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in 6 volumes

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PLENARY LECTURES

THE STORY OF SINGLE MOLECULES, FROM EARLY HIGH-RESOLUTION SPECTROSCOPY IN SOLIDS, TO SUPER-RESOLUTION NANOSCOPY IN CELLS AND BEYOND

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In the late 1970s and 1980s, many researchers around the world were exploring a novel optical storage concept, frequency domain optical storage, which was based on spectral hole-burning in the zero-phonon lines of impurities in solids at low temperatures. In 1989, experiments aimed at establishing the ultimate limits this optical storage idea led to the first optical detection and spectroscopy of a single molecule in the condensed phase using laser FM spectroscopy. This represented optical exploration of the ultimate limit of one individual molecule at a time, an amount of material equal to (1/Avogadro's Number) of mol. As one might expect from an unexplored new regime, many surprises occurred where single molecules showed both spontaneous changes (blinking due to spectral diffusion) and also light-driven control of emission. These properties were subsequently also observed in 1997 at room temperature with single green fluorescent protein variants, and blinking, or reversible entry into dark states, was found to occur in many situations. In 2006, PALM and related approaches showed that Abbe's optical diffraction limit of ~200 nm can be circumvented to achieve super-resolution fluorescence microscopy, or nanoscopy, with relatively nonperturbative visible light. Essential to imaging with single molecules beyond the diffraction limit are several requirements: single-molecule fluorescence imaging, active control of the emitting concentration, and sequential localization of single fluorophores decorating a structure. Super-resolution microscopy has opened up a new frontier in which biological structures and behavior can be observed in live cells or other materials with resolutions down to 20-40 nm and below. Examples range from protein superstructures in bacteria to bands in axons to details of the shapes of cytoskeletal structures, amyloid fibrils and much more. Current methods development research addresses ways to extract more information from each single molecule such as 3D position and orientation, and to assure not only precision, but also accuracy. Still, it is worth noting that in spite of all the current interest in super-resolution microscopy of extended structures, even in the "conventional" single-molecule tracking regime where the motions of individual biomolecules are recorded in solution or in materials, much can be learned about the dynamics of nanoscale processes when ensemble averaging is removed.

FROM CATENANES AND ROTAXANES TO MOLECULAR MACHINES

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The simplest catenane, a [2] catenane, consists of two interlocking rings. Rotaxanes consist of rings threaded by acyclic fragments (axes). Interlocking ring compounds have attracted much interest in the molecular sciences, first as pure synthetic challenges and, more recently, as components of functional materials. In particular, these compounds appear as perfect precursors to dynamic systems for which motions can be triggered and controlled in a precise manner. This property led to the use of catenanes and rotaxanes as *molecular machine prototypes*.

Subsequently, the research field of artificial molecular machines has experienced a spectacular development, in relation to molecular devices at the nanometric level or mimics of biological motors. In biology, motor proteins are of the utmost importance in a large variety of processes essential to life (ATPase, a rotary motor, or the myosin-actin complex of striated muscles behaving as a linear motor responsible for contraction or elongation). A few recent systems are based on simple or more complex rotaxanes or catenanes acting as switchable systems or molecular machines. Particularly significant examples include a "swinging catenane", "molecular shuttles" as well as multi-rotaxanes reminiscent of muscles or able to act as molecular compressors or switchable receptors. The molecules are set in motion using electrochemical, photonic or chemical signals. Examples will be given which cover the various approaches used for triggering the molecular motions implied in various synthetic molecular machine prototypes. The work of various groups using non interlocking compounds will also be briefly discussed. Potential applications of rotaxanes and molecular machines will also be mentioned.

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J.-P. SAUVAGE, "From Chemical Topology to Molecular Machines", Angew. Chem. Int. Ed., 2017, 56, 11080.

CATALYSIS AND THE PERIODIC TABLE OF ELEMENTS

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Catalytic technologies are currently used in the production of the vast majority of chemicals and materials and about 90% of all contemporary industrial technologies involve catalytic processes. As we have mentioned before, interdisciplinary projects, which interconnect the fields of catalysis, organic synthesis and organometallic chemistry, have quickly and drastically changed the image of the chemical industry [1]. It is important to note that numerous developments made by organic chemists in the field of catalytic technologies find rapid implementation in the industry and facilitate appearance of innovative products.

In this lecture we will touch upon the phenomenon of catalysis in terms of the diversity of catalytic processes, with the emphasis on the unique features of the application of different elements of the Periodic Table in catalytic reactions.

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MATERIALS FOR DEVELOPMENT OF ARCTIC AND COLD TERRITORIES

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The success of the development of cold areas, including the Arctic, largely depends on the availability of materials that can work effectively in hard climatic conditions. The development of cold zones has a long history, but the Arctic materials science (AMS) was formed a few decades in modern form. Now there is an intensive search, synthesis and experimental studies of the arctic materials, but there is virtually no generalizing analysis of the current state of AMS and not formulated trends in its development[1]. Domestic AMS significantly behind the indicators of industrial development of the Arctic in the Russian Federation, although to succeed, the trend should be reversed.

The number and variety of materials used in cold climate zones is great: construction, functional, fuel and lubricants and other auxiliary materials of natural and anthropogenic origin and different chemical composition (metal, ceramic, low and high molecular weight, etc.). The specific features and requirements for these materials give reason to allocate AMS in a special section of material sciences. The evolution of AMS has features characteristic of modern materials science: the transition from natural materials to anthropogenic, the chemical and morphological composition and structure, versatility and giving the materials smart elements, etc. The report discusses the climatic factors of the Arctic and the mechanisms of their impact on the properties of materials, formulated requirements for arctic materials necessary for their operation. The classification of arctic materials, taking into account their properties, structure and application in technical devices and constructions is offered. Obtaining Arctic materials are adaptation of existing materials for the Arctic conditions and development of new specifically for Arctic. The report will give examples of the creation of some Arctic materials obtained in domestic scientific organizations. The methods of studying the structure of Arctic materials, their laboratory and nature tests, including the influence of climatic factors, were also discussed. Analysis of the survey of experts and international bibliometric databases revealed research organizations with the greatest competence in certain areas of AMS. The features of interaction between researchers and between scientific structures are evaluated, and proposals to improve the cooperative climate are made.

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SYNCHROTRON RADIATION AND INVESTIGATION OF CATALYTIC SYSTEMS

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Over recent years the progress in development of material science and adjacent fields such as energetics, catalysis, membrane and sensor technologies, elemental base of micro- and nanoelectronics is largely defined by the level of a country's research infrastructure including the sources of synchrotrone radiation and neutrons, in other words, by the presence of “mega-science” plants. We can rely on the international cooperation in conducting such studies assuming the use of the international centers of competence in this field, HZB (known before as BESSY-II) and DESSY in Germany, ESRF in France, Daresbury in Great Britain, centers of synchrotron radiation within the National Laboratories in the USA. Indeed, these options are available and should be used, albeit on a competitive basis; however, the existence of the domestic “mega-science” plants, their regular use and upgrading would not only increase the time for such studies and widen the circle of objects over the technological tasks, but also keep up the research and methodological level of the scholars participating in this international differentiation of labor as well as the technological level of production of non-standard equipment for various purposes.

In my lecture I intend to argue for the importance of using the potential of synchrotron radiation for catalytic studies; I will present not only the forming tendencies but also the latest research results obtained lately while studying the structure of active centers of heterogeneous catalysts in various centers of synchrotron radiation. I will also show the latest results of our experiments on studying the bimetallic Pd-Au catalysts of low-temperature oxidation with CO (the XPS experiments were carried out on the RGBL and ISISS stations of the Berlin source of synchrotron radiation, HCB), the Pt/Al_2O_3 nanocatalysts of the total methane oxidation (studied at the station of the Kurchatov center of synchrotron radiation upgraded for the in-situ XRD and XAFS measurements with our participation), reactions of methane oxidation in the self-oscillation regime on Ni catalyst (studied at the XRD station of the Siberian center of synchrotron radiation in Budker Institute of Nuclear Physics SB RAS).

In conclusion I would analyze the possible directions of development of this approach to the basic research in the field of catalysis, already employed in some countries (Germany, USA, Great Britain, Scandinavian countries), for example by creation of national catalytic hubs with the purpose of coordination of means for conducting the oriented studies including those in the interest of industrial partners as well as the Russian national network of “mega-science” plants planned to be built.

CHEMISTRY OF 2D MATERIALS: FROM 2D MOLECULAR MAGNETS TO HYBRID MOLECULAR/2D HETEROSTRUCTURES

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Graphene and other 2D materials are a hot focus of interest in physics, chemistry and materials science. These materials are almost exclusively based on inorganic lattices and cover a wide range of electronic and magnetic properties: from insulators to superconductors, from diamagnetic to ferromagnetic (FM) and from metallic to non-metallic compositions. Except for the chemical functionalization of the surface of the 2D material, molecules have been scarcely considered in this field. In this talk I will emphasize the role of chemistry in this area paying particular attention to the magnetic properties. In the first part I will show how coordination chemistry can provide examples of molecular 2D magnets that, in contrast to what happens with the inorganic 2D magnets, are chemically stable in open air, keeping their magnetic properties preserved upon functionalizing their surface with different organic molecules.1 In the second part I propose to create hybrid heterostructures by interfacing a layer of a functional molecular material with a 2D material. The aim is that of tuning the properties of the "all surface" 2D material via an active control of the hybrid interface.[2] To reach this goal the molecular system of choice will be based on spin-crossover complexes able to switch between the two spin states upon the application of an external stimulus (temperature, light or pressure). This concept will provide an entire new class of stimuli-responsive molecular/2D heterostructures, which may be at the origin of a novel generation of hybrid materials and devices of direct application in highly topical fields like electronics, spintronics and molecular sensing.

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ORIGIN OF ELEMENTS AND CHEMISTRY IN SPACE

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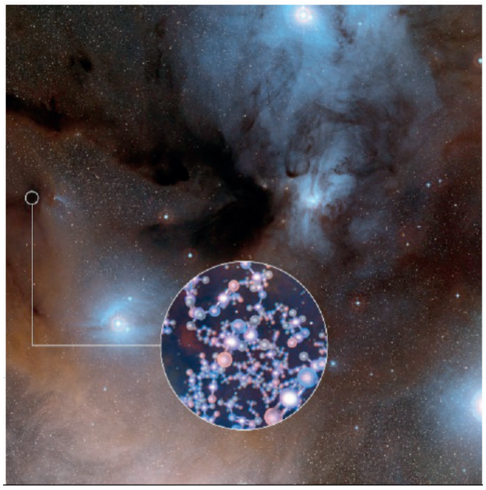
'We are all stardust'. Most of the elements in the periodic table were formed in space. The simplest species - H, D, He, and Li - were made shortly after the Big Bang in the early Universe, whereas the rest of the elements that make 'us' were produced by nuclear fusion in the interior of stars, gradually enriching the Universe with heavier elements. A brief overview of the production of the main elements that are important for interstellar chemistry will be given.[1]

Chemistry starts in the cold and tenuous clouds between the stars. In spite of extremely low temperatures and densities, these clouds contain a surprisingly rich and interesting chemistry, as evidenced by the detection of more than 200 different molecules, from simple to complex[1]. Chemistry takes place both in the gas and on the surfaces of interstellar dust grains.[1,2] New facilities such as ALMA allow us to zoom in on the formation sites of new stars and planets with unprecedented sharpness and sensitivity. Spectral scans of young protoplanetary disks contain tens of thousands of rotational lines[3], revealing water and a surprisingly rich variety of organic materials, including simple sugars[3], molecules with peptide bonds[4] and high abundances of deuterated species[3]. What are the dominant chemical processes at work? How common are they? What material is available to build new exo-cometary and planetary systems?



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NON-CRYSTALLINE NANOSTRUCTURED MATERIALS: THE WAY TO NEW SOLIDS WITH NEW STRUCTURES AND PROPERTIES

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Today's technologies are based primarily on utilizing crystalline materials (e.g. metals, semiconductors or crystalline ceramics). The way to new technologies may be opened by nanostructured materials that are totally or partially on non-crystalline. One group of them are nano-glasses. They consist of nanometer-sized glassy regions connected by (nanometer-wide) interfacial regions with atomic and electronic structures that do not exist in melt-cooled glasses. Due to their new atomic/electronic structures, the properties of nano-glass differ from the corresponding properties of melt-cooled glasses. For example, their ductility, their biocompatibility, their catalytic and ferromagnetic properties are changed by up to several orders of magnitude. Moreover, they permit the alloying of components e.g. ionic materials (e.g. SiO) and metallic materials (e.g. PdSi glasses) that are immiscible in the crystalline state. The properties of nano-glasses may be controlled by varying the sizes and/or chemical compositions of the glassy clusters which opens the perspective of a new age of technologies - a ”glass age”. A second group of nanostructured partially non-crystalline materials with tunable properties are nano-porous metals with electrolyte filled prores. By applying an external voltage between the electrolyte and the nano-porous metal their properties e.g. their superconductivity, magnetic moment, electric resistivity may be varied. Single or multi-atom switchable contacts represent a third group of these materials. They open the way to spontaneously formed single-atom or multi-atom transistors which allow quasi solid state bi-stable switching between quantized conduction levels of $2e^2/h$ or multiples of $2e^2/h$.

THE FUNCTION OF FUNDAMENTAL STUDIES IN DEVELOPMENT OF THE NEW GENERATION MATERIALS

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Director General of FSUE "VIAM" SSC RF , Head of Руководитель top-priority technological direction "technologies of materials science", Academician of RAS

New generation materials are the basis for development of the competitive civil and special equipment on the world market. The "Strategic directions for the development of materials and technologies of their treatment for the period up to 2030" developed upon the VIAM initiative and approved by the Science & Technology Council of the Military-Industrial Commission of the Russian Federation determine the approaches and implementation phases of fundamental and applied studies in the field of materials science.

The main principles of creation of the new generation materials are materialized on the basis of unity paradigm "material – technology – design". During the development of the new generation materials the multilevel approach is used: material modeling on nano-, micro, meso- and macro-levels, study of mechanisms of elemental samples behavior with results validation for structural elements and goods. Today the development of the new generation materials is impossible without computer modeling of materials and mathematic models of their manufacturing. They allow optimizing the parts and structures production technology by conditions of strain-stress state; evaluate the influence of the initial stock on physical and mechanical properties of the materials; reduce the value of the development of the new materials.

The development of the new generation polymer composite materials (PCM) is the most important direction of growth of the Russian economy. This calls for the new high-strength, high-modulus fillers, foremost – the carbon fiber. It should be noted that nowadays Russia does not possess both the production of intermediate modulus carbon fibers similar to T700 and T800 in their properties and the capacity of the end-to-end cycle of PAN-fiber production, the quality of which predefines the properties of carbon fiber. At the same time the development of PCM branch is in direct dependence on the achievements of the chemical industry. The main task is to develop the components of polymer matrices – olygomers, catalyst systems meeting the high requirements not only to properties, but also to ecological compatibility of production. Under present conditions the technological breakthrough is closely connected with the intense development and wide application of principles of "green chemistry" and molecular design, development of atomic-molecular engineering during the new compounds production. It is necessary to generate the program of manufacturing process management for the highly purified materials for microelectronics, photonics, optoelectronoics and biomedicine, as well as to determine the competence center – an industry organization in charge of technologies and production development for chemical compounds of highly purified materials.

The digital and additive technologies play the key part in improvement of the manufacturing process of complex technical systems parts. They allow manufacturing of high-quality parts by means of direct material synthesis ("addition"); it is impossible to create these parts by means of traditional "extracting" technologies, such as welding, mechanical treatment, etc. Additive technologies are rightfully the technologies of 21st century and they have great potential in the realm of energy cost reduction during the various products manufacturing. Thus, it is evident that the intensity index of using of the additive technologies is one of the indicators of industrial and innovative national development.

In general the joint achievements of the Russian Academy of Sciences, state scientific centers and the leading institutes of chemistry and materials science allow creating the basis for the development of the new generation materials. At present it is necessary to expand the scope of application of the scientific knowledge and discoveries and to intensify the innovative activity of scientific facilities and business by means of formation of consortia for implementation of large-scale projects of end-to-end innovative cycle (idea – material – technology – production of innovative products).

SYSTEMS THINKING TO EDUCATE ABOUT THE MOLECULAR BASIS OF SUSTAINABILITY

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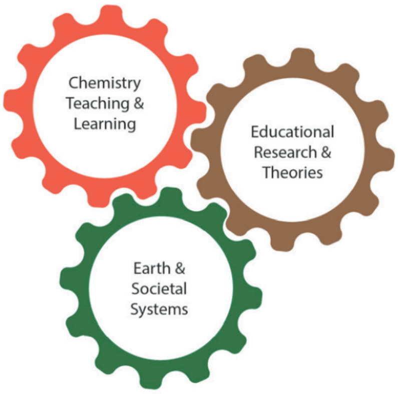
A Systems Thinking in Chemistry Education (STICE) frameworki has been developed by a global IUPAC project team with the goal of moving learners from fragmented knowledge of chemical reactions and processes toward a more holistic understanding of the field. Systems thinking shows promise in guiding students to see the relevance of their chemistry education for addressing multiple emerging global challenges such as sustainability, alternative energy, planetary boundaries, and the UN Sustainable Development Goals. We will explore progress to date in implementing the IUPAC STICE project and suggest approaches that can be used by chemistry educators to help students develop a deeper understanding of the molecular basis of sustainability.ii To give chemists and educators a concrete example of how systems thinking can be used, we will consider the Haber-Bosch process for the synthesis of ammonia, and the way systems thinking visualization tools can help students move beyond a narrow view of this process to consider chemical and energy inputs, reaction conditions, outputs such as the Ostwald Process leading to ammonium nitrate, and the intended uses of nitrogenous compounds derived from ammonia in agriculture and munitions, as well as unintended consequences resulting from the overuse of reactive nitrogen. Next steps for the IUPAC STICE project will be discussed, including suggestions arising from contributions to a special issue of the Journal of Chemical Education on "Reimagining Chemistry Education: Systems Thinking and Green & Sustainable Chemistry," to be published in late 2019.iii

Abstract graphic (if one can be used):



Systems Thinking in Chemistry Education
An IUPAC Project

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THE CHEMICAL ELEMENT: HOW CHEMISTRY IS KEY TO SOLVING OUR GLOBAL CHALLENGES

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Chemistry is a global endeavor that has greatly contributed to improving our quality of life by protecting us against illness and by putting food and clean water on our table.[1] But now, our global challenges are so big that only if we focus all our efforts in solving our most pressing problems we can create a sustainable and better future for all.[2] From climate change to our dependence on finite natural resources, many of our most global challenges require a technical solution that only better science and technology in general and chemistry in particular can provide.[3] During its almost 100 years of existence, IUPAC has created universally accepted chemistry nomenclature and terminology as well as a global platform to discuss and advance some of the most relevant topics on pure and applied chemistry.

Chemistry education is of particular importance. We must train, engage, and inspire the new generation of young chemists able and committed to building a more sustainable future.[4,5] In order to get there, science education, from primary school to college, needs to be reinvented to put the student at the center of the learning process and provide him or her with the skills needed to become a more complete and creative scientist.

There is still a significant gap between academia and industry that needs to be bridged by bold entrepreneurs able to connect these two worlds and successfully commercialize the new and exciting research carried out in universities. Entrepreneurship is another important part of the equation, taking the discoveries made in the lab to the market place is essential to implementing the solutions we need, and scientists have a key role to play here.[6]

During the presentation some examples and various ideas will be shared to accelerate the discovery and application of chemistry breakthroughs that, hopefully, will ignite a thriving and constructive discussion.

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ELECTROCATALYTIC PRODUCTION OF H_2 FROM WATER WITH F-ELEMENT-BASED MOLECULAR CATALYSTS

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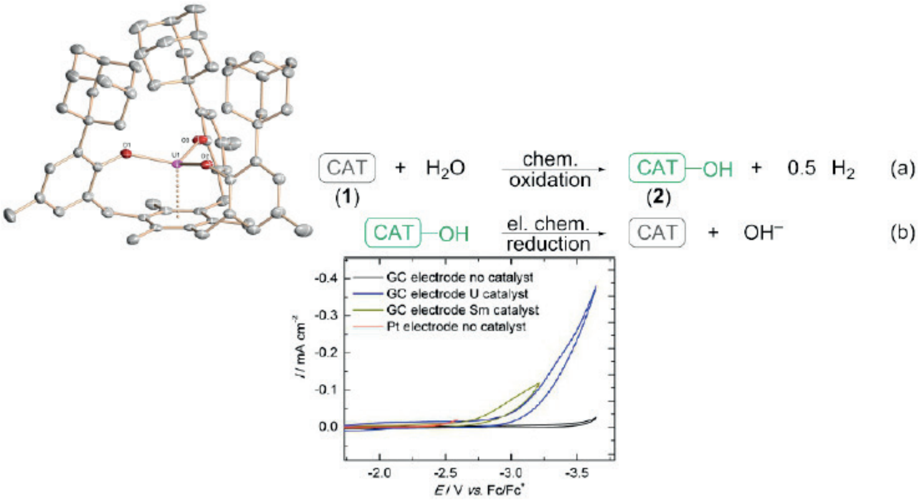
Research on renewable energies and energy storage, such as H_2 production from H_2O, has become a key challenge for our society. The low efficiency of conventional H_2O electrolysis precludes large-scale applications. Thus, catalysts are desired to make this otherwise convenient strategy more applicable. Due to the high reactivity and oxophilicity of trivalent uranium complexes, as well as the large-scale availability of depleted uranium, uranium complexes are widely discussed as effective and economic catalysts for stable substrates.

In our previous studies of the arene-anchored tris-aryloxide uranium complex $[U(^{Ad,Me}ArO)_3mes)]$ (1), unique electrochemical and well-defined synthetic behavior were found, rendering 1 a perfect candidate for electrocatalysis.

Indeed, trivalent uranium coordination complex 1 was found to be the first molecular uranium catalyst for electrocatalytic H_2 production. Utilization of 1 during H_2O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance by 3 orders of magnitude. Isolation of key intermediates and *in situ* EPR experiments allowed to determine the reaction mechanism of H_2O reduction with low valent U(III). This reactivity is now studied in a series of lanthanide complexes $[Ln(^{Ad,Me}ArO)_3mes)]$ (2–Ln), which allows for fine-tuning of overpotential and reactivity of the catalyst by choice of the 4*f* ion.



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PERIODIC TABLE AFTER 150 YEARS

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One of the fundamental consequences of the modern theory of atomic nuclei (1969) is the prediction of an ‘Islands of Stability’ in the region of hypothetical super heavy elements (SHEs). In a heavy nucleus, going through the large-scale deformation on the way to fission, the motion of single nucleons is coupled with the collective degrees of freedom of the whole system. The most striking effect of this coupling is obtained for the case of fission of the heaviest nuclei, whose existence is defined entirely by the nuclear structure, i.e. by the shell effect.

From this point of view, the synthesis and study of properties of super heavy nuclei (SHN) is a direct way for checking the basic statements of the microscopic nuclear theory. On the nuclide map, SHN outline the border of the heaviest nuclear masses. SHN set the limits of the periodic system of chemical elements. The study of possible existence of SHN in nature offers a way for testing different scenarios of astrophysical nucleosynthesis.

The talk presents results concerning the synthesis and decay properties of the super heavy nuclei from this ‘Stability Islands’ of SHEs obtained in cold and hot fusion reactions. The region of heavy nuclei have expanded and advanced up to mass of 294. New elements filled the 7th row of the Periodic Table of Elements. The results of the first chemical experiments and theoretical predictions about the influence of the "relativistic effect" on the electronic structure of the SH atom are presented.

Super heavy atoms are synthesized today in unit quantities. Theoretical expectations of the chemical properties of the new elements with respect to their light homologues is discussed in connection with the synthesis of elements heavier than 118. A significant increase in the sensitivity of experiments is expected with accelerator complexes of the new generation. At one of them, the “SHE Factory” in JINR (Dubna) the first beam was obtained in the end 2018.

The talk used results of the experiments conducted in 2000-2015 at FLNR (JINR, Dubna) at the U400 heavy ion accelerator in collaboration with researchers from national laboratories and universities: LLNL (Livermore, USA), ORNL (Oak-Ridge, USA), IAR (Dimitrovgrad, Russia), Vanderbilt, Knoxville and Texas A & M Universities (all in USA), as well as data obtained at national nuclear centers: GSI (Darmstadt, Germany), GANIL (Caen, France) and RIKEN (Wako-shi, Japan).

THE PERIODIC TABLE AT 150: METALS, HEALTH AND MEDICINAL APPLICATIONS

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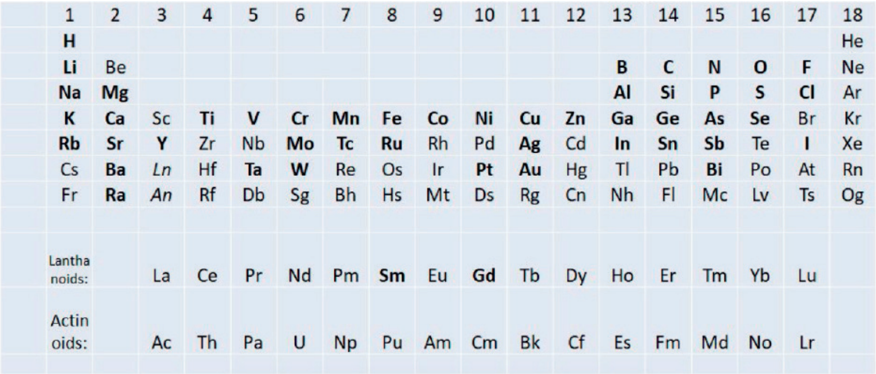
Elements of the Periodic Table have been known since ancient times, even before elements were known and recognized as such. No doubt Gold, Silver and Copper were the first of such metals, and were generally used in jewelry and coins, and in some cases also as weapons (Cu). By the time the Periodic System was tabulated in 1869, one was already aware that some elements and metal-containing compounds were needed for life (like Fe) and others were known to be very toxic, like As, Hg.

Already in the ancient times, some of the elements were used to treat diseases, like colloidal gold. The dosage of many of such metallic elements to humans, to cure or prevent diseases has been a subject of study for many decades. In the last 50 years the usage of metal compounds to diagnose or cure diseases has been rapidly grown.[1] The Periodic Table shown below, has elements that are known to play a role in health of humans bold printed.

Elements needed for live and used in curing and diagnosis



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	H																	He
	Li	Be											**B**	**C**	**N**	**O**	**F**	Ne
	Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	Ar
	K	**Ca**	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	Br	Kr
	Rb	**Sr**	**Y**	Zr	Nb	**Mo**	**Tc**	**Ru**	Rh	Pd	**Ag**	Cd	**In**	**Sn**	**Sb**	Te	**I**	Xe
	Cs	**Ba**	*Ln*	Hf	**Ta**	**W**	Re	Os	Ir	**Pt**	**Au**	Hg	Tl	Pb	**Bi**	Po	At	Rn
	Fr	**Ra**	*An*	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
Lanthanoids:			La	Ce	Pr	Nd	Pm	**Sm**	Eu	**Gd**	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinoids:			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

In the lecture examples of drugs to cure diseases will be presented, with a focus on treatment of cancers by metal compounds, in particularly by certain platinum compounds.2,3 The mechanism of action of such compounds will be discussed as well.

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MENDELEEV’S GIFT TO EDUCATION (AND TO ME)

Sir Poliakoff M.

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2019 has been declared the International Year of the Periodic Table in celebration of the 150th anniversary of Dmitri Mendeleev’s first publication of his Periodic Table.[1] The purpose of this lecture is to demonstrate that Mendeleev’s genius was to create something that anyone can use as a highly flexible framework for expressing their chemical ideas. I shall do this by giving examples of a whole variety of periodic tables ranging from one of the oldest surviving examples of periodic table intended to be shown in a lecture theatre[2] to the periodic table recently devised specifically by the European Chemical Society (EuChemS) for the IYPT, highlighting some of the elements which are becoming scarce.[3] I shall also highlight how the Periodic Table has impacted my own career and research. as well as mentioning our own contribution to the debate about designs of the periodic table.[4]

Acknowledgements: I thank all of my colleagues, collaborators, co-workers as well as our technicians. In particular, I thank Professor Mike George, Brady Haran and Neil Barnes. I also thank the Engineering and Physical Sciences Research Council, The Bill and Melinda Gates Foundation and The Garfield Weston Trust for financial support.

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FROM MATERIALS INNOVATIONS TO NEW SUSTAINABLE BATTERY CHEMISTRIES

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Research's progresses in rechargeable batteries are driven by ever increasing demands for portable electronic devices as well as for powering electric vehicles and providing load-leveling for mass storage of renewable energy. Li-ion batteries are the systems of choice for the aforementioned applications. Therefore, for this to fully happen, new concepts and new sustainable chemistries are sorely needed, and this is what this presentation will address.

Firstly, regarding new concepts, we will show how the discovery of a new Li reaction mechanism that involves the anionic network with the reversible formation of dimers (O-O) represents a transformational approach for creating electrode materials with exacerbated capacities. Towards, higher energy density systems, recent advances on solid state Li batteries will be discussed. Concerning new chemistry, our new findings with the Na-ion chemistry which enlists novel materials/electrolyte designs together with the assembly of 18650 prototypes together with our work on Zn-MnO2 aqueous systems will be presented. Lastly, an indirect way to enhance simultaneously energy density and sustainability via the use of sensing and self-healing functionalities will be introduced. Through these examples, the importance of materials design will be emphasized together

Altogether, these examples have been selected to show that the future of battery offers new opportunities for materials scientists as long as we are willing to play with the Mendeleev table and explore new risky paths. .

BIOMASS CHEMISTRY: BIOFUELS AND BIOPLASTICS

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The lecture is devoted to the analysis of the achievements and trends in the renewable raw materials conversion into energy carriers and biomaterials.

The demand for new technologies for producing fuels and polymeric materials is determined by the raw materials sources growing shortage and the need to create fundamentally new large-scale environmentally acceptable methods for chemical industry.

The lecture discusses:

- Trends in the development of biofuels production and use;
- Biomethane and biohydrogen, chemical processes and the basis of technology for biogas production;
- Catalytic ethanol conversion processes;
- New fuels based on bioresources;
- Biotechnological processes for the butanol, acetone, other organic solvents and fuels production;
- Obtaining "bio-oil" and "synthesis oil" by biomass and polymeric materials pyrolysis;
- Biocatalytic synthesis of organic acids and plastics based on them;
- Polyhydrooxyalkanoates - natural biodegradable polymers;
- Polyamides based on natural amino acids solid-phase polymerization;
- Bacterial cellulose - biocatalytic synthesis and use;
- Natural rubber - new biotechnological synthesis methods.

The rates of new renewable resource sources development, qualitatively new biofuels and bioplastics properties are considered.

SECTION 1

FUNDAMENTAL PROBLEMS OF CHEMICAL SCIENCE

Co(II) BASED SINGLE ION MAGNETS AND THEIR ADVANTAGES FOR THE DESIGN OF NEW MAGNETIC MATERIALS

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The structure and magnetic properties of single ion magnets (SIM) related to Co(II) complexes have been considered. Specific features of the structure and magnetic anisotropy of Co complexes with coordination number being, 4, 5, 6, 7, and 8, and the influence of the ligand surrounding on the distortion of Co coordination and slow magnetic molecule relaxation are under consideration.

Particular attention has been paid to the results of experiments and theoretical modeling of hexacoordinated complexes of Co(II) with negative and positive magnetic anisotropy. To analyze magnetic anisotropy of these complexes, additional experimental techniques, such as SQUID magnetometry, Multi High Frequency EPR Spectroscopy, and Far-infrared Magnetic Spectroscopy have been used, as well as theoretical modeling using parametrized Griffith's Hamiltonian with parameters obtained from ab initio calculations. As follows from the analysis, magnetic anisotropy of these complexes is mainly triaxial, with different signs of axial components. Independently on the sign of the axial anisotropy, Co(II) complexes exhibit a slow paramagnetic relaxation in the constant magnetic (DC) field, i.e., belong to the class of field induced non-monoaxial single ion magnets (FI-SIMs). Such type of SIM behavior is due to Kramer's character of Co(II) ion.

Effect of the axial crystal field in quasioctahedral high-spin Co(II) complexes on the rates of direct one-phonon relaxation processes is being discussed. Strongly axially distorted complexes (regardless of the sign of distortion) were shown to exhibit slower relaxation than more symmetric (undistorted) octahedral complexes, this being important to take into account while designing SIMs based on quasi-octahedral Co(II) complexes. Possibility to produce new magnetic materials based on these compounds is being discussed.

This work was performed in accordance with the state task, state registration No 0089-2019-0011.The work was financially supported by the Ministry of Education and Science of Rus-sian Federation (Agreement No. 14.W03.31.0001-Institute of Problems of Chemical Physics of RAS, Chernogolovka).

EFFICIENT CATALYTIC SYSTEMS FOR CARBON-HETEROATOM AND CARBON-CARBON BONDS FORMATION

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Transition metal catalysis is the most powerful technique for carrying selective organic synthesis in a diverse range of reactions developed in academic research and transformed as core methodologies for industrial processes. Exploring dynamic phenomena in catalysis brings a new wave in sustainable development [1], usage of novel type of reagents [2], resolving reproducibility issues [3], mechanistic understanding [4] and organic synthesis [5].

New opportunities and challenges of dynamic phenomena in catalytic systems will be presented and discussed in view of organic synthesis and sustainable development.

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Acknowledgement. The study was supported by Russian Science Foundation (RSF Grant 19-13-00460).

POSITIVELY CHARGED METAL CENTERS AS NUCLEOPHILES TOWARD σ-HOLE AND π-HOLE DONORS

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The past few years have seen a precipitous growth in the number of publications related to various aspects of weak interactions, both in chemistry and biology. Compared to covalent bonds, intra- and intermolecular noncovalent interactions are weak. They have much lower energy, fluctuating in the range from several units to several tens of kcal/mol, as well as less directed orientation. Depending on specific chemical elements or building blocks based on these elements, noncovalent interactions are classified into hydrogen, halogen, chalcogen, pnictogen, metallophilic, lp–π interactions, π-stacking, and a number of others; this classification is continuously expanded and refined.

Despite the low energy of noncovalent interactions, in many cases they act collectively and the sum of their actions can play a significant role in the various transformations of chemical compounds, synthesis and catalysis, including organic catalysis. Crystal engineering makes extensive use of interactions between multiple noncovalent bonds, allowing the design and production of associates, clusters, extended supramolecular systems and ultimately functional materials.

Non-metal centers bearing lone pairs such as, e.g., O, N, S, halogens, etc. are typically applied as acceptors for crystal engineering studies that utilize interactions with σ-hole or π-hole donors. Recently, however, we have established that even metal centers could serve as effective σ-hole acceptors and, in particular, NiII, RhI, PdII, PtII, and AuI with certain ligand environment behave as nucleophiles. If the interaction of positively charged metal centers with σ-hole donors is uncommon, interaction with π-hole donating centers is nearly unique as only a very few examples of π-hole•••metal contacts are known. In the talk, all these examples will be considered and appropriate data systematized.

ACKNOWLEDGEMENTS. I am deeply indebted to my former and current co-workers, postdoctoral fellows, and students who shared with me the fascination of this area of chemistry. Financial support from the Russian Foundation of Basic Research (grant 18-29-04006) is gratefully acknowledged.

ALKENE METATHESIS: SILICON AND GERMANIUM VERSIONS

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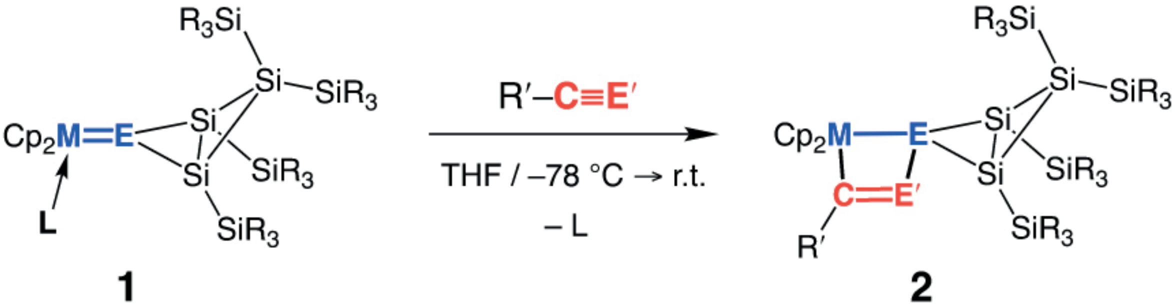
Alkene metathesis is one of the very important industrial processes for the production of alkenes, catalyzed by the transition metal carbene complexes >M=C< (M = transition metal). The latter complexes are classified as either Fischer or Schrock-type, depending on the interaction mode between the transition metal and the carbene ligand. In this presentation, we report a general synthetic approach towards the isolation of the readily available unique examples of the Schrock-type silylene and germylene complexes of the group 4 metals >M=Si(Ge)< (M = Ti, Zr, Hf) 1 (Scheme). These 18-electron complexes 1 feature loosely bound and readily removable Lewis base ligands L (thf, phosphine, isocyanide, etc.), providing a vacant site for coordination of unsaturated substrates at the transition metal center and thus ready access to unprecedented (sila/germa)metallacyclobutenes 2, as the "frozen" intermediates of the silicon/germanium versions of metathesis.1-3 The peculiar structural features of both 1 and 2, as well as the bonding nature (metallacycle vs. π-complex) of 2 will be also discussed.



[$\mathbf{M}$ = Ti, Zr, Hf; $\mathbf{E}$ = Si, Ge; E' = CH, N; R' = H, ^{n}Bu, Ph, $SiMe_3$; R_3Si = $SiMe^tBu_2$]

Scheme.

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WHAT DETERMINES THE NATURE OF HYDROGEN ATOMS ON M° SURFACES? M°-NANOPARTICLES CATALYZE THE REDUCTIVE DE-HALOGENATION OF HALO-ORGANIC COMPOUNDS BY BH_4^- IN AQUEOUS MEDIA.

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The mechanisms of formation of M°-NPs (nano-particles) via the reduction of M_{aq}^{n+} by weak reducing agents is considerably more complex than usually considered.

M°-NPs catalyze the reaction of BH4- with water to form hydrogen:
(1) $(M^\circ\text{-NP}) + nBH_4\text{-} + 4nH2_O \text{ -> } \{(M^\circ\text{-NP})\text{-}H_{4n}\}^{-4n} + nB(OH)_3 + 3nH_3O^+$
(2) $\{(M^\circ\text{-NP})\text{-}H_{4n}\}^{-4n} + mH_3O \text{ <-> } \{(M^\circ\text{ -NP})\text{-}H_{4n+m}\}^{(4n-m)}\text{-} + mH_2O$ (Volmer)
(3) $\{(M^\circ\text{-NP})\text{-}H_{4n+m}\}^{(4n-m)}\text{-} \text{ -> } \{(M^\circ\text{-NP})\text{-}H_{4n+m-2}\}^{(4n-m)}\text{-} + H_2$ (Tafel)
(4) $\{(M^\circ\text{-NP})\text{-}H_{4n+m}\}^{(4n-m)}\text{-} + H_3O\text{+}/H_2O \text{ -> } \{(M^\circ\text{-NP})\text{-}H_{4n+m-1}\}^{(4n-m-1)}\text{-} + H_2 + H_2O/OH\text{-}$
(Heyrovsky)

Isotopic labeling experiments point out that the mechanism of the process observed depends on $[BH_4^-]$: The higher the concentration the relative contribution of the Heyrovsky mechanism increases and that of the Tafel decreases. Surprisingly the rate constant k_{-2} is slow. The relative contributions of the two mechanisms differ considerably for M° = Au° and Ag°.

When halo-organic acids, $X_kH_{3-k}CO_2^-$, X = Cl or Br are present reactions (5) and/or (6) compete with reactions (2) - (4).
(5) $\{(Au^0\text{-NP})\text{-}H_n\}^{m-} + X_kCH_{3-k}CO_2^- \text{ -> } \{(Au^0\text{-NP})\text{-}H_n\}^{(m-1)-} + X^- + X_{k-1}CH_{3-k}CO_2^{\cdot-}$
(6) $\{(Au^0\text{-NP})\text{-}H_n\}^{m-} + X_kCH_{3-k}CO_2^- \text{ ->} \{(Au^0\text{-NP})\text{-}H_{n-1}\}^{m-} + X^- + H^+ + X_{k-1}CH_{3-k}CO_2^{\cdot-}$
These reactions are followed by reaction (7):
(7) $\{(Au^0\text{-NP})\text{-}H_n\}^{(m-1)-} + X_{k-1}CH_{3-k}CO_2^{\cdot-} \rightarrow \{(Au^0\text{-NP})\text{-}H_n\}\text{-}CX_{k-1}H_{3-k}CO_2^{m-}$

The mechanisms of decomposition of the transients $\{(Au^0\text{-NP})\text{-}H_n\}\text{-}(CX_{k-1}H_{3-k}CO_2^{m-})$l thus formed depends on $[BH_4^-]$ in an analogous way to that reported above. It depends also on the nature of M° and X.

CAN A MATERIAL PERFORM AS AN ENGINE?

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Recently a number of reports demonstrated successful developments of microswimmers. These are small objects with the size of micrometers or even smaller. Qualification of polymer objects to undergo autonomous motion, i.e., driven and directed (i) rotation, (ii) vibration/oscillation or (iii) translation requires the particles to do work. This in turn requires a local energy input. Examples in which a micro-object can undergo a directed motility by body shape deformation, mimicking the locomotion of bacteria, are rare and incomplete. In the case of low Reynolds numbers, the actuation must not generate a reciprocating change in the particles conformation or shape and furthermore, such a motility requires that the micro-objects undergo a displacement directed by itself, just like a human swimmer, who moves forward by recurring strokes. A cyclic body shape deformation, however, represents a clockwise repetition. If this should be autonomous, it will represent another challenge.

Here we report on LCST-hydrogel micro objects for which the body shape variation can be precisely controlled by the (i) design of the geometrical shape, (ii) the widely variable material properties and (iii) by the energy intake via infra-red irradiation. The volume change is not caused by heating of the whole system, but by strictly localized heat generation inside the particles. For this purpose the gels were equipped with 1-4 gold nanorods per ∓ m^3 that absorb light at 780 nm and convert it practically instantaneously to heat. It will be shown that a cyclic deformation can be controlled to follow a different path in space and time during the “forward” and the “backward” stroke. In first instance the deformation cycle has been controlled from outside by switching on and switching off the irradiation as the driving energy input. In a higher developed version, we attempted and succeeded to cause the repetitive deformation by continuous irradiation. This required the introduction of an autonomous feedback mechanism by which the energy uptake ceased upon raising the temperature and a hysteretic bistability by which we could prevent that the system could adopt a shape corresponding to a steady state equilibrium.

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P,T–SENSORS BASED ON COPOPER–NITROXIDE COMPLEXES

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A study of the properties of molecular magnets is the subject of active interdisciplinary fundamental research in view of the high potential in creation of a new generation of functional materials and spintronic devices. A wide range of molecular magnets are known in which the structure and functional properties can change under the influence of external factors, for example, irradiation or variation of temperature, pressure, or electromagnetic field, or during redox processes. The effect of the external pressure remains least understood. The data of studies that compared the polymorphic transformations induced by temperature variation at different external pressures are especially scarce, though they provide important information about the fundamental properties of objects and serve as a basis for creating energy-independent pressure sensors for space and seismological studies and original devices capable of light emission at increased pressure or work at low temperatures under conditions of underground and deep-sea exploration. Heterospin compounds based on copper complexes with nitroxides, exhibiting effects similar to spin-crossover, belong to interesting objects for investigating the temperature-induced phase transformations at different pressures. The increase of pressure provokes a transition from high-spin to low-spin state, which again transforms into the high-spin state when the external load is removed. The solids under discussion are elastic and show reversible phase transformation which accompanied by a reversible contrastive change of color. Moreover, a study of the dynamics of the single-crystal-to-single-crystal transformation induced by temperature variation for some compounds showed that an increase in the hydrostatic pressure completely changes the intracrystalline displacements of molecules relative to one another. This, in turn, significantly affects the interaction energy of the unpaired electrons of the paramagnetic centers and hence the form of the temperature dependence of the effective magnetic moment. This phenomenon is under discussion as well.

The study was supported by the Russian Science Foundation (18-13-00380).

RECENT ADVANCES IN PHOSPHORUS CHEMISTRY

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In this lecture some of the most recent achievements in the field of the chemistry of elemental phosphorus, deriving from the author's own research in Florence (Italy) during the last two decades, will be presented and discussed.

The lecture will encompass the three allotropes of elemental phosphorus with particular emphasis to the extremely reactive and toxic white allotropic form and, on the opposite end, to the incredibly inert black allotrope. More in details, the lecture will include:

i) the ruthenium mediated activation of white phosphorus pointing out the unusual and fascinating hydrolytic degradation of the P4 molecule which follows its η1-coordination to the metal. The stepwise hydrolysis results in a variety of unusual Px fragments ($x \leq 4$), such as P-oxyacids, mono-, di-, and triphosphanes and hydroxyphosphanes, stabilised by coordination to one or two metal centers;[1]

ii) our most recent results in the chemistry of the less reactive allotrope of the element, i.e. black phosphorus, which may be easily exfoliated to form 2D-flakes of phosphorene (the all-P analogue of graphene).[2] This new material exhibits intriguing electronic properties and behaves as a perfectly tailored platform to host transition-metal nanoparticles[3] and, likely, to coordinate different transition metal fragments.[4,5]

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MP thanks all the coworkers listed in the references for their invaluable help in developing this chemistry. Thanks are also expressed to the European Research Council (ERC Grant Agreement No. 670173) for funding the project PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" through an ERC Advanced Grant. Finally, the Italian Ministry for Education and Research (MIUR) is kindly acknowledged for financial support through Project PRIN 2015 (grant number 20154X9ATP).

HIGHLY REDUCING ORGANIC PHOTOREDOX CATALYSTS AND THEIR APPLICATION TO FLUOROALKYLATION OF OLEFINS

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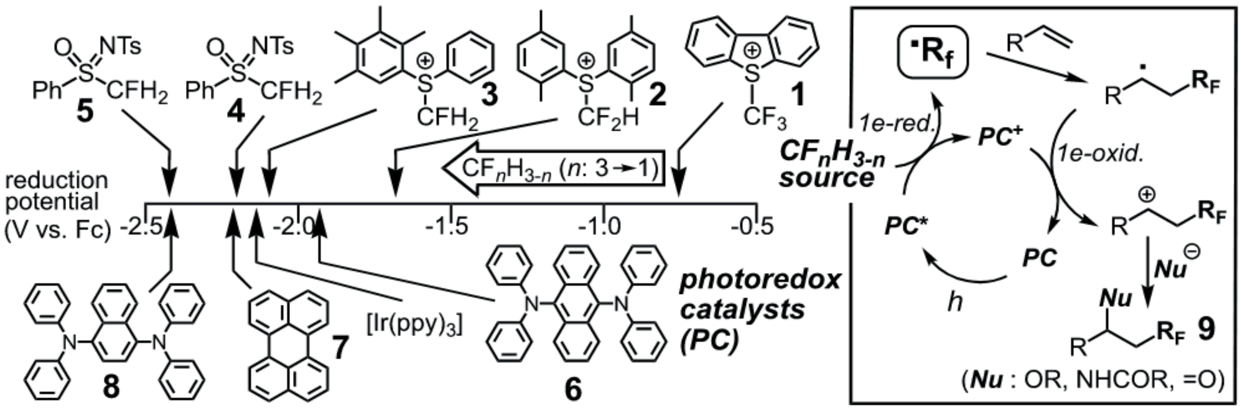
Fluoroalkyl groups (R_f) such as CF_nH_{3-n} groups are versatile structural motifs, especially in the fields of pharmaceuticals and agrochemicals, and development of simple methodologies for efficient and selective incorporation thereof into various organic skeletons is therefore highly demanded. On the other hand, *photoredox catalysis* via radical interediates[1] has attracted increasing attention as *a practical, green synthetic chemical process*, because it is promoted by visible light including sunlight. Herein we will present *various fluoroalkylations of olefins promoted by highly reducing organic photoredox catalysts*.

Cationic trifluoromethylating reagents such as Umemoto's reagent 1 turn out to be excellent CF_3 radical sources upon 1e-reduction by the action of photoredox catalysis ($PC^* \rightarrow PC^+ + 1e^-$).[2] But replacement of the most electron-withdrawing fluorine atom by a hydrogen atom (2, 3) causes significant negative shifts of the reduction potential. In addition, neutral precursors (4, 5) are more difficult to be reduced compared to the cationic ones, as readily anticipated. In order to expand the scope of not only fluoroalkylation via Rf radicals but also photoredox catalysis it has been demanded to develop highly reducing photoredox catalysts.



Taking into account this situation we developed highly reducing polyaromatic hydrocarbon catalysts 6 - 8, which were (1) even stronger than fac-[Ir(ppy)3] and (2) effective for various fluoroalkylative difunctionalization of olefins giving 9.[3]

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PALLADIUM-CATALYZED AMINATION IN THE SYNTHESIS OF CHIRAL MACROCYCLIC COMPOUNDS FOR FLUORESCENT ENANTIOSELECTIVE DETECTION

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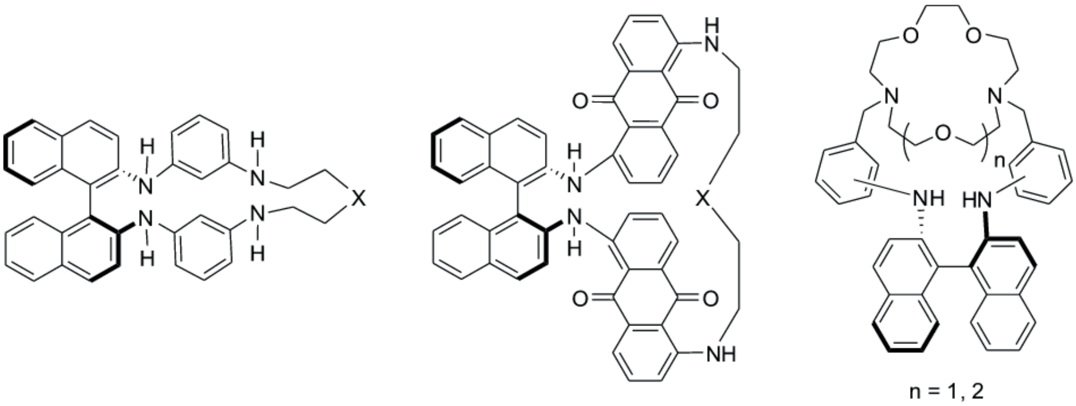
The development of the methodology of efficient detection of enantiomers of organic compounds envisages the use of fluorescent spectroscopy. In this connection the creation of detectors comprising chiral and fluorophore groups is actual. Such detector should be able to bind the analytes like amino acids and their derivatives, amino alcohols, diamine and diols. In this work we elaborated the synthetic approaches to various macrocyclic compounds containing polyoxadiamine fragments. The key step in the synthesis of such molecules is Pd(0)-catalyzed amination of aryl halides. As a result, we obtained planar-chiral macrocycles and macrobicycles on the basis of 1,5-diaminoanthraquinone, macrocyclic compounds comprising C2-chiral (S)-2,2'-dimino-1,1'-binaphthalene (BINAM) and various aromatic spacers. Also macrobicyclic BINAM derivatives on the basis of diazacrown ethers and tetraazamacrocycles (cyclen, cyclam) were synthesized. The investigations were carried out revealing the possibility to detect amino alcohols using fluorescent spectroscopy, the distinguishing between individual enantiomers was demonstrated.



The work was financially supported by RFBR, project No 18-03-00709.

ELECTRIFICATION OF ORGANIC SYNTHESIS. ON THE VERGE OF A RENAISSANCE

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We live in the period of integration of various fields of science, as a result of which their mutual enrichment takes place. The methodology of classical synthetic organic chemistry is increasingly evolving due to new approaches and principles that use in situ reagents, new materials and technological solutions. Direct use of electricity in organic synthesis is currently undergoing a renaissance. An important aspect of the electrochemical methodology is that many electrochemical processes meet the requirements of environmental cleanliness. From the point of view of implementation, such reactions have several advantages: mild conditions, high rates, process selectivity, as well as convenient operational control using parameters such as current density and potential, and the control is easy to automate.

Then organic chemistry is currently aimed at the development of ideal transformations to synthesize the complicated molecules that are effective, economical and environmentally friendly. Functionalization of carbon-hydrogen bonds catalyzed by transition metals, which convert the widespread, but, as a rule, inert C–H bonds directly to C–C and C–heteroatom bonds are very promising in this regard. An idea arose to use the possibilities of organic electrosynthesis with the participation of metal-complex catalysts for solving these problems, both homogeneous catalysts and those immobilized on silicate matrix. Nanocatalysis allows to make the chemical process more environmentally acceptable, to regenerate the catalysts. The use of electrocatalysis by transition metals for the purpose of aromatic C–H functionalization, that is, the introduction of perfluoroalkyl, fluorine and phosphonate groups, showed a high potential of this method, which allows to obtain various practically important products. The proposed approaches represent a new practical way to synthesize valuable fluorinated and phosphorylated products, potentially important in the pharmaceutical and agrochemical industry, with the most atom-saving, environmentally acceptable, meeting the high requirements of modern chemistry.

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COMPARATIVE ANALYSIS OF THE EFFICIENCY OF METHODS OF CONTROLLED RADICAL POLYMERIZATION (ON THE EXAMPLE OF SYNTHESIS ACRYLONITRILE POLYMERS)

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Controlled synthesis of polymers under the conditions of radical initiation is one of the priorities for the development of the synthetic chemistry of polymers and is an effective tool for macromolecular design. In particular, using this methodology, it is possible to synthesize high-molecular compounds of a given structure with certain molecular mass characteristics, which ultimately determines the properties of polymer molecules and materials based on its.

Experimental data on the laws of the synthesis of acrylonitrile homo- and copolymers by three main methods of controlled radical polymerization are analyzed: reversible inhibition (in the presence of nitroxyl radicals of various structures), reversible chain transfer (with the participation of a number of sulfur-containing compounds) and atom transfer (complexes of copper, ruthenium, iron and other transition metals). It has been established that polymerization by atom transfer mechanism involving copper complexes with nitrogen-containing ligands is the most effective tool for the directed synthesis of acrylonitrile (co) polymers as precursors for the production of high-strength carbon fiber.

The effect of various comonomers and composition of the monomer mixture, as well as the ligand environment of the metal complex and initiator structure on the molecular mass characteristics of the synthesized co- and terpolymers based on acrylonitrile and other (meth)acrylic monomers, was evaluated.

The effect of the composition of these polymers on their thermodynamic properties is estimated by the method of scanning calorimetry. It has been shown that the introduction of methyl acrylate and dimethyl itaconate units, as well as a number of other (meth) acrylic comonomers into the polyacrylonitrile molecules, significantly reduces the probability of carbon fiber destruction at high temperature and leads to a smoother course of the process of thermal exposure of the polymer during carbon fiber formation.

This work was supported by the Russian Foundation for Basic Research, project No. 17-03-00498.

CHARGE-TRANSFER CHEMISTRY OF CHALCOGEN-NITROGEN Π-HETEROCYCLES

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Chalcogen-nitrogen π-heterocycles (chalcogen: S, Se and Te) and their derivatives and hybrids possessing positive electron affinity (EA) are used in the design and synthesis of perspective multifunctional building blocks for molecule-based magnetic, conducting and light-emitting functional materials.[1-5]

This report will present and discuss recent achievements in the charge-transfer chemistry of the title heterocycles, mostly 1,2,5-chalcogenadiazoles. A large series of these species with EAs up to ~3 eV were designed on the basis of quantum chemical calculations.[6] Derived radical anions (RAs), RA salts, charge-transfer (CT) complexes, and metal coordination compounds were prepared and structurally and functionally characterized. Magnetic properties of RA salts, photoconductivity of CT complexes, and light-emitting properties of metal coordination compounds were studied experimentally and analyzed using DFT calculations.

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DEVELOPMENT OF PHOTOACTIVE SUPRAMOLECULAR DEVICES AND MACHINES

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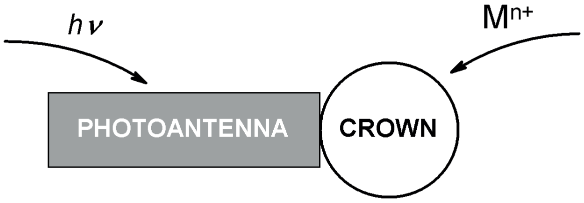
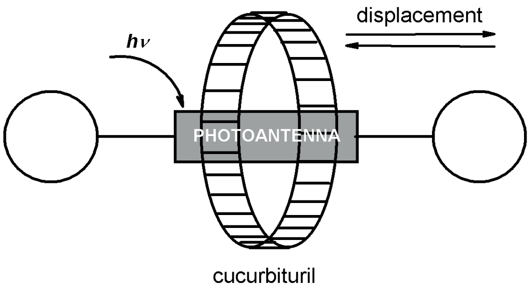
We propose an unique class of polyfunctional photoactive compounds: unsaturated (polymethine) dyes. A large body of research has been performed for their synthesis, determination of their spatial structures, study of self-assembly features to give supramolecular systems, and also study of fluorescent, photochemical and complexing properties.

Resulting from the research, we elaborated for the first time universal supramolecular meccano, allowing one to accomplish building-up, with using a limited number of complementary compounds with participation of metal cations and hydrogen bonds, photoactive supramolecular systems of varied architecture with adjusted properties. Within the same class of compounds one can construct in solution, solid and at the air-water interface new types of photoswitchable supramolecular devices and photocontrolled supramolecular machines susceptible to all of the key photoprocesses.



supramolecular devices



supramolecular machines

The high practical value of these studies deserves attention. They provide a new strategy for the design of materials for supramolecular and organic nanophotonics, which was demonstrated, first of all, by the creation of practically important sensor and photochromic materials.

This work was supported by the RFBR (project No. 18 03 00214), the Russian Science Foundation, the RAS, the Ministry of Science and Education, the Moscow Government, the INTAS, the CRDF, the DFG, the Royal Society, and the ISF.

AMINO ALCOHOLS AND THEIR TIN DERIVATIVES. SIMPLE CHEMISTRY WITH ECONOMIC POTENTIAL

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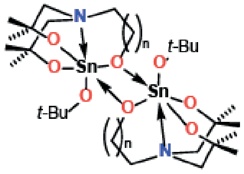
The first report on amino alcohol derivatives of tin dates back to 1967[1]. Since then a number of papers have appeared on both Sn(IV) and Sn(II) amino alcohol derivatives including so-called stannabicyclo[3.3.0]octanes, $RN(CH_2CH_2O)_2M$ (M = Sn, SnX_2, X = organic substituent, halogen, alkoxide etc.), and stannatranes, $N(CH_2CH_2O)_3SnR$. The chemistry of these compounds has been thoroughly reviewed [2-4]. Motivated by the extraordinary delayed-action catalytic activity of novel inorganic, non-toxic representatives of these compounds in polymerization reactions,[5] we looked again into this chemistry. The syntheses, the structures in solution and in the solid state, and the reactivity of novel Sn(II) and Sn(IV) derivatives that are based on structurally modified and in part chiral amino alcohols[6-8] will be presented. Controlled hydrolysis of selected stannatranes provided novel tin oxoclusters such as A – C.



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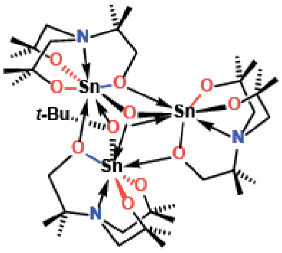

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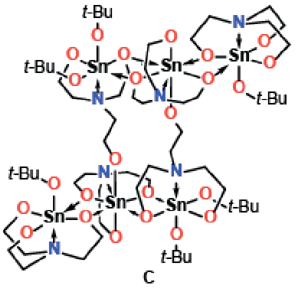

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DESIGN OF NOVEL LUMINESCENT COMPLEXES BASED ON CYCLIC HYBRID PHOSPHINES

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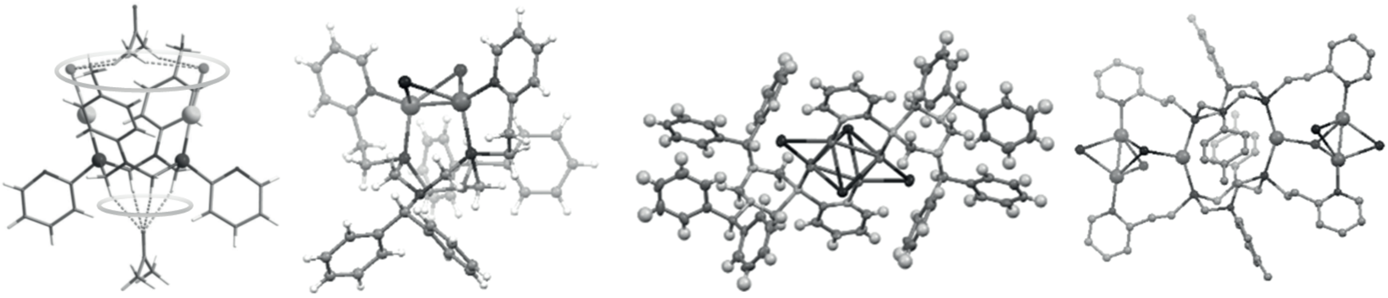
Within the last decade a variety of gold(I) and copper(I) complexes based on cyclic phosphine scaffold has been obtained.[1] Due to the presence of exocyclic chromophoric pyridyl or thienyl groups in the ligands complexes demonstrate noticeable luminescence in visible and near infrared regions. Cyclic nature of the phosphine ligands is responsible for supramolecular host-behavior of the complexes. [2,3]



Unique structure of the complexes favors the stimuli-induced structural reorganizations followed by stimuli-responsive luminescence. Organic molecules and cations are revealed as the "guests" inducing concentration-dependent changes in the emission of the complexes.[2-4] The fluorescent response of gold complexes stabilized in hydrophilic core-shell colloids on L-cysteine as biorelevant representative of thiols enables to recognize it in the buffer solutions with the detection limits about 1 μM.[5] Number of novel polynuclear copper clusters with Cu_2I_2, Cu_4I_4 and unusual Cu_3I_3 metal cores demonstrate temperature dependence of luminescence in wide range of external temperatures. Therefore, the complexes are versatile building blocks for bottom-up design of smart nanomaterials for analytical and biomedical applications.

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METAL COMPLEXES IN THE SYNTHESIS OF BIODEGRADABLE POLYMERS

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Biodegradable polymers gain the increasing value for the industry, health care and other industries of human activity every year. First of all use of these compounds instead of classical materials on the basis of polyolefins allows to minimize human activity consequences, in particular pollution by not decomposed plastic, for planet ecology. On the other hand biodegradable polymers are broadly used in medicine, for example as a suture material and containers for drugs of the prolonged action.

The most important among these substances are polymers of cyclic esters: polylactide, polyglycolide, poly-ε-caprolactone. At the same time constantly grows the need for new types of such polymers and copolymers considerably differing with the physical and chemical characteristics in connection with expansion of a range of problems which solve with use of biodegradable polymers.

The main approach to their synthesis realized now commercially is ring open polymerization (ROP) of cyclic ethers under action of the initiator to which in most cases serves the complex of metal which is Lewis acid. It is well known that the structure of a ligand environment most defines the geometry and electronic structure of metal complex. Varying of the structure of a ligand allows to vary both geometry of a coordination polyhedron of metal, and its effective charge, and, therefore, defines properties of the obtained polymer.

In the report will are presented the researches for the last few years devoted to synthesis of new ligands NO -, to NNN-, NNO-, NOO-, NOOO-, NNNN-, NNOO types, to preparation on the basis of these ligands of the Al, Ga, In, Ge, Sn, Zn and Ti complexes, to studying of structure and properties of these substances, including activity as the initiator in ROP reactions.

The represented researches were partially supported by grants of RNF (14-13-01456), the Russian Federal Property Fund (09-03-00536-a, it 12-03-90020-is white, 12-03-00206-a, 18-29-17029), the Russian President's grant for young doctors of science (MD-3634.2012.3).

CATALYTIC HYDROGENATION WITH PARAHYDROGEN

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Hydrogenation of unsaturated compounds with molecular hydrogen can lead to significant signal amplification in NMR and MRI, if parahydrogen is used instead of ordinary H_2. This provides important information on the existence and the nature of the active catalytic sites that can implement the pairwise addition of H_2 to a substrate. We have established the fact that such centers of pairwise H_2 addition do exist on supported metal catalysts, which was rather unexpected since such a reaction mechanism is usually associated with homogeneous hydrogenation through the formation of a dihydride metal complex. The pairwise addition of H_2 is demonstrated by us for other types of heterogeneous catalysts as well, including metal oxides, their sulfides, carbides, etc.

With the purpose of a deliberate creation of catalysts possessing centers of pairwise hydrogen addition to a substrate, we used isolated metal-based structures on the surface of a support, such as single-site/single-atom catalysts[1]. Examples of such systems for which we were able to observe the pairwise addition of hydrogen include isolated Co(II),O centers on SiO_2, Cr(III),O on SiO_2-Al_2O_3, oxo-vanadium complex on SiO_2, and others. The greatest activity in pairwise hydrogen addition was observed, in particular, with bimetallic catalysts. These include catalysts with the Aushell-Pdcore nanoparticle structure deposited on pyrolytic graphite, as well as Pd-In/Al_2O_3 catalysts - single-site systems in which the active metal atom is isolated by a group of atoms of an element which is inactive in the reaction.

The enhancement of the NMR/MRI signals using parahydrogen in catalytic hydrogenation reactions, in addition to important mechanistic information about these processes, makes it possible to perform MRI studies of operating reactors, as shown by the example of model systems with Rh nanoparticles on a TiO_2 layer deposited on glass tubes or plates. This approach allowed us to visualize the catalytically active regions of the model reactor during the hydrogenation of propene[2].

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EFFECT OF VARIOUS FACTORS ON SPIN-CROSSOVER CHARACTERISTICS IN IRON(II) COMPLEXES WITH NITROGEN-CONTAINING LIGANDS

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Spin-crossover (spin transition) in the coordination compounds of 3d-metals with d^4-d^7 electron configuration represents one of the most interesting phenomena in chemistry of coordination compounds [1, 2].

The change in the spin multiplicity occurs under the action of external factors such as temperature, pressure, or light irradiation with a certain wavelength. The compounds that exhibit "bistability" properties, i.e., the ability to exist in the two states such as a low-spin state ($S = 0$) and a high-spin state ($S = 2$) having a sufficiently long lifetime, could be used as materials for molecular electronics, in particular, in order to make displays and systems of memory.

The report is devoted to the synthesis and study of iron(II) complexes with three classes of heterocyclic ligands containing several nitrogen atoms: 1,2,4-triazoles, *tris*(pyrazol-1-yl)methanes and 2,6-*bis*(benzimidazol-2-yl)pyridine (L). The study of the dependence $\mu_{eff}(T)$ have shown that the mentioned compounds exhibit spin-crossover $^1A_1 \leftrightarrow {}^5T_2$. Iron(II) complexes with 1,2,4-triazoles having different compositions exhibit SCO temperature (T_c) values ranging from 200 to 400 K, whereas Fe(II) complexes with tris(pyrazol-1-yl) methanes show the SCO temperature to be in the range of 340–470 K. For both classes under consideration, T_c considerably depends on the composition of the complexes, i.e. on the type of ligand, on the type of anion, and on the number of crystallization water molecules. We have obtained novel Fe(II) sulfate, hexafluorosilicate and perrhenate complexes with 2,6-bis(benzimidazol-2-yl)pyridine (L). For $[FeL_2](ReO_4)_2$, abrupt spin-crossover is observed with the hysteresis on the $\mu_{eff}(T)$ curve ($\Delta T = 21$ K),

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HETARYLFUROXANS – PERSPECTIVE NO-DONORS: SYNTHESIS AND CYTOTOXIC ACTIVITY

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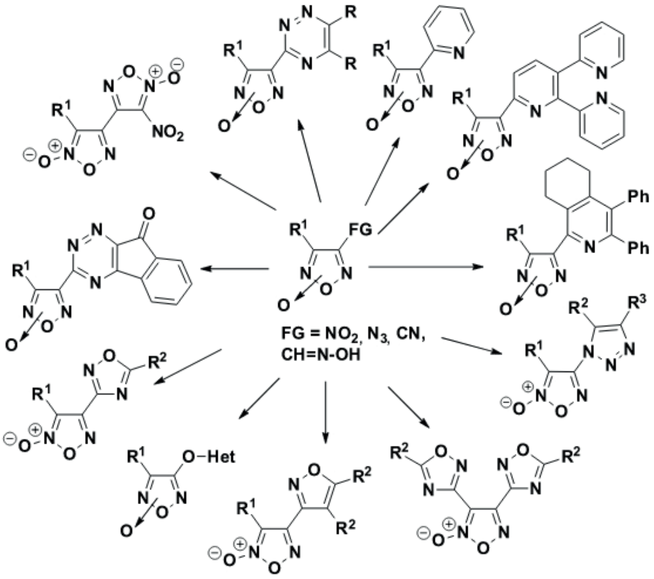
One of the widespread approaches for the design of potential drugs with improved pharmacokinetic profile is based on the synthesis of hybrid structures including a frameworks capable to nitric oxide (NO) release. The furoxans (1,2,5-oxadiazole 2-oxide) are one of the most effective NO-donors.[1,2]

In this work the package of new, simple, regio- and diastereoselctive methods for the synthesis of wide set of hetarylfuroxans - potential NO-donors, comprising of furoxan moiety and pharmacophoric heterocycles has been presented. The methods are based on the transformations of different available functional furoxan derivatives (NO_2, N_3, CN, CH=NOH). Along with synthesis the cytotoxic activity of some synthesized hetarylfuroxans was revealed and experimental evaluation of their NO-donor capacity was performed.[3-6]



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NOVEL UNUSUAL CHEMICAL COMPOUNDS AT HIGH PRESSURES AND IN LOW DIMENSIONS

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Until mid-2000s it was thought that crystal structures are fundamentally unpredictable. This has changed, and a special role in this was played by our evolutionary method/code USPEX (uspex-team.org). USPEX, developed by my group since 2004, now has over 5000 registered users worldwide. With USPEX it is routinely possible to predict stable crystal structures for a given chemical composition], and even to predict all stable compounds formed by given elements. I will describe results of our recent works along several lines:

1. Discovery of novel chemical phenomena: transparent non-metallic allotrope of sodium, counterintuitive novel sodium chlorides, chemical reactivity of helium.
2. Prediction and experimental realization of new high-temperature superconductors, approaching room-temperature superconductivity.
3. Prediction of novel chemistry of nanoparticles and possible explanation of carcinogenicity of oxide dust.

I will explicitly mention currently open problems in interpreting these new results, as well as current limitations and future prospects of structure prediction methods.

CHEMICAL ASPECTS OF LUMINESCENCE AND MODERN TRENDS FOR DEVELOPMENT OF NEW LUMINOPHORES

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Luminescence as a physical phenomenon, inherent only to special substances - luminophores, capable of emitting light under external influence, has been known for almost 300 years, but its practical application luminescence began to find only in the middle of the last century as a result of the creation of a scientifically based theory of luminescence, rapidly penetrating into all spheres of human activity.

Development of phosphors and luminescent materials is an urgent task of fundamental and applied chemistry. Luminophores are widely used not only for luminescent analysis and diagnostics in engineering, physics, chemistry, biology, medicine, criminology, etc., but also in multi-tonnage production of various luminescent materials, fluorescent paints, light-emitting devices for various purposes, including fluorescent and led lamps, electronic information display systems.

Over the past period, three generations of phosphors have been replaced. Initially, these were inorganic crystallophores, the glow of which is due to the presence in the crystalline substance of a small amount of luminescent ions of transition and rare earth metals.

Then another class of phosphors began to be actively introduced - molecular organic and organometallic phosphors, spectral luminescent properties of which are achieved by chemical design of the structure of luminescent molecules using wide range of methods of fine chemical synthesis, and the necessary performance characteristics through the use of polymeric binders.

Recently, a new promising class of phosphors has appeared - quantum dots (QDs) with a narrow luminescence band of 20-30 nm, the position of which in the spectral range from 350 to 3500 nm is set by changing the average size of the QDs in the range from 2 to 10 nm.

The report presents an analysis of the current state of the fundamental physical and chemical bases of luminescent properties of the substance, discusses the chemical aspects and current trends in the creation of new fluorescent materials, problems and prospects of their application.

ELECTRICAL EFFECTS IN COMMON POLYMERS AND COMPOSITES DURING IRRADIATION

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This work discusses the present-day situation in experimental and theoretical studies of radiation induced conductivity (RIC) and bulk charging of polymer dielectrics.

It has been established that RIC as a rule is determined by transport of a one-sign carrier and namely, a hole. Effect of molecular relaxations on hole transport is considered. Dispersed fillers are shown to increase RIC of composites. For a number of polymers and composites, experimental results for irradiations 40 ns to 100 s long have been compared with numerical simulations including model parameter extraction.

RIC behavior at strong pre-breakdown fields are discussed. Numerical simulations of the bulk charging of polymers by fast electrons have been done. Time dependence of non-stationary currents in polymer dielectrics under electron irradiation have been described with due account of RIC kinetic features at strong electric fields.

THE NEW THREE-COMPONENT REACTIONS OF POLYFLUOROALKYL-3-OXO ESTERS, METHYL KETONES AND AMINES

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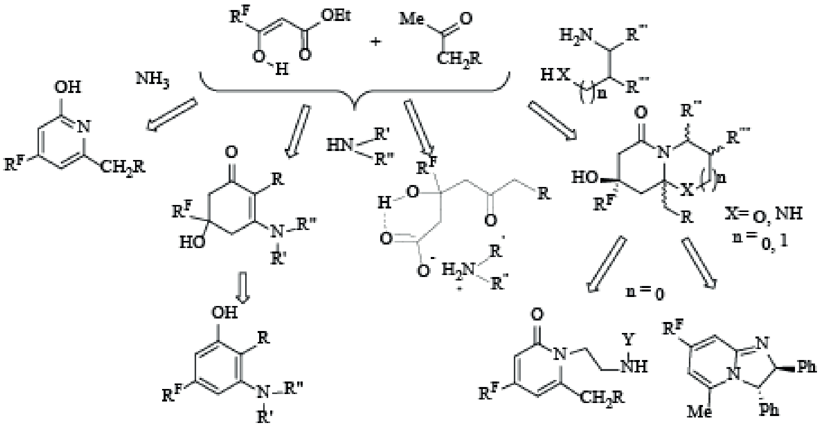
Multicomponent reactions are one of the main trends of the modern organic chemistry. The known Biginelli's and Hantzsch's cyclizations, which are extensively used in various syntheses, are based on the transformations of 3-oxo esters with aldehydes and amines.[1] Recently, we have found the new three-component transformations of polyfluoroalkyl-3-oxo esters with methyl ketones and amines. The routes of these reactions are established to essentially depend on being used amine. Variation of the amine component allows us to obtain a wide range of compounds, including pyridine derivatives and their heterocondensed analogs[2,3], 3-aminoalkylcyclohexenones and etc.[4] The aspects of the targeted synthesis of the certain class of products are discussed in the report. The special attention is paid to the mechanisms of these reactions. In addition, the data on the biological activity of the synthesized compounds are presented.



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FORMATION AND GROWTH OF MULTICOMPONENT BUBBLES AND DROPLETS

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There are two general approaches to theory of first-order phase transitions in a closed system with a limited availability of the nucleating species: the approach with the mean-field supersaturation and the approach with the excluded volume. The first approach implies that nucleation and growth of supercritical new-phase particles is governed by stationary diffusion of molecules and accompanied by a synchronous and uniform decrease in the mean supersaturation.[1,2] The excluded volume approach is based on a self-similar solution for non-stationary diffusion onto the growing supercritical particles and takes into account that the nucleation of new particles is strongly suppressed around growing particles.[3-6]

In this communication, we report new theoretical results for the nucleation stage of gas bubble formation in liquid solutions and droplet nucleation in supersaturated vapors with arbitrary number of components and any supersaturation values. The nucleation stage is an important stage of degassing in decompressed liquid-gas solutions and condensation in supersaturated vapors, on which a certain size distribution of gas bubbles or liquid droplets is formed, being the starting point for further growth. It has been recently shown[7] that the initial composition and size dependence of the surface tension of a small supercritical bubble does not affect the peculiarities of the development of the nucleation stage, but affects the rate of nucleation at the initial total supersaturation. Analysis of the effects of non-stationary diffusion confirmed that they can be very significant in the growth of multicomponent bubbles and, in particular, are responsible for large swelling and foaming the decompressed liquid solution. An extended mean-field approach that allows one to find all vapor supersaturations and the distribution of supercritical droplets in sizes as functions of time on the nucleation stage, has been proposed[8] for a real multicomponent solution in the droplets.

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GALLIUM COMPLEXES OF METHYLIDENEMALONATES AND DONOR-ACCEPTOR CYCLOPROPANES – PROSPECTS OF APPLICATION IN ORGANIC CHEMISTRY

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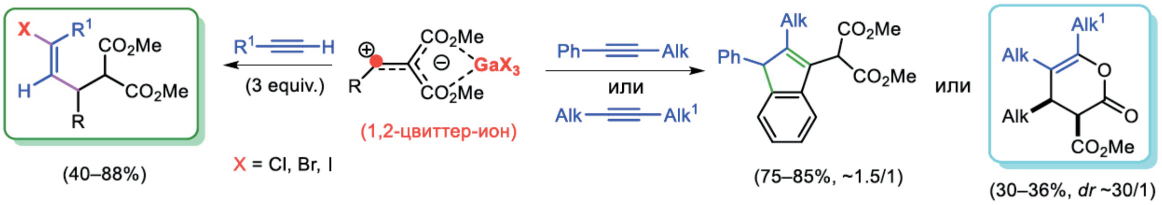
New processes involving reactions of donor-acceptor cyclopropanes (DAC), in particular, 2-arylcyclopropane-1,1-dicarboxylates (ACPC), or substituted methylidenemalonates, with various acetylenes in the presence of gallium halides have been developed[1,2]. The key step of these processes involves generation of 1,2-zwitterionic intermediates followed by addition of the latter to the triple bond in acetylenes. The subsequent reactions of the intermediates that are formed (vinyl cations) are determined both by the nature of the substrates used and the reaction conditions. For example, selective formation of substituted (3-haloallyl)malonates is rather a common process of the reactions of ACPC or methylidenemalonates with terminal alkynes in the presence of GaX_3. In addition to the main process, the reaction may also follow other pathways. For instance, reactions of alkynes Ar–C≡C–Alk with benzylidenemalonate in the presence of $GaCl_3$ gives products of annulation of the malonate substrate at the aromatic ring to give isomeric indenes in high yields, whereas in the case of alkylidenemalonates, another interesting process occurs to give 6-membered lactones with high diastereoselectivity. In this case, the vinyl cation is stabilized by one of the ester groups.



We also studied the complexation of methylidenemalonates with metal halides[2], including $GaCl_3$ and $GaBr_3$, where three malonate ligands are coordinated to one gallium atom to give three GaX_4^- anions.

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ISOTOPIC RESONANCE - THE FIRST DECADE

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Isotopic resonance (IsoRes) is a postulation that the rates of chemical and biological reactions are affected nonlinearly and non-canonically by the specific ratios between different stable isotopes. The average terrestrial isotopic compositions of the elements C, H, N and O happen to be close to the resonance values. The IsoRes hypothesis formulated in 2008 predicted that the terrestrial IsoRes affected all chemical and biochemical reactions on Earth and enhanced the chances of early life to either emerge or take root on our planet [1]. For the following decade, the existence of the IsoRes phenomenon in biology and biochemistry has been extensively tested experimentally and verified by at least two independent groups. Of the important IsoRes isotopic compositions, besides the terrestrial one, is the monoisotopic resonance as well as the resonances at around 350 ppm deuterium [2] and another one at 3.5% ^{15}N [3], with all other isotopic ratios being normal. The fact that both Mars and Venus seem to have no resonance, underlies the potential importance of the IsoRes phenomenon in space exploration and astrobiology [4].

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REACTION OF NITROALKENES WITH INDOLES AS ROUTE TO SPIRO[INDOLE-3,5'-ISOXAZOLES] WITH ANTICANCER ACTIVITY

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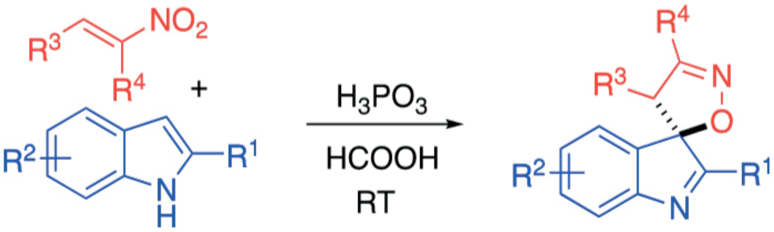
Development of synthetic approaches towards alkaloid analogs containing indole fragment, can be considered one of the central topics of modern organic and medicinal chemistry. Recently we communicated on the novel investiga-tions of antitumor properties of 2-aryl-2-(3-indolyl)acetohydroxamic acids that demonstrated significant activities against glioma, melanoma, esophageal carci-noma and many other cancer cell lines inherently resistant to the apoptosis in-duction and poorly responsive to the medical treatment with traditional pro-apoptosis medicinal agents. Expanding the scope of the structures we faced a necessity to develop synthetic approaches towards structural analogs unavailable via previously used methods. The scope of such analogs would include both hydroxamic acids and their cyclic derivatives. The latter class comprises, for example 4’H-spiro[indol-3.5’-isoxazoles], which not only related to hydroxamic acids structurally, but also can be viewed as analogs of some natural products, and therefore are very attractive objects for biological studies.

An unusual asid-assisted transformation of nitrostyrenes was discovered, which permits the employment of these readily available synthons as 1,4-CCNO-dipole surrogates in a highly diastereoselective (4+1)-cycloaddition of indoles to afford 4'H-spiro[indole-3,5'-isoxazoles] in a diastereomerically pure form:



The mechanism of this transformation was investigated and optimization of reaction conditions was performed. Acetic and Formic acids proved to be opti-mal solvents for the featured process. The influence of different Bronsted acids was also investigated.

This project was supported by grants from the Russian Science Foundation (Grant number 18-13-00238).

2-KETIMINO-1,8-BIS(DIMETHYLAMINO)NAPHTHALENES IN THE SYNTHESIS OF 9-DIMETHYLAMINOBENZO[G]INDOLES

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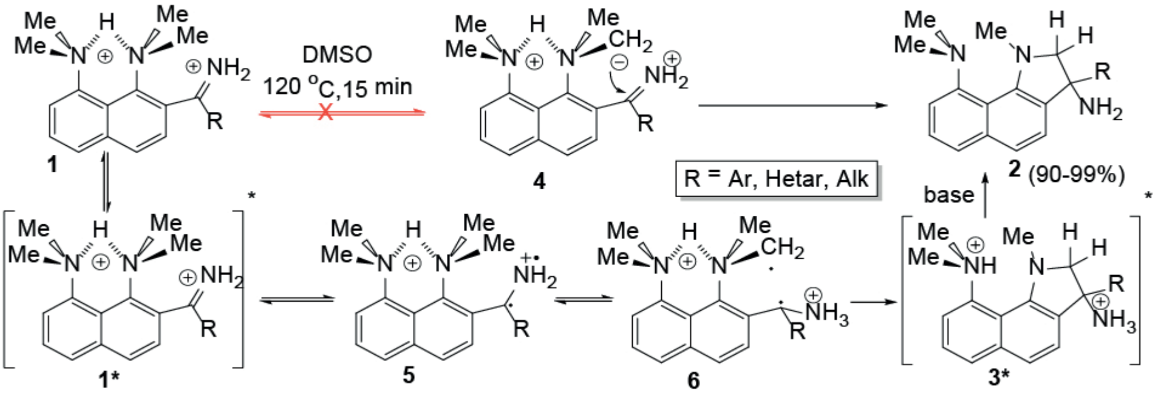
Pyrroles, including condensed ones, are one of the most common types of heterocyclic systems in nature and the pharmaceutical industry. This is the reason why dozens of methods of synthesis of these important heterocycles were developed in the past two decades. *Ortho*-ketimines of 1,8-bis(dimethylamino)naphthalene (DMAN) were reported by our research group as convenient substrates for the synthesis of ketones, oximes and benzo[h]quinazolines.[1–3] Recently we have shown that DMAN *ortho*-ketimines can easily form stable dications 1 upon treatment with tetrafluoroboric acid.[4] Surprisingly, heating of 1 in DMSO leads to the fast and selective cyclisation into 2,3-dihydro-benzo[g]indoles 2 with excellent yield:



It is unlikely that the mechanism of this unusual transformation involves acidic ionization of an NMe group, since it is difficult to imagine the formation of the zwitterionic intermediate 4 under these essentially acidic conditions. Performed quantum chemical calculations have demonstrated that this reaction occurs as a radical process somewhat like the Norrish type II reaction via the biradical 6. It is not yet clear what the source of this radical formation is, since the reaction proceeds in darkness and no oxidant is used.

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NEW LUMINESCENT COPPER(I) AND SILVER(I) COMPLEXES BASED ON P,N-LIGANDS

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Over the past decades, complexes based in coinage metals (Cu^I, Ag^I, Au^I) have attracted considerable attention as an alternative for commonly used luminescent materials.[1] Therefore, the search of new effective emitting group 11 metal based complexes represents a challenging task.

Recently, we have synthesized and studied a series of new brightly emitting Cu^I and Ag^I complexes with tris(2-pyridyl)phosphine and related ligands (Figure 1).

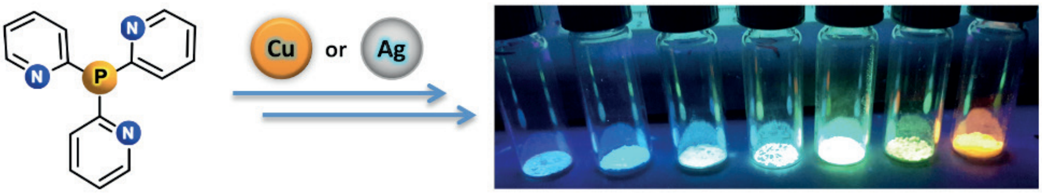

Рисунок 1.

The report discusses: luminescent Cu^I complexes with tris(2-pyridyl)phosphine and similar ligands;[2,3] structurally unprecedented Ag^I clusters with tris(2-pyridyl)phosphine;[4] mechanochemical synthesis of CuI-based coordination polymers; thermo-, mechano- and vapochromшс luminescence of the Cu^I and Ag^I complexes with P,N-ligands.

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SYNTHESIS AND TRANSFORMATIONS OF BRIDGEHEAD AZOLES

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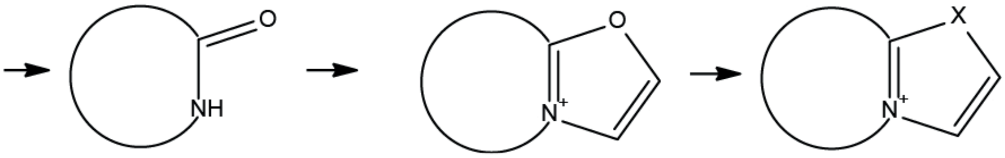
Bridgehead azoles, and in particular oxazolo[3,2-a]pyri(mi)dines and their analogs containing oxazole fused with 4-, 5- and 6-membered saturated cycle, are important and not well examined class of heterocycles.[1,2]



The talk is devoted to the synthesis of such fused oxazole structures and their behavior towards attack of (bi)nucleophiles leading to exchange of oxygen in the ring to one or two carbon or nitrogen atoms.

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STUDY OF THE FORMATION OF HIGHLY BRANCHED POLYACRYLONITRILE

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Hyper- and highly branched polymers (HBP) are a class of compounds with an unusual topology and a number of unique properties compared to their linear or cross-linked analogues. In particular, HBP have a nanoscale structure, good solubility, high sorption capacity, low viscosity of solutions and melts, etc. These properties provide the use of HBP, for example, as additives to traditional polymers to modify their physico-chemical, mechanical and technological pro-perties. So, one of the important current tasks in creating carbon fibers based on polyacrilonitrile (PAN) synthesized by radical polymerization is to reduce viscosity/increase the concentration of spinning solutions during the molding of polyacrylonitrile fibers (PAN precursor). This is important in terms of im¬proving the quality of the «white» fiber and reducing the cost of the final carbon fiber. Using HBP, that reduce the viscosity of spinning solutions and at the same time have a composition similar to PAN, seems promising. High-branched polyacrylonitrile which is the subject of this work may meet these required needs.

The report presents the method for obtaining and ways of managing the properties of the highly branched PAN synthesized by anionic polymerization of acrylonitrile under the action of the initiating system that we have developed: 1,4-diazabicyclo [2.2.2] octane - ethylene oxide. Properties of the branched PAN depending on the conditions of polymerization were studied, the mechanism of its formation was proposed and the estimated values of the average number of branches per macromolecule were obtained using experimental and theoretical approaches.

The study was carried out with the financial support of the Russian Founda-tion for Basic Research in the framework of research projects No. 18-03-00612 and No. 18-29-17058.

SMART CONTROL OF NITROXIDE-MEDIATED POLYMERIZATION INITIATORS' REACTIVITY BY PH, COMPLEXATION WITH METALS, AND CHEMICAL TRANSFORMATIONS

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Because alkoxyamines are employed in a number of important applications, such as nitroxide-mediated polymerization [1], radical chemistry, redox chemistry, and catalysis, research into their reactivity is especially important. Typically, the rate of alkoxyamine homolysis is strongly dependent on temperature. Nonetheless, thermal regulation of such reactions is not always optimal. There are several factors that influence reactivity of alkoxyamines. Among them, electron-withdrawing and electron-donating properties of substituents are of special importance in terms of the influence on reactivity of the C–ON bond. In this report we overview various ways to reversibly change the rate of C–ON bond homolysis of alkoxyamines at constant temperature. The major methods influencing C–ON bond homolysis without alteration of temperature are protonation of functional groups in an alkoxyamine [2], formation of metal–alkoxyamine complexes [3-5], and chemical transformation of alkoxyamines [6]. Depending on the structure of an alkoxyamine, these approaches can have a significant effect on the homolysis rate constant, by a factor of up to 30, and can shorten the half-lifetime from days to seconds. These methods open new prospects for the application of alkoxyamines in biology and increase the safety of (and control over) the nitroxide-mediated polymerization method.

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NEW SYNTHETIC SOLUTIONS TO OBTAIN BIOLOGICALLY ACTIVE ORGANIC POLYSULFIDES

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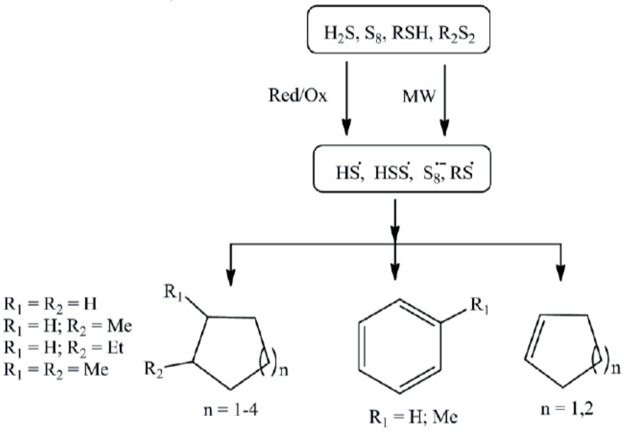
In the paper, a new approach to the synthesis of different polysulfides (R2Sn, n = 2-4) is proposed. This method is based on the electrochemical and microwave activation of the available sulfur-contaning reagents. S-functionalization of inert hydrocarbons proceeds under mild conditions due to the generation of reactive, sulfur-centered intermediates.



As a result of the reactions, symmetric and asymmetric R_2S_n were synthesized. The yield of polysulfides depends on the method of reagent activation, the electrolysis time (or time of MW), the electrode surface area (irradiation power) and the ratio of components. Along with direct redox activation of sulfur reagents, the synthesis of R_2S_n with the participation of organic and metal complex mediators was carried out. The application of reagents mixtures ($H_2S + S_8$, $RSH + S_8$, $H_2S + R_2S_2$) made it possible to significantly increase the selectivity of reactions for tri- and tetrasulfides.

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NONCOVALENT INTERACTIONS INVOLVING SQUARE-PLANAR NICKEL(II) COMPLEXES

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The study of noncovalent weak interactions involving transition metal complexes attracts a permanent interest due to the possibility of controlling the useful properties of materials based on these complexes, i.e. various types of biological activity, luminescent, magnetic, catalytic properties, etc.1–2. Complexes exhibit great possibilities for manifestation of noncovalent interactions of various types. Square-planar nickel(II) complexes bearing organic ligands are able to form short contacts both with involvement of functional groups from an organic ligand and/or a sterically accessible metal center.

X-ray diffraction structures of various adducts of the bis-chelate nickel(II) complexes $[Ni\{NH{=}C(NR_2)NN(O)\}_2]$ (R_2 = Me_2, Me/Ph, C_5H_{10})[3–4] and $[Ni\{o\text{-}C_6H_4(NO)(NOH)\}_2]$[5] with such halogen bond (XB) donors as molecular I_2, tetrafluorodiiodobenzenes (1,2-$C_6F_4I_2$ and 1,4-$C_6F_4I_2$), sym-trifluorotriiodobenzene (1,3,5-$C_6F_3I_3$) were studied and XB and semicoordination linkages contacts were recognized. Existence of weak noncovalent interactions that involve organic ligands, viz. hydrogen bonding, XB, π-stacking etc., was identified based upon XRD parameters and appropriate DFT calculations. We demonstrated that nickel(II) centers can form semicoordination bonds and contact, which is intermediate between semicoordination and metal-involving XB.

The structural features of the obtained associates and noncovalent bonding patterns will be discussed. Special emphasis will be put on contacts involving metal centers.

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This work was supported by RSF (project 19-13-00013).

CREATION OF NEW SKELETON PHOSPHONATES - SEMI-PRODUCTS FOR THE DESIGN OF DIFFERENT TYPES OF LINEAR AND MACROCYCLIC PHOSPHORUS CONTAINING STRUCTURES

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The chemistry of organophosphorus skeleton compounds has recently achieved significant success, both in synthetic and applied aspects. To date, significant data have been accumulated in the literature on the synthesis of skeletal compounds, the cyclic skeleton of which is formed from various types of endocyclic P – E bonds (E — oxygen, nitrogen, carbon atoms). Practical interest in such rigidly structured structures is determined by the possibility of using them as complex-forming agents, ligands in metal-complex catalysis, organocatalysts, as well as wide-spectrum drugs. This report presents the results of our work on the synthesis of previously unknown symmetric skeleton phosphonates obtained as a result of a new cascade reaction of 2-ethoxyvinyl dichlorophosphate with various phenols; demonstrated an original approach to the synthesis of a new class of skeleton phosphonates of asymmetric structure on the platform of phosphorinin derivatives; The first results of the synthesis of regioisomeric skeleton phosphonates are presented. The creation of new types of receptor systems on the platforms of symmetric and asymmetrical skeleton phosphonates is discussed.

The reported study was funded by RFBR according to the research project № 17-03-00254

SYNTHESIS OF PYRAZOLYLPYRAZOLO[1,5-a]PYRIMIDINES BY RECYCLIZATION OF 2-(ETHOXYCARBONYL)METHYL-1,4,6-TRIMETHYLPYRIMIDINIUM IODIDE

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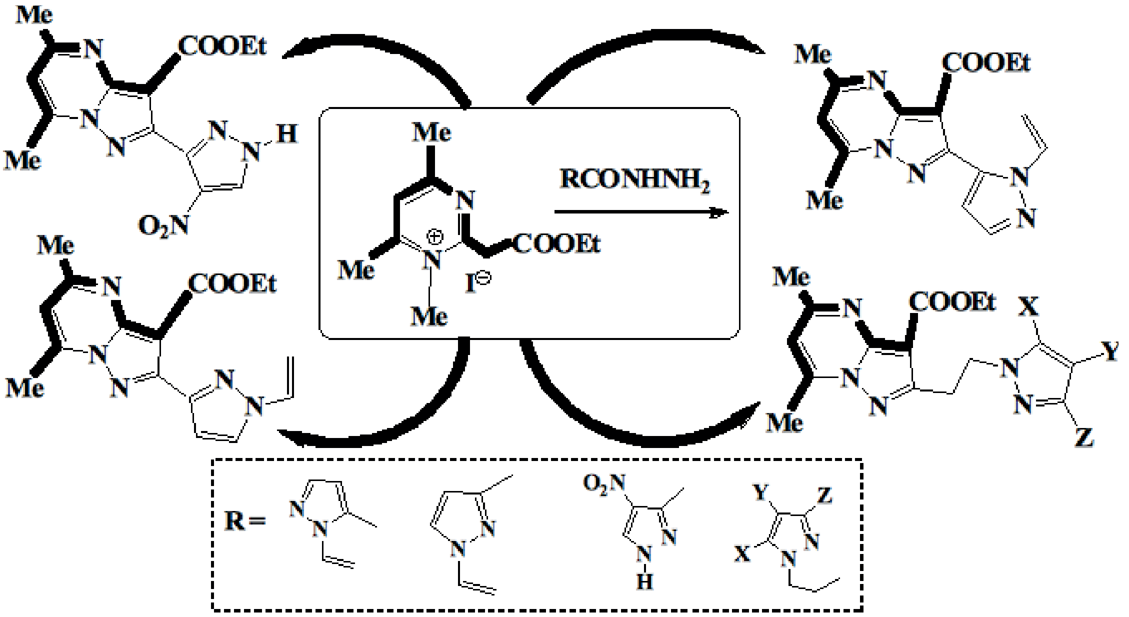
During an earlier study of reactions between pyrimidine derivatives and nitrogen-containing nucleophilic agents, we identified an unusual transformation of 2-(ethoxycarbonyl)methyl-1,4,6-trimethylpyrimidinium iodide in the presence of certain acyl hydrazides, which unexpectedly provided pyrazolo[1,5-a]pyrimidine derivatives. We studied the reaction of 2-(ethoxycarbonyl)methyl-1,4,6-trimethylpyrimidinium iodide with hydrazides of N-pyrazolyl- and C-pyrazolyl-substituted carboxylic acids. This reaction was shown to result in recyclization and formation of ethyl 2-(pyrazol-1-ylalkyl)- and 2-(pyrazol-3-yl)-5,7-dimethylpyrazolo[1,5-a] pyrimidine-3-carboxylates.



The research was carried by the funds allocated under the subsidy of the Ministry of Education and Science of the Russian Federation to finance research activities at Russian-Armenian University, as well as under grant 18T-1D249 of thematic financing of the Republic of Armenia.

NEW METHODS, REAGENTS AND OPPORTUNITIES OF DIAZONIUM CHEMISTRY

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In recent years, we have obtained a number of arenes(heteroarenes)diazonium sulfonates Ar(Het)$N_2^+RSO_3^-$ (ADS) and have shown that they have advantages over the known diazonium salts. Most of them are stable when stored in a dry state and safe (low energy of thermal decomposition), well soluble in both polar and non-polar solvents. At the same time, ADS show high reactivity in known diazonium transformations and enter into reactions that are not typical for traditional diazonium salts[1-5]. Experimental and theoretical methods determined the effect of the Ar(Het) and RSO_3^- structure on the reactivity, stability, and physicochemical properties of ADS. Many examples have demonstrated that, due to its availability, safety and variety of chemical transformations, ADS can be convenient "workhorses" of both laboratory and industrial organic synthesis in obtaining a wide range of practically important aromatic and heterocyclic compounds.

In the study of ADS, detected stable clusters (Ar(Het)N2+)n (RSO3-)m by various ESI MS methods and discovered previously unknown diazonium reactions in the gas phase, which opens up fundamentally new prospects in the chemistry of diazonium salts. A special type of diazonium salts, the aminodiazonium triflate $H_2N\text{-}N_2^+TfO^-$, was obtained and identified for the first time, and it was established that this compound, depending on the pH of the medium, is capable of electrophilic aminating some arenes and heterocycles or alternatively being a strong oxidizing agent.

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CATALYTIC CHEMISTRY OF UNSATURATED STRAINED CARBOCYCLIC COMPOUNDS

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Strained unsaturated carbocyclic hydrocarbons, having a norbornene structure, are important objects in organic chemistry. The use of catalytic methods and approaches allows to obtain on their basis unique compounds with desired properties using a very limited number of process steps. A feature of such reactions is the realization possibility of using additional carbocyclic strain energy for solving questions of the selectivity of various levels – regio-, stereo-, enantio-.

Selectivity problems in multipath reactions involving norbornadiene (NDB) and its derivatives become more important. Using the example of the reactions of homodimerization and allylation of NBD and norbornenes, codimerization of NBD with acrylic acid esters and methyl vinyl ketone, the possibility of controlling the speed and selectivity of various levels is shown. The ways of formation of nickel and palladium catalysts are investigated, key intermediates are identified by spectral and isotopic methods, kinetic regularities are established, and consistent mechanisms are proposed. In a number of cases, paramagnetic nickel complexes (I) and (II -), potential catalysts or intermediates of processes involving NBD, have been detected. The mechanism of their formation is proposed. However, the role of these complexes in catalysis remains unclear.

New technologically advanced heterogeneous catalysts for reactions involving NDB were developed. A comparison of the effectiveness of their use between them and metal-complex analogues was made.

Quantum-chemical modeling of nickel-catalyzed processes with the participation of NBD was performed. Theoretical approaches made it possible to carry out molecular design of catalytic systems, to detail the mechanisms, to predict the most probable reaction routes, and to optimize the conditions of their conducting.

This work was supported by the Russian Science Foundation (Grant No. 18-13-00415).

ACID-CATALYZED CASCADE REACTIONS OF FUNCTIONALIZED ACETALS WITH (HETERO)AROMATIC NUCLEOPHILES: A VERSATILE ONE-POT ACCESS TO VARIOUS HETEROCYCLES.

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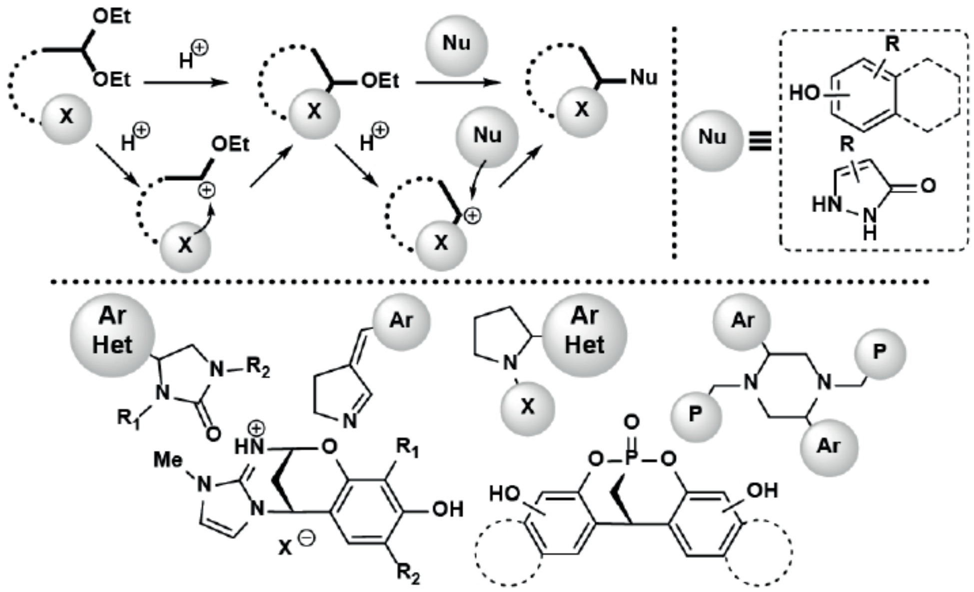
Acetals possessing various functional groups are widely used as building blocks in the synthesis of heterocycles. Their reactions with aromatic nucleophiles play an important role in these syntheses. In most cases, these reactions are intramolecular with the aromatic nucleophile being a part of the acetal molecule. Intermolecular reactions of functionalized acetals with aromatic nucleophiles received much less attention from the researchers.

Herein we summarize the results of our studies of acid-catalyzed cascade intermolecular reactions of nitrogen- and phosphorus-containing acetals with aromatic and heterocyclic C-nucleophiles and demonstrate their considerable potential in the synthesis of various classes of new heterocyclic compounds.



The work was supported by a grant from the President of the Russian Federation for support of young Russian scientists (MD-585.2019.3)

TRANSITION METAL COMPLEXES WITH REDOX ACTIVE DIIMINE TYPE LIGANDS: SYNTHESIS, STRUCTURES, ELECTROCHEMICAL AND CATALYTIC PROPERTIES

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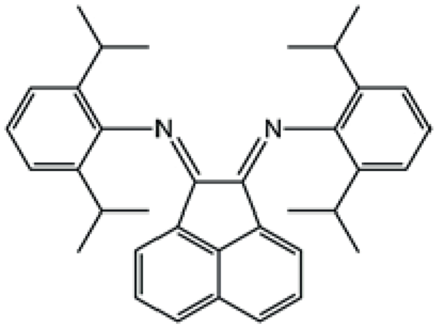
In modern chemistry, an important place is occupied by coordination compounds of transition and non-transition metals with redox-active ligands. In particular, diimine ligands of the bis-(imino)acenaphthenes class (abbreviated, bian) are attracting increasing interest. A key feature of these compounds as strong π-acceptor molecules is their ability to reversibly accept up to four electrons and exchange them reversibly with a metal center, which leads to the implementation of multi-step redox processes and can be used in multi-electron activation of small molecules and catalytic reactions based on redox transformations.



This paper presents the results on the use of diimine-type compounds (dpp-bian, bpy, phen) for the preparation of complexes of early and late transition metals. The synthesis of new compounds, their molecular and electronic structure, magnetic and electrochemical properties, and catalytic activity in oxidation reactions of organic substrates and carbon dioxide reduction are discussed.[1-3]

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DEVELOPMENTS OF PROCESS

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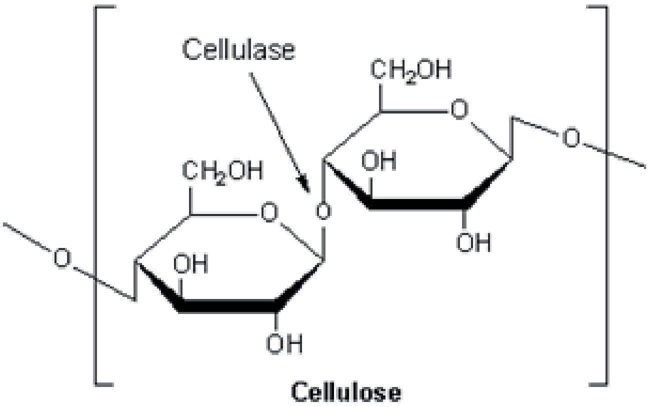
Ethanol is used today as an alternative fuel, a fuel extender, an oxygenate, and an octane enhancer. From just over 10 million gallons of production in 1979, the U.S. fuel ethanol industry has grown to more than 1.8 billion gallons of annual production capacity.[1]



The application of cellulase to the breakdown of cellulosic biomass into sugars for fermentation to ethanol and other commodity products would provide tremendous environmental, economic, and strategic benefits.[2]

However, the key challenge is to make biomass depolymerization more rapid and less costly, but the question remains.[3-4]

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STRUCTURAL DYNAMICS OF FREE MOLECULES AND CONDENSED MATTER

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The study of the structural dynamics of matter with a high spatial-temporal resolution represents a new direction of modern science, which is a necessary step to explain the relationship between the elements of the structure-dynamics-property triad in physics, chemistry, biology, and materials science. The method of ultrafast electron and X-ray diffraction made it possible to combine the high temporal resolution provided by a pulsed laser source with the atomic spatial resolution inherent in diffraction methods.

Advances in the development of pulsed laser technology have predetermined a further breakthrough in the field of research into ultrafast structural dynamics of nuclei and electrons. As a result of this progress, the use of femto- and attosecond laser pulses, both to excite the sample and to form ultrashort photoelectron bunches synchronized with optical pulses to probe matter, opened up the possibility of observing coherent dynamics of nuclei and electrons in the studies of matter on the required space-time scales.

A colossal breakthrough is the possibility of direct observation of the reaction process. How can this information and the new view on reactionary dynamics be used in the future? This question was raised in connection with the development of a new conceptual foundation of the natural sciences, which marks the convergence of experimental and theoretical tools in the study of systems of any level of complexity with atomic resolution. The main conclusion is that the implementation of the "atomic-molecular movie" is carried out using the complementary information obtained in the triune approach based on the combined use of ultrafast electron and X-ray diffraction, spectroscopy and the theory of non-equilibrium dynamics of complex quantum systems.

This work was supported by the RFBR, Project 16-29-11679 OFI - m.

ISOXAZOLE-AZIRINE ISOMERIZATION: A POWERFUL TOOL FOR THE SYNTHESIS OF HETEROCYCLES

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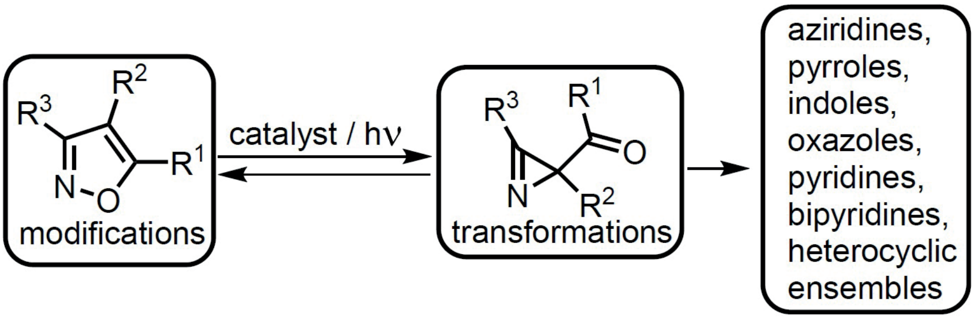
Search for solutions to the reactivity and selectivity problems is key fundamental challenge in organic synthesis. Isoxazoles and 2H-azirines are widely used in the synthesis of various heterocyclic compounds. Isoxazoles in many cases are much more available and stable than azirines and this facilitates modifying of substituents without ring opening. On the other hand, highly strained azirines are much easier to undergo ring expansion under the action of electrophilic, nucleophilic, and other reagents, leading to the formation of various heterocycles.[1] The high reactivity of azirines permits the use of milder reaction conditions and more selective reagents. The combination of these two different reactivity modes, taking into account the synthetic equivalence of isoxazoles with 2-carbonyl-substituted 2*H*-azirines due to easy interconversion, creates new opportunities for synthetic chemists in functional heterocyclic design. This was exemplified by recent examples of use catalytic isoxazole–azirine isomerization as a basis for the development of the methods of preparation of heterocycles and heterocyclic ensembles.[2-6]



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MODERN APPLICATIONS OF METAL COMPLEXES WITH ISOCYANIDES AND ACYCLIC DIAMINOCARBENES

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Isocyanides are versatile C-ligands combining both σ-donor and π-acceptor properties. Coordination of isocyanides to a metal leads to change in properties of both the isocyanide ligand and the metal center itself. Thus, the coordination to a metal center affects dramatically the reactivity of isocyanides[1]. A particular interest represents the coupling with bifunctional N,N-nucleophiles as it poten-tially leads to more complex but easily tunable aminocarbene ligands, that are of great significance in transition metal catalysis. In this project, we established general rules controlling regio/chemoselectivity of such reactions and prepared several different types of metal-aminocarbene species by coupling of Pd-bound isocyanides with hydrazides, hydrazones, and benzenediamines. Prepared aminocarbene species were studied as catalysts for Sonogashira and Suzuki–Miyaura (yields up to 99, TONs up to 10^4) coupling under mild conditions[2]. On the other hand, coordination isocyanides to a metal center alters the elect¬ron density on the metal potentially leading to metal systems with interes¬ting photophysical and catalytically properties. Herein, we showed that cyclometallated iridi¬um(III) complexes with isocyanides, viz. $[Ir(ppy)_2Cl(CNR)]$ and $[Ir(ppy)_2(CNR)_2](OTf)$, are the first silicon cross-linking catalyst operating at high temperatures (150–180 °C)[3]. In this report, we provide an overview of modern application of metal-isocyanides and aminocarbenes, focusing, in particular, on catalysis and materials sciences.

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ELECTRONICALLY MEDIATED REACTIONS IN METAL THERMAL REDUCTION OF THE VI GROUP METAL OXIDE COMPOUNDS

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Usually, reduction reactions occur through direct contact between the reagents. However, it has been demonstrated that reactions can occur without direct physical contact between the reagents[1,2]. They are referred to as electronically mediated reactions (EMR). The essence of the experiments confirming the occurrence of such reactions is as follows: the substance to be reduced and the reducing agent in separate containers are placed into molten salts. The containers have openings that allow the reagents to contact with the melt and are also connected by an external circuit. When the external electrical circuit is closed during the reduction, a current of electrons formed due upon the ionization of reducing metal flows through it, and the molten salt serves as the electrolyte.

This paper presents an attempt to explain the anomalous phenomenon of the reaction products separation during the reduction of a number of oxide compounds of the metals of the VI Group (MoO_3, $MgMoO_4$, $CaMoO_4$, WO_3, $MgWO_4$, Cr_2WO_6, $MgW_xMo_{1-x}O_4$ and $CaW_xMo_{1-x}O_4$) by vapours of alkaline-earth metals (Mg, Ca) by an electronically mediated reaction in the absence of a molten salt.

The equipment, methods of conducting experiments and studying the characteristics of the obtained powders were similar to those used previously[3]. After reduction under conditions of residual argon pressure deposits of MgO, CaO or their mixture were found on the surface of the reaction products. The reaction mass under the oxide layer was a black powder consisting of a mixture of a reduced metal and an oxide of an alkaline earth metal, which was part of the precursor. When vacuum reduction took place separation of the reaction products were not observed.

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PHOSPHORYLATED ANILINE AS A PRECURSOR FOR PINCER LIGANDS AND PALLADIUM COMPLEXES ON THEIR BASE

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The so-called pincer complexes with tridentate monoanionic ligand framework, which offers multiple options for directed structural modifications, are of particular interest owing to their broad spectrum of practically important properties. A convenient precursor for the synthesis of new pincer-type ligands can be meta-phosphorylated aniline (Fig. 1).[1,2] Using this functionalized aniline as a starting compound, we developed synthetic routes to several series of pincer ligands with different ancillary donor groups. It was shown that the resulting compounds readily undergo direct cyclopalladation under mild conditions, leading to mono- and ditopic palladium(II) pincer complexes in high yields. The peculiarities of synthesis and structures as well as the physicochemical properties of the new palladacycles will be discussed.

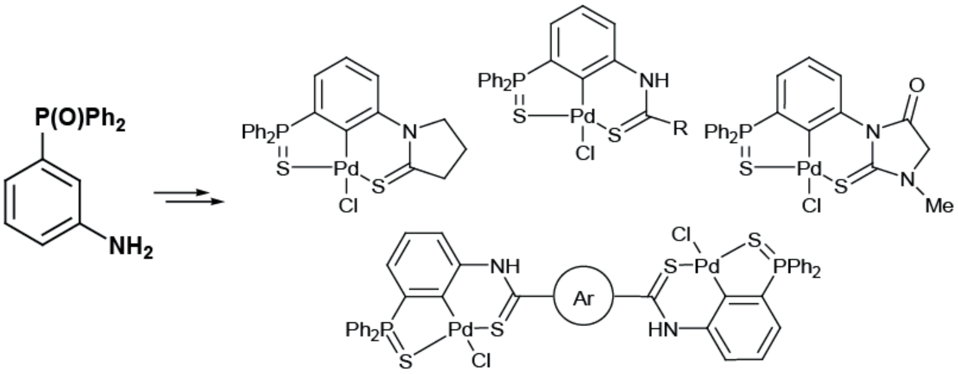

Figure 1. Pincer complexes based on meta-phosphorylated aniline.

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PYRANOSIDE-INTO-FURANOSIDE REARRANGEMENT: FROM A SIDE REACTION TO A NEW SYNTHETIC METHOD

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Great interest to natural furanoside-containing compounds has challenged the development of preparative methods for their synthesis. Herein we report new results achieved using a novel reaction in carbohydrate chemistry, namely a pyranoside-into-furanoside (PIF) rearrangement permitting transformation of selectively O-substituted pyranosides into the corresponding furanosides, including studies of its mechanism,[1] driving force,[2] synthetic scopes and limitations[3] and most recent synthetic applications.[4-8] The discovered process, which has no analogy in organic chemistry, includes acid-promoted per-O-sulfation of pyranosides which is accompanied by ring rearrangement into the furanoside form followed by solvolytic O-desulfation. Some interesting conformational effects occurring in exhaustively sulfated monosaccharides were observed during the mechanistic investigations.[9] Their possible role in governing the PIF transformation is discussed in this communication. The reported reaction was shown to be a very useful tool for the preparation of furanoside-containing complex oligosaccharides, which was demonstrated by syntheses of oligosaccharides related to bacterial and fungal cell-wall polysaccharides.

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MACROMOLECULAR REACTIONS INVOLVING METATHESIS POLYMERS

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Our studies[1-4] of cross-metathesis and chemical modification of macromolecules in the blends of unsaturated polyolefins are discussed. Using ruthenium Grubbs' catalysts of different generations, copolymers of norbornene with cyclooctene, cyclopentene, cyclododecene, butadiene, and isoprene, which are difficult to obtain by other methods, have been synthesized. The possibility of introducing functional groups (acetoxy-, carboxy-, hydroxy-, trimethylsilyl-, and bromine) into copolymers through the use of substituted monomers in the synthesis of initial homopolymers or by post-modification of cross-metathesis products has been shown. Kinetic studies using in situ 1H and ex situ 13C NMR made it possible to describe the evolution of Ru-carbene complexes (active centers of cross-metathesis) and diad composition of the resulting copolymers. Analysis of the mechanism and individual stages of the reaction makes it possible to adjust the degree of copolymer blockiness by variation of the reaction time, ratio of the reacting polymers, and amount of catalyst. The chain structure determines the crystallinity and other properties of the resulting copolymers, which were studied using DSC (including thermal fractionation) and rheological methods. At low concentrations of the reacting polymers, intramolecular cross-metathesis leading to the formation of cyclic macromolecules should be taken into account. Our studies expand the synthetic possibilities toward multiblock copolymers, the growing interest in which is due to their use as promising functional materials with improved mechanical properties.

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N-AMINOAZIRIDINES IN ORGANIC SYNTHESIS

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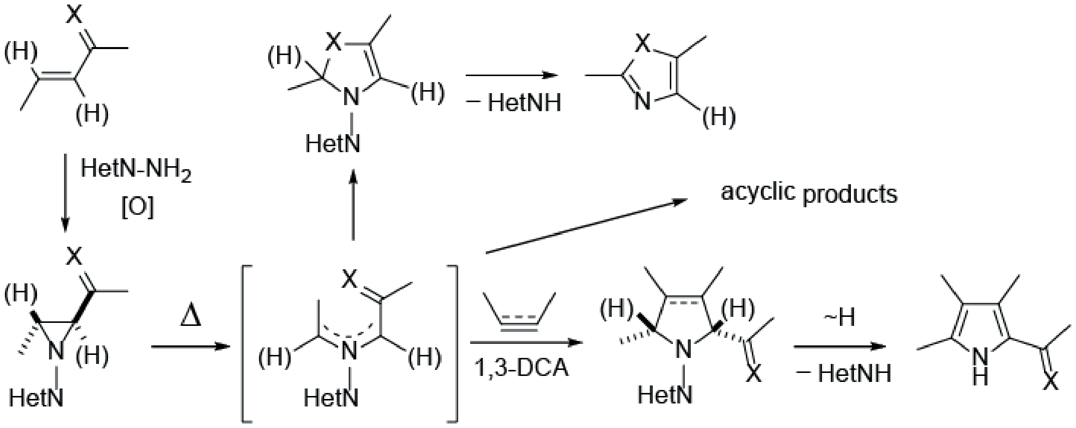
Strain energy of N-aminoaziridines is a driving force for a wide range of their intra- and intermolecular transformations which offer novel synthetic approaches to various nitrogen heterocycles and their derivatives.[1-5] Oxidative addition of easily accessible N-aminoheterocycles to unsaturated compounds (oxidative aminoaziridination)[1] provides a general method for the preparation of N-aminoaziridines.



As a rule, thermal transformations of N-aminoaziridines proceed via stereospecific generation of 1,3-dipoles, azomethine ylides, which can be involved in 1,3-dipolar cycloaddition reactions or intramolecular electrocyclic processes. A plenty of azaheterocycles such as pyrrolines, pyrroles, oxazoles, triazoles, pyrazoles, and imidazoles, as well as unsaturated acyclic compounds are thus obtainable in high yields.

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DESIGN OF HOMO- AND HETEROGENEOUS CATALYSTS FOR CO_2 FIXATION INTO CYCLIC CARBONATES

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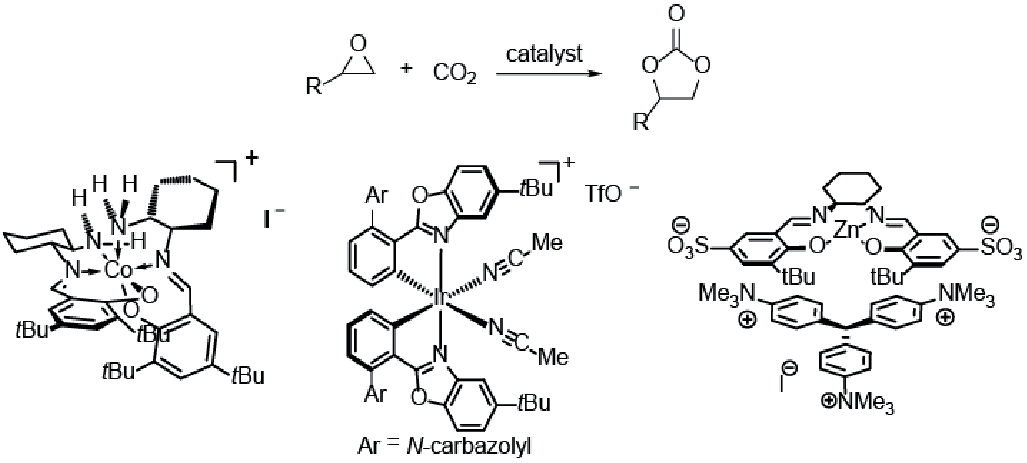
The reaction of epoxides with CO_2 to form cyclic carbonates has attracted much attention as CO_2 constitutes a sustainable C1 feedstock. Furthermore, the reaction features perfect atom economy, and cyclic carbonates are important synthetic building blocks.[1]



Here we report the design of new classes of homo- and heterogeneous catalytic systems based on stereochemically inert co-ordinatively saturated chiral complexes of cobalt(III),[2] bis-cyclometalated chiral-at-iridium complexes[3] and self-assembled ionic composites of negatively charged Zn(salen) complexes and triphenylmethane derived polycations.[4]

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PHYSICAL - CHEMICAL PROPERTIES OF MATTER UNDER EXTREME CONDITIONS

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According to modern conceptions[1], more than 90% of the observed matter in the Universe is under conditions of extremely high pressures and temperatures. The questions of the behavior of the structure of matter under extreme conditions, the expected new chemical effects, methods for obtaining extreme states in the laboratory and the study of physical and chemical properties of substances are considered in the review[2].

The report discusses the state of the problem of experimental and theoretical study of the fundamental physical and chemical properties of substances under extreme conditions, the description of physical and chemical transformations, the phase boundaries of melting and evaporation, the effects of restructuring of the electronic structure, ionization, metallization and dielectrization.

The results of calculations of the properties of metals and structural materials are presenting with the use of wide-range models of physical - chemical properties in comparison with the available theoretical and experimental data under extreme conditions. Discussing are problems of the numerical simulation of physical-chemical processes of various nature under conditions of high energy density, implementation of models of substance properties in numerical codes, the quality of descriptions and the reliability of the modeling results. Examples of 3-and 2-dimensional numerical modeling of high-energy-density processes are given, the importance of reliable description of physical and chemical properties of matter in a wide area of the phase diagram is indicated.

The problems of development, functioning and presentation of experimental data and approximations of thermodynamic properties of substances in the form of an online data bank are discussing.

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LIGAND-TO-METAL CHARGE TRANSFER EXCITED STATES BASED ON GROUP IV METALLOCENES

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Molecular electronically-excited states are of great fundamental and technological importance. The current state of knowledge on ligand-to-metal charge transfer (LMCT) excited states based on organometallic compounds indicates that such studies are few and rather unsystematic. Organometallic compounds are an important class of materials in many areas of science and technology. Group IV metallocenes RCp_2MX_2 [Cp = cyclopentadienyl; M = Ti, Zr, Hf; R – substituent(s) or bridging group(s)] have provided impetus for a new generation of a large family of highly reactive organometallics, for years successfully used in the fields of homogeneous and heterogeneous catalysis[1]. In this report, emphasis will be given to redox, photophysical, photochemical properties, and their generalization regarding extremely rare LMCT excited states of group IV metallocenes[2–6], experimental quantities of frontier molecular orbitals. The tendency in the observed photophysics (absorption and luminescence spectra, experimental and radiative lifetimes, emission quantum efficiencies, etc.) in the group IV metallocenes will be discussed in view of the nature of a d^0 metal ion and coordination sphere of organometallic complexes. Orbital interactions between d^0 bent metallocenes, unsaturated hydrocarbon substrates, and organic solvents will be detailed.

There is great scope for novel chemical, photophysical, and photochemical studies of organometallic species, having long-lived emissive LMCT excited states, and their organized systems.

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CHANGE IN THERMODYNAMIC PROPERTIES WITH ISOBARIC REDUCTION OF NANOCRYSTAL SIZE

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Based on the Mie-Lennard-Jones pair potential of the interatomic interaction and the method presented in[1], the isotherms of the state equation are calculated: P(T, v), for Si, Ge crystals and Si-Ge solid solution. Here T is the temperature; v is the specific (per atom) value of the volume. For Si and Ge, the parameters of the Mie-Lennard-Jones potential were determined in[2], and for the Si-Ge solid solution, in[3]. Calculations were carried out both for a macro-crystal (at $N = \infty$) and for a cubic nanocrystal, consist of $N = 223$ atoms. The changes in thermodynamic properties at isobaric ($P = 0$) decrease in crystal size for isotherms T = 100, 300, 1000 K were calculated.

The following properties were calculated: Θ is Debye temperature and $\Theta'(P) = (\partial\Theta/\partial P)_T$; three Gruneisen parameters: $\gamma = -[\partial\ln(\Theta)/\partial\ln(V)]_T$, $q = [\partial\ln(\gamma)/\partial\ln(V)]_T$, $z = -[\partial\ln(q)/\partial\ln(V)]_T$; BT is the elastic modulus and $B'(P)$; α_p is the thermal expansion coefficient and $\alpha_p'(P)$; $\alpha_p \bullet B_T = (\partial P/\partial T)_v$; C_v and C_p are the specific (per atom) isochoric and isobaric heat capacities; $C_v'(P)$ and $C_p'(P)$; σ is the specific (per unit area) surface energy; $\sigma'(T)_v = (\partial\sigma/\partial T)_v$; $\sigma'(T)_p = (\partial\sigma/\partial T)_p$; $\sigma'(P) = (\partial\sigma/\partial P)_T$; μ_p is the Poisson's ratio.

It is shown that at the isobaric ($P = 0$) transition from macro- to nano-crystal, the following properties decrease: Θ, q, z, BT, σ, and the melting temperature. At this increases the values of the following properties: v, $\Theta'(P)$, γ, $B'(P)$, α_p, $|\alpha_p'(P)|$, $\alpha_p \bullet B_T$, C_v, $|C_v'(P)|$, C_p, $|C_p'(P)|$, μ_p, $|\sigma'(T)_v|$, $|\sigma'(T)_p|$, $\sigma'(P)_T$.

In the transition from macro- to nano-crystal, the following parameters change slightly: at T = 100 K: γ, z, $B'(P)$, μ_p; at T = 300 and 1000 K: γ, z, $B'(P)$, $\alpha_p \bullet B_T$, C_v, $C_v'(P)$, C_p, μ_p. Therefore, under the given P-T-conditions, the values of these parameters obtained for the macro-crystal can be used.

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The reported study was funded by RFBR according to the research project № 18-29-11013_mk and the Program of the Presidium of the RAS (program № I.13).

STABILIZATION OF «NON-TRADITIONAL» HIGH OXIDATION STATES OF 3D-ELEMENTS IN THEIR COMPLEXES WITH TETRAAZAPORPHINE DERIVATIVES AND FLUORIDE-ANIONS: QUANTUM-CHEMICAL DESIGN

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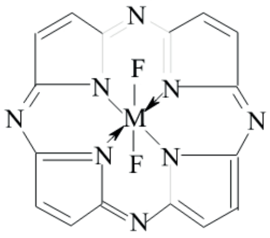
In this overview report, on the basis of quantum-chemical calculation data obtained by using the OPBE/TZVP and DFT B3PW91/TZVP DFT methods, possibility of existence (at least in the gas phase) of heteroligand complexes Cu(IV) and Zn (IV) as well as similar in composition M(IV) complexes of other 3d-elements (M = Ti, V, Cr, Mn, Fe, Co, Ni) with tetraazaporphin, its diphenylene and tetraphenylene substituted and fluoride anions of types I, II and III, respectively, has been shown.



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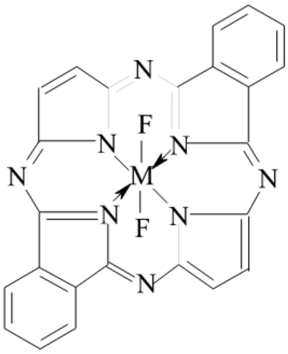

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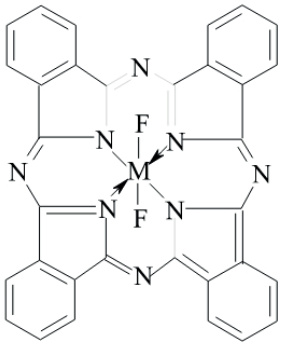

III

The key parameters of the molecular structures of these coordination compounds [bond lengths, bond and torsion (dihedral) angles], and, also, their dipole moments and spin multiplicities of their ground states, are calculated. It is noted that complexes of type I contain flat MN_4 chelate nodes and are generally practically coplanar, whereas in complexes II and III, there is a slight deviation from co-planarity, and both in the MN_4 chelate node and in the phenylene fragments; in general, in complex III, such a deviation is more pronounced than in complex II. The standard thermodynamic parameters of the formation of these complexes are also determined.

THERMOPHYSICAL PROPERTIES OF XENON AT HIGH DYNAMICAL PRESSURES

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The report presents the overview of the results of the investigations of the equation of state, transport and optical properties of the dynamically compressed xenon up to the megabar pressure range. The highly time-resolved diagnostics permit us to measure the behavior of shock Hugoniots and isentropes, electrical conductivity, Hall effect parameters, emission spectra and reflectivity of the xenon at extremely high coupling. “Pressure ionization” is the most prominent effect at high compression ratios. Comparison of the data obtained with different theoretical models is presented. We pay great attention to the analysis of behavior of the shear viscosity at strong coupling and to the verifying the hypothesis that the ratio of shear viscosity coefficient to volume density of entropy of any physical system has a lower quantum bound. New experiments on polarized reflectivity of dense xenon plasma are presented. The research of polarized reflectivity properties of xenon was accomplished using laser beams at different wave lengths and at incident angles up to θ = 70 degrees. These experiments allow us to determine permittivity of shock compressed xenon and kinetics of the ionization process.

MOLECULAR DESIGN AND CRITERIA FOR THE FORMATION OF LUMINESCENT MECHANO-AND CHEMOSENSORY PROPERTIES IN BORON AND LANTHANIDES COMPLEXES

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The report presents data on the relationship between geometric and electronic structure of boron and the lanthanides complexes and their chemosensory, triboluminescent and mechanofluorescent properties.

The information about the new lanthanides triboluminophors and "switching-on" luminescent chemosensors based on boron, europium and terbium compounds inducing their own luminescence under mechanical impact (triboluminophors, mechanochromes) or by binding of substrate (analyte) due to intra- and intermolecular processes of charge transfer (optical chemosensors) is given. We have first proposed a model and possible mechanism of formation triboluminescent (TL) properties in lanthanide complexes, revealed a key role of the cleavage planes, introduced the concept of the zone and width of zone of destruction in the crystal under mechanical impact1. In a series of beta-diketonates and ketoiminate difluoride boron, we have obtained effective mechanochromes changing optical properties under external stimuli (heat, rubbing, pressure). Our optical chemosensor compositions based on lanthanide and boron complex compounds are promising for environmental monitoring and medicine2.

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Financial support of this work by the Russian Foundation for Basic Research, grant 19-03-00-409 is gratefully acknowledged.

THE TRANSFORMATION OF PROPELLANIC BOND IN 1,3-DEHYDROADAMANTANE BY ACTION OF NUCLEOPHILES AND ELECTROPHILES

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The transformations of propellanic bond in briged [3.3.1]propellane I (tetracyclo[3.3.1.1.^{3,7}.0.^{1,3}]decane, 1,3-dehydroadamantane, 1,3-DHA) and it's alkylated homologs II-IV in reactions with electrophiles and nucleophiles are investigated.

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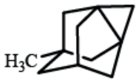

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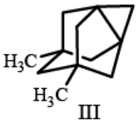

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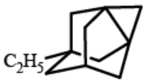

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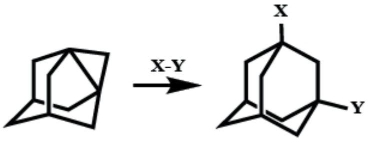

$X = H^+, Y = Nu^-; X = E^-, Y = M^+; X = Y = R^•$

The reactions of 1,3-DHA with different nature substrates: C-H, N-H, O-H and S-H–acids, alkylhalogenides, carboxylic acid halogenanhydrides, amines, Grignard reagents, diarildiselenides, di- and trisulphides and others are done. It is found, that the major reaction of 1,3-DHA is the cleavage of propellanic bond between C^1 and C^3 inverted carbon atoms, which results in recovery of adamantane structure. The dependence of reaction rate from substrate structure and it's acidity is studied.

It is shown, that depending on reaction conditions and substract used 1,3-DHA is able to generate different intermediates (cation, biradical, cation-radical), that leads to changing of chemo- and regioselectivity of proceeding reactions. First time by 1,3-DHA radiolysis in freon matrix at low temperatures was registered an EPR-spectrum of radical-cation of 1,3-DHA. Recovered an unusual ability of 1,3-DHA undergo reaction with alkyl groups of alkylaromatic hydrocarbons.

Discovered an easiness of adamantyl-cation generation from 1,3-DHA in presence of acidic catalysts and it's further reactions with aromatic and heterocyclic substances.

The perspectivity of 1,3-DHA using for synthesizing of hard to reach adamantane derivatives is shown, especially while using of substances, unstable at elevated temperatures: hydroperoxides, nitrogroup-containing substances, also for synthesizing of compounds, which impossible to obtain by combinatorial chemistry methods.

SYNTHESIS FEATURES OF GRAFTED FUNCTIONAL POLYMERS ON THE METAL AND POLYMERIC SUBSTRATES

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The grafting of polymers to the surface of substrates of various nature is a relevant field for the development of materials science. The combination of characteristics of the substrate and polymeric modifier makes it possible to make materials with fundamentally new properties, which opens up broad prospects for creating of modern sensitive sensors, medical drugs, filter elements, organic current sources etc.

At this work two approaches to the synthesis of grafted polymers based on methacrylic monomers on the surface of materials “grafting from” and “grafting to” are discussed. Some metallic and polymeric materials were used as substrates. The advantages of epoxy reagents, in particular polyglycidyl methacrylate, to use as “anchor” compounds are discussed. The synthesis of polymers was carried out by the methods of atom transfer radical polymerization (ATRP) or free-radical polymerization.

The lyophilic properties control of the materials’ surfaces bases on the obtaining of grafted functional polymethacrylates determining the properties at the interface. The grafting of hydrophilic polymers and polyelectrolytes to the surface with multimodal roughness allows to give the superhydrophilic properties with contact angles less than 10º. The grafting of polyalkylmethacrylates allows to achieve the superhydrophobic state, which characterized by contact angles up to 170°.

The surface modification by polymers has several advantages compared with low molecular weight modifiers. The main is the possibility to form a variety of cooperative bonds with functional groups of the substrate that leads to greater resistance of the coatings to the effects of aggressive media. In addition a series of functional polymethacrylates having the adaptive properties gives to the surface the ability to respond to external stimulus.

The work was supported by the Russian Foundation for Basic Research (RFBR), project 16-29-05364.

EXPANDED RING N-HETEROCYCLIC CARBENES – VERSATILE LIGANDS FOR TRANSITION METAL MEDIATED CATALYSIS AND LIGHT EMITTING MATERIALS

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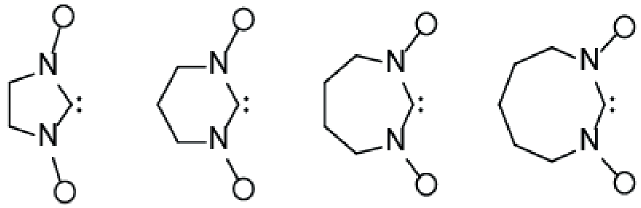
N-heterocyclic carbenes (NHCs) are highly tunable ligands for construction of transition metal complexes. The core of NHC can consist of five-, six-, seven-, and even eight-membered ring heterocycle. By varying the size of the cycle, donor and steric properties can be tuned in a wide range. Expansion of the ring leads to significant increase in electron donating properties, as well as increase in steric hindrance of the carbene. Additionally, steric and electronic properties of NHCs can be varied by changing the nature of the core heterocycle. Complexes of transition metals bearing NHCs based on mono-, di-, tri-, and tetrazoles were obtained.

In this contribution we present an overview of our results in carbene chemistry in last decade:

- Theoretical considerations of electronic structure and properties of various carbenes.
- Methods of synthesis of carbene ligands and their transition metal complexes.
- Design, synthesis and optical properties of iridium-based materials for OLED.
- Applications of Pd, Au, Cu complexes in homogeneous catalysis.



AZAPOLYENE STRATEGY FOR THE SYNTHSIS OF NITROGEN HETEROCYCLES

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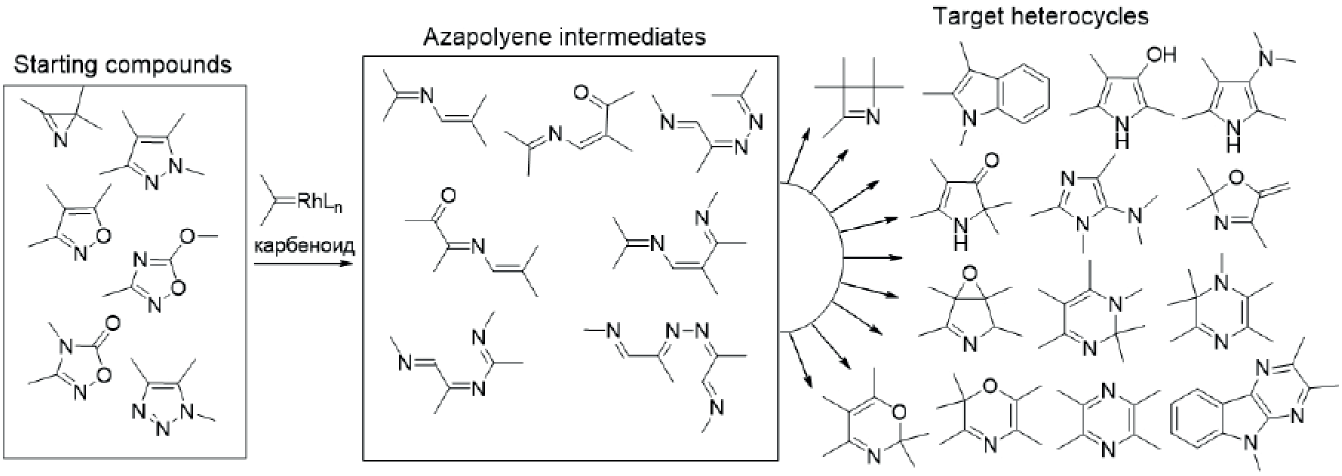
The development of efficient methods for the synthesis of new organic com-pounds with useful properties, most of which belong to the class of nitrogen-containing heterocycles, is one of the fundamental tasks of synthetic organic chemistry. The report discusses one of the strategies currently being developed for the formation of monocyclic, *ortho*-fused and bridged heterocyclic systems, based on carbenoid-mediated generation of azapolyene intermediates and their subsequent pericyclic, pseudopericyclic or nucleophile-initiated cyclizations.[1,2] The high synthetic potential of the proposed approach is due to the wide range and synthetic availability of the starting compounds, as well as to the high reac-tivity of the azapolyene intermediates themselves, which under mild conditions can form small strained rings, can involve stable benzoid aromatic systems in the cyclization process, and also can react with weak nucleophiles as cyclization initiators.



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This work was supported by Russian Science Foundation, grant 17-13-01078.

PHYSICO-CHEMICAL SPECTRAL METHODS, MECHANISMS OF ELECTRON-NUCLEAR INTERACTIONS IN ELECTRONIC EXCITED STATES AND REACTIVITY OF SUBSTITUTED N -,O -,S-COMPOUNDS OF THE BENZENE, FURAN, THIOPHENE, OXAZOLE, OXADIAZOLE, PYRIDINE AND VARIATION OF CONDITIONS

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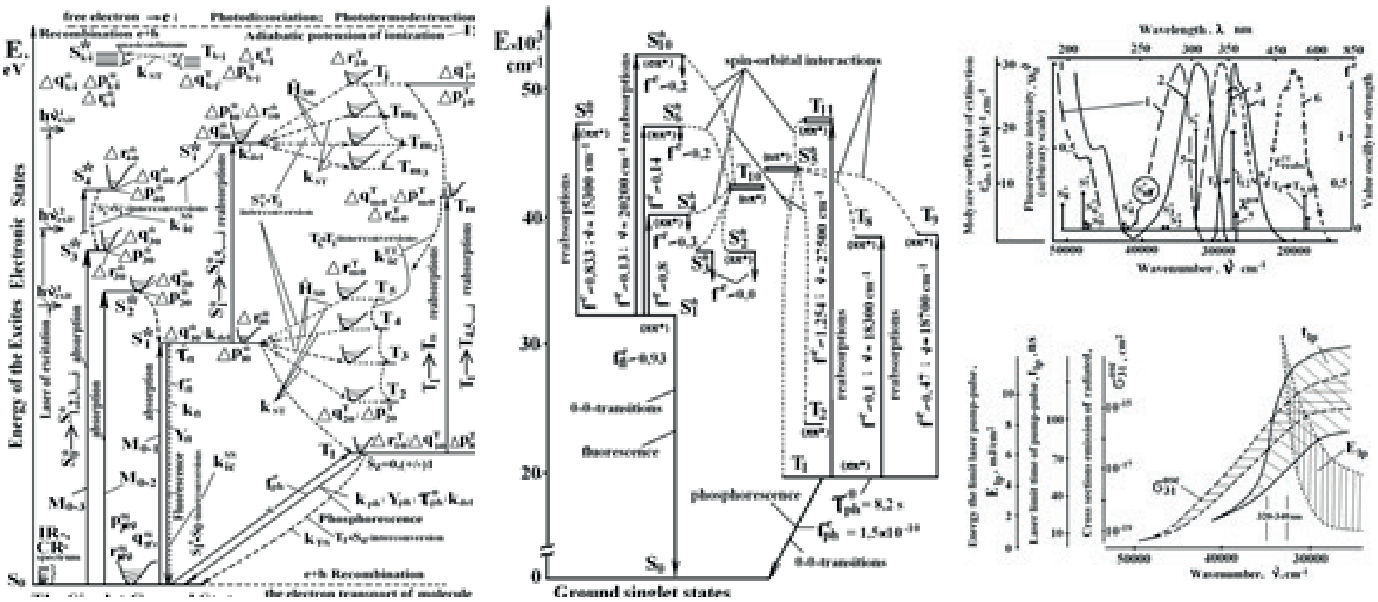
The intramolecular mechanisms of ultrafine electron-nuclear interaction forming the characteristics of the spectra: NMR, EPR, IR and UV absorption, Raman, luminescence at different temperatures (from 298 to 2,6oC) and pump types is the lasers, ions and electrons the use as additives of different functions N-,O-,S-compounds for fuel and lubricants were a studied (Fig. 1) [1].



(I) (II)

Fig. 1. (I) is the scheme of the radiative and nonradiative multistage of transitions in the full spectra S_i*T_jElExSt («elementary act») for polyatomic compounds (is doublet D*m and quartet Q^*_n of ions and radicals); $\{r_n\}$ are the coordinates of the localized electrons on LCAO-MO-SCF-CI INDO/S for the induced of active quasioscillators in structure between the intermediate ElExSt, {l} is the quasicontinuum of inactive vibrational levels, V_n is the matrix elements of the spin-orbit interaction of factors multiplied by a Frank-Condon; V_{nl} is the matrix elements of the operator of anharmonisms, $\{G_n\}$ is the width of the levels of active oscillation during of relaxation, M_{0i} is the matrix moments of electric dipole transitions. Free electron from mechanism of multistage photo-ionization. Vertical arrows is frequencies and forces the oscillators of transitions $S_1^* \rightarrow S_0$, $S_1^* \rightarrow S_i^*$, $T_1 \rightarrow S_0$ and $T_1 \rightarrow T_j$ formed by pumping, and $\Delta r_{\mu\nu}$, $\Delta p_{\mu\nu}$ and $\Delta q_{\mu\nu}$, $\Delta\rho_{\mu\nu}$ is the lengths, orders valence bonds, charges and total electron densities on atoms; (II) Full diagram the S_i*T_jElExSt is nπ*- and ππ*-type of the following and UV and Fluorescence spectra of the 2,5-diphenyle-1,3-oxazole (POP).

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NI(II) CATALYZED ASYMMETRIC ADDITION OF CARBONYL DERIVATIVES TO NITROALKENES: SIMPLE AND EFFICIENT ROUTE TO POLYFUNCTIONAL NON-RACEMIC COMPOUNDS

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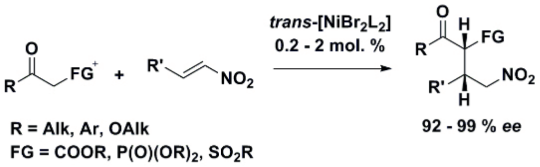
The development of effective approaches to the synthesis of polyfunctional compounds with several stereocenters is one of the major challenges in modern organic chemistry.

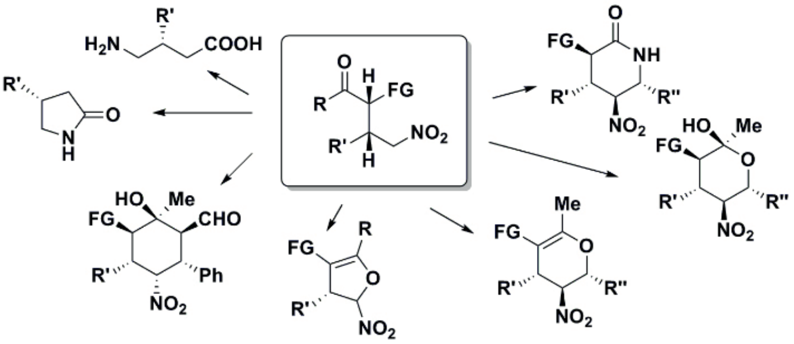
Asymmetric addition of 1,3-dicarbonyl compounds, β-keto phosphonates and β-keto sulfones to nitroalkenes is an effective method for obtaining chiral intermediates of neurotropic drugs - analogues of GABA and polysubstituted heterocycles. We have shown that the octahedral complexes of Ni(II) with chiral vicinal diamines are effective catalysts for this reaction.



The reaction mechanism and the ligands effect on the catalytic activity of the complexes and the enantioselectivity of the reaction are discussed.

Methods for the synthesis of non-racemic 3-alkyl, aryl and adamantyl-substituted GABA analogs via Ni(II)-catalyzed Michael addition were developed.

The cascade transformations of chiral Michael adducts were used for the synthesis of polyfunctional cyclohexanes, piperidinones, tetrahydropyranes and dihydrofuranes with several contiguous stereocenters.



This work was supported by the Russian Science Foundation (grant no. 18-13-00447).

OXIDATION OF MONOTERPENE THIOLS WITH CHLORINE DIOXIDE

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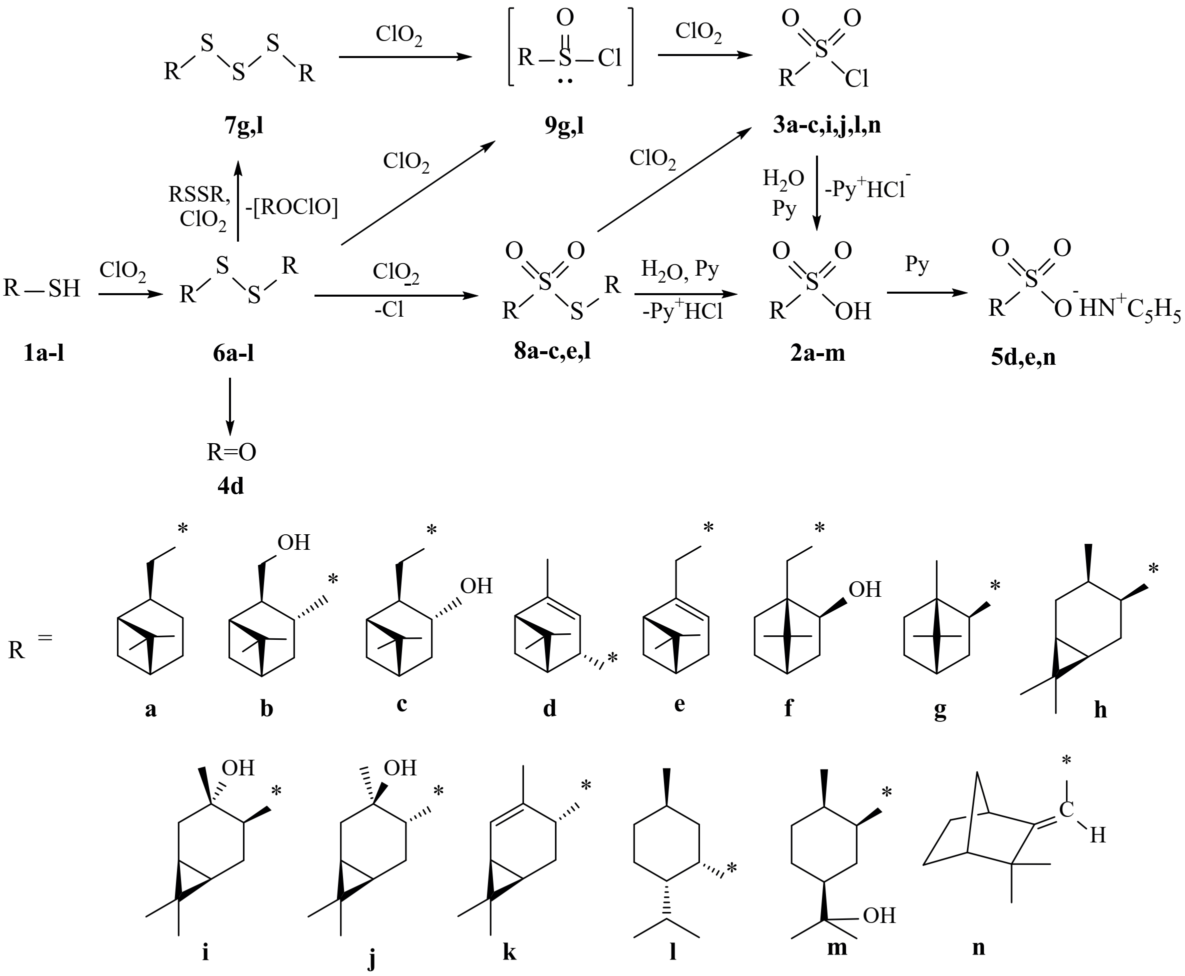
The interest in the chemistry of oxidative transformations of sulfur-containing terpenoids is due to a wide spectrum of biological activity of oxidation products. Chlorine dioxide (ClO_2) being used for pulp bleaching and water treatment is one of the most promising and available oxidizing agents produced on an industrial scale. Herein, we summarized the results of the oxidation of monoterpene thiols with chlorine dioxide.



The work was financially supported by the Ural Branch of the RAS (Project No. 18-3-3-17) and implemented using the Shared Use Center «Chemistry» equipment of the Institute of Chemistry of Komi SC UB RAS.

THEORETICAL CHEMISTRY OF FULLERENES: CURRENT STATE AND PROSPECTIVE

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Unique properties of fullerenes and their derivatives originate from the rich spheroid systems of π-electrons and the regular structure of their molecules.[1] The report is devoted to a theoretical study of the mechanisms of formation and synthetic transformations of fullerenes, prediction of the properties of their compounds and the isomeric diversity of organic functional fullerene derivatives.

The report presents the results of quantum-chemical modeling of the reactions of fullerenes with radicals and molecules resulting in the formation of exo- and endohedral derivatives of C_{60} and C_{70}. An overview is given on the application of the computational data to understand the mechanisms of the fullerene antioxidant and inhibitory effects on the oxidation of organic compounds[2,3] and radical processes in polymeric[4] and biological systems (degradation of lipid membranes).[5] After the discovery of C_{60} in the interstellar medium, the search for its compounds in astronomical objects began. The possibility of the formation of fullerene hydrides $C_{60}H_x$ is discussed from the point of view of thermochemical estimates, structure and polarizability of $C_{60}H_x$.[6]

The design of fullerene compounds with desirable properties includes the machine search for possible regioisomeric adducts $C_{60}X_n$[7] and predicting their properties by quantum-chemical methods and/or QSAR. Applications of both methodologies to screening efficient fullerene-based acceptors for organic solar cells and other photovoltaic devices are discussed.[8,9]

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STRUCTURE AND SOLVATION CHARACTERISTICS OF PROTIC IONIC LIQUIDS

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Studies of the solvation characteristics of ionic liquids are of great interest for their prospective applications in industrial processes. In the last 10–15 years, thermodynamics of solvation of various substances in a wide variety of aprotic ionic liquids (AILs) has been extensively studied. At the same time, there are virtually no data on the thermodynamic functions of solvation in protic ionic liquids (PILs). The presence of a network of hydrogen bonds in molecular solvents always leads to a decrease in solubility and an increase in the activity coefficients of low polar compounds. Therefore, it could be concluded that hydrocarbons should have significantly higher activity coefficients in the PILs than in the AILs.

For the first time, we have shown that for solutions in PILs such as alkylammonium nitrates and thiocyanates, the opposite is observed: the activity coefficients of hydrocarbons are much lower than in AILs with similar molar volumes [1]. This fact is explained by the structural features of these PILs – the presence of polar and apolar domains. The solvation of hydrocarbons occurs predominantly in apolar domains, which causes an increase in their solubility. At the same time, there are PILs that do not have a domain structure, e.g. 2-hydroxyethylammonium nitrate. The activity coefficients of hydrocarbons in this solvent turned out to be significantly higher than in alkylammonium nitrates. Using molecular dynamics simulations, we have proven that the observed effects are caused by the relatively low values of the Gibbs free energies of cavity formation in alkylammonium salts due to the predominant formation of the cavities in apolar domain. For 2-hydroxyethylammonium nitrate, very high values of the Gibbs free energy of cavity formation were obtained.

Thus, the supramolecular structure of the liquid phase of PILs determines their solvation characteristics. On the other hand, thermodynamic data can be used as a simple indicator of the presence or absence of a domain structure in these liquids.

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CLUSTER IODIDES OF EARLY TRANSITION METALS

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Chemically robust octahedral cluster halide complexes of early transition metals, $[\{M_6(\mu_3\text{-}X)_8\}L_6]$ and $[\{M_6(\mu_3\text{-}X)_{12}\}L_6]$ (M = Nb, Ta, Mo, W; X = Cl, Br or I; L = neutral or anionic ligands) are stable, chemically robust and easily available. The iodide clusters of Mo and W exhibit superior emission lifetime and quantum yield values. We are carrying out systematic studies on the influence of terminal ligands L on the properties of the $[\{M_6I_8\}L_6]$ clusters, in order to achieve predictable tuning of their potentially useful characteristics such as the redox, spectroscopic and photophysical behaviour, that is intrinsically due to the presence of the $\{M_6I_8\}^{4+}$ cluster core, by the choice of an appropriate L. Coordination chemistry, photocatalytic activities on the water reduction reaction and other possible applications of the $[\{M_6I_8\}L_6]$ clusters will be discussed.

Coordination chemistry of Nb and Ta iodide clusters is virtually non-existent. Nevertheless, these iodides merit attention owing to unique combination of properties, offered by the cluster iodides of tantalum: the $[\{Ta_6(\mu_3\text{-}I)_{12}\}L_6]$ clusters will have 18 heavy (i.e., strongly X-ray absorbing) atoms per molecule. This makes them good candidates for new X-ray contrast agents. Additionally, their redox and optical properties makes them a good candidates for hydrogen generation from water using sunlight. In this work we will report preparation, photocatalytic and reactivity studies of some key $[\{Ta_6(\mu_3\text{-}I)_{12}\}L_6]$ clusters.

Nb and Re cluster iodides will be also covered.

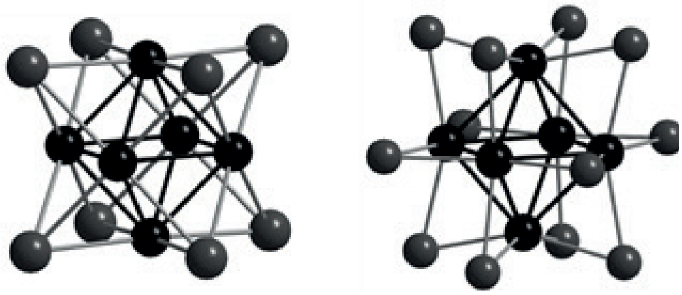

Figure 1. Octahedral cluster cores: $\{M_6I_8\}$ (left), $\{M_6I_{12}\}$ (right)

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CHEMICAL CRYSTALLIZATION OF DIAMOND: THE METHOD EMERGENCE AND SOME TRENDS IN MODERN DEVELOPMENT

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A brief overview of the emergence and development of a fundamentally new synthesis of diamond from the vapor phase (CVD process), starting with the initial simplest processes to widely and successfully used at the present time main methods of the activated chemical crystallization of diamond at pressures near and below 1 atm. The key role of atomic hydrogen generated in the activated crystallization medium, which provides selective (not accompanied by the release of non diamond carbon) growth of diamond on the diamond seed crystal, as well as heterogeneous and homogeneous nucleation of diamond under thermodynamic metastability conditions established for the first time in IPCE RAS. The main reasons for the reduction of surface energy at nucleation of diamond from the vapor phase and the factors that ensure high growth rate are considered. The advantages of diamond film doping processes in the growth from activated gas media, allowing to obtain equilibrium and superequilibrium solid solutions of an impurity elements, are noted. The synthesized diamond films have special optical and electrical properties (semiconductor conductivity and superconductivity). The opportunities of new methods of synthesis for providing new properties to synthetic diamond surpassing the determined by Nature, to obtain a “super diamond” are demonstrated. For the first time the heteroepitaxy of wide band diamond like aluminum nitride on diamond was experimentally established and investigated. Some of the most important, according to the authors, modern scientific and technical achievements in the field of CVD diamond are presented. The most challenging new issues for the near future are outlined.

NEW SUPRAMOLECULAR MESOMORPHIC MATERIALS FOR TRIBOSYSTEMS

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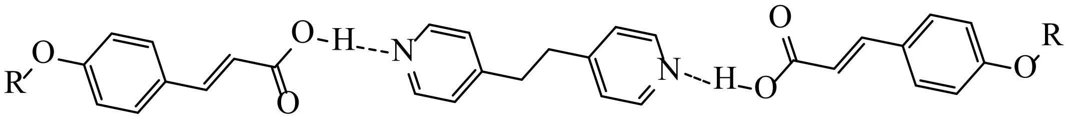
New supramolecular complexes based on mesogenic 4-n-alkyloxycinnamic acids (n-AOKK, n = 2,3,7,8) and 1,2-bis(4-pyridyl) ethane nemesogen (BPE) were obtained from the melt of their mixtures with a molar ratio of 2:1, respectively. The formation of complexes was confirmed by IR spectroscopy. Using the methods of differential scanning calorimetry and polarization thermomicroscopy, it was demonstrated that the obtained complexes have mesomorphic properties. The temperature range of the nematic mesophase existence increases for all H-complexes under study and their temperature of phase transition to isotropic liquid decreases, as compared with individual acids. The structural formula of the H-complexes supermolecules is given below.



We used the obtained compounds as additives to lubricants at boundary friction. High tribological efficiency was showed. We conducted a study on the friction and wear of lubricant compositions of these substances in the conditions of lean lubrication with reciprocating motion of the slider at a specific pressure at the contact of 80 MPa and a sliding speed of 2 mm / s, which showed that the wear resistance of the oil film of the lubricant with additives of these compounds increased tenfold compared to the base solvent oil and the prototype compositions. Currently, the developed lubricants undergo the procedure of patenting. In addition, prospects for the practical use of the compounds under study as triboactive additives to lubricating oils for friction units operating under high pressure and boundary lubrication (sliding bearings, etc.) are determined.

This work was supported by the Russian Foundation for Basic Research, project 18-43-370027.

NEW HIGHLY EFFICIENT BIOCATALYSTS IN HYDROXYLATION AND BAEYER–VILLIGER REACTIONS

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Stereoselective hydroxylation and Baeyer–Villiger reactions are widely used in pharmaceutic industry and fine organic synthesis. The mostly used enzymes are Cytochrome P450 monooxygenase (CYP450, hydroxylation) and different monoxygenases (MO, Baeyer–Villiger reaction). As a result target products can be obtained with yield up to 99-100% and enantiomeric excess 98-99% and higher. Both reactions require organic substrate, oxygen and reduced coenzyme NADPH. NADPH is expensive (about 10 000 Euro per kg). To reduce cost of the process the second enzyme reaction is used to regenerate product of main reaction $NADP^+$ back to NADPH. Mutant $NADP^+$-specific formate dehydrogenase (FDH) is one of the most suitable enzyme for that. Using X-ray analysis we solved 3D structures of FDHs from bacterium and yeasts and the structures were used for rational design of FDH coenzyme specificity from NAD^+ to $NADP^+$. In practice the enzymes are used as pair of purified proteins (CYP450 - FDH or MO – FDH) or two enzymes are co-expressed in one E.coli cell (whole cell biocatalysts). Unfortunately efficiency за biocatalysts is not high due low specific activity of CYP450 and MO. To increase total process efficiency we prepared genetic constructions expressing hybrid biocatalysts which have in one polypeptide chain both enzymes connected with linker. Construction with different genes order – CYP450-FDH (two variants), FDH-CYP450 (two variants), MO-FDH and FDH-MO (with two types of FDH) were made and fusion proteins were expressed as active enzymes, purified and tested in some reactions. It was found that hybrid fusion biocatalysts show higher total process efficiency (several fold) compared to use of separate enzymes.

This work was funded by Russian Foundation for Basic Research grants 17-04-01469, 17-04-01662, 18-34-20098, RFBR and Moscow city Government grant 19-34-70036 and Russian Science Foundation grant 18-74-00146.

NEW PHTHALOCYANINE COMPLEXES AND THEIR APPLICATION AREAS

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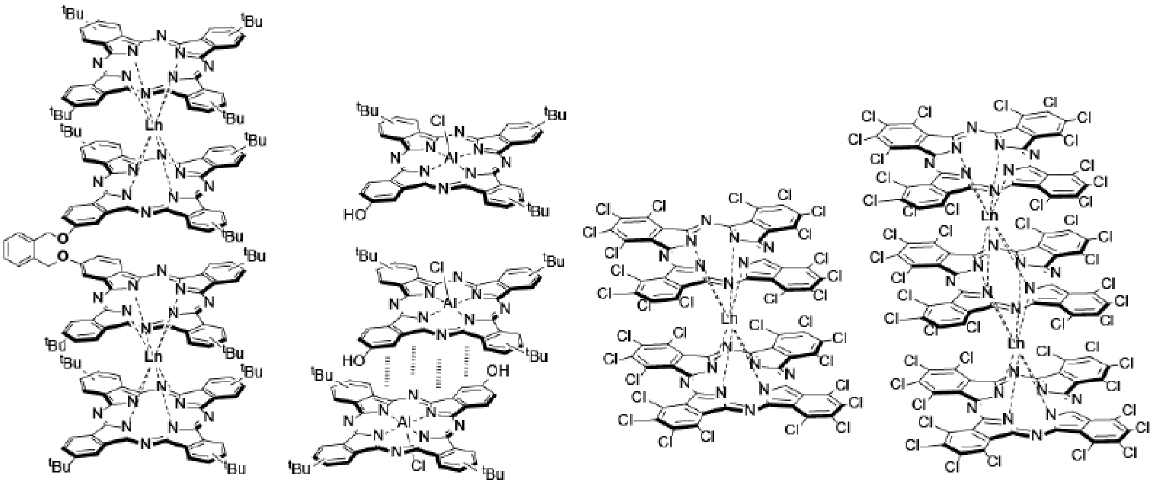
Recent advances in chemistry of new complexes with phthalocyanines (Pcs) and their closest analogues are presented. Special attention is given to compounds based on Pc-spacer-Pc ligands, which can be classified as .[1]

We obtained new quadruple-deckersandwich complexes of lanthanides (III), based on phthalocyanine clamshell ligands with high yields up to 90%.[2] The study of the complex with Tb using the SQUID magnetometry method suggests that this complex possesses magnetic properties.



Ln = Eu, Gd, Tb, Er, Lu

supramolecular *J*-type dimer

sandwich-type complexes with
electron-withdrawing functional groups

Novel hexadecachloro-substituted phthalocyanine complexes of Ln was synthesised and comparison of linear and nonlinear optical properties was carried out. The values of the absorption cross-sections of the first excited state were determined using z-scan technique. The highest value ($\sigma1 = 1.96\times10^{-16}$ sm^{2}) was observed for terbium complex.[3]

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UNIFORM LAW OF VARIATIONS IN DIFFERENT PROPERTIES OF ORGANIC COMPOUNDS WITHIN HOMOLOGOUS SERIES

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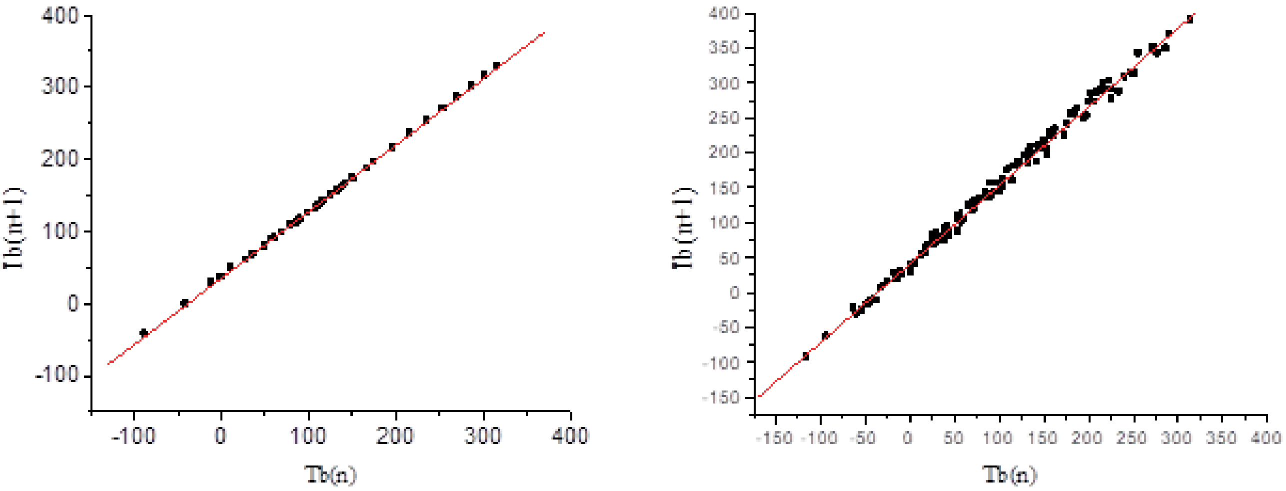
Approximation of various physicochemical properties (A) of homologs of organic compounds has always been among the most important problems in che¬mistry. Unusual general solution of this task becomes possible using linear (first order) recurrent relations:

$$A(n+1) = aA(n) + b \qquad (1)$$

where *A(n)* in the value of the property *A* for homolog containing *n* carbon atoms in a molecu-le, *A(n*+1) is the same for homolog, containing (*n*+1) carbon atoms, coefficients *a* and *b* are calculated with Least Square Method. Correlation coefficients *(R)* for various properties of homologs most often exceed 0.999.

The dependence (1) allows evaluating the properties of the following homologs based on the data for the previous members of series. Its applicability was demonstrated on the examples of normal boiling point (T_b) (Fig. 1a), refractive index (n_D^{20}), relative density (d_4^{20}), dielectric permittivity (ε), acidity constant (pK_a), and so on. Moreover, the single relations (1) characterize various homologous series with the same homologous differences, at first CH_2 (Fig. 1b)



(a) (b)

Figure 1. The plots of the linear recurrent dependence of normal boiling points (T_b,°C) of alkanes C_nH_{2n+2} (N = 39, R = 0.9997), and joint linear dependence for compounds of diffe¬rent series (N = 131, R = 0.9988).

PHOSPHONATE-SUBSTITUTED RU(II) COMPLEXES WITH 1,10-PHENANTHROLINE: SYNTHESIS AND APPLICATION TO PHOTOCATALYSIS

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Ru(II) complexes of 1,10-phenanthroline and its derivatives possess unique luminescent, electrochemical and photochemical properties1 due to which they find wide applications as fluorescent markers, photocatalysts and photovoltaic cell elements.

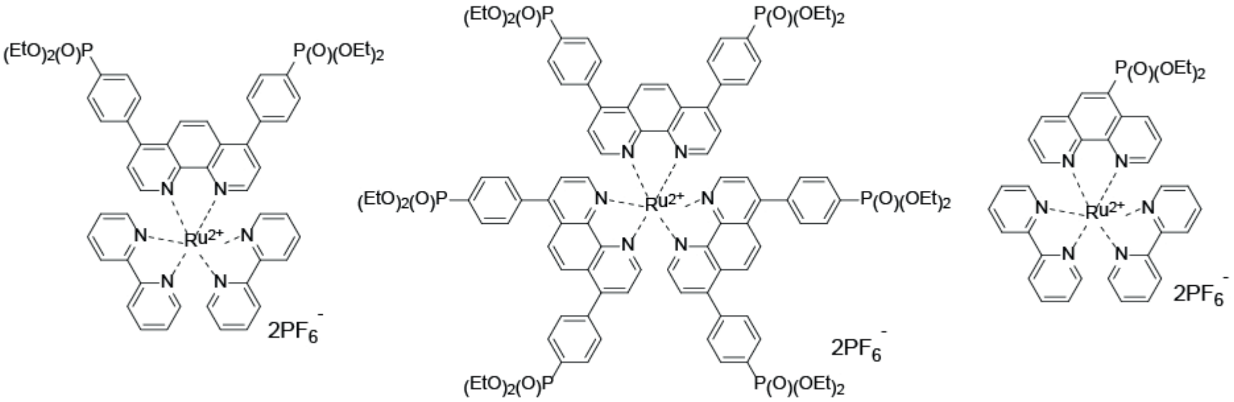

Figure 1. Examples of synthesized phosphonate-containing complexes.

In this work using Hirao and Suzuki-Miyaura reactions we obtained various derivatives of 1,10-phenanthroline with phosphonate groups linked to the heteroaromatic moiety either directly or through the phenylene linker. These ligands were used to synthesize heteroleptic Ru(II) complexes with additional 2,2'-bipyridyl ligands. We studied the spectral properties of obtained complexes and the possibility to employ them as photocatalysts in the oxidation of arylboronic acids into phenols.

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The work was financially supported by RFBR (project No 18-33-00279).

DIASTEREOSELECTIVE FORMAL [4+1] CYCLOADDITION OF INDOLES IN REACTION WITH UNSATURATED NITRO COMPOUNDS.

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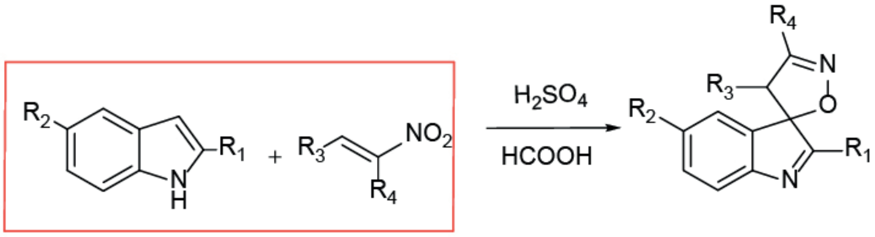
Heterocyclic compounds with 4’H-spiro[indoline-3,5’-isoxazole] and 4’H-spiro[indole-3,5’-isoxazole]cores do not occur in nature, these synthetic drugs can potentially demonstrate promising biological activity. Our group has interest in the development of Bronsted acid-assisted cascade heterocyclizations of nitro-compounds. Nitroalkenes are multipurpose reagents in organic synthesis, which are more often used as electrophilic components in Michael addition reactions, as dipolarophiles in some [3+2] cycloadditions and as electron poor dienophiles in Diels-Alder or hetero Diels-Alder reactions.

In the transformation that we recently discovered, nitroalkenes were successefully employed as synthetic equivalents of 1,4-dipoles of CNNO-type in a hightly diastereoselective formal [4+1]-cycloaddition reaction of indoles to afford 4’H-spiro[indole-3,5’-isoazole]derivatives. About these transformations,will be discussed in this report.



This work was supported by the Russian Science Foundation (Grant № 18-13-00238).

INFLUENCE OF CATALYST ON ANILINE POLYMERIZATION KINETICS

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In the past few decades, intensive studies have been carried out in the field of the use of polyaniline derivatives (PANI)[1]. For its synthesis, constant monitoring of various physicochemical parameters of the medium is important, which is successfully carried out by measuring the open-circuit potential (OCP) during polymerization2.

In this work, we studied the catalyst (cobalt phthalocyanine) effect for the oxidative polymerization of aniline on the change in OCP with time (Fig. 1).

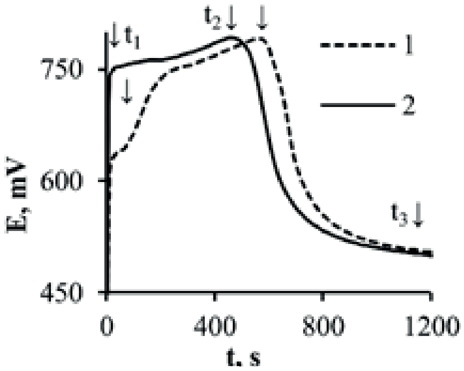

Figure 1. The change in the potential of the open circuit during the reaction: 1- without a catalyst, 2- with a catalyst

Changes in the OCP profile are in good agreement with the known two-step mechanism for the polymerization of aniline2. The obtained data indicate both a reduced induction period (t_1) and shortened time of the formation of insoluble precipitate PANI (t_2). The time of complete consumption of the oxidant (t_3) does not change.

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This work was carried out within the framework of the state task program no. AAAA-A19-119020890014-7.

FORMATION OF THE STRUCTURE OF ABRASIVE RESISTANT ALLOYS UNDER THE INFLUENCE OF ULTRADISPERSED TIN AND TICN PARTICLES IN ARC AND ELECTROSLAG SURFACING

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The introduction of modifiers into the weld pool during the deposition process contributes to the improvement of the mechanical and operational properties of the weld metal1.

Disclosure of the mechanisms of metal structure formation under the influence of particles of refractory chemical compounds will allow scientifically substantiate the principles of creating new abrasion-resistant weld alloys and develop materials for their surfacing.

It has been established that the introduction of ultrafine TiCN particles in the composition of nickel-based microgranules into the weld pool at electroslag surfacing helps to reduce their dissociation of the reaction zones. The initial TiCN particles with a size of 100 ... 600 nm are fixed in the metal of droplets forming in the slag at the end of the filler wire. Serving as crystallization centers in a deposited metal of the type Fe-Cr-Ni-Ti-C-B, TiCN particles contribute to the formation of a significant amount of TiC carbides in its structure. A similar function is performed by nanoscale (up to 500 nm) oxide inclusions of CaO and Al_2O_3, the source of which is slag, as well as endogenous TiO. Structural changes cause an increase in hardness and wear resistance of the weld metal.

It was revealed that the introduction of micro- and nanoparticles TiN into the low-temperature region of the weld pool during arc surfacing promotes their partial preservation in the melt and the formation of carbides $(Ti, Mo) C_{1-x}$ 1 ... 4 microns in size on them. These phases are also formed on endogenous TiN nano-sized inclusions. An increase in the volume fraction of hardening phases, along with the dispersion of the eutectic matrix, contributes to an increase in the hardness and durability of the metal of the Fe-Cr-Mo-Ti-Ni-C-B system to abrasive wear at temperatures up to 500 °C.

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OXIDATIVE ADDITION REACTIONS OF TRIARYLANTIMONY WITH FLUORINATED Β-DIKETONES

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β-Diketones, being O,O-ligands, have high complexing ability. It was previously shown that reactions of triphenylantimony with peroxides in the presence of β-diketones of $CF_3C(O)CH_2C(O)Alk$ type lead to the formation of cyclic diolate six-coordinated antimony (V) complexes.[1]

We have found for the first time that the interaction of triarylantimony with fluorinated β-diketones in the presence of peroxides results in the formation of binuclear triarylantimony carboxylates with a bridging oxygen atom:

$Ar_3Sb + CF_3C(O)CH_2C(O)R + ROOH \rightarrow [CF_3C(O)O]Ar_3SbOSbAr_3[OC(O)R]$
Ar = Ph (1,2), *m*-Tol (3), *p*-Tol; R = CF3 (1), C2F5 (2,3).

Compounds were characterized by IR, NMR spectroscopy and X-ray diffraction analysis (Fig. 1).

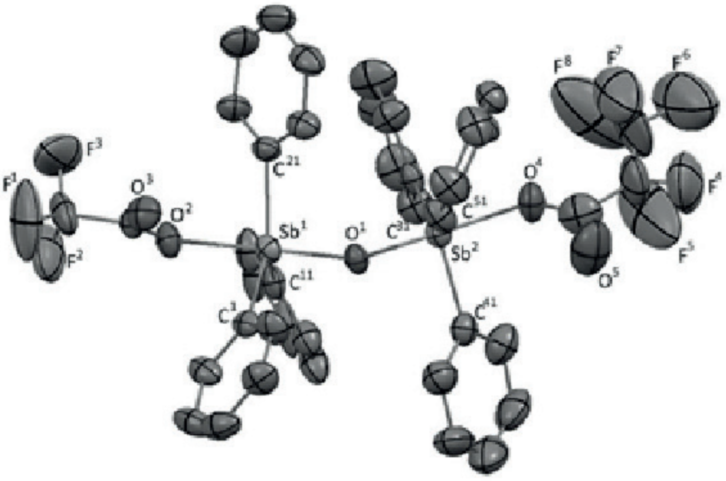

Figure 1. The structure of the molecule $[CF_3C(O)O]Ph_3SbOSbPh_3[OC(O)C_2F_5]$ showing thermal ellipsoids for 30% probability. Hydrogen atoms have been omitted for clarity.

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NEW PROPERTIES OF EARLY TRANSITION METAL CHALCOGENIDES

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This paper presents a new look at the known chalcogenides of transition metals of groups IV-VI, taking into account the trends and analytical capabilities of modern science. Phases of different stoichiometry and structures are formed in the systems "transition metal - chalcogen" MQ_n (M = Ti, Zr, V, Nb, Ta, Mo, W, Re; Q = S, Se), among them simple chalcogenides as well as polychalcogenides containing $(Q\text{-}Q)^{2-}$ groups can be found. Low-dimensional (1D and 2D) structures are of special interest here.

Experimental and theoretical studies of chalcogenides with different compositions and structures were carried out at compounds containing metal chains M_2Q_3, MQ_3, VS_4, as well as layered MQ_2. Nature of polymorphism was examined by example of composition "Nb_2Q_3". Formation features and nature of solid solutions were studied for non-isoelectronically doped MoS_2 (Mo/Nb and Mo/Re).

Owing to low-dimensional character of the structures MQ_n, their exfoliation with formation of particles 100-400 nm in diameter and up to 10 nm thick was shown. The colloid particles were used for obtaining of films and composites with noble metal nanoparticles.

Particular attention is paid to the study of the properties of polychalcogenides, including X-ray amorphous ones. The polysulfides were shown to have increased reactivity due to presence of $(Q\text{-}Q)^{2-}$ groups. This feature along with semiconductivity and other physical properties allows considering polysulfides as promising electrode materials with increased capacitance, sensors, and catalysts.

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STUDY OF BIOLOGICALLY ACTIVE SUBSTITUTED BENZALDEHYDES

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Substituted benzaldehydes, which are widely distributed in nature, exhibit antibacterial, anti-inflammatory, antiviral, anticarcinogenic activity with low toxicity, which makes them promising in medicine. The report presents the results of experimental and theoretical studies of spectral-luminescent properties of four substituted benzaldehydes: o-anisic and lilac benzaldehydes, vanillin and 2,3-hydroxybenzaldehyde. Experimental absorption, fluorescence and fluorescence excitation spectra were obtained. A structure of the molecules studied depends on the pH of medium and therefore, in addition to neutral, their ionic forms (cations and anions) also appear. Absorption and fluorescence spectra, rate constants of photophysical processes (radiative and nonradiative) and physico-chemical properties of neutral and ionic forms of molecules are calculated by INDO method with original spectroscopic parametrization. Calculations have shown that in the neutral forms of all the compounds studied, the state S1 is formed by the transition of nπ * -type both in absorption and in fluorescence. The main channel for the decay of the fluorescent state in them is ST-conversion. Therefore, neutral forms of substituted benzaldehydes are not the source of fluorescence observed experimentally. In ionic forms, inversion of nπ* and ππ* states takes place, and fluorescence of vanillin, anisic and lilac aldehydes is emitted by cationic forms of these compounds in ethanol. The ultimate goal of research is the development of new criteria and methods for predicting the pharmacological activity of biomolecules.

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The results were obtained in the framework of the implementation of the state task of the Ministry of Education and Science of the Russian Federation, project No. 4.6027.2017/8.9.

RESEARCH OF COMPETITION OF PHOTOPHYSICAL AND PHOTOCHEMICAL PROCESSES

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A.N. Terenin combined interrelated photophysical and photochemical processes in the photonics of organic compounds [1]. We were tasked with developing a quantum-chemical model for studying the competition of photophysical and photochemical processes during the dissociation of single chemical bonds in excited molecule. To study the reaction of photo-breaking of bonds, an approach was developed, the main provisions of which were formulated as follows [2].

1. The breaking of a chemical bond can occur only with the participation of s-electrons, i.e. mainly in σσ*-, σπ*-, πσ*-type states.
2. The probability of breaking this bond in this excited state is determined by degree of localization of the electronic excitation energy on this bond, as well as by reducing the strength of the broken bond in the photodissociative state. The bond strength (energy) was assumed to be proportional to electron density (population) of the bond.
3. A potential repulsion curve corresponds to the photodissociative state, while ground state corresponds to Morse potential.
4. In absence of possibility of direct excitation of the photodissociative state, it must be possible to populate it through intramolecular photophysical processes or by multi-stage absorption.

The report presents the possibilities of proposed quantum-chemical approach for the study of photochemical properties of molecules.

The results of quantum-chemical calculations and the approach based on them to the study of photodissociation of chemical bonds in specific polyatomic compounds made it possible to determine orbital nature, energy and probability of population of the photodissociative state, mechanism of primary stage of photoreaction, role of proton donor medium.

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The results were obtained in the framework of the implementation of the state task of the Ministry of Education and Science of the Russian Federation, project No. 4.6027.2017/8.9.

SYNTHESIS AND TRANSFORMATION OF HEXAHYDROPYRIMIDINES AND 1,3,5-HEXAHYDROTRIAZINES

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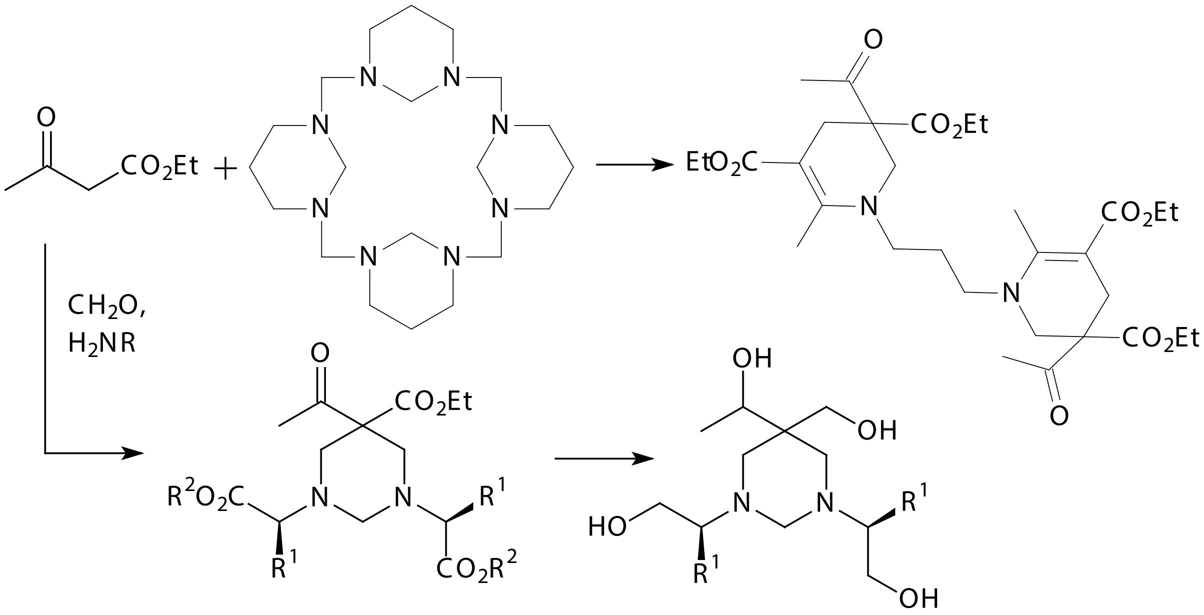
Hexahydropyrimidines and 1,2,3,4-tetrahydropyridines are not only structural fragments of many biologically active compounds, but also have significant synthetic potential. We have developed selective methods for the preparation of 5-acetylhexahydropyrimidine-5-carboxylates and 3-acetyl-6-methyl-1,2,3,4-tetrahydropyridine-3,5-dicarboxylates based on the reaction of acetoacetate ester with 1,3,5-hexahydrotriazines or formaldehyde and esters of natural amino acids[1].



The interaction of alkyl 5-acetylhexahydropyrimidine-5-carboxylates with NH_3, $N_2H_4 \cdot H_2O$ and $LiAlH_4$ obtained hexahydropyrimidines derivatives containing in their structure pharmacophoric 1,3-propylenediamine and 1,3-propanolamine fragments.

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The work was funded the Ministry of Education and Science of the Russian Federation through the State order (project no. AAAA-A17-1170011910021-8, contract no. 4.2703.2017/PCh)

REACTIONS OF 1-[(Z)-1,4-DIBROMOBUT-2-EN-2-YL]ADAMANTANE WITH 1,3-DICARBONYL COMPOUNDS AND THEIR ANALOGUES

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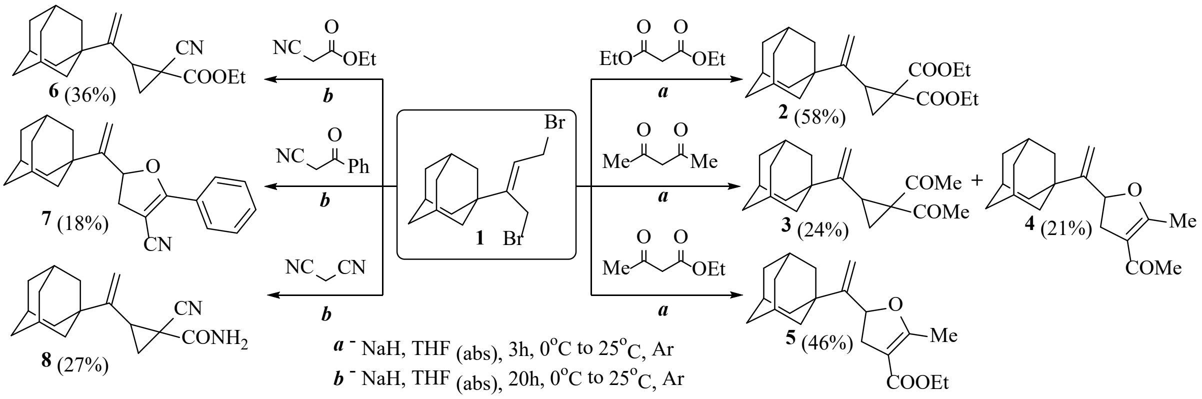
It is known that β-dicarbonyl compounds are easily alkylated with allyl halides in the presence of bases to form the corresponding γ, δ-unsaturated dicarbonyl compounds. In the case of 1,4-dihalobut-2enes, the resulting alkylation products can undergo further transformations, as a result of which carbocyclic and heterocyclic compounds are formed[1-3].

So, as a result of the reactions of 1-[(Z)-1,4-dibromobut-2-en-2-yl] adamantane 1 with diethyl malonate, acetylacetone and acetoacetic ester in the presence of sodium hydride, adamantane-containing vinyl cyclopropanes 2,3 and vinyl dihydrofuranes 4,5 , depending on the structure of the starting β-dicarbonyl compound.



a - NaH, THF (abs), 3h, 0°C to 25°C, Ar
b - NaH, THF (abs), 20h, 0°C to 25°C, Ar

Similar products were obtained by the reaction of dibromide 1 with ethyl cyanoacetate, benzoylacetonitrile and malononitrile. Amide 8, apparently, is formed as a result of the hydrolysis of the intermediate adamantane-containing cyclopropanedinitrile.

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This study was performed under financial support by the Russian Foundation for Basic Research (project no. 18-33-00994).

INFRARED SPECTROSCOPIC STUDY OF (4-METHYLPENT-3-EN-1-YNYL)METHYLTHIOCARBEN AND ITS PHOTOCHEMICAL TRANSFORMATIONS IN AN ARGON MATRIX

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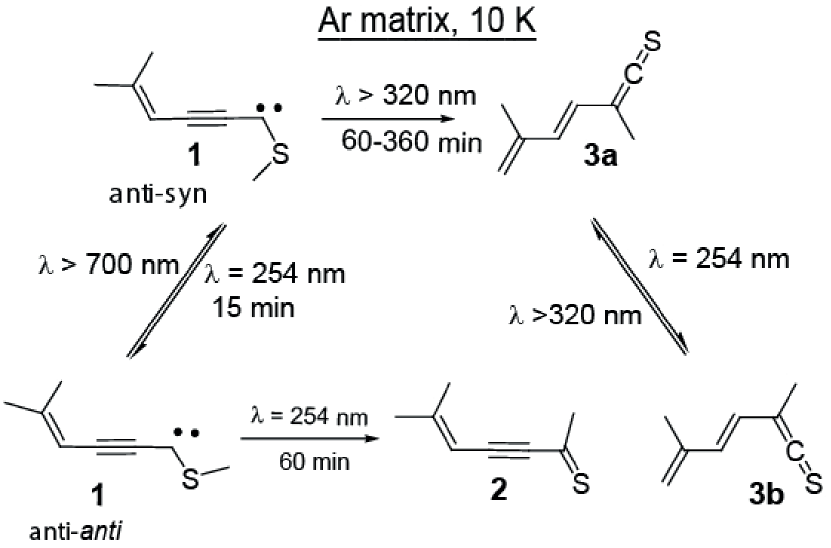
(4-Methylpent-3-en-1-ynyl)methylthiocarbene (Me$_2$C=CH–C≡C(MeS)C:) (1) was generated from 3,3-dimethyl-5-methylthioethynyl-3H-pyrazole by the UV photolysis (λ~ 350 nm) and subsequent irradiation at λ> 490 in Ar matrix at 10 K. The comparison of FTIR spectroscopy data with the results of quantum chemical calculations (B3LYP/aug-cc-PVTZ) allowed us to determine that 1 has a singlet ground state with the localization of the unpaired spins on the carbon atom in α-position to methylthio fragment.



The short time (15 min) UV photolysis of this carbene by λ = 254 nm light results to the isomerization of its more stable *anti-syn* rotamer into *anti-anti* rotamer. Upon further irradiations at λ > 700 nm, the *anti-syn* form is partially recovered. Prolonged irradiation of studied carbene by 254 nm light produced photochemically stable thioketone (Me(C=S)–C≡C–CH=CMe$_2$) (2), whereas irradiation at λ > 320 nm leads to the formation of labile thioketenes (S=C=C(Me)–CH=CH–CMe=CH$_2$) (3a,3b).

Work was supported by a grant of the RFBR (Project 18-03-01037a).

CH-FUNCTIONALIZATION OF 2-ARYL(HETARYL)SUBSTITUTED PYRIDINE-N-OXIDES BY DIALKYLCYANAMIDES

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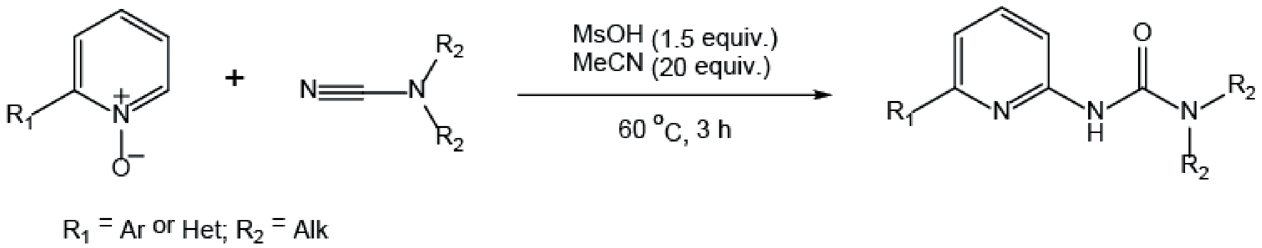
Ureas bearing heterocyclic moiety are attractive targets for medicinal chemistry because of a wide range of their therapeutic applications[1]. There is additional interest due to their ability to form coordination compounds with transition metals, some of which also have valuable properties, for example, antiproliferative activity[2].

Previously, the simple protocol for the preparation of N-pyridylureas via CH-functionalization of pyridine-N-oxides by dialkylcyanamides in acidic medium has been developed by our group3. Herein work is aimed at further studying the synthetic perspectives of this reaction by expanding the range of substrates to pyridine-N-oxides containing aromatic and heterocyclic substituents in the second position of the pyridine ring (scheme 1). First of all, this refers to phenylpyridine and bipyridine, modification of which provides access to new types of bi- and tridentate chelate ligands.



Scheme 1. Reaction of pyridine-N-oxides with dialkylcyanamides.

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Physicochemical studies were performed at the Center for Magnetic Resonance Research and Center for Chemical Analysis and Materials Research (both belong to Saint Petersburg State University).

SYNTHESIS OF DIHYDRO- AND TETRAHYDRO-CHROMENO[3,2-C] PYRIDINES AND THEIR N-OXIDES BASED ON 4A-(MORPHOLIN-4-YL)-HEXAHYDRO-1H-CHROMENO[3,2-C]PYRIDIN-10-OL

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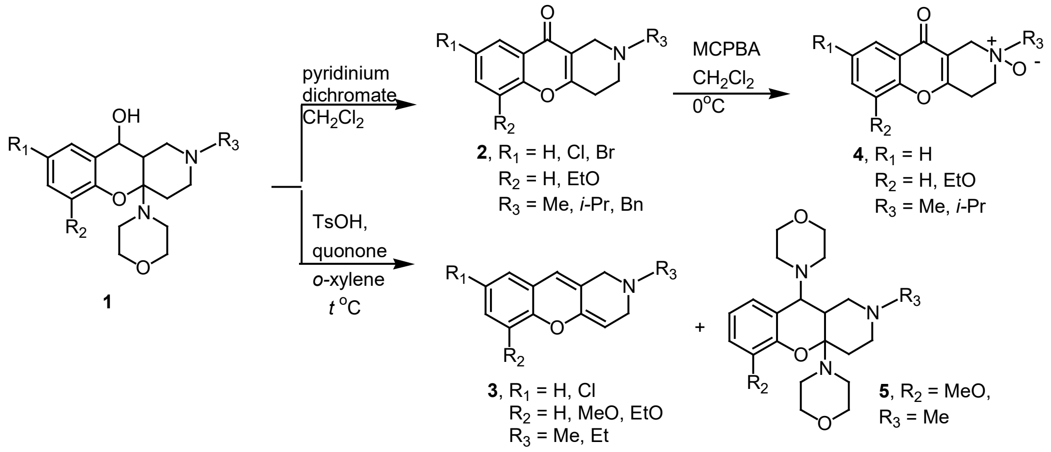
Recently we have studied the reactions of chromeno[3,2-c]pyridines with activated alkynes under different conditions[1] and found that initial chromenopyridines and their derivatives are promising inhibitors of acetylcholinesterase (AChE inhibitors) and monoamine oxidase (MAO inhibitors)[1,2]. Supposing that variation of the substituents or changes in chromenopyridine core will enhance biological properties of the products , we synthesized a series of compound 2-5. The starting chromenopyridines 1 were prepared using earlier described two-step procedure starting from N-substituted piperidones and aromatic aldehydes[3]. The target compounds 2-5 were obtained from chromenopyridines 1 through oxidation or acid-catalyzed oxidative dehydratation in o-xylene. The structure of unusual product 5, containing two morpholine fragments, was confirmed by X-ray spectroscopy (Fig. 1). N-oxides 4 were synthesized by oxidation of compounds 2 using MCPBA.



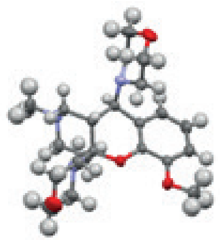


Figure 1. Molecular structure of compound 5

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Mass and IR spectra were registered using instruments of the Shared Research and Educational Center of Physic-Chemical Studies of New Materials, Substances and Catalysis of RUDN. The publication has been prepared with the support of the "RUDN University Program 5-100".

THE REACTIONS OF FLUORINATED 1-ARYLHYDRAZONES OF 1,2,4-TRICARBONYL COMPOUNDS WITH AMINES

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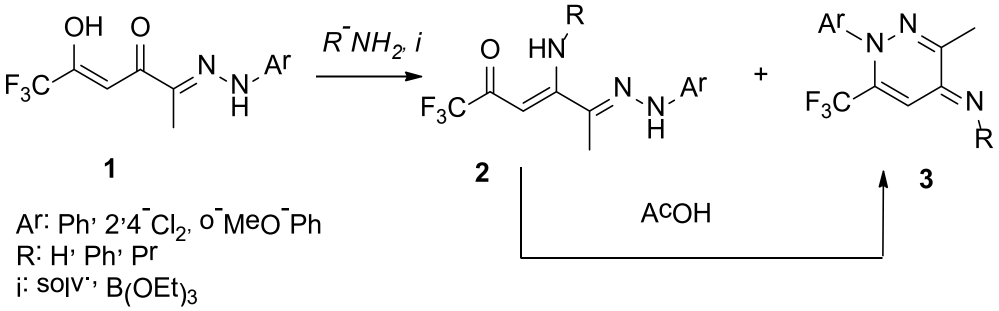
Recently we have described 1-arylhydrazones of 4-fluoroalkyl-1,2,4-tricarbonyl compounds that can be considered as a novel fluorinated building-block for construction of fictionalized five- and six-membered heterocycles. For example, aryl hydrazones of fluorinated pyrazolylketones were have obtained reacting these reagents with hydrazines. The aryl hydrazone group can be used in further transformations.

Here we report on reactions of 1-arylhydrazones 4-fluoroalkyl-1,2,4-tricarbonyl compounds 1 with amines (aniline, n-propylamine) and ammonia. We found that diketohydrazones 1 react non readily with these reagents: prolonged refluxing leads to degradation of 1. It is gratifying, amination of diketohydrazones 1 at their 1,3-diketone fragment is effectively mediated with triethyl borate to give ketoaminoenones 2 bearing a terminal arylhydrazone group.



When 1 reacted with aniline, some amount of pyridazin-4-imines 3 (R = Ph) was observed in reaction mixtures. On the other hand, it was found that compounds 3 (R = H, Pr, Ph) can be readily obtained by cyclization of the corresponding ketoaminoenones 2 in an acidic medium.

COMPLEXATION OF HAFNIUM (IV) - CITRIC ACID IN AQUEOUS SOLUTIONS

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PH-metric titration is used to study the complexation in the $HfOCl_2$ - citric acid system at the molar ratio of metal-ligand 1:1, 1:2, 1:3 in the pH range from 1.3 to 10.5. The determination of stoichiometry and calculation of the equilibrium composition of the formed hafnium (IV) citrates are carried out, using the program CPESSP by Professor Yu. I. Salnikov. In the preparation of the stoichiometry matrix, while describing the equilibrium in the system of $Hf4^+$- citric acid, we rely on the previously obtained data on the composition and stability of the zirconium (IV) - citric acid system zirconium (IV)[1,2].

In the system under study, at the equimolar metal-ligand ratio, complex forms of 4:4 composition are predominantly formed, which may be associated with the preservation of the Hf4. The formation of $[HfHCit]^+$, [HfCit] complexes is recorded in the acidic region. With an excess of citrate – ligand, 4:8 composition complex forms of varying degrees of deprotonation are formed. Constants of formation and shares of accumulation of these complex forms are calculated. The composition and stability of hafnium (IV) citrate complexes and zirconium (IV) citrate complexes are correlated. Compared to the same hafnium (IV) complexes, zirconium (IV) citrates possess higher resistance.

Thus, we have shown that in the hafnium (IV) – citric acid complex forms of 1:1, 4:4, 4:8 compositions, different degrees of deprotonation exist in a wide range of pH values.

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CH-FUNCTIONALIZATION OF PHENOL AND HAPHTHOL IN THE SYNTHESIS OF PHENOL SULPHANYLALKYL DERIVATIVES

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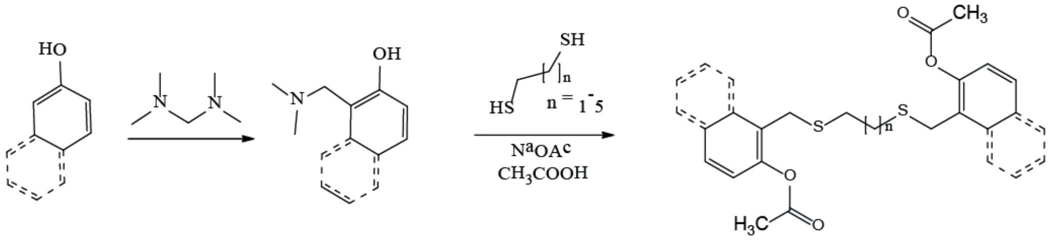
Amino and thiomethylated phenol derivatives are known to exhibit antioxidant, anti-radical, anti-inflammatory and anti-tumor properties. Earlier[1], we synthesized sulfanyl-substituted 1,3-dicarbonyl compounds (DCC) by the reaction of CH_2O and SH-acids via activating the protons of CH_2-methylene in DCC by Luis acids or bases. This report discusses approaches to the design of sulfonyl-substituted phenol derivatives. Thiomethylation of phenols in DCC conditions occurs simultaneously on O- and *ortho,para*-C-sp^2-positions of substrates with the formation of products as mixture.

The approach we developed is to react the C – H amino-functionalization of phenol (naphthol) under the action of N,N,N′,N′-tetramethyl methane diamine to form N, N- (dimethylaminomethyl) phenol (naphthol) with a yield of more than 90%.

Next, the reaction of substitution of the amino function under the action of the corresponding α,ω-dithiol in the environment of the acetate buffer was carried out.



Thus, a method has been developed for obtaining new derivatives of phenol and naphthol, which are promising for the creation of bioactive agents.

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This work was supported by the Russian Foundation for Basic Research and the Academy of Sciences of the Republic of Bashkortostan (project № 17-43-020292 r_a) and AAAA-A19-119022290010-9

COMPOSITION AND STABILITY COMPLEXES OF FE (III) AND AG (I) WITH THIOSEMICARBAZIDES

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Thiosemicarbazide (TSC) and its derivatives have neurotropic activity and are used in medical practices. In [1] provides detailed information on the pharmacological, biochemical, pathophysical effects of TSC, as well as their application in medicine. These compounds are considered biologically active substances and good complexing agents. In this connection, the study of the complexation Fe (III) and Ag (I) with thiosemicarbazide (TSC), 1-formyl-3-thiosemicarbazide (1-FTSC) and 1-acetyl-3-thiosemicarbazide (1-ATSC), the establishment of their stability and biological activity is an important scientific task. Our studies have shown that in aqueous solutions of Fe (III) and Ag (I) with TSC, 1-FTC and 1-ATSC, they enter into step-complexing. The number of complex particles formed in the solution was determined by the Yacimirk method. To determine the overall stability constants of the complexes Fe (III) and Ag (I) with TSC, 1-FTSK and 1-ATSK, we used the nonlinear least squares method. The table 1 shows the overall stability constants of the complexes of Fe (III) with TSC and 1-FTSC at 298K.

Table 1. General stability constants of complexes of Fe (III) with TSC and 1-FTC

[Fe(TSC)]3+ lgβ1	[Fe(TSC)2]3+ lgβ2	[Fe(TSC)3]3+ lgβ3	[Fe(1-FTSC)]3+ lgβ1	[Fe(1- FTSC)2]3+ lgβ2
4,65±0,04	6,34±0,03	7,80±0,07	4,21±0,08	6,14±0,12

These tables show that the introduction of the formyl group into the thiosemicarbazide molecule affects both the number of complex particles formed in the solution and their stability. Studies have shown that, depending on the nature of the ligand, the stability of three-substituted silver (I) complexes with TSC and its acyl derivatives at 298 K varies in the following row: TSC> 1-FTC> 1-ATSC. The proximity of the numerical values of the stability constants of the Ag (I) complexes with TSC, 1-FTSC and 1-ATSC indicates that all three compounds are coordinated to Ag(I) by the same atom. The decrease in the overall stability constants of the Fe (III) and Ag (I) complexes during the transition from TSC to 1-FTC and 1-ATSC is associated with the redistribution of electron density in the TSC molecule with the introduction of acyl groups.

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Work performed at the department of inorganic chemistry, TNU.

THEORETICAL STUDY OF THE RELATION STRUCTURE – PROPERTIES IN OXIDES OF CHROMIUM

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The object of research is new complexes of chromium oxides. The aim of the work was to determine the criteria of stability of these complexes, the conditions of their ferromagnetic or antiferromagnetic properties. The geometrical and electronic structures of the Cr_2O_n and $Cr_2O_n^-$ clusters are computed using density functional theory with a generalized gradient approximation in the range of $1 \leq n \leq 14$. For each value of n the most probable cluster structures with all possible spin multiplicity values are calculated. Then among them the structure with the lowest total energy was chosen, which was considered the ground state of the cluster for this value n. Thus, more than 500 Cr_2O_n and Cr_2On^- cluster structures were calculated. In the lowest total energies states of Cr_2O_2, Cr_2O_3, Cr_2O_4, Cr_2O_{14}, $Cr_2O_3^-$, $Cr_2O_4^-$ and $Cr_2O_{14}^-$ total spin magnetic moments of the Cr atoms are quite large and antiferromagnetically coupled. In the rest of the series, at least one of the Cr atoms has no spin-magnetic moment at all. The computed vertical electron-detachment energies of the $Cr_2O_n^-$ are in good agreement with experimental values obtained in the $1 \leq n \leq 7$ range. All neutral Cr_2O_n possess electron affinities larger than the electron affinities of halogen atoms when $n > 6$ and are thus superhalogens. It is found that the neutrals and anions are stable with respect to the abstraction of an O atom in the whole range of n considered, whereas both neutrals and anions became unstable toward the loss of O_2 for $n > 7$. The polarizability per atom decreases sharply when n moves from one to four and then remains nearly constant for larger n values in both series.

The work was done on the theme of the state task № 0089-2014-0026

THE TRIPLE CL/BR/I HALOGEN ISOMORPHOUS EXCHANGE IN CRYSTALS OF PALLADIUM(II) ISOCYANIDE COMPLEXES

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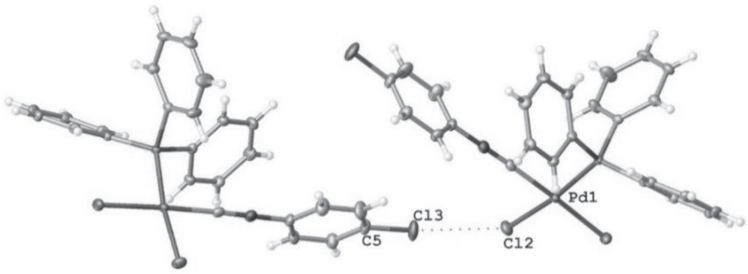
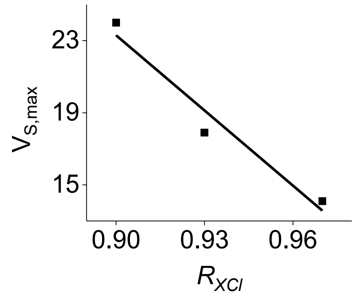
Halogen bonding (XB) is considered to be comparable with hydrogen one[1] in strength and directionality ant thus often acts as a crystal structure determining interaction. Dependence of the strength of XB on the type of a halogen was studied theoretically by P. Politzer.[2] It was predicted by him that the XB energy must increase when XB donor is being changed from Cl to Br to I. However, his considerations were not fully confirmed for a solid phase, limiting XB usage in crystal engineering and making it difficult to control a crystal structure when the XB donor is replaced.

In this work we perform two series of structures *cis*-$[PdCl_2(CNC_6H_4\text{-}4\text{-}X)(PPh_3)]$[3] and ^{trans}-$[PdI_2(CNC_6H_4\text{-}4\text{-}X)_2]{\bullet}2I_2$ (X = Cl, Br, I) with isomorphous Cl/Br/I exchange and with preservation of XBs. In both structures calculated maximum positive potential $V_{S,max}$ of the XB donor[4] depends linearly on distances between XB donors and acceptors divided by their van der Waals radii which finally experimentally proves Politzer theory for a solid phase.





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The work was supported by the Russian Foundation for Basic Research (18-33-20073) and Grant Program of the President of Russian Federation (MK-4457.2018.3). Physicochemical studies were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research (all belonging to Saint Pe-tersburg State University).

LUMINESCENT PROPERTIES OF SELECTED QUINOXALINE AND QUINOXALINONE DERIVATIVES. EXPERIMENTAL AND THEORETICAL STUDY

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Organic electronics nowadays is one of the most promising and actively developing directions of modern material science. Molecules composed of electronic-donating and electronic-withdrawing moieties (D-π-A) are paid especial attentions being utilized as functional layers in nonlinear optical materials (NLO), organic light-emitting diodes (OLEDs), sensory applications of different types, and organic photovoltaics. D-π-A systems often demonstrate remarkable sensitivity of the photophysical properties dependent on structural modification and environment, allowing fine-tuning of their properties toward possible applications. In particular, we have demonstrated high sensitivity of luminescent signal to position of donor fragment, solvent polarity, and H-bond donors of quinoxaline/quinoxalinone derivatives [1,2].

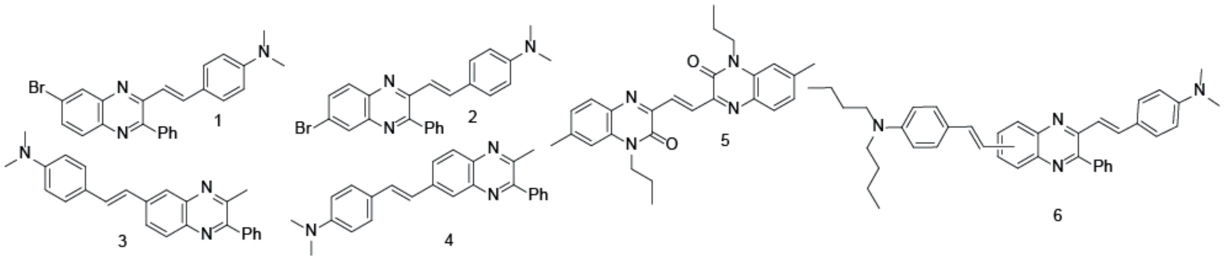

Figure 1. Chemical structures of considered systems.

Herein we report on experimental and theoretical study of the photophysical properties in the series of related compounds (Figure 1). Chosen computational approach was found as very effective for interpretation and prediction of electronic absorption spectra, as well as for reveling of transition natures.

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The reported study was funded by Russian Science Foundation (project № 18-73-00165)

PRODUCTS OF REACTION $Ra(NO_3)$ AND $RaCO_3$ WITH IRON AND NICKEL

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JSC “SSC RIAR” develops the production technology of short-lived alpha emitters for medical purposes (^{223}Ra, ^{224}Ra, ^{227}Th, etc.) from ^{226}Ra irradiated in nuclear reactor. After irradiated material dissolution in HCOOH, the solution contain the large concentrations of iron, chromium and nickel salts, which hurdles the isolation and purification of ^{227}Ac.

The probable reason for this is the reaction of radium with inner surface of target claddings to form compounds $Ra_xM_yO_z$ (where M = Ti, Cr, Fe, Ni), which could dissolve in formic acid. In this work, the products of the chemical interaction of $RaCO_3$ and $Ra(NO_3)_2$ with metallic Fe and Ni at a temperature of 800° C were studied.

In samples, obtained by calcinations radium salts with iron traces of phases similar to $BaFeO_{3-x}$ were found. Due to low content of barium salts in radium preparation these phases can be attributed to previously unknown compound $RaFeO_{3-x}$. It was found that a similar barium compound is easily soluble in formic acid. The combination of these facts allows us to explain the high rate of corrosion of radium target claddings when dissolution of the irradiated material.

In samples, obtained by calcinations radium salts with nickel there was a very weak group of reflexes close to $BaNiO_x$, which can be interpreted as $RaNiO_x$. A few reflexes were related to a phase analogous to BaO_2 (probably RaO_2), which may play the role of an intermediate in the mechanism of metal surface oxidation.

An increase radium peroxide stability compared to barium peroxide is a possible reason that radium salts are more chemically active than barium in these reactions.

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 18-33-00145.

SYNTHESIS OF HYDANTOINS AND ITS THIO- AND SELENO-ISOSTERIC ANALOGS WITH ADAMANTANE MOIETY

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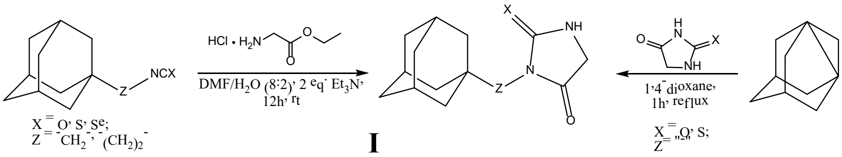
Derivatives of hydantoin and its thio- and seleno-isosteric analogs (2-thiogidantoin and 2-selenohydantoin) show anticonvulsant, fungicidal, antiviral and antimutagenic activities and other types of biological activity. The adamantyl fragment is a highly frequently used structural element in medical chemistry [1]. However, the number of publications on the synthesis of 1-adamantyl-containing hydantoins and its S- and Se-isosteric analogues is extremely small.

Synthesis of 3 - [(adamantan-1-yl) alkylene] hydantoins, of general formula I, and its 2-thio- and 2-seleno-isosteric analogues, was carried out in two stages: the reaction of heteroallenes with glycine ethyl ester hydrochloride in the presence of Et_3N and the subsequent cyclization of the formed adamantyl-containing ethyl ureido-acetates *in situ* with a yield of 75–85%.

However, these reactions with the use of 1-adamantyl isocyanate (or isothiocyanate) were not successful. Therefore, to introduce the 1-adamantyl group into the 3-position of hydantoin and 2-thiohydantoin, the bridge [3.3.1] propellant (1,3-dehydro-adamantane, 1,3-DHA) was used. The reaction was carried out in boiling 1,4-dioxane for 1 h. The yields were 75-80%.



Thus, methods for preparation of hydantoins and its S- and Se-isosteric analogues, containing a N^3-1-adamantyl group, separated or not separated by an alkylene bridge, with yields of 75-85%, have been developed.

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This work was supported by the Ministry of Education and Science of the Russian Federation (base part of state assignment for 2017–2019; project no. 4.7491.2017/BCh) and performed on the equipment purchased by the funds of the Program of Strategic Development of VSTU in 2012-2016.

THE REGULARITIES OF CHANGE OF STRUCTURE AND PROPERTIES OF N,O-COORDINATED COMPLEXES OF TRANSITIONAL METALS IN THE ROWS OF THE PERIODIC TABLE IN THE RELATION TO THEIR ELECTRONIC STRUSTURE

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The regularities of change of structure and properties of N,O-coordinated nitrilo-*tris*-methylenephosphonic complexes of 3*d*- and 4*f*-metals from Mn to Zn and from La to Tb respectively are studied. The coordination complexes of said metals with completely deprotonated nitrilo-*tris*-methylenephosphonic acid (NTP) are synthesized and isolated. For each of these complexes the atomic-molecular and crystal structure by precision single-crystal X-ray diffraction, the electron-energy structure of the valence band and the core levels by XPS, the thermochemical behavior and the reaction ability are investigated. Some of a synthesized compounds show properties of effective corrosion inhibitors. Comparatively analysis with coordination complexes of said metals with partially deprotonated NTP is carried out.

The regularities of change of interatomic distances of *M*–N and *M*–O, characteristics of the respective coordination bonds and properties of coordination compounds caused by them are shown. It is shown that change of structure and properties of coordination complexes is caused by change of electron-energy structure of metal atom, in particular, change of binding energy of electrons of *p*- and *d*-sublevels of a preouter electron shell. This change influences a possibility of formation of lowest occupied valence orbital at overlapping of the said *p*- and *d*-sublevels of a preouter electron shell of the central atom with N2s- and O2s-sublevels of the donor centers of the ligand molecule.

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The work was performed in the framework of the state assignment, subj. No. AAAA-A17-117022250040-0..

PHOTODEHYDROGENATION OF DIHYDROHETARENES IN THE PRESENCE OF BENZOQUINONE

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We previously found that in the presence of perchloralkanes (σ-electron ac-ceptors) various dihydrohetarenes undergo effective photodehydrogenation. It was shown that such reactions most likely proceed by the ion-radical mechanism and are accompanied by an increase in the acidity of the medium both in solutions of organic solvents and in polymer films[1-3].

In this report we inform that the photodehydrogenation of dihydrohetarenes in the presence of benzoquinone (π-electron acceptors) proceeds even more efficiently and with higher speed than in the presence of perchloralcans[4]. We have found that reaction photodehydrogenation of dihydrohetarenes in the presence of benzoquinone are not accompanied by an increase in the acidity of the medium and proceed by a radical mechanism.

New photodehydrogenation reactions of dihydrohetarenes have been used for optical information recording[5], may be of interest for the design of new sensory elements, to be useful in the preparative preparation of the corresponding hetarenes, as well as in the study of redox processes in biochemical systems.

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This work is supported by the Russian Science Foundation, grant 17-13-01302.

SYNTHESIS OF STABILIZERS BASED ON 3-(2,6-DI-TRET-BUTYL-HYDROXYPHENYL)PROPYLCHLORIDE AND THE EFFICIENCY OF THEIR ACTIVITY UNDER CONDITIONS OF HIGH-TEMPERATURE OXIDATION OF INDUSTRIAL OIL

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By a series of sequential transformations a number of polyfunctional inhibitors of oxidation processes based on 2,6-di-tert-butyl-4-(3-hydroxypropyl)phenol were synthesized: bis-(3,5-di-tert-butyl-4-hydroxy-phenyl)propyl)phosphite (I), di-[3-(2,6-di-tert-butyl-hydro-syphenyl)propyl]-sulfide (II), 1,6-di-(2,6-di-tert-butyl-hydroxy-phenyl)hexane (III). The structure of the compounds was established by methods of IR-, NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, the composition was confirmed by elemental analysis.

The effectiveness of the synthesized compounds was defined under conditions of thermal oxidation of industrial oil (I20A). Accumulation of low molecular weight volatile acids (A_{lmw}), acid number (AN) and the amount of precipitate formed in the oil (m) were used as criteria (Table 1). The known stabilizer Agidol-70 was used as comparative antioxidant.

Table 1. Characteristics of the stabilizers' efficiency in the oxidation conditions of industrial oil brand I20A (GOST 981-75, 170 °C, 5 hours in the presence of 0,25% wt. of the stabilizer)

Compounds	$A_{lmw} \times 10^{-3}$	AN	m, g
I	1,4373	0,2567	0,0173
II	19,6570	2,7467	0,5045
III	19,5080	1,6700	0,3751
N-(3,5-di-tert-butyl-4-hydroxybenzyl)benzo-thiazol-2-thione (Agidol-70)	22,8183	2,5033	0,7376

Experimental data has shown (Table 1), that synthesized products inhibit industrial oil thermal oxidation, reducing the amount of acids and precipitate formed. The synthesized stabilizers are superior to Agidol -70 by antioxidant efficiency.

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ESTIMATION OF MELTING CHARACTERISTICS OF ALKALI METAL HALIDE SALTS AT THE INCLUSION OF POLARIZATION EFFECTS IN THE ENERGY OF MELTS WITHIN THE THERMODYNAMIC PERTURBATION THEORY

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The forces acting between ions in the molten salts are classified according to the number of particles entering into the interaction energy. The first group includes the pair interactions: repulsion at short distances, the Coulomb interac-tions, etc. The greatest difficulty is the consideration of the second group of interactions, namely, polarization interactions. Point is that the charge of a given ion induces dipole moments on neighboring ones, which will not only interact with each other, but also induce dipole moments on other ions. However, the polarization energy can be calculated for the molten salts by introducing a dielectric constant to avoid the many-body problem of polarization forces. Within the statistical thermodynamics this problem is more convenient to solve by means of thermodynamic perturbation theory (TPT). The expression for the free energy of melts taking into account the polarization of ions based on the model of charged hard spheres with different diameters in the TPT-method is

$$F_{liq} = F_0 + \frac{1}{4\pi^2}\sum_{i,j}\left[\sqrt{x_i x_j}\int_0^\infty \varphi_j^1(k)\left(S_j^0(k)-\delta_j\right)k^2 dk - 2\pi^2\rho\, x_i x_j \varphi_j^1(0)\right],$$

where $S_j^0(k)$ are the structural factors of the reference system in the inverse Fourier space, $\varphi_j^1(k)$ is the perturbing ion-dipole additive to the pair potential in the Fourier space, F^0 relates to the free energy of the reference system of charged hard spheres, and the other two terms describe the polarization additive to the free energy of the system.

Further calculation of the temperatures and thermodynamic characteristics of melting is based on the standard rule for the equality of the chemical potentials of the liquid and solid phases at the phase equilibrium point. Herewith, the free energy of the solid phase is calculated using three main contributions: Madelung energy of the ionic crystal, Born repulsion of the electron shells, and vibration contribution within the Debye model.

The calculated results of the temperatures and thermodynamic characteristics of the melting for all alkali metal halide salts will be presented in the report, and a comparison with experimental data available in the literature will be made.

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MODELING OF THE THERMODYNAMIC PROPERTIES OF MOLTEN SODIUM AND CESIUM HALIDES CONSIDERING POLARIZATION EFFECTS BY MEANS OF VARIATIONAL THERMODYNAMIC PERTURBATION THEORY

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When describing the thermodynamic properties of liquid-salt electrolytes, in addition to electrostatic interactions, polarization effects between ions must also be taken into account. The tasks of accounting for ionic polarization in molten salts are successfully solved using ab initio methods and molecular dynamic modeling. The difficulty of statistical-thermodynamic calculations is the absence of exact solutions for complex interaction models (e.g., at inclusion of polarization), therefore, within the statistical theory of liquids, the problem of taking into account polarization interactions in molten salts has not been resolved so far.

The inclusion of polarization interactions in the energy of molten salts is im-plemented within the Gibbs-Bogolyubov method of thermodynamic perturbation theory. This approach makes it possible to considerate complex polarization interactions based on simpler analytical models. The model of charged hard spheres with different diameters was chosen as the reference system for this purpose. Then the expression for the free energy of melts in the Fourier space is

$$F \le F_{CHS} + \frac{1}{4\pi^2} \cdot \sum_{i,j} \sqrt{x_i x_j} \int_0^\infty \varphi_{ij}^{Pol}(k) \left(S_{ij}^{CHS}(k) - \delta_{ij} \right) k^2 dk - \frac{\rho}{2} \cdot \sum_{i,j} x_i x_j \varphi_{ij}^{Pol}(0) ,$$

where $S_{ij}^{CHS}(k)$ is the structural factor of the reference system, $\varphi_{ij}^{Pol}(k)$ is the ion-dipole additive in the pair interaction potential:

$$\varphi_{ij}^{Pol}(k) = \pi k E_{ij} \cdot \left(\frac{\sin kd_{ij}}{k^2 d_{ij}^2} + \frac{\cos kd_{ij}}{kd_{ij}} - \mathrm{Si}(kd_{ij}) \right).$$

Here $\mathrm{Si}(kd_{ij})$ is the integral sinus, E_{ij} depends on the polarizabilities and deter-mines the intensity of the ion-dipole influence of ions. The expression for the free energy of the reference system F_{CHS} includes three components: the energy of ideal-gas mixture, the hard-sphere term within the MCSL approximation, and the electrostatic contribution within the mean spherical approximation (MSA).

The report will present the results of modeling the heat content and entropy of molten sodium and cesium halides in comparison with experimental data.

The reported study was funded by RFBR according to the research project №18-33-01234.

STUDYING OF COMPLEX FORMATION OF RUBEANATE OF COPPER (II) IN AQUEOUS SOLUTION

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In chemical analysis, sorbents containing functional groups of rubeanic acid (RA) use to extract copper (II) ions. According to previously conducted studies[1] of the sorption properties of a polysiloxane modified with RA, it is known that at pH = 6, the highest value of the selectivity coefficient $K^{Ag/Cu}$ is achieved under competitive sorption. Extraction of metal ions from a solution occurs due to the formation of a complex compound - rubeanate, the composition and properties of which are not fully understood. To explain the obtained results, we decided to investigate the complexation of copper (II) rubeanate in an aqueous solution at pH = 6.

Copper (II) rubeanate is a dark olive color, slightly soluble substance in an aqueous medium, therefore, to increase solubility, in order to study it by a spectrophotometric method of analysis, a 5 % solution of sodium alkylbenzenesulfonate was introduced into the test solution. To create ionic strength, a 0.01 M KCl solution was used; to maintain the acidity of the medium, a universal buffer mixture was used.

According to the obtained absorption spectra, the maximum absorption wavelength of 375 nm was chosen. When studying the kinetics of complexation, it was found that copper (II) rubeanate is formed in less than 10 minutes, the value of optical density remains unchanged during the day, and there is a gradual destruction of the complex. The composition of copper rubeanate was established by the methods of isomolar series and molar relations, and the stability constant was calculated. The ratio of RA : copper (II) was 3: 2, the stability constant by the method of isomolar series was $7{,}57 \cdot 10^7$, by the method of molar ratios - $3{,}73 \cdot 10^5$.

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SYNTHESIS OF ARYL-SUBSTITUTED THIENO[2',3':4,5]THIENO[3,2-B] INDOLES

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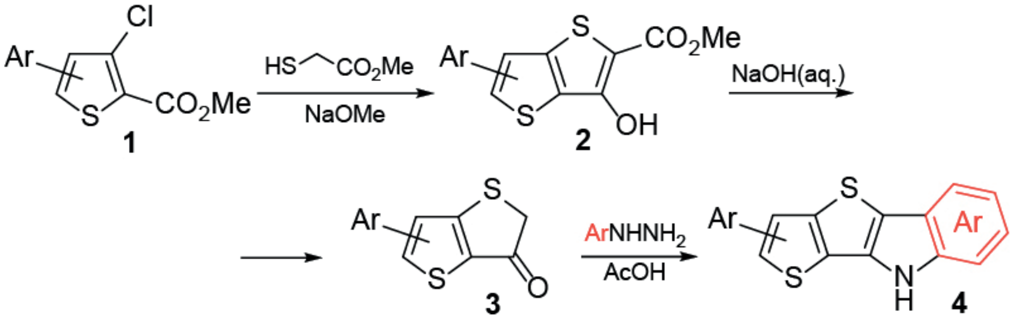
The rapid development of organic electronics leads to a high demand for new semiconductor materials, the structural basis of which are π-conjugated condensed molecules. In this case, one of the most frequently used elements in such systems are the heterocyclic moiety of thiophene and pyrrole.

In this paper, an effective approach to the synthesis of substituted thieno[2',3':4,5]thieno[3,2-*b*]indoles 4 was proposed, making it possible to easily obtain wide series of these compounds. The method involves the preparation of thieno[3,2-*b*]thiophene derivatives from esters of 3-chlorothiophene-2-carboxylic acid 1 by the Fiesselmann reaction, the subsequent saponification with decarboxylation of the resulting esters 2 to thiophene-3(2H)-ones 3, and the synthesis of the target compounds 4 by the Fisher reaction (Scheme 1).



Scheme 1. Scheme for the preparation of aryl-substituted thieno[2',3':4,5]thieno[3,2-b]indoles

This work was supported by the Russian Foundation for Basic Research, project 18-33-20083.

SELECTIVE SYNTHESIS OF CYCLIC ORGANOIODINE(III) WITHOUT CONTAMINATION OF HAZARDOUS PENTAVALENT COMPOUND

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The first report of hypervalent iodine compound in history was 1886, where iodobenzene dichloride ($PhICl_2$, Willgerodt reagent) was accidentally obtained during the attempt of chlorination of iodobenzene by chlorine gas.[1] A century later, hypervalent iodine reagents showing a variety of unique reactivities have received attention as useful oxidant due to their characteristics meeting green chemistry, such as low toxicity, ready availability, and easy handling. Particular noteworthy, they have replaced highly toxic heavy metal oxidants, i.e., lead(IV), mercury(II), and thallium(III) reagents, in modern organic synthesis. The details of their synthetic versatility are well documented in several review articles by key contributors in the fields.[2]

Five-membered hypervalent iodine(III) compounds, such as 2-iodosylbenzoic acids (IBAs), have recently emerged as reagents for developing new synthetic transformations and photo-catalyzed reactions.[3] For the preparation of pure IBAs, we now suggest an improved method not causing formation and contamination of hazardous pentavalent IBXs. The reaction system consistsing of the suitable oxidant[4] smootly produces IBAs under mild conditions,[5] and co-existing catalyst suppresses undesired IBX formations[6] derived from disproportionation of IBA compounds.

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PREDICTION OF THE STRUCTURES OF NEW METASTABLE NITRIDES S3N2, S3N4, SN2, Os3N8, Re3N7, WN2, MoN2 AND WAYS OF THEIR SYNTHESIS

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Binary and numerous complex sulfur nitrides have been obtained for a long time. At the same time, sulfur nitrides with pure oxidation states +II, +IV, +VI have not yet been obtained. There are almost no theoretical publications about them either. However, nitride $(S_3N_2)_4$ should be expected from $S_4(NH)_4$ and SCl_2 in the presence of suitable buffers (Fig. 1) with cubic symmetry molecules. Of the known precursors of $S_4N_5^{+1}$, $S_3N_3Cl_3$, $S_4N_4F_4$, SN_2^{-2}, several pathways can lead to molecules $(S_3N_4)_2$ (one of the 4 isomers in Fig. 1). There are also possible ways to nitride S(VI) SN_2. Elementary acts and products of such reactions are reproduced by semi-empirical methods AM1, PM3 and PM6 in HyperChem and MOPAC programs.

Numerous triple and quadruple nitrides and nitride derivatives for d-elements with oxidation states up to +VIII: $Os(NC(CH_3)_3)_4$, $Li_5[ReN_4]$, $Li_6[MN_4]$ (M = Cr,Mo,W), $Li_7[MN_4]$ (M = V,Nb,Ta) and many others have been obtained long ago. There is no data on the interaction of these complex nitrides with well-known nitride-halides of these elements $ReNCl_4$, $WNCl_3$ etc. and the behavior of these nitrides and nitride-halides in liquid ammonia, and the binary higher nitrides of these elements (except Ta_3N_5) has not been synthesized. It is logical to look for the ways of synthesis of new metastable nitrides in such liquid-phase reactions of finite molecules and ions that do not require high temperatures. The structures of molecular forms $(Os_3N_8)_2$ (1 of 19 isomers in Fig. 1) and $(Re_3N_7)_3$ (1 of 8 isomers in Fig. 1) are predicted theoretically. For SN_2, WN_2, MoN_2, and CrN_2, the preferred structure is expected to be glassy SiO_2. But polycondensation in the confined spaces of the cavities of the zeolites can be and the way to hypertetrahedral molecules $(MN_2)_{10}$ (M=S, W, Mo, Cr) (Fig. 1).

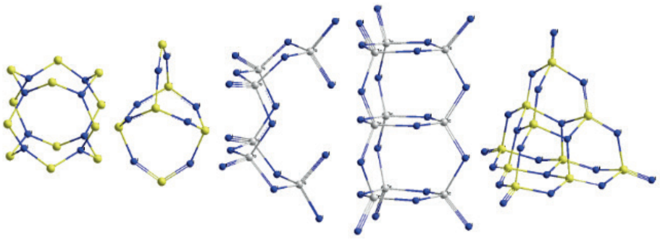

Figure 1. Structures of predicted nitrides (from left to right): $(S_3N_2)_4$, $(S_3N_4)_2$, $(Os_3N_8)_2$, $(Re_3N_7)_3$, $(SN_2)_{10}$

DENDRIMERIC DESIGN PRINCIPLE OF NEW ALLOTROPES OF NITROGEN, CHLORINE, AND THEIR OXIDES

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Increased coordination numbers of nonmetals can stabilize in such molecules, the geometry of which does not allow low-barrier electrocyclic rearrangements, leaving possible only the rupture of single chemical bonds into radicals or ions. This condition is automatically satisfied for chain or dendritic structures that do not contain cycles. The simplest known example of this method of stabilization is ozone – "oxygen dioxide OO_2" in structure. The same stable allotropes is possible for the Halogens, for example, $ClCl_3$ and $ClCl_5$, are isostructural known ClF_3 and ClF_5. In contrast to the non-existent $(N_5^{+1})(N_3^{-1})$, azides of larger polynitrogen cations $(N(N_3)_4^{+1})(N_3^{-1})$, $(N(NN(N_3)_3)_3^{+1})(N_3^{-1})$ (Fig. 1) etc. are expected to be more stable. This method of stabilization makes possible new low-volatile molecular forms of nitrogen, chlorine and bromine oxides, e.g. $(N_2O_5)_2 = ON(ONO_2)_3$, $(Cl_2O_7)_3 = OCl(OClO_3)_5$ (Fig. 1), and their analogues without a part of the terminal atoms of O or with the replacement of the end groups by branched. The range of applicability of the principle of dendrimeric stabilization has been extended to new allotropes of the chalcogens and pnictogens involving cycles. The geometry and stability of new allotropes were studied by semi-empirical methods AM1, PM3, PM6 in HyperChem and MOPAC programs, and for systems up to 10 atoms and non-empirically in the 6-31G* MP2 approximation.

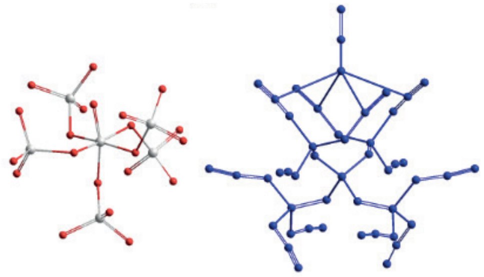

Figure 1. The calculated structures of $OCl(OClO_3)_5$ (left) and $(N(NN(N_3)_3)_3^{+1})(N_3^{-1})$ (right).

SYNTHETIC STRATEGIES FOR PREPARATION OF HYBRID TETRAPYRROLO-CAPPED 3D-METAL CLATHROCHELATES: THEIR XRD AND ELECTRONIC STRUCTURES

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Macrobicyclic cage complexes with encapsulated metal ion(s) (clathrochelates)[1] form a separate class of coordination compounds possessing uncommon chemical robustness and unusual physical and spectral properties caused mainly by isolation of the cage metal ion from external factors. Paramagnetic complexes of this type seem to be prospective paramagnetic and optical probes for biomedical applications.

Di- and tritopic metalloporphyrinato-capped[2], as well as the ditopic metallophthalocyaninato-capped[3] macrobicyclic iron(II) dioximates have been prepared *via* transmetallation reaction of their labile triethylantimony-capped precursors. Using the same synthetic approach, the polynuclear pseudomacrobicyclic iron and nickel(II) tris-pyridineoximates which are cross-linked by metal(IV) phthalocyaninates[4] and porphyrinates have been prepared.

Recently, we were able to elaborate a new efficient synthetic pathway for preparation of the metallophthalocyaninato-capped iron and nickel(II) tris-pyridineoximates[5]. This synthetic approach is based on the *one-pot* template condensation of 2-substituted pyridine-, pyrazole- and imidazoleoximes with zirconium and hafnium(IV)phthalocyaninates on the corresponding metal(II) ion as a matrix.

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2-NITROGUANIDINE IN THE SYNTHESIS OF AZAHETEROCYCLES

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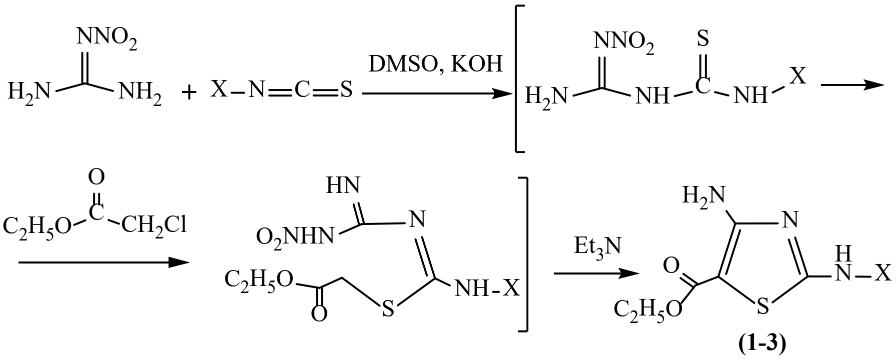
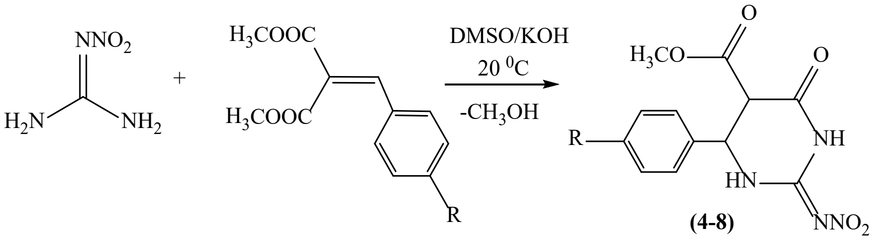
Derivatives of azoles and azines are attractive for their potential biological activity; among them are substances with analgesic, antihypoxic, antitumor, antifungal, and other beneficial properties. A convenient building block for the construction of nitrogenous heterocycles is 2-nitroguanidine. We carried out a three-component one-pot synthesis with the participation of 2-nitroguanidine, commercially available isothiocyanates and ethyl ester of chloroacetic acid, resulting in 4-amino-2-(arylamino)-5-ethoxycarbonyl-1,3-thiazolam (1-3) with yields up to 87%.



X= C_6H_4-CH_3^{-n} (1); C_6H_4-Cl^{-n} (2); C_6H_4-OCH_3^{-n} (3)

The use of preparatively available substituted dimethyl 2-benzylidene malonates in the reaction with 2-nitroguanidine as bielectrophilic reagents allowed us to obtain in yields up to 80% new representatives of methyl 6-aryl-2-nitroimino-4-oxo-5,6-dihydropyrimidin-5 carboxylates (4–8).



R= CH_3 **(4)**’ OCH_3 **(5),** $N(CH_3)_2$ **(6)**’ Cl **(7)**’ NO_2 **(8)**

The structure of the obtained heterocyclic compounds (1-8) was established on the basis of the complex use of modern spectral methods: IR, ^{1}H and ^{13}C- {^{1}H} NMR with the involvement of heteronuclear experiments (^{1}H-^{13}C HMQC, HMBC), as well as X-ray diffraction.

SYNTHESIS AND STRUCTURE OF THE [PH3SB(CL)O]3C • PHH COMPLEX

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By now, a small number of compounds containing the centrosymmetric group $C(OMXY)_3$ (where M is a transition metal) is known[1,2]; however, for non-transition metals, such complexes are unknown.

We have isolated a minor product $[Ph_3Sb(Cl)O]_3C$ • PhH from products of the ligand redistribution reaction between Ph_3SbCl_2 and $Ph_3Sb(OC_6H_3Br_2\text{-}2,4)_2$ in benzene in air atmosphere. According to X-ray diffraction data, the compound has crystallized as a solvate with benzene (Fig. 1).

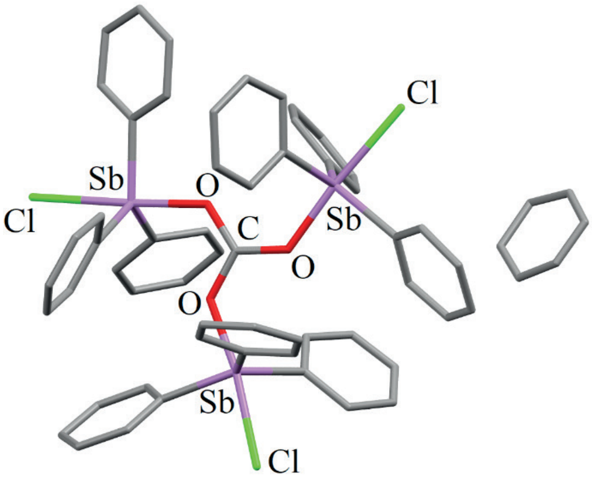

Figure 1. Structure of the $[Ph_3Sb(Cl)O]_3C$ • PhH complex

The C–O shortened distances (1.365(15)–1.385(15) Å) compared to the sum of the covalent radii of carbon and oxygen atoms (1.51 Å) indicate an increase in the multiplicity of these bonds. The abnormal reduction of the Sb–O distances (1.986(7), 2.001(7), 2.011(7) Å) in the neutral molecule of the minor product compared to the sum of the covalent radii of antimony and oxygen atoms (2.14 Å) implies delocalization of the electron density in the CO_3Sb_3 core. It is interesting to note that the Sb–Cl distances are longer than those in triphenylantimony dichloride.

The formation of the crystal structure is due to the weak hydrogen bonds such as C···H and Cl···H.

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REGULARITY OF SEPARATION AREA IN SALT – ETHOXYLATED SURFACTANT – WATER SYSTEMS

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The results of phase equilibria study in a number of inorganic salt – ethoxylated surfactant – water systems in a wide temperature range allowed us to propose nine schemes of temperature transformation of separation area depending on the salting-out ability of the salt and physical and chemical properties of surfactant. The micelle formation processes and specific interactions of salt ions with surfactant micelles have led to the emergence of new types of phase diagrams that are not characteristic of generalized scheme of the topological transformation of phase diagrams of the inorganic salt – binary solvent systems[1].

The analysis of developed schemes allowed to propose an approach to the qualitative and quantitative assessment of salting-out ability of inorganic salts by studying polytherm of isoconcentrating section containing a fixed surfactant amount and subsequent mathematical processing of the obtained data.

The approach was tested on a number of technical ethoxylated surfactants – monoalkyl polyethylene glycols (syntanols ALM-10 and DS-10), ethoxylated nonylphenols (neonols AF 9-12 and AF 9-25), ethoxylated tertiary amines (ethomeen C/15), potassium bis(alkyl polyethylene)phosphate (oxyphos B) and found that the temperature and concentration parameters of the existence of phase separation area with the specified surfactants are defined as the competing processes of dehydration of surfactant's micelles and hydration of ions, produced by the salt dissociation, and specific interactions of salt ions with surfactant's micelles – ion-dipole interaction of cations and anion adsorption.

The obtained data allowed to formulate a general approach to the selection of salting-out agent for extraction in systems based on ethoxylated surfactants and to propose a number of new extraction systems.

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COMPLEXES OF DICYANOAURATES AND DICYANODIHALOAURATES WITH TETRAORGANYLPHOSPHONIUM AND -STIBONIUM CATIONS

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Creating complexes of different cations with $[Au(CN)_2]^-$ anions is an actual task. Many of these derivatives possesses useful optical and magnetic properties1,2. However, there is almost no mention of such tetraorganylphosphonium and -stybonium complexes in the literature. As part of our study, we obtained a series of compounds: $[Ph_3PR][Au(CN)_2]$ (R=$CH_2C_6H_4$, $CH_2C_6H_4F$ 4, CH_2OMe, CH_2CN), $[Ph_4Sb][Au(CN)_2]$ и $[Ph_3PCH_2C_6H_4F\text{-}4][Au(CN)_2Cl_2]$, $[Ph_3PCH_2C_6H_4(F\ 4)][Au(CN)_2Br_2]$, $[Ph_3PCH_2C_6H_4F\text{-}4][Au(CN)_2I_2]$, $[Ph_3PCH_2OMe][Au(CN)_2Br_2]$, $[Ph_4P][Au(CN)_2I_2$-*trans*], $[Ph_3PCH_2Ph][Au(CN)_2I_2]$, $[Ph_3PEt]_2[Au(CN)_2I_2]$, $[Ph_3PEt]_2[Au(CN)_2I_2][I_3]$, $[Ph_3PCH_2CN]_2[Au(CN)_2I_2][I_3]$, $[Ph_4Sb][Au(CN)_2I_2]$, [*p*-$Tol_4Sb][Au(CN)_2I_2]$, [*p* $Tol_4Sb]_2[Au(CN)_2I_2][I_3]$, $[Ph_3PMe][Au(CN)_2I_2]$ *via* interaction of corresponding tetraorganylphosphonium, stybonium halides with $K[Au(CN)_2]$ and $K[Au(CN)_2Hal_2]$ (Hal = I, Br, Cl) salts in water. The structures of the synthesized compounds were characterized by IR, NMR ^1H, ^{13}C spectroscopy and X-Ray analysis. The structure of $[Au(CN)_2]$- anions in the complexes is almost linear. Anion of $[Au(CN)_2Hal_2]$- represent the distorted square.

Tetrafenylstibonium dicyanoaurate shows the expressed activity with respect to the degradation of organic dyes in water under the action of UV radiation.

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SYNTHESIS AND STUDY OF SPECTROSCOPIC AND CATALYTIC PROPERTIES OF D- AND F- ELEMENTS PHTHALOCYANINATES WITH THERMINAL CYANO- GROUPS

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Materials based on phthalocyanines have long been proven in areas such as medicine, nonlinear optics, industrial catalysis. This is associated with a number of unique properties of compounds of this class. The presence in the structure of the molecule of *d*- or *f*- metal atom opens up possibilities for the extra-coordination of certain ligands, for usage of phthalocyanines as catalysts, and the extended conjugated aromatic π-system causes the presence of unique spectroscopic and luminescent properties.

This paper presents the synthesis and study of the spectroscopic and catalytic properties of cyano-substituted phthalocyaninates of *d*- and *f*- elements. The complexes were btained by template fusion of the corresponding phthalonitrile with a metal salt in a molar ratio of 4 : 1. The compound was purified by column chromatography with silica gel as an eluent and with chloroform as a solvent. The structure of all the compounds obtained was confirmed using MALDI-TOF mass spectrometry, IR, ^{1}H NMR spectroscopic methods, as well as according to elemental analysis. Further, the spectroscopic and fluorescent characteristics of the phthalocyanine metal complexes obtained in various organic solvents were studied, and the aggregation behavior of phthalocyaninates in the extra-coordination processes of small organic ligands was analyzed. Finally, the catalytic activity of the complexes was investigated using a model oxidation reaction of sodium diethyldithiocarbamate.

The work was supported by the Russian Science Foundation (project No. 17-73-20017).

SYNTHESIS OF ANALOGUES OF CALANOLIDE A, HIV REVERSE TRANSCRIPTASE INHIBITOR

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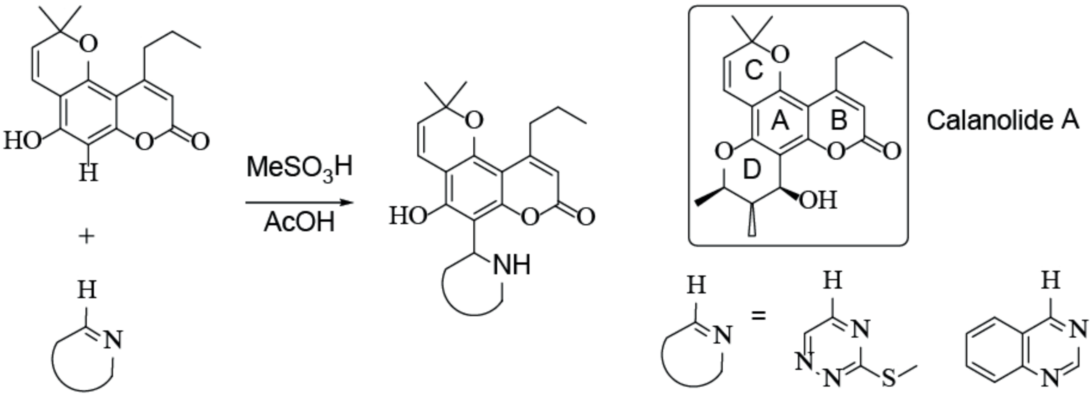
Calanolide A is a natural tetracyclic benzopyrone identified as non-nucleoside reverse transcriptase inhibitor. Ring D of Calanolide A contains three stereocenters, which hinder the full effective synthesis of this anti-HIV agent.

QSAR analysis of Calanolide A analogues revealed that the activity was sensitive to the modification of the ring D of the tetracyclic structure.[1,2] In this connection we see promising modification of the ring D of Calanolide A to the aim of search of the more active analogues compared with parent Calanolide A.

In the present work we demonstrated synthesis of azaheterocyclic derivatives of Calanolide A via the direct C-H/C-H coupling of the 2,2-dimethylpyranocoumarin with 1,2,4-triazine and quinazoline in the presence of methanesulfonic acid as catalyst.



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COMPUTATIONAL REACTOR FOR CHEMICAL SYNTHESIS PLANNING: GENERATION OF POSSIBLE REACTIONS INVOLVING GIVEN CHEMICAL COMPOUND

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The key challenge in the computer planning of chemical synthesis is generation of new compounds from the set of available molecules. As part of this work, we have developed an algorithm that generates new chemical structures from a given molecules, using transformation rules extracted from database of chemical reactions. This approach has one major advantage: information about mechanism of the transformation is saved.

List of possible reactants was extracted from databases of commercially available chemical building blocks, which were stored in reactant database based on our in-house Python-based CGR-DB cartridge. Chemical structures were indexed based on functional groups present in them. Transformation rules were classified into one-, two- and multi-component based on number of molecules required to perform reaction transformation. Based on extracted transformation rules, functional groups that are subjected to transformations were identified.

At the stage of generation of products, system identifies functional groups present in the initial molecule, and extracts from database only those transformation rules that can be applied to a given molecule. If selected transformation rule requires two or more reactants, the second reactant is also selected based on the list of functional groups. The groups absent in starting molecule but required for transformation rule is identified and corresponding molecules are extracted from the database. Having all required molecules reaction product is generated based on the transformation rule. In such a way, algorithm does not try to do unnecessary transformations with unsuitable molecules and it quickly generates new compounds and reactions.

Possibility to generate the whole reaction was also implemented. Algorithm was tested, speed and quality tests were performed.

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X-RAY SPECTROSCOPIC STUDY OF ELECTRONIC STRUCTURE OF TRINUCLEAR METAL CHALCOGENIDE CLUSTER COMPLEXES

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Transition metal cluster complexes represent a rapidly growing class of inorganic compounds. Among the various types of cluster compounds, complexes in which metal clusters are coordinated by chalcogenide and polychalcogenide ligands occupy a special place. Study of the electron density distribution in complexes and the features of metal–chalcogen electron interactions is great interest for understanding the physical and chemical properties.

Modern X-ray spectroscopy is effective method for studying of the electronic structure of various substances and materials. Experimental and theoretical study of the electronic structure of the trinuclear chalcogenide complexes of molybdenum and tungsten $\{M_3Q_4\}^{4+}$ and $\{M_3Q_7\}^{4+}$ (M = Mo, W; Q = S, Se) was carried out.

X-ray emission (XES), X-ray absorption (XAS) and X-ray photoelectron (XPS) spectra of trinuclear complexes and transition metal polysulfides containing both S^{2-} and $(S_2)^{2}$- bridge ligands were obtained. XES and XAS spectra of valence levels, which provide information on the energy position and partial atomic composition of occupied and unoccupied molecular orbitals of the complexes, and quantum chemical calculations using density functional theory allowed determining the changes in the electronic structure of trinuclear complexes depending on the nature of the terminal ligand. XPS spectra provided information on the distribution of the electron density on the bridging chalcogenide and dichalcogenide ligands.

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The Siberian Branch of the Russian Academy of Sciences (SB RAS) Siberian Supercomputer Center is gratefully acknowledged for providing supercomputer facilities.

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STRUCTURAL ORGANIZATION OF THE MESOMORPHIC "4-N-DODECYLOXYBENZOIC ACID: 4-PYRIDYL 4′-N-DODECYLOXYBENZOATE" SYSTEMS

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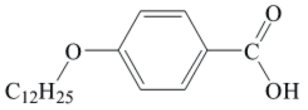
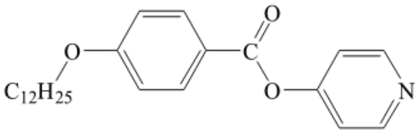
The mesomorphic and volumetric properties of the 4-n-dodecyloxybenzoic acid (A) and 4-pyridyl 4'-n-dodecyloxybenzoate (B) system were studied by the polarization thermomicroscopy and by the dilatometric method. IR spectra of individual A and B compounds as well as IR spectra of 2A:1B and 1A:1B systems were recorded.



4-n-dodecyloxybenzoic acid (A)



4-pyridyl 4'-n-dodecyloxybenzoate (B)

For the assignment of the experimental vibrational spectra a series of quantum chemical calculations of DFT(B97D)/6-311++G** level was carried out. Hydrogen-bonded complexes of types A•••A, A•••B, A•••A•••B and A•••B•••A that can be formed at different component ratios in system A-B were simulated. The geometric structure of these complexes was optimized and the vibrational frequencies were calculated.

It was determined that the IR spectrum of compound A corresponds to the existence of cyclic dimers A•••A_{cycl}, while in a system with a component ratio of 1A:1B, the complexes A•••B are formed. The analysis of the IR spectrum of the 2A:1B mixture led to the conclusion that the expected stoichiometric A•••A•••B, A•••B•••A and A•••A_{op}•••B complexes are not formed, and the 2A:1B crystalline system consists of rod-like complexes A•••B and A•••A_{cycl} in the ratio 2:1.

The conclusions made basing the analysis of the IR spectra and the free energies of the possible processes are confirmed by the density measurement of the system A-B with different ratios of the A and B components.

Analysis of the obtained data shows that H-complexes of A•••B type are formed in the systems under study with an equimolar ratio of components; in other cases, there is a coexistence of two types of complexes A•••A_{cycl} and A•••B in different ratios. Thus, conducted studies open up prospects for managing the process of obtaining cocrystals of a specified composition.

The work was supported by Ministry of Science and Higher Education 4.7121.2017/8.9

THEORETIC AND EXPERIMENTAL STUDY OF THE INTERACTION OF 1,3,5-TRIARYL-1,3,5-TRIAZACYCLOHEXANE TRICARBONYLMETAL COMPLEXES OF THE CHROMIUM GROUP

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To optimize the existing and develop new catalytic processes, it is necessary to study the structure of the active intermediates of the catalytic reaction and the factors controlling their formation. Therefore, we decided to conduct a theoretical and experimental study of the interaction of dialkyl-H-phosphonates with η^3-(1,3,5-triorganyl-1,3,5-triazacyclohexane)¬tricarbonyl derivatives of chromium group metals.

Table 1. Calculated (B3LYP/LANL2Z) free energies values for η^3-[(1,3,5-triphenyl)-1,3,5-triazacyclohexane]tricarbonylmetals(0) with diethyl-H-phosphonate.

	$\Delta G_{reaction}$, kJ/mole		
Metal	**Cr**	**Mo**	**W**
Reaction **(1)**	-23.9	-28.0	-22.8
Reaction **(2)**	-0.3	-4.1	+2.3
Reaction **(3)**	-10.8	-14.8	-11.7
Reaction **(4)**	+29.8	+19.2	+22.1
Reaction **(5)**	+19.8	+14.3	+18.2
Reaction **(6)**	-41.0	-34.0	-22.8
Reaction **(7)**	-16.3	-5.7	-2.4
Reaction **(8)**	-28.1	-14.8	-14.6
Reaction **(9)**	+8.6	+4.4	+13.5

In accordance with the quantum-chemical calculations, the most favorable route for the interaction of diethyl-H-phosphonate and a triazine-tricarbonyl complex of the chromium metal is the reaction, which results in the binding of two ionized molecules to the transition metal atom due to lone phosphorus pairs, and a η^3 → η^1 coordinated regrouping occurs 1,3,5-triphenyl-1,3,5-triazacyclohexane. The free energy of this process is –34.0 kJ / mol. The calculated theoretical data were confirmed experimentally.

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QUANTUM-CHEMICAL STUDY OF THE PROCESS OF COPOLYMERIZATION OF METHYL METHACRYLATE AND STYRENE IN THE PRESENCE OF METALLOCENES

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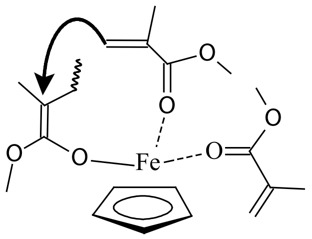
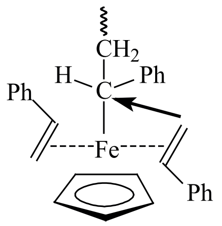
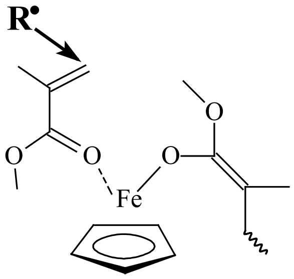
It was previously shown that metallocenes have a significant influence on the process of radically initiated copolymerization of methyl methacrylate and styrene[1]. The presence of metallocenes in the composition of the initiating system influenced the composition, molecular weights and microstructure of the copolymers obtained, as compared with copolymers obtained by initiating only benzoyl peroxide. This was associated with the formation of two types of active centers: free-radical and coordination, by analogy with the homopolymerization of these monomers[2,3]. In the latter case, using quantum-chemical calculations, the possibility of the formation of coordination centers and their structure was established. In particular, it was shown that the coordination centers formed during the polymerization of styrene have a structure that differs from the structure of the active centers formed during the polymerization of methyl methacrylate[4-6] (arrows indicate the direction of reactions of coordination chain growth):

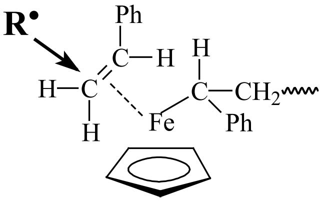




Therefore, the question arose of how these active centers can work in the copolymerization of methyl methacrylate and styrene, provided that there are no homopolymers in the composition of the polymerization mass[1]. In this regard, in this work, quantum-chemical calculations were carried out in order to establish the scenario of copolymerization of methyl methacrylate and styrene initiated by benzoyl peroxide in the presence of ferrocene. It was found that as a result of a series of transformations, including the release of the growth radical from the complex, the subsequent coordination of the "foreign" monomer, as well as reactions of the addition of free radicals to the molecules of metal-coordinated monomers, it is possible to rearrange one type of active site to another.

High probability of the formation of copolymers is not in the coordination sphere of the metal, as in the case of coordination growth of the homopolymer chain, but due to the addition of radicals by coordinated monomers, as shown in the diagram below:





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SOLUBITITY OF LITHIUM, SODIUM AND POTASSIUM CHLORIDES IN SOLUTIONS WITH ETHYL ALCOHOLS

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Chlorides of lithium, sodium and potassium, having ionic bonds, dissolve well in a highly polar (ε = 78,53 aqueous medium. The study carried out in this work showed that when the less polar (ε =24,3) ethanol alcohol is added to the aqueous solutions of the studied salts, the solubility decreases. As can be seen from the table, with an increase in the volume fraction of alcohol to 90%, the mass fraction of lithium chloride, sodium and potassium decreases from 40 to 400 times. The concentration of salts in the studied solutions was determined by titration with silver nitrate.

Table 1. Mass fraction of lithium chloride, sodium and potassium, depending on the volume fraction of alcohol

V% alcohol	ω% LiCl	ω% NaCl	ω% KCl
0	45,35	28,32	71,23
10	36,02	24,85	67,06
20	31,50	21,96	44,46
30	24,68	17,66	30,98
40	21,90	15,35	22,91
50	17,09	13,79	11,87
60	9,42	10,79	6,25
70	7,19	9,04	3,55
80	2,23	3,16	1,77
90	0,11	0,71	1,35

The crystal-optical method of research has shown that in water-alcohol solutions the morphology of the formed crystals is disturbed in comparison with the crystals released from aqueous solutions. Moreover, the addition of alcohol leads to a reduction in the size of salt crystals up to 600 times.

TRIANGULAR MOLECULES $C_{45}H_{21}$, $C_{24}E_{21}H_{21}$ AND $E_{24}C_{21}H_{21}$ (E = SI, GE): A DFT STUDY

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Nowadays graphene nanoflakes and nanoribbons are among the focus research subjects. Graphene nanoflakes are classified by their edge type and close or open shell. Open-shell systems are in particularly interest because of their potential use in spintronic applications.

Among zigzag-edged polycyclic aromatic hydrocarbons (PAH) triangular graphene nanoflakes occupy the special place being high spin alternant non-Kekulé hydrocarbons. Smallest compounds of this PAH series are fenalenile and tringulene (or Clar's hydrocarbon) being doublet and triplet state respectively. Triangulene family also shortly called "triagulenes", and we will follow this name. Whereas carbon triangulenes are fairly well studied, their main group element analogues received much less attention. Various triangulene compositions of the group 14 elements were studied recently.[1]

One of the possible modifications of the triangulenes is holes in the skeleton[2] leading to the new spin state (Figure 1). In this work we present DFT calculations on structures and properties of a series of group 14 elements (C, Si, Ge) hollowed triangulenes.

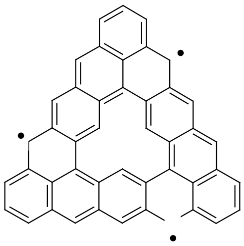

Figure 1. Hollowed triangulene, S=3/2

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THE NATURE OF DUAL-EMISSION OF THE OCTAHEDRAL CU$_4$I$_4$ CLUSTERS AND THEIR UTILIZATION IN THE LUMINESCENT THERMOMETRY

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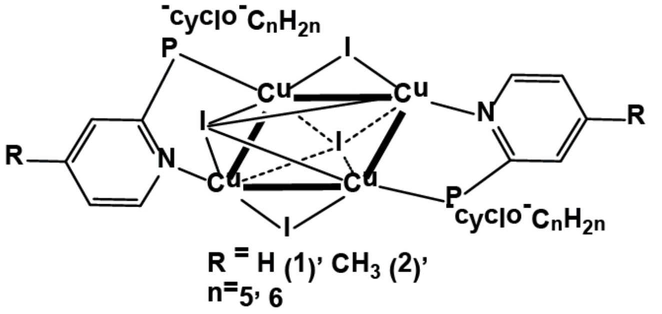
Luminescence thermometry has emerged as one of the most promising non-contact techniques due to its simplicity, noninvasiveness and possibility to work in biological fluids, strong electromagnetic fields and fast-moving objects. One of the approach of optical sensing is based on the temperature dependence of ration between intensities of two emission bands and can be achieved with a combination of two emissive dyes or with single dye displaying dual emission. Among single dyes with dual-emissive luminescence polynuclear copper (I) complexes arose interest due to the tunable phosphorescence emission with large Stokes shifts, long lifetimes and high quantum yields at room temperature demonstrated by this class of compounds.

Recently, the copper (I) complexes with Cu$_4$I$_4$ core of octahedral type demonstrating the temperature-dependent dual-luminescence have been synthesized[1].



Quantum chemical computations revealed two lowest triplet excited states, T$_1$ and T$_2$. According to computations the highest occupied molecular orbitals (HOMO) for both T$_1$ and T$_2$ states are located at metal-halide core and the lowest unoccupied molecular orbitals (LUMO) are contributed by pyridyl moieties. Thus, one can conclude that both bands are of ^{3}(X+M)LCT character.

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INTERACTION OF 4-(2-THIAZOLYLAZO)CATECHOL WITH NON-FERROUS METAL IONS ON THE SURFACE OF SULFIDE ORES AND IN A SOLUTION

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4-(2-thiazolylazo)catechol (TAC) evinced good flotation characteristics towards the copper-nickel sulfide ore, so it was of interest to study the mechanism of its interaction with metal ions on the ore surface.

According to the present-day concepts, chemosorption is considered as formation of a surface coordination compound via the donor-acceptor mechanism. Consequently, the complexation processes on the surface of a mineral and in a solution are analogous, since the mechanism of the complex formation in the solution is also based on the formation of a donor-acceptor bond between a reagent and a metal cation. Thus, the interaction between reagents and metal ions in solution can serve as a model for understanding the processes occurring on the ore surface.

To determine the nature of interaction of the reagent with Cu-Ni sulfide ore, its adsorption and desorption processes were studied. The isotherms of the both processes do not coincide; consequently, chemosorption of TAC occurs on the surface of the ore. The Henry adsorption constant has been calculated (0.0182 l/g).

The adsorption mechanism being chemical, it was of interest to study the complex formation of the reagent with the metal ions contained in the ore sample, in solution, in order to understand what complexes are formed in the chemosorption process. The pH intervals in which the TAC complexes exist: with Cu(II) ions – 5.8-11.1 and 12.3-13.2, Co(II) – pH 8.5-9.9, Ni(II) – pH 8.5- 9.8, Zn(II) – pH 9.3-10.0. In a slightly alkaline medium, Cu(II), Co(II), Ni(II) and Zn(II) form cationic complexes at a ratio [M(II)]:[TAC] = 1:1. In a strong alkaline medium, copper(II) forms an anionic complex at the ratio [Cu(II)]:[TAC] = 1:2. The stability constants of the complexes have been calculated (table 1). The structures of the complexes have been proposed.

Table 1. The stability constants of TAC complexes with metal ions

M(II)	Cu(II) 1:1	Cu(II) 1:2	Co(II) 1:1	Ni(II) 1:1	Zn(II) 1:1
lg Kst	6.90 ± 0.06	12.5 ± 0.4	4.7 ± 0.2	4.9 ± 0.3	4.8 ± 0.4

Since the Cu(II) - TAC complex at the ratio 1:2 cannot be formed on the ore surface due to steric obstacles, formation of complexes at the ratio 1:1 is most likely.

The work was financially supported by the RFBR (Project Nr. 17-03-00727 a).

MOLECULAR DESIGN OF ADAPTIVE HYBRID MATERIALS BASED ON POLYURETHANE UREA THERMOPLASTIC ELASTOMERS

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Among the adaptive polymers, polyurethane urea thermoplastic elastomers (TPUU) reveal particular interest. These materials have found applications in industry and medicine due to their combination of strength and elasticity.

In the presented work the method of synthesis of new di- and triblock TPUU copolymers and their composites with silver nanoparticles at low concentration was developed. For triblock copolymers, we demonstrate the possibility to control kinetics of physical network formation by the mutual influence of crystallizable blocks of polybutylene glycoladipinate diol (PBA) and poly-ε-caprolactone diol (PCL). The introduction of the second crystallizable component allows to optimize the crystallization kinetics and final distribution of the crystallites in TPUU matrix. Thus, the mechanical characteristics and their evolution of the TPUUs can be tunes by variation of chemical composition of the soft block. For diblock copolymers with different isocyanates (aromatic, aliphatic and cycloaliphatic nature) in the rigid block, the role of phase-separated domain interphase in structure formation was addressed by a combination of differential scanning calorimetry and synchrotron X-ray diffraction analysis. The choice of isocyanate allows controlling of crystallization kinetics in geometrical confinement of nanosized domains of the soft block. This opens possiblity to control the mechanical properties of the material and the parameters of the shape memory effect. Based on developed TPUUs, prototypes of "smart" patches for medical applications have been designed.

In the presented work the equipment of the Analytical Center for Collective Use of the IPCP RAS was used. The work is carried out on the topic of the State Assignment, State Registration No. 01201361836. The authors are grateful to the Russian Foundation for Basic Research for financial support (project № 19-53-15016/19).

THERMODYNAMIC PARAMETERS OF PROTOLYTIC AND COORDINATION EQUILIBIA FOR SOME ALKYLENEDIAMINEPOLYCARBONIC ACIDS

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This work presents results of potentiometric, spectrophotometric and calorimetric investigations of the acid-base interaction and magnesium(II), calcium(II), zinc(II), cadmium(II), copper(II), nickel(II), cobalt(II), manganese(II) complexation processes in aqueous solutions of ethylenediamine-N,N,N',N'-tetraacetic, trimethylenediamine-N,N,N',N'-tetraacetic, tetramethylenediamine-N,N,N',N'-tetraacetic, hexamethylene-diamine-N,N,N',N'-tetraacetic, 2-hydroxypropylene-1,3-diamine-N,N,N',N'-tetraacetic, ethylenediamine-N,N'-diacetic-N,N'-dipropionic, ethylenediamine-N,N,N',N'-tetrapropionic, N-methylethylenediamine-N,N',N'-triacetic, N-(β-hydroxyethyl)ethylenediamine-N,N',N'-triacetic and ethylenediamine-N,N'-diglutaric acids. Thermodynamic parameters (logK, ΔG, ΔH, ΔS) for the relevant equilibria have been determined at 298.15 K and ionic strength values from 0.1 up to 1.5 M. The results obtained were compared with the reference data on related monoamine compounds: alanine, serine, homoserine, aspartic, imino-N,N-diacetic, N-methylimino-N,N-diacetic, N-(β-hydroxyethyl)imino-N,N-diacetic and nitrilo-N,N,N-triacetic acids. The influence of background electrolyte character and concentration on the protolytic and coordination equilibria was under consideration. The standard thermodynamic parameters have been evaluated for the corresponding reactions. A plausible explanation of changes in these quantities has been suggested in view of the metal ion and ligand structures (type of coordination, denticity, presence of hydrophobic and hydrophilic fragments, solvation features of the zwitter ions). As ancillary part of this study, the spatial, electronic and energy parameters for isolated molecules and ions of these complexones have been computed. The data obtained were compared with results of structural and thermochemical investigations for the relevant complexones in an aqueous solution and crystalline state.

This work was performed at the Research Institute of Thermodynamics and Kinetics of Chemical Processes, Ivanovo State University of Chemistry and Technology in accordance with a state assignment (basic part), project 4.7104.2017/8.9.

NEW MIXED-VALENCE NEPTUNIUM COMPOUNDS

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Two neptunium molybdate compounds with outersphere guanidinium cations (HGuan+ = $C(NH_2)_3^+$) have been synthesized. The compounds contain simultaneously dioxocations of hexavalent (NpO_2^{2+}) and pentavalent (NpO_2^+) neptunium.

Crystallographic data:

$(HGuan)_3[(Np^VO_2)(Np^{VI}O_2)(MoO_4)_3(H_2O)]\cdot 3H_2O$: *a* = 12.3393(3), *b* = 12.9270(3), *c* = 17.3818(3) Å, β = 99.249(1)º, V = 2736.53(10) Å3, sp. gr. P21/n, *Z* = 4, R1 = 0.0298.

$(HGuan)_3[(Np^VO_2)(Np^{VI}O_2)(MoO_4)_3(H_2O)]\cdot H_2O$: *a* = 11.3515(18), *b* = 11.7584(18), *c* = 19.030(3) Å, V = 2540.1(7) Å3, sp. gr. P212121, *Z* = 4, R1 = 0.0229.

Both compounds contain anionic layers $[(Np^VO_2)(Np^{VI}O_2)(MoO_4)_3(H_2O)]_n^{3n-}$, guanidinium cations and crystallization water molecules are placed between the layers. Three crystallographically independent molybdate-ions are tridentate-bridging between three neptunium atoms. The atoms of penta- and hexavalent neptunium occupy separate positions and have the same coordination number 7, but differ significantly by Np-O distances. The Np-O distances in dioxocations of hexavalent neptunium are from 1.755 to 1.770 Å, in dioxocations of pentavalent neptunium - from 1.823 to 1.852 Å. The Np-O distances for O atoms of molybdate-ions in the equatorial plane of dioxocations are from 2.321 to 2.406 Å for hexavalent and from 2.415 to 2.461 Å for pentavalent neptunium. The water molecule in both cases is coordinated to Np(V) atom.

In earlier studied[1] mixed-valence neptunium compound $Na_6[(Np^VO_2)_2(Np^{VI}O_2)(MoO_4)_5]\cdot 13H_2O$ the atoms of penta- and hexavalent neptunium also occupy separate positions, but in chloride compound $Cs_7[(Np^VO_2)(Np^{VI}O_2)_2Cl_{12}]$ – the same position[2].

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THE COMPARISON OF THE POSSIBILITIES OF Pd(0)- AND Cu(I)-CATALYZED ARYLATION OF OXADIAMINES

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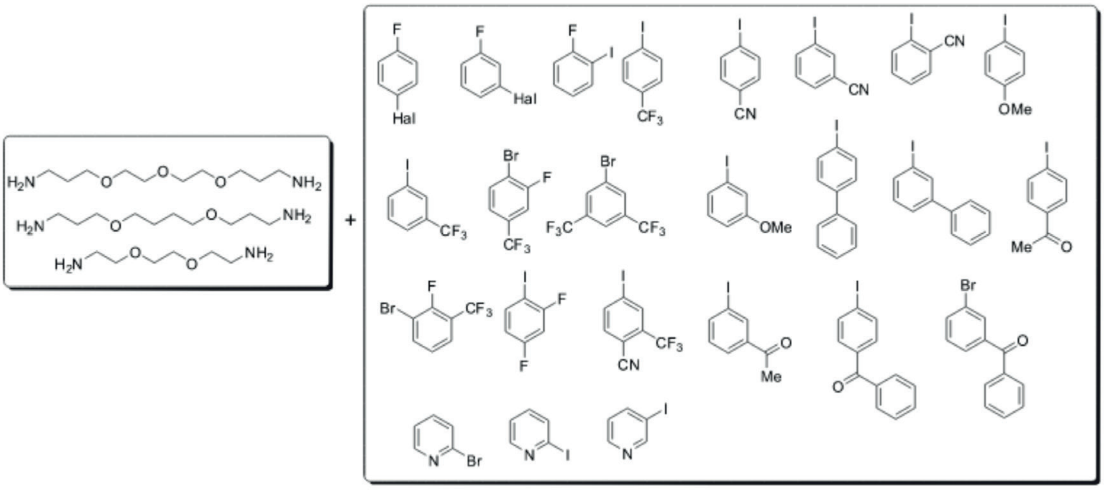
Due to a great need to replace expensive palladium for much cheaper copper in the catalysis of C-N bonds formation a thorough investigation was carried out to explore the possibilities and limitations of the catalysts of both types in the synthesis of N,N'-di(hetero)aryl derivatives of polyoxadiamines. Three oxadiamines were used as starting compounds which differ by the number of oxygen atoms and methylene groups between nitrogen and oxygen atoms. As aryl halides substituted bromo- and iodobenzenes were tested containing the following substituents: F, CF_3, CN, Ph, COMe, COPh, COOEt, OMe. To conduct the heteroarylation reactions, 2-bromo-, 2-iodo- and 3-iodopyridines were applied. As catalytic systems $Pd(dba)_2$/BINAP and $Pd(dba)_2$/DavePhos were used in Pd series, CuI/2-isobutyrylcyclohexanone and CuI/BINOL were taken in Cu series. In many cases the possibility of successful synthesis of the target compounds was demonstrated using both Pd(0)- and Cu(I)-catalyzed approaches, excluding the amination of *ortho*-substituted halogenobenzenes. In this case Pd catalysis was found to be much more efficient.



The work was financially supported by RFBR, project No 17-03-00888.

CARBORANE COMPLEXES OF RUTHENIUM (II) WITH BI- AD TRIDENTATE PHOSPHOROUS LIGANDS: SYNTHESIS AND USE IN CATALYSIS

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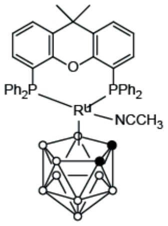
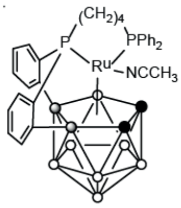
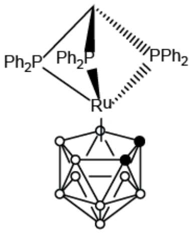
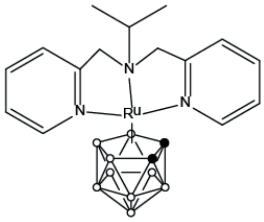
One of the promising and practically significant areas of application of coordination compounds is the catalysis of various processes of organic synthesis. These include, in particular, the polymerization of vinyl monomers via Atom Transfer Radical Polymerization (ATRP) mechanism. Among the compounds exhibiting high catalytic activity in such processes carborane clusters of ruthenium with *nido*-C_2B_9-carborane ligand should be noted.

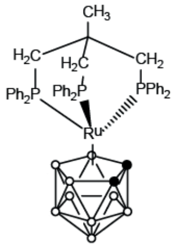
For the purpose of the development of new highly efficient catalytic systems for the controlled syntheses of polymers, new metallacarborane complexes of ruthenium with chelate phosphine and nitrogen-containing ligands were synthesised.











Novel clusters were explored by means of NMR-, IR-spectroscopy, MALDI TOF and X-Ray analysis methods. The redox properties of complexes were studied using cyclic voltammetry showed the reversible nature of Ru (II) - Ru (III) transition. Consequently, the resulting nitrile complexes can be used in controlled radical polymerization by an atom transfer mechanism as catalysts.

The polymerization of methacrylic monomers in the presence of Ru (II) compounds proceeds with a higher rate than the similar polymerization in the presence of the previously proposed trivalent ruthenium complexes.

During the process, molecular weight and conversion grow linearly. The polymers obtained have a polydispersity coefficient not exceeding 1.5.

This work was supported by the Russian Science Foundation (project 18-73-10092).

PHOTO-CONTROLLED RADICAL POLYMERIZATION OF METHACRYLIC MONOMERS UNDER THE ACTION OF PHENYLPHENOTHIAZINE BY METAL-FREE ATRP MECHANISM

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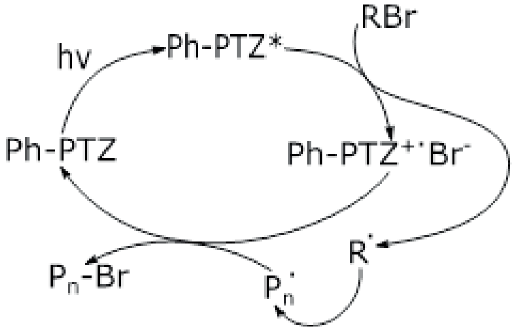
In recent years, photo-controlled radical polymerization using metal-free organic compounds as catalysts (Metal-Free ATRP) is considered as a powerful tool for obtaining polymers with given molecular weights (MM) and narrow molecular weight distribution (MMD) as well as various macromolecular structures. The methodology is based on the ability of some organic compounds in the excited state of reversible activation of a carbon-halogen bond, leading to the appearance of active radicals that mediate the process of controlled polymerization in accordance with scheme:



Scheme 1. Metal-Free ATRP mechanism.

In this research polymerization of methyl methacrylate (MMA) and glycidyl methacrylate (GMA) in the presence of phenylphenothiazine (Ph-PTZ) under the action of UV radiation was studied. Polymerizations were conducted in N,N-dimethylformamide, N,N-dimethylacetamide and dimethyl sulfoxide as solvents. Ethyl-2-bromoisobutyrate (EBiB) and carbon tetrachloride (CCl_4) were used the initiators. The polymerization was carried out in degassed tubes with a different molar ratio between the reagents and under the action of sources of UV radiation with radiation maximum at 254 nm and 360 nm. The research showed that the process of polymerization of MMA and GMA is accompanied by a uniform growth in molecular weight with increasing conversion and leads to synthesized samples with narrow MWD. The implementation of the Metal-Free ATRP mechanism is also confirmed by the presence of halogen atoms at the ends of the “dormant” polymer chains, found by the time-of-flight MALDI mass spectrometry.

The work was supported by Russian Science Foundation (proj. No 18-73-10092).

INTERACTION OF PENTAPHENYLPHOSPHORUS WITH POLYFUNCTIONAL CARBOXYLIC ACIDS

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Pentaphenylphosphorus reactions with polyfunctional carboxylic acids are not always unambiguous. Thus, during interaction of pentaphenylphosphorus with maleic and tetrafluorophtalic acids, bis(tetraphenylphosphonium) carboxylates are formed, but only the hydroxyl group takes part in its reaction with 2-hydroxyisophtalic acid, the carboxyl group does not take part in the reaction.

It has been found that pentaphenylphosphorus reacts with succinic acid (2:1 mol, toluene) with the formation of bis(tetraphenylphosphonium) succinate (toluene solvate). The product of the reaction between pentaphenylphosphorus and 2,6-dihydroxybenzoic acid is tetraphenylphosphonium 2,6-diyhydroxybenzoate (benzene solvate) regardless of the mole ratio.

According to the X-ray analysis the crystals of synthesized compounds are formed from tetrahedral cations $[Ph_4P]^+$ and carboxylate anions (Fig. 1). The formation of crystal structures is conditioned by the weak C−H···O hydrogen bonds.

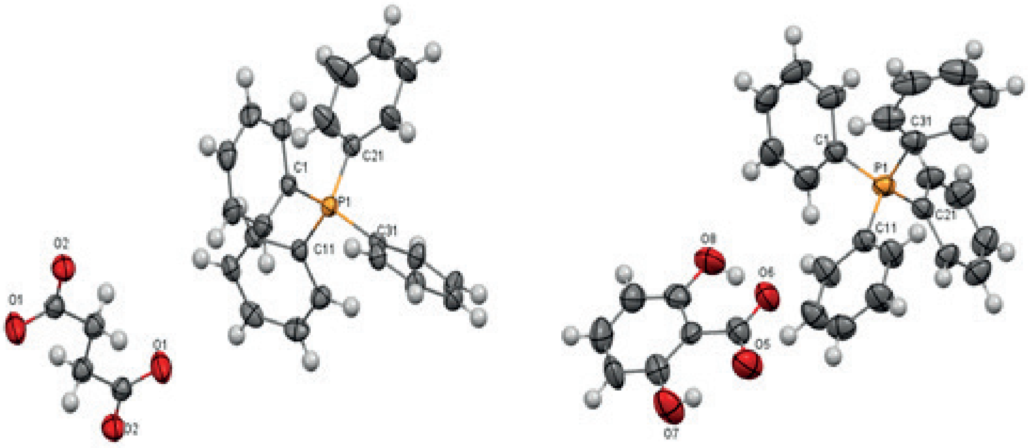

Figure 1. Molecular structure of bis(tetraphenylphosphonium) succinate and tetraphenylphosphonium 2,6-diyhydroxybenzoate *(solvate molecules are not shown)*

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ALKYLTHIO(ALKYNYL)CARBENES: PHOTOLYTIC GENERATION AND REACTIONS WITH ALKENES AND ALCOHOLS

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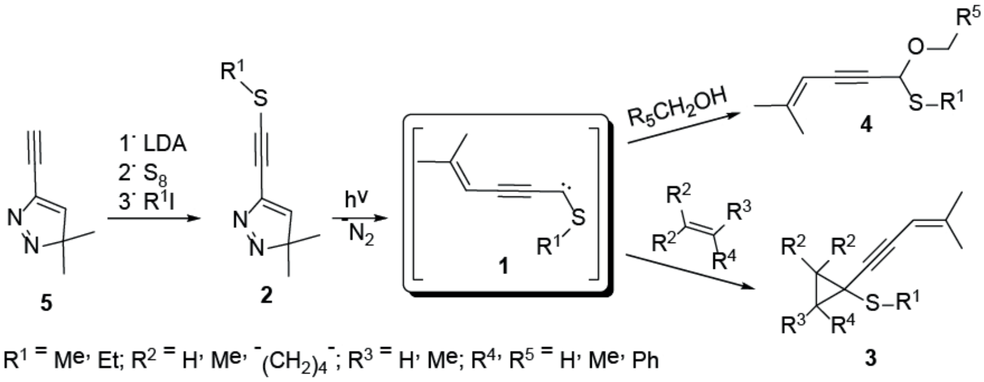
An original approach to the generation of previously unknown singlet alkylthio(alkynyl)carbenes 1, based on photolytic decomposition of corresponding 5-alkylthioethynyl-3,3-dimethyl-3H-pyrazoles 2, was proposed.

It was found[1], that these species are able to add to the double bond of alkenes with formation of corresponding unsaturated cyclopropanic adducts 3 with yields up to 60%, as well as to insert into O-H–bonds of alcohols giving mixed propargylic acetals 4. The data, pointing to the significant role of steric factors in the reactions with participation of carbenes 1, was obtained.



R^1 = Me, Et; R^2 = H, Me, $-(CH_2)_4-$; R^3 = H, Me; R^4, R^5 = H, Me, Ph

Starting pyrazoles 2 were synthesized with yileds up to 55% from compound 5 by sequential treatment of the latter with lithium diisopropylamide, sulfur and appropriate iodoalkane.

The developed approach is promising for direct synthesis of new functionalized alkynylcyclopropanes as well as for further investigation of carbenic species 1 by matrix IR spectroscopy.

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This work was financially supported by RFBR, project 18-03-01037 A.

BISHYDROPHOSPHORYLATION OF UNSATURATED ELECTROPHILIC COMPOUNDS UNDER TERTIARY PHOSPHINES CATALYSIS

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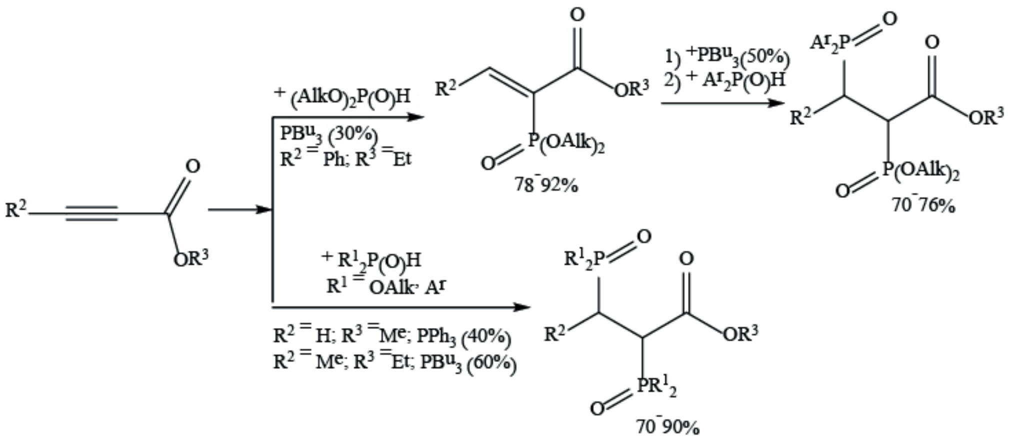
The aim of the project is development of new highly efficient organocatalytic methods of preparation of cyclic and acyclic bisphosphonates, phosphinates and phosphine oxides on the basis of one-step phosphorylation reactions of electron-deficient alkynes.

It was established that diarylphosphinites are more reactive in phosphine-catalyzed bishydrophosphorylation reaction than dialkylphosphites. A number of bisphosphoryl compounds based on ethyl phenylpropiolate, ethyl 2-butynoate and methyl propiolate were obtained.

Optimization of the bishydrophosphorylation reaction conditions has resulted than increase of rate and chemoselectivity of the process. The best results were provided when the reactions were performed using nucleophilic aliphatic phosphine PBu3 as a catalyst.

The examination of solvent effects with PBu3 as the catalyst revealed that polar solvents such as MeCN, DMF and DMSO can significantly facilitate the reactions, and the best results were obtained using acetonitrile as a solvent.

The use of tri-n-butylphosphine as a catalyst in the reactions of highly reactive methyl propiolate was not useful. The use of less nucleophilic triphenylphosphine turned out to be more effective. It was found that proton-donating solvent, isopropanol, facilitate minimization of side processes.



This research was supported by a grant of Russian Foundation for Basic Research (project 18-33-00047).

STEREOSELECTIVE FOUR-COMPONENT SYNTHESIS OF TETRAHYDROPYRIDINE

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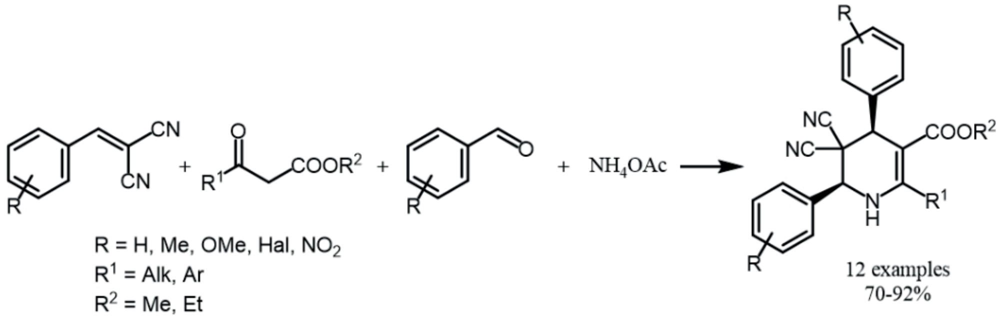
Tetrahydropyridines are an important class of biologically active compounds. For example, arecoline is a nicotinic acid alkaloid that has a stimulating effect as a muscarinic acetylcholine receptor. Betanin, a plant pigment, is a natural product containing a tetrahydropyridine unit, used as a food additive[1]. Among a wide range of heterocyclic compounds, piperidine derivatives are of particular interest in the pharmaceutical industry because of their versatility and broad spectrum of action for various types of diseases. Namely, they have anti-cancer, anti-inflammatory, sedative, antimicrobial, antiviral properties[2].

Piperidine derivatives have found application as synthetic drugs broad pharmacological actions: analgesics, Anesthetics, antipsychotics, antidepressants agonists, opiate receptors and many others.

The stereoselective four-component synthesis of substituted tetrahydropyridines was carried out.



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INFRARED LUMINOPHORS BASED ON LANTHANIDE COMPLEX COMPOUNDS

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At present, the great attention is paid to preparation of the infrared luminophors. Such materials may be used as converters of ultraviolet and visible radiation into emission of the near infrared range, that is important for solution of biomedical problems. These converters may find application as luminescent marks in the immunofluorescent analysis, in silicon receivers, in optoelectronics for night vision equipment and lasers.

New Nd(III), Yb(III), and Er(III) complex compounds with carboxylic acids as well nitrogenous- and phosphorous – containing neutral ligands displaying intensive luminescence in the IR range were synthesized. Their composition and structure were determined by the chemical elemental analysis, X-ray diffraction, X-ray electron, thermal and IR spectroscopy methods.

The spectral luminescent properties of the mixed-ligand rare-earth complex copounds with carboxylic acids were studied. The dependence of the luminescence intensity on the composition of their coordination sphere was stated. The lanthanide complexes displaying the maximum intensity in the near IR range were revealed[1,2].

The polymer luminescent compositions based on Nd(III), Yb(III), and Er(III) compounds, polyethylene and methacrylate were obtained. Kinetics of their decay was studied.

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The work was supported by the Russian Government State Order, project no 0265-2014-0001.

ACCUMULATION AND MIGRATION OF HEAVY METALS IN WATER-SOIL-PLANT SYSTEM

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Heavy metal contamination is the globaly recognised environmental issue. The aim of this study was quantify the concentration heavy metals including (Mn, Ni, Zn, Pb, As, Cd, Cu, Fe) in water-soil and plant (rice) system, and to investigate the bioavailability of heavy metals in water-soil-plant. The mobility of heavy metals from soil into the food chain and their bioaccumulation in rice has increased from safety point to view. The metal concentrations were determined by Flame Atomic Absorption and ICP-MS.

MULTICOMPONENT SYNTHESIS OF 2,6-DIARYL-3,3,5,5-TETRACYANO PIPERIDINES

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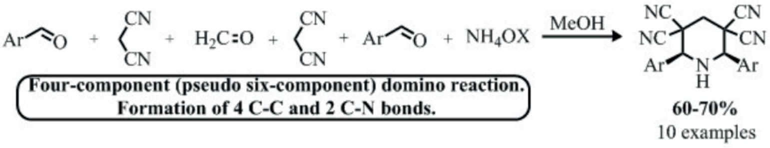
Piperidine containing compounds have been used as synthetic drugs broad pharmacological actions. There are derivatives of piperidine exhibiting antiviral activity (N-methyl-2,4,6-triphenylpiperidine is effective against smallpox virus)[1]. Presently a few examples of synthesis of substituted piperidines is known in the literature[2]. The development of cost-effective methods for the synthesis of derivatives of piperidine is an actual problem of modern organic chemistry.



We have established that four-component (pseudo six-component) domino reaction of malononitrile, formaldehyde and aromatic aldehydes in the presence of ammonium acetate or ammonia hydrate in methanol results in to the formation of 2,6-diaryl-3,3,5,5-tetracyanopiperidines, with 60-70% yields:

The procedure found by us utilizes simple equipment; it is easily carried out and is valuable from the viewpoint of environmentally bening diversity-oriented large-scale processes. Final compounds do not require further purification and isolated by simple filtration followed by washing with a small amount of methanol.

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This study was financially supported by Russian Science Foundation (grant no. 17-73-20260).

MOLECULAR DESIGN OF NEW LUMINESCENT COMPLEXES OF PLATINUM METALS

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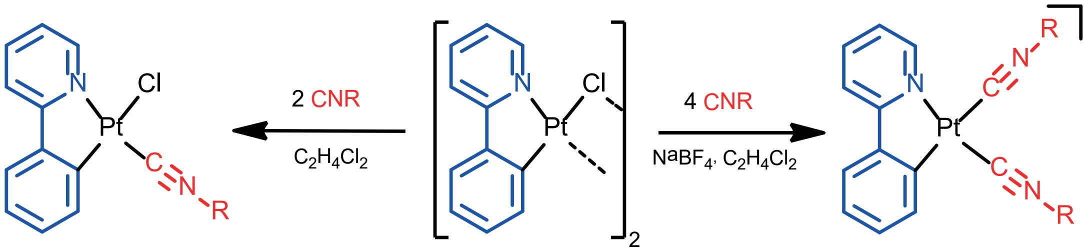
Molecular design, synthesis and study of luminescent complexes is one of the most relevant fundamental research in the coordination chemistry. In this case, the luminescent platinum (II) complexes with cyclometalated arylpyridine ligands are the most perspective for light-emitting materials. Moreover, the strong σ donor CC^N atom affords the metal ion a very strong ligand field, raising the energy of the nonradiative metal-centered (d-d) excited states to relatively inaccessible energies. Additionally, the introduction of strong-field ancillary ligands in the complex increases the energy gap, ΔE, between the lowestlying excited state (IL/MLCT) and higher-lying d-d state, so the nonradiative decay is inhibited.

A series of cyclometalated platinum(II) complexes, [Pt(C^N)(CNR)Cl] и $[Pt(C^N)(CNR)_2]X$ (C^N – phenylpyridine) have been designed and synthesized (yield 70-90%).

All prepared complexes were isolated and characterized by elemental analyses (C, H, N), HRESI$^{\pm}$-MS, IR, ^{1}D (^{1}H,^{13}C{^{1}H}, ^{195}Pt) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{1}H-NOESY) NMR spectroscopies, and by X-ray diffraction.



R = Xyl, Mes, 2-Cl-6-MeC_6H_3, naphth-2-yl,
4-Cl-C_6H_4, 4-Br-C_6H_4, 4-I-C_6H_4, t-Bu,

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This work was supported by grant of the President of the Russian Federation, project MK-1476.2019.3. Physicochemical studies were performed at the Center for Magnetic Resonance and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).

SYNTHESIS, STRUCTURE AND PHOTOPHYSICAL PROPERTIES OF CYCLOMETALATED COMPLEXES OF IRIDIUM(III) WITH CYANAMIDE AND ISONITRILE LIGANDS.

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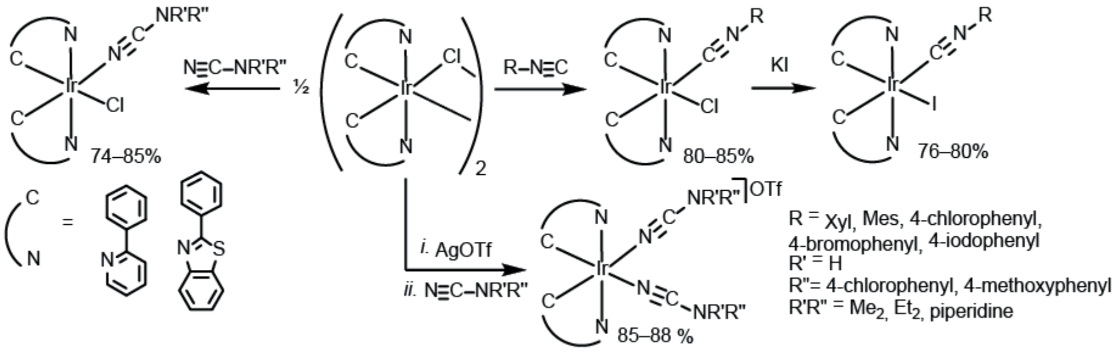
Cyclometalated complexes of iridium(III) $[\mathrm{Ir(C^{\wedge}N)_2(L,L')}]^Z$ are perspective materials, which has application as biological labels, photoredox catalysis and LEDs because of luminescence in the entire visible range. We can tune photophysical properties by changing cyclometallating(C^N) or auxiliary ligands(L, L').

In the course of our studies on chemistry of platinum metals complexes with various cyclometalated and auxiliary ligands, we have synthesized several new complexes $[\mathrm{IrCl(ppy)_2(NCNR_2)}]$, $[\mathrm{Ir(ppy)_2(NCNR_2)_2}]\mathrm{OTf}$, $[\mathrm{IrCl(ppy)_2(CNR)}]$, $[\mathrm{IrI(ppy)_2(CNR)}]$, $[\mathrm{Ir(bt)_2(NCNHR)_2}]\mathrm{NO_3}$[1].



Complexes exhibited intense and long-lived luminescence in the blue-green and yellow-red region of visible range. All obtained complexes have been characterized by ^{1}H, ^{13}C{H} NMR and IR spectroscopies, ESI$^+$ MS, elemental analyses and structurally characterized by X-ray crystallography.

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This work has been supported by the Russian Science Foundation (18-33-20073) and grant of the President of the Russian Federation, project MK-1476.2019.3. Physicochemical measurements were performed at the Center for Magnetic Resonance, X-ray Diffraction Center, and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).

REACTION OF THE DIISOPROPOXYDITHIOPHOSPHORIC ACID WITH THE ENAMINES

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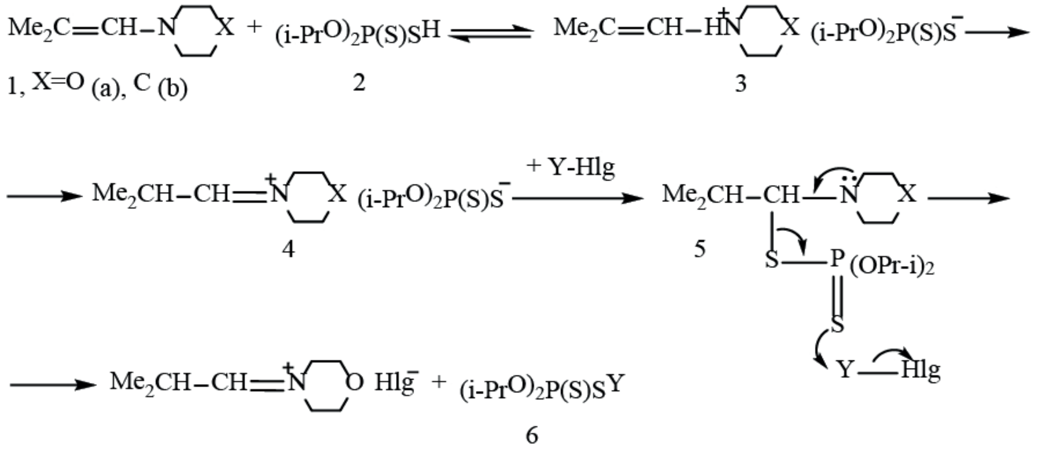
Earlier it was supposed[1] that an interaction of O,O-dialkyldithiophosphoric acids $(RO)_2P(S)SH$ with N-alkyl-2-haloimines $Me_2C(Hlg)CH{=}NR$ proceeds via the intermediate formation of enamine[1]. But the reactions of enamines with the P(IV) dithioacids were not studied. We found out, that enamines 1 react with the diisopropoxydithiophosphoric acid 2 to give iminium dithiophosphate 4. Probably initial protonation of enamine nitrogen atom takes place with the formation of ammonium dithiophosphate 3 which transforms into the salt 4 owing to the prototropic process. When X=C the salt 4b is stable and it was isolated as an individual substance. Salt 4a is not stable and transforms into the product 5 of addition of acid 2 to enamine 1. We also established that compound 5 react with organic halides (sulfenyl, acyl halides and α-chloroethes) to form substitution products 6.



6, Y=$(RO)_2P(S)S$ (a), RCO (b), $(RO)_2CH$ (c)

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DERIVATIVES OF FULLERENES: MORE THAN ONE-THIRD OF ELEMENTS OF MENDELEEV PERIODIC TABLE ARE INSIDE AND OUTSIDE OF THEM

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In fact, now it is well known that more than forty elements of Mendeleev periodic table are attached chemically to fullerene cages. Some of them are covalently bonded outside of them i.e. *exohedral* derivatives, but most of them, which named *endohedral* fullerenes, contain inside the cages atom(s) of noble gases, almost all lanthanides, some actinides, and rare-earth as well transition metals, atomic clusters etc. and even small molecules. The volume of the fullerene molecular cavity makes it possible to put them in. An important feature of endohedral metallofullerenes is that they generate a big family of derivatives of fullerenes, which cannot be obtained as pristine, i.e. empty fullerenes. Between them are non-IPR fullerenes and also very interesting group of *radical fullerenes* both IPR and non-IPR ones. Radical fullerene has unpaired electrons being very unstable one. Such a radical fullerene is stabilizing by metal cation inside anionic fullerene cage in the process of its obtaining in DC arc charge, for example. This peculiarity shed light on details of fullerene electronic structures. Moreover, it gives the information about some earlier undisclosed episodes of mechanism of fullerene formation. Keeping in mind the very short historical period of our knowledge of fullerenes and unusual structure of their molecules, in general, experimental synthetic and structural data often outpace their explanations. Indeed, quantum-chemical calculations are very useful and serve sometimes as predictive models. In our report we show some new theoretical rationales concerning influence of geometrical and electronic structures of fullerene molecules on properties of exohedral and endohedral fullerenes, mainly fullerenes stability.[1-3]

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VIBRATIONAL SPECTROSCOPY STUDY OF P-SULFONATOCALIX[4]ARENES

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Calixarenes with sulfonate groups on the upper rim are soluble in water and play a particular role in the interaction with biological objects. They interact with cells, are used as bacteria sensors and for drug delivery. Calixarene sulfonates have been shown to be biocompatible and non-toxic.

In this work, changes in the infrared spectra in the process of heating p-sulfonatocalix[4]arene are studied. It is important to detremine how bands of polar sulfonate groups appear in the vibrational spectra of calixarene and their modification in the conformational transformation process. The DFT method was used to interpret the IR and Raman spectra of p-sulfonatocalix[4]arene. Characteristic bands of sulfonate substituents were identified. In addition, using the TGA method, we tried to establish how the sulfonate groups affect the thermal stability of calixarenes.

Vibrational spectra of p-sulfonatocalix [4] arene were investigated. The geometrical parameters, the energies, the frequencies and the intensities of the bands in the IR and Raman spectra were obtained for four possible conformations. The most stable conformation of the p-sulfonatocalix[4]arene is the cone due to the cooperative cyclic intramolecular hydrogen bond system. The strength of the hydrogen bonds and the orientation of the aromatic moieties depend on the type of substituent on the upper rim of the calixarene molecules. The process of destruction of calixarenes is studied by the methods of IR spectroscopy and TGA. Characteristic bands for each conformation were selected. HOMO covers aromatic units with notable conjugation and LUMO belongs to sulfonate groups.

We thank the Russian Science Foundation for the financial support of this work (project №15-13-20017). Synthesis of (thia) calix[4]arene derivatives was supported by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities (4.5151.2017/6.7).

NOVEL WATER-SOLUBLE FLUORESCENT CHEMOSENSORS BASED ON 2,3-DIPHENYLQUINOXALINE

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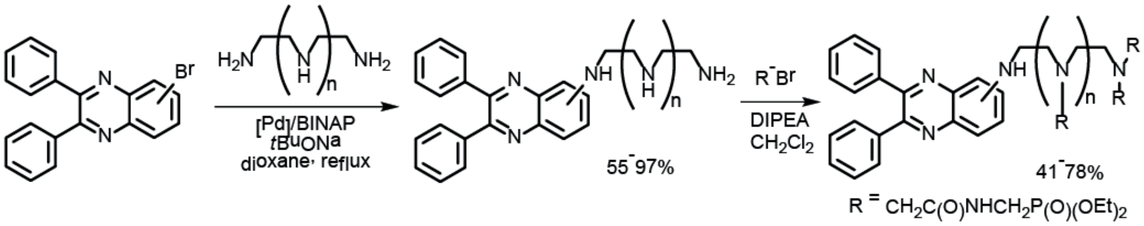
Fluorescent sensors for metal cations, gases and small molecules find wide applications in various areas of chemistry, ecology and medicine due to high selectivity and sensitivity. The synthesis of the fluorescent sensors for metal detection in aqueous media is a challenging task as it demands the combination of water solubility, emissive properties and selectivity towards the analyte.



In this work we studied synthetic approaches to prospective fluorescent chemosensors for metal cations based on 2,3-diphenylquinoxaline. Pd-catalyzed amination reaction was used as a key step which allowed to bind the fluorescent heteroaromatic moiety directly to a receptor polyamine group. We investigated the introduction of the receptor units into positions 5 and 6 of 2,3-diphenylquinoxaline. target compounds were obtained in yields up to 97%. To prepare water-soluble fluorescent ligands, arylated polyamines were modified with phosphonate-containing substituents. The possibility of the metal cations detection using these ligands at the biological pH level (7.4) was studied.

The work was accomplished in the frames of the French-Russian associated laboratory LIA LAMREM and financially supported by RFBR (project No 17-53-16012) and CNRS.

DECOMPOSITION OF TERTIARY HYDROPEROXIDES BY METAL COMPLEXES OF CALCIUM METALS

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Supramolecular complexes of crown ethers and alkaline earth metals' halides are widely used in the industrial syntheses and in the interfacial catalysis. Also, they are quite an attractive objects of the study of the hydroperoxide decomposition reactions because of their ability of making the complexes with the organic molecules.

To determine the value of the catalytic activity of the metal compounds of the second subgroup, we made a research of the catalytic decomposition of the tertiary hydroperoxides (the isopropyl benzene and the tertiary butyl) in the presence of the dibenzo-18-crown-6 crown ether complexes (DBC). These complexes contained the calcium chloride ($CaCl_2$), the strontium chloride ($SrCl_2$) and the barium chloride ($BaCl_2$).

The reactions of the tertiary butyl hydroperoxides' (TBHP) decomposition and the isopropyl benzene hydroperoxides' (IPBHP) decomposition have been accelerated with all the studied compounds. The studied catalysts are ordered by the activity as follows: $SrCl_2 \bullet DBC > CaCl_2 \bullet DBC > BaCl_2 \bullet DBC$.

It has been kinetically proven that the TBHP is forming a 3-to-1 proportional intermediate with all the complexes. The IPBHP decomposition forms the complex consisting of the following poroportions: ROOH : Kat = 2:1.

Both of the hydroperoxides have quite a branched structure. However, the presence of a benzene ring in IPBHP, obviously, creates a steric obstacle to the 3-to-1 complex formation.

The decomposition proceeds sequentially: several complexes of different stoichiometry (3ROOH·Kat, 2ROOH·Kat, ROOH·Kat) decompose simultaneously, which leads to the high values of the decomposition rate constants and lowered activation energies. The TBHP's decomposition rate is higher than IPBHP's, because in the first case 3 intermediates of different stoichiometry are getting decomposed simultaneously, and only 2 of them are getting decomposed at the same time in the second case.

The formation of intermediate complexes in the hydroperoxide-catalyst system was confirmed by a quantum-chemical method. The optimized structure was determined, and the stepwise mechanism of intermediate complexes' formation and decomposition was established.

The work was done with the financial support of the Ministry of Education and Science of the Russian Federation as part of the State Mission No. 10.956.2017 (PNIL 25.17).

PYRIMIDINE SYNTHESIS BY PHOTOCHEMICAL REACTION OF 2-AZIDOCINNAMATES

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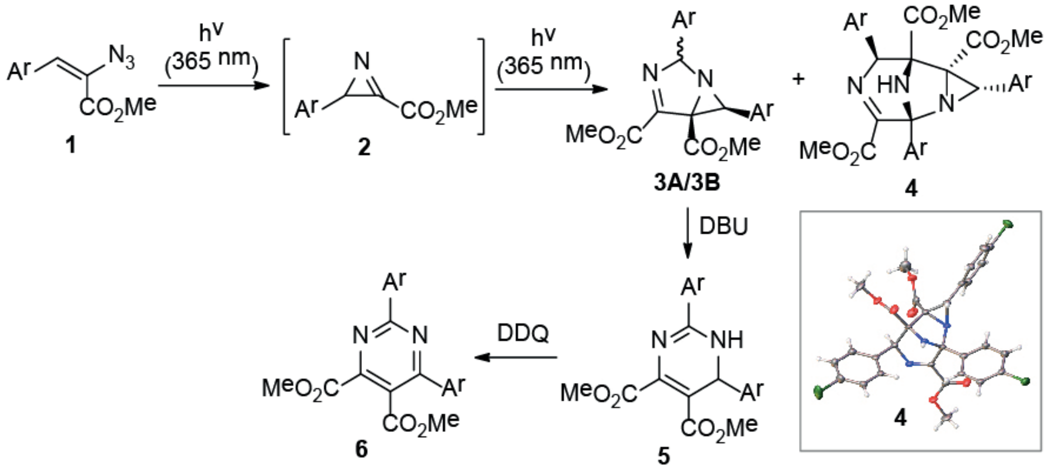
Many natural bioactive compounds and drugs contain pyrimidine cycle[1], so development of new method for the synthesis of pyrimidines is an actual task. In this work, we suggested the new way of pyrimidine synthesis from 2-azidocinnamates.

When 2-azidocinnamates 1 are irradiated, they turn into azirines 2, which upon further irradiation give isomeric bicycles 3A/3B[2] and compound 4. Under treatment with a base 3A/3B convert to dihydropyrimidines 5, which can be oxidized to pyrimidines 6. The structures of the compounds were determined by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and high resolution mass-spectrometry. The structure of tricyclic compound 4 was confirmed by X-ray diffraction analysis.



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The work was supported by the Russian Foundation for Basic Research (18-33-20073) and Grant Program of the President of Russian Federation (MK-4457.2018.3). Physicochemical studies were performed at the Center for Magnetic Resonance Research, Center for X-ray Diffraction Studies and Center for Chemical Analysis and Materials Research (all belong to Saint Petersburg State University).

THEORETICAL STUDY OF DERIVATIVES OF CLOSO-BORATE ANIONS WITH EXO-POLYHEDRAL CARBONILE GROUPS

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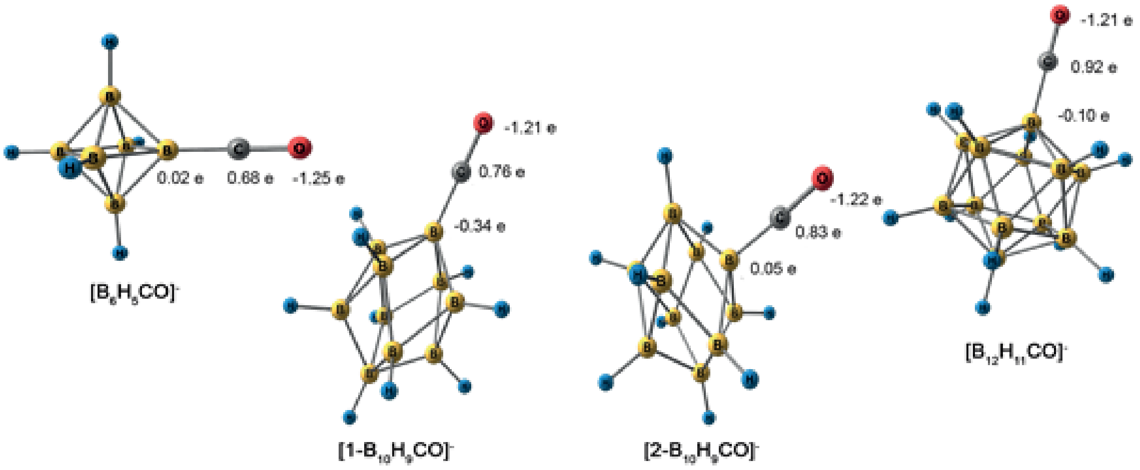
This study focused on the structure, bonding, and reactivity analysis of the derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12) and $[B_nH_{n-1}COR]^-$ (n = 6, 10, 12, R=OH, OCH_3, NH_2, H, CH_3). DFT calculations at the ωB97X-D3/6-31++G(d,p) level of theory have been performed. The B–B, B–H, B–C and C–O bonding interactions have been theoretically studied under the perspective of the Quantum Theory of Atoms in Molecules (QTAIM) and several local and integral topological properties of the electron density involved in these interactions have been computed. We have discovered the good correlation between results of Wiberg bond order analysis and QTAIM analysis of B-C and C-O interactions. Also, different chemical reactivity descriptors have been calculated via conceptual density functional theory (DFT). The active sites suitable for nucleophilic attacks have been selected using the Fukui function indices based on the NBO and AIM atomic charges.



$[B_6H_5CO]^-$ $[1\text{-}B_{10}H_9CO]^-$ $[2\text{-}B_{10}H_9CO]^-$ $[B_{12}H_{11}CO]^-$

This work was supported by the Russian Science Foundation (projects no. 18-73-00049).

TRANSFORMATION OF EPIMINOMETHANOCYCLOPENTAINDENES UNDER UV-IRRADIATION

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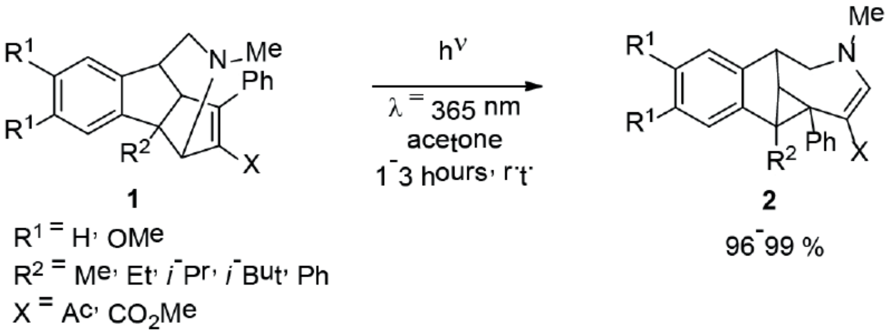
The vinylcyclopropane rearrangement is well studied in the literature. A lot of transformations of compounds containing a vinylcyclopropane fragment into cyclopentene derivatives and alicyclic diene systems under the action of temperature, light or catalysts was described. Such rearrangements occur in both cyclic and heterocyclic systems[1-2].

In our laboratory, the thermolysis reaction of heterocyclic allenes was earlier carried out[3], which resulted in the production of complex skeleton structures - condensed cyclopentenes 1, as well as vinylcyclopropanes 2 isolated in small quantities, which were intermediate products of thermal transformations of azacyclic allenes into condensed cyclopentenes 1.

It was noted that compounds 1 under the action of light can be transformed into cyclopropan-containing compounds 2. It was found that epiminomethanocyclopentaindenes 1 in acetone under the influence of UV radiation for 1-3 hours entirely converted into azabenzocyclopropaazulenes 2 containing a vinylcyclopropane fragment.



The structure of compounds 2 was proved by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and IR spectroscopy.

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THE EFFECT OF ULTRAVIOLET IRRADIOATION ON THE PROCESSES OF ELECTROOXIDATION OF HYDROGEN SORBED ON PALLADIUM DEPOSITS

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Stripping voltammetry is used by us to study the effect of ultraviolet (UV) irradiation on the kinetics of the processes of electrooxidation of hydrogen adsorbed by the electrolytic deposit of palladium and absorbed by the palladium deposit on the surface of a graphite electrode (GE).

From the literature data it is known that in acidic background electrolytes at the limit current potential of palladium(II) ions there is a conjugated process of electrodeposition of hydrogen and palladium.

During the electrooxidation of the deposit, a curve with multiple peaks of current is recorded on the voltammogram. In the potential range of 0.1...0.3 V, selective electrooxidation of hydrogen adsorbed on palladium precipitate occurs; at potentials of 0.4...0.6 V, selective electrooxidation of hydrogen from palladium absorbed by the deposit and electrooxidation of palladium occurs. The kinetics of electroreduction of palladium together with hydrogen without UV and with UV irradiation of solution is considered. The study of the kinetics of the solid-phase process of electrooxidation of hydrogen from palladium was carried out using the Abraham equation, on the temperature dependences of the logarithm of the current on the reciprocal temperature, on the basis of phenomenological dependence of hydrogen desorption from palladium surface on UV irradiation time.

It is established that the process of electrooxidation of hydrogen absorbed by palladium is limited by the diffusion of hydrogen from palladium. Determined kinetic parameters of adsorption processes of hydrogen by electrodeposits of palladium and processes, desorption of hydrogen from the electrolytic precipitation of palladium (the heat of hydrogen adsorption, the rate constants of hydrogen desorption, the diffusion coefficient of hydrogen absorbed by the palladium deposit).

SYNTHESIS AND STRUCTURE OF COORDINATION COMPOUNDS OF TRIS(HYDROXYMETHYL)AMINOMETHANE

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Tris(hydroxymethyl)aminomethane (trisamine) is a non-toxic aminoalcohol and is widely used in medicine and molecular biology. Trisamine has an osmotic diuretic effect and is used for correction of the acid-base composition of the blood in acidosis of various etiologies. The trisamine salt with a pyrrolizine carboxylic acid derivative is a nonsteroidal anti-inflammatory drug that has a pronounced analgesic effect.

With the aim of obtaining new biologically active compounds we have investigated the interaction of trisamine with biogenic metals salts. New coordination compounds of trisamine were synthesized by the interaction of trisamine with copper (II), nickel (II), cobalt (II) and zinc (II) valinate, benzoate and cinnamate at different molar ratios of reagents. The composition and structure of the synthesized complexes were confirmed by the data of mass spectrometry, electron and IR spectroscopy, elemental analysis.

The crystal structure of the trisamine complex with copper (II) cinnamate, $[Cu(Tris)_2]Cin$, was established by X-ray diffraction. The copper atom is tetracoordinated by two trisamine ligands through nitrogen and oxygen atoms. The bond lengths of Cu-N and Cu-O are 2.0099(14), 2.0039(12) Å and 1.9380(12), 1.9532(12) Å, respectively. The other two hydroxymethyl groups of trisamine are not involved in coordination with the metal. Cinnamate anions form the outer sphere of the complex and participate in the formation of hydrogen bonds with hydroxymethyl and amino groups of trisamine.

Antimicrobial activity of the synthesized coordination compounds of trisamine was investigated.

The reported study was funded by RFBR according to the research project № 18-33-00216.

The scientific research was performed at the "Centre for Optical and Laser Materials Research," "Chemical Analysis and Materials Research Centre," "Centre for X-ray Diffraction Studies," "Magnetic Resonance Research Centre" of Research park of St. Petersburg State University.

COORDINATION COMPOUNDS OF TRIS(2-HYDROXYPROPYL)AMINE

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Tris(2-hydroxypropyl)amine (TPA) is the closest structural analogue of tris(2-hydroxyethyl)amine and its interaction with acids, metal salts and organoelement compounds also leads to the formation of chelate compounds – atranes.

In order to obtain new compounds, the interaction of TPA with carboxylic acids – cinnamic, benzoic, salicylic, nicotinic, succinic, malonic and oxalic, as well as with Cu(II), Co(II), Ni(II) and Zn(II) salts was studied. The target compounds were obtained and isolated as powders or viscous liquids by the interaction of TPA with the corresponding acid. The obtained tris(2-hydroxypropyl) ammonium salts, $[NH(CH_2CH(CH_3)OH)_3]_nX$, were characterized by NMR (^1H, ^{13}C), IR spectroscopy and elemental analysis. The crystal structure of tris(2-hydroxypropyl)ammonium hydromalonate was determined by single crystal X-ray diffraction. The cation is characterized by bicyclic *endo-exo*-conformation: two hydroxypropyl branches surround the hydrogen atom HN with the formation of two intramolecular hydrogen bonds. It should be noted that in the case of tris(2-hydroxyethyl)ammonium hydromalonate [1], tricyclic *endo*-conformation of the cation was observed, which is characteristic for the majority of tris(2-hydroxyethyl)ammonium salts (protatranes).

The composition and structure of coordination compounds of TPA were confirmed by mass spectrometry, IR spectroscopy and elemental analysis. The structure of TRA complex with nickel (II) cinnamate was established by single crystal X-ray diffraction.

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The reported study was funded by RFBR according to the research project № 18-33-00216.

The scientific research was performed at the "Centre for Optical and Laser Materials Research," "Chemical Analysis and Materials Research Centre," "Centre for X-ray Diffraction Studies," "Magnetic Resonance Research Centre" of Research park of St. Petersburg State University.

SYNTHESIS OF SUBSTITUTED BENZAZECINES.

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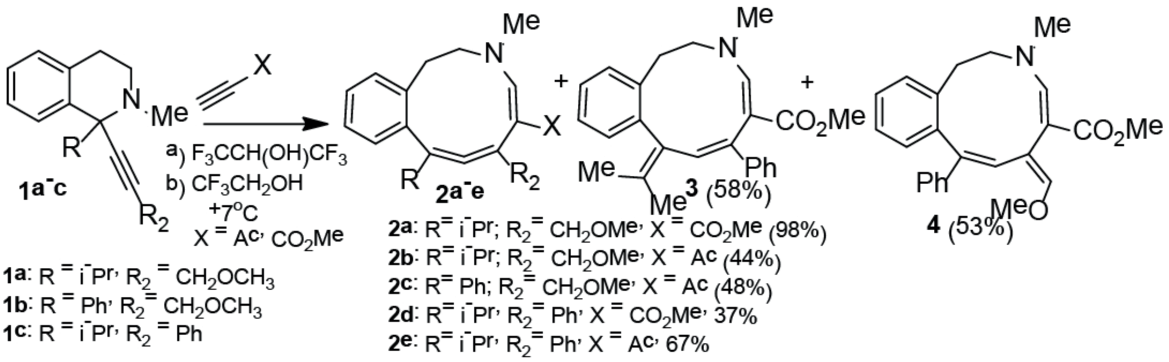
A large number of alkaloids are known, among of which compounds with the azacine fragment can be found. These natural substances include protopine and allocryptopine. Benzazecines have a wide range of beneficial properties: they can be used as antagonists of dopamine 5-HT2A, they are potential antipsychotics [1] and acetyl and butyrylcholinesterase inhibitors.

In this research, we have developed some methods for the synthesis of substituted benzazecines. Reactions of 1-methoxymethyl(phenyl)ethynyl-substituted tetrahydroisoquinolines with terminal activated alkynes in trifluoroethanol or hexafluoroisopropanol were carried out at + 7°C. Azacyclic allenes 2 are the main products of the transformation of the cycle of tetrahydropyridine. In some cases, we found two ways to stabilization of a strained cyclic cumulated system 2 into ylidene substituted benzazecines 3 and 4. The presence of a methine or methylene group at the allene's fragment can lead to [1,3]-hydrogen shift, and the assistance of a proton solvent in these processes cannot be ruled out.



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REACTIONS OF LEVULINIC ACID AND PSEUDOLEVULINIC ESTERS WITH VARIOUS C-NUCLEOPHILES

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Pseudolevulinic esters, 5-methyl-5-methoxydihydrofuran-2(3H)-one and 2-methyl-5-oxotetrahydrofuran-2-yl acetate (acetoxy γ-valerolactone), may also be promising reagents; their syntheses are simple and their synthetic potential is associated with a possibility of generating oxocarbenium ions whose chemistry has been developed extensively.[1-4]

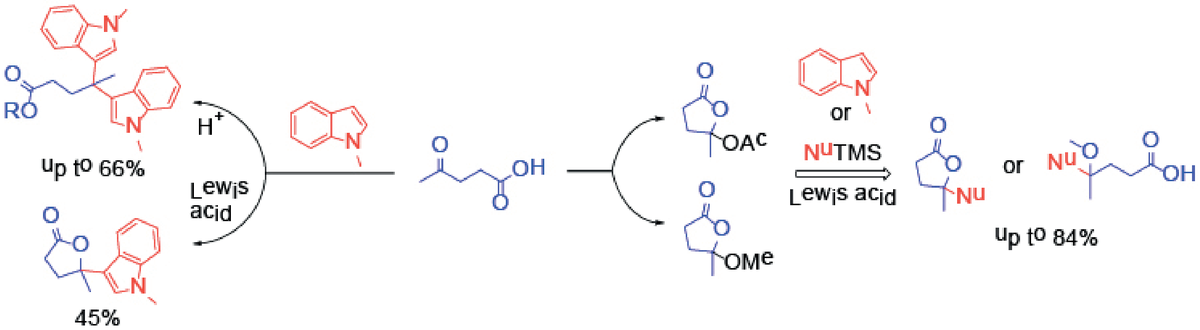

Figure 1. Reactions of levulinic acid and its esters with C-Nucleophiles

The reactions of levulinic acid and its pseudo esters, which are readily available from carbohydrate-containing raw materials, with various C-nucleophiles are described. Different reaction pathways were demonstrated depending on the nature of the leaving groups and nucleophiles. For 5-methyl-5-methoxydihydrofuran-2(3H)-one, the reaction was found to proceed by a route giving hept-6-enoic acid derivatives. In contrast, the reaction of 2-methyl-5-oxotetrahydrofuran-2-yl acetate proceeds via intramolecular cyclization to form γ-valerolactone derivatives[5].

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ESTIMATION OF EXTRACTION SELECTIVITY OF METALS UNDER THE CONDITIONS OF COMPETITIVE SORPTION ON MODIFIED SILICA GELS

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Our team conducts systematic studies of silica gels with covalently immobilized thiosemicarbazide and formazan groups under the conditions of competitive sorption from multicomponent systems and has proposed a methodological approach to determine the selectivity of the modified sorption material with regard to Cu(II), Ni(II), Co(II), Cd(II), and Zn(II) under these conditions. This approach includes the following steps:

– the behavioral study of binary systems containing a modified silica gel and a metal cation (at pH of the medium providing the maximum distribution coefficient of metal ion), plotting of sorption isotherms, and calculation of the maximum sorption capacity;

– the behavioral study of a multicomponent system under equilibrium and competitive sorption conditions when the molar ratio of functional groups and analytes is 1 : 1;

– plotting of kinetic sorption curves for binary and multicomponent systems when the amount of functional groups is considerably (more than 50–100-fold) higher than that of metal ions. The resulting integral kinetic curves are processed in the coordinates of pseudo-first- and pseudo-second-order equations and the Elovich equation;

– the adequacy of application of the kinetic equation (for selected concentration level) is assessed comparing the approximation coefficient and the calculated inadequacy variance with table values. The maximum sorption capacity for selected initial concentration of sorbate is calculated from kinetic equations and compared with its experimental value;

– series of the surface affinities of selected metal cations are plotted based on the reached equilibrium capacities calculated from kinetic equations for binary and multicomponent systems, which are then used to build up eluotropic series of affinity and to assess the mutual influence of analytes when the number of functional groups considerably exceeds the content of analytes.

This work were supported by the Russian Ministry of Higher Education and Science (project no. 4.4892.2017/8.9).

NEW OPPORTUNITIES FOR SYNTHESIS OF QUINAZOLIN DERIVATIVES

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Quinazoline derivatives are one of the most important classes of heterocyclic compounds that are widely common in nature and are part of various drugs.

We have determined the reduction potentials for quinazoline 1 and its proton salt by voltammetry methods. The appearance of a low-voltage peak at –0.55 V is associated with the reduction of the –C=NH$^+$– quaternary quinazoline proton salt fragment and indicates the electron-acceptor properties of the molecule.

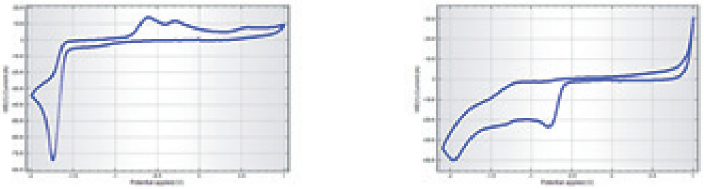
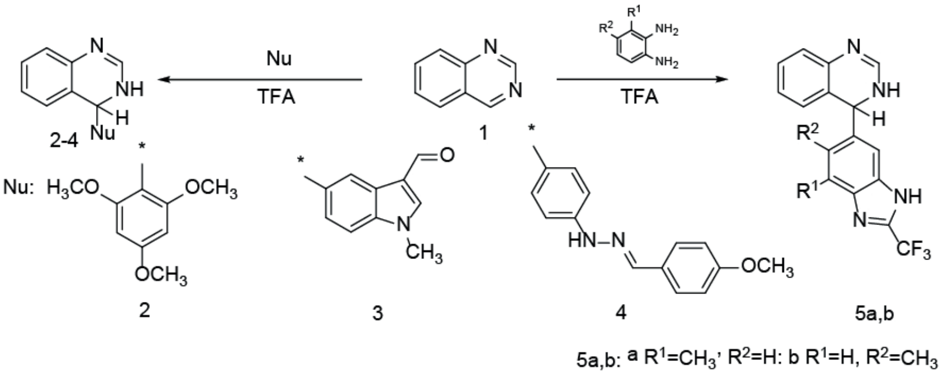


Fig. 1. CV for comp. 1 (1.0*10-4 M): a) without acid; б) with acid (18,6•10-3 M) HCl.

It was found that quinazoline 1 reacts with C-nucleophiles when heated in the presence of trifluoroacetic acid with the formation of stable σ-adducts 2-4.



A multicomponent reaction was found in the study of the interaction of quinazoline 1 with o-phenylenediamines when heated in the presence of TFA. σ-adducts 5a,b were obtained as a result of the reaction

This work was supported by the Russian Foundation for Basic Research (grant 18-33-00727).

STERIC EFFECT OF SUBSTITUENTS IN HIGH-SPIN POLYBROMPHENYL NITRENES ON THE SPIN-ORBIT CONTRIBUTION TO THE ZERO-FIELD SPLITTING

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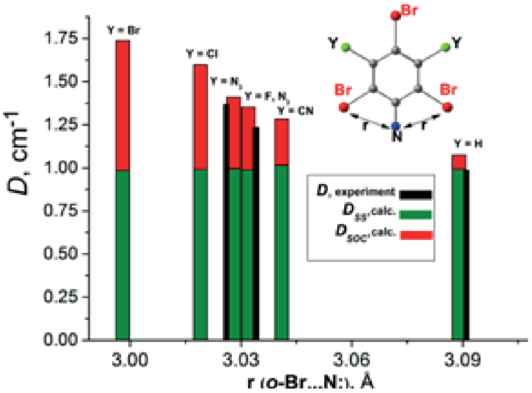
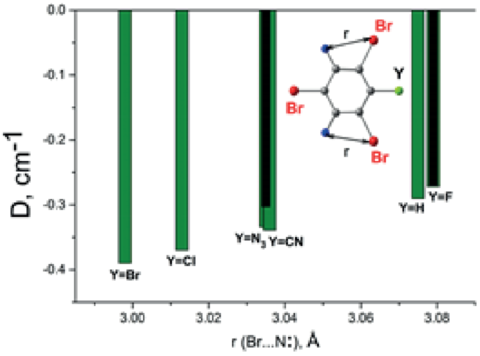
Recently we reported on the first high-spin arylnitrenes with the predominant spin-orbit contribution to the zero-field splitting parameters D due to the presence of bromine atoms (the "heavy atom effect")[1]. Further development of these works showed that, unlike the septet (S = 3) and quintet (S=2) polynitrenes, the "heavy atom effect" in triplet (S=1) bromine and iodophenylnitrenes does not manifest itself [2,3], but can be modulated by some substituents in the phenyl ring[3,4].





In this work, at the experimental and theoretical levels, the "heavy atom effect" in the series of triplet and quintet 2,4,6-tribromophenylnitrenes is studied in detail. The steric nature of the influence of the substituents Y on the spin-orbit contribution (D_{SOC}) to the parameter *D* is established. This effect is expressed in the decreasing of the distance between the o-Br substituents and the nitrene center.

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This work has been supported by the Russian Foundation for Basic Research, 19-03-00644.

CHARGE TRANSFER COMPLEXES OF LANTHANIDE 3,5-DINITROBENZOATES WITH AMINOBENZENES

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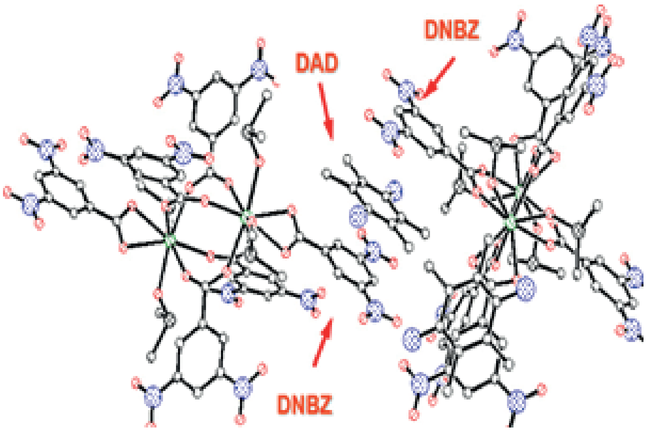
One of the problems in the development of the magnetic materials on a basis of the lanthanides is the presence of diamagnetic ligands, the “spin ballast” in the complexes. Conversion of the ligands into magnetically active ones is possible due to formation of a charge transfer complex (CTC) between an electron donor molecule and an electron-acceptor ligand. Recently we obtained and studied CTCs containing binuclear Ln 3,5-dinitrobenzoates and N,N-dimethylaniline[1] or N,N,N',N'-tetramethylphenylenediamine[2] ($[Ln_2(DNBZ)_6(DMSO)_4]$•xDON•yMeCN; DON = Me_2NPh; x = 3, 4, 5; y = 0; or DON = $1,4\text{-}(Me_2N)_2C_6H_4$; x = 1 or 3; y = 1 or 0; DNBZ = $3,5\text{-}(NO_2)_2C_6H_3CO_2^-$)). Using diaminodurene, (DAD), and 1,2-phenylenediamine (PDA), two new original series of CT adducts, $[Ln_2(DNBZ)_6(DMSO)_4]$•4DAD (Ln = Sm, Gd-Er, Y; DAD = $1,4\text{-}(H_2N)_2C_6Me_4$) (Fig.1, left) and $[Ln_2(DNBZ)_6(DMSO)_2]_2$•PDA•4MeCN (Ln = Gd-Er), were obtained.

CT in the complexes was characterized by UV-vis and reflectance spectra. CT also brings about paramagnetism of Y compound with DAD which was studied by EPR and magnetic measurements; thus, a new way for magnetic activation of ligands is found.



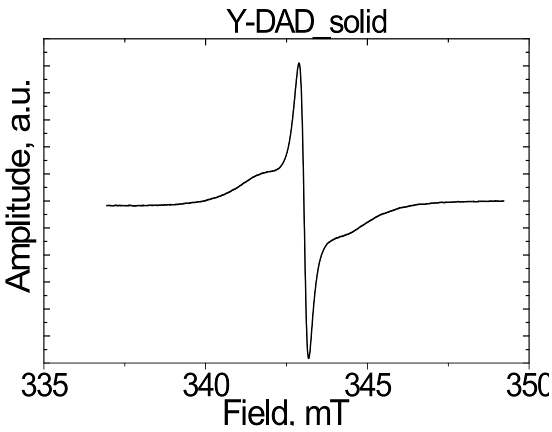


Fig. 1. Fragment of the supramolecular structures of compounds $[Ln_2(DNBZ)_6(DMSO)_4]$•4DAD (left), and EPR spectrum of the Y compound (right).

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The work was supported by the Russian Science Foundation (grant 16-13-10407).

TWO NOVEL SERIES OF 3D-3D´-4F-COMPLEXES ON A BASIS OF ORGANOMETALLIC LIGANDS

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Heterometallic complexes containing organometallic ligands are still poorly studied. In recent years we have obtained and studied several series of *3d-4f*-complexes containing cymantrene[1] (CymH, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$) or ferrocene[1,2] (FcH, $(\eta^5\text{-}C_5H_5)_2Fe$) and benchrotrene[3] ($(\eta^6\text{-}C_6H_6)Cr(CO)_3$) fragments.

Using $FcCO_2H$ and triethanolamine (H_3tea), we obtained new isostructural *3d-3d´-4f*-complexes $[Ln_2Cr_2(OH)_2(FcCO_2)_4(NO_3)_2(H_2tea)_2]$•2MePh•2THF (Ln = Tb (1), Dy (2), Ho (3), Er (4), Y (5)) (Fig. 1, left). Complexes 1-4 show single-molecule magnet (SMM) properties (Δ_{eff}/kB values of 56, 80, 48, and 14 K). Thermolysis of 1 - 5 under air leads to trimetallic $LnFe_{0.25}Cr_{0.75}O_3$ phases.

Using $CymCO_2H$ and $Fe(\eta^5\text{-}C_5H_4P(O)Ph_2)_2$ ligand ($DppfO_2$), a series of new heteroleptic *3d-3d´-4f*-complexes $[Ln(CymCO_2)_2(DppfO_2)_2]NO_3$•Solv (Ln = Tb (6), Dy (7), Ho (8), Er (9); Solv are the lattice solvent molecules) was obtained. The Ln^{3+} ions in the bulky $[Ln(CymCO_2)_2(DppfO_2)_2]^+$ cations are eight-coordinate (Fig.1, right). According to AC magnetic studies, complexes 9 and 10 are the SMMs with Δ_{eff}/kB values of 3.8 and 10.1 K, respectively.

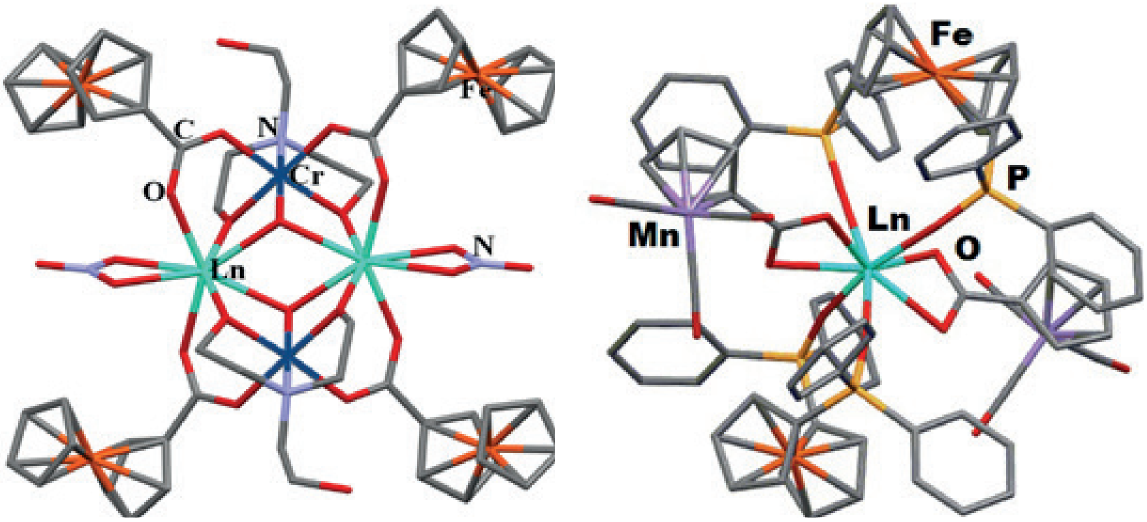

Fig. 1. Structures of complexes 1-5 (left) and of bulky cations in compounds 6-9 (right).

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The work was supported by the Russian Science Foundation (grant 16-13-10407).

COMPLEX COMPOUNDS OF TRANSITION METALS WITH α-CARBONYL CONTAININD ARYLHYDRAZONES

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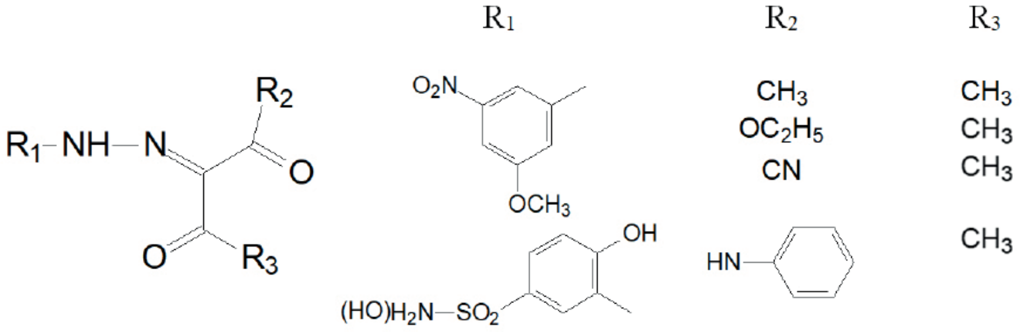
Variety of aspects of application of hydrazones attracts a great interast to their stydies. One of the most valuable property is their high physiological activity. Among them, herbicides, insecticides, nematocides, fugnicides, ratitcides and regulators of growth of plants are found1.

The authors of the present communication isolated and studied by a set of methods (elemental analysis, XRD, structure determination, IR, 1H NMR, electronic spectroscopy, EPR) complex compounds of transition metals with a series of α-carbonyl containing hydrazones:



The problems of ionic and tautomeric transformations of the organic molecules under the conditions of complex formation, equilibrium processes in the solutions, formation constants of metal complexes, crystal and molecular structures of non-coordinated ligands and the corresponding complex compounds are highlighted.

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INVESTIGATION OF ADAMANTYLTHIACALIX[4]ARENES BY IR SPECTROSOPY

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The introduction of four atoms of sulfur instead of methylene links leads to changes in the size of macrocycle, conformation, and ability to chemical modification. Unlike chemistry of classical calixarenes, only a small number of examples of derivatives of thiacalixarenes on the upper rim can be found in the literature.

The objective of this work was to study the normal vibrations, conformations, and hydrogen bonds in molecules of thiacalix[4]arenes with different types of substituents on upper rim, based on an experimental study of FTIR spectra at various temperatures in solid state and solution and quantum chemical calculations using density functional theory. It seems to us important to establish a reciprocal relationship between the structure of thiacalixarenes molecules, conformation, hydrogen bonding, and infrared spectra.

Thiacalix[4]arene (TC4A), *p*-*tert*-butylthiacalix[4]arene (*t*-BuTC4A) and *p*-(1-adamantyl)thiacalix[4]arene (1-AdTC4A) IR spectra were studied. Calculated energies and IR spectra of the various conformers (cone, partial cone, 1,2-alternate, and 1,3-alternate) were compared. The cone is the most stable conformation for all studied thiacalix[4]arenes. Theoretical IR spectrum of adamantylthiacalix[4]arene molecule in the form of a cone is consistent with experiment. Classification of bands in the IR spectrum of adamantylthiacalix[4]arene has been implemented. The strength of H-bonding in the thiacalix[4]arenes depends on the type of the substituent. In the conformation of the cone cyclic system of H-bonds are implemented for all the studied thiacalix[4]arenes. Introduction of adamantyl substituents leads to convergence of oxygen atoms in molecules of thiacalix[4]arene and H-bonds are strengthened. Conformation cone of molecules of thiacalix[4]arenes does not change when heated to a temperature of 180ºC and dissolving in a neutral solvent.

NEW DATA ON THE MOLECULAR STRUCTURE OF GIANT FULLERENES C_{100} AND C_{108}

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Theoretical modeling of the electronic structure of fullerene molecules[1,2] of IPR isomer 450 (D_5) of C_{100} and IPR isomer 1771 (D_2) of C_{108} was carrying out. The data about the distribution of single, double and delocalized π-bonds in the fullerene molecules are presented for the first time and structural formulas of these isomers are shown (Fig.). It is revealed that isomer 450 (D_5) of fullerene C_{100} has an open electronic shell; its molecule contains pair of equivalent substructures consisting of condensed phenalenyl-radicals at the poles of the molecule. The isomer 1771 (D_2) of fullerene C_{108} has a closed electronic shell; its molecule resembles a short closed nanotube. The bonds distribution a priori made according to our approach was successfully confirmed by quantum-chemical calculations.

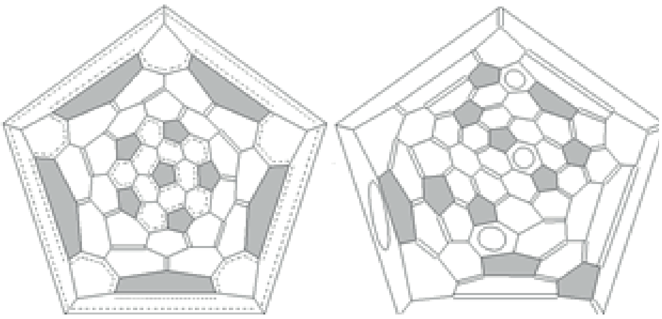

Figure. Schlegel diagrams of the IPR isomer 450 (D_5) of fullerene C_{100} and isomer 1771 (D_2) of the fullerene C_{108}. Single and double bonds are marked respectively. Dotted lines are for radical substructures, and circles are for delocalized bonds in hexagons..

The efficiency of the developed by us approach has been shown in determining the structure of molecules of giant fullerenes.

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INFLUENCE OF FREE STABLE MACRORADICALS ON THE AGGREGATIVE STABILITY OF LATEX SYSTEMS

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On a model latex system (polystyrene and copolymers of styrene with polar monomers acrylonitrile and ethoxyethylacrylate) it is showed that one of the reasons of synthetic latexes aggregative stability loss can be free stable macroradicals accumulated in polymer-monomer particle (PMP) during the polymerization process[1]. These macroradicals decrease protective ability of hydrate adsorption layer of PMP and in case of insufficient adsorption protection lead to aggregative stability loss and gel formation in latex. Further recombination of macroradicals leads to increase of polymer molecular weight and polydispersity[2].

Radical polymerization inhibitors increase aggregative stability of latexes, providing free macroradicals termination. Investigating of macroradicals termination kinetics showed that it has two stages: rapid and slow stabilization of latexes by inhibitors. Studying of latexes by EPR method showed correlation between inhibitor concentration and aggregative stability of latexes.

We assume that influence of macroradicals on aggregative stability of latexes is anionic in nature.

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SYNTHESIS OF BLOCK COPOLYMERS VIA PSEUDOLIVING RADICAL POLYMERISATION OF VINYL ACETATE AND ITS ACTIVITY

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Polyvinylacetate is one of the abundant polymers characterazied by high coating ability and capacity for a work in water or water-organic mixtures1. In this study copolymers of polyvinyl acetate block synthesized via pseudoliving polymerization in the presence of addition fragmentation chain transfer agents(dibenzyltritiocarbonate) with water-soluble monomers (N-vinyl pirrolidone, acrylic acid, acrylamide) have been obtained. Some aspects of application these block copolymers are considered.

The possibility of polyvinyl acetate–*b*–poly-N-vinyl pirrolidone to stabilize silver sols particles in organo-aqueous medium has been shown. This effect ensure the achievement of nano size particles of silver.

Also this copolymer display the inhibiting effect with reference to zinc and zinc-galvanized steel in neutral medium. The tendency to cathodic polarization of zinc and inhibition of dissolving process of zinc oxide coating formed as a result of depolarization has been established in this presence.

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REACTIVITY OF AROMATIC CARBOXYLIC AND SULPHONIC ACIDS HYDRAZIDES AND AMIDES IN SULPHONYLATION

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Amides and hydrazides of aromatic carboxylic and sulfonic acids are widely used in organic synthesis as monomers for polycondensation polymers (in particular, spongy rubber and foams), many of their derivatives exhibit biological activity and are used as medicines and inhibitors of important enzymes.

In the literature, there are practically no kinetic data on the N-acylation of compounds of these classes, which is associated with the thermal instability of aromatic sulfonic acids hydrazides (when heated above 350 K, they decompose with release of nitrogen) and the low amides reactivity, due to the presence of electrophilic centers – carbonyl and sulfonyl near NH_2-group.

Currently, systematic studies of the kinetics of sulfonylation of benzoic and benzenesulfonic acid hydrazides, as well as a number of amides: benzamide, benzenesulfonamide and saccharin are carried out by our group in aqueous-organic media containing 2-propanol, acetonitrile, 1,4-dioxane and THF as the non-aqueous component. It is established that the composition of the solvent has the same effect on all the reactions studied: with an increase in the water part in the system, the acylation rate constant (k) increases by an average of 2–5 times (see table).

Table. Range of change in rate constants of the reaction with 3-NO2C6H4SO2Cl, 298 K

№	Acylated agent	Solvent	*k*, l•mole^{-1}•s^{-1}
1	$C_6H_5CONHNH_2$	water (10-70 mass.%) – 2-propanol	0,140 – 1,530
		water (30-60 mass.%) – 1,4- dioxan	0,061 – 0,251
		water (10-50 mass.%) – THF	0,035 – 0,104
		water (10-50 mass.%) – acetonitrile	0,20 – 0,326
2	$C_6H_5SO_2NHNH_2$	water (20-50 mass.%) – 1,4- dioxan	(4,7 – 11,9)•10^{-3}
3	$C_6H_5CONH_2$	water (20 mass.%) – 1,4-dioxan	3,92•10^{-2}
4	$C_6H_4COSO_2NH$		1,66•10^{-4}
5	$C_6H_5SO_2NH_2$		3,37•10^{-3}

The results of chromato-mass spectrometry investigations suggest that the reaction product № 2 is thermally more stable than the original hydrazide.

INVESTIGATION OF THE ELECTRONIC STRUCTURE AND THE CHEMICAL BONDING FOR SEVERAL $[M^{IV}_2S_4(H_2O)N]_4^+$ TRANSITION METAL CLUSTERS: A DFT STUDY

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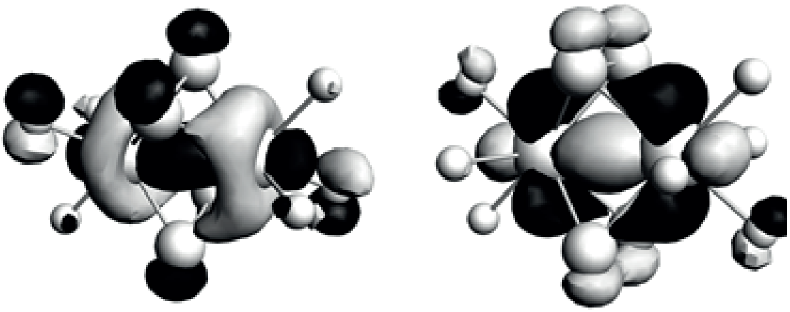
For more than half a century metal–metal bonding hold on interest as one of the central concepts of modern chemistry. Dinuclear complexes with symmetrical central cores are the simplest units that can incorporate metal–metal bonds. They represent the first step in chemical complexity in going from monomers to clusters. For example, the disulfide-bridged clusters of V, Nb, Mo and W containing a $\{M_2(\mu_2\text{-}S_2)_2\}$ unit with a direct M–M bond, supported by two $\mu_2\text{-}S_2^{2-}$ bridges, are long known and rather stable.[1-2] But there are few examples of other transition metals binuclear complexes containing such $\mu_2\text{-}S_2$ bridges. Only one $\{Zr_2(\mu_2\text{-}S_2)_2\}^{4+}$ complex, and several examples of $\{Ru_2(\mu_2\text{-}S)(\mu_2\text{-}S_2)\}$ complexes were described, without M–M bonding.[3]

In order to estimate the electronic structure and possibility of a M–M bond formation (and potential existence) of $\{M_2(\mu_2\text{-}S_2)_2\}$-containing clusters, quantum chemical calculations were performed on a series of model complexes with $\{M_2(\mu_2\text{-}S_2)_2\}^{4+}$ central core (M is 2nd-row transition metal from Zr to Ru, and actinides from Th to Pu). The $[M^{IV}_2S_4(H_2O)_8]^{4+}$ complexes were used as entry model to perform optimization and topological analysis using Bader QTAIM theory with the ADF program.[4] Preliminary results show that only d^1-d^1 pairs (Mo^V_2, Nb^{IV}_2, Pa^V_2) form direct M–M bonding (σ-bond). Further population of the d-level either cancels out the M–M bonding due to filling of the σ* (M–M antibonding orbital) or leads to dissociation of two H_2O ligands.



Molecular orbitals showing σ-bonding in $[Mo_2S_4(H_2O)_6]^{4+}$ (left) and $[Nb_2S_4(H_2O)_8]^{4+}$ (right)

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THE PROBLEM OF "ZERO ELEMENTS" IN THE WORKS OF D.I. MENDELEEV. NEUTRON MATTER AND ITS PLACE IN THE PERIODIC TABLE OF CHEMICAL ELEMENTS

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D.I. Mendeleev was convinced of the existence of elements before hydrogen[1]. Elements before hydrogen inevitably fall into the zero group. “This position of argon analogs in the zero group is a strictly logical consequence of the understanding of the periodic law,” stated D.I. Mendeleev. He allowed the existence of the elements - X (“newtonia”) and Y (“coronia”) before hydrogen in the zero group. It should be recalled that Mendeleev had not been mistaken in his predictions of new elements! It should be noted that after D.I. Mendeleev's question about “zero” elements was repeatedly raised by many authors both in the past and in the present centuries, however, for brevity, we only mention the very first and most famous ones: for example, Ernest Rutherford in 1920 and Andreas von Antropoff in 1926 as a designation for a hypothetical element with atomic number zero, which he placed at the beginning of the periodic table. A. Antropov was the first to suggest the term "neutronium"[2] . Currently, neutron matter, like neutron stars, is a recognized reality in astro- and nuclear physics. Neutron matter from the standpoint of General chemistry can be classified as chemically simple (i.e., cannot be decomposed into simpler chemical means), then inevitably the question arises about the Element corresponding to it and its place in the Periodic System. Based on the logic of the Periodic Law - (sequence number - electric charge) - the sequence number of neutron matter will correspond to zero, which makes us remember and develop the ideas of Dmitry Ivanovich Mendeleev about the zero group and period[3].

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TRANSFORMATIONS OF FUNCTIONALLY SUBSTITUTED 2-(ADAMANTAN-1-IL)OXIRANES

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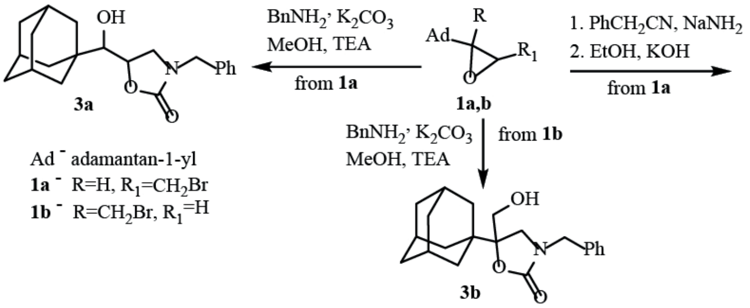
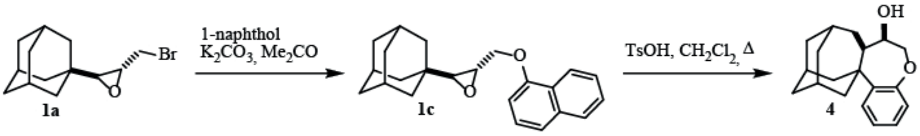
Oxiranes are important intermediates for the synthesis of valuable natural compounds and medicinal substances[1-3]. The introduction of a volume and conformationally rigid adamantane fragment and functional groups into the structure allows to significantly expand the synthetic capabilities of oxirans and to obtain a variety of heterocycles.

The interaction of bromoxirane 1a with phenylacetonitrile in the presence of $NaNH_2$ yields bicyclic lactone 2, and the reaction of 1a, b with benzylamine in the presence of K_2CO_3 and TEA is oxazolidin-2-ones 3a, b.



When heated oxirane1c with TsOH in methylene chloride, the rearrangement product is obtained - naphthooxepin-3-ol of the homoadamantane structure4.



IR, NMR spectroscopy and chromatography-mass spectrometry, confirmed the structure of the compounds obtained.

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A COMPARATIVE STUDY OF LIQUID INTERMEDIATES ARISING IN SYNTHESIS OF Au- AND Pt-BEARING NANOPARTICLES

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Noble metal nanoparticles attract much attention due to various application fields such as catalysis, nanoelectronics, biomedicine etc. Formation of extra-ordinary large-scale (in comparison with the size of classical nuclei) pre-nucleation species has been observed in a range of processes such as crystallization of calcium carbonate, calcium phosphate, silica gel formation, and protein crystallization [1]. Recently, we found a series of long-lived liquid pre-crystallization intermediates to arise in processes of reduction of $HAuCl_4$ and H_2PtCl_6 with trisodium citrate or sodium sulfide in aqueous solutions [2]. Loh et al. has published a paper [3], in which the formation of dense droplets in the course of aqueous gold (III) reduction by citrate has been confirmed using in situ TEM. Due to the relatively slow reaction rates, those reactions emerge as convenient ones for studying (pre-)nucleation stages. In this contribution, based on atomic force microscopy (AFM) in situ, dynamic light scattering (DLS) and small angle x-ray scattering (SAXS) data, we tried to explore and to compare a few different kinds of liquid intermediary structures. In addition, after the deposition onto highly oriented pyrographite the intermediates and products of their evolution were examined by XPS, XANES, EXAFS, HRTEM (along with EDX, SAED) etc.

In case of the Au(III)-Na_2S and Pt(IV)-Na_2S reactions, an accumulation of reduced $Me_mS_n{\cdot}pH_2O$ (Me=Pt or Au) solutes (referred as pre-nucleation clusters) form dense liquid domains of various dimensions, including “liquid clusters” less than about 20 nm, globules about 50 nm and their submicrometer aggregates. Nucleation was suggested to proceed within “dense droplets”, which are large enough to accumulate necessary amount of Me-S substance formed via coalescence of the above fluid species. In comparison with the sulfide-bearing systems, citrate intermediary species, at least in case of Au, consist of metallic “cores” embedded into highly disordered “liquid” matter, which facilitates their coalescence into “dense” globules, which give rise to metal nanoparticles.

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CATALYTIC ARYLATION AND HETEROARYLATION OF ADAMANTANE-CONTAINING AMINES

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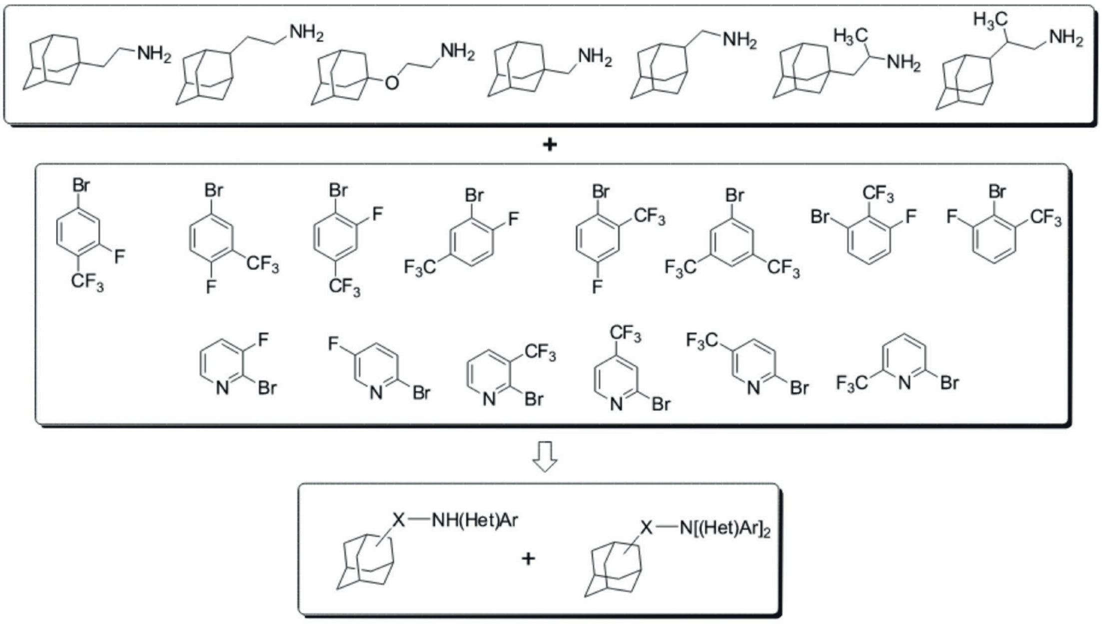
A complex investigation of the Pd(0)-catalyzed arylation and heteroarylation of a series of adamantane-containing amines was conducted using bromosubstituted benzenes and pyridines. Adamantane-containing amines differ by the spatial hindrances at the amino group, bromo(hetero)arenes contain fluorine and CF_3 group at various positions of the aromatic ring. The study of the dependence of the ratio of the products of mono- and di(hetero)arylation on the nature of the phosphine ligand was studied, the influence of the sterical hindrances at the amino group and at the bromine atom on the reaction outcome was shown. The best catalytic system for the amination of the substituted bromobenzenes was found to be Pd(dba)$_2$/BINAP while for the amination of 2-bromopyridine derivatives Pd(dba)$_2$/DavePhos proved to be optimal. The best yields of N-aryl derivatives reached 93%, and those of N-pyridinyl derivatives attained 95%.



The work was financially supported by RFBR, project No 17-03-00888.

LOOKING FOR ALTERNATIVES TO THE SUPERSPACE DESCRIPTION OF ICOSAHEDRAL QUASICRYSTALS

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Discovery of quasicrystals by Shechtman is now counted as one of the milestones in the development of modern crystallography. It led to paradigm shift in our understanding of the nature of chemical structures. Under the term *crystal* we now understand any solid having an essentially discrete diffraction pattern. According to the strict mathematical definition, an aperiodic crystal is a distribution of discrete point masses that has a pure point Fourier transform. The ordinary crystals are periodic distributions with periodic spectra, whereas quasicrystals are self-similar distributions with self-similar spectra.

The structure of quasicrystals is usually described within the superspace formalism by using the cut-and-project construction.[2] We offer an alternative approach based on the Socolar-Steinhardt tiling combined with the quasi-unit cell formalism.[3] Four types of quasi-unit cells fill the space without gaps and overlappings. Every cell in the whole tiling is uniquely decorated by specific atoms and associated with a triad: type, position, and orientation. The key issues of the proposed approach are the subgroup/coset decomposition of the icosahedral symmetry group (stabilizer and orbit), original substitution rules, and recursive inflation/deflation rules for the general space filling algorithm.[4-6] Our method has been proven effective in the field of photonic quasicrystals.[7] The similar approach can be adopted to other types of quasicrystals including those with the 7-fold symmetry.[8,9]

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THERMAL BEHAVIOUR OF THE GLASSES ON THE BASE OF OXYFLUORONIOBATES $MNbOF_5$ (M – CD, MN)

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The glasses based on the oxyfluoroniobates may be both the new functional glass materials and the basis for the transparent oxyfluoride glass ceramics with incorporated crystalline phases. An increase in the size of crystallites already present in glass or an emergence and growth of crystallites of a different structure may take place in the process of the crystallization. In this work we present the synthesis of the glasses on the base $MNbOF_5$ (M – Mn, Cd) with introduction of glassforming component of InF_3 and their thermal study with X-ray analysis (XRD), IR- and Raman spectroscopy, differential scanning calorimetry (DSC). By DSC method the process of the crystallization in the glasses was studied at various temperatures and time exposure. The analysis of the X-ray patterns showed that for the most of the In-containing glasses on the base of $MnNbOF_5$ after one hour exposure at temperatures close to the peaks of crystallization the crystal phases $Ba_3In_2F_{12}$ and $BaNbOF_5$ were formed. As for as of the In-containing glasses on the base of $CdNbOF_5$ at devitrification of the samples at different characteristic temperatures the cubic crystalline phase of the CdF_2 was revealed fist. The further crystalline phases of barium oxyfluoroniobate BaNbOF5 and fluoroindate $Ba_3In_2F_{12}$ were recognized. It should be noted that used by us the IR- and Raman methods were more sensitive to the appearance of the crystalline phases in the glass matrix. While X-ray analysis showed the amorphous state of the sample at the certain temperatures, in the IR-spectra, the position and shape (transition from gentle to narrow peaks) of the bands changed in going from glass to the crystalline state, in the Raman spectra the form and intensity of the “bozon” peak were changed. To obtain the nanocomposite glass-ceramic materials in which the particles of the compounds possessing of the definite properties crystallize, it is necessary to study the processes of glass formation and crystallization taking into account the composition of the charge and varying it with certain glass-forming additives.

Acknowledgments
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ANTIMONY(III) COMPLEX FLUORIDE COMPOUNDS WITH AMINO ACIDS

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A great number of works including those carrying out at the Institute of chemistry are devoted to the coordination chemistry of the fluorous compounds of the non-transition metals. In the framework of the investigations of the structure and properties of the complex fluorides of the metals of groups III-V of the Periodic table carried out at the laboratory of rare metals chemistry we prepared a series of new antimony(III) fluorides with various amino acids (AA) in the crystal state. The main purpose of this work consisted in obtaining new data on the conditions of synthesis of albuminous acids complexes with inorganic components displaying potential activities and on the types of AA coordination in the antimony(III) complexes as well as in study of their properties. We prepared some antimony fluoride coordination compounds with amino acids (glycine, alanine, valine, leucine, serine, and phenylalanine) which can be divides in the three types: molecular complexes, tetrafluoroantimonates(III) with protonates AA cations, and antimony(III) complex fluoride with the structure built of DL- serinium cations and anionic dimeric complexes $[Sb_2F_7]^-$.

The structures of the twelve antimony(III) complex fluorides with AA prepared in result of the present work were determined and the new structural types were revealed. Using the ^1H, ^{19}F NMR method, we investigated stability of the complex fluoroantimonates(III) with AA in aqueous solutions and ion mobility. [1-3]

Use of aqueous solutions of tetrafluoroantimonates(III) with protonated AA cations was shown to be perspective for obtaining metal polycrystal antimony. It was also stated that some these complexes displaied antimicrobe activity in vitro to strains of pathogenic microorganism cultures.

The knowledge obtained makes a certain contribution to the theory of purposeful synthesis of complexes with a desirable composition and structures and may be used for creation of new functional materials including those for medical purpose.

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SYNTHESIS OF HETEROCYCLES BY MODIFICATION OF 2-(2-AMINOVINYL)-BENZOFURAN-5,6-DICARBONITRILES

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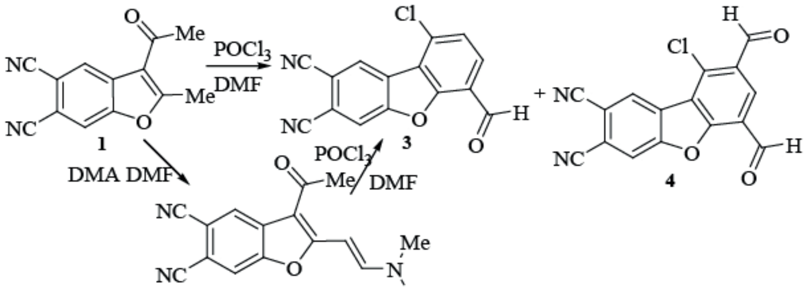
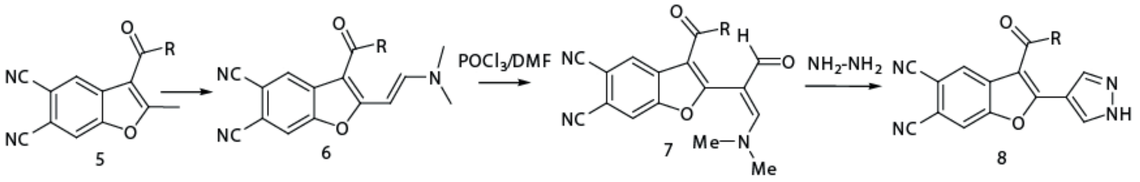
Synthesis of various condensed and annelated benzofurans is a promising line of development of heterocyclic chemistry. Interest in compounds of these series is determined by their diverse pharmacological activity.

We have proved that benzofurans 1 or 2 reacted with Vilsmeier reagent to give a mixture of mono- and diformyldibenzo[*b,d*]furan-2,3-dicarbonitriles 3 and 4, the former prevailing (Scheme 1). The product ratio 3 and 4 depended on the amount of Vilsmeier reagent, temperature, and reaction time[1].



Scheme 1

A new method for the synthesis of 3-substituted 2-(1*H*-pyrazol-4-yl)-benzofuran-5,6-dicarbonitriles 8 was based on condensation of aminovinylbenzofuranes 7, preparation from corresponding benzofurans 5 by two-step method, with hydrazine hydrate in refluxing acetic acid[2] (Scheme 2) .



R = Ar, Het
Scheme 2

The structure of synthesized compounds was confirmed by data IR, NMR, and mass spectra.

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CHIRAL MACROCYCLIC COMPOUNDS COMPRISING ENDOCYCLIC FRAGMENT OF 2,2’-DIAMINO-1,1’-BINAPHTHALENE

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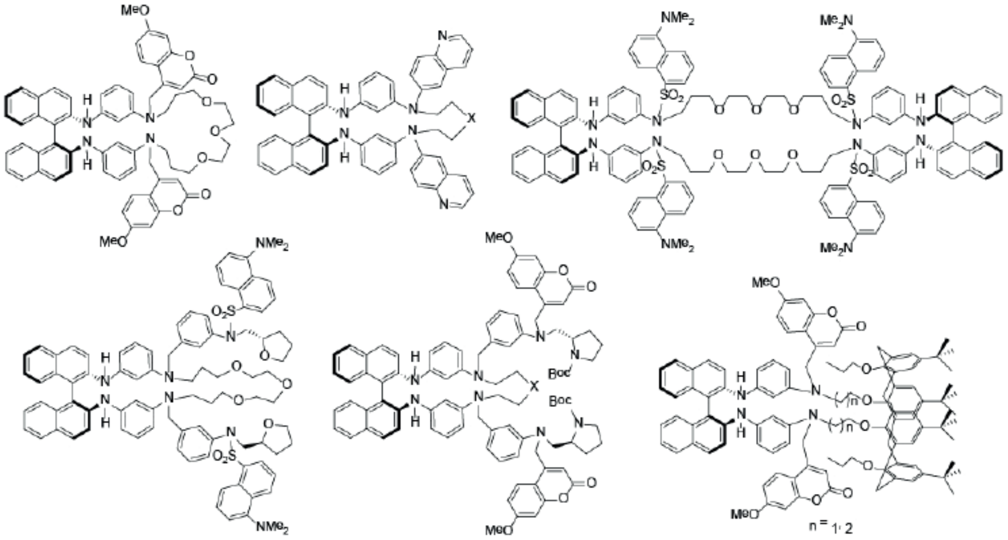
Pd(0)-catalyzed amination was successfully applied to the synthesis of the macrocyclic compounds comprising endocyclic chiral fragment of (S)-2,2’-diamino-1,1’-binaphthalene (BINAM). Macrocycles differ by the nature of the aromatic spacer (phenylene, naphthalene), the length of the polyoxadiamine chain, the presence of the exocyclic fluorophore groups (dansyl, coumarin, quinoline) and additional chiral substituents with nitrogen and oxygen atoms increasing the number of coordination sites of the molecules. Thus synthesized macrocycles were investigated as enantioselective fluorescent detectors of six pairs of chiral amino alcohols, the possibility of the use of selective quenching or enhancement of the emission by one of enantiomers for detection was demonstrated.



The work was financially supported by RFBR, project No 18-03-00709.

P *, P * -BISDIAMIDOPHOSPHITE LIGANDS WITH OXALAMIDE FRAGMENT IN PD- AND RH-CATALIZED TRANSFORMATIONS

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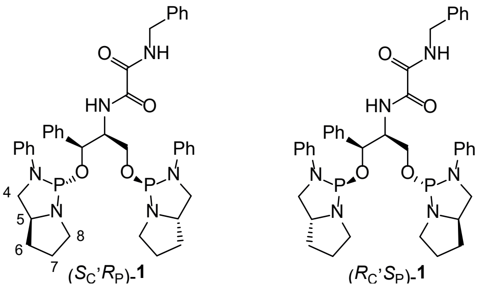
Diastereomeric P*,P*-bisdiamidophosphite ligands with 1,3,2-diazaphopholidine cycles and oxalamide fragment was synthesized.



A possibility of its application in the palladium- and rhodium-catalyzed transformations was demonstrated.

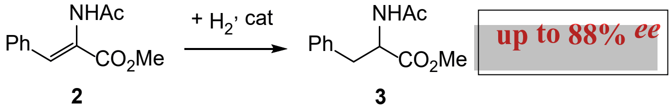


Схема 1. Rh-catalyzed asymmetric hydrogenation of (*Z*)-methyl 2-acetamido-3-phenylacrylate (2).

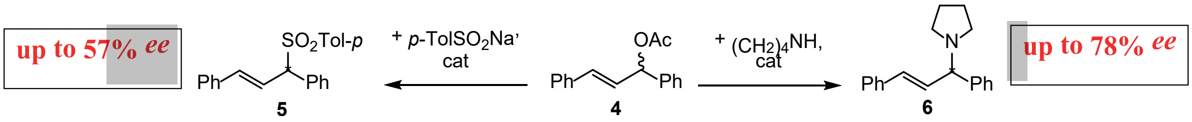


Схема 2. Pd-catalyzed asymmetric allylation of (*E*)-1,3-diphenylallyl acetate (4).

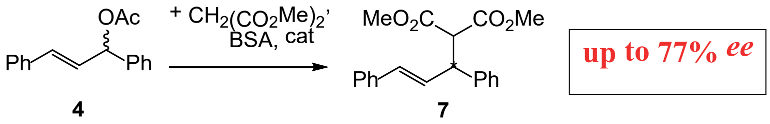


Схема 3. Pd-catalyzed asymmetric alkylation of (*E*)-1,3-diphenylallyl acetate (4).

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MORPHOLOGICAL MEMORY OF DISPERSE SOLID SUBSTANCES AND POLYMERS AND ITS USE IN CREATION OF NEW GENERATION MATERIALS

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Currently, many dispersed systems have been studied in such detail that it became possible to use the results of their study when searching for optimal ways to create new materials. Realization of such a possibility should be facilitated by the fact that dispersed systems have a morphological memory. This is indicated by the ability of particles of many solids and polymers to maintain their morphological properties for a long time, allowing subsequent repeated detection of these changes using optical and electron microscopy without destroying the particles. With this in mind, the foundations of the methodology for using morphological memory when searching for optimal conditions for the production of dispersed substances with multiparameter characterization of particles in accordance with the requirements for new generation materials have been developed. Frequency functions that characterize the relationship between the distribution functions of particles in terms of morphological parameters of a state and molecular motion were introduced. A computer-aided system for extracting information about frequency functions from the morphological memory of dispersed substances has been developed.

Using morphological memory, it was established that the formation of a dispersed substance in a supersaturated solution or a vapor can be multi-stage, ensuring the predominance of the nucleation and growth of primary and microparticles in the first stage, the combination of primary and microparticles into aggregates in the second stage and the formation of clusters of aggregates in the third stage. The acceleration of aggregation by the current of electrons at the second stage and the unification of clusters of aggregates into particles with the desired hierarchical structure at the third stage were found.

NEW PERSPECTIVE ON THE MECHANISM OF OXIDATIVE POLYMERIZATION OF AROMATIC AMINES

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Oxidative polymerization comprises a variety of reactions for synthesis of macromolecules and is characterized by fundamental patterns, which distinguish it among other methods for production of polymers. Generally oxidative polymerization is an autocatalytic process and is sensitive to presence of “inert” substances, while the reaction order with respect to the monomer may vary with changing temperature and monomer concentration. Interpretation of such specific aspects is a matter of debate and is related to study of mechanisms that suggest various nature of active centers1,2.

This paper presents the results of investigation of the kinetics and the mechanism of oxidative polymerization of aromatic amines and pyrroles and demonstrates the potential for understanding many distinctive properties of such reactions through assuming the formation of a complex with the transfer of the charge occurring in the adsorption layer between the monomer and the electron-deficient regions of the growing chains.

The following kinetic equation (1) was developed viewing oxidative polymerization as a heterogeneous process, and its generality for synthesis of polyaniline, polypyrrole and derivatives thereof was demonstrated.

$$-\frac{d[M]}{dt} = W_s + \frac{k([M]_0-[M])[M]}{1+K[M]} \qquad (1)$$

where: [M]_0, [M] are the initial and immediate monomer concentrations; [Ox] is the oxidant concentration; W_s is the rate of one-electron oxidation of the monomer; k is the rate constant of the interaction of the adsorbed monomer with the electron-deficient chain fragments; K is the constant of adsorption equilibrium of the monomer on the surface of the particles.

Special focus was made on the influence of water-soluble polymers’ addition on the rate of oxidative polymerization of aromatic amines; some properties of the forming disperse systems were analyzed, as well as application potential thereof was outlined.

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ONCE MORE ABOUT THE ORIGIN OF CHEMICAL ELEMENTS

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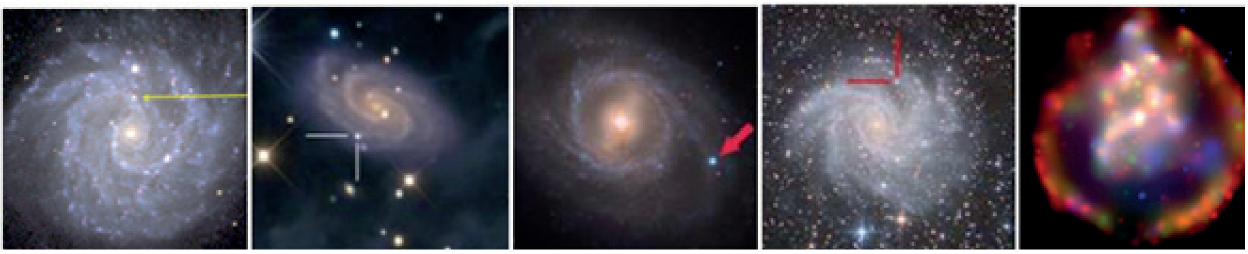
Humanity has been convinced that *”the hydrogen in your body, present in every molecule of water, came from the Big Bang. There are no other appreciable sources of hydrogen in the Universe. The carbon in your body was made by nuclear fusion in the interior of stars, as was the oxygen. Much of the iron in your body was made during supernovas of stars that occurred long ago and far away. ”*[1].

Where do supernovas flare up in spiral galaxies? As seen from (Pic.1a-d), there, where massive stars form, and these areas lie along swirling blue spiral arms. The study of supernovas shows, that after the flash their remnants most often they are rounded, within which the substance discharged by the flash remains (Pic.1e). Therefore, they are not responsible for the appearance of heavy elements in the Universe.



a b c d e

Picture 1. Supernovas: a) in NGC 3184 (14.04.2003)[2]; b) in NGC 981 (13.08.2005)[3]; c) in M95 (22.03.2012)[4]; d) in NGC 6946 (25.05.2017)[5]; e) in SNR 0103-72.6[6]

Since nowhere is it considered, what the swirling arms of galaxies are: what their nature is, what the cause of the supernova explosion is, - this paper is devoted to the consideration of these questions.

As we have noted earlier that outer space is permeated by magnetic flux lines, created by objects of different sizes in the Universe[7]. This makes it possible to assert that chemicals are formed not only in the stars, but also in the small bodies of the Universe – the planets (including the Earth), comets, asteroids by dissipation of a substance from their kernels by excitation by magnetic fluxes, arriving from the space.

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NEW ON THE STRUCTURE OF AN ATOM IN THE PERIODIC SYSTEM OF CHEMICAL ELEMENTS OF D.I.MENDELEEV

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After the discovery of the Periodic law in 1869 D.I. Mendeleev improved his wording two years and finalized it as follows (1871) : *"The properties of the elements, and therefore, the properties of simple and complex bodies formed by them are arranged on periodically depending on their atomic weight."* [1]

With the development of atomic and quantum physics, not knowing what charge was, they gave other definition to the Periodic Law of D.I. Mendeleev: *"Properties of chemical elements and also the forms and properties of simple substances and compounds formed by them are in periodically dependence on the amount of charges of their atoms nuclei."* [2]

Carried by us the fundamental researches of the nature of a charge led to the discovery of vortex dynamics of a substance in an atom, which is responsible for appearance of a charge: – the radiation, extending beyond the outer shell of the atom-vortex[3-4]; which, in turn, depends on degree of its excitation. The analysis of various characteristics of chemical elements is carried out; during that their new fundamental characteristic was open - **the size of the circulation of the velocity of transfer of a substance *(v•r)*** in them, which is responsible for the appearance of the Periods themselves in the Periodic System[3].

The discovery of this value allowed us to understand and to contemplate the genial idea of D.I.Mendeleev, who divided the noble gases into "Zero" group, placed them, even then, at the beginning of the Periodic System. This was reflected in his last edition by life "The Principles of Chemistry" (1906)[1]; although the report about this was notified in his brochure "An Attempt of Chemical Understanding of the World Ether" (1902).

The obtained data point to the need for a review of a modern-day version of the Periodic System, it was essential to put noble gases at the beginning of new periods (Table 2)[3], because **(v•r)** of this group significantly differs from that Period, to which they belong now, and also to consider that *their atomic weight is being as the main characteristic of atoms, what the author of the System thought.*

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NEW ABOUT THE NATURE OF MAGNETISM OF ATOMS OF A SUBSTANCE

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Nuclear magnetic resonance methods by measuring radiation or absorption of electromagnetic energy by a substance have the ability to determine the chemical structure of substances, molecular conformations, effects of mutual influence, intramolecular transformations and much more.

But what is the nature of magnetism, there is still no answer.

In this work it is considered, how the mass itself of a liquid homogeneous rotating self-closing spherical vortex [1,2], creates within itself two fluxes of matter, moving one towards the other in its axial part – a vortex kernel, and being self-closing fluxes of magnetic induction through the cross-section of the kernel. This closure leads to, that the sink of the vortex filament with fluxes of magnetic induction coincides with its source in the kernel of the vortex. Therefore, the Maxwell equation ***Div B = 0***, indicating closed magnetic induction lines, is done.

The fundamental property of closed magnetic induction lines was discovered. Being vortex fluxes, the substance of lines of magnetic induction, returning into atom's kern, brings with it a twisting moment. With this they support not only the rotation of the atom itself, but also contribute to his excitation:

- in an arc or spark by conducting spectral analyzes or in plasma;
- the appearance of radiation (photons) by excitation;
- the appearance of radiation treated as a charge in electrostatics.

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This work was held on personal fund of the authors.

IMPURITIES IN NATURAL DIAMONDS - THE KEY TO DECODING THE APPEARANCE OF CHEMICAL ELEMENTS ON THE EARTH

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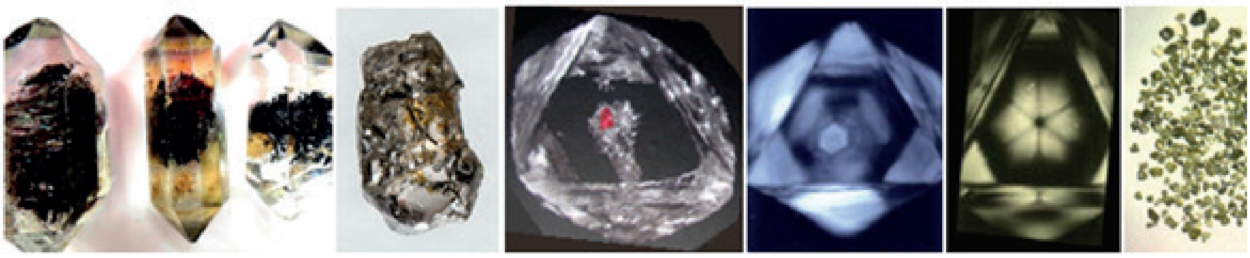
Earlier we pointed out that the cause of the appearance of chemical elements in the Universe is the dissipation of matter discharged by the central kernel of the rotating mass of the vortex object itself when it is excited[1].

Information about the processes in the depths of our planet which are carried by kimberlite diamonds recorded in their volume (Pic.1) all changes in the chemical composition of its crystallization medium during the cooling of the deep plasma fluid, carried them to the Earth's crust [2-5].



a b c d e f

Picture 1. a) oil in diamonds[2]; b) ringvudit in diamond from Brazil[3]; c) inclusion of garnet in diamond, the Arkhangelsk Pipe[4]; d) nitrogen in diamond [photo by V.A.Milyuvene]; e) oxygen in diamond [photo by V.A.Milyuvene]; f) diamonds of the Flat Tolbachik[5].

Analysis shows, that the chemical composition of inclusions and impurities in diamonds: (*) - oil (Pic.1 a); water in ringvudit (Pic.1 b); N – in zones with blue glow (Pic.1 d); O – in zones with yellow-green glow and in diamonds of the volcano Tolbachik (Pic.1 f); (**) - Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni - in minerals - inclusions (Pic.1 b, 1c) in diamonds belonging to different mantle horizons, give the most complete information about the chemical composition of abyssal plasma fluid, enduring growing diamond crystals of diamond and other minerals to the Earth's crust. The presence of hydrocarbons in diamonds – oil (Pic.1a) confirms the theory of inorganic origin of oil promoted by D.I.Mendeleev in 1877.

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This work was held on personal fund of the authors.

MANGANESE AND COPPER POLYFLUORINATED METAL COMPLEXES BASED ON 2,2'-BIPYRIDINES AND 1,2,4-TRIAZINES

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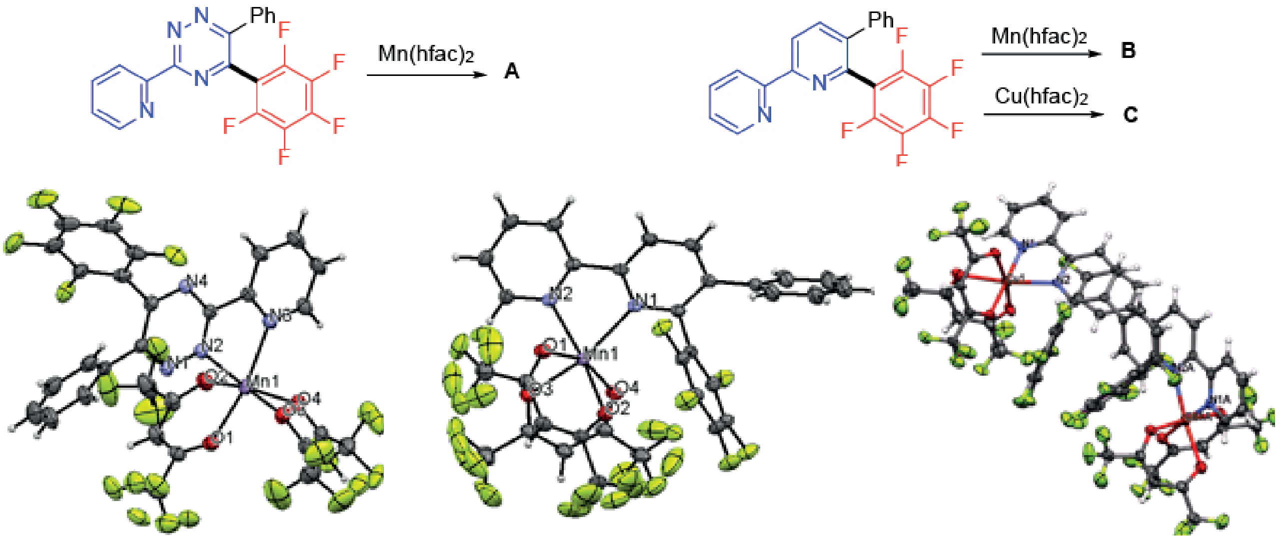
The increased interest in organofluorine heterocyclic compounds in modern organic chemistry is due to the fact that incorporating fluorine atom or fluorine-containing group in organic structure is able to tremendously change physics and chemical properties of target compounds in comparison with the non-fluorine analogs. In this regard, polyfluorinated nitrogen-containing ligand systems based on 2,2'-bipyridines and 1,2,4-triazines are of interest in coordination and supramolecular chemistry. In this project, the complexing ability of synthesized pentafluorophenyl-containing bidentate ligands based on 1,2,4-triazine with manganese (II) hexafluoroacetylacetonate and based on 2,2'-bipyridine with copper (II) hexafluoroacetylacetonate and copper (II) has been studied.



A B C

Scheme 1. Synthesis of manganese and copper complexes based on polyfluorinated 2,2'-bipyridyl and 1,2,4-triazines

Metal complexes of various architectures based on 2,2'-bipyridines and 1,2,4-triazines, which are of interest in the field of coordination and supramolecular chemistry, have been synthetized, their properties have been studied. The structure of the synthesized metal complexes was confirmed by X-ray structural analysis.

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of a research project 18-33-00226.

METHODOLOGY C(SP2)-H FUNCTIONALIZATION IN THE SYNTHESIS PERFLUOROPHENYL SUBSTITUTED 2H-IMIDAZOLES, 1,2,3-TRIAZOLES AND N-OXIDES

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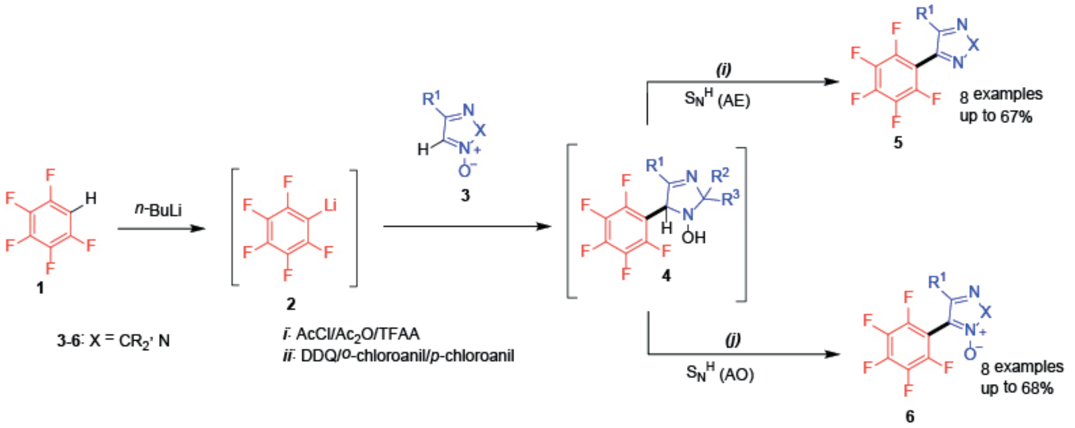
Organic compounds containing one or more fluorine atoms are widely used as promising materials for medicinal and cryochemistry, molecular electronics, and other fields of science and industry. Due to unique properties of fluorine atom, such as high electronegativity and small size of nucleus, incorporation of this atoms in molecules improve bioavailability, physical and photophysical properties of materials.

The development of new and high effective methods for the synthesis azaheterocyclic containing pentafluorophenyl moety, is one of the urgent tasks in modern organic chemistry. Methodology C(sp^2)-H functionalization of 2*H*-imidazoles-1-oxides and 1,2,3-triazoles-1-oxides 3 by the action of perfluorophenyllithium 2 is a powerful synthetic tool for these transformations, because additional catalyst or using protection group are not required.

There are two protocols of accomplishing these reactions. The first one is the addition-elimination S_N^H(AE), which takes place, when a deoxygenating agent was added after the σ^H-adduct was formed in reaction mixture, compounds 5 being obtained. If an oxidant was added instead of a deoxygenating agent, reaction could occur through addition-oxidation mechanism S_N^H(AO) to result in compounds 6.



Scheme 1. C-C coupling of pentaluofophenyllithium with 2*H*-imidazoles-1-oxides and 1,2,3-triazoles-1-oxides

The study was carried out with the financial support of the Russian Science Foundation as part of a research project 18-73-00088.

SYNTHESIS OF AMINOMETHYLATED DERIVATIVES OF FLAVONOIDS

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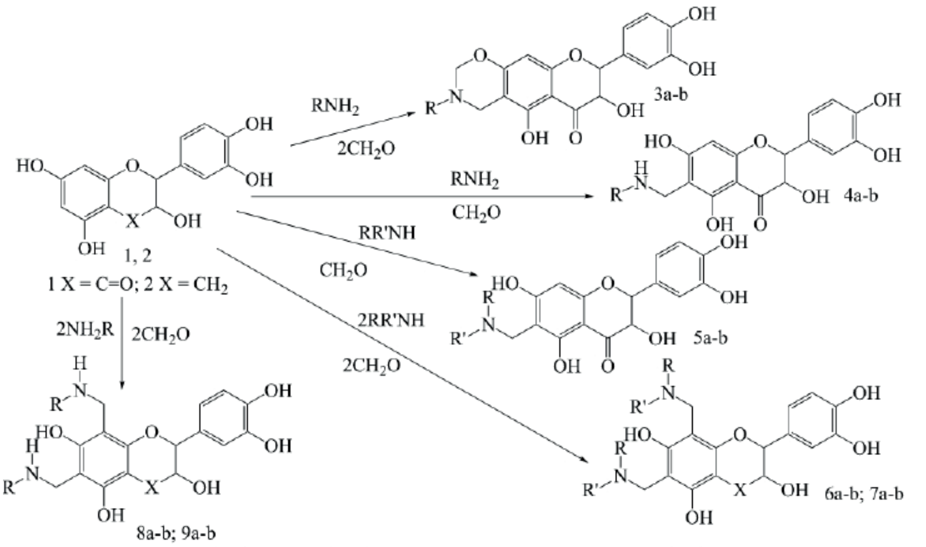
Dihydroquercetin (Taxifolin) (1) readily undergoes the Mannich reaction with formaldehyde and amines of different structure (3a-b, 4a-b, 5a-b, 6a-b). Alkanols of different structure at different concentrations were used as solvents to conduct the reaction.

In contrast to dihydroquercetin, catechol did not react with formaldehyde and secondary amines in alcohols of different structure. When dioxane was used as a solvent, we managed to perform aminomethylation at the molar ratio catechol : formaldehyde : amine = 1 : 2 : 2 (7 a-b).

We accomplished the selective bisaminomethylation of dihydroquercetin and catechin with participation of amino acids (8a-b, 9a-b). The reaction was carried out at the molar ratio flavonoid : formaldehyde : amino acid of 1 : 2 : 2 in aqueous ethanol.



3a, 4a R = t-Bu; 3b, 4b R = $CH_3(CH_2)_4$; 5a, 6a X = C=O, R = R' = sec-Bu; 5b, 6b X= C=O, R = Me, R' = Bn;
7a X = CH_2, R = R' = i-Pr; 7b X = CH_2, R = Me, R' = Bn; 8a X = C=O, R = CH_2COOH;
8b X = C=O, R = $(CH_2)_2COOH$; 9a X = CH_2, R = CH_2COOH; 9b X = CH_2, R = $(CH_2)_2COOH$

This work was performed under financial support of RFBR, project 18-03-00466 A.

DIFFUSION OF SURFACTANT IN AQUEOUS MICELLAR SOLUTIONS

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The interest in the diffusion of surfactants in aqueous micellar solutions is due to the use in both theoretical investigations and the development of technological processes relevant to the transport properties of surfactants.

In a wide range of concentrations have been used to study aqueous micellar solutions of alkyl(triphenylphosphonium and trimetylammonium) bromides, of monoalkyl ethers of polyethylene glycols, (C_8E_4 and $C_{12}E_5$) and of octyl-β-D-glucopyranoside (OBG) by dynamic light scattering[1–3].

A local increase in the diffusion coefficient (D) has been discovered for all ionic surfactants at concentrations higher than the critical micelle concentration (CMC). At the same alkyl chain length and counterion nature, the increase in the D with surfactant content becomes more pronounced with a reduction in CMC. The OBG diffusion coefficient has a general tendency toward a reduction with an increase in the surfactant content in a solution, although this tendency is not as pronounced as it is for C_8E_4 and $C_{12}E_5$.

The concentration dependences of the diffusion coefficients have been explained in terms of a previously proposed theory[5–7] formulated for ideal micellar systems[4]. The methods for introducing initial calculation parameters and the computational scheme for an ideal mixture of monomeric ions and micelles, as well as the correction for a deviation from ideality, varying in solution viscosity and the aggregation number micelles, have been considered. The combined correction widens the range of agreement between the theory and experimental data.

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The study was carried out within the framework of a state assignment

CYCLOADDITION OF AZIDE ION TO HETEROCUMULENES, NITRILES AND TERMINAL ALKYNES IN PRESENCE OF ZINC(II) CHLORIDE

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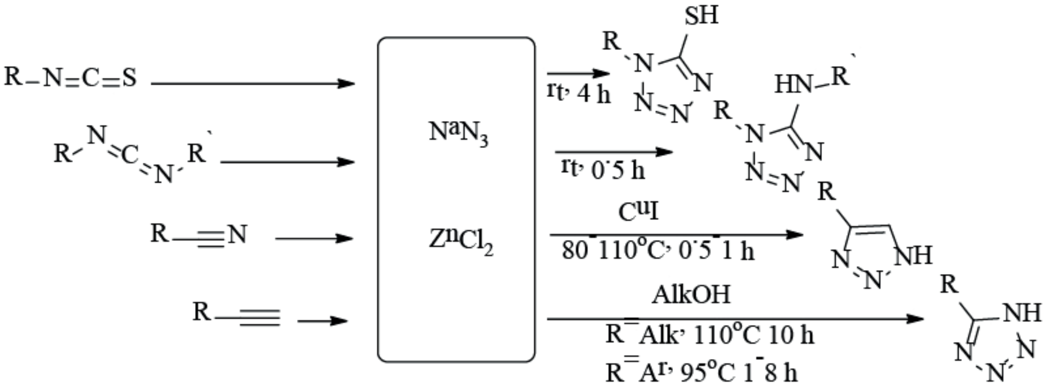
Vicinal polynitrogen-containing aromatic heterocycles have recently become of considerable research interest for their potential application as pharmaceuticals, energetic materials, and for certain other purposes. The primary method for the preparation of this type of compounds is cycloaddition of azide to triple (C≡N, C≡C) or cumulative double (N=C=X; X = NR', O, S) bonds. The synthesis of substituted tetrazoles from nitriles, isothiocyanates, isocyanates, and carbodiimides is the most common among these transformations. In most cases, the cycloaddition requires prolonged heating of unsaturated compound in the presence of an azide source - HN_3, NaN_3, $TMSN_3$, etc. A catalyst is often added to the reaction mixture, while Lewis acids are most commonly used. The topical issues for all mentioned transformations are to reduce the reaction time and temperature, to minimize risk of HN_3 evaluation during the synthesis and to obtain products containing reactive functional groups.

We found that system of NaN3–$ZnCl_2$ in organic solvents is effective for azide ion cycloaddition to heterocumulenes, nitriles[1] and terminal alkynes.



Resented procedures for synthesis of 1,2,3-triazoles from terminal alkynes and tetrazoles from nitriles are one of the most effective today. In the case of heterocumulenes these transformations fall into the category of click reactions.

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PHYSICO-CHEMICAL PROPERTIES OF ALKALI METAL SULPHATES IN AQUEOUS-ALCOHOLIC SOLUTIONS

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It is known that the addition of alcohol (ethanol, isopropanol) to an aqueous solution of lithium, sodium and potassium sulfates reduces the solubility of salts. The study of the properties of aqueous-alcoholic solutions by the method of conductometry showed that, along with solubility, the constant and the degree of electrolytic dissociation of the studied salts decrease as the concentration of alcohol in the solution increases. In solutions with a volume fraction of ethanol of more than 50% and isopropanol of more than 30%, sulfates of lithium, sodium, and potassium exhibit the properties of a weak electrolyte.

The decrease in the degree of electrolytic dissociation of salts in the liquid phase as the addition of alcohols has a significant impact on the structure and size of crystals that precipitate from aqueous-alcoholic solutions. X-ray phase analysis showed that $Li_2SO_4 \cdot H_2O$, $Na_2SO_4 \cdot 10H_2O$ and anhydrous K_2SO_4 salt are separated from aqueous solutions. With aqueous-alcoholic solutions (with an alcohol content of up to 30% by volume) mixtures of crystals in the form of crystalline hydrates and anhydrous salts of Li_2SO_4 and Na_2SO_4 are in equilibrium. With a high alcohol content (more than 50% by volume), only anhydrous salt crystals precipitate from solutions. Crystal optic analysis revealed a violation of the initial morphology of crystals as alcohols were introduced to an aqueous solution of lithium, sodium, and potassium sulfates. Additives of alcohols simultaneously reduce to 600 times the size of the resulting crystals. The observed patterns of phase equilibria in aqueous-alcoholic solutions of lithium, sodium, and potassium sulphates are also confirmed by the IR spectra of the resulting salt crystals.

THE HYDROGENATION OF UNSATURATED HYDROCACBONS IN THREE-PHASE SYSTEM CATALYZED BY IMMOBILYZED TRANSITION METAL NANOPARTICLES

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Unsaturated cyclic hydrocarbons serve as a basis for synthesizing of a number of valuable products of medium and low tonnage organic synthesis. As an example, dicyclopentadiene is a raw material for adamantane synthesis and for production of high-calorie fuel; 1,5-cyclooctadiene is used for suberic acid production; 1,5,9-cyclododecatriene is used for dodecanamide and 1,10-dacanedicarboxylic acid obtaining. The key stage in their production is exhaustive hydrogenation.

The investigation of hydrogenation processes of unsaturated cyclic hydrocarbons in presence of immobilized transition metal nanoparticles (such as: Ni, Co, Cu, Fe) in three-phase system at atmospheric hydrogen pressure was done.

The catalysts were prepared by impregnation of support by water solution of precursor and subsequent reduction of metal of surface of support by sodium borohydride or hydrazine monohydrate. Zeolite NaX, γ-Al_2O_3 and cation-exchange resin Purolite CT-175 were used as supports.

As a result of investigations done was shown, that nickel nanoparticles on γ-Al_2O_3 exhibit the highest catalytic activity is studied processes. This catalyst allows to synthesize products of hydrogenation of corresponding unsaturated cyclic hydrocarbons with up to 100% yields and total conversion of raw materials at 160°C and atmospheric hydrogen pressure. In case of 1,5-cyclooctadiene it also allows to obtain it's semihydrogenation product with selectivity up to 98%.

The investigation was done with financial support of RFBR within of scientific project № 18-33-00183.

SYNTHESIS AND REACTIVITY OF CLOSO-DODECABORATE ANION [B12H12]2- DERIVATIVES WITH EXO-POLYHEDRIC NITRILIUM SUBSTITUENTS

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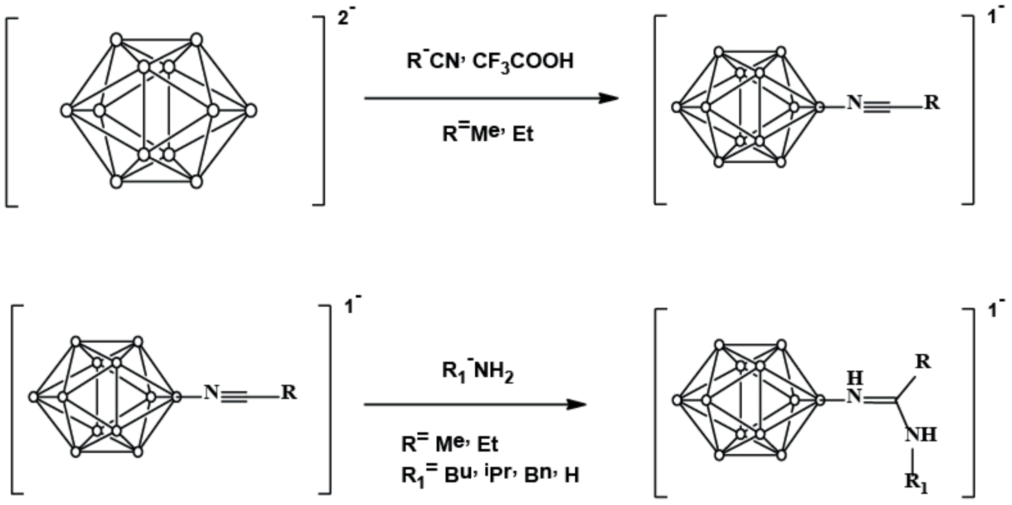
The closo-dodecaborate anion $[B_{12}H_{12}]^{2-}$ is the boron cluster anion, which are of considerable interest for the synthesis on their basis drugs for cancer treatment.

Earlier, it was shown that the modification of nitrilium substituents in $[B_{10}H_{10}]^{2-}$ anion is a convenient method for synthesis of substituted *closo*-borates of various structures, including bioinorganic systems [1-3]. However, such derivatives for the ^{closo}-dodecaborate anion $[B_{12}H_{12}]^{2-}$ are less investigated.

The purpose of this work was the obtaining of nitrilium derivatives of the *closo*-dodecaborate anion and studying of their reactivity under the conditions of the nucleophilic addition process of aliphatic and aromatic amines.



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The work was performed as part of the state assignment of the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences in the field of fundamental scientific research and Grant of the President of the Russian Federation NSh 2845.2018.3.

NEW METHOD OF 4-(2-HYDROXY-1-NAPHTHYL) QUINAZOLINE DERIVATIVES OBTAINING

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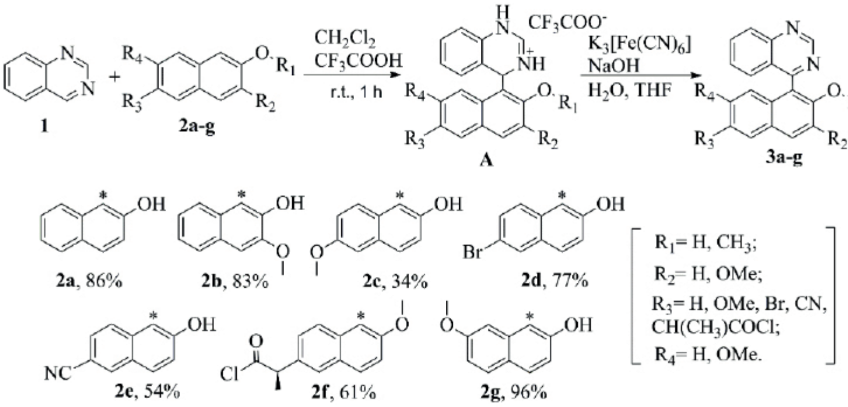
(R) or (S)-4-(2-Diphenylphosphino-1-naphthyl)quinazolines (Quinazolinap) are perspective the axially chiral P,N-ligands successfully used in asymmetric synthesis reactions1.

Here we propose a new approach to the oxidative coupling of quinazoline 1 with 2-hydroxynaphthalene derivatives 2, based on the methodology of nucleophilic aromatic substitution of hydrogen (S_N^H reaction) (Scheme 1). S_N^H reactions can be carried out both by isolating σ^H-adducts A and in one-pot method with similar yields of the target products (34-96%).



Scheme 1. Oxidative coupling of quinazoline with 2-naphthol derivatives

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The research was financially supported by the Russian Foundation for Basic Research (18-33-00927).

COMBINATION OF REVERSIBLE ADDITION-FRAGMENTATION CHAIN-TRANSFER POLYMERIZATION AND CLICK-REACTIONS FOR SYNTHESIS OF POLYMERS WITH DEFINED ARCHITECTURE

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Last year's achievements in the field of chain-transfer radical polymerization allow to obtain macromolecules with defined architecture. Special place among these processes takes reversible addition-fragmentation chain-transfer radical polymerization due to tolerance to monomer's functional groups and soft conditions. This process based on the use of sulfur-containing compounds with general structure Z–C(=S)S–R. If conditions are selected correctly, obtained macromolecules contain α- and ω-end-groups, whose structure is defined by chemical nature of RAFT-agent used (R- and Z-C(=S)S- respectively). The use of RAFT-agents with alkyne and azide R-group, or post-modification of Z-C(=S)S- group to SH or C=C, gives us molecules that can be used as basic units for click-reactions.

The purpose of this work was the synthesis of poly(methyl methacrylate) (PMMA) and polystyrene (PS) via RAFT-polymerization with narrow dispersity and given end-group functionality, the development of dithiocarbonyl group modifications methods and the search for optimal conditions for click-reactions with synthesized polymers.

Using dithiobenzoate and asymmetric thrithiocarbonate monofunctional RAFT-agents with different R-groups PMMA and PS samples with MM up to 104 were synthesized. The conditions of dithiobenzoate and thrithiocarbonate group modification to vinyl C=C (thermolysis), thiol (aminolysis and reduction), cyanoisopropyl (radical substitution) were developed. Various options of click-reactions for synthesis of homo- and block-copolymers were tested.

This research was supported by RFBR (№ 19-03-00900).

THE EFFECT OF ENVIRONMENT AND N-CONTAINING GROUPS ON THE OPTICAL PROPERTIES OF THE DYE BODIPY: EXPERIMENT AND COMPUTER SIMULATION STUDIES

Nevidimov A.V.,[a,b] Gadomska A.V.,[a,b] Nikolenko L.M.,[a,b] Ozivskaya E.V.,[a,c] Razumov V.F.[a,b,c]

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A complex experimental (spectroscopy) and theoretical (quantum chemistry, GAMESS) study of a number of nitrogen-containing dye derivatives of 4-boro-3a,4a-diaza-s-indacene (BODIPY) has been carried out (Fig.1). It was shown that the simultaneous presence of electron-donating and electron-withdrawing groups in the structure of BODIPY molecule makes this molecule extremely sensitive both to the choice of the groups themselves and to the environment [1,2]. For example, in polar solvents complete quenching of the luminescence occurs regardless of the location of the N-groups, while in benzene and toluene, the position of the amino group (R_2) is decisive.

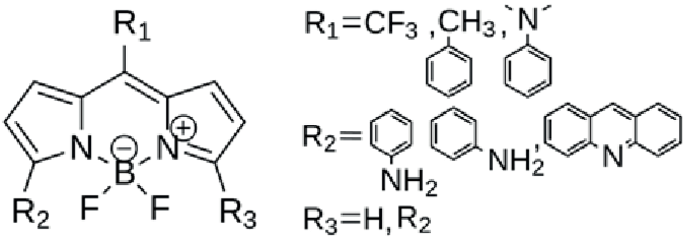

Figure 1. The structures of investigated BODIPY molecules.

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This work was performed under the State Assignment (no. 0089-2019-0003) and supported by the Ministry of Education and Science of the Russian Federation under the Program for Increasing the Competitiveness of the Moscow Institute of Physics and Technology "5–100" among the world's leading research and educational centers for 2016–2020 (no.074-02-2018-286).

NANO-CLUSTERS OF COLLOIDAL QUANTUM DOTS AS A LIGHTING-COLLATING ANTENNAS FOR LUMINESCENT CHEMOSENSORS: A COMPUTER SIMULATION STUDY

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A large-scale computer simulation of the Förster nonradiative transfer of electronic excitation energy in the hybrid nanosystems "Nanocluster of colloidal quantum dots / porphyrin dye" was performed[1,2]. In such systems, a nanocluster acts as a light-collecting antenna, the absorption cross section of which is 2 3 orders of magnitude larger than that of the dye. Due to the migration of electronic excitation to the dye molecule, a multiple increase in the intensity of its luminescence spectrum occurs. This effect can be used to lower the detection limits of both the dye itself and various substances, such as metal cations, which form stable complexes with the dye.

The efficiency of the hybrid system is determined by the ratio of the luminescence spectra of the dye before (I_0) and after (I) the formation of nanoclusters and depends on the cluster size (N is the number of quantum dots) and the probability of excitation transfer (P) from cluster to dye. In this work, the dependences of P on various factors were studied: N, particle size distribution (D), length of protective ligand shell (L), quantum yield of quantum dots (φ), fraction of luminescent particles (ϕ), spatial organization of the cluster.

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This work was performed under the State Assignment (no. 0089-2019-0003) and supported by the Ministry of Education and Science of the Russian Federation under the Program for Increasing the Competitiveness of the Moscow Institute of Physics and Technology "5–100" among the world's leading research and educational centers for 2016–2020 (no.074-02-2018-286).

IBRIDIZATIONS S + P AND ELECTRONEGATIVITY

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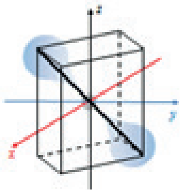
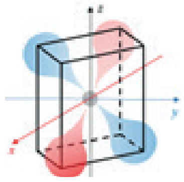
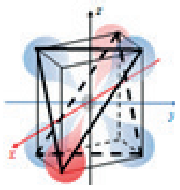
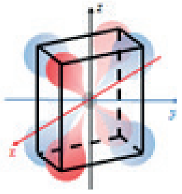
The electrons belonging to energy sublevels s and p of the same energetic level do not coexist separately in blocks but are added together, reaching a maximum of 8 (2 + 6). The quantity of electrons present on the shell s + p and the way in which they are placed in the orbitals creates a variety in the structure of the shell s + p, which requires a distinction based on the quantity of orbitals present, respectively the shell with 1, 2 , 3 or 4 orbitals.

The electrons s + p "occupy" the orbitals that are composed of 2 lobes present on opposite sides of the nucleus, which can be occupied by a single electron and a hole, by two electrons and by two holes. The electron is here represented by a black circle, a hole by an empty circle, as shown in the drawing below.

We propose to measure the electronegativity of the elements belonging to the same period of the periodic table by calculating the ratio between the quantity of electrons and the quantity of lobes and then transforming this ratio into a percentage, calculating as 0 the value of the electronegativity of the shell in which both lobes are occupied.

The ranking of the electronegativity obtained in this way and shown in the table below will be useful in understanding the characteristics of different compounds, for example the difference between atmospheric nitrogen and the nitrogen of the ammonia, different energy degrees of carbon in CO2, in the carbonate group or in methane.

value of electronegativity	shell with 1, 2 , 3 or 4 orbitals			
				
87,5				F
83,3			$\mathrm{N}_{(3\ \mathrm{orbitals})}$	
75,0		$\mathrm{B}_{(2\ \mathrm{orbitals})}$		$\mathrm{O}_{(4\ \mathrm{orbitals})}$
66,6			$\mathrm{C}_{(3\ \mathrm{orbitals})}$	
62,5				$\mathrm{N}_{(4\ \mathrm{orbitals})}$
50,0	$\mathrm{Li}_{(1\ \mathrm{orbitals})}$	$\mathrm{Be}_{(2\ \mathrm{orbitals})}$	$\mathrm{B}_{(3\ \mathrm{orbitals})}$	$\mathrm{C}_{(4\ \mathrm{orbitals})}$
0,0	$\mathrm{Be}_{(1\ \mathrm{orbitals})}$	$\mathrm{C}_{(2\ \mathrm{orbitals})}$	$\mathrm{O}_{(3\ \mathrm{orbitals})}$	$\mathrm{Ne}_{(4\ \mathrm{orbitals})}$

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NEW WAY OF CONCEIVING THE STRUCTURE OF BENZENE

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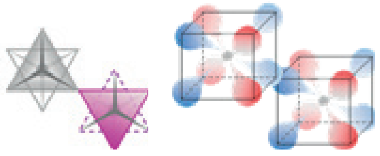
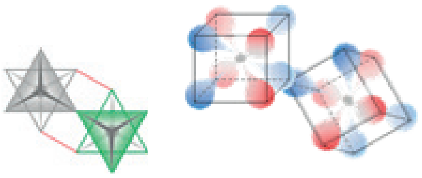
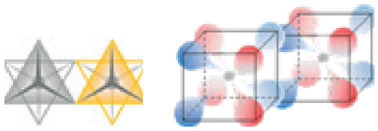
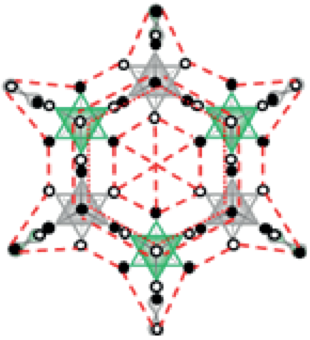
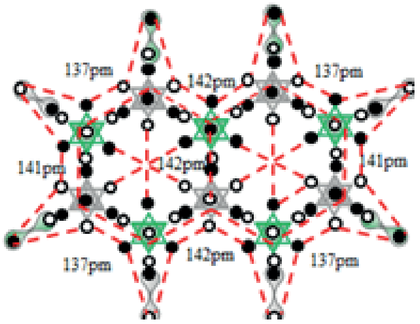
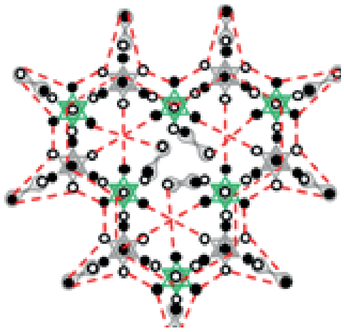
The electrons belonging to energy sublevels s and p of the same energetic level do not coexist separately in blocks but are added together, reaching a maximum of 8 (2 + 6). In the alkanes, alkenes and alkynes the atoms do not change the way of distributing the orbitals around the nucleus but the atoms with 4 orbital s + p of which the vertices form the cube change the reciprocal spatial relations.

alkanes	alkenes	alkynes
		

The electrons s + p "occupy" the orbitals that are composed of 2 lobes present on opposite sides of the nucleus, which can be occupied by a single electron and a hole, by two electrons and by two holes. The electron is here represented by a black circle, a hole by an empty circle, as shown in the drawing below.

This new model of benzene is able to explain different characteristics of this compound and its derivatives, for example the differentiation of spin density of adjacent hydrogens in the ring, differentiation between the activating and deactivating substituents of electrophilic substitutions , degrees of aromaticity of the condensed rings and the annulenes.

benzene	naphthalene	12-aromatic annulene
		

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STUDY OF CHANGES OF CATALYTIC PROPERTIES OF SYSTEMS WITH IMPROVED THERMAL CONDUCTIVITY

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A significant number of chemical catalytic processes occur with a change in the enthalpy of the reaction, leading to the instability of catalysts' performance due to the uneven temperature profile. Therefore, in order to increase activity and stability of the catalysts, it is necessary to provide effective heat transfer in their layer1.

The methanol dehydration (ΔH = 50,1 kJ/mol) was carried out in the flow-type reactor at temperatures 150÷250 ºC and feedstock space velocity 1÷12 h^{-1}. The thermal conductivity of the catalyst was increased by the method of even injection of heat-conductive additive by the volume. The samples treatment in the microwave field was carried out in the current of hydrogen. The analysis of the obtained products was performed using gas chromatography. The physical and chemical properties of the samples of catalytic systems were determined, as well as x-ray phase analysis of them was performed.

The study of the structure and chemical composition of the catalyst showed that microwave treatment more effectively restores the active component compared to other activation methods, as well as increases its dispersion by 20÷22 %. Increasing the thermal conductivity up to 0,7÷1,3 W/(m·K) increases the process selectivity up to 70%, with the maximum yield of methyl formiate reaching 16%, and the performance of the active component increasing up to 1,7 $g_{MF}/(g_{cat\ Cu}\cdot h)$ at 200 ºC and feedstock space velocity 3 h^{-1}. The effect of the microwave radiation power on the thermal conductivity and specific surface area of the systems has been showed.

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THEORETICAL STUDY OF H_2O_2 DECOMPOSITION MECHANISM CATALYZED BY $Au_{25}(SCH_3)_{12}$ GOLD CLUSTER

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The $Au_{25}(SG)_{18}$ gold cluster stabilized by glutathione shell the under the action of H_2O_2 loses 6 glutathione ligands SG.[1] It was established experimentally that various catalytic reactions take place in this system, both decomposition of hydrogen peroxide and oxidation of substrates, the mechanisms of which are not fully established. In this regard, quantum-chemical modeling of the H_2O_2 decomposition reaction was carried out when interacting with the simplest model gold cluster $Au_{25}(SCH_3)_{12}$ in order to establish the nature of the intermediate complexes that could act as active sites in the oxidation of alkanes. When a H_2O_2 molecule interacts with a cluster, its coordination occurs on the Au* atom of one of the six "staples" [-(SCH_3)-Au*-Au-(SCH_3)-] on the cluster surface with a gain of 7.9 kcal/mol. The cleavage O-O bond in the H_2O_2 molecule occurs through a four-cent transition state (Figure 1) with an activation energy of 9.5 kcal/mol. This forms the terminal OH group on the Au* atom and the OH bridge group between the Au* and Au atoms. The transfer of the proton from the bridge to the terminal OH group leads to the formation of an H_2O molecule and a monooxygenated cluster with a μ_2-O atom. Its subsequent reaction with H_2O_2 leads to a cluster with two O atoms which can serve as an active center.

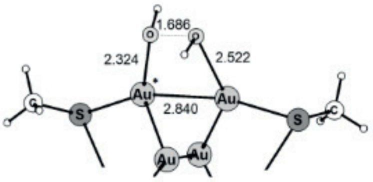

Figure 1. Fragment of the transition state structure

The calculations were performed by the PBE/SBK approach using computational facilities at the Joint Supercomputer Center, Russian Academy of Sciences.

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ELECTRICAL CONDUCTIVITY OF MGO SUSPENSIONS IN MOLTEN TERNARY CARBONATE EUTECTIC

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Molten alkali carbonates thickened with chemically inert oxide materials can be used to improve the performance of carbonate fuel cells. The electrical conductivity of the working electrolyte is one of the most important characteristics of the operation of the fuel cell.

The specific electrical conductivity of composite electrolytes containing nanodispersed MgO powder and molten carbonate eutectic $(Li_2CO_3–Na_2CO_3–K_2CO_3)_{eut}$ were investigated by AC impedance method. The system shows dependence of the electrical conductivity upon the temperature and the MgO content (Fig.1). Empirical equation describing electroconductivity of the $MgO/(Li_2CO_3–Na_2CO_3–K_2CO_3)_{eut}$ system as a function of solid content and temperature was derived on the basis of experimental data:

$\log(\sigma) = 2.138924711 - 9.3895.10^{-5}\varphi(MgO) -1796.79243/T$,

where σ – electroconductivity, S/cm; T – temperature, K; φ(MgO) – MgO concentration, (vol. %). The equation is valid for the MgO content from 0 to 50 vol. % in the temperature range from 680 to 873 K. The multiple regression coefficients for this dependence is 0.99, the average deviation is 1%.

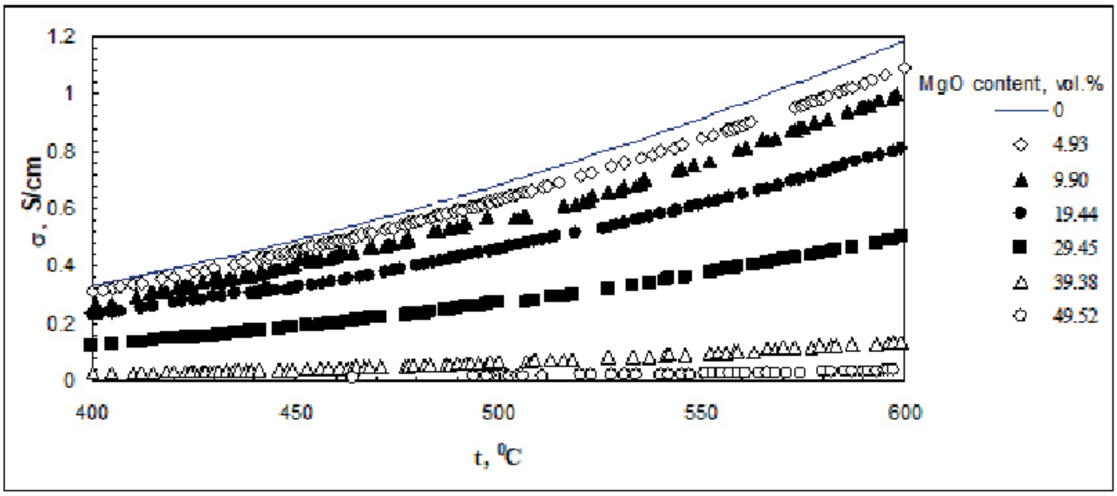

Figure 1. Temperature and composition dependence of the electrical conductivity for $MgO/(Li_2CO_3–Na_2CO_3–K_2CO_3)_{eut}$ system.

ELECTROCONDUCTIVITY OF MOLTEN SYSTEM $GdCl_3$ – KCL – Gd_2O_3

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The dependence of the electrical conductivity of the molten eutectic $GdCl_3$(0.515) – KCl(0.485) on the concentration of gadolinium oxide have been investigated in the temperature range 860 – 960 K.

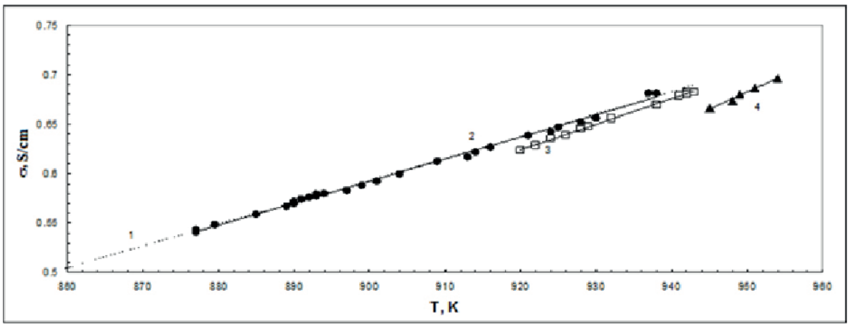

Figure 1. Temperature and composition dependence of electrical conductivity of $GdCl_3$ – KCl – Gd_2O_3 system with Gd_2O_3 concentration: 0 mol. %, (1); 1.02 mol. % (2); 2.00 mol. % (3); 2.83mol. % (4).

Figure 1 shows the temperature dependence of the conductivity of the homogeneous molten $GdCl_3$(0.515) – KCl(0.485) with Gd2O3 additives up to 2.83 mol. %. It is seen that Gd_2O_3 additives lead to a decrease in the conductivity of the system.

Additives up to 1 mol. % gadolinium oxide practically does not change the electrical conductivity at temperatures above 900 K. At 950 K, the electrical conductivity of the homogeneous system decreases by 3 % with the introduction of 2.83 mol. % of Gd_2O_3. The decrease in the electrical conductivity of the system with the introduction of oxide may be associated with the formation of oxychloride complexes in the melt, the stability of which decreases with temperature.

The study was financially supported by the Russian Foundation for Basic Research (project no. 18-03-00561 A).

COMPLEX-FORMATION OF 3D-METALS WITH OPTICAL ISOMERS OF MONOMAMINE COMPLEX OF N- (CARBOXYMETHYL) ASPARAGIC ACID

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The synthesis of optical isomers of the monoamine type of complexones has been carried out by the interaction of chloroacetic acid with optical isomers of aspartic acid[1]. The study of the complexation of Ni^{2+}, Cu^{2+}, Zn^{2+} ions with complexone optical isomers was performed by pH-potentiometric titration. For both isomers, in the range of values up to the pH jump, the neutralization curves in the presence of 3d-metal ions coincide with the neutralization curves of free complexones.

Such a coincidence indicates the absence of complexation processes, and the discrepancy between the titration curves in the region where the pH increases, and the complexon exists mainly as a free ligand, indicates the formation of metal complexonates.

Table 1. Logarithms of stability constants of complexes of 3d-elements with L-КМАК (X) and D-КМАК (Y), t = 25ºC, I = 0,1

Комплекс*	Ni^{2+}	Cu^{2+}	Zn
MeX	10,49±0,03	12,63±0,04	9,09±0,08
MeY	9,96±0,05	11,09±0,02	8,52±0,09
MeX2	16,11±0,2	16,78±0,04	12,34±0,05
MeY2	14,96±0,1	15,44±0,05	11,29±0,06
MeHX	15,09±0,04	16,69±0,02	12,29±0,03
MeHY	13,62±0,03	14,97±0,06	13,64±0,05

* Anion charges omitted

An increase in the stability of the complexes by 1.5–2 orders of magnitude in the L-CMAC compared with the D-CMAC is observed, which is explained by the increase in the dentateness of the compounds studied.

For complexes of both complexons with 3d-metal ions, the change in stability is consistent with a decrease in the atomic radius in the Irving-Williams series Ni^{2+} <Cu^{2+}> Zn^{2+} and is explained by the stabilization of the complexes in the field of nitrogen and oxygen-containing ligands compared to aquions.

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VOLUME PROPERTIES OF IODIDE AMMONIUM SOLUTIONS IN DIMETHYLSULFOXIDE–WATER MIXTURES AT 298.15 K

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The densities (ρ) of solutions of ammonium iodide in dimethylsulfoxide (DMSO)–water mixtures were measured at 298.15 K over the entire range of mixed solvent compositions. The density of solutions was measured on a precision pycnometer with accuracy $1•10^{-5}$ г•см$^{-3}$. The data obtained were used to calculate the apparent molar volumes Φv of ammonium iodide in DMSO−water mixtures. The concentration dependences of the apparent molar volumes are described by the Masson equation.

To determine the standard partial molar volumes of ammonium iodide in DMSO−water mixtures at infinite dilution $(\overline{V_2^0})=\Phi_V^0$, the dependences $\Phi v=f(m^{1/2})$ were approximated by linear regression equations. The values obtained for ammonium iodide in DMSO−water mixtures are listed in Table.

Table. Standard partial molar volumes of ammonium iodide in DMSO−water mixtures at 298,15 К

ХДМСО	0,1	0,3	0,5	0,75	0,9	1,0
$(\overline{V_2^0})$, cm3•mole-1	57,9	60,1	55,7	50,4	48,7	47,6

It is noteworthy that the dependences $(\overline{V_2^0})$ have extrema located in the range of ~0.3 mole fractions of DMSO. This character of curves $(\overline{V_2^0})=f(X_{DMSO})$ indicates that the specific interaction occurring between the components in a binary DMSO –H_2O system and leading to the formation of the most stable associates of the DMSO•$2H_2O$[1] composition also determines the formation of ternary NH_4I – DMSO –H_2O solutions. The presence of the electrolyte does not change the sign of deviations of V from additivity; rather, it lowers the magnitude of these deviations and, the most dramatic drop occurs in mixtures with X_{DMSO} contents 0.3–0.5.

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IONIC MOLECULAR INTERACTIONS IN SOLUTIONS OF CADMIUM HALOGENIDES IN N-METHYLPYRROLIDONE IN THE PRESENCE OF IONS OF ALKALINE METALS AND ALKALINE-EARTH METALS

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The heat capacities (C_p) and densities (ρ) of three-component solutions NaI–CdI_2–N-methylpyrrolidone (NMP), KI–CdI_2–NMP, RbI–CdI_2–NMP, BaI_2–CdI_2–NMP, at 298.15 K are investigated via calorimetry and densimetry.

In our view, the competition between two processes that occur upon mixing binary solutions - the formation of acidocomplexes and the redistribution of the effect ions have on the solvent due to their different solvation capabilities - have the greatest effect on changes in heat capacity and volume (V) in systems with possible complexation. Adding a second electrolyte with the same anion strengthens the formation of acidocomplex and the desolvation of cations.

The processes of desolvation lower the C_p and raise the V of a system[1]. The process of resolvation is in turn typical of systems with great differences between the enthalpies of solvation of ions, accompanied by opposite changes in C_p and V[1].

Based on the experimental data for C_p and V, additivity coefficients δ_C and δ_V were determined. Values $\delta_C < 0$ and $\delta_V > 0$, testifying to the predominance of the formation of acidocomplexes in all of the investigated systems. Even in the solutions NaI–CdI_2–NMP, KI–CdI_2–NMP, and RbI–CdI_2–NMP, where the NMP molecules are also redistributed in favor of the better solvating Cd^{2+} cation and the effect of complexation is largely compensated for, δ_C and δ_V do not change sign, and they remain relatively high in their absolute values.

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DECOMPOSITION OF TERTIARY HYDROPEROXIDES BY METAL COMPLEXES OF CALCIUM METALS

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Supramolecular complexes of crown ethers and alkaline earth metals' halides are widely used in the industrial syntheses and in the interfacial catalysis. Also, they are quite an attractive objects of the study of the hydroperoxide decomposition reactions because of their ability of making the complexes with the organic molecules.

To determine the value of the catalytic activity of the metal compounds of the second subgroup, we made a research of the catalytic decomposition of the tertiary hydroperoxides (the isopropyl benzene and the tertiary butyl) in the presence of the dibenzo-18-crown-6 crown ether complexes (DBC). These complexes contained the calcium chloride ($CaCl_2$), the strontium chloride ($SrCl_2$) and the barium chloride ($BaCl_2$).

The reactions of the tertiary butyl hydroperoxides' (TBHP) decomposition and the isopropyl benzene hydroperoxides' (IPBHP) decomposition have been accelerated with all the studied compounds. The studied catalysts are ordered by the activity as follows: $SrCl_2 \bullet DBC > CaCl_2 \bullet DBC > BaCl_2 \bullet DBC$.

It has been kinetically proven that the TBHP is forming a 3-to-1 proportional intermediate with all the complexes. The IPBHP decomposition forms the complex consisting of the following poroportions: ROOH : Kat = 2:1.

Both of the hydroperoxides have quite a branched structure. However, the presence of a benzene ring in IPBHP, obviously, creates a steric obstacle to the 3-to-1 complex formation.

The decomposition proceeds sequentially: several complexes of different stoichiometry (3ROOH·Kat, 2ROOH·Kat, ROOH·Kat) decompose simultaneously, which leads to the high values of the decomposition rate constants and lowered activation energies. The TBHP's decomposition rate is higher than IPBHP's, because in the first case 3 intermediates of different stoichiometry are getting decomposed simultaneously, and only 2 of them are getting decomposed at the same time in the second case.

The formation of intermediate complexes in the hydroperoxide-catalyst system was confirmed by a quantum-chemical method. The optimized structure was determined, and the stepwise mechanism of intermediate complexes' formation and decomposition was established.

The work was done with the financial support of the Ministry of Education and Science of the Russian Federation as part of the State Mission No. 10.956.2017 (PNIL 25.17).

DMITRY I. MENDELEEV IS THE FOUNDER OF SCIENTIFIC SCHOOL OF CHEMISTRY AND TECHNOLOGY OF ENERGETIC COMPOUNDS AND MATERIALS IN RUSSIA

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In 1891, by the initiative and with the assistance of D.I. Mendeleev, a Navy scientific and technical laboratory (NTL) was created at St. Petersburg University to study the manufacture of smokeless powders for the naval artillery, where he invited S.P. Vukolov. In a short time, Mendeleev and Vukolov carried out systematic studies of the cellulose nitration processes with sulfur-nitric nitrating mixtures to produce high quality nitrocellulose, as well as new energy-rich material (pyrrocollody). This research and development were designed to eliminate the backlog of the Russian military industry.

Picture 1. In the center: S.P. Vukolov, D.I. Mendeleev during the expedition to the Urals (1899).

After 1905, the functions of NTL were significantly expanded and, apart from smokeless powders, S.P. Vukolov began research on a wide range of munitions used in naval artillery. The successor of the Mendeleev – Vukolov scientific school is Professor Lev I. Bagal, who created in the USSR a unique school of chemical technologists who made an invaluable contribution to the Victory in the Great Patriotic War (1941-1945)1.

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REACTIONS OF B-CARBONYL SUBSTITUTED 4H-CHROMENES WITH ELECTRON-RICH AROMATIC AMINES

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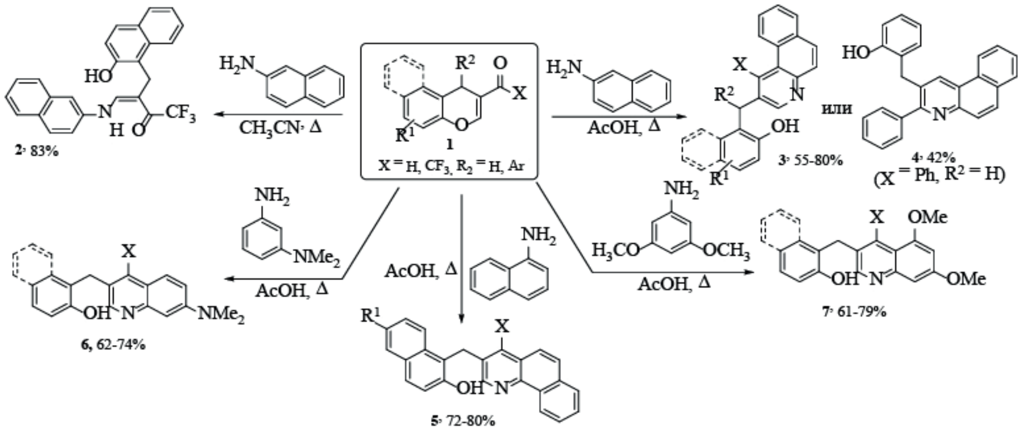
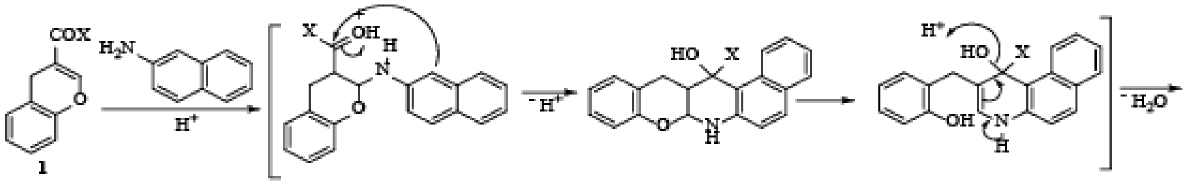
Highly polarized chromenes 1 are promising starting compounds for the synthesis of a wide variety of heterocyclic systems, which is due to the presence of several reaction centers in their structure. When 2-aminonaphthalene reacts with 2-trifluoroacetyl-1H-benzo[f]chromene in acetonitrile, the corresponding enamine 2 is formed. At the same time, carrying out the reaction in boiling acetic acid provides access to benzo[f]quinolines 3. It is interesting to note that 2,3-disubstituted benzoquinoline 4 is formed in the case of 3-benzoyl-4H-chromene. 1-Aminonaphthalene, 3,5-dimethoxyaniline and N,N-dimethyl-m-phenylenediamine have also been successfully introduced into the reaction with 4H-chromenes 1.



According to the mechanism, this transformation is related to the preparation of quinolines according to Doebner-Miller method.



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COMPLEXES OF POLYETHYLENIMINE WITH COPPER, COBALT AND NICKEL IONS AS PRECURSORS FOR PARTICLES SYNTHESIS

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Composite materials based on macromolecules of polymers and nano-sized particles are widely used in catalysis, lubrication systems, in the production of antibacterial drugs, additives to motor oils, etc. The synthesis of metal particles in the presence of macromolecules of polymers is realized in the form of the so-called pseudomatrix synthesis. To obtain particles with narrow size distribution the speed of interaction between particles and macromolecules should be as high as it is possible. In dilute polymer solutions it can be achieved when the formation of the new phase occurs not in the bulk of the solution but inside macromolecular coils. This condition can be fulfilled when at least one of the components of future solid phase is inside macromolecular coils and forms a complex with macromolecular units.

In aqueous solutions, polyethyleneimine macromolecules form stable complexes only with copper and cobalt ions. The composition and dissociation constant of the complex of polyethylenimine with copper ions were determined by potentiometric analysis. The compositions of polyethyleneimine complexes with copper and cobalt ions were determined by a spectrophotometric method of analysis. These methods showed that the complex of polyethyleneimine with nickel ions is not formed. The effect of pH on the stability of polyethyleneimine complexes with copper and cobalt ions was evaluated. It was shown that the complexes dissociate, but the complete decomposition of the complexes does not occur even with a significant excess of acid. Copper and cobalt particles were synthesized in the presence of polyethylene imine (under the conditions of formation of polyethyleneimine – metal ion complexes) and nickel particles (under conditions when the complex with polyethylene imine is not formed) by chemical reduction of the corresponding metal ions. It was shown that only in the case of copper and cobalt were nanoscale particles with a narrow size distribution obtained by transmission electron microscopy.

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SYNTHESIS AND COMPLEXATION OF NEW BENZOAZACROWN ETHERS AND IT DERIVATIVES

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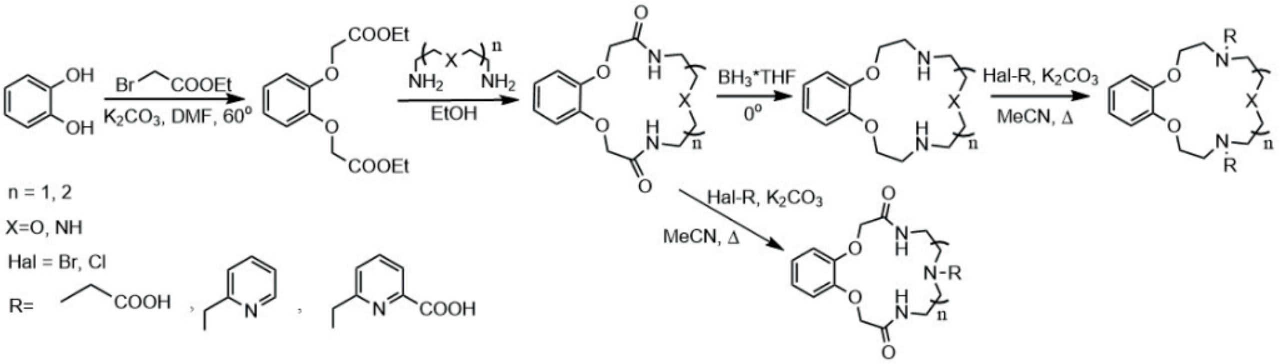
Azacrown compounds are widely used in many fields: as contrast agents for MRI[1] and fluorescent probes[2], components of radio-pharmaceuticals[3], agents for the chelating treatment[4] and chemosensors[5]. This diversity in the practical application of azacrown compounds is due to their ability to dissolve in both organic and aqueous media and also the ability to adjust the properties of ligand by introducing various coordinating groups.

The aim of our work is the synthesis of benzoazacrown ethers with various chelating groups and studying of their complexing properties. By the reaction of N-alkylation various chelating groups are introduced into their structures: carboxyl, pyridine and picolinate.



The structure of the obtained compounds was proved by ^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy and x-ray diffraction of free ligands and their complexes with metal cations.

At the present time a study of the stability of complexes of benzoazacrown compounds with heavy metal cations by potentiometric titration is being carried out. The results will allow to determine the influence of the macrocyclic cavity size and the nature of the chelating groups on the complexing properties of the benzoazacrown ethers obtained.

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HYDROMETALLURGICAL TECHNIQUES IN THE TECHNOLOGY OF COMPLEX PROCESSING OF PYROCHLORE-MONAZITE-GOETHITE ORES

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Complex ore deposits are the most important source of raw materials for the production of many deficient rare metals. Rare-metal raw materials are characterized by a complex chemical and polymineral composition, which determines the use of effective methods of processing with the extraction of all valuable components.

Good example of complex rare-metal raw materials can be the ore of the Chuktukon ore field. The ore layer is characterized by mineral varieties, characterized by significant variations in content Nb_2O_5 (0,18-1,73%), REE (La_2O_3 0,16 - 2,55%; CeO_2 0,34 - 3,33%), manganese oxides (2,92 - 27,12%), iron oxides (31,80 - 68,52%) and ratios of ore and rock-forming minerals.

The autoclave nitric acid technology for ore decomposition is proposed as the ores are practically non-rich due to the high dispersion of minerals, the formation of complex types of coalescence of iron hydroxides with pyrochlore, monazite, thin germination with minerals of the crandallite group. The technology allows selective transfer of REE and Mn in the nitric-acid solution for further extraction and redistribution of obtaining individual rare-earth metals, and the filter cake from the leach to concentrate Nb, Fe and P.

The traditional method of sintering with NaOH followed by water and acid leaching was tested for the processing of leaching cake from nitric acid. However, this technology is multi-stage, energy-consuming, requires the use of large amounts of opening reagent to form a significant amount of man-made waste requiring expensive disposal.

We have conducted research on the extraction of niobium from the cake leaching mixture HF + H_2SO_4. For application of this technological procedure and evaluation of the behavior of niobium in acidic media was tested by solvent extraction Nb of TBF by setting the contact time of the phases, the ratio of the concentrations of HF+H_2SO_4 and the influence of impurity elements such as silicon.

POLYMERS FOR SELECTIVE GAS SEPARATION: «STRUCTURE-PROPERTIES» RELATIONS

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Membrane-forming polymers have a great importance for modern industry, resource-saving and " green " technologies. However, only a few high-molecular compounds have found practical application for effective separation of gas mixtures. First of all, they include silicium- or germanium-containing disubstituted polyacetilenes[1], which thin films are characterized by a large free volume. In recent years, novel polymers suitable for membrane gas separation have been synthesized – substituted poly(norbornenes) and poly(tricyclononenes) (Fig. 1), having high gas permeability and selectivity coefficients in films. They can be obtained by additive (Fig.1) or metathesis synthesis using different types of catalysts and commercially available monomers.[2,3]

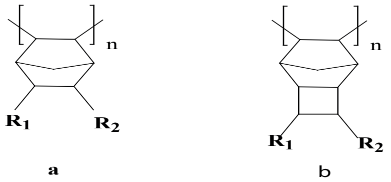

Рис. 1. Monomer units of additive poly(norbornene) (a) and poly(tricyclononene) (b). Side substituents of norbornene: $R_1=R_2=Si(CH_3)_3$; R_1=no, $R_2=Si(CH_3)_3$; R_1=no, R_2= $=CH-CH_3$; R_1=no, R_2= $-CH=CH_2$; side substituents of tricyclononene: $R_1=R_2=Si(CH_3)_3$; R_1=no, $R_2=(Si(CH_3)_3)_2$.

Investigation of molecular properties of poly(norbornenes)/poly(tricyclononenes) in solutions[4,5] and comparative study of their gas transport properties in films[2,3] allowed us to reveal the influence of chemical structure on equilibrium and kinetic rigidity of polymer chains, as well to determine how the synthesis conditions and monomer structure can contribute to targeting of gas permeability of membranes based on these compounds.

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ADAMANTYL DERIVATIVES OF VARIOUS NAPHTHALENEDIOLS

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The naphthalene core exists extensively in natural products and bioactive molecules.[1] A wide application of adamantane derivatives allows to suggest that containing in its structure various naphthalenediols are of definite practical interest.[2]

The interaction of adamantane derivatives with different naphthalenediols (1,2-; 1,3-; 1,4-; 1,5-; 1,6-; 1,7-; 1,8-; 2,3-; 2,6 - and 2.7-) has not been studied systematically before. We have shown that the interaction of 1-adamantanol (1-AdOH) with naphthalenediols in such acid media as CF_3COOH or $CH_3COOH:H_3PO_4$ are convenient method of C-alkylation of these compounds with formation mono- and di-adamantyl substituted derivatives. Moreover, we developed environmentally friendly solvent free and metal catalyst free method (1-AdOH with 1-bromoadamantane (1-AdBr) as an alkylation agent in a sealed tube at 200 ^{0}C) for the preparation of diadamantyl-substituted naphthalenediols.

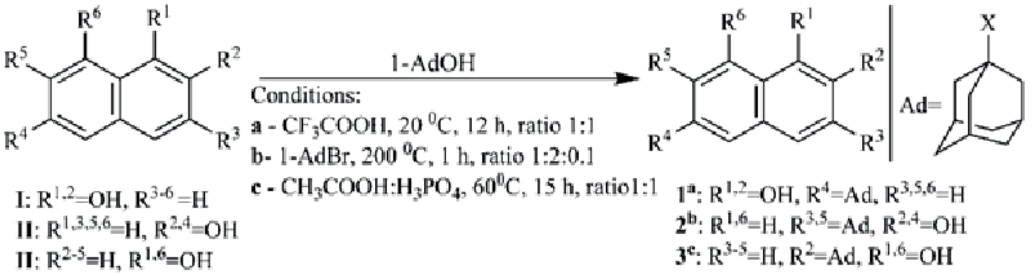

Figure 1. Examples of schemes for synthesis of adamantyl derivatives of naphthalenediols.

Thereby, series of fifteen mono- and di-adamantyl-substituted naphthalenediols were synthesized and characterized by 1D and 2D NMR spectroscopy (Bruker Avance III 600, Krasnoyarsk regional research equipment centre of Siberian branch Russian academy of science).[3]

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LUMINESCENCE AND CHEMOSENSOR PROPERTIES OF EUROPIUM BETA-DIKETONATES

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Intensive stadies in the development of polyfunctional materials with optical chemosensing properties are now being conducted. The need for sensors that control the presence of environmentally harmful vapors of volatile organic compounds is dictated by the need for constant monitoring of the environment.

One of the promising classes of compounds for optical chemosensors are lanthanide-containing complexes with luminescent properties.

Chemosensor optical properties of tris-β-diketonates ($Eu(\beta)_3$•nH_2O) and carboxylate-β-diketonates ($Eu(\beta)_2Acid$•nH_2O) were investigated. Plates for thin-layer chromatography by Sorbfil were used as a matrix for immobilization of compounds. Polymer sensory compositions with different content of luminophors in polyethylene, polymethylmethacrylate and polystyrene were also prepared.

Under the action of ammonia vapors or aliphatic amines on complex compounds, a sharp optical response is observed: a significant increase in the intensity of Eu(III) luminescence. The analyte vapour detection process is completely reversible: after removal of ammonia vapours, the original Eu(III) luminescence is restored [1, 2].

The mechanism of luminescence sensitization consists in bonding of an analyte molecule with a water molecule into the coordination sphere of Eu(III). As a result, the bond of a water molecule with the luminescence centre weakens and the blockage of the quenching of luminescence on OH-vibrations takes place.

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CATALYTIC ACTIVITIES OF NiO-V_2O_5 COMPOSITIONS IN ETHYLBENZENE AND TOLUENE CONVERSIONS

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Using XRD and IR techniques, in combination with the results of thermoanalytical experiments, the processes of phase composition and structure formation of binary NiO-V_2O_5 catalysts, have been studied. The catalysts were prepared by mixing aqueous solutions of ammonium metavanadate (V) and nickel (II) nitrate hexahydrate in various ratios, followed by thermal treatment of evaporated precipitates in air at T ~ 120, 180, 220, 300, 400, 500 and 700^0C for 3-6 h. It has been shown that after thermal treatment at T ≥ 300^0C, the phase composition of NiO-V_2O_5 samples is presented by mostly crystal phases of corresponding metal oxides and/or nickel (II) vanadates [$Ni_2V_2O_6$, $Ni_2V_2O_7$ or $Ni_3V_2O_8$]. The formation of these phases occurred via generating intermediate structures of $(NH_4)_2V_6O_{16}$•H_2O, $(NH_4)_2V_{12}O_{29}$, $Ni_3(NO_3)_2(OH)_4$ and/or $Ni(NO_3)_2$•$4H_2O$ types, depending on the catalyst composition. The structure of nickel (II) orthovanadate, $Ni_3(VO_4)_2$ (or $Ni_3V_2O_8$), is finally formed after thermal treatment of the 75 mol.% NiO-25 mol.% V2O5 sample at only T ~ 700^0C, and its formation is preceded by the appearance of nickel (II) meta- and pyrovanadates ($Ni_2V_2O_6$ and $Ni_2V_2O_7$, respectively).

The catalytic activity of binary NiO-V_2O_5 systems in the reaction of ethylbenzene dehydrogenation (T = 600°C; PHe = 0.1 MPa; τc = 1 s) has been found to be mainly due to the presence of the V_2O_5 phase (i.e., it is associated with vanadium ions); other phases present in NiO-V_2O_5 samples catalyze mainly the cracking and dealkylation reactions of ethylbenzene.

The catalytic activity of NiO-V_2O_5 samples in the hydrodealkylation of toluene is mostly related to nickel (II) meta- and pyrovanadates. Under the reaction conditions chosen (T = 420°C; PH2 = 0.1 MPa; τc = 1 s), pure V_2O_5 and NiO facilitate the development of toluene condensation reactions and heavy hydrocarbons (≥C8) formations, but do not show noticeable activity in the dealkylation of toluene, while NiO, modified with small amounts of V_2O_5 (10-25 mol.%), catalyzes the processes of toluene hydrogenolysis only.

SYNTHESIS OF POLYFUNCTIONAL FURANS BASING ON TRANSFORMATIONS OF 4-FURYL-1,2,3-CHALCOGENODIAZOLES

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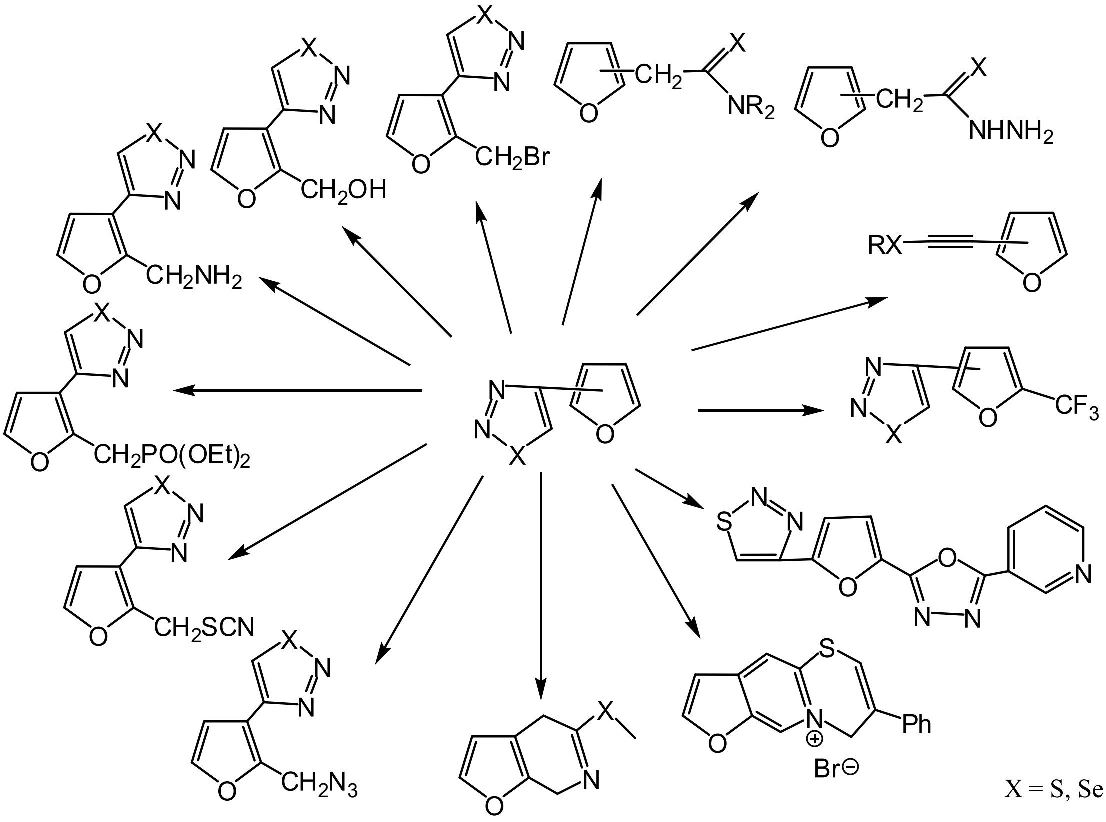
Starting from the derivatives of acetylfuran method of synthesis 4-furyl-1,2,3-thia- and –selenadiazoles, new hybride dipolar bis-heterocycles, is developed. Thermal stability of furylchalcogenodiazoles is provided by presence of electron-accepting substituent such as the ester or amido group in the furan ring. Broad possibilities of obtaining of polyfunctional furan derivatives on the basis of transformation of furylchalcogenodiazoles are shown.



The work was carried out with the financial support of Ministry of science and education of Russia (project № 4.5554.2017/8.9).

SYNTHESIS AND HALOCYCLIZATION OF SUBSTITUTED 6-ALLYLSULFONYLPURINES

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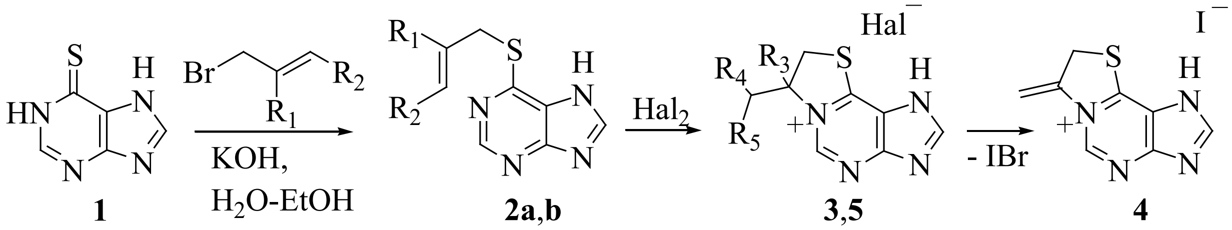
It is well known that purine-6-thione (1) and its condensed derivatives exhibit antitumor activity[1].

We were the first to synthesize 6-(2-bromoprop-2-enyl)sulfanylpurine (2a) and 6-(3-phenylprop-2-enyl)sulfanylpurine (2b) by alkylation of purine 1 with

2,3-dibromopropene and with cinnamyl chloride in aqueous alcohol solution in the presence of potassium hydroxide.



1 **2a,b** **3,5** **4**

2a $R_1 = Br$, $R_2 = H$, **2b** $R_1 = H$, $R_2 = Ph$,
3 Hal = I, $R_3 = Br$, $R_4 = I$, $R_5 = H$, **4** Hal = Br, $R_3 = H$, $R_4 = Br$, $R_5 = Ph$

We have found that the reaction of bromoallylsulfide 2a with iodine in chloroform leads to the formation of 7-methylene-7,8-dihydro[1,3]thiazolo[2,3-i]purinium iodide (4). Iodide 4 is formed from 7-bromo-7-(iodomethyl)-7,8-dihydro[1,3]thiazolo[2,3-i]purinium iodide by elimination of iodine monobromide molecule.

The reaction of cinnamyl sulfide 2b with bromine gives 7-bromo(phenyl)methyl-7,8-dihydro[1,3]thiazolo[2,3-i]purinium bromide (5).

Thus, the iodocyclization of 6-(2-bromoprop-2-enyl)sulfanylpurine and bromocyclization of 6-(3-phenylprop-2-enyl)sulfanylpurine go with the formation of thiazolopurines. Structures of compounds 2a,2b,4,5 have been confirmed confirmed by nuclear magnetic resonance spectroscopy.

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THE INFLUENCE OF HARDNESS SALTS ON THE FORMATION OF GALLSTONES

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It is known that the formation of organomineral aggregates (gallstones, urinary stones, salivary stones) is influenced by consumed water, which contains in its composition hardness salts - slightly soluble calcium and magnesium salts[1]. The formation of gallstones begins when an excess amount of radical particles appears in the body. One of the sources of the appearance of radical particles are hardness salts. In this regard, it is relevant to study the effect of hardness salts on the formation of gallstones.

According to X-ray analysis (XRD), the composition of gallstones is a mixture of phases: cholesterol, bilirubin and calcium carbonate in the form of calcite and vaterite. XRD hardness salts showed the presence of calcium carbonate phases in them of various polymorphic modifications.

Analysis of the electron paramagnetic resonance (EPR) spectra of gallstones revealed the presence of paramagnetic centers characteristic of the high-spin state of iron(III) with nuclear 5/2 spin, copper(II), manganese(II), bio-organic complexes of copper(II) and free radicals. In the EPR spectrum of the pigment part, obtained by separating gallstones into the cholesterol and pigment parts, a sextet related to Mn** was observed. Comparison of the EPR spectra of the pigment part of gallstones with the EPR spectra of hardness salts suggested that the processes of their formation are identical. The EPR spectra of hardness salts contain lines characteristic of iron and copper paramagnetic centers and a sextet line, which corresponds to manganese paramagnetic centers. The appearance in the hardness salts of the paramagnetic center of manganese can be explained by the fact that manganese can easily be incorporated into the crystal lattice of calcium carbonate.

Therefore, the process of formation of gallstones is influenced by the water consumed. The high content of hardness salts in it promotes the appearance of an additional amount of radical particles in the body.

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ON THE PROCESS OF FORMATION OF ORGANOMINERAL AGGREGATES

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Organomineral aggregates are neoplasms in the human body of complex composition, which is associated with the presence of both organic and inorganic compounds. These organomineral aggregates include biliary, urinary, and salivary stones. The reason for the formation of such tumors is associated with various factors, such as diseases of the body, nutrition, the environment, etc.

The data of photon correlation spectroscopy (FCS) for solutions of gallstones in benzene, followed by the addition of n-hexane, make it possible to judge the processes occurring during the formation of organomineral aggregates like gallstones.

Gallstones were dissolved in benzene in ratios from 1: 10 to 1: 50, thus the colloidal system was obtained. According to FCS data, the investigated systems showed a decrease in particle size from 1950 to 250 nm with an increase in the solvent fraction.

A colloid particle is an associate whose center is a particle with an unpaired electron, around which spin-compensated molecules are present that are present in this solution. With a small amount of solvent, colloidal particles are at small distances from each other, which leads to their merging into a larger unit, which precipitates. With a larger amount of solvent, the agglomeration of the particles occurs either very slowly or does not occur at all, since the distance between the particles increases, and the interaction energy between them decreases.

Adding 0.1 ml of n-hexane to such a system results in the aggregation of particles of the "gallstone-benzene" colloidal system. So in colloid systems "gallstone - benzene" with a small amount of benzene (1: 10, 1: 20, 1: 30) with the addition of n-hexane, the average size of the associates reaches ~ 600 nm, and in those systems where the benzene content is 1 : 40 and 1: 50 the size of the associates is ~ 250 nm. This behavior is due to an increase in the frequency of collisions between particles, due to both spatial difficulties and the introduction of a different nature into the system.

THEORETICAL PREDICTION OF THE ACIDITY OF DIALKYLPHOSPHITES COORDINATED WITH A CHROMIUM ATOM

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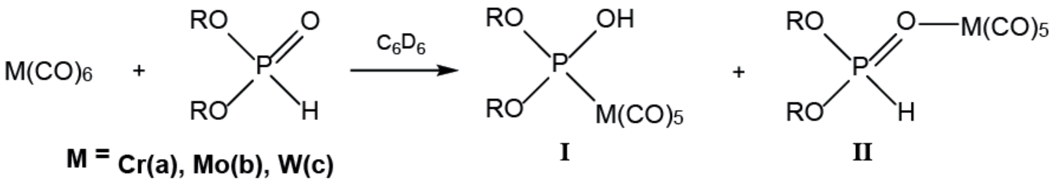
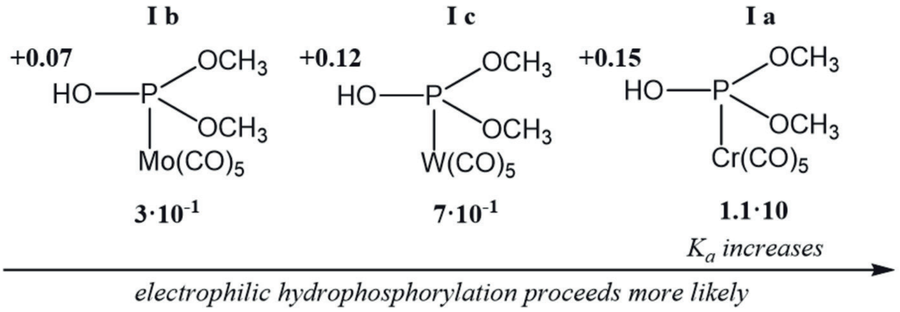
Previously we have found that the interaction of dimethylphosphite with the chromium group metals' hexacarbonyls leads to the formation of complexes having been coordinated with the hydroxy-tautomeric form of phosphite. The form mentioned possesses the significant acidity of the PO–H moiety[1].



To optimize the existing and develop new catalytic processes, it is necessary to study the structure of the active intermediates of the catalytic reaction and the conditions controlling their formation. Therefore, it was decided to conduct a theoretical study of the interaction of H-phosphonates with the chromium group metals' hexacarbonyls. We have estimated the effective positive charge of the P-OH hydrogen atom in compounds notes as I via quantum-chemical modeling using the density functional method (B3LYP / LANL2DZ). We also has conducted a quantum chemical determination of the static and dynamic acidity of model compounds with chromium.



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CATALYZED ADDITION OF HYDROPHOSPHORYL COMPOUNDS TO ALKENES

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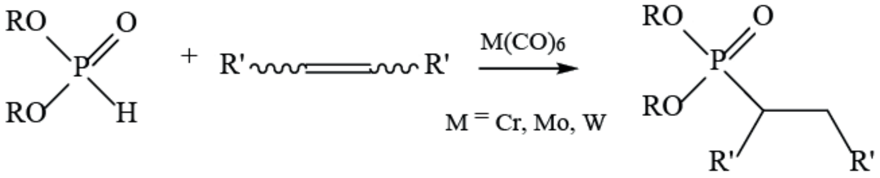
In the twentieth century, a number of methods were developed for the synthesis of organophosphorus compounds. They include Arbuzov, Abramov, Kabachnik-Fields, and Pudovik reactions. However, metal-catalyzed reactions outperform most of conventional methods in efficiency and selectivity. Application of homogeneous metal complex catalysis for the formation of carbon-phosphorus bonds in the hydrophosphorylation of unsaturated compounds that are inert classic Pudovik reaction seems to be a convenient synthetic method for the formation of P-C bonds.

This report considers the results of our study of the catalyzed via hexacarbonyl complexes of the chromium group metals ($Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$) interactions of inert unsaturated substrates, such as 1,2-dichloroethylene and 1,1,2,2-tetrachloroethylene, with hydrophosphoryl compounds –dimethyl-H-phosphonate and dodecyl-H-phosphonate.



The interaction of organophosphorus compounds and olefins was carried out in reaction mixtures comprising equimolar amounts of these reagents and also containing 10 mol. % of $M(CO)_6$. All components were dissolved in benzene. The resulting reaction mixtures were refluxed in sealed ampoules for 5 hours, and then were studied via ^1H, $^{13}C\{1H\}$ и $^{31}P\{1H\}$ NMR spectroscopy.

The products of the catalytic reactions are corresponding phosphonates. The highest yields are observed in the reaction of 1,2-dichlorethylene with dodecyl-H-phosphonate when $Mo(CO)_6$ is used as a catalyst.

This work was supported by Russian Foundation for Basic Research, project 18-33-00445.

MECHANOHROMISM OF Β-DIKETONATES AND Β-KETOIMINATS OF BORON DIFLUORIDE

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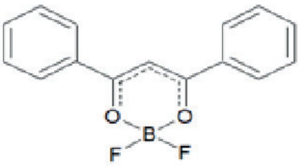
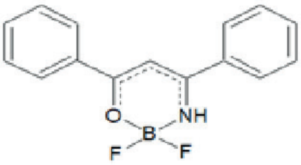
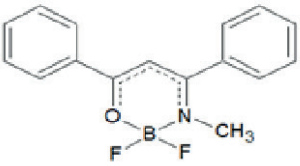
Due to intense luminescence in the crystalline state in the VIS and IR region, thermo- and mechanochromism, ability to aggregation and crystallization-induced emission, β-diketonates and β-ketoiminates of boron difluoride represent a promising class of solid-state fluorophores for smart materials1-3.

The ability of thermo- and mechanohromism were revealed for dibenzoylmethanate of boron difluoride and for its ketoiminate derivatives with hydrogen and methyl substituents at the nitrogen atom.







The hypochromic shift of the J-aggregate band in the excitation spectrum was observed for grinding methyl-substituted β-ketoiminate, in addition monomer excitation band appears, which almost disappears when heated. A similar change in the luminescent properties is observed for other compounds under mechanical pressure and heating. From the data of stationary and time-resolved spectroscopy we concluded that the observed effects are due to dissociation and the formation of J-aggregates.

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PHOTOCHROMISM OF THE (NITROARYLMETHYL)BENZAZOLES

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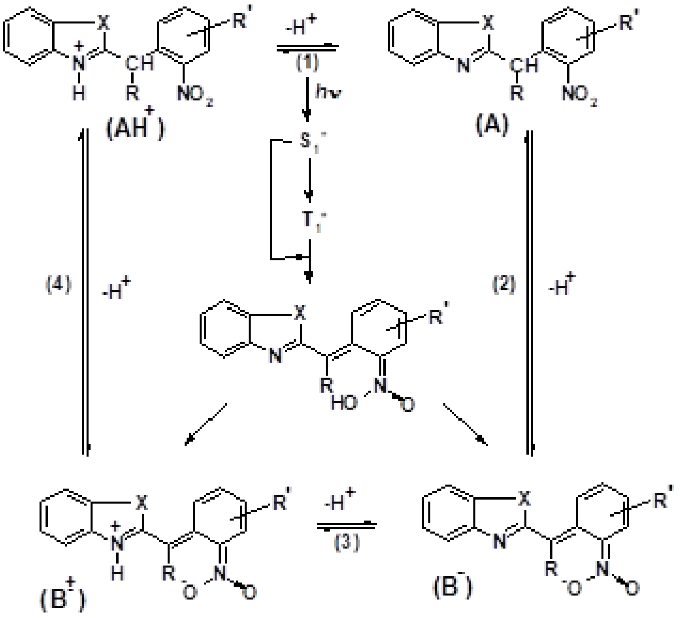
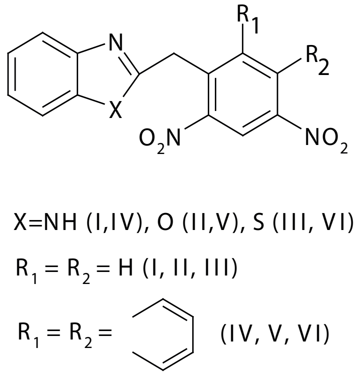
The photochromism of o-nitrotoluenes is caused to the formation of colored aci-nitroacids and/or their anions. The replacement of one of the hydrogen atoms of the methyl group of nitrotoluene by a basic heterocycle capable of accepting a proton leads to the formation of colored azamerocyanines ($B^{\pm}$).





X=NH (I,IV), O (II,V), S (III, VI)

$R_1 = R_2 =$ H (I, II, III)

$R_1 = R_2 =$ (IV, V, VI)

In the series of dinitrobenzyl (I, II, III) and dinitronaphthylmethyl (IV, V, VI) benzimidazole derivatives (I, IV), benzoxazole (II, V) and benzothiazole (III, VI), the dependence of photocoloring intensity on the basicity heterocycle in polar (ethanol) and non-polar (hexane) solvents has been studied. A measure of the intensity of photocoloring in the series of the studied compounds was chosen as the integral value of the optical absorption $S=\int D d\nu$ (D is the optical density, ν is the wave number, cm^{-1}) of photo-colored forms in the frequency range from 27000 to 15300 cm^{-1}. It has been established that with an increase in the basicity of heterocycle, the quantum yield of photocoloration compounds (I-VI) increases in both polar and non-polar solvents. This conclusion allows to conduct a targeted search for the most promising photochromes.

The work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (4.4697.2017/6.7) and the Russian Foundation for Basic Research (grant 19-08-01232).

FORMATION KINETICS STUDY OF CHROMIUM(III)-HEDP COMPLEXES

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The study of various aspects of the kinetics and the formation of chromium(III) complexes in solutions is an important task as it allows to clarify the features of coordination compounds of this metal and the new possibilities for their practical application[1-4].

The kinetics of the complexation of chromium (III) with 1-hydroxyethane-1,1-diphosphonic acid (HEDP) in solutions was studied by a spectrophotometric method. Component concentrations, as well as pH, ionic strength and temperature of the solutions varied. It was found that the complexation process was a first-order reaction with a rate constant $7.78 \bullet 10^{-7}$ s^{-1} and the limiting stage of complex formation was the transformation of an ionic pair of hexa-aqua-chrome(III) with protonated ligand anions into the inner-sphere complex. The associative mechanism of the complexation reaction was confirmed by the low value of the activation energy of the reaction: 125±6 kJ/mol. A decrease in the chelation rate was observed with an increase in the ionic strength of the solution. An increase in the pH of the solutions in the optimal for chelation of chromium (III) ions range from 1.5 to 4.5 provided an increase in the reaction rate due to the combination of simultaneously occurring deprotonation reactions of aqua-complexes of chromium(III) and protonated anions of the complexing agent. It was found that the equilibrium mixture of complexes $[CrH_4L]^{2+}$, $[CrH_3L]^{+}$ and $[CrH_2L]^{0}$ formed in solutions with the pH range 1.5-4.5. The corresponding logarithms of the stability constants were 1.83±0.06, 2.83±0.09 and 7.14±0.35 respectively and were in good agreement with the previously obtained data[5].

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MIXED LIGAND NITRILOTRIACETATE COMPLEXES OF NICKEL(II) AND COPPER(II) WITH POLYAMINES

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The increased interest in mixed ligand complexing in multicomponent solutions is due to the need to improve the composition of technological solutions with desired properties and performance characteristics, as well as the possibility of obtaining biologically active compounds[1,2].

A detailed study of the formation of mixed ligand complexes in ternary systems containing nickel(II) or copper(II) cations, nitrilotriacetic acid and polyamine ligand (ethylenediamine, diethylenetriamine or triethylenetetramine) was performed by spectrophotometric method. A set of factors contributing to the formation of mixed-ligand complexes of the metals with the composition $[ML_1L_2]$ (M = Ni(II), Cu(II); L_1 = nitrilotriacetic acid; L_2 = polyamine ligand) in multicomponent aqueous solutions was studied. It was found that all mixed ligand complexes were characterized by preferential polydentate chelating coordination of polyamine ligand with the addition of the coordination sphere of the central atom by nitrogen and oxygen atoms of the amino carboxylate ligand.

Under conditions of equimolar content of components in aqueous solutions, in the system Cu(II) - nitrilotriacetic acid - triethylenetetraamine the polyamine ligand was characterized by the maximum discriminating effect and lack of coordination of the amino carboxylate complexing agent. The data on the thermodynamic stability of the compounds studied were obtained. It was found that an increase in the denticity of the polyamine ligand while maintaining the number of chelate metallocycles in the coordination polyhedron provides an increase in the values of the stability constants of the resulting complexes.

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CHEMICAL BOND IN BI-INTERCALATED $TiSe_2$

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Intercalated compounds of titanium dichalcogenides TiX_2 intercalated with alkaline, noble and transition metals in the thermodynamic sense are solid solutions with a limited region of stability. When going beyond this region, decomposition occurs with the release of intercalated metals or their compounds (depending on the conditions of the decomposition reaction). In this case, due to the high anisotropy of the diffusion coefficient (the D||/D⊥ ratio, where $D_{\|}$ и D⊥ - the difference of diffusion coefficients along and across the lattice layer TiX_2, is at least 10^5 [1]) decay products are encapsulated in the interlayer space of the TiX2 lattice. This opens up the possibility of obtaining nano-scale composites with attractive functional properties.

In present work we are investigate chemical bond and charge transfer in bi-intercalated system $Cu_xNi_yTiSe_2$. Investigations were performed by classical X-ray methodic: XPS (X-ray photoelectron spectroscopy), XAS (X-ray absorption spectroscopy), ResPES (resonance photoelectron spectroscopy). All measurements were performed on BACH beamline at ELETTRA synchrotron.

It was established, that main contribution in change of chemical bond between $TiSe_2$ hast lattice and intercalated atoms are introduce the Ni atoms, whereas Cu atoms act as electron donor and not interact with other atoms directly.

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The results were obtained within the state assignment of Minobrnauki of Russia (theme "Spin" No. AAAA-A18-118020290104-2). This work was supported in part by RFBR grant 18-32-20141.

STUDYING OF THE CuxZrSe$_2$ COMPOUND BY THE OCV METHOD OF ELECTROCHEMICAL CELL

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The crystal structure of the layered transition metal dichalcogenides makes it possible to consider them as a two-dimensional object. It is a sequence of Se-Zr-Se layers. Among themselves, such layers are separated by a gap and are connected by a weak bond of the Van der Waals type. Copper intercalation was performed at room temperature by solid-phase synthesis using metal dispersed copper and previously prepared ZrSe2 powder. Diffractograms were taken on a Shimadzu XRD 7000 Maxima diffractometer. Diffractograms of CuxZrSe2 in the whole investigated range of copper contents ($0.05 \leq x \leq 0.3$) are indexed in the group P-3m1, the trigonal syngony. In the range of $0 < x \leq 0.2$ with an increase in x, copper atoms partially transfer from tetrahedral to octahedral positions. At $x \geq 0.2$, the filling of tetrahedral positions with copper atoms increases, and the octa- positions are empty.

The OCV method has proven itself quite well when studying layered intercalate compounds. The high sensitivity of the OCV method will provide information on phase equilibria in intercalates systems. From the results of OCV measurements, it can be seen that the region in the range $0 < x < 0.2$ corresponds to a monotonic increase in the Fermi level in the CuxZrSe2 phase, which agrees well with the literature data1. It is also seen here that a monotonous decrease in the OCV also corresponds to an increase in the parameter C

References:
1. Band Gap Width Control by Cu Intercalation Into ZrSe2 / A.S.Shkvarin, A.I.Merentsov, Yu.M.Yarmoshenko et al // Journal of Physical Chemistry C. — 2019. — V. 123. — P. 410—416.

The research was performed within the state assignment of FASO of Russia "Spin" No. AAAA-A18-118020290104-2.

REACTION OF AMIDOXIMES WITH 7-OXABICYCLO [2.2.1] HEPTENE-EXO-2,3-DICARBOXYLIC ACID ANHYDRIDE

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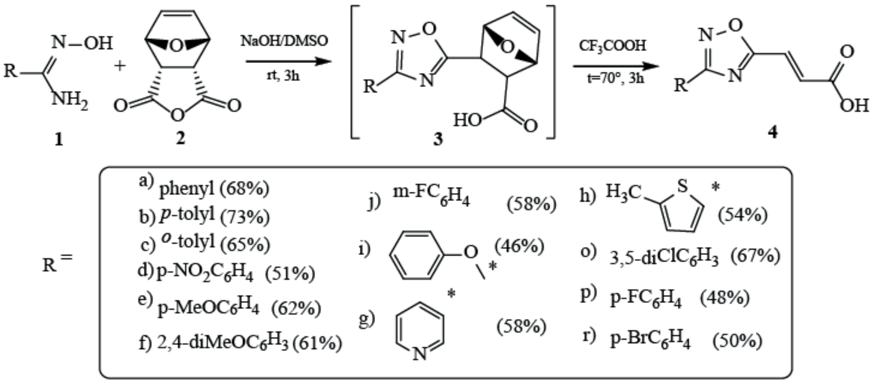
During of our earlier work1, the reaction of amidoximes with 7-oxabicyclo [2.2.1] heptene-exo-2,3-dicarboxylic acid anhydride in a supebasic NaOH/DMSO medium was investigated.



It was shown that in the absence of superbasic activation, the reaction of amidoxime 1 with anhydride 2 doesn't occur. At the same time, the reaction of the amidoxime anion in DMSO initially leads to the acid (3). It was found that when reaction mass work up with hydrochloric acid, 3 undergo a partial transformation to previously newly trans-acrylic acids containing the 1,2,4-oxadiazole ring (4) due to the retro-Diels-Alder reaction with furan cleavage.

It has been established that the heating of acids 3 in the presence of sulfuric and trifluoroacetic acid catalyzes the retro-Diels-Alder reaction and leads to the complete conversion of the starting acids 3 to compounds 4 with 48-73% yields.

Compounds 4a-r were evaluated for antibacterial activity. Compounds 4a, 4b, 4d, 4f, 4o, 4f showed moderate bacteriostatic activity against E. Coli (C600) and S. Aur. (ATCC 25923).

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This work was financially supported by the Russian Foundation for Basic Research (RFBR) grant No. 18-33-01108.

ICOSAHEDRAL STRUCTURE AS A 10-FOLD TWIN CRYSTAL

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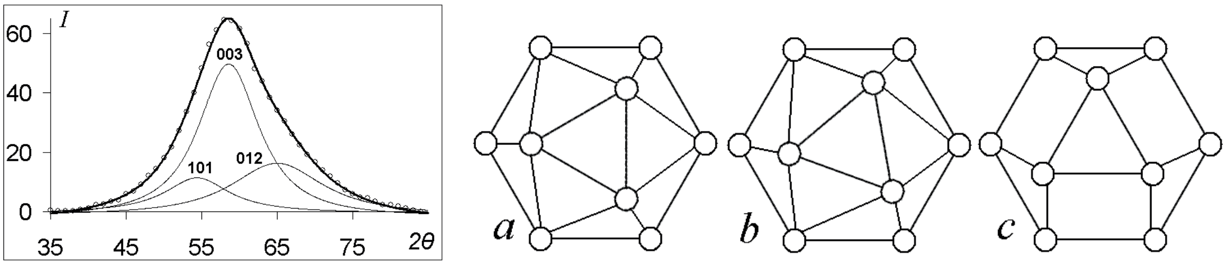
The icosahedral quasicrystalline structure (IQS) is realized in metals and their alloys. It is a 10-fold twin crystal of antisymmetric trigonal pyramid pairs (in the shape of an hourglass) with a distorted FCC lattice described in the hexagonal aspect (left figure) with parameters uniquely determined by the geometry of the icosahedron: $a = R(2(1 - 5^{-0.5}))^{0.5}$, $c = R(3(1 + 2 \bullet 5^{-0.5}))^{0.5}$, where R is the shortest interatomic distance. The icosahedron is easily transformed into a cuboctahedron (FCC structure) and vice versa.



Representation of the X-ray diffraction profile of the IQS of nickel in three reflections in the hexagonal aspect to the left; the scheme of transformation of the icosahedron into a cubic octahedron *(a–c)* and back *(c–a)* to the left.

IQS is characteristic of very small metal clusters and is the primary structure when many metals are formed as a result of crystallization from the melt or in the reduction[1,2]. As a result of enlargement, as well as with decreasing temperature, the normal FSS structure becomes energetically more advantageous, which can easily be turned into a BCC structure.

The transformation of IQS and FCC into HCP proceeds through the displacement of layers and is more difficult, however, low-melting metals (Mg, Zn, Cd) can crystallize immediately in the HCP form.

The report also discusses the results of the synthesis and analysis of nickel and Fe – Co solid solutions by methods of wide and small angle X-ray diffraction, as well as by methods of molecular dynamics.

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SYNTHESIS AND STUDY OF PYROCATECHOL DERIVATIVES OF B KETOIMINATES OF BORON

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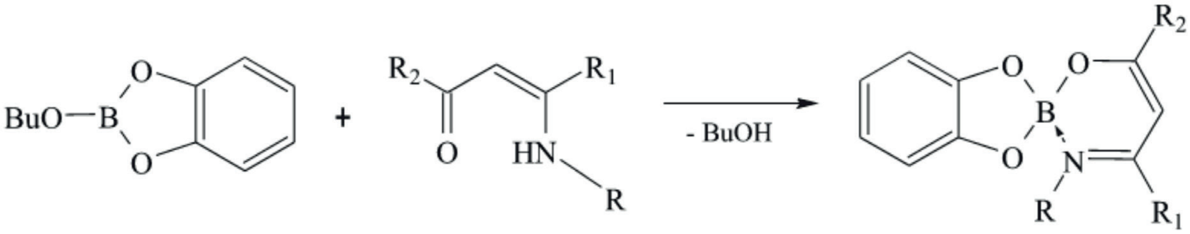
Interest in the chemistry of spirocompounds of tetracoordinated boron has been observed since the early 60s of the last centuries and has been noted to date by a series of publications[1–4] on the synthesis and study of their physicochemical properties. The features of the structure of boron spirochelates constantly attract the attention of researchers, following reports of the synthesis of this class of compounds in the 60s of the last centuries was followed by several publications describing the spectroscopic properties of individual representatives.5 Unlike numerous compounds of three-coordinated boron, in spiroborate boron is tetra-coordinated, which is confirmed by the optical activity of these compounds[1–4] and has a formal negative charge, i.e. compounds are bipolar.

The synthesis and study of properties of fluorescent N-methyl and N-phenyl analogs β-diketonates boron.



где R=H, CH_3, Ph и R_1=R_2=Ph, CH_3; R_1= CH_3 R_2=Ph

The structure of the obtained compounds was proved by the methods of IR, NMR spectroscopy, MASS spectrometry, and TLC.

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CATALYTIC METHOD FOR THE SYNTHESIS OF SUCROSE ESTERS IN THE PRESENCE OF CESIUM CONTAINING ZEOLITES

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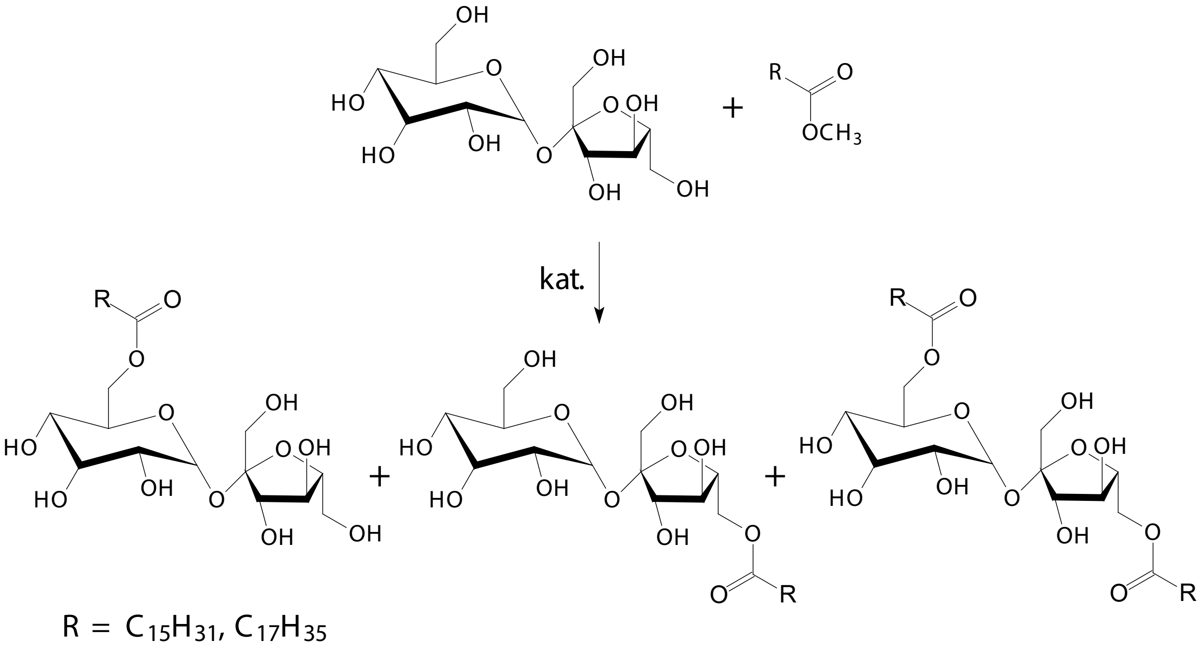
Cesium forms of zeolites were synthesized by ion exchange of Na-forms in an water solution and their activating effect on the transesterification of fatty acid methyl esters was established.

The interaction of methyl esters of palmitic and stearic acid with sucrose at 100 ° C in the presence of cesium-modified zeolites obtained 6-O-mono-, 6'-O-mono- and 6,6'-di-O-esters of sucrose with yields 91-96 %.



The influence of the nature of aluminosilicate zeolites on the yield and composition of sucrose esters obtained was established. Catalytic transesterification in the presence of the obtained catalysts proceeds selectively along the hydroxymethyl groups of sucrose.

The work was funded the Ministry of Education and Science of the Russian Federation through the State order (project no. AAAA-A17-1170011910021-8, contract no. 4.2703.2017/PCh).

HEAT CAPACITY AND VOLUME OF MULTIVALENT CATIONS IN DIMETHYLSULFOXIDE AND DIMETHYLFORMAMIDE AT 298.15 K

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The heat capacities and volumes of dimethylsulfoxide (DMSO) and dimethylformamide (DMFA) solutions of barium and cadmium iodides at 298.15 K were measured by calorimetry and densimetry.

The apparent molar heat capacities Φ_C and volumes Φ_V of barium and cadmium iodides in DMSO and DMFA were calculated from the experimental data. The concentration dependences of Φ_C and Φ_V have a positive slope, which is typical for solutions of inorganic salts in nonaqueous solvents.

To determine the standard partial molar quantities $\bar{C}^{o}_{p,2} = \Phi^{o}_{C}$ and $\bar{V}^{o}_{2} = \Phi^{o}_{V}$, corresponding to an infinitely dilute solution, the dependences $(\Phi_C\ \Phi_V = f\ m^{1/2}$ were approximated by linear regression equations.

The quantities $\bar{C}^{o}_{p,2}$ and $\bar{V}^{o}_{2}$ were separated into ionic components based on the additivity of the partial molar quantities values of $\bar{C}^{o}_{p,i}$ and $\bar{V}^{o}_{i}$ for the iodide ion in DMSO and DMFA[1,2]. The $\bar{C}^{o}_{p,i}$ and $\bar{V}^{o}_{i}$ values of barium and cadmium ions in DMSO and DMFA are shown in Table.

	Ba^{2+} (DMSO)	Cd^{2+} (DMSO)	Ba^{2+} (DMFA)	Cd^{2+} (DMFA)
$\bar{C}^{o}_{p,i}$, J(mole•K)$^{-1}$	-133±15	-126±15	35±15	43±15
$\bar{V}^{o}_{i}$, cm^3•mole^{-1}	6.4±0.3	8.2±0.3	–2.7±0.3	17.7±0.3

Comparison of values $\bar{C}^{o}_{p,i}$ and $\bar{V}^{o}_{i}$ of barium and cadmium ions in DMSO and DMFA, shows that specific interactions between cadmium ions and molecules of solvents result in an increase in volume, but do not lead to considerable changes in heat capacity.

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TERMODYNAMICAL PROPERTIES OF AMMONIUM THIOCYANATE IN N-METHYLPYRROLIDONE AT 298.15 K

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Senchurova D.A.,[b] Salomasova G.G.[b]

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Earlier, we studied heat capacities and volume properties of different type electrolyte solutions in N-methylpyrrolidone (MP) and proposed a system of standard values of heat capacity and ions volume in MP[1,2]. To confirm the validity of the proposed system, it is of interest to expand the range of investigated electrolytes.

The heat capacity (*Cp*) and density (*ρ*) of ammonium thiocyanate solutions in MP are measured at 298.15 K by calorimetric and densimetric means. Apparent molar heat capacities Φ_C and volumes Φ_V of ammonium thiocyanate in MP were calculated from the experimental *Cp* and *ρ* data, and the standard partial molar values of $C_{p,2}^{\bar{o}} = \Phi_C^{o}$ and $V_2^{\bar{o}} = \Phi_V^{o}$ were determined.

The $C_{p,2}^{\bar{o}}$ and $V_2^{\bar{o}}$ values on ionic components were separated using $C_{p,i}^{\bar{o}}$, $V_i^{\bar{o}}$, for ammonium ion, obtained on the basis of a system of standard values of heat capacity and volume of ions in MP[1,2] with the condition of the additivity of partial molar values. The obtained values of $C_{p,i}^{\bar{o}} = 112$ J(mole•K)$^{-1}$, $V_i^{\bar{o}} = 30{,}5$ cm^3•mole^{-1} for CNS– ion in MP are within the error of calculation in good agreement with our data obtained earlier for potassium and cadmium thiocyanate solutions in MP3 confirming the validity of our system of the standard values of heat capacity and volume of ions in MP.

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APPLICATION OF ETHYL-2-DIAZO-3-OXOBUTANOAT IN THE SYNTHESIS OF HETEROCYCLES

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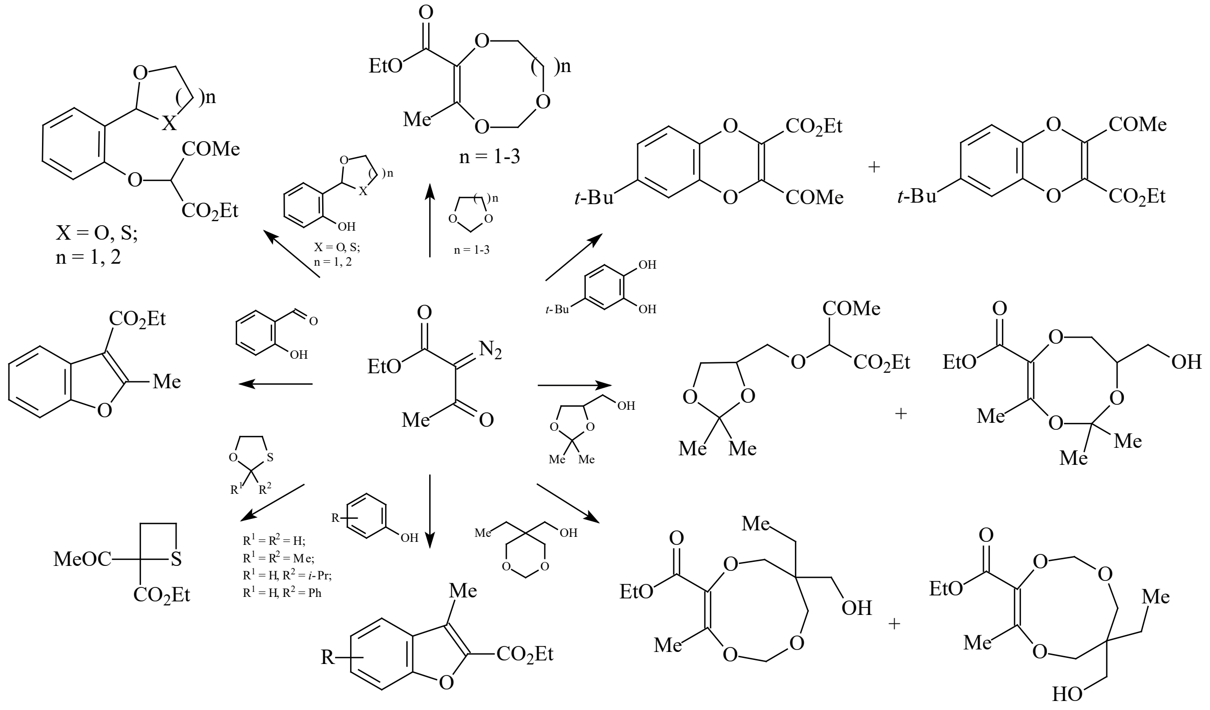
This paper presents the results of studies of the catalytic interaction of ethyl 2-diazo-3-oxobutanoate with cyclic acetals, alcohols and phenols in the presence of rhodium and copper compounds in order to develop approaches to the synthesis of functionally substituted heterocycles that are difficult to access, including macrocycles, oxoethers and benzofurans.



The report discusses in more detail the possible reaction mechanisms, the effect of the reaction conditions on the nature of the initial substrates, the catalyst.

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This work was supported by the grant of the Republic of Bashkortostan for young scientists (from 08.02.2019).

OBTAINING 5,7-DIETHYNYL-[1,2,4]TRIAZOLO[1,5-A] PYRIMIDINES BY SNH METHODOLOGY

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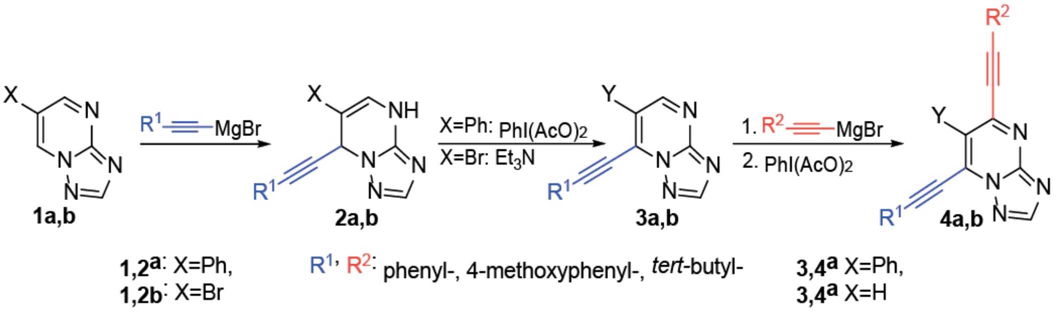
[1,2,4]Triazolo[1,5-*a*]pyrimidines (TAP) attract a great attention of scientists due to their wide range of applications. The π-deficient TAP system can be used as a building block in creating push-pull molecules which are widely used as materials for optical and electronic devices.

Previously we have showed the possibility of the direct C–H functionalization of TAPs by the action of Grignard reagents. The resulting 5,7-disubstituted TAPs demonstrated interesting optical properties, including high quantum yields up to 55% [1].

This study was devoted to the synthesis of TAPs with an expanded π-system using substituted ethynyl magnesium bromides.



Picture 1. The scheme for obtaining 5,7-dietynyl TAPs.

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This work was supported by the grant of the Russian Science Foundation № 19-13-00234.

APPLICATION OF ETHYL-2-DIAZO-3-OXOBUTANOAT IN THE SYNTHESIS OF HETEROCYCLES

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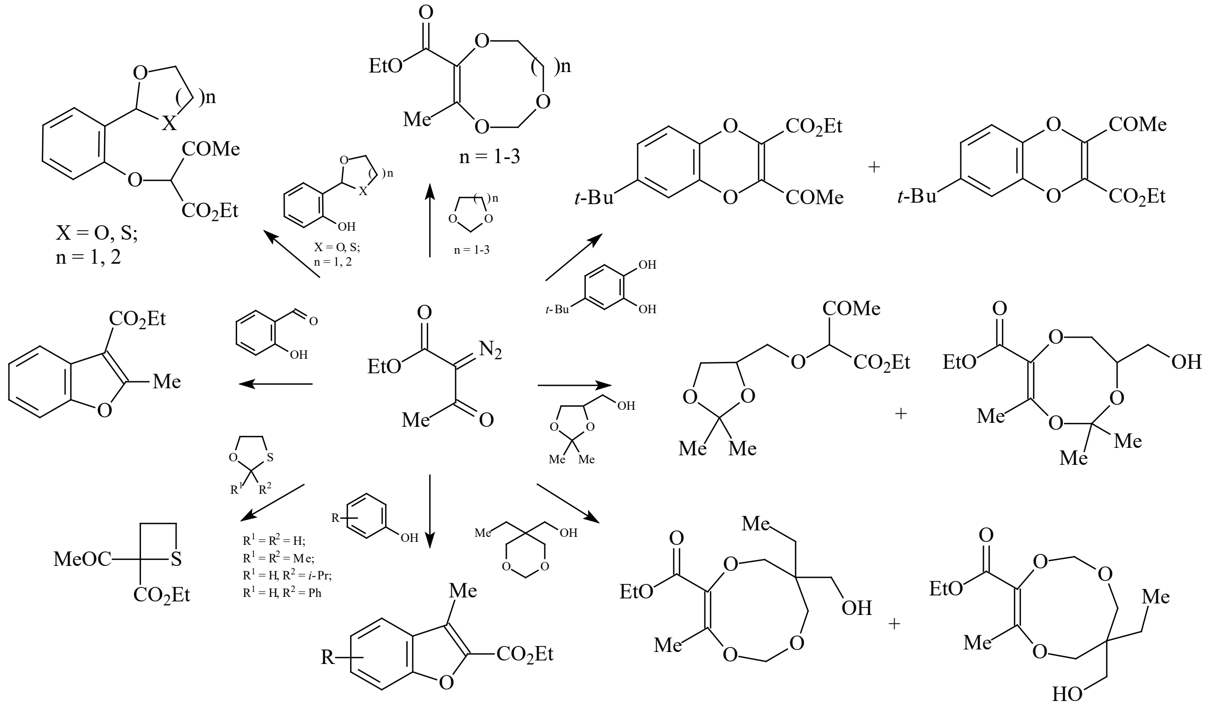
This paper presents the results of studies of the catalytic interaction of ethyl 2-diazo-3-oxobutanoate with cyclic acetals, alcohols and phenols in the presence of rhodium and copper compounds in order to develop approaches to the synthesis of functionally substituted heterocycles that are difficult to access, including macrocycles, oxoethers and benzofurans.



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This work was supported by the grant of the Republic of Bashkortostan for young scientists (from 08.02.2019).

SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF IONIC LIQUIDS BASED ON 1,2,3,4-TETRAHYDROPYRROLO [1,2-A] PYRAZINIUM CATION

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The widespread use of polymer-containing composites in supercapacitor assemblies is limited, on the one hand, by the wettability of their surface with an electrolyte solution and, on the other hand, by the high contact resistance arising at the boundary of the electrode material - current collector. The ability to electropolymerize a pyrrole-containing ionic liquid (IL) at low potentials makes it possible to obtain a layer of conducting redox polymer on the surface of the current collector and carbon material, leading to an increase in the capacity of the composite due to the redox processes. In this work, for the first time, the complete synthesis of two pyrrole-containing ILs based on alkyl substituted pyrrolo[1,2-a]pyrazines was carried out (Fig. 1).

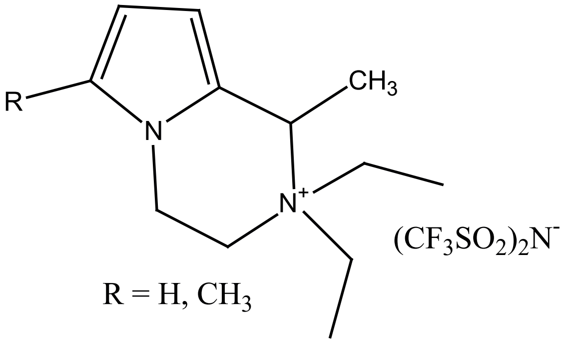

Figure 1. The structure of the obtained IL.

The composition and structure of the obtained ILs were confirmed by XPS and ^{1}H and ^{13}C NMR. The study of electrical conductivity and the electrochemical stability of acetonitrile solutions synthesized IL was performed using the impedance spectroscopy and cyclic volamperometry.

The work was supported by the Russian Science Foundation under grant 18-13-00-217.

DESIGN OF LUMINESCENT SILVER (I) COMPLEXES BASED ON 1,3-N,S LIGANDS

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Silver(I) molecular complexes and coordination polymers are of great interest due to their structural diversity and a wide range of applications. In recent years, these compounds have received attention because of remarkable luminescent properties1.

In the course of searching new efficient Ag(I)-based phosphors, a series of reactions with 1,3-N,S 2-alkylsulphanylazine ligands with silver(I) salts (e.g. AgOTf, $AgNO_3$, $AgClO_4$, $AgBF_4$) have been studied systematically. It was shown that the structure of resulting products – ranging from molecular complexes to coordination polymers – strongly depends on the counterion and azine heterocycle, as well as on crystallization conditions (Fig. 1). In the report, the structures of synthesized compounds, and the photoluminescent properties are discussed.

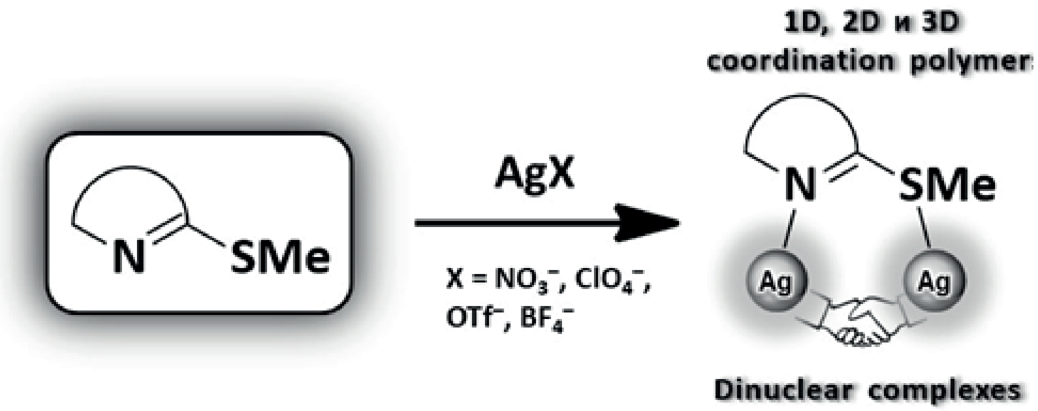

Fig. 1. Design of luminescent silver(I) complexes based on 1,3-N,S ligands

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The research is supported by the Russian Science Foundation, project №18-73-10086

PERSISTENT TRIS(TETRATHIAARYL)METHYL RADICALS – A NEW GENERATION OF SPIN LABELS DESIGNED FOR STUDYING THE STRUCTURE OF BIOPOLYMERS

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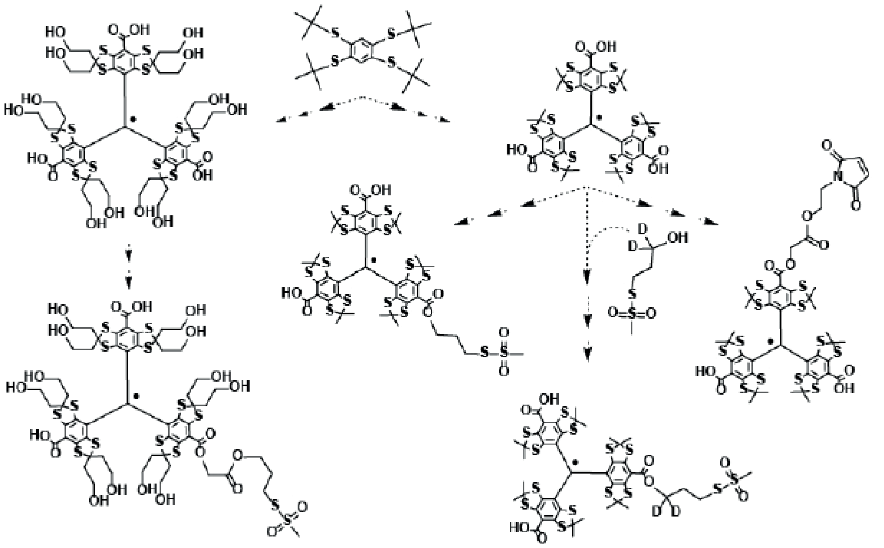
Recently bulky tris(p-carboxyltetrathiaaryl)methyl radicals (TAM) are brought into service as a promising source of a new generation of spin labels that provide a variety of capabilities.[1] Here we present the results obtained for a new methanethiosulfonate, maleimide and N-hydroxysuccinimide derivatives of a Finland and OX063 trityls, which react readily and selectively with biopolymers at predefined sites in their structure.



These labels have been successfully used in applications of DEER and DQC techniques to nanoscale distance measurements in doubly labeled oligonucleotide duplexes, and in elucidation of peptide structure based on pulsed ESR spectroscopy and site-directed spin labeling.

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This study was supported by the Russian Ministry of Science and Education within Grant 14.W03.31.0034 (megagrant).

SYNTHESIS OF DEHYDROABIETINTHIOL AND ITS SULFUR-CONTAINING DERIVATIVES

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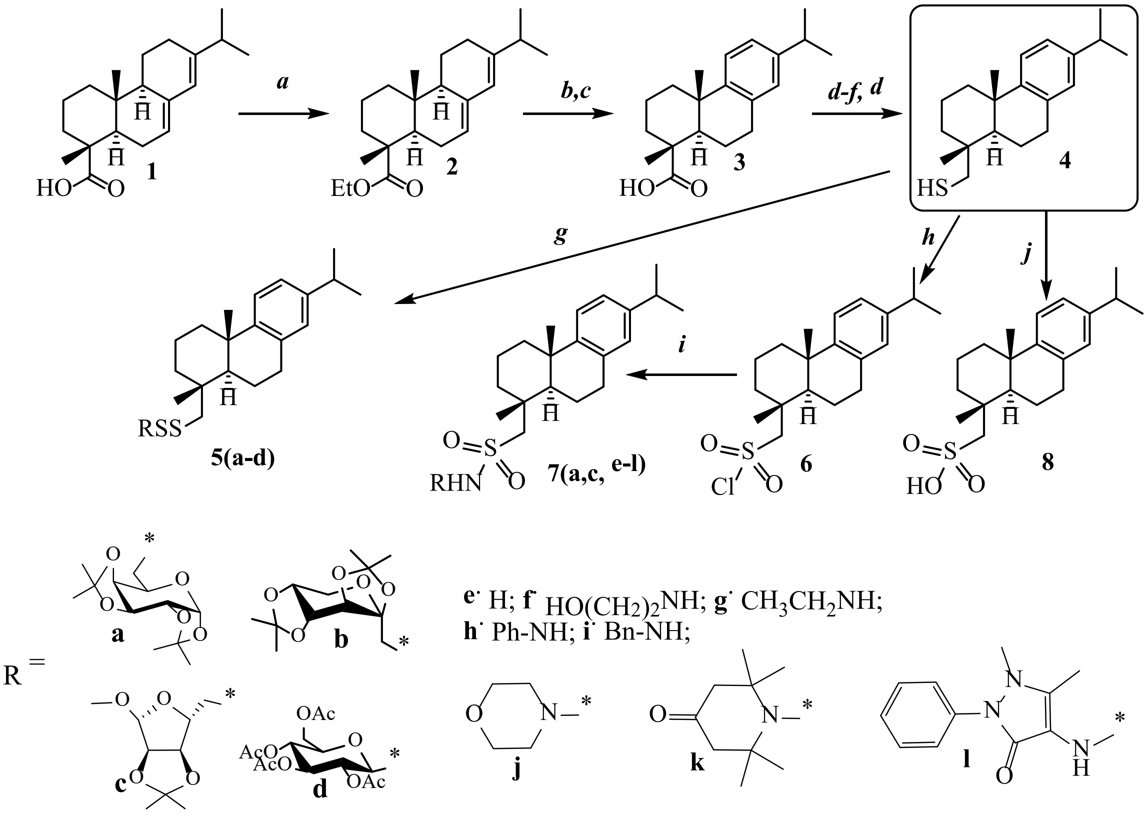
Dehydroabietic acid 3, belonging to the class of diterpene compounds, is a convenient and promising scaffold for the production of biologically active substances of various structures. For the first time, proceeding from it, thiol 4 was obtained, which was studied in the reaction of oxidation with chlorine dioxide. As a result, sulfochloride 6 and sulfonic acid 8 were synthesized. By the reaction of thiol 4 with monosaccharide thiols, and sulfochloride with different-structure amines, disulfides 5 and sulfonylamides 7 were synthesized, respectively.



e: H; f: HO(CH2)2NH; g: CH_3CH_2NH;
h: Ph-NH; i: Bn-NH;

Reagents and conditions: *a*) EtBr, K_2CO_3; *b*) S, I_2’ 200°C ; *c*) *t*-BuOK, DMSO; *d*) $LiAlH_4$, Et_2O; *e*) I_2, benzimidazole, PPh_3’ toluene; *f*) AcSK, DMF; *g*) RSH, I_2’ EtOH; *h*) ClO_2’ H_2O, VO(acac)$_2$’ $CHCl_3$; *i*) RNH_2’ $CHCl_3$’ *j*) ClO_2’ H_2O, Py .

The work was financially supported by the RFBR (project No. 18-33-00486 mol_a), the Ural Branch of the RAS (Project No. 18-3-3-17) and implemented using the Shared Use Center «Chemistry» equipment of the Institute of Chemistry of Komi SC UB RAS.

SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES STUDY OF THE PYRIDYL CAMPHORSULFONATES - NEW REAGENTS FOR ORGANIC SYNTHESIS

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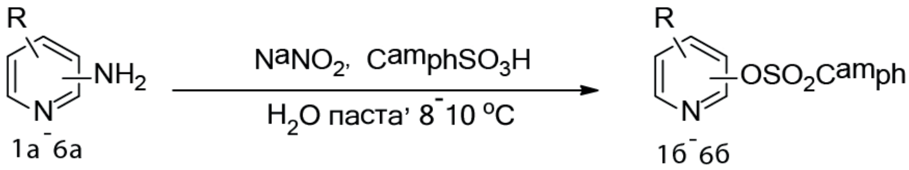
Sulfonate groups (p-toluenesulfonate (tosylate), trifluoromethanesulfonate (triflate)) have low nucleophilicity and can be relatively easily replaced with other functional groups[1, 2]. Earlier in the Kizhner research center developed effective methods for the synthesis of pyridyl- and quinolyl triflates and tosylates via diazotization in the presence of TfOH / p-TsOH[3-5].

We showed for the first time that the diazotization of aminopyridines (1a-6a) in the presence of camphorsulfonic acid leads to the formation of previously unknown pyridyl camphorsulfonates (1b – 6b) (scheme 1). The reaction is carried out in aqueous paste that meets modern requirements for chemical processes. The structure of the obtained compounds (1b – 6b) is confirmed by modern physicochemical methods.



Scheme 1.

For the first time, it was found that pyridyl camphor sulfonates (6b) compared with the corresponding triflates and tosylates show the highest reactivity in SN reactions (the method of competing reactions)

It has been shown that, when boiled in aliphatic alcohols (ethyl, allyl and amyl alcohols), pyridylcamphorsulfonates can be relatively easily converted into the corresponding alkoxypyridines, which are important intermediates of organic synthesis.

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NOVEL SYNTHESIS OF DIHYDROQUINOXALINONE DERIVATIVES

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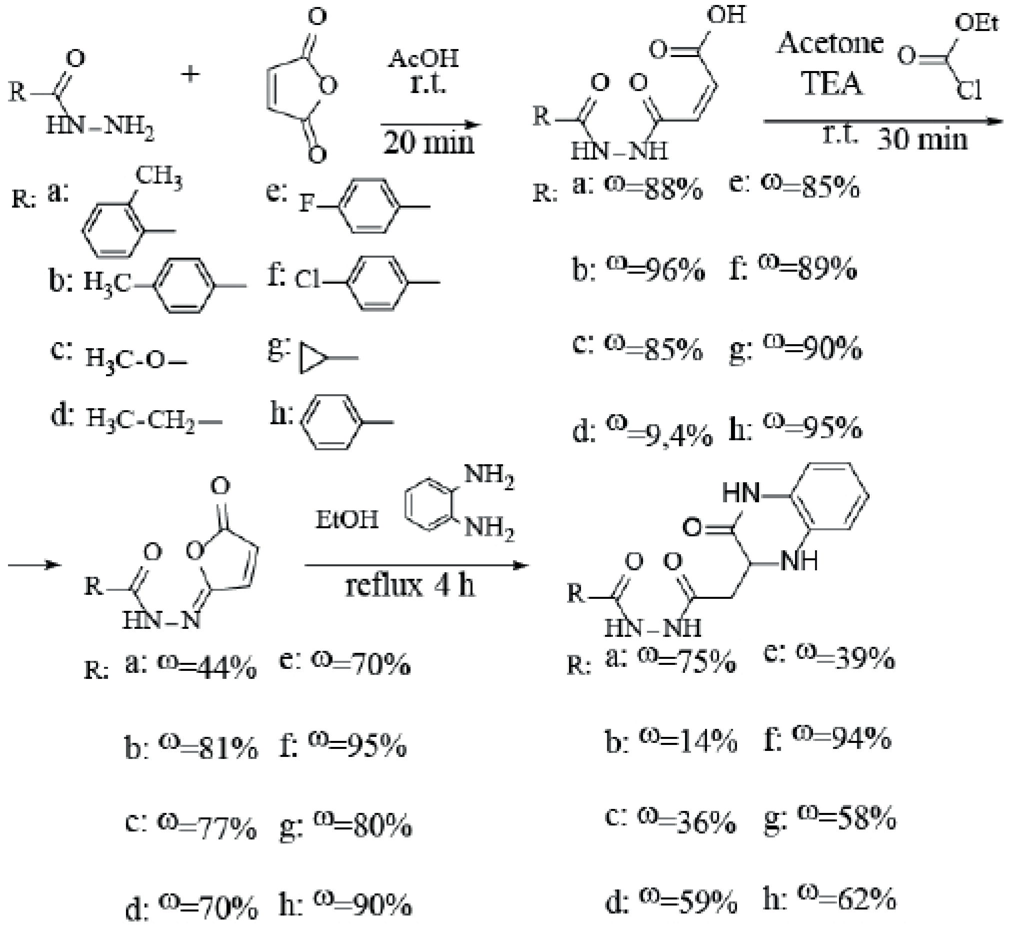
Derivatives of dihydroquinoxaline often exhibit various types of biological activity and are currently being used as antimicrobial, antifungal, antidepressant, and other drugs. In this regard, the interest in convenient and practical methods for the synthesis of dihydroquinoxalinone derivatives remains an actual task. We managed to develop a new method that allows to obtain products with higher yields and purity. The compounds synthesized can find application in combinatorial libraries design for bioscreening of new drugs. The structure of the compounds is confirmed by NMR ^{1}H and ^{13}C spectroscopy.



WETTING PROPERTIES OF A SURFACTANT CONTAINING SHORT PERFLUOROALKYL CHAINS COMBINED WITH CONVENTIONAL BRANCHED SURFACTANTS

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Fluorinated surfactants are known as unsurpassed surface-active agents for reducing the surface tension of water and various solvents up to ultra-low values. However, disadvantages of the surfactants containing long C_6F_{13}-C_8F_{17}-chains are related to their environmental impact, associated with their worth biodegradation, bioaccumulation, and toxicity [1]. A proper alternative to such surfactants is a new type of amphiphiles containing several short perfluoroalkyl chains. These surfactants are not subject to restrictions on marketing and use whereas their effectiveness is almost the same as of long-chain fluorinated surfactants [2-4].

Our study focuses on the wetting properties of Tivida FL 2300 (TFL), new fluorosurfactant kindly provided by Merck KGaA. This eco-neutral anionic surfactant contains three perfluoropropyl chains connected via a spacer to hydrophilic group. Surprisingly, aqueous solutions of this fluorosurfactant in a certain range of concentrations exhibit synergistic wetting of Parafilm M with ethoxylated (×5 EO and ×6 EO) wetting agents, derivatives of branched decanol (Guerbet alcohol). The wetting rate and contact angles on the Parafilm surface were examined for solutions ofthe surfactants and their mixtures using a digital camera in video mode at 25°C.

It was shown that the even small additives of TFL to ethoxylated alcohols significantly accelerate the spreading of water drops on the hydrophobic Parafilm surface. Probably, this nonideal behaviour is essentially of the same kind as the known cases of “fluorophobic effect”, which is typical for other mixtures of a fluorinated surfactant and hydrocarbon molecules. On the other hand, the attractive interaction of hydrophilic moieties can take place. Associative behaviour of TFL and branched alcohol ethoxylate in mixed solutions is examined by various methods. Anyway, anionic TFL and ethoxylated alcohols show a certain independence of their action at the liquid/air surface and the liquid/solid interface. As it was proposed before [5], the comparison of isotherms $\gamma = f(\log C)$ and $\gamma \bullet \cos\theta = f((\log C)$ offer the suggestion on the concentration ranges of surfactant adsorption on these surfaces. TFL adsorption at the Parafilm/air surface is possible as revealed by Zisman’s plot. The obtained data allow us to conclude that the synergistic mixtures of short-chain fluorinated surfactant and branched decanol ethoxylates represent a promising eco-friendly and cost-effective alternative to other wetting agents, particularly with regard to the high adsorption rate and proper wetting in such compositions as sprayable coatings, inks, and surface cleaners.

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HETEROLIGAND COMPLEXES OF CHROME(III) WITH NITRILOTRIACETIC AND MALONIC ACIDS

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Complexes of transition metals with carboxylate ligands including com-plexes with malonate ones are promising components of optical, magnetic and sorption materials, antibacterial and antifungal drugs[1,2]. This explains the interest in the synthesis and study of the physicochemical properties of homo- and heteroligand complexes with malonic acid and its derivatives[3].

Study of homo- and heteroligand complexes of chromium(III) with nitrilotriacetic and malonic acids in aqueous solutions was carried out by the spectrophotometric method. It was found that the presence of malonic acid in the composition of both homo-and heteroligand complexes of chromium(III) provided an increase in the hydrolytic stability of the complexing agent in aqueous solutions with an widening of the pH range corresponding to the stable existence of the chelates. Under optimal conditions for complexation in solutions with an equimolar ratio of components, a deprotonated malonato nitrilotriacetate complex of chromium(III) was formed. The corresponding logarithm of the stability constant was 20.9±0.1. The introduction of malonic acid anions into the coordination sphere of the chromium(III) nitrilotriacetate complex ensured the formation of an additional six-membered metallocycle. This led to an increase in the thermodynamic stability of the heteroligand chelate compared to the homoligand complex.

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STUDY OF EQUILIBRIUM COMPOSITION CHANGE OF COBALT(II)-HEDP COMPLEXES IN AQUEOUS SOLUTIONS

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Complexes of d-block elements with 1-hydroxyethane-1,1-diphosphonic acid (HEDP) are widely used in various industries. The study of the composi-tion and stability of the metals phosphonates in multicomponent aqueous so-lutions is an important and urgent problem. Currently, methods for synthesiz-ing cobalt(II)-HEDP complexes in the solid state have been developed and the crystal structure of some chelates has been investigated. However information on the kinetic stability of these compounds in solutions is very few.

A detailed study of the equilibrium composition dynamics of cobalt(II)-HEDP complexes with different content of components in various media was carried out by the spectrophotometric method. It was found that the amorphous form of poorly soluble chelates was formed after a few hours in solutions with an equimolar ratio of cobalt(II):HEDP and $\Delta pH = 2.8–3.7$. Keeping the solutions for a longer period led to an increase in the pH range ($\Delta pH = 1.7–9.8$) in which hydrates of cobalt(II) di-, mono- and deprotonated 1-hydroxyethane-1,1-diphosphonates precipitated. Under conditions of a twofold excess of the complexing agent, the pH range of chelates crystallization after a month was limited to $\Delta pH = 2.9–4.8$ and triprotonated cobalt(II) bis-phosphonate was released. Preserving the homogeneity of liquid-phase complexes cobalt(II)-HEDP in time was provided by more than threefold excess of the complexing agent in a wide pH range. It was found that binuclear, equimolar and bis-phosphonates of cobalt(II) were formed in freshly prepared alkaline solutions, but storage of the solutions caused a change in the composition of the coordination sphere of cobalt(II) with the predominant formation of mono- and tris- chelates of cobalt(II).

CARBONYLCYCLOPROPANES OF SPIRO STRUCTURE: SYNTHESIS AND SYNTHETIC APPLICATION

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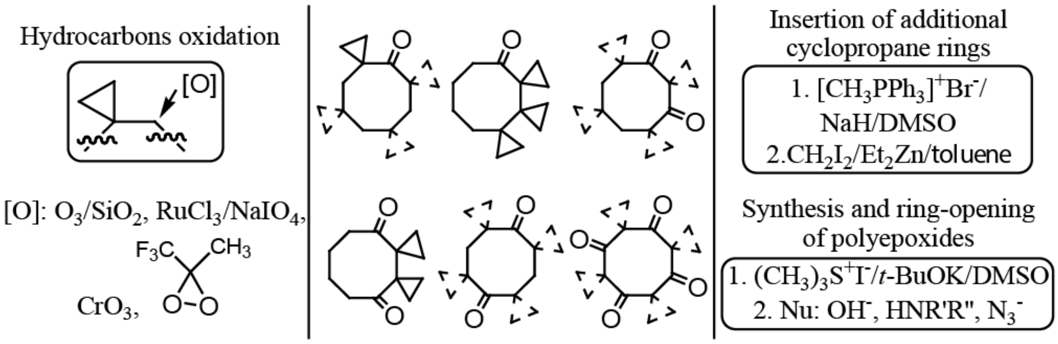
The development of synthetic approaches to the novel types of polyfunctional compounds, containing the functional groups linked by a carbocyclic core, is an actual problem from the point of view of the search of multivalent ligands for the use in medicinal chemistry.

The approaches to unique ketones and polyones of spiro structure were elaborated basing on the reactions of oxidation of cyclopropane hydrocarbons under the treatment with various oxidative systems.[1,2]



Carbonyl and polycarbonyl compounds were investigated in two synthetic sequences: 1) methylenation and cyclopropanation of the obtained vinylcyclopropanes and 2) synthesis and ring-opening of epoxides under the treatment with various nucleophiles. As a result, a series of novel hydrocarbons, containing spiro-annelated cyclopropane moieties, as well as spirocyclic epoxides and polyepoxides and polyfunctional cyclooctane derivatives were obtained.

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TUNABLE IONIC LIQUIDS SYSTEMS FOR CHEMICAL WASTE

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Chemical compounds of different nature are daily released into the water, air, and soil, thereby increasing the risk of irreversible environmental pollution. Nowadays the problem is a top priority challenge, demanding the designing of new concepts to develop “smart” systems for capture, storage, and treatment of toxic contaminants.

In recent decades, ionic liquids due to their unique properties have been used to solubilize and extract substances of different nature.[1] Ionic liquids properties can be adapted to each particular pollutant by changing their cationic or anionic part, mixing with other ionic compounds and adding small amounts of solvents. Systems based on ionic liquids with low water content ("solvent in salt" or more precisely "water in ionic liquid") have received considerable attention in recent years due to the ability of water to form heterogeneous nano- and microstructures (drops and channels).[2]

It was shown that ionic liquid systems better than traditional organic solvents and water retain toxic substances.[3] The process of encapsulating chemicals in the ionic liquid at the micro level was demonstrated using field emission scanning electron microscopy. The possibility of reverse isolation of all substances without changing the structure of the ionic liquid was shown by slice-selective NMR spectroscopy.[4]

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2,2,3,3,4,4,5,5-OCTAFLUOROPENTANOL-1 AND ITS CARBONATE IN ALKYLATION REACTIONS

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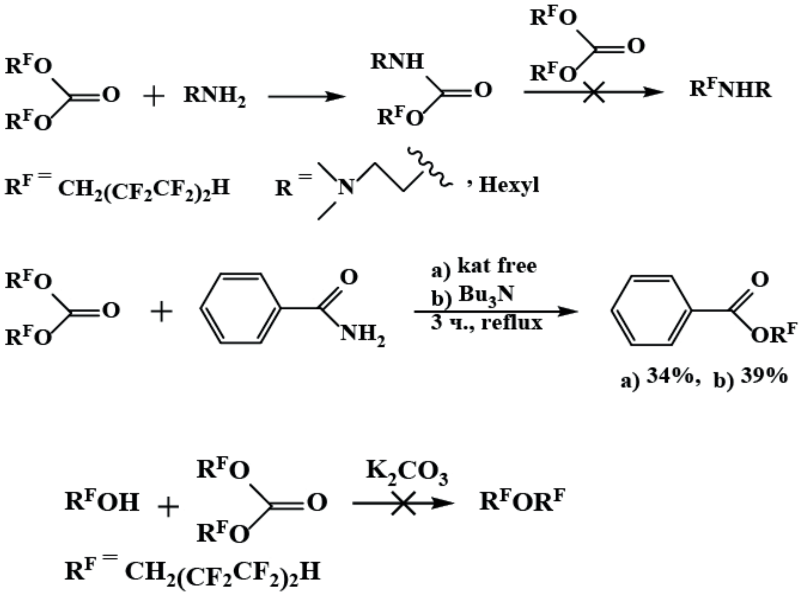
Alkylation reactions are of great scientific interest because they are useful for introduction of protective groups into molecules of phenols, amines and indoles [1,2]. Dialkyl carbonates are known to be alkylation agents [1-3]; however, fluorinated dialkyl carbonates are not known to undergo alkylation reactions in literature.



We demonstrate that 2,2,3,3,4,4,5,5-octafluoropentanol-1 carbonate does not undergo alkylation reactions when interacting with 2,2,3,3,4,4,5,5-octafluoropentanol-1, N,N-dimethylethylenamine and various amides. The reaction stops at the step of monoacylation on the nitrogen atom.

$$R^FOH + Br(CH_2)_3Br \xrightarrow[24\ ч]{K_2CO_3} R^FO(CH_2)_3Br + R^FO(CH_2)_3OH + R^FOCH_2CH{=}CH_2$$

However, it was found that upon interaction of 2,2,3,3,4,4,5,5-octafluoropentanol-1 with 1,3-dibromopropane in DMF, along with monoalkylation of telomeric alcohol, there occurs partial hydrolysis of thus formed bromide derivative and its partial dehydrobromination, which produces O-allyl telomeric alcohol.

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ENANTIOMERICALLY ENRICHED FERROCENNYLAZINES IN THE ASYMMETRIC SYNTHESIS

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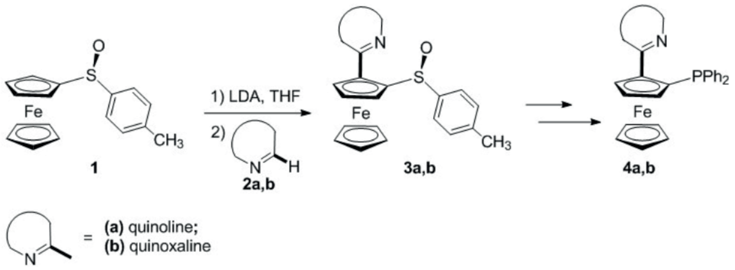
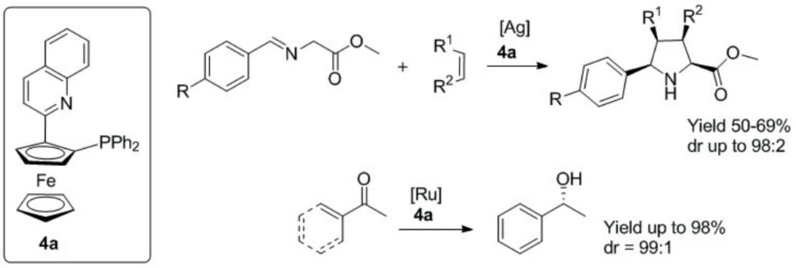
Previously it has been described synthesis of the enantiomerically enriched ferrocennylazines (4a,b) based on the oxidative CDC process of azines with (S)-ferrocenyl-p-tolylsulfoxide 1. The exchange in sulphoxides 3 with diphenylphosphines affords the complexes 4 (Scheme 1)[1].



Scheme 1

Successful examples of the ferrocennylazines systems application are the reactions of asymmetric [3+2]-cycloaddition azomethine ylides and olefins and the asymmetric transfer hydrogenation of ketones (Scheme 2)[2].



Scheme 2

In those reactions 4a showed high catalytic activity. The desired products were isolated with good yields and selectivity.

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The research was financially supported by the Russian Foundation for Basic Research (18-33-00927), the Ministry of Education and Science of the Russian Federation grant number 4.6351.2017/8.9.

ALKYLATION OF POLYPHOSPHOCYCLIC DERIVATIVES OF RESORCINARENES: FACTORS AFFECTING ON THE PROCESS EFFICIENCY

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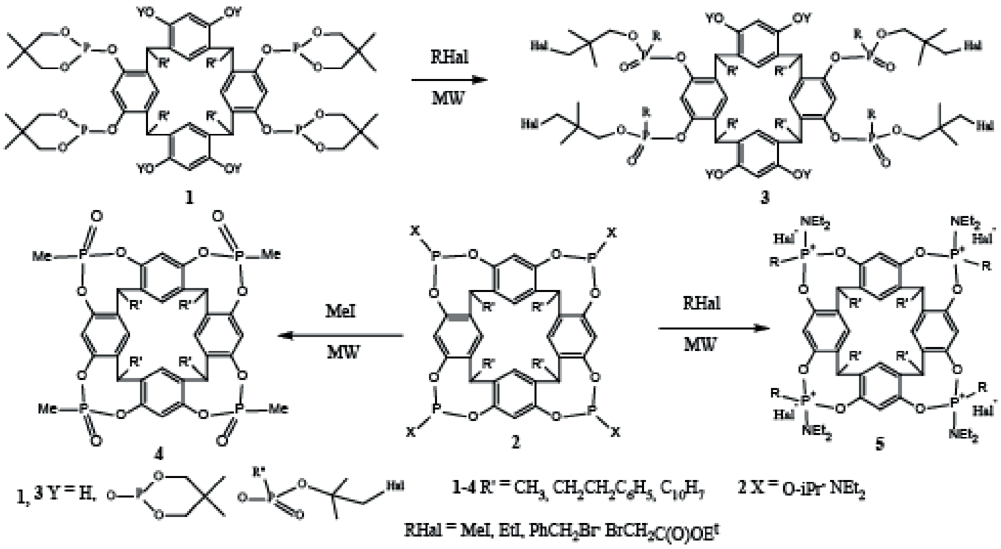
The alkylation of polyphosphorylated derivatives of resorcinarenes 1,2 differing in macrocyclic core structure, size and topology of the phosphocyclic fragments was considered.



In the main, the regiodirection of processes depended on structural factors. Conformationally flexible resorcinarenes 1 with dioxaphosphinane fragments located on the molecule periphery interacted with haloderivatives with the opening of cycles and the formation of linear phosphonates 3 [1]. The alkylation of phosphocavitands 2 with a rigid frame structure didn't lead to disclosure of phosphocyne cycles, the main products of the reaction were phosphonates 4 and quasiphosphonium salts 5. In all cases, the reaction was most efficiently in the microwave reactor, the use of which made it possible to increase the yield of target products with a significant reduction in the duration and lowering the process temperature.

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This work was supported in part by the Russian Foundation for Basic Research (grant no. 18-03-00347a).

CHIRAL DERIVATIVES OF BIPHENYL AND NAPHTHALENE: SYNTHESIS AND APPLICATION IN FLUORESCENT ENANTIOSELECTIVE DETECTION

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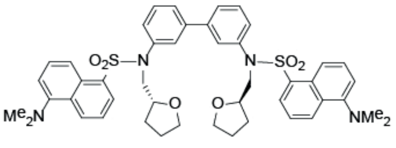
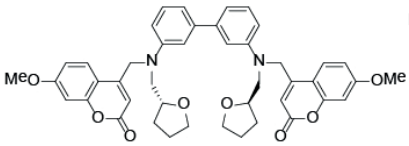
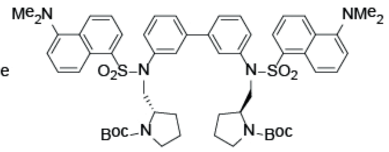
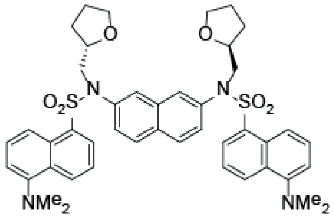
Using Pd(0)-catalyzed amination we synthesized a series of 3,3'-diaminobipehnyl derivatives containing chiral substituents and fluorophore groups like dansyl, coumarin, quinoline.

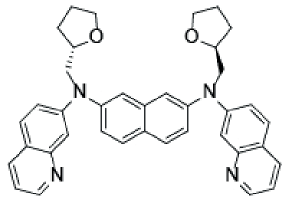


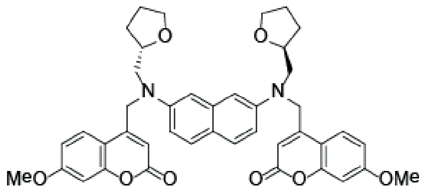


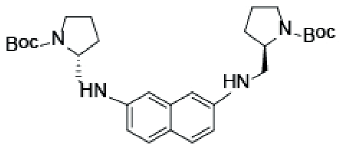


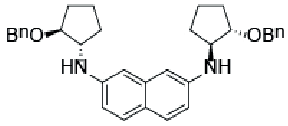
Similarly the derivatives of naphthalene were obtained, including those without additional fluorophore groups as 2,7-diaminonaphthalene exhibit fluorescent properties itself.

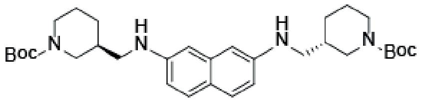












We also demonstrated the possibility of the synthesis of macroyclic derivatives of biphenyl modified with exocyclic substituents. Several compounds were shown to selectively quench or enhance the emission in the presence of one enantiomer of amino alcohols.

The work was financially supported by RFBR, project No 18-03-00709.

THE IMPROVED METHOD TO OBTAIN 5-CHLOROMETHYL ISOXAZOLES FROM EPICHLOROHYDRIN PRODUCTION WASTE

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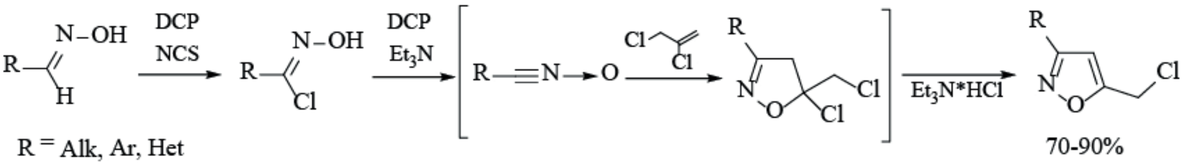
2,3-Dichloropropene (DCP) is one of the by-products of large-scale production of epichlorohydrin by the “chlorine method” and should be subject to recovery.1

In this work, we suggest a simple one-pot method for the preparation of 5-chloromethylisoxazoles based on aldoximes and DCP. The method is convenient because it does not require the use of any solvents and catalysts, the initial reagents are readily available, the reaction proceeds quickly and with the high yield of the target products. The process is slightly dependent on the nature of oxime and proceeds well for both aliphatic and aromatic aldoximes. There is no need to prepare individual chloroximes.



In the proposed one-pot approach in the first two stages (synthesis of chloroxime and its dehydrochlorination) DCP is used as solvent, and at the final stage also as a substrate in the reaction of 1,3-dipolar cycloaddition of nitrile oxides. At the end of the reaction unreacted DCP is recovered by distillation.

Target adducts are useful scaffolds in fine organic synthesis and pharmaceutical chemistry. Due to the presence of the chloromethyl group, they can be functionalized with various N-, O-, S-nucleophiles, that is used to introduce the pharmacophoric isoxazole fragment into a large number of substrates.

Thus, in the present work, a simple convenient method for the synthesis of 5-chloromethylisoxazoles is proposed.

Literature
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NMR PARAMAGNETIC PROBING OF IRON (III) COMPLEXES WITH DIOXYBENZIC ACIDS IN WATER AND IN ORGANIZED MEDIA

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Identifying the features of the interaction of metal ions with polydentate aromatic ligands in organized media is one of the main tasks of coordination chemistry. Thus, among the aromatic ligands, special mention should be made of the mono- and dioxy derivatives of benzoic acid, with which the iron (III) ions form the strongest complexes. The presence of a large magnetic moment of Fe (III) and the high stability of Fe (III) complexes with DHB allows us to consider them as models of contrast agents for magnetic resonance imaging. Earlier in our research group, the effect of cationic surfactants on the state of iron (III) tironate complexes was tested. It is shown that the addition of surfactants to the system Fe (III) -tiron contributes to the formation of iron (III) tironates.

In the present work, the state of iron (III) complexes with DHB in water and micellar media by NMR relaxation was studied. The possibility of stimulating the formation of these complexes in the presence of cationic micelles of surfactants has been tested. The composition, equilibrium constants of formation, and spectral parameters of iron (III) complexes with DHB in micellar solutions were determined by electron spectroscopy. The spectral and magnetic relaxation characteristics of Fe (III) complexes with 2,6-DHB in water, dodecylpyridinium bromide (DPyB), cetylpyridinium bromide (CPyB), cetyltrimethylammonium bromide CTAB have been established. The apparent equilibrium constants in the corresponding media are calculated. It was found that the structure and content of surfactants affects the formation of bis- and tris-ligand complexes of Fe (III) with 2,6-DHB. The presence of surfactants below CMC leads to the formation of precipitation. At optimal surfactant concentration, they practically do not affect $[Fe (HL)_2]^-$ and significantly contribute to the formation of $[Fe (HL)_3]^{3-}$. However, a high surfactant content destroys all metal complexes due to strong competitive binding of the ligand to micelles. It was shown that with an increase in the length of the alkyl radical surfactant and the replacement of the pyridinium head group with the trimethylammonium group, an increase in the binding of 2,6-DHB with micelles is observed.

"The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 18-33-00441."

ELECTROCHEMICAL OXIDATIVE C-H PHOSPHORYLATION OF AZINES

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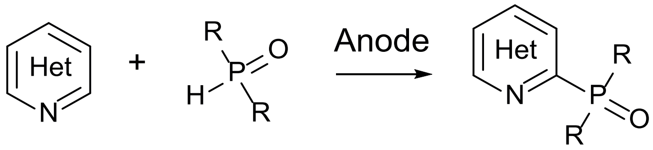
The formation of a carbon-phosphorus bond by the direct functionalization of C (sp^2)-H bonds is a highly attractive methodology for obtaining various compounds, which are widely used in organic synthesis, advanced materials and as ligands in catalytic reactions. Phosphonate fragments are presented in many biologically active compounds that exhibit antiviral, antibacterial, and anticancer activities. However, examples of selective, low-waste, metal-free, one-step and convenient methods of the construction of C(sp^2)-P bonds in the literature are rare.

Meanwhile, an alternative and simple way to obtain phosphorylated heteroaromatic compounds may be an electrochemical synthesis.

In this work, we would like to report a convenient and effective electrochemical method for the C-H phosphorylation of a number of azines.



This simple and practical method of building the C-P bond provides a high yield of products under mild conditions, thus complying with the principles of green chemistry.

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NOVEL DESIGN OF MONONUCLEAR HEXACOORDINATED Co(II) COMPLEXES WITH SINGLE-ION MAGNET BEHAVIOR

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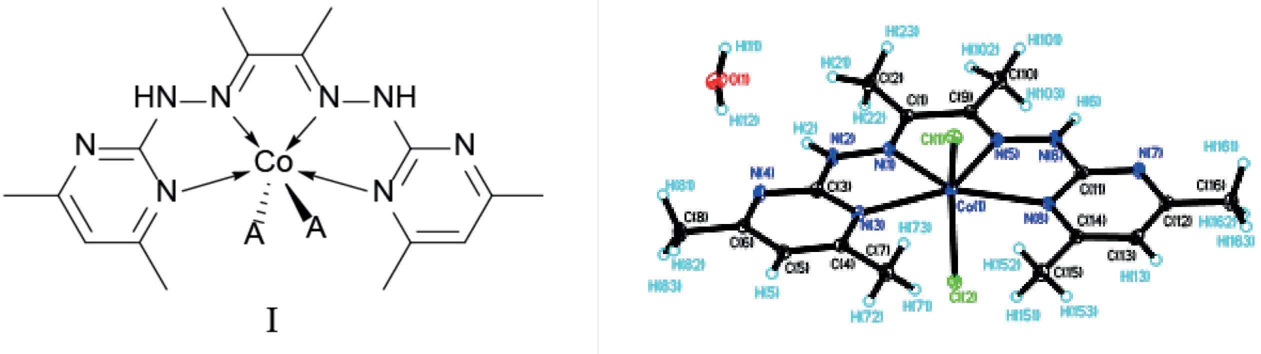
Novel design of mononuclear Co(II) coordination compounds with chemically stable coordination number six showing single-ion magnet properties is proposed. Rigid tetradentate ligand capable to form three chelate cycles (5+5+5) dictates heavily distorted (trapezoid) coordination environment in the plane of the ligand. With two additional monodentate ligands hexacoordination environment of metal center is formed with local axial C2 symmetry. Two compounds I (A = Cl^-, NCS^-) of such type were synthesized and their magnetic susceptibility in DC and AC magnetic fields was studied [1]. Both compounds show large axial zero-field splitting (ZFS) and field-induced slow relaxation of magnetic susceptibility in AC field.



I

Fig.1. Complexes I (A=Cl^-, NCS^-), molecular structure of I, A = Cl^-

Presence of solvation water molecules in crystal structure of I (A=Cl^-, see Fig.1) results in formation of intermolecular hydrogen bond network favoring weak antiferromagnetic exchange interaction between paramagnetic centers. In I (A=NCS-) DMSO molecule is present, preventing exchange interaction between Co(II) ions. Quantum-chemical modelling of ZFS parameters were performed at CASSCF/NEVPT2 theory level.

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The work was supported within internal research grant of Southern Federal University № VnGr-07/2017-29

COPPER SALTS (I, II) AS CATALYSTS IN THE REACTION OF THE INTRA-MOLECULAR CYCLISATION OF GUANIDINES

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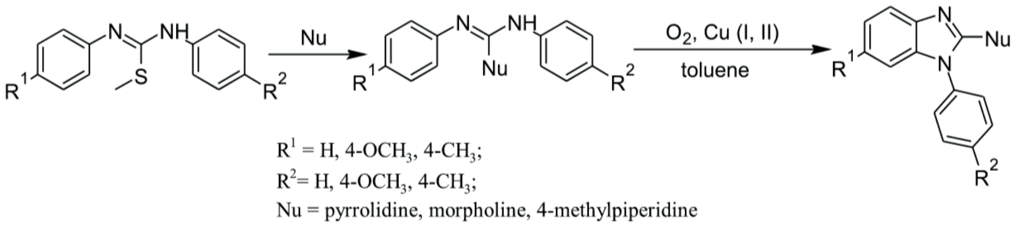
It is known that copper (I, II) salts are used as reoxidizers of reduced palladium in catalytic reactions of the formation of a carbon – carbon bond or carbon – heteroatom [1] and recently it was reported that it can be used as catalysts in reactions proceeding via the «C – H» mechanism of activation [2]. We have implemented work on the search for catalytic systems based on copper (I, II) salts in the «C – H» reactions of activation using the example of intramolecular cyclization of guanidines to the corresponding 2-aminobenzoimidazoles.



R^1 = H, 4-OCH_3, 4-CH_3;
R^2= H, 4-OCH_3, 4-CH_3;
Nu = pyrrolidine, morpholine, 4-methylpiperidine

We have found that copper (II) acetate and copper (I) chloride can be used as catalysts in the cyclization reaction, and the developed method allows to obtain 2-amino-benzoimidazoles with high yield and without using expensive palladium-based catalysts.

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SYNTHESIS OF NEW FUNCTIONALLY SUBSTITUTED HETEROCYCLIC COMPOUNDS BASED ON 5-ACETYL-4-HYDROXY-2H-1,3-TIAZIN-2,6 (3H) -DIONE

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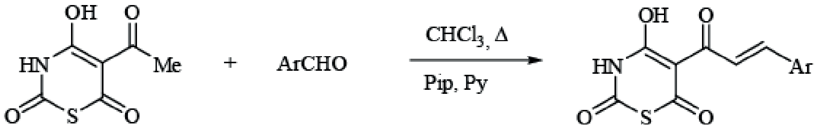
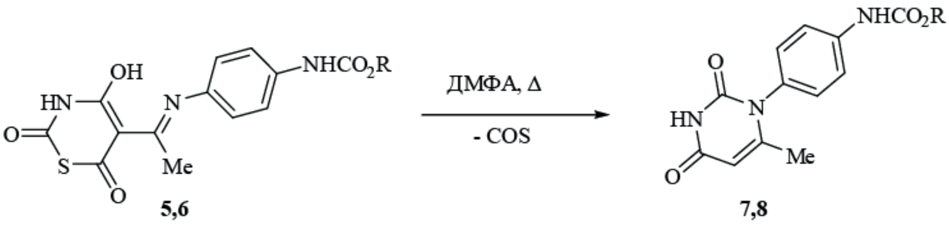
By condensation of 5-acetyl-4-hydroxy-2H-1,3-thiazin-2,6 (3H)-dione (1)[1] with aldehydes in chloroform in the presence of catalytic amounts of piperidine and pyridine, were obtained the corresponding hybrid chalcones (2-4).



1 **2-4**

2-4, Ar=4-ClC$_6$H$_4$, 4-MeOC$_6$H$_4$, 5-(4-бромфенил)-фуран-2-ил

The corresponding azomethines (5,6) were obtained by condensation of compound 1 with alkyl N-(4-aminophenyl)carbamates, which, when boiled in dimethylformamide, were converted to the corresponding uracils (7,8).



5,6 **7,8**

R=*цикло*-C$_6$H$_{11}$ (**5,7**); PhCH$_2$ (**6,8**)

The structure of the synthesized compounds was confirmed by IR, ^{1}H, ^{13}C NMR spectroscopy.

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This study was performed under financial support by the Ministry of Education and Science of the Russian Federation (project no. 4.9288.2017BCh)

RADICAL POLYMERIZATION OF PROTONED DIALYLAMMONIUM MONOMERS IN THE PRESENCE OF RAFT AGENT

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Protonated diallylammonium polymers (PDAA) obtained by the radical polymerization of diallylammonium trifluoroacetate salts (DAATFA) possess strong antimicrobial activity, including action against M. *tuberculosis*. [1-3] Due to a potential for creation of novel biocidal materials based on PDAA, a problem arises to control radical polymerization in order to obtain polymers with predicted MW and narrow polydispersity index (PDI). In the presented work, an adaptability of the radical polymerization technique termed as the reversible addition fragmentation chain transfer (RAFT) process for the polymerization of DAATFA monomers, which occurs with effective chain transfer to monomer, has been studied. There was the purpose to depress effective chain transfer to monomer by the competitive transfer reaction with RAFT agent that to prepare polymers with narrow PDI and predicted MW. The polymerization of DAATFA monomer in aqueous solutions upon several ratios of the initiator and RAFT agent concentrations was performed. As the results of studies by NMR and IR-Fourier spectroscopy, and hydrodynamics and light scattering methods, it has been shown that the effective chain transfer to monomer can be kinetically depressed by the transfer reaction with the RAFT agent at the appropriate conditions. At these conditions, the RAFT agent controls preparation of PDAA samples with narrow PDI (1.3) and small MW (9000-14000 g/mol) increased with an increase in polymerization duration. Polymers with end dithiocarbonate group are the main product of the polymerization.

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ACOUSTIC AND ELECTROMAGNETIC PROPERTIES OF WATER

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Water, as an open, thermodynamically nonequilibrium, extremely dynamic supramolecular aqua-system constantly not only evaporates, but also is a natural source of acousto-electromagnetic (AEM) aqua-emissions: wave ensembles of acoustic and electromagnetic coherent oscillations, matched and conjugate to each other. The spectrum of AEM aqua-emission is linear, low-intensity (W < 10-10 W/cm2 “white noise”) and extremely broad-band — from fractions of Hz to 1017 Hz. Since water is the source of AEM-aquatic emissions and is sensitive to different emissions, it is a natural aqua-radio system [1]. This ability is due to the high dynamism of a large set of H_2O dipole molecules, aqua-ions, with a very low concentration ($c \approx 10^{-7}$ mol/l) and aqua-radicals, whose concentration is still significantly lower, as well as a constant vibrationally excited state of the whole supramolecular system and its particles, and most importantly - a single network of hydrogen bonds. AEM-emissions can initiate resonant-wave interaction with oscillations of the medium and the formation of short-term dynamic waveguides in these environments. Water and all flesh are natural universal aqua-radio systems, since they are sources of AEM aqua-emissions, receivers of external emissions, their converters and amplifiers. The phenomenon of aqua-communication is characteristic of living and inanimate water-containing systems [1]. There is no existence of bio-field, since there are existing only fundamental fields and elastic oscillations of the medium. Mitogenetic radiation is the AEM aqua- emissions of a cellular aqua-system during mitosis.

Aqua-radio properties of aquatic systems of the human body and the ability of their aqua-emissions to resonant-wave interaction is the basis of materiality: consciousness, thinking, psyche, spirituality, emotions and feelings, including remote sensitivity, as the basis of aqua-location ability of the living.

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MORPHOLINE-CONTAINING NAPHTHOPHOSPHACYCLOPHANES

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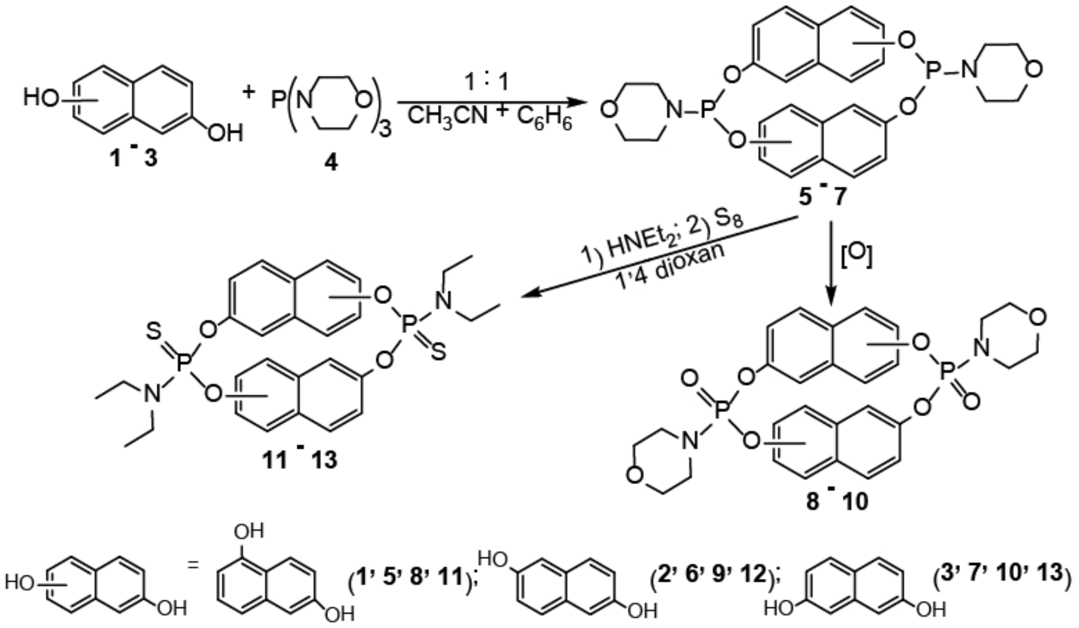
Chemistry of macrocyclic compounds is an emerging area of modern science. Application of naphthalene units as building blocks of macrocyclic compounds is widely used in synthetic practice[1]. Further introduction of phosphorus centers bearing morpholine substituents can extend the area of functional possibilities of macrocyclic systems. Morpholine and its derivatives find applications in various fiends of science and technology as anticorrosive agents, synthetic precursors for antibiotics and enamines, plasticizers for synthetic caoutchouc, etc.

We have studied phosphorylation of dihydroxynaphthalenes 1-3 with spatially separated hydroxyl groups by trimopholylphosphite 4. The features of chemical behavior and activity of uniform naphthophosphacyclophanes are discussed. Reactions of phosphorus centers oxidation and morpholine fragments substitution were investigated.



All synthesized compounds were isolated and characterized by modern physical-chemical methods (^{1}H-, ^{13}C- and ^{31}P-NMR, MALDI TOF MS).

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ZINC AND CADMIUM COMPLEXES WITH BENZIMIDAZOLE DERIVETIVES: STRUCTURE AND LUMINESCENT PROPERTIES

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Biologically active benzimidazole derivatives are widely used in coordination chemistry as ligands for synthesis of complexes with various topology and dimension because the ligands have different ways of coordination[1-3]. Coordination compounds with these ligands can have optical, magnetic and biological activities. However, the luminescent properties of complexes with benzimidazole derivatives are not widely studied.

In this work two benzimidazole derivatives were used as ligands: bis(benzimidazol-2-yl)methane (L^1) and 1-(1H-benzimidazol-1yl-methyl)-1H-benzo-triazole (L^2). Zinc and cadmium polycrystalline coordination compounds with these ligands were characterized using elemental analysis and IR-spectroscopy. The molecular and crystal structures some of the complexes were determined by single-crystal X-ray analysis. The luminescent properties of all obtained compounds were studied: the luminescence excitation and emission spectra of ligands (Fig.) and complexes were received. Also the quantum yields and lifetimes of excited states were measured.

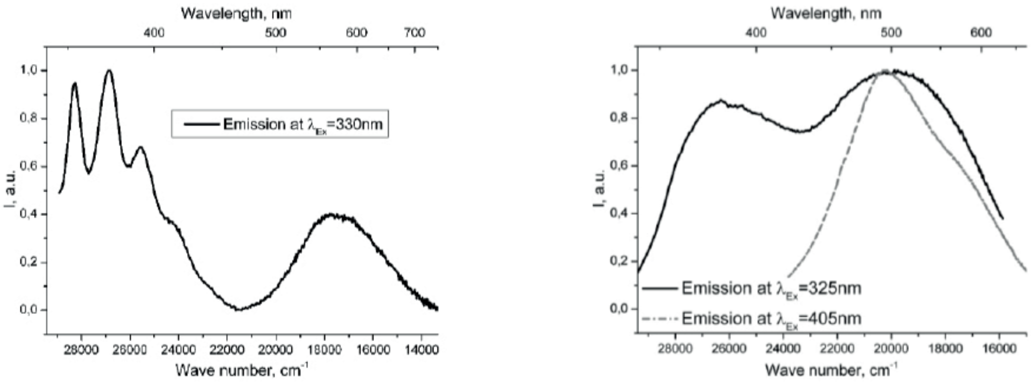

Figure. The emission spectra of ligands L^1 (left) and L^2 (right)

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RUSSIAN CHEMICAL BULLETIN (IZVESTIYA AKADEMII NAUK. SERIYA KHIMICHESKAYA)

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The *Russian Chemical Bulletin (Izvestiya Akademii Nauk: Seriya Khimicheskaya)* is a peer-reviewed Russian journal covering all branches of chemistry. Founded in 1936 and published in English since 1951, now the *Russian Chemical Bulletin* publishes nearly 500 original articles per year. The Journal offers to the chemists an exciting mixture of Review-type articles, Full Papers, Brief Communications, and Letters to the Editor. Contributed by leading scientists from Russia and throughout the world, all papers are rigorously refereed and edited to the highest international standards. The topics related to the Journal include but not limited to general and inorganic chemistry, theoretical and computational chemistry, physical chemistry, organic chemistry; organometallic chemistry, chemistry of natural compounds, bioorganic chemistry, and materials science.

The Journal metrics are summarized in Fig. 1.

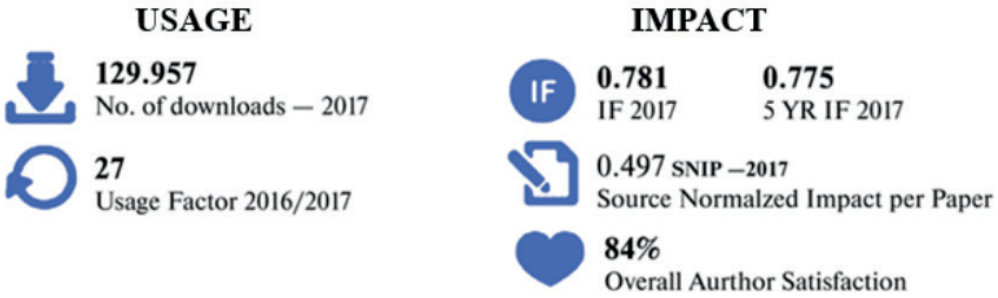

Fig. 1. The Russian Chemical Bulletin metrics (IF is impact factor; 5 YR IF is 5 Year Impact Factor.

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NEW METHOD OF SYNTHESIS OF SUBSTITUTES PYRROLIDINES BASED ON REACTIONS 3-ARYLIDEN-1-PYRROLINES AND DERIVATIVES 4,4-DIETOXIBUTAN-1-AMINE WITH C-NUCLEOPHILES

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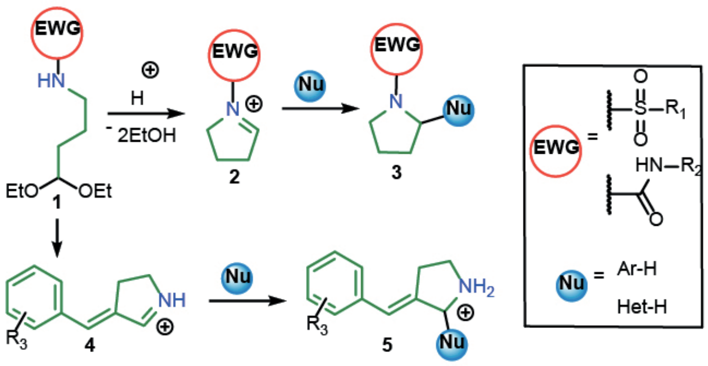
Pyrrolidine moiety is a frequently appearing motif in a variety of natural alkaloids and pharmaceuticals. We have developed an original approach to the substituted pyrrolidines 3 based on the acid-catalyzed reaction of 4,4-diethoxybutan-1-amine 1 derivatives with aromatic/heterocyclic nucleophiles. Moreover, we have discovered a novel reaction of N-(4,4-diethoxybutyl)-1-arylmethanimine 1 derivatives which leads to the formation of heterocyclic compounds 3-arylidene-1-pyrrolines 4, which may serve as starting compounds for the 2-substituted pyrrolidines 5 synthesis. Unlike previously known methods the proposed approach does not require use of expensive reagents and/or catalysts and allows to obtain target compounds with high yields under mild conditions without intermediate products isolation.



This work was supported by the Russian Science Foundation (Grant No. 16-13-10023).

EMULSION POLYMERIZATION OF ELEMENTAL SULFUR UNDER HIGH ENERGY RADIATION

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Elemental sulfur is one of the important types of large-scale chemical raw materials. At the beginning of the industrial production of mineral fertilizers, sulfur, as the main component, was constantly in short supply, and a permanent increase in its production was required. Currently, the situation has drastically changed: global production of sulfur is much larger than its global consumption, and this excess will continue for the observable future[1]. Since the existing methods of producing polymer sulfur have a number of disadvantages, the search for new ways of processing elemental sulfur into a polymer form is relevant. There are various methods of polymer synthesis, one of them being the emulsion polymerization. One of the traditional methods of obtaining stable polymer dispersions is emulsion polymerization. It is characterized by high rates and degrees of polymerization in various systems, which opens the opportunity to try its application in the formation of sulfur-containing substances[2]. Emulsions with different surfactants were obtained and their stability was investigated. The most stable emulsions were irradiated at the MRX-γ-100 unit, the precipitate obtained after irradiation was investigated using a scanning electron microscope JSM 6510 LV SSD X-MAX with probe micro-analysis and JEOL sputtering unit, as well as x-ray diffractometry at the Drone-3M unit. The results of the analysis showed that the precipitate formed consists of sulfur-containing crystals, the shape of which is typical for elemental sulfur, and particles of amorphous-fibrous structure, which can be a sign of oligomeric or polymeric structure. The equipment of the D. I. Mendeleev Center for Collective Use was used in the research.

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COMPLEXES OF IRON(III) WITH HYDROXYAROMATIC ACIDS IN AQUEOUS SOLUTIONS OF POLYETHYLENYMINE AND STABILIZED MAGNETITE NANOPARTICLES

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Nanoparticles of iron oxide (II, III) (IONPs) have a set of unique physical, chemical, thermal and mechanical characteristics, which leads to their wide scope. In particular, colloidal dispersions of nanosized magnetite particles are used in magnetic resonance imaging (MRI) as negative (T_2-weighted) contrast agents (CA). Thus, among commercial contrasting MRI agents, a number of magnetite-based preparations are known, namely, Lumiren and Sinerem (particles of magnetite with a diameter of 300 and 30 nm, respectively, coated with dextran-type polymers and auxiliary medicinal substances). However, a number of CA based on iron (II, III) oxide particles also have disadvantages: increased toxicity and ability to aggregate in a physiological environment. Due to non-specificity, low efficiency, toxicity, as well as increased cost of commercial preparations, and due to the growing number of MRI studies, the development of CA combining high relaxation efficiency (bimodal T_1, T_2 contrasts) with low toxicity of components is relevant. Earlier, we discovered the effect of the growth of the relaxation efficiency of low molecular weight iron (III) complexes with some aromatic acids in the presence of polyethyleneimine. It is shown that such complexes are able to act as models of positive (T_1 – weighted) CA. The combination of low-molecular complexes of iron (III) (T_1-image) and magnetite nanoparticles (T_2-image) would achieve the best contrasting ability and create innovative CA. This paper presents data on the synthesis of magnetite nanoparticles modified by low molecular weight iron (III) complexes with 2,4-, 3,4-dihydroxybenzoic acids (DHB). The synthesized modified magnetite nanoparticles were characterized by IR spectroscopy, DLS, and TEM. The effect of the salt background, the acidity of the medium, biomolecules, and temperature on the relaxivity of the modified magnetite nanoparticles obtained was studied.

"The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 18-33-00441."

COMPOSITE ELECTRODES MATERIALS BASED ON THE RUTHENIUM AND PLATINUM OBTAINED BY SHORT-PULSE LASER RADIATION

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For the development of energy and fuel cells necessary to conduct research on the development of manufacturing techniques and methods for producing catalytic electrode materials with a long service life and power, will be more resistant to poisoning even under working in conditions of contaminated hydrogen.

The goal of our study was to examine the properties and characteristics of catalytic electrode materials based on ruthenium and platinum obtained by short-pulse laser radiation. This method of obtaining electrode materials allows you to control the structure of catalysts based on platinum-ruthenium composite systems and to achieve the greatest efficiency.[1]

In this work we discuss characteristics of nanostructured electrode materials based on ruthenium and platinum prepared by laser synthesis. Commercially available planar three-electrode samples as the basic electrodes ware used. Samples were obtained as follows: ruthenium and platinum solutions in different ratios were applied on the surface of the working electrode, after was complete drying of the surface of electrodes was used the short-pulse laser treatment was performed in argon.

The electrode materials were studied by cyclic voltammetry on a potentiostat in a wide range of input potentials and scanning speeds, the regime of chronopotentiometry open circuit potential method. With the use of transmission electron microscopy images of surface of electrode materials were obtained. This report covers functional characteristics of the electrode that demonstrate high performance of materials.

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IRON (II) COMPLEXES OF 1,5-DIAZA-3,7-DIPHOSPHACYCLOOCTANES

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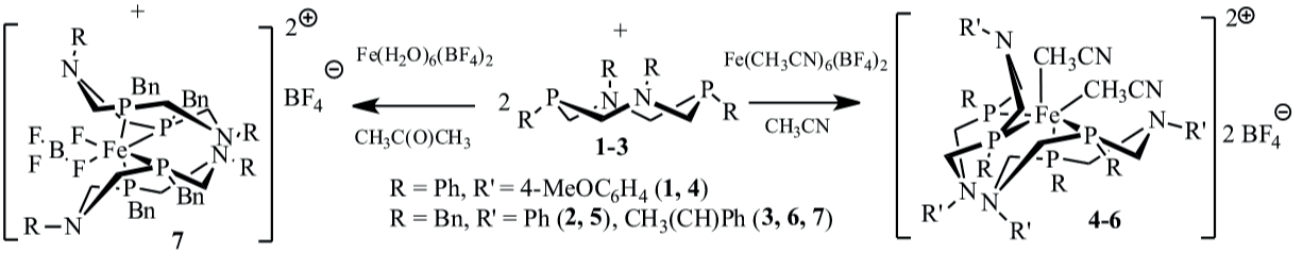
The search for new available and inexpensive metal complex systems capable to activate small molecules and transform them into practically useful derivatives is intensively carried out at the last time[1,2]; various P, N-containing phosphines are widely proposed as the ligands[1-4].

New iron (II) *cis*-complexes 4-7 with diazadiphosphacyclooctanes 1- 3 were synthesized in yields of 63-87%. In complexes 4-6 on the basis of Fe $(CH_3CN)_6$ $(BF_4)_2$, the coordination sphere of Fe (II) is complemented by two acetonitrile molecules, whereas in complex 7 based on a similar aquacomplex this sphere includes two fluorine atoms of tetrafluoroborate anion. The close proximity of iron ion and nitrogen atoms of the ligands (X-ray) indicates the possibility of activation of small molecules due to secondary interactions with the substrate.



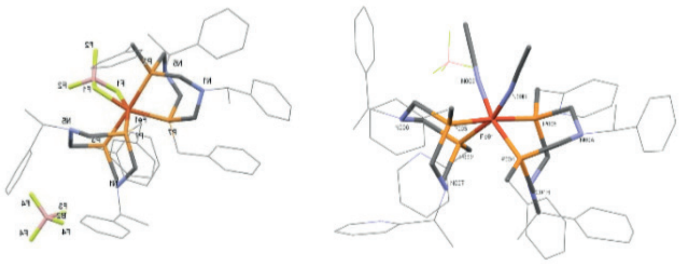


Figure 1. Molecular structures of the complex 7 (left) and of the complex 6 cation (right)

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CONTROLLED (CO)POLYMERIZATION OF ACRYLONITRILE IN THE PRESENCE OF CATALYTIC SYSTEMS BASED ON COPPER BROMIDE (I)

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Atom Transfer Radical Polymerization (ATRP) is one of the most effective methods for the preparation of functional polymers with predetermined composition and molecular weight characteristics. One of the applications of such copolymers is the production of polyacrylonitrile (PAN) fibers used as carbon fibers precursors. A significant task in this area is the methods design for obtaining copolymers, characterized by a narrow molecular weight distribution, high values of molecular weight with relatively high rates. One of the ways to solve this problem is the selection of a suitable metal catalyst and process conditions.

In this work the synthesis of acrylonitrile homo- and copolymers in a controlled mode in the presence of a catalytic systems based on copper bromide (I) and nitrogen-containing ligands was studied. Tris(2-pyridylmethyl)amine (TPMA), N,N,N’,N’-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) and 2,2′-bipyridyl (BiPy) were used as ligands to obtain copper complexes. It was shown that the use of these compounds as ligands allows carrying out the polymerization in accordance with the atom transfer mechanism. The controlled nature of the process is evidenced by an increase of molecular weight throughout the reaction and sufficiently narrow molecular weight distribution of the synthesized samples (1.3-1.6). Moreover, the obtained values of molecular weights are in good agreement with the theoretically calculated ones. It has been established that to achieve a high yield of the target product in the shortest time (9 hours), the most appropriate is the use of a catalytic system containing TPEN, TPMA and Me6TREN.

The work was supported by Russian Foundation for Basic Researches (Proj. № 18-43-520016).

SYNTHESIS OF (E)-4-(NITROMETHYLENE)-4H-CHROMEN-2-AMINES FROM 1-(2-IMINO-2H-CHROMEN-3-YL)PYRIDIN-1-IUM PERCHLORATES AND NITROMETHANE UNDER ACTION OF BASE

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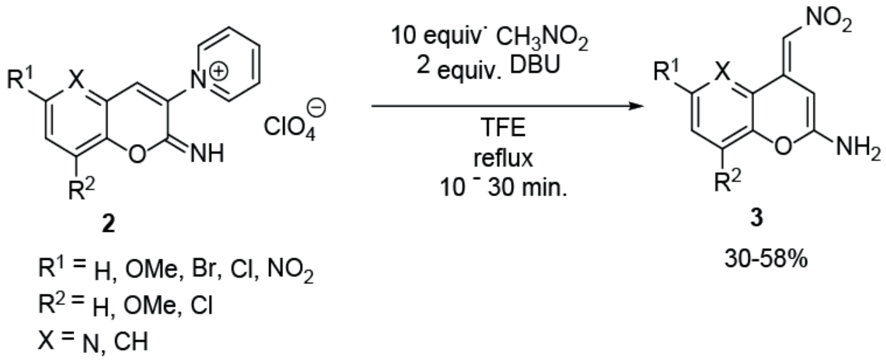
2-Aminochromenes belong to favored and privileged scaffolds in medicinal chemistry and exhibit a wide range of biological activity, particularly, great interest of researchers is related to the antiproliferative properties of several representatives.

Here we describe a new approach towards 2-aminochromes via reaction of 1-(2-imino-2H-chromen-3-yl)pyridin-1-ium perchlorates with nitromethane (Scheme 1), that presumably proceeds through the initial Michael addition to the 2-iminochromene followed by the formation of cyclopropane intermediate, which in its turn cleaves and tautomerization finally gives the 2-aminochromene.



Scheme 1

The reported study was funded by RFBR according to the research project № 18-33-00536

NMR STUDY OF THE SODIUM ION MOBILITY IN THE COMPLEX MOLYBDENE AND TUNGSTEN OXIDES

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The aim of the study is to establish the mechanism of ion transport in the complex sodium-containing oxides, promising as the basis for new solid electrolytes. The double and triple molybdates and tungstates with open framework structures of the alluaudite type, $Na_5R(MoO_4)_4$ (R = Sc, In), $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = In, Sc), $Na_{4-2x}M_{1+x}(MoO_4)_3$ (M = Cd, Mg, Zn); NASICON type, $Na1{-}xM_{1-x}R_{1+x}(XO_4)_3$ (M = Mg, Co, Mn; R = Al, Sc, In; X = Mo, W); glaserite type, $A_3Na(XO_4)_2$ (A = K, Rb, Cs; X = Mo, W), were studied.

The NMR experiments have been performed in the external magnetic fields (9.4 and 11.7 T) and acquisition modes (static and with magic angle spinning, MAS) and in a wide temperature range 300 – 750 K. It allowed to attribute the observed NMR signals to different groups of Na+ ions in the structures. It was found that the second order quadrupole effects are the main factor determining the shape of the ^{23}Na NMR spectrum. The results of the ^{23}Na NMR spectrum analysis are confirmed by ab initio calculations of the electronic structure and parameters of the electric field gradients near magnetic nuclei. The temperature dependences of different NMR parameters allowed us to establish the mechanism of Na+ ions diffusion in the studied compounds. In particular, we first showed that, in addition to 1D diffusion of sodium along the crystallographic c axis in the alluaudite-type molybdates, there are also fast (on the NMR frequency scale) ionic jumps through nonequivalent positions in the bc plane.

This work was supported by the Russian Science Foundation, project No. 18-12-00395.

MECHANISM OF SODIUM DIFFUSION IN POLYANIONIC MOLYBDATES AS PROMISING MATERIALS FOR SODIUM BATTERIES

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Recently, sodium-ion batteries have attracted a renewed interest as a promising alternative to the widely used lithium-ion batteries. New perspective classes of polyanionic oxides are proposed as electrolyte and/or cathode materials for sodium batteries.[1-3] First-principles methods have been extensively used to predict the diffusion and intercalation mechanisms in Na-ion materials. In this work we present the results of ab initio studies of Na-ion diffusion in polyanionic molybdates with crystal structures of alluaudite, glazerite and NASICON. The density functional theory (DFT) calculations were performed using the projector-augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP). The ion diffusion barriers for sodium were calculated using the nudged elastic band (NEB) method.

For the first time, we calculated the electronic structure of alluaudite-type $Na_5R(MoO_4)_4$ (R = Sc, In) and $Na_{4-2x}M_{1+x}(MoO_4)_3$ (M = Cd, Mg, Zn, Mn, Fe, Co, Ni), glaserite-type $A_3Na(MoO_4)_2$ (A = K, Rb, Cs) and NASICON-type $Na_{1-x}Al_{1-x}R_{1+x}(MoO_4)_3$ (M = Mg, Co, Mn). For all molybdates, the electric field gradient (EFG) tensors were calculated on sodium nuclei, which are necessary for interpretation of the experimental ^{23}Na NMR spectra. The various occupancies of atomic positions were considered within the different structure models. The migration barriers for Na-ion were calculated for the various pathways in these molybdates and their strong dependences on the sodium positions, the type of metals and concentrations were established. Our results show that the alluaudite-type and NASICON-type molybdates are promising electrolyte and/or cathode materials for sodium batteries.

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This work was supported by the Russian Science Foundation, Grant No. 18-12-00395.

STRUCTURAL ORGANIZATION OF THE MESOMORPHIC “4-N-DODECYLOXYBENZOIC ACID : 4-PYRIDYL 4′-N-DODECYLOXYBENZOATE” SYSTEMS

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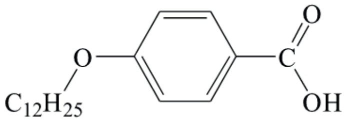
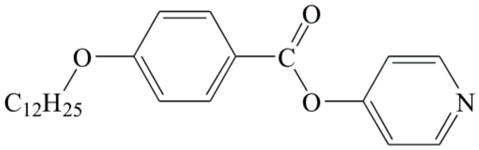
The mesomorphic and volumetric properties of the 4-n-dodecyloxybenzoic acid (A) and 4-pyridyl 4'-n-dodecyloxybenzoate (B) system were studied by the polarization thermomicroscopy and by the dilatometric method. IR spectra of individual A and B compounds as well as IR spectra of 2A:1B and 1A:1B systems were recorded.



4-n-dodecyloxybenzoic acid (A)



4-pyridyl 4'-n-dodecyloxybenzoate (B)

For the assignment of the experimental vibrational spectra a series of quantum chemical calculations of DFT(B97D)/6-311++G** level was carried out. Hydrogen-bonded complexes of types A•••A, A•••B, A•••A•••B and A•••B•••A that can be formed at different component ratios in system A-B were simulated. The geometric structure of these complexes was optimized and the vibrational frequencies were calculated.

It was determined that the IR spectrum of compound A corresponds to the existence of cyclic dimers A•••A$_{cycl}$, while in a system with a component ratio of 1A:1B, the complexes A•••B are formed. The analysis of the IR spectrum of the 2A:1B mixture led to the conclusion that the expected stoichiometric A•••A•••B, A•••B•••A and A•••A$_{op}$•••B complexes are not formed, and the 2A:1B crystalline system consists of rod-like complexes A•••B and A•••A$_{cycl}$ in the ratio 2:1.

The conclusions made basing the analysis of the IR spectra and the free energies of the possible processes are confirmed by the density measurement of the system A-B with different ratios of the A and B components.

Analysis of the obtained data shows that H-complexes of A•••B type are formed in the systems under study with an equimolar ratio of components; in other cases, there is a coexistence of two types of complexes A•••A$_{cycl}$ and A•••B in different ratios. Thus, conducted studies open up prospects for managing the process of obtaining cocrystals of a specified composition.

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THE RESEARCH OF PATTERNS OF CALCIUM IONS ADSORPTION BY MINERAL SORBENTS

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In order to use natural materials as carriers for the creation of friction anti-icing materials[1] were studied the patterns in the adsorption of calcium ions on inorganic sorbents of the Astrakhan region. There was found out that the adsorption equilibrium is satisfactorily described by the Freundlich isotherm. Graphical locating and theoretical calculating the constants lead to the conclusion that the greatest contribution to the limiting stage is made by the internal diffusion for marl and clay and the external one for the opal of marl type. The irreversible character of the adsorption of a certain fraction of calcium ions makes possible the assumption that the chemical interaction of sorbate ions with the surface of sorbents contributes to the overall rate of the process[2]. This is confirmed by the accordance in the experimental data to the Ho-McKay kinetic model (table 1).

Table 1. The adsorption characteristics of natural sorbents

Sorbents	Parameters						
	$1/n$	K_F	Q_∞^{exp}, mmol/g	$D{\bullet}10^3$, cm^2/min	B_i	k_2, g/ mmol•min	E_{act}, kJ/mol
Marl	1,1	64,1	0,245	0,14	275	45,48	38,22
Clay	1,2	2072	0,250	8,65	50	21,83	30,56
Opal of marl type	0,8	68,6	0,166	0,23	0,002	345,34	21,68

The obtained kinetic data including the kinetic equation of pseudo-second order, the low values of the activation energy in the diffusion process and the negative activation entropy values as well as the isosteric heat values, the results of calculations by the Elovich model, indicate the presence of sorbate-sorbate interactions, and the formation of intermediates.

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SYNTHESIS AND STUDY OF PROPERTIES OF WATER-SOLUBLE PHENYLOXY- SUBSTITUTED PHTHALOCYANINES

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The introduction of sulfo groups into the phthalocyanine molecule adds them solubility in water and expands the areas of its practical application. There are references in the literature about possibility of practical usage of water-soluble substituted phthalocyanines as catalysts1 for various purposes, photosensitizers for photodinamic therapy of cancer diseases2. Present work is devoted to synthesis and study of physicochemical properties of tetrasubstituted cobalt, copper and zinc phthalocyanines containing substituted sulfophenoxy- groups on the periphery.

The most effective method of phthalocyanines obtaining is nitrile one. In this cause, by the nucleophilic substitution of the nitro-group in 4-introphthalonitrile with biphenyloxy, 4-benzyloxyphenoxy and 2,4,5-trichlorophenoxy one's the corresponding phthalonitriles were obtained. At the next stage, by heating the resulting phthalonitriles with cobalt acetate at 190–200°C, the corresponding metal complexes were synthesized, which were further subjected to sulphonation with oleum or sulfochlorination followed by hydrolysis to sulphonic acids. Purification of the target compounds was carried out by column chromatography on silica gel M60.

The structures of all compounds obtained was confirmed by elemental analysis, MALDI-TOF mass spectrometry, ^{1}H NMR, IR and absorption spectroscopy.

The spectroscopic properties of compounds synthesized were studied in organic and water mediums. The influence of substituent nature and metal cation in the macrocycle on the type of electronic spectra and position of Q-band were revealed. The catalytic activity of the synthesized water-soluble complexes of cobalt in the oxidation reactions of DTC and 2-mercaptoethanol was studied. The catalytic properties of the studied compounds are compared with the influence of the nature of the terminal fragments in the phthalocyanine macrocyclic cycle.

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SEARCH AND RATIONAL DESIGN OF BIOCATALYSTS FOR CHIRAL AND FINE ORGANIC SYNTHESIS

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Enzymes are unique biocatalysts which permit to carry out of processes of chiral and fine organic synthesis with yield up to 99-100% and optival purity ee 99% and higher. Each process requires enzyme(s) with certain optimal properties. In our laboratory we carry out systematic studies for search and production of biocatalysts with desired properties. The first step includes “genome mining” of genes of enzymes of interest. In the next step gene is cloned and overexpressed in E.coli cells. After purification and characterization new enzymes are crystallized and 3D structure is solved using X-ray analysis. Data of structure analysis are used to select position ofr site-directed mutagenesis. The best changes are combined in multi-point mutants. Using this approach genes of formate dehydrogenases (used in chiral synthesis with oxidoreductases) from bacterium Staphylococcus aureus, yeasts Ogataea parapolymorpha and moss мха Physcomitrella patens were cloned and new biocatalysts with higher activity and improved thermal and chemical stability were created. Genome mining of yeasts Hansenula polymorpha resulted in cloning and preparation of three new D-amino acid oxidases (DAAO) and one D-aspartate oxidases. New DAAOs showed narrow spectrum of substrate specificity and the highest activity with D-Ala. For DAAO from yeast Trigonopsis variabilis (used in industrial process of preparation of 7-aminocephalosporanic acid from Cephalosporine C) structure analysis was used to produce multi-point mutans and it was shown that new mutant TvDAAOs have higher activity and stability compared to initial enzyme.

This work was funded by Russian Foundation for Basic Research grants 17-04-01469, 17-04-01487, 17-04-01662, 18-34-20098.

1-MORPHOLINO-2-CYANOETHYLENE IN THE SYNTHESIS OF AZOLO[5,1-C][1,2,4]TRIAZINES

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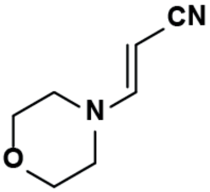
We have proposed a simple compound for the preparation of azolotriazines - 1-cyano-2-morpholinoethylene 1.



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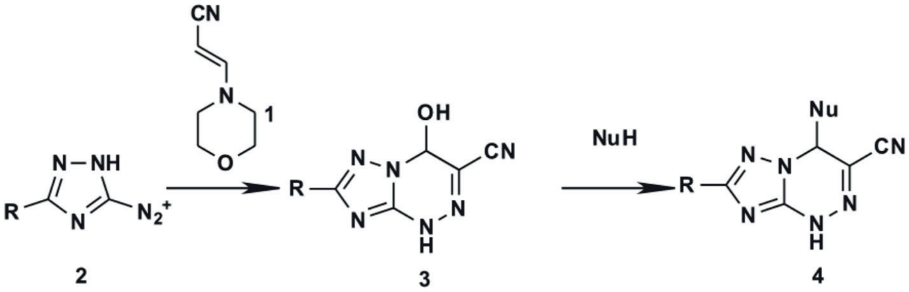
We have developed a new synthetic approach to the synthesis of cyanotriazolotriazines(3). Heterocycles 4 react with nucleophiles easily results in the formation of adducts 4.



R: H, SMe, Me, CF_3, Ph,

The hydroxy group in azolotriazines 4 is mobile, i.e. is easily replaced by C- or O-nucleophiles. This way, one can introduce additional pharmacophore groups that can make other kinds of biological action.

SUPRAMOLECULAR STRUCTURE OF THE BINUCLEAR OXOCHLORIDE CLUSTER $Li_8Ru_2OCl_{14}$ AND STUDYING OF THE WATER OXIDATION REACTION IN ARTIFICIAL PHOTOSYNTHESIS

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Artificial photosynthesis - a chemical process that biomimics the natural process of photosynthesis to convert water into H_2 and O_2 - is one of perspective methods of receiving renewable energy. We need highly effective catalysts for formation of molecular products (in addition to the division of photogenerated charges) for the organization of effective process of water decomposition. Complexes of Ru and Co attracts the attention of scientists now. Not only the nature of transition metal and its ligands environment, but also cations and acidity have an impact on efficiency and stability of complexes. The structure of the $Li_8Ru_2OCl_{14}$ ($Ru^{IV}Ru^{IV}$) is presented in this work. We have studied the reaction of self-reduction of the complex with formation of O_2 and also the reaction of water oxidation by Ce^{+4} as an one-electron oxidant. The last reaction was catalyzed by the cluster which is formed as a result of self-organization. Electrochemical researches of $Ru^{IV}Ru^{IV}$ behavior showed formation of a dimeric intermediate of mixed oxidation state with a ratio of the Ru^{IV}:Ru^{III} = 1:1 in the acidic environment (0.2-0.8 M of HCl). This intermediate decays into Ru^{IV} and Ru^{III} monomers. Its formation was excluded by increasing of HCl concentration to 2M and above. Kinetics of the self-reduction of Ru^{IV}-Ru^{IV} by coordinated water have been described by a bimolecular law with a reaction rate constant $k = 0.22$ l mol^{-1} min^{-1} up to 80 % conversion. That means that binuclear complexes self-organizes into the tetranuclear catalyst which oxides the water by tetra-electronic manners to O_2. The process of stoichiometric reduction is described by the equation: $[Ru^{IV}Ru^{IV}]_2 + 2\ H_2O \rightarrow [Ru^{III}Ru^{III}]_2 + O_2 + 4\ H^+$. ESI-mass-spectrum confirms the formation of a tetranuclear catalyst $[2H_2O{\bullet}Ru_4O_6(OH)]^{3+}$ with m/z = 553.29. The catalytic water oxidation by the one-electron oxidant $(NH_4)_2Ce(NO_3)_6$ in the coordination sphere of $[Ru^{IV}Ru^{IV}]_2$ also leads to the four-electronic oxidation of two water molecules into one oxygen molecule: $4\ Ce^{4+} + 2\ H_2O \rightarrow 4\ Ce^{3+} + O_2 + 4\ H^+$. The oxygen formation rate is high (turnover frequency TOF = 0.012 mmol / min), the turnover number of the catalyst during 3 h of the reaction TON = 260.

This work was performed in accordance with the state task of the Federal Agency for Scientific Organizations (no. 0089-2014-0024).

CHEMICAL TRANSFORMATIONS OF B-KETOESTERS OF HOMOADAMANTANE SERIES

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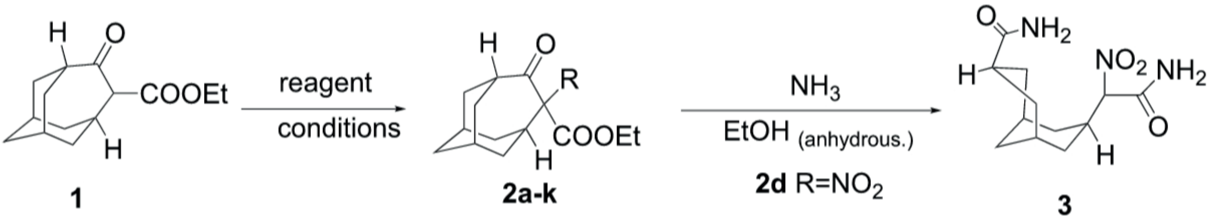
In order to synthesize 4,5-substituted derivatives of homoadamantane, it is convenient to use α-R-homoadmantan-4-ones as a starting material. Ethyl 5-oxohomoadamantyl-4-carboxylate (1) is the one of the most suitable substrate to reach that purpose.

The presence of the β-ketoester moiety in structure 1 means the ability for its facile and selective α-functionalization with the possibility of subsequent hydrolysis and decarboxylation.

A series of 4-R-5-oxohomoadamantyl-4-carboxylates (2a-k) was obtained by reactions of 1 with alkyl halides, Michael acceptors, halogens, etc. under basic or acid catalysis considering a number of features in the chemical behavior of 1. It is necessary to note the results of the transformations of 1 in nitrosation reaction, reactions with dichlorocarbene, and peracids with the formation of α-nitroxy (2a), α-dichloromethyl (2b), and α-hydroxy derivatives (2c), respectively.



R=ONO2 (**2a**), CHCl2 (**2b**), OH (**2c**), NO2 (**2d**), Br (**2e**), Cl (**2f**), CH_3 (**2g**), CH_2COOR (**2h**), CH_2CN (**2i**), CH_2CH_2COOR (**2j**), CH_2CH_2CN (**2k**)

Nevertheless, the study of nucleophilic cleavage reactions of α-R-keto esters of type 1 is even more promising, but it was not possible to carry out such transformations on α-R derivatives (2a-k) and on the 1 itself1 - the classical acid cleavage method leads to detachment of ester group in all cases. However, during the reaction of nucleophilic cleavage of the substituted β-ketoester - 4-nitro-5-oxohomoadamantyl-4-carboxylate (2d) in an alcoholic ammonia solution, the formation of *endo,endo*-bicyclo[3.3.1]nonane structure 3 was observed.

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OXIDATIVE PHOTOCATALYTIC NUCLEOPHILIC C-H FUNCTIONALIZATION OF AZINES

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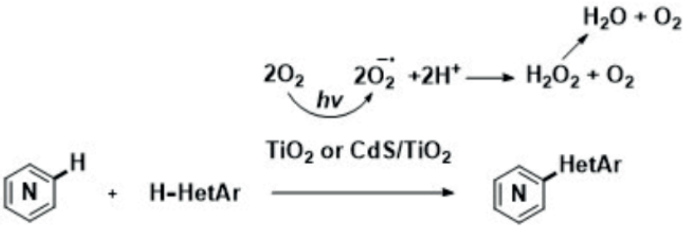
In the last decade, oxidative C-H functionalization has received particular attention, since the formation of new bonds in these processes occurs with high atomic efficiency, does not require the introduction of additional functional groups into molecules and the use of metal catalysis.

A variation of the non-metal oxidative functionalizations of the C-H bond in arenes and heteroarenes is the reaction of nucleophilic aromatic substitution of hydrogen (S_N^H reaction). One of the key issues in carrying out such transformations is the search for the optimal oxidizing agent, since not only the intermediate, but also the nucleophile are sensitive to oxidation.

We have investigated the possibility of using a heterophase photocatalytic system of air O_2 / TiO_2 catalyst / light irradiation in the oxidative C-H functionalization of azines with (hetero)aromatic nucleophiles. It is important to note that the presented transformations correspond to the signs of "green" chemistry: the absence of homocoupling products, the oxidizing agent — air oxygen, the by-product - water, easily separated heterophase catalyst. The method allows in mild conditions to obtain the biheteroaryls of interest to study of physiological activity.



This work was supported by the Russian Foundation for Basic Research, project 18-33-00927.

CRYSTALLIZATION-INDUCED EMISSION OF BORON DIFLUORIDES B-KETOIMINATES

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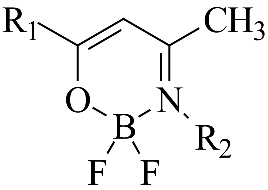
An important class of organic luminophores are β-ketoiminates of boron difluoride due to their ability to aggregate and crystallization-induced emission[1]. Aggregation-induced emission, which special case is crystallization-induced emission is a key phenomenon for overcoming of aggregation-caused quenching effect and obtaining efficient luminophores in the crystal state, that can be used as luminescent sensors and smart materials[2,3].

The comparative study of boron difluoride β-ketoiminates and their oxygen-containing analogs by the methods of stationary and time-resolved luminescence spectroscopy and quantum chemistry simulation has been performed.



The ability of boron fluoride β-ketoiminates with aromatic substituents in the α-position of the chelate cycle and small substituents at the nitrogen atom to crystallisation-induced emission, due to blocking of rotation of the aromatic substituent, has been revealed. The dependence of the quantum yield of luminescence of crystals on the nature of the substituent at the nitrogen atom has been established.

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This work was supported by Russian Foundation for Basic Research, (project No. 18-33-00281).

FEATURES OF THE FORMATION OF THE ADSORPTION CENTERS OF THERMALLY MODIFIED HIGH-SILICA POROUS GLASSES

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It is known that the surface of high-silica porous glass (PG) is a combination of Lewis and Brønsted centers with different pKa values, which characterize their acid-base and donor-acceptor properties[1,2]. For the directed synthesis of new composite materials with adjustable properties, for example, luminescent ones[3], information on the functional composition of the surface of the PG pores and the development of approaches to its regulation are needed. In the present work, high-silica PG obtained as a result of through acid etching of two-phase alkali borosilicate glasses of the composition (mol.%) (92-97) SiO_2, (0.2-0.6) R_2O (R = Na, K), (3-7) B_2O_3 were investigated. The porous structure of the PG plates was thermally modified at 120–750 °C. The study of surface active centers with various acidic forces was carried out by the indicator method4, based on the selective adsorption of acid-base indicators from aqueous solutions on the surface of solids. The parameters of the porous structure of PG were studied by the method of thermal desorption of nitrogen at 77 K using a specific surface analyzer Sorbtometer-M.

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The work was carried out under financial support of the Russian Foundation for Basic Research (project No. 18-03-01206).

STUDY OF COMPLEX FORMATION OF IONS OF SOME 3D-METALS BY CHELATE-FORMING SORBENT

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A complexing sorbent based on urea, formaldehyde and hydrazine hydrate (KFGG) was synthesized in molar ratios 1: 2.5: 1 of starting materials at a temperature of 80 ° C. The active functional hydrazogroup in the KFGG sorbent has a weak basic property than the amino group; in a weak alkaline and neutral environment, it exhibits reducing properties with respect to metals. As a result of studying the acid-base properties of the sorbent, it became known that at pH = 3.4-3.7, the medium of the hydrazogroup solution is protonized. In complex compounds of the sorbent in the spectral region at 1639 and 1550 cm^{-1}, a decrease in the vibration frequency by 25–32 and 22–48 cm^{-1} is observed. This is evidence of the coordination of the central atom through the atoms of carbonyl oxygen and hydrazone nitrogen. To determine the stability constant of the coordination compounds synthesized by complexing polyfunctional sorbents with some d-metals, potentiometric titrations were used.

Table. The results of the determination of the concentration stability constant of the synthesized coordination compounds

Metal	pH	[M], mcg / ml	[L], mcg / ml	lg[L]	$K_{stability}$, n=1	$lgK_{stability}$
Cu (II)	3,4-3,7	0,0016	$1,28\cdot10^{-4}$	-3,89	$5,48\cdot10^{4}$	4,74
Zn (II)	6,2-6,5	0,0019	$1,46\cdot10^{-5}$	-4,83	$4\cdot10^{5}$	5,6
Cd (II)	4,5-5	0,0017	$1,14\cdot10^{-4}$	-3,94	$5,93\cdot10^{4}$	4,8

SYNTHESIS OF (PYRROLIDIN-2-YL) PHOSPHINE OXIDES VIA REACTION OF CHLOROPHOSPHINES WITH 1-(4,4-DIETHOXYBUTYL) UREAS AND 1-SULFONYL-2-ETHOXYPYRROLIDINES

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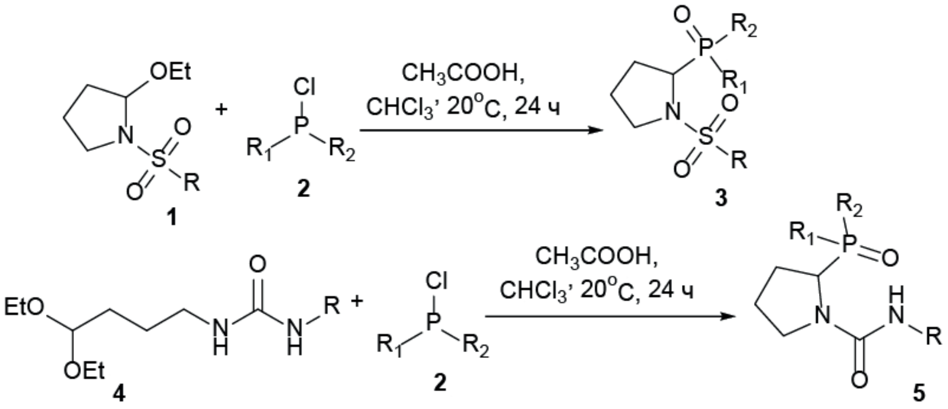
Pyrrolidine core is a structural motif of many biologically active compounds, both natural and synthetic. Considering this, it is not surprising that a lot of efforts devoted to the development of novel approaches to these compounds. Among them, pyrrolidine derivatives possessing phosphoryl moiety are of a special interest due to their unique biological properties.

We have developed a novel approach to the (pyrrolidin-2-yl) phosphine oxides 3,5 based on acid-catalyzed reaction of 1-(4,4-diethoxybutyl) ureas 4 and 1-sulfonyl-2-ethoxypyrrolidines 1 with chlorophosphines 2. The proposed approach benefits from mild reaction conditions, good yields of target compounds and readily available starting materials and catalyst.



The work was supported by a grant from the President of the Russian Federation for support of young Russian scientists (MD-585.2019.3)

NEW BRANCHED ORGANOSILICON PHOSPHORS: SYNTHESIS, STRUCTURE, OPTICAL PROPERTIES

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The development of optical chemical sensors for the determination of metal cations in aqueous media is a dynamically developing area of modern chemistry. At the same time, more and more attention is paid to the synthesis, the study of physicochemical properties and the use of compounds of the dendrimeric structure, due to the unique properties that such compounds possess. Of particular interest are the photochemical and photophysical properties of dendrimers.

In the present work, a series of photoactive organosilicon phosphors of a dendrimeric nature of various degrees of functionalization was developed. The composition and structure of the compounds obtained were established by modern methods. Optical characteristics were studied: absorption spectra, excitation spectra, and luminescence emission spectra were studied; sensory characteristics were investigated in relation to a wide range of metal cations; The methods of quantum-chemical modeling optimized the geometry and investigated the electronic structure of the ground and excited states of the compounds obtained.

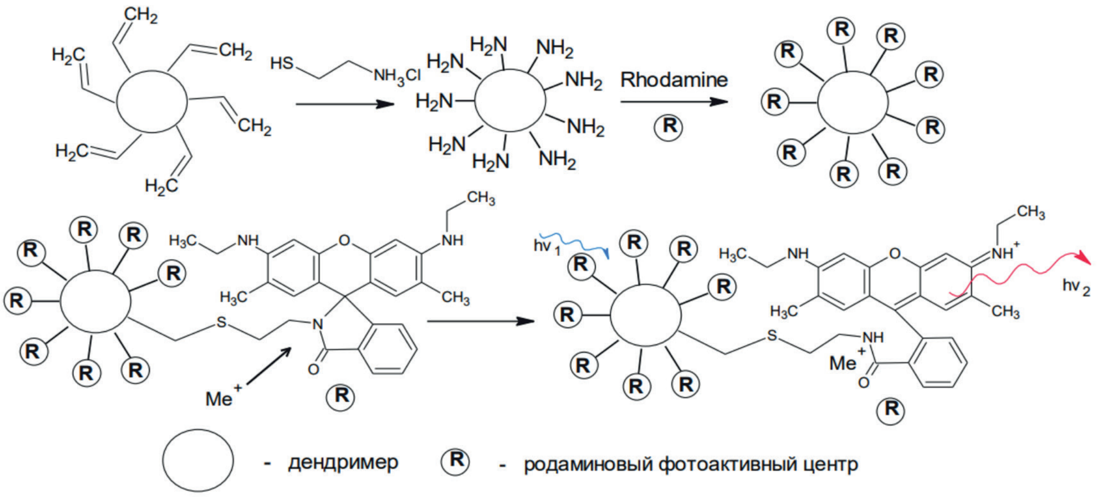

Figure 1. Schematic diagram of the synthesis and sensory properties of the obtained phosphors.

The reposted study was funded by RFBR according to the research project # 18-33-00459.

KINETIC RESOLUTION OF 2 PIPECOLINE WITH ACTIVE ESTERS OF (RS)-2-PHENOXYPROPIONIC ACID

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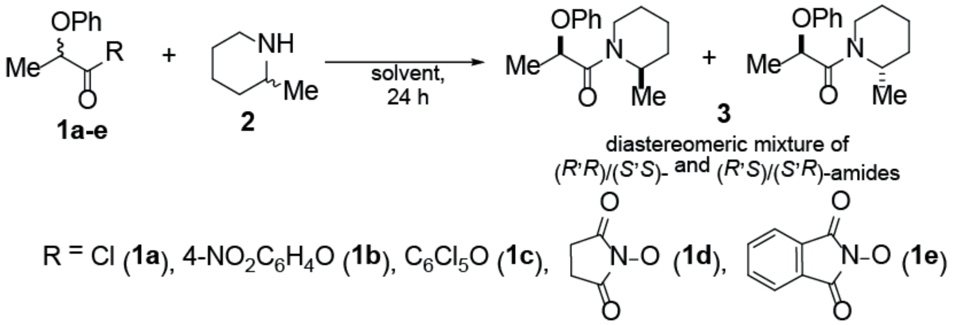
We have previously developed the methods for preparation of individual enantiomers of heterocyclic arylamines via kinetic resolution (KR) of their racemates with acyl chloride (R)-1a.[1,2] Unfortunately, this reagent turned out to be inefficient for KR of racemic alkylamines. In this work, we carried out mutual KR of (RS)-2-pipecoline (2) and active esters of (RS)-2-phenoxypropionic acid 1b-e during the diastereoselective acylation in toluene at +20°C. The reactions of amine (RS)-2 and esters (RS)-1b-e led to a mixture of (R,S)/(S,R)- and (R,R)/(S,S)-diastereomeric amides 3. A ratio of the formed amides, which is equal to the selectivity factor (s), was determined by GLC. It has been shown that the acylation with succinimidyl-2-phenoxypropionate (1d) proceeds most selectively (s 14). In order to select the optimum solvent, acylation of racemic amine 2 with racemic ester 1d was carried out in different solvents, such as C_6H_5Cl, CH_2Cl_2, $CHCl_3$, CCl_4, MeAc, MeCN, EtOAc, THF, Et_2O, and MeOH. The best stereochemical outcome was obtained in chloroform (s 19).



The obtained data indicate the prospects for using succinimidyl-2-phenoxypropionate (1d) as a chiral resolving agent for KR of racemic heterocyclic alkylamines.

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The work was financially supported by the Russian Foundation for Basic Research, grant 18-33-00027 mol_a.

SYNTHESIS OF 5-(4-ALKOXYPHENYL)-6-PENTAFLUOROPHENYL-2,2'-BIPYRIDINES

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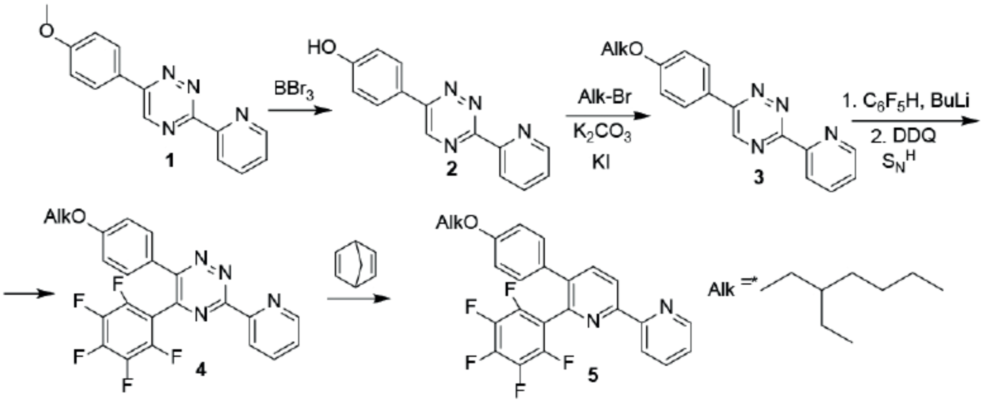
Organic compounds bearing long aliphatic chains in their structure are of interest for obtaining perspective liquid-crystal materials on their basis. In this study, a convenient synthetic approach towards 5-aryl-2,2'-bipyridines containing both pentafluorophenyl residue and the long aliphatic chain at the aromatic moiety has been developed.

6-(4-Methoxyphenyl)-3-(2-pyridyl)-1,2,4-triazine 1 has been chosen as The starting material. It has been found that removal of the methyl protection from the phenolic hydroxy group, alkylation reactions, nucleophilic substitution of hydrogen, and aza-Diels-Alder transformations, lead to bipyridines 5 bearing both pentafluorophenyl and aliphatic chain residues.



The structure of the product has been proved by the data of ^{1}H, ^{13}C, ^{19}F NMR spectroscopy, mass spectrometry, and elemental analysis.

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of a research project 18-33-00226.

ATOM-EFFICIENT APPROACH IN THE SYNTHESIS OF NOVEL POLYFTORARYAL HETEROCYCLIC LIGAND SYSTEMS

Varaksin M.V. ,[a,b] Nikiforov E.A.,[a] Moseev T.D.,[a] Gorlov D.A.,[a] Lavrinchenko I.A., Starnovskaya E.S.,[a] Kopchuk D.S.,[a,b] Chupakhin O.N.,[a,b] Charushina V.N.[b]

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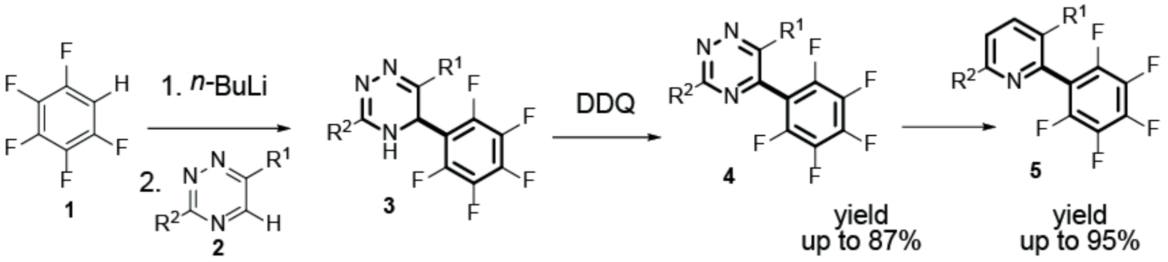
The use of effective pot, atom, and step economy (PASE) approaches in the synthesis of organic molecules has become one of the promising methodologies in modern organic synthesis. The unique properties of (poly)organofluorine compounds cause the wide distribution of the latter both in molecular electronics and in the development of modern instrumental methods for early diagnostics of socially significant diseases.

Among the known methods for constructing C–C bonds, the strategy of sequential reactions of nucleophilic substitution of hydrogen in 1,2,4-triazines (S_N^H) using pentafluorophenyl lithium 2 as a nucleophile (obtained from pentafluorobenzene 1 and n-BuLi) and aza-Diels-Alder reactions is most attractive in terms of compliance with the basic principles of green chemistry.



As a result, new pentafluorophenyl-substituted aza-heterocyclic derivatives of various structures that are of interest in the field of molecular electronics and coordination chemistry have been obtained. The synthesized pentafluorophenyl-containing ligands were then used in the synthesis of metal complexes with transition metals of various architectures.

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The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of a research project 18-33-00226.

NOVEL METHODS OF FUNCTIONALIZATION OF THE ISOXAZOLE RING BASED ON THE REACTION OF THE AROMATIC NUCLEOPHILIC SUBSTITUTION

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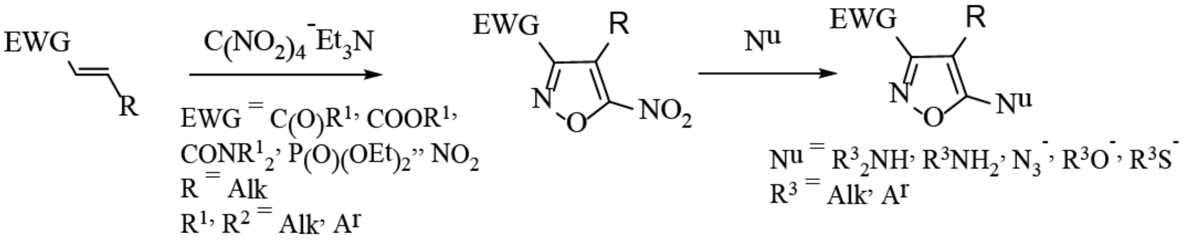
Recently we have developed the general synthetic approach to polysubstituted 5-nitroisoxazoles based on heterocyclization of electrophilic alkenes under the treatment of activated tetranitromethane (TNM) 1-3. Studying the reactivity of the 5-nitroisoxazoles bearing a variety of electron withdrawing functional groups, we have found that the nitro group can be substituted under the treatment of various N-, O-, S-nucleophiles. The reaction was found to be applicable to a wide range of 5-nitroisoxazoles substituents.



The elaborated novel methods of functionalization of the isoxazole ring can be used to obtain the libraries of compounds with promising biological activity.

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NOVEL FLUOROPHORES BASED ON 4-NITROISOXAZOLES

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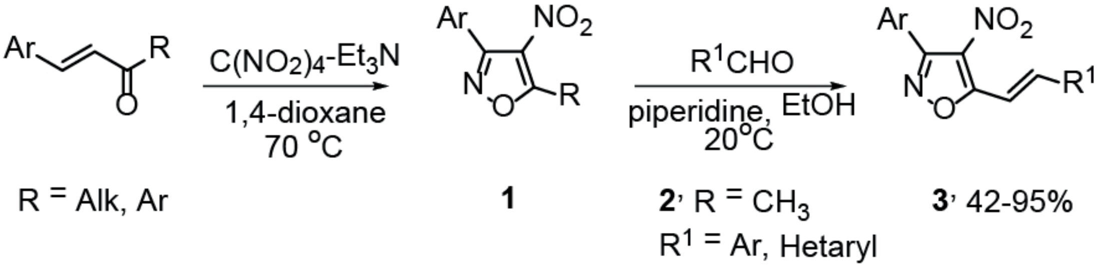
This work is a recent trend in research of our laboratory which concerns the development of methods for the synthesis and functionalization of the isoxazoles[1-3]. We have found that the heterocyclization of aryl substituted α,β-unsaturated ketones under the treatment of complex $C(NO_2)_4$-Et_3N proceeds with the formation of 3,5-disubstituted 4-nitroisoxazoles 1, which are interesting for the synthesis of previously unknown π-conjugated systems based on isoxazole with intramolecular charge transfer.



A series of 4-nitro-5-methylisoxazoles 2 was investigated in the condensation with aromatic aldehydes and the preparative method for the synthesis of novel type of isoxazole-based fluorophores has been developed. We have studied photophysical properties of the obtained π-conjugated heterocycles 3 and have found that reported structural type of the isoxazole derivatives possesses the emission wavelength maximum in the visible range of spectrum (λ^{em}_{max} over 600 nm).

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RELATIONSHIP OF THE PHYSICOCHEMICAL CONSTANTS WITH PERIODIC LAW

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Different relationships between the various physical and chemical properties of isostructural compounds take place according to the Periodic Law that is a fundamental basis of Chemistry. Previous review articles evidenced the relation of thermodynamic data with Periodic Law [1-4] and established a strict relationship between the enthalpy of formation, melting point and the atomic numbers of components in the semiconductor $A^{III}B^{V}$ phases, with diamond-like structure of sphalerite and wurtzite types. The proposed model was used for the critical assessment of the thermodynamic properties of isostructural compounds. The relationship between the reduced enthalpy ($\Delta_f H^o_{298}/T_m$), standard entropy (S^o_{298}), reduced Gibbs energy and the sum of the atomic numbers ($Z_i = Z_A + Z_B$) has been used for a critical assessment of the thermodynamic properties of $A^{III}B^{V}$ phases.

The Similarity Method was used for the critical analysis of specific heats $C^o_p(T)$ for solid state of the $A^{III}B^{V}$ isostructural phases. A critical analysis of heat capacities $C^o_p(T)$ was carried out for the pure elements of the Periodic System fourth group (C, Si, Ge, Sn) and isostructural phases $A^{III}B^{V}$ and $A^{II}B^{VI}$. It was found that the dependence of the heat capacities $C^o_p(T)$ from 0 to 1500 K follows certain regularity. Phases with the same sum of the atomic numbers of elements (Z_i), such as BN (hex) Z_i = 12 and glassy pure carbon Z = 6; BP and AlN (Z_i = 20); AlP (Z_i = 28) and pure Si (Z = 14); BAs and GaN (Z_i = 38); AlAs and ZnS (Z_i = 46); AlSb, GaAs, InP, CDs (Z_i = 64) and pure Ge (Z = 32); GaSb, InAs, and CdSe (Z_i = 82); InSb, CdTe (Z_i = 100) and pure grey Sn (Z= 50); have the same heat capacity experimental values of the solid state within the experimental uncertainty.

The second group is concerned of the rare earth metals and their compounds and the actinides. The "tetrad-effect" phenomenon was established and used for the analysis, correction and prediction of thermodynamic data for the lanthanide (Ln) compounds and the pure actinides (Ac). They are connected to the 4f-electrons of the lanthanide elements (Ln: La-Lu; their atomic numbers are 57-71) and 5f-electrons of the actinides with atomic numbers from89 to 102. The most sensitive to the tetrad-effect the thermodynamic functions of lanthanide and actinide compounds are standard entropies and entropies of formation, because they are the most susceptible to the influence of the 4f- and 5f electrons of the lanthanides and the actinides. We analyzed some classes of lanthanides with other elements of the Periodic Table, which account for only a sampling of the thousands of similar binary compounds possible. As an example, we use the tetrad-effect concept for the analysis and prediction of the standard entropies of the solid phases as the Ln2X3 (X=O, S, Se, Te) [5]. This approach can also be applicable to other classes of the Ln compounds as LnN, LnB_2, LnB_4, LnB_6, LnF_3, $LnIn_3$ [6, 7] and other compounds. Unfortunately, the actinides and the alloys on the base these elements are studied insufficiently, but it is possible to apply to them the same laws.

Keywords: Semiconductor (AII-BVI, AIV, AIII-BV) and lanthanide compounds, thermodynamic properties, entropy, Debye's functions, crystal structure, critical assessment, tetrad-effect

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SYNTHESIS OF NEW FUNCTIONALLY-SUBSTITUTED HETEROCYCLES WITH CARBAMATE FUNCTION

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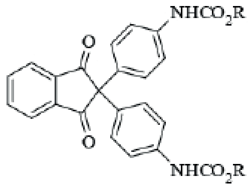
Based on ninhydrin, 2-hydroxy-2,2-biindan-1,1′,3,3′-tetrone and functionally substituted alkyl N-phenylcarbamates, new poly(hetero)cyclic compounds (1-9) were obtained.[1] The compounds obtained have a significant potential for biological activity, and can also serve as intermediates in the synthesis of new poly(hetero)cyclic compounds.



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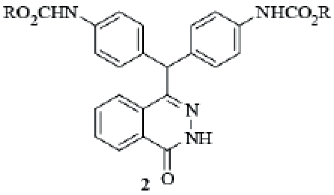

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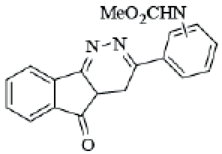

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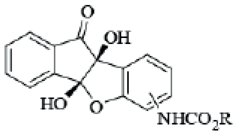

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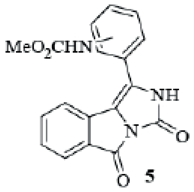

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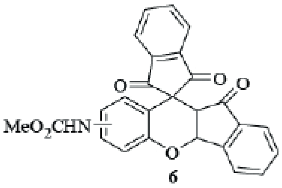

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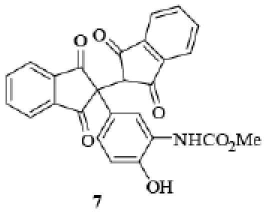

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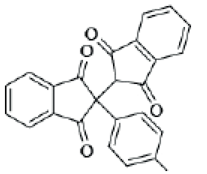

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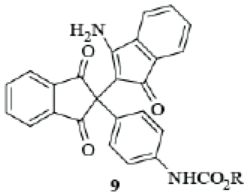

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The structure of the synthesized compounds was confirmed by IR, ^{1}H, ^{13}C NMR spectroscopy.

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THEORETICAL STUDY OF THE REACTIONS OF DIMETHYL (CHLOROETHYNYL)PHOSPHONATE WITH 5-METHYL-1,3,4-THIADIAZOLE-2(3H)-THIONE AND 1-METHYL-1H-IMIDAZOLE-2(3H)-THIONE

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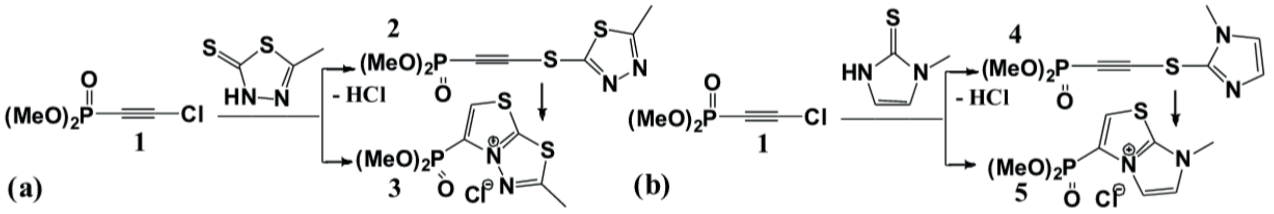
An original procedure for the synthesis of 3-phosphorylated N,S-heterocycles via the reaction of chloroethynylphosphonates with various thioazoles was described recently in paper[1]. We conducted a theoretical study of the reaction mechanisms of addition 5-methyl-1,3,4-thiadiazole-2(3h)-thione (scheme 1a) and 1-methyl-1h-imidazole-2(3h)-thione (scheme 1b) to the dimethyl (chloroethynyl)phosphonate 1 [DFT B3PW91/6-311++G(df,p)], the possible products of which are linear substituted ethynylphosphonates 2, 4 or bicyclic salts 3, 5.



Scheme 1.

Thermochemical parameters of the reactions were determined: for 2 ΔH_p 0.6 kJ/mol, ΔG_p 1.9 kJ/mol; for 3 ΔH_p 5.1 kJ/mol, ΔG_p 23.7 kJ/mol; for 4 ΔH_p 36.8 kJ/mol, ΔG_p 38.4 kJ/mol; for 5 ΔH_p 2.6 kJ/mol, ΔG_p 23.4 kJ/mol. Transition states of the transformation 2 into 3 (ΔH# 72.0 kJ/mol, ΔG# 85.0 kJ/mol) and 4 into 5 (ΔH# 61.3 kJ/mol, ΔG# 71.4 kJ/mol) were found. Probably, there is a synchronous process of the HCl elimination and internal heterocyclization, possibly with the participation of the solvent.

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CONFORMATIONAL ANALYSIS OF ORGANOPHOSPHORUS COMPOUNDS WITH P=SE AND P–SE BONDS IN SOLUTION. EXPERIMENT AND THEORY

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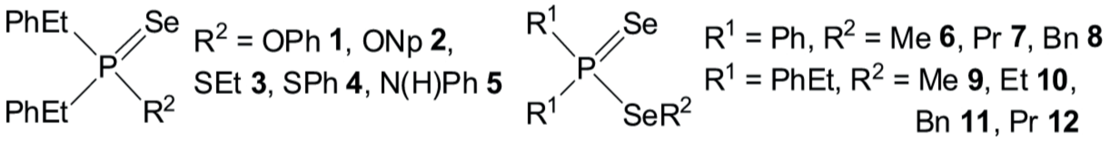
The derivatives of seleno- and diselenophosphinic acids have attracted considerable attention due to their applications as ligands, nanomaterials and drug intermediates, heavy metal extractants, and building blocks in synthesis.1

Experimental and theoretical conformational analysis of selenophosphinates 1-5 and diselenophosphinates 6-12 was carried out by the methods of dipole moments, IR spectroscopy, and quantum chemical calculations DFT in the gas phase and in benzene solution (B3PW91/6-311++G(df,p)+CPCM).



R^2 = OPh **1**, ONp **2**, SEt **3**, SPh **4**, N(H)Ph **5**

R^1 = Ph, R^2 = Me **6**, Pr **7**, Bn **8**
R^1 = PhEt, R^2 = Me **9**, Et **10**, Bn **11**, Pr **12**

Comparison of experimental data (dipole moments, IR spectra) and theoretical results for possible conformers 1-12 indicates that in solution these phosphinates exist as conformational equilibrium of several forms with staggered gauche- and trans- or eclipsed cis-orientation of the substituents located in the form of a propeller relative to the P=Se bond. In preferred conformers, the presence of cis-orientations is due to the formation of intramolecular H…Se bonds with the participation of one of the hydrogen atoms of thioethyl (3), Se-alkyl(benzyl) or phenyl (6-12) substituents at the phosphorus atom and the selenium atom of the P=Se group. For 1-12, experimental and theoretical data are in a good agreement. The CPCM model is the best choice for the calculation of the theoretical polarity for the substituted diselenophosphinates 6-12.

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N-DOPING OF CARBON NANOTUBES UNDER HYDROTHERMAL CONDITIONS

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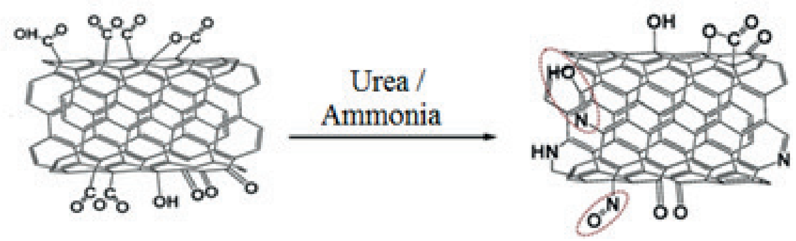
Special electrical, thermal and mechanical properties of carbon nanotubes (CNT) allow to use it in a wide variety of applications, including nanoscale devices and sensors, electronic emitters, supercapacitors, anode materials and membranes.[1] CNT's properties can vary depending on defectiveness of their structure and presence of functional groups or impurities. For example, CNT doped with nitrogen are studied for use in lithium-ion batteries, materials for hydrogen storage, nanocomposites, etc.[2]

The aim of the work was to identify the optimal parameters of post-doping (T,p), as well as to compare the efficiency of nitrogen introduction by using ammonia and urea under hydrothermal conditions.



In this work, the nitrogen-containing functional groups were introduced by hydrothermal treatment of CNT in ammonia and urea solutions. Various microscopic and spectroscopic investigations, including SEM, TEM, XPS and TGA, revealed the optimal temperature (220°C) and time (3 hours) of post-doping using both nitrogen agents. According to the XPS, the nitrogen content in doped nanotubes slightly increased during the transition from urea to ammonia.

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INTRAMOLECULAR N-ARYLATION OF HETEROCYCLIC IODONIUM SALTS

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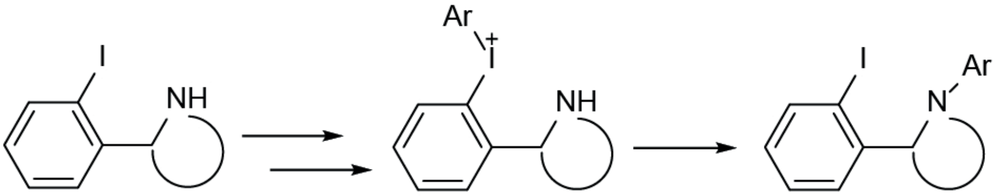
N-Aryl heterocycles, such as N-arylpyrroles, N-arylpyrazoles, and N-arylimidazoles, are considered to be an important and merit building blocks in pharmaceutical, biological, and material chemistry.[1-2]

Many efforts have been devoted to the development of new methodology for the C–N bond formation catalyzed by transition metals and without it. Among these, various progressive strategies of direct N-arylation of heterocycles have been realized using Pd- and Cu- catalyst systems in reaction with aromatic halogen compounds.[3-4] Meanwhile, it's worth mentioning that the arylation methods of N-heterocycles with aryl boronic acids have been discovered.[5]

Hypervalent iodine compounds are getting popularity due to the growing interest in the synthesis of environmental, non-toxic reagents for various selective transformations. These reagents have been applied in a wide variety of organic reactions, including N-arylation.[6-8]

We have developed a method of intramolecular N-arylation of heterocyclic iodonium salts through the intramolecular migration of an aryl radical. This method has significant synthetic potential in the preparation of N-substituted heterocycles bearing active iodine atom.



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ELECTRONIC STRUCTURE OF SR-DOPED LASCO3 UNDER H2 AND H2O UPTAKE

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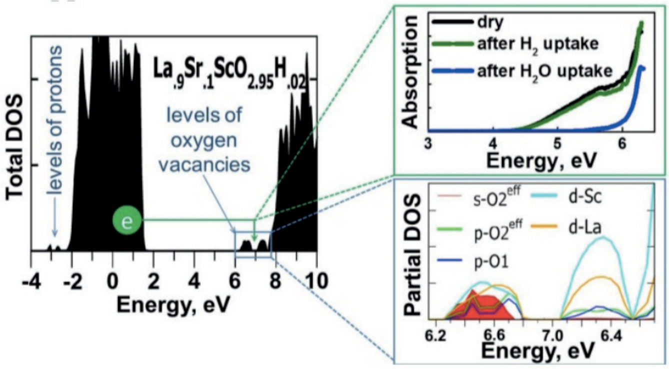
Sr-doped $LaScO_3$ is one of the perspective materials for application as electrolyte in various high-temperature electrochemical devices based on the effect of proton conductivity.[1-2] It efficiently uptakes protons from humid atmospheres, like water vapor (H_2O), and its electrochemical properties under this conditions are rather well studied.[3] Recently, using isotopic exchange method we have shown that it also uptakes hydrogen from dry H_2 atmosphere, however efficiency of such uptake in this case is about one order of magnitude lower.[4] In order to better understand mechanisms of proton uptake from H_2 and H_2O atmospheres in this oxide and in perovskite-type oxides in general, we have studied corresponding changes in the electronic structure in the vicinity of the band-gap of the Sr-doped $LaScO_3$. For this, methods of diffuse reflectance spectroscopy and coherent potential approximation (CPA) calculations were applied.



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INFLUENCE OF BOILING ON THE HIERARCHY OF RADICAL EXCHANGE AND RECOMBINATION UNDER RADIOLYSIS

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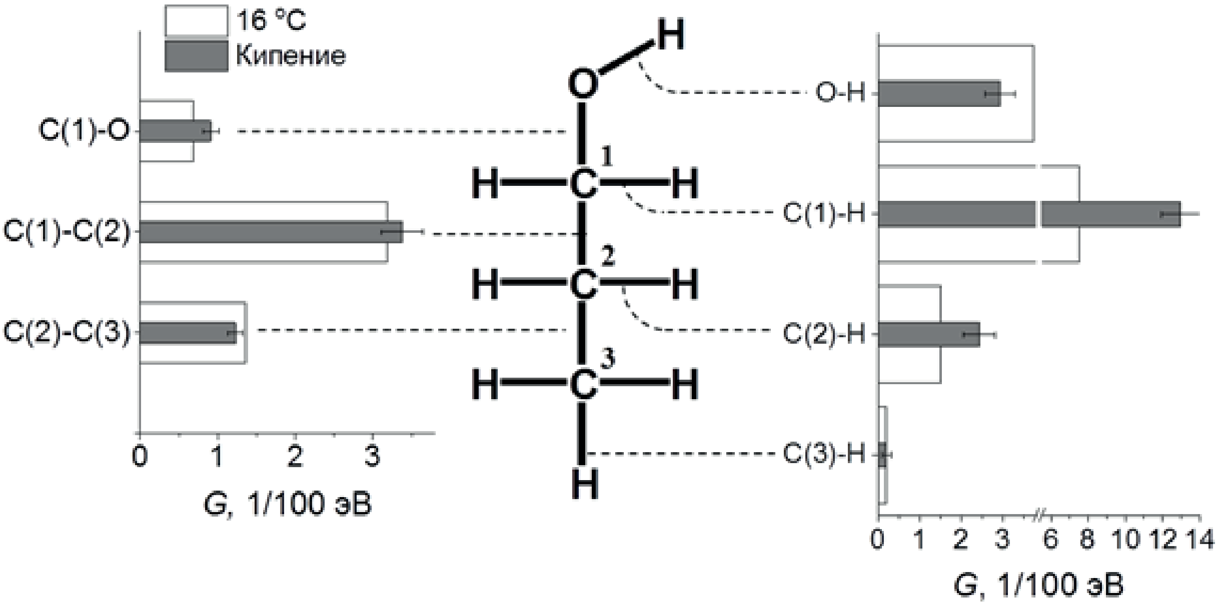
Boiling, being one of the extreme states, significantly affects the mechanism and hierarchy of chemical processes in a substance. In the present work, the radiolysis of oxygen-containing solvents (diglyme, n-propanol, acetone, methyl ethyl ketone and 4-methyl-2-pentanone) in a boiling state under the action of accelerated electrons was studied for the first time. Boiling increases the total yield of radiolytic cleavage of chemical bonds. For example, in n-propanol, there is an almost 1.5-fold increase in the yield (G) of cleavage of the C(1)-H and C(2)-H bonds:



The efficiency of radiolytic ionization and excitation of molecules depends little on temperature. As a consequence, the observed effect is due to a weakening of the cage effect, acceleration of the processes of radical exchange and an increase in the dissociation yield of certain primary radical-cations and radicals. An increase in the yield of H2 is observed, accompanied by an increase in the yields of products of a combination of heavy radicals, which indicates the appearance of additional H atoms due to thermal dissociation of intermediates. An increase in the total yield of heavy products and a decrease in the yield of light products suggests a beneficial effect of boiling on the combination of heavy radicals. Boiling weakens steric limitations and accelerates the structural relaxation of transitional complexes during the combination of radicals.

CROSS-COUPLING PROCESS INVESTIGATION BASED ON BIFUNCTIONAL CLOSO-DECABORATES

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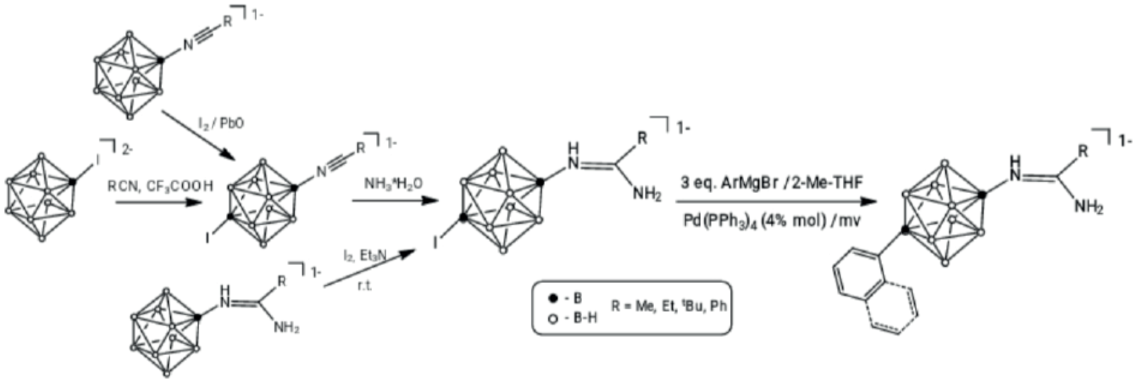
Series of amidine-iodine-*closo*-decaborates was synthesized and its reactivity under palladium catalyzed cross-coupling conditions was investigated.

Introduction of positively charged exo-polyhedric substitutes into boron carcass changes general charge of the system and electron density distribution in substituted *closo*-decaborates, which drastically affects reactivity of such compounds under conditions of further cross-coupling processes. Nitrile groups and its derivatives can be introduced into boron cluster to reduce the system charge. Under the conditions of Kumada reaction, it's impossible to use $[ee\text{-}B_{10}H_8I(NCR')]^{1-}$ (R' = Me, Et, ${}_t$Bu, Ph) anions due to electrophilic nature of nitrile group. Because of that we've synthesized series of iodine derivatives of closo-decaborates with general formulae $[ee\text{-}B_{10}H_8I(NHC(NH_2)R')]^{1-}$ (R' = Me, Et, ${}_t$Bu, Ph). Such second-generation *closo*-decaborates can be obtained either from iodine-closo-decaborates, unsubstituted amidines $[2\text{-}B_{10}H_9(NHC(NH_2)R'')]^{1-}$ or nitrile derivatives of *closo*-decaborate anion.



Further, disubstituted derivatives of closo-decaborate anion was introduced into palladium catalyzed cross-coupling reaction with Grignard reagents in ether solvents (THF, 2-Me-THF, 1,4-dioxane) in order to prevent oxidation side processes.

This research was supported by RFBR (17-03-01013 A) and Grant of the President of the Russian Federation 2403.2019.3.

INVESTIGATION OF THE HALOGEN EFFECT ON SELF-AGGREGATION OF PT (II) COMPLEXES BY NMR SPECTROSCOPY

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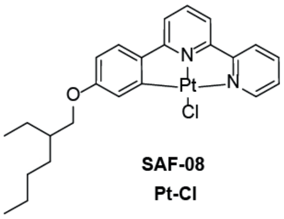
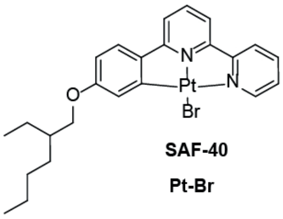
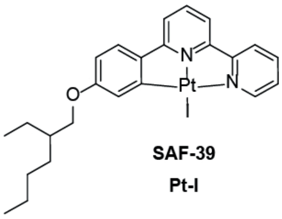
Square planar Pt(II) complexes are widely utilized in supramolecular chemistry due to their rich scale of useful and interesting properties[1-4]. In continuation previous work[5] we report the ^1H and ^{195}Pt analysis of self-association of three cyclometallated Pt(II) complexes (SAF-08, SAF-40 and SAF-39) of NNC type that have different halide auxiliary ligands.



SAF-08
Pt-Cl



SAF-40
Pt-Br



SAF-39
Pt-I

All complexes show concentration-dependent NMR spectra. Their self-association was studied by dilution method monitoring both the 1H as well as 195Pt nuclei. Both techniques show similar results validating that 195Pt NMR is an important methodology to study self-association of potentially any Pt complex regardless of the nature of the ligands. It was found that the nature of the halide auxiliary ligands does not significantly influence the aggregation of these complexes.

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A MECHANISTIC STUDY OF THE SONOCHEMICAL REACTION OF THE C_{60} AND C_{70} FULLERENES WITH ETHYLENE GLYCOL IN HETEROGENEOUS MEDIUM

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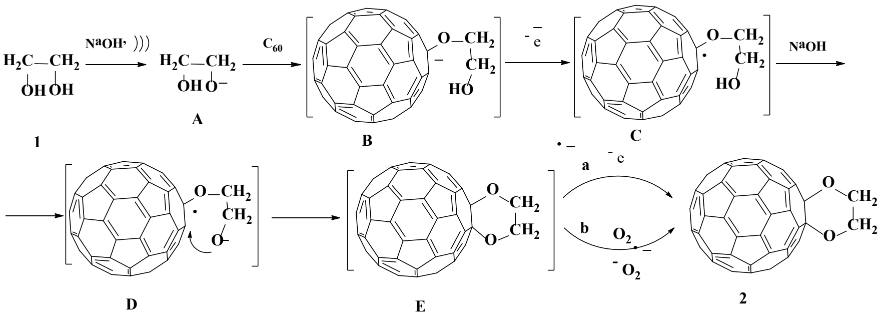
We have selectively synthesized the dioxane–C_{60} and dioxane–C_{70} monoadducts through the sonochemical reaction between the fullerenes and 1,2-diols in o-DCB in the presence of NaOH in heterogeneous medium.[1,2]

In the present work, we have performed a UV-spectroscopic/HPLC study of the kinetics and mechanism of the reaction underlying these syntheses on the example of the C_{60} interaction with ethylene glycol (o-DCB is a solvent). For this purpose, we have introduced to the reaction mix, the following inhibitors: hydroquinone, iodine, 2,2-diphenyl-1-picrylhydrazyl (DPPH) and Coppinger radical (galvinoxyl). The decay of the stable radicals DPPH and galvinoxyl was monitores spectrophotometrically as the lowering absorbance at intensities $\lambda_{max} \sim 520$ nm and $\lambda_{max} \sim 430$ nm, respectively. Depending on the nature of the inhibitor, the yield of the C_{60}–dioxane adduct 2 decreases to 30–60%. Herewith, the maximal inhibition is observed for the radical inhibitors (DPPH and galvinoxyl). The increase in polarity of the medium for reaction of C_{60} with 1 in the presence of NaOH reduces three times the reaction time (o-DCB:CH3CN = 1:1, 1 hour) but the bis- and trisadducts are formed in addition to monoadduct 2.

The states of several chemical bonds are simultaneously changed due to the redistribution of the electrons under this cycloaddition reaction, so the process is neither pure homolytic or heterolytic. Based on the experimental data above, we propose the mechanism of the formation of product 2 (Scheme). Here, NaOH in sonochemical reaction between C_{60} and 1 accepts the proton of the OH group. This facilitates the formation of alkoxide anion, a key intermediate of the reaction, which further leads to 2.



The contribution of path b (Scheme) of the transformation of E to 2 is negligible because the air oxygen has almost no effect on the yield. Thus, when the reaction is performed in argon, the yield reduces only by 5%. Obviously, C_{60} is the main electron acceptor in the reaction system as such electron transfer reactions are typical for fullerenes.

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The work is financially supported by the Russian Foundation for Basic Research (project number 19-03-00716).

NOVEL AMINO DERIVATIVES OF 1,10-PHENANTHROLINE-3,8-DICARBOXYLIX ACID

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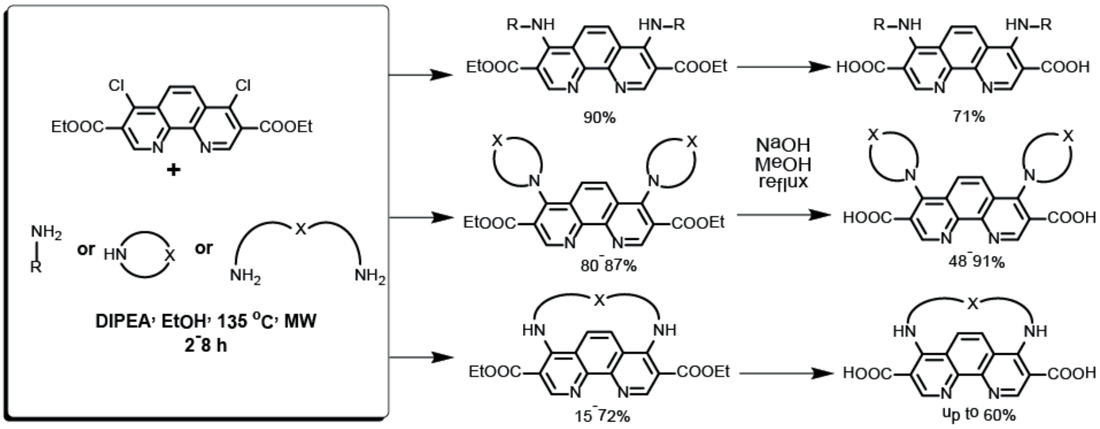
Metal-organic frameworks (MOFs) are of great interest due to their module structure and ample possibilities to achieve various properties of materials by varying their structural fragments. Among such materials UiO67 based on Zr and biphenyl-4,4'-dicarboxylic acid is well known[1].



In this work we studied the synthetic approaches to prospective building blocks based on 1,10-phenanthroline-3,8-dicarboxylic acid which is a geometric analogue of biphenyl-4,4'-dicarboxylic acid. For this purpose we investigated the non-catalytic amination of chloro derivatives of 3,8-di(carboxyethyl)phenanthrolines with various amines including di- and poly(oxa)diamines. The conditions for the synthesis of the primary and secondary amines derivatives were found, among them different macrocyclic ditopic ligands. The hydrolysis gave functionalized dicarboxylic acids for their further introduction into metal-organic frameworks.

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The work was financially supported by RFBR (project No 18-29-04030)

STUDY OF THE MECHANISM AND KINETICS OF OXIDATION OF FE2+ IONS BY LOW-TEMPERATURE PLASMA OF DISCHARGE

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The treatment of model solutions containing Fe(II) salts in the range of Fe^{2+} ions concentrations of 20-500 mg/dm^3 was carried out at the laboratory set of water purification by low-temperature plasma discharge during the registration of changes in the Red-Ox potential and pH of solutions, the Fe^{2+} concentration and the emission discharge spectrum. The ions concentration was measured by atomic absorption spectroscopy.

During the experiments, data on the residual concentration of Fe^{2+} from the time of exposure of solutions, which are curves characteristic of the development of branched chain reactions, were obtained:

$$n = \frac{r_0}{f\text{-}g} e^{[t(f\text{-}g)]}$$

(1)

where n – the concentration of active particles, f – the effective constant of the chain branching rate, g – the effective constant of the chain breakage rate, r0 – the chain nucleation rate. To explain the observed regularities, a possible mechanism of the oxidation process Fe^{2+}, including the branching stage (4):

O2 → $O^{\bullet}$ + $O^{\bullet}$ (2) $O^{\bullet}$ + H2O → ${}^{\bullet}OH$ + ${}^{\bullet}OH$ (4)
$O^{\bullet}$ + O_2 → O_3 (3) ${}^{\bullet}OH$ + ${}^{\bullet}OH$ + M → H_2O_2 + M (5)
${}^{\bullet}OH$ + $Fe^{2+}(H_2O)_n$ = Fe^{3+} + all possible reaction products (6)

Assuming the residual concentration is inversely proportional to the concentration of active particles (${}^{\bullet}OH$), therefore the equation (1) is the kinetic equation of the oxidation process. Indeed, the experimental points in the coordinates lnα-t, где $\alpha=(C_0\text{-}C_1)/C_0$ are approximated along lines at all values of $C_0(Fe^{2+})$ with slope angle tangent (f-g).

The study was financially supported by the Ministry of Education and Science of the Russian Federation. Unique identifier of the agreement RFMEFI58317X0068.

STUDY OF THE MECHANISM OF OXIDATION OF ORGANIC SUBSTANCES IN THE PLASMA OF A GLOW DISCHARGE WITH LIQUID CATHODE

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Oxidation of organic substances in a DC discharge between the electrode and the liquid surface is a promising object of study of interaction of intense energy fluxes with matter.

Deciphering the emission spectra of the discharge with a liquid cathode showed the presence of OH–radical emission bands and molecular nitrogen N2, as well as lines of atomic hydrogen H and oxygen O. Figure 1 shows the distribution of luminescence intensity of the main oxidizer - OH-radicals and N2 depending on the distance from the electrode to the surface of the liquid cathode containing 16.7 mmol/l 2-propanol.

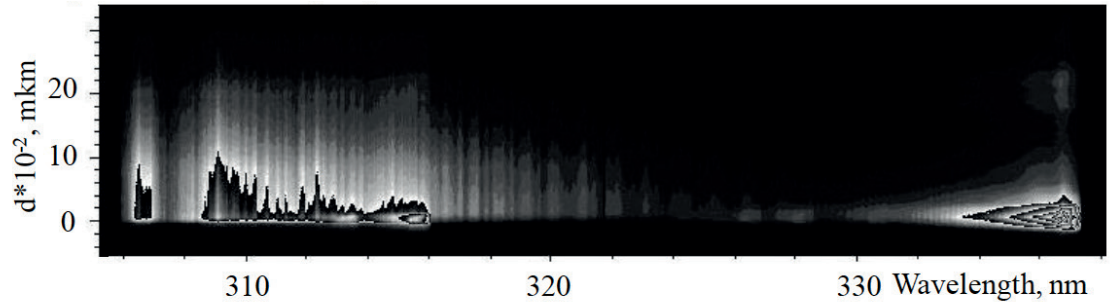
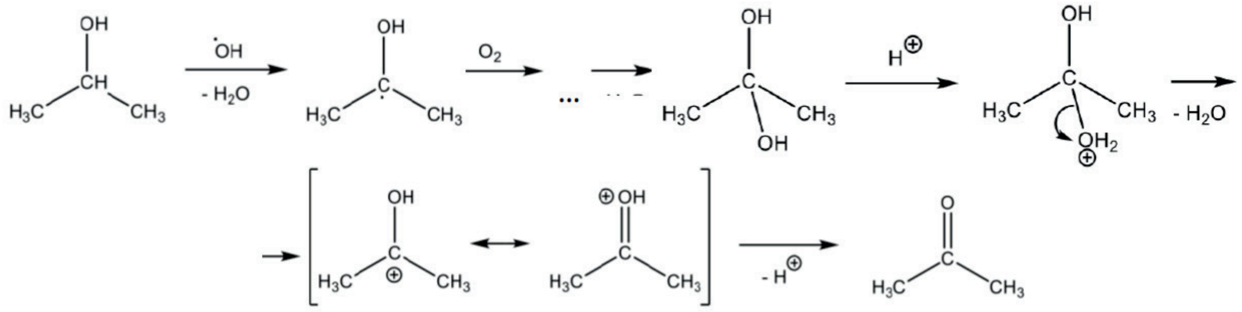


Figure 1. The luminescence intensity distribution of the bands of HE-radicals and N_2 (d is the distance from the electrode to the surface of the liquid; the discharge current 100 mA)

During the plasma-chemical exposure of the model solution by gas-liquid chromatography, a decrease in the concentration of 2-propanol and an increase in the concentration of 2-propanone and carboxylic acids were determined. The mechanism of radical oxidation at pH<7 is proposed.



This work was partially supported by the RFBR grant No. 19-08-00592.

IRON (II) IODIDE COMPLEXES WITH N-, P-DONOR LIGANDS: SYNTHESIS, STRUCTURE, MAGNETIC PROPERTIES

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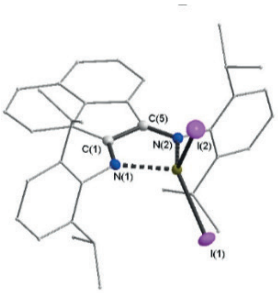
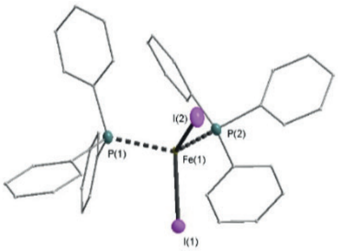
Recently, many polynuclear compounds with the properties of Single Molecular Magnet (SMM) have been obtained[1]. These complexes are mainly synthesized by the solvothermal method, which makes synthetic control impossible. In our opinion, a simpler approach is the synthesis of mononuclear compounds — their coordination sphere is easier to control. The first example of a monometallic 3d SMM was the high-spin iron (II) complex K[(tpa^{Mes})Fe][2]. Because of their specific electronic structure, iron (II) ions are promising for creating SMM on their basis.

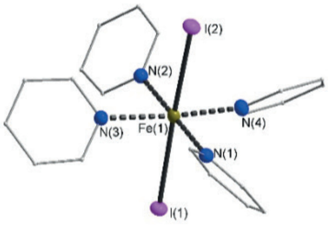
In this work, we describe the synthesis of a series of iron (II) iodide complexes with N-, P-donor ligands, describe their magnetic measurements, compare them with similar SMMs based on Co (II) nuclei[3].

Changing the ligands structure, we can control the coordination sphere of the iron (II) atom; we can also control the iodine-iron-iodine' angle.

Synthesis of complexes, their structure, magnetic behavior will be discussed in the report in details.







Acknowledgements
This work was financially supported by the Russian Science Foundation (project 19-13-00436).

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NI(II)-MEDIATED CYANAMIDE-PYRAZOLE COUPLING

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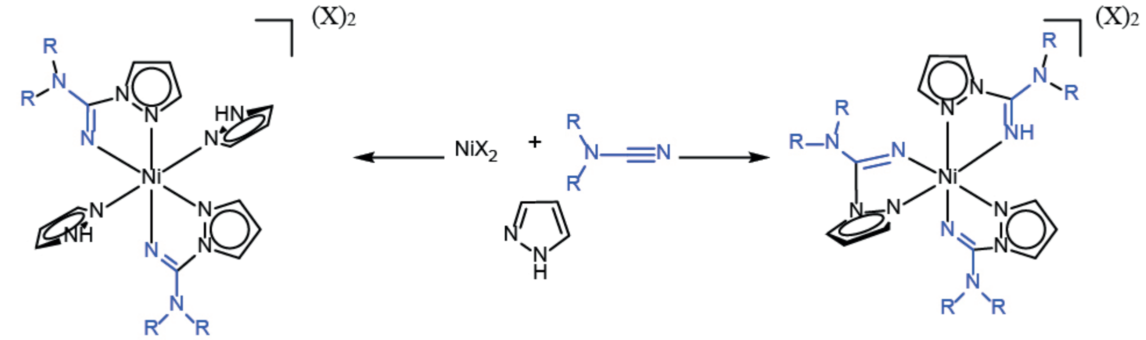
Chemistry of cyanamides attracts constant and non-decreasing attention for recent two decades due to pronounced ligand properties and enhances reactivity of NCNR.[1-3]. Commonly chemistry of cyanamide ligands is compared with widely applied nitriles, which coordination chemistry is well studied4. However, metal-activated nitriles and cyanamides could demonstrate differences in degree of activation and in composition of the products.

In continuation of our studies of nickel(II)-mediated reactions of cyanamides, we turned our attention to system nickel(II)/NCNR2/PzH (PzH – unsubstituted pyrazole) and found that cyanamides gave coordinated addition product {NH=C(NR2)Pz}Ni(II), similarly to conventional nitriles. However, under much milder conditions and using only stoichiometric amounts of reagents



R = Me, Et, $-(CH_2)_4-$, $-(CH_2)_5-$, $-[(CH_2)_2-O-(CH_2)_2]-$
X = Cl, Br, NO_3, ClO_4, OTf, OTs

Scheme 1. NI(II)-mediated cyanamide-pyrazole coupling.

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PHOSPHINE-CATALYZED CYCLOADDITION REACTIONS OF MBH-CARBONATES TO ADAMANTANE-CONTAINING MALEIMIDES AND ISOTHIOCYANATES

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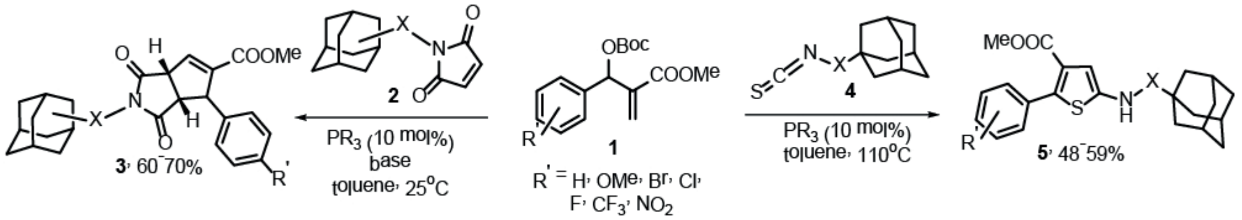
An important modern trend of the organic chemistry is the investigations of organocatalyzed cycloaddition reactions as this process proceeds under mild conditions providing high yields and enantioselectivity[1].



In this work we studied organocatalysis in the synthesis of polysubstituted heterocycles incorporating adamantane pharmacophore moiety. The phosphine-catalyzed cycloaddition reactions of Morita-Beylis-Hillmann (MBH) carbonates 1 to adamantine-containing maleimides 2 and isothiocyanates 4 were investigated. [3+2]-Cycloaddition reaction of MBH-carbonates to maleimides proceeds at room temperature in the presence of triphenylphosphine and small amount of sodium tert-butoxide giving bicyclic condensed compounds 3. Their yields strongly depend on the nature of substituents in starting compounds. The cycloaddition of the MBH-carbonates to isothiocyanates demands more harsh conditions and leads to substituted 2-aminothiphens.

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The work was supported by RFBR (project No 16-03-00349)

THE SYNTHESIS, PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF ZINC PHTHALOCYANINES BEARING DIFFERENT PHENYLPYRAZOLE HETEROCYCLES

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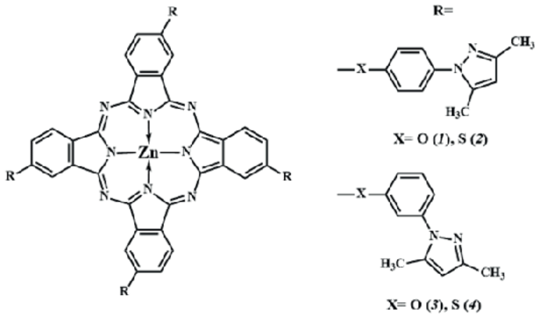
Phthalocyanines are used as traditional dyes and pigments and thanks to the unique physical and chemical properties, as photosensitizers for photodynamic therapy of cancer. The only a few works devoted to phthalocyanines and porphyrin containing pyrazole substituents are known.



In the work we report the methodology for the synthesis of new zinc phthalocyanines containing phenylpyrazole heterocycles with different linker heteroatoms and the position of the heterocycle. The spectral characteristics (aggregation, solvatochromic effects, thermal and photostability, quantum yields of singlet oxygen) of the compounds will be presented.

The work was performed in the framework of the basic part of the State contract with the Ministry of Education and Science (contract no. 10.7608.2017/8.9)

SYNTHESIS OF ACETYLENE ALCOHOLS BASED ON PHENYLACETYLENE AND SOME KETONES

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In world for synthesis of aromatic acetylene alcohols management of their physic-chemical properties, broadening of ranges of their using and elaboration of technologies of their production investigation are carried out by following priorital directions: using of nanocatalysts Et_2O+PhMe+Hex, $TiCl_4/Me_2S$, $Et_3N/Zn(OTf)_2$, $Ti(OiPr)_4$ and $Cl_2Ti(OPh)_2$ at synthesis of aromatic acetylene alcohols, using of waste of production at extraction oil and gas and chemical industry for aromatic acetylene alcohols production, elaboration and obtain of pharmaceutical products on the base of aromatic acetylenic alcohols new cross-linking agents and on base of vinyl ester polymers, resins, rubbers, nanomaterial's for molecular electronics.

In that work synthesis of new biologically-active acetylene alcohols containing in composition of their molecules aromatical, cyclical and hydroxyl-groups and also triple bond by reaction of enantioselective alkylation of some cyclic ketones such as cyclohexanon, 2-methylcyclohexanon, menton and camphora with phenylacetylene in the presence of 3,3′-diphenylbinaphtol has been investigated. New methods of synthesis of acetylene alcohols and mechanisms of corresponding reactions were preposed. Influence of nature of initial compounds, catalysts and solvents on carring out of reaction and yields of products has been determined. On the base experimental results optimal condition of carring out of reactions have been also determined. It was shown that in solution of TGF the mole ratio phenylacetylene: keton 1:2, temperatupe 0 oC, duration of reaction 120 min. are the optimal conditions of carring out of investigated reactions. Structure of synthesized alcohols:

1-(2-phenylethynil)cyclohexanol, 2-methyl-1-(2- phenylethynil)cyclohexanol,

2-isopropyl-5-methyl-1-(2-phenylethynil)cyclohexanol and 1,7,7-threemethyl-2-(2-phenylethynil) biciclo[2,2,1]-heptanol-2 has been proved and also their purity was determined by some physico-chemical methods.

Determination the most anticorrosion action of aromatic acetylene alcohols against microorganism cause biocorrosion of metal and steel equipment of processing of oil and gas.

This work was supported by the Ministry of Innovation Development of the Republic of Uzbekistan (CA6-001, 2016-2019).

SYNTHESIS AND STUDY OF PROPERTIES OF MIXED-SUBSTITUTED PHTHALOCYANINES CONTAINING TURT-BUTYL GROUPS

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Recent years, phthalocyanines have attracted much attention due to their potential usage as organic semiconductors, solar cells, liquid crystals and medicines. Since the first appearance of this macrocycle in 1907, a huge number of phthalocyanine derivatives have been synthesized. The nature of the peripheral substituents in the phthalocyanine molecule has an extremely strong effect on the basic properties of phthalocyanines, such as the state of aggregation, the intensity of light absorption in the visible range, thermal and chemical stability. Among the various substituted phthalocyanines, tert-butyl-substituted phthalocyanines are distinguished by their chemical resistance, versatility and high solubility, and also due to the fact these phthalocyanines exhibit a number of valuable applied properties, such as nonlinear optical [1], sensory (iodine [2] and toluene [3] definition), electrocatalytic [4] properties. By varying the nature of the peripheral substituents located in the phthalocyanine molecule along with tert-butyl groups and coordination metal in the macrocyclic cavity there is become possible to establish new patterns of the substituted phthalocyanines structure influence on their physicochemical properties, as well as to obtain compounds with potentially useful applied properties. In this regard, the purpose of this work is to synthesize and to study the physicochemical properties of metal complexes of octa-substituted phthalocyanines combining tert-butyl and nitro or phenylsulfanyl groups at the periphery.

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SYNTHESIS AND STRUCTURE MALONATE BIS(TETRAPHENYLANTIMONY)

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Carboxylates antimony(v) is the most characterized on the example of compounds of the general formula Ar_3SbX_2 and Ar_4SbX, where X is the residue of a monocarboxylic acid at the same time, the synthesis and structure organic antimony derivatives of dicarboxylic acids remains a little studied question organometallic chemistry, and therefore relevant[1].

We studied the interaction of bromide tetraphenylantimony with malonate silver (2 : 1 mol/mol) in toluene with heating according (60°C) to the scheme:

$2Ph_4SbBr + AgO(O)CCH_2C(O)OAg \rightarrow Ph_4SbO(O)CCH_2C(O)OSbPh_4 + 2AgBr.$

The output of malonate bis(tetraphenylantimony) 1 is 76%.

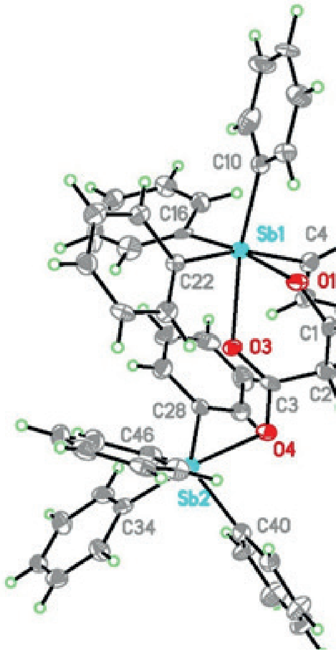

Figure 1. General view of the compound 1 molecule.

According to X-ray diffraction in compound 1 (Fig. 1) tridentate carboxylate ligand is chelated. The coordination number of the Sb1 atom in contact with the carbonyl oxygen atom increases to 6 (the Sb1–O3 distance is 2.362 Å), the Sb2 atom remains fivecoordinate, as a result of which the antimonium fragments have distorted octahedral and trigonal pyramidal coordination, respectively.

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IMPACT OF FLUORINE BY HYDROXIDE SUBSTITUTION ON PROPERTIES OF PHOSPATE APATITE SINGLE ION MAGNETS

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Single ion magnets – paramagnetic compounds that could possess a macroscopic magnetic moment without external magnetic field – are the subject of intensive scientific research because they can be used as a tiny magnets in spintronics or high density magnetic storage devices. Usually single ion magnets represent organic complexes of d- or f-elements with volumetric ligands and a minor part of them are d- or f-element paramagnetic ions inserted in inorganic matrix. We suggested phosphate apatites as a such matrix and demonstrated that it could be used for constructing of novel single ion magnets based on such metals as cobalt or dysprosium.

Phosphate inorganic matrix providing chemical and thermal stability also allows to dilute paramagnetic centers as well as tune the magnetic properties by changing the nearest environment of magnetic ions. So barium for calcium substitution leads to substantial growth of remagnetization energy barrier U_{eff} up to 1040 cm^{-1} in Dy containing phosphates. In this work we have investigated impact of fluorine by hydroxide substitution on magnetic properties of such compounds. Hydroxides are the second surrounding of magnetic ions and also could affect on their properties.

Dy containing calcium phosphates[1] as well as cobalt containing barium,[2] strontium and calcium[3] phosphates were investigated. All the series keep their magnetic properties so magnetic centers in such compounds are quite stable. Dy containing samples show a small growth of U_{eff} with fluorine introduction. U_{eff} of cobalt containing samples stay nearly the same after fluorine insert but the observed paramagnetic centers concentration falls substantially due to competition with fluorides for positions inside the trigonal channels. This effect also causes the disappearance of single ion magnet properties in strontium and barium compounds with very high fluorine and the smallest cobalt concentrations.

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ANISOTROPY OF ELECTRONIC CHARGE DENSITY IN MESOGENIC COMPOUNDS

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The most important components for the development of liquid crystal materials are cyanoderivatives of various chemical classes. Cyanogroup is a highly polar substituent with a dipole moment of $13.4 \cdot 10^{-30}$ C•m (when attached to the aromatic fragment). Therefore, the distribution of the electron charge density in the corresponding molecules is anisotropic. The degree of polarity of a molecule, as is known, is characterized by its dipole moment as a measure of asymmetry in the distribution of the molecular charge.

The table shows the modulus of the dipole moment vector and its projection on the axes of the Cartesian coordinate system for 4-n-pentyl-4'-cyanobiphenyl (BP5) and 4-pentoxy-4'-cyanobiphenyl (OBP5). They are calculated using the second order perturbation theory and density functional theory.

Table. Components of the dipole moment vector (D) of BP-5 and OBP-5 molecules

Method	µX	µY	µZ	µTot
MP2/ 6-31G(d, p)	6.131 -6.899*	0.641 -0.366*	0.675 0.096*	6.201 6.910*
MP2/ 6-31++G(d, p)	6.377 -7.133*	0.637 -0.367*	0.671 0.096*	6.444 7.143*
B3LYP/ 6-31G(d)	5.885 -7.042*	0.598 -0.217*	0.630 0.064*	5.949 7.046*
B3LYP/ 6-31G(d, p)	5.888 -7.038*	0.595 -0.218*	0.628 0.064*	5.951 7.042*
B3LYP/ 6-31++G(d, p)	6.211 -7.302*	0.604 -0.242*	0.637 0.069*	6.273 7.307*

* Data for OBP-5

The influence of the basis and the method of calculation is noticeable (perturbation theory leads to overestimated values, and an increase in the basis functions entails an increase in dipole moments), although there are no qualitative changes in magnitude, order and direction of the moment. Common to the methods is a significant dipole moment, indicating an anisotropic charge distribution in molecules.

QUANTUM-CHEMICAL EVALUATION OF THE POLARIZABILITY OF THE MESOMORPHIC COMPOUNDS

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Mesomorphic compounds are characterized by a set of physico-chemical parameters, such as phase transition temperatures, viscosity, elasticity, dielectric and optical properties.

In determining the optical activity and other optical properties of substances, polarizability plays an important role. It also largely determines the dielectric properties of substances, the magnitudes of dipole moments induced on the bonds by intramolecular electric fields created by a set of charges of the molecule. In many cases, the influence of substituents on the physico-chemical properties of molecules is also primarily due to their polarizability.

The components of the polarizability tensor (α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{yz}, α_{xz}) and the average polarizability of some liquid crystal molecules, calculated using the B3LYP / 6-31G (d, p) quantum chemical method, are listed in the table.

Table. Comparison of α polarizabilities of molecules

	α, B^3						α_{av}, B^3
	Compound	xy	yy	xz	yz	zz	
4-n-pentyl-4’-cyanobiphenyl	352.141	14.755	160.292	20.979	-18.555	115.953	215.188
4-pentoxy-4’-cyanobiphenyl	393.769	-12.121	177.927	0.007	0.008	92.446	217.345
4-propyl-4’-methoxystilbene	276.023	15.154	110.104	6.389	-3.444	96.764	160.998
4-propyl-4’-ethoxystilbene	277.341	-14.658	116.474	-9.135	-4.823	89.956	161.841
4-propyl-4′-cyanazobenzene	331.478	-7.090	155.431	0.115	0.038	56.645	181.138
4-ethoxy-4’-cyanazobenzene	335.589	17.724	121.648	1.329	-0.904	104.478	187.764

The highest values of polarizability are observed for molecules with a polar cyan group. An increase in the number of conjugated fragments in the examined molecules increases the average polarizability (exaltation of polarizability) and affects the molecular anisotropy of polarizability.

CLEAVAGE OF 2- (3-OXO-2-ARILILINDOLIN-2-YL)-2-ARYL-ACETONITRILES BY MEANS OF ALTERNATIVE METHODS OF ACTIVATION

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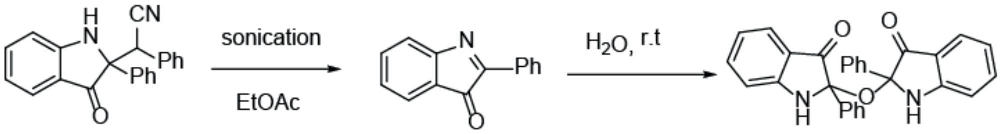
2-Phenyl-3H-indole-3-ones are attractive building blocks in organic synthesis. For example, in one of the last works[1] these compounds enter into condensation with various carbonyl compounds. Recently, we have found that 2- (3-oxo-2-arylindolin-2-yl)-2-arylacetonitriles are cleaved by ultrasound in ethyl acetate. The 2-phenyl-3H-indol-3-ones obtained in this way, when standing in solution, absorb water to form 2,2'-oxybis (2-phenylindolin-3-ones), the structure of which was confirmed using the XRD method. These semi-aminals are fairly stable during storage, but can be easily dehydrated under the influence of various reagents, which opens up possibilities for further transformations.



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This study was performed under financial support by the President of the Russian Federation (program for state support of young Russian scientists—Candidates of Sciences, project no. MK-3089.2018.3)

THE SYNTHESIS OF 1,3-OXAZOLIDINES AND 1,4-DIHYDRO-2H-3,1-BENZOXAZINES CONTAINING (η6-ARENE)TRICARBONYLCHROMIUM GROUP

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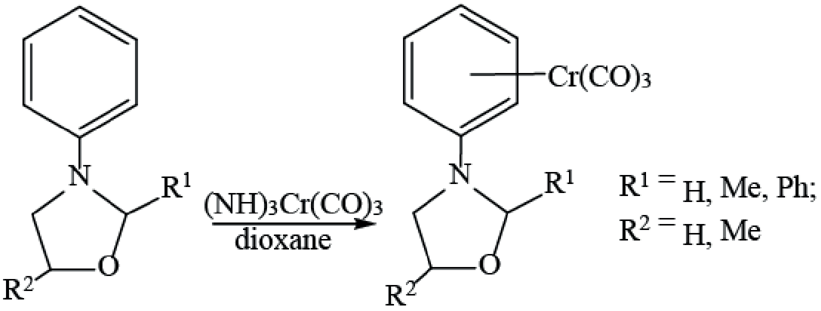
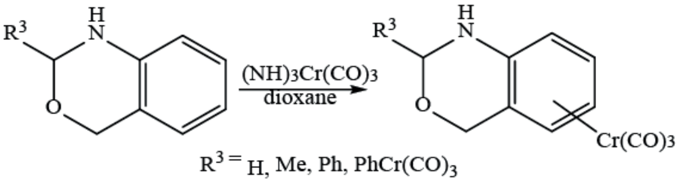
The synthesis of transition metal complexes with N,O-heterocyclic ligands, such as 1,3-oxazacycloalkanes, is interesting both for applied and fundamental chemistry. The most perspective method for the synthesis of such π-complexes is the direct reaction of aromatic derivatives of 1,3-oxazolidines and 1,4-dihydro-2H-3,1-benzoxazines with $(NH_3)_3Cr(CO)_3$. As known, interaction of oxazolidines with carbonyl complexes leads to the opening of the heterocycle and the formation of n-donor type coordination compounds. We found that $CH_3C(O)$-, t-$C_4H_9OC(O)$-; a good protecting group is also a phenyl group. The complexation reaction with $(NH_3)_3Cr(CO)_3$ gives high yields of π-arene derivatives.



In the case of benzoxazines, due to the presence of conjugation, the process leads to the formation of π-complexes with absence of protective groups at the nitrogen atom.



The obtained products after isolation and purification were characterized using HPLC, UV-, IR-, ^1H NMR-spectroscopy, mass-spectrometry and X-ray diffraction.

COMPLEXES FE(II) AND FE(III) WITH BIBENZIMIDAZOL

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Bibenzimidazol and its complexes, as analogs of natural compounds, show biological activity.

In this work, formation of iron(II, III) complexes with 2,2'-bibenzimidazol (BBI, H_2X) in solution was investigated, and complexes were isolated as solids.

For researching complex formation in solution, electrometric and conductometric methods were used.

The method of electrometric titration (EMT) confirmed existence of complex formation in the Fe(II)–BBI–H_2O–DMFA and Fe(III)–BBI–H_2O–DMFA systems, since titration of BBI in the presence of iron(II, III) salts showed considerable shift of titration curves to acidic area as compared to the titration curve for BBI. With the use of the BBI EMT curve, step constants of acidity were calculated for H_4X^{2+} ($K_{a,1} = 5{,}93\cdot10^{-3}$; $K_{a,2} = 2{,}21\cdot10^{-3}$; $K_{a,3} = 6{,}35\cdot10^{-12}$; $K_{a,4} = 1{,}93\cdot1^{0-13}$). From titration curves for the solutions containing mixtures of BBI with metal salts, stability constants (table 1) were calculated.

Table 1. Logarithms of stability constants

	lgβ	
	$[M(H_2X)_3]$	$[M(HX)_3]$
Fe^{3+}	11,81	30,15
Fe^{2+}	11,96	19,09

Dependence of capacity for the iron(II) and iron(III) systems vs. BBI concentration showed formation of complexes with the metal : ligand ratio of 1 : 1 and 1 : 3 for Fe(II), 1 : 1 for Fe(III).

Conductometric titration of solutions of metal salts with the neutralized BBI solution confirmed formation of the Fe(II)–BBI complex with the 1 : 3 ratio and revealed formation of the iron(III) complex with the 1 : 2 ratio.

For preparing solid complexes, reagents were kept for several hours at 80–85°C in a DMFA–water solution. The resulting crystals were filtered off and washed with water. The composition was confirmed with the use of IR- and mass-spectroscopy methods.

HYDROXYETHYLENE DIPHOSPHONIC ACID IN REACTIONS OF THE COMPLEX FORMATION WITH REE

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The study of the complexing properties of organophosphorus ligands with rare earth elements (REE) is performed for selecting extractants for the separation of REE with similar properties.

In this work, we studied the processes of the complex formation of oxyethylenediphosphonic acid (HEDP, H_5X) with the Y^{3+}, Ce^{3+} and Eu^{3+} ions in an aqueous solution.

Potentiometric titration curves ($pH = f(a_{NaOH})$) of mixtures of ligand with metal salts are shifted to a more acidic region relative to the HEDP titration curve, which is evidence of processes of complexation in the systems under study. Complexation begins at pH = 2.5 and ends at pH = 11.0 - 12.0 in all three systems.

To determine the composition of the complexes, the methods of potentiometric (with EMF measurement) and conductometric titration of the metal with a ligand were used. In all three systems, the formation of complexes of the same metal: ligand ratio 1 : 1 was found.

Table 1. Logarithms of the stability constants of HEDP complexes with REE

	Y^{3+}			Ce^{3+}			Eu3^{+}		
Measured parameter	pH[1]	EMF[2]	Electrical conductivity[3]	pH[1]	EMF[2]	Electrical conductivity[3]	pH[1]	EMF[2]	Electrical conductivity[3]
$[MeH_3L]^+$	2,38		2,30	2,37		2,25	2,36		2,24
$[MeH_2L]$	4,34	4,00		5,88	4,24		5,02	4,00	
$[MeHL]^-$	5,12			6,38			5,65		
$[MeL]^{2-}$	5,54			6,47			6,83		

For all obtained titration curves, the stability constants (Table 1) of the resulting complex particles were obtained using the three calculation methods.

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QUANTUM THEORY OF STRUCTURE OF ATOM OF HYDROGEN

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Oscillation and wave processes can be described by identical equations following the law of harmonic motion, but a separate particle cannot spread as a wave, it can only oscillate. The oscillating body (particle) placed in a resilient environment creates in it indignations or deformations, spreading in this environment as waves. Therefore, the question asked by Louis de Broglie about the presence of wave properties in a separate particle was not correct. Due to this, debates have gone on over for 90 years about the correctness of solutions given to Schrödinger's equation for the description of motion of an electron in the atom of hydrogen. The opponents of young physics asserted that all these objects conflicting with good physical sense were simply the result of imperfection of mathematical formulae, (i.e. the equation itself). So, in many works a strange solution to Schrödinger's electron-equation showing the superposition of two flat monochromatic waves of identical frequency, spreading in opposite directions. Furthermore, in its final form Schrödinger's equation usually will be transformed to this:

$$\nabla^2 y + \frac{8p^2 m}{h^2} E_k y = 0$$

and fully identically to that gotten by the author1 for a photon the model of which appears to consist of two differently charged particles. Experimentally, it appears as if, the presence of wave properties was confirmed even in single electrons that are flying through two cracks. To add to this, a separately flying electron was seen either behind one or the other crack, but not simultaneously before two. Thus, on the screen an interference picture was demonstrated, seemingly confirming the wave properties of electrons. It is related to the fact that around electrons there is an electromagnetic photonic field1. Therefore, an electron does not possess wave properties, but it can create a wave in the surrounding electromagnetic field if its photonic field co-operates with the environment around it. The front of the solitonic wave formed by it in the electromagnetic field passes through both cracks and creates an interference picture. Thus, the application of Schrödinger 's equation to the electron of the atom of hydrogen is a fundamental error in physical and chemical sciences.

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DINITRONES IN THE SYNTHESIS OF POLY(METHYL METHACRYLATE)

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The development of new and improvement of traditional methods of the synthesis of macromolecules in recent decades has led to the possibility of obtaining polymers of the most diverse chemical structure. Among the developed technologies, controlled radical polymerization has occupied key positions in the creation of polymers with a specific architecture.

In this regard, the purpose of our work is to develop a new approach to the controlled synthesis of poly(methyl methacrylate) (PMMA) in the presence of small amounts of acrylonitrile (AN), vinyl acetate (VA) and styrene (ST) comonomers and sources of stable nitroxyl radicals: C-glyoxal N-methyl nitrone (MDN), C-glyoxal N-tert.-butyl nitrone (BDN), C-glyoxal N-phenyl nitrone (PDN). The influence of the nature of the second monomer, the steric factors of the dinitrone substituents, and the temperature condition on the patterns of PMMA synthesis is analyzed.

It has been established that in the case of homopolymerization of MMA in the temperature range of 70–110° C, the introduction of dinitrones as sources of nitroxyl radicals leads to the regulation of kinetic parameters, a decrease of the molecular masses and polydispersity of PMMA. However, the polydispersity index is about 2.0, which is caused by the prevalence of disproportionation reactions between growth radicals and nitroxyl radicals.

To reduce the contribution of disproportionation reactions, the MMA polymerization process was carried out in the presence of small amounts of second comonomers (AN, VA, ST) in a ratio of 91:9 mol.%. It allowed improving the molecular weight characteristics of poly(methyl methacrylate). It has been shown that the structure of nitrones, which are the sources of stable nitroxyl radicals formed in situ, plays the primary role in the synthesis of narrowly dispersed PMMA. Thus, in the case of the most spatial phenyl substituent, the Mw/Mn value is not lower than 2.0. The samples with a polydispersity of 1.48 were synthesized in the presence of nitrones with methyl and t-butyl fragments in the structure.

This work was supported by the Russian Foundation for Basic Research, project №17-03-00498.

NEW SYNTHESIS OF 1,2,4-TRIAZOLE-CONTAINING HETEROCYCLES BY REACTION OF ACTIVATION OF ALIPHATIC NITROCOMPOUNDS IN PPA

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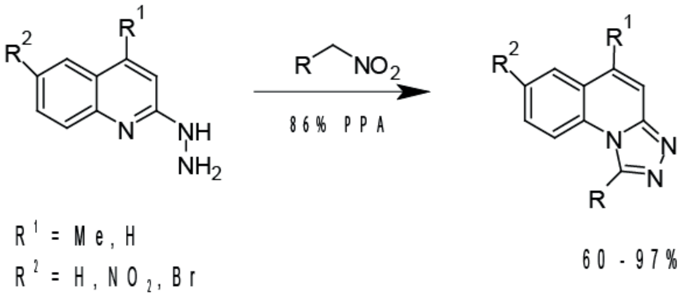
Our recent studies of a reaction of hydrazides of carboxylic acids with nitroalkanes in polyphosphoric acid (PPA) led to the discovery of an efficient synthesis of 2,5-disubstituted 1,3,4-oxadiazoles with excellent yields1.

In this work, we attempted to transfer this reaction to 2-hydrazinoquinolines derivatives, which led to a new efficient synthesis [1,2,4]triazolo[4,3-a]quinoline (Scheme 1).



Scheme 1.

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This work was financed by the Russian Foundation for Basic Research (grant #18-33-20021 mol_a_ved)

INFLUENCE OF ULTRASOUND AND COMPOSITE FLOCCULANTS ON THE STABILITY OF MONTMORILLONITE HYDROSUSPENSION

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Water-soluble polymers are widely used to regulate the stability of dispersed systems – for flocculation of dispersed phase particles at low concentrations of water-soluble polymers or, conversely, to stabilize the system at their high concentrations.This report discusses the results of a joint study of mechanical action, the effect of electrolyte and surfactant on the effectiveness of the water-soluble polymers flocculating action on the montmorillonite hydro suspension1.

Used: colloidal fraction of Na-montmorillonite Taganskogo field (East Kazakhstan), polydimethyldiallylammonium chloride, chitosan, notredameuniversityi. The kinetics of flocculation was studied by optical method, determining the number R proportional to the number of elementary particles in the aggregate (floccule)2.

It was found that the units formed under the action of NaCl and CaC are destroyed by ultrasound treatment (ultrasonic bath Tesla, Austria). This is manifested in the mixing of the differential curves of the size distribution of aggregates in the region of small sizes.

The kinetic dependence of R shows that the chitosan with more than Polydimethyldiallylammonium chloride, speed flocculent particles montmorillonites, although both polyelectrolyte eventually form floccule with the same degree of aggregation of the particles (R). Flocculating action Polydimethyldiallylammonium chloride and Chitosan in the presence of Ca , thus reducing the negative potential of the colloidal particles of montmorillonite are enhanced with the addition of NaДДБС. This is a consequence of NaДДБС with cationic polyelectrolytes, the decrease of the electric charge and the compaction of the macromolecules.

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EXTENDED OUTLOOK ON DEFECT'S CONCEPTION TOWARDS SPECIFICITY OF PROTON TRANSFER

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"Grotthuss mechanism of proton conductivity" like "Frenkels defect pair" are widely used definitions in the literature on Ionic Process different kinds. Although they are appeared 212 and 93 years ago correspondingly, and, moreover, initially have related to distinguished phase states (liquid or solid), at present the evident community of Grotthuss and Frenkel conceptions seems attractive to understand the phenomenon of proton transfer in different forms. Such conclusion could be received from two point of view: as historical as well physical ones.

1. History of the interest in ionic conductivity in condensed matter has arisen more than 250 years ago after pioneering Volta's discovery of the electrochemical cells, based on systems metal-electrolyte. The absence of charged particles in liquid water needed an answer on 'simple' question: "What happens at water electrolysis?" The pioneering creative idea on the heteropolar dissociation was advanced, as it is universally recognized, by Theodor Grotthuus [1,2]. However, it has turned out, that main physical reason for the dissociation is the interaction of ions and molecules inside liquid phase. Main questions was to understand how and why atoms (or ions) could migrate inside strongly ordered lattice. Nobelist W.Röntgen proposed for A.Joffe (from St-Petersburg) to study experimentally the conductivity of any solids (1904 year, Mũnchen Univ.) [3]. Later A.Joffe could supported Ya.Frenkel to advance very creative, now universally recognized conception on defects, which are formed at the dissociation as the result of thermal movement of atoms (ions) [4,5].

2. At continuing study of the role of defect in hydrogen containing materials it was revealed that the phenomenological approach to analyses showed that it is necessary to include into consideration the interstitial position of lattice as the active component of system as it was noted by Frenkel in [4]. Small mass and size of proton at 3250 K is not the same as e.g. Ag+.

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THE ROLE OF HETERONUCLEAR AND HETEROLIGAND COMPLEXES IN THE PROCESSES OF ELECTROCHEMICAL ALLOY FORMATION

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One of the priority areas of work in the field of electrochemistry is the improvement of the known and creation of new alloys in order to obtain effective protective and functional properties of coatings. An important place in solving these problems at the present stage is given to issues of ecology, efficiency and intensification of technological processes.

Significant progress in this direction has been achieved on the basis of fundamental studies of the kinetics and mechanism of electrode reactions, taking into account the role of complexation and the proton effect in electrochemical systems.

The expedience of this approach is relevant in obtaining alloys for difficult-to-coprecipitate from aqueous solutions by electrochemical reduction of the ingredients, or in the case of processes occurring with a very low current efficiency.

The rationale for the study of the role of heteronuclear and heteroligand complexes, as well as the possibility of obtaining positive effects in the co-precipitation of different metals, or a metal with a non-metallic element, can serve the following views.

In the heteronuclear and heteroligand complexes, the donors of the components of the coprecipitated elements are in the same chemical compound and have common molecular orbitals. Adsorption of the considered complexes on the cathode, or their formation directly on the electrode surface, can change the characteristics of a potential barrier in the path of charge transfer and bring together the discharge potentials of the coprecipitated elements.

The purpose of this work is to analyze the experimental results on the effect of heteronuclear and heteroligand complexes in the processes of obtaining coatings from zinc-chromium and nickel-phosphorus alloys.

The laws of influence of heteronuclear, heteroligand complexes have been studied and established. It has been shown that the finding of donors of the components of the electroplated coating in the internal sphere of the heteronuclear or heteroligand complexes contributes to their joint electrochemical reduction.

KINETIC PARAMETERS OF ELECTROCHEMICAL REACTION IN THE CONDITIONS OF STATIONARY AND PULSE POLARIZATION

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In order to explore the role of the pulsed current at the stage of electron transfer, the values of the exchange current density and the effective activation energy of the discharge reactions of aqua-and glycinate zinc complexes at the zinc electrode are determined. Exchange current densities obtained by cyclic galvanostatic method are 2.5 ... 3 times greater than those calculated from stationary polarization curves.

If, when processing oscillograms, we use not the maximum values of the potential, but the charge transfer overvoltage, determined from the potential drop curves, then the exchange current density on the zinc electrode is also higher than that obtained from the stationary polarization curves.

As is known, the exchange current depends on the structure, the electronic structure of the metal, the concentration and nature of the particles in the reaction zone, as well as on the transfer coefficient, i.e. from charge transfer mechanism.

Based on the above factors affecting the exchange current, its increase in the conditions of pulsed polarization of the electrode can be due to the following reasons.

With pulsed polarization, the rate of nucleation is higher due to high amplitude current densities. It is known that the more nuclei are formed, the smaller the final size of the crystals. Thus, one of the reasons for the increase in the exchange current density under the conditions of pulsed polarization of the electrode can be an increase in the number of ad-atoms on the cathode surface.

In the case of a pulsed current, the effective activation energy of the discharge of glycinate complexes of zinc is approximately two times less than for the stationary mode and has values at potentials, B: –1.05; - 1.10; - 1.15, respectively, values, kJ/mol: 18.1; 17.0; 9.8. To explain the reasons for the decrease in the effective activation energy when zinc glycinate complexes are restored under conditions of cathode pulsed polarization, a process model with the participation of anionic water clusters is considered.

The possibility of changing the kinetic parameters in the work is also confirmed by a comparative analysis of their values for simple redox electrodes, determined by stationary and relaxation methods.

ASSOCIATION OF ANIONIC POLYELECTROLYTES AND CATIONIC SURFACTANTS IN MICROFLUIDIC CHANNELS

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Microfluidics offers new opportunities for controlled synthesis of multifunctional soft matter systems with high degree of ordering[1,2]. This project is focused on synthesis of polyelectrolyte-surfactant complexes (polyacrylic acid or sodium polyacrylate as polyelectrolytes and cetyltrimethylammonium bromide as a surfactant) in microfluidic systems[3] (Fig. 1).

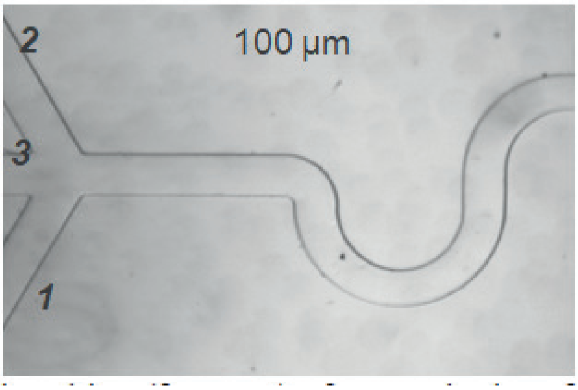

Figure 1. A microfluidic chip (fragment) for synthesis of polyelectrolyte-surfactant complexes in microchannels (1 – polymer, 2 – surfactant, 3 – aqueous or organic solvent).

The flowrates of polyelectrolytes, surfactant and cosolvents were varied in a 5-50 µl/min range. With these flowrates, the hydrodynamic radius of complexes was found to be in the 100-250 nm range. The measurements were repeated three times to prove that the synthesis process can be controlled and the results can be reproduced. Convection-diffusion equation was used to model radial and axial distribution of components and products inside a microchannel.

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This research was supported by the Republic of Tatarstan Grant "Algarysh", Project # 67/18. The author extends his gratitude to the team of Complex Fluids Engineering Center at Carnegie Mellon University, where these experiments were performed.

STUDY OF THE INTERACTION OF PYROMELLITIC DIANHYDRIDE WITH [2-(AMINOMETHYL)BICYCLO[2.2.1]HEPT-3-YL]ANILINES BY A CALORIMETRIC METHOD

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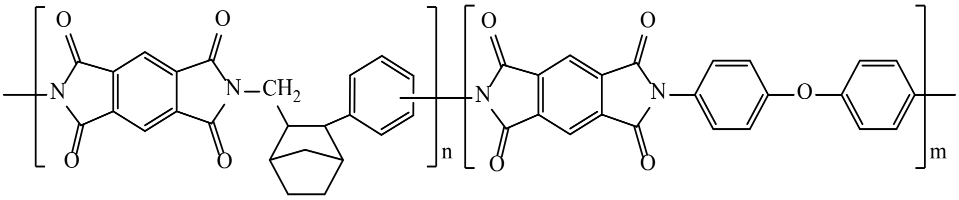
The study of the reactivity of new monomers is an important step in the development of polymers with improved characteristics. In this regard, we have carried out kinetic studies of the formation of polyamic acids based on pyromellitic dianhydride (PM) and [2-(aminomethyl)bicyclo[2.2.1]hept-3-yl]anilines (AMBHA).



For comparison, the rate constants of the reaction of the same dianhydride with 4,4′-diaminodiphenyl ether (DADPHE) have also been determined.

The kinetic was studied by calorimetric method using Calve C80 microcalorimeter. DMF was used as a solvent.

We have determined the changes in enthalpy of reaction, the values of the effective rate constants and the activation energy of the reaction in the temperature range 303-313 K.

Analysis of the data obtained indicate that for the studied bicyclic diamines, the effective rate constants of the acylation reaction are greater than for the aromatic diamine taken for comparison. This fully agrees with the pKa values of the diamines in nitromethane. It should be noted that the values of kef for 4-AMBHA are slightly higher than for 3-AMBHA, which is probably due to steric factors.

The kinetic studies carried out demonstrate the high reactivity of AMBHA in polyamic acid formation reactions, which allows one to predict the possibility of obtaining polymers with a sufficiently high molecular weight on their basis.

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation in the context of the basic part of the state task using CUC "Physicochemical research methods" FSBEI HE VSTU equipment.

ANTIMICROBIAL MICELLAR SYSTEMS BASED ON MONO- AND BISQUATERNIZED DERIVATIVES OF 1,4-DIAZABICYCLO[2.2.2]OCTANE AND FURAZOLIDONE

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Currently, one of the promising areas of supramolecular chemistry is the creation of new non-toxic delivery systems based on cationic surfactants (CS). For this purpose, the most attractive are CS, containing natural fragments and having a low critical micelle concentration (CMC). Earlier in our research group, some interesting features were found in the aggregation behavior and functional activity (high catalytic effect, solubilizing properties, antimicrobial activity) of CS - amphiphilic 1,4-diazabicyclo[2.2.2]octane derivatives (DABCO). Hexadecyl derivative DABCO has been shown to be non-toxic in the presence of N-methyl-D-glucamine and has antimicrobial activity.1

The purpose of this work was to establish the relationship between the structure and the solubilizing properties of DABCO derivatives in water in relation to poorly soluble dyes (Orange OT, Sudan I) and the antimicrobial drug furazolidone. The nuclear magnetic resonance method with a magnetic field pulse gradient was used to investigate the self-association processes of amphiphilic mono- and bisquaternized 1,4-diazabicyclo[2.2.2]octane derivatives (mono-DABCO-n and di-DABCO-n, where n = 12, 14, 16, 18). The influence of the DABCO structure (the head group and the length of the alkyl chains) on the CMC, as well as a number of aggregation and solubilization properties were studied. It is shown that CMC values of mono-DABCO-n are lower than those for di-DABCO-n. The solubility of the poorly water soluble antibacterial drug furazolidone was improved by micellar solubilization based on mono- and di-DABCO-n. Mono-DABCO-n are the best solubilizing agents in relation to furazolidone. The use of a mixed composition of mono-DABCO-16-furazolidone provides a significant increase in the level of antimicrobial activity.

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"The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project № 18-43-160015."

NOVEL APPROACH TO SYNTHESIS OF PHARMACEUTICAL SUBSTANCES BY THE METHYLATING REACTION OF TERTIARY AMINES

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Quaternary ammonium compounds are characterized by a wide spectrum of biological activity, the most important of them met in nature - choline, acetylcholine, alkaloid trigonellin.1-3

We have found a new approach to obtaining quaternary ammonium compounds (their gegenion being 1,1-dicyano-2-methoxy-2-oxoethane-1-ide) by the influence of methanol and ethene-1,1,2,2-tetracarbonitrile (ETCN) dissolved in it upon tertiary amines (Fig. 1).

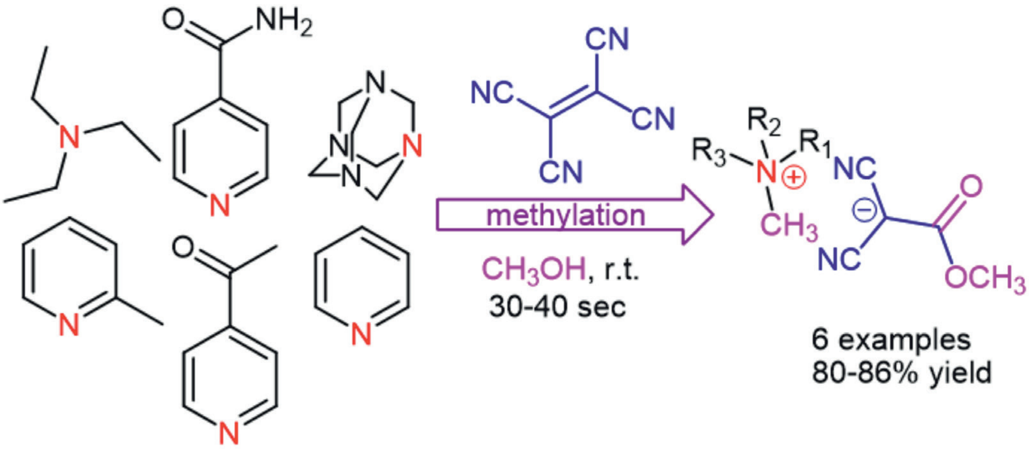

Figure 1. Reaction of tertiary amines and ETCN in methanol.

This method is notable for the simplicity of syntheses that run immediately in mild conditions at room temperature. At a molecular level it combines at least two procedures: methylating nitrogen atom in tertiary amine and forming an anion of 1,1-dicyano-2-methoxy-2-oxoethane-1-ide.

Received compounds was identified by the methods of IR, 1H NMR, 13C NMR -spectroscopy and X-ray crystal structure analysis.

We suppose that tertiary amines methylation with methanol in the presence of ETCN is a useful instrument for modification of pharmaceutically important chemical substances.

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HYDRAZONES OF α,β-UNSATURATED ALDEHYDES IN [2+2]-CYCLOADDITION WITH TETRACYANOETHYLENE

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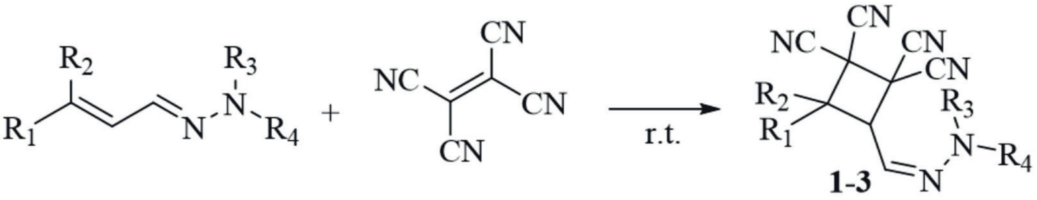
The Diels−Alder reaction of dienes and alkenes is one of the most frequently used reactions in organic chemistry [1-6]. The hydrazones of α,β-unsaturated aldehydes typically react with dienophiles producing standard Diels-Alder products in synchronous manner.

To verify our theoretical predictions we carried out a series of reactions with ethene-1,1,2,2-tetracarbonitrile (TCNE) and different hydrazones of α,β-unsaturated aldehydes (Fig. 1).



R_1 = Ph (1), Me (2), $(CH_2)_2CHC(CH_3)_2$ (3)
R_2 = H (1-2), Me (3)
R_3 = Me (1a, 2a, 3a), Ph (1b), H (1c-d, 2c-d, 3c-d)
R_4 = Me (1a, 2a, 3a), Ph (1b-c, 2c, 3c), C(S)NH_2 (1d, 2d, 3d)

Figure 1. Experimentally studied cycloaddition reactions

Received compounds was identified by the methods of IR, 1H NMR, 13C NMR -spectroscopy and X-ray crystal structure analysis.

In conclusion, we have shown by means of quantum chemical calculations that the preference toward the C–C bond formation over C–N can be used to avert the Diels-Alder reaction and direct the reaction to the otherwise unfavorable [2+2] cycloaddition.

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IR SPECTROSCOPY AS A METHOD OF STUDING THE COMPLEXES STRUCTURE EXTRACTED WITH BENZO-15-CROWN-5

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Extraction systems based on benzo-15-crown-5 are very promising for solving one of the most important tasks of radiochemistry – lithium isotopes separation. To optimize these processes, it is necessary to understand chemical transformations and structure of compounds formed in the separation process during extraction.

With ATR method of IR spectroscopy the spectral studies of aqueous and organic phases, as well as the solid samples isolated from these phases were carried out. Comparison of X-ray diffraction data and spectral results allowed to determine the complexes structure in solutions.

Complexation of B15C5 and lithium salts with various anions: CH_3COO^-, CCl_3COO^-, $CClH_2COO^-$, CCl_2HCOO^- and their protonated forms was studied.

The IR spectra of B15C5 solutions show that crystalline crown ether changes the conformation upon dissolution, while the conformation of the dissolved crown ether does not differ from the conformation of its complex in solution.

It was shown that the composition of the complexes formed as a result of extraction includes water molecules, which can exhibit both electron donor and electron acceptor properties. In the first case, the oxygen atom of the water molecule enters first coordination sphere of lithium. In the second case, the hydrogen atom of water forms bifurcated bonds with the oxygen atoms of crown ring, and the electrons of water oxygen atoms participate in the formation of bonds with HOOCR acid molecules. In the IR spectra, the multifunctionality of water molecules is depicted in the region of stretching vibrations of OH groups – 3600–3300 cm^{-1} as shifting and splitting of bands. The hydrogen bonds O...H are also represented in the spectra.

In the IR spectra of organic phases of extraction from aqueous solutions in B15C5 in chloroform, shifts of the vibration bands ν(HC) and ν(CCl) of chloroform are observed, which allows us to conclude that solvent molecules are involved in the formation of complexes.

The study has been supported by the Ministry of Education and Science of the Russian Federation (subject No. 22, state registration No. AAAA-A16-116110910010-3)

METHOD FOR OBTAINING ORGANOPHOSPHORUS ACIDS FROM STYRENE AND RED PHOSPHORUS IN A SUPERBASIC SYSTEM

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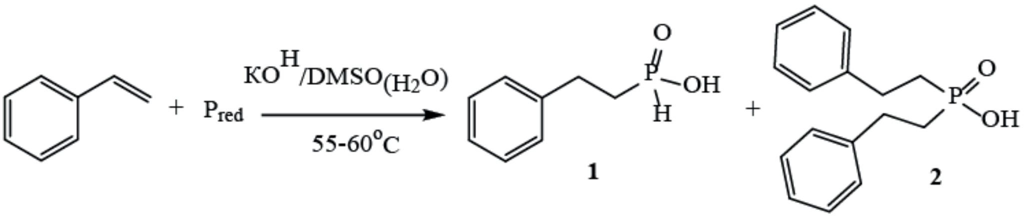
Organophosphorus acids are a promising class of compounds due to their use as precursors of drugs, catalysts, adsorbent modifiers, as well as for creating coordination polymers[1].

We have shown that styrene reacts with red phosphorus in the superbasic KOH / DMSO system in the presence of small amounts of water at 55–60°C to form 2-phenylethylphosphinic acid 1 and bis(2-phenylethyl) phosphinic acid 2, yield (determined by NMR ^{31}P) which depends on the ratio of initial reagents and reaction time.

So, when carrying out the reaction for 4 h using the molar ratio P_{red} : styrene = 3.4 : 1, 2-phenylethylphosphinic acid 1 is formed almost selectively with a yield of 31%. A decrease in the mole fraction of styrene with respect to phosphorus and an increase in heating time up to 6 hours leads to the preferential formation (yield 16%) of bis(2-phenylethyl) phosphinic acid 2, and the yield of phosphinic acid 1 is 6%.



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TETRAORGANIC ANTIMONY PERCHLORATE

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Perchlorates, as a rule, are low-stable and explosive substances. They are part of the compositions of rocket fuels, explosives, dehydrators, used in organic synthesis, in particular, in the acylation of arenes, aminoalkylation of aldehydes, alkylation of anilines. Organic perchlorates Sb(V) remain poorly understood. Therefore, the development of methods for the synthesis of tetraorganic antimony perchlorates is an important task.

The purpose of our study is to obtain the stibonium perchlorates of the gen-eral formula $[Ar_3RSb]ClO_4$ (R = Alk).

Or a long time, the main method of obtaining compounds of the common formula $[Ar_3RSb]^+X^-$ (R = Alk) was the alkylation of triarylantimony with active agents: boron fluoride trimethyloxonium or diphenyliodonium. For the first time, the authors[1]. Have succeeded in attaching halide alkyls to triarylantimony.

We studied the alkylation of *tris*(2,6-dimethoxyphenyl)antimony with ethyl iodoacetate[2], iodide isobutyl, ethyl iodide followed by the exchange of iodide ion for the perchlorate group (solvent – chloroform) according to the following schemes:

$$Ar_3Sb + RI \rightarrow [Ar3RSb]I,$$

$$[Ar_3RSb]I + AgClO_4 \rightarrow [Ar_3RSb]ClO_4 + AgI,$$

$$Ar = 2,6\text{-}(MeO)_2C_6H_3;\ R = CH_2C(O)OEt,\ i\text{-}Bu,\ Me.$$

Tris(2,6-dimethoxyphenyl)alkylantimony perchlorates (yield up to 78%) are beige crystals, melting with decomposition, readily soluble in polar organic sol-vents.

The IR spectra (Fourier spectrometer FSM 1201) of compounds contain the characteristic absorption bands of the perchlorate group[3] (ν, cm^{-1}): 1089 [$\nu_{as}(ClO_4)$], 622 [$\delta(ClO_4)$]. The iodine content is determined by the gravimetric method on the form of AgI.

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KINETIC PROPERTIES OF SULFUR AND NITROGEN-CONTAINING ANIONITE

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The object of study is the effective anion exchange resin based on thiourea, epichlorohydrin and melamine1,2 and its kinetics of exchange capacity for copper and nickel ions. In the study of the kinetics of ion exchange, a limited volume method and an installation were used, which includes a thermostat and a reactor with a stirrer with a capacity of 1 liter. A preprepared solution was placed in the reactor in an amount of 1 l with a concentration of components of 0.2 mol / l. With a constant grain size of the swollen ion exchanger, the temperature in the experiments varied: 25°C, 45°C, 60°C. 1 g of swollen ion exchanger was placed in the solution. The analysis of all solutions for the content of elements was carried out by trilonometric and potentiometric titration. For comparison, the kinetic properties of the industrial polymerization anion exchanger EDE-10P were investigated. The total exchange capacities of these anion exchangers in the OH - form were determined according to a 0.1N CuSO4 solution: EDE-10P– 3.2 mg eq / g, TEM - 4.6 mg eq / g

The calculated value of the copper diffusion coefficient after the 7-hour phase contact is $6.3 \cdot 10^{-8}$ for the TEM anion exchanger, and $5.6 \cdot 10^{-8}$ for the EDE-10P anion exchanger. The research results show that the obtained anion exchange resin by its sorption and kinetic properties is not inferior to the industrial anion exchange resin EDE-10P.

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REACTIONS OF SALT COPPER (II) WITH CARBONYL-CONTAINING (SPYROHYDRO)CHROMANES AND CONDENSED 2H-PYRAN-2-ONES

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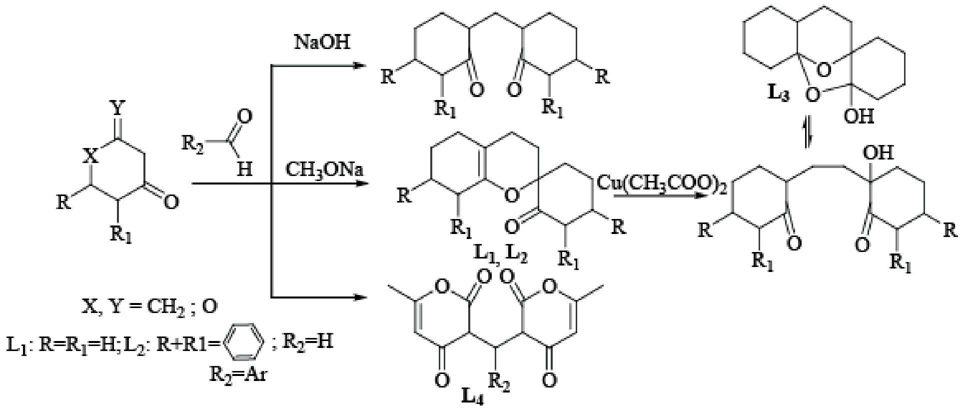
Organic compounds that include biometal – copper – in their structure are similar in properties to metal-enzyme-substrate complexes that are participants in various redox processes occurring in a living organism.

We have implemented a targeted approach to the synthesis of complex compounds based on methylene(aryl)bistetrahydronaphthalinones and their functionalized O-heteroanalogs and spirocyclization products, characterized by high antiphage activity against T4 phage.



It is shown that copper acetate catalyzes not only the semi-ketalization of the ligand L1, but also the decyclization of L2, L3, followed by complexation of the carbonyl and hydroxyl functional groups in the complexes of the following composition.

$$\begin{tikzcd}
{[Cu(L^4)_2](H_2O)_n} & Cu(CH_3COO)_2 \arrow[l, "L^4"'] \arrow[r, "L^1; L^3"] \arrow[d, "L^2"] & {[CuLH_2O][Cu(CH_3COO)_3]} \\
 & {[CuL^2(H_2O)_2][Cu(CH_3COO)_3]} &
\end{tikzcd}$$

When introduced in the reaction of arylmethylenbis-2H-pyran-2-ones with L4 acetate copper(II) monohydrate formed the bidentate compound with inclusion of three or four molecules of crystallization water the external field which was confirmed by the spectral and DTA-analysis.

SYNTHESIS OF LUMINESCENT Cu_4I_4 – COMPLEXES WITH N-ALKYL-10-(ARYL)PHENARSAZINES

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The complexes of copper (I) halides have been of great interest due to the large variety of their photophysical properties associated with the ability of copper (I) halides to form various types of structures.1

This report is devoted to the synthesis of Cu (I) iodide complexes of N-alkyl-10-(aryl)-phenarsazines with a tetrameric Cu4I4-core.

Complexes 1 and 2 of the composition Cu4I4L4 are obtained by the reaction of N-alkyl-10-(aryl)-phenarsazine ligands (L) with copper iodide in the equal molar ratio in acetonitrile (Figure 1). The structures of 1 and 2 were analyzed by the X-ray crystallography (Figure 2).

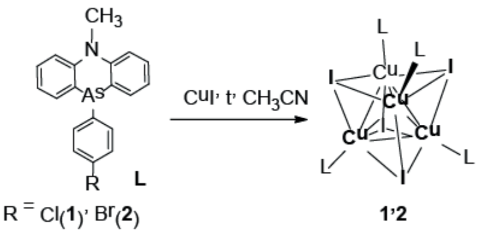

Figure 1.Synthesis of complexes 1 and 2

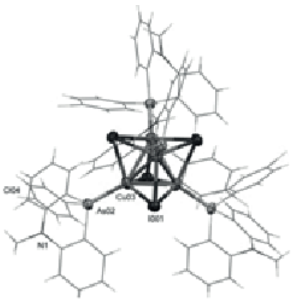

Figure 2. Structure of 2

Complexes 1 and 2 exhibit intense green solid state luminescence under UV irradiation.

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Acknowledgements
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THE SELECTION OF OPTIMAL CONDITIONS FOR AMINO ACID SEGREGATION FROM WATER-SALT SOLUTIONS BY DIALYSIS THROUGH MK-40 MEMBRANE

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Donnan dialysis is an environmentally rational method for separating electrolyte and non-electrolyte solutions on electrically charged membranes. It does not require the consumption of electricity and chemicals.

It was pointed out that the separation of phenylalanine and sodium chloride by dialysis with sulfonic cation-exchange membrane is most effective from dilute solutions of $C<3\cdot10^{-2}$ M with a membrane in the hydrogen form due to the effect of “facilitated” diffusion of amino acids and Donnan's exclusion of a strong electrolyte in ion-exchange membranes (fig. 1). Changes in the volume morphology and surface because of profiling of sulfonic cation-exchange membranes lead to an 8-fold increase in the flux density of the alkylaromatic amino acid phenylalanine compared with the commercially available MK-40 membrane.

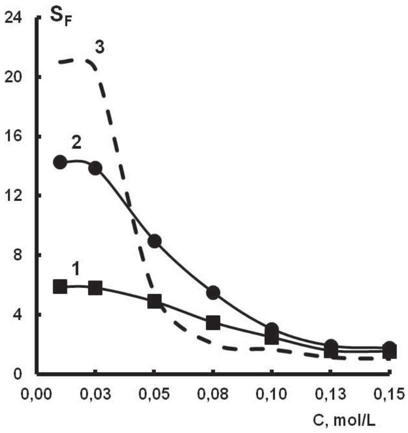

Figure 1. Concentration dependence of the separation factor during dialysis of solutions of equimolar mixtures (1, 2) of phenylalanine and sodium chloride through the membrane MK-40 (1) and MK-40pr (2, 3). Curve 3 is calculated from the results of the transfer of components from individual solutions.

It has been detected that for sulfonic cation-exchange membrane, the conjugation of fluxes leads to a less efficient separation of substances (Fig. 1, curves 2, 3). The use of the profiled membrane MK-40pr provides more than a 2-fold increase in the SF separation factor compared with the commercial membrane MK-40 (Fig. 1, curve 1).

This work was supported by the Russian Foundation for Basic Research (project No 18-08-01260).

INFLUENCE OF MANUFACTURING TECHNOLOGY OF CATION-EXCHANGE MEMBRANES ON THE PROPERTIES OF THEIR SURFACE

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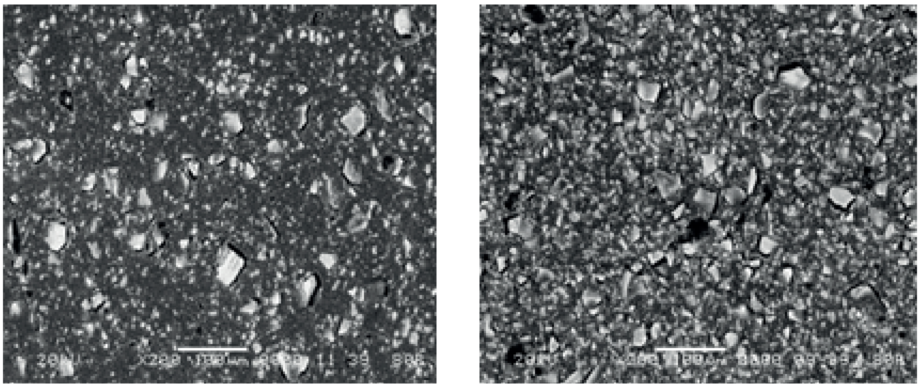
One of the priorities of modern membrane electrochemistry and technology is the creation of ion-exchange membranes with optimized surface morphology for high-intensity electrodialysis. The task of this work is to analyze the electrical surface heterogeneity of experimental heterogeneous membranes with different fractions of a sulfocation-exchanger by scanning electron microscopy.

The objects of study were experimental samples of heterogeneous sulfocation-exchange membranes Ralex CM Pes ("MEGA" a.s., Czech Republic) with a different ratio of conductive (ion-exchanger) and non-conductive (polyethylene) regions. With an increase in the bulk fraction of the ion-exchange resin in the mixture used in the manufacture of membranes, from 45 to 70%, an increase in the area of conductive regions on the surface of the swollen samples by 1.9 times was found. In this case, the sizes of ion-exchange particles remain constant and amount to 1-36 microns. The length of non-conductive membrane regions with 45% ion exchanger content is twice as much as for a sample with 70% ion-exchanger fraction. An increase in the fraction of macropores on the surface by 60% was established with an increase in the content of the ion-exchanger in the composition of the experimental membranes.



a b

Figure 1. SEM images of the surface of the swollen cation-exchange membranes Ralex CM Pes. Ion exchanger content: 45 % (a) и 70 % (b).

The work is supported by the grant of the President of the Russian Federation MK-925.2018.3. The authors are grateful to the «MEGA» a.s. company (Czech Republic) and its owner Mr. L. Novak for providing experimental samples of the Ralex CM Pes.

PHYSICO-CHEMICAL CHARACTERISTICS OF INCLUSION COMPOUNDS ON THE BASIS OF METAL COMPLEXES AND CUCURBIT[N]URILS: DFT FORECASTS

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An important feature of cucurbit[n]urils ($C_{6n}H_{6n}N_{4n}O_{2n}$, CB[n], n=5-10) is their ability to form supramolecular inclusion compounds according to the host-guest mechanism. Using a series of guest metal complexes as an example, an approach for quantum chemical predicting the formation of inclusion compounds with CB [n] is proposed.[1] It is shown that for a correct assessment of the energy of formation of such compounds in aqueous solutions, it is necessary to take into account the water structuring inside the cavities of macrocyclic cavitands. The water structuring in CB[n] in the form of $c(H_2O)_m$ clusters is established.[2] Studies of the structure of inclusion compounds based on metal complexes and CB[n] have revealed the key role of water molecules in the fixation of complexes inside the cavitands due to the network of hydrogen bonds of water molecules with ligands of complexes and portal oxygen atoms.[3] It was proposed to consider the reaction of inclusion of a complex into CB[n] as a substitution reaction, in which the guest complex displaces completely or partially of the water molecules preexisting inside the cavitand in aqueous solution. Quantitative estimates of the Gibbs free energy of such a reaction make it possible to predict the thermodynamic possibility of the formation of an inclusion compound. It is known that the inclusion of complexes in CB[n] can lead to a change in their physico-chemical characteristics, as well as reactivity. One of the important characteristics of a metal complex is its standard redox potential. In this work, for the first time it was made an attempt of calculating the redox potential of the inclusion compounds Fe(III)@CB[n]/Fe(II)@CB[n] (n = 6–8) in comparison with the experimental redox potential of Fe(III)/Fe(II) in the bulk of aqueous solution.

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SYNTHESIS AND RESEARCH OF LUMINESCENT PROPERTIES OF BORON DIFLUORIDE DIBENZOYLMETHANE DICULFIDE

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The derivatives of β-diketonatonates of boron difluoride are of interest due to the fact that some of them have intense luminescence1. Also, the luminescent properties of boron difluoride β-diketonates solutions, unlike the properties of most known luminophores, depend significantly on the concentration of the solution that gives a unique possibility to control the optical properties of functional materials containing them[2].

In the present work, we synthesized some boron diafluoride diketonate disulfides (Fig. 1), and also investigated their consumption and luminescence spectra.

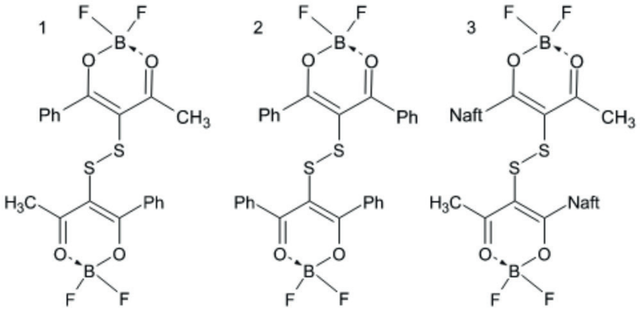

Figure 1 - 1. Disulfide dibenzoylmethionate boron difluoride ((SDBMBF2)2);
2. Boron disulfide benzoylacetonate disulfide ((SBAcBF2)2);
3. Naphthoylacetonate disulfide boron difluoride ((SNaftAcBF2)2)
Structural substances were proved by the methods of IR and NMR 1H, 13C spectroscopy.

In the study of the absorption spectra of solutions, compounds were obtained that can be detected in insignificant amounts of bathochromic displacement of the absorption spectra, which may indicate a low degree of conjugation of the benzoyl acetonate complex system.

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NEW MOLECULES OUT THE OLD-STYLE HUTCH

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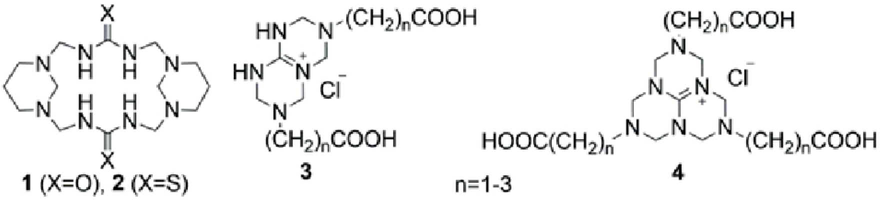
Revision of publications referring to the urea, thiourea, and guanidine aminomethylation has rather surprisingly resulted to obtaining of new bi- and tricycle substances. So, bridged macrocycles – 1,3,5,7,11,13,15,17-octaazatricyclo[15.3.1.1^{7,11}]docosane-4,14-dione 1 and its thio-analog 2 – were obtained from urea or thiourea, respectively, formaldehyde, and 1,3-propandiamine[1,2].



1 (X=O), **2** (X=S) **3** **4**

Bicyclic 3,7-bis(carboxyalkyl)-1,2,3,4,6,7,8,9-octahydro[1,3,5]triazino[1,2-a][1,3,5]triazin-5-ium chlorides 3 or tricyclic 2,5,8-tris(carboxyalkyl)-2,3,5,6,8,9-hexahydro-1H,4H,7H-2,5,6a,8,9a-pentaaza-3a-azoniaphenalene chlorides 4 were obtained from guanidine hydrochloride, formaldehyde, and amino acids depending on the reactant ratio. It is possible to pass from 3 and 4 to zwitteriones or betaines, respectively[3].

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ELECTRON EXCHANGE IN 1,2,4,1′,2′,4′-HEXA¬METHYL-FERROCENE/ 1,2,4,1′,2′,4′-HEXAMETHYL¬FERRICE¬NIUM ¬HEXA-FLUORO¬PHOS¬PHA¬TE AND SYM. OCTA¬METHYL¬FERROCENE/SYM. OCTAMETHYL¬FERRICENIUM HEXAFLUOROPHOSPHATE SYSTEMS

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The study of redox couples – 1,2,4,1′,2′,4′-hexamethylferrocene/1,2,4,1′,2′,4′-hexamethylferricenium hexafluorophosphate ($Me_6Fc^{+/0}$) and sym. octamethylfer-rocene/sym. octamethylferricenium hexafluorophosphate ($Me_8Fc^{+/0}$) is important in view of the need of replacing the ferrocene/ferricenium ($Fc^{+/0}$) reference electrode which manifests instability in a number of solvents with a more stable system [1].

We obtained ^{1}H NMR spectra of diamagnetic complexes Me_6Fc, Me_8Fc, para-magnetic salts $Me_6Fc^+PF_6$, $Me_8Fc^+PF6^-$, and of the process of electron exchange in the systems $Me_6Fc^{+/0}$ and $Me_8Fc^{+/0}$ in deuteroacetone at 25°C (Bruker-300 MHs).

Based on data [isotropic shifts (Δv), half-widths of resonance lines (W_D, W_P and WDP) and molar fractions of reagents (fD, fP)] from individual experiments, we measured exchange rate constants (k_{ex}) depending on the concentration of each reagent. The values obtained for k_{ex} show that the electron exchange in the systems $Me_6Fc^{+/0}$ and $Me_8Fc^{+/0}$ obeys the kinetic equation of the second order:

$$\text{Exchange rate} = k_{ex}\,[Me_nFc] \cdot [Me_nFc^+] \quad (mol/l \cdot sec) \quad (n = 6, 8)$$

Compared with the unsubstituted ferrocene-ferri¬cenium system [k_{ex} ($Fc^{+/0}$) = 4,6 $\cdot 10^6$] [2], the emergence of six and eight methyl groups in the molecule of each of the reagents in $Me_6Fc^{+/0}$ and $Me_8Fc^{+/0}$ redox systems increases the exchange rate constant [k_{ex} ($Me_6Fc^{+/0}$) = 1.50 • 10^7 and k_{ex} ($Me_8Fc^{+/0}$) = 2.20 • 10^7 (l/mol • sec)] by approximately 3.3 and 4.8 times, respectively.

The rise in exchange rates in the series $Fc^{+/0}$ • $Me_6Fc^{+/0}$ • Me8Fc+/0 is interpreted as a result of a decrease in the reorganization energy of the solvent (acetone) with an increase in the volume of reagents in redox couples $Me_6Fc^{+/0}$ and $Me_8Fc^{+/0}$.

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INTEGRAL THEORY OF ACIDS AND BASES

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In the evolution of ideas about acids, bases, their "strength", salts, mechanisms of acid-base reactions, neutralization, etc. - the general principle of the progressive development of the theory is implemented: each subsequent one includes the previous one, as a particular case.

In the proposed theories, two fundamental approaches can be distinguished for explaining acidic and basic properties: 1. - The presence of a acid and base particles; 2. - The structure of chemical compounds. But, as shown by experimental studies of electrical conductivity and complexation in non-aqueous solutions, it is impossible to unambiguously determine this acid or base from the composition and structure of compounds. This led to the rejection of the concepts of "acid" and "base" as classification features.

Acidity and basicity began to be considered as a chemical function that any substance can manifest in a particular reaction.

According to Usanovich: a compound that donates a cation or an attaching anion is an acid; the base is a compound giving away an anion or an attaching cation. According to Lewis: acid is an electron pair acceptor; the base is an electron pair donor.

Usanovich's approach can be characterized as heteropolar-electrophore, and Lewis's approach is homopolar-structural. Each of these approaches has its own limitations and areas of application.

The paper deals with a more general interpretation and definition of acid and basic functions.

The "acid function" of a substance is an increase in a negative charge (or electron density) or a decrease in the positive charge of atomic-molecular particles forming this substance during a chemical reaction.

Under the "base function" should be understood an increase in negative charge (electron density) or a decrease in the positive charge of atomic-molecular particles involved in the process of chemical reaction.

These definitions cover all previously formulated definitions of the concepts "acid", "base" and acid-base interaction. The result of the acid-base reaction is the reduction (neutralization) of the acid and the main function of the reaction participants.

The "strength" of an acid, a base is determined by the density of the effective charges on the atoms and atomic groups involved in the reaction.

VISCOSITY AND ELECTRICAL CONDUCTIVITY OF SODIUM-BORING MELTS CONTAINING MECHANO-ACTIVATED OXIDES: SM, EU AND ER, TM

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The electrical conductivity (æ) of sodium borate melts, containing 1 wt. % of mechanically activated oxides of lanthanides (Sm, Eu, Er, Tm), was measured in the range of 950–1650 K by AC bridge method. The temperature and concentration dependences of the electrical conductivity values were definedIt is known that in borate melts of current carriers there are cations: ions of alkaline and rare earth elements (REE) and free hydroxide ions [1-2]. Depending on the magnitude of electrical conductivity. The technique for measuring electrical conductivity is described in detail in [3]. Logarithm æ dependences on inverse temperature revealed high and low temperature regions with different activation energies. Viscosity (η) of sodium borate melts, containing 1 wt % of mechanically activated oxides of lanthanides (Sm, Eu, Er, Tm) were measured by vibrating viscometer (T=950-1650K). The temperature and concentration dependences of the viscosity values and starting temperature of solidification of melts were defined. High and low temperature regions with different activation energy of viscous flow revealed on the dependences of the viscosity's logarithm from inverse temperature. The activation energy of a viscous flow depends on the concentration of the B^{III}-O-B^{IV} and B^{IV}-O-B^{IV} bridging fragments of ring polyborate groups, that is, on the structure of average order.

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The work was performed in the framework of the state assignment of IMET Ural Branch of the Russian Academy of Sciences on the equipment of the CCU "Ural-M"

SYNTHESIS AND CHEMICAL PROPERTIES OF 7-LITHIOPYRAZOLO[5,1-C][1,2,4]TRIAZINES

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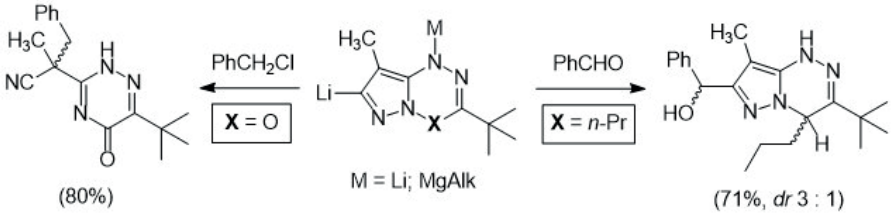
C-Lithiated azolo[1,2,4]triazines represent a relatively poorly studied class of heterocyclic compounds, and are of considerable synthetic interest. In continuation of the recent works[1,2], the chemical properties of C(7)-lithiopyrazolo[5,1-c][1,2,4]triazines have been studied[3]. It was found that the stability of 7-lithio species depended highly on the substitution pattern at the C(4) ring position. The rate of the pyrazole ring opening reaction increased in a row CH–Alk ~ CH$_2$ < CH–Ar < C=O ~ CH–C≡CPh (Ar = Ph, 4-MePh; Alk = *t*-Bu, *n*-Bu, *n*-Pr) and roughly followed the order of the electronegativity of substituents.



Thus, the unstable 4-oxo derivatives underwent rapid ring opening already at –112^{o} ÷ –97^{o}C, with formation of the corresponding monocyclic 1,2,4-triazines. However, an electrophile trapping of stable 4-alkyl-1,7-metalated derivatives at –97^{o} ÷ –84^{o}C using DMF or PhCHO allowed the selective side-chain functionalization3. The quantum chemical studies of the ring opening reaction were in accordance with the experimental results. The structures of the isolated products were established on the basis of IR, NMR, high resolution mass spectra and X-ray powder diffraction analysis.

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The work was financially supported by RFBR, grant 18-33-00019.

COMPLEXATION AND IONOPHORIC PROPERTIES OF 2,4,6-TRIS[(2-DIPHEHYLPHOSPHORYL)-4-ETHYLPHENOXY]-1,3,5-TRIAZINE WITH ALKALY METAL CATIONS

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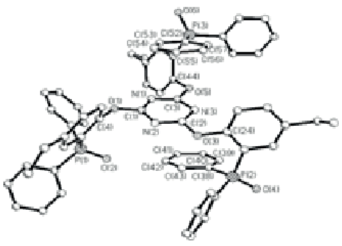
New ligand – 2,4,6-tris[(2-diphehylphosphoryl)-4-ethylphenoxy]-1,3,5-triazine (L) was synthesized. Crystal structures L•H_2O (I), [LiL(ClO_4)…(H_2O)LLi](ClO_4)•11H_2O (II), [LiLI…(H_2O)LLi]I•18H_2O (III), and [K_2L_2I]I•7.2H_2O (IV) were determined by X-ray diffraction.



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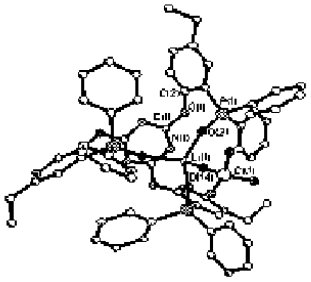
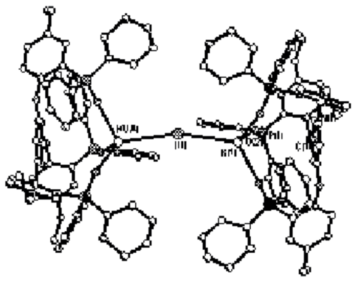


II



IV

Stability constants of complexes of L with lithium and sodium cations in MeCN were determined by spectrophotometric titration.

reaction	log *K*	*ε (λ, nm)*, cm^{-1} M^{-1}	*HRF, %*	R_{det}^2
$Li^+ + L = Li^+L$	6.23 ± 0.04	15877 ± 84 (249)	0.522	0.9998
$Na^+ + L = Na^+L$	4.90 ± 0.09	3222 ± 178 (285)	0.375	0.9999

Ionophoric properties of L were studied. It was determined that L as the active component of the polymeric plasticized membrane of ISE, exhibits selectivity towards lithium cation and shows good lithium/sodium selectivity. The results of study of ionophoric properties are in good agreement with spectrophotometric studies.

This work was financially supported by the the Presidium of Russian Academy of (program no. 1.4P). Part of the work was performed on the government assignments for 2019 year of Kurnakov Institute of General and Inorganic Chemistry, Frumkin Institute of Physical Chemistry and Electrochemistry and Institute of Physiologically Active Compounds.

SIZE-CONTROLLED SYNTHESIS OF THE GOLD NANOPARTICLES IN THE PRESENCE OF DNA

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Colloidal Au is known as a promising material for creating efficient catalysts1, nanoelectronics and different sensors[2]. Synthesis of Au nanoparticles (AuNPs) in the presence of DNA is an attractive choice to obtain stable AuNPs due to efficient interaction between DNA and Au species[3,4]. The main goal of this work was to synthesis stable Au nanoparticles of tunable size assisted by DNA.

The interaction of DNA with $HAuCl_4$ in an aqueous solution was studied at different molar ratios (1:0.25, 1:1, 1:5, 1:20 per a nucleotide unit, $c(HAuCl_4)$ = 0.4 mM). The interaction process was accompanied by an increase in absorbance in the range of 400–500 nm. The rapid increase in absorbance was completed within 2 hours. Addition of excess of $NaBH_4$ at that moment led to the appearance of a peak at 520-530 nm, corresponding to the characteristic surface plasmon resonance absorption of AuNPs.

It should be noticed that strong scattering was observed in the long-wavelength region in the spectra of samples with Au-DNA ratio of 1:0.25, which indicated the formation of larger particles. That fact was also evidenced by the sedimentation instability of that system during centrifugation. The preparation of nanoparticles of tunable size was also confirmed by transmission electron microscopy (TEM).

We performed screening of the catalytic activity of the synthesized AuNPs in a standard model reaction of p-nitrophenol reduction. The reaction rate constant varied, depending on the size of the gold nanoparticles, from 1.2 min_{-1} to 2.3 min_{-1}.

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The study was supported by the Russian Foundation for Basic Research, grant no. 17-08-01087/17

REACTION OF THE DICHLOROMETHYLARENES WITH O-METHYL DIETHYLTHIOPHOSPINATE

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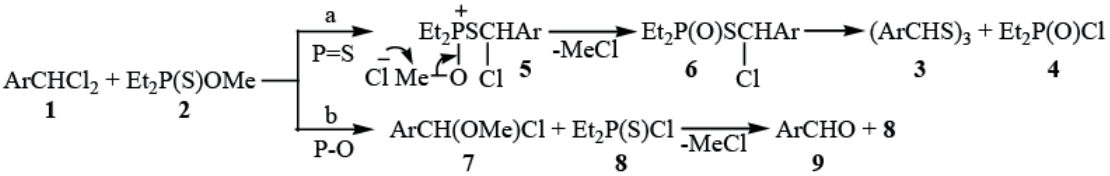
We have studied for the first time the reaction of the functionally substituted benzylidene chlorides 1 with O-methyl diethylthiophosphinate 2, which is one of the ambident (P=S, P-O)-nucleophiles. The arenecarbthioaldehyde trimers 3 and diethylphosphinoyl chloride 4 were formed. This result suggests an initial attack of the thione sulfur (P=S) on the methyne carbon in 1, i.e. the realization of route a. Intermediate phosphonium adduct 5 eliminates methylchloride to produce the product of substitution of one chlorine atom in 1 by dieth-ylphosphinothioyl group 6 (dechlorodiethylphosphinylthioylation). Intermediate 6, like its oxygen analog1, 2, is unstable and decomposes under the reaction conditions (100°C), yielding diethylphosphinoyl chloride 4 and arenecarbthioaldehyde which exists exclusively as trimer[3].



Scheme 1. Reaction of dichloromethylarenes 1 whith O-methyl diethylthiophosphinate 2

Arenecarbaldehyde 9 and diethylphosphinothioyl chloride 8 were not ob-served among the reaction products. It means that initial attack of the ester oxy-gen on the methyne carbon in 1 to form α-chlorether 7 (dechloromethoxylation, route b) is not realized.

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TI-MG-CATALYZED ETHYLZINCATION OF 1-ALKYNYLPHOSPHORSULFIDES

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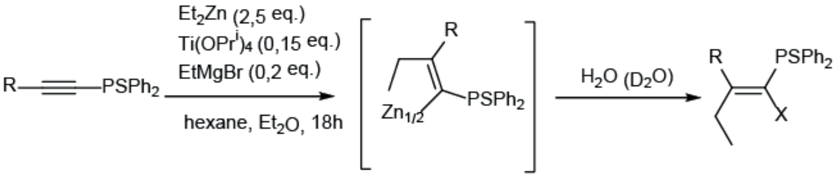
Previously we have shown that 1-alkynylphosphines are useful substrates for the synthesis of 1-alkenylphosphines by Zr-catalyzed cycloalumination with Et_3Al[1]. Tertiary phosphines and their oxides are widely used ligands in organometallic and coordination chemistry. In order to develop new methods for the synthesis of various alkenylphosphorsulfides, we studied the Ti-Mg-catalyzed reaction 1-alkynylphosphorsulfides with Et_2Zn. We found that the reaction of 1-alkynylphosphorsulfides 1 with 2.5 equivalents of Et_2Zn (1 M in hexanes) in the presence of 10 mol. % Ti(O-*i*Pr)$_4$, (0.5 M in hexanes) and 20 mol. % EtMgBr (2.5 M in Et_2O) carried out in diethyl ether at room temperature for 18 h, followed by deuterolysis (or hydrolysis) furnishes Z-configured 1- alkenylphosphorsulfides 3,4. The structure of the alkenylphosphorsulfides was established using 1D and 2D NMR spectroscopy for the products of deuterolysis and hydrolysis.



1 2 3, 4

3a: R = *n*-Bu; X = H; **3b**: R = *n*-Hex, X = H; **3c**: R = *n*-Pent, X = H; **4a**: R = *n*-Bu; X = D.

The strategy we developed opens up the way to the synthesis of heterofunctional alkenes of various structure via catalytic zincoethylzincation of functionally substituted alkynes.

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This work was supported by the Russian Foundation for Basic Research (grant no. 18-03-00817) and by Grant of the RF President (Sci. Sh.-6651.2016.3) which are gratefully acknowledged.

SYNTHESIS AND HALOGENCYCLIZATION OF 2-ALKENYLSULFANYLPYRIDINES

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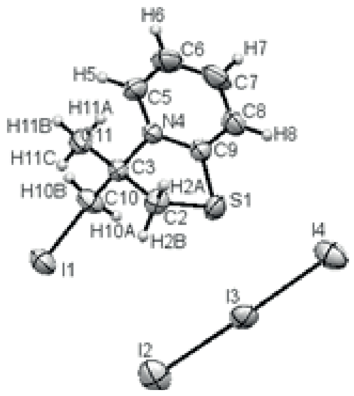
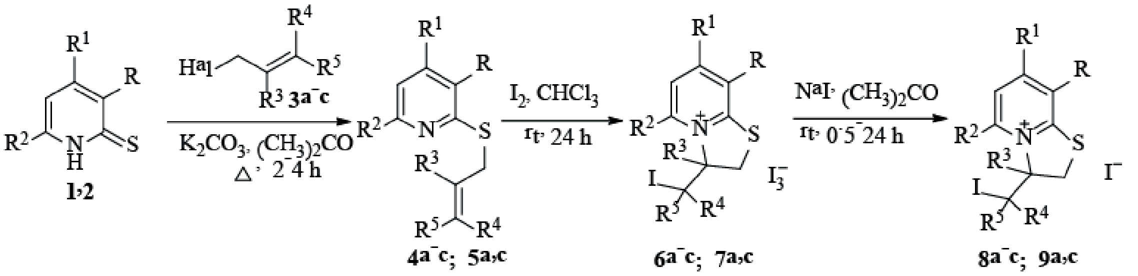
For derivatives of [1,3]thiazolo[3,2-a]pyridinium detected analgesic, anti-inflammatory and hypoglycemic activity.

In order to study alkenyl derivatives of 2-pyridinthione in the halogencyclization reaction, we carried out the interaction of 2-pyridinthione (1) and 4,6-dimethyl-3-cyano-2-pyridinthione (2) with alkenyl halides (3a-c) in the presence K2CO3 in acetone. The reaction proceeds regioselectively, the first time we synthesized 2-methallylsulfanylpyridine (4a) 2-(2-bromoallylsulfanyl)pyridine (4b), 2-prenilsulfanylpyridine (4c) 4,6-dimethyl-3-cyano-2-methallylsulfanylpyridine (5a) and 4,6-dimethyl-3-cyano-2-prenylsulfanylpyridine (5c).

We have shown that as a result of the reaction of 2-alkenylsulfanylpyridines 4a-c and 5a,c with iodine, a five-membered cycle is annulated to form previously unknown 3-iodomethyl-2,3-dihydro[1,3]thiazolo[3,2-a]pyridinium triiodides (6a-c and 7a,c) whose structure is established by X-ray diffraction and 1H NMR.





1,4,6,8: $R = R^1 = R^2 = H$; **2,5,7,9**: $R = CN$, $R^1 = R^2 = CH_3$; Hal = Br, Cl;
a: $R^3 = CH_3$, $R^4 = R^5 = H$; **b**: $R^3 = Br$, $R^4 = R^5 = H$; **c**: $R^3 = H$, $R^4 = R^5 = CH_3$

Sulfides 4a-c and 5a,c react with bromine to form bromocyclization products and bromine addition products on a double bond.

This study was performed under financial support by the government of the Russian Federation (Resolution no. 211, March 16, 2013; contract no. 02.A03.21.0011) and by the Ministry of Education and Science of the Russian Federation in the framework of state assignment no. 4.9665.2017/8.9.

TANDEM OXIDATION-HALOGENATION REACTION OF SECONDARY ALCOHOLS BY MEANS OF H_2O_2-HHAL SYSTEMS. NEW METHOD FOR HALOGENO KETONES SYNTHESIS.

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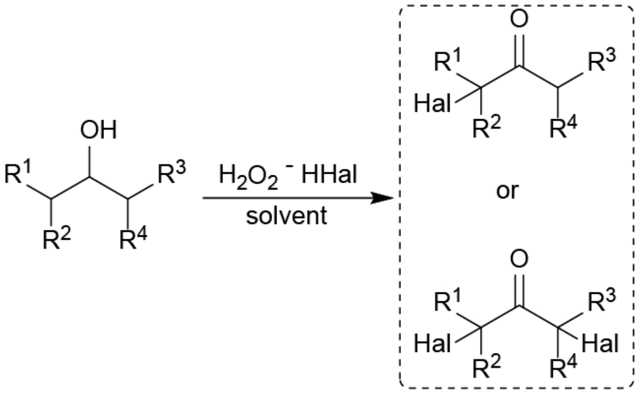
Ketones are one of the main classes in the range of organic compounds. The compounds containing keto-group are included in the composition of natural objects, many drugs, pesticides, pheromones, perfume compositions, dyes, solvents, detergents and cleaning products. Halogen in a ketone molecule increases their potential as synthons, allows the introduction of double bonds and functional groups in the molecule and thus expands the boundaries of their use in organic synthesis.

We carried out the oxidative halogenation of secondary alcohols in chlorine and bromo ketones under the action of the H_2O_2/HHal systems. The transformation of alcohols into halogeno ketones proceeds as a one-pot process without isolating intermediate ketones. On the basis of this reaction, a new, easy-to-use, method for producing mono- and dihalogeno ketones has been developed.



This process expands the field of application of hydrogen peroxide, one of the most popular oxidizing agents in organic synthesis.

This work was supported by the Russian Foundation for Basic Research (Grant no 18-03-00122 A).

STUDY OF THE INTERACTION OF ACETYLACETONATES OF BORON, GERMANIUM AND TIN DIHALOGENIDES WITH POLYPHENYLSILSESQUIOXANE IN CONDITIONS OF MECHANOCHEMICAL ACTIVATION

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Boron difluoride acetylacetonate, germanium and tin dichlorides bis-acetylacetonates were reacted with polyphenylsilsesquioxane in a Pulverisette 6 planetary ball mill with a frequency of 600 rpm, the ratio of the nozzle mass to the mass of the useful load was 1.8, the molar ratio Si/E was 1:1. The reaction mixture was divided into soluble and insoluble in toluene fraction (table). The composition and structure of the products of the syntheses were studied by the methods of elemental, X-ray phase and gel chromatographic analyzes, IR and NMR spectroscopy, HPLC (ESI-MS / MS).

Source derivative	№ synth.	Wfr., %	Found / calculated, %				
			Э	Si	C	F (Cl)	Si/Э
F_2BAcAc E=B	1	100	$[(PhSi(F)O)OBAcAc]_n$				
			3.5/4.1	10.3/10.5	50.3/49.7	7.3/7.1	1.1:1
$Cl_2Sn(AcAc)_2$ E=Sn	2	SF1 38.0	$[(PhSiO_{1.5})_{0.87}(PhSi(Cl)O)(SnO_{0.5}Cl(AcAc)_2]_n$				
			20.5/17.7	9.5/9.0	40.0/41.0	11.5/11.4	1.87:1
		SF2 48.3	$[(AcAc)_2Sn(Cl)O_{0.5}]_2OSiPh(OH)$				
			27.1/27.1	3.4/3.2	36.1/35.6	14.5/12.1	1:1.88
$Cl_2Ge(AcAc)_2$ E=Ge	3	ISF 54.1	$(PhSiO_{1.5})_{0.09}\cdot(AcAc)_2GeCl_2\cdot 0.11CH_3C_6H_5$				
			20.5/20.0	0.7/0.7	38.4/37.3	20.1/19.5	0.09:1
		SF 45.9	$[(PhSiO_{1.5})_6(OGe(AcAc)_2(OGeCl_2)\cdot 0.61CH_3C_6H_5]_n$				
			12.5/11.4	13.8/13.1	43.2/43.7	9.8/9.5	2.86:1

The insoluble fractions of syntheses 2 and 3 are a mixture of the starting materials and their decomposition products. Soluble fractions of syntheses 1 and 3, fraction 1 of synthesis 2 - polymeric products. Fraction SF2 is a previously not described crystalline substance, its formula is given in the table.

Reactions proceeded with the participation of the halogen radical. The fluorine radical is the most reactive, which explains the correspondence of the obtained Si/B ratio to the given one and the absence of an insoluble fraction.

The results of the synthesis depended on the nature of the metal. Breaking the Sn-Cl bond was easier than Ge-Cl due to the large radius of the tin atom, which resulted in a larger proportion of soluble fractions in synthesis 2.

COMPLEXATION OF GALLIUM(III) WITH 1,7-DIAMINO-4-OXYHEPTANE-1,1,7,7-TETRAPHOSPHONIC ACID

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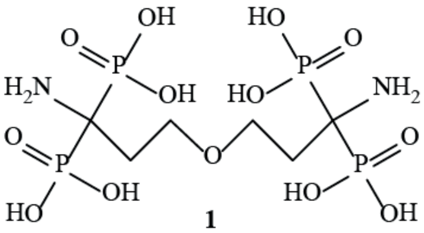
Aminodiphosphonic acids are promising components of radiopharmaceuticals because they can effectively bind cations of diagnostic or therapeutic radiometals and can deliver it to the bones due to their affinity for binding with hydroxyapatite, the main component of bone matrix. ^{68}Ga is one of the popular diagnostic isotope in nuclear medicine. Therefore in this work we study complexation of stabile Ga^{3+} with earlier synthesized 1,7-diamino-4-oxyheptane-1,1,7,7-tetraphosphonic acid 1[1] by potentiometric titration.



1

Dissociation constants of 1 and stability constants of its complexes with Ga^{3+} were obtained for the first time. Species distribution diagrams of the protonated forms of 1 and its complexes as a function of pH were plotted. Reaction of Ga^{3+} with 1 at the different pH was studied by NMR. Spectral and potentiometric data were compared. It was found that there are several forms of protonated complexes in solution at pH>8. Moreover, complex predominantly are in the GaH_3L^{2-} form at pH≈6.5. It leads to the formation of three groups of signals in 31P NMR due to the phosphorous atoms nonequivalence.

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SYNTHESIS AND STUDY OF NITROGEN-, OXYGEN-, PHOSPHORUS-CONTAINING SORBENT

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Studies have been conducted to study the effect of temperature on the process of polycondensation of urea, formaldehyde, and phosphoric acid (MFP). The process of polycondensation was studied at temperatures: 70, 80, 90 and 100°C. At the same time, the reaction duration, the specific volume of the sorbent in water, and the static exchange capacity (SOC) of 0.1 N HCl solution were established.

From the experimental data, it follows that at a temperature of 70 °C, the duration of the polycondensation reaction is 10 hours, the exchange capacity of the ion exchanger is 3.7 mEq / g. This is due to the low activity of the reactants at a given temperature. With an increase in the reaction temperature to 100 °C, the polycondensation process proceeds rapidly and the reaction time decreases to 1.5-2 hours, however, the magnitude of the exchange capacity and the swelling capacity of the ion exchanger also decrease. This is apparently due to the fact that at a given temperature the structure of the resulting ion exchanger becomes more dense, as a result of which the mobility of ionic groups is hampered. The optimum temperature of polycondensation was 90°C, the reaction time was 3.5-4 hours, the reaction was more uniform, and the exchange capacity of 0.1 N HCl solution reached 5.5 mEq / g.

To obtain an ion exchanger with a different number of cross-links, various samples of ion exchangers were synthesized. On the basis of the conducted studies, ionites with the best indicators were obtained at a 1: 2: 1 ratio of urea, formaldehyde and phosphoric acid, respectively.

The IR spectra of the obtained compound contain bands in the region of 3439 cm^{-1}, corresponding to the valence vibrations of the secondary N – H groups. The appearance of bands in the 1640 cm^{-1} region indicates a bound C = O group, and in the 1431 cm^{-1} region, we observe resolved resonances of the CH_2 groups. Free and related P = O groups appear in the regions of 1119 cm^{-1} and 932 cm^{-1}.

SYNTHESIS AND RESEARCH OF PHOSPHORUS-CONTAINING POLYMERIC LIGAND

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Despite the large range of polymer ligands, many of them have a number of drawbacks that limit the possibilities and their scope. To improve the kinetic and sorption properties of polymeric ligands, it is advisable to synthesize them from multifunctional compounds containing electron-functional groups.

8 g (0.0315 mol) of potassium di- (2-aminoethyl) -dithiophosphate were placed in a three-necked flask equipped with a reflux condenser and mechanical stirrer and 5.8 g (0.063 mol) of epichlorohydrin were added dropwise at a temperature of 40°C. Then, the temperature was increased to 85-90 °C and at this temperature, after 1.5-2 hours, a resinous mass was formed, which was transferred to a porcelain dish and dried at 80-90 °C for 24 hours. The resulting product is a gel grayish brown granules. Exit 87%. The results of elemental analysis - calculated: H - 4,92%, C – 32,78%, S – 17,48%, K – 10,65%; найдено: H - 4,85%, C – 32,67%, S – 17,43%, K – 10,71%. General formula $[(–OCH_2CH(CH_2))_2(ClH_2NC_2H_4O)_2PS_2K]_n$. In the IR spectrum was observed, cm -1: ν(NH) 3324, νs(CH2) 2963, δ(CH2)+δ(CN) 1614, $\delta_{as}(CH_2)$ 1454, $\delta_s(CH_2)$ 1342, ν(C-O) 1070, ν(POC) 979, ν(C-C) 830, ν(P-O) 752, ν(P=S) 665, ν(P-S-) 516.

According to the results, the molar ratio of di- (2-aminoethyl) -dithiophosphate potassium: epichlorohydrin is 1: 2.

Table. Physico-chemical properties of the obtained polymer ligand

The molar ratio of the starting materials	Output, %	Bulk weight, g / ml	Specific volume, ml / g	Static exchange capacity for 0.1 N solutions, mEq / g		
				$CuSO_4$	$NiSO_4$	$AgNO_3$
1:2	87	0,43	2,7	3,7	3,5	4,5

ELECTROPHILIC ACTIVATION OF NITROALKANES IN SYNTHESIS OF N-HETEROCYCLES

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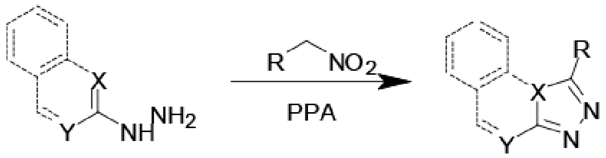
Recently we reported efficient synthesis of 1,3,4-oxadiazoles, containing different substituents in 2 and 5 positions via electrophilic activation of nitroalkanes in polyphosphoric acid and further cyclocondensation with acylhydrozides.

We wondered about the possibility of employing 2-hydrazinoquinoline and other heterocyclic hydrazines en route to [1,2,4] triazolo[4,3-a]quinolone scaffolds (Scheme 1). The reaction proceeds at 130°C with high yields (60-99%).



X = O, S, N
Y = Alk, (het)Ar, NH_2, CH
R = H, Alk, Ar,

Scheme 1.

The novel one-pot multistep reaction sequence involving cyclocondensation with nitroalkanes has been investigated..

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INTERPHASE CHARACTERISTICS OF HYMATOMELANIC ACID FRACTIONS AT THE LIQUID-GAS INTERFACE

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In this work, the interphase characteristics of the hymatomelanic acids (HMA) fractions at the liquid-gas (L-G) interface were investigated using the dilatational rheology method (Tensiometer PAT-2P SINTERFACE Technologies, Germany). Humic acids were isolated from brown coal samples at t = 100°C (HA_{100}). HMA were obtained from HA_{100} by single extraction with ethyl alcohol at t = 80 and 20°C (HMA_{80-100} and HMA_{20-100}).

The HMA_{20-100} fraction is characterized by abnormally high values of viscoelasticity (|E| = 117 mN/m) and elasticity (E_r = 115 mN/m). Probable causes for this behavior were identified. The dependence $|E| = f(C_{HMA})$ for the $HMA2_{0-100}$ fraction in the framework of the polymolecular adsorption model for polyelectrolytes of protein nature[1] obeys the equation of trilayer adsorption, and the HMA_{80-100} fraction – the equation of bilayer adsorption. The fraction HMA_{20-100} has a low average molecular weight ($\overline{M}$), contains more carboxyl groups, also it is characterized by significant aliphatic part in macromolecules (Table). The ratio between the aromatic and aliphatic parts in macromolecules of humic compounds is related to the ratio of absorption coefficients at 465 nm and 665 nm, E_{465} / E_{665}[2]. High values of E_{465}/E_{665} also indicate the predominance of aliphatic fragments in the structure of macromolecules.

Table. The maximum values of the rheological characteristics of the natural polyelectrolytes surface layers at the liquid-gas interface

Polyelectrolyte	|E|, N/m	Er, N/m	$\overline{M}$	E_{465} / E_{665}	[-COOH], mg-eq/g	[-OH], mg-eq/g
HA_{100}	55	54	15000	5,92	2,8	2,4
HMA_{80-100}	60	59	12000	8,50	2,4	3,2
HMA_{20-100}	117	115	5000	12,13	3,2	2,8
Albumin	70	68	65000	-	-	-
β-casein	10	9	24000	-	-	-

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STUDY OF HYDROGELS SYNTHESIZED ON THE BASIS OF STARCH COPOLYMERS

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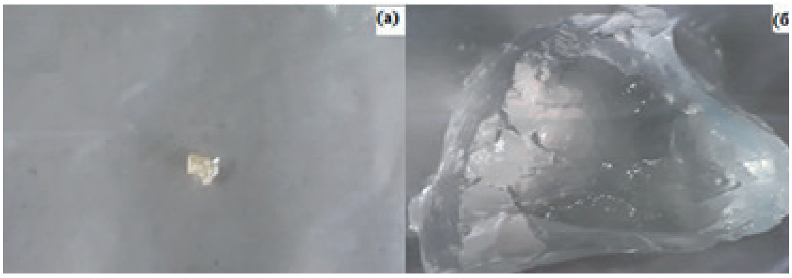
Acrylamide-based and starch-based hydrogels are among the most water-absorbing, and the use of bentonite clay in a starch-acrylamide hydrogel improves water absorption, improves mechanical properties, and reduces cost. Bentonite mineral reserves a lot, and it is very cheap.

In the copolymerization reaction, various substances can be used as a binder, such as methylene bisacrylamide, such as potassium persulfate or ammonium persulfate. As synthetic hydrogels, hydrogels derived from starch copolymers do not release toxic substances into the environment and do not degrade the soil.

The starch/acrylamide/bentonite-based hydrogel reaction can be carried out using radical polymerization for 3 hours at 70°C. After completion of the reaction, the product is hydrolyzed to pH = 7 with a solution of sodium hydroxide or potassium, and then it is washed several times in distilled water. Then dried at 60°C to a continuous mass. At the same time, a highly swollen hydrogel is formed.

Figure shows dry (a) and swollen (b) starch/acrylamide/bentonite based hydrogel.



Picture. Dry (a) and swollen (b) hydrogel based on starch, acrylamide and bentonite

The figure shows that the ratio of the swollen hydrogel to the dry mass is several hundred times greater. Hydrogel can be used several times depending on the composition of water and soil, but after drying the hydrogel, the degree of swelling decreases with the next soaking. Hydrogels based on polysaccharides, like hydrogels based on synthetic materials, leave behind a lot of fertilizers that do not leave toxic residues for them at the end of their work.

NEW SYNTHESIS OF 2-ETHYL-1,5-DIPHENYL-4,5-DIHYDRO-1H-IMIDAZOLE VIA ELECTROPHILIC ACTIVATION OF NITROALKANES

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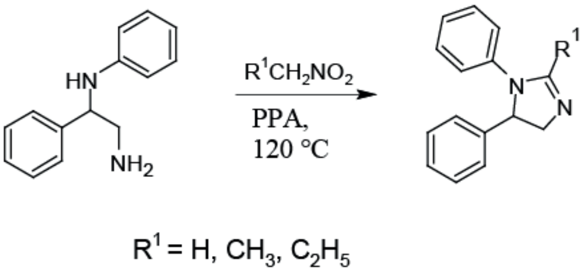
Imidazole he has become an important part of many pharmaceuticals. Synthetic imidazoles are present in many fungicides and antifungal, antiprotozoal, and antihypertensive medications. Imidazole is part of the theophylline and in the anticancer medication mercaptopurine, which combats leukemia by interfering with DNA activities.

New efficient synthesis of 2-ethyl-1,5-diphenyl-4,5-dihydro-1*H*-imidazole, from different diphenylethane-1,2-diamines via electrophilic activation of nitroalkanes in polyphosphoric acid and further cyclocondensation is reported.

We wondered the way of employing N1,1-diphenylethane-1,2-diamine and his derivatives en route to 2-ethyl-1,5-diphenyl-4,5-dihydro-1*H*-imidazole scaffolds (Scheme 1). The reaction proceeds at 120°C with middling yields (~40 %).



Scheme 1

Thus, a new reaction of N1,1-diphenylethane-1,2-diamine was found in the PPA medium with activated nitroalkanes under mild conditions, including cyclocondensation.

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LIQUID CHROMATOGRAPHY OF AROMATIC HETEROCYCLES

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Heterocyclic compounds varied in structure, composition and number of nitrogen atoms have attracted researchers attention due to their practical application[2] and as models to establish the relationship between the structure and their physico-chemical properties and, in particular, chromatographic retention.

We investigated the laws of chromatographic retention in the series of triazole, benzotriazole, quinoline, and 1,2,3,4-tetrahydroquinoline derivatives. To establish the dependence of retention on the structure of the compounds, some physicochemical characteristics of these substances were calculated. Also, we optimized the structure and calculated the molecular characteristics using the Spartan-14 program. V 1.4 in the framework of the density functional theory (DFT).

Obtained data demonstrates that the increase the number of nitrogen atoms in the molecules of the studied compounds leads to the significant decrease in the values of the retention characteristics. In general, there are significant differences in the patterns of retention of azoles and quinoline derivatives due to changes in the solvation energy and dipole moment of these compounds and the differences in the geometry of their molecules. The final conclusions about the laws of sorption of these classes of nitrogen-containing aromatic compounds can be made on the basis of a set of data on the thermodynamics of sorption and solvation, as well as taking into account the results of modeling the sorption complexes in our chosen chromatographic systems.

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CHEMICAL MESOSCOPICS IN MESOPARTICLES REACTIONS

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The Chemical Mesoscopics is the scientific trend studied the mesosystems activity at the beginning of formation and at further active behavior in media and in materials. The theoretical basis of this trend give the explanation for peculiarities of nanostructures formation including reaction within nanoreactors as well as the behavior of minute quantities of them in media and materials with properties change of latest.

The fundamental postulates of Chemical mesoscopics, according to which a) regulated mesosystem must be many much little than macrosystem which is found in contact with it, b) the charges (negative and positive) quantization is observed, d) such phenomena as interference with chemical bonds and also annihilation with the creation of radiation and direct electromagnetic fields, that stimulate the electron shift in high energetically region.

The Chemical Mesoscopics postulates for the metal/carbon nanocomposites synthesis and their modification reactions are considered. These processes for above mesoparticles and mesosystems proceed owing to the reduction-oxidation process on the interface boundary of metal containing substances and polymeric phases. In all cases the realization of above processes lead to the metal reduction and the formation of Carbon shell from Carbon fibers. In turn the Carbon fibers consist from fragments of poly acetylene and carbine. On the joints of these fragments the unpaired electrons are appeared. In this case it's possible the formation of electric circuit. The formation of unpaired electrons on d orbital's of metal leads to the metal atomic magnetic moment growth and also to the creation of magnetic flow disposed perpendicularly to the plane of formed circuit. That structure of mesoparticle (nano granule) is confirmed by the complex of methods (x-ray photoelectron spectroscopy, AFM, TEM, EPR) as well as by the investigations of mesoparticles activity in redox processes.

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REGULARITIES OF "STRUCTURE-PROPERTY" IN THE SERIES OF ALKYLATED 3,5-DIAMINO-1,2,4-TRIAZOLES

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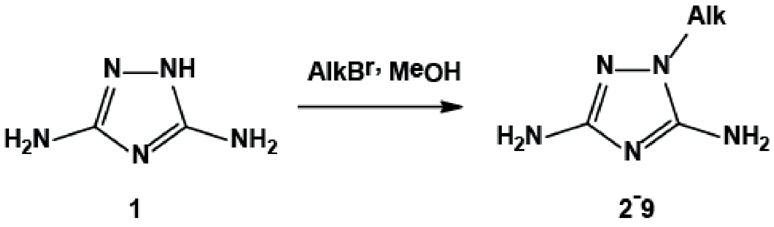
Analysis of the literature showed that alkyl derivatives of nitrogen-containing heterocycles are most widely used in the creation of devices operating on liquid crystals, as well as in various antimicrobial drugs. In accordance with method1, we synthesized a series of 1N-alkyl derivatives of 1,2,4-triazole 2-9, which was studied further in the applied aspect.



Alk = CH_3(**2**); C_3H_7 (**3**); C_5H_{10} (**4**); C_7H_{15} (**5**);C_8H_{19} (**6**); $C_{10}H_{21}$ (**7**); $C_{12}H_{25}$ (**8**); $C_{16}H_{31}$ (**9**)

Initially, compounds 2–9 were investigated for the manifestation of mesomorphic properties. The phase transition temperatures of the synthesized products were determined by the method of thermomicroscopy. It turned out that in the series of 1N-alkyl-3,5-diamino-1,2,4-triazoles, with an increase in the alkyl chain, the ability to exhibit mesomorphic properties — $C_{10}H_{21} < C_{12}H_{25} < C_{16}H_{33}$ — increased.

Studies of the antibacterial properties of the disc diffusion method have shown that compositions created on the basis of 1-decyl-3,5-diamino-1,2,4-triazole 7 have a high antibacterial activity and can be used for the preparation of medicinal dressings.

Thus, an increase in the alkyl chain contributes to the manifestation of properties that are promising in practical terms, which will make it possible in the future to use such compounds to create organic materials with predictable characteristics.

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POLIDENTANTE LIGANDS BASED ON HYPERBRANCHED POLYESTERS CONTAINING TERMINAL BENZOYLCARBAMATE AND THIOCARBAMATE GROUPS

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Hyperbranched polymers, having a high concentration of functional groups at the periphery, can act as effective polydentate ligands[1].

Hyperbranched polyethers of the second generation containing terminal benzoylcarbamate (1) and benzoylthiocarbamate (2) fragments were synthesized. 1H NMR spectroscopy was employed to establish that compound (1) contains 6 benzoylcarbamate, and compound (2) has 7 benzoylthiocarbamate groups. On the basis of these compounds, complexes with Cu (II) and Co (II) ions were obtained. IR spectroscopic data indicate the participation of oxygen and sulfur atoms of the carbonyl and thiocarbonyl groups in the formation of coordination bonds with metal ions.

To confirm the structure of the synthesized compounds, we have obtained dendrons simulating terminal fragments of hyperbranched polyesters. Benzoylcarbamate and benzoylthiocarbamate derivatives of 2,2-dimethylopropanoic acid ethyl ester have been synthesized. By 1H NMR spectroscopy, it was found that both hydroxyl groups of the ester were modified. Complexes of dendrons with Cu (II) and Co (II) ions were synthesized. IR spectral data indicate the coordination of metal ions with oxygen and sulfur atoms of the benzoyl carbamate and α-thiocabamate groups.

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HYPERBRANCHED POLYESTER POLYOLS CONTAINING FUNCTIONAL GROUPS, IONS AND NANOPARTICLES OF D-METALS

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Academic interest in the creation and research of composite materials based on hyperbranched polymers and their derivatives containing functional groups, ions and metal nanoparticles is due to the possibilities of their practical application as part of promising materials for biotechnology, medicine and pharmacy.

The conditions of formation, morphology, aggregation and functional activity of metal complexes and nanoparticles of biophilic metals (Co, Cu, Ag, Au) on the base of hyperbranched polyester polyols and their derivatives containing fragments of acrylic and propanoic acids in terminal positions were studied. It was established that the stabilization of metal ions with the subsequent formation of the corresponding metal complexes and nanoparticles is due to their coordination and electrostatic interactions with the oxygen atoms of the carbonyl and hydroxyl groups of polyester polyols or carboxylic groups of polycarboxylic acids.

Co(II) ions with polydentate ligands were composed of coordination nodes with octahedral (MO_6) and tetrahedral (MO_4) symmetry for polypropanoic and polyacrylic acids, respectively. For the Cu(II) ion, increase in the functionalization degree of polyacrylic acid leads to a change in the geometry of the coordination unit from tetrahedral to octahedral. Powders and colloid-stable solutions containing polymer-stabilized Co^0 nanoparticles (8 nm) with superparamagnetic properties, Cu^0 nanoparticles (24-40 nm), Ag^0 nanoparticles (34-400 nm), Au^0 nanoparticles (50-100 nm) have been synthesized.

The prospects for use of the synthesized polyester polyacids as self-organizing systems for doxorubicin transport were revealed. Metal complexes and nanoparticles of copper, cobalt, silver and gold on the basis of hyperbranched polyester polyols and polyacids possess antiproteinase and antifungal activity.

METHODOLOGICAL ASPECTS OF THE PERIODIC SYSTEM CHEMICAL ELEMENTS D. I. MENDELEEV CONSTRUCTION

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The analysis of the relativistic Hamiltonian for various forms of quantum mechanics – instantaneous, point, frontal, proposed in the works of Dirac[1,2]. On the basis of the analysis of the relativistic Hamiltonian for the K-shell of atoms is shown that the number of elements of the periodic system is limited and equal to 137[3]. The existence of elements with a charge of the nucleus 137 and more is impossible, since the electron *K*-shell of the atom is unstable. The total number of elements of the periodic system is determined by one of the fundamental quantities – the speed of light equal to 137,03604 atomic units of speed in the atomic coordinate system.

All elements periodic table in the proposed final version are placed in eight periods and eight groups, Fig.1. The last three periods – the sixth, seventh and eighth form families consisting of 14 elements. In the eighth period, the shell *R* in elements 119, 120 is filled. In the analogs of the element 121, the 6*f*- shell is filled, so it is possible that the elements 122 ... 135 are similar in properties to the actinium series. The last two elements of the periodic table on the structure of electronic configurations can be attributed to the *d*-elements.

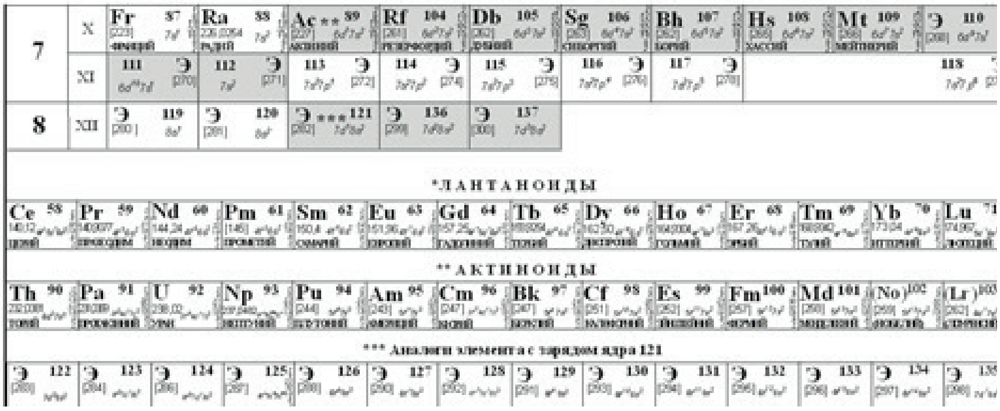

Figure 1. The proposed lower part of the final version of the periodic table of chemical elements D. I. Mendeleev-7.8 periods

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DECAY OF HYDROGEN PEROXIDE IN THE PRESENCE OF FULLERENES AND CARBON NANOTUBES

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In our laboratory, we undertake experiments to determine the effect of carbon nanostructures (CNS) on the decomposition of hydrogen peroxide (H_2O_2) and the subsequent oxidation hydrocarbons, petroleum fractions. These studies are conducted both in the aspect of studying the kinetic patterns of aerobic-peroxide oxidation of hydrocarbons, and in the catalytic action of various CNS on the yield and selectivity of final products [1-2]. In this aspect, it is extremely impor-tant to know what is rate of decomposition of H_2O_2 at moderate temperatures. The thermal decomposition intensity of H_2O_2 in aqueous solutions is characterized in the literature by various figures, since peroxide is extremely sensitive to any, even the smallest impurities, which catalyze its decay. Thus, in order to study the kinetics of hydrocarbon oxidation with H_2O_2 and to have accurate quantitative information, necessary first carefully study the thermal decompo-sition of H_2O_2 at operating temperatures under the most sterile conditions.

The present report is devoted to studying the kinetics of the thermal decomposition of aqueous solutions of H_2O_2 solely and in the presence of fullerenes and multi-walled carbon nanotubes (MWCNTs) by means of the volumetric analy-sis. As a result of experiments it has been inferred: 1. Rates of oxygen evolution during the thermal decomposition of H_2O_2 at 60°C were precisely obtained. 2. The rate of released oxygen is directly proportional to the concent¬ration of H_2O_2 – the thermal decomposition of H_2O_2 proceeds according to the first-order mode. Experiments conducted in the presence of fullerenes and MWCNTs have shown that decomposition of H_2O_2 is substantially catalyzed by the nanocarbon patterns. It has been found that the catalytic activity of fullerene soot turns out to be 4 times higher than fullerene C_{60}. Seemingly, fullerene soot contains admix-ture compounds, which have an additional catalytic effect on the decomposition of H_2O_2.

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CORRELATION OF THE CLUSTER AND ASSOCIATED MODEL OF VISCOSITY WITH A FRENKEL EQUATION

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The cluster and associative model of the temperature dependence of viscosity is based on the idea of the virtual existence in a liquid of fragments of a solid phase – clusters and their associates. Clusters retain the structural motifs of the crystalline phase, and the probability of their formation and destruction is determined by the energy barrier, commensurate with the heat of melting of the crystal. Associates form such a virtual arrangement of clusters in which they are connected by weaker molecular attraction forces, and their formation and destruction depends on the energy of van der Waals attraction. The result is a hierarchical model1

$$\eta=\eta_1\,(T_1/T)^{\,(a=a_2\,(T_2/T)^b\,)},$$

where is the bottom level $\eta_1(T_1/T)$ responsible for the formation of clusters, and the top $a = a_2(T_2/T)^b$ – for the formation of associates. On this basis, when adapting the cluster and associative model to the experimental data, the indicator a determined in this case has the meaning of the degree of cluster association, that is, the average number of clusters in the associate.

This is confirmed when determining the activation energy by the Frenkel's equation based on the adaptation of the same experimental data together with those calculated by the cluster and associate model in logarithmic coordinates. When processing linearized plots, the value of activation energy found when dividing by the degree of cluster association gives values in all cases related to the interval of van der Waals attraction energy, 2-20 кДж/моль[2,3].

Thus, it is substantiated that a viscous flow is the destruction of associates without the destruction of clusters. This is confirmed by an analysis of the temperature dependences of the viscosity of simple substances, inorganic compounds, and slag systems.

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EQUILIBRIUM IN SYSTEMS, CONTAINING STRONG CATION EXCHANGERS - BIVALENT METAL-IONS

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The report presents the results of the equilibrium, kinetics and thermo-dynamics of the interaction of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions with strongly acid Amberlite IR 120H, Dowex 50W×8 and Diaion RCP 160M cation exchangers. The thermodynamic description of the exchange of the studied ions by cation exchangers was carried out under the assumption that the solid phase is ideal, i.e. without taking into account the coefficients of ion activity in the sorbed state. Sorption isotherms were studied at concentrations from 0.25 to 2.50 $gMe^{2+}.L^{-1}$. The dependence $A=f(C_e)$ had the form of the Langmuir isotherm for all the systems studied. The parameters of the Freundlich equation were also calculated, and the corresponding equations were proposed. Since the results of the sorption of the studied ions depend on a linear dependence in the coordinates $C_e/A– C_e$ with a high correlation coefficient, this dependence allows determining the Amax and K with good accuracy. The selectivity of sorption of the studied ions with ion exchangers increases, and then decreases with an increase in their molar fractions in the solid phase. Since the kinetics of the processes was studied in solutions with a concentration of $C_0=1$ $gMe^{2+}.L^{-1}$, the number of metal ions passing into the solid phase is small, and the K values vary in the range of 1,3-1,9. But from concentrated solutions of more than 2 g $Me^{2+}.L^{-1}$, the values are 4–5 times higher for K. The diffusion coefficients of ions in ionites with different granules in solutions of different concentrations were calculated. Using the calculated Bio criteria, the mechanism of the processes under study, corres-ponding to the internal diffusion kinetics, was revealed. At the same concentra-tion, the sorption rate of the studied ions is the higher, the more selective the cation exchanger is to the ion under study. The enthalpy of the processes was determined by the ratio of the released amount of heat to the amount of sorbed ions. The sorption processes of the studied ions are exothermic and are characterized by a decrease in exothermicity as they are absorbed by the ions. The reason for the subsequent decrease in the intensity of the heat flux may be the need for diffusion of sorbed ions into the depth of the grain, which is associated with additional energy costs. By sorption and kinetic parameters, Diaion RCP 160M far exceeds the other two. The calculated all thermodynamic parameters are negative, therefore the exchange of the studied ions for H^+ is accompanied by heat release, a decrease in the entropy and Hibbs free energy.

INVESTIGATION OF THE BROMINATION REACTIONS OF PYRROLE DERIVATIVES IN DIFFERENT CONDITIONS

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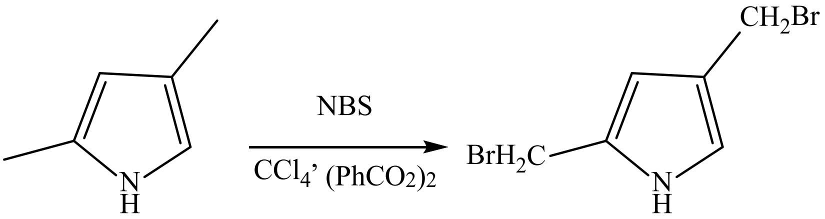
It is known that pyrrole and its derivatives are convenient synthons in the synthesis of new biologically active compounds[1,2]. Despite the availability of the preparation, Knorr pyrrole remains insufficiently studied in terms of the functionalization of its structure. Many questions related to the conditions of the Knorr pyrrole reactions are little studied to the present. In this regard, we have carried out investigation of the bromination reaction of Knorr pyrrole with the help of N-bromosuccinimide according to the allylic substitution scheme. It was found that the reaction depended on the nature of the solvent. Thus, no visible changes were observed when using dry ethyl acetate. At the same time, when using carbon tetrachloride purified over phosphorus pentoxide as a solvent, the target product, 2,4-dimethylbromo-3,5-diethoxypyrrole (1), was obtained with a yield of 76% and m.p. 125^{0}C.



(1)

The reaction was carried out in the presence of a radical initiation catalyst, benzoyl peroxide. The reaction completes in 2 hours with the release of succinimide on the surface of the solvent. The resulting reaction product (1) is a convenient synthon for further functionalization.

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REACTIONS OF ALKYL (GEM-DICHLOROCYCLOPROPYL-METHYL)-4-(2,5-DIOXO-2,5-DIHYDRO-1H-PIRROLYL) BENZOATES AND PHENYLACETATES WITH SECONDARY AMINES

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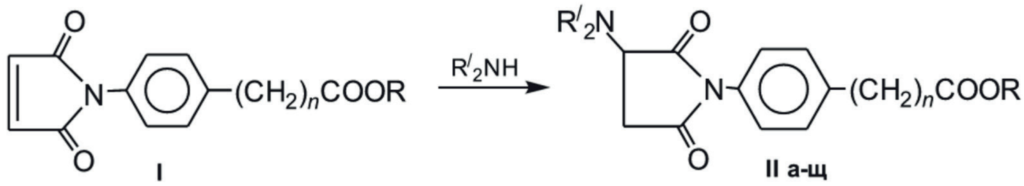
It is known that 4-aminobenzoic acid esters (anesthesin, novocain, dikan, etc.) are used as strong local anesthetic agents. In order to expand the range of such drugs, of particular interest is to obtain esters of 4-aminobenzoic and 4-aminophenylacetic acids containing succinimide cycle as a substituent, since hypnotic, anticonvulsant, antiarrhythmic and other types of activity of N-aryl-3-dialkylamino-2,5-dioxo-2,3,4,5-tetrahydro-1*H*-pyrrolins are described[1-3]. We have shown that the esters of 4-N-maleimidobenzoic and phenylacetic acids (I) react with diethylamine, piperidine, and morpholine in dioxane at 45-90°C to form alkyl (or heme-dichlorocyclopropylmethyl)-4-(3-dialkylamino)-2,5-dioxo-2,3,4,5-tetrahydro-1*H*-pyrrol-1-yl)benzoates and phenylacetate (II a-x):



I **II а-щ**

II: n=0, R=Me, R'=Et (а), $(CH_2)_5$ (б); R= Et, R'=Et (в), $(CH_2)_5$ (г), $(CH_2)_2O(CH_2)_2$ (д); R=CH_2CH_2Cl, R'=Et (е), $(CH_2)_5$ (ж), $(CH_2)_2O(CH_2)_2$ (з); R=C_4H_9, R'=Et (и), $(CH_2)_5$ (к), $(CH_2)_2O(CH_2)_2$ (л); R=$CCl_2CH_2CHCH_2$, R'=Et (м), $(CH_2)_5$ (н), $(CH_2)_2O(CH_2)_2$ (о); n=1, R=Me, R'=Et (п), R=Et, R'=Et (р), $(CH_2)_5$ (с), $(CH_2)_2O(CH_2)_2$ (т); R=CH_2CH_2Cl, R'=Et (у), $(CH_2)_5$ (ф), $(CH_2)_2O(CH_2)_2$ (х); R=C_4H_9, R'=Et (ц), $(CH_2)_5$ (ш), $(CH_2)_2O(CH_2)_2$ (щ).

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REACTIONS OF 1-ALKENILTRYCHLOROPHOSPHONY HEXACHLOROPHOSPHATES WITH CARBAMIDE DERIVATIVES

Mitrasov Yu.N., Savinova N.P., Lukicheva N.A., Smolina I.N., Chigarova N.A.

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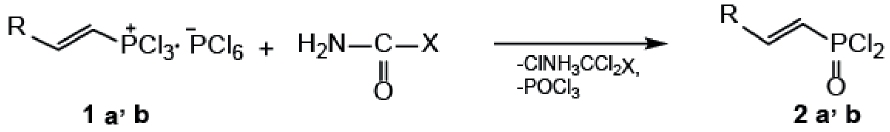
Earlier, in papers[1–4], we have proposed to use N-oxides of pyridines, lactams, oximes, amides of carboxylic and dithiocarbonic acids as transformers of intermediate C-nucleophiles adducts with phosphorus pentachloride. However, their activity in these reactions is not high enough. Therefore, with an aim to search for new, more efficient N-functionalized oxygen-containing transformers, and in the continuation of work[5,6], we studied the reaction of 2-phenyl- (or 2-ethoxy) ethenyltrichlorphosphonium hexachlorophosphates (1a, b) with carbamide derivatives.

We have shown that the adducts (1a, b) react easily with urea, biureth and acetylurea at an equimolar ratio of the reactants at room temperature with the formation of 2-phenyl (or 2-ethoxy) ethylphosphonic acid dichlorides (2a, b):



R=C_6H_5 (a), C_2H_5O (b); X=NH_2, NHC(O)NH2, NHC(O)CH3

The structure of dichloroanhydrides (2a, b) was confirmed according to the data of the IR, NMR ^{1}H and ^{31}P spectroscopy, and the composition was confirmed by elemental analysis.

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OBTAINING NANOCELLULOSE FROM COTTON

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Today, despite the extensive amount of research, there is an urgent need to modernize and intensify the technologies for producing nanocellulose (NC)[1,2].

We have investigated the possibility of obtaining NC using the stage of physico-chemical activation on a modified extrusion unit. The extrusion unit may include up to 8 cylinder working zones. The installation consists of a central auger, which is engaged with satellite augers performing the function of grinding elements. In turn, the augers satellites are engaged with the inner surface of the extruder working cylinder. Processing of pulp on the extrusion unit leads to its intensive grinding and defibrillation in the working cylinder of the extruder. This effect is achieved by cycling pulsating loads, which create high shear stresses that effectively act on the polymer chains of cellulose. If necessary, the number of zones of the extruder, as well as the number and type of augers satellites can be changed.

The production of NC from cotton was carried out by successively performing such operations as processing raw materials in distilled water, physico-chemical activation of wet cellulose on a modified extrusion unit, acid hydrolysis, dialysis, ultrasonic treatment.

According to the results of research, it can be concluded that processing cotton raw materials on a modified extrusion unit can reduce its degree of polymerization by 2.6 times, reduce the consumption of H_2SO_4 at subsequent stages of producing NC (2 times), and also increase the yield of nanoparticles with sizes less 100 nm by 24%. Cotton raw materials and the obtained NC samples have a structural modification of cellulose I. An increase in the number of zones of the modified extrusion aggregate leads to an increase in the proportion of particles with the smallest size increases.

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SUPRAMOLECULAR INCLUSION COMPLEX WITH CYCLODEXTRIN HAVING ROOT ACTIVITY

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The most interesting and practically significant properties of cyclodextrin (CD) is the ability to form inclusion complexes of the “host-guest” type, in which the CD plays the role of a “host”. In the process of formation of cyclodextrin complexes, many of the original properties of the “guests” —connected compounds — change, which makes it possible to improve the applied properties of the substances forming the complex. CD and complexes based on them are used in a wide variety of fields: in medicine and veterinary medicine, in perfumery and cosmetics, in agriculture, in food industry, biotechnology and ecology, in chemical technologies.

Synthesis of the supramolecular inclusion complex prop-2-ynylmorpholindi thiocarbamate (PMDK) with β-cyclodextrin (β-CD) was developed. The supra-molecular β-CDA/PMDK complex is synthesized by the interaction of PMDK substrate with β-CDA in DMSO at a reagent ratio of 1: 0.5 and a reaction tem-perature of 55 ° C for 10 hours. As a result of isolation, the complex was obtained in 57% yield.

The formation and structure of the supramolecular complex was confirmed by 1H and 13C NMR spectroscopy. Comparison of the integrated intensities of the PMR signals of the substrate molecules and the β-CD receptor has shown that a complex of one guest molecule per host molecule is formed.

The influence of the synthesized complex on the growth and development of the root system of the scirius spiraea (Spiraeasalicifolia) was studied. It was established that the treatment of seedlings with the complex β-CD / PMDK activates the formation of the root system and shoots in comparison with the control standard. Thus, at a concentration of 0.001%, the length of the roots reaches 6.4 cm, the number of formed shoots is 1.5 and the average length of these shoots is 1.4 cm. The β-CD/PMDC inclusion complex has root-forming activity and can be used in plant growing as a root-formation stimulator for ornamental shrubs.

ALTERNATIVE MECHANISMS OF THE PRIMARY ACT OF THE GAS-PHASE MONOMOLECULAR DECOMPOSITION OF ISOMERIC MONO-, DI- AND TRINITROPHENOLS

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The B3LYP/6-31+G(df,p) method was used to study the series of primary act mechanisms of monomolecular decomposition of all isomeric mono-, di-, and trinitrophenols: radical breakoffs of NO_2• and CH_3• groups and nitro-nitrite regroupings, formation of isomerous and substituted 7-oxa-8-azabicyclo[4.2.0]-octa-1(8)-2,4-triene-*n*-ol 8-oxide (where n is position of the OH group). For nitrophenols with the *ortho*-position of CH_3• and NO_2• groups (2-nitrophenol, 2,3-, 2,4-, 2,5- and 2,6-dinitrophenols, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5- and 2,4,6-trinitrophenols), we studied formation of *aci*-forms. For nitrophenols with neighboring nitrogroups, we studied the processes of formation of isomerous and substituted 1,4-dioxo-1,4-dihydro-2,3,1,4-benzodioxadiazine-1,4-diiums (2,3- and 3,4-dinitrophenols, 2,3,4-, 2,3,5-, 2,3,4-, 2,3,6-, 2,4,5- and 3,4,5-trinitrophenols). It was determined that the most energy favorable mechanism of the primary act for o-substituted nitrophenols is the reaction of formation of *aci*-forms. The transfer of hydrogen from oxygen of hydroxyl group to oxygen of NO_2 group and its turn around NO bond in the N(O)OH group takes place in one stage.

The mechanism of destraction of o-nitrophenol is most studied by us at the moment time. Secondary processes are limiting in this case. As well as for o-nitrotoluene [1], for o-nitrophenol is possible the motion of the =N(O)OH group around the double bond, and not the transfer of a hydrogen atom between two oxygen atoms in this group, that is more process expected in this system. However, the energetically favorable mechanism of o-nitrophenol *aci*-form further decomposition isn't found yet. All possible ways of development of reaction investigated by us have the energy barriers exceeding experimental values. This statement belongs to various alternative mechanisms of primary act of thermodestruction o-nitrophenol.

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STUDY OF THE PHYSICAL AND CHEMICAL PROPERTIES OF THE SYNTHESIZED OLIGOMER NDA-6

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Physical and chemical properties were studied: density, melting point, solubility, IR-spectroscopy and DSC in sulfur-, nitrogen- and phosphorus-containing oligomers. The physico-chemical characteristics of the synthesized high-filling oligomer of the brand NDA-6 (Ammophos with sulfur-containing organic compounds) are presented in the table.

Table. Physico-chemical indicators of thiokol oligomer NDA-6

Properties	Indicators
Density, g / cm3 GOST 15139-69	1,40
T melting oC	130
Ƞхв	0,070
Solubility	dimethylformamide
Appearance and color	brown viscous substance

On the IR spectrum of NDA-6 in the regions of 3300-3440 cm^{-1}, corresponding to the secondary –CONHR groups. The deformation vibrations of all active groups are manifested in the form of strong narrow bands between the usual deformation vibration bands –CH_2 – CO– in the region of 1400 - 1465 cm$^{–1}$. The absorption bands in the regions of 800 and 1600 cm$^{–1}$ confirm the presence of –NH_2 groups. The presence of groups containing phosphorus P=O and P–O–C in the range of 1000–1180 cm$^{–1}$ is confirmed by the broad intense band and sulfur-containing compounds in the ranges of 400–900 cm$^{–1}$, 1040–1060 cm$^{–1}$ and 1100–900 cm$^{–1}$.

Conducted a thermal study of the oligomer NDA-6. The mass of the NDA-6 sample does not change to 207 ° C. On the DSC curve in the temperature range of 20-207 °C, there is one endothermic peak (at 184.1 °C), which corresponds to the melting of the sample. Above the temperature of 207 ° C, the sample begins to decompose in two stages - up to 265 °C at a rate of 6%/min, and above 265 °C at a rate of 2.5%/min, with a total mass loss of 73%.

SYNTHESIS AND ANTIRADICAL ACTIVITY OF HINDERED PHENOL DERIVATIVES OF BENZAZOLE-2-THIONES

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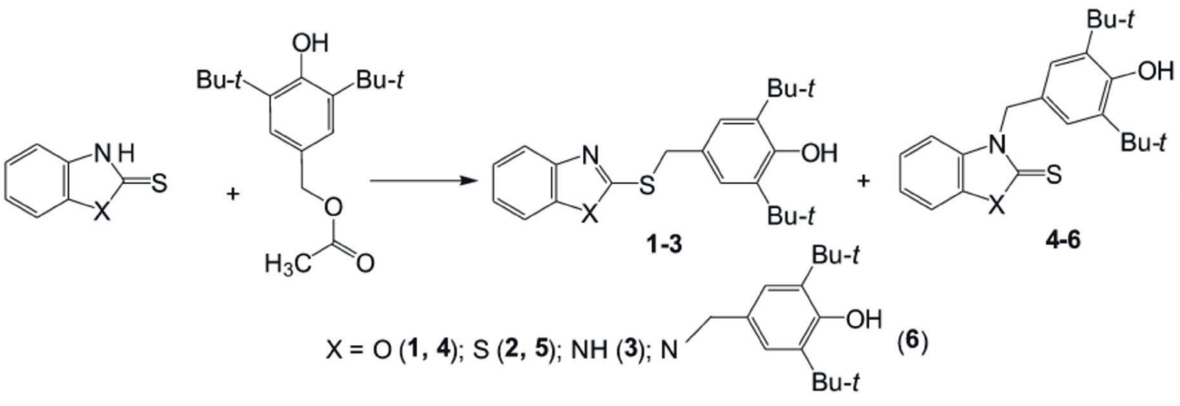
In the present work we determined conditions for the synthesis of S- and N-benzylation products of benzothiazole(oxazole, imidazole)-2-thiones in the reactions of the corresponding benzazole-2-thiones with 3,5-di-tert-butyl-4-hydroxybenzyl acetate. The synthesized derivatives of benzazol-2-thiones (1-6) are interesting as stabilizing additives to polymers and biologically active substances.



It was shown that antiradical activity of S- and N-3,5-di-tert-butyl-4-hydroxybenzyl derivatives of benzothiazole(oxazole, imidazole)-2-thione with respect to 2,2-diphenyl-1-picrylhydrazyl is varies widely. S-Benzyl derivatives exhibit higher reactivity at 30°C.

Table 1. Kinetic parameters of the reactions of substituted benzazole-2-thiones with 2,2-diphenyl-1-picrylhydrazyl in 1,4-dioxane

Соединение	k_2 *at 30°C*, L mol^{-1} s^{-1}	E_a kJ/mol	$\Delta S\neq$, J K^{-1} mol^{-1}
1	0.05625 ± 0.00089	56.7 ± 1.0	-90 ± 3
2	0.164 ± 0.0014	36.4 ± 0.8	-150 ± 3
3	0.032*	50.9 ± 1.6	-114 ± 5
4	0.0158 ± 0.00006	38.5 ± 2.5	-161 ± 8
5	0.0346 ± 0.0005	46.1 ± 0.3	-129 ± 6
6	0.0389 ± 0.0002	34.4 ± 0.4	-167 ± 4

* The value was calculated using the Arrhenius equation.

This work was carried out within the framework of the governmental task of the Ministry of Science and high Educationof the Russian Federation (№ 10.1718.2017/4.6).

SYNTHESIS AND STRUCTURE OF O-CINNAMOYLLUPININE

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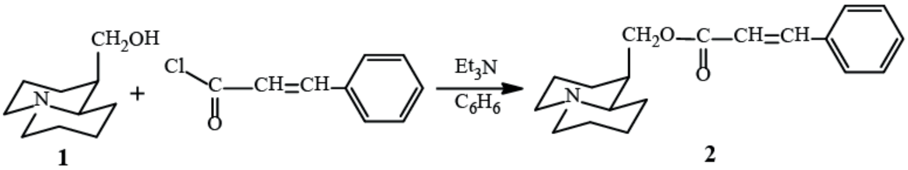
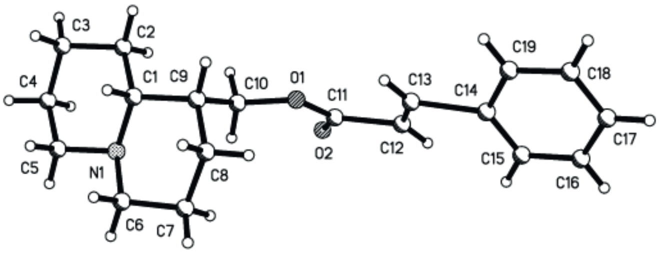
In continuation of the study of bicyclic heterocycles comprising quinoline fragment, we studied the interaction of the alkaloid lupinine 1 chloride cinnamoyl. The acylation reaction was carried out in a benzene medium in the presence of triethylamine, which resulted in a final product 2 with an output of 82% (MP 75-78°C). The structure of product 2 data set the spectral methods (IR, UV, NMR ^{1}H-, ^{13}C-) and identified as O-cinnamoyllupinine.



The spatial structure 2 is confirmed by x-ray diffraction. Analysis of the geometry of molecule 2 showed that the bond lengths in the phenyl radical, as well as the atoms connecting the lupin frame and the phenyl cycle, O1-C11 1.363, C11-C12 1.642, C12-C13 1.063 and C13-C14 1.759 Å are significantly deviated from the standard due to the large thermal vibrations of these atoms (U_{eq}. are 0.096-0.125 Å^2).



The conformation of the six-membered cycles C1-C2 ... N1 and C1...C9 are in the form of an almost ideal chair (ΔC_S^2=0.9° and $\Delta C_2^{3,4}$=0.7° for the first, ΔC_S^8=0.3° and $\Delta C_2^{7,8}$=1.5° for the second).

The work is executed at financial support of Committee of Science of MES RK №BR05236438.

SYNTHESIS, ISOMORPHIC CAPACITY AND CRYSTAL CHEMISTRY $Zn_{2-2x}M_{2x}SiO_4$ (M = Mn, Ni, Mg, Cu)

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Zinc orthosilicate with willemite structure, activated by manganese ions, Zn_2SiO_4: Mn, is an effective luminescent substance of green luminescence. The structure of Zn_2SiO_4 is characterized by the presence of two crystallographically nonequivalent positions of the metal atom. The formation of substitution solid solutions in such structures can be associated with the non-statistical filling of nonequivalent positions with dopant metal atoms. The study of isomorphic capacity of substitution solid solutions $Zn_{2-2x}M_{2x}SiO_4$ (M = Mn, Ni, Mg, Cu) obtained by solid-phase synthesis was performed using powder diffraction data analysis, followed by calculation of the parameters of the unit cells. The effective Shannon radii and the volumes of the coordination polyhedra [ZnO_4] were chosen as the size factors for estimating the length of solid solutions. The homogeneity range of the solid solution $Zn_{2-2x}M_{2x}SiO_4$ (M = Mn, Cu, Ni, Mg) increases sequentially: 13 at.% in $Zn_{2-2x}Mn_{2x}SiO_4$, 15 at.% in $Zn_{2-2x}Ni_{2x}SiO_4$ and 50 at.% in $Zn_{2-2x}Mg_{2x}SiO_4$ and $Zn_{2-2x}Cu_{2x-}SiO_4$. Changes in the crystal chemical parameters of $Zn_{2-2x}M_{2x}SiO_4$ (M = Mn, Ni, Mg, Cu) were analyzed and compared. Due to the presence of a rigid anionic group $[SiO_4]^{4-}$, unchanged during the formation of solid solutions, there is no significant change in the linear and volume coefficients of thermal expansion. It was found that small changes in the unit cell parameters of $Zn_{2-2x}M_{2x}SiO_4$ with increasing concentrations of Ni^{2+}, Mg^{2+} and Cu^{2+}, having a smaller radius compared to Zn^{2+}, are associated with a predominant substitution of zinc in a position with a smaller volume of coordination polyhedron. While the thermal expansion of the structure as a whole is due to the deformations of the larger polyhedron. The absence of the possibility of shear deformations of the crystal lattice due to the crystallization of Zn_2SiO_4 in the hexagonal syngony leads to the fact that as the relative difference in the effective radii of interchangeable cations decreases, the homogeneous regions of the $Zn_{2-2x}M_{2x}SiO_4$ solid solutions increases in the range of dopants M = Mn, Ni, Mg, Cu.

This work was supported by the Russian Foundation for Basic Research, project 19-03-00189.

PHENYLMETHYLENE AS AN INTERMEDIATE OF THE ACID-CATALYZED MOLECULAR OXYGEN CONSUMPTION BY STYRENE EPOXIDE IN ALKOHOL SOLUTION

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Oxygen absorption mechanism by acid catalyzed consumption of styrene epoxide (ES) essentially differs from usual mechanism of radical (chain -radical) hydrocarbons oxidation, although any external similarity is evident: radical particles, appearing by the rupture of three-membered cycle C – C bond react with O_2, in Ar atmosphere they destroy hydroperoxides[1]. The confirmation of carbene phenylmethylen (FM) formation assumption by p-toluenesulfonic acid catalyzed ES decreasing[1] was received in[2] with using of "pyridine sample technique"

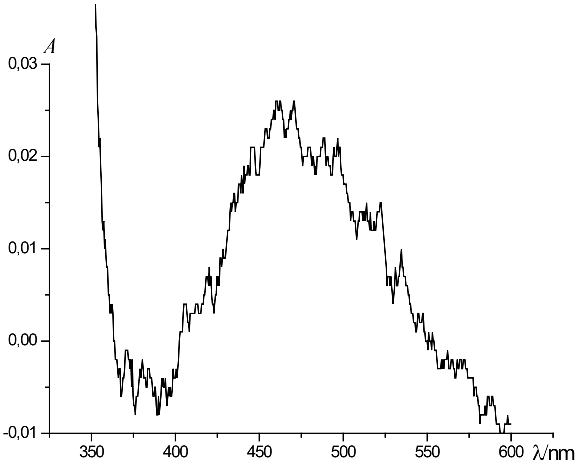

Figure 1. Absorption spectrum of iminium ylide FM, system ES−perchloric acid−Py.

Similar investigation with chemical traps (Py and O_2) and by immediate spectrophotometry utilization was made in system ES – perchloric acid in mixture solution Bu^tOH – chlorobenzene (9:1 vol.), 343 K, fig. 1. In two systems ES – acid ylide product of Py with FM reaction (λ_{max} = 450 – 470 nm), and in O_2 atmosphere spectra of FM carbonyloxide were observed accordingly (λ_{max} = 400 – 408 nm). These finds confirm forming carbene nature particles by acid – catalyzed ES transformation in polar solution.

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Work performed under the subject state assignments number state registration 1201361859.

CATALYTIC OXYGEN ABSORPTION BY TERNARY SYSTEM STYRENE EPOXIDE – 1,4-DIHYDROXYBENZENE – COPPER (II) CHLORIDE IN AQUEOUS TERT-BUTANOL

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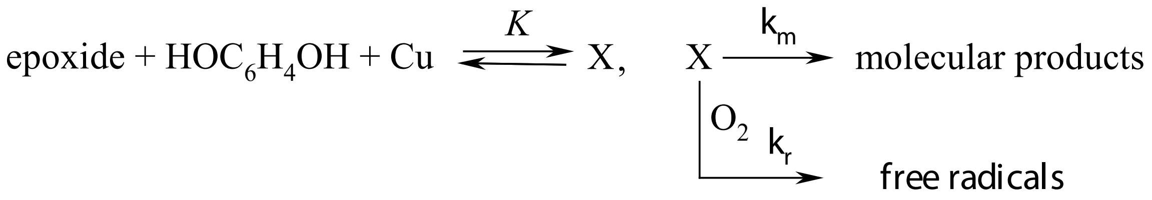
Ternary system styrene epoxide – 1,4-dihydroxybenzene – copper(II) chloride oxidation by molecular oxygen is investigated by 323 – 343 K in mixed tert-butanol – water solution (4:1 vol.). Oxidation rate expression is $V = k\,[CuCl_2]^1[epoxide]^0[HOC_6H_4OH]^0$, $[epoxide] > [HOC_6H_4OH] > [CuCl_2]$.

This expression is explained by preliminary ternary reagents complex formation and its following reaction with oxygen. Effective rate constant general expression is as follows: $k = 92.5 \exp(-22\ kJ.mol^{-1}/RT)\ c^{-1}$ (323 ÷ 343 K). Oxidation is catalytic formal, values of oxygen consumed and copper salt concentrations ratio $[O_2]/[\ CuCl_2]] >> 1$. Reaction scheme:



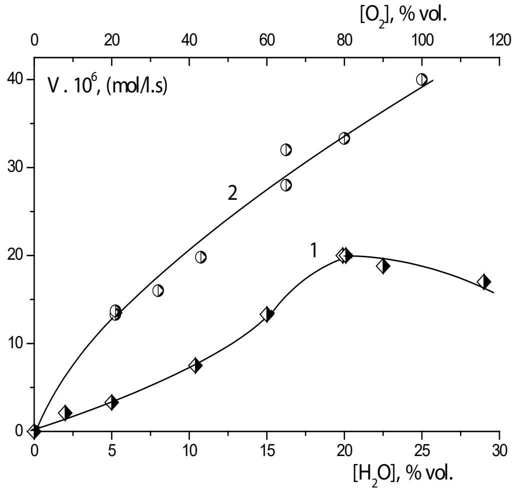


Figure 1. Dependences of oxygen consumption rate by ternary system (0.35 mol/l epoxide, 0.021 1,4-dihydroxybenzene) from contents of: 1 – water in mixture with tert-butanol (5.6 · 10-4 mol/l CuCl2); 2 – oxygen in gas mixture (1.12 · 10-3 mol/l CuCl2). 333 K.

Work performed under the subject state assignments number state registration 1201361859.

CHANGE OF CHLORIDES LOWEST HYDRATES THERMAL STABILITY IN CERIUM SUBGROUP OF RARE EARTH ELEMENTS

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Synthesis and thermal stability of the lowest hydrates (monohydrates) of the rare earth elements chlorides (REE) are of considerable scientific and practical interest – on dehydration of these hydrates anhydrous chlorides can be obtained. The latter are used to produce rare earth metals, which are becoming increasingly and widely used in various fields of industry, electronics, medicine and in everyday life. Previously, we have studied the processes of synthesis and thermal decomposition of the lowest hydrates of lanthanum chloride [1], cerium chloride [2] and neodymium chloride [3].

Figures 1 and 2 show the dependence of the water vapour pressure for these monohydrates (lnP atm, extrapolation to the temperature of 20 °C) and the dependence of the heat of their dehydration (ΔHo°, kJ/mol) on the ordinal number of REE. As one can see from figures 1 and 2, the observed monotonic dependence allows to estimate these values for the not yet studied praseodymium chloride monohydrate (only its synthesis conditions are determined using the controlled isothermal drying method for the subsequent study of its thermal stability).

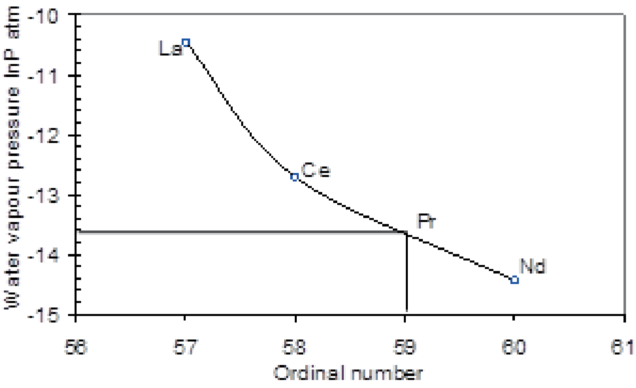

Figure 1. Dependence of pressure on №

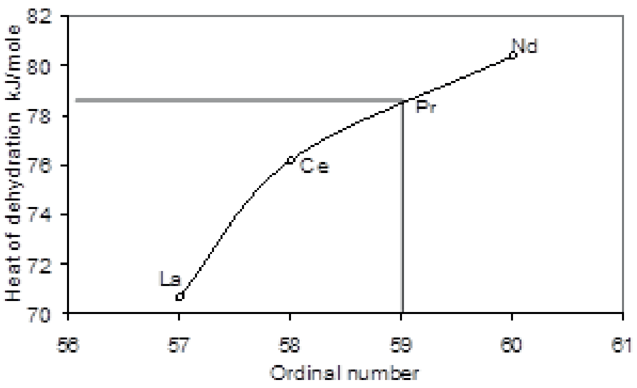

Figure 2. Dependence of enthalpy on №

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THE EFFECT OF CH3O GROUPS IN POSITIONS 6 AND 7 OF A-(3,3-DIMETHYL-3,4-DIHYDROISOQUINOLYL-1) NITROSOACETO-NITRILE ON THE STRUCTURE AND PHYSICO-CHEMICAL CHARACTERISTICS OF ITS COMPLEX WITH NI (II) ACETATE

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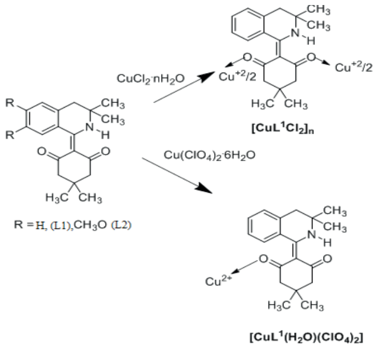
In the course of systematic studies of 1-substituted 3,3-dimethyl-3,4-dihydroisoquinoline and their metal complexes, we established the dependence of the composition and structure of some metal complexes on the presence of CH_3O groups at positions 6 and 7 of the benzene cycle of ligand molecules. Thus, the interaction of $CuCl_2$ and $Cu(ClO_4)$2 with 3,3-dimethyl- and 3,3-dimethyl-6,7-dimethoxy-derivatives of 1- (4′, 4′-dimethylcyclohexa-2′, 6′-dione- 1′-yl) -3,4-dihydroisoquinoline (L^1 and L^2), led to the formation of significantly different metal complexes (Scheme 1).

To further study of this effect, the complex of Ni (II) acetate with α- (3,3-dimethyl-6,7-dimethoxy-3,4-dihydroisoquinolyl-1) nitrosoacetonitrile (HL3) of the composition [Ni3(μ3-OH)(μ2-L3)3 (μ2-CH3COO) (CH3COO) (H2O)2]•2H2O (I), where L3 is the deprotonated ligand HL3.



Scheme 1

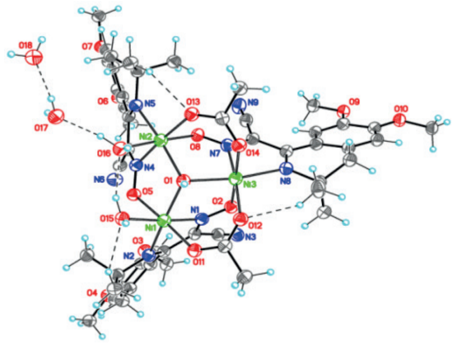


Fig. 1 Complex structure I

A comparative analysis of the structure and characteristics of complex I with the previously described complex $[Ni_3(\mu_3\text{-OH})(\mu_2\text{-}L^4)_3(\mu_2\text{-}CH_3COO)\ (CH_3COO)\ (H_2O)_2] \cdot H_2O$ (II), in which L^4 does not contain groups OCH_3. Complex I has the same trimeric structure (Fig. 1), as complex II. The compositions of the coordination polyhedra of each of the three Ni (II) atoms, the isomeric form and the L^3 coordination method were determined. The OCH_3 groups in positions 6 and 7 of the HL^3 molecule do not actually affect the complex formation process, in contrast to the complex formation of Cu (II) salts with L^1 and L^2. Compound I is characterized by IR and electron spectroscopy data.

FEATURES OF REACTIONS OF FURAN COMPOUNDS WITH HYDROGEN PEROXIDE DEPENDING ON THE SUBSTITUENT IN THE CYCLE AND THE TYPE OF CATALYST

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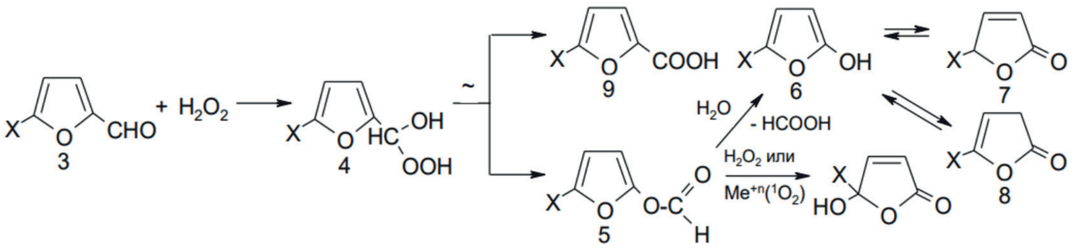
It was found that furan (1) and 2-methylfuran (2) do not react at 25 ^{0}C in aqueous and aqueous-alcoholic media with H_2O_2. The reaction is possible only in the presence of catalysts based on the elements of V and VI groups. However, the process is quite long, and the complete conversion of the furan is not achieved. The oxidation time of 2-methylfuran decreases sharply, and the total yield of products increases.

2-Formylfuran (3), unlike furan, reacts with aqueous H_2O_2 already at 25^{0}C. Oxidation takes place through the formation and intensive transformation of hydroxyhydroperoxide 4 and is accompanied by the release of heat. The aromaticity of the furan cycle is higher than that of furans 1 and 2. Therefore, the center of the reaction attack is not a cycle of compound 3, but its carbonyl group, which is involved in simultaneous electrophilic and nucleophilic addition of H_2O_2 (Scheme 1). The Bayer-Villiger rearrangement of the peroxide 4 leads to ether 5 which is hydrolyzed to 2-hydroxyfuran (6) and formic acid. The latter further serves as a catalyst. Tautomeric lactone forms 7 and 8 are formed as a result of keto-enol rearrangement of intermediate 6.



Scheme 1.

The electron density in the cycle of produsts 5 and 6 is increased as a result of its conjugation with exocyclic oxygen. Molecules H_2O_2 or $^1O_2$ in the pres-ence of compounds V and VI groups are easily attached to the diene system of the cycle in contrast to furans 1 and 2.

The formation of peroxides 4 is accelerated by both electron-donor (CH_3) and electron-acceptor (NO_2) substituents, which also affect the rearrangement of peroxides. Electron-acceptor substituents in the cycle prevent its migration to the electron-deficient oxygen of the peroxide bond.

NEW FUNCTIONALIZED METHYLENEDIPHOSPHONIC ACIDS WITH AZAHETEROCYCLES AND AMINO ACIDS MOIETIES AS EFFECTIVE LIGANDS AND BIOACTIVE COMPOUNDS

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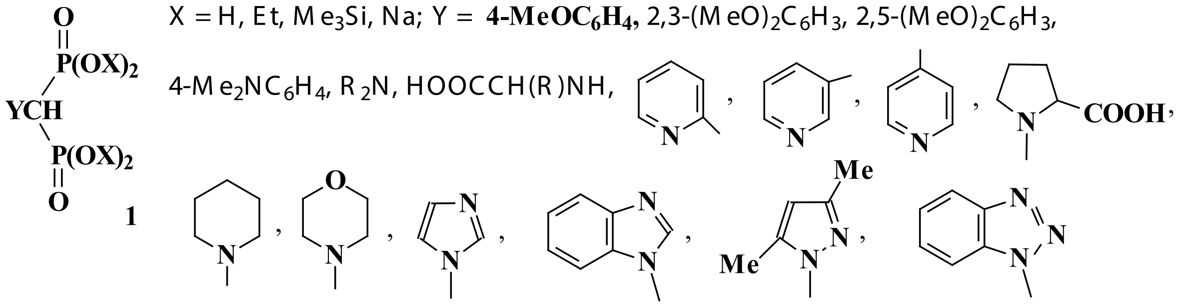
Functionalized methylenediphosphonic acids and their derivatives with aromatic and heterocyclic moieties are well-known biomimetics of hydroxy- or aminocarboxylic acids and natural pyrophosphates, and some of them such as zoledronic, risedronic, and minodronic acids are widely used in medicine[1]. Organosilicon-mediated synthesis of functionalized organophosphorus acids and their derivatives was used recently by us as convenient method of creating of P-C bonds. We have synthesized the new functionalized methylenediphosphonic acids and their derivatives 1 including aromatic, azaheterocyclic, and amino acids moieties via addition of tris(trimethylsilyl) phosphite to corresponding formamides in the presence of effective catalyst – trimethylsilyl triflate under mild conditions [2,3]. Also trimethylsilyl-containing organophosphorus compounds easily react with methanol excess or with sodium methylate in methanol giving water soluble acids or their sodium salts in high yields.



1

X = H, Et, Me_3Si, Na; Y = **$4-MeOC_6H_4$,** $2,3-(MeO)_2C_6H_3$, $2,5-(MeO)_2C_6H_3$, $4-Me_2NC_6H_4$, R_2N, HOOCCH(R)NH,

The resulting compounds are the perspective biologically active substances and polydentate ligands with versatile properties as well as the promising precursors for multitarget drug discovery.

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NEW ORGANOPHOSPHORUS DERIVATIVES OF HYDROXYMETHYL PIPERIDINES AND THEIR POLYCYCLIC ANALOGS WITH PROSPECTIVE MULTIFACTOR ACTIVITY

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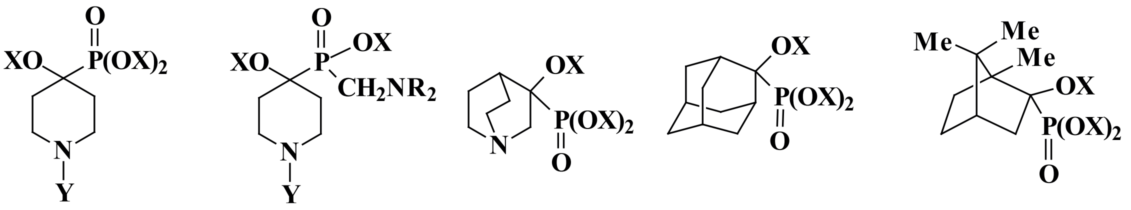
Functionalized hydroxymethylphosphonates and -phosphinates are widely used as polydentate ligands and biologically active substances with various properties. Thus, these compounds with hydrolytically stable P-C bonds are widely used as effective herbicides and the structural core of new types of antibiotics[1]. Phosphorus-containing cyclic analogs of 4-aminobutyric acid with piperidine fragments are of particular interest due to their antitumor properties and their activity as effective neuromodulators. The diverse biological activity of the polycyclic piperidine analogs, including fragments of quinuclidine, nitrogen-containing adamantane derivatives, adamantane carboxylic acids and bornan (camphane), which are widely used in pharmaceutical synthesis, are also well known.

Now the convenient methods for synthesis of various functionalized hydroxymethylphosphonates and -phosphinates with fragments of piperidine and its polycyclic analogs - quinuclidine, adamantane and bornan are proposed via the addition of tris(trimethylsilyl) phosphite excess to various corresponding ketones in the presence of trimethylsilyl triflate as a catalyst leading target compounds under mild conditions in high yields[2].



X = H, Me_3Si, Na; Y = H, Me, Et, *i*-Pr, Bn, Ac, $MeSO_2$.

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This work was financially supported by the RFBR (grant number 17-03-00169).

MODIFIED CITRUS PECTIN IN THE PROCESS OF FLOCCULATION DISPERSE SYSTEMS

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Modification of natural polysaccharides is a promising molecular design method that opens the possibility of synthesizing new organic hybrid composites with unique specific properties[1]. Polysaccharides are widely used as the form of individual additives and in the composition of organic hybrids for the separation of disperse systems containing various impurities of inorganic and organic nature.

In this work, modified polysaccharides were synthesized by the method of chemical interaction of citrus pectin and cationic monomer (1,2-epoxypropyl) triethylammonium chloride in an alkaline medium and with under the microwave radiation on a microwave-ultrasonic-ultraviolet synthesis reactor system. Data of IR spectroscopy initial citrus pectin and the products of its modification with acrylamide are compared. Organic hybrids were obtained based on natural polysaccharides (pectin, chitosan) according to the method described by us[2]. The concentration effect of citrus pectin, its modified samples, chitosan and their organic hybrids on flocculation properties was studied in the free mode sedimentation using model dispersion system — TiO_2 suspension in aqueous and salt-water media. The choice of TiO_2 suspension is determined by their stable characteristics of average size $R_{cp} = 1{,}5 \cdot 10^{-6}$ m, polydispersity in size, and physicochemical properties of the interface between TiO_2 particles ($\xi = -11$ mV). High efficiency of flocculation in TiO_2 suspension with the participation of hybrids based on modified pectins and chitosan was established. The effect of ionic strength on the conformational state of macromolecules of natural polysaccharides and the aggregation of titanium dioxide particles has been analyzed.

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ICOSAHEDRAL STRUCTURE AS A 10-FOLD TWIN CRYSTAL

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The icosahedral quasicrystalline structure (IQS) is realized in metals and their alloys. It is a 10-fold twin crystal of antisymmetric trigonal pyramid pairs (in the shape of an hourglass) with a distorted FCC lattice described in the hexagonal aspect (left figure) with parameters uniquely determined by the geometry of the icosahedron: a = R(2(1 – 5–0.5))0.5, c = R(3(1 + 2•5–0.5))0.5, where R is the shortest interatomic distance. The icosahedron is easily transformed into a cuboctahedron (FCC structure) and vice versa.

Representation of the X-ray diffraction profile of the IQS of nickel in three reflections in the hexagonal aspect to the left; the scheme of transformation of the icosahedron into a cubic octahedron (a–c) and back (c–a) to the left.

IQS is characteristic of very small metal clusters and is the primary structure when many metals are formed as a result of crystallization from the melt or in the reduction1,2. As a result of enlargement, as well as with decreasing temperature, the normal FSS structure becomes energetically more advantageous, which can easily be turned into a BCC structure.

The transformation of IQS and FCC into HCP proceeds through the displacement of layers and is more difficult, however, low-melting metals (Mg, Zn, Cd) can crystallize immediately in the HCP form.

The report also discusses the results of the synthesis and analysis of nickel and Fe – Co solid solutions by methods of wide and small angle X-ray diffraction, as well as by methods of molecular dynamics.

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DROP BY DROP THE ADAMANTANE OXIDATION WITH HYDROGEN PEROXIDE IN THE PRESENCE OF DIMETHYLGLYOXIME COMPLEX OF COPPER IN ACETONITRILE

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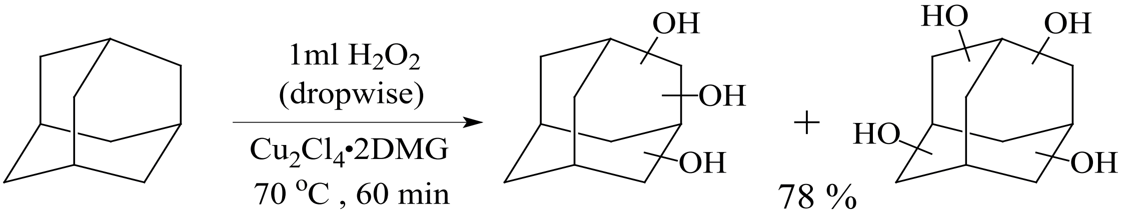
Found the conditions in which the impact of a 50% aqueous solution of hydrogen peroxide to adamantane (Tricyclo[3.3.1.1(3,7)] decane, 30 mg) at the full conversion leads to preferential (total 78 %) the formation of tri- and tetra-oxygenated adamantane. This result was obtained with a slow drop-by-drop introduction of a small (1 ml) amount of the oxidizer into the reaction mixture containing adamantane and a catalytic amount of dimethylglyoxymic (DMG) copper dichloride complex in an acetonitrile solution at 70 °C.



It is shown that under such conditions adamantane is consistently oxidized to mono-, bi-, tri- and tetra- oxygenated products, starting with 1- and 2-oles and then 2-one. Oxidation occurs at the copper complexes, which include molecules of acetonitrile.

With the rapid (no more than 3 seconds) introduction of 1.5-10 ml of the oxidizer partial and/or complete replacement of acetonitrile molecules with water molecules in copper complexes occurs and the conversion and yields of tri- and tetra-oles of adamantane are sharply reduced. At 50 °C with an increase to 1.5, 2.0 and 10 ml of oxidant volumes, adamantane conversion decreases linearly to 66, 65 and 44%, respectively, and the correlation coefficient $R^2 = 1$. With the rapid introduction of 2 and 10 ml of the oxidizer, the total amount of tri- and tetra-oles of adamantane, respectively, was 44 and 1% of the total content of all products of adamantane oxygenation.

SYNTHESIS OF [1,3]THIAZINO[3,2-B][1,2,4]TRIAZINIUM SYSTEMS BY HETEROCYCLIZATION OF 3 ALKENYLSULFANYL 5 PHENYL 1,2,4 TRIAZINES

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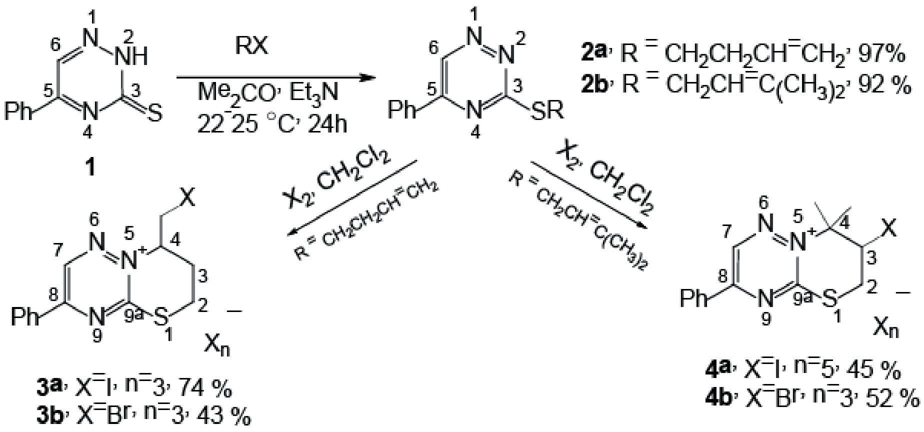
Previously we have describe that *trans*-5-phenyl-3-cinnamylsulfanyl-1,2,4-triazine can be used as a starting compound in the heterocyclization reaction with the aim of obtaining condensed heterocyclic systems of ionic type with the bridging N-atom[1]. In continuation of our study we have obtained the previously unknown 3-butylsulfanyl - and 3 prenylsulfanyl-5-phenyl-1,2,4-triazine (2a,b) by the alkylation of 5-phenyl-2,3-dihydro-1,2,4-triazine-3-thione (1) 4-brombach-1-ene and 1 bromo-3-methylbut-2-ene, respectively. Synthesis of polyhalides 8 halomethyl-6,7-dihydro[1,3]thiazino[3,2-b][1,2,4]triazinium (3a,b) and 7-halo-8,8-dimethyl-6,7-dihydro[1,3]thiazino[3,2-b][1,2,4]triazinium (4a,b) proceeds via electrophilic heterocyclization of butenyl- and prenylsulfide 2a,b, respectively, under the action of halogens.



The structure of polyhalides 3a,b and 4a,b identified by ^{1}H, ^{13}C NMR. Structure of triiodide 3a, pentaiodide 4a and tribromide 3b were investigated by X-ray analysis.

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SORPTION ABILITY OF BENTONITE OF THE TAGANSK DEPOSIT TO THE CATIONS OF VANADIUM (IV)

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Existing methods for purification of aqueous media from the cations of heavy metals, including the vanadium ions are costly and multi-step. Currently, sorption methods using not expensive, available natural sorbents are the most promising.

The study of the process of sorption of V^{4+} cations was carried out in the model $VOSO_4 \cdot 3H_2O–H_2O$ system under mixing conditions. The effect of temperature, time and norm of bentonite (S: L) was studied at constant C_V equal to 200 mg/l. As seen from the figure (a) the temperature increase from 25 to 70°C reduces the degree of sorption of V^{4+} ions by 21.1% due to their desorption from the sorbent into the solution. The increase in the degree of sorption of V^{4+} ions with increasing S:L is due to an increase in the mass of bentonite (Fig. b). Sorption curves of time and concentration have minimum at 45 min and 400 mg/l V (Fig. c, d). The extreme nature of the curves is probably due to the tendency of the system to equilibrium. The sorption of V^{4+} ions does not depend on the pH of the medium. Under optimal conditions (25°C, 60 min, S:L = 1:1.5) in low concentrated solutions (50-100 mg/l V) the degree of sorption reaches (94.2-73.7)%, and in highly concentrated (500 mg/l V) - 47.2%.

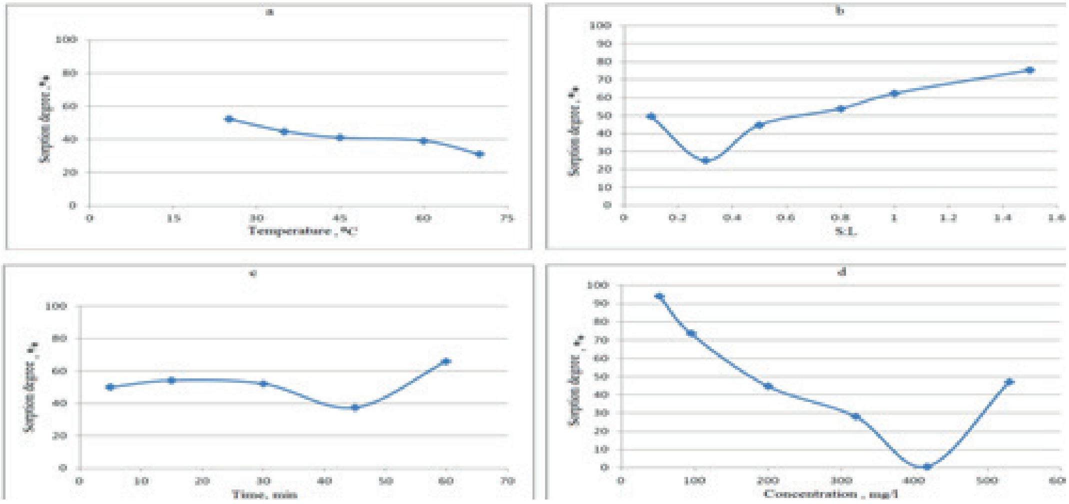

Figure - Sorption of cations V^{4+} depending on time (a), S:L (b), temperature (c) and C_V (d)

MECHANISTIC STUDY OF THE REACTION OF TERTIARY PHOSPHINES WITH ALKENES ACTIVATED BY ELECTRON-WITHDRAWING GROUPS ON THE BASIS OF SECONDARY KINETIC ISOTOPE EFFECT DATA

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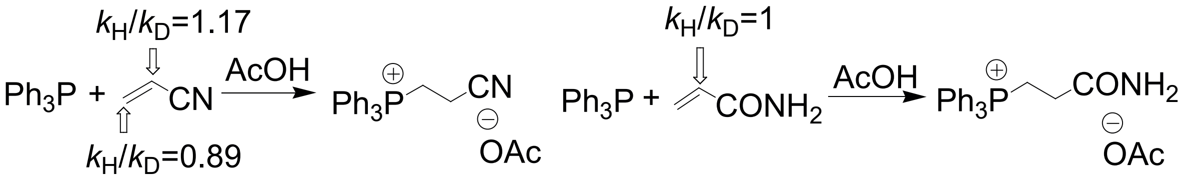
Secondary kinetic isotope effects (KIEs) were determined for the reaction of triphenylphosphine with 2-D-acrylonitrile, D3-acrylonitrile, and 2-D-acrylamide in acetic acid solution.[1,2]



The isotope labeling at the α-position of acrylonitrile surprisingly led to normal secondary KIEs (k_H/k_D=1.17±0.02). These normal effects were interpreted in terms of known vibrational-rotational (Coriolis) coupling between the out-of-plane and the in-plane C–C≡N bending modes resulted from rapid rotation of acrylonitrile molecule with an angular velocity strongly dependent on the H/D substitution.3 By the influence of the Coriolis force, the out-of-plane bending in the isotopomeric acrylonitriles contributes differently to the in-plane bending, which defines the reaction coordinate during rehybridization of nitrogen atom from sp in the CN group to sp^2 in enimine moiety (C=C=NH) at the rate-determining protonation of phosphonium zwitterionic intermediate by acetic acid. The observation of normal secondary KIEs became possible due to dynamic behavior of the intermediate zwitterion, whose very high potential energy allows to convey the history of its formation on the second reaction step of proton transfer. Calculated lifetime of the zwitterionic intermediate was only 138 femtoseconds. The untypical origin of secondary KIEs related to the α-position of acrylonitrile was evidenced by the absence of such effect for the reaction of 2-D-acrylamide (k_H/k_D=1.01±0.02).

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This work was supported by Russian Science Foundation (project 18-73-00018).

ADDITION OF P(O)–H BONDS TO A,B-UNSATURATED ELECTROPHILIC COMPOUNDS UNDER TERTIARY PHOSPHINE CATALYSIS

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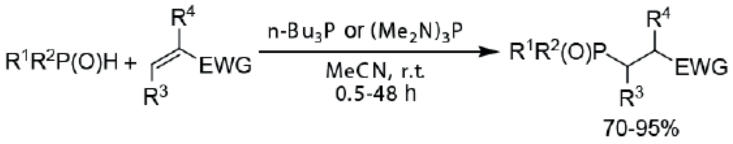
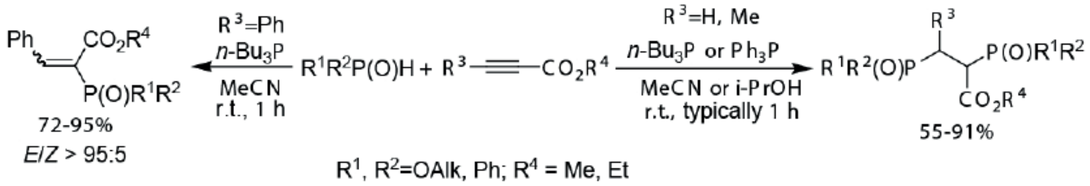
Addition of P(O)–H compounds to carbon-carbon multiple bonds is one of the most atom-economical and straightforward approaches to organophosphorus compounds. Using cheap and commercially available tertiary phosphines, *n*-Bu_3P, $(Me_2N)_3P$, and Ph_3P, we developed highly efficient protocols for addition of P(O)–H compounds to electron-deficient alkenes and alkynes.[1-3]



R^1, R^2=OAlk, Ph; R^3=H, Me, Ph; R^4 = H, Me, CH_2CO_2Me; EWG = CO_2Me, CN, $CONH_2$



R^1, R^2=OAlk, Ph; R^4 = Me, Et

The operational simplicity of the developed methods lies in the use of mild conditions (room temperature, no need of protective inert atmosphere), high selectivity and short reaction times, highlighting practical conditions for these reactions.

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This work was supported by Russian Science Foundation (project 18-73-00018).

FLUORO–CONTAINING IMIDAZOTHIAZOLS AND THIOGLYCOLURILS: SYNTHESIS FROM PERFLUOROBIACETYL

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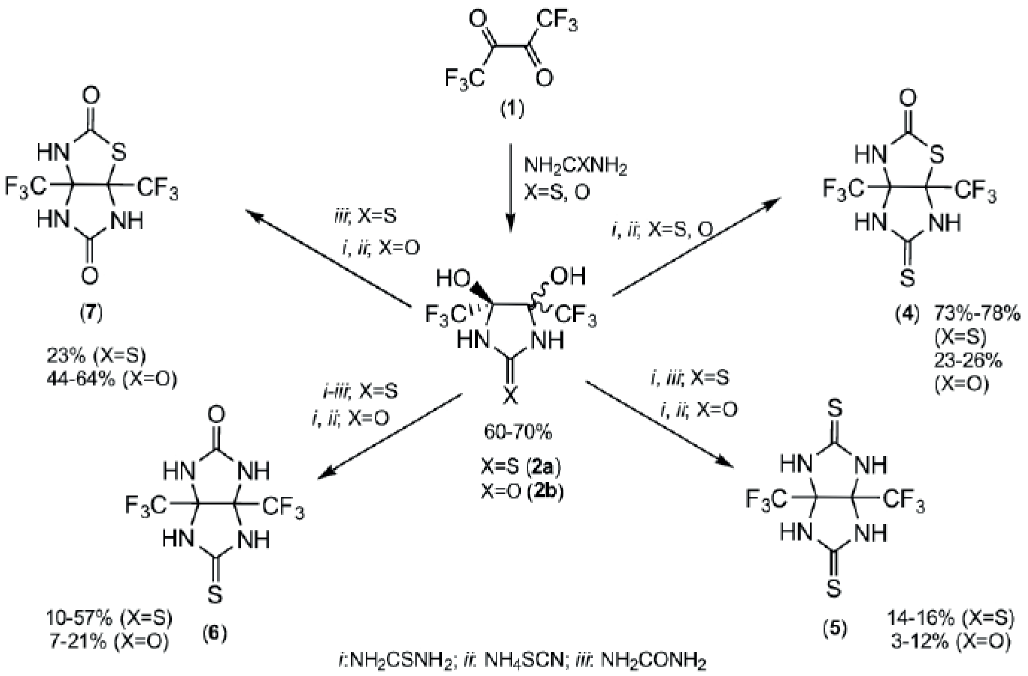
The reaction of perfluorobiacetyl (1) with thiourea and urea produced imidazolidine-2-thione(one)s (2a, b) as mixtures of *cis*-, *trans*-isomers. Imidazolidines (2a, b) were introduced in the condensation with thiourea in bipolar aprotic solvent at elevated temperature and unexpected fluoro-containing thioxo(oxo)imidazothiazolones (4, 7) were obtained (yield ~23–73%). A similar reaction of imidazolidines (2a, b) with NH4SCN afforded the same compounds (4, 7) (yield ~26–78%). In contrast to it, the condensation of imidazolidine-2-thione (2a) with urea gave mainly thioglycoluril (6) in ~57% yield and dithioglycoluril (5) as minor product (yield ~16%). Possible mechanisms of compounds (4-7) formation are discussed.



i: NH_2CSNH_2; ii: NH_4SCN; iii: NH_2CONH_2

SYNTHESIS OF COMPLEX COMPOUNDS OF CHLORIDES OF POLYVALENT ELEMENTS WITH SULFUR TETRACHLORIDE

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Sulfur in compounds with chlorine may have a different valence. The higher (IV, for chlorides) valence state of sulfur low-stable already at room temperature stabilizes when it enters in the composition of the outer-sphere cations SCl3+ in known compounds of the type $[SCl_3]_k$•$[M_mCl_n]$, where M = Al, Sb, Zr, Nb, Fe, Au, Ir.

In the present work, a search for new chloride complexes was carried out. The interaction of the corresponding chlorides was investigated in the presence of liquid or gaseous Cl_2 at elevated pressures (up to 60 atm). In this case, sulfur together with the corresponding element (Be, In, V, Ti, Sn, Ge, P) or chloride ($ZnCl_2$, $PbCl_2$, $GaCl_3$, $AlCl_3$, $HfCl_4$) was kept for several days at 18–25 °C in sealed quartz ampoules with anhydrous liquid Cl_2. In some cases, the reagents, taken in different proportions, were additionally heated for 5–10 hours at 80–150 °C. Under these conditions, elemental substances (S, P, Be, In, etc.) were chlorinated.

The formation of ionic compounds of the type $[SCl_3]_k$•$[M_mCl_n]$, which have low solubility in liquid chlorine, was recorded by the appearance of the characteristic bands of their constituent SCl_3+ complex cations and $M_mCl_n^{k-}$ anions in the Raman spectra of solid samples. The spectra were recorded using a Renishaw U1000 spectrometer (25 mW laser, λ = 514.5 nm) directly through the glass walls of sealed reactive ampoules with liquid Cl_2[1].

Several new and known compounds have been synthesized according to the described method: $[SCl_3].[BeCl_3]$, $[SCl_3].[AlCl_4]$, $[SCl_3].[GaCl_4]$, $[SCl_3].[Ga_2Cl_7]$, $[SCl_3].[InCl_4]$, $[SCl_3].[Ti_2Cl_9]$, $[SCl_3]_2.[SnCl_6]$, $[SCl_3]_2.[HfCl_6]$, $[SCl_3].[Hf_2Cl_9]$, containing the pyramidal group SCl_3^+. Their spectroscopic characteristics were obtained and systematized.

In general, the $[SCl_3]_k$•$[M_mCl_n]$ family is found to be smaller in the number of formed compounds as compared with the previously investigated by us family of $[PCl_4]_k$•$[M_mCl_n]$ chloride complexes.

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MECHANISM OF METHATHESIS OF N-METHYLFORMAMIDE WITH DIMETHYL CARBONATE WITH PARTICIPATION OF Ϭ-BONDS

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Esters of carbamic acid - carbamates - have a very wide range of applications. They are used in the production by isocyanate free methods of large-capacity polymers - polyurethanes. A number of carbamates exhibit the properties of pesticides, insecticides, and herbicides. Thermal decomposition of carbamates is one of the promising phosgene-free methods for the production of isocyanates.

The most widely known method of obtaining carbamates with good yield is the reaction of alcohols with isocyanates, which are obtained by phosgenation of amines. This process has several significant drawbacks, therefore, the methods for producing carbamates continue to be improved. One of the promising methods for obtaining carbamates is the metathesis of N-alkyl- and N-aryl formamides and organic carbonates:

Neither the mechanism nor the thermodynamic parameters of dimethylcarbonate metathesis reactions with formamides remain unknown. In order to clarify these issues, we studied the mechanism of N-methylformamide with dimethyl carbonate with the participation of σ-bonds leading to the formation of N, O-dimethylcarbamate using the density functional method B3LYP / 6-311 ++ G (df, p). The reaction can proceed as a bimolecular interaction, and as catalyzed by alcohols (monomers and dimers) conversion. The reactions catalyzed by methanol can develop in two different directions. One of these directions is characterized, compared with the bimolecular interaction, by significantly lower activation enthalpies. However, all reactions involving methanol and its dimer are characterized by significantly lower activation entropies compared to the bimolecular transformation. This leads to greater free energy barriers in their path compared to the bimolecular transformation.

All reactions proceed through cyclical coordinated transition states in which the destruction of old and the formation of new chemical bonds occurs simultaneously.

MICROEMULSION FOR DIRECTED DELIVERY OF BIOLOGICALLY ACTIVE SUBSTANCES AND DRUGS

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The using of supramolecular systems for controlled drugs and biologically active substances (BAS) delivery has the great interest in the field of medicine, cosmetology and pharmacology. In this aspect, self-organizing structures, such as microemulsions (ME), occupy an advantageous position due to their nanometer-sized particles, their ability to increase solubility (solubilization) of the drug, bioavailability, thermodynamic stability, and ease of preparation.

The aim of this work was to obtain microemulsion systems based on biodegradable surfactants for the transportation of biologically active substances, as well as to study the interaction of BAS molecules with the components of ME system.

The complex of physicochemical research methods (NMR and fluorescence spectroscopy, dynamic light scattering and X-ray analysis) were used to obtained and characterized of the water / lecithin / propylene glycol / vaseline oil1 and water / AOT / isopropyl myristate systems. It has been shown that these systems are stable and in certain concentration ratios are reverse micro emulsions with a maximum droplet size of 100 nm. Phase diagrams of the studied systems were constructed. Microemulsion, liquid crystal regions, as well as areas of macroemulsions and gel systems were found. By entering fluorescent probes of pyrene and laurdan, the possibility of studying transitions in self-organizing systems, as well as modeling the location of incorporated molecules in them, were shown. The release of amino acids that differ in functional groups (L-lysine, L-syrin,β-alanine and glycine) as well as the antibiotic cefotoxime from the ME systems by the method of equilibrium dialysis using Franz cell was studied. It has been shown that the release has a prolonged nature. The ME systems as shown are an effective carriers of biologically active substances and can be used in transdermal patches for medical purposes.

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ANALYSIS OF REACTION PHASE TRAJECTORIES FOR ESTABLISHING FUNDAMENTAL ASPECTS OF CATALYTIC SYSTEMS OPERATION

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The establishing of fundamental patterns of operation of catalytic systems of complex reactions is non-trivial scientific task because of proceeding of several coupled consecutive-parallel processes in such systems. The studies of kinetic regularities of reactions proceeding is one of the most effective tools for establishing of their mechanisms. We proposed and tested the approach based on the analysis of differential selectivity of a catalytic reaction under competition of several (pair, as minimum) similar substrates using so-called phase trajectories of the competing reactions being interdependences of the yields of the products formed in the competing reaction. [1]. The analysis of patterns of phase trajectories' changes with varying different reaction parameters, such as the nature and concentration of the substrates and components of the catalytic systems used, allows for solving a lot of questions appearing under establishing the catalytic reaction mechanism (i.e., nature of intermediates participating in the elementary steps of catalytic cycles, the degree of reversibility of the steps, a mechanism of their coupling with each other, distinguishing between homogeneous and heterogeneous catalysis mechanisms, etc.). The main advantage of the approach over traditional kinetic studies of the rates of reactions is the independence of its results on substantially changing during the reaction concentration of catalytically active species that usually cannot be measured correctly. The results of the application of the approach to several cross-coupling reactions with aryl bromides and unreactive aryl chlorides complicated by intensive processes of catalyst deactivation are discussed in the report.

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The work was supported by Russian Science Foundation, project 19-13-00051.

SYNTHESIS AND STRUCTURE OF COPPER COMPLEX $[CuBr_2(O\text{-dmso})_3]$

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Molecular halide complexes of copper (II) containing coordinated dmso molecules are structurally characterized by a small number of examples[1]. By dissolving copper bromide (II) in dimethyl sulfoxide, followed by slow evaporation of the solvent, we obtained the complex $[CuBr_2(O\text{-dmso})_3]$ represented by air-resistant yellow-green crystals.

According to X-ray diffraction data, the complex has a monomeric structure, the copper atom has a distorted trigonal bipyramidal coordination with axially located dimethyl sulfoxide ligands connected to central atoms by oxygen atoms (valent angle OCuO 165.68(11)°); there are two bromine atoms and a dimethyl sulfoxide molecule in the equatorial plane (fig. 1). The sum of the angles in the equatorial plane is 360°. Bond lengths Cu–Br are unequal (2.4681(14) and 2.5922(14) Å), Cu–O distances are varied in the interval 1.944(3)–2.054(3) Å. It should be noted, that by the slow evaporation of a $CuBr_2$–dimethyl sulfoxide–ethanol solution, a polymer complex $[CuBr_2(O\text{-dmso})_2]_n$ was obtained, in which the structural fragments are connected of μ_2-bridge bromine atoms[2].

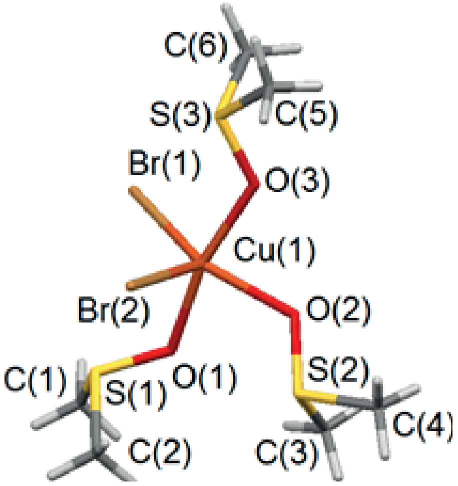

Fig. 1. Structure of $[CuBr_2(O\text{-dmso})_3]$

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Complete tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structure Database no. 1883471; http://www.ccdc.cam.ac.uk. We thank prof. V.V. Sharutin for X-ray analysis of the crystal compound.

SYNTHESIS AND STRUCTURE OF RHODIUM COMPLEXES $[Rh_2(OAc)_4{\cdot}(Diox)_2]$ AND $[Rh_2(OAc)_4{\cdot}((C_6H_4\text{-}F\text{-}4)_3Sb)_2]$

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Dimeric rhodium acetate (II) shows a tendency to form adducts of the general formula $[Rh_2(OAc)_4{\cdot}L_2]$, where L is *N*-donor molecules[1]. By dissolving rhodium acetate in dioxane, as well as mixtures of rhodium acetate and *tris*-4-fluorophenyl antimony in acetonitrile, followed by slow evaporation of the solvent, we have obtained the adducts $[Rh_2(OAc)_4{\cdot}(Diox)_2]$ (1) and $[Rh_2(OAc)_4{\cdot}((C_6H_4\text{-}F\text{-}4)_3Sb)_2]$ (2).

According to X-ray diffraction data, in centrosymmetric molecules 1 and 2, the rhodium atoms have a slightly distorted octahedral coordination with the oxygen atoms of dioxane and antimony in axial positions and with the oxygen atoms of the acetate groups in the equatorial positions (fig. 1). The *trans*-angles ORhRh, ORhO and SbRhRh, ORhO are varied in the intervals of 176.56(6)°–177.72(4)° (1), and 173.590(19)°–175.48(10)° (2), the sum of the angles of ORhO in the equatorial plane are 359.8° (1), 359.62° and 359.64° (2). In 1, the axial bond Rh – OD$_{iox}$ (2.335 (3) Å) is longer than the equatorial Rh – O$_{acetate}$. (2.037(3)–2.046 (3) Å), in 2 the axial Rh–Sb bonds are 2.7113(13), 2.7120(13) Å, the equatorial bonds Rh–O are varied in the interval 2.033(3)–2.044(3) Å.

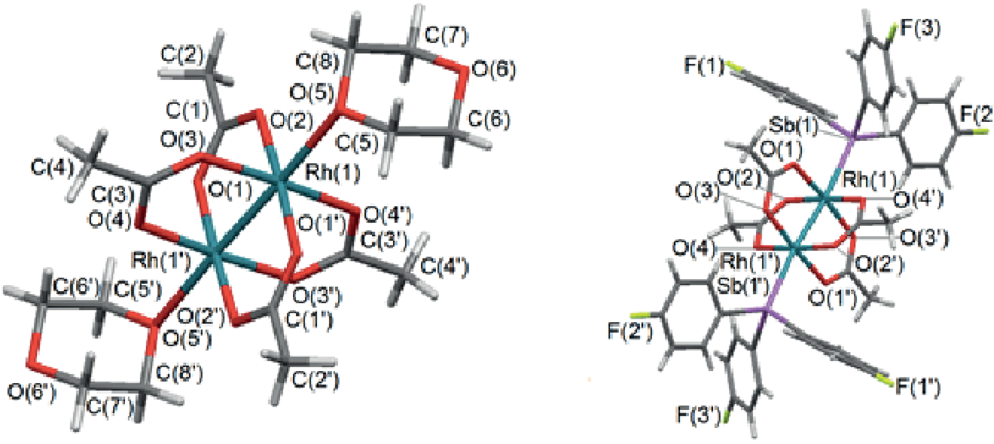

Fig. 1. Structure of $[Rh_2(OAc)_4{\cdot}(Diox)_2]$ (1) and $[Rh_2(OAc)_4{\cdot}((C_6H_4\text{-}F\text{-}4)_3Sb)_2]$ (2)

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Complete tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structure Database no. 1840624 (1), 1840625 (2); http://www.ccdc.cam.ac.uk. We thank prof. V.V. Sharutin for X-ray analysis of the crystal compounds.

FLOW SYNTHESES OF THE GLYCINE OLIGOPEPTIDES WITH THE PARTICIPATION OF THE SODIUM TRIMETAPHOSPHATE

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One of the most important and unresolved problems of modern science is prebiotic peptide synthesis. To develop this problem we previously investigated the kinetics of the formation of oligopeptides in the glycine – sodium trimetaphosphate – imidazole system in an aqueous medium at different temperatures and pH values, revealed the catalytic effect of imidazole, and using ^{31}P NMR spectroscopy studied the transformations of particles containing various forms of phosphorus[1,2].

This work is a continuation of the mentioned studies and is aimed at establishing optimal conditions for the formation of oligopeptides in the presence of sodium trimetaphosphate, as well as a more detailed understanding of the mechanism of synthesis.

Syntheses have been performed on the ASIA-330 flow system (Syrris). The kinetics of the processes was monitored using the Knauer Smartline HPLC system, as well as by NMR spectra recorded on the Bruker Avance III 400 spectrometer. Not only imidazole was used as a catalyst, but also heterocyclic compounds such as N-methylimidazole, pyrimidine, etc.

The structures of reagents, products, intermediates, and some transition states have been optimized by the GAMESS program3 on the CAM-B3LYP/TZVP computation level. The polarizable continuum model (C-PCM) was used to account for solvent effects.

The rather good yields of oligopeptides (up to 52% for glycylglycine) were reached in the investigated reactions. The present systems can serve as good models of peptide syntheses under prebiotic conditions.

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ETHERS OF TRIFUNCTIONAL ORGANYLSILANES BASED ON RICINOLEIC ACID

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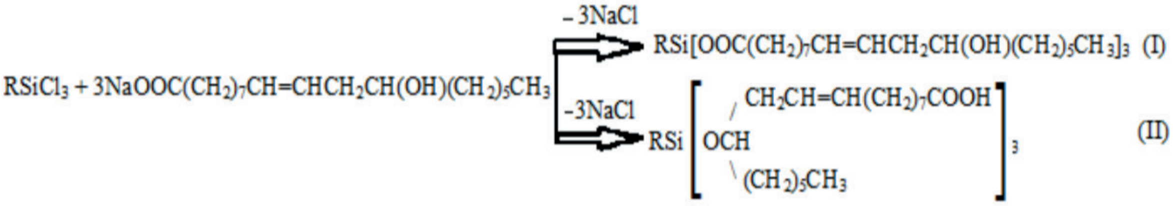
Triglyceride of ricinoleic acid (castor oil) is one of the components of high-quality lubricants[1]. This fact determined the interest towards silicon-containing ethers of ricinoleic acid, since synthesizing additives for motor oils with advanced properties for decreasing the friction coefficient is of high priority. These ethers were prepared by condensation of the acid with tetraethoxysilane, silicon tetrachloride[2]. In the present study, the reaction of sodium ricinoleate with organylhalogensilanes was investigated according to the equation:



where R – H, CH_3, C_6H_5, C_8H_{17}

The behavior and structure of the silicon-containing ethers varies depending on the solvent nature. In case of nonpolar solvents (hexane, toluene), the reaction proceeded on the hydroxyl of the carboxyl group (equation I). When a polar solvent was applied (alcohol, tetrahydrofuran), the reaction mainly proceeded on the alcohol hydroxyl (equation II). The reaction of sodium ricinoleate with chlorosilane proceeded in a rather uncommon fashion. It is complicated by splitting of tetrahydrofuran, and the synthesized ether interacts with ricinoleate, while the presence of the hydrogen atom by silicon leads to a formation of the addition products. The composition and structure of the synthesized compounds were determined by means of the element analysis data, IR- and NMR-spectroscopy, and gel chromatography.

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MICROBIOLOGICAL DEGRADATION OF UNSATURATED COMPOUNDS

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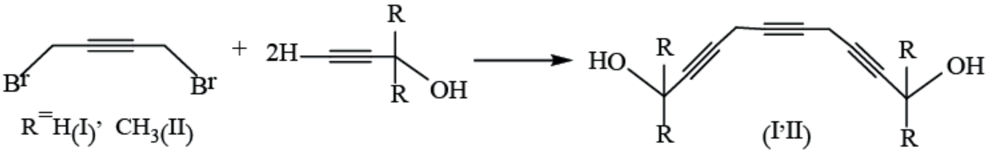
The investigations in the field of thin organic synthesis with participation of microorganisms can be recognized as advisable and are one of the main directions of the organic chemistry. The new reactions realized by microorganisms more expand a circle of the converted substances; attract new taxonomic groups of microorganisms [1, 2].

In connection with above-mentioned ones in this work for biodegradation of the polyacetylene compounds the separate microbial cultures have been used. The investigations showed that in interaction of 1,4-dibromobutine with monosubstituted acetylene alcohols (propargyl alcohol and dimethyl ethynylcarbinol) in the presence of the catalytic system consisting of the copper bromide, triethylamine and K2CO3 the reaction proceeds at 55-600C in a medium of dimethylformamide with formation of unconjugated polyacetylene diols (I, II) with yields of 65-70% on scheme:



It should be noted that as a result of an introduction of the functional groups with use of microorganisms in molecules of unsaturated hydrocarbons and their mutual conversion, it can be prepared the new types of practically valuable compounds, the preparation of which is chemically difficult or almost impossible. Also, the preparation of the organic compounds by microorganisms is more economical and safer than with use of the chemical methods. The main objects of the carried out investigations were micromycetes (*Pencillium, Aspergillus, Cephalosporium, Fusarium, Mucor, Trichoderma*) and bacteria (*Micrococcus, Bacillus, Pseudomonas*), isolated from water and soil of Absheron Peninsula.

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ACETYLENE –CONTAINING MORPHOLINE DERIVATIVES

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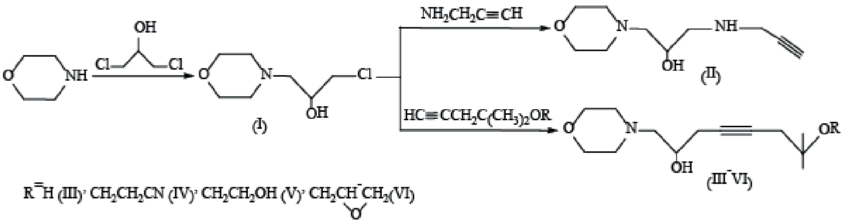
One of the important tasks of synthetic organic chemistry is the search of new biologically active substances. In spite of a considerable number of the prepared synthetic chemical and pharmaceutical preparations with medicinal action, a task of search of new more effective biologically active substances is of particular interest. Among them, the acetyl-containing morpholine derivatives, which are an important group of physiologically active compounds, take a special place. An introduction of a triple bond in molecule favors biological activity (medicinal properties, growth of regulating activity, pesticide and herbicide action), decrease of toxicity and irritant action.

Therefore, the investigations in this direction are of special interest. Taking into account the above-mentioned ones, in this paper the methods of the synthesis of acetylene-containing morpholine derivatives are presented. It has been shown that on the basis of the morpholine reaction with 1,3-dichloropropen-2-ol it is formed the corresponding chlorine-containing alcohol (I), which further undergoes the reaction with propargyl amine and monoacetylene ethers forming the corresponding acetylene-containing morpholine derivatives (II_VI) on scheme:



The structure of the synthesized compounds has been confirmed by IR- and NMR 1H-spectroscopy, and the purity was controlled by thin-layer chromatography.

Thus, it has been established due to the high reactivity that the synthesized acetylene-containing morpholine derivatives can be widely used as synthons in the various syntheses for preparation of practically useful, including biologically and physiologically active products and semi-products.

SYNTHESIS OF FUNCTIONALIZED ALKYNYL- AND VINYLIDENECYCLOPROPANES FROM 1-ALKYNYL-1-CHLOROCYCLOPROPANES

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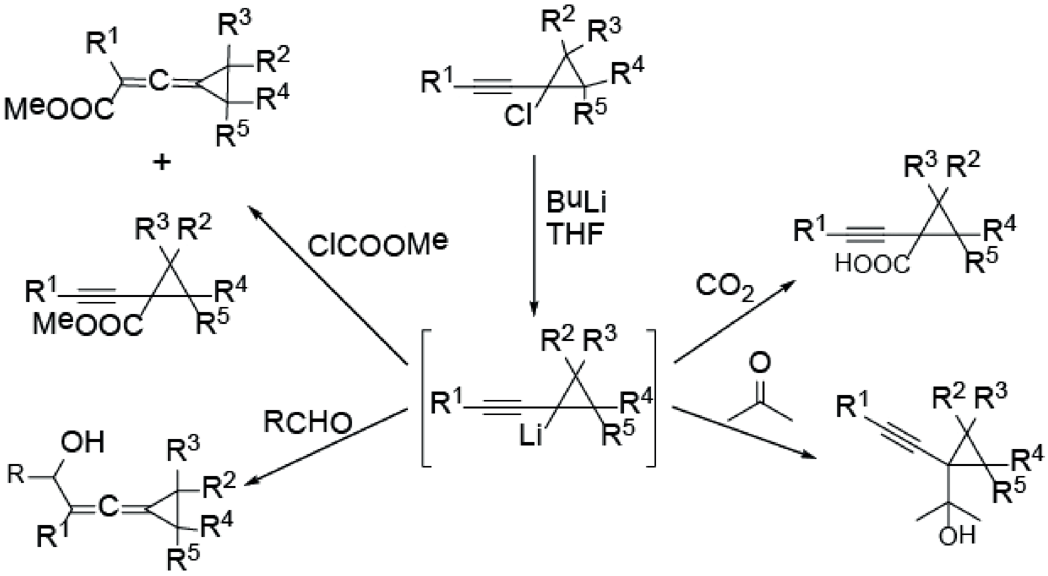
Functionalized alkynyl- and vinylidenecyclopropanes are widely used in various chemical transformations, play an important role in biochemical processes and exhibit valuable pharmacological properties.



We have found, that 1-alkynyl-1-chlorocyclopropanes under the action of n-BuLi in THF at -40 – 0 °C undergo chlorine-lithium exchange. Forming organolithium derivatives react with carbon dioxide and acetone with selective formation of previously unknown 1-alkynylcyclopropanecarboxylic acids and corresponding alcohols with yields up to 74%. Similar reactions with methyl chloroformate give mixtures of cyclopropylacetylenic and vinylidenecyclopropanic esters, whereas using of aliphatic aldehydes as electrophiles results in the formation of secondary allenic alcohols with yields up to 64%.

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SOLVENT EXTRACTION OF TITANIUM(IV) WITH ORGANOPHOSPHORUS EXTRACTANTS

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Titanium dioxide is used in the production of a wide range of products for various purposes. The technological schemes for TiO_2 production consist of the sulphate and chloride processes. The most known and widely used sulphate process for processing of ilmenite concentrates with production of titanium dioxide, which is carried out according to a complex multistage scheme[1]. As alternative approach to obtaining high quality of titanium dioxide is to separate titanium and iron from the ilmenite sulfuric acid leachate prior to hydrolysis. Solvent extraction is one of the most effective technologies for recovery of titanium from technological solution[2].

In the present study, the feasibility of extraction of titanium from ilmenite sulphuric acid leach liquor[3] using Cyanex 925 and isoamyl-dialkylphosphine oxide (different-radical phosphine oxide - POR) in diluent with the addition of aliphatic alcohols of various structures was investigated. As the diluents used o-xylene, ShellSol 2046 and Isopar H. The effect of contact time, concentration of extraction mixture components, O/A phase ratio, and temperature on the separation of titanium from iron were examined.

The efficient extraction of titanium from sulfuric acid solutions is possible with the use of concentrated solutions of extractant (25-30 vol.%). The efficiency of using aliphatic alcohols as a kinetic accelerator is shown. Extraction efficiency and selectivity of titanium with Cyanex 925 is found to be better as compared to POR.

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DYNAMIC PROCESSES IN THE PHOSPHORYLATION REACTION OF PIPERITENONE BY P–H PHOSPHONIUM SALTS

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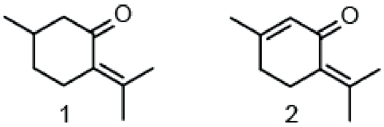
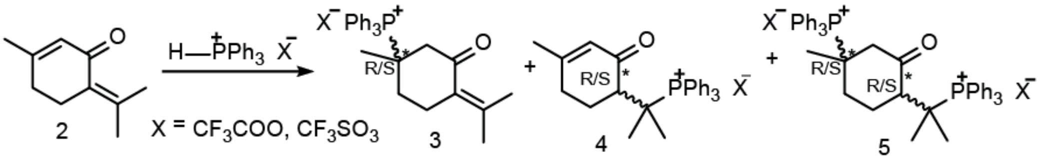
We have previously shown that the reaction of cyclic monoterpenoids containing activated C=C double bonds (using R-pulegone (1) as an example) with P-H phosphonium salts is a convenient way to form chiral cyclic γ-ketoalkylphosphonium salts. To evaluate the relative reactivity of semi- and endocyclic activated C=C bonds piperitenone (2) was involved in the reaction with P–H phosphonium salts.



It was shown that in the reaction of piperitenone (2) with P–H phosphonium salts (triphenylphosphonium trifluoroacetate and triphenylphosphonium triflate) three products are formed: bisphosphonium salt (5) and two monophosphonium salts (3, 4).



It was found that the ratio of phosphonium salts depends not only on the conditions of the reaction, but also changes over time. Regardless of the ratio of piperitenone to P–H phosphonium salt (1 : 1 or 1: 2), compound (3) is formed first. It's observed at the ^{31}P–{^{1}H} NMR spectrum giving singlet at δ_P 34 ppm. In course of time, product (3) content in the reaction mixtures decreases, and and the signals of compounds (4 and 5) are observed in the ^{31}P NMR spectra.

This work was funded by RFBR (grant №18-33-00224) and by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities (4.5151.2017/6.7).

FEATURES OF CHITOSAN-SURFACTANT COMPLEXES FORMATION IN AQUEOUS-ALCOHOL MEDIUM

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In recent decades, chitosan has been the subject of intense research. This is due to the complex of unique properties of this polysaccharide - the ability to biodegrade, compatibility with the tissues of living organisms, high complexing ability. The interaction of chitosan with oppositely charged surfactants leads to the formation of polymer-colloidal complexes. The clearly pronounced cooperative character of binding and stability of complexes are determined by hydrophobic interactions of electrostatically bound surfactant ions. The complex formation of polyelectrolytes with surfactants in mixed aqueous-organic media is the most complicated.[1]

The goal of this research was to study the effect of the nature and medium composition on the cooperativity of the binding of anionic surfactants to chitosan in mixed aqueous-alcoholic solvents. Chitosan with a molecular weight of $M\eta$ 38700 and a degree of deacetylation of 80% was used in the research. Sodium dodecyl sulfate (SDS) was used as anionic surfactant. The main research method was a potentiometric method using ion-selective electrodes. As a criterion for the cooperativity of SDS binding, we used the parameter of cooperativity U, which was determined from the slope of the binding isotherms of SDS with a degree of binding θ equal to 0.5.

It has been established that the greatest cooperativity of SDS binding is manifested in mixed solvents with an alcohol concentration of 10÷20 vol. %. However, the intensity of cooperative of the binding depends on the nature of the organic co-solvent. In aqueous-methanol solvents, the parameters of cooperativity are less than in aqueous media. At the same time, the imposing of ethanol and propanol-2 into the solvent is accompanied by a pronounced increase in the cooperativity of the binding of SDS in comparison with the aqueous solution.

Thus, it is shown that the introduction into the solvent 10÷20 vol. % ethanol and propanol-2 leads to increased cooperativity of the binding of sodium dodecyl sulfate by chitosan compared with aqueous solutions.

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THE HYDROGENATION OF FURAN DERIVATIVES IN PRESENSE OF NEW NICKEL CATALYSTS

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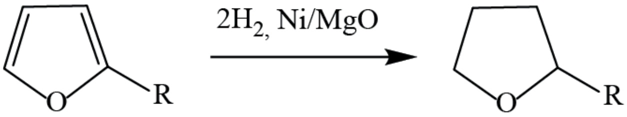
Increasing importance for chemical industry acquires development of processes based on renewable raw materials. The biomass is of particular interest, it is an ideal raw material for obtaining of different organic compounds. Currently, one of the main compounds, produced from biomass is furfural. Thereby development of new and improvement of current processes of furfural processing into different organic compounds, such as furfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran, furan, tetrahydrofuran, tetrahydrofurfuryl alcohol and others.



We investigated processes of hydrogenation of furan derivatives in presence of new nickel catalysts under atmospheric pressure of hydrogen.

Catalysts were prepared by means of impregnation of aqueous solution of precursor and further reduction of nickel on the surface of a support by sodium tetrahydroborate in water. A specially prepared MgO served as a support.

In the result of investigations done was shown, that nickel nanoparticles supported on MgO exhibit high catalytic activity in hydrogenation of furane, 2-methylfurane, furfuryl alcohol and furfural. This catalyst allows to synthesize products of hydrogenation of corresponding furane derivatives with yields up to 100% and total conversion of raw materials at 100-160°C and atmospheric hydrogen pressure.

THERMAL ANALYSIS OF 6-O-CARBOXYMETHYL CHITIN IN THREE FORMS

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Features of the structure of chitin derivatives are manifested in the study of their thermal stability, the evaluation of which is of practical interest.

The authors conducted studies using TGA and DSC methods of three forms of 6-O-carboxymethyl chitin (CMC) in an Ar atmosphere in the temperature range 30–550 ºC. From the analysis of DSC data, it can be concluded that the thermal transformations of all three forms of CMC to a salt (CMC-Na) containing a carboxyl group in the form of the –COONa salt, to an acidic (CMC-H) containing a carboxyl group in the form of –COOH and mixed (CMC-50H), which contains an equal proportion of chain links in acid and salt forms in a macromolecule, is carried out in three stages. The first stage (up to 140–150 ºC) is associated with the evaporation of both free and bound water present in the lyophilized samples of three forms of CMC. At the second stage, when the sample was heated above 170 ºC, an exothermic peak was recorded, which is associated with the decomposition of the polymer (deacetylation, decarboxylation, etc.). At the third stage, weight loss at a temperature of 335 ºC and higher was associated with the carbonization of samples due to the cleavage of polymer macromolecules by glycosidic bonds.

The amount of water sorbed by the polymer depends on the form in which the CMC is located. So, CMC-H at room conditions absorbs ≈9% of water, CMC-50H about 13% of water, and in CMC-Na - 20%. Thus, the most salt form of CMC-Na is the most hygroscopic.

The temperature of the onset of decomposition of CMC, which is in various forms, was different. For CMC-H it was 197 ºC, for CMC-50H 221 ºC and for CMC-Na 262 ºC. Note that CMC-Na also had the largest coke residue. Thus, the salt form of CMC is characterized by the highest thermal stability, and the H-form is the least thermally stable. Apparently, the presence of free carboxyl groups in CMC-H contributes to the occurrence of such reactions as decarboxylation, the formation of anhydride bonds, etc., accompanying the thermal transformations of the polymer.

SYNTHESIS OF CARBOXYLIC ACID AMIDES USING PHOSPHORUS TRICHLORIDE

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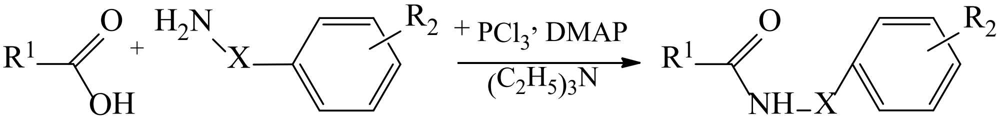
Carboxylic acid amides are an important raw material for producing various pharmaceuticals and agrochemicals. Adamantyl carboxamides are not only intermediates of synthesis of compounds with antiviral and anticonvulsant activity, but also are biologically active compounds1.

We have developed a new method of producing carboxylic acid amides from carboxylic acid and amine using PCl_3 in the presence of 4-(N,N-dimethylamino) pyridine (DMAP) catalyst) and hydrogen chloride acceptor triethylamine (TEA) in one step without isolation of the intermediate chlorides, which are easily hydrolyzed in the presence of moisture.



where R^1= Ph, R^2= H, X= bond; R^1= Ad, R^2= H, *p*-C_4H_9, *m*-NO_2, *p*-NO_2, *p*-Br, *p*-Cl, o-CH_3, *m*-CH_3, *p*-CH_3, X = CH_2, bond ; R^1= $AdCH_2$, R^2= H, X = bond

Amides are obtained with high yield in the medium of absolute acetonitrile at the molar ratio carboxylic acid: amine: PCl_3: DMAP: TEA = 1:1:1:1:1 at the temperature 800C for 2–8 hours.

Table. Yields of carboxylic acid amides:

SUBSTANCE	YIELD, %	SUBSTANCE	YIELD, %
$PHC(O)NHC_6H_5$	81	$ADC(O)NHC_6H_4CL_{-P}$	67
$ADC(O)NHC_6H_5$	78	$ADC(O)NHC_6H_4CH_{3-O}$	88
$ADC(O)NHC_6H_4C_4H_{9-P}$	85	$ADC(O)NHC_6H_4CH_{3-M}$	82
$ADC(O)NHC_6H_4NO_{2-M}$	77	$ADC(O)NHC_6H_4CH_{3-P}$	87
$ADC(O)NHC_6H_4NO_{2-P}$	84	$ADC(O)NHCH_2C_6H_5$	70
$ADC(O)NHC_6H_4B_{R-P}$	79	$ADCH_2C(O)NHC_6H_5$	69

Thus, a convenient one-step method for the synthesis of carboxylic acid amides, occurring in relatively mild conditions with a high yield of target products, has been developed.

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SHOCK WAVES AND CATALYSIS IN PREBIOTIC SYNTHESES ON THE BASIS OF WATER–FORMAMIDE SYSTEMS

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Tereshkina I.A.,[b,c] Koshkin S.A.,[a] Bukharov M.S.,[a] Gilyazetdinov E.M.,[a]
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One of the biggest problems of modern science is the problem of the origin of life whose solution requires clarifying the conditions and mechanisms of effective prebiotic syntheses of organic compounds on our planet. As the most promising way of realization of prebiotic syntheses, we consider the impact of shock waves on water-formamide systems which can be universal precursors of all major components of living organisms, including nucleic bases, nucleosides, nucleotides, amino acids, sugars, amino sugars and carboxylic acids.

In this work, we studied the impact on water-formamide systems placed in a stainless steel conservation capsule in an N2 atmosphere with different pH values of the medium (6-10.5) and additions of natural components, including $KHCO_3$, $Na_3P_3O_9$, $Cu_2(OH)_2CO_3$, fine-dispersed powders of Fe, Ni, FeS, NiS and some natural zeolites. The calculated maximum temperature and pressure in the capsule reached 575 K and 13.4 GPa, respectively, through 0.8 µs after the impact. According to the results of the LC-MS-MS analysis in the studied systems after shock, over 50 compounds of various classes were identified.

It has been established that the Fischer-Tropsch-type syntheses with heterogeneous catalysis on the surface of stainless steel of the capsule associated with reactions of the adsorbed HCN molecules, transamidation processes, as well as the classical Wöhler's and Butlerov's reactions, play a major role in the shock experiments performed. Key reaction schemes for the formation of identified compounds have been proposed.

Based on the collection of the obtained by us and literature data, it was concluded that life could have originated on the early Earth due to the impact of iron-nickel meteorites on alkaline water-formamide lakes (pH ~9) located near active volcanoes.

The work was supported by Russian Foundation for Basic Research, grant 17-03-00133.

SYNTHESIS OF TETRASUBSTITUTED GLYCOLURILS WITH HETEROFUNCTIONAL SUBSTITUENTS

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N-alkyl-substituted 2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-diones (glycolurils) exhibit a broad spectrum of biological activity; in particular, tetramethyl glycoluril (Mebicar) and 2,6-diethyl-4,8-dimethyl-glycoluril (Albicar) are compounds with tranquilizing properties[1].

The starting disubstituted glycolurils were prepared via cyclization of monosubstituted urea with glyoxal by the reported procedure[2]. N-alkylation reactions of di-tert-butyl glycoluril and diiso-butyl glycoluril with some alkane halo derivatives were effected (Fig. 1).

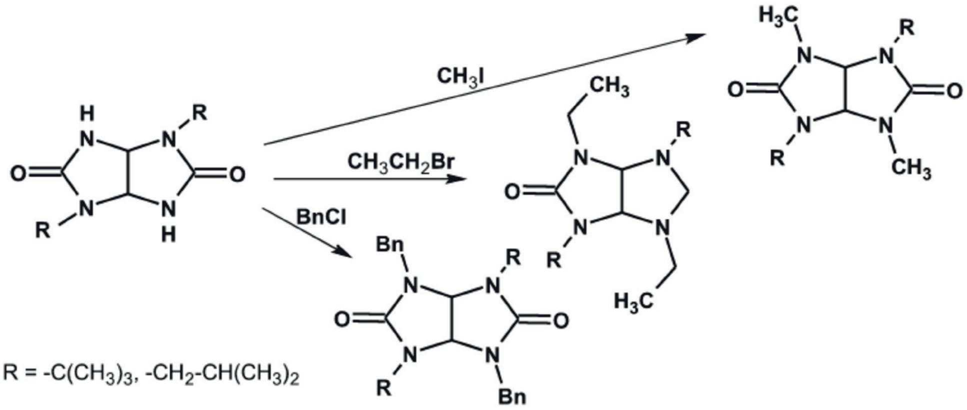

Figure 1. A scheme of N-alkylation reaction of disubstituted glycolurils

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ON THE ISSUE OF A POSSIBLE SOLUTION TO THE PROBLEM OF CHEMISTRY'S FUNDAMENTAL DEVELOPMENT IN XXI CENTURY

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Nowadays, the main problem of chemistry's development, in authors' opinion, is that its fundamental formation is not complete yet[1,2]. This can be demonstrated by the fact that chemical science still lacks the two major criteria of its fundamental maturity, which would be accepted by a wide chemical scientific community: *a unified theory of structure of chemical compounds' (chemical substances') and a system that would unite the latter on a fundamental basis*[1]. For example, like the D.I. Mendeleev's Periodic system, which unites the physical compounds of elementary particles in the form of atoms[1,2].

The main reasons, which have led to occurrence of such a problem, are as follows: 1. the bias of research in chemistry from theory towards practice; 2. fragmentation of chemistry into more than 70 "independent" chemical disciplines; 3. utter dependence of chemistry on physics in development of theoretical and fundamental basis. This is supported by the fact that nowadays the list of scientific specialties by Higher Attestation Commission lacks such a specialty, which is important for development of chemistry's fundamental principles, as "Theoretical and general chemistry" or "General and inorganic chemistry". Apparently, this is due to the fact that in the Brussels' Universal Decimal Classification[3] UDC 541 "Theoretical and general chemistry" was replaced by UDC 544 "Physical chemistry".

The authors see the solution to the above problem of the fundamental development of chemical science in the XXI century through the development of *a symbiosis of D.I. Mendeleev's ideas (composition) and ideas of A.M. Butlerov (chemical structure of matter), a unified model of chemical bond, a system of chemical bonds and compounds* in the form of a "Chemical Triangle" and *a unified theory of the structure of chemical compounds*[4].

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PATTERNS OF THE EFFECT OF COMPOSITION AND CHEMICAL BOND TYPE ON STRUCTURE AND PROPERTIES OF HOMO- AND BINARY HETERONUCLEAR COMPOUNDS OF ELEMENTS

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Today in the chemical scientific literature there are practically no data on the systemic assessment of the complex effect of the composition and type of chemical bonding of elements on the structure and characteristic properties of chemical substances. The paper attempts to solve the above problem with the support of a unified chemical bond model[1], combining its covalent, metal and ionic varieties into a single whole, and a system of chemical bonds and compounds[1,2].

As a result, a number of different in nature patterns of the complex effect of composition and type of homo- and heteronuclear chemical bonding of elements on structure and characteristic properties of chemical substances were found[1,2,3,4] for the first time, including:

- on length and energy of homo- and heteronuclear (element-oxygen, etc.) bonds between the elements of D.I. Mendeleev's Periodic system;
- on the nature of transformation of chemical structure of homo- and heteronuclear binary compounds of elements with element-oxygen bonds from low-, oligo-, high-molecular to non-molecular metallic or ionic, as well as on the ability to undergo crystallisation or amorphisation, glass formation, etc .;
- on the possibility of assessing the energy of the intermolecular physical interaction of molecules, using an assessment of the contribution of two or three components of chemical bonds that form the molecules;
- on the regular change of chemical (redox properties, thermal effect of reactions, etc.) and physico-mechanical properties of substances (electrical and thermal conductivity, plasticity, brittleness, etc.), their density, physical state, etc.

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BASIC PRINCIPLES OF THE UNIFIED THEORY OF STRUCTURE OF CHEMICAL COMPOUNDS

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After the scientific community adopted in 1860 in the city of Karlsruhe a two-level view of structure of matter in the form of atomic-molecular theory, as early as in 1861 the great Russian chemist A.M. Butlerov laid the foundations of the theory of chemical structure, thereby substantiating the fundamental difference in structure and properties of a molecule and an atom.

As part of its evolutionary development into a unified theory of structure of chemical compounds of elements, based on the symbiosis of the fundamental ideas of A.M. Butlerov (1861) and D. I. Mendeleev (1869), the authors formulated three main principles[1,2,3], determining the *formation* (1), features of *chemical structure* (2) and *properties* (3) of chemical substances in contrast to other substance varieties (physical - elementary and atomic, biological, etc.).):

- the formation of a chemical compound of elements, as a qualitatively new in comparison with an atom objectively existing quantum chemical species of a substance, and its stable existence is determined by the possibility of an effective overlapping of the electron shells of individual atoms, which leads to the emergence of collectivised electrons and chemical elements in the form of nuclei or atomic cores linked by exchange-electrostatic interaction;
- the structure of a chemical compound is determined by its composition (homo- and heteronuclear), its elemental nature (s-, p-, d-, f-), the type of a chemical element (atomic cores of various types), their number and spatial arrangement, characterised by the degree of electrons' collectivisation, character of their localisation - delocalisation, or the type of intermediate chemical bond between them;
- properties of a chemical compound (chemical substance) are determined by its structure (chemical structure).

The principles of this theory are based on the unified model of chemical bond, the system of chemical bonds and compounds in the form of a “Chemical Triangle”, including variants of the D.I. Mendeleev's Periodic table, in which the atoms are replaced by chemical bonds of elements and substances formed by them.

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QUANTUM-CHEMICAL MODELING OF MAGNETIC BISTABILITY MECHANISMS IN DINUCLEAR MIXED-LIGAND METAL COMPLEXES

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Magnetically active coordination compounds are regarded as a promising basis for molecular electronics and spintronics devices. The most widespread spin-state-switching mechanisms in transition metal complexes are spin-crossover (SCO)[1] and redox-isomerism, or valence tautomerism (VT)[2].

With the aim to search for compounds prone to spin-state-switching rearrangements via both SCO and VT, the quantum-chemical calculations (DFT UTPSSh/6-311++G(d,p)) of bimetallic (Fe, Co) complexes of 5,6-bis(salicylideneimino)-1,10-phenanthroline have been performed. It is expected that when forming salicylideneimine cobalt and iron complexes and their subsequent adduct formation with one or two pyridine molecule, ligand field strength sufficient for the occurrence of thermally initiated SCO transitions can be achieved. On the other hand, coordination of bis-o-benzoquinone cobalt complex to the phenanthroline moiety allows obtaining redox-active center.

As a result of quantum-chemical study of homo- and heterometallic complexes of 5,6-bis(salicylideneimino)-1,10-phenanthroline, a possibility of controlling energy and magnetic characteristics of isomers of these compounds by means of modification of the metal nature, variation of the auxiliary ligands and coordination of additional nitrogen-containing base has been revealed. Capability of considered adducts to undergo thermally initiated intramolecular rearrangements accompanied by switching the spin states has been predicted.

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ELECTROPHORETIC DETERMINATION OF STABILITY CONSTANTS OF COMPLEXES OF ETHER BETULIN DERIVATIVES WITH HYDROXYPROPYL- γ-CYCLODEXTRIN

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Betulin (Fig. 1) and its derivatives exhibit antimicrobial, antivirus, and antitumor activity. Bioavailability and pharmacological activity can be increased by obtaining inclusion complexes with cyclodextrins (CDs), natural macrocycle molecules built up from residues of α-1,4-bonded D-glucopyranose. Recently, the interaction of betulin derivatives with β-CD[1] and with (2-hydroxypropyl)-β and γ-cyclodextrin[2-4] has been studied.

The aim of this study was to determine the stability constants of complexes of the ether derivatives of betulin with (2-hydroxypropyl)-γ-cyclodextrin by affinity capillary electrophoresis (ACE). The study was carried out using a capillary electrophoresis system with a diode-array detector Agilent 7100 (Agilent Technologies, Waldbronn, Germany) of the Krasnoyarsk Regional Center of Research Equipment, Siberian Branch of the Russian Academy of Sciences. The values found of log K were > 5.

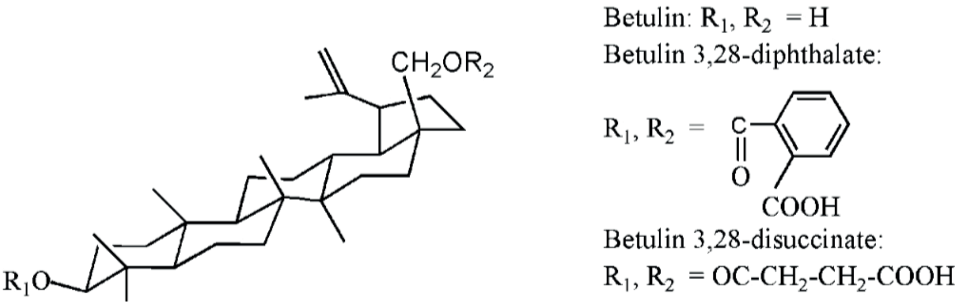

Figure 1. Structural formulas of betulin and the ether derivatives of betulin studied

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COMPLEXES OF RHODIUM (III) WITH ASPARTIC ACID AND HYPOXANTHINE

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Synthesis, study of the properties and structure of complex compounds of platinum metals with ligands containing several donor centers (amino acids, purine and pyrimidine bases) occupy an important place in modern coordination chemistry. The ligands have different types of denticity which depends on the nature and relative position of the nucleophilic centers in the ligands, the electronic configuration of complexing agents and the conditions for the synthesis of compounds. Data on rhodium(III) complexes with biologically active ligands are very limited [1-3].

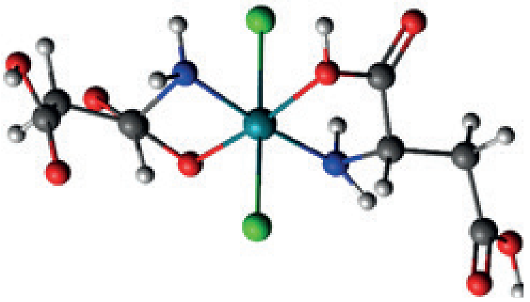
Sufficiently high stability of Rh(III) complexes with amino acids and nucleobases is established by potentiometric titration [4].

The compounds were synthesized according to approved procedures: $(Rh(Asp)(Asp\text{-})Cl_2]\cdot H_2O$, $[Rh(Hyp)_2Cl_3]\cdot H_2O$.

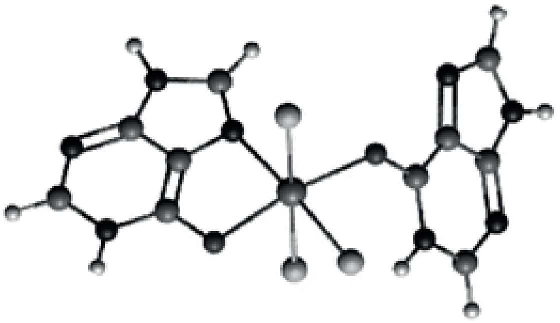
$RhCl_3 \bullet 3H_2O + 2\ Asp\ pH = 4 - 6)\ \ Rh\ (Asp)(\ Asp^{-})Cl_2 \bullet H_2O + 2\ HCl + 2H_2O$ (a)

$RhCl_3 \bullet 3H_2O + 2Hyp\ pH = 4 - 6\ Rh(Hyp)_2\ Cl_3 \bullet H_2O + 2H_2O$ (б)

The composition and structure of the obtained complexes were confirmed by the methods of elemental analysis, DTA, IR and NMR spectroscopy, as well as X-ray absorption spectroscopy EXAFS/XANES.



(a)



(б)

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UNCONVENTIONAL METAL CLUSTERS IN CRYSTALS WITH BREATHING PYROCHLORE SUBLATTICES

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The structural mechanisms of phase transitions (real or virtual) in geometrically frustrated crystals $MgTi_2O_4$, $CuTi_2S_4$, $CuZr_{1.86}S_4$ and AlV_2O_4 are studied theoretically. The spin ($MgTi_2O_4$, $CuTi_2S_4$, $CuZr_{1.86}S_4$) and chard (AlV_2O_4) degeneracy removes due to geometric frustration that occurs as a result of lattice distortion, atomic and orbital ordering, and also cluster formation. Thus, metallic pico- and nanostructures are formed in the tetragonal phase of $MgTi_2O_4$: Ti_2 dimers, two types of helical filaments along the axes of the second and fourth orders of the tetragonal cell, and two types of one-dimensional filaments of titanium ions[1-3]. The bunch of dimers, are formed in rhombohedral thiospinels $CuTi_2S_4$ and $CuZr_{1.86}S_4$[5]. The trimers are formed in the rhombohedral modification of AlV_2O_4[6]. Universal mechanism of tetrahedral metal clusters formation in crystal with geometrically frustrated pyrochlore sublattices is proposed. The formation of tetrahedral metal cluster in ordered spinels, ordered lacunar spinels, ordered Laves phases ($MgCu_4Sn$ structural type) and ordered pyrochlore is considered.

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GROUP-THEORETICAL DESIGN OF NEW FERROELECTRICS WITH A PYROCHLORE STRUCTURE

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The design of ferroelectrics, materials with polarization that is switched by the electric field, has become one of the key areas in materials science throughout most of the XXth century. Ferroelectrics with pyrochlore structure are distinguished by relatively high dielectric constant values and low dielectric losses, which makes them a promising basis for creating capacitor materials[1-3]. The purpose of this study was to establish all possible low-symmetry phases of proper and improper ferroelectrics formed from the archetype high-symmetry phase with the structure of cubic pyrochlore as a result of real or virtual phase transitions.

Six symmetrically permissible phases of proper ferroelectrics and 16 phases of improper ferroelectrics were found. Proper and improper order parameters, as well as theoretically calculated structures (space groups, multiplications of primitive cells, Wyckoff position splitting) are calculated for each of these phases. The invariant analysis was performed and the types of mixed invariants (for improper ferroelectrics) in the thermodynamic potential are determined. The contributions of proper and improper order parameters to the atomic displacements of known ferroelectrics with the pyrochlore structure, for example, Cd2Nb2O7, are estimated. The results obtained in the work can be used in combination with the first-principles calculations for the design of new functional materials with the pyrochlore structure for application in electronics industry.

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HYDROGEN BONDS IN A-GLYCINE: RESULTS OF SIMULATION

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Currently, to create many drugs, amino acids and their derivatives are increasingly used. This is due to the safety, the absence of allergenic effects, as well as the low severity of side effects of these compounds.[1] Polymorphism is characteristic of amino acid crystals; therefore, the ability to predict the existence of all possible polymorphic modifications is required. Developing methods for the desired structures and preventing their uncontrolled conversion to other forms are also relevant.[2] For example, α-, β- and γ-modifications are characteristic of glycine. Article[3] showed how the α and γ forms of glycine differ in biological activity. They block the spontaneous activity of pyramidal neurons with different temporal dynamics. γ-glycine more actively affects the transport of nano-sized particles to the brain, etc. β-Modification of glycine is metastable, but it also exhibits bioactivity[4]. In this regard, the study of the instability of hydrogen bonds (H-bonds) in amino acid crystals plays an important role. When simulating α-glycine dimer[5], the interaction energy value was -58.28 kcal / mol, which corresponded to two strong H-bonds. Simulation of a fragment of crystal consisting of 5 and 6 molecules showed[6] that H-bonds were formed inside the layer and between the layers. The difference in energy is significant, which indicates the possibility of saving small clusters during dissolution process.

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SYNTHESIS OF 5-HYDROXYBENZO[A]PHENAZINE 12-OXIDES BASED ON 2-ARYLAMINO-1,4-NAPHTHOQUINONES

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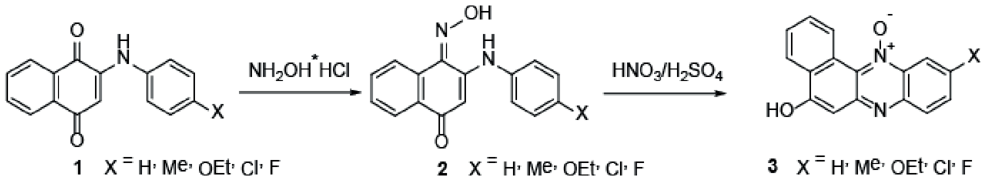
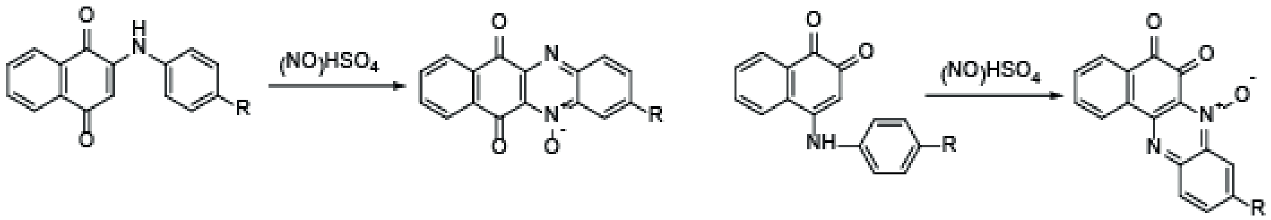
Oximation of 2-arylamino-1,4-naphthoquinones (1) was found to result in 2-arylamino-1,4-naphthoquinone-1-oximes (2). When treating with the nitrating mixture in acetic acid, oximes 2 were cyclized to 5-hydroxybenzo[a]phenazine 12-oxides (3).



The 2→3 reaction resembles the known heterocyclizations of 2-nitrosodiarylamines to pnenazine-N-oxides[1,2].



Interestingly, the 2→3 cyclization is accompanied by the removal of both carbonyl groups from the initial substrates in contrast to the previously described reactions, which occur with 2-arylamino-1,4-naphthoquinone or 4-arylamino-1,2-naphthoquinone under the action of nitrosylsulfuric acid3,4.

Obviously, the 2→3 cyclization occurs via the radical mechanism. The structures of phenazines 3 were confirmed by their chemical transformations and the X-ray and two-dimensional NMR data.

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COMPLEXES OF DICYANOAURATES AND DICYANODIHALOAURATES WITH TETRAORGANYLPHOSPHONIUM AND -STIBONIUM CATIONS

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Creating complexes of different cations with $[Au(CN)_2]$- anions is an actual task. Many of these derivatives possesses useful optical and magnetic properties[1,2]. However, there is almost no mention of such tetraorganylphosphonium and -stybonium complexes in the literature. As part of our study, we obtained a series of compounds: $[Ph_3PR][Au(CN)_2]$ ($R=CH_2C_6H_4$, $CH_2C_6H_4F$-4, CH_2OMe, CH_2CN), $[Ph_4Sb][Au(CN)_2]$ и $[Ph_3PCH_2C_6H_4F\text{-}4][Au(CN)_2Cl_2]$, $[Ph_3PCH_2C_6H_4(F\text{-}4)][Au(CN)_2Br_2]$, $[Ph_3PCH_2C_6H_4F\text{-}4][Au(CN)_2I_2]$, $[Ph_3PCH_2OMe][Au(CN)_2Br_2]$, $[Ph_4P][Au(CN)_2I_2$-*trans]*, $[Ph_3PCH_2Ph][Au(CN)_2I_2]$, $[Ph_3PEt]$2[Au(CN)2I2], $[Ph_3PEt]_2[Au(CN)_2I_2][I_3]$, $[Ph_3PCH_2CN]_2[Au(CN)_2I_2][I_3]$, $[Ph_4Sb][Au(CN)_2I_2]$, [*p*-Tol_4Sb][Au(CN)2I2], [*p*-$Tol_4Sb]_2[Au(CN)_2I_2][I_3]$, $[Ph_3PMe][Au(CN)_2I_2]$ *via* interaction of corresponding tetraorganylphosphonium, stybonium halides with $K[Au(CN)_2]$ and $K[Au(CN)_2Hal_2]$ (Hal = I, Br, Cl) salts in water. The structures of the synthesized compounds were characterized by IR, NMR ^1H, ^{13}C spectroscopy and X-Ray analysis. The structure of $[Au(CN)_2]^-$ anions in the complexes is almost linear. Anion of $[Au(CN)_2Hal_2]^-$ represent the distorted square.

Tetraphenylstibonium dicyanoaurate shows the expressed activity with respect to the degradation of organic dyes in water under the action of UV radiation.

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ANALYSIS OF ION-EXCHANGE PROPERTIES OF NATURAL SORBENTS RELATIVE TO COPPER AND LEAD CATIONS

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In the work there were studied the regularities of copper (II) and lead (III) cations extraction from aqueous solutions with the help of natural sorbents from the Astrakhan region such as the marl of the Baskunchak deposit, the Kamennyy Yar deposit and the clay of the Volzhsky deposit. A comparative study was made of the applicability of the adsorption models to describe experimental isotherms of the adsorption of mentioned cations on the surface of aluminosilicates[1]. The comparison of the regression coefficients shows that the Temkin model is suitable for describing the adsorption equilibria in the "M^{2+} - clay" systems. The Freundlich model more accurately from the mathematical point of view describes the experimental data in the "M^{2+} - marl / opoka" systems which reveals the heterogeneous surface of both of these materials with a large number of energetically dissimilar active centers[2].

The Dubinin-Radushkevich model can be used to describe the process of lead (II) ions concentration on the marl surface of the Baskunchak deposit and the Kamennyy Yar deposit, the calculated values of the free energy of adsorption were 4.17 and 11.2 kJ / mol, accordingly. The process of lead cations attaching on these natural sorbents in the Astrakhan region proceeds according to the ion-exchange mechanism. The adsorption activity of Cu^{2+}, Pb^{2+} ions on the surface of sorbents is confirmed by the calculated values of Gibbs energy and entropy. According to the adequacy of the description of cations adsorption on the examined materials of the model there were formed the following series:

Cu^{2+}: *clay* (Freundlich < Temkin m.) ≤ *marl* (Dubinin-Radushkevich m.) < Temkin < Freundlich m.) < *opoka* (Langmuir < Dubinin-Radushkevich < Temkin < Freundlich m.) (1)

Pb^{2+}: c*lay* (Langmuir ≤ Temkin m.) < *opoka* (Dubinin-Radushkevich < Langmuir < Freundlich m.) < *marl* (Dubinin-Radushkevich ≤ Freundlich m.). (2)

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SYNTHESIS, STRUCTURE AND ANTIMICROBIAL ACTIVITY OF TRIMETHYLAMMONIUM HEXACHLOROPLATINATE

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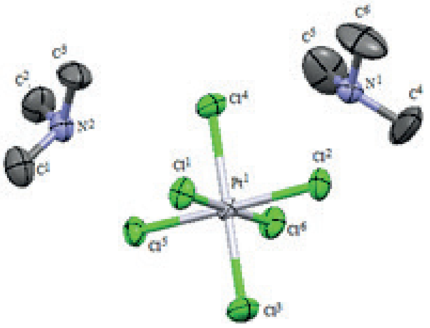
Synthesis of platinum complexes exhibiting antimicrobial properties against gram-positive and gram-negative bacteria is one of the main objectives in the field of drug design of platinum series[1].

The reaction of trimethylammonium chloride with hexachoroplatinic acid in acetonitrile (mole ratio of reagents 1: 1) is accompanied by formation of complex 1:



Structure of complex 1 was determined by the X-ray structural analysis. The crystals of complex 1 consists of tetrahedral cations of trimethylammonium and hexachloroplatinate octahedral anions.

The values of the CNC valence angles approach the ideal tetrahedral angles [109.0(16)°−115(3)°]. In the slightly distorted octahedral anions $[PtCl_6]^{2-}$ of complex 1 the ClPtCl trans-angles approach 180°, cis-angles are [88.82(17)°–91.09(12)°]. The Pt–Cl distances vary within [2.317(5)–2.334(3) Å].

The aqueous solution of complex 1 at concentrations of 0.0029 and 0.00029 mol/L in 0.9% NaCl solution was found to have antimicrobial activity against Escherichia coli strain ATCC 25922 at a concentration of 108 CFU/ml.

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SYNTHESIS OF NEW ARYL-SUBSTITUTED UREAS WITH A SUBSTANTIAL CYTOTOXICITY

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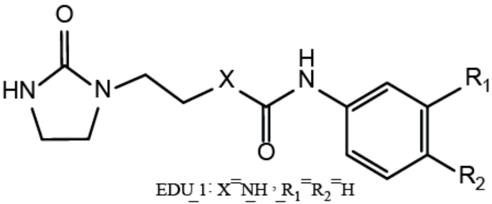
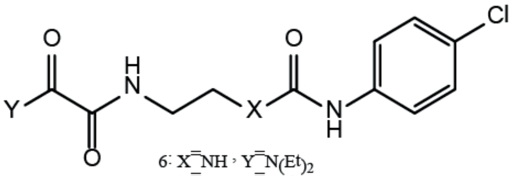
Adenine type natural cytokinins possess a pronounced anticancer activity but are hard to synthesize. Cytokinin-like aryl ureas are similar in their biological properties to the natural adenine-type cytokinins but are significantly more synthetically available compounds. Thus, the development of their novel analogs is of significant interest.

The purpose of this research was to synthesize a series of cytokinin-like aryl-substituted ureas and carbamates and to study their biological activity.



EDU 1: X=NH, R_1=R_2=H
2: X=O, R_1=R_2=Cl
3: X=NH, R_1=R_2=Cl
4: X=O, R_1=H, R_2=Cl
5: X=NH, R_1=H, R_2=Cl



6: X=NH, Y=N(Et)$_2$
7: X=NH, Y=OEt
8: X=O, Y=OEt

A cytokinin-like agrochemical preparation Kartolin-2 and a compound with similar structural framework ethylene diurea (EDU) were chosen as templates for chemical synthesis. Their analogs 2-8 were synthesized and tested for an acute cytotoxic activity in four lines of human tumor cells: melanoma A-375, glioblastoma U-87 MG, breast cancer MDA-MB-231, neuroblastoma SH-SY5Y.

It was found that the compounds synthesized have substantial cytotoxicity against breast and neuroblastoma cancer lines.

The work was supported by the RFBR projects No. 19-03-00492 A and projects No 18-33-01128 mol_a

SYNTHESIS OF DITHIOACETYLENIC CYCLIC ALCOHOLS

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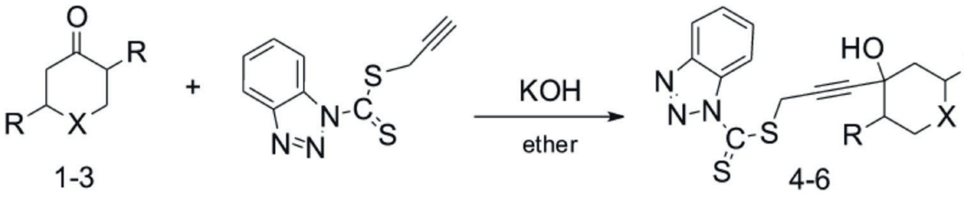
Compounds containing in its structure the benzotriazole moiety and several functional groups attract interest from point of view of their potential biological activity.

The nucleophilic addition reaction of prop-2-ynyl-1H-benzo[d][1,2,3]triazole-1-carbodithioate on the carbonyl group of the cyclic ketones cyclohexanone, 2,5-dimethyltetrahydrothiopyran-4-one and 1-methylpiperidine-4-one was studied. The condensation reaction was carried out in the presence of a 4-fold excess of technical KOH at room temperature in diethyl ether.



X = CH_2, R = H (1,4); X =S, R =CH_3 (2,5); X = NCH_3, R = H (3,6)

As a result of separation from the reaction mixture in individual form, the tertiary dithioacetylenic alcohols were obtained in the corresponding yields: 3-(1-hydroxycyclohexyl)prop-2-ynyl-1H-benzo[d][1,2,3]triazole-1-carbodithioate 4 (48.5%); 3-(4-hydroxy-2,5-dimethyltetrahydro-2H-thiopyran-4-yl)prop-2-ynyl-1H-benzo[d][1,2,3]triazole-1-carbodithioate 5 (85%); 4- (3-(1H-benzo[d][1,2,3]triazol-1-yl)prop-1-ynyl)-1-methylpiperidin-4-ol 6 (57.6%). The composition and individuality of the synthesized alcohols 4-6 were confirmed by the data of the elemental analysis, TLC and IR spectroscopy.

The IR spectra of the dithioacetylenic alcohols 4-6 are characterized by the presence of broadened absorption bands in the region of 3400–3500 cm– 1 characteristic for stretching vibrations of the hydroxyl group. The weak absorption band at 2100 cm-1 indicates the presence of triple acetylene bond in the alcohols.

The work was carried out by the financial support of the SC MES RK in the framework of the scientific and technical program № BR05236420 “Green technologies based on supercritical media”.

NEW PYRIDYLCONTAINING LIGAND-DIETHYL(PYRIDIN-2-YL) PHOSPHINE OXIDE AND ITS COORDINATION PROPERTIES

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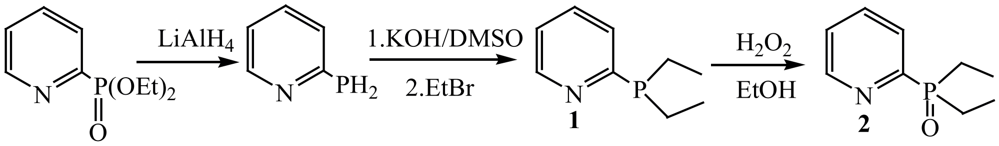
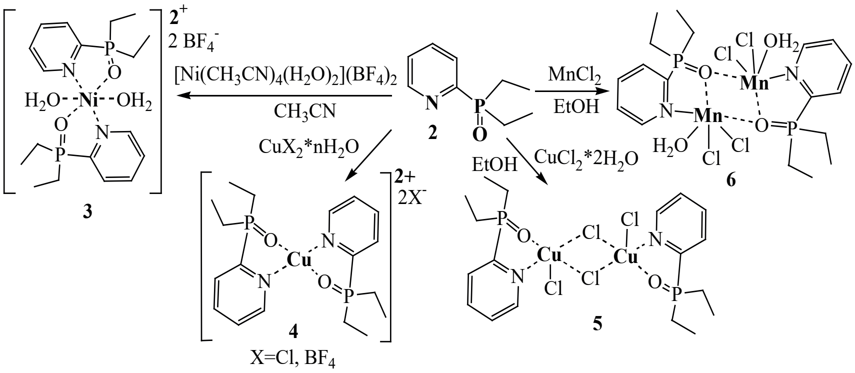
Pyridylcontaining phosphine oxides and their metal complexes attract a great interest due to their application as combustion inhibitors[1], extractants for separation of actinides and lanthanides from the nuclear wastes[2], and oxygen transfer agents in epoxidation of olefins[3]. Despite the high applicability of these compounds, pyridyl-substituted phosphine oxides with alkyl substituents at the phosphorus atom and their metal complexes reported scarcely. With the aim to expand the library of N,O-hybrid phosphine oxide ligands and their metal complexes a novel diethyl(pyridin-2-yl)phosphine oxide, its complexes with Ni(II), Cu(II) and Mn(II) metal-ions were synthesized (Scheme 1 and 2).



Scheme 1. Synthesis of diethyl(pyridin-2-yl)phosphine oxide 2.



Scheme 2. Synthesis of transition metal complexes with obtained ligand 2.

Ligand 2 reacts with and manganese(II), nickel(II), and copper(II) metal-ion sources in MeCN or EtOH in different metal:ligand ratio giving the corresponding mononuclear and binuclear complexes 3-6 (Scheme 2). The composition and structure of 3-6 were established using a set of physicochemical analysis methods including X-ray analysis.

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MORPHOLOGICAL AND RHEOLOGICAL FEATURES OF POWDERY COMPOSITES BASED ON OXYGEN-FREE GRAPHENE AND ZRO2

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The morphological and rheological properties comparative study of hybrid nanopowders based on ZrO_2 and graphene with different amounts of 0.3-1.4 wt.% was carried out. These powders are intended for sintering fine-grained ceramics. The method main idea is a combination of sol-gel synthesis of a Zr-containing sol and a sonochemical method for producing oxygen-free graphene. In one case, the graphene suspension was mixed with as-prepared sol, and the sol→gel transition followed by crystallization of ZrO_2 occurred on graphene sheets with the formation of K1 hybrid system. In another case, two suspensions were used for synthesize the K2 composite: calcined (500°C) ZrO^2 nanopowder with a crystallite size of 3-30(8) nm and graphene. It was found that ZrO^2 dispersion in the K1 composite was several times higher than in the single ZrO^2 nanopowder and in the K2 composite. The rheological characteristics of composites and single ZrO^2 nanopowder were investigated on INSTRON machine in the constant plunger movement speed mode. It was found if calcined ZrO^2 was used in the synthesis of K2 composite, the compressibility modulus of it decreased by 36% compared to the single ZrO^2 indicator. When as-prepared Zr-containing sol was used in the synthesis, the resulting K1 composite had a compressibility modulus 2 times higher than single ZrO^2. The limit values of the strain on the linear section of the stress-strain curve also differed significantly: for the K1 composite this value was 1.2 times higher, and for the K2 composite, it was 2.6 times lower than for single ZrO^2. Thus, it was shown that the method of introducing graphene into ZrO^2 nanopowders in amounts not exceeding 1.5 wt.% make a strong impact on the formation of composites rheological properties.

This work was supported by the Russian Foundation for Basic Research, grant № 19-03-00554_a.

STRUCTURAL FEATURES OF THE INTERACTION OF PHOSPHOLIPIDS WITH NANOPARTICLES AT THE INTERFACE

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The scientific and applied significance of the study is determined by the role of associates of surfactants, polymers and lipids in associates with nanoparticles (NPs) in the regulation of biochemical processes occurring at the interfaces with different polarities. The structural features of the interaction of phospholipids (basic lipids of biomembranes) such as phosphatidic acid (PA) with different NPs at the water/air interface were investigated. The studies were carried out by methods of surface spectroscopy and microscopy, allowing to evaluate the organization and interaction of the resulting supramolecular structures. Initially, monolayers of individual PAs were investigated, which immediately after the application of the corresponding solution exists in a liquid-expanded state (LE) and formed a relatively uniform film (with small "open" sections of water). After the start of monolayer compression, i.e. reduce the surface area, PA formed domains, which with further compression disappeared and became as liquid-condensed (LC) state of the monolayer. An increase in surface pressure led to a collapse of the monolayer. Further, mixed monolayers of PA and QDs with different QD contents (1% and 10%) were obtained and studied. When applying all mixtures of PA:QDs immediately formed a non-uniform layer at the interface. Two types of structures were observed in the monolayer, the first of which related to QD aggregates of submicron size; the second type of structures - homogeneous sections. With further compression of the LE state of the monolayer, the PA and QD sections were separated for a short time. Almost immediately after separation, the QD aggregates were mixed with PA and form a more uniform layer in the LC state. The subsequent compression of the mixed monolayer led to the formation of an almost homogeneous monolayer having a “granular” structure. In general, mixed monolayers of PA:QDs both with high and low QD content, can be characterized by similar phase behavior and the formation of a stable granular structure with preservation of the boundaries between the formed aggregates.

This work was supported by the Russian Foundation for Basic Research, project 19-03-00717.

THE 2,2-DINITRO-2-(2-METHYLTETRAZOL-5-YL)ACETONITRILE IN REACTIONS OF CYCLOADDITION WITH NITROGEN 1,3-DIPOLES

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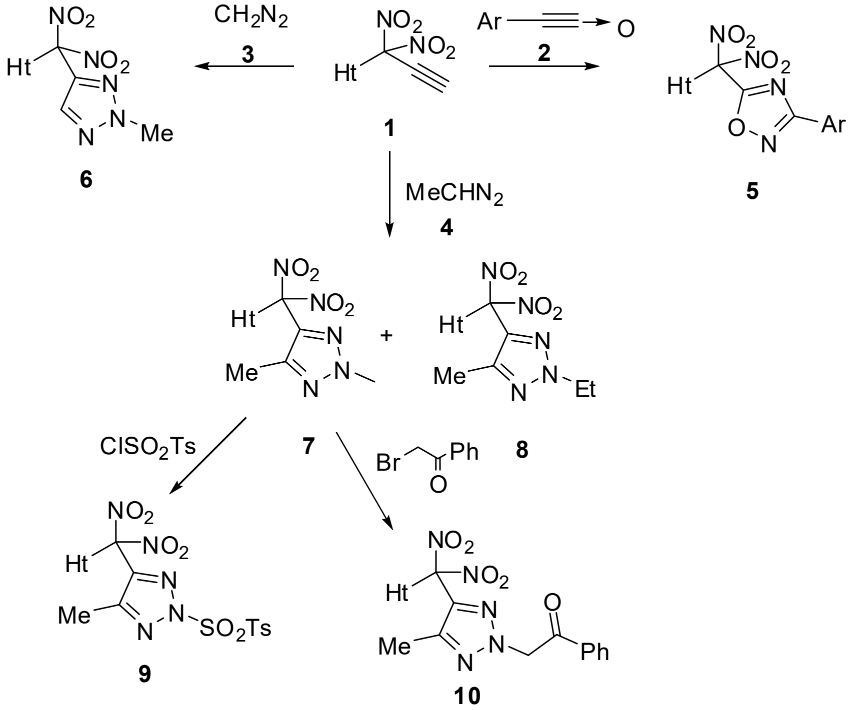
Reactions of 2,2-dinitro-2-(2-methyltetrazol-5-yl)acetonitrile (1) with N-oxides of aromatic nitriles (2), diazomethane (3) or diazoethane (4) resulted in 5 [dinitro(3-phenyl-1,2,4-oxadiazol-5-yl)methyl]-2-methyltetrazol (5), 2-methyl-5 -[(2-methyl-1,2,3-triazol-4-yl)(dinitro)methyl]tetrazole (6) or separable mixture of 2-methyl-5-[(5-methyl-1,2,3-triazol-4-yl)(dinitro)methyl]tetrazole (7) and 2-methyl-5-[5-methyl-2-ethyl-1,2,3-triazol-4-yl)(dinitromethyl]tetrazole (8)[1].



Ht= 2-methyltetrazol-5-yl

The possibility of integrating tosyl (9) and phenacyl (10) fragments into the 1,2,3-triazole cycle of compound (7) is shown.

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This work was supported by the Ministry of Education and Science of the Russian Federation (project no 4.9288.2017BCH)

APPLICATION OF MICROWAVE RADIATION FOR THE INITIATION OF H2S REACTIONS WITH CONDENSED BICYCLIC HYDROCARBONS

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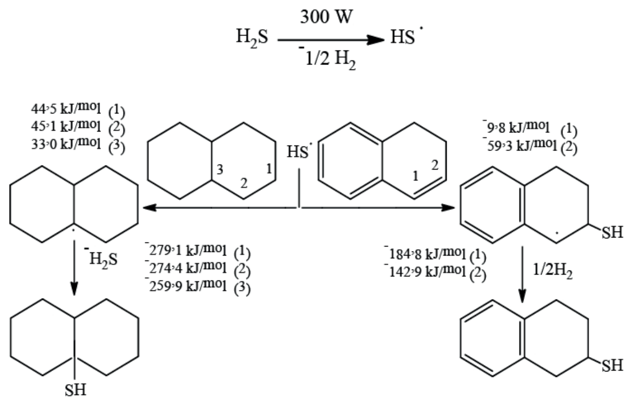
Recently, microwave irradiation (MWO) has acquired the greatest popularity in organic synthesis due to a number of advantages. Earlier, we successfully carried out electro- and microwave synthesis of thiolation products of cycloalkane $C_{5-}C_8$ by H_2S.[1,2] In this work, the reactions of thiolation of decaline I and 1,2-dihydronaphthalene II with H_2S under MWO conditions (30 min) are studied.



Quantum-chemical calculation of the thermal effects of reaction stages was carried out using the Gaussian 03 program (BLYP functional, basis 6-31G (d, p)). R2S2 was obtained as secondary products of RSH transformations in the following ratio 1.0: 3.6 (I); 1.0: 4.4 (II). The potential possibility of using RSH as muco-membrane protectors, stimulants of kidney function and drugs for the treatment of phobic disorders has been established (PASS program, a probability of 75.2-87.0%).

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This work was supported by the Russian Foundation for Basic Research (№ 18-29-24001)

ONE-POT SYNTHESIS, STRUCTURE AND WAYS OF FORMATION OF SUBSTITUTED AZOLOAZINES

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One of the tasks of modern chemistry of heterocyclic compounds is directed synthesis based on simple and accessible reagents of heterosystems with predictable properties that are similar in structure to natural ones.

This paper summarizes the new data we obtained on the synthesis and determination of the structure of triazolo- (thiazolo-) hydropyrimidines, quinazolines, containing pharmacophoric fragments and groups that are heteroanalogs of purines, the significance of which is well known. Synthetic approaches are based on the use of a methodology of multicomponent reactions that meets the criteria of environmental friendliness, economy, and stage efficiency.

With a three-component condensation of (hetero) aromatic aldehydes, cyclohexanone and 1,2,4-triazol-3-amine, a series of isomeric triazologohexahydroquinazolines was obtained. The spectral data and the isolation of intermediates made it possible to determine the route for the formation of reaction products with the azomethine – amino ketone – hydroxyhydroquinazoline – hexahydroquinazoline sequence.

With the o-pot interaction of ethyl acetoacetate, aromatic aldehydes and 1,3-thiazol-2-amine (20º, UZ), substituted thiazolopyrimidinecarboxylates are obtained, the formation of which due to the high CH-acidity of the methylene component flows through α, β -unsaturated ketone, its interaction with the nucleophilic reagent and azocyclization. Ortho-substituents in the benzene ring of aldehyde have a decisive influence on the direction of the reactions - the formation of N, O-heterocyclization products or acyclic systems.

Detailed one- and two-dimensional NMR studies of newly synthesized compounds on the ^{1}H, ^{13}C, HPLC nuclei made it possible to establish that, depending on the aminoazole used, azoloazines with different types of articulation of rings are formed, containing the azine fragment of the enamine or imine structure, which indicates different ways of their formation.

Compounds with pronounced cytotoxic activity in relation to HeLa cell culture, promising for further research, were isolated among the series of substances obtained.

EXTRACTION OF COPPER WITH VERSATIC ACID HYDRAZIDES 1519 FROM AMMONIA SOLUTIONS

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This work is a continuation of the study of the extraction properties of α-branched tertiary carboxylic acids Versatik $C_{15} – C_{19}$ hydrazides (GVIK 1519). In the previous paper this reagent was suggested for extraction of copper (II) and associated metals from sulfuric acid solutions [1].

It is that in ammonia solutions hydrazides carboxylic acid (HL) are known to form complex compounds [Cu(II)]: [HL] = 1:1 and 1:2 with copper(II) ions. When extraction these compounds are gradually transferred into the organic phase [2]. The aim of the present paper is to study extraction properties of GVIK 1519 in relation to copper (II) in ammonia media.

It has been established that during extraction of copper (II)with 0.4 mol/l GVIK 1519 solution in kerosene at an initial copper(II) concentration of 1 g/l, the extraction degree is 98-99% in pH-range of 0.5 – 9.0 at the phase volume ratio Vo : Vw = 1 : 1 and phase contact time 3 min. The extraction capacity in relation to copper at 0.1 mol/l GVIC 1519 has been found to be 2.8 g/ l.

Ammonium salts are added to increase leaching rate. It is necessary to know how the presence of these salts affects the extraction. The extraction degree of copper at one extraction step has been decreased from 98.7% to 91.8% the initial solution pH-value of 8.0 and $(NH_4)_2SO_4$ concentration of 200 g/l.

The re-extraction of copper with sulfuric acid solutions has been studied. The re-extraction degree was 99-100% at H_2SO_4 concentration of 147 g/l, the contact time of the phases of 3 min and the phase volume ratio Vo: Vw = 1: 10.

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This work was financially supported by the Comprehensive Program of Ural Branch of the Russian Academy of Sciences (Project Nr. 18-3-3-24).

LIQUID PHASE CATALYED OXIDATIVE TURNOVER OF PENTAETERITRITE

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One of the methods for producing methane tetracarboxylic acid (MTCA), which has a wide prospect of application in various branches of the chemical industry, is the liquid-phase oxidation of pentaerythritol (2,2-bis (hydroxymethyl)-1,3-propanediol) tetrahydric alcohol. The known methods of oxidative transformations of pentaerythritol are multistage and expensive.[1] In this work, we studied the possibility of synthesizing MTCA by oxidizing pentaerythritol (PE) by an oxidizing system based on H_2O_2 and a catalyst – H_2MoO_4.

To identify the patterns of the process under study, the kinetic patterns of accumulation of peroxide compounds and acids in the reaction products were studied. The concentration of acids was determined by alkalimetric, and the content of peroxo compounds - by iodometric methods. It is shown that during the oxidation of PE in aqueous medium at 80 °C for 9 h by the oxidizing system "$H_2O_2 + H_2MoO_4$", the yield of acids increases with increasing initial concentration of H_2O_2 and H_2MoO_4; in the reaction system, the consumption of H_2O_2 is accompanied by the formation and subsequent consumption of peroxo compounds of pentaerythritol. The following scheme is proposed for the initial stages of peroxidation catalyzed by pentaerythritol in an aqueous medium:

$H_2O_2 + H_2MoO_4\ ^{K1} \leftrightarrow H2O + H2MoO5$
$H_2MoO_5 + PE\ ^{K2} \leftrightarrow H_2MoO5 \cdots PE$
$H_2MoO_5 \cdots PE\ ^{k3} \rightarrow H_2MoO_4 + H_2O + PECHO$
$PECHO + O_2\ ^{k4} \rightarrow PECOOOH$
$PECOOOH\ ^{k5} \rightarrow PECOOH$

Kinetic analysis of the scheme for the oxidation of PE allowed us to theoretically obtain the following equation for the accumulation of carboxyl groups:

$[–COOH]= k_4/2\ .\ k_3\ .K_1\ .\ K_2.\ [H2O2]_{equally}\ .\ [H_2MoO_4]_{equally}\ .\ [PE]_{equally}.\ t^2/[H_2O]_{equally},$

describing the experimental data.

Laboratory studies have shown that catalyzed peroxidation of PE is promising as a one-pot method for producing polycarboxylic acids.

Literature
1. Patent RU 2487862, Cl. IPC SS 51/295, SS 55/24, publ. 07/20/2013.

MODELING OF TRANSPORT PROCESSES IN CONCENTRATED ELECTROLYTE SOLUTIONS USING BI-VELOCITY METHOD

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Highly concentrated electrolyte solutions, as well as electrolyte melts and solid electrolytes, are widely used in various electrochemical systems, because they allow one to improve significantly the characteristics of such systems. The transport processes in the highly concentrated electrolyte solutions can be de-scribed by the hydrodynamic model of homogeneous multicomponent mixtures and Stefan-Maxwell multicomponent diffusion model. These models have a number of disadvantages. In recent years, so-called "bi-velocity approach" for modeling of transport processes in the concentrated solutions has been developed. The bi-velocity approach postulates that the velocity of any component of solution can be represented as the sum of two velocities: (1) the velocity of the diffusion-migration transport of the component, which depends on the gradient of electrochemical potential and does not depend on the choice of coordinate system; (2) the velocity of the entire solution, which is the same for all components of solution and depends on the choice of coordinate system.

The aim of this work is to develop the bi-velocity approach to the modeling of transport processes in the concentrated solutions and to compare various models of transport processes in the complex electrochemical systems.

The mathematical model of ionic transport in the concentrated electrolyte solutions is developed using the bi-velocity approach. The model involves the Nernst-Planck equations in the approximation of solution electroneutrality and the law of volume conservation. Within the framework of bi-velocity method, the equations for the diffusion-migration fluxes of solution components and for the hydrodynamic velocity common to all components are obtained. A scheme of numerical solution based on the conservative finite volume method is developed. The results of modeling are presented for a number of electrochemical systems.

The work was performed with support of Ministry of Science and Higher Education of Rus-sian Federation.

EFFECT OF MIGRATION ON HOMOGENEOUS REDOX ELECTROCATALYSIS AT ROTATING DISK ELECTRODE

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Electrocatalysis is important to many applications in the electrochemistry. A large number of works have been devoted to the experimental and theoretical study of homogeneous redox electrocatalysis. The theory of homogeneous electrocatalysis is most well-developed for polarography; however, in some works, variously shaped electrodes and chemical reactions of various orders were considered. In all works devoted to the theoretical study of homogeneous redox electrocatalysis, the ionic migration was ignored. In many cases, the supporting electrolyte is present in the solution. It almost completely suppresses the migration of electroactive ions. However, in some cases, the concentration of supporting electrolyte can be rather low or it is absent at all. In this case, the migration transfer of all types of ions, which are present in the solution, should be taken into account.

This work is devoted to the theoretical study of the effect of migration on the homogeneous redox electrocatalysis of electrochemical reactions at the rotating disk electrode. The mathematical model involves the Nernst-Planck equations that take into account diffusion, migration, convection, homogeneous chemical reactions, and electroneutrality condition. For the convenience of solving and analyzing the results, the mathematical model was reduced to the dimensionless form. The numerical solution was performed by the finite volume method on the nonuniform grid. Based on the results of computational experiments, for the electrocatalytic reduction of hydrogen peroxide in the presence of ferric ions, three zones were observed in the plane of concentrations of H_2O_2 – H_2SO_4. These zones differ in the nature of the limiting current: for H^+ ions, Fe^{+2} ions, and hydrogen peroxide H_2O_2. The dependences of the limiting current on the concentrations of H_2SO_4 and H_2O_2 were determined with and without consideration of ionic migration. It was found that the ionic migration may be ignored only in the cases that the concentration of H_2SO_4 is significantly higher than that of H_2O_2.

The work was performed with support of Ministry of Science and Higher Education of Rus-sian Federation.

STUDY OF THE MECHANISM OF THE INTERACTION OF 4-N,N-DIMETHYLAMINOBENZALACETOPHENONE WITH 2-NAPHTHYLAMINE BY CHROMATOMASS-SPECTROMETRY METHOD

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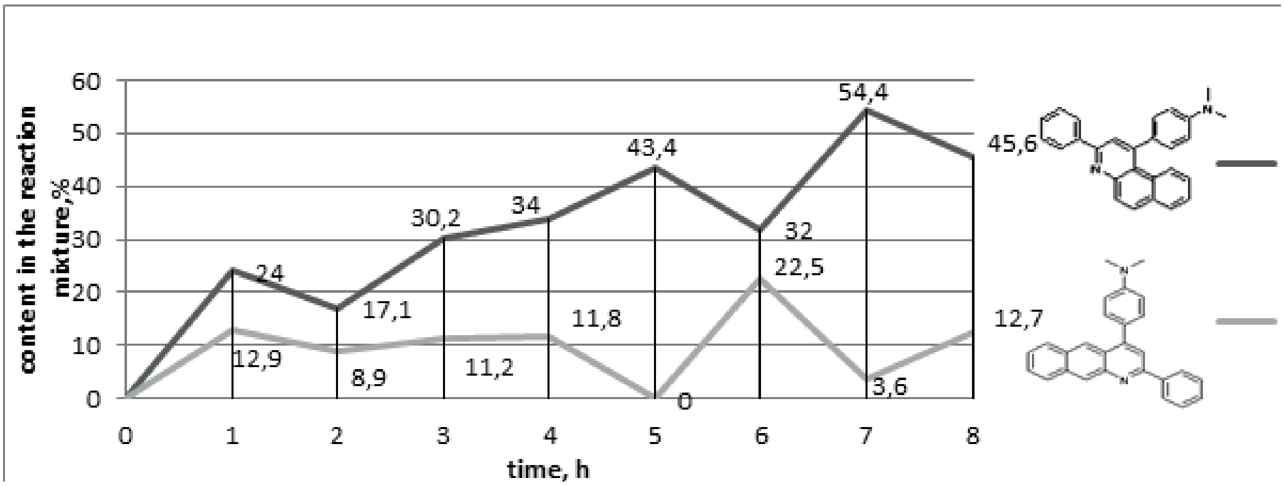
The study of the regioselectivity of the reaction of ambident electrophiles - chalcones with 2-naphthylamine showed the formation of two isomeric heterocyclic systems benzo[g]- and benzo[f]quinolines - products of heterocyclization of azomethine or aminoketone intermediates. We have previously suggested that the process regioselectivity is observed not only at the stage of formation of intermediates but also at the stage of their heterocyclization1. A detailed study of the reaction of 4-N,N-dimethylaminobenzalacetophenone with 2-naphthylamine at 338K showed an interesting pattern of changes in the ratios of isomeric benzoquinolines to the duration of heating.



The dependence of the change in the content of isomeric forms of benzoquinolines in time has a mirror-symmetric form. Such behavior, in our opinion, presumably speaks of the mutual transformation of heterocyclic reaction products, i.e. cyclotransformation (rearrangement) 4-(N,N-dimethylaminophenyl)-2-phenylbenzo[g]quinoline to 1-(4-N,N-dimethylaminophenyl) -3-phenylbenzo[f]quinoline. This process is likely to be reversible, as evidenced by fluctuations in the concentration graph.

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THE METHOD OF ESTIMATION ANTIOXIDANT ACTIVITY OF THE COMPOUNDS ACCORDING TO QUANTUM-CHEMICAL PARAMETERS

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The evaluation of antioxidant activity (AOA) of substances is an urgent task for chemistry, biology, medicine. The experimental methods used for this purpose are very diverse, however, it is worth noting that the range of results is wide and they are not always comparable. Therefore, the researcher is faced with the task of choosing the method of evaluation of AOA. An alternative to the experiment may be a method based on the results of quantum chemical calculations of the electronic structure of antioxidant molecules. The calculation has been implemented on the example of chemical structures, in which AOA was acknowledged (trolox, Quercitin, Gallic and ascorbic acids, etc.) The energy characteristics of the molecules were determined by method of DFT B3LYP/6-31G(d,p) by program [1] with the full energy optimization and the calculation of normal oscillation frequencies. The calculated energies of the highest the occupied (E_{homo}) and the lowest the vacant (E_{lvmo}) molecular orbitals, electronegativity (χ), "chemical hardness" (η) and electrophilicity (ω) play an important role in the chemical stability of the molecule and allows to make conclusion about the possibility of sending or receiving an electron. The indices of the reaction ability of antioxidants were calculated. The relationship of the reaction ability of antioxidants from energy of the lower vacant molecular orbital is constructed according to these indices. The linear equations with good correlation coefficients describes obtained relationships.

For example, for electronegativity such relationship has the form:

χ = -13.453 Enuma+64.691; (R2=0.8672)

The indicators of antioxidant activity of compounds, which need to estimate, compare with indicators of the selected standard antioxidant (reference), according to the results of quantum-chemical calculations of the value (E_{lvmo}). The graphical comparison has the greatest usability and visibility. The compounds with indices of reaction ability on the graph relationship χ, η, ω from (E_{lvmo}) which can see on the left of the standard show weak antioxidant properties, on the right of the standard are strong antioxidant properties. The difference in indexes can serve as criterion of quantitative estimation of relative activity of antioxidants.

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SYNTHESIS AND PROPERTIES OF NOVEL Π-CONJUGATED (OLYGO) THIENYL- AND SELENOPHENYL-1,3,4-OXADIAZOLES

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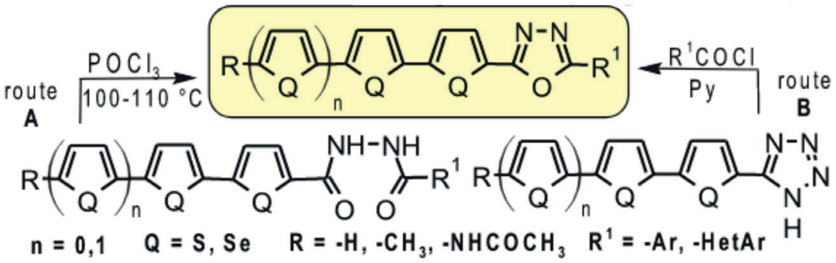
Polycyclic chained arenes with endo- and exocyclic atoms of nitrogen, oxygen, sulfur and selenium, which also include derivatives of 2,2'-bithiophene, 2,2'-biselenophene and 2,2':5',2"-terthiophene, have interest as promising perspective organic luminophores, fluorescent sensors and sintones for the synthesis of different azolylderivatives[1]. Diaryl 1,3,4-oxadiazoles are known as effective scintillators and laser dyes[2].

Research of methods for synthesis 5-R,2-(olygo)thienyl-1,3,4-oxadiazoles allowed to use the most useful reactions: Robinson-Gabriel synthesis (route A) or thermal acylation (route B).



Different electronic nature of groups and their location in thiophene and oxadiazole fragments allowed us to evaluate their effect on physico-chemical properties. For example, an insertion of electrondonating group into the bithiophene, biselenophene or terthiophene structure leads to a maximum bathochromic shift with a high Stokes shift (up to 7000 cm-1). New compounds are effective fluorophores with intensive longwave absorption band *fe* within 1.1-2.8 and emission quantum yield 0.4-0.8 in the region from 420 to 540 nm. The most of the synthesized olygothiophenes refer to V luminescent orbital type, which are promising as active media for quantum generators (efficiency is up to 0.4). However, presence in the tetraene structure of two "super heavy" selenium atoms reduces photostability of biselenophene structure and leads to a significant chemical degradation at the excitation state.

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ON THE STRUCTURE OF THE ELECTRON

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To build a theoretical model of atoms, modern science lacks knowledge about the internal structure of the electron. The electron is invisible, so its structure can be known only by theoretical methods.

The classical radius of an electron is calculated incorrectly. Theorists mistakenly compared the internal energy of the electron (511004 eV) with the energy of the external interaction of the electron according to Coulomb's law (maximum 13.6 eV) and received an absurd radius of 2.8 fm. However, this radius was given the status of a fundamental constant and recorded in all directories.

In the probabilistic concept of the atom, theorists generally deprived the electron of size and integrity, smeared on the orbitals absent in atoms. The Schrodinger equation is not applicable to describe electrons because its wave function has no physical meaning. The uncertainty principle is applicable only to the measurement of particle parameters, but it was applied to the structure of particles.

These errors of modern theory need to be corrected. To construct a theoretical model of atoms, it is proposed to replace the Schrodinger equation with a refined Compton equation: $\lambda = \hbar c/\alpha W = 52.9$ pm. The clarification is that the electron consists of 137 ($1/\alpha$) photons. This gives the constant fine structure of the physical meaning, and also explains the wave-particle dualism: inside the electron there are continuous electromagnetic processes, and their closed set forms a complete dynamic system, called the particle. Electromagnetic oscillations are directed in all directions of space and are superimposed on each other by the middle of the wave.

Electrons with a diameter of 52.9 pm cannot rotate around the nucleus. They do not need to rotate, because the electrostatic attraction of the external field inside the electron is replaced by an electrodynamic oscillation of forces.

The nucleus of an atom is between two electrons, which become the first shell and the axis of the atom. The following electrons are arranged around the axial rings in the form of 4, 8, 16, 32 electrons, which causes the periodicity of the properties of chemical elements. The degree of filling of the ring with electrons determines the valence of atoms. The different arrangement of electrons in the atom causes a difference in quantum numbers, which explains Pauli's ban. But the main thing - the proposed ideas open a real way to knowledge of the internal structure of the electron.

IN SITU RAMAN SPECTROSCOPIC INVESTIGATION OF SOLVATION IN THE DISPERSE SYSTEM Li$_2$Co$_3$–Na$_2$Co$_3$–K$_2$Co$_3$-MELT–MgO-NANOPOWDER

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The physicochemical properties of high-temperature disperse systems based on alkali-metal-carbonate melts must be studied to optimize the carbonate-fuel-cell operating environment. Raman spectroscopy is used to study such systems and enables in situ information about inter particle interactions and the behavior of CO_3^{2-} in the presence of a nanodisperse filler to be obtained.

As results the chemical inertness of MgO in $(Li_2CO_{3-}Na_2CO_{3-}K_2CO_3)_{eut}$ melt was demonstrated using in situ Raman spectroscopy. At the same time, analysis of the spectral data showed that the system contains two types of carbonate anions: in the volume of the melt and anions adsorbed on the solid-particle surfaces. Salt anions adsorbed on nanopowder-particle surfaces formed solvate shells that should have considerably affected the physicochemical properties of the high-temperature disperse system. In particular, coagulation of the solid particles and their subsequent sedimentation were expected to be suppressed in suspensions with relatively low contents of oxide phase, which was an important factor for stabilizing highly disperse systems with a liquid dispersant. Solvation of salt-melt ions on solid-particle surfaces of pastes and oxide matrix elements with a developed interface interfered considerably electrical charge transfer.

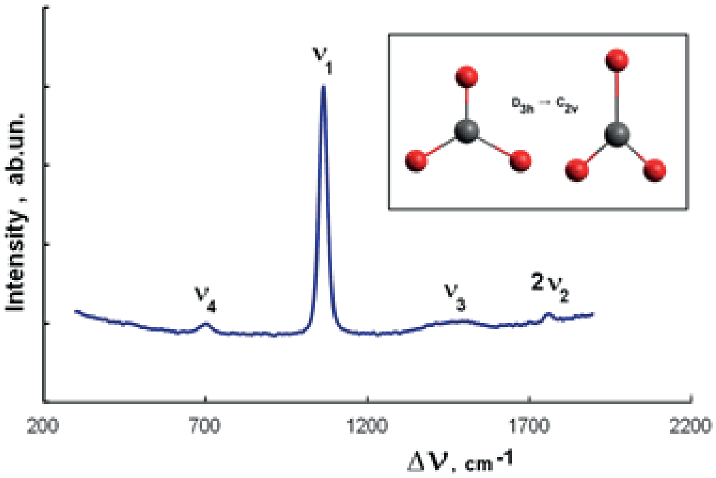

Figure 1. Raman spectrum of disperse system containing $(Li_2CO_{3-}Na_2CO_{3-}K_2CO_3)_{eut}$ melt and 32 vol.% MgO nanopowder (d = 95 нм, S = 9.35 м2/г), 500 oC (in the inset, diagram of symmetry change of CO32- in solvate shells).

THE STRUCTURE OF GD2O3-GDCL3-KCL OXIDE-SALT MELTS FROM IN SITU RAMAN SPECTROSCOPY

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Rare-earth metals (REM) are widely used in various fields of production, science and technology. The main way to obtain REM is the electrolysis of their anhydrous chlorides in the environment of molten alkali metal chlorides. In the process of electrolysis of chloride melts containing REM ions, upon their contact with components of the air atmosphere, the formation of oxygen-containing impurities not rule out.

The report presents the results of in situ studies on the structure of homogeneous oxide-salt melts Gd_2O_3 - $GdCl_3$ - KCl, obtained using the original high-temperature device [1] by Raman spectroscopy. It was shown that octahedral groups $[GdCl_6]$ are present in the $GdCl_3$ – KCl melts, and binuclear oxychloride groups $[Gd_2OCl_n]$ are present in the homogeneous Gd_2O_3 – $GdCl_3$ – KCl melt.

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The study was in part financially supported by the Russian Foundation for Basic Research (Project No. 18-03-00561).

REDUCTION OF [B10H9NCR]- ANIONS – NEW SYNTHETIC APPROACH TO OBTAINING OF FUNCTIONAL SUBSTITUTED CLOSO-DECABORATES.

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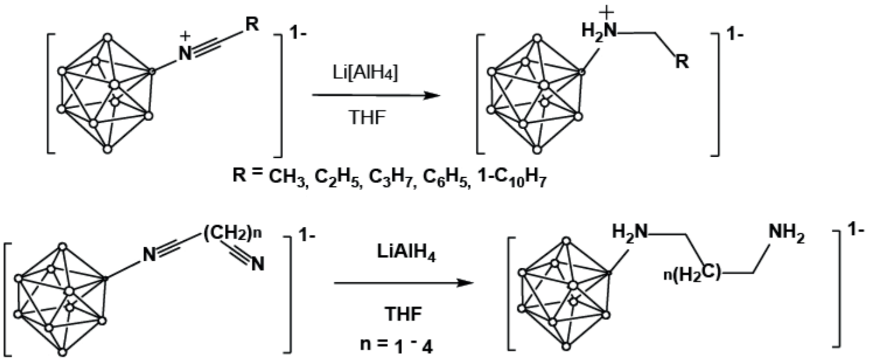
In the work, the reduction process of nitrilium derivatives of the closo-decaborate anion by lithium aluminum hydride was studied. The process proceeds under mild conditions with good yields to form mono-alkyl-ammonium derivatives of the *closo*-decaborate anion. The proposed method allows to obtain derivatives with aromatic functional groups, and pendent amino groups in the case of reduction of dinitrile derivatives.



The structure of one of the products was confirmed by single crystal XRD.

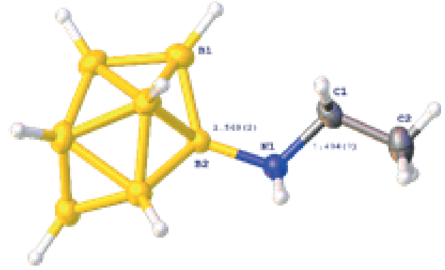


Figure. Structure of [2-$B_{10}H_9NH_2CH_2CH_3$]- anion.

This study was supported by Grants of the President of the Russian Federation NSh 2845.2018.3 and MD 265.2019.3.

SYNTHESIS AND PHOTODYNAMIC ANTIMICROBIAL ACTIVITY OF AMPHIPHILIC CATIONIC PORPHYRINS

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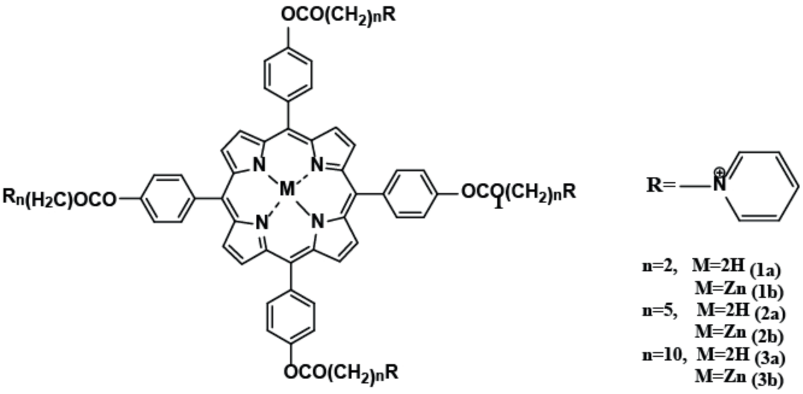
This work is devoted to the synthesis of new photosensitizers for photodynamic antimicrobial therapy (PACT) and to the study of their dark and photoinduced activity against E.coli and S.aureus bacteria.



The target compounds were synthesized using monopyrrole condensation according to the Lindsay method, followed by chemical modification of the terminal groups to obtain cationic porphyrins. The structure of the obtained products was confirmed by UV-, ^{1}H-, ^{13}C-NMR spectroscopy, and mass spectrometry.

Further, the dark toxicity and photoinduced activity of compounds 1-3a,b against to E. coli and S. aureus bacteria in suspension and their biofilms were carried out. It has been shown that aqueous solutions 1-2a,b,3a rather strongly inhibit the growth of both gram-positive S.aureus bacteria and gram-negative E.coli without irradiation with light. Light irradiation leads to an increase in S.aureus inhibition compared with the dark control only in the case of free-basic porphyrins 1a, 2a. The PD activity of the compounds with respect to the biofilms of the E.coli and S.aureus bacteria was also investigated. For compounds 1-2a,b, 100% inhibition of viable bacteria was achieved at concentrations of 10–20 µM. Porphyrins 1a and 2a act most effectively on E.coli biofilms upon irradiation.

This work was supported by the Russian Science Foundation (grant No. 17-73-10470).

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The mission of the Foundation is to preserve and enhance the cultural heritage of Russia, support the country's scientific and sports potential, and create an inclusive socio-cultural environment.

The Art, Science and Sport Foundation is a dynamic non-profit institution actively integrated into the professional charity community. For several years, the Foundation has been a full member of the Donors Forum, an association of the largest grant-giving organizations working in Russia. Moreover, the Foundation with its own projects and programs participates in all major economic and cultural forums in Russia and abroad.

Patronage activities are carried out in the following areas:

- **Culture and art**: support for the leading cultural institutions of Russia. Many of the projects implemented with the assistance of the Art, Science and Sport Foundation and the personal participation of Alisher Usmanov have become iconic in the cultural life of the country.

- **Science and education**: support for projects on the exchange of experience and opinions between specialists from various fields of science and education, assistance to educational institutions at all levels, including higher education institutions.

- **Sport**: promotion of a healthy lifestyle and physical culture, popularization of sports in Russia.

The Foundation is actively developing its own projects and programs:

- **The Special Vision support program for people with visual impairment** has been implemented by the Foundation since 2013 with the goal of creating an accessible sociocultural environment in Russia and solving problems of social integration of blind and visually impaired people.

- In 2017, the Art, Science and Sport Foundation established the **ART-WINDOW arts festival**, which was created with the aim of ensuring free creative dialogue between the regions and cultural centers of Russia. In 2019, the project changed the vector of activity and turned into the ART-WINDOW cultural platform, promoting the development of the urban cultural environment.

- **The “With Confidence in the Future” project** has been implemented by the Art, Science and Sport Foundation since 2013. During its existence, the project has been transformed from providing targeted assistance into a comprehensive program that provides assistance in developing potential and acquiring knowledge and skills necessary for confident entry into adulthood and the choice of profession.

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[1] Source: IFA, Fertecon, CRU

[2] Source: CRU, RAFP

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In March 2013, PhosAgro, UNESCO and the International Union of Pure and Applied Chemistry (IUPAC) signed a partnership agreement on the establishment of a grant program for young scientists as part of the joint project “Green Chemistry for Life”. The agreement provides financial and scientific support to researchers involved in the development of new advanced technologies based on the green chemistry principles to solve the problems of environmental protection and healthcare, nutrition, energy efficiency and the rational use of natural resources.

The uniqueness of the program lies in the fact that for the first time in the long history of UNESCO and the entire UN system, such an initiative is being implemented on an extra-budgetary basis at the expense of Russian business funds. Over the first five years of the program's existence, the jury reviewed more than 600 applications, and 34 young scientists from 26 countries became grantees. Given the success of the project, it has been extended till the end of 2022.

Furthermore, PhosAgro is the general partner of the IUPAC Postgraduate Summer Schools on Green Chemistry. In 2019, a record number of delegates attended the event in Dar es Salaam (Tanzania) - more than 100 young professionals and 30 world-class teachers from 43 countries.

The summer school curriculum focuses on the 17 United Nations Sustainable Development Goals. The main topics of the training session concerned the exploitation of natural resources, green methodologies, material synthesis, green technologies and waste management. 35 Of the 50 winners of the Summer School receiving financial support represented the African nations.

PhosAgro is aware that without innovation it is impossible to ensure competitiveness and high growth rates of a company: science in industry is not noticeable, but its absence is immediately apparent. In total, investments in expanding production using the best available technologies, increasing its efficiency and R&D exceeded 180 billion rubles over the past 5 years.

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