

# **ADVANCES IN SYNTHESIS AND COMPLEXING**

**Book of abstracts**

**The Fifth International Scientific Conference**

*In Two Parts*

**Volume 2**  
**Inorganic and Coordination Chemistry**  
**Section**  
**Physical and Colloidal Chemistry Section**

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The present publication was designed to popularize scientific research activity in the field of chemistry and to discuss modern chemical problems on the international level. The digest is intended for scientists, students, postgraduates and for wide range of readers interested in problems in chemistry.

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Dear Colleagues,

I'd like to personally welcome each of you to the 5-th International conference "Advances in Synthesis and Complexing" (RUDN University, Moscow, Russia).

RUDN University is confronting a time of many changes and we're meeting these changes during a time of larger nation-wide and global change. This series of conferences has attracted many leading scientists.

The 5-th International conference "Advances in Synthesis and Complexing" addresses the following research topics

*- Modern problems of organic chemistry. New methods in organic synthesis, synthesis and properties of heterocyclic compounds, multi-component and domino reactions, stereochemistry of organic compounds, chemistry of macrocyclic compounds, biologically active compounds, chemistry of natural products.*

*- Heterogenic and homogenic catalysis. Physico-chemical methods of investigation, quantum-chemical calculations.*

*- Modern problems of inorganic chemistry. Complexing of metals with polyfunctional N,O,S-containing ligands, physico-chemical investigations of inorganic and coordination compounds and new materials, solidphase synthesis. X-RAY analysis.*

This conference is a platform for promoting cooperation between scientists sharing scientific interests in organic, inorganic and physical chemistry as well as interdisciplinary research in this field.

We are most grateful to all the scientists who have travelled from all corners of the world to Moscow. Throughout this conference, I ask you to stay engaged, keep us proactive and help us shape the future of RUDN University.

My personal respect and thanks goes out to all of you.

We hope that you will find your participation in the 5-th International conference "Advances in Synthesis and Complexing" intellectually stimulating and socially enjoyable.

Chair of the organizing committee

Prof. Dr. Leonid G. Voskressensky



# Plenary Lectures



## From Interlocked and Knotted Rings to Molecular Machines

Sauvage J.-P.

*Institut de Science et Ingénierie Moléculaire (ISIS)*  
*University of Strasbourg*  
*8 allée Gaspard Monge, F-67000 Strasbourg, (France)*  
*e-mail: jpsauvage@unistra.fr*

The area referred to as "Chemical Topology" is mostly concerned with molecules whose molecular graph is non-planar, i.e. which cannot be represented in a plane without crossing points. The most important family of such compounds is that of **catenanes**. The simplest catenane, a [2]catenane, consists of two interlocking rings. **Rotaxanes** consist of rings threaded by acyclic fragments (axes). These compounds have always been associated to catenanes although, strictly speaking, their molecular graphs are planar. Knotted rings are more challenging to prepare. One of the most spectacular topologies in this respect is the **trefoil knot**. Our group has been much interested in knots and, in particular, in their properties in relation to coordination chemistry or chirality.

Since the mid-90s, the field of **artificial molecular machines** has experienced a spectacular development, in relation to molecular devices at the nanometric level or as mimics of biological motors. In biology, motor proteins are of utmost importance in a large variety of processes essential to life (ATP synthase, a rotary motor, or the myosin-actin complex of striated muscles behaving as a linear motor responsible for contraction or elongation). Many examples published by a large number of highly creative research groups are based on complex rotaxanes or catenanes acting as switchable systems or molecular machines. Particularly significant examples include a "pirouetting catenane", "molecular shuttles" (Stoddart and others) as well as multi-rotaxanes reminiscent of muscles. More recent examples are those of multi-rotaxanes able to behave as compressors and switchable receptors. The molecules are set in motion using electrochemical, photonic or chemical signals. Particularly impressive light-driven rotary motors have been created by the team of Feringa.

Finally, potential applications will be mentioned as well as possible future developments of this active area of research.

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## Very strong and confined acids enable a general approach to asymmetric Lewis acid catalysis

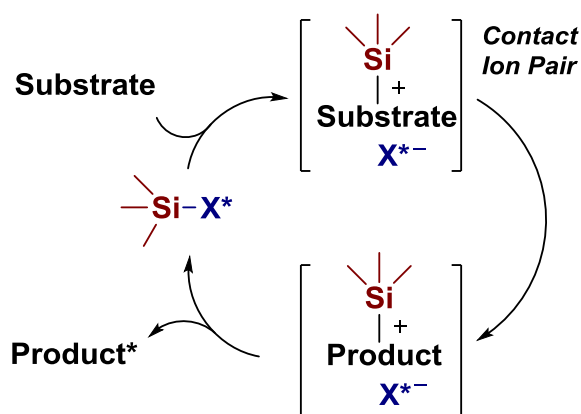
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*Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany  
e-mail: list@mpi-muelheim.mpg.de*

As a fundamental activation mode, Lewis acid catalysis enables key reactions in chemical synthesis, such as the Diels–Alder and Friedel–Crafts reactions, and various aldol, Mannich, and Michael reactions. Consequently, substantial efforts have been directed towards the development of enantiopure Lewis acids, which have enabled important asymmetric variations of such reactions. Despite the plethora of elegant catalysts and methodologies developed in this context, a key limitation of enantioselective Lewis acid catalysis is the frequent need for relatively high catalyst loadings, which result from issues such as insufficient Lewis acidity, product inhibition, hydrolytic instability, and background catalysis.

We have recently proposed a new design for asymmetric Lewis acid catalysis. We developed in situ silylated disulfonimide-based organocatalysts, which address some of the above problems in various highly enantioselective Mukaiyama-type reactions involving silicon-containing nucleophiles with unprecedentedly low catalyst loadings. As an example of asymmetric counteranion-directed catalysis (ACDC), these reactions proceed via silylation of an electrophile, generating a cationic reactive species that ion-pairs with an enantiopure counteranion and reacts with a silylated nucleophile. We became interested in expanding this “silylium-ACDC” concept to, in principle, all types of Lewis acid catalyzed reactions, including those that do not involve silylated reagents. In my presentation, I will discuss how the concept evolved from our studies on ACDC. I will furthermore describe its first realization with the development of extremely active organic Lewis acid catalysts that enable asymmetric versions of highly challenging Diels–Alder reactions. The confined acids that form the basis of our latest catalyst design not only enable the utilization of small and unbiased substrates but, because of their high acidity, also the activation of previously inaccessible substrates for organocatalysis.

Katalysatordatenbank



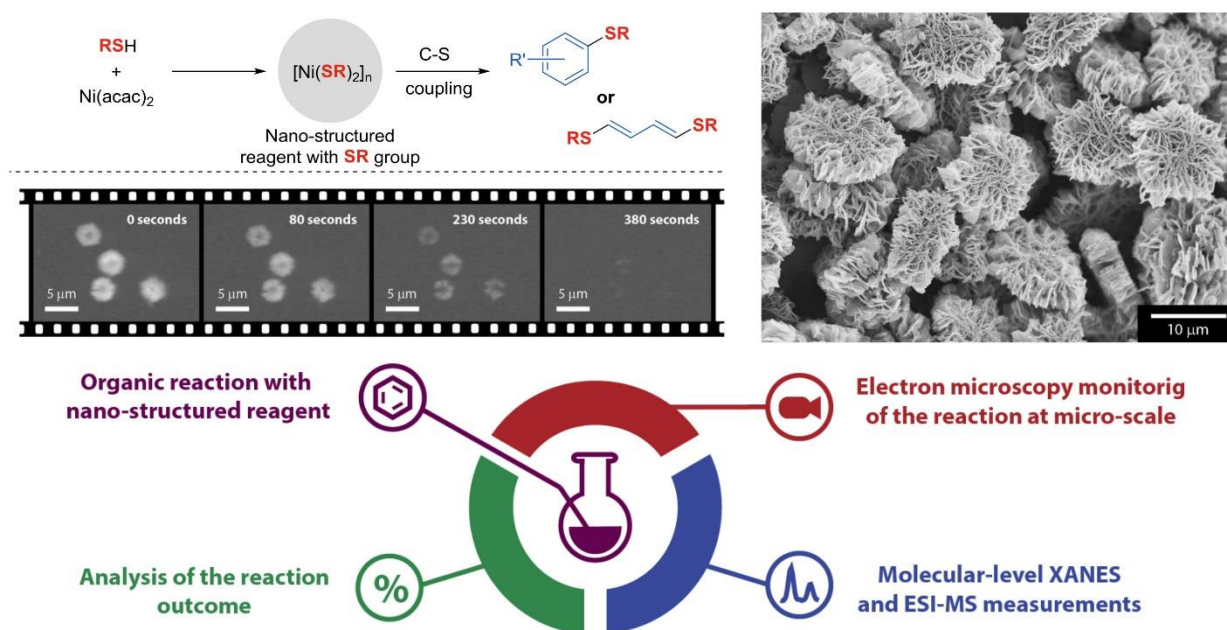


# Dynamic catalytic systems for organic synthesis and sustainable development

Ananikov V.P.

*Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences  
Leninsky Prosp. 47, Moscow, Russia.  
e-mail: val@ioc.ac.ru; http://AnanikovLab.ru*

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] and mechanistic understanding [4].



**Figure 1.** Dynamic catalytic system with nanostructured reagents [2].

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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## Development of novel C–H functionalization methodologies

Gevorgyan V.

*University of Illinois at Chicago, USA*  
*e-mail: vlad@uic.edu*

We have developed a set of new transition metal-catalyzed C-H functionalization methodologies employing a silicon-tether motif. These methods feature: (a) use of silyl group as a tether between a substrate and a reagent, thus transforming intermolecular reaction into intramolecular reaction; (b) employment of a silicon-tethered directing group, which is traceless or easily convertible into valuable functionalities; (c) use of silyl-tethered hydrosilane reagent; and (d) introduction of new N/Si-chelation concept that allows for a remote activation of aliphatic C-H bonds.

We have also uncovered new reactivity of hybrid Pd-radical species, generated at room temperature under visible light without exogenous photosensitizers, which lead to development of novel transformations, including new types of Heck reaction, aliphatic C–H functionalization methods, as well as new cascade transformations. These methods employ removable silicon-based, and amide linkers.

The scope of these transformations will be demonstrated and the mechanisms will be discussed.

## **Nickel catalysis for C-C and C-heteroatom bond forming reactions**

Rueping M.

*King Abdullah University of Science and Technology, KAUST; Thuwal KSA  
RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany  
e-mail: Magnus.Rueping@Kaust.edu.sa*

Catalytic C-C and C-heteroatom bond forming reactions represent key transformations for the synthesis of valuable products or advanced intermediates. In this presentation our introduction to the field of C-O bond activation as well as our the recent efforts for the development of new and valuable nickel catalyzed functional group interconversions will be highlighted. These include direct dealkoxylative, decarbonylative, deformylative and decarboxylative reactions [1-2] Furthermore, light mediated combined metal and photoredox catalyzed transformations, including C(sp<sup>3</sup>)-H functionalizations and olefin functionalizations will be presented.

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## **2D materials: Inorganic nanotubes and fullerene-like nanoparticles at the crossroad between materials science and nanotechnology and their applications**

Tenne R.

*Department of Materials and Interfaces, Weizmann Institute,  
Rehovot 76100, Israel*

*e-mail: [reshef.tenne@weizmann.ac.il](mailto:reshef.tenne@weizmann.ac.il)*

*web site: <http://www.weizmann.ac.il/materials/tenne/>*

After almost 100 years of research inorganic layered (2D) materials, like MoS<sub>2</sub>, are currently used as catalysts, lubricants, and perhaps most importantly in rechargeable Li-ion batteries. Much research is currently focused on monolayers (beyond graphene) of 2D materials and hybrids thereof in relation to their electronic and optoelectronics properties. After a short briefing on the history of 2D materials research,<sup>1</sup> the concepts which led to the first synthesis of hollow-cage nanostructures, including nanotubes (INT) and fullerene-like (IF) nanoparticles from 2D compounds, will be presented. The progress with the high-temperature synthesis and characterization of new inorganic nanotubes (INT) and fullerene-like (IF) nanoparticles (NP) will be presented. In particular, the synthesis and structure of nanotubes from the ternary and more recently quaternary “misfit” layered compounds (MLC), like LnS-TaS<sub>2</sub> (Ln= La, Ce, Gd, etc), CaCoO-CoO<sub>2</sub> and numerous other MLC will be discussed.

Major progress has been achieved in elucidating the structure of INT and IF using advanced microscopy techniques, like aberration corrected TEM and related techniques. Mechanical, electrical and optical measurements of individual WS<sub>2</sub> nanotubes reveal their unique quasi-1D characteristics. This analyses demonstrate their altered behavior compared with the bulk phase, including quasi-1D superconductivity. Applications of the IF/INT as superior solid lubricants and reinforcing variety of polymers and light metal alloys was demonstrated. Some of this research resulted in commercial products (a few spin-off companies) which are exploited world-wide with rapidly expanding marketshare. Few recent studies indicate that this brand of nanoparticles is less toxic than most nanoparticles. With expanding product lines, manufacturing and sales, some of these nanomaterials are gradually becoming an industrial commodity.

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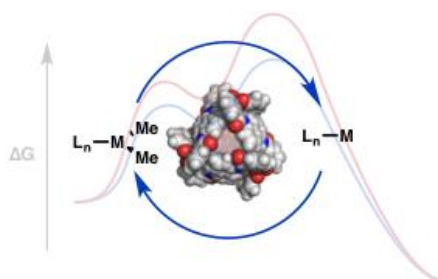
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## Catalysis in confined spaces

Toste F. D.

*Department of Chemistry, University of California and Chemical Science, Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720*  
*e-mail: fdtoste@berkeley.edu*

We have been exploring organic and organometallic reactions that occur in the confined space of self-assembled water-soluble tetrahedral  $M_4L_6$  clusters. For example, cationic phosphinegold(I) complexes encapsulated by an anionic  $Ga_4L_6$  tetrahedral demonstrated higher turnover numbers, rate acceleration and/or produced different products compared to the unencapsulated catalysts [1]. In addition to serving as hosts for transition metal catalysts, these supramolecular assemblies can serve as catalysts themselves, both for organic and organometallic reactions (Figure 1) [2]. This lecture will focus on our most recent studies of reactions promoted by encapsulation in these supramolecular hosts, induced thermally and/or photochemically, and the mechanisms of these reactions [3].



**Figure 1.**

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## **The use of Kramers ions for the design of new single magnets and molecule-based magnetic materials**

Aldoshin S.M.<sup>1</sup>, Korchagin D.V.<sup>1</sup>, Palii A.V.<sup>2</sup>

<sup>1</sup> *Institute of Problems of Chemical Physics, RAS, Chernogolovka, Russia;*

<sup>2</sup> *Institute of Applied Physics, Chisinau, Moldova*

*e-mail: sma@icp.ac.ru*

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.

*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 Russian Federation (Agreement No. 14.W03.31.0001-Institute of Problems of Chemical Physics of RAS, Chernogolovka)*

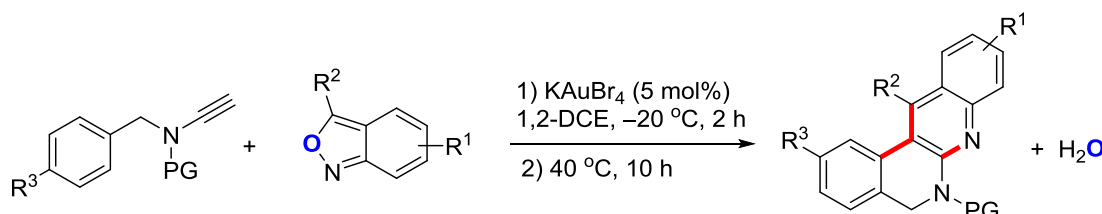
## Gold catalysis: functionalized carbenes, dual activation, light

Hashmi A.S.K.

*Organisch-Chemisches Institut, Heidelberg University, Im Neuenheimer Feld 270, 69120  
Heidelberg, Germany  
e-mail: hashmi@hashmi.de*

Only after two papers from 2000 had demonstrated the full potential of gold catalysis for organic transformations by a high increase of molecular complexity, [1, 2] homogeneous gold catalysis was developed to a versatile tool for organic synthesis [3, 4]. For a long time, the field was exclusively focused on electrophilic and nucleophilic species, radical intermediates were not involved, but this changed in 2013 [5].

Apart from the synthesis of different heterocycles, the use of these principles also allows a number of C-C coupling reactions, which in a formal sense can also address C-H bonds [6]. Principles like dual activation, and the use of di- and even mononuclear gold(I) complexes for photochemical reactions will be discussed.



**Scheme 1.** Intermolecular reaction of an anthranil derivative with an ynamide to provide a multi-annulated heterocyclic system in only one step.

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# Inorganic and Coordination Chemistry Section

## Key-note Speakers and Invited Lectures



## **Novel N-donor extraction systems for lanthanide/minor actinide separation**

Kalmykov S., Matveev P., Petrov V., Ustinyuk Yu.

*Lomonosov Moscow State University, Moscow, Russia*  
*e-mail: stepan\_5@hotmail.com*

Lanthanide / minor actinide separation is a challenging task within the nuclear fuel cycle of a new generation (fast neutron reactors). Long-lived Am isotopes could be burned-up while lanthanides (Eu-152, 155 are the most important) and Cm-244 could be disposed at the near-surface nuclear waste repositories. Such an approach would allow minimizing the volume of long-lived nuclear wastes that should be directed to deep repositories.

This paper describes the application of various novel phenanthroline, diamide and dilactam ligands for effective Eu/Am and Am/Cm separation. At the first step the DFT calculations allowed to choose 4-8 ligands for synthesis that would demonstrate high separation factors together with high solubility in industrial diluents. Extraction and stripping tests are done at various acidities of nitric acid, total metal ion concentrations and competing ion concentrations. The introduction of electron acceptor substitutes, like Cl to the molecule of diamide phenanthroline dicarboxylic acid increase the separation factor for Am/Cm pair from 1.5 to c.a. 6.

The structure of the complexes was studied by  $L_{III}$  EXAFS that was in consistence with theoretical calculations. The radiation stability was studied using Cs-137 external gamma-source up to the doses of 500 kGy. The Mayer estimation of bond sequence and Fukui surface calculations for resistance to radical reactions is applied to estimate the radiation stability. The theoretical calculations well fit to the experimental tests that were done using ESI-MS to detect the radiolysis products. The substitution of Cl by CN-moiety result in keeping record high Am/Cm separation factors with sharp increase of radiation stability.

As a result the CN-substituted diamide phenanthroline dicarboxylic acid was tested at industrial scale using simulated high level nuclear waste solutions containing mg quantities of Am-241 and Cm-244. It was shown that Am-241 with the purity of 99.9% and yield of 99.9% could be separated using cascade of 10 extraction units, 10 rinsing steps and 3 stripping steps.

## Functional metal-organic architectures: from design to applications in catalysis and materials chemistry

Kirillov A.M.

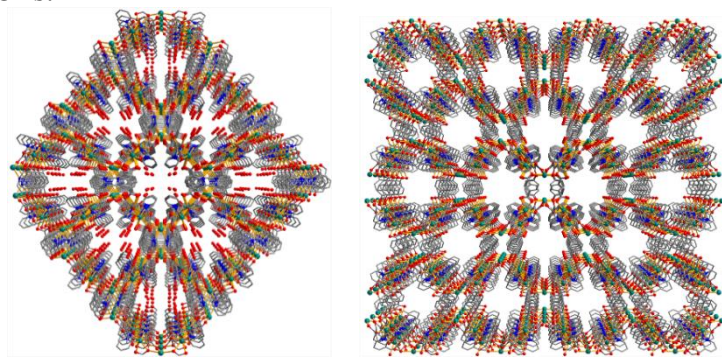
*Centro de Química Estrutural, Instituto Superior Técnico, University of Lisbon, Av. Rovisco Pais, 1049-001, Lisbon, Portugal; Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya st., Moscow, 117198, Russia  
e-mail: kirillov@tecnico.ulisboa.pt*

This contribution will highlight our recent research on the use of versatile self-assembly and hydrothermal synthetic methods for the design of a wide diversity of metal-organic architectures, including metal-organic frameworks (MOFs), coordination polymers (CPs), and multinuclear metal complexes [1,2]. These compounds were generated from various aminoalcohol, aminophosphine, and/or carboxylic acid building blocks and simple metal salts as metal sources. The presentation will focus on the following main topics.

(1) Aqueous medium self-assembly, structural and topological features of Cu coordination polymers and multinuclear cores driven by aminoalcohol building blocks and carboxylate linkers. Application of these compounds as bioinspired catalysts in mild oxidative C–H functionalization of hydrocarbons and other substrates.

(2) Hydrothermal crystal engineering and structural diversity of MOFs and CPs driven by multifunctional polycarboxylates with biphenyl and phenyl-pyridine cores and various metal nodes (Cu, Fe, Co, Mn, Ni, Zn, Cd, or Ln). Examples of functional applications of these compounds and derived materials as recoverable heterogeneous catalysts, selective sensors, adsorbents, or luminescent probes.

(3) Design of bioactive metal-organic architectures toward applications as topical antimicrobial agents, antibiofilm materials, and drug-releasing systems. New class of Ag, Cu, and Zn-based bioMOFs.



*This work was supported by the Foundation for Science and Technology (FCT) and Portugal 2020 (projects LISBOA-01-0145-FEDER-029697, UID/QUI/00100/2013), RUDN University (RUDN University Program 5-100), and the EU COST Action CA15106 (CHAOS)*

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## **A water soluble aminophosphine: coordination chemistry and catalysis**

Guedes da Silva M.F.C.

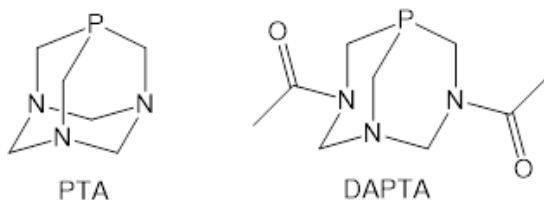
*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,  
Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.*

*e-mail: fatima.guedes@tecnico.ulisboa.pt*

*<https://fenix.tecnico.ulisboa.pt/homepage/ist90142>*

The cage-like monodentate phosphine 1,3,5-triaza-7-phosphadamantane (PTA) is among the most interesting water-soluble phosphines. The role of PTA as ligand is highly established in coordination chemistry and its functionalization with different substituents is largely expanded.

Among the large family of PTA derivatives, 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA) is the di-*N*-acylated open cage derivative of PTA. Despite the synthesis and characterization of DAPTA has long been established its coordination chemistry is significantly scarce when compared with PTA.



Recent examples will be given on the synthesis and characterization of metal complexes bearing DAPTA as ligand, as well as its oxidized form, DAPTA=O. Applications in catalysis will be illustrated with focus on nitroaldol (Henry) reaction, and azide-alkyne (Huisgen) cycloaddition reaction.

*This work has been partially supported by the Fundação para a Ciência e Tecnologia, Portugal, namely through the project UID/QUI/00100/2019*

## **Expanded ring N-heterocyclic carbenes – versatile ligands for transition metal complexes**

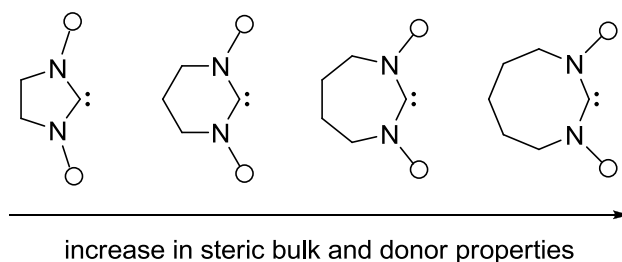
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Tukov A.A., Nechaev M.S.

*M.V. Lomonosov Moscow State University, 119991, Moscow, Leninskie gory 1(3);  
A.V. Topchiev Institute of Petrochemical Synthesis, RAS, 119991, Leninsky prosp., 29.  
e-mail: m.s.nechaev@org.chem.msu.ru*

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.



# Oral Reports





## The studies of NbCl<sub>5</sub> with acetylene reaction products as a new precursors for simple and economical synthesis of ceramic NbC/C nanocomposite

Il'in E.G.<sup>1</sup>, Parshakov A.S.<sup>1</sup>, Iskhakova L.D.<sup>2</sup>

<sup>1</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Russia, 119991, Moscow, Leninsky Pr., 31

<sup>2</sup> Fiber Optics Research Center, Russian Academy of Sciences, Russia, 119333, Moscow, Vavilov str. 38  
e-mail: eg\_ilin@mail.ru

At present, the active interest of researchers is manifested in develop of new methods for obtaining nanocomposites based on IV-VI groups transition metals carbides in dispersed carbon. A composite containing nano-sized stoichiometric Mo<sub>2</sub>C in the matrix of carbon nanotubes (Mo<sub>2</sub>C/CNT), in addition to traditional applications as super refractory and super hard materials, has used as the catalyst for the one-stage hydrodeoxygenation of natural oils into diesel fuel [1]. It has been shown that carbide niobium - carbon composites NbC/CNT are universal precursors of materials for high-power supercapacitors and electrodes of high-energy Li-ion batteries [2].

The usual methods for preparing ceramic IV-VI groups transition metals carbide/carbon nanocomposites Me<sub>x</sub>C/C are multi-step: sol-gel synthesis, including the hydrolysis of metal halides, alkoxides or alkoxy-acetylacetonates, followed by controlled polycondensation and gelling, step drying in the temperature range of 20-250°C, carbonization in an inert or reducing atmosphere at 350-600°C using phenol-formaldehyde resins or others carbon containing polymers and pyrolysis at 1200-1500°C.

Previously [3] we have synthesized the composite of crystalline molybdenum carbide Mo<sub>2</sub>C in finely dispersed carbon by the thermal decomposition of the MoCl<sub>5</sub> with C<sub>2</sub>H<sub>2</sub> reaction products.

Now, we propose simple and low-energy method for the preparation of a ceramic NbC/C nanocomposite, by using as a precursor of the products of reactions of NbCl<sub>5</sub> with C<sub>2</sub>H<sub>2</sub>, followed by their thermal decomposition. In this work present the results of the studies of reaction products in different conditions and the solid products of their thermal decomposition.

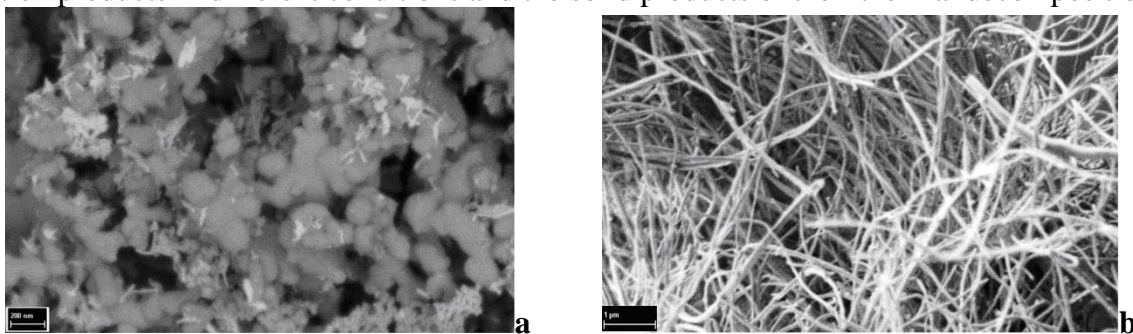


Fig.1. ASM surface micrograph of the NbCl<sub>5</sub> with C<sub>2</sub>H<sub>2</sub> reaction products: **a** – in benzene solution; **b** – interaction of components in glass tube.

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## Bimetallic copper(I) helicates– mechanism of action in cells

Fik M.A.<sup>a</sup>, Belter A.<sup>b</sup>, Szymańska M.<sup>a</sup>, Czepa W.<sup>a,c</sup>, Kubicki M.<sup>a</sup>, Patroniak V.<sup>a</sup>

<sup>a</sup>Faculty of Chemistry, Adam Mickiewicz University in Poznań, 61614, Poznań, Umultowska 89b, Poland

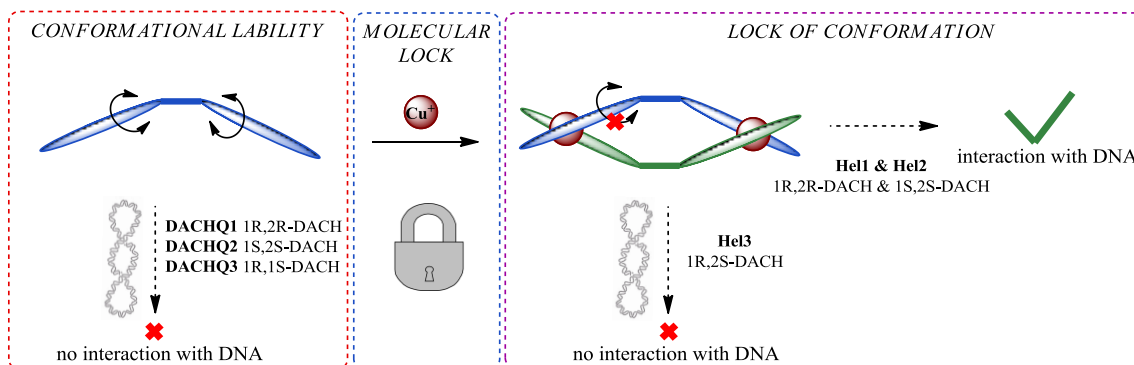
<sup>b</sup>Institute of Bioorganic Chemistry, Polish Academy of Science, 61704, Poznań, Noskowskiego 12/14, Poland

<sup>c</sup>Center for Advances Technologies, 61614, Poznań, Umultowska 89c, Poland  
e-mail: marta fik@amu.edu.pl

Understanding the mechanism of action of novel potential metallodrugs is of a high interest nowadays. Herein, we present the synthesis and chemical characterization of 3 diastereoisomeric ligands **DACHQ1-3** composed of 1,2-diaminocyclohexane (**DACH**) core and quinoline (**Q**) based arms and their helical complexes with Cu<sup>+</sup> **Hel1-3** (Fig.). All compounds were tested for their influence on living cells (healthy and tumorigenic).

Enantiopure **DACH** is one of the most important building blocks for chiral ligands. **DACH** based ligands occurred to be a great core for construction of helicates, preferentially formed in the presence of tetrahedral metal ions (Cu<sup>+</sup>, Ag<sup>+</sup>) [1]. Noteworthy, quinoline-based complexes with Cu<sup>+</sup> exhibit significant activity in biological systems and its cytotoxicity towards a few cancer cell lines was investigated so far [2].

Designed helical systems differ in their cytotoxic mechanism in cells. **Hel1** and **Hel2** that comprise (1R,2R)-*trans*-1,2-DACH and (1S,2S)-*trans*-1,2-DACH possess high affinity towards double helix of DNA and most probably bind in the grooves, while **Hel3** comprising (1R,2S)-*cis*-1,2-DACH causes cell cycle arrest in a concentration dependent manner through a different mechanism. All 3 complexes differ in their behaviour in healthy and tumorigenic cells. It needs to be mentioned that **DACHQ** ligands are not toxic towards tested cell lines and do not bind with DNA [3].



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## **Structure–reactivity relationship, biological activity of the bis-pyrazolylpyridine Rh<sup>III</sup> complexes**

Bogojeski J., Petrović A., Milutinović M.M., Živanović M., Milivojević N., Puchta R., Scheurer A., Korzekwa J., Klisurić O.R.

*University of Kragujevac, Faculty of Science, 34000 Kragujevac, Radoja Domanovića 12,  
Serbia,  
e-mail: jrosic@kg.ac.rs*

Kinetically-inert transition metal complexes, such as Rh(III) complexes have attracted increasing attention as leading scaffolds for the development of potent pharmacological agents for disease treatment due to their inertness and stability [1]. Therefore, we have designed and fully characterized a few novel rhodium(III) complex [Rh<sup>III</sup>(X)Cl<sub>3</sub>] (X = pyridin-bis(pirazole) ligands) with tridentate nitrogen–donor chelate system. A single crystal X-ray structure analysis has been done. The reactivity of the synthesized complex toward small biomolecules (L-methionine (L-Met), guanosine-5'-monophosphate (5'-GMP), L-histidine (L-His) and glutathione (GSH) and to a series of duplex DNAs and RNA was investigated. These measurements showed that the synthesized complex has a good affinity toward studied ligands and the obtained order of reactivity is: 5'-GMP > GSH > L-Met > L-His. Duplex RNA reacts faster than duplex DNA, while shorter duplex DNA (15mer GG) reacts faster compared with 22mer GG duplex DNA. In addition, a higher reactivity is achieved with a DNA duplex with centrally located GG-sequence than with 22GTG duplex, in which GG sequence is separated by a T base [2].

Furthermore, the interaction of this metal complex to calf thymus DNA (CT-DNA) and bovine serum albumin (BSA) was further examined by absorption (UV-Vis) and emission spectral studies (EB displacement studies). Overall, the studied complex exhibited good DNA and BSA interaction ability. The impact of the metal complex on cytotoxicity was tested by MTT assay on HCT-116 line. As well as DFT calculation was performed.

All obtained results in this study indicate that the introduction of pincer-type spectator ligand can be used to improve the reactivity of rhodium(III) complexes. Together, these observations show the reactivity characteristics needed for a potential anti-tumor agent, with the ability to target both DNA and proteins. Every new contribution in this field highly is warranted due to the current lack of clinically used metallo-based alternatives to cisplatin.

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## Synthesis and coordination chemistry of new Janus-type bis(NHC) ligands

Grineva A.A.,<sup>1,2</sup> Valyaev D.A.,<sup>2</sup> César V., Filippov O.A.,<sup>3</sup> Khrustalev V.N.,<sup>4,5</sup> Nefedov S.E.,<sup>2</sup> Lugan N.<sup>2</sup>

<sup>1</sup> Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne,  
31077 Toulouse Cedex 4, France

<sup>2</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
31 Leninsky Pr., Moscow, 119991, Russia

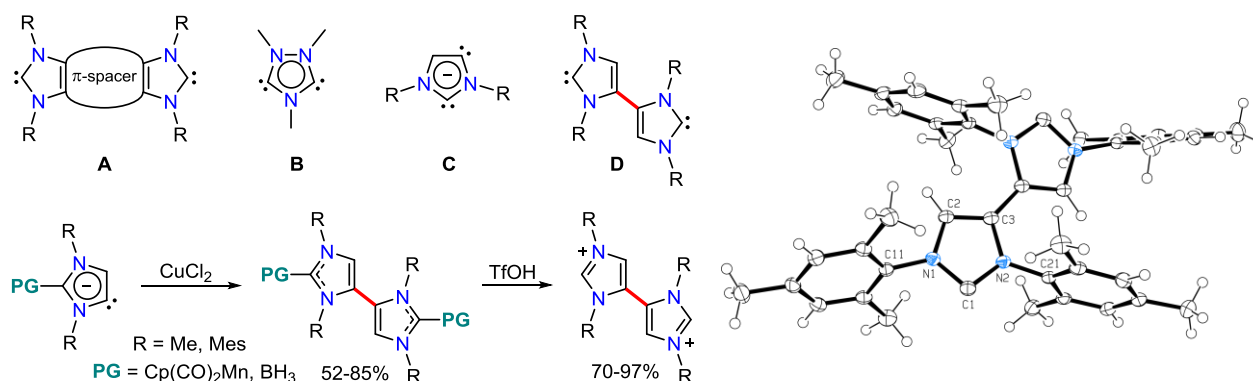
<sup>3</sup> A. N. Nesmeyanov Institute of Organoelement Compounds (INEOS) Russian Academy of  
Sciences, GSP-1, B-334, 28 Vavilov str. 119991 Moscow, Russia

<sup>4</sup> Peoples Friendship University of Russia, Inorganic Chemistry Department, 6 Miklukho  
Maklaya Str, Moscow, 117198, Russia

<sup>5</sup> National Research Center "Kurchatov Institute", 1 Kurchatova pl., 123182, Moscow, Russia

Transition metal complexes bearing so-called Janus-type N-heterocyclic carbenes (NHCs) (**A-C**, see Scheme below) have recently found numerous applications in homogeneous catalysis [1] and material science [2]. Up to now the design of these molecular architectures was based either on the assembly of two NHC moieties by the aromatic spacer (**A**), or the creation of two carbenic units within the same heterocycle (**B** et **C**).

We report here the synthesis of novel type of Janus-type NHC scaffold (**D**) featuring two imidazol-2-ylidene moieties directly linked on the backbones by simple C–C bond [3]. The precursors of these bis(NHC)s, difficult to prepare by traditional methods of heterocyclic chemistry, were obtained by unprecedented oxidative coupling of anionic abnormal NHCs protected in C2 position by [Cp(CO)<sub>2</sub>Mn] or BH<sub>3</sub> groups followed by deprotection with acid.



Unexpectedly, bis(IMes) ligand (R = Mes) shows an almost planar conformation stabilized by two C–H...π interactions, allowing the efficient electronic communication observed in bimetallic Mn(I) and Rh(I) complexes. The coordination chemistry of bis(IMes) ligand including the preparation of heterobimetallic complexes will also be discussed.

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## Synthesis and biological applications of copper(II) complexes with triketone-like ligands

Khamidullina L.A.<sup>1,2</sup>, Puzyrev I.S.<sup>2</sup>, Khrustalev V.N.<sup>3,4</sup>, Dorovatovskii P.V., Veretennikova E.A.<sup>1</sup>, Pestov A.V.<sup>1,2</sup>

<sup>1</sup>Ural Federal University, 620002, Ekaterinburg, 19 Mira St.

<sup>2</sup>Postovsky Institute of Organic Synthesis, UB RAS, 620990, Ekaterinburg, 22 Sofia Kovalevskaya St.

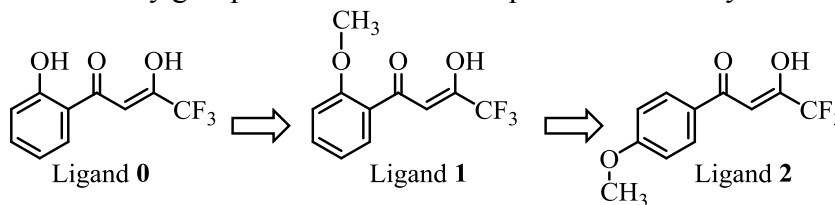
<sup>3</sup>Peoples' Friendship University of Russia, Russia, 117198, Moscow, 6 Miklukho-Maklay St.

<sup>4</sup>National Research Centre "Kurchatov Institute", 123182, Moscow, 1 Acad. Kurchatov Sq.  
e-mail: lili.khamidullina@gmail.com

Transition metal complexes with organic ligands play a significant role in biological processes. The copper ion is essential for aerobic microorganisms, plants, and animals because it binds molecular oxygen in oxygen-transport proteins and participates in the electron transport. Due to its important role in biological systems, copper(II) complexes are considered as promising antimicrobial agents, good alternatives to platinum anticancer drugs, potential modulators of inflammatory and autoimmune responses.

The nature of the ligand has a paramount impact on the bioactivity of metal complex. In particular, fluorine and fluorine-containing substituents as well as diketo groups affect the biological properties of organic compounds and their derived metal complexes. Also minor changes in the ligand structure can cause dramatic alterations in the structure and properties of the metal complexes. Copper(II) complexes with  $\beta$ -diketones are known to possess interesting biological properties.

Herein we report the synthesis and biological properties of copper(II) complexes based on  $\beta,\delta$ -triketone-like ligands. The ligand **0** is a diprotic acid and has the maximum denticity of three, which bear an extra complexing group, *viz.*, phenolic group, in addition to enol group [1]. In the structure of the ligand **1** the aromatic hydroxy group is converted into a methoxy group [2]. Hence, the ligand becomes a monoprotic acid of a different Lewis basicity with a retention of the general arrangement of all donor atoms therein. The ligand **2** differs in a spatial arrangement of the methoxy group in the structure and potential denticity.



Biological activity of ligands and their copper(II) complexes towards *Tobacco mosaic virus*, four anthropopathogenic bacterial species, which included three Gram-positive bacteria (two *S. aureus* strains, *B. subtilis*), one Gram-negative bacteria (*E. coli*), two Gram-negative phytopathogenic bacteria (two *P. atrosepticum* strains), nine fungi (*P. infestans* (Mont.) de Bary, *C. arachidicola*, *A. solani*, *B. cinerea*, *G. zeae*, *P. piricola*, *S. sclerotiorum*, *R. cerealis*, *P. sasakii*), and yeast strain (*C. albicans*), was evaluated. Minimum inhibitory concentrations (MIC) of the compounds towards bacterial and yeast strains and  $IC_{50}$  towards fungi were determined.

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## Complexes of $\text{Bi}^{3+}$ , $\text{Eu}^{3+}$ , $\text{Sc}^{3+}$ , $\text{Y}^{3+}$ with conjugates DOTA-tetrapeptide and DOTA-pentapeptide for the diagnosis and therapy of cancer

Yakusheva A.O.<sup>1</sup>, Egorova B.V.<sup>1</sup>, Matazova E.V.<sup>1</sup>, Titchenko N.A.<sup>2</sup>,  
Kalmykov S.N.<sup>1</sup>, Avdeev D.V.<sup>3</sup>, Osipov V.N.<sup>4</sup>, Khachatryan D.S.<sup>3</sup>

<sup>1</sup>Lomonosov Moscow State University, 119991, Moscow, Leninskiye gory, 1

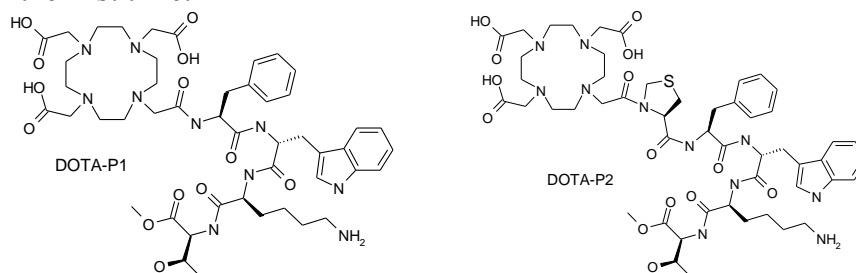
<sup>2</sup>D.Mendeleev University of Chemical Technology of Russia, 125047, Moscow, Miusskaya sq., 9

<sup>3</sup>NRC «Kurchatov Institute» - IREA, 107076, Moscow, Bogorodskiy Val st., 3

<sup>4</sup>«N.N. Blokhin National Medical Research Centre of Oncology» of the Health Ministry of Russia, 115478, Moscow, Kashirskoe sh., 24  
e-mail: angie.chem.msu@gmail.com

Neuroendocrine tumors are a type of oncological diseases characterized by increased expression of somatostatin receptors on their surface. For the diagnosis and therapy of such diseases, peptide analogues of the hormone somatostatin, which have a shorter amino acid sequence and a longer biological lifetime, are being actively developed. It has been established that the sequence of a four amino acids Phe – D-Trp – Lys – Thr is critical for the cytotoxic and antitumor activity of such peptides [1,2].

For this work, two new short tetra- (P1) and pentapeptide (P2) conjugates were synthesized for the first time:



For the complexation analysis radionuclides  $^{207}\text{Bi}$  and  $^{152}\text{Eu}$  were selected as they are the long-lived analogues of  $^{213}\text{Bi}$  [3] and other rare earth elements ( $^{177}\text{Lu}$ ,  $^{149}\text{Tb}$ ), which can be used in nuclear medicine.  $^{44}\text{Sc}$  is a potential radionuclide for positron emission tomography (PET) [4] and  $^{90}\text{Y}$  is a therapeutic radionuclide [5]. All these metal cations mentioned above form stable complexes with the macrocyclic chelator DOTA.

Labeling reactions were carried out by varying different factors: conjugate concentration, temperature, pH and time of reaction. The resulting complexes were analyzed by thin layer chromatography (TLC) and high-performance liquid chromatography (HPLC).

Optimal conditions of complex preparation with the labeling yield not less than 95-98% were found for each complex Me-DOTA-P. All complexes have high stability in serum, isotonic solution and in the excess of biogenic cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ).

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## Structure-activity relationship of metal-based complexes with targeting ligands

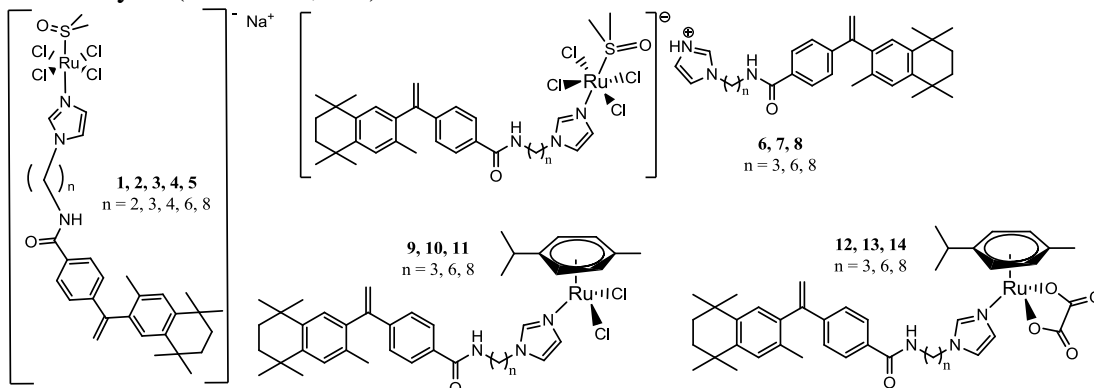
Shutkov I.A., Tyurin V.Yu., Nazarov A.A.

M.V. Lomonosov Moscow State University, 119991, Moscow, Leninskie Gory 1/3

e-mail: ilya-shutkov@chemmsu.ru

After antitumor platinum drugs the most promising is ruthenium compounds with another mechanism of antiproliferative activity, also they are less toxic and have reduced side effects. Several Ru(III) complexes are under clinical investigation and some Ru(II) compounds - in advance preclinical studies. The widely used approach in medicinal chemistry is a combination of biologically active part and metal-based structure in one compound aiming to increase activity and selectivity [1,2].

Ruthenium compounds with imidazole modified bexarotene (agonist of RXR) had been obtained. Analogs of NAMI and NAMI-A was synthesized and characterized by ESI-MS and elemental analysis (Scheme 1, **1-8**).



To improve the stability in biological solutions of the Ru(II)-arene compounds with targeting ligands the oxalate living group were introduced into a structure and new compounds were fully characterized by NMR, MS and elemental analysis (Scheme 1, **12-14**).

Investigations of *in vitro* cytotoxicity of Ru(II/III) complexes show activity in the area of micromolar concentrations, all investigated compounds are more active then starting bexarotene drug.

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## The synthesis of new chromium(III) complex compounds and their application in catalysis

Babenko I.A., Bezborodov V.A., Vilms A.I.

*Irkutsk State University, 664003, Irkutsk, Karl Marx str. 1  
e-mail: legatt112@yandex.ru*

The catalytic transformation of ethylene using of chromium(III) complex compounds in higher linear alpha olefins is one of the topical issues today. This is due to their widespread use in large-scale industrial copolymerization processes, as well as the use in the synthesis of various low-molecular-weight products, such as higher alcohols, detergents, bases for synthetic oils, etc.

In order to create new catalysts, we synthesized new chromium(III) complex compounds [1] with tridentate chalcogen-containing ligands [2] according to the reaction:

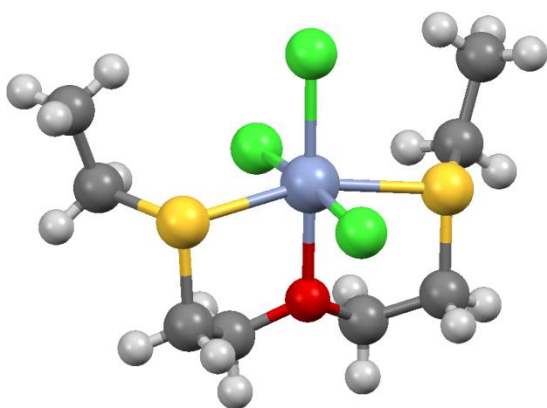
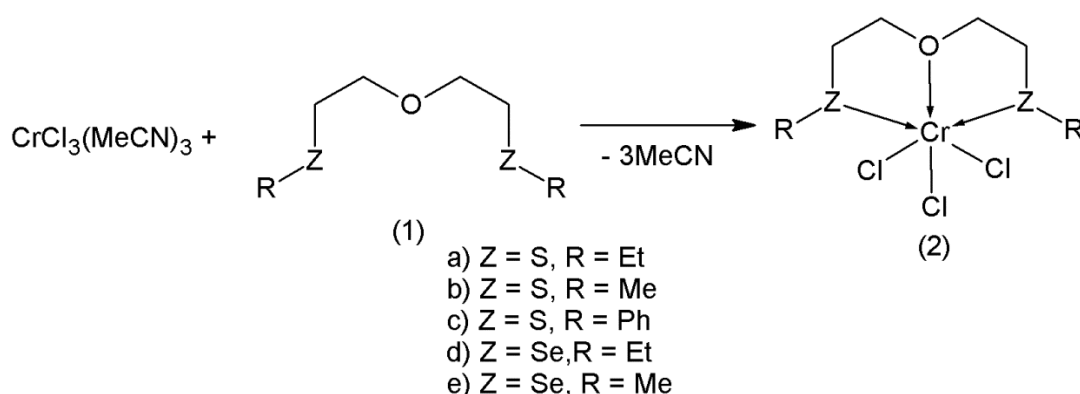


Fig. 1

As a result of the syntheses, 5 new chromium(III) complex compounds were obtained, isolated as individual substances and characterized by TG/DSC, IR and EPR spectroscopy. For the complex  $[\text{Cr}((\text{EtSCH}_2\text{CH}_2)_2\text{O})\text{Cl}_3]$ , a single crystal was obtained and characterized by X-ray diffraction (fig. 1).

Complexes  $[\text{Cr}((\text{EtSCH}_2\text{CH}_2)_2\text{O})\text{Cl}_3]$ ,  $[\text{Cr}((\text{MeSCH}_2\text{CH}_2)_2\text{O})\text{Cl}_3]$  and  $[\text{Cr}((\text{MeSeCH}_2\text{CH}_2)_2\text{O})\text{Cl}_3]$  was tested on catalytic activity in the ethylene oligomerization reaction. As a result of testing this complexes exhibited catalytic activity. The highest selectivity for hexene-1 was 33 wt.%.

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## New alkali metal diphosphates how materials to preserve the security of the environment: $\text{CsNaCu}(\text{P}_2\text{O}_7)$ , $\text{Rb}_2\text{Cu}(\text{P}_2\text{O}_7)$ and $\text{CsNaCo}(\text{P}_2\text{O}_7)$ synthesis and crystal structure determination

Chernyatieva A.P., Spiridonova D.V., Filatova A.A., Krivovichev S.V.

*Crystallography Department, Geology faculty, St. Petersburg State University,  
199034, University Emb. 7/9, St. Petersburg, Russian Federation  
e-mail: nastya250@mail.ru*

In this work we describe preliminary results of the synthesis and of a crystal-chemical study of synthetic phosphates with transition metals. Due to the increasing requirements for environmental safety specialists from various industries, we are searching for sustainable forms of immobilization of hazardous waste during storage. We are also developing a component-based waste for new materials. In our continued exploratory synthesis of compounds containing transition-metals, we were able to produce the new diphosphate phases  $\text{CsNaCu}(\text{P}_2\text{O}_7)$ ,  $\text{Rb}_2\text{Cu}(\text{P}_2\text{O}_7)$  and  $\text{CsNaCo}(\text{P}_2\text{O}_7)$ .

A crystal chemical study has allowed us to identify new phosphates. Crystals of  $\text{CsNaCu}(\text{P}_2\text{O}_7)$  (Phase 1) is orthorhombic, crystallizes in space group  $Pmn2_1$ , with  $a = 5.147(8)$ ,  $b = 15.126(2)$ ,  $c = 9.717(2)$  Å,  $V = 756.20$  Å<sup>3</sup>,  $R_1 = 0.066$  and  $\text{Rb}_2\text{Cu}(\text{P}_2\text{O}_7)$  (Phase 2) is orthorhombic as well, crystallizes in space group  $Pmcn$ , with  $a = 5.183(8)$ ,  $b = 10.096(1)$ ,  $c = 15.146(3)$  Å,  $V = 793.55$  Å<sup>3</sup>,  $R_1 = 0.063$ , they have been obtained by high-temperature reaction of  $\text{RbNO}_3$ ,  $\text{CsNO}_3$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{NaOH}$  and  $(\text{NH}_4)_4\text{P}_2\text{O}_7$ . Synthetic crystals of the phosphate of copper and rubidium were studied in detail by us on the structures of  $\text{Rb}_2\text{Cu}(\text{P}_2\text{O}_7)$  and  $\text{Rb}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2$  - new alkali metal copper diphosphates (Chernyatieva et al., 2008). Here we report the synthesis, the structure and the properties of the title compounds and we compare these phases with the previously discovered  $\text{K}_2\text{CuP}_2\text{O}_7$  (ElMaadi et al., 1995) and  $\text{CsNaMnP}_2\text{O}_7$  (Huang et al., 1998). These structures crystallize in other space groups, although their structures are also based on 2-D layers, formed by  $\text{P}_2\text{O}_7$  groups combined with polyhedra of the transition metals (Chernyatieva et al., 2012).

A crystal chemical study has allowed us to identify even new diphosphates  $\text{CsNaCo}(\text{P}_2\text{O}_7)$  (Phase 3). Crystals of  $\text{CsNaCoP}_2\text{O}_7$  is monoclinic, space group  $P2_1/n$ , with  $a = 7.424(2)$ ,  $b = 7.648(1)$ ,  $c = 12.931(3)$  Å,  $\beta = 90.71(2)^\circ$ ,  $V = 734.2(3)$  Å<sup>3</sup> and  $R_1 = 0.060$ . The structure is based framework of Co tetrahedra and  $\text{P}_2\text{O}_7$  groups. The structure of the  $[\text{Co}(\text{P}_2\text{O}_7)]^{2-}$  framework in more detail. The phosphate groups and tetrahedra coordinate cobalt ions form topology. This is a unique 4-coordination topology, where Co and  $\text{P}_2\text{O}_7$  groups in the structure are topologically equivalent.

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## Structural features of the new mixed-GP complex (H<sub>3</sub>NCH<sub>2</sub>COO)<sub>2</sub>[CoMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>][H<sub>3</sub>O]<sub>4</sub> • 4H<sub>2</sub>O

Nguyen B.V.\*, Kaziev G.Z.\*, Stepnova A.F.\*, Khrustalev V.N.\*\*\*,  
Simakova E.A.\*\*, Quenones S.H. \*\*\*

\* Moscow State Pedagogical University, Moscow

\*\* Peoples' Friendship University of Russia, Moscow,

\*\*\* Universidad Autonoma Metropolitana (Azcapotzalco), México  
e-mail: tvph.novo.kinhbac@gmail.com

This work describes the synthesis, structural and spectroscopic characterization of a new glycine hexamolybdocobaltate (H<sub>3</sub>NCH<sub>2</sub>COO)<sub>2</sub>[CoMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>][H<sub>3</sub>O]<sub>4</sub> • 4H<sub>2</sub>O (I), which is an efficient building block in a design of more complex supramolecular assemblies promising as catalysts or single-molecule magnets. It has been prepared and studied by means of chemical analysis, single-crystal X-ray diffraction, NMR and IR spectroscopy. The crystal system is monoclinic, space group is P2<sub>1</sub>/n, unit cell parameters *a* = 11.031(2) Å, *b* = 12.055(2) Å, *c* = 12.492(3) Å, β = 94.18(3)°. The structure of (H<sub>3</sub>NCH<sub>2</sub>COO)<sub>2</sub>[CoMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>][H<sub>3</sub>O]<sub>4</sub> • 4H<sub>2</sub>O includes an isolated heteropoly anion [CoMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>]<sup>4-</sup> that can be classified as the Perloff's-type anion, two zwitterionic glycine molecules <sup>+</sup>H<sub>3</sub>NCH<sub>2</sub>COO<sup>-</sup>, four outer-sphere hydronium cations H<sub>3</sub>O<sup>+</sup>, and four hydration water molecules (Figure 1). The Co heteroatom has a coordination number of 6 and is located in the center of the inner octahedron of the complex anion. Its vertices are formed by OH-groups with an average Co-O bond length of *d* ~1.912 Å. The cobalt atom is characterized by an oxidation state +2, which is supported by its coordination pattern.

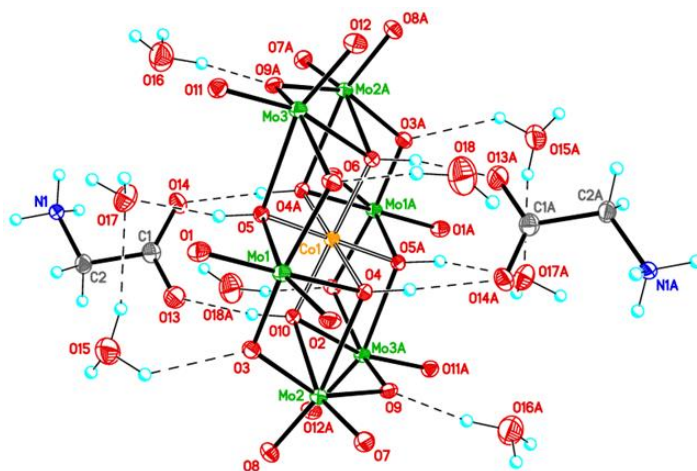


Figure 1. The structure of acidic hydrated complex of  
(H<sub>3</sub>NCH<sub>2</sub>COO)<sub>2</sub>[CoMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>][H<sub>3</sub>O]<sub>4</sub> • 4H<sub>2</sub>O

The data of IR spectroscopic analysis confirm the structure of the compound (I), (*ν*, cm<sup>-1</sup>): 3128,5; 1971,1; 1557,5; 1408,5; 1333,0; 1110,1; 876,6; 623,9; 583,2; 514,8; NMR (*δ*, м. д.): 4,66; 3,45; 2,11.

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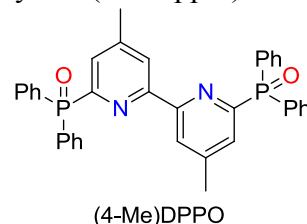
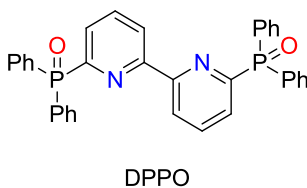
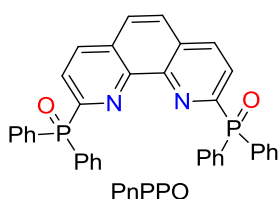
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## Structure and stability of the complexes of N-heterocyclic diphenylphosphine oxides with 4f-elements

Sumyanova Ts.B., Borisova N.E., Zakirova G.G., Korotkov L.A.

Lomonosov Moscow State University, 119991, Moscow, Leninskiye Gory, 1 str. 3  
e-mail: ts.sumyanova90@gmail.com

One of the tasks of coordination chemistry is to study the effect of structure on the composition and properties of complex. We study of influence the structure diphenylphosphine oxides on the stability of complexes ( $\lg\beta_1$ ) to understand the complexation of phosphine oxides with lanthanides nitrates  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln}=\text{La}-\text{Gd}$ ) in “dry” acetonitrile ( $40 \pm 5$  ppm).



The composition of complexes in solution was established using the methods of Job's plot, titration curves and factor analyzes. It has established that only one complex with a metal-ligand ratio (1:1) is formed in the solution. The stability constants of complexes were determined by spectrophotometric titration. The results were processed using the HypSpec2014 program (Figure 1). The results show that the stability of complexes for DPPO with lanthanum ion ( $6.82 \pm 0.04$ ) is higher than for the PnPPO ( $6.18 \pm 0.04$ ). Surprisingly, the introduction of donor methyl groups into the bipyridyl fragment of DPPO led to a decrease in the stability of complexes ( $5.96 \pm 0.09$ ). On the curve of dependence of the stability of complexes on the ionic radius of lanthanides from La to Gd, a maximum is observed on Nd.

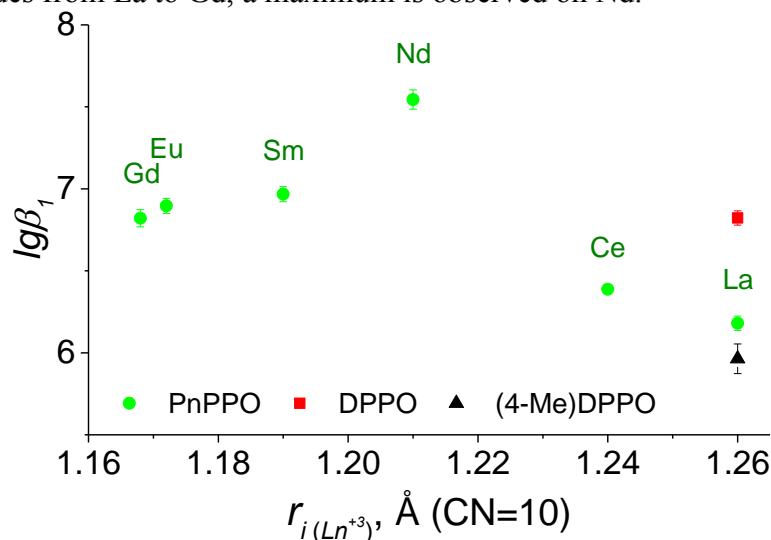


Figure.1 Dependence the value  $\lg\beta_1$  on the ion radius of lanthanide for diphenylphosphine oxides

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## Copper(II) bromide complex with caffeine: synthesis, structure, cytotoxicity

Rukk N.S.<sup>1</sup>, Davydova G.A.<sup>2</sup>, Kuzmina L.G.<sup>3</sup>, Ivanova T.V.<sup>1</sup>, Buzanov G.A.<sup>3</sup>, Belus S.K.<sup>4</sup>,  
Kozhukhova E.I.<sup>4</sup>, Retivov V.M.<sup>4</sup>

<sup>1</sup>RTU MIREA, M.V. Lomonosov Institute of Fine Chemical Technologies, 119571 Moscow,  
Vernadsky av. 86, Russian Federation

<sup>2</sup>Institute of Theoretical and Experimental Biophysics of the Russian Academy of Sciences,  
Pushchino, 142290 Moscow region, Institutskaya str., 3, Russian Federation

<sup>3</sup>Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences  
(IGIC RAS), Leninskii pr. 31, 119991 Moscow, Russian Federation

<sup>4</sup>The Federal State Unitary Enterprise "Institute of Chemical Reagents and High Purity  
Chemical Substances of National Research Center "Kurchatov Institute"" (NRC—"Kurchatov  
Institute"—IREA), Bogorodskii val, 3, 107076 Moscow, Russian Federation  
e-mail: taru-lankinen@bk.ru, roukkn@inbox.ru

Copper belongs to essential trace elements (group III), which deficiency leads to disorders, while bromine is a promotive trace element [1]. Copper-containing compounds demonstrate their selective cytotoxicity towards malignant cells due to the hypoxic environment of cancer cells that promotes the reduction of Cu(II) to Cu(I), leads to a pro-apoptotic oxidative stress, DNA double strand breaks and catalyzes the formation of reactive oxygen species (ROS) in a larger amount than in non-cancer cells [2]. It has been demonstrated [3] that the compound planarity is the important factor for its ability to intercalate and interact with the DNA duplex with subsequent antitumor effect [3]. Previously [4] we have studied zinc(II) and cadmium(II) halide complexes with caffeine (1,3,7-trimethylpurine-2,6-dione, caf), the latter possessing antitumorigenic effect.

The aim of the present work consists in the synthesis, identification and cytotoxicity studies of copper(II) bromide complex with caffeine. The complex  $[\text{Cu}(\text{caf})_2\text{Br}_2]$  (**1**) has been prepared in aqueous solution at room temperature from stoichiometric amounts of  $\text{CuBr}_2$  and caffeine. The identity of (**1**) has been confirmed by elemental analysis, powder and single crystal X-ray diffraction, IR-, <sup>1</sup>H NMR- and ESI spectra studies. The prepared compound is characterized by monoclinic unit cell, sp. gr.  $\text{P2}_1/\text{n}$  ( $Z = 4$ ). The coordination polyhedron is square planar and the central copper atom in  $[\text{Cu}(\text{caf})_2\text{Br}_2]$  is surrounded by two bromide ions in *trans*-position and two caffeine molecules coordinated via their N<sup>9</sup> atoms. The signal at 8.77 ppm in the <sup>1</sup>H NMR ( $\text{D}_2\text{O}$ ) spectrum of compound (**1**) in comparison with 7.77 ppm for pure caffeine is assigned to proton of CH (A) group due to coordination of a ligand. IR- and ESI-MS spectra studies also confirm the ligand coordination mode and the existence of complex species in solution. Preliminary results on the cytotoxicity of (**1**) with respect to different cell lines were obtained and compared with those for other caffeine containing complexes.

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## Modulation of geometry and reactivity of cyclometalated complexes of Ir(III) with 2-arylphenanthroimidazoles

Kalle P.<sup>1,2</sup>, Bilyalova A.A.<sup>1,2</sup>, Tatarin S.V.<sup>2</sup>, Dolzhenko V.D.<sup>2</sup>, Bezzubov S.I.<sup>1</sup>

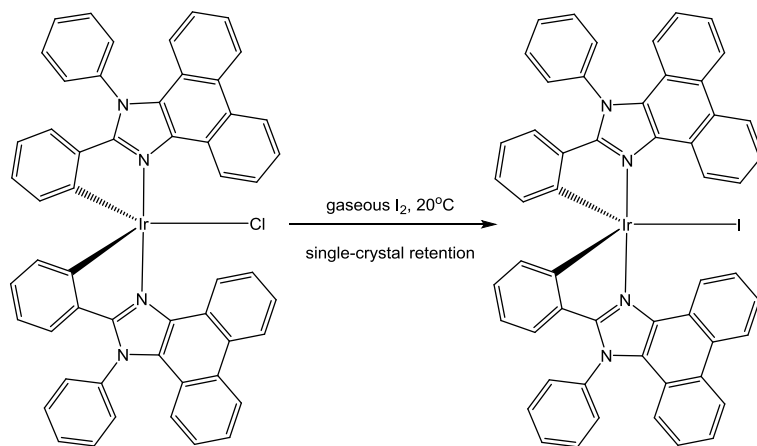
<sup>1</sup>Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 119991, Moscow, Leninsky prospect 31

<sup>2</sup>Lomonosov Moscow State University, 119991, Leninskie Gory  
e-mail: p10051997@yandex.ru

Cyclometalated iridium(III) complexes are widely used in various fields of chemistry due to their unique photophysical and electrochemical properties as well as their exceptional stability. Still, for some important medicinal and catalytic applications kinetically labile Ir(III) complexes are needed. However, these complexes not easily available because Ir(III) forms inert coordination compounds with octahedral geometry.

We supposed that sterically hindered ligands could destabilize the octahedral geometry of the Ir<sup>3+</sup> ion and increase the lability of the complexes. We studied two bis-cyclometalated complexes of Ir(III) with 2-phenylphenanthroimidazole (**1**) and 1-phenyl-2-(3,4-dimethoxyphenyl)-phenanthroimidazole (**2**), containing large rigid phenanthrene moieties. X-ray structure analysis showed that the first complex crystallizes in the monomeric form with rare trigonal-bipyramidal geometry, while the second was obtained in the common dimeric form with octahedral geometry. These results suppose a dynamic equilibrium monomer-dimer in solution.

The reactivity of complex **1** was demonstrated in an unprecedented gas-solid reaction of **1** with iodine. The ligand exchange was monitored by single-crystal X-ray analysis. Structure elucidation of the reaction dynamics reveals an exceptional stereoselectivity of the reaction caused by the crystal packing peculiarities.



In conclusion, we have revealed a way to control the reactivity of cyclometalated iridium(III) complexes by modulating the geometry of the ligands. A stereoselective ligand exchange reaction in a pentacoordinated Ir(III) complex with crystal retention was characterized by X-ray analysis.

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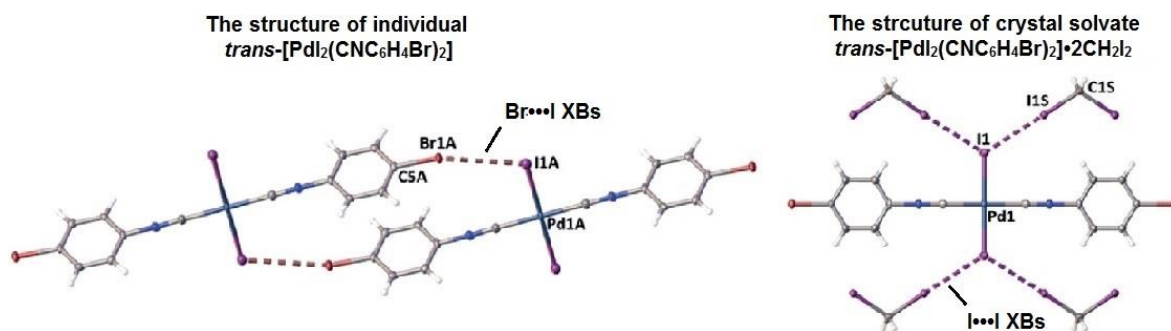
## Weak interactions in crystal structure on Pd/Pt isocyanide complexes and the role of the solvent•••complex halogen bonding

Kashina M.V., Kinzhalov M.A.

Saint Petersburg State University, 199034, Saint Petersburg, Universitetskaya nab. 7/9  
e-mail: st040562@student.spbu.ru

Studies on supramolecular systems involving metal species are among frontier fields of research because of application in catalysis [1], molecular recognition [2] and other relevant areas. Halogen bonding (XB), alongside the other non-covalent interactions (e.g., hydrogen bonding (HB),  $\pi$ - $\pi$ -stacking etc.) is successfully applied in crystal engineering for selective assembly of supramolecular structures. However, the understanding of contribution of each interaction and the possibility to manage the self-assembly are recognized problems in crystal engineering. Its solution will allow to obtain materials with desired structure and properties.

For this study we employed the dihalomethanes  $\text{CH}_2\text{X}^{\text{S}}_2$  ( $\text{X}^{\text{S}} = \text{Cl}, \text{Br}, \text{I}$ ) as bidentate XB donors and a series of *trans*- $[\text{MX}^{\text{M}}_2(\text{CNC}_6\text{H}_4\text{X}^{\text{C}})_2]$  ( $\text{M} = \text{Pd}, \text{Pt}$ ,  $\text{X}^{\text{M}} = \text{Br}, \text{I}$ ,  $\text{X}^{\text{C}} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) was used as XB acceptors. Isocyanide complexes were found to cocrystallize with  $\text{CH}_2\text{X}^{\text{S}}_2$  forming heterotetrameric clusters by two molecules of dihalomethanes and one molecule of metal species. The crystal structures of solvates demonstrate three types of short contacts, viz.  $\text{H}_2\text{X}^{\text{S}}\text{C}-\text{X}^{\text{S}}\cdots\text{X}^{\text{M}}$  XB,  $\text{X}^{\text{C}}\cdots\text{M}$  semicoordination bond, and  $(\pi\text{-hole})\cdots\pi$  contacts between the C atoms from the isocyano groups and  $\pi$ -system of a phenyl ring. The energy of interactions were calculated and differences in structures were recognized.



**Figure 1.** The structures of *trans*- $[\text{PdI}_2(\text{CNC}_6\text{H}_4\text{Br})_2]$  in individual form and as solvate.

As a result, we established that both HBs and XBs not only affect the crystal structure but they may play crucial role in solvation. Thus, the solubility of a number of organometallics is noticeably improved in  $\text{CH}_2\text{I}_2$  when compared to other haloalkane solvents [3]. This was associated with the formation of the uniquely strong solvent-(metal complex) XB, which is attenuated by the introduction of additional halogens to the organometallic species due to the competitive formation of more favourable intermolecular complex-complex XB. Exceptional solvation properties of  $\text{CH}_2\text{I}_2$  and its inertness towards organometallics make this solvent a good candidate for NMR solvent-of-choice.

*These studies were funded by the Russian Foundation for Basic Research (18-33-20073) Measurements were performed at the Center for Magnetic Resonance, the Center for X-ray Diffraction Studies, the Center for Chemical Analysis and Materials Research, and the Chemistry Educational Centre (all belonging to Saint Petersburg State University)*

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## Series of isostructural crystals with palladium(II) isocyanide complexes assembled by halogen bonding

Buldaikov A.V., Novikov A.S., Kinzhalov M.A.

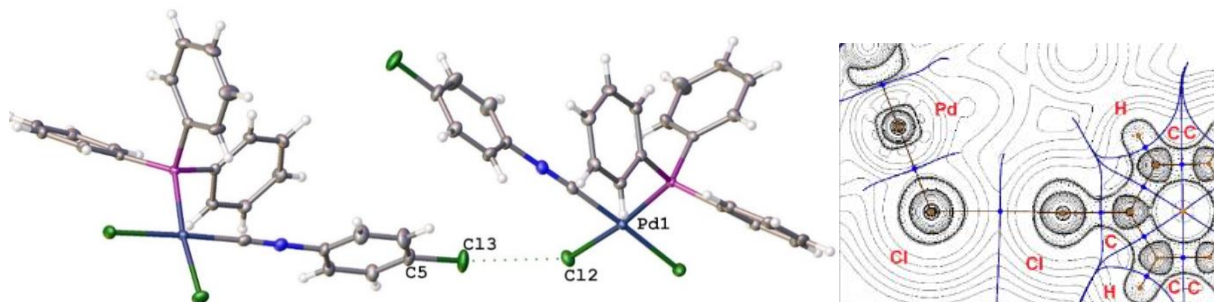
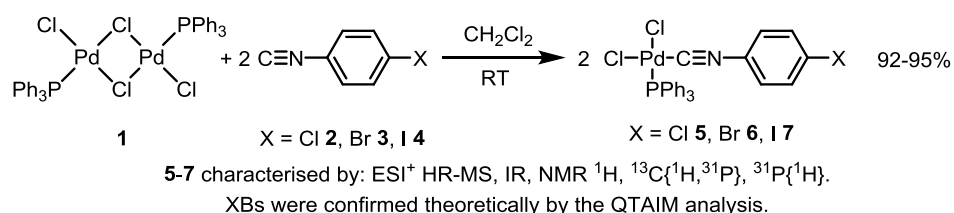
Saint Petersburg State University, 199034, St. Petersburg, University Emb. 7/9  
e-mail: st055690@student.spbu.ru

The ability to predict and control the structure of molecular crystals is a key to the synthesis of functional molecular solids by design [1]. However, controlling crystal structure is frequently not an easy task due to appearance of unpredictable polymorphic forms [2]. The opposite of polymorphism is isostructurality, i.e. when crystals possess the same structure albeit not necessarily the same cell dimensions or chemical composition.

Earlier we conducted a study on palladium(II) iodide complexes with ancillary *para*-halogen substituted phenylisocyanides [3]. It was shown that these species can crystallize with or without the solvent – CH<sub>2</sub>I<sub>2</sub>. In both cases, the crystal structure was supported by the halogen bonding, and in each case only double isostructural halogen exchange was present.

In order to conduct triple isostructural halogen exchange, we reduced steric influence of isocyanide halogen by replacing one isocyanide with Ph<sub>3</sub>P and making the new complexes to possess *cis*-configuration by replacing iodide ligands with chlorides.

Complexes *cis*-[PdCl<sub>2</sub>(CNR)(PPh<sub>3</sub>)] (**5–7**) were synthesized by the interaction of [Pd<sub>2</sub>Cl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**1**) with isocyanide in CH<sub>2</sub>Cl<sub>2</sub> at RT [4] with 92–95% yields and characterized by ESI<sup>+</sup> HR-MS, IR and NMR <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P}, <sup>31</sup>P{<sup>1</sup>H} spectroscopy. Complexes **5–7** were crystallized from CH<sub>2</sub>Cl<sub>2</sub> solutions in unsolvated isostructural crystalline form.



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 Petersburg State University)

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## **Zinc(II) halide complexes with caffeine and urea: specific features of structure and cytotoxicity**

Rukk N.S.<sup>1</sup>, Davydova G.A.<sup>2</sup>, Kuzmina L.G.<sup>3</sup>, Krasnoperova V.N.<sup>1</sup>, Buzanov G.A.<sup>3</sup>, Belus S.K.<sup>4</sup>,  
Kozhukhova E.I.<sup>4</sup>, Retivov V.M.<sup>4</sup>

<sup>1</sup>*RTU MIREA, M.V. Lomonosov Institute of Fine Chemical Technologies, 119571 Moscow,  
Vernadsky av. 86, Russian Federation*

<sup>2</sup>*Institute of Theoretical and Experimental Biophysics of the Russian Academy of Sciences,  
Pushchino, 142290 Moscow region, Institutskaya str., 3, Russian Federation*

<sup>3</sup>*Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences  
(IGIC RAS), Leninskii pr. 31, 119991 Moscow, Russian Federation*

<sup>4</sup>*The Federal State Unitary Enterprise "Institute of Chemical Reagents and High Purity  
Chemical Substances of National Research Center "Kurchatov Institute" (NRC—"Kurchatov  
Institute"—IREA), Bogorodskii val, 3, 107076 Moscow, Russian Federation  
e-mail: v-krasnoperova@mail.ru, roukkn@inbox.ru*

Metal-based complexes have been proposed as alternatives to platinum containing compounds in order to overcome their toxicity and drug-resistance and to achieve higher selectivity and activity. Zinc is a relatively abundant element in biological objects and plays an essential role in a large number of enzymatic reactions. Anticancer activity of zinc-containing complexes with 1-phenyl-3-methyl-4-acyl-5-pyrazolones and 2-aminonicotinaldehyde has been demonstrated in [1] and [2], respectively. Caffeine and its derivatives can be used in a combined therapy for brain tumors due to their possibility to penetrate through the Blood-Brain-Barrier (BBB) [3].

The aim of the present work consists in the synthesis, identification and cytotoxicity studies of zinc(II) halide complexes with caffeine (caf) and urea (Ur), the latter ones being taken for comparison. The complexes have been synthesized in an aqueous medium from zinc(II) halides and ligands taken in the molar ratio  $\text{ZnX}_2\text{:caf} = 1(3)\text{:}1$  and  $\text{ZnX}_2\text{:Ur} = 1\text{:}2$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ).

The prepared complexes –  $[\text{Zn}(\text{caf})(\text{H}_2\text{O})\text{X}_2]$  and  $[\text{Zn}(\text{Ur})_2\text{X}_2]$  – have been characterized by elemental analysis, powder and single crystal X-ray diffraction, IR-, <sup>1</sup>HNMR- and ESI spectra studies, thermal analysis. All the studied complexes are the molecular ones with the tetrahedral coordination mode, the ligands being coordinated via oxygen (Ur) or N<sup>9</sup> (caf). The compounds cytotoxicity has been determined by the MTT test with respect to postnatal dental pulp stem cells (DPSC) and MCF-7 breast cancer cell line.

All the studied compounds demonstrate the dose-dependent behavior and suppress cellular survivability of both cell types at  $1 \cdot 10^{-3}$  -  $1 \cdot 10^{-4}$  mol/L.  $[\text{Zn}(\text{caf})(\text{H}_2\text{O})\text{Br}_2]$  is more active towards cancer cells (survivability < 20%), while for stem cells it is near 70-80%. The cytotoxicity varies in the sequence  $[\text{Zn}(\text{caf})(\text{H}_2\text{O})\text{Br}_2] > [\text{Zn}(\text{caf})(\text{H}_2\text{O})\text{Cl}_2] > [\text{Zn}(\text{caf})(\text{H}_2\text{O})\text{I}_2]$  in accordance with the N(caf)–O (water) distance which is near the same as the distance between the neighboring base pairs along the DNA spiral for  $[\text{Zn}(\text{caf})(\text{H}_2\text{O})\text{Br}_2]$  in contrast to other zinc halide complexes with caffeine. The same tendency has been observed for the urea-containing complexes.

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## Cleavage of the acyclic diaminocarbene ligand bound to iridium(III) center

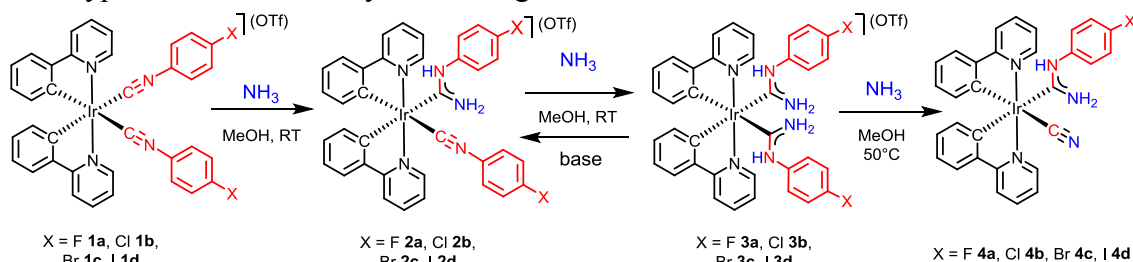
Eremina A.A., Kinzhalov M.A.

Saint Petersburg State University, 199034, Saint Petersburg, Universitetskaya Emb., 7–9  
e-mail: st040551@student.spbu.ru

Acyclic diaminocarbenes (ADCs) are powerful ancillary ligands with a broad scope of applications in organometallic chemistry and catalysis. Upon coordination to a metal center, ADC ligands exhibit strong  $\sigma$ -donor properties. ADCs are recognised as persistent ligands, albeit an extent of their thermodynamic and chemical stability, and pathways to decomposition, are rarely assessed. [1] One of the most simple method of preparation of ADC complexes is a nucleophilic addition to metal-bound isocyanides. Complexes of many metals were prepared via this route with a clear prevalence of palladium(II), platinum(II), and gold(I) species. However, nucleophilic additions to iridium-bound isocyanides are limited to but a couple of examples. [2].

Cyclometalated iridium(III) complexes are actively investigated due to their superior optoelectronic properties such as long excited-state lifetimes and high phosphorescence quantum yields. Heteroleptic cyclometalated iridium complexes such as  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{LL}')^{0/+}]$ , are of particular interest because the structures of the  $\text{C}^{\wedge}\text{N}$  and  $\text{LL}'$  ligands control the emission energy and tunes the excited-state character [3].

In the course of our studies on preparation and application of metal complexes with isocyanide and aminocarbene ligands, we aimed to expand the range of iridium(III)-ADC complexes by application of the ammonia towards iridium(III)-bound isocyanides. *Bis*ADC complexes **3** were successfully generated by reaction of *bis*isocyanide complexes **1** with gaseous ammonia. After that we observed an unusual base-mediated follow-up transformation of these complexes leading to two different products: *mono*-isocyanide **2** and cyanide **4** complexes. These experimental observations demonstrate that diaminocarbene ligands in *bis*ADC complexes **3** may be subject to a fragmentation via two competing routes, viz. by the splitting of either  $\text{C}-\text{NH}_2$ , or  $\text{C}-\text{NHR}$  bonds in the carbene fragment. Thus, we have discovered a previously unknown type of reaction activity of ADC ligands.



Compounds **1–4** were obtained in 75–87% yields and were fully characterized by ESI<sup>+</sup>-MS, IR and <sup>1</sup>H, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies, the structures of 6 complexes were also confirmed by the X-ray diffraction method.

*These studies were funded by the Russian Foundation for Basic Research (grant 18-33-20073) and grant program of the President of the Russian Federation (project MK-4457.2018.3). Measurements were performed at Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Center for Thermogravimetric and Calorimetric Research and Chemistry Educational Centre (all belong to Saint Petersburg State University)*

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## The study of the process of complexing Fe(III) with thiourea

Samadov A.S., Gorichev I.G., Kaziev G.Z., Kuzin A.V., Stepnova A.F.

Moscow State Pedagogical University

e-mail: s.s.rasul@mail.ru

The complex formation of  $\text{Fe}^{\text{III}}$  with thiourea in the system « $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}\text{-}0.05 \text{ mol/l H}_2\text{SO}_4$  thiourea» was studied by potentiometry. The redox potential platinum electrode system was measured relative to the silver chloride electrode. The results of measuring the potential from the logarithm of the concentration of thiourea are presented in Fig. 1. To determine the amount of complex particles formed in the system and to calculate the instability constants,  $\Delta E$  versus  $\lg[L]$  curves were constructed using the method described in [1]. During the titration of the thiourea solution with Fe(III) and Fe(II), the system potential decreases, which indicates the formation of the Fe(III) –thiourea complex. The Fe(II) ions did not the effect on the titration process practically.

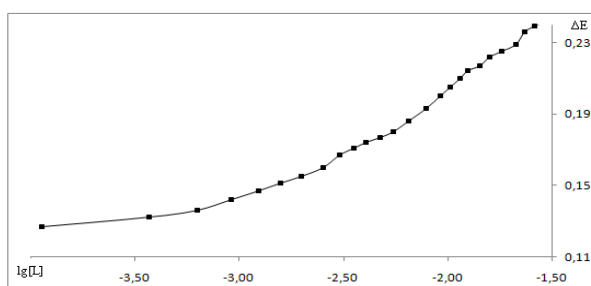


Fig.1 The curves of  $\Delta E$  (B) versus  $\lg[L]$  (mol / l) at  $T=298 \text{ K}$  and an ionic strength of  $0.1 \text{ mol / l NaNO}_3$ .

The curves of  $\Delta E$  versus  $\lg [L]$  are nonlinear, which indicates the stepwise formation the complex Fe(III) – thiourea. From the curves of  $\Delta E \lg[L]$  (Fig. 1) using the methods [1,2] found that two complex particles are formed in the system. The logarithms of the stability constants of complexes are:  $\lg K_1=4,97$  ( $[\text{FeL}]^{3+}$ ) and  $\lg K_2=6,85$  ( $[\text{FeL}_2]^{3+}$ ). Using the found values of the constants, the relative distribution of the complex ions in the solution was calculated (Fig. 2).

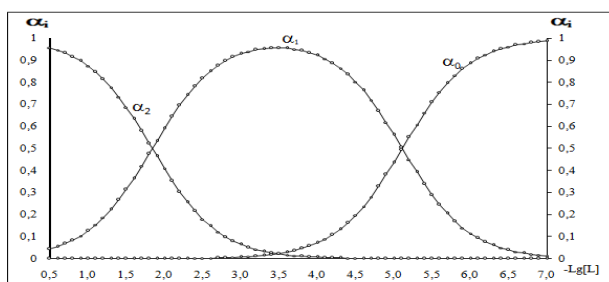


Fig.2. Distribution curves of complexes Fe(III)- thiourea in  $0.05 \text{ mol / l H}_2\text{SO}_4$  at  $T=298 \text{ K}$ :  $\alpha_0\text{-}[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $\alpha_1\text{-}[\text{FeL}(\text{H}_2\text{O})_5]^{3+}$ ,  $\alpha_2\text{-}[\text{FeL}_2(\text{H}_2\text{O})_4]^{3+}$ .

Distribution curves for complex shapes (Fig. 2) provide an opportunity to dominance identify areas of each of the complex particles.

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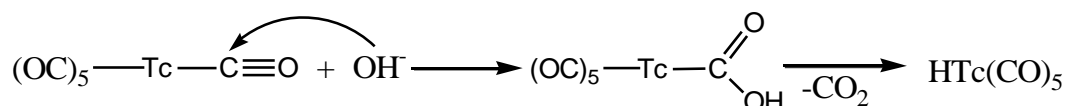
## Preparation of the technetium(I) pentacarbonyl hydride in the absence of reducing agent

Shishkina A.P.

*Saint-Petersburg State University, 198504, Saint-Petersburg, Universitetsky av., 26  
e-mail: annash000@gmail.com*

Technetium and rhenium pentacarbonyl hydride was obtained for the first time by reduction of  $M_2(CO)_{10}$  ( $M = Tc$  and  $Re$ ) with sodium amalgam, followed by treatment with phosphoric acid [1, 2]. Also, rhenium pentacarbonyl hydride was obtained by interaction between rhenium pentacarbonyl bromide, zinc dust and acetic acid [3]. This method was successfully realized by us for preparation of  $TcH(CO)_5$ . The product, that appeared as colorless gas, was characterized by IR-spectroscopy in the vapor phase and in a hexane solution. Thus, all the above methods require the presence of a reducing agent.

We now wish to report a new method for preparing technetium(I) pentacarbonyl hydride in the absence of a reducing agents.  $TcH(CO)_5$  appears as alkaline hydrolysis product of technetium hexacarbonyl cation. In this case carbonyl ligand acts as a intramolecular reducing agent. The estimated mechanism of the reaction is based on the results of DFT calculations.



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## Synthesis and properties of cage-like metallagermsesquioxanes

Kulakova A.N.<sup>1,2,3</sup>, Bilyachenko A.N.<sup>1,2</sup>, Khrustalev V.N.<sup>1</sup>, Larionova J.I.<sup>3</sup>, Korlyukov A.A.<sup>2</sup>

<sup>1</sup> Peoples' Friendship University of Russia, Moscow, Russia;

<sup>2</sup> A. N. Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia;

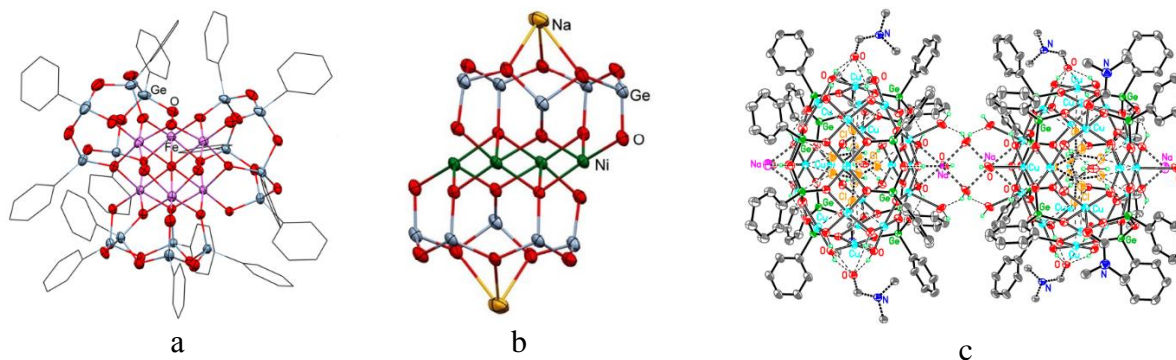
<sup>3</sup> Institute Charles Gerhardt, UMR5253, University of Montpellier, Montpellier, France

e-mail: alenkulakova@gmail.com

The interest to framework (cage) organometallic complexes containing transition metal ions is due to a variety of their structural organizations and topologies, which may be controlled by means of coordination chemistry tools through modulation of various parameters, including the nature and connectivity of building blocks and metal ions, as well as through the nature of organic ligands. In addition, these compounds exhibit catalytic activity, as well as magnetic and optical properties, which makes them an interesting subject for study.

Notably, some amount of the reported cage-like metal complexes were isolated using branched sesquioxane units. The majority of such products were made with (RSiO<sub>1.5</sub>) silsesquioxane ligands, while analogous architectures based on germanium sesquioxanes are poorly reported in the literature. The main approach for obtaining structures with Ge-O-M units is the hydrothermal method, characterized by the long time of the reaction and harsh conditions [1].

Here we present an alternative, mild conditioned, approach to obtaining a new class of compounds containing Ge-O-M fragments (M = Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>), based on a self-assembly reaction between the building blocks, PhGe(OMe)<sub>3</sub> (or PhGeCl<sub>3</sub>) and metal ions in the presence of NaOH, with the formation of [(Ph<sub>5</sub>Ge<sub>5</sub>O<sub>10</sub>)<sub>3</sub>Fe<sub>6</sub>(OH)<sub>3</sub>(O)Na<sub>2</sub>] [2], [(PhGeO<sub>1.5</sub>)<sub>10</sub>(NiO)<sub>4</sub>(NaO<sub>0.5</sub>)<sub>2</sub>] [3], (C<sub>144</sub>H<sub>164</sub>Cu<sub>42</sub>Ge<sub>24</sub>Na<sub>4</sub>O<sub>102</sub>) [4]. Furthermore, the study of catalytic activity and magnetic properties of these complexes was performed.



The molecular structure of a) [(Ph<sub>5</sub>Ge<sub>5</sub>O<sub>10</sub>)<sub>3</sub>Fe<sub>6</sub>(OH)<sub>3</sub>(O)Na<sub>2</sub>], b) [(PhGeO<sub>1.5</sub>)<sub>10</sub>(NiO)<sub>4</sub>(NaO<sub>0.5</sub>)<sub>2</sub>], c) (C<sub>144</sub>H<sub>164</sub>Cu<sub>42</sub>Ge<sub>24</sub>Na<sub>4</sub>O<sub>102</sub>)

This work was supported by the RFBR 19-03-00488

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## The impact of asymmetrical binding subunits on the richness of (metallo)supramolecular architectures

Brykczyńska D.A., Jezierska Z., Bocian A., Gorczyński A., Patroniak V.

Adam Mickiewicz University, ul. Wieniawskiego 1, 61-712 Poznań, Poland  
e-mail: darbry@st.amu.edu.pl

Supramolecular chemistry is a domain associated with non-covalent interactions such as hydrogen or coordination bonds, which may result in difficulties in terms of the *a priori* design and prediction of chemical structures [1]. Mutual interaction of the ligand and the metal atom results in the synthesis of compounds with different properties such as biological, catalytic or fluorescent ones [2,3]. An attempt to an accurate prediction of complex supramolecular architectures may be realized by creation of libraries of similar coordinating systems, with subtle changes in the organic framework, while retaining the same binding motif.

In our work, having such a library consisting of twelve ligands (Fig. 1), we synthesized a series of complexes to see which structural elements are responsible for creating the obtained architectures such as: “open” system (1:1), “closed” system (2:1) and cuban-type system (4:4) (Fig. 2) [4].

Figure 1 – Schematic representation of the ligand structures utilized in the study.

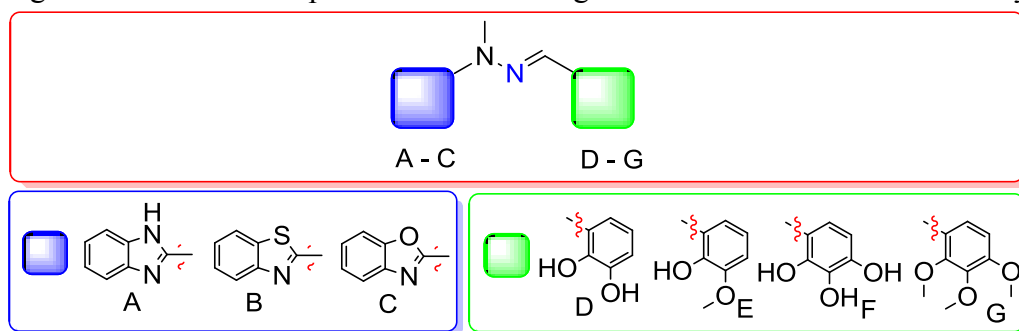
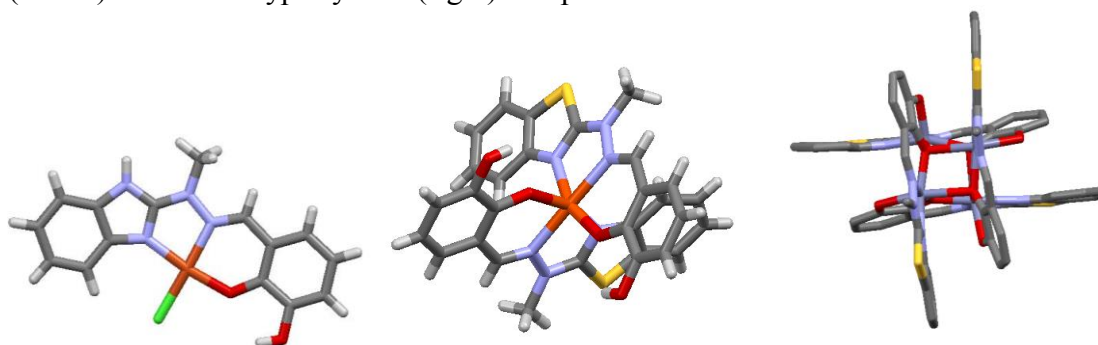


Figure 2 – Crystal structures of exemplary “open” system (1:1) (left), “closed” system (2:1) (center) and cuban-type system (right) complexes.



*This research was carried out as a part of the Polish Ministry of Science and Higher Education project “Best of the best! 3.0”*

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## **Design and synthesis of H-bonded porous iron(III)/chromium(III) materials for selective removal of CO<sub>2</sub> from the environment**

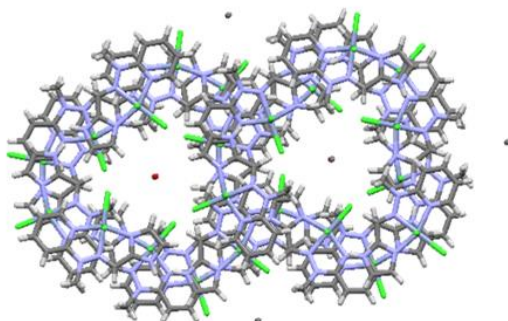
Marcinkowski D., Gorczyński A., Bocian A., Pakulski D., Michalkiewicz B., Serafin J., Zieliński M., Kubicki M., Patroniak

*Adam Mickiewicz University Faculty of Chemistry, Poznań, Poland*  
*e-mail: dawid12326@gmail.com*

World is endangered by global warming, which is regarded to be one of the major civilization problems and can be partially attributed to an increase in the emissions of greenhouse gases such as carbon dioxide (CO<sub>2</sub>). [1] Global warming leads to droughts, floods, heat waves, and destruction of ecosystems. [2]

For the capture, storage and utilization of CO<sub>2</sub>, solid CO<sub>2</sub>-adsorbents are widely used. The process of capturing CO<sub>2</sub> with a dry adsorbent involves the selective separation of CO<sub>2</sub> based on a gas-solid interaction. Particular attention should be devoted to such systems as Metal-Organic Frameworks (MOFs), Covalent-Organic Frameworks (COFs) and hydrogen-bonded organic frameworks (HOFs). [3]

Herein, we would like to present iron(III)/chromium(III) complexes that are based on simple N-heterocyclic Schiff bases ligands. These complexes have characteristic pores in their lattice, which allow and facilitate adsorption of CO<sub>2</sub>. Complexes were characterized by spectroscopic methods and then submitted to an examination of adsorption using volumetric method in the pressure range from 1-50 bar at a temperature from 0-100°C. The results have been satisfactory: under a pressure of 1 bar and temperature of 0°C adsorption of CO<sub>2</sub> was 0.17 mmol/m<sup>2</sup>, whereas 0.10 mmol/m<sup>2</sup> at 25°C. The CO<sub>2</sub>/N<sub>2</sub> selectivity was high at the low pressure except at temperature of 100°C. Continuation of this project encompasses synthesis of new iron(III) complexes with others N-heterocyclic ligands so that we can find crucial elements within ligands framework that are responsible for enhancement of adsorption properties.[4]



*This research was carried out as a part of the Polish Ministry of Science and Higher Education project! «Best of the best! 3.0»*

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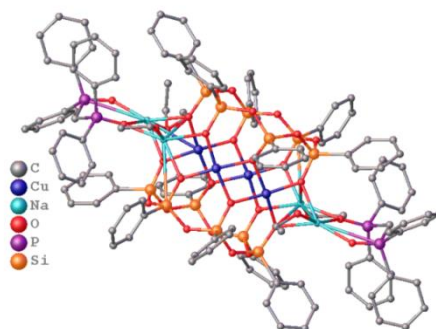
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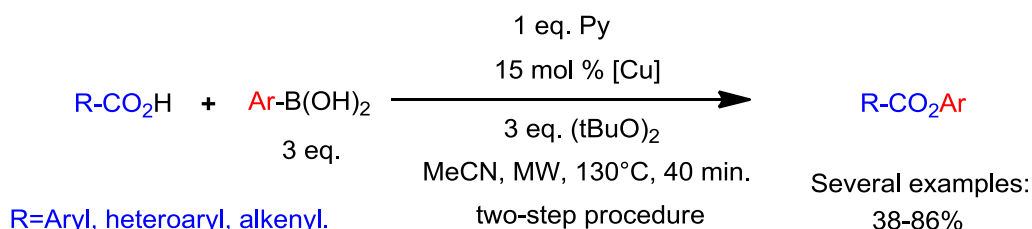
## Copper silsesquioxanes and their catalytic properties

Astakhov G.S.<sup>1,2</sup>, Bilyachenko A.N.<sup>1,2</sup>, Levistky M.M.<sup>2</sup><sup>1</sup> RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6;<sup>2</sup> INEOS RAS, 11999, Moscow, Vavilova St. 2.

e-mail: astakhovgrigorii@gmail.com

**Figure 1. Molecular structure Cu<sub>4</sub>Na<sub>4</sub>-silsesquioxane complex with dppmO<sub>2</sub>**

The cage-like structures based on metallsesquioxanes are attracted the attention of many research groups, because they demonstrate intriguing catalytic properties [1]. In recent years the Chan-Evans-Lam (CEL) coupling reaction, copper-catalyzed interaction of H-nucleophiles (amines, amides, carbamates, phenols *etc.*) and boronic acids, became popular instrument of fine organic synthesis [2]. Here we show that several copper-based cage-like silsesquioxanes catalyze coupling of boronic acids and carboxylic acids under microwave (MW) conditions. In comparison to published results [3a-e], Cu<sub>4</sub>Na<sub>4</sub> complex (**Fig. 1**) exhibit high catalytic activity on conditions of low loading of copper source and added base [4]. To the best of our knowledge, this is a first example of CEL reaction by making C-O bond in MW.



Work was supported by RFBR (project 19-03-00488)

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## **New helical complexes of Schiff base ligands**

Kurkiewicz A.,<sup>a</sup> Fik M.A.,<sup>a</sup> Belter A.,<sup>b</sup> Hnatejko Z.,<sup>a</sup> Kubicki M.,<sup>a</sup> Patroniak V.<sup>a</sup>

<sup>a</sup> *Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61614 Poznań, Poland*

<sup>b</sup> *Institute of Bioorganic Chemistry, Polish Academy of Sciences, Noskowskiego 12/14, 61-704 Poznań, Poland*

*e-mail: adakurkiewicz96@gmail.com*

Schiff's bases are products that arise from the condensation of primary amines and carbonyl compounds. Schiff base ligands are important in the field of coordination chemistry, especially in the development of transition metal complexes because they are potentially capable of forming stable entities. They have imine bonds which determine their biological properties. They are antibacterial, antifungal, antiviral and antineoplastic compounds. [1] As biological models, they help to understand the structure of biomolecules and biological processes in living organisms. [2]

Three new silver and copper complexes of the formula  $[\text{Cu}_2(\text{L}_2)](\text{OTf})_2$ ,  $[\text{Ag}_2(\text{L}_2)](\text{OTf})_2$  and  $[\text{AgCu}(\text{L}_2)](\text{OTf})_2$  were synthesized. Ligand [L] is a Schiff base formed by the condensation of p-xylenediamine and 2-quinolinecarboxylic aldehyde. It was successfully synthesized and characterized by EA, NMR, ESI-MS and UV-VIS spectroscopy. Spectrophotometric titration, circular dichroism method and determination of  $T_m$  allowed to determine the affinity of helical complexes to DNA. In vitro cytotoxicity of the ligand and complexes for cancer and healthy cells was also investigated.

*This research was carried out as a part of the Polish Ministry of Science and Higher Education project «Best of the best! 3.0.» and National Science Centre Grant SONATINA 2017/24/C/ST5/00181*

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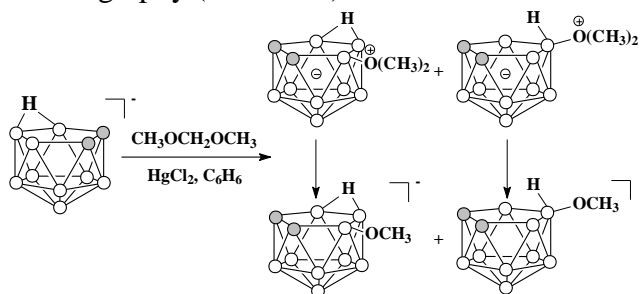
## Synthesis of new derivatives of *nido*-carborane and based on them cobalt and iron bis(dicarbollides)

Erokhina S.A., Stogniy M.Yu., Sivaev I.B., Bregadze V.I.

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,  
28 Vavilov Str., 119991, Moscow, Russia  
e-mail: erokhina.sv@rambler.ru

Since its discovery 7,8-dicarba-*nido*-undecaborate anion and its derivatives for many years attracted attention as unusual three-dimensional  $\pi$ -ligands as well as water-solubilizing boron moieties in design of potential drugs for boron neutron capture therapy of cancer [1]. That's why the development of effective methods for the synthesis of new *nido*-carborane derivatives remains one of the important areas in boron chemistry.

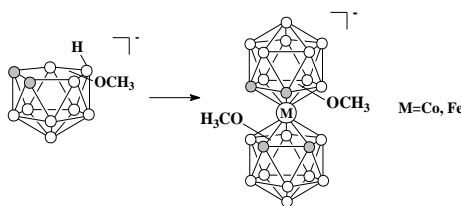
It was found out that potassium salt of *nido*-carborane  $K[7,8-C_2B_9H_{12}]$  reacts with dimethoxymethane in the presence of  $HgCl_2$  in benzenes giving the unsymmetrical and symmetrical dimethyloxonium and metoxy derivatives of *nido*-carborane ( $9-Me_2O-7,8-C_2B_9H_{11}$ ,  $10-Me_2O-7,8-C_2B_9H_{11}$ ,  $9-MeO-7,8-C_2B_9H_{11}^-$  and  $10-MeO-7,8-C_2B_9H_{11}^-$ , respectively) that can be separated by column chromatography (Scheme 1).



Scheme 1

The dimethyloxonium derivatives of *nido*-carborane can be used as methylating agents and the reactions of  $9-Me_2O-7,8-C_2B_9H_{11}$  and  $10-Me_2O-7,8-C_2B_9H_{11}$  with different N-nucleophiles were investigated.

On the base of metoxy derivatives of *nido*-carborane  $9-MeO-7,8-C_2B_9H_{11}^-$  and  $10-MeO-7,8-C_2B_9H_{11}^-$  unsymmetrical and symmetrical cobalt and iron bis(dicarbollides) were obtained (Scheme 2).



Scheme 2

These synthesized bis(dicarbollide) complexes can be used for preparing of new electrically conductive and magnetic materials.

*This work was supported by the Russian Foundation for Basic Research  
(grant № 18-33-20115)*

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## **Analysis of sand in Nafud desert province, Saudi Arabia**

Nawal M.S.

*Department of chemistry, Faculty of Education, Khartoum University, P.O.Box 406 Omdurman  
Sudan*

*e-mail: nawalmahgoub@gmail.com*

In this present study, soil samples were collected from an agriculture area of Zilfi Province of Saudi Arabia approximately 260 km northwest, of the capital city Riyadh. The area of study (Nafud Desert in Zilfi Province) was surveyed during December 2012 collecting 21 samples from 7 places (Al sabla, Almata, Jaway, Alaaga, Magra, Shlwan, and Althware, by taking 3 samples from each place at the surface, 20 cm and 40 cm depth. The concentrations of some elements such as Si, Na, Mg, Ca, K, Al, P, S, Ti, V, Mn, Fe, Ni, Cu, As, Au, Pb, Cr, Co, Cd, and Zn were measured, using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), after sieving and digestion using HNO<sub>3</sub>, HCl and HF. In most of the samples the elements (Au or Cd), found to have low concentrations while the element S found to have the highest concentrations. The concentrations of toxic trace elements (Ni, Cd and As), were found have values more than background concentrations found in the literature of sandstone. The maximum concentrations of the elements: Pb, Zn, Na, Ca and Cd were found at Al sabla region. On the other hand, the maximum concentrations of the elements: As, and V were found in Shlwan region, while the maximum concentration of Cr was found in Alaaga region. Magra region shows maximum concentrations of elements Au, Si, Ti, P, Al, Fe, Mg, and S. High concentration of elements Cu, Mn and K were found in Althware region, while Ni in Jaway region, and Co in Magra and Althware regions [1]. In addition, elemental composition was determined using X-ray fluorescence spectrometry, while mineral content and crystallography analysis were performed using X-ray diffraction. Analysis results revealed that silicon was abundant in the area, in homogeneous amounts. Silica was found in concentrations of around 93% per sampled mass, and silicon concentrations were around 42%, in the surface layers down to the depth of 40 cm. Thus, according to the results, the Nafud Desert is a rich source of silicon that can be exploited very cheaply because of the presence of the raw material on the surface [2].

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## **Extraction - photometric determination of chromium in urban dust**

Zalov A.Z.<sup>1</sup>., Verdizadeh N.A.<sup>1</sup>, Hasanova N.A.<sup>2</sup>

<sup>1</sup>*Department of Chemistry, Azerbaijan State Pedagogical University,  
U. Gadzibekov street 68. Baku, AZ 1000 Azerbaijan*

<sup>2</sup>*Azerbaijan State University of Oil and Industrial, Department of Chemistry and Technology  
inorganic substances, Azadlg street 34, Baku, 1000 Azerbaijan  
e-mail: Zalov1966@mail.ru*

In this paper we present the results of our spectrophotometric investigation of chromium (VI) complexes with 2-hydroxy-5-iodothiophenol (HITP) and aniline (An).

Chloroform and chlorobenzene are best extractants of organic solutions. In one extraction with chloroform we got 98.4% of the chromium(VI) in the form of Cr(VI)-HITP-An. The maximum percent of complex extraction is observed at pH's between 4.0-5.2. The result of increasing acidity is a smaller concentration of the ionic form of HITP and a smaller percent of hydroamines protonization. The complete extraction of complex occurs in excess reagent. Optimal concentration of HITP is  $1.3 \times 10^{-3}$  mol/l and for An,  $1.2 \times 10^{-3}$  mol/l. At pH 4, the complex's absorbency has a maximum at 628 nm. The absorbency of the vanadium-complex extract shows the formation of one compound. The molar absorbency coefficient of different complexes equal to  $3.6 \times 10^4$ . The optimal volume of water-phase is 20 mL and of organic phase is 5 mL. Increasing the water-phase volume to 90 mL does not influence the complex's optical properties. The complex forms as the reagents are mixed and is stable in chloroform for more than two days.

The molar component balance in the complex is established by different physical-chemical methods of analysis. It was found that the spectrophotometric characteristics of the mixed-ligand complexes of Cr(VI) and Cr(III) were identical, i.e., in the interaction with HITP, Cr(VI) was reduced to Cr(III) and  $\text{Cr}^{3+}$  was the complex-producing form. This fact was also confirmed by ESR spectrometry.

We observed absorbency to be in accordance with Beer's Law for complex extracts with chloroform in intervals of concentration between 0.05 to 2.8 mg / 5 mL. We found the corrected linear equation to be:  $y = 0.345x + 0.19$ . The Limit of detection (LOD) of chromium(III) is 0.0011 mg/mL.

The interference of Fe(III) was eliminated by thioglycolic acid; Cu(II), V(IV,V) and Mn(VII) were masked by thiourea; Ti(IV), ascorbic acid; and Zr(IV), Nb(V), and Ta(V), by fluoride ions. Ions of Mo(VI), W(VI), Ti(IV), Nb(V), and Ta(V) form with HITP and An colored compounds and interfere with the determination of chromium. However, these elements form complexes in more acidic medium.

Dust sample obtained by pumping air through the filter, ashed, the ash is mixed in a ratio of 2: 1 with  $\text{HNO}_3$  and sintered samples and vanadium extracted with water. We then added a little chromium-sulphate with 10  $\mu\text{g}$  of chromium, 2-3 mL of concentrate HCl and corrected the volume with distilled water. To a given quantity of this solution, we added 0.5 g of thiocarbamide, 2.5 mL of 0.01 M HITP and 2.5 mL of 0.01 M An. After shaking we increased the volume of solution to 25 mL with distilled water. We separated the organic-phase from the water-phase and sured the optical absorbency of the extract at 590 nm using the CFC-2. The concentration of chromium was determined and corrected statistically.

The results of the analysis of urban dust by this method: 0.045  $\mu\text{g/L}$  ( $n=5$ ;  $p=0.95\%$ ) vanadium in good agreement with the results obtained by dithiol 0.049  $\mu\text{g/L}$  ( $n=5$ ;  $p=0.95\%$ ).

## Luminescent properties of some difluoroboron $\beta$ -diketonate complexes containing both electron donor and electron acceptor groups

Puzyrev I.S.<sup>1</sup>, Khamidullina L.A.<sup>1,2</sup>, Khrustalev V.N.<sup>3,4</sup>, Dorovatovskii P.V.<sup>4</sup>, Pestov A.V.<sup>1,2</sup>

<sup>1</sup>Postovsky Institute of Organic Synthesis, UB RAS, 620990, Ekaterinburg,  
22 Sofia Kovalevskaya St.

<sup>2</sup>Ural Federal University, 620002, Ekaterinburg, 19 Mira St.

<sup>3</sup>Peoples' Friendship University of Russia (RUDN University), Russia, 117198, Moscow,  
6 Miklukho-Maklay St.

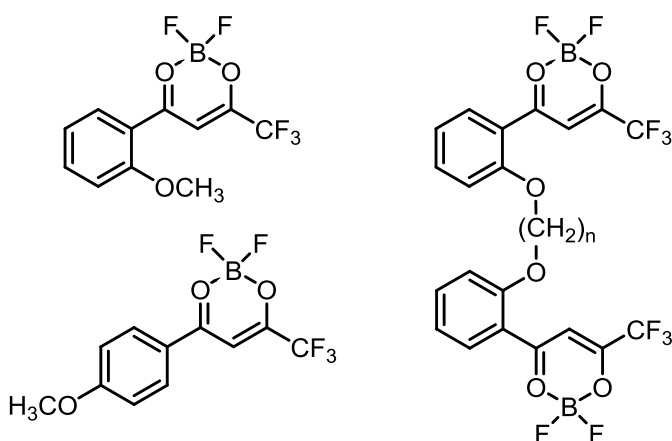
<sup>4</sup>National Research Centre "Kurchatov Institute", 123182, Moscow, 1 Acad. Kurchatov Sq.  
e-mail: igor.puzyrev@gmail.com

Organic luminescent materials are of great importance in various applications such as chemsensing, biolabeling, bioimaging and organic light emitting diodes (OLEDs) [1].

Luminescent properties of difluoroboron complexes of  $\beta$ -diketones have attracted much attention [2,3]. Particular emphasis is placed upon such complexes due to their unique characteristics, large molar extinction coefficients, and highly efficient photoluminescence quantum yields.

Most studied boron difluoride  $\beta$ -diketonate complexes are 4,6-diaryl-substituted 1,3,2-dioxaborines. Modification of the structure of the ligand leads to a considerable changing in properties of complexes. Moreover, boron-containing fluorophores are known to form excimers, and as a consequence their luminescent properties are influenced by the intermolecular interactions.

In our work, we synthesized difluoroboron complexes with  $\beta$ -diketonate and bis- $\beta$ -diketonate ligands containing both electron donor (methoxy) and electron acceptor (trifluoromethyl) groups in the same molecule. The compounds were studied using a single crystal X-ray analysis, photoluminescence spectroscopy. Also the influence of crystal packing and intermolecular interactions on optical properties was considered.



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# Alcoholysis of transition metal tetrahydroborates and BH/OH activation

Golub I.E.<sup>1,2</sup>, Filippov O.A.<sup>2</sup>, Shubina E.S.<sup>2</sup>

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6*  
<sup>1</sup>*Peoples' Friendship University of Russia (RUDN University), 117198, 6 Miklukho-Maklay St, Moscow, Russia*

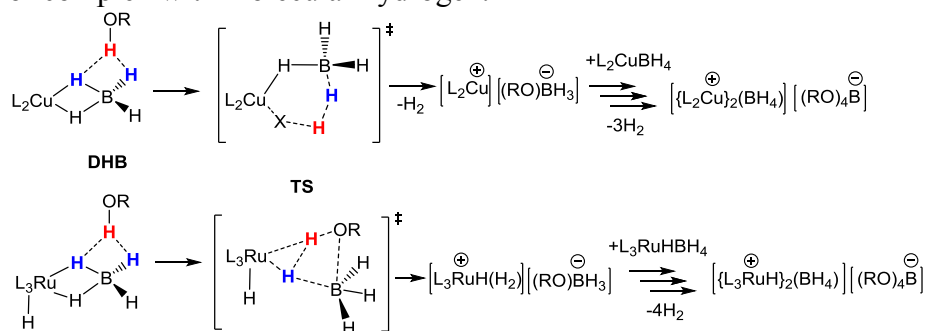
<sup>2</sup>*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991, 28 Vavilova St, Moscow, Russia*  
*e-mail: seraph347@gmail.com*

Boron hydrides are widely used as selective reducing agent, catalyst of polymerization/isomerization reaction, precursors at the creation new materials and by its gravimetric and volumetric hydrogen density this compounds are perspective for hydrogen storage systems.

Optimal system for hydrogen storage should combine high hydrogen density and low energy cost for its release. The hydrolysis and alcoholysis process are certainly significant for release of large quantities of hydrogen gas from boron hydrides.

The non-covalent intra- and intermolecular interactions (e.g. (di)hydrogen bonds) are known to have a great impact on reactivity of boron hydrides in reactions with proton transfer and hydrogen evolution. The first proton transfer reaction, whis is going via preliminary dihydrogen-bonded complexes formation is rate-limiting stage of overall alcoholysis process, further acceleration of reaction rate related to increasing hydride donor ability in alcoxyboron hydrides [1].

Herein we present comprehensive investigation of the reactivity  $[BH_4]^-$  and transition metals (Cu, Ru, Pd) tetrahydroborate and hydrido-tetrahydroborate complexes with in alcoholysis reactions [2-3]. The first proton transfer reaction is rate-limiting stage of overall alcoholysis process, further acceleration of reaction rate related to increasing hydride donor ability in alcoxyboron hydrides. The nature of transition metal in their borohydride complexes determines the overall mechanism of activation of the borohydride fragment and the ways of stabilization of complex with molecular hydrogen.



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## New ferrocene-based N-heterocyclic carbenes: simple and versatile ligand platform

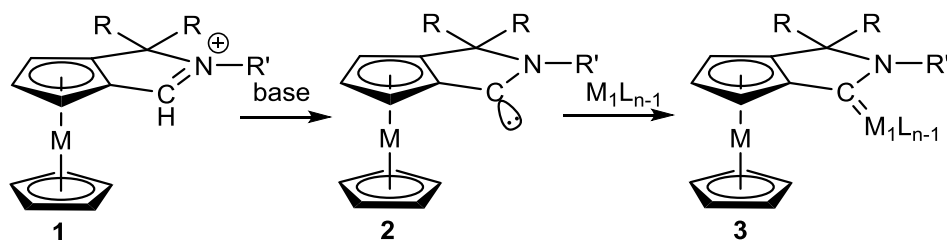
Polezhaev A.V.<sup>1,2</sup>, Nikovski I.A.<sup>1</sup>, Platonova E.O.<sup>2</sup>, Zakharova D.V.<sup>1,2</sup>,  
Nelyubina Yu.V.<sup>1</sup>, Pavlov A.A.<sup>1</sup>.

<sup>1</sup>*A.N.Nesmeyanov Institute of Organoelement Compounds, 119334, Vavilova, 28, Moscow, Russia*

<sup>2</sup>*N.E.Bauman Moscow State Technical University, 105005, 2 Baumanskaya, 5/1, Moscow, Russia*  
*e-mail: aleksandr.polejaev@gmail.com*

Over the last two decades, the replacement of phosphine ligands by carbenes on transition metal centers has led to considerable improvements in catalyst development. Catalysis demands a large variety of ligands with different electronic and steric properties. Several types of carbenes have been prepared, but a wider diversity is still needed to match their phosphorus-based counterparts. It was shown that a window of NHCs donor abilities is at least 3 times smaller than achieved for phosphines in late 70s. Enlargement of a window of steric and electronic properties of NHC ligands, using simple modular synthetic routes, is a central theme in design of carbene ligands. In recent years a numerous approaches to modify their  $\sigma$ -donor/ $\pi$ -acceptor properties have been implemented, such as backbones forcing different NCN-angles, variation of the heteroatoms adjacent to carbon, abnormal and remote carbenes, acyclic carbenes, anti-Bredt NHCs, push-pull carbenes. A less explored approach relies on NHCs comprising organometallic fragments, redox-switchable NHCs, and chiral carbenes. Those approaches, especially combined in one scaffold, are potentially a very attractive for ligand modification.

We combined in one easy-to-modify scaffold several features that can significantly broaden utility of NHC: a metallocenyl(Mc)-based heterocyclic carbenes (MB-NHC) that incorporates organometallic unit directly in  $\pi$ -system of NHC. The main purposes of MB-NHC are 1) enlarge a window of NHC donor abilities in both directions 2) make NHC ring plane chiral for application in asymmetric catalysis 3) make ligand redox-switchable for application in sensors and redox-switchable catalysis. The general structure of the proposed scaffold is shown on Fig 1 and consist of metallocene unit annelated with NHC ring. Proposed MB-NHC also provides a variety of simple synthetic opportunities for final tuning of both electronic and steric properties of the ligand (Cp, X and R' modification). MB-NHC precursor could be obtained in a few steps from metallocenes using well developed and inexpensive organic methodology and should be stable enough to be isolated and characterized and then installed on catalytically active metal.



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(grant № 18-73-00208)*

## New metal complexes based on 2-benzazol-2-yl-1,3-tropolones and their rearrangement products

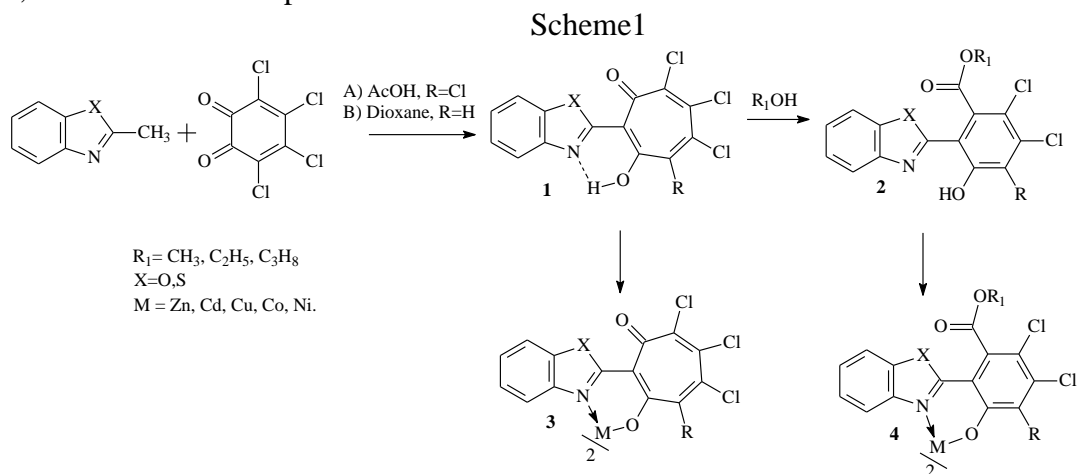
Tupaeva I.O.,<sup>1</sup> Sayapin Yu.A.,<sup>2</sup> Gusakov E.A.,<sup>1</sup> Guseva A.A.,<sup>1</sup> Sobol' D.G.,<sup>1</sup>  
Nikolaevskii S.A.,<sup>3</sup> Metelitsa A.V.,<sup>1</sup> Minkin V.I.<sup>1,2</sup>

<sup>1</sup> Institute of Physical and Organic Chemistry, Southern Federal University,  
pr. Stachki 194/2, Rostov-on-Don, 344090, Russia, e-mail: [iotupaeva@sfdedu.ru](mailto:iotupaeva@sfdedu.ru)

<sup>2</sup> Southern Scientific Center, Russian Academy of Sciences, ul. Chekhova 41, Rostov-on-Don,  
344006 Russia.

<sup>3</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
Leninskii pr. 31, Moscow, 119991 Russia.  
e-mail: [sayapin@ipoc.rsu.ru](mailto:sayapin@ipoc.rsu.ru)

In order to synthesize a ligand system exhibiting advanced capabilities to form complex, we have obtained a series of 2-benzazol-2-yl-1,3-tropolone **1** based on the acid-catalyzed reaction between *o*-chloranil and methylene-active five-membered heterocyclic compounds (2-methylbenzoxazoles, 2-methylbenzothiazoles) and products of their rearrangement **2** – hetaryl-substituted 2-alkoxycarbonyl-6-hydroxyphenylols (Scheme 1) [1]. Based on ligand systems **1** and **2**, we synthesized new metal complexes **3** and **4** (M = Zn, Cd, Cu, Co, Ni) [2]. By analogy with photochromic spiropyrans, the obtained metal complexes can be considered as spirocyclic systems, with metall ion as spiroatom.



The structures of new compounds were confirmed by NMR <sup>1</sup>H, <sup>13</sup>C, IR-spectroscopy, high resolution mass spectrometry, elemental analysis and X-ray analysis (for key organic and most of coordination compounds). Absorption and fluorescent properties of the compounds obtained were studied by the methods of stationary and time resolved spectroscopy [1,2].

*The reported study was funded by RFBR according to the research project  
№ 18-33-01137*

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## Formation and structural characteristics of solid solutions in (1-x) (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub>- x (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>

Bronnikova S.I.<sup>1</sup>, Fortalnova E.A.<sup>1,2</sup>, Safronenko M.G.<sup>1</sup>, Politova E.D.<sup>2</sup>

<sup>1</sup> Peoples' Friendship University of Russia (RUDN University), 117198,  
Miklukho-Maklaya str. 6, Moscow, Russia; e-mail:

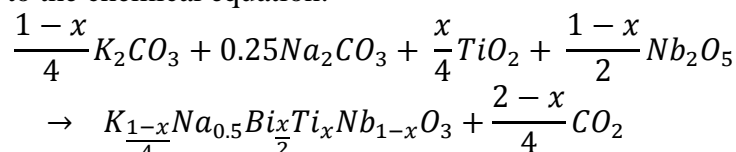
<sup>2</sup> L.Ya.Karpov Institute of Physical Chemistry, 105064, Obukha s.-st., 3, Moscow, Russia  
e-mail: chemistann@gmail.com

In the last decade, interest in the development of new materials capable of replacing the widely used lead containing phases based on lead zirconate-titanate Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub> (PZT) has increased.

The most prospective materials for PZT substitution are ceramics based on (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> (KNN), (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> (NBT) and (K<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> (KBT) with perovskite structure [1,2]. KNN is characterized by the high temperature of phase transition (~ 420°C), large values of dielectric and piezoelectricity characteristics. However, it is difficult enough to obtain its dense ceramic. KBT ceramics has a good sintering along with high Curie temperature (~ 320°C) and large value of dielectric permittivity.

That is why the investigation of phase formation in the (1-x)KNN – xKBT system, where 0.0 ≤ x ≤ 0.1 at Δx = 0.02, has an interest considering the advantages of both phases.

The samples were obtained by the solid state reactions method. The carbonates of potassium and sodium and oxides of bismuth(III), titanium(IV), niobium(V) were used as a starting reagents, according to the chemical equation:



The muffle furnace was used for temperature treatment of regrinded and pressed initial mixtures at 800 and 950°C.

According to the X-ray data (DRON-7, CuK<sub>α</sub>-radiation), after the second heating at 950°C, all the samples are of single phase and their crystal structure belongs to perovskite type. These results are confirmed by the FTIR-spectroscopy data (Nicolet 6700 (Pike), 4000 - 400 cm<sup>-1</sup>, diamond).

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# Poster Session



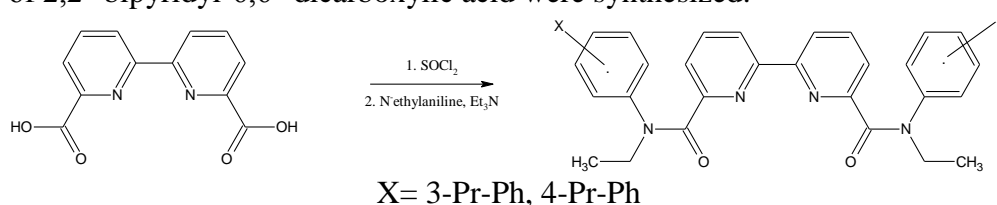
## Complexes of lanthanide nitrates with bis(*n*-ethyl-3(4)-propylanilide) of 2,2'-bipyridyl-6,6'-dicarboxylic acid. Investigation of luminescent properties

Abramova O.A., Ivanov A.V., Kharcheva A.V., Borisova N.E.

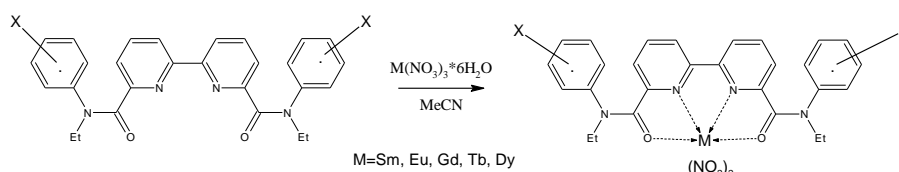
*Lomonosov Moscow State University, Moscow, Russia*  
e-mail: olga.abramova.msu@gmail.com

The binding of f-block elements by ligands of O,N,N, O-type, possessing both hard (O) and soft (N) binding centers have been studied thoroughly [1],[2]. These ligands can be used to selective separation of lanthanides and actinides [3],[4]. The aim of the research as the creation of new complexes containing propyl group in meta- and para-position and the investigation of the photophysical properties of their complexes with f-block elements.

Starting from the substituted 3-propyl-N-ethylaniline and 4-propyl-N-ethylaniline two diamides of 2,2'-bipyridyl-6,6'-dicarboxylic acid were synthesized:



The synthesized ligands reacts with lanthanides nitrates in acetonitrile with the formation of corresponding mononuclear complexes:



The composition and structure of the resulting compounds were confirmed by mass spectrometry. Also, their luminescent properties were investigated.

*The results have been obtained under support of the RSF  
grant no. 16-13-10451*

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## **Wet synthesis and characterization of hybrid nanopowders based on oxygen-free graphene and ZrO<sub>2</sub>**

Afzal A.M.<sup>1,2</sup>, Trusova E.A.<sup>2</sup>, Kirichenko A.N.<sup>3</sup>, Titov D.D.<sup>2</sup>, Polikarpov K.V.<sup>1,4</sup>,  
Safronenko M.G.<sup>1</sup>

<sup>1</sup>*Peoples' Friendship University of Russia, 6 Miklukho-Maklaya str., Moscow 117198, Russia*

<sup>2</sup>*Institution of the Russian Academy of Sciences A.A. Baikov Institute of Metallurgy and Materials Science of RAS, 49 Leninsky pr., Moscow 119334, Russia*

<sup>3</sup>*Technological Institute for Superhard and Novel Carbon Materials, 7a Tsentralnaya str., Troitsk, Moscow 142190, Russia*

<sup>4</sup>*Dmitry Mendeleev University of Chemical Technology of Russia, 9 Miusskaya sq., Moscow 125047, Russia*

*e-mail: asya.afzal@mail.ru*

In the last decade, the growing interest of researchers has been turned to graphene-ZrO<sub>2</sub> hybrids, as promising raw materials designed to produce new functional materials of a wide range of purposes: fuel cells, solar cells, supercapacitors, electronic devices, catalysts, thermal barrier coatings, biocompatible matrix for protein immobilization, transistors. We present a wet method for the synthesis of graphene-ZrO<sub>2</sub> hybrid nanostructures with homogeneous dispersion of graphene and ZrO<sub>2</sub> crystallites in the material volume. A oxygen-free graphene suspension in N,N-dimethyloctylamine-aqua emulsion was obtained from synthetic graphite by ultrasonic treatment [1] and used in the further syntheses [2]. As-prepared suspension of ZrO<sub>2</sub> nanopowder calcined at 500°C with crystallite sizes of 10-15 nm [3] was combined with sedimented and decanted graphene suspension under heating and stirring. Because the graphene sheets fixation on ZrO<sub>2</sub> crystallites surface, the graphene shells formed substantially around each ZrO<sub>2</sub> crystallite. Further, the hybrid structure formed from such fragments. Subsequent heat treatment at 400°C results in a nanostructured hybrid with high chemical homogeneity. The specific surface of the hybrids with a graphene content of 3.5–3.6 wt.% increases one and a half times as compared with the initial ZrO<sub>2</sub> nanopowder. The absence of new chemical bonds in the hybrid was proved by the vibrational spectroscopy methods. This indicates the formation of van der Waals system and the preservation of unique electrophysical properties of graphene in its composition. In the hybrid structure, the thickness of graphene sheets does not exceed 10 (3-6) nm. The synthesized nanostructured powders with a graphene content of 1.2–3.6 wt.% were characterized using XRD, TEM, HRTEM, IR-, UV-Vis-, Raman spectroscopy, N<sub>2</sub> adsorption-desorption, elemental analysis. Also, comparative rheological studies of single ZrO<sub>2</sub> nanopowder and synthesized graphene-ZrO<sub>2</sub> hybrids were carried out. These powders are the promising raw materials for (photo)catalysts and fine-grained ceramics of a wide range of applications.

*E.A. Trusova and A.N. Kirichenko thank Russian Foundation for Basic Research for the financial support of the study (Grant No: 17-02-00759\_a)*

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## **Phase equilibrium in systems MnSe-Bi**

Ajdardova D.S., Maksudova T.F., Huseynova E.S., Rahimova V.M., Mammadov Sh.H.,  
Guluzade E.S.

*Academician M.Nagiyev Institute of Catalysis and Inorganic Chemistry of ANAS  
Baku, Azerbaijan, AZ 1143, H.Javid Ave. 113,  
e-mail: chem@science.az*

There is information on the interaction in triple system Mn-Bi-Se in literature [1]. Its authors studied the section MnSe-Bi<sub>2</sub>Se<sub>3</sub> by physical-chemical analysis and state diagram, establishing the formation of two intermediate triple peritectic compounds at ratio of components 1:1 and 1:3 - MnBi<sub>2</sub>Se<sub>4</sub>, Mn<sub>3</sub>Bi<sub>2</sub>Se<sub>6</sub> correspondingly, has been constructed.

Syngony was determined and parameters of unit cell of obtained peritectic compounds were calculated. Information about binary systems which make up triple Mn-Bi-Se is presented in literature [2]. Manganese with selenium forms two compounds. One of them is MnSe, which congruently melts at a temperature higher than 1540°C with polymorphic transformations at 650°C, 850°C. Crystals of MnSe have a cubic lattice of type NaCl, where  $a=5,46 \text{ \AA}$ .

The section MnSe-Bi was studied to detect the character of chemical interaction in triple system Mn-Bi-Se. The investigation of alloys of the system was conducted by methods of physical-chemical analysis: differential-thermal (DTA), X-ray phase, microstructural (MSA) analyses and by measuring micro hardness. During synthesis of alloys we used Bi of type Bi-000; selenium rectifier (frequency 99.9998) and manganese - electrolytic.

Obtaining of complex selenides of manganese has experimental difficulties due to high reactivity of manganese with container material, that's why synthesis of alloys is conducted in graphitized quartz ampoules pumped off till residual pressure  $10^{-3}$  mm of mercury. Ampoule was heated in one temperature furnace vertical at temperatures 100°C higher than liquidus with further annealing one month at temperatures 50°C lower than solidus (150°C). Equilibrium was controlled by measuring micro hardness by its unchanged values.

According to the data of DTA in alloys of system MnSe-Bi in manganese-rich region besides endoeffects of liquidus and solidus, effects of corresponding polymorphous conversions of manganese were observed thermograms. They were carried out at low temperatures by metathetical reactions at lower temperatures than for MnSe. Transition of  $\gamma$ -MnSe to  $\beta$ -MnSe modification in the system occurs at 780°C, but in  $\alpha$  - MnSe it is at 550°C. At the range of concentration 10 mol% of MnSe only two effects are fixed in alloys, the higher one conforms to liquidus, but the other one corresponds to eutectic equilibrium and has similar stopping temperature at 250°C (content of eutectic 98 mol% Bi).

MSA data shows the existence of two phases. Determination of micro hardness of alloys showed that two rows of values were obtained: 140 kG/mm<sup>2</sup> (MnSe) and 90 kG/mm<sup>2</sup> (Bi). According to the results of thermal analysis state diagram of MnSe-Bi was plotted.

State diagram was confirmed by the data on determination of micro hardness, MSA and X-ray analysis. Liquidus of the section MnSe-Bi consists of two branches of initial crystallization of phases.

The section MnSe-Bi is quasibinary section of triple system Mn-Bi-Se and is related to eutectic type.

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## **Synthesis and structural-chemical study of phthalate and terephthalate Cr(II) in aqueous environment**

Usubaliyev B.T., Munshiyeva M.K., Aliyeva G.M., Rahmanova S.Y., Mammadova G.F.

*Academician M.Nagiyev Institute of Catalysis and Inorganic Chemistry of NAS of Azerbaijan,  
Baku, Azerbaijan, H.Javid Ave. 113,  
e-mail: qudrataliyeva@gmail.com*

Earlier we have synthesized and studied compounds of phthalic and terephthalic acids with transition metals. It was established that these metals with mentioned acids form polymer-laminated channel structure [1].

Syntheses were conducted using the known method [2]. Initial substances were o- $\text{C}_6\text{H}_4(\text{COOH})_2$  (phthalic acid), p- $\text{C}_6\text{H}_4(\text{COOH})_2$  (terephthalic acid),  $\text{CrSO}_4$ ,  $\text{NaHCO}_3$  qualification of chemically pure (GOST 3759-75). For synthesis we took 1,661 g (0,01 mol) of phthalic or terephthalic acids to which 100ml of distilled water and then 1,680 g (0,02 mol) of powder of sodium hydrogen carbonate were added in portions with heating ( $80^\circ\text{C}$ ). After full dissolution of acids 1,480 g (0,01 mol) of  $\text{CrSO}_4$  was added, and were heated up to boiling to avoid formation of hydroxycomplexes.

During interaction of sodium salt of acids with chromic sulphate (II) first the deposit of violet color is formed. Deposit formed with terephthalate is filtered after cooling of solution and was washed with distilled water and then benzene and dried on a filter-paper at  $40\text{-}50^\circ\text{C}$ .

The deposit formed with phthalate does not pass through filter, that's why we could not filter it. In aqueous environment this deposit gradually changes its color to dark green. Crystals were deposited from dark green solution. Filtered and dried crystals began to jump on filter-paper and the heat flow is emitted from them. This process continued nearly three hours, that's why we called these crystals "jumping".

We were not able to explain this. But suggest that this process may be due to intracellular reconstruction of crystalline structure.

It should be emphasized that these processes (change of color, heat release) do not occur with chromium(II) terephthalate.

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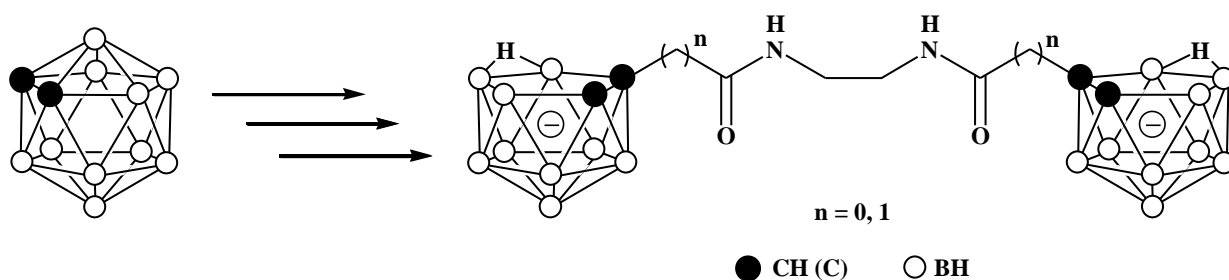
## Synthesis of carborane ligands for Gd-guided BNCT

Arsent'eva A.V., Anufriev S.A., Sivaev I.B., Bregadze V.I.

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,  
119991, Moscow, Vavilov Str. 28  
e-mail: lapppysya@mail.ru

Neutron capture cancer therapy is a promising method of cancer treatment based on selective accumulation of compounds containing non-radioactive isotopes possessing a high thermal neutron capture cross section in the tumor and their subsequent irradiation with a thermal neutron flux, which has relatively little effect on the normal tissues surrounding the tumor. At present, neutron-capture therapy is based on the use of compounds containing isotope  $^{10}\text{B}$ , which has a rather large thermal neutron capture cross section, and is capable to form stable covalent compounds, of which the most interesting are polyhedral boron hydrides containing 10 or more boron atoms per a molecule [1]. An interest in gadolinium-neutron capture therapy emerged in the early 1990s with the introduction of gadolinium-containing drugs for magnetic resonance contrast diagnostics [2]. It was supposed that dual boron-gadolinium agents could be used for MRI-guided BNCT treatment [3].

In this work we propose a possible strategy for introducing isotopes  $^{10}\text{B}$  and  $^{155}\text{Gd}$  (or  $^{157}\text{Gd}$ ) into one molecule by synthesizing carborane ligands containing carboxamide groups. This should lead to the formation of chelate complexes, in which the oxygen atom of the carboxamide substituent takes the place on free sites of gadolinium. To achieve this we synthesized *ortho*-carboranylcarboxylic acid by reacting *ortho*-carborane with butyllithium, followed by treatment with carbon dioxide. The resulting acid reacts with phosphorus pentachloride to give *ortho*-carboranylcarboxylic acid chloride, which was converted into the desired diamide by reacting with ethylene diamine. Diamide of *ortho*-carborane acetic acid was synthesized in a similar way starting from the sodium derivative of *ortho*-carborane and bromoacetic acid. The resulting diamide compounds will be converted into the corresponding *nido*-carborane ligands to form gadolinium bis(dicarbollide) complexes thereof.



*This work was supported by the Russian Foundation for Basic Research  
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## Preconcentration of thorium(IV) with sorbtion – photometric methods

Bahmanova F.N., Hajiyeva S.R., Chiragov F.M.

*Baku State University, Baku, Azerbaijan, Az 1148, Z. Khalilov, street 23  
e-mail: fidan\_chem@rambler.ru*

In the presented work has been used chelatoformed sorbent on the basis of sterol-malein anhydride copolymer. Determination was spent by spectrophotometric method. For this purpose the reagent 2,2',3,4-tetrahydroxy-3'-sulpho-5'-chlorazobenzol (R) has been used. For creation of necessary acidity we have used phyxanal HCl (pH 0-2) and ammonium-acetate buffer solutions (pH 3-11). pH solutions were measured by ionomere I-130 with a glass electrode. Optical density of solutions measured on photocalorimetre KФК 2 (l=1cm)

Table1. Spectrophotometric characteristics of complex of thorium(IV) with R

pH <sub>opt</sub>	$\lambda_{\max}$ , nm	Composition	$\epsilon_{\max} \cdot 10^{-4}$	Interval of submission to Beer's law $\mu\text{g/ml}$
4	490	1 : 2	$0.60 \pm 0.02$	0.928 – 9.280

The of sterol malein anhydride copolymer had been modifikated with 2-aminophenole4,6-disulpho acid in precense formaldegide. Sorbent synthesized by known methods [1]. The sorbtion of thorium(IV) has been studied by the synthesized sorbent with influence of acidity of environment, time, and concentration of thorium(IV), ionic force on sorbtion has been investigated.

Table 2. Optimal conditions of concentration of thorium(IV) ions by polymer sorbent in static conditions

SC, mg/g	pH <sub>opt</sub>	$\mu^*$ , mol/l	Time, clocke	d, mm
270	4	0,6	3,0	0,14

\*- ionic force which leuds to significant reduction of sorbtion

Also the desorbtion of sorbented ions of thorium(IV) has been studied. Influence of different mineral and organic acids on desorbtion of ions has been investigated. Experiment has shown, that maximal desorbtion of thorium(IV) occurs in perchloric acid.

*This work was supported by the Grant project at BSU "50 + 50"*

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**Complex compounds of Rh(III) with DNA's components**

Bondarchuk A.V., Kurasova M.N., Andreeva O.I., Esina N.Ya.

*Peoples' Friendship University of Russia (RUDN University), 117198, Moscow,  
Miklukho-Maklaya str. 6  
e-mail: heyteufel@gmail.com*

Platinum group metals represent interesting subject for research mainly because of their extraordinary ability for complexation and properties of synthesized complexes, which can be applied in various areas such as chemistry, medicine, engineering, etc. Depending upon the donor atom and pK values exhibited by the group present in the ligands, it is expected that each donor atom will bind to its own preferred metal ion [1]. Compounds of Rh(III) with nucleic acids and their derivatives have been extensively studied as it relates to the understanding of the mechanism of action of the anticancer complexes, and platinum complexes in particular [2]. Metal complexes specifically recognizing individual nucleobases (adenine, guanine, cytosine, and thymine or uracil) would provide a wide range of applications, leading us to investigate a structural basis for their base-specific metal bonding properties. For the time being rhodium complexes with a very good selectivity to some kinds of cancerous cells have been synthesized [3].

With regard to information below the assigned task was to determine composition of products, which were obtained by reaction of rhodium(III) with adenine (C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>) and cytosine (C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>O) according to approved methodology. It turned out, that the method of coordination of ligands with Rh(III)-cation and the composition of resulting compounds depend primarily on the acidity of the reaction mixture. That is why the synthesis was carried out in a slightly acidic solution (pH = 5) to prevent hydrolysis of rhodium(III) chloride.

The synthesis of compounds was carried out following these schemes:



The solutions were treated by by an alcohol-acetone mixture and precipitates of orange (I) and light-brown (II) colors were obtained. Both proved to be insoluble in organic solvents (acetone, ether, chloroform) and poorly soluble in water.

IR-spectra of both compounds show bidentate ligands coordination by N(3) and N(7) in adenine and by heterocyclic nitrogen and C=O group in cytosine.

Formulae of complexes are calculated based on analysis results and are preliminary requiring further investigation.

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## Synthesis and structure of organoantimony derivatives of 2,5-dinitrophenol

Efremov A.N., Sharutin V.V., Sharutina O.K.

South Ural State University (National Research University),  
454080, Chelyabinsk, Lenin Avenue, 76  
e-mail: efremov\_an94@mail.ru

Currently, organic compounds of antimony are being intensively studied, with special attention being paid to tri- and tetraarylantimony aroxides, of which the 2,5-dinitrophenol derivatives are less studied.

$\mu_2$ -Oxobis[(2,5-dinitrophenoxo)triphenylantimony] (1) and  $\mu_2$ -oxobis[(2,5-dinitrophenoxo)tris(*para*-tolyl)antimony] (2) were synthesized by the oxidative addition reaction between triphenyl- and tris(*para*-tolyl)antimony, 2,5-dinitrophenol and *tert*-butylhydroperoxide (1:1:1 mol.) in diethyl ether. After recrystallization of the solid residue from a benzene–isopropanol mixture (2:1), crystals suitable for X-ray diffraction analysis were obtained in a yield of up to 87%. This method of synthesis is one-stage and is characterized by mild reaction conditions (20 °C, 12 h).

Tetraphenyl- and tetra(*para*-tolyl)antimony 2,5-dinitrophenoxides were obtained by a substitution reaction between pentaphenyl- and penta(*para*-tolyl)antimony and 2,5-dinitrophenol (1:1 mol.) in benzene with a yield of up to 95% and by the ligand redistribution reactions between compounds 1, 2 and pentaarylantimony with a yield of up to 92%.

According to X-ray diffraction data, the molecules of  $\mu_2$ -oxobis[(2,5-dinitrophenoxo)triarylantimony] have an angular structure of the SbOSb fragment with a bridging oxygen atom (figure).

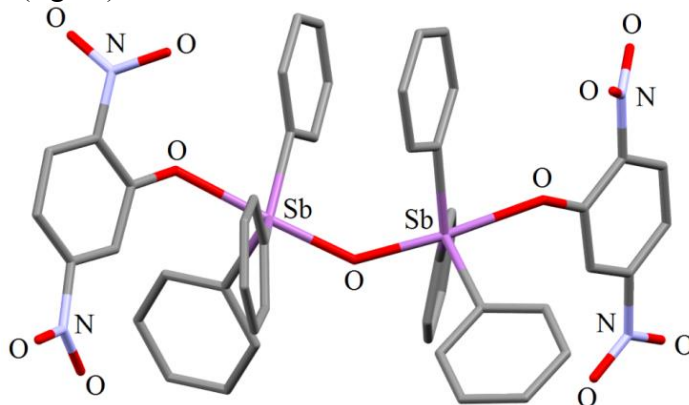


Fig. Molecular structure of  $\mu_2$ -oxobis[(2,5-dinitrophenoxo)triphenylantimony]

The antimony atoms have a distorted trigonal-bipyramidal coordination with oxygen atoms in axial positions. The terminal Sb–O bonds are longer than the Sb–O bonds with a bridging oxygen atom. A similar coordination of an antimony atom with an oxygen atom of an aroxide ligand and a carbon atom of aryl ligand in axial positions is observed in molecules of tetraarylantimony 2,5-dinitrophenoxides. The equatorial substituents are closer to the central atom than the axial ones. The antimony atoms are deviated from the equatorial plane  $C_3$  towards the carbon atom in the axial position by no more than 0.317 Å.

Molecular packing in crystals of the obtained compounds is characterized by the presence of weak intermolecular contacts  $C(Ph)\cdots H$ ,  $N-O\cdots H$  and the stacking effect. In all structures, intramolecular interactions  $C-O\cdots O-N$  are observed.

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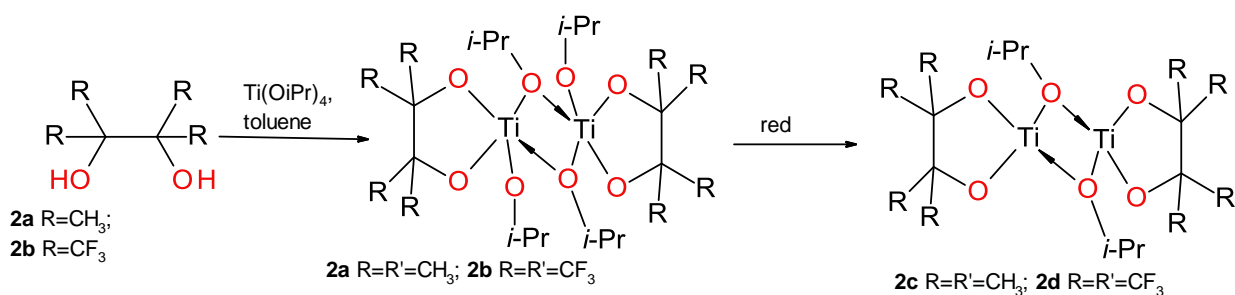
## Novel titanium(IV, III) complexes with 1,2-diolate ligands: synthesis, structure and catalytic activities polyethylene production

Gagieva S.Ch.<sup>a,b</sup>, Tuskaev V.A.<sup>a,b</sup>

<sup>a</sup>Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation

<sup>b</sup>A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation

A series of titanium(IV) **2a,b** and titanium(III) complexes **2c,d** stabilized by 1,2-diolate ligands **1 a,b** have been synthesized. Structures of complexes **2a** and **2c** have been determined by X-ray diffraction. Titanium atoms in these complexes have a distorted square-pyramidal environment created by four oxygen atoms. All resulting complexes are highly active in ethylene polymerization in the presence of {3Et<sub>2</sub>AlCl + MgBu<sub>2</sub>} or {1.5Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> + MgBu<sub>2</sub>} binary co-catalysts. In the latter case, higher molecular weights of UHMWPE samples (up to 7.7 10<sup>6</sup> g/mole) are achieved.



The present work aims to investigate the relationship between the structures of novel 5-membered diolate titanium(IV) complexes and their activity in ethylene polymerization, and mainly with their ability to catalyze the production of disentangled UHMWPE.

It is known that the introduction of highly fluorinated fragments into the diol ligands significantly increases their acidity.

Alkoxo-titanium complexes have been obtained by the interaction of toluene solutions of ligands **1a,b** with titanium(IV) tetraisopropoxide at room temperature. The resultant complexes **2a-d** have been identified on the basis of <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra, IR spectroscopy and elemental analysis.

All complexes reported herein have been tested for their ability to catalyze the ethylene polymerization. The polymerization was carried out under the same conditions such as temperature, Al/Ti ratio, solvent and ethylene pressure. The most relevant results of ethylene polymerization using pre-catalysts **3a-d** in the presence of Et<sub>2</sub>AlCl or Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> as co-catalyst have demonstrated rather low catalytic activity and yielded only the trace amounts of the polyethylene. Introduction of dibutylmagnesium to the catalytic systems containing aluminum alkyl chlorides leads to a significant increase in activity (up to 3700 kg of PE mol<sup>-1</sup>h<sup>-1</sup> atm<sup>-1</sup>).

*This work was supported by the Russian Foundation for Basic Research (grants № 17-03-00234 and 19-03-00312)*

## The synthesis of rhodium(III) complex compounds with aspartic acid and threonine

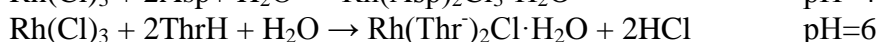
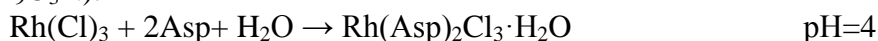
Godzishvskaya A.A., Kurasova M.N., Andreeva O.I., Esina N.Ya.

Peoples' Friendship University of Russia (RUDN University), 117198, Moscow,  
Miklukho-Maklaya str. 6  
e-mail: kovalevskaya2804@mail.ru

The first mention of rhodium(III) chloride antitumor activity is dated 1953, more than ten years earlier than cis-platinum ones. But only recently rhodium(III) complex compounds, considered as non-perspective before, received great attention. Their reactivity, coordination priority and cell penetration highly depend on ligands combination and geometry of obtained complexes [1]. The combined results of NMR spectroscopy, X-ray crystallography, and various biochemical tools of Rh(III) compounds provide incontrovertible evidence that dinuclear complexes are favorably poised to bind to purine nucleobases, DNA fragments, and double-stranded DNA [2]. On the other side, this data shows that rhodium bimetal peptides can effectively repress cell activity of chemotherapy drugs due to overlap between nuclei (Rh-Rh) and strong ligand bond [3].

The synthesis of new complex compounds with chemical structure different from cis-platinum by replacing kind of ligand can lead to creation of new compound, which has higher antitumor activity and lower toxicity. All the above is the reason of necessity to launch our studies.

We synthesized and extracted rhodium(III) complexes with aspartic acid ( $C_4H_7O_4N$ ) and threonine ( $C_4H_9O_3N$ ).



$Rh(Asp)_2Cl_3 \cdot H_2O$  is dark-brown powder,  $Rh(Thr)_2Cl \cdot H_2O$  is light-orange powder. Both complexes are well soluble in water, poorly soluble in ethyl alcohol, insoluble in acetone, ether, carbon tetrachloride, chloroform.

Chemical, thermogravimetric analysis and IR-spectroscopy were done to determine obtained compounds.

It is worth noting the explosive way of thermal decomposition of rhodium complex with threonine. Complex destruction starts at 180°C and has a strong exothermic effect. Decomposition of complex (I) undergoes more calmly; a peak of exothermic effect is indicated at 491°C.

The analysis of IR-spectra shows the difference of coordination of these two amino acids with rhodium, what is probably related to the medium's acidity in the reaction. Carboxylic groups of aspartic acid was protonated and couldn't form bonds with metal cation. Therefore, aspartic acid coordinates with rhodium as a monodentate ligand by  $NH_2$ -group, and threonine coordinates with cation by carboxylic and amino groups, forming a chelate complex.

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## Synthesis and structure of terbium and dysprosium complexes with diethyl-dithiocarbamate and bipyridine

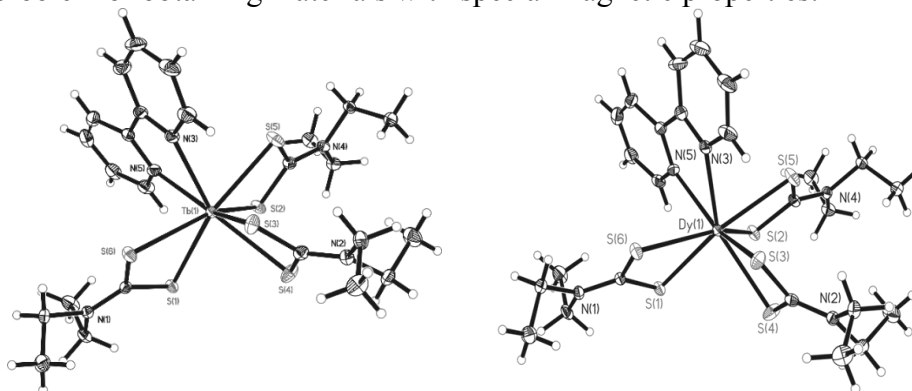
Gorshkov E.V.<sup>1,2</sup>, Korchagin D.V.<sup>1</sup>, Rudneva T.N.<sup>1</sup>

<sup>1</sup>*Institute of Problems of Chemical Physics, RAS, 142432, Chernogolovka, Moscow region, Russia*

<sup>2</sup>*Lomonosov Moscow State University, Faculty of Fundamental Physical and Chemical Engineering, 119991, GSP-1, 1-51 Leninskie Gory, Moscow, Russia*  
e-mail: 19goga99@bk.ru

The lanthanide complexes attract the researchers' attention as potential candidates for creating single-ion magnets (Ln-SIM), liquid crystals and information storage devices due to their unique properties: anisotropy of magnetic susceptibility and saturation magnetization. Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup> ions have the highest values of magnetic susceptibility anisotropy, and it is possible to create materials on their basis controlled by weak magnetic fields.

Synthesis and study of new complex compounds of the above lanthanide ions can help in solving the problem of obtaining materials with special magnetic properties.



**Fig. 1** The complex **I** (left) and **II** (right) structures

We synthesized (2,2'-dipyridyl)-tris(diethyldithiocarbamato-S,S')terbium(III) [Tb(Et<sub>2</sub>Dtc)<sub>3</sub>(bipy)] (the complex **I**) and (2,2'-dipyridyl)-tris(diethyldithiocarbamato-S,S')dysprosium(III) [Dy(Et<sub>2</sub>Dtc)<sub>3</sub>(bipy)] (the complex **II**) and investigated the molecular structure of these complexes by X-ray analysis (Fig. 1), IR- and UV-spectroscopy. The temperature dependence of the magnetic susceptibility is measured in the temperature range from 2-300 K with a constant magnetic field of 0.1 T. The  $\chi_m T$  values are 12.03 and 14.37 at room temperature. When the temperature decreases to 2 K, the value of  $\chi_m T$  decreases to  $\approx 7-9$  cm<sup>3</sup>K/mol. The plot of  $1/\chi$  (T) is described by a linear function and corresponds to the Curie law.

The field dependence of the magnetization  $M/N_A \mu_B$  at 2 K does not reach saturation up to 5 T for both complexes and has a maximum value of 6.53 and 7.30, which differs from the theoretical saturation value of 10. At the same time, the curves of the magnetization at different temperatures cannot be superimposed on each other, indicating magnetic anisotropy.

Frequency dependencies were measured for complex **II** in the absence of a field and in a constant magnetic field of 0.2 T in the temperature range 2–10 K. The actual absence of a maximum in the dependence of the imaginary part of  $\chi''$  susceptibility on frequency indicates that in the temperature and frequency range considered the complex **II** does not show the properties of a monomolecular magnet even in an applied magnetic field.

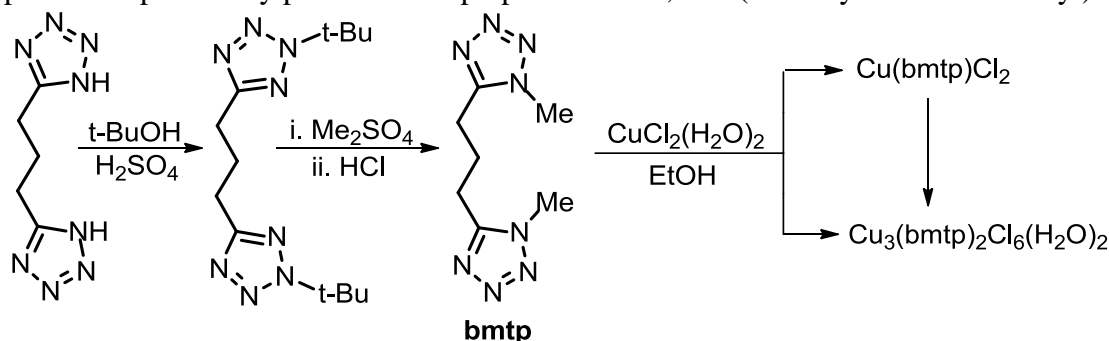
*This work was supported by the Ministry of Education and Science of Russian Federation (Agreement No. 14.W03.31.0001)*

## Synthesis and complexation of 1,3-bis(1-methyl-1*H*-tetrazol-5-yl)propane

Voitekhovich S.V., Grigoriev E.Y., Lyakhov A.S., Ivashkevich L.S.,  
Grigoriev Y.V., Ivashkevich O.A.

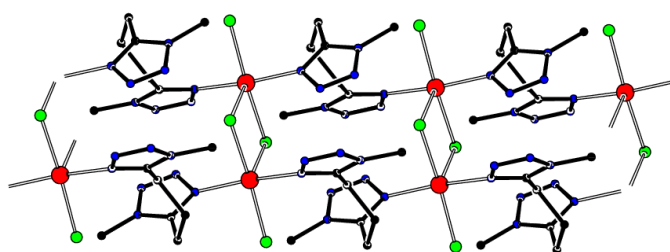
Research Institute for Physical Chemical Problems of the Belarusian State University, 220006,  
Minsk, Leningradskaya str., 14,  
e-mail: azole@bsu.by

The rational design of coordination compounds with multidentate organic ligands showing networking ability has represented active area of research in chemistry of materials. In this regard, tetrazole derivatives, in particular binuclear ones, offer an excellent class of linkers due to their capability to bridge metal atoms by means several electron-donating nitrogen atoms of heterocycle. At the same time, the data on complexation of N-substituted binuclear tetrazoles are rather restricted. Here we report preparation of a novel binuclear tetrazole, namely 1,3-bis(1-methyl-1*H*-tetrazol-5-yl)propane (bmtp), and its complexation. It was prepared by three-step procedure previously published for preparation of 1,2-bis(1-methyl-1*H*-tetrazol-5-yl)ethane [1].



Ligand bmtp was found to react with copper(II) chloride dihydrate in ethanol to give the complexes  $\text{Cu}(\text{bmtp})\text{Cl}_2$  and  $\text{Cu}_3(\text{bmtp})_2\text{Cl}_6(\text{H}_2\text{O})_2$  depending on the reagents ratio.

According to single crystal X-ray analysis,  $\text{Cu}(\text{bmtp})\text{Cl}_2$  exists in three polymorphic forms. All they are 1D coordination polymers, in which polymeric chains include dimeric fragments  $\text{Cu}_2\text{Cl}_4$ , linked to each other by two bridging ligands *via* the tetrazole ring  $\text{N}^4$  atoms.



Complex  $\text{Cu}_3(\text{bmtp})_2\text{Cl}_6(\text{H}_2\text{O})_2$  presents 3D coordination polymer. Its complex structure includes  $\text{Cu}_3\text{Cl}_6$  fragments, connected by ligands through the tetrazole ring  $\text{N}^4$  atoms as well as through the tetrazole ring  $\text{N}^3\text{--N}^4$  bridges.

The transformation of  $\text{Cu}(\text{bmtp})\text{Cl}_2$  into  $\text{Cu}_3(\text{bmtp})_2\text{Cl}_6(\text{H}_2\text{O})_2$  was observed in ethanol solution.

*This work was supported by Belarusian Republican Foundation for Fundamental Research (grant X18P-043)*

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## Heterocyclization of 2-pyridylselenenyl bromide with acetonitrile

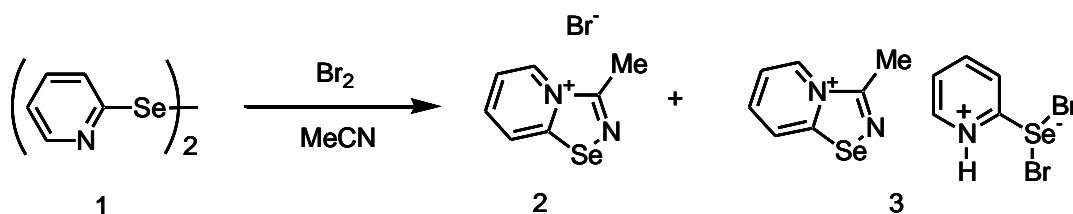
Grishina M.M., Lukiyanova J.M., Matsulevich Zh.V. Khrustalev V.N., Borisov A.V.

RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: mmgri@yandex.ru

Chemistry of selenium-containing heterocycles is currently undergoing extremely rapid development, which is associated with the reveal of a large number of representatives in this class of compounds with various types of high biological activity [1,2].

In this paper, we studied two routes for the involvement of 2-pyridineselenenyl bromide in the reaction with acetonitrile with the formation of selenium-, nitrogen-containing heterocycles – derivatives of 1,2,4-selenadiazole [3]. The first route includes the reaction between acetonitrile and pre-synthesized reagent, the second one is with the reagent prepared *in situ* by the halogenation of di(2-pyridyl) diselenide **1** in acetonitrile with bromine.

In the reaction between selenenyl bromide and acetonitrile, the product of selenating reagent cycloaddition via a carbon-nitrogen multiple bond was identified as 3-methyl[1,2,4]selenadiazolo[4,5-a]pyridinium-4 bromide **2** and obtained in 93% yield.



The heterocyclization product **2** was isolated in 84% yield from the reaction mixture after bromination of di(2-pyridyl) diselenide **1** in acetonitrile. However, a crystalline product consisted of salt **2** and T-shaped 1H-pyridine-2-selenenyl bromide **3** in equimolar ratio was also isolated in yield 8% from this reaction.

All compounds obtained were structurally characterized by X-ray diffraction.

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## Synthesis and characterization of novel bioactive bismuth(III) complexes with sterically hindered phenolic compounds

Gvozdev M.Y., Loginova N.V., Ksendzova G.A., Osipovich N.P.,  
Kovalchuk-Rabchinskaya T.V.

Belarusian State University, Research Institute for Physico-Chemical Problems of the  
Belarusian State University, 220030, Minsk, Leningradskaya str. 14  
e-mail: loginonv@gmail.com

Bismuth(III) compounds have received increased interest recently due to their multiple applications in diverse areas including medicine, materials, organic synthesis, and catalysis [1]. These compounds have been used for centuries in the treatment of a variety of microbial infections due to their high efficacy and low toxicity. More recently, the discovery that bismuth(III) compounds inhibit the growth of *Helicobacter pylori* (gram-negative bacteria which can cause peptic ulcer disease and gastric cancer) and are effective in eradicating these bacteria when administered in combination with antibiotics has rekindled interest in the use of bismuth compounds for chemotherapy [2]. An important virulence factor for these bacteria is urease, an enzyme which plays a crucial role for bacterial colonization of the human gastric mucosa. It is known that some bismuth(III) drugs (bismuth subsalicylate, colloidal bismuth subcitrate and ranitidine bismuth citrate) possess urease-inhibition activity. However, these pharmaceutical formulations are not very well defined or stable, bismuth compounds are not very soluble, and the active species are not well characterized. The hydrolysis of bismuth(III) ions and ability to expand the coordination sphere of the metal center make the control of the reactions and characterization of the bismuth(III) compounds a difficult task. A way of attenuating the hydrolysis of bismuth(III) ions in aqueous solution with the formation of the bismuthyl species is the incorporation of N, O or S donor atoms into coordinating ligands. These aspects have stimulated the development of novel bismuth-based urease inhibitors. Bismuth(III) complexes with sterically hindered phenolic compounds present a promising field of search for compounds useful in producing such antibacterial agents. Moreover, these ligands exert antioxidant and antiviral activity, while demonstrating low toxicity.

Bi(III) complexes with *N'*-(4,6-di-*tert*-butyl-2,3-dihydroxybenzylidene)isonicotinohydrazide (I), 2-(4,6-di-*tert*-butyl-2,3-dihydroxybenzylidene)hydrazine carboxamide (II), 1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-3-phenylurea (III), 1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-3-adamantylurea (IV) and a sulfur-containing sterically hindered diphenol derivative 2-(4,6-di-*tert*-butyl-2,3-dihydroxybenzylidene)hydrazine carbothioamide (V) were synthesized and characterized by means of elemental analysis, TG/DTA, FT-IR, UV-Vis, XRD and conductivity measurements. Some bismuth(III) complexes were isolated from acidic medium where phenolic ligands are protonated, and thus no bonding between the ligand and bismuth(III) was observed. The bismuth(III) ions are coordinated by chloride ions forming binuclear anions  $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ . The charge of this ion is compensated with protonated phenolic ligands (ionic interactions). According to the results of pharmacological screening bismuth(III) complexes may be considered as potential chemotherapeutic agents with urease-inhibition activity comparable to those of widely used bismuth-containing drugs.

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## Optically transparent films based on the Eu(III) mesogenic complex with intense red luminescence

Karyakin M.E., Ziyatdinova R.M., Knyazev A.A., Galyametdinov Yu.G.

Kazan National Research Technological University, 420015, Kazan, K. Marks str. 68  
e-mail: belgesto@list.ru

Unique luminescent properties of coordination lanthanide compounds open the possibility of their using as materials for optoelectronics. In contrast to organic luminescent materials and semiconductors, lanthanide compound emission spectra exhibit narrow luminescence lines, their position being determined by the central metal atom and practically independent of its coordination environment. This causes high purity of the emitted light and accurate colour rendition. However, the main disadvantages of the known compounds of lanthanides, which prevent their wider use, are low photo and thermal stability, as well as crystallizability, which make it difficult to obtain transparent film materials.

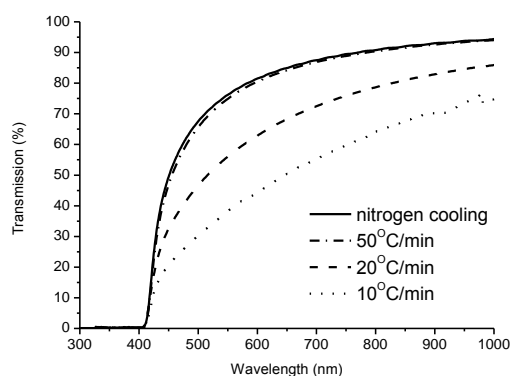


Fig. 1 The light transmission spectra of the complex Eu(12-14)Phen, depending on the cooling rate of the films

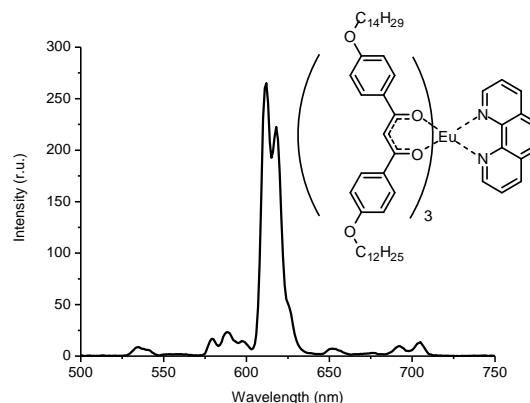


Fig. 2 The luminescence spectra of the complex Eu(12-14)Phen

We propose an approach to eliminate these drawbacks through the use of anisometric analogues of the known coordination compounds of the lanthanides. The advantage of these compounds over known analogues is the ability to form optically transparent low-defect films when cooled from the isotropic phase [1]. The light transmission of the films obtained in this way can reach 94% in almost the entire visible and near-IR range (Fig. 1). It should be noted that by changing the cooling rate, we can obtain films with different transmittance. The obtained films have effective red luminescence (Fig. 2) and can be used as emitting components for luminescent materials [2].

*This work was supported by the Ministry of Education and Science of the Russian Federation, state project № 4.5557.2017/BCH*

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## Influence of transition metals nature on the coordinating properties of the ligand di-[(2-(3,4-dimethoxy)pyridylmethyl)selenide]

Khromova O.V.<sup>1</sup>, Matsulevich Zh.V.<sup>2</sup>, Khrustalev V.N.<sup>1</sup>, Borisov A.V.<sup>2</sup>

<sup>1</sup>Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6

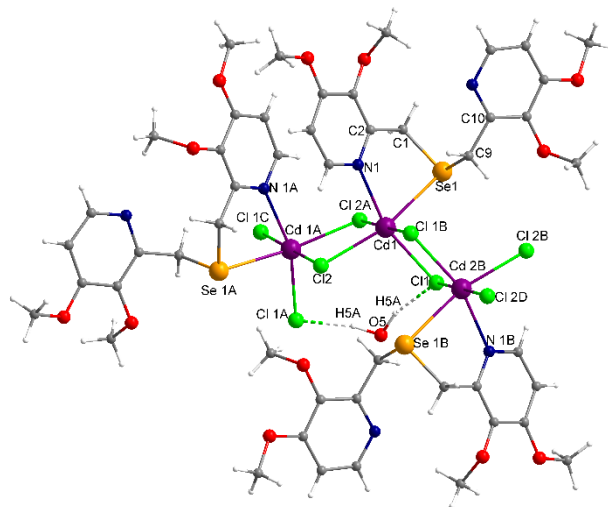
<sup>2</sup>Nizhegorodskiy gosudarstvennyy tekhnicheskii universitet im. R. Ye. Alekseyeva,

Nizhniy Novgorod, Russia

e-mail: olvichrom@gmail.com

Chalcogen-containing organic compounds and their transition metal complexes were studied in the range from antioxidant and antitumor activity to materials for optical electronics and LEDs. With current investigations of sulfur-rich metalloenzyme active sites as well as the antioxidant activity of ergothioneine, selenoneine, and thione-containing anti-thyroid drugs, the coordination chemistry of thione and selone ligands with biologically common first-row transition metals has sparked considerable recent interest [1]. In this study, we focused on the synthesis and characterization of new coordination compounds of transition metals with N,Se-donor ligand.

Novel complexes of cobalt(II), copper(II), zinc(II) and cadmium(II) with di[(2-(3,4-dimethoxy)pyridylmethyl)-selenide] were obtained and extracted. Spectral methods of analysis studied the crystal and molecular structure of the complexes and the effect of the nature of the complexing metal on the structural characteristics of the complexes was also established. It is established that the cadmium complex is a polymer with a binuclear elementary link containing chelating selenorganic ligands coordinated by selenium and nitrogen atoms (fig. 1).



**Fig. 1.** The structure of the elementary unit of the cadmium polymer complex.

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**Synthesis and analysis of the double complex salts**  
 **$[\text{RhEn}_3]_2[\text{Pd}(\text{NO}_2)_4]_x[\text{Pt}(\text{NO}_2)_4]_{3-x} \cdot n\text{H}_2\text{O}$**   
**– precursors of the three-way catalysts**

Kirilovich A.K.<sup>a</sup>, Plyusnin P.E.<sup>a,b</sup>, Shubin Yu.V.<sup>a,b</sup>, Vedyagin A.A.<sup>c</sup>, Korenev S.V.<sup>a,b</sup>

<sup>a</sup>Novosibirsk State University, Novosibirsk, Russia.

<sup>b</sup>Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia.

<sup>c</sup>Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia.

e-mail: anastasiya.kiril@mail.ru

Modern three-way catalysts (TWC) are employed for neutralization of harmful components of exhaust gases of gasoline-powered engines ( $\text{CO}$ ,  $\text{NO}_x$  and  $\text{HC}$ ). Three-way catalysts contain as active components nanoparticles of Pd and Rh [1]. Such catalysts operate at high temperature, so a major part of active component is deactivated. Also the formed ions of Rh diffuse into the support bulk and cause the phase transformation of  $\gamma$ -alumina into  $\alpha$ -phase already at a temperature of 1000 °C [2]. Also, to optimize the properties, it is possible to introduce into the composition of the catalyst a third metal, for example, Pt, which also has significant activity and was previously widely used in TWC. Since Rh-Pt and Pd-Pt are unlimited mixing systems, it is possible to increase the activity and stability of the catalysts due to synergism.

Nowadays incipient wetness impregnation of the support with aqueous solutions of precursors is used to prepare Pd-Rh catalysts. The impregnated samples are dried in furnace at 105 °C for 4 h, then heated in different temperature conditions. As the precursors, most often used are various compounds:  $\text{H}_2[\text{PdCl}_4]$ ,  $\text{H}_3[\text{RhCl}_6]$ ,  $\text{PdCl}_2 \cdot n\text{H}_2\text{O}$ ,  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{Pd}(\text{CH}_3\text{COO})_2$ ,  $\text{Rh}(\text{CH}_3\text{COO})_3$ ,  $[\text{Pd}(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ ,  $[\text{Rh}(\text{H}_2\text{O})_x(\text{NO}_3)_{6-x}]$ , etc. But the use of this approach doesn't guarantee stability of nanoparticles on the surface of support.

Prospective multicomponent precursors for the preparation of nanoscale alloys for the preparation of catalysts are double complex salts containing in their composition simultaneously the atoms of palladium, rhodium and platinum. It was shown earlier that the thermal decomposition of double complex salts deposited on the surface of the support makes it possible to obtain these metals in the state of an alloy (solid solution), which increase their catalytic activity and stability [3].

The report presents the synthesis and properties of double complex compounds with different ratio of metals. The possibility of obtaining nanoparticles of solid solutions in a Pd-Rh-Pt system with a different component ratio is shown.

The most promising compounds were used for the synthesis of bimetallic particles on the surface of oxide support. The properties of the double complex salts deposited on  $\gamma\text{-Al}_2\text{O}_3$  have been studied by a complex of physicochemical methods. It was also established that in the process of thermal decomposition it is possible to obtain alloyed bimetallic and threemetallic nanoparticles  $\text{Rh}_{0.6}\text{Pd}_{0.4-x}\text{Pt}_x$  fixed on the surface of the oxide support. The activity and stability of the resulting catalyst compositions were confirmed in model reactions of CO oxidation and hydrogenolysis of the C-C bond.

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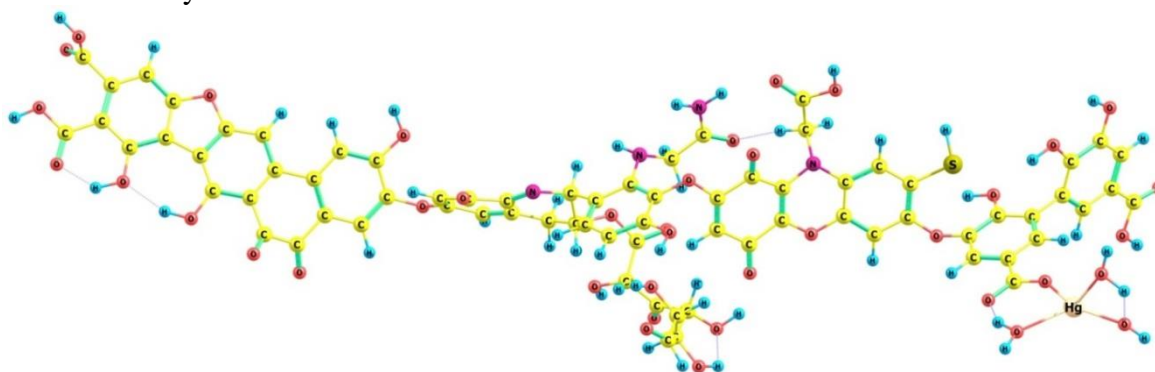
## Theoretical study of $\text{Hg}^{n+}$ complexing with humic acids

Konkova E.S.<sup>1,2</sup>, Shishilov O.N.<sup>1</sup>

<sup>1</sup> Russian Technological University – MIREA, Institute of Fine Chemical Technologies,  
Vernadskogo avenue 86, Moscow, 119571, Russia.

<sup>2</sup> Yu.A. Izrael Institute of Global Climate and Ecology  
e-mail: e.konkova.igce@gmail.com

Humic acids (HA) are widespread natural complexing agents. Their sophisticated structure is resulting in high capacity of complexing with many different substances. HA are at the same time consist of aromatic and aliphatic structural units that contain oxygen, nitrogen and sulfur functional groups. As a result, HA are to incline form hydrogen bonds with many organic substances and complex most of heavy metals. Humic acids can be used for wastewater treatment to remove not only heavy metals but wide row of organic substances as well, e.g. pesticides, etc., can bind of that pollutants in the natural environment, accumulate and store them in the form of complexes and prevent their further spread into the surroundings. In the present study we concentrate on possible complexation of mercury as one of the most dangerous polluting metals with humic acids. Main goals of the study ware to reveal possible binding sites in humic acids for  $\text{Hg}^{n+}$  ions and to evaluate stability of corresponding complexes. Humic acids are high molecular weight compounds with irregular structure and variable composition, so for theoretical study simplified model was Stevenson's of humic acids structure [1,2,3], however, these model is not optimal for consideration of mercury binding, first of all, due to lack of SH-groups, which are considered to be most favorable binding site for  $\text{Hg}^{n+}$  ions. So at the first step we modified Stevenson's model with SH-group and determined the most probable location of it in the molecule structure. Then we estimated energies for different isomers of corresponding  $\text{Hg}^{n+}$  complexes. All calculations were performed in the frame of scalar-relativistic approximation of DFT method in the Priroda program [4]. Studied complexes are  $[(\text{HA}_{\text{H}})\text{Hg}(\text{OH})(\text{H}_2\text{O})_2]$  (see figure below), where  $\text{HA}_{\text{H}}$  is deprotonated humic acid and formal oxidation state of mercury is (+2). PBE exchange-correlation functional and basis set SBK were used. Energy of isomers with Hg coordinated to sulfur of thiolate groups were found to be at least 10 kcal/mole lower in energy against isomers with Hg coordinated to oxygen of hydroxyl or carboxylate groups, so we can conclude that SH-groups are most likely binding sites for Hg as it could be expected. We are planning to check results of this theoretical investigation in experiment with natural humic acids and synthetic humic like substances.



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## Aluminium phthalocyanine complexes: selective synthesis and properties

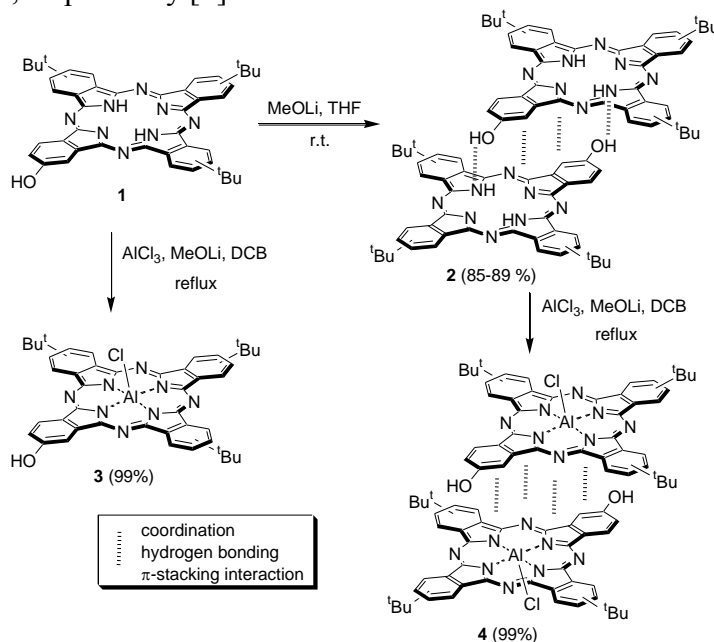
Korostei Yu.S.,<sup>a,b</sup> Tolbin A.Yu.,<sup>a,b</sup> Dzuban A.V.,<sup>b</sup> Pushkarev V.E.,<sup>a,b</sup> Sedova M.V.,<sup>c</sup>  
Maklakov S.S.,<sup>c</sup> Tomilova L.G.<sup>a,b</sup>

<sup>a</sup>*Institute of Physiologically Active Compounds, Russian Academy of Sciences, 1 Severnyi Proezd, 142432 Chernogolovka, Moscow Region, Russian Federation*

<sup>b</sup>*Department of Chemistry, M.V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation*

<sup>c</sup>*Institute for Theoretical and Applied Electromagnetics, Russian Academy of Sciences, Izhorskaya St. 13, 125412, Moscow, Russian Federation*  
e-mail: jkorostei@mail.ru

Efficient direct synthesis of new monomeric and stable *J*-type dimeric species of 2-hydroxy-9(10),16(17),23(24)-tri-*tert*-butylphthalocyaninato aluminum with high yields, including preparation of the corresponding dimeric free-base ligand at ambient conditions, has been developed. The compounds were characterized by the UV–Vis spectroscopy as well as MALDI-TOF mass-spectrometry and thermogravimetry data. The in-depth study of the produced aluminum complexes by 1D and 2D <sup>1</sup>H NMR techniques was carried out owing to elaboration of disaggregating CD<sub>3</sub>ONa/CD<sub>3</sub>OD system featuring formation of phthalocyanine phenolate anions. Surface morphology of thin films formed by the complexes was studied by scanning (FE-SEM) and atomic force (AFM) microscopies. According to the AFM data, the films are characterized by granular structure, while the grain diameter accounts for 50 and 100 nm for the monomeric and dimeric complex, respectively [1].



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## Correlation between charge transfer degree and ionization potentials of the donors in the adducts of rare earth 3,5-dinitrobenzoates with aminobenzenes

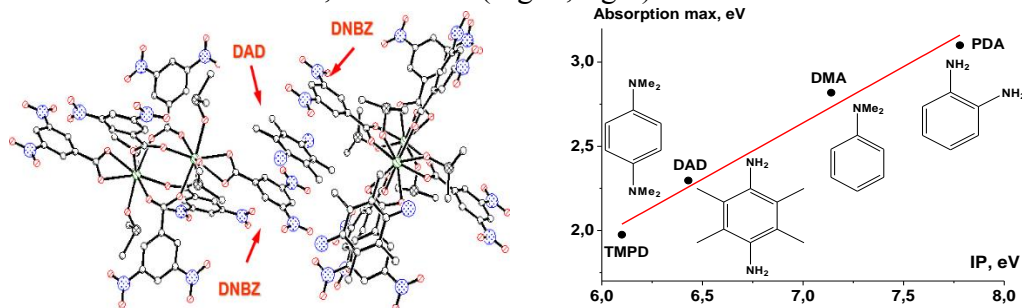
Koroteev P.S., Efimov N.N., Ilyukhin A.B., Minin V.V., Dobrokhotova Zh.V.

N.S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences,  
119991, Leninsky prosp., 31, Moscow, Russia.

e-mail: pskoroteev@list.ru

Molecular charge transfer complexes (CTC) have long been known [1,2]. Such compounds are formed of two electrically neutral molecules, one of which (a donor) has excess electron density in comparison with the other one, an acceptor. Electron transfer in CTC can vary from negligible to almost complete, in the latter case the complexes exhibit distinct paramagnetism.

Typical CTC are built of two single organic moieties. Recently we have obtained and studied CTC containing binuclear lanthanide 3,5-dinitrobenzoates and *N,N*-dimethylaniline [3] ( $[\text{Ln}_2(\text{DNB})_6(\text{DMSO})_4] \cdot x\text{Me}_2\text{NPh}$ ;  $x = 3, 4$ , or  $5$ ;  $\text{DNB} = 3,5\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{CO}_2^-$ ) or *N,N,N',N'*-tetramethylphenylenediamine [4] ( $[\text{Ln}_2(\text{DNB})_6(\text{DMSO})_4] \cdot x1,4\text{-(Me}_2\text{N)}_2\text{C}_6\text{H}_4 \cdot y\text{MeCN}$ ;  $x = 1$  or  $3$ ;  $y = 1$  or  $0$ ). Structures of those hybrid compounds are formed due to stacking interactions between donor aromatic amine molecules and acceptor 3,5-dinitrobenzoate fragments. With use of *p*-diaminotetramethylbenzene (diaminodurene, DAD), a new series of isostructural CTC,  $[\text{Ln}_2(\text{DNB})_6(\text{DMSO})_4] \cdot 4\text{DAD}$  ( $\text{Ln} = \text{Sm}(1), \text{Gd}(2), \text{Tb}(3), \text{Dy}(4), \text{Ho}(5), \text{Er}(6), \text{Y}(7)$ ;  $\text{DAD} = 1,4\text{-(H}_2\text{N)}_2\text{C}_6\text{Me}_4$ ), was prepared (Fig. 1, left). CT in the complexes was characterized by reflectance spectra. CT also brings about significant paramagnetism of Y compound; thus, a new way to activate magnetically the ligands in metal complexes is found. Using 1,2-phenylenediamine (PDA), the complexes  $[\text{Ln}_2(\text{DNB})_6(\text{PDA})_2(\text{DMSO})_2]_2$ , in which PDA takes part in CT interaction with DNB ligand and coordinates  $\text{Ln}^{3+}$  ion via  $\text{NH}_2$  group at the same time, were obtained. A correlation between the maxima of CT absorption band in reflectance spectra and the ionization potentials of the donor molecules, was found (Fig. 1, right).



**Fig. 1.** Fragment of the supramolecular structures of compounds 1-7 (left), and correlation between ionization potentials (IP) of the donors and CT bands maxima in reflectance spectra of the complexes with different aminobenzene derivatives as donors (right).

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

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## Synthesis and photophysical properties of Ru(II)-terpyridine complexes

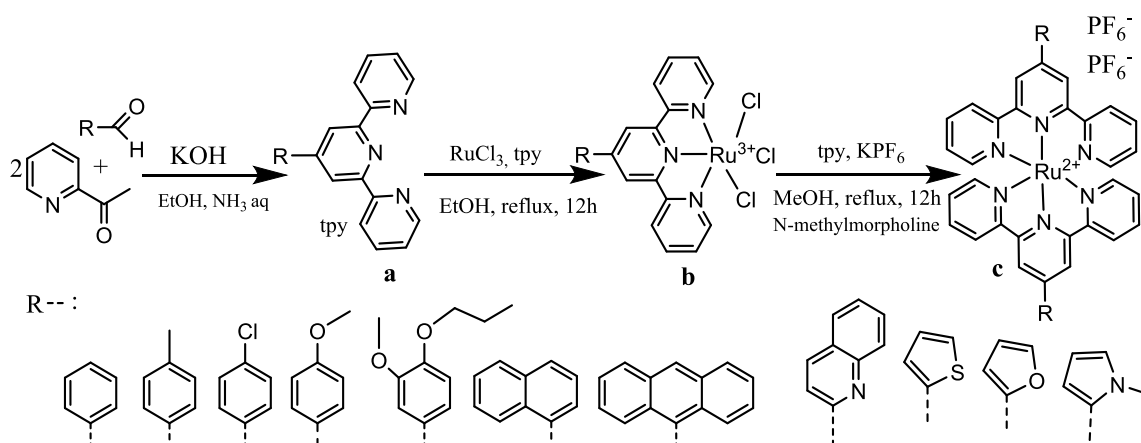
Kostenko E.A., Eliseenkov E.V., Boyarskiy V.P.

Saint Petersburg State University, 7/9 Universitetskaya Nab., St. Petersburg 199034, Russia  
e-mail: mausjan@yandex.ru

Terpyridines (tpy) as ligands are noticeable building blocks in organic and inorganic chemistry because of their ability to non-covalent interactions, directional hydrogen bonding and coordination properties. Considerable attention has also been drawn to their photophysical and electrochemical properties. A lot of studies revealed that electron withdrawing and electron-donating substituents may be used to alter the redox and photophysical properties of free terpyridines and their transition metal complexes. The donor-acceptor system has been proven to be an effective approach to adjust the optical properties of organic and organic-inorganic hybrid materials.

Metal complexes based on terpyridine ligands or their derivatives are extensively investigated due to wide potential applications in catalysis, molecular electronics and supramolecular chemistry [1]. Among terpyridine complexes special attention is paid to complexes with ruthenium(II) due to their photophysical and redox properties.

As a part of our research on this topic we synthesized a series of terpyridine based Ru(II)-complexes (including not previously described). We obtained ligands **a** with varied aryl substituents (yields = 22–67%) and the corresponding homoleptic ruthenium ion complexes **c** in two stages (yields = 32–98%).



Absorption and luminescence spectra were measured for all complexes, the lifetime of the excited state and the quantum yield also were measured. The average lifetimes of the excited state are 3.7–4.9 ns respectively.

*The authors greatly appreciate financial support from the Russian Science Foundation, grant 18-03-00119. The work was carried out using equipment of Centers for Magnetic Resonance, for Optical and Laser Materials Research, and for Chemical Analysis and Materials Research (Research Park of St. Petersburg State University)*

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## **Copper(II)-histidine complex formation specifics**

Kozhukhova I.I., Esina N.Ya., Kurasova M.N., Andreeva O.I.

*Peoples' Friendship University of Russia (RUDN University), 117198, Moscow,  
Miklukho-Maklaya str. 6  
e-mail: kozhukhova.1995@mail.ru*

Peptides, widely used as antiviral drugs, are complex protein molecules whose terminal units contain amino acids, histidine in particular. The efficiency of transport of these compounds into cells significantly depends on the compactness of the macromolecule, which greatly increases with the introduction of biometal cations into the structure [1]. Histidine (HisH) is coordinated by  $\text{Cu}^{2+}$  binuclear centers of cytochrome *C* oxidase; binds to  $\text{Cu}^{2+}$  in many metalloenzymes, such as hemocyanins [2]. Studies have shown that during formation of complexes with transition metals, peptide interacts with copper cation through the His-tag fragment. Despite large number of works devoted to the study of interaction of copper(II) ions with amino acids, structure and properties of compounds are not well understood due to the difficulty of isolation in crystalline state.

The purpose of this study is to examine the features of complex formation of copper with histidine and to determine synthesis conditions for preparation of crystal structures.

Coordination compound of copper(II) with histidine  $\text{Cu}(\text{His}^-)_2 \cdot 2\text{H}_2\text{O}$  was obtained by approved method [3]. Synthesized compound is a bright blue powder, soluble in water, insoluble in alcohol, ether, acetone and chloroform.

Identity of copper(II) complex synthesized is confirmed by X-ray and chemical analysis. The results of chemical analysis (found/calculated) are: Cu (14.7/15.6), C (34.6/35.1), H (5.9/5.4), N (19.8/20.5).

Thermogravimetric analysis showed, that the compound thermolysis proceeds with strong exoeffects, the destruction of the complex starts at the temperature of 175°C, the maximum effect is noted at 387°C, final product is  $\text{CuO}$ .

Three donor centers of histidine provide a wide range of coordination capabilities of this ligand, specific type of which is determined by many factors according to Pearson's theory [4]. The IR-spectra of the synthesized compound unambiguously showed the ligand tridentate: the  $\text{Cu}^{2+}$  cation coordinates the amino acid through the amino- and carboxyl groups to form a chelate and through the N3 heterocycle.

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## Luminescent materials based on an anysometric tris( $\beta$ -diketonate) europium adducts

<sup>a</sup> Krupin A.S., <sup>a</sup> Knyazev A.A., <sup>a,b</sup> Galyametdinov Yu.G.

<sup>a</sup> Kazan National Research Technological University, 420015, Kazan, K. Marx str. 68

<sup>b</sup> Kazan Physical-Technical Institute RAS, 420029, Kazan, Sibirsky tract, 10/7

e-mail: krupin\_91@mail.ru

Coordination compounds of lanthanides(III) are an interesting class of substances that can be used as efficient luminescent materials for various applications [1]. Their main property and advantage is the effective luminescence provided by the Ln(III) ion and not by organic ligands. In such compounds, a central ion possesses poor absorptive capacity, so excitation energy is transferred through surrounding organic ligands ("antenna effect"). The important advantage of anysometric lanthanide complexes is their high solubility in organic solvents and capability to incorporate, in view of some structural resemblance, namely, possessing an anisotropic form and the presence of terminal alkyl chains, into the structure of the conductive conjugated polymers [2].

A new series of anysometric Ln(III) tris( $\beta$ -diketonate) adducts with different Lewis bases has been synthesized (fig. 1). The structural features of the presented compounds allow to create vitrified optically isotropic and self-organized films with effective luminescence (fig. 2).

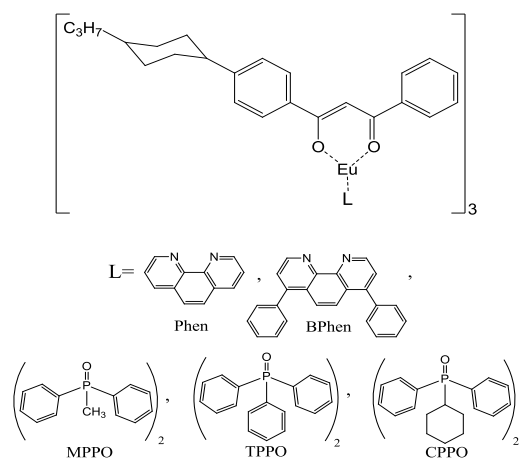


Figure 1. Chemical Structures of Eu(III) Complexes

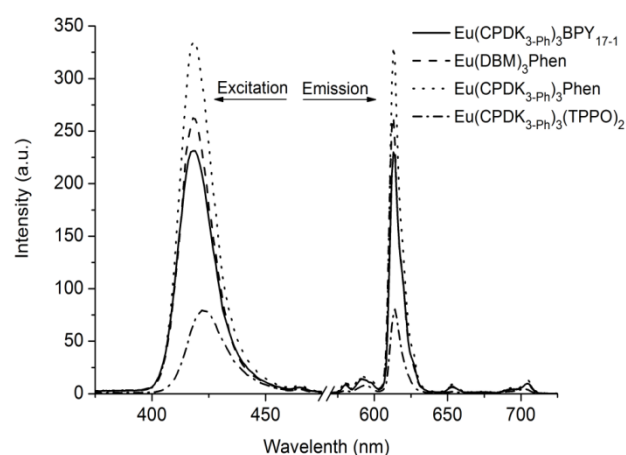


Figure 2. The excitation and luminescence spectra of Eu(III) complexes

Anisometric analogues of well-known  $\text{Eu}(\text{DBM})_3\text{Phen}$  complex have been studied to show that the geometry of a complex may exert considerable influence on the luminescence properties of the blends including a conjugated polymer and a Ln(III) complex. It is shown that in blends of PVK and some studied complexes the emission intensity per a complex mole increased by 3.9 times, and intrinsic quantum yield increased by 40% in comparison with individual compounds. The presence of alkyl and cyclohexane substituents in the structure of  $\beta$ -diketone ligands, in contrast to commercial DBM, hinders crystallization, inhibits formation of defects in the structure of films, and demonstrate good dispersibility in PVK films.

*This work was supported by the Russian Science Foundation (RSF)  
(grant № 18-13-00112)*

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## **Extractive-spectrophotometric determination of cobalt(II) with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines**

Kuliyev K.A., Verdizadeh N.A., Suleymanova G.S.

*Department of Chemistry, Azerbaijan State Pedagogical University,  
U. Gadjibekov street 68. Baku, AZ 1000, Azerbaijan  
e-mail: kerim.kuliev.69@mail.ru*

Mixed-ligand complexes of Cobalt(II) with dithiolphenol (DP) {2, 6-dithiolphenol (DTP) and its derivatives (2, 6-dithiol-4-methylphenol (DTMP), 2, 6-dithiol-4-propylphenol (DTPP), 2, 6-dithiol-4-tert-buthylphenol (DTBP)} in the presence of hydrophobic amines (Am) have been studied by spectrophotometry. As hydrophobic amine aniline (An) and N-methylaniline (mAn) were used.

Co(II) reacts with dithiolphenols (DP) and gives a yellow colored complexes. These complexes are insoluble in non-polar solvents. Chloroform, dichloroethane and chlorobenzene appeared to be the best extractants. All the further investigations were carried out with chloroform. After a single extraction with chloroform, 96.9-99.2% of cobalt was extracted as an ion associate.

The absorbance was found to be maximum in the pH range 4.1-5.6. For the formation and extraction of MLC, a 20-25-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by  $1.0 \times 10^{-3}$  M DP and  $(0.92-1.24) \times 10^{-3}$  M Am. Neither the metal ion nor the reagent has appreciable absorbance at specified wave-lengths. Hence further studies were carried out at 550-560 nm. The reagent has minimum absorbance at the maximum absorbance of the complex. Hence further absorbance measurements were made at 540 nm. The molar absorptivity of the complex was calculated with Komar method to be  $\epsilon = (2.56-3.15) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods were employed to elucidate the composition of the complex. The results suggest the complex composition of 1:2:2 (Co : DP : Am). The formation of MLC can be presented in the following way. When cobaltion interact with two molecules of DP, they form doubly-charged anionic complexes, which are extracted with two molecules of protonated Am. Formed ion-association complex between anionic chelates of cobalt(II) with DP and hydrophobic aromatic amines. The stability constant of Co(II)-DP-Am complexes was calculated and found to be  $\lg \beta = 7.19-11.25$  at room temperature.

It was found using the Nazarenko method that Co(II) in the complexes was present in the form of  $\text{Co}^{2+}$ . The number of protons replaced by cobalt in one DP molecule appeared to be one. The disappearance of the pronounced absorption bands in the  $3200-3600 \text{ cm}^{-1}$  with a maximum at  $3460 \text{ cm}^{-1}$  observed in the spectrum of DTPP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area  $2580 \text{ cm}^{-1}$  shows that one of the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at  $2380 \text{ cm}^{-1}$  indicates the presence of a protonated aniline. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Co(II) may be determined in the range  $0.05-3.2 \text{ } \mu\text{g/ml}$ . The proposed method under the already established optimum conditions was applied for the determination of Co(II) in steel, in the Sewage water and Bottom sediments.

## Perchlorinated europium, terbium and lutetium mono(phthalocyaninates): synthesis and investigation of physicochemical properties

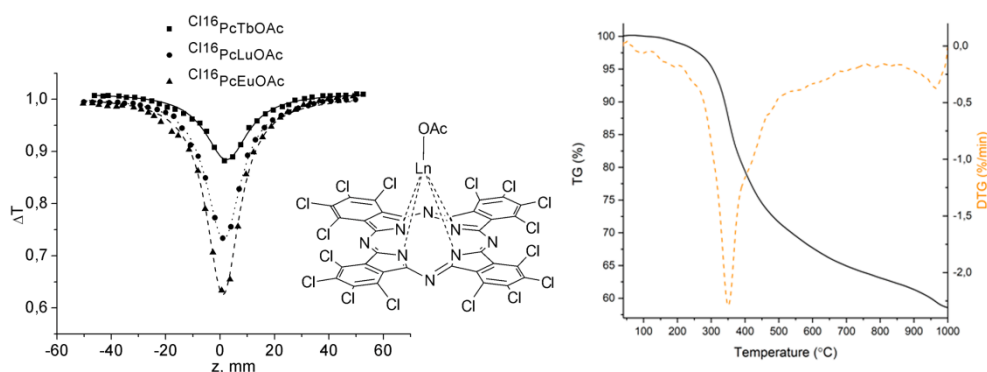
Kuzmina E.A., Dubinina T.V., Krasovskii V.I., Tomilova L.G.

Department of Chemistry, M.V. Lomonosov Moscow State University, 119991 Moscow,  
Leninskie Gory 1

e-mail: lena.kuzmina94@gmail.com

A novel hexadecachloro-substituted terbium(III) mono(phthalocyaninate) was obtained using two approaches: template synthesis and metallation of the phthalocyanine ligand (a two-stage method).

It was observed that the yield of the target complex was higher in the template approach. The terbium complex was identified by high-resolution mass-spectrometry, IR and UV/Vis spectroscopies. Sufficiently high thermal stability up to 220°C was shown for the perchlorinated europium, terbium and lutetium mono(phthalocyaninates) using thermogravimetric analysis. The linear and nonlinear optical properties of the target terbium compound were compared with the corresponding ones for Cl<sub>16</sub>PcEuOAc and Cl<sub>16</sub>PcLuOAc [1,2]. A decrease in the extinction coefficients simultaneously with the ionic radii on going from Eu<sup>3+</sup> to Lu<sup>3+</sup> was observed. This result correlates with the corresponding increase in proneness of the  $\pi$ - $\pi$  stacking interactions.



The influence the nature of the lanthanide ions on their nonlinear optical properties was investigated using the z-scan technique. The values of the absorption cross section of the first triplet excited state were determined using the z-scan technique. The highest value ( $\sigma_{T1} = 1.96 \times 10^{-16} \text{ cm}^2$ ) was observed for the terbium complex. This value is higher than the corresponding ones found for planar and sandwich-type phthalocyanines bearing electronreleasing functional groups. It can be concluded that thanks to their enhanced nonlinear optical properties and high thermal stability, the target complexes can be used for novel organic nonlinear optical materials for optoelectronic applications.

*This work was supported by the Russian Science Foundation  
(Grant 17-13-01197)*

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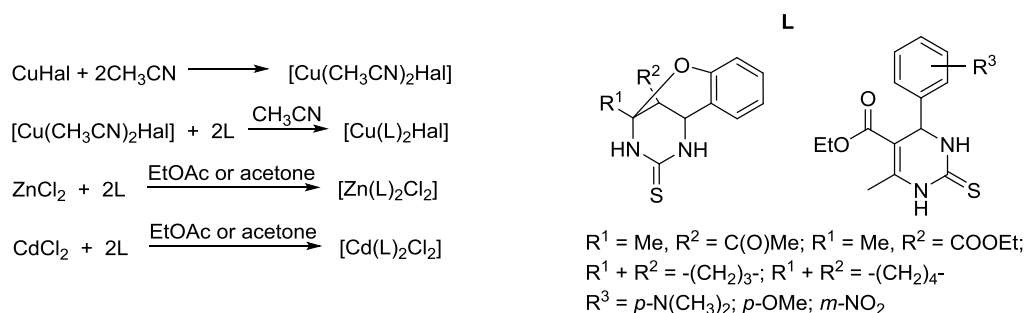
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## Coordination compounds of pyrimidine-2-thiones and [1,3,5]oxadiazocine-4-thiones

Kuzovlev A.S., Volkova D.A., Parfenova I.V., Kulakov I.V.

University of Tyumen, 625003, Tyumen, Volodarskogo str. 6  
e-mail: a.s.kuzovlev@gmail.com

Pyrimidine-2-thiones and [1,3,5]oxadiazocine-4-thiones exhibit a wide diversity of biological activities and can serve as efficient antibacterial [1], antiviral [2], antidiabetic [3] and antifungal [4] agents. Coordination significantly changes their biological, physical and chemical properties, and is therefore very attractive for the development of innovative materials. However, complexes of pyrimidine-2-thiones and [1,3,5]oxadiazocine-4-thiones remain underexplored. Thus, development of new methods for the synthesis of such coordination compounds and investigation of their properties are topical problems of modern chemistry.



The novel complexes of highly functionalized pyrimidine-2-thiones and [1,3,5]oxadiazocine-4-thiones with copper, palladium, zinc and cadmium salts were synthesized. Coordination occurs through the thiocarbamide fragments of heterocycles (proved by IR, UV, NMR spectroscopy and X-ray diffraction). Biological activity of obtained compounds was investigated. Several complexes demonstrated good antibacterial activity.

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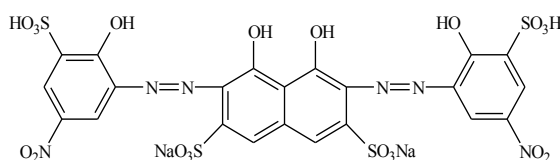
## Spectrophotometric determination of copper(II) with azo derivative of chromotropic acid in the presence of third components

Mardanova V.I., Hajiyeveva S.R., Chyragov F.M.

Baku State University, Az1148 Baku, Z.Xalilov str. 23  
e-mail: vusala\_chem@mail.ru

It is known that due to the improvement of the analytical parameters of the reaction, mixed-ligand complexes have found wide use of the spectrophotometric determination of elements. In the present work, the complex formation of copper (II) with 2,7-bis (azo-2-hydroxy-3-sulfo-5-nitrobenzene)-1,8-dihydroxy-neftalin-3,6-disulfonatrium (R) in the presence of ethylenediamine (Ed), diphenylguanidine (DFG), triphenylgufnidine (TFG), non-ionic surfactant Triton X-114 (TX-114) and dantipyrylmethane (DAM).

The reagent has been synthesized by a known method. The composition and structure of the synthesized compounds installed by elemental analysis, IR and NMR spectroscopy.



To establish the complexation of copper(II) ions with this reagent, the absorption spectra of the complexes in the presence and absence of the third components, depending on the acidity of the medium, were taken. It was studied that for complete binding of copper(II) to the complex, a double excess of the reagent is necessary. The effect of time and temperature was investigated. The correlation of components is installed by methods of Starik-Barbanel, shift of the equilibrium and isomolar series. There are determined the concentration intervals, which obey to Beer's law and also the molar coefficients of complexes are determined from curves of saturation. The results of the analysis are presented in table 1.

Complexes	pH <sub>opt</sub>	$\lambda_{\text{max}}$ , nm	$\epsilon$	M : R	Liney.grad interval. schedule, mkg/ml	Lg $\beta$
Cu-R	3	538	10400	1:2	0.12-2,32	8,75±0,05
Cu-R-Ed	1	523	13000	1:2:2	0,07-2,32	9,35±0,05
Cu-R-DFG	2	491	15500	1:2:2	0,07-2,32	9,85±0,05
Cu-R- TFG	2	572	16000	1:2:2	0,07-2,32	9,92±0,04
Cu-R- TritonX-114	1	512	15000	1:2:2	0,07-2,32	9,59±0,05
CuR-DAM	2	511	12000	1:2:2	0,07-2,32	9,09±0,03

The effect of interfering ions and masking agents has been learned. The determination of copper(II) is not interfered alkaly metals and ions of Ca(II), Ba(II), Mn(II), Cr(III), Sn(IV), Ga(III), In(III), Zr(IV) is not interfere. These methods is highly sensitive and selective. It is a very rapid and a simple technique.

The developed technique is applied to the determination of copper in peas ( $(7,58 \pm 0,02) \times 10^{-1}$ ) and buckwheat ( $(6,35 \pm 0,05) \times 10^{-1}$ ).

## Synthesis of nanostructured graphene-NiO hybrid

Mashal D.A.,<sup>1,2\*</sup> Trusova E.A.,<sup>2</sup> Kirichenko A.N.,<sup>3</sup> Polykarpov K.V.<sup>1,4</sup>  
Fedorov S.V.<sup>2</sup>, Safronenko M.G.<sup>1</sup>

<sup>1</sup>RussiaPeoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup>Institution of the Russian Academy of Sciences A.A. Baikov Institute of Metallurgy and Materials Science of RAS, 119334, Moscow, Leninsky pr. 49

<sup>3</sup>Technological Institute for Superhard and Novel Carbon Materials, 142190, Moscow Troitsk, Tsentralnaya str., 7a

<sup>4</sup>Dmitry Mendeleev University of Chemical Technology of Russia, 125047, Moscow Miusskaya sq.9

e-mail: dariosha97@yandex.ru

Magnetic nanoparticles based on graphene and NiO have been used in biomedical applications such as biosensing, drug delivery, hyperthermia, magnetic resonance imaging and cellular capture. We have developed a low cost and technologically promising method for the synthesis of nanostructured graphene-NiO composite, using a combination of sol-gel and sonochemical techniques [1]. According to the TEM and XRD data, the powder consisted of composite nanoparticles with sizes of  $\leq 15$  nm, consisting of well-crystallized NiO (96 wt.%) with Ni<sup>0</sup> impurity ( $\leq 3$  wt.%); the carbon content was  $\sim 1$  wt.%. The synthesized hybrid nanoparticles have pronounced magnetic properties. Confocal laser scanning microscopy was used to visualize the orientation of composite nanoparticles on the surface of a magnetic stirrer core (Fig. 1). The results of 3D profilometry of 5 mm<sup>2</sup> area show that hybrid nanoparticles have formed a dense shell of varying thickness (up to 4 mm) on the surface of the magnet. The shell was formed by "columns" perpendicular to the surface of the magnetic core.

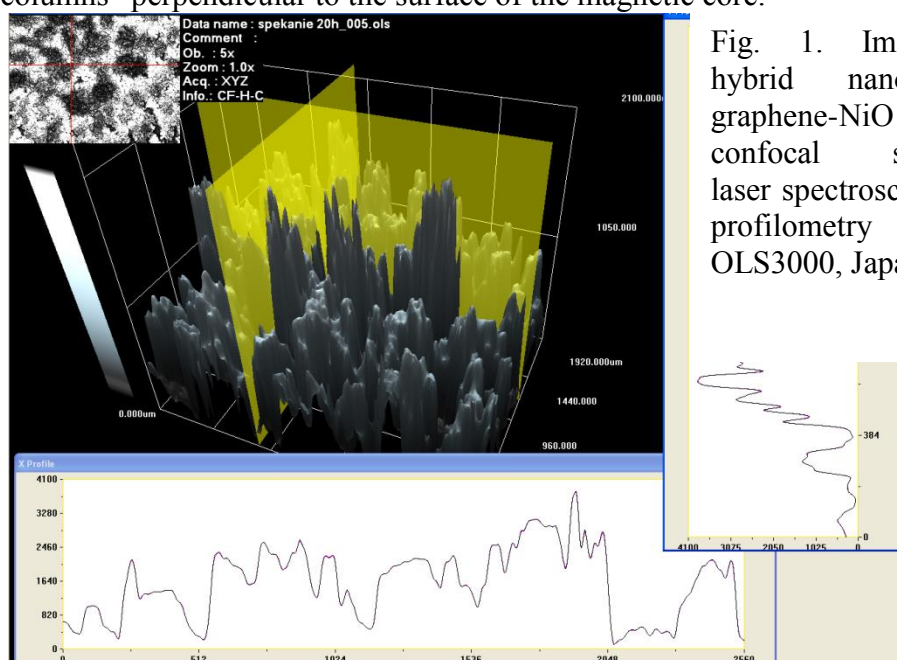


Fig. 1. Image of hybrid nanopowder graphene-NiO by confocal scanning laser spectroscopy and profilometry (LEXTOOLS3000, Japan)

The work is supported by RFBR, Grant No: 17-02-00759\_a

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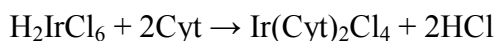
## Synthesis of complex of iridium(IV) with cytozine

Mitrofanova E.S., Kurasova M.N., Andreeva O.I., Esina N.Ya.

*Peoples' Friendship University of Russia (RUDN University), 117198, Moscow,  
Miklukho-Maklaya str. 6  
e-mail: elizaveta.mitrofanova.97@mail.ru*

Metal complexes based on iridium and rhodium have recently become a potentially attractive alternative to existing platinum and ruthenium drugs with anticancer activity. The study of the cytotoxic mechanism of action of iridium complexes on cancer cells showed that hydrolysis, DNA cleavage and depolarization of mitochondrial membrane potential (MMP), apparently, are not the main mechanism of their action, and their anti-cancer effectiveness is shown, causing cell death, disrupting the cell cycle and increasing the number of free radicals (ROS) inside the cells. At the same time, iridium-based drugs can not only be effective against several forms of cancer, but also inhibit the development of metastases [2]. Scientific developments of recent years [3] show that the reactivity and biological activity of iridium and rhodium complexes can be enhanced by a proper selection of auxiliary ligands similar in composition and properties to proteins and enzymes.

Coordination compound Ir(IV) with cytosine (C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>O) was synthesized and isolated in the individual state.



The synthesized compound is a powder of dark brown color, well soluble in water, poorly soluble in ethyl alcohol, insoluble in acetone, ether, carbon tetrachloride, chloroform. Chemical analysis results show the followings (found/calculated): Ir (33.75/34.53), C (8.21/8.63), H (0.9/0.9), N (7.12/7.55), O (2.65/2.88). It was determined by means of argentometric titration that 2 chlorine ions are found in the outer sphere of the complex.

IR spectrum analysis of the complex compound showed a clear shift of the ligand carbonyl group band (1550 cm<sup>-1</sup> – ligand, 1660 cm<sup>-1</sup> – complex), indicating the interaction of iridium (IV) with the ligand through C=O group. Valence vibrations displacement of the ring (1360 cm<sup>-1</sup> – ligand, 1396 cm<sup>-1</sup> – complex) suggests that the nitrogen of the heterocycle is also involved in coordination with the metal cation. Thus, the cytosine in this compound acts as a bidentate ligand.

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## **Effect of substitution with REE(III) and Nb(V) ions on phase formation and properties of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$**

Mitrofanova A.V.<sup>1</sup>, Fortalnova E.A.<sup>1,2</sup>, Safronenko M.G.<sup>1</sup>, Politova E.D.<sup>2</sup>

<sup>1</sup> *Peoples' Friendship University of Russia (RUDN University), 117198, Miklukho-Maklaya str. 6, Moscow, Russia*

<sup>2</sup> *L.Ya. Karpov Institute of Physical Chemistry, 105064, Obukha s.-st., 3, Moscow, Russia  
e-mail: chemistann@gmail.com*

The synthesis and study of the physical and chemical properties of perovskite-like compounds with Aurivillius structure is an important issue, because such compounds are prospective materials from the point of the further application in modern technology [1]. According to a number of works [2-3] cation substitutions in various positions of  $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$  significantly affect the physical and electrical properties of these Aurivillius phases.

The goal of present research is to study the influence of partial cation substitutions with  $\text{Tb}^{3+}$  and  $\text{Nb}^{5+}$  for  $\text{Bi}^{3+}$  and  $\text{Ti}^{4+}$ , respectively, on phase formation, physical-chemical and electrical-physical properties of  $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ .

The samples of  $\text{Bi}_5\text{Fe}_{1+y}\text{Ti}_{3-2y}\text{Nb}_y\text{O}_{15}$  (BFTNb) with  $0.0 \leq y \leq 1.0$ ,  $\Delta y = 0.2$  and  $\text{Bi}_3\text{Tb}_2\text{Fe}_{1+y}\text{Ti}_{3-2y}\text{Nb}_y\text{O}_{15}$  (BTbFTNb) with  $0.0 \leq y \leq 0.6$ ,  $\Delta y = 0.2$  were obtained by the solid state reaction method, using microwave and muffle types of heating. The microwave annealing was more efficient for this synthesis, since expands the area of perovskite-like phase homogeneity, at the same time lowering the temperature and reducing the time of synthesis.

Despite the large number of papers reporting the formation of a layered perovskite structure with such substitutions [3-5], our results indicate the formation of a perovskite structure in a narrow concentration range of  $y$ . The obtained X-ray diffraction data show that the samples of BFTNb with  $0.0 \leq y \leq 0.4$  are of single-phase perovskite-like compounds, while the crystal structure of BTbFTNb samples changes with growing  $y$  in the series from a perovskite-like structure to a pyrochlore structure.

According to the X-ray diffraction, DTA, FTIR and dielectric spectroscopy data, an increase in the  $\text{Fe}^{3+}$ ,  $\text{Nb}^{5+}$  cations content leads to an increase in the unit cell volume of BFTNb solid solutions and accompanied by a decrease in the ferroelectric phase transition temperature.

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## Perrhenates of purine nitrogen heterocycles

Novikov A.P.<sup>1</sup>, Grigoriev M.S.<sup>2</sup>, Safonov A.V.<sup>2</sup>, German K.E.<sup>2</sup>, Khrustalev V.N.<sup>1</sup>

<sup>1</sup>Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup>The Institute of Physical Chemistry and Electrochemistry RAS, 119071, Leninsky prospect 31/4  
e-mail: tony.novickoff@yandex.ru

Perrenate ion is readily available from the <sup>188</sup>W/<sup>188</sup>Re generator and it is interesting in nuclear medicine for diagnostic and therapeutic applications [1]. In recent years, neutral hosts of a complex structure with internal cavities containing nitrogenous bases have been developed [2]. In case of effective binding with perrhenate anions, they can be promising suppliers of rhenium to cells of various organs and tissues. Purine nitrogen heterocyclic molecules are important elementary molecular components in modeling the creation of similar hosts for ReO<sub>4</sub><sup>-</sup>.

Two new perrhenates with adenine and guanine cations (isothermal evaporation of solutions of magnesium perrhenate and nitrogenous bases in HCl) were synthesized as single crystals in this study. An X-ray diffraction study was performed (automatic diffractometer Bruker KAPPA APEX II). Crystallographic data: H<sub>2</sub>Gua(ReO<sub>4</sub>)<sub>2</sub> (**I**):  $a = 5.2014(2)$ ,  $b = 15.7463(6)$ ,  $c = 14.9004(5)$  Å,  $\beta = 92.908(2)^\circ$ , at 100 K,  $Z = 4$ , space gr.  $P2_1/n$ ,  $R1 = 0.0199$ ; H<sub>2</sub>Aden(ReO<sub>4</sub>)<sub>2</sub> (**II**):  $a = 16.0078(8)$ ,  $b = 5.0950(2)$ ,  $c = 16.2841(9)$  Å,  $\beta = 116.078(2)^\circ$ , at 100 K,  $Z = 4$ , space gr.  $P2_1/c$ ,  $R1 = 0.0176$ .

In both compounds, the nitrogenous base molecules are twice protonated. All nitrogen atoms are protonated in **I**, and the nitrogen atom in the *para*-position to the amino group is not protonated in **II**. The NH and NH<sub>2</sub> groups in both compounds are proton donors in hydrogen bonds, and the oxygen atoms of perrhenate ions act as proton acceptors. One bond between the amino group and the perrenate ions in structure **I** is bifurcate. The oxygen atom of the guaninium cation in structure **I** does not participate in hydrogen bonds. In structure **I**, each cation is linked by hydrogen bonds with six anions, and in **II** - with four.

The crystal packing in structures **I** and **II** can be represented as consisting of cationic and anionic columns. In both structures, each cationic column is surrounded by 6 anionic ones and each anionic one is surrounded by 3 cationic ones. In both structures, there is no  $\pi$ -stacking interaction. The study showed that the similar nature of cations and the similar composition of compounds lead to the formation of crystalline packings of the same type, despite some differences in the system of hydrogen bonds.

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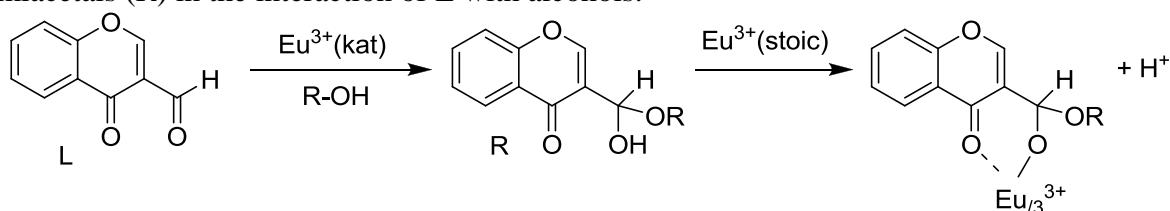
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## Interaction between $\text{Eu}^{3+}$ and 4-oxo-4H-1-benzopyran-3-carboxaldehyde in alcoholic medium

Novikova N.S., Zseltvay I.I., Kondratyeva R.V., Kuz'min V.E.

A.V.Bogatsky Physico-chemical institute of NAS Ukraine, 65080, Odessa, Lustdorfskaja str. 86  
e-mail: nadyas.n73@gmail.com

Under certain conditions, 4-oxo-4H-1-benzopyran-3-carbaldehyde (L) interacts with transition metal salts forming  $[\text{ML}_2]\text{A}_2 \cdot x\text{H}_2\text{O}$  adducts, where  $\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$ ,  $\text{A} = \text{Cl}^-, \text{ClO}_4^-$  [1,2]. We first discovered that in the presence of lower alcohols: methanol, ethanol, 1-propanol, 2-propanol, used as solvent L, europium(III) salts form chelates of composition  $\text{EuR}_3$ , which do not contain a nonorganic anion. These chelates were not formed in the environment of other solvents: dioxane, acetone, DMFA, DMSO, acetonitrile. The process of complexation can be presumably explained by a scheme that takes into account the formation of hemiacetals (R) in the interaction of L with alcohols.



Meanwhile the europium(III) ion catalyzed the conversion of aldehyde to hemiacetal in the first stage [3], and in the second stage the europium(III) ion stabilized it due to complexation.

The resulting europium(III) complex was well extracted from the aqueous-alcoholic medium with organic solvents (preferably chloroform, dichloroethane,  $\text{CCl}_4$ ) and brightly luminesced in red when irradiated with soft ultraviolet (390-400 nm). The emission spectrum was a discrete nature and was connected with the intramolecular transfer of excitation energy from the organic ligand to the  $\text{Eu}^{3+}$  ion. This complex was at the level of the best samples of organic-inorganic phosphors based on  $\beta$ -diketones, including with tenoyltrifluoroacetone according to its spectral-luminescent characteristics (luminescence intensity, intrinsic quantum yield, average lifetime of the excited state).

The complex was separated in solid form. Its composition and structure were confirmed by mass spectral, IR spectroscopic and thermogravimetric methods.

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## Synthesis and crystal structure of complex scandium sulfates

Pasechnik L.A., Yatsenko S.P., Chufarov A.Yu., Enyashin A.N., Kozhevnikova N.S.

*Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences,  
620990, Ekaterinburg, 91, Pervomayskaya Str.  
e-mail: pasechnik@ihim.uran.ru*

Hydrated and anhydrous metal sulfates are formed as a result of exchange reactions in geological processes of mineral formation, as well as during hydrochemical processing of feedstock. Sulfuric acid is extensively used as one of the most active and available reagents. As a result of sulfatization of feedstock, rare and rare-earth elements (REE) pass into a sintered mass, from which sulfates are leached by water. The deposition of complex REE sulfates with alkali metal cations or ammonia is based on the difference in the solubility values of simple and double sulfates [1]. Scandium sulfate, as distinct from REE sulfates, exhibits an anomaly of properties. Sc(III) has a large similarity to cations of a small ionic radius ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$  etc.). Such behavior explains the scarcity of scandium minerals in the nature and its isomorphic incorporation into the crystal structures of other minerals.

In order to separate scandium from concomitant metals in concentrate, produced from bauxite residue, we have developed the conditions of selective deposition of scandium sulfates  $\text{NH}_4\text{Sc}(\text{SO}_4)_2$  and  $(\text{NH}_4)_3\text{Sc}(\text{SO}_4)_3$ . The literature data on the crystal structure and properties of double scandium sulfates are limited [2]. Developing the scandium technology on model systems, we determined the region of existence of structural polytypes and conditions of polymorphic transformations for both compositions [2, 3]. The uniting factor for these structures is their crystallization from stable solutions, containing complex anions  $[\text{Sc}(\text{SO}_4)_2]^-$  and  $[\text{Sc}(\text{SO}_4)_3]^{3-}$ . A trigonal  $1T'$  and rhombohedral  $3R$  layered modifications with an irreversible phase transition  $1T' \rightarrow 3R$  due to mechanical action have been discovered for  $\text{NH}_4\text{Sc}(\text{SO}_4)_2$ . The basis of the framework architecture of two saturated compounds  $(\text{NH}_4)_3\text{Sc}(\text{SO}_4)_3$  is  $[\text{M}^{3+}(\text{SO}_4)_3]_\infty^{3n-}$  columns, in which two neighboring  $\text{MO}_6$  octahedra are connected by three  $\text{SO}_4$  tetrahedra. A reversible transition from monoclinic ( $P21/c$ ) modification to rhombohedral ( $R3c$ ) modification is observed at 81.7 °C. Ammonium cations in all compounds are held either between layers or columns by weak hydrogen bonds  $\text{N}-\text{H}\cdots\text{O}-\text{S}$ . The relative stability of the experimental crystal structures is confirmed by the results of DFT calculations.

Solutions of complex scandium sulfates were successfully applied for Sc-doping of nanocrystalline  $\text{TiO}_2$  via the sol-gel method. The Sc-doped powder-like product was a mixture of anatase/brookite or anatase/brookite/amorphous nanoparticles. The quantum chemical calculations distinguished both brookite and amorphous  $\text{TiO}_2$  phase as the most preferred hosts for substitutional Sc atoms among all  $\text{TiO}_2$  polymorphs. Substitutional doping of  $\text{TiO}_2$  by scandium did not modify the electronic structure near the band gap edges.

*The work was supported by the Russian Science Foundation  
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## Synthesis and properties of InSb<Mn, Ni>

Pashkova O.N., Sanygin V.P., Izotov A.D.

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
11999, Moscow, Leninsky pr 31  
e-mail: [olg-pashkova@yandex.ru](mailto:olg-pashkova@yandex.ru)

The main task of spintronics is the integration of magnetic systems into semiconductor electronics. Composites consisting of ferromagnetic clusters in the nonmagnetic semiconductor matrix  $A^{III}B^V$  are perspective materials in this direction [1].

The semiconductor InSb doped with Ni (0.8, 1; 1.2 at.%) and Mn (1 at.%) was chosen as the object of study. The synthesis of alloys was carried out at a temperature  $T = 1100$  K, kept at this temperature for 40 h, and then quenched in ice water.

X-ray diffraction (XRD) analysis of the samples was performed at room temperature with a Bruker D8 Advance automatic diffractometer (CuK $\alpha$  radiation, Ni filter,  $2\theta$  range  $10^\circ$ – $80^\circ$ , scan step  $\Delta 2\theta = 0.02^\circ$ ). X-ray diffraction spectra contained mainly peaks related to the InSb phase.

Measurements of magnetic characteristics confirmed that the ferromagnetism of InSb <Mn, Ni> alloys is due to the formation of clusters  $Ni_{2-x}Mn_xSb$  ( $0 \leq x \leq 1$ ). The Curie temperature of the obtained samples depended on the Ni content and was in the range from 661 to 670 K. From a comparison of the obtained results with the data of [2], it follows that the clusters have a phase composition near to  $Ni_{1.1}MnSb$ . The magnetization curves of InSb <Mn> samples are typical of a magnetically soft material with a coercive force of  $\sim 30$  Oe at  $T = 4$  K and  $\sim 19$  Oe at  $T = 300$  K (Fig.1). The samples had metallic conductivity and positive magnetoresistance at temperatures below room temperature.

The results of the study demonstrate the ability to control the magnetic properties of the sample by changing the concentration of doping elements forming magnetic clusters.

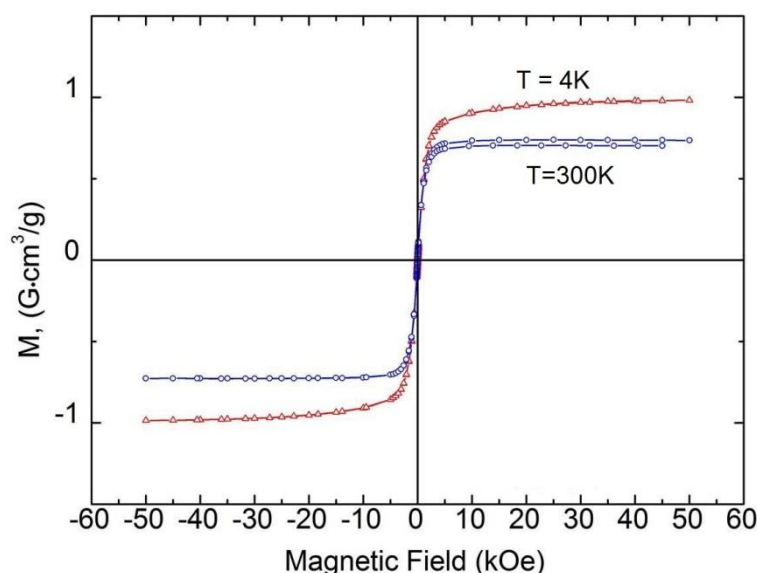


Fig. 1. Field dependences of magnetization for a InSb(1 at.% Ni, 1 at.% Mn) at 4 and 300 K.

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## Synthesis and crystal structure of a novel nickel complex with $\alpha$ -(3,3-dimethyl-3,4-dihydroisoquinolyl-1) hydroxyiminoacetonitrile

Polyakova E.I.,<sup>a</sup> Davydov V.V.,<sup>a,\*</sup> Dorovatovskii P.V.,<sup>b</sup>  
Zubavichus Ya.V.,<sup>b</sup> Khrustalev V.N.,<sup>a,b</sup> Shklyayev Yu.V.<sup>c</sup>

<sup>a</sup> Peoples' Friendship University of Russia (RUDN University), Moscow 117198, Russia

<sup>b</sup> National Research Center "Kurchatov Institute", Moscow 123182, Russia

<sup>c</sup> Institute of Technical Chemistry, Ural Branch of RAS, Perm 614990, Russia

$\alpha$ -(3,3-dimethyl-3,4-dihydroisoquinolyl-1) hydroxyiminoacetonitrile (**LH**, compound **1**), belongs to polyfunctional organic ligands and contains several functional groups capable of coordination with metals. It is also a derivatives of 3,3-dimethyl-3,4-dihydroisoquinoline, which is a structural fragment of some natural alkaloids, that have antimicrobial, antispasmodic, antihypertensive, choleric, anti-inflammatory activity. In the presence of the -C (R) NOH group allows us to classify the molecule as an oxime derivative. It is known that such compounds also exhibit biological activity, in particular antidiabetic, antiallergic, sedative, anti-cancer and fungicidal. We calculated the biological activity for compound **1**, according to the PASS program (Prediction of Activity Spectra for Substances). According to the evaluation, compound **1** with a probability of 65% and 51% potentially has anticancer and hypotensive activity.

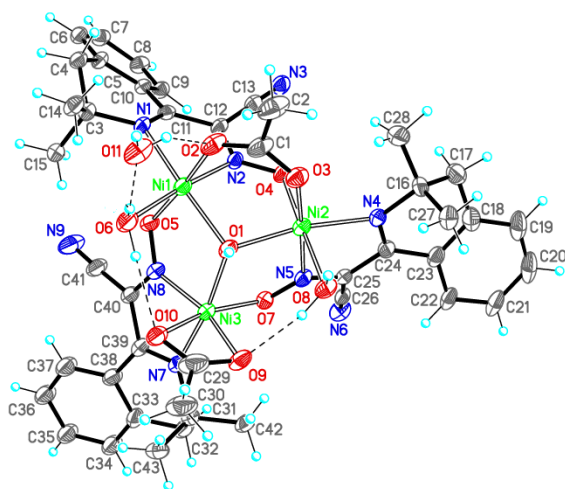
These characteristics determine the interest for studying compound **1** and its metal complexes, as precursors of new drugs or new materials for various purposes.

A novel complex of Ni(II) acetate with  $\alpha$ -(3,3-dimethyl-3,4-dihydroisoquinolyl-1) hydroxyiminoacetonitrile corresponding to stoichiometry  $[\text{Ni}_3(\mu_3\text{-OH})(\mu_2\text{-L})_3(\mu_2\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**2**) (fig.1) was synthesized and studied by X-ray diffraction, IR and UV-vis spectroscopy. The spectroscopic data and geometric features of obtained substance **1** were compared with previously described complexes of Cu(II), Cu(I) and Co(II) with the same ligand. It was shown that, depending on the nature of metal and the salt anion the structure of the isolated compounds was different.

Complex **2** has a trimeric structure. All three ligand molecules are deprotonated (**L**) in **1** and in the form of the *E*-s-cis-isomer. Nickel atoms are linked together by a bridging hydroxyl group and chelate **L** ligands. The ligand **L** is coordinated to Ni(II) simultaneously through the N and O atoms of the oxime group and the N atom of the dihydroisoquinoline moiety. One of the

acetate anions is coordinated in a bidentate chelate manner. The second one occupies a bridging position between two neighboring Ni(II) atoms. The coordination environment of all three Ni atoms can be described as octahedral.

In IR spectrum position of bands corresponding to mixed vibrations  $\nu(\text{C}=\text{N} + \text{C}=\text{C})$  over the range  $1620\text{--}1500\text{ cm}^{-1}$  can be used as a criterion pointing to the participation of the N atoms of the dihydroisoquinoline and oxime groups in coordination with the metal. In the spectrum of complex **2** this bands drifted to 1606, 1580, 1571, and  $1548\text{ cm}^{-1}$ . Their relative intensities are also redistributed upon complexation.



**Fig. 1.** Molecular structure of  $[\text{Ni}_3(\mu_3\text{-OH})(\mu_2\text{-L})_3(\mu_2\text{-CH}_3\text{COO})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

## **The effect of inert atmosphere and pre-activation of dimethyl sulfoxide osmium(IV) complexes on hydrosilylation C=C and C=O bonds**

Popova A.S.<sup>1</sup>, Kultyshkina E.K.<sup>1</sup>, de Vekki D.A.<sup>2</sup>, Tereshina T.A.<sup>1</sup>,  
Dobrokhotova E.V.<sup>1</sup>, Rudnitskaya O.V.<sup>1</sup>

<sup>1</sup> *Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6*

<sup>2</sup> *Saint-Petersburg State Institute of Technology (Technical University), 190013,  
Saint-Petersburg, Moscow prospect str. 26  
e-mail: popova-ansr@rudn.ru*

Hydrosilylation is one of the widely used methods for the synthesis of organosilicon compounds [1]. The use of osmium compounds, especially sulfoxide complexes, as catalysts is a new approach to development of this field of chemistry. Only a few papers [2] are devoted to such studies.

The catalytic activity of osmium sulfoxide complexes discovered by us in the hydrosilylation reactions of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane and acetophenone 1,1,3,3-tetramethyldisiloxane became the starting point of research.

This work is devoted to the study of the catalytic activity of osmium(IV) complexes  $[H(dmsO)_2]_2[OsX_6]$ ,  $[H(dmsO)_2][OsX_5(dmsO)]$  ( $X = Cl, Br$ ) in the above mentioned hydrosilylation reactions, the influence of inert atmosphere and pre-activation of catalysts by reactants.

Experimental conditions: ampoule method, temperature 100–120 °C, catalyst concentration  $(1.0\text{--}1.5) \cdot 10^{-3}$  mol/l; inert atmosphere – argon. Pre-activation consisted in heating the complex with one of the reactants, followed by the addition of the second reactant after a certain period of time. The control of the hydrosilylation process was carried out by GLC and NMR.

By this work, we demonstrate the effectiveness of pre-activation of all studied osmium complexes with acetophenone: the time to achieve maximum acetophenone conversion and the yield of hydrosilylation by-products decrease by two times, while the preliminary activation of 1,1,3,3-tetramethyldisiloxane and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane does not have a significant effect on the hydrosilylation process. The exception is  $[H(dmsO)_2][OsBr_5(dmsO)]$ , the pretreatment of which with divinylsiloxane leads to an increase in the rate and selectivity of hydrosilylation of the latter: the yield of  $\beta$ - and  $\beta\beta$ -addition products increases, the yield of by-products decreases as compared with catalysis on the untreated complex.

Conducting of experiments in an inert atmosphere also showed the quite effectiveness: a selectivity of the process and an yield of the target product increase, and, in the case of acetophenone, the rate of hydrosilylation is further increased. Apparently, the destruction of osmium sulfoxide complexes occurs in humid air, which leads to a decrease in catalytic activity.

Summarizing the above, we can conclude that the inert atmosphere and the pre-activation of osmium complexes with acetophenone and divinylsiloxane are promising for catalytic hydrosilylation and deserve further study. For example, the activation of platinum catalysts by reactants is more effective in the case of hydrosiloxanes [3].

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## Comparative analysis of methods for the synthesis of coordination compounds Ni(II) with cytosine

Qi S., Esina N.Ya., Kurasova M.N., Andreeva O.I.

*Peoples' Friendship University of Russia (RUDN University), 117198,  
Miklukho-Maklaya str. 6, Moscow, Russia  
e-mail: qishenghua12345@163.com*

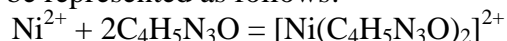
Despite the fact that nickel is a biologically active metal, its excessive content in the body causes toxic changes in the cell [1]. The combination of the bioeffects of nickel(II) with biologically active substances - amino acids, purine and pyrimidine bases, which are part of proteins and DNA, very often leads not only to a decrease in toxicity, but also to the manifestation by such compounds of pharmacological and antibacterial activity [2-3]. Moreover, the biological activity of complex compounds, where nickel(II) coordinates the ligand in the form of a chelate, increases due to the greater compactness of the compounds formed and, consequently, greater ease of assimilation of the obtained complexes [4].

The study of the correlation between the structure, stability and reactivity of complex compounds of nickel(II) with bioligands is important for the development of both coordination and bioinorganic chemistry.

Methods for the synthesis of the complex compound Ni(II) with methionine were studied in [5]. The analysis confirmed the maximum yield and purity of the compound obtained using the sodium salt of the amino acid. But this technique is unacceptable for the synthesis of complex compounds of Ni(II) with purine (pyrimidine) bases. Therefore, the next stage of the study was to obtain a complex compound of Ni(II) with cytosine using various methods and to choose the optimal one.

As starting materials containing Ni(II), to obtain the complex compound, freshly precipitated Ni(OH)<sub>2</sub>, 0.1M solution of NiCl<sub>2</sub> and crystalline Ni(NO<sub>3</sub>)<sub>2</sub> were used.

The reaction scheme can be represented as follows:



The criteria for the selection of methods for the synthesis were purity, ease of product isolation and the percentage of its output. Studies of the isolated complex compounds (IR spectroscopy, thermo gravimetric analysis, chemical analysis, titrimetry and X-ray diffraction analysis) clearly showed that the purest product is obtained using nickel chloride in the synthesis. The complex of nickel(II) with cytosine, which is a light green powder, is highly soluble in water, alcohol, and slightly soluble in acetone and ether. In the coordination compound, cytosine is most likely a bidentate ligand coordinated by a metal ion through the N3 and C=O group.

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## **Functionalization of the MOF with thienthiophene-containing building blocks**

Samsonova A.M., Bolotov V.A., Samsonenko D.G., Dybstev D.N., Fedin V.P.

*Novosibirsk State University, 117198, Novosibirsk, Russian Federation, Pirogova str. 2  
e-mail: lipa\_anna@rambler.ru*

Metal-organic frameworks (MOF) are a class of materials in which cations (or clusters) of metals are coordinated by organic bridging ligands. MOFs are of great interest to the scientific community due to their unique properties, such as crystalline nature, high porosity, and potential scalability on an industrial scale. Another important property is the high specific surface area of the framework and, consequently, high values of sorption capacity with respect to various gases and liquids, which is one of the most promising areas of application of porous MOFs [1].

In this paper, we use thieno[3.2b]thiophene 2,5-dicarboxylic acid ( $H_2[3.2b]ttdc$ ). The sulfur atom of this group is relatively easily polarizable and contains a free (not participating in conjugation) lone electronic pair, and can act as sorption centers for various gases. First of all, this applies to gases whose molecules are easily polarizable, molecules having a significant dipole moment, as well as atoms of heavy chalcophilic metals. The increase in the sorption capacity is associated with local dipole moments present in the thiophene group, as well as with the features of the electronic structure of the conjugated heterocyclic ligands. Functionalization of the MOF through the use of organic ligands containing thienthiophene building blocks is effective and leads to a significant increase in the sorption capacity of structurally similar materials with respect to various gases and liquids.  $H_2[3.2b]ttdc$  is of considerable interest because of its complete geometric analogy of terephthalic acid, which is the most common organic building block.

The World Health Organization (WHO) has set the maximum level of contamination with mercury in drinking water at 1 ppb [2]. However, the efficiency of mercury removal using traditional technologies for removing ultra-low concentrations of  $Hg^{2+}$  is not fully realized. In this paper, we report on the development of a series of materials based on a sulfur-containing bridging ligand — thienothiophenedicarboxylate and various metals, including zirconium. Some materials exhibit thermal and chemical stability with respect to various media, which is typical for this class of materials. Recent studies have shown that one of the developed materials has some ability to clean the aqueous medium from mercury ions, as well as the ability to regenerate the material, which is one of the few examples to date among the coordination polymers that exhibit similar activity with respect to mercury ions.

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## Topographic analysis of the surface of the GaSb<Mn> magnetic semiconductor

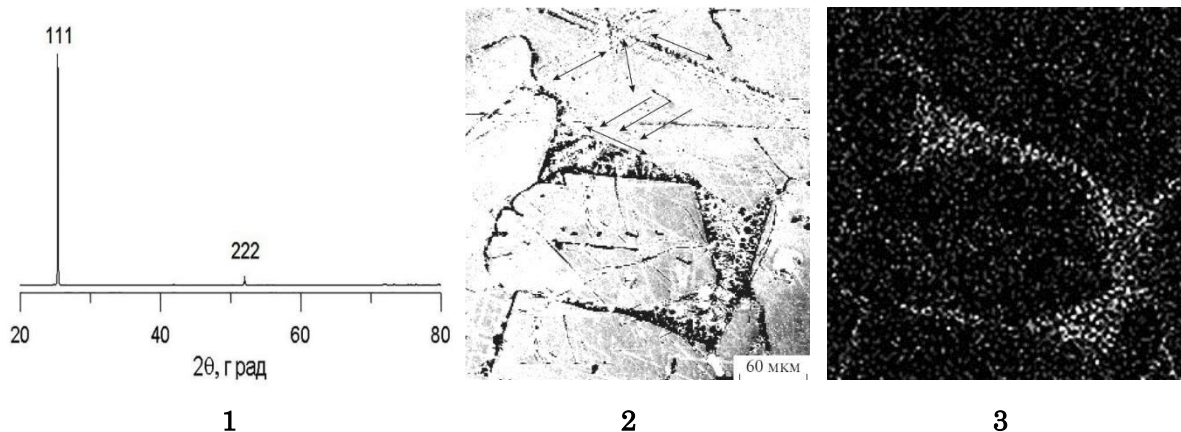
Sanygin V.P., Izotov A.D., Pashkova O.N.

*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
119991, Moscow, Leninsky pr. 31  
e-mail: sanygin@igic.ras.ru*

The effect of doped dislocations on the properties of magnetic materials is basic to the concept of impurity–dislocation magnetism, which can be used in creating new anisotropic materials containing magnetic linear lattice defects [1].

GaSb containing 2 at. % Mn ingot was prepared by water-quenching a melt. According to the magnetic measurements, the ferromagnetism of the alloy GaSb<Mn> is due to Mn<sub>1.1</sub>Sb phase inclusions [2].

The crystal structure of the GaSb<Mn> sample was studied by X-ray diffraction on a Bruker diffractometer. According to diffraction data, the material of the sample in the form of a polished section of GaSb<Mn> has a well-defined (111) growth texture (1).



The sample GaSb<Mn> was examined by scanning electron microscopy on a Carl Zeiss NVision40 Cross Beam workstation. The surface consisted of microscopic inhomogeneities in the form of straight segments, triangular blocks, and microcracks (2). The arrows show dislocation motion directions. The electron probe scans of this area in MnK $\alpha$  radiation indicated that these inhomogeneities were manganese pile-ups (3).

According to the analysis results, the straight line segments are dislocation slip planes. They can be classified as surface defects, and the microcracks originate from dislocation mechanisms behind the onset of crystal fracture and can be classified as three-dimensional defects in the crystal lattice of the GaSb.

It has been shown using X-ray diffraction and scanning electron microscopy that the generation of dislocations and their motion during quenching play a key role in determining the microstructure of the GaSb <Mn> magnetic semiconductor.

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## Synthesis, spectra and structure of new iron and cobalt(II) macrobicyclic tris-dioximates with terminal biorelevant substituents

Semenov A.V.,<sup>1,2</sup> Chuprin A.S.,<sup>2,3</sup> Dudkin S.V.,<sup>2</sup> Voloshin Ya.Z.<sup>2,4</sup>

<sup>1</sup>MIREA – Russian Technological University, 119571, Moscow, Vernadskogo pr. 86

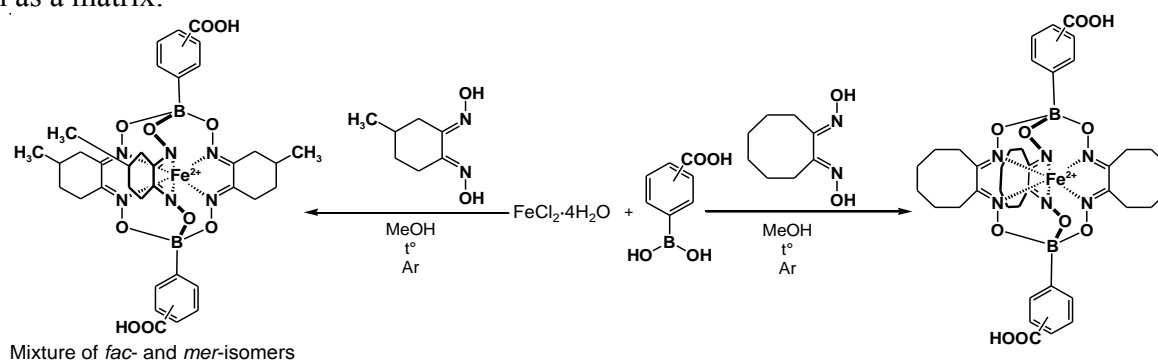
<sup>2</sup>Nesmeyanov Institute of Organoelement Compounds RAS, 119991, Moscow, Vavilova str. 28

<sup>3</sup>Frumkin Institute of Physical chemistry and Electrochemistry RAS,  
19907, Moscow, Leninskiy pr. 31, korp. 4

<sup>4</sup>Kurnakov Institute of General and Inorganic Chemistry RAS, 119991, Moscow, Leninskiy pr. 31  
e-mail: artzemmen@gmail.com

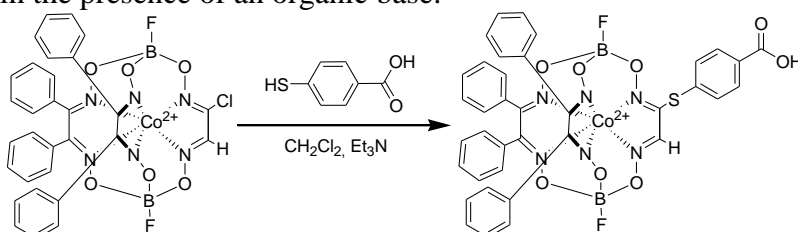
Cage metal complexes (clathrochelates) [1] with terminal reactive, donor or biologically relevant groups are prospective, chemically robust, three-dimensional molecular platforms and building blocks for the design of new types of (photo)electronic devices, modern functional materials and prodrugs as well.

New macrobicyclic iron(II) complexes with equivalent carboxyphenyl apical groups were obtained through the template condensation by scheme 1 of the corresponding  $\alpha$ -dioximes as the ligand synthones with Lewis-acidic *para*- and *meta*-carboxyphenylboronic acids on the iron(II) ion as a matrix.



Scheme 1

The cobalt(II) cage complex with one carboxyphenylsulfide ribbed substituent was obtained by scheme 2 using a nucleophilic substitution of the single chlorine atom of its monochloro clathrochelate precursor with an anionic form of *para*-mercaptobenzoic acid generated *in situ* in the presence of an organic base.



Scheme 2

The obtained complexes were characterized using UV-Vis, MALDI-TOF MS, IR and multinuclear 1D and 2D NMR spectra.

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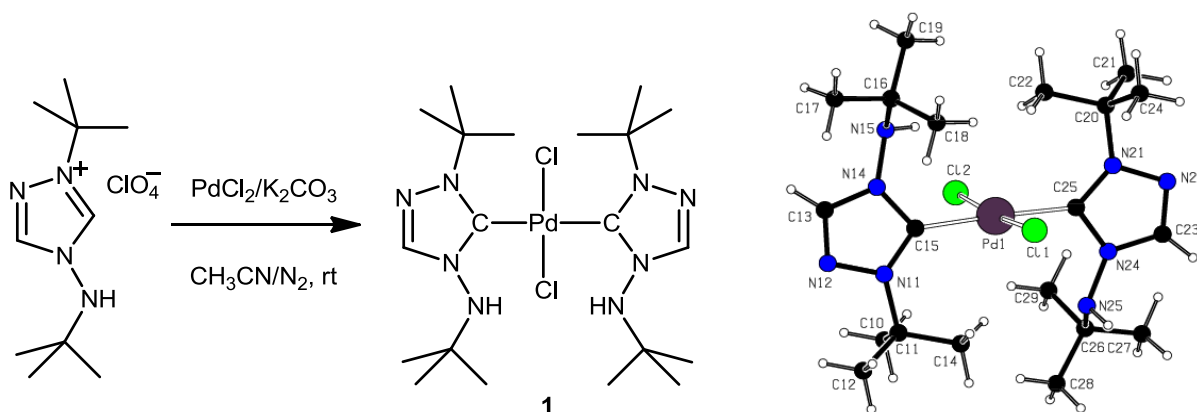
# Synthesis and structure of *trans*-dichloridobis(1-*tert*-butyl-4-(*tert*-butylamino)-1,2,4-triazol-5-yliden)palladium(II)

Serebryanskaya T.V., Lyakhov A.S., Grigoriev Yu.V.

Research Institute for Physical Chemical Problems of Belarusian State University, 220006,  
Minsk, Belarus, Leningradskaya str. 14  
e-mail: serebryanskaya.t@gmail.com

Palladium complexes bearing N-heterocyclic carbene (NHC) ligands are widely used as versatile catalysts [1] and also attract attention as potential metal-based antitumor agents [2]. In comparison with imidazole- and benzimidazole-based NHC derivatives, properties of NHC metal complexes derived from polynitrogen heterocycles are significantly less studied.

Here, we report synthesis and structure of a novel functionalized triazole-based Pd(II) NHC species, namely *trans*-dichloridobis(1-*tert*-butyl-4-(*tert*-butylamino)-1,2,4-triazol-5-yliden)palladium(II) (**1**). The title compound was obtained by the reaction of PdCl<sub>2</sub> with 1-*tert*-butyl-4-(*tert*-butylamino)-1,2,4-triazolium perchlorate in the presence of K<sub>2</sub>CO<sub>3</sub> using the standard Schlenk technique. The complex was characterized by means of elemental analyses, HR ESI(+)-MS, IR and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopies, DCS/TG and single-crystal X-ray crystallography.



According to the X-ray data, complex **1** crystallizes in monoclinic *P*2<sub>1</sub>/*c* space group. It is a molecular complex featuring square planar geometry with *trans* configuration of the ligands in the coordination sphere of Pd(II). There is a system of non-classic intermolecular C–H···Cl hydrogen bonds in crystals of **1**.

*This work was supported by the Belarusian Republican Foundation for Fundamental Research (grant № X17PM-028)*

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## Synthesis of a complex salt of Co(II) based on histidine

<sup>1</sup> Zeynalov S.B., <sup>1</sup> Sharifova S.K., <sup>1</sup> Huseynov E.R., <sup>1</sup> Abdullayeva F.A., <sup>2</sup> Sharifova A.K.,  
<sup>1</sup> Sadikhova G.K., <sup>1</sup> Lutvelizade I.S., <sup>1</sup> Behbudova S.K.

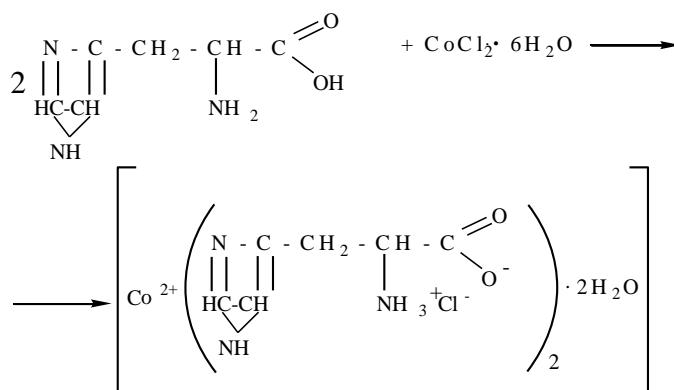
<sup>1</sup>Academician M.Naghiyev Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences, AZ 1143, Baku, H.Javid Ave. 113, Azerbaijan

<sup>2</sup>Azerbaijan Medical University, AZ 1022, Baku, Bakikhanov str. 23.  
 e-mail: chemistry@science.az

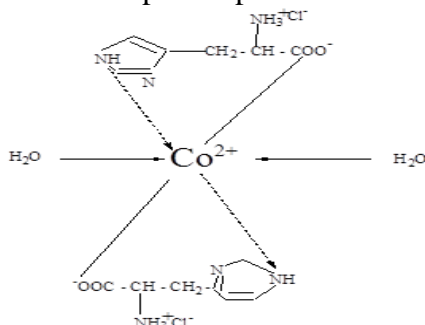
For the first time coordination compounds of amino acids was identified in the middle of XIX century. The structure of  $\alpha$ -amino acids creates the possibility of forming different forms of complex compounds with metal ions.

It is known that histidine (His) is heterocyclic  $\alpha$ -amino acid, one of 20 proteinogenic amino acids. Histidine residue is a part of active centers of many ferments and is a precursor in biosynthesis of histamine. Histidine is one of the essential amino acids, contributes to the growth and restoration of tissues, and is found in large amounts in hemoglobin.

The present research work deals with studying the formation of a complex salt  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with histidine at 35-38°C, with ratio of components 1:2 for 5 hours in aqueous medium by continuous mixing. Yield of reaction product made 76 %. The precipitated crystals are blue-black, insoluble in alcohols and other organic solvents, but well soluble in water. Histidine participates in the formation of the complex in the form of bipolar ion. Formation reaction of the complex salt of cobaltichloride(II) with His can be presented by the following scheme:



The structure of synthesized complex is provided below:



It was established that synthesized complex exhibits biological activity and has antiviral, antimicrobial, antibacterial, sedative, psychotropic properties.

## Synthesis of multicomponent heterostructures for quantum electronics devices

Shelyakin A.A., Vasil'ev M.G., Izotov A.D.

*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991, Moscow, Leninsky pr 31  
e-mail: mgvas@igic.ras.ru*

Epitaxial growth is a heterogeneous process occurring at the liquid – solid interface. Analysis of the conditions of contact of the substrate with a nonequilibrium liquid or gaseous phase indicates the complexity of the contact phenomena occurring at the interface. In this regard, the preparation of indium phosphide substrates for epitaxial growth can be crucial for the synthesis of structures [1], including quantum electronics devices.

In this work, complex studies of technological operations for the preparation of indium phosphide substrates for the processes of epitaxial growth of heterostructures were carried out. The morphology and state of the surface of indium phosphide for the orientation of (100) substrates were studied. Various chemical etchants have been tested for finishing surface chemical treatment. It is shown that two-sided, two-stage chemical-mechanical polishing is optimal. The first stage is a zeolite suspension based on deionized water with the addition of ammonium fluoride and hydrogen peroxide. The second stage is a suspension of zeolite based on isopropyl alcohol with 5% iodine addition. The finishing chemical polishing in the etchant is a mixture of bromine with isopropyl alcohol. Based on the studies performed, complex nano heterostructures were synthesized on planar and profiled surfaces (Fig. 1). It is shown that the optimal mode of substrate preparation is a fundamentally important process for the synthesis of thickened instrument heterostructures of quantum electronics.

These structures were used to create semiconductor single-mode laser diodes with high quantum efficiency.

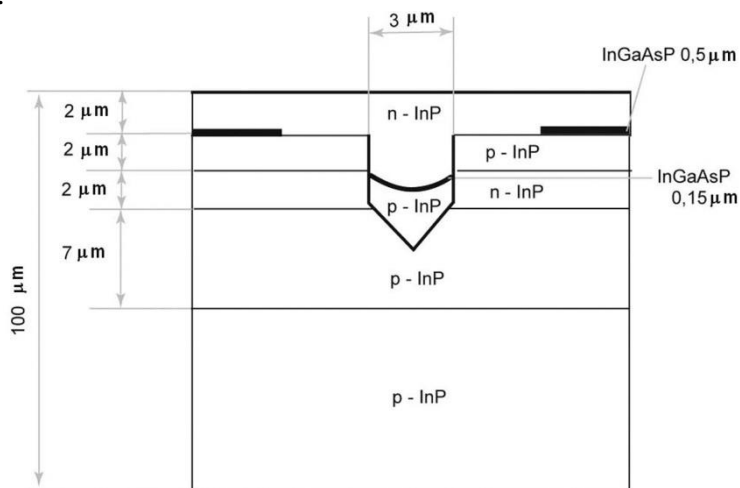


Fig. 1. Laser nanoheterostructure with a channel in the substrate.

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## Fe(III) spin-crossover complexes with gold bis(dithiolene) anions

Spitsina N.G.,<sup>a</sup> Shvachko Y.N.,<sup>b</sup> Lahderanta E.,<sup>c</sup> Zorina L.V.,<sup>d</sup> Simonov S.V.,<sup>a,d</sup> Blagov M.A.,<sup>a,e</sup> Yagubskii E.B.<sup>a</sup>

<sup>a</sup>Institute of Problems of Chemical Physics, RAS, Chernogolovka, MD, 142432, Russia

<sup>b</sup>M.N. Miheev Institute of Metal Physics, UB RAS, Yekaterinburg 620137, Russia

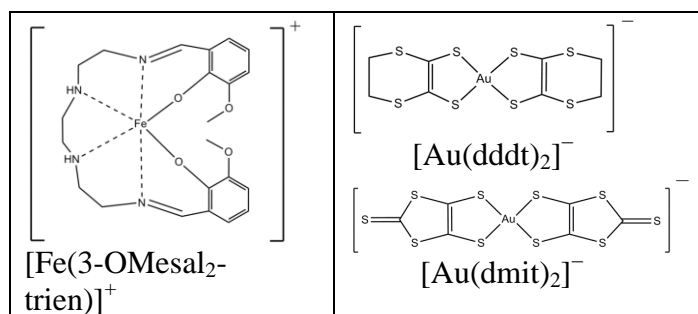
<sup>c</sup>Lappeenranta University of Technology, FI-53851 Lappeenranta, Finland

<sup>d</sup>Institute of Solid State Physics, RAS, Chernogolovka, MD, 142432, Russia

<sup>e</sup>Faculty of Fundamental Physical and Chemical Engineering MGU, Moscow, 119991 Russia

The synthesis of multifunctional materials which exhibit long-range magnetic order in addition to other functionalities such as spin-crossover transition (SCO) or electrical conductivity is current focus in molecular materials research, because the interplay of these properties may lead to novel behavior. The hybrid structures implementing efficient exchange interaction between the SCO and conducting subsystems would facilitate the development of new molecular spintronic devices where the spin transport is controlled by spin-crossover complexes [1]. Metal bis(dithiolene) complexes, as organic donors and acceptors, possess a delocalized electron system as a planar central core  $M(C_2S_2)_2$  and present different formal oxidation states. This type of complexes has been intensively studied as the component of molecular conductors [2-3]. In the last decade, the new trend is associated with the use of the octahedral cation complexes of Fe(III), showing reversible SCO between high-spin (HS) and low-spin (LS) states of the metal ion, in combination with the radical anion conducting subsystems [4].

We report synthesis, crystal structure, and magnetic properties of  $[Fe(3-OMesal_2-trien)][Au(dmit)_2]$  (**1**),  $[Fe(3-OMesal_2-trien)][Au(dmit)_2]_3 \cdot CH_3CN$  (**2**) and  $[Fe(3-OMesal_2-trien)][Au(ddd)_2] \cdot CH_3CN$  (**3**) involving a nonmagnetic gold bis(dithiole) anions. The compounds **1**, **3** were insulator with  $\sigma_{300} = 1.3 \cdot 10^{-9} \text{ Ohm}^{-1} \text{ cm}^{-1}$ , while for **2**  $\sigma_{300} = 1 \text{ Ohm}^{-1} \text{ cm}^{-1}$ . The incomplete SCO conversion was observed in **2**, **3** and was not in the compounds **1**, where 100% of Fe(III) ions remained in HS state.



*This work was done on the topic of the State task (No. 0089-2019-0011) with using of the Analytical Center for Collective Use of the IPCP RAS tool base*

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## Structure and properties of pure and intermetallic gold clusters

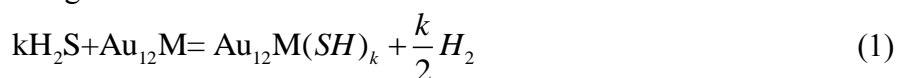
Teplyakov E.A.<sup>1,2</sup>, Yarzhemsky V.G.<sup>1,2</sup>, Izotov A.D.<sup>2</sup>

<sup>1</sup>*Moscow Institute of Physics and Technology 141700, Dolgoprudny, Moscow region, Institutsky lane. 9,*

<sup>2</sup>*Kurnakov Institute of General and Inorganic Chemistry, 119991, Moscow Leninsky pr.31  
e-mail: egery23@gmail.com*

Gold nanoparticles and clusters have a wide range of functional properties, such as catalytic activity, luminescence, the formation of self-organizing layers with a thiol terminal group [1]. The chemical properties of gold clusters are determined both by the cluster structure and by the interactions of gold atoms with each other and with ligands. Since the energy of bonding of SH group in gold clusters is significantly smaller than that of the clusters of 5d-elements, its changes due to the doping by other elements can influence significantly on functional properties. The 18-electron ionic cluster  $W@Au_{12}$  is a perfect icosahedron and extremely stable due to closed electronic shell  $a_{1g}^2 t_{1u}^6 h_g^{10}$ . The cubooctahedral clusters  $M@Au_{12}M$  ( $M = Hf, Ta, Re, Os$ ) are stabilized and become icosahedral, when the electrons are added (removed) to reach out the magic number 18.

In the present work the quantum chemical calculations in lanl2dz/b3lyp approach were performed for the above mentioned clusters with SH and H ligands. It is obtained that adding of SH and 2(SH) to  $Re@Au_{12}$  and  $Os@Au_{12}$  respectively results in more symmetric structure. To investigate the changing of functional properties, namely attaching thiol terminal group, the energy of the following reaction was calculated :



It is seen from the table 1, that in the cases of stable symmetric clusters  $Au_{32}$  and  $Au_{18}$  the reaction energy is relatively small. In the case of  $Au_{12}$  the reaction energy is relatively large due to significant changes of its structure. In the cases of  $ReAu_{12}$  and  $OsAu_{12}$  the reaction energy is larger due to the change of the shape from  $D_{2h}$  to  $I_h$  symmetry.

Table1. Theoretical energy of reaction (1) in eV per SH group

$Au_{32}$	$Au_{32}(SH)_2$	0.20
$Au_{18}$	$Au_{18}(SH)_2$	0.24
$Au_{12}$	$Au_{12}(SH)_2$	0.68
$WAu_{12}$	$W@Au_{12}(SH)_2$	-0.04
$ReAu_{12}$	$Re@Au_{12}SH$	0.44
$Os@Au_{12}$	$Os@Au_{12}(SH)^{1)}$	0.34

Hence it follows from the obtained results, that the energy reaction of gold clusters with thiol terminal group can be modified by doping of 5d elements.

*This work was supported by the Presidium of RAS grant I 37*

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## Synthesis and structure of $\text{Na}_2[\text{OsCl}_6]$

Tereshina T.A., Dobrokhotova E.V., , Kultyshkina E.K., Rudnitskaya O.V., Khrustalev V.N.

RUDN University, 117198, Moscow, Miklukho-Maklaya str.6  
e-mail: tereshina-ta@rudn.ru

The most important osmium coordination compounds that are widely used in preparative and analytical practice are chlorocomplexes [1-3]. The potassium salt  $\text{K}_2[\text{OsCl}_6]$  is well studied and often used, but its use is limited by low solubility in aqueous solutions and organic solvents. The sodium salt  $\text{Na}_2[\text{OsCl}_6] \cdot 2\text{H}_2\text{O}$  [3] is highly soluble in water and alcohol, however, we could not find the crystal structure data of either this salt or the sodium salts of hexachlorocomplexes of other platinum metals. This work is devoted to the synthesis and the crystal structure of the salt  $\text{Na}_2[\text{OsCl}_6]$ .

The compound  $\text{Na}_2[\text{OsCl}_6]$  was obtained during long-term boiling of a mixture of  $\text{H}_2[\text{OsCl}_6] \cdot n\text{H}_2\text{O}$  and  $\text{NaCl}$  (molar ratio Os: Na = 1: 1) in concentrated  $\text{HCl}$ . The resulting substance is a red crystal, cubic form. The UV/Vis spectra of water and DMSO solutions of  $\text{Na}_2[\text{OsCl}_6]$  correspond to the absorption of the  $[\text{OsCl}_6]^{2-}$  ion; the IR spectrum contains bands of  $\nu_3 = 314$  and  $\nu_4 = 174 \text{ cm}^{-1}$  of the octahedral  $[\text{OsCl}_6]^{2-}$  ion [4,5]. The absorption bands of crystallization water molecules in the IR spectrum are absent.

X-ray diffraction analysis showed that the compound consists of the  $[\text{OsCl}_6]^{2-}$  complex anion and  $\text{Na}^+$  cations (figure). The anion is a regular octahedron with the distances Os—Cl equal to 2.325 (3) Å. The  $\text{Na}^+$  cation is surrounded by twelve Cl atoms with a  $\text{Na} \cdots \text{Cl}$  distance of 3.448 (4) Å. Thus, its coordination polyhedron can be described as a cubooctahedron.

It should be noted that the classical method of synthesis of sodium salt leads to the release of the crystalline hydrate upon dissolving melt in water and the subsequent saturation of the  $\text{HCl}$  solution [3]. In our case, when the processes occurring in aqueous solution are similar, anhydrous complex is released.

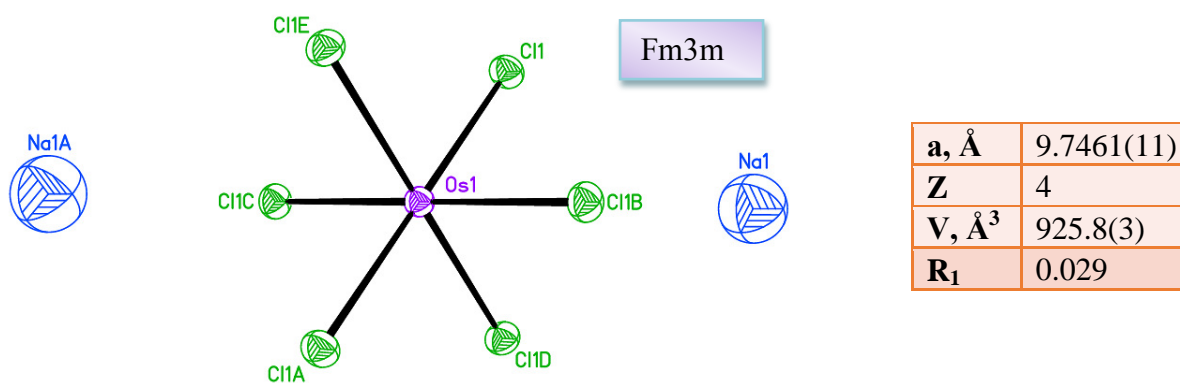


Fig. Structure  $\text{Na}_2[\text{OsCl}_6]$

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**Anticancer Pt(IV) complexes with a selective inhibitor of glycolysis**

Zenin I.V., Shutkov I.A., Okulova Y.N.

Lomonosov Moscow State University, Department of Medicinal Chemistry and Fine Organic Synthesis, 119991, Russia, Moscow, Leninskie Gory, 1/3  
e-mail: iliazenin.msu@gmail.com

Nowadays Pt(II) anticancer drugs, cisplatin, carboplatin, and oxaliplatin, are widely used in the treatment of the malignant tumors. However, they have several severe side effects: intrinsic or acquired resistance, general toxicity. Octahedral Pt(IV) complexes are of interest because of their kinetic inertness, low general toxicity and the possibility for oral administration.

Combinations of two drugs in one molecule are the widespread approach in medicinal chemistry. In our work, we introduced lonidamine, an inhibitor of aerobic glycolysis in cancer cells, as an axial ligand in Pt(IV) complexes [1, 2]. As a platinum moiety Pt(IV) analogs of cisplatin and oxaliplatin and ethylenediamine derivatives were used. We obtained two types of complexes: with direct conjugation of lonidamine to platinum (**1** - **4**) and using a linker bridge (**5**-**7**). In this presentation synthesis and characterization by NMR, ESI-MS of new Pt(IV) complexes are reported. Anticancer activities of the complexes were investigated using SW480 (colon carcinoma), A549 (non-small cell lung cancer), MCF7 (breast cancer), and MCF7D (doxorubicin/cisplatin-resistant analog of MCF7) cell lines by means of standard MTT colorimetric assay. For the complexes with direct binding of lonidamine moiety cytotoxicity is higher than for cisplatin, with some cases IC<sub>50</sub> values are in a nanomolar range. The results of *in vivo* studies for the most active complex **2** will be presented.

Comp.	IC <sub>50</sub> (μM)		
	SW480	A549	MCF7D
<b>1</b>	1±0.5	2.1±0.7	0.6±0.15
<b>2</b>	<b>0.13±0.06</b>	1.5±0.9	<b>0.07±0.02</b>
<b>3</b>	0.7±0.2	1.2±0.4	0.33±0.0
<b>4</b>	2.1±1.0	3.9±2.4	0.5±0.1
<b>5</b>	48±6	>100	53±7
<b>6</b>	43±1	>100	<b>5,9±0,1</b>
<b>7</b>	>100	>100	>100
CisPt	14±4.4	29.0±10	75±5.8

*This work was supported by the Russian Science Foundation  
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Physical and Colloidal  
Chemistry Section  
Key-note Speakers and  
Invited Lectures

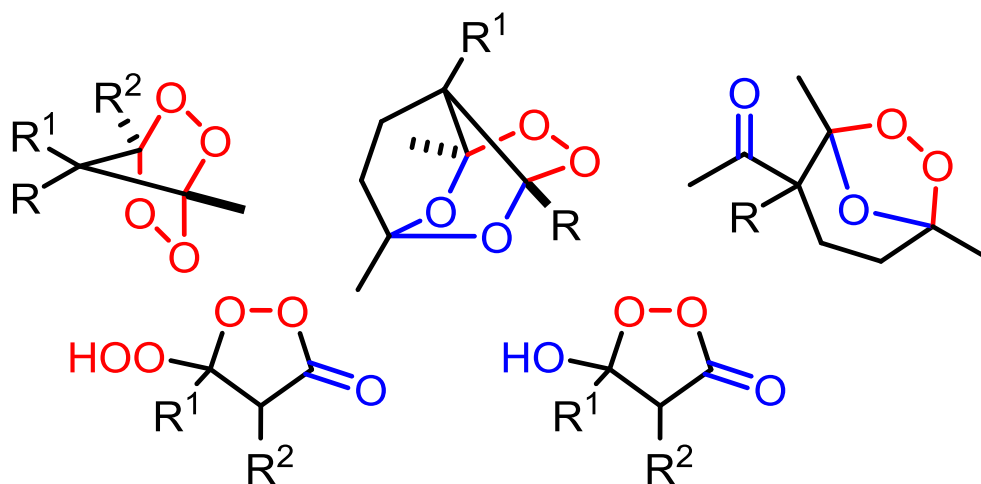


## Cyclic peroxides as a base for antiparasitic and anticancer drugs

Terent'ev A.O., Radulov P.S., Belyakova Yu.Yu., Barsegyan Y.A., Bityukov O.V.

*N. D. Zelinsky Institute of Organic Chemistry RAS, 119991, Moscow, Leninsky prosp. 47  
e-mail: alterex@yandex.ru*

In the last decades, organic peroxides have received considerable attention from chemists and drug design experts, which is associated with a need in the search for drugs for the treatment of parasitic diseases, such as malaria and helminth infections. Considerable progress has been made in the design of effective peroxide antimalarial drugs. Some synthetic peroxides exhibit activity equal to or higher than that of artemisinin. Peroxides having antitumor or growth-regulatory activity were also documented. In our works [1, 2] we developed new and green methods for synthesis of various types of peroxides using hydrogen peroxide and carbonyl compounds.



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## Green catalytic synthesis of aliphatic aldehydes and esters

Cortés C.V.

*Institute of Catalysis and Petroleumchemistry (ICP), CSIC, 28049 Madrid, Spain  
e-mail: vcortes@icp.csic.es*

Many aldehydes and ketones with lineal, aliphatic carbon chain, and wax esters are high value compounds used in perfumes, pharmaceutical and cosmetic applications, emulsifiers and lubricants. They could be prepared by selective oxidation of higher alcohols ( $C_{6+}$  linear alkanols) present in wastes from forestry, agriculture and the paper industry. But this reaction faces two challenges: avoiding the environmental impact of conventional processes using stoichiometric oxidants and the specific issues caused by their physicochemical characteristics (hydrophobicity, high melting and boiling points, etc.) and low reactivity [1].

Nano gold catalysts have been shown to catalyze this reaction under demanding 'green' conditions (liquid phase, low temperatures, oxygen at atmospheric pressure as oxidant, no base addition) [2], using mostly n-octanol as a model molecule.

Oxidation of n-tetradecanol on similar catalysts showed the effect of the alcohol carbon-chain length: decrease of activity and increase of selectivity to aldehyde. The detailed analysis of the influence of reaction parameters (run time and temperature) of this latter reaction on 2%Au/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed a drastic change of selectivity as a function of alcohol conversion, revealing a mechanistic effect of the support, that allows to get high selectivity to either aldehyde or ester by proper selection of reaction conditions [3].

It was found that the catalytic performance of nano gold catalysts depend strongly on the nature of the support, and more specifically of its surface. This opens a way to improve their activity by modifying the support surface prior to deposit the gold active phase. Doping the titania support with La and Ce increased four- and two-fold, respectively, the activity of Au/TiO<sub>2</sub> under the same reaction conditions [4].

The application of this strategy of modification has allowed to obtain nanosilver catalysts as active as their nanogold homologues, despite of the lower intrinsic catalytic activity of Ag compared to that of Au [5]. In addition these Ag nano catalysts show a higher selectivity to aldehyde than nano Au catalysts, thus offering new ways to control selectivity in the oxidation of these alkanols.

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**Interlayer dynamics of the active sites of transition metal sulfide-based catalysts and the mechanisms of hydrodesulfurization of oil fractions and synthesis gas conversion into higher alcohols and other oxygenates**

Kogan V.

*N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991,  
Russia  
e-mail: vmk@ioc.ac.ru*

Short Description of what will be discussed during the presentation Recently suggested concept on the dynamic nature of active sites (AS) of the catalysts (Dynamic Model - DM) based on transition metal sulphides bases a hypothesis, that AS formed and functioning under the reaction conditions can oscillate between layers of promoted molybdenum sulphide. The DM assumes the existence of the AC of different types and the possibility of their mutual transformation due to the reversible migration of sulphur and promoter between the crystallite layers in a hydrogen atmosphere. The DM explains a series of “structure – property” correlations. The results suggest that the catalytic activity in hydrodesulphurization (HDS) and hydrogenation (HYD) reactions depends on the shape of crystallites of the active phase. Alkali-modified CoMoS is a promising catalytic system both for hydrotreating of FCC gasoline and synthesis of higher alcohols from synthesis gas. According to quantum chemical calculations potassium donates electronic density onto the Co atoms of CoMoS phase AS. Reduction of metal atoms of the AS leads to a decrease in Lewis acidity and in the CO and H<sub>2</sub> adsorption energy as well as promoting the oxidative addition of H<sub>2</sub>. The influence of ethanol addition to synthesis gas on its conversion and the product composition results in sharp increase of CO conversion in the presence of ethanol. A reaction network of CO conversion on the KCoMoS catalyst active sites depending on the catalyst composition and reaction conditions was suggested. The proposed model makes it possible to develop criteria for the evaluation of the efficiency of catalytic performance for HDS of oil crudes of various types, for syngas conversion with formation of higher alcohols and their followed conversion into wide range of oxygenates.

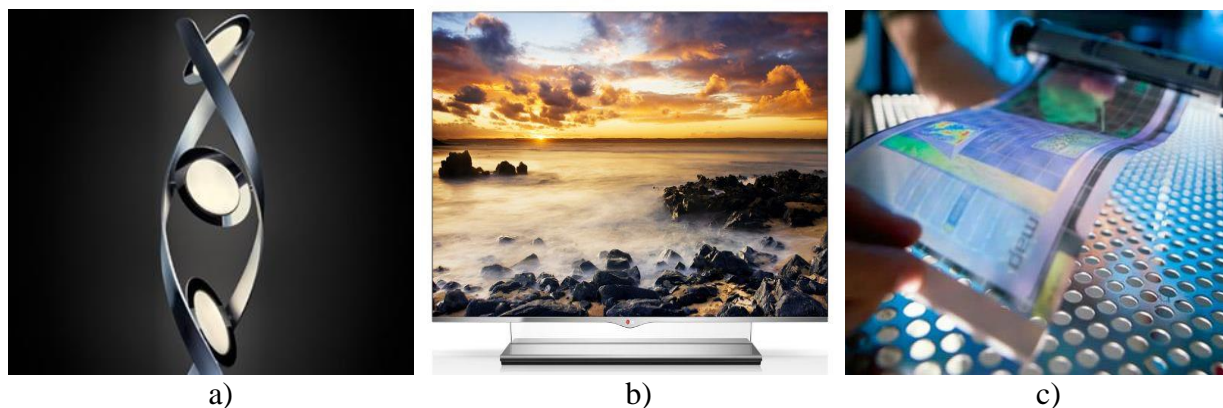
## Materials for organic light emitting devices: synthesis and application

Cherednichenko A.G.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: sorbotek@yandex.ru*

Organic light emitting devices (OLED) have been one of the most attractive research topics in materials science for the last three decades. The attractiveness of this area is due to the interdisciplinary nature of the approach, which includes synthetic and physical chemistry, electronic and engineering science. The link between fundamental and applied science and the huge industrial and commercial interest in its application is particularly attractive. Industrial interest in organic electroluminescent materials arose from the hope that the future display technology will be mainly based on organic light-emitting diodes and will have advantages such as high brightness, wide viewing angles, manufacturability and low cost [1].

The appearance of electrophosphorescent emitters based on coordination compounds of rare metals with organic ligands determined a further milestone on the way to improve the efficiency of these devices. Currently, high-performance TVs, monitors, lighting sources are produced on the basis of organic emission materials (Fig.1).



**Fig. 1.** Modern OLED devices based on organic semiconductor materials: lighting devices (a); TVs and monitors (b); devices on a flexible substrate (b).

The complete structure OLED is made of 10-12 nanoscale layers of various functional purposes. The method of vacuum thermal deposition is used to solve this problem. The efficiency of the OLED device depends on the nature of the materials used, their properties, the absence of impurities and the optimal combination of emission and auxiliary materials [2].

For further development of this technology it is necessary to synthesize new effective organic electroluminescent materials and to optimize the composition and structure of OLED devices.

*The publication has been prepared with the support of the  
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## Thermochemistry of some polyazocontaining compounds. Enthalpies of formation and reorganization of radicals

Miroshnichenko E.A.<sup>1</sup>, Pashchenko L.L.<sup>2</sup>, Kon'kova T.S.<sup>1</sup>

<sup>1</sup>*N.N. Semenov Institute of Chemical Physics RAS, 119991, Moscow, Kosygin str. 4, Russia*

<sup>2</sup>*Chemistry Department, Lomonosov Moscow State University, 119991, Leninsky Gory1, Russia  
e-mail: eamir02@mail.ru*

Polyazocontaining compounds are important industrial chemicals with a broad range of applications. This class of compounds is widely used in the synthesis of many diverse products. Some compounds are highly explosive. To investigate the stability and performance of these chemicals, knowledge of the enthalpy of formation ( $\Delta_f H^\circ_{298}$ ) is an essential requirement. Other thermo chemical properties, such as enthalpies of vaporization ( $\Delta_{\text{vap}} H^\circ_{298}$ ) and energies of reorganization of radicals are needed for the characterization of the chemical degradation pathways of their compounds. Despite the extensive studies of their compounds, available thermo chemical experimental information is often scarce and frequently presents significant discrepancy among published results.

In this work the enthalpies of formation,  $\Delta_f H^\circ_{(\text{cond})}$ , and vaporization  $\Delta_{\text{vap}} H^\circ$ , of some polyazocontaining compounds are determined, a namely phenylazide **I** ( $\text{C}_6\text{H}_5\text{N}_3$ ), benzylazide **II** ( $\text{C}_6\text{H}_5\text{CH}_2\text{N}_3$ ), three-phenyl-methylazide **III** ( $(\text{C}_6\text{H}_5)_3\text{CN}_3$ ), three-nitromethylazide **IV** ( $(\text{NO}_2)_3\text{CN}_3$ ) и 1-azido-1, 1-dinitroethane **V**  $\text{CH}_3(\text{NO}_2)_2\text{CN}_3$ . Using experimentally obtained values of  $\Delta_f H^\circ_{(\text{cond})}$  and  $\Delta_{\text{vap}} H^\circ$  the standard enthalpies of formation in gas phase are calculated. The bond dissociation energies,  $D$ , C – N are calculated (Table 1).

Using fundamental equations of the chemical physics, the calculation scheme by “double difference” method of the enthalpy of formation of radical and energies of reorganization of molecule fragments into radicals is offered. The new calculation method is offered to determine the energy of reorganization of molecule fragment  $\text{N}_3$  into radical  $\text{N}_3 \cdot$ . Reorganization energies of radicals and bond dissociation energies,  $D$ , are calculated, ( $\text{kJ} \cdot \text{mol}^{-1}$ ). See below. Significant thermochemical characteristics of investigated by us compounds are given in Table 1.

**Table 1.** Thermochemical characteristics of polyazocontaining compounds ( $\text{kJ} \cdot \text{mol}^{-1}$ )

	$\Delta_f H^\circ_{(\text{cond})}$	$\Delta_{\text{vap}} H^\circ$	$\Delta_f H^\circ_g$	$D$
<b>I</b> (l)	$345.2 \pm 2.5$	$44.8 \pm 0.8$	$389.9 \pm 3.4$	362.3
<b>II</b> (l)	$368.2 \pm 1.2$	$48.1 \pm 0.4$	$416.3 \pm 1.7$	205.8
<b>III</b> (cr)	$486.2 \pm 1.2$	$120.5 \pm 1.2$	$606.7 \pm 2.5$	199.6
<b>IV</b> (l)	$306.3 \pm 5.4$	$46.0 \pm 2.1$	$352.3 \pm 6.2$	286.6
<b>V</b> (l)	$196.6 \pm 2.9$	$56.5 \pm 0.8$	$253.1 \pm 3.8$	270.3

The new calculation method for determination of the enthalpy of formation and the energy of reorganization of radicals gives a way to calculate ( $\text{kJ} \cdot \text{mol}^{-1}$ ): the enthalpy of formation of radical  $(\text{N}=\text{NC}_6\text{H}_5) \cdot$  - 275.7, bond dissociation energy  $\text{C}_6\text{H}_5 - (\text{N}=\text{NC}_6\text{H}_5)$  - 207.5, median thermo chemical bond energies  $E$  (C – N) - 362.3,  $E$  (N = N) - 489.1,  $\Sigma E \text{N}_3$  - 1004.2,  $\Sigma E \text{N}=\text{NC}_6\text{H}_5$  - 5904.5. Reorganization energies of radicals ( $\text{kJ} \cdot \text{mol}^{-1}$ ) are calculated, namely  $(\text{N}=\text{NC}_6\text{H}_5) \cdot$  - 154.8, which is near to energy of reorganization of acetylene radicals,  $\sim 160 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{C}_6\text{H}_5\text{CH}_2 \cdot$  - 40.5;  $(\text{C}_6\text{H}_5)_3\text{C} \cdot$  - 85.4;  $(\text{NO}_2)_3\text{C} \cdot$  - 16.3,  $\text{N}_3 \cdot$  - 0 and  $\text{CH}_3(\text{NO}_2)_2\text{C} \cdot$  - 8. 5. Bond dissociation energies,  $D$ , which listed in Table 1 and in calculation process of radical's reorganization energy are obtained from the standard enthalpies of formation in gas phase of compounds I – V.

Obtained by us data on reorganization energies of radicals and bond dissociation energies are needed for energy calculations of the kinetics of the reactions involving azido- and polyazo-containing compounds.

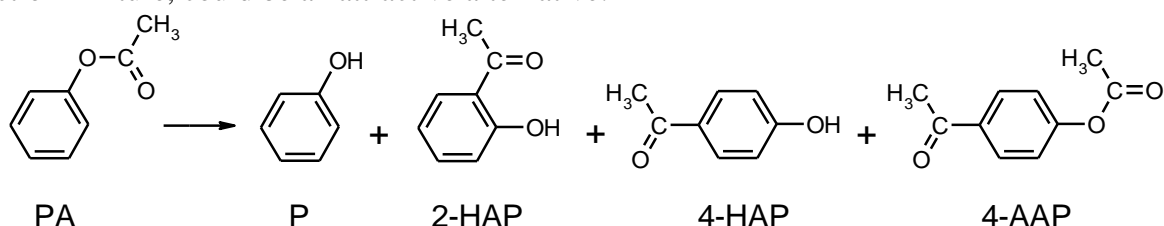
## Heterogeneous catalysis meets organic synthesis a case study: fries - rearrangement of phenylacetate

Roessner F.

Carl v. Ossietzky University, Industrial Chemistry 2, D-26111 Oldenburg  
e-mail: frank.roessner@uni-oldenburg.de

Fries - rearrangement of phenyl acetate to hydroxyaryl ketons is a commercially important process for the synthesis of fine chemicals and pharmaceuticals. Since the turnover number on the added  $\text{AlCl}_3$  is only one, the process does not belong to catalytic conversion.

Therefore, the usage of heterogeneous catalysts, which could be easily separated from the reaction mixture, could be an attractive alternative.



Crystalline microporous aluminosilicates (zeolites) are suitable catalysts to substitute the co-reactant  $\text{AlCl}_3$ . Interestingly, activity of the studied catalysts rather correlates with the number of Brönsted acidic groups than with Lewis centers, as known for homogeneous catalysis. However, two effects accompany their application: (i) mass transfer limitation and, (2) deactivation. Furthermore, temperature control seems to be a crucial moment for reproducibility of experiments.

Usually, a rigid stirring is used for homogenisation of the reaction mixture. In case of heterogeneous systems, diffusion layers are formed around the catalyst particles resulting in

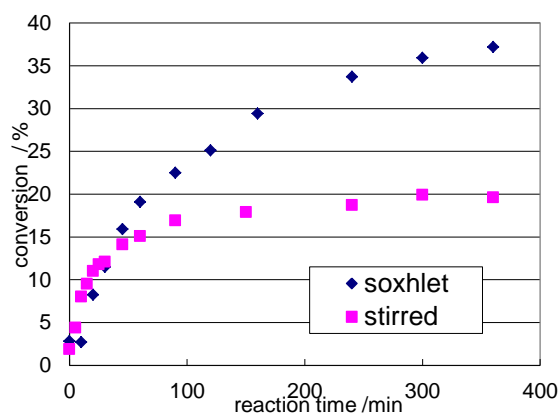


Figure 1 Conversion of phenyl acetate in

the nature of used solvents. Here, the activity in conversion of phenyl acetate correlates with donor strength of the solvent and not with its polarity. The donor strength was determined by  $^{23}\text{Na}$  NMR.

It was shown, that heterogeneous catalyst are also able to catalyse the conversion of functionalised organic compounds. Knowledge of principles of chemical engineering will give a great impact in understanding reaction behaviour. This will be necessary for upscaling of target reactions.

lower reaction rate. Therefore, a new reactor based on a soxhlet system was created. The permanent flow of condensate creates a state similar to a plug flow reactor. As a result, the conversion increased nearly twice at the same conditions (Fig. 1).

Calculating the mass balance of the acetyl groups, it was found, that two effects influence the deactivation: (i) product inhibition by acetoxyacetophenone, and (ii) polymerization of ketenes bound to the surface resulting in coke formation and blocking of pore entrance.

The conversion was also influenced by

## Nanocatalysts based on metal/hypercrosslinked polystyrene composites

Matveeva V.G.<sup>1,2</sup>, Sulman E.M.<sup>1</sup>, Sulman M.G., Sidorov A.I.<sup>1</sup>, Nikoshvili L.Zh.<sup>1</sup>,  
Manaenkov O.V.<sup>1</sup>, Bykov A.V.<sup>1</sup>, Shkileva I.P.<sup>1</sup>, Doluda V.Yu.<sup>1</sup>

<sup>1</sup>Tver State Technical University, 170026, Tver, A. Nikitin str. 22

<sup>2</sup>Tver State University, 170100, Tver, Zhelyabova str: 33

e-mail: matveeva@science.tver.ru

Recent years, hypercrosslinked polystyrene (HPS) became a widely used material as a support for metal nanoparticles (NPs) [1]. These catalysts not only demonstrated high activity in the liquid phase oxidation and hydrogenation but also proved to be stable. Metal resides on the porous surface of HPS in a dispersed form with the particle size of 1-4nm. Active metal particles are tightly bound to the surface of HPS and are not removed by aqueous solutions. It is already well established that catalytic NPs possess unique catalytic properties due to large surface areas and a considerable number of surface atoms leading to an increased amount of active sites [1-3].

Catalytic oxidation and hydrogenation of mono- and disaccharides allows avoiding protection and deprotection stages of various functional groups. This work is devoted to the formation of Pd, Pt and Ru-containing HPS-based nanoparticulate catalysts and study of their catalytic properties for the synthesis of fine chemicals. HPS was purchased from Purolite Int. as MN270 (non-functionalized) and MN100 (bearing amino-groups). The following metal precursors were used:  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{PdCl}_4$ , and  $\text{Ru}(\text{OH})\text{Cl}_3$ . Additionally  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ ,  $(\text{PhCN})_2\text{PdCl}_2$ ,  $(\text{Sty})(\text{CH}_3\text{CN})\text{PdCl}_2$ ,  $(\text{StyPdCl}_2)_2$  were used. THF, MeOH,  $\text{H}_2\text{O}_2$ , D-glucose, and D-maltose were purchased from Sigma-Aldrich.

The samples of the catalysts with different metal loading varied from 1% up to 5% (wt.) were prepared by the impregnation method. Oxidation reaction was conducted batchwise in isothermal glass batch reactor, while for hydrogenation various reaction setups were used: PARR 4200 apparatus; PARR 5000 multi-reactor system and stainless steel autoclave reactor specially developed by the group of Tver Technical University. Experiments were performed in an aqueous reaction medium at the variation of substrate concentration, temperature, pH and oxygen flow rate (for catalytic oxidation) and hydrogen pressure (in the case of hydrogenation). For all the catalysts the physicochemical investigations were conducted via TEM, XPS, XFA, and liquid nitrogen physisorption.

We studied the influence of such key parameters as NP morphology, metal precursor type, the presence of large pores and pore functionality on catalytic behavior of nanoparticulate catalysts. We demonstrated that nanocomposites based on catalytic metal (Pt, Pd, Ru, Au) NPs formed in micro/mesoporous HPS show high activity, selectivity, and stability. In all the cases we suppose that the formation of well-defined metal-containing NPs can be controlled in the pores of HPS.

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*Authors thank Dr. Liudmila Bronstein (Indiana University) for TEM study of the catalysts.*

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## NASICON type catalysts $\text{Na}(\text{Cs})_{1-2x}\text{M}_x\text{Zr}_2(\text{PO}_4)_3$ for aliphatic alcohols' vapor-phase conversions

Mikhaleiko I.I., Pylinina A.I., Knyazeva E.I.

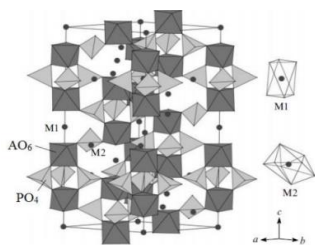
Peoples Friendship University (RUDN-University) Moscow, Russia  
Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: mikhaleiko\_ii@pfur.ru

Among the ways of practical application of complex zirconium phosphates belonging to NASICON-type frame structure (ionics, sensors, ion-exchange materials) the catalysis is very attractive for hydrogen and olefin production from C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> alcohols. Catalytic conversion of propanols on Li-Zr-phosphates results in 100% selectivity to propene [1].

In our work ternary orthophosphates  $\text{Na}(\text{Cs})_{1-2x}\text{M}_x\text{Zr}_2(\text{PO}_4)_3$  were obtained by sol-gel procedure and studied for dehydration and dehydrogenation of isobutanol (iC<sub>4</sub>) and isopropanol (iC<sub>3</sub>) in the temperature range 200-400°C. The chemical composition and homogeneity of the samples were verified on scanning electron microscope with microprobe analysis and XRD method. By partially replacement of conducting ions  $\text{Na}^+$  or  $\text{Cs}^+$  by cations  $\text{M}^{2+} = \text{Ni}, \text{Co}, \text{Cu}$  we obtain the catalytic active sites. The data of thermal desorption and reactivity kinetic order for adsorbed alcohols on  $\text{Na}_{0.5}\text{M}_{0.25}\text{Zr}_2(\text{PO}_4)_3$  showed the difference in iC<sub>3</sub> and iC<sub>4</sub> linkage on catalysts surface. The activation energy of iC<sub>3</sub> desorption increases in a row  $\text{Ni} (92) > \text{Co} (125) > \text{Cu} (167 \text{ kJ/mol})$  as a linear function of ionic radii  $\text{M}^{2+}$  [2]. The ratio of iC<sub>4</sub> adsorbed and reactive in dehydrogenation increases in series  $\text{Cu} \rightarrow \text{Ni} \rightarrow \text{Co}$  with 40% for Co.

For M-doped Zr-phosphates (ZP) we'll discuss the temperature hysteresis observed in vapor-phase iC<sub>3</sub> conversions over NaMZP [3] and iC<sub>4</sub> over CsMZP treated in Ar or H<sub>2</sub> plasma.

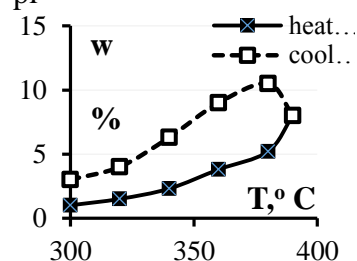
**Fig.1.** NASICON structure



Changes in acetone yield  $\Delta N$  and apparent activation energy  $E_a$

$\text{M}^{2+}$	$\Delta N, \% \text{ at } 320^\circ\text{C}$	$\Delta E_a^{C=O} = E_{a\downarrow} - E_{a\uparrow} \text{ kJ/mol}$
Co	+90	26
Ni	-57	19
Cu	+10	16

**Fig.2.** iC<sub>4</sub> conversion to aldehyde on CsCo<sub>0.15</sub>ZP Ar pl



From the table it can be seen that significant hysteresis of “anticlockwise”-type for acetone formation ( $\Delta N = N_{\downarrow} - N_{\uparrow}$ , when reaction temperature is down  $\downarrow$  or up  $\uparrow$ ) was found for Co<sub>0.125</sub>-ZP catalyst with increase of the activation energy value for dehydrogenating reaction. The same result is possible for “clockwise” hysteresis in case of Ni<sub>0.125</sub>-ZP. Olefin formation on CsCo(Ni)ZP catalysts proceeded without hysteresis effect. Preliminary treatment of Cs<sub>0.7</sub>Co<sub>0.15</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> in high frequency H<sub>2</sub> or Ar discharge lead to “anticlockwise”-hysteresis (fig.2). Note, that the basic reaction on CsCo(Ni)ZP was iC<sub>4</sub> dehydration with S~86%.

So, varying conducting ion, dopant M in ZrP catalyst and special pretreatments procedure we can regulate activity and selectivity of such type catalysts in alcohol conversion processes.

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# Oral Reports



## Hydrogen desorption from activated palladium-yttrium foil

Mikhaleenko I.I.<sup>1</sup>, Gorbunov S.V.<sup>2</sup>, Roshan N.R.<sup>2</sup>, Burchanov G.S.<sup>2</sup>

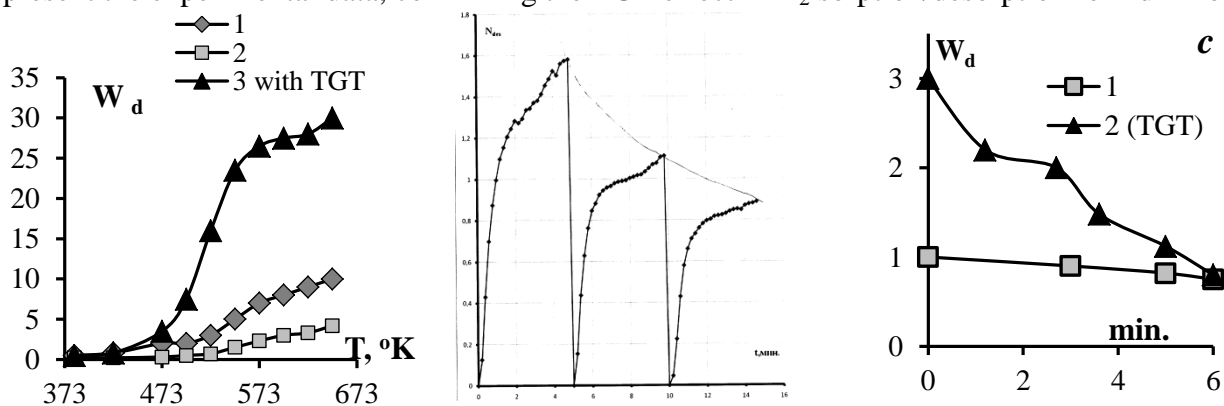
<sup>1</sup> RUDN-University, 117198, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup> Baikov Institute of Metallurgy and Material Science RAS, Moscow, Russia  
e-mail: sgorbunov@imet.ac.ru

Academician Gryaznov V.M. (1922-2001) head of physical and colloid chemistry department in Peoples Friendship University from 1962 to 2001 years. His pioneered works on hydrogen diffusion through thin-walled Pd or Pd alloys and Pd membranes application in heterogeneous catalysis started in 1970-72 in collaboration with institutes of Russian Academy of Sciences (Baikov Institute, Topchiev Institute of Petrochemical Synthesis). Palladium foils were studied as membrane catalysts for dehydrogenation/hydrogenation reactions occurred on input and output side with hydrogen penetration throw Pd. Now palladium membrane technologies [1] include not only chemical applications (solar steam reforming, IGCC, NGCC, CHP plants) but a high purity hydrogen production (99,999% H<sub>2</sub>).

By alloying Pd with other metals (Ru,Pt,Ag,Cu) the chemical stability, surface reactivity, H<sub>2</sub> permeability can be improved and the operating temperature range can be broadened. Among investigated palladium alloys the best characteristics showed membrane with 7 wt.% Y [2]. Sufficient mobility of surface atoms of noble metal and formation of surface defects can be achieved by use of thermo graduated treatment (TGT) in vacuum.

The basic result of our previous study of PdY properties in H<sub>2</sub> sorption/desorption processes as perspective membrane for high purity hydrogen production was the inhibiting effect of preliminary dissolved hydrogen on adsorption capacity of the foil [3]. In this paper we will present the experimental data, confirming the TGT effect in H<sub>2</sub> sorption/desorption for Pd-Y foil.



**a.** Temperature dependences of desorption rate ( $W_d \cdot 10^{15}$  molec.H<sub>2</sub> min.<sup>-1</sup>); **b.** Desorption cycles at 648 K, **c.** Initial rate of H<sub>2</sub> desorption ( $W_{0,d} \cdot 10^{15}$  molec.H<sub>2</sub> min.<sup>-1</sup>) in cycles at 648 K.

The rise of  $W_d$  values in 3 times is connected with the increase of total quantity sorbed hydrogen that strongly bonded with Pd foil. Activation energies of desorption are 36 (1) vs. 62 kJ/mol (3).

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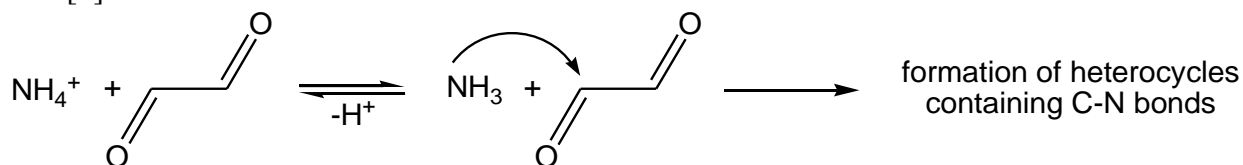
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## Condensation of glyoxal with ammonia in aqueous solution: A DFT study

Tuguldurova V.P., Fateev A.V., Kotov A.V., Poleschuk O.Kh., Vodyankina O.V.

*Tomsk State University, 36 Lenin ave., Tomsk, Russia 634050*  
*e-mail: tuguldurova91@mail.ru*

The reactions of glyoxal with ammonia, ammonium salts, and amines cause the formation of the secondary organic aerosol (SOA) components (imidazole and its derivatives) in the atmosphere [1].



The basic products and the kinetic functions of the reactions between glyoxal and ammonia in a solution have been identified [2], and different reaction schemes have been proposed [3,4]. However, there is no detailed explanation of the mechanism of the formation of imidazoles and their derivatives during the interaction of glyoxal with ammonium salts. Therefore, our research goal is to identify the main routes of the glyoxal interaction with ammonia in aqueous solution using quantum chemical calculations.

The calculation was carried out using the Gaussian'16 program package installed at the ANNEMARIE – Cluster of the Hochschulrechenzentrum of the Philipps-Universität Marburg at the B3LYP-D3/6-311G(d,p) level of theory. The solvent effect was accounted by the PCM solvation model and a recalculation of the obtained data using the low-frequency corrections and correction from the gas with the pressure of 1 atm applied to a solution with a concentration of 1 mol/l by using the freely available GoodVibes script developed by the Paton and Funes-Ardoiz [5].

A detailed mechanism of the formation of the key intermediates, namely, ethanediimine, diaminoethanediol, and aminoethanetriol, required for the imidazole ring cyclization, is proposed, and its potential energy surface (PES) is constructed. The mechanism includes the experimentally identified intermediate compounds and takes into account the conformational and hydration equilibria of glyoxal. The schemes are proposed for further conversion of the key intermediates to the products of the glyoxal–ammonia condensation in the aqueous solution, C–N cyclic oligomers, that were identified. The products are shown to correspond to low positions on the PES in terms of Gibbs free energy, from  $-30.8$  to  $-67.5$  kcal/mol, which confirms the high probability of their formation. The preferable thermodynamic pathway for the formation of the imidazole products does not comprise the conversion of the diimine intermediate with the participation of the proton, but rather includes the interaction of either the diaminoalcohol with glyoxal monohydrate or two monoamine derivatives between themselves (aminoethanetriol and aminohydroxyacetaldehyde).

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## **Novel highly ordered liquid crystals resulting from the complexation of alkyl- and alkoxybenzoic acids**

Gorbacheva S.N., Konstantinov I.I., Ilyin S.O.

*A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences  
29 Leninsky prospekt, 119991 Moscow, Russia*

A study was carried out of the rheological and thermophysical properties of individual nematogenic p-alkyl- and p-alkoxybenzoic acids as well as their binary mixtures. Alkoxybenzoic acids are characterized by higher viscosity, activation energy of viscous flow, melting and clearing temperatures compared to alkylbenzoic acids with comparable molecular weight. Mixing the alkyl- and alkoxybenzoic acids leads to the formation of a homogeneous solution, this is characterized by a lower melting point, as compared to the melting points of individual compounds, and a clearing temperature, which is intermediate in value. In mixtures of nematogenic acids, a polymorphism is found, consisting in the formation of a smectic mesophase in addition to the nematic one. The smectic mesophase is characterized not only by a many times higher viscosity compared with the nematic one, but also by viscoplastic behavior, which is expressed in the presence of yield stress and viscoelasticity. Varying the ratio of acids in a mixture affects transition temperatures: an increase in the proportion of the lower-melting component shifts the transition points to the low-temperature region — insignificantly in the case of the melting temperature and greatly in the cases of clearing and polymorphic-transition temperatures. In mixtures of acids, regardless of component ratio, neither rheological nor calorimetric methods reveal transitions characteristic of individual compounds. Alkyl- and alkoxybenzoic acids in mixtures always form unsymmetrical dimers using hydrogen bonds. The existence of such dimers leads to a new complex of properties, and the presence of additionally symmetric dimers in the system does not lead to phase separation and additively affects the properties. Thus, the use of alkyl and alkoxybenzoic acids in mixtures allows one to expand the region of existence of the liquid crystalline state and to obtain a more highly ordered mesophase.

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## **A mass spectrometric study of the cadmium pivalate phenanthroline complex**

Kayumova D.B., Malkerova I.P., Shmelev M.A., Sidorov A.A., Eremanko I.L., Alikhanyan A.S.

*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
119991, Moscow, Leninskii pr. 31  
e-mail: dkayumova@gmail.com*

Cadmium oxide belongs to the group of transparent conducting oxides (TCO) and because of its electrical, optical, chemical, and physicochemical properties, it is fairly promising as a working medium for the design of analytical instruments, sensors, transistors, field emission displays, etc. Functional film materials based on the multicomponent oxide systems with TCO can be prepared by chemical vapor deposition (CVD) in which volatile complexes of trimethylacetic acid (pivalates) were used as precursors.

A preliminary investigation of a polymeric cadmium pivalate has shown that evaporation of this compound is accompanied by complete thermal decomposition to give cadmium atoms, carbon dioxide, and carbonyl, carboxyl, and other gaseous products. An approach that allows one to suppress polymerization of the condensed phase and thus to obtain volatile compounds to be used as CVD precursors consists in saturation of the central ion coordination sphere with additional ligands such as o-phenanthroline (Phen). So, it was interesting to investigate the vaporization processes and thermodynamic characteristics of the cadmium pivalate phenanthroline complex.

Evaporation of the complex  $\text{Cd}_2\text{Piv}_4\text{Phen}_2$  was studied by the Knudsen effusion method with mass spectral analysis of gas phase composition on an MC 1301 instrument in the temperature range of 450–520 K. Molybdenum Knudsen cells were used, with the ratio of evaporation area to effusion area being  $\sim 600$ . The temperature was measured by a Pt/Pt-Rh thermocouple and maintained to an accuracy of  $\pm 1^\circ$ .

The dissociative ionization of saturated vapor molecules and complete isothermal vaporization of a known weighed sample were experimentally studied for determining the molecular composition of the gas phase, the absolute partial pressures, and the character of congruent sublimation of complex.

The experiment was demonstrated that the evaporation is congruent, and the gas phase consists of  $\text{CdPiv}_2\text{Phen}$  molecules. The standard enthalpy of sublimation of these molecules was found and its recommended value is  $\Delta_s H^\circ_{298} = 186.9 \pm 4.6$  kJ/mol. The upper and the lower limits of the enthalpy of dissociation of  $\text{CdPiv}_2\text{Phen}$  molecules to cadmium pivalate and phenanthroline by the reaction



were estimated and can be represented as  $177.5 \leq \Delta H^\circ_{500} \leq 260$  kJ/mol

In conclusion, it can be noted that the thermodynamic characteristics of cadmium phenanthroline complex make it suitable as a precursor for CVD production of oxide coatings or nanocrystalline films.

*The work was carried out within the State Assignment on Fundamental Research to the  
Kurnakov Institute of General and Inorganic Chemistry*

## **Spectral features of difluoroboron $\beta$ -diketonates with aromatic substituents: an analysis based on DFT and TD-DFT calculations**

Gelfand N.A., Freidzon A.Ya., Vovna V.I.

*Far Eastern Federal University, 690092, Vladivostok, 8 Sukhanova St.  
e-mail: gelfand.na@dvfu.ru*

Difluoroboron  $\beta$ -diketonates are tetracoordinate boron complexes exhibiting phosphorescence at room temperature, solvatochromism, thermochromism, and mechanochromism. The wide diversity of important optical properties makes these dyes promising for use in optoelectronics and photonics as biological and chemical optical sensors.

In many cases, these dyes have complicated long-wave absorption spectra. Understanding the nature of their absorption features may shed light on their emission properties and make it possible to effectively design optical chemo-, thermo-, or mechanosensors. This is why their electronic structure and spectral characteristics are actively studied by theoretical and experimental methods.

In the present study, we make a step toward better understanding of spectral features of a series of difluoroboron  $\beta$ -diketonates with an extended  $\pi$  system. The UV-Vis absorption spectra of difluoroboron  $\beta$ -diketonates with aromatic substituents at the  $\beta$ -carbon are studied thoroughly using DFT and TD-DFT with the CAM-B3LYP functional. The vibronic absorption bandshape is studied using time-dependent formalism and displaced harmonic oscillator model.

The complicated experimental spectra of these dyes can be correctly interpreted by considering their structural features. A closer look at the calculated data shows that the conformational flexibility of these compounds markedly influences their spectral shape. For the complexes with an extended  $\pi$  system, several conformers with significantly different absorption spectra are present in the equilibrium mixture in solution. Introducing a donor group alters the electronic structure of the complexes, so the charge distribution asymmetry in the molecules increases and the nature of the electronic transitions changes. Thus, both types of substituents, aromatic and donor ones, affect the spectral shape. Understanding their roles may help one to explain the absorption spectra of these and similar compounds and predict their response to analytes and other factors.

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Far Eastern Computing Resource "IACP FEB RAS, Computing Center FEB RAS, Joint  
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## Formation and growth of barium titanate nanocrystals in water vapor

Kholodkova A.A.<sup>1,2</sup>, Danchevskaya M.N.<sup>1,2</sup>, Ivakin Yu.D.<sup>1</sup>, Fionov A.S.<sup>3</sup>, Ponomarev S.G.<sup>2</sup>

<sup>1</sup>Chemistry Department, Lomonosov MSU, 119991, Moscow, Leninskie Gory 1-3,

<sup>2</sup>Moscow Polytech, 115280, Moscow, Avtozavodskaya str. 16,

<sup>3</sup>Kotel'nikov Institute of Radio-Engineering and Electronics of RAS, 125009, Moscow,

Mokhovaya str. 11-7,

e-mail: anastasia.kholodkova@gmail.com

Recently, a method of fine-crystalline BaTiO<sub>3</sub> synthesis in water vapor was performed as a promising route to produce nanoscale and submicron powders that can be used as raw materials for dielectric ceramics [1,2]. In this work, we studied kinetics of BaTiO<sub>3</sub> formation from oxides (BaO and TiO<sub>2</sub>) in a medium of water vapor in equilibrium with a liquid. Using HRTEM, it was found that the process involved amorphization of TiO<sub>2</sub> and crystallization of BaTiO<sub>3</sub> in the solid phase. The introduction of protons into the reaction medium by addition of various acids contributed to the acceleration of BaTiO<sub>3</sub> formation. The activation energy of the considered reaction in vapor was about 57 kJ/mol, which was significantly lower than the activation energy of the solid-state reaction of BaTiO<sub>3</sub> formation in air (361 kJ/mol [3]). Phase boundary diffusion appeared to be the limiting stage of the reaction in vapor. Water molecules possessed an activating effect on solid reagents by dissociative adsorption on their surfaces, diffusion of protons into the crystal lattice, and breaking metal-oxygen bonds. This led to an increase in the structural mobility of the oxides and facilitated diffusion processes in the solid phase. It was shown by TEM that the recrystallization processes in the BaTiO<sub>3</sub> particles occurred by solid-state diffusion. In contrast to the conditions of high-temperature solid-state synthesis of BaTiO<sub>3</sub> in air, in water vapor the formation of undesired side phases of barium polytitanates was not observed regardless of the molar ratio of the starting oxides. An excess of BaO with respect to TiO<sub>2</sub> in the reaction mixture led to an increase in the average size of the crystals from nanometric to submicron.

Ceramic materials with a dielectric constant of 1600–1800 at room temperature in the frequency range of 20 Hz – 2 MHz were manufactured from a powder of barium titanate synthesized in the vapor medium, by means of semi-dry pressing at a pressure of 100–200 MPa and sintering at 1300°C.

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## Protective conversion titanium-oxide nanocoatings on iron and non-ferrous metals

Vagramyan T.A., Abrashov A.A., Grigoryan N.S., Vasilenko O.A., Shcherbina E.A.

*Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Miusskaya sq. 9  
e-mail: vagramyan@muctr.ru*

Currently in technologies of painting of metal surfaces as an alternative to the adhesive phosphate and chromatic layers on the steel in the world have become increasingly used nanoscale adhesive coatings obtained from solutions hexafluorotitanic and hexafluorozirconic acids. The advantages of these new technologies are their lower energy consumption and technological effectiveness comparing with phosphating and chromating processes. Solutions for application of these coatings do not require heating, strict control of process, easy to apply and give less toxic sludge [1-7].

Formation of adhesion titanium-oxide layers on steel, aluminum and zinc-plated surface was studied. The process is less toxic than chromate treatment and easier than phosphating. The solution used contained  $\text{H}_2\text{TiF}_6$  2 g/l;  $\text{Ni}^{2+}$  0,08 g/l;  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  0,1-0,3 g/l; pH 4,0-5,0 at 18-25°C. After etching time of 3-5 min coatings formed on steel contain following elements: Ti, Fe, Mo, F and O. Ni content as ions and nickel metal. After 80 min of etching practically all Ni in metallic form and there is no ionic Ni. Iron of the 20 min etching is also in metallic form, indicating to the end of coating etching. In the coating Fe is contained as mixture of FeO and  $\text{Fe}_2\text{O}_3$ . Thus, the existence of contact-reduced Ni was shown in this study. The coatings formed have amorphous structure.

Corrosion tests have demonstrated good results. In spite of lower thickness and mass their protective characteristics are not worse than those of phosphate or chromate coatings. These coatings have protective characteristics which are highly competitive with silicone and amorphous phosphate coatings and are similar to the protective characteristics of crystalline phosphate coatings.

During this work the process of applying the adhesive ceramic titanium-oxide nanoscale coatings under the paint layer was developed.

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## **Metal and toxin-binding ability of pectin polysaccharides obtained by the method of combined fractionation**

Gorshkova R.M.<sup>1</sup>, Slobodova D.A.<sup>1,2</sup>, Novoselov N.P.<sup>2</sup>, Panarin E.F.<sup>1</sup>

<sup>1</sup>*Institute of Macromolecular Compounds, Russian Academy of Sciences,  
199004, Saint-Petersburg, Bolshoy pr. 31*

<sup>2</sup>*Saint-Petersburg State University of Industrial Technologies and Design,  
191186, Saint-Petersburg, Bolshaya Morskaya, 18  
e-mail: gorshkova.raisa@gmail.com*

Pectic polysaccharides are one of the most complex classes of biopolymers, differing both in structure and in physicochemical parameters. Regardless of the nature of the raw materials and the method of production, they are united by a common property: in the gastrointestinal tract they are not hydrolyzed by amylases of the salivary and pancreatic glands and are not absorbed from the intestine into the blood, however, in the large intestine they are degraded by bacterial microflora enzymes. A number of diseases can be prevented due to the biological activity inherent in pectin polysaccharides, the study of which was the purpose of this work.

Pectin polysaccharides were obtained by the developed method of combined fractionation in a column-type reactor. The advantage of this method is the possibility of timely isolation of the extracted pectin macromolecules, which makes it possible to prevent their degradation, to ensure a high yield and to maintain optimal physicochemical parameters and properties. Secondary resources of the food industry were used as raw materials: apple (AP) and peach pomace (PchP), as well as sunflower heads (SH)). The hydrolyzate solution was divided into three fractions: a water-swallowable polymer with a network structure - microgel (MG), water-soluble pectin substances (PS) and low molecular weight residues - oligosaccharides (OS).

For microgel and pectin substances, metal binding and hepatoprotective properties have been studied. In vitro, it was established that all samples of MG and PS have greater sorption activity with respect to heavy metal ions and bilirubin, as compared with pharmacopoeial preparations, as well as with pectic polysaccharides obtained by traditional technology. It is shown that microgel and pectin substances of sunflower have the highest sorption capacity. At the same time, the coefficients of affinity and strength of the formed bonds, as well as an indicator of the intensity of sorption processes of MG and PS SH, significantly exceed similar parameters of other samples, which once again confirms their high binding activity.

In vivo conditions revealed that the use of microgel and pectin substances of sunflower promotes a dose-dependent decrease in the amount of lead deposited in the organs of experimental animals with enteric lead intoxication, as well as a decrease in the activity of alanine aminotransferase, aspartate aminotransferase, total and direct bilirubin in tetrachloromethane intoxication. In this case, the greatest therapeutic efficacy is observed after the use of MG and PS in the maximum dose.

It has been shown that low molecular weight water-soluble degradation products PP - oligosaccharides have a pronounced ability to increase the latent period of narcotic sleep in a dose-dependent way, accelerate the way out of alcohol intoxication and reduce the toxicity of toxicity, thus weakening the acute toxic (narcotic) effect of ethyl alcohol in experimental animals.

Thus, the decomposition products of protopectin, obtained in a dynamic mode, can be considered as additional means in the complex treatment of diseases accompanied by intoxication phenomena.

## Nanocarbon formation in dry reforming of methane over supported Ni

Murga Z.V.<sup>1</sup>, Mikhaleiko I.I.<sup>1</sup>, Eyubova S.<sup>2</sup>, Gasymov V.<sup>3</sup>

<sup>1</sup>RUDN-University, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup>Institute of Petrochemical Processes NAS, Baku, Azerbaijan

<sup>3</sup>Institute of Catalysis and Inorganic Chemistry NAS, Baku, Azerbaijan

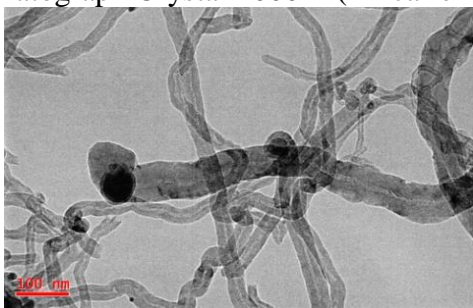
e-mail: mikhaleiko\_ii@pfur.ru

The activity, anti-coking enhancement and lower reaction temperature depend on selection of active metal, supports and promoters in performance of catalysts for such extremely endothermic reaction  $\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$  ( $\Delta H_{298\text{K}} = +247 \text{ kJ mol}^{-1}$ ). The lowering  $\text{H}_2/\text{CO}$  ratio syngas produced is preferable for the production of hydrocarbons via Fischer-Tropsch synthesis. Alumina and silica with supported nickel are the most wide spreading catalysts. Different types of carbon deposited on the catalysts' surface are discussing in DRM mechanism.

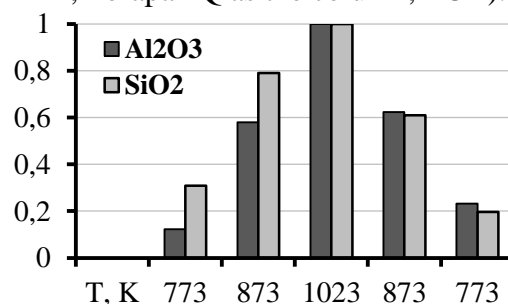
We have recently reported some characteristics of Ni,Co-alumina reforming catalysts with Ni loading 5% wt. We found that cobalt additives and Ni catalysts treatment in high frequency Ar plasma provided the activating effect.

This goal of this study is to compare the activity of Ni(5% wt.) and Ni(5%)Co supported on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  ( $S_{\text{sp}} \sim 100 \text{ m}^2/\text{g}$ ) catalysts in focus of carbon deposits.

For catalyst characterization we used XRD, XPS spectra, EDS, ESR spectra, TEM. Catalytic tests were performed in flow mode in temperature range 673-1023<sup>0</sup>K with online gas chromatograph Crystal 2000M (Ar-carrier gas, 30 mL·min<sup>-1</sup>, Porapak Q as the column, TCD).



**Fig.1.** TEM image of CNTs with Ni NPs



**Fig.2.** Relative  $\text{H}_2$  yield on supported NiCo

The comparison XRD data for Ni/ $\text{Al}_2\text{O}_3$  before (1) and after (2) catalysis shows no presence of Ni and NiO phases, the increase of degree for  $\text{Al}_2\text{O}_3$  crystallinity (35% vs.45%) after catalysis and the decrease of alumina crystallite size of from 71 to 44 nm with dominating  $\alpha$ -phase. ESR spectra 1 and 2 are with a broad resonance line indicating the multiple signals' superposition of different magnetism for Ni-containing particles. The comparison XRD data for Ni/ $\text{Al}_2\text{O}_3$  before (1) and after (2) catalysis showed no presence of Ni and NiO phases, the increase of degree for  $\text{Al}_2\text{O}_3$  crystallinity (35% vs.45%) after catalysis and the decrease of alumina crystallite size of from 71 to 44 nm with dominating  $\alpha$ -phase. ESR spectra of 1 and 2 were different with a broad resonance line indicating the multiple signals' superposition of different magnetism. Binding energies of Ni2p peaks correspond of  $\text{Ni}^{+2}$  with small quantity  $\text{Ni}^0$ . Catalytic carbon is in form of carbon nanotubes (CNTs) with encapsulated Ni nanoparticles (**fig.1**) and in of carbide form. Deactivating of "fresh" bimetallic catalysts surface due to initial carbon formation is bigger for silica (**fig.2**). The apparent activation energy of products' formation depends on surface state, but always  $E_{a \text{ H}_2} > E_{a \text{ CO}}$ . Products' molar ratio ( $\text{H}_2/\text{CO} = 0,5 \div 1$ ) augments with temperature rise for supported NiCo catalysts, but remains constant  $\sim 0,8$  for Ni/ $\text{Al}_2\text{O}_3$ .

## Synthesis, structural organization of ruthenium complex $\text{Li}_8\text{Ru}_2\text{OCl}_{14}$ and its catalytic properties in the water oxidation reaction

Tkachenko V.Yu.<sup>1</sup>, Dzhabieva Z.M.<sup>2</sup>, Shilov G.V.<sup>2</sup>, Dzhabiev T.S.<sup>2</sup>

<sup>1</sup>*M.V. Lomonosov Moscow State University, Russia*

<sup>2</sup>*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Moscow Region,  
Chernogolovka, Russia  
e-mail: timur@cat.icp.ac.ru*

No alternative to solar energy over the long run. It is clear that, in the future, energy demands will be satisfied via solar radiation transformed into a convenient energy carrier (heat, chemical fuel, electricity, etc.) by some method. One of the promising ways for transforming solar energy is its biomimetic recycling, which is similar to oxygenic photosynthesis to a certain extent and is therefore called "artificial photosynthesis". The aim of artificial photosynthesis is the photoinduced water splitting to hydrogen, which is an environmentally friendly chemical fuel, and water oxidation products. In addition to the photophysical and photochemical stages, artificial photosynthesis includes two catalytic stages, of which the stage of water oxidation with single-electron oxidizing agents is less developed.

Here we report on the synthesis of a new ruthenium binuclear complex  $\text{Li}_8\text{Ru}_2\text{OCl}_{14}$  (**1**). Molecular structure of **1** was determined by X-ray diffraction. Thermoanalytical studies of and infrared and electronic spectroscopy studies showed that **1** is not only highly thermally stable and chemically stable in an acidic environment, but also is an active water oxidation catalyst.

The mechanism by which  $\text{Ru}^{\text{IV}} \text{Ru}^{\text{IV}}$  is reduced to  $\text{Ru}^{\text{III}} \text{Ru}^{\text{III}}$  in HCl solution has been elucidated using of electrochemical and spectrophotometric methods. In dilute acid solution the reduction mechanism proceeded, through a dimeric intermediate of mixed oxidation state, but that in 2.5 M HCl and greater, no intermediate compound was formed. In dilute HCl electrolytes, dimeric intermediate of mixed oxidation state undergoes a rapid ligand exchange which renders its reoxidation more reversible. The stoichiometric self-reduction reaction of a binuclear complex  $\text{Ru}^{\text{IV}} \text{Ru}^{\text{IV}}$  in 3 M HCl was studied by the spectrophotometric method. Kinetics of the disappearance of  $\text{Ru}^{\text{IV}} \text{Ru}^{\text{IV}}$  described by a bimolecular law with a reaction rate constant  $k = 0.22 \text{ l mol}^{-1} \text{ min}^{-1}$  up to 80 % conversion. The stoichiometric reduction process is described by the equation  $[\text{Ru}^{\text{IV}} \text{Ru}^{\text{IV}}]_2 + 2 \text{ H}_2\text{O} \rightarrow [\text{Ru}^{\text{III}} \text{Ru}^{\text{III}}]_2 + \text{O}_2 + 4 \text{ H}^+$ .

The catalytic water oxidation by the one-electron oxidant  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in the coordination sphere of  $[\text{Ru}^{\text{IV}} \text{Ru}^{\text{IV}}]_2$  also leads to four-electronic oxidation of two water molecules into one oxygen molecule:  $4 \text{ Ce}^{4+} + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ Ce}^{3+} + \text{O}_2 + 4 \text{ H}^+$ .

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.

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## Thermochemical study of some perfluoroorganic compounds

Pashchenko L.L., Miroshnichenko E.A.

Department of Chemistry, Lomonosov Moscow State University,  
Leninskie Gory 1, bl.3, Moscow, 119991, Russia  
e-mail: lara.paschenko@gmail.com

The standard vaporization enthalpies,  $\Delta_{\text{vap}}H$ , of seven PFOC (perfluoroorganic compounds) namely *cis*- and *trans*- perfluorodecaline (PFD), perfluoro-N-(4-methylcyclohexyl) piperidine (PMCP), perfluorothreebutylamine (BAF-3), perfluorothreepropylamine (PAF-3), perfluorooctylbromide(PF-octylBr) и perfluorodibutyl ether  $(\text{C}_4\text{F}_9)_2\text{O}$  were determined using Wadso calorimeter. Using Sventoslavsky ebulliometer, temperature dependences of vapor pressure,  $p_s$ , for these seven PFOC were determined. The densities of their liquids were determined by picnometrically. The novel method of calculation of oxygen capacity of liquid PFOC,  $\phi\text{O}_2$ , based on the definition of the enthalpies of vaporization,  $\Delta_{\text{vap}}H$ , the vapor pressures,  $p_s$ , and densities in dependence on the temperature is proposed. In Table 1 given vaporization enthalpy,  $\Delta_{\text{vap}}H^\circ$ , vapor pressure,  $p_s$ , calculated oxygen capacity,  $\phi\text{O}_2$  (1) and experimental oxygen capacity,  $\phi\text{O}_2$  (2) for seven studied perfluoroorganic compounds.

**Table 1.** Vaporization enthalpies, vapor pressures and oxygen capacities of PFOC

Compound	PFD - <i>cis</i>	PFD - <i>trans</i>	PMCP	BAF-3	PAF-3	PF-octylBr	$(\text{C}_4\text{F}_9)_2\text{O}$
$\Delta_{\text{vap}}H^\circ$ , kJ/mol	45.5±0.5	44.8±0.5	56.6±0.2	58.9±0.8	46.9	47.7±0.3	39.3±0.4
$p_s$ , Pa, at 37°C	15.6	17.3	0.81	1.71	14.7	13.8	82.2
$\phi\text{O}_2$ (1), cm <sup>3</sup> /100ml	40.3	41.1	40.0	41.9	47.4	46.6	51.2
$\phi\text{O}_2$ (2), cm <sup>3</sup> /100ml	40.3 <sup>1</sup>	42 <sup>1</sup>	-	40 <sup>1</sup>	46.5 <sup>1</sup>	-	51 <sup>1</sup>

The obtained values of oxygen capacity,  $\phi\text{O}_2$  (1), of PFOC are in a good agreement with the experimental literature data,  $\phi\text{O}_2$  (2), from Ref.<sup>1</sup> Among the studied compounds PAF-3 and  $(\text{C}_4\text{F}_9)_2\text{O}$  have the highest values of oxygen capacity. When choosing PFOC as blood substitutes, the determining factors, along with the vapor pressure, are the stabilities of their emulsions. Quantitative characteristics of the stability of PFOC emulsions are the values of the densities of cohesion energy,  $C$ .  $C = \Delta_v E / V_m$  ( $\Delta_v E$  - cohesive energy,  $V_m$  - molar volume). At temperatures significantly below the critical, (298 K), the cohesive energy,  $\Delta_v E$ , is calculated by the formula based on the enthalpy of vaporization,  $\Delta_{\text{vap}}H$ , at a temperature T.  $\Delta_v E = \Delta_{\text{vap}}H - RT$  ( $R$  – universal gas constant).

In Table 2 given the values of the density of cohesion energy,  $C$ , calculated for six PFOC based on the enthalpies of vaporization measured calorimetrically in this work, where (PFI) - *cis*-perfluorobicyclononane(perfluoroindane), (PMCP)-perfluoro-N-(4-methylcyclohexyl)piperidine.

**Table 2.** Densities of cohesion energy and molar volumes of PFOC

Compound	PFD- <i>cis</i>	PFI- <i>cis</i>	PMCP	BAF-3	$(\text{C}_4\text{F}_9)_2\text{O}$	$(\text{C}_5\text{F}_{11})_2\text{O}$
$C \cdot 10^{-4}$ , kJ/m <sup>3</sup>	18.0	18.1	19.2	16.2	14.3	15.1
$V \cdot 10^4$ , m <sup>3</sup> /mol	2.40	2.19	3.30	3.58	2.67	3.12

The obtained values of the density of cohesive energy PFOC are in a good agreement with the experimental literature data on reduction dispersity of their emulsions [2], a namely the stability of PFOC emulsions is proportional to the increase of the density of cohesion energy,  $C$ .

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## Effect of high-frequency hydrogen and argon plasma treatment on the microstructure of NASICON type catalysts

Lobanov N.N., Pylinina A.I., Romanenko E.V., Chernyshova M.N.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: romanenko-ev@rudn.ru*

The structure of complex framework zirconium phosphates with superionic conductivity belonging to the NASICON type (Na-Super-Ionic-CONductor) allows using them as effective and stable catalysts of acid-base and redox types.

Changes in the properties of solid electrolytes under the influence of various types of radiation, waves and vibrations are well studied, but the effect of plasma-chemical processing at the level of the microstructure is not so widely reported in the literature. As a result, it seems relevant to study the patterns of changes in the crystal structure of NASICON type cesium-zirconium phosphates where cesium ions partially replaced by nickel and cobalt ions before and after high-frequency (HF) plasma treatments.

In the present work, we synthesized double and triple cobalt- and nickel-containing NASICON phosphates and studied the effect of plasma-chemical treatment on the microstructure using X-ray diffraction data.

Samples of  $\text{Cs}_{1-2x}\text{Co}(\text{Ni})_x\text{Zr}_2(\text{PO}_4)_3$ , where  $x = 0.15, 0.25$ , and  $0.50$ , were obtained by the sol-gel method [1]. The phase composition and structural properties of the samples obtained studied by XRD confirmed NASICON structure for these phosphates. The X-ray diffraction spectral data for these samples was carried out on a DRON-7 automatic diffractometer with stepwise scanning using  $\text{CuK}_\alpha$ -radiation. A profile analysis of the most intensive reflexes was carried out and parameters of the unit cells were calculated. Treatment with high-frequency (HF)  $\text{H}_2$  and Ar plasma was performed in a vacuum facility. The samples were placed into a quartz cell and treated with an HF discharge at a gas pressure of approximately 0.1 mm Hg.

It was shown a decrease of the parameters of the unit cell with increase of the dopant cations content. The introduction of nickel leads to a significantly greater reduction in micro deformations compared to cobalt. The correlations obtained are in complete agreement with the ionic radii of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ .

The influence of plasma-chemical treatment also leads to a change in the microstructure. It is shown that the parameters of the unit cell  $\text{Cs}_x\text{Me}_{1-2x}\text{Zr}_2(\text{PO}_4)_3$  ( $x = 0.15; 0.25$ ) with  $\text{Me} = \text{Co}, \text{Ni}$  increase after high-frequency electrodeless plasma in hydrogen treatment. This indicates, apparently, the introduction of hydrogen atoms into the crystal lattice of these compounds. After argon plasma treatment, the parameters of the unit cell decrease, which is connected, apparently, with the recovery of their crystal structure and the release of dislocations to the surface. It was shown the microdeformations depends on the type of HF-plasma and dopant ion: for example, after Ar-plasma for Ni-content sample the deformations increase but the microdeformations of Co-content sample decrease.

The treatment with hydrogen and argon plasma affects the catalytic characteristics of samples in various ways. The activated character of the double phosphates for ethanol transformation retains after their treatment with HF  $\text{H}_2$  plasma.

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## Functionalization of halloysite by aminoalkoxysilanes

Osipova V.A.<sup>1</sup>, Pestov A.V.<sup>1</sup>, Kovaleva E.G.<sup>2</sup>, Tambasova D.P.<sup>2</sup>, Antonov D.O.<sup>2</sup>

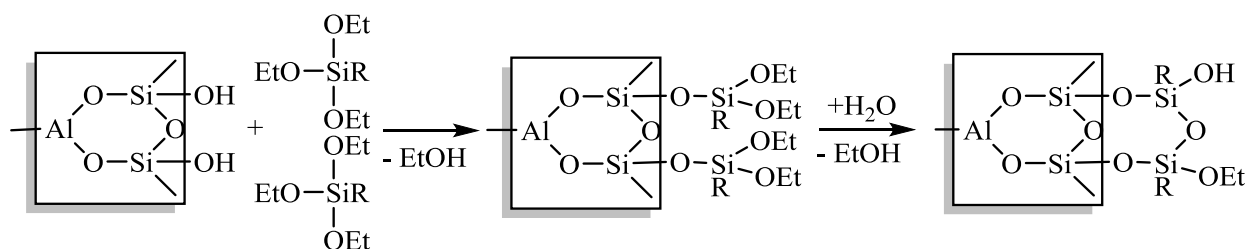
<sup>1</sup> Postovsky Institute of Organic Synthesis Ural Branch of the Russian Academy of Sciences,  
Yekaterinburg, Russia,

<sup>2</sup> Ural Federal University named after the first President of Russia B.N.Yeltsin,  
Yekaterinburg, Russia  
e-mail: osipova.sva@gmail.com

Modification of aluminosilicate minerals of the montmorillonite or calionite groups makes it possible to widely use these materials in sorption, complexation, pharmacology and catalysis [1]. The differences between compositions of the inner and outer layers of halloysite nanotubes affect the properties of the material. The outer surface of such particles consists of silicon oxide; therefore, for its modification, the functionalization by the aminoalkyl group of such reagents as aminopropyltriethoxysilane and aminoethylaminopropyltrimethoxysilane is used.

The procedures described in the literature for these syntheses are based on early work with pure silica [2]. Generally, they use such stages as preliminary heat treatment of halloysite, dispersion by ultrasound and long boiling.

In order to determine the optimal synthesis conditions, we carried out the modification of halloysite with an amine-containing silane at concentrations of halloysite dispersion in an organic solvent of 0.01 g/L and 0.04 g/L.



R - (CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>, (CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>

According to the results of thermogravimetric analysis of halloysite, the first mass loss of 2% was observed approximately from room temperature to 140°C, due to dehydration. Based on this, a number of solvents with different boiling points were selected to determine the optimal synthesis temperature: toluene, ethanol, dioxane-1,4, butanol, acetonitrile and TGF.

The best solvent for a concentration of 0.04 g/L of a halloysite dispersion providing a degree of functionalization of 19,12% is toluene. With a more dilute reaction mixture, acetonitrile makes it possible to achieve a degree of functionalization of 18,03% compared with the degree of functionalization in toluene 13,66% at the same concentration.

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## The influence of hydrothermal synthesis temperature on luminescence changing of sensitive element of biosensor based on ZnO films under the action of DNA

Hayrullina I.<sup>1</sup>, Nagovitsyn I.A.<sup>3,4</sup>, Sheshko T.F.<sup>1</sup>, Chudinova G.K.<sup>2,3</sup>

<sup>1</sup>Peoples' Friendship University of Russia (RUDN University), Faculty of Science, Physical and Colloidal Chemistry Department, Miklukho-Maklaya Str.6, Moscow, 117198, Russia Federation

<sup>2</sup>National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, Russia

<sup>3</sup>General Physics Institute RAS, Moscow, Russia

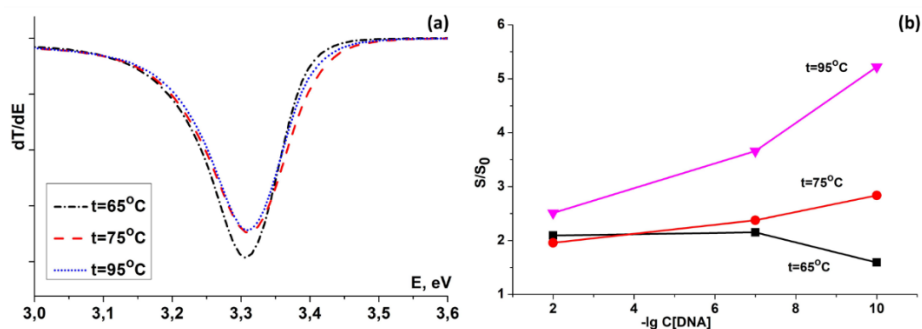
<sup>4</sup>Semenov Institute of Chemical Physics RAS, Moscow, Russia  
e-mail:spaldingtm@mail.ru

The optical properties of ZnO bilayer films were studied by absorption and luminescence spectroscopy (Shimadzu UV-250 and RF-5300pc spectrometers). The films were obtained on glass support by sequential application of two ZnO layers in according to sol-gel method and hydrothermal synthesis. With a view to prepare the seed film, a mixture of monoethanolamine and zinc acetate (molar ratio 5:2) in 2-ethoxyethanol was used. During the hydrothermal synthesis, the temperature of the reaction media, contained  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution, hexamethylenetetramine and polyvinylpyrrolidone (MW = 12600 g / mol), was changed (65, 75 и 95°C). Meanwhile the spincoating method (Elecon centrifuge TsLMN-P10-02, 2500 rpm) was applied for deposition of solution in the sol-gel method as well as DNA on the two-layer film surface.

Due to the transmission spectra analysis, it becomes possible to determine the optical band gap ( $E_g$ ): 3,306 eV for all films obtained at different temperatures. This fact points out no relation between sample conductivity and temperature (Fig.a). However, increasing the fluorescence intensity of ZnO at ( $\lambda_{\text{em}} = 358\text{-}360\text{nm}$ ) occurs along with the synthesis temperature, probably on account of improved uniformity of the film.

The best of our knowledge, the application of DNA from calf thymus (Sigma-AldrichCo) to the films surface from an aqueous solution with concentrations of  $10^{-2}$  -  $10^{-10}$  generally leads to the ignition of the ultraviolet fluorescence band of zinc oxide. And besides, its intensity depends on the content of DNA. What is more, the samples synthesized at a temperature of 75°C and 95°C shows high fluorescence intensity within decreasing DNA concentration from  $10^{-2}$  to  $10^{-10}$  mg/ml.

In conclusion, the obtained systems can be good candidates for use in sensitive biosensor devices with fluorescence detection of low concentrations of DNA and other biomacromolecules.



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## Adsorption of benzene onto activated carbon AR-A and onto activated carbons of the Baojun activated carbon Co

Kasatkin E.M., Cherednichenko A.G.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: kasatkin.1991@list.ru*

One of the most common sources of environmental pollution are the volatile organic compounds (VOCs) among which the most known is benzene and its derivatives representing significant hazard to human health and the environment [1]. One way to remove benzene or to reduce its concentration to the required minimum is to clean the gas emissions by passing them through a layer of sorbent, and activated carbons are usually used as it [2].

The purpose of this work was to determine the sorption characteristics of activated carbon AR-A and activated carbons of Baojun Activated Carbon Co. (China) during the purification of gaseous media from benzene, and to study and simulate the adsorption process.

In a study of benzene adsorption onto the Russian active carbon AR-A and the Chinese active carbons of Baojun Activated Carbon Co. it was found that the highest adsorption capacity for benzene is shown by the active carbon Baojun 4.0/90 (the first number in the title is diameter in mm, the second is adsorption efficiency of carbon tetrachloride, %) and the lowest one is shown by AR-A (Fig. 1).

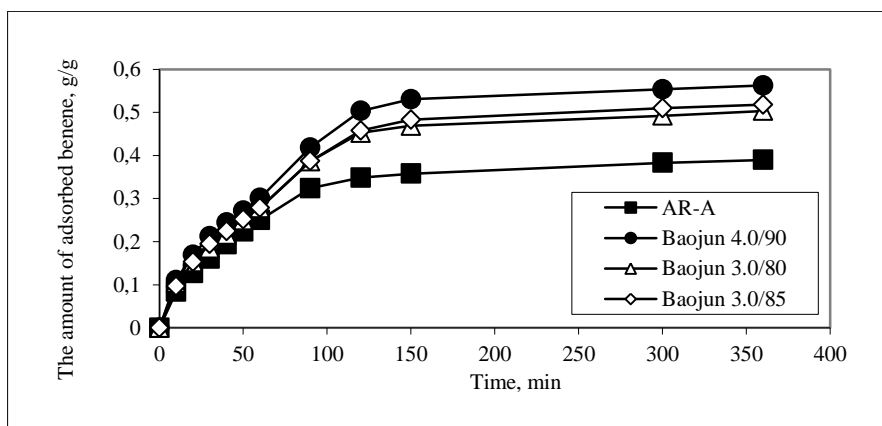


Fig. 1. Dependence of benzene adsorption on contact time

The kinetic research was performed using the pseudo-first-order Lagergren and the pseudo-second-order Ho and Mackay equations, the simplified Elovitch equation and the Morris-Weber diffusion equation. The best correlation with the experimental data was obtained in the case of a pseudo-second-order model. Analysis of the used Morris-Weber model allows us to make a conclusion about the rate control of the phenomenon under study by diffusion of benzene vapor to the external surface of the activated carbons through the adsorbate film and further diffusion in the intrapore space.

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## The study of the catalytic activity of nanocrystalline powders of gadolinium complex oxides

Kovtun S.O.<sup>1</sup>, Popov V.V.<sup>2</sup>, Markova E.B., Menushenkov A.P.<sup>2</sup>, Molokova A.Yu.<sup>2</sup>, Schetin I.V.<sup>3</sup>, Ponkratov K.V.<sup>4</sup>, Tsarenko N.A.<sup>5</sup>

<sup>1</sup>Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup>National Research Nuclear University «MEPhI» (Moscow Engineering Physics Institute)

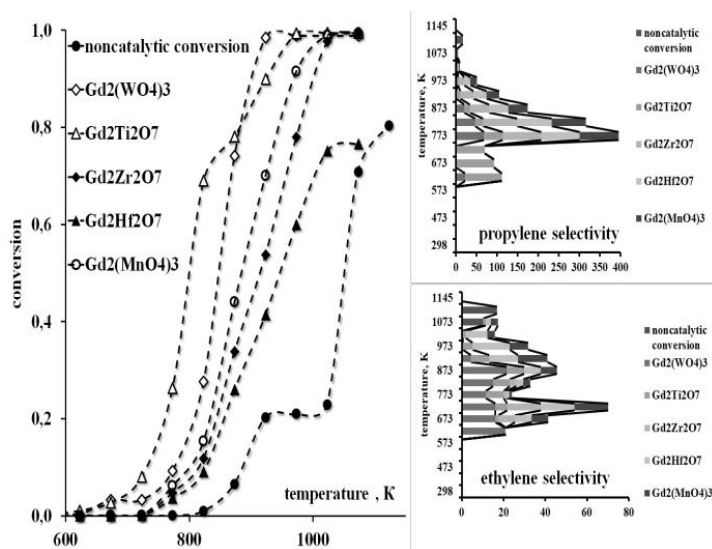
<sup>3</sup>National University of Science and Technology «MISIS»

<sup>4</sup>Renishaw plc., Moscow

<sup>5</sup>Leading Scientific Research Institute of Chemical Technology «VNIHT»

e-mail: svetlana-479@yandex.ru

Due to a set of unique physicochemical properties, REE complex oxides are interesting from both scientific and practical points of view and have recently attracted the attention of numerous researchers [1].



The aim of the work was to study the catalytic activity of nanocrystalline powders of Gd complex oxides with different chemical and phase composition ( $\text{Gd}_2\text{M}_2\text{O}_7$  where  $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ;  $\text{Gd}_2(\text{M}^*\text{O}_4)_3$  where  $\text{M}^* = \text{Mo}, \text{W}$ ).

Nanocrystalline oxides form different types of crystalline structure: cubic in the case of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  (space group  $Fd-3m$ ),  $\text{Gd}_2\text{Zr}_2\text{O}_7$  ( $Fm-3m$ ),  $\text{Gd}_2\text{Hf}_2\text{O}_7$  ( $Fm-3m$ ); orthorhombic  $\text{Gd}_2(\text{MoO}_4)_3$  ( $Pba2$ ) and monoclinic  $\text{Gd}_2(\text{WO}_4)_3$  ( $C2/c$ ). The obtained diffraction data correlated well with the results of Raman spectroscopy.

During catalytic experiments, it was found that the formation of a cubic structure promotes an increase of propane conversion degree and a shift of cracking temperatures to a lower region. The formation of this type of nanocrystalline oxides promotes dehydrogenation reaction with propylene selectivity up to 80% at temperatures up to 700K. The formation of the orthorhombic structure of  $\text{Gd}_2(\text{MoO}_4)_3$  leads to a shift in the degree of conversion to a region of catalytic temperatures of 700-900K with a prevalence of the dehydrogenation reaction by 80%. In the case of the monoclinic structure of  $\text{Gd}_2(\text{WO}_4)_3$  the destruction reaction proceeds in parallel in the same cracking temperature regions, which reduces the propylene selectivity to 50%, while promoting the yield of ethylene in an amount of 30%.

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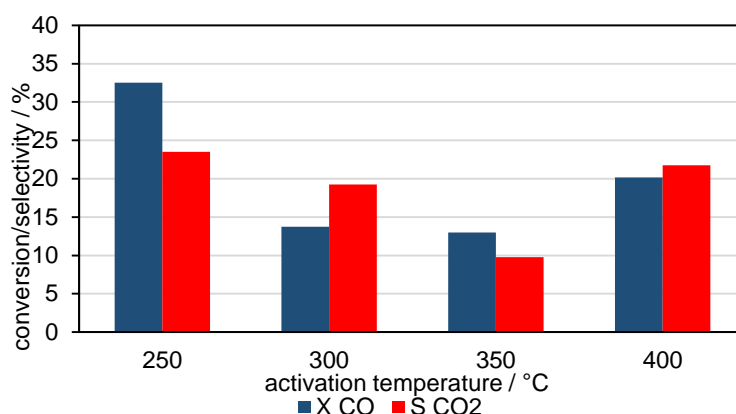
## Influence of promoters and reaction conditions on the iron based Fischer-Tropsch synthesis

Einemann M., Roessner F.

*Carl v. Ossietzky University, Industrial Chemistry 2, D-26111 Oldenburg,  
e-mail: frank.roessner@uni-oldenburg.de*

In the last years, research on the Fischer-Tropsch synthesis regains attention, since with this technique hydrogen and carbon monoxide are converted to hydrocarbons with different chain length. By this reason, it might be a key technology in the upcoming energy supply revolution. Different catalyst systems, usually based on iron or cobalt, are active for the Fischer-Tropsch reaction. Depending on the catalyst composition and the reaction conditions the desired product distribution can be achieved [1,2].

In this work, focus was directed on iron based catalysts. The influence of reaction temperature, pressure and hydrogen to carbon monoxide ratio is well described in literature. Less attention is paid to the influence of the activation temperature. Here, a hematite bulk catalyst was used. During activation in hydrogen atmosphere, the hematite phase is reduced to other iron oxide phases or metallic iron, depending on the activation temperature. The composition of the iron phase is a crucial point in the Fischer-Tropsch process. In a temperature range between  $T = 250\text{ }^{\circ}\text{C}$  and  $T = 400\text{ }^{\circ}\text{C}$ , it was shown, that highest conversions with the lowest selectivity towards the side product carbon dioxide was found for an activation temperature of  $T = 350\text{ }^{\circ}\text{C}$ . This is probably related to the reduction to magnetite at this temperature. Interestingly, a significant variance in the hydrocarbon selectivity was not observed.



**Fig. 2:** Dependence of carbon monoxide conversion and carbon dioxide selectivity of a bulk iron catalyst on activation temperature,  $T_{\text{reaction}} = 300\text{ }^{\circ}\text{C}$ ,  $p = 3.4\text{ bar}$ ,  $\text{GHSV} = 6000\text{ h}^{-1}$ ,  $\text{CO:H}_2 = 1$ .

In recent years, different promoted catalysts were tested. However, the determination of influences of promoting elements is challenging, because of different conditions in the test plants, different supports or varying concentrations of the investigated element. For investigation of the influence of the promoting elements on the iron oxide phase, XAS measurements were carried out, showing slight differences between the different promoted iron samples.

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## Fine nanoparticle deposition on the porous supports using subcritical water

Stepacheva A.A.<sup>1</sup>, Markova M.E.<sup>1,2</sup>, Gavrilenko A.V.<sup>1</sup>, Sidorov A.I.<sup>1</sup>, Matveeva V.G.<sup>1,2</sup>,  
Sulman M.G.<sup>1</sup>, Sulman E.M.<sup>1</sup>

<sup>1</sup>Tver State Technical University, 170026, Tver, A. Nikitin str. 22

<sup>2</sup>Tver State University, 170100, Tver, Zhelyabova str: 33

e-mail: a.a.stepacheva@mail.ru

The modern tendencies in industry require the development of highly active and stable catalysts for different processes. Supported metal nanoparticles are one of the most prospective catalysts involved in the majority of the reactions (i.e. hydrogenation, oxidation, hydroformylation etc.), particularly in the size-sensitive processes [1]. Such nanocatalysts are characterized by unique properties (high surface area, high surface energy) and enhanced reactivity. However, the main problem of the metal nanoparticles is fast aggregation. In order to solve this problem, two main directions are used: (i) the search for highly effective stabilizers, and (ii) the development of novel synthesis methods.

Last years, the interest in the application of super- and subcritical fluids for the synthesis of the supported nanoparticles is raised. The formation of the metal particles in super- and subcritical fluids is classified as physical and chemical deposition [2]. This method is interesting from the point of view of the achievement of high dispersed nanoparticles with unique physical and chemical properties. It can concur with the classical wetness impregnation in terms of efficiency, rapidity, and safety. The use of water in the sub- or supercritical state in the catalyst synthesis (so-called hydrothermal synthesis) allows obtaining ultrafine metal oxides or metal nanoparticles from inorganic salts [3]. The metal precursor undergoes hydrolysis resulting in the formation of metal hydroxide, which then is converted into metal oxide or metal particles [4].

In this work, we report the physics-chemical study of the structure and catalytic performance of metal-containing catalysts synthesized in subcritical water. The catalysts were prepared in the superheated water ( $T = 200\text{ }^{\circ}\text{C}$ ,  $P = 6.0\text{ MPa}$ ) for 15 minutes with the following reduction in a hydrogen flow. Hypercrosslinked polystyrene (HPS) and silica were used as catalyst supports. Both the porous structure and the composition of the active phase were investigated in order to determine the processes taking place during the hydrothermal synthesis. The catalytic activity of the resulted supported materials was studied in a variety of the processes aimed at the production of liquid transportation fuel from the renewable sources.

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## Dehydration of ethanol on ZSM-5 zeolites modified with nanodispersed titanium dioxide

Kirushkina V.V.<sup>1</sup>, Chuklina S.G.<sup>1</sup>, Fionov Y.A.<sup>1</sup>, Pylinina A.I.<sup>1</sup>, Kravchenko G.V.<sup>2</sup>, Kuzmicheva G.M.<sup>2</sup>

<sup>1</sup> Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup> Department of Physics and Chemistry of Materials, MIREA-Russian Technological University, 119454, Moscow, Vernadsky pr 78  
e-mail: sofyaogan@gmail.com

The production of ethylene by the dehydration of ethanol, which can be produced from fermentation processes using renewable substrates such as glucose, starch and others looks like alternative reactions to produce green ethylene due to rising oil prices [1].

Recently it was reported that during the last few decades, ethanol dehydration to ethylene has been extensively studied over a variety of heterogeneous catalysts including alumina, zeolites, transition metal oxides and heteropolyacids. Among the catalysts studied zeolites (e.g., ZSM-5) have received the most attention for their high activity and selectivity [2].

Despite the great interest in these systems as catalysts for the dehydration of ethanol, the process of creating an effective catalyst for the low-temperature process ethylene and diethyl ether production without deactivating requires more detailed studies.

In this study we investigated the effect of various methods of synthesis and modification of zeolites on selectivity in ethanol conversion. A series of catalysts based on ZSM-5 (MFI) zeolites with different zeolite modules Si/Al=12, 25, 40 with the functional basis of nanosized titanium oxides (IV) (NTO) were obtained by various methods: (1) titanium sulfate hydrate [3] and (2) from titanium tetra-butoxide and tested in ethanol conversion. The samples were characterized by XRD, XPS and N<sub>2</sub>-adsorption. Ethanol conversion was carried out at 160°C-380°C with chromatography analysis of gas mixture (FID, helium as a carrier gas).

The main directions of this reaction were intermolecular (DEE) and intramolecular dehydration (ethylen) of ethanol with the maximum activity and selectivity to ethylene formation at the temperature above 300°C. For a composite with NTO obtained on zeolite functional basis (NTO/ZSM-5) compared to pure zeolite ZSM-5, the reaction goes to a lower temperature range. When the ratio of Si/Al = 40, the catalytic system gives a more stable result, i.e. the same data for catalytic activity in heating and cooling mode.

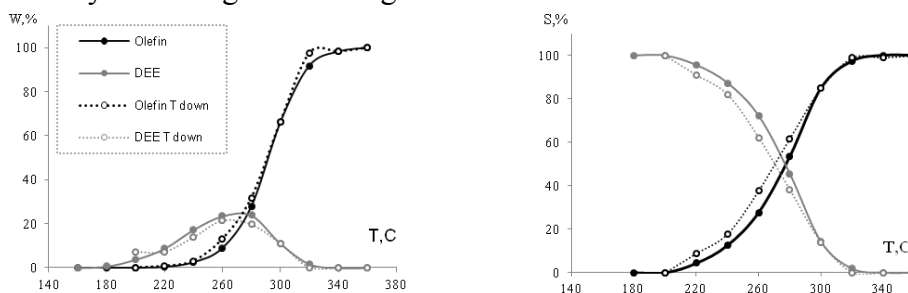


Fig. NTO/ZSM-5(40) method 2.

The reported study was funded by RFBR according to the research project № 18-33-00922

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## Encapsulated Pt-particles for bifunctional catalysis

Damps A., Roessner F.

Carl v. Ossietzky University, Industrial Chemistry 2, D-26111 Oldenburg  
e-mail: alexander.damps1@uni-oldenburg.de

The idea of poison-resistant catalysts can be traced back as early as 1966, where Firth and Holland kept large molecules (carbon tetrachloride) from the active center (Pd) [1].

The investigation in this research area continues due to the advantages in petrochemical applications [2a, b]. Recent advances in synthesis of core-shell nanoparticles offer new poison-resistant catalysts [3].

The idea of our research is based upon the spatial separation of two catalytic centers and protecting one of them by a SiO<sub>2</sub> shell as in a core-shell system. The investigated reaction is the hydroisomerization of *n*-hexane, where acidic and hydrogenating/dehydrogenating sites are needed. This could lead to a universal hydrogen activating catalyst, which could facilitate the design of a poison-resistant catalyst [4].

The preparation of the catalysts was done by ion-exchange of a platinum salt with layered materials (e.g. Magadiite). During calcination, the layers collapse and embed the Pt-particles inside the matrix. Alternatively, Pt/SiO<sub>2</sub> was covered by hydrolysis of tetraethoxysilane (TEOS). The Pt-catalysts were mixed with H-ZSM-5 (Si/Al : 25) and tested in a micro fixed-bed reactor setup.

Catalytic results indicate a successful encapsulation by maintaining catalytic activity, but the yield drops significantly for the isomerization products (Iso) versus the products of acidic cracking (Crack) as seen in figure 1.

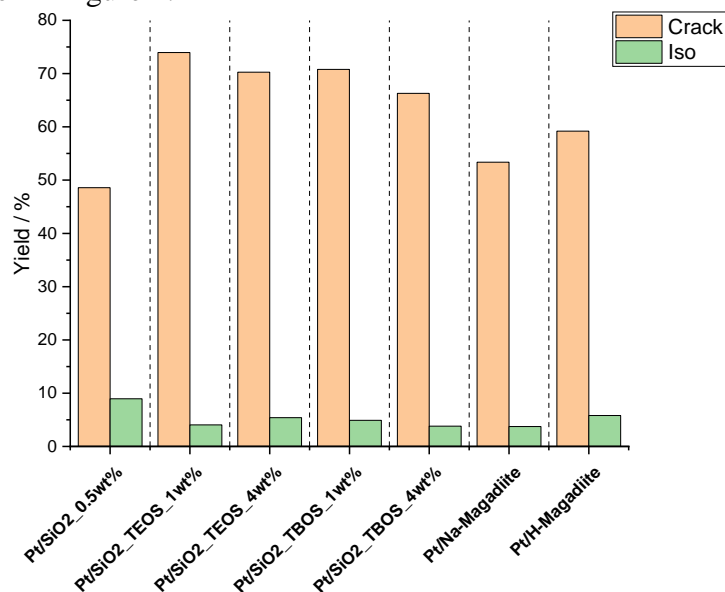


Figure 3: Yield of the isomerization and crack products for a variety of catalysts.

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## Analysis of amino acid synthesis kinetic in organic raw materials bioconversion

Molchanov V.P., Sulman M.G., Kisakova D.

*Tver State Technical University, 170026, Tver, A. Nikitin str. 22,  
e-mail: science@science.tver.ru*

The bioconversion process of the organic stock-breeding waste and difficultly hydrolyzing vegetable raw material mixture has been studied. The end product of this process can be used as food addition. The process was regulated by additional introduction of biologically active stimulators to the initial mixture to accelerate the organics mineralization and to contribute to secondary metabolites active biosynthesis. Cobalt, sodium, potassium, calcium, zinc or iron ascorbinates have been used as biostimulators. It accounts for the ability of micro- and macroelements forming part of ascorbic acid salts to produce favourable effect on the metabolism of the microorganisms performing bioconversion process. Besides, ascorbic acid is necessary for livestock normal vital functions.

During the mixture bioconversion sampling has been carried out. The presence and change of free amino acids content in the samples have been determined to ascertain possible value of the end product. The analysis of the kinetic regularities of the process studied has shown that free acids accumulation in the fermented mixture can be accurately enough described by a degree equation similar to the classical equation of the formal kinetics of fractional order. According to the experimental data obtained the computation has been performed to determine kinetic parameters of the equation suggested for different conditions of the process realization. The fact that not only the nature of the biostimulator added (Table 1) but its concentration (Table 2) produce a considerable influence on the order of magnitude is of special interest.

Table 1. Kinetic parameters of the bioconversion process (introduction of different salts of ascorbic acid)

Introduced ascorbate	Reaction order n	Rate constant k, 1/hour
Co ascorbate	0,9	0,013
Na ascorbate	1,8	0,009
K ascorbate	2,1	0,010
Ca ascorbate	1,8	0,019
Zn ascorbate	0,9	0,040
Fe ascorbate	0,2	0,047
without ascorbinates	1,4	0,007

Table 2. Kinetic parameters of the bioconversion process varying Fe ascorbate concentration in the initial mixture

Ascorbate concentration, %	Reaction order n	Rate constant k, 1/hour
0,025	1,8	0,015
0,030	0,9	0,034
0,045	0,2	0,047
0,055	1,0	0,030
0,070	1,3	0,020
0,090	2,1	0,012

The data presented show that the reaction order decreases with the most effective stimulators (zinc and iron ascorbinates) addition and on the contrary it increases while introducing the other ascorbinates which intensifies a little the process of free amino acids accumulation. Such an effect is probably connected with the process of activation of different ferment systems of microbial cells under the influence of the metals included in the salts used.

It is seen from Table 2 data that rate constant and reaction order considerably change at the increase or decrease of biostimulator's concentration beginning with the value optimal for amino acids accumulation in the mixture (0,045%). A considerable decrease of the reaction order value can be caused by such amount of Fe ascorbate. In this case the rate of amino acids formation according to the kinetic equation depends in the least on the substrate content of the bioconversion process.

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## Quantum-chemical simulation of the adsorption induced reduction of strength of siloxane bonds

Flyagina I.S., Malkin A.I., Dolin S.P.

*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, 119071, Moscow, Leninsky avenue 31 k. 4  
e-mail: irina.fliagina@gmail.com*

It is well known that the strength of silicates in contact with water solutions often appears to be significantly less than that in inactive environments, and the reason of this is the phenomenon of the adsorption induced reduction of strength (AIRS). It is established that the strength of silicates drops as a result of an auto-catalytic reaction between the siloxane bonds and hydroxyl groups adsorbed on the surface of silica [1,2]. However, it is not clear yet why hydroxyl groups induce the greatest effect of strength reduction compared to other components of water solutions, e.g. hydronium ions. In order to answer this question, we performed a quantum-chemical simulation of tensile deformation of the siloxane bond in the presence of various adsorbates.

The simulations were carried out using the ORCA 4.0 code [3] within the wB97X-D3/def2-TZVP level of theory. The rupture of the siloxane bond was modelled using the simplest model cluster  $\text{H}_3\text{Si-O-SiH}_3$ , and the effect of the AIRS was simulated by adding the following species to the model cluster:  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{H}^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ .

Table 1 presents some of the calculated characteristics of the siloxane bond rupture. The calculated activation energy of breaking the siloxane bond in the absence of adsorbates is in a reasonable agreement with the experimental value of 418 kJ/mol [1]. The calculated activation energies also indicate that the mechanism of nucleophilic substitution is more kinetically favourable than the electrophilic substitution, and the strength of the siloxane bond decreases with increasing nucleophilicity of the adsorbates. It is also found that the activation energy of rupture correlates with electron density, changing in the presence of the adsorbates, rather than with the heat of adsorption.

**Table 1.** Calculated characteristics of rupture of the siloxane bond.

Molecular system	Heat of adsorption, kJ/mol	Activation energy, kJ/mol	Work of rupture, kJ/mol	Electron occupancy of the ruptured Si-O bond	
				Bonding orbital	Anti-bonding orbital
$\text{OSi}_2\text{H}_6$	-	540	540	1.99	0.02
$\text{OSi}_2\text{H}_6\cdots\text{H}^+$	-282	277	277	1.99	0.03
$\text{OSi}_2\text{H}_6\cdots\text{H}_3\text{O}^+$	-90	191	127	1.99	0.03
$\text{OSi}_2\text{H}_6\cdots\text{H}_2\text{O}$	-12	211	28	1.99	0.03
$\text{OSi}_2\text{H}_6\cdots\text{Cl}^-$	-787	194	194	1.94	0.13
$\text{OSi}_2\text{H}_6\cdots\text{OH}^-$	-159	113	113	1.93	0.18

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## Methods for the improvement of physicochemical parameters of petrodiesel and *Jatropha curcas* L biodiesel using eco-friendly materials and gamma radiation

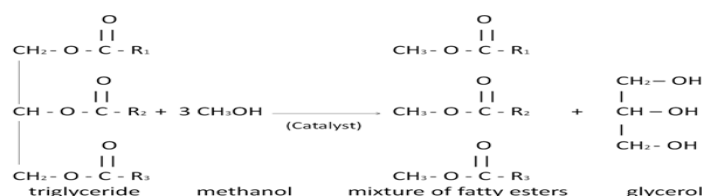
Osman M.E.A.<sup>1,2</sup>

<sup>1</sup>Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup>Omdurman Islamic University, 231902, Khartoum, Elfatih str. 59

e-mail: Wadalmsna3.com@gmail.com

Biodiesel produced from *Jatropha curcas* L fixed oil by trans-esterification process represents one of the most alternative fuel options to replace depleting fossil fuels. Physico-chemical parameters such as density, kinematic viscosity, flash point, cloud point, ash content, sulphur content, water content, colour, copper strip corrosion, carbon residue and cetane number, were determined for diesel fuel samples (S1, S2, S3 and S4). Results obtained were found to be within the limits assigned by American Society for Testing and Materials (ASTM) except the water content of sample (S1) was found to be 0.052 % w/w. the cetane number was found to be 56.14, 54.72, 57.89 and 56.9 for samples S1, S2, S3 and S4, respectively. The *Jatropha curcas* oil was converted to biodiesel using homogenous and heterogeneous catalysts (NaOH and Natrolite). Cetane number of biodiesel and petrodiesel, after treatment with furfural, has been improved from 60.8 to 64.1 and from 54.46 to 58.36, respectively. Improvement accomplished by the eco-friendly blend furfural has removed 13 and 81 aromatic, cyclic and branched organic compounds from biodiesel and petrodiesel respectively, Such compounds exhibits a negative effect on the cetane number of diesel fuel. In the case of petrodiesel sample after treatment by furfural have shown a decrease in the elements composition of Na, Mg, K, Fe, Al and As, the result led to the decrease of ash content. Conversion process adopted using gamma radiation has slightly improved the cetane number from 60.8 to 61.2 and 61.9 of *Jatropha curcas* biodiesel under the doses 3KGy and 6KGy, respectively, but the cetane number was decreased after been exposed on 10KG. The value obtained from *Jatropha* biodiesel closely matched the value of conventional diesel as the (ASTM) and as it been used in the existing diesel engines without any modification.



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## Optical properties of cerium doped zinc oxide nanoparticles synthesized on molybdenum surface

Shulga A.<sup>1</sup>, Butusov L.A.<sup>1,2</sup>, Chudinova G.K.<sup>2,3</sup>, Sheshko T.F.<sup>1</sup>

<sup>1</sup> Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaa str. 6

<sup>2</sup> A. Prokhorov Institute of General Physics. RAS, 119991, Moscow, Vavilov str. 38.

<sup>3</sup> National Research Nuclear University MEPhI, 115409, Moscow, Kashirskoye sh. 31.

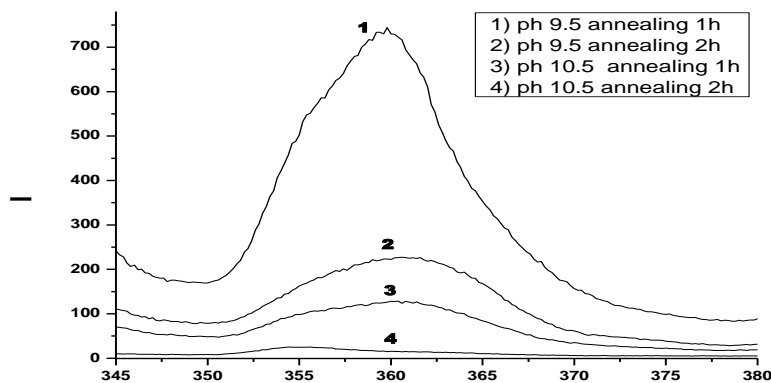
e-mail: aleksandra-box@mail.ru

Zinc oxide nanoparticles have been a popular science field for a long time. Nano-dimension allows for various chemical, physical and biological properties of the material, and the variety of geometric structures of zinc oxide is enormous as well as areas of application - electronics, optoelectronics, sensors, photonic devices and photo catalyst [1].

The properties of structures can be controlled in a controlled manner by using either a specific synthesis technique or by introducing dopants like cerium.

Injection of cerium atoms in a hexagonal structure of zinc oxide can increase the absorption in the ultraviolet region, which in turn makes the particles obtained are highly effective as catalysts for photo-degradation reactions and thus has high practical significance in the purification of water [2]

In our work, we used zinc and cerium oxalates mixed in a mass ratio to obtain ZnO nanoparticles doped with 1% of  $\text{Ce}^{3+}$ , alkaline environment, ultrasound instead of the usual mechanical mixing, microwave irradiation of solutions to obtain germ nanoparticles 200-350 nm diameter. Germ particle solutions were deposited by backspacing on molybdenum substrates and annealed at its oxidation temperature of 600 °C to create porous surface saturated by nanostructures at the boundaries of the pores and further study of photoluminescent properties presented in Figure 1.



**Fig.1.** Substrate's photoluminescence intensity in UV region

Optical properties of the obtained composite materials showed a clear dependence on the time effects of temperature and alkalinity. Longer thermal exposure or higher pH values of germ solution led to cracking of the composite structures or decrease growth rate but the samples obtained by annealing for 1 hour and pH 9-9.5 had the highest photoluminescence value and therefore the most effective catalytic activity.

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## Study of influence solid phase formation of silica gel on the optical properties of 4 - DASPI

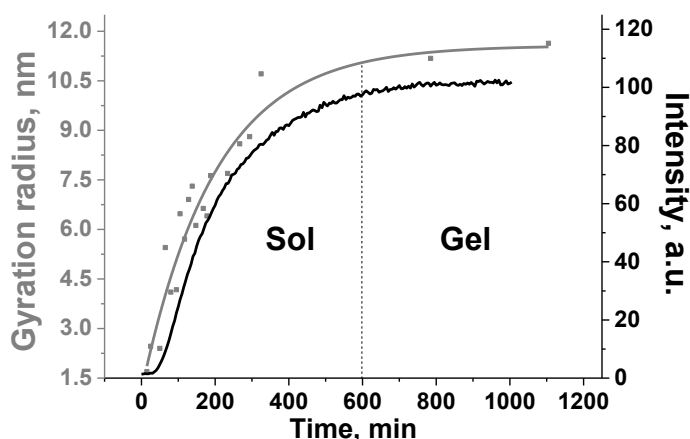
Medvedeva A.A., Koshkin A.V.

«Photochemistry Center» RAS, FSRC «Crystallography and Photonics» RAS,  
119421, Moscow, Novatorov str. 7a/1  
e-mail: Medvedeva.mipt@gmail.com

The formation processes of the silica solid phase were investigated by different methods, in particular, by the method of fluorescent analysis by using of 4-DASPI styryl dye as a label. Up to date there is no precise data on the mutual influence of the solid phase formation and optical dyes properties in the process of sol-gel synthesis, which makes it difficult to interpret the observed effects.

In our study, we obtained a silicate hydrogel matrix based on the water-soluble precursor tetrakis(2-hydroxyethyl)orthosilicate (THEOS) by the sol-gel synthesis. The choice of fluorescent probe was due to a dramatic change of its fluorescence intensity in the viscous media [1,2].

Comparing the kinetic curve of growth of the particle gyration radius and the kinetic curve of the fluorescence intensity, one can note a good correlation of the obtained data. This allows to suggest the increase in fluorescence intensity to be associated with the formation of a silica nanoparticles. Comparing the change of the spectral properties of the dye and the kinetics of the solid phase formation, it is possible to track time of phase transition.



**Fig. 1.** Grey – growth kinetics of particle gyration radius; black – kinetics of fluorescence intensity ( $\lambda_{\text{exc}} = 500 \text{ nm}$ )

As a result of the study, a model was proposed for the solid phase formation of a silicate hydrogel in the presence of a fluorescent dye 4-DASPI.

*This work was supported by the Russian Foundation for Basic Research in part of SAXS measurements (grant № 16-29-11763)*

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## **Influence of composition and thermal treatments on Cu-containing Zr-Al oxides catalysts in ethanol dehydrogenation reaction**

Maslenkova S.A., Chuklina S.G., Kharlamova M.Y., Pylinina A.I., Fionov Y.A.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: sveta.maslyonkova@yandex.ru*

Currently, the use of ethanol as an alternative fuel and a precursor for obtaining valuable chemical raw materials seems to be the most promising long-term solution of some ecological and ecological problems since ethanol is absolutely harmless that can be easily obtained from bio-organic masses, and its transformations does not caused excretion of harmful by-products. However, existing catalytic systems show unsatisfactory reaction yields or are too expensive for production [1-3].

Copper catalysts that extensively used in environmental catalysis reactions seems to be promising for ethanol conversion. Among wide variety of materials that has been developed as catalyst supports mixed oxide of ceria, zirconia and alumina should be paid attention as they have good structural characteristics and thermal stability and have several applications in heterogeneous catalysts [4-5]. In this study we investigate the effect of thermal pre-treatments and supports composition on catalytic performances of 5%Cu/ ZrCeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> in conversion of ethanol.

The systems of the following composition were tested in the catalytic reaction: 5% Cu/ZrCeO<sub>2</sub>, 5% Cu/(5% Al<sub>2</sub>O<sub>3</sub>-95%ZrCeO<sub>2</sub>), 5% Cu/(50% Al<sub>2</sub>O<sub>3</sub>-50%ZrCeO<sub>2</sub>). Oxide supports were obtained by the sol-gel method at different final synthesis temperature with the following impregnation of 5% Cu from an aqueous solution. Systems are undergone by treatment at critical temperature (cooling to -195.75°C) additionally. Catalytic activity of the systems was studied in a model reaction of the conversion of ethanol in the temperature range of temperatures of 250–400° C in a flow-through catalytic installation with gas chromatographic analysis of the products. In addition, the physical and chemical properties of the catalysts were further studied by XRD, EXAFS and XANES-spectroscopy, low-temperature adsorption of N<sub>2</sub> and electron microscopy. Catalytic systems demonstrated 83% conversion of ethanol with 97% selectivity in acetaldehyde. The experiments revealed that preparation temperature and amount of aluminum oxide strongly affects the reaction selectivity and hence the structural characteristics. The effect such activation methods as critical temperatures have been also shown. Moreover, it was found that cryo-treatment affects differently on the activity of the different catalysts in this reaction. It has been established that the opposite effect of critical cooling is associated with the formation of the crystalline phase of zirconium oxide in Al<sub>2</sub>O<sub>3</sub>-ZrCeO<sub>2</sub> supports, which occurs at higher final temperature of carrier synthesis.

Thus, a change in the physico-chemical and structural characteristics of the Cu/ZrCeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems during thermal treatments and changes of the structure of oxide carriers formed during the synthesis process lead to the formation of catalytic centers of different nature and changes of their number.

*The reported study was funded by RFBR according to the research project № 18-33-00922*

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## Acidic properties of $Mn_{0,5(1+x)}Al_xTi_{2-x}(PO_4)_3$ catalysts: effect on ethanol dehydration activity

Akhmedova L.S.<sup>1</sup>, Pylinina A.I.<sup>1</sup>, Knyazeva E.I.<sup>1</sup>, Abrosimova S.M.<sup>2</sup>, Glukhova I.O.<sup>2</sup>, Asabina E.A.<sup>2</sup>, Pet'kov V.I.<sup>2</sup>, Fionov Y.A.<sup>1</sup>, Osaulenko D.A.<sup>1</sup>, Sokolova E.A.<sup>1</sup>

<sup>1</sup>Peoples' Friendship University of Russia, (RUDN University) 117198, Moscow,  
Miklukho-Maklaya str. 6

<sup>2</sup>Lobachevsky State University of Nizhni Novgorod (UNN) 603950, Nizni Novgorod,  
Gagarina str.23

e-mail: luisaakhmedova@gmail.com

The main goal of green chemistry is the search for environmentally friendly, renewable energy sources. Bioethanol is a product of biomass processing and also one of the main biofuels currently used as source for industrially important compounds, such as hydrocarbons, ethers, aldehydes, ketones, hydrogen. For this reason, it is crucial to find suitable catalysts capable of effectively converting alcohols into these products. Nowadays, the complex phosphates with NASICON structure are widely considered to be the most prospective catalysts in alcohol conversion cause of their unique set of properties as high ionic conductivity, low thermal expansion coefficient. The composition modification of the framework phosphates led to variance in their catalytic activity and selectivity for alcohol conversion due to changes in the acidity, specific surface area, and particle size of the catalysts [1,2].

The change in the activity of alcohol decomposition was useful to detect the effect of type and content of cation in the acid-base properties of promoted catalysts. In this study we have investigated the catalytic activity and stability of systems  $Mn_{0,5(1+x)}Al_xTi_{2-x}(PO_4)_3$  with  $x=0; 0,2; 0,3; 0,4$  (series 1),  $Cu_{0,5(1+x)}Al_xTi_{2-x}(PO_4)_3$  with  $x=0; 0,2$  (series 2), in ethanol conversion reaction in a catalytic flow system at 280-400 °C with chromatographic analysis of products. All catalysts were synthesized by the Pechini technique and characterized using X-ray, IR-spectroscopy, electron microscopy. The structural type NZP was confirmed by X-ray phase analysis. Nevertheless, the further addition of aluminum to the catalyst (series 2) doesn't lead to obtain NZP-structure. The alcohol transformation was proceeded in three directions with ethylene, acetaldehyde and diethyl ether formation. It is worth pointing out that all considered catalysts show stability and efficiency in ethanol dehydration. The selectivity of the catalysts for dehydration reaction strongly depends on their composition (Table).

**Table.** Dehydration selectivity and total ethanol conversion at 400°C

	$Mn_{0,5(1+x)}Al_xTi_{2-x}(PO_4)_3$				$Cu_{0,5(1+x)}Al_xTi_{2-x}(PO_4)_3$	
X	0,0	0,2	0,3	0,4	0,0	0,2
$S_{ethelene}, \%$	66	38	46	63	61,5	81
$S_{DE}, \%$	31	49	48	31	12,5	7
$W, \%$	47	37	44	62	26	30

The best ethylene selectivity in dehydration reaction is obtained using the Mn-containing mixed phosphate catalysts. Dehydration activity was more sensitive for the Mn-promoted catalysts than the Cu-promoted ones, showing an important role of cation nature (radius and electronic structure) in the acidic and catalytic properties of these complex phosphates.

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## Cluster approach in liquid structure modeling

Grinvald I.I., Kalagaev I.Yu., Spirin I.A., Kapustin R.V.

*Nizhniy Novgorod State Technical University n.a. R.E. Alekseev  
Minin str. 24, 603950 Nizhniy Novgorod, Russia  
e-mail: grinwald@mts-nn.ru*

Common knowledge considers a condensed phase formation as the superposition of weak coulomb interaction, arising between dipoles. In some cases for organic liquids the reason of phase stability is the hydrogen bonding (or other type of strong non-covalent interaction). But in terms of such interpretation seem to be not clear the nature of phase stability for many non-polar and hydrogen bondless compounds, for example, alkanes or alkenes, benzene, especially taking into account their high boiling temperature, i.e. the destruction energy of liquid phase. It is known the cases, when this temperature can be higher than for polar organic compounds or systems with hydrogen bond. Moreover the more polar molecules can be the gases and less polar ones are liquids as it is observed for carbon tetrahalides.

In this work the IR spectroscopic findings, obtained for such organic liquids as tetrachlorides of carbon, silicon and germanium, benzene, as well as for methyl iodide and acetonitrile at ambient condition also for their vapours and solid films at low temperature are presented in order to discuss the mechanism of molecular interaction in condensed state. The selected compounds have either negligible total and bond dipole moments, strong bond dipole moment only, or considerable bond and total dipole moments.

Benzene is a planar molecule assigning to  $D_{6h}$  symmetry point group. It means that only one CH stretching IR band (E-specie) for similar molecule should be active in accordance with the selection rules. However three bands are observed in real spectra of liquid benzene. The picture in CH stretching region can be caused by the existence of clusters. In this case the cluster formation can be assigned to the carbon-carbon binding between parallel rings. This assignment is confirmed by the spectra of benzene vapour at ambient conditions. The complicated view of absorption with the manifestation of rotational structure is the display of low-symmetrical shape with several bonded molecules. At heating up to 473K the vapour spectra are simplified and manifest the superposition of cluster and non-bonded shape.

The molecules of tetrachlorides ( $ECl_4$ , where E=C, Si, Ge) attribute to high symmetry  $T_d$  point group. The selection rules require the occurring of only one stretching ECl band in IR spectra. However, carbon tetrachloride in liquid state and in solid film at 25K has two bands at 786 and 761  $cm^{-1}$  with approximately equal intensities. The second component disappears at heating the sample up to 423K. At the same time for silicon and germanium tetrachlorides only one E-Cl stretching band was found. Therefore, the appearance of two bands in  $CCl_4$  spectrum cannot be assigned to the CCl stretching of chlorine isotopes and is the manifestation of cluster formation, for example of  $(\cdots C-Cl \cdots C-Cl)$  bonded chains. Unlike  $CCl_4$  in tetrachlorides of silicon and germanium the clusters exist due to the  $d-d$  orbitals interaction of central atoms. It does not lead to the sufficient distortion of initial molecular symmetry.

During the transition from liquid to solid state (film at 25 K), the  $CH_3I$  spectrum changes, namely, only one band remains in the region of stretching vibrations of CH bonds. It indicates on a change of the molecular symmetry type (transformation from  $C_{3v}$  to  $D_{3h}$ ). It can be caused due to the shift of iodine atom to neighboring molecule and formation of almost planar  $CH_3$  fragment. The IR stretching of CN bond in acetonitrile has two components instead of an expected one. This effect justifies the interaction between molecules under CN group. The second component disappears at heating the sample up to 423K. The presented data can be taken as reliable evidence of existence in condensed phase of the interaction between molecules, different from coulomb and H-bonding mechanism, leading to formation of cluster shapes.

## Investigation of the catalytic activity of heteropoly compounds on the propane cracking model reaction

Stepnova A.F.<sup>1</sup>, Kaziev G.Z.<sup>1</sup>, Markova E.B. Ошибка! Залкадка не определена.<sup>2</sup>

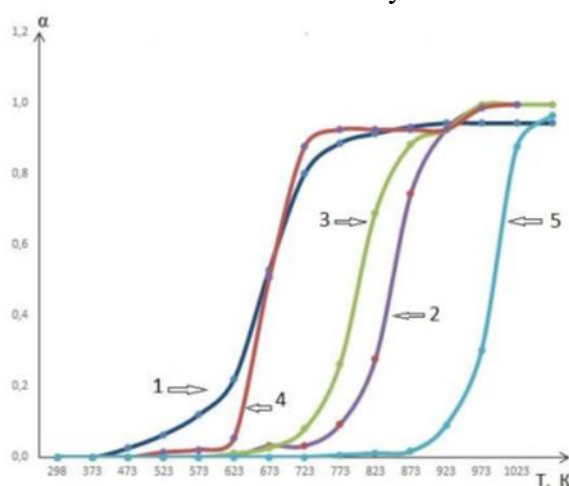
<sup>1</sup>Moscow State Pedagogical University, Moscow

<sup>2</sup>Peoples' Friendship University of Russia, Moscow

e-mail: af.stepnova@mpgu.su

During last years, the petrochemical industry has seen an increasing role of the catalytic cracking process on finely fragmented catalysts in order to obtain not only high-octane gasolines, but light olefins, which is associated with tightening of environmental requirements for motor fuels and enhanced growth of propylene use in the petrochemical industry [1]. It is known that some heteropoly compounds (HPS) are superior in their catalytic activity to aluminosilicate and zeolite catalysts [2]. This work is devoted to the study of the catalytic activity of four different types of HPS in the context of the model reaction of propane cracking, which has actual and industrial significance. The obtained data were compared with the results of thermal cracking.

The product of the cracking reaction was a mixture of methane, ethylene, ethane, propylene, and propane. It was shown that the using of HPS as catalysts led to a significant decrease in the gas conversion temperature, while the coalification processes occurred at higher temperatures in comparison with thermal decomposition (fig. 1). These factors, as well as the analysis of the reaction products depending on the temperature, unambiguously indicate the presence of catalytic properties in the substances under study.



**Fig 1.** Propane conversion rate: 1-  $[\text{Cr}(\text{H}_2\text{O})_6]\text{H}_3[\text{V}_{10}\text{O}_{28}]\cdot 2\text{H}_2\text{O}$ ; 2-  $(\text{NH}_4)_6\text{H}_6[\text{Ca}_4\text{V}_{12}\text{O}_{40}]\cdot 12\text{H}_2\text{O}$ ; 3-  $(\text{NH}_4)_2[\text{Co}(\text{H}_2\text{O})_4]_2\text{H}_2[\text{Mo}_8\text{O}_{27}]\cdot 6\text{H}_2\text{O}$ ; 4-  $(\text{C}_6\text{NO}_2\text{H}_5)_2\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}$ ; 5-thermal cracking

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## Catalytic behaviour of surface cobalt on GdFeO<sub>3</sub> perovskite in the syngas production

Kost V.V.<sup>1</sup>, Kryuchkova T.A.<sup>1</sup>, Sheshko T.F.<sup>1</sup>, Bazhenova O.O.<sup>1</sup>, Chislova I.V.<sup>2</sup>, Yafarova L.V.<sup>2</sup>, Zvereva I.A.<sup>2</sup>

<sup>1</sup> Peoples' Friendship University of Russia (RUDN University), Faculty of Science, Physical and Colloidal Chemistry Department, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation

<sup>2</sup> Saint-Petersburg State University, Petrodvorets, Universitetsky pr. 26, Saint-Petersburg, 198504 Russian Federation  
e-mail: kryuchkova-ta@rudn.ru

In recent years, many researches have been devoted to natural gas converting methods. Using methane for the synthesis gas production by oxidative reactions is of particular interest, mainly dry reforming of methane (DRM) [1]. Still, that process faces their problems on the way of being fully launched on industrial scale: the absence of an active and stable catalyst without a tendency to form surface carbon at the same time. Consequently, in order to achieve significant results at relatively medium temperatures, these drawbacks must be overcome. Thus, perovskite-type catalysts ABO<sub>3</sub> (A = lanthanide, B = transition metal) become relevant for the study due to their high activity and thermal stability [2]. It is widely accepted that partial substitution of atoms at A- and B- sites of the perovskite structure can highly contribute to the improvement of catalytic performance [3]. While metal deposition on the surface itself inhibits carbon formation.

In the present work, complex perovskite-type oxides GdFeO<sub>3</sub> and GdCo<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> synthesized by the citrate sol-gel method and GdFeO<sub>3</sub> modified with cobalt (5% in weight) by impregnation, were studied as catalysts for DRM process. All of the samples were investigated by a series of physicochemical analyzes: XRD, SEM, BET, XPS, TPR are among them. The results established the single-phase catalysts with orthorhombic perovskite crystal structure, possessing high porosity and average particle size of 100-200 nm.

The catalytic activity tests showed that doping by cobalt on the surface of gadolinium ferrite, as well as the Co-introduction into the anion sublattice, led to the synergistic effect and the appearance of new catalytically active centers. As a result, reagent conversions and product yields increased as follows: 5wt.%CoO/GdFeO<sub>3</sub> > GdCo<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3</sub> > GdFeO<sub>3</sub>. Furthermore, surface cobalt sample remains more resistant to coke than the rest ones. This phenomenon can be associated with the stronger interaction of Co particles with the support or with Co<sup>3+</sup> to Co<sup>2+</sup> transition and a defective oxygen compound formation.

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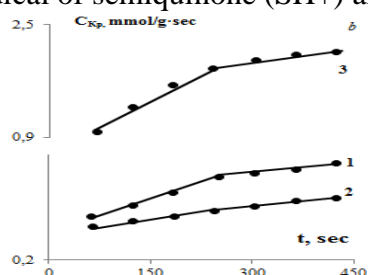
## Study of the acidity of the NZP-catalyst surface on the basis of the indicator reaction

Knyazeva E.I., Akhmedova L.S., Chuklina S.G., Pylinina A.I., Sokolova E.A.

*RUDN university, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: knyazeva-ei@rudn.ru*

Superionic conductors (SICs) with a high conductivity in sodium NZP respectively, represent a new class of catalysts, which have attracted considerable attention in recent years. The crystalline structure of these compounds has nanosized conduction channels. The properties of phosphate catalysts are largely determined by the acidity of the surface, an analysis of which is based on the use of the adsorption of bases and indicator reactions [1]. The concentration of electron-acceptor (Lewis) sites on the surface of catalysts and adsorbents can be measured using the one-electron oxidation of p-phenylenediamine (PPD) with the formation of semiquinone cation-radical  $SH^+$ , as well as a more complex process of catalytic formation of a dye, the first and limiting stage of which is the formation of  $SH^+$ . At the next stage  $SH^+$  is oxidized to quinonediimine (QDI), which, in turn, interacts with naphthol to form leucobase (LB) and then a blue dye. *Therefore*, it was interesting to study the activity of 3d-ions on an acidity of the  $M^{2+}/NZP$  surface by using the spectrokinetic measurements of the formation of dyes.

Samples with the compositions  $Na_{0.5}M_{0.25}Zr_2(PO_4)_3$  ( $M^{2+} = Co, Ni, \text{ and } Cu$ ) were synthesized by the sol-gel method. The X-ray diffraction data substantiated the structure of NZP: the positions and relative intensities of diffraction maxima were close to those reported in the literature. The acidity of the surface was controlled spectrokinetically on a Specord UV-VIS spectrophotometer by using the indicator reactions of oxidation of the PPD derivative to the cation-radical of semiquinone ( $SH^+$ ) and of catalytic formation of a dye.



**Fig.** Kinetic dependences of the test reaction with the dye Kr formed on  $M_x$ -NZP,  $M^{2+}=Ni$  (1), Co (2), Cu (3)

$W_{Kp},$ $mmol \cdot l^{-1} \cdot sec^{-1}$	$M_{0.25}$		
	Ni	Co	Cu
$W_1$	0.30	0.29	0.65
$W_2 \times 10^3$	0.71	0.30	5.22
$W_3 \times 10^3$	0.26	0.25	1.28
$W_1/W_2$	423	970	125
$W_2/W_3$	2.7	1.2	4.1

**Table.** Kinetics data of the indicator reaction

The dye yield formed in the heterogeneous reaction rises with increasing M content (fig.). Therefore, the electron-acceptor centers are Ni-Cu-Co dopant ions. Three types of acid sites, differing in the formation rate of the Kp dye and containing 3d-metal ions, have been established. Values of speeds and their ratios are presented in table. The centers  $W_1, W_2, W_3$  differ in the localization of M type ions: 1 and 2 demonstrate surface centers, type 3 indicates centers in the conduction channels with different positions. The speeds values  $W_1$  and  $W_2$  are maximum for Cu-NZP, which is also consistent with the reduction potential ( $E_{red}^0$ ) in the series  $Co^{+2} (-0.27) < Ni^{+2} (-0.25) < Cu^{+2} (+0.34)$ .

*The reported study was funded by RFBR according to the research project № 18-33-20101*

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# Poster Session





## Chelating sorbents- sorption equilibrium in the system of non-ferrous metal ions

Abbasov A.D., Mammadova F.S., Mammadova S.I., Askarova M.N.

*Natural Resources Institute of Nakhchivan Branch of ANAS, Nakhchivan city, Azerbaijan*  
e-mail: ada.nat.res@mail

In the present report, the results related to the sorption equilibrium, kinetics and thermodynamics of ions studied by chelating ionites involved in an investigation have been presented. Sorption equilibrium of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ -ions with macroporous Amberlite IRC-748 (iminodiacetic acid functional group), Amberlite GT 73 (thiol functional group), Duolite C 467 (amino-phosphonic functional group) and Dowex M 4195 (bis-picolylamine functional group) chelating sorbents. Sorbents are respectively characterized by 4.4; 3.9; 3.5; 35g  $\text{Cu}^{2+}$ /L sorption capacities. Sorption isotherms of metal ions were taken in the interval of 0.50-2.50 gMe<sup>2+</sup>/L by exchanging concentrations method, it was confirmed by calculations that isotherms obey Langmuir equation with certain deviations in all cases, and formulas relevant to Langmuir equation of isotherms were suggested. At the same time the parameters of Freundlich equation were calculated, it was determined that the areas of isotherms which is relevant to 0.5-1.5 gMe<sup>2+</sup>/L concentration oblast obey this equation, relevant calculation equations were suggested by using the dependences set in the  $\lg C_e - \lg E$  coordinates. Notwithstanding in all cases, the selectivity of sorption is considerably higher in the low concentrations, it drops sharply by increasing of the molar share in the sorbent phase of ions. The fact that realizing of chelates imine nitrogen created by metal ions by Amberlite IRC-748, sulfur atom by Amberlite GT 73, oxygen atom combined with double communication to phosphor atom by Duolite C467, nitrogen atom and pyridine nitrogen-  $\text{C}_5\text{H}_4\text{N}-\text{CH}_2-\text{N}(\text{polymer})-\text{CH}_2-\text{C}_5\text{H}_4\text{N}$  which connects picolyl groups by Dowex M 4195 by means of unbreakable electron pairs was confirmed by IR-spectroscopy method. Although Dowex M4195 is intended for the sorption of  $\text{Cu}^{2+}$  ions from the discharge water of metallurgical facilities, the high capacity and selectivity of this sorbent against  $\text{Pb}^{2+}$ - ions is also determined: 160.65mg/g. During the sorption of the studied ions by Amberlite IRC-748  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+}$ , bu Duolite C467  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+}$ , by Amberlite GT 73  $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$  orders were determined. Although Dowex M 4195 has good sorption ability against  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ -ions, it does not show any intrinsic resistance to other ions. The maximal sorbent capacity of sorbents for each ion and the possibility of separating of  $\text{Cu}^{2+}$ - $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ - $\text{Cd}^{2+}$ -ions by Amberlite IRC-748 and Duolite C467 from binary solutions in which the two ions are combined are determined according to the values of coefficient. The value of the diffusion coefficients were calculated during the absorption of ions studied by different solids. In all cases, the value for diffusion coefficients for  $\text{Cu}^{2+}$  was higher than values for other ions. The linear dependence of  $F$  from  $t^{1/2}$  up to the 0.4-0.45 values, the characterization of Bio criterion by  $>50$  values, show that the speed of the results processes obtained from the "kinetic memory" experiments is controlled by internal diffusion. Being exothermic from 1.00gMe<sup>2+</sup>/L concentrated solutions of the sorption of studied ions by sorbents, the decreasing of exothermicity is observed parallel to that of filling of ionites with ions from more concentrated solutions. The decline in the heat flow intensity is probably due to additional energy consumption during the diffusion of ions into the ionic particles. By using the diffusion coefficients and activation energy, the values of activation entropy were calculated by R.Barrer equation:  $D_0 = d^2(ekT/h)\exp(\Delta S/R)$ :  $ekT/h=1,69 \times 10^{13} \text{sec}^{-1}$ ,  $d=0,5 \text{ nm}$ . The values of free energy and entropy multiplier were calculated, it was proved that selectivity is controlled by entropy factor in all processes accompanied by the separation of heat and decreasing of entropy, the factor that stipulates higher selectivity was the decreasing of entropy. Since all thermodynamic functions are negative, sorption of ionites with ions is accompanied by the separation of heat, decreasing entropy and free energy. One of the most important results of the theoretical and practical plan of the work carried out is the evidence of the interaction between the selectivity of sorption and kinetic abilities of ionites: the rise of kinetic indicators of ionites is accompanied by the increase of selectivity of sorption.

## Fenozan derivatives and its activities at colloidal systems

Alekseeva O.M.<sup>1</sup>, Golochshapov A.N.<sup>1</sup>, Kim Yu.A.<sup>2</sup>

<sup>1</sup>*N.M. Emanuel Institute of Biochemical Physics of Russian Academy of Sciences,  
Moscow, Russia,*

<sup>2</sup>*Institute of Cell Biophysics of Russian Academy of Sciences, Pushchino, Moscow region,  
Russia  
e-mail: olgavek@yandex.ru*

Synthetic hydrophobic substance - antioxidant fenozan ( $\beta$  - (4-hydroxi-3, 5-di-tert-butylfenil) propionic acid) was synthesized by V.V. Ershov and Nikiforov G.A at Institute of Chemical Physics of USSR Academic of Science RAS [1]. Fenozan formed the micelle suspension at aqua medium, contained salts and buffers (neutral pH). These suspensions were soluted to small concentrations. Fenozan and its derivatives were tested by DSC method with using of biological experimental on models of multilayer cell membranes.

The multilayer membranes were formed as multilamellar liposomes [2] contained only one phospholipid - dimyristoilphosphatidylcholine (DMPC). DMPC is synthetic phospholipid without any charges. Fenozan easily incorporated to bilayer of these multilamellar liposomes and destroyed its structure. Suspensions influenced in concentration dependence manner to the microdomain organization of DMPC bilayer. These suspensions with varied concentrations of fenozan we tested by adiabatic differential scanning micro calorimetric method (DSC) on models of multilayer cell membranes with using DASM-4 [3].

By using the derivatives of fenozan – ICHFANs, that were synthesized by Nikiforov G.A at Institute of Biochemical Physics of RAS [4]. ICHFANs - hydrophobic hybrid antioxidant with quaternized long chains, with number of carbon atoms from 8 up to 16, - alkyl halogenides alkyl-dimethyl- $[\beta$ -(4-hydroxi-3,5-di-tret-butilphenil) propionyl ethyl] ammonia halogenides. Its micelle suspension influence to DMPC membrane. By DSC method we obtained data, suggested that ICHFANs can incorporate to easily, and change its microdomain structure. And ICHFAN-16 forms its own faze at bilayer.

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## **Features of calcium carbonate crystallization during heating hard water passed through microporous membranes**

Ananyeva E.A., Kuchuk G.S., Mesyats E.A., Mindlina T.B.

*National Research Nuclear University MEPhI, Moscow, 115409 Russia  
e-mail: [eaananyeva@mephi.ru](mailto:eaananyeva@mephi.ru)*

In the present work the effect of various microporous filtering materials on the subsequent crystallization of calcium carbonate when heating hard water was investigated. Filtration through a microporous membrane does not change the hardness of water, but reduces the amount of deposition that forms on the surface, due to the predominant crystallization of hardness salts in the volume of water in the form of aragonite. Aragonite needles have poor adhesion to the substrate; they do not form dense deposits on the heat exchanger tubes. This effect is called “quasi-softening,” since the hardness of the source water does not change during microfiltration. In order to clarify the mechanism of “quasi-softening” hard water, microfiltration experiments were carried out using filter elements based on a polymer with a spatial-globular structure (SGS-polymer) with a pore size of 3  $\mu\text{m}$  and membrane filter with 0.45  $\mu\text{m}$ . It was found that calcite crystallizes from the source water, and from the filtrates subjected to boiling, obtained using filtering elements (FE) based on SGS-polymer crystallizes the mixture of calcite crystals, vaterite and aragonite, and filtrates using the “Millipore” installation crystallizes mainly aragonite. Previously, this effect, found on filtrates through membranes of SGS-polymer, was explained by the special properties of the polymer, due to which a change in the hydration shells occurs during the movement of water [1]. However, the description of this effect given in [1] by the change in the ion hydration shell is not in accordance with the results of structure study of the ion hydration shell in nanoscale pores. In [2], using the Monte-Carlo computer simulation, the structure of ion hydration shell was studied in the size range from 1 to 100 molecules at a temperature of 298 K in a flat model nanopore 0.7 nm wide. It has been established that the perturbations produced by the walls of such a nanopore lead to the decomposition of ion hydration shell into components differing in their spatial organization and orientational molecular order. Therefore, it can be assumed that a noticeable change and destruction of hydrated shells is possible only using nanofiltration. Thus, the effect of “quasi-softening” is not a specific property of filter materials with a spatial globular structure. This effect is observed when filtering through other microporous materials and depends on the pore size.

It can be assumed that the effect of “quasi-softening” is due to the removal of calcite microcrystals during microfiltration, thus creating conditions for the formation of aragonite crystals, which corresponds to the well-known “rule of steps” Ostwald [3]. The free energy of the aragonite phase transition to calcite is approximately 1.1 kJ / mol. The energy barrier of such a transition is large enough, so the unstable form - aragonite can persist indefinitely.

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## Modeling of CO, O<sub>2</sub> adsorption and O<sub>2</sub> dissociation on platinum and platinum-copper clusters

Bandurist P.S., Nikitina N.A., Pichugina D.A., Kuzmenko N.E.

*Department of Chemistry, Moscow State University, Moscow,  
e-mail: monbar-95@yandex.ru*

Development of a catalyst for the oxidation of CO to CO<sub>2</sub> is one of the most urgent tasks. Noble metal catalysts, such as platinum, are traditional in CO oxidation. The insertion of another metal can increase the catalytic ability of platinum and reduce the cost of the catalyst. In this work, the adsorption of CO, O<sub>2</sub> and the dissociation of oxygen, which is one of the stages in the oxidation of CO, were considered.

The purpose of this study was to compare the processes of CO, O<sub>2</sub> adsorption and oxygen dissociation occurring on two different catalytic systems: platinum and platinum-copper using methods of quantum chemistry. Catalysts based on Pt<sub>13</sub> [1] and Pt<sub>12</sub>Cu clusters were considered. The optimization of the structure and the calculation of the energy of the reaction participants were carried out using the PBE96/SBKJC method in the program «Priroda» on the MSU supercomputer «Lomonosov» [2].

At the beginning of the work it was established how the insertion of an additional copper atom affects the structure of the platinum cluster. The most stable structure of the Pt<sub>12</sub>Cu cluster is that in which the copper atom is located on the edge. There are no special changes in the cluster geometry when it is doped. Next, we simulated the adsorption of molecular oxygen and carbon monoxide on two Pt<sub>13</sub> and Pt<sub>12</sub>Cu clusters. The most beneficial interaction of carbon monoxide on a bimetallic cluster is realized as far as possible from the copper atom. When oxygen interacts with a platinum cluster, superoxide and peroxide complexes are formed, and with a bimetallic platinum-copper cluster, only peroxide complexes are formed. When considering the dissociation of oxygen, a transition state and activation energy were found on two model catalytic systems. The introduction of a copper atom into the Pt<sub>13</sub> cluster reduces the activation energy in the oxygen dissociation reaction. The most advantageous position for the adsorption of the oxygen molecule on a bimetallic cluster is a position that is not in close proximity to the copper atom. It can be assumed that the role of copper is to change the electronic properties of the cluster, contributing to an increase in its reactivity.

*The work was performed using the resources of the Supercomputer  
Complex of Moscow State University.*

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## The quantum chemical modeling of adamantane reactions with propylene

Baranov N.I.<sup>1</sup>, Safir R.E.<sup>1</sup>, Bozhenko K.V.<sup>1</sup>, Cherednichenko A.G.<sup>1</sup>, Bagrii E.I.<sup>2</sup>

<sup>1</sup>Physical and colloidal chemistry department, Peoples' Friendship University of Russia,  
117198, Moscow, Miklukho-Maklaya street 6

<sup>2</sup>A.V.Topchiev Institute of Petrochemical Synthesis, 11991, Moscow, Leninsky prospekt 29  
e-mail: 1042182094@rudn.ru

The main purpose of conducted research is to investigate the mechanism of chemical reactions during the interaction of adamantane with unsaturated hydrocarbons, e.g. propylene. The products of such complex transformations vary by the structure, physical and chemical properties. Nevertheless, experimental data and the results of quantum chemical calculations demonstrate that the main products of reactions, carried out in the presence of aluminum catalysts, are n-alkanes with n-alkenes. Computational modeling aims at understanding of reaction stages, including the geometrical and electronic structure of transition states. Knowing these processes let scientists change the experimental conditions to obtain the necessary products with the sufficient yields. The substituted adamantanes might be used as missile fuels.

The geometry optimization and normal-mode analysis for the studied systems were carried out using B3LYP version 1 functional with 6-31G\* basis set as implemented in Gamess US program. Energetically, the most preferable way of adamantane substitution with hydrocarbon radicals undergoes through 1-adamantyl cation (figure 1).

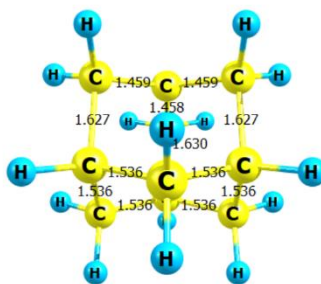


Figure 1. 1-adamantyl cation

It was shown by quantum chemical calculations that the tertiary adamantyl cation is more stable by 11 kcal/mol comparing with secondary ones. 1-adamantyl cation interacts with hydrocarbon radical forming positively charged intermediates. Adding one more adamantane molecule leads to 1,n-propyladamantane, and this reaction is barrierless. The heat effect of summary reaction, calculated from total energy with zero-point energy corrections, totals -18,56 kcal/mol. However, forming 1,n-propenyladamantane in trans- and cis- forms requires to overcome the transition state complex, containing Ad-CH<sub>2</sub>-CH<sup>+</sup>-CH<sub>3</sub> cation with aluminum tetrachloride. The conducted calculations support the previous experimental data concerning adamantane reactions with unsaturated hydrocarbons.

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## **Novel composite nano-catalysts based on titanium dioxide modified by bivalent transition cations**

Isaeva N., Bratchikova I.G., Cherednichenko A.G., Absalan Y., Kovalchukova O.V.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: bratchikova\_ig@pfur.ru*

Liquid phase photocatalytic transformations of organic harmful impurities from the waste waters is of the particular focus in connection with the development of new photocatalytic methods. The transition from micro to nano-dispersed catalysts increases the efficiency of the processes. Titanium dioxide nano-particles are known as good catalytic objects for photodegradation of phenol containing impurities which are active under UV irradiation. Incorporation of colored transition cations in its composition shifts the absorption bands of the composite to longer waves and make the catalysts active under the condition of visible irradiation.

For this, we isolated novel composite nano-catalysts based on titanium dioxide modified by some bivalent transition cations of the composition  $(MTiO_3)_x(TiO_2)_y$  (M denotes Co, Cu, Ni, Fe) and studied the characteristics of their surface and photocatalytic activity. According to the synthesis, while organometallic complexes as a precursor was being reacted with the metal, the energy band gap has been decreased markedly. The result shows this type of experiment can help to obtain  $MTiO_3$ -nanoparticle at less temperature, than in previous work we reported [1].

The samples thus obtained were characterized by UV-VIS, FT IR spectrophotometry, XRD, thermal analysis, SEM and EDAX analysis, BET method. Based on the results obtained, we can conclude that thermal decomposition of bimetallic complexes of titanium and transition metals with the organic polyphenols leads to formation of nano-sized composites  $(MTiO_3)_x(TiO_2)_y$  which possess good catalytic activity in the reactions of photodegradation of phenols.

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## Application of microwave initiation process of synthesis of iridium coordination compounds

Cherednichenko A.G., Zakharov S.V., Markova E.B.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: sorbotek@yandex.ru*

Coordination compounds of iridium with organic ligands are widely used as emission materials in organic light emitting devices and heterogeneous catalysis [1]. Their synthesis is carried out in two stages to obtain an intermediate dimer product. Both stages of the process are very slow. The reaction time is 24-48 hours. One of the modern methods of initiation of chemical reactions is microwave radiation. this type of initiation can reduce the time of the chemical reaction in question several times while maintaining the value yield and quality of the final product [2].

The use of microwave initiation for synthesis of tris(1-phenylisoquinolate) iridium allows you to carry out the entire process in one hour (Fig.1). The total yield was 44,0-45,0 %. To obtain a high-purity product, a synthesized sample of tris(1-phenylisoquinolate) iridium was placed in the loading chamber of a laboratory sublimator and purified by sublimation at a temperature of 320-340 °C in a deep dynamic vacuum. Similar results were obtained for coordination compounds of iridium with other organic ligands. The analysis of the synthesized products was carried out by NMR, ICP-MS and LC-MS methods.



**Fig.1.** Synthesis of complex microwave initiation CEM Explorer 48 NP-1002: general view of the installation (a) and the reactor with a tris(1-phenylisoquinolate) iridium ((b).

Luminescent properties of the material were investigated on a spectrometer Fluorolog FL3-22. The synthesized sample of the material showed luminescence in the red region of the spectrum at  $\lambda_{\max}=366$  nm. Multilayer structures of organic light-emitting diodes (OLED) were manufactured to study the electroluminescent properties of the material and their characteristics were determined.

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## Development of catalytic systems for the synthesis of unsaturated hydrocarbons based on the principles of green chemistry

Dementieva M.V., Sheshko T.F.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: dementyeva\_mv@rudn.university*

Improving the quality of life, the protection of public health, the environment is the main objective of development of industrial production, including chemical and petrochemical, and introduction of innovative products. Also, necessary to consider that any industrial production has the potential to technogenic danger-mechanical, radiation, chemical or biological [1]. The special place among the technological dangers is chemical. The problem of chemical safety is to protect people and the environment, where the risk of negative effects of dangerous chemical agents is reduced to an acceptable level, in modern conditions is becoming increasingly important. Currently, the framework for the creation of mechanisms of protection against chemical pollution is the green chemistry. Following one of its principles it is possible to receive unsaturated hydrocarbons ( $C_2H_4$ ,  $C_3H_6$ ), using the technological emissions of the production enterprises containing the carbon oxides.

As a result of the work was created catalytic nanosystems based on nanopowders iron and manganese matrixed in oxides substrate ( $Fe/Al_2O_3$ ,  $Fe/SiO_2$ ,  $Fe/ZrO_2$ ,  $MnOx/SiO_2$ ,  $Fe-MnOx/ZrO_2$ ,  $Fe-MnOx/Al_2O_3$ ,  $Fe/ZrO_2-SiO_2-MnOx/SiO_2$ ) and iron oxides of complex of gadolinium ( $GdFeO_3$ ,  $SrFeO_{3+x}$ ,  $GdSrFeO_4$ ,  $Gd_{2-x}Sr_{1+x}Fe_2O_7$ ) for utilization of greenhouse gases with hydrogen at atmospheric pressure. The selectivity of the process for unsaturated olefins amounted to 42%. In articles [2,3], the reaction mechanisms described in detail extending with the catalysts described above. The successful results show that this utilization of greenhouse gases industrial production technology must be fixed in law and implemented in the industrial enterprises, along with the same rate as the required payment of environmental tax.

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## Experimental vs DFT calculated NMR spectra of the 2-methyl-2,3,4,5-tetrahydro-1H-[1]benzothieno[2,3-c]azepine

Eresko A.B.<sup>1</sup>, Muratov A.V.<sup>1</sup>, Voitash A.A.<sup>1</sup>, Raksha E.V.<sup>1</sup>, Tolkunov V.S.<sup>2</sup>, Tolkunov S.V.<sup>2</sup>

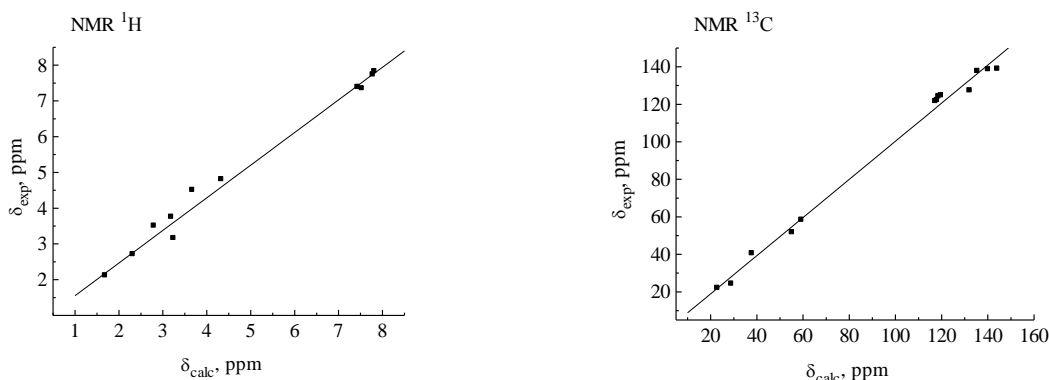
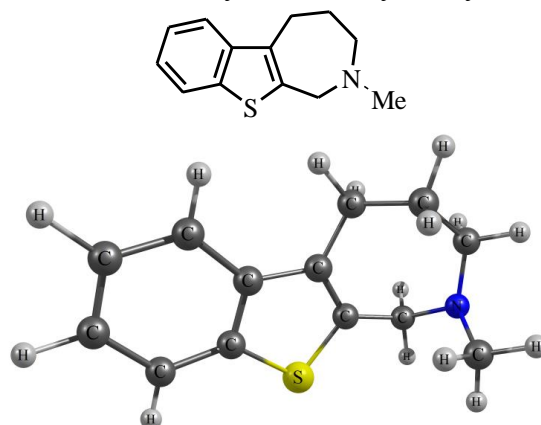
<sup>1</sup>L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, Ukraine 83114, Donetsk, R. Luxemburg str., 70

<sup>2</sup>L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, Ukrainian Academy of Sciences, 50, Kharkiv road, Kyiv, 02160, Ukraine  
e-mail: a\_eresko77@mail.ru, elenaraksha411@gmail.com

As a continuation of our research on the synthesis and reactivity of heterocyclic systems based on 1,2-diazepine and azepine, this we present the results of the molecular modeling of the structure and NMR spectra of 2-methyl-2,3,4,5-tetrahydro-1H-[1]benzothieno[2,3-c]azepine.

2-Methyl-2,3,4,5-tetrahydro-1H-[1]benzothieno[2,3-c]azepine was obtained from [3-(1-benzothien-3-yl)propyl]amine by interaction with mixture of formic acid and formaldehyde in the conditions of the Eschweiler-Clark reaction. Its structure was confirmed by NMR <sup>1</sup>H and <sup>13</sup>C spectroscopy (DMSO-d<sub>6</sub> solution).

Molecular geometry optimization for the studied azepine was carried out by B3LYP/6-31G(d,p)/PCM method (solvent - DMSO). Parameters of molecular geometry as well as electronic structure for the azepine ring were estimated. Only conformer with the lowest total energy was further considered for studied molecule (Fig. 1). The azepine optimized geometry was used for magnetic shielding tensors calculation by standard GIAO method. The patterns of the NMR <sup>1</sup>H and <sup>13</sup>C spectra for 2-methyl-2,3,4,5-tetrahydro-1H-[1]benzothieno[2,3-c]azepine are correctly reproduced at used computational level. Linear correlations between the theoretical and experimental chemical shifts are clearly visible on Fig. 2.



**Fig. 2.** Linear correlations between the calculated (B3LYP/6-31G(d,p)/PCM) and experimental (DMSO-d<sub>6</sub> solution) <sup>1</sup>H and <sup>13</sup>C chemical shifts of the 2-methyl-2,3,4,5-tetrahydro-1H-[1]benzothieno[2,3-c]azepine (R = 0,993 for <sup>1</sup>H, R = 0,997 for <sup>13</sup>C)

## Green synthesis of gold nanoparticles in sodium alginate media

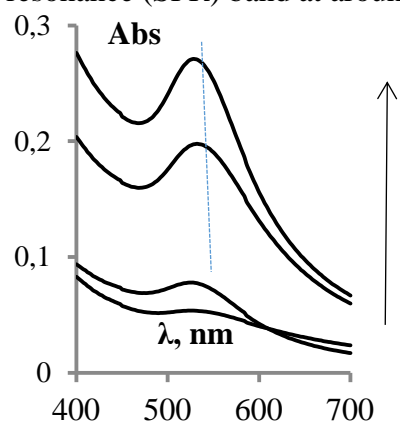
Fedoseeva M.A., Mikhaleiko I.I., Kononova E.A.

Peoples Friendship University, Moscow, Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: mikhaleiko\_ii@pfur.ru

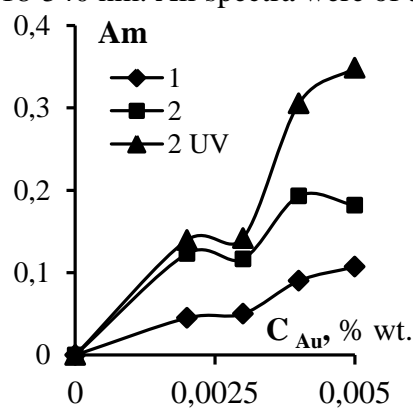
Alginates as polysaccharides from renewable natural resources are eco-friendly reducing agents and stabilizers for a perspective use in green synthesis of nanotechnology. Na-Alginate is one of the few important naturally occurring polyelectrolyte polymers used in preparation of hydrogel matrix. In recent reports [1,2] the producing of silver and gold nanoparticles (NPs) in biopolymer media by means of green sonochemical methods has been used.

In our work gold NPs were synthesized by reducing  $\text{AuCl}_3$  in aqueous Na alginate solution without and under stimulation by tannin additive or/and ultraviolet (UV) light. The different sols' synthesis were carried out with varying the concentration of precursor, alginate (0,2 ÷ 0,8 % wt.), tannin and irradiation time. The formation of NPs was determined by using UV-visible spectroscopy (TM Ecoview B-1200, Russia).

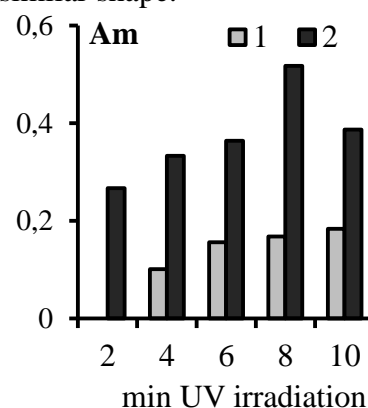
Figure 1 shows one example of the absorption spectra with characteristic surface Plasmon resonance (SPR) band at around 518-540 nm. All spectra were of a similar shape.



**Fig.1.** Plasmon spectra of Au-NPs in alginate sol with tannin content increase ↑



**Fig.2.** Gold concentration dependence of  $A_m$  for Au-NPs in Alg sols without tannin T



**Fig.3.**  $A_m$  values of Au-NPs Plasmon spectra in Alg sols without (1) and with T (2)

The increasing of substances concentration – tannin,  $\text{AuCl}_3$  (figure 2), alginate, and time irradiation (Figure 3) caused the increased SPR absorbance. SPR shifted to the higher wavelength (red-shift from 518 to 538 nm) with Au content increase, but weak blue-shift in case of Alginate. These effects can be explained by changes of the average size of flocculated particles. Tannin presence and UV treatment do not influence the absorbance maximum of Au-NPs spectra. But tannin addition and UV irradiation greatly enhanced the Au-NPs formation.

The special analysis of absorption spectra [3] based on Mie theory permits us to calculate such characteristics of Au-NPs as volume fraction of metallic NPs ( $N_v$ ), concentration of conducting electrons ( $N_e$ ) and damping coefficient of plasma oscillation ( $\gamma$ ). The latter parameter includes the number of surface defects and the cross section of electron scattering on defects.

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## **The ability of humic substances of peats and microorganisms of the genus *Rhodococcus* to stabilize emulsions of oil and oil products in water**

Gertsen M.M., Dmitrieva E.D.

*Tula State University, Tula, Russian Federation*  
*e-mail: mani.leontyeva@gmail.com*

The problem of environmental protection is becoming particularly acute due to the pollution of aquatic ecosystems with oil and oil products. There are methods for detoxifying contaminated natural objects with petroleum hydrocarbons by using a complex of microorganisms, oil destructors and environmentally friendly, natural compounds - humic substances (HS) [1].

The purpose of this work is to study the stabilizing ability of humic substances of peats separately and in the joint presence with microorganisms of the genus *Rhodococcus* in the relation to oil hydrocarbons.

The objects of the study are humic substances of peats from Tula region: reed fen peat (RFP), black alder fen peat (BFP), sphagnum high-moor peat (SHP) and sphagnum transition peat (STP), identified by the method described in the previously published work [2]; bacteria strains *Rhodococcus erythropolis* S67, *Rhodococcus erythropolis* X5, provided by the plasmid laboratory of the Institute of Biochemistry and Physiology of Microorganisms n. a. G. K. Scriabin RAS (Pushchino). Model pollutants: hexadecane (a representative of the light fraction of oil), diesel fuel from the Rosneft filling station and oil from the refinery of GAZPROMNEFT JSC.

The study of the effect of HS preparations on the aggregate state of oil products was carried out in fresh water at room temperature with recalculation of the optical densities of the solutions on the transmittance (T, %), the values of which served as a criterion for the stability of an oil-in-water emulsion [3]:

$$T = 10^{-D} \cdot 100\% \quad (1)$$

where D is the optical density.

The peripheral parts of the HS molecules are associated with the light fractions of oil, mostly paraffins, due to hydrophobic bonds, the interaction of the aromatic framework with the heavy fractions proceeds according to the "stack-interaction" type, which is carried out between parallel arranged aromatic structures due to van der-Waals forces combining several types of intermolecular interactions. Persistent, difficult to exfoliate emulsions are formed, since the dispersed phase droplets, protected by a peculiar shell — an adsorption film — cannot merge with each other. Drops of petroleum products, surrounded by molecules of humic substances, acquire negative buoyancy and pass from the surface into the water column, where they are intensively decomposed by microorganisms-oil destructors due to the large contact surface.

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## Assessment of chemical air pollution in moscow emissions of thermal power plants

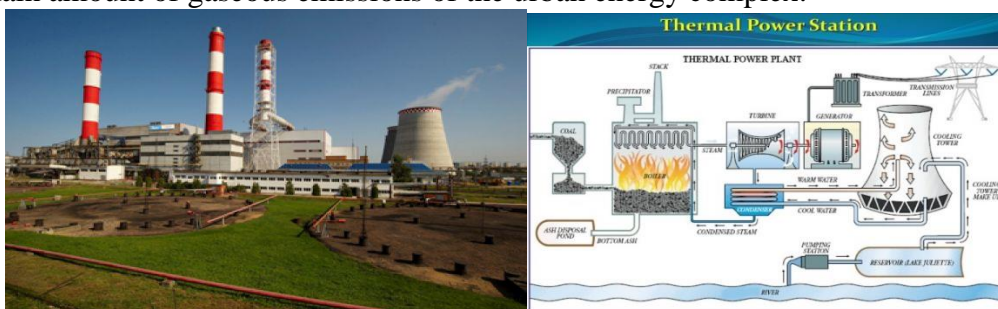
Mayorova Y.V., Martishov A.V., Danacheva M.N., Glebov V.V.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: vg44@mail.ru

The problem of reducing the harmful effects of the energy complex is most acute for large cities due to the concentration of industry, utilities and the population, the concentration of various types of power plants in a limited area.

One of the most important issues is to determine the contribution of the thermal power plants (TPP) to the surface gas content of the city, since the level of pollution is directly related to the cost of protecting the atmosphere [1].

As energy facility, which conducted field studies of the spread of harmful emissions in the city, was chosen TPP #21 JSC "Mosenergo". The choice of TPP #21 is due to the fact that it is one of the most powerful Moscow power plants with a pipe height of 120 m, which accounts for the main amount of gaseous emissions of the urban energy complex.



During field experiments, emissions of sulfur and nitrogen oxides from TPP varied widely. Thus, the ratio of the maximum value of emissions to the minimum in different series of experiments changed for  $\text{NO}_x$  – in 1,2 - 2,1, for  $\text{SO}_2$  - in 2,8 - 4,7 times. Therefore, when processing the results, sub-flare surface concentrations were recalculated for the same emission of harmful substances equal to 1 g/s. data relating to conditions with the same characteristics were analyzed [2].

Oxide and nitrogen dioxide have different maximum permissible concentrations (MPC):  $\text{MPC NO} = 0.49 \text{ mg/m}^3$ ,  $\text{MPC NO}_2 = 0.092 \text{ mg/m}^3$ , i.e. nitrogen dioxide is 4.8 times more toxic than nitrogen oxide.

The assessment of  $\text{NO}_x$  transformation according to the ozone diffusion method showed that the share of  $\text{NO}_2$  in the total amount of nitrogen oxides from TPP emissions averages 32-43% for the cold season. The results of the study confirmed the position that the complete transformation of nitric oxide into dioxide is practically not observed.

It is revealed that with increasing wind speed the contribution of the energy complex to the total gas content of the air increases significantly in the range of 4-8 m/s and practically stabilizes at a speed greater than 8 m/s. For the summer period, the share of energy in the gas content of the air basin can be considered conditionally constant, starting from the wind speed equal to 6 m/s.

*The publication has been prepared with the support of the «RUDN University Program 5-100»*

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## The sorption activity of minerals on the absorption of heavy metals

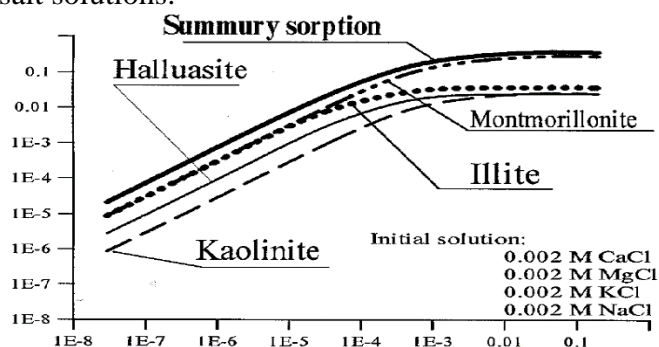
Mikhailichenko K.Yu., Kulieva G.A., Glebov V.V., Erofeeva V.V., Maksimova O.A.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: vg44@mail.ru

Investigated sorption of ions  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , nano-sized particles of the mineral kaolinite, pre-treated diesel fuel. Sorption isotherms are obtained, on the basis of which the sorption capacities of kaolinite with respect to these ions and their sorption constants are determined. It was found that the treatment of kaolinite with diesel fuel reduces the sorption properties of this soil mineral.

Heavy metals (HM) are extremely dangerous pollutants that are constantly released in the biosphere during many natural and anthropogenic processes [1]. Often contaminated ecosystems contain high concentrations of organic toxicants, such as petroleum products, together with heavy metals. The aim of our study was to study the effect of petroleum products (diesel fuel) on the sorption of heavy metal ions by highly dispersed soil mineral (kaolinite).

**Method of research.** Processes of sorption of ions  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  by kaolinite were investigated by potentiometric method. Using ionomer (I-130) was measured potentials of chalcogenide ion-selective electrode Chg-Cu-001 and Chg-Cd-001, Chg-Zn-001 silver chloride relative to the reference electrode. The concentrations of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  ions in the working solutions were calculated on the basis of electrode functions obtained by calibrating these electrodes in standard salt solutions.



**Results and discussion.** Using the Langmuir adsorption equation converted into a linear form, the sorption capacities of  $Q_{\text{max}}$  kaolinite (the number of reactive surface centers of the mineral) and  $KL$  adsorption coefficients were calculated, which showed the bond strength of the metal cation with the active groups of the mineral.

The sorption capacity of kaolinite with respect to  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  ions in the absence of diesel fuel was 40.1-41.3  $\mu\text{mol/g}$ , and with the addition of diesel fuel – 19.7-19.8  $\mu\text{mol/g}$ , while the conditional sorption constants were close: their logarithms were 4.4 - 4.5 (pH 4.8).

**Conclusion.** As a result of the experimental study of the sorption of ions  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  by the highly dispersed mineral kaolinite, it is shown that the sorption capacity of kaolinite after its treatment with diesel fuel decreases. In this regard, it can be assumed that contamination of soils and bottom sediments with petroleum products leads to a decrease in the sorption properties of soil minerals in relation to heavy metals, resulting in the mobility and bioavailability of heavy metal ions in the soil and their migration increase.

## Accumulation of zinc in the test cultures at the dust load in cement production in east kazakhstan region

Askarova D.A., Glebov V.V., Shevtsov V.V., Akhmedzyanov V.R., Nikitin D.S.

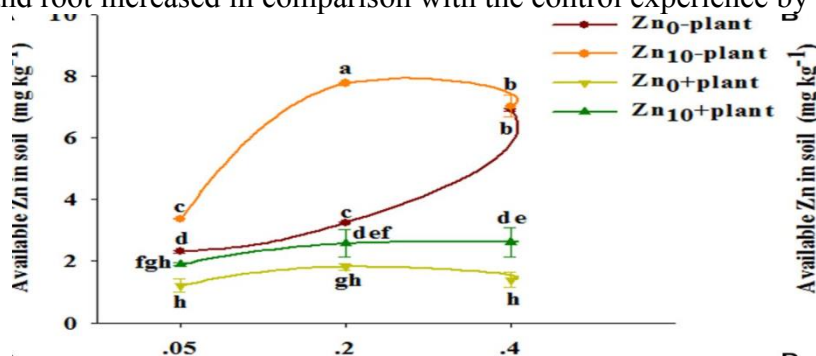
Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: vg44@mail.ru

Plant food is the main source of heavy metals (HM) in humans and animals. According to various data, together with food comes from 40 to 80% of TM [1]. Therefore, the level of accumulation of metals in plants used in food, largely depends on the health of the population [2].

**Organization and methods of research.** We conducted studies to assess the accumulation of heavy metals in various plants (*Brassica juncea* L., *Lepidium sativum* L., *Pisum sativum* L.). Cement dust was introduced in the concentration of 0.1%, 5%, 10%.

**Obtained result.** In *Brassica juncea* L. the concentration of zinc in the aboveground part was higher than in the root by 1.3 times compared with the control experience (in the aboveground part – 29.1 and in the root – 22.5 mg/kg). With the increase in the introduced dose of dust, the accumulation of zinc by the bodies of test cultures (above-ground part - roots) increased.

When cement dust was introduced into the soil, the concentration of zinc in the aboveground part of *Lepidium sativum* L. was 1.7 times less than in the root. In the control version of the experiment, the concentration of zinc in the above-ground part of *Lepidium sativum* L. was 3.2 mg/kg, and in the root – 6.0 mg/kg. Naturally, with an increase in the dose of contamination in the soil, the accumulation of metals by test cultures increases from the control. Thus, when applying different doses (5.0%), dust into the soil, the concentration of zinc in the aboveground part and root increased in comparison with the control experience by 1.8 times.



The concentration of zinc in the aboveground part of *Pisum sativum* L. when making 10% of the dust in the aboveground part was less than 1.5 times in the root. Zinc content in the aboveground part and root compared with the control experience was (2.3 mg/kg) and increased by 1.56 times.

**Summary.** The dust of cement production for plants is less toxic. All test cultures grew at 5.0% and some at 10.0% dust content in the soil. The accumulation of zinc above ground is the following decreasing series: *Brassica juncea* L. > *Lepidium sativum* L. > *Pisum sativum* L.

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## Membrane palladium-based alloys for high purity hydrogen production

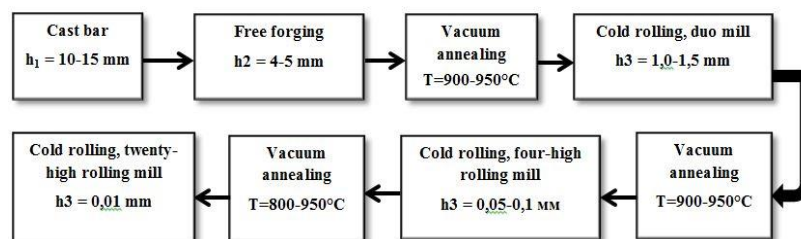
Gorbunov S.V., Chistova T.V., Roshan N.R., Chistov E.M., Burchanov G.S.

*Baikov Institute of Metallurgy and Material Science RAS, Moscow, Russia  
IMET RAS, 119991, Moscow, Leninskiy prospect, 49  
e-mail: sgorbunov@imet.ac.ru, tchistova@imet.ac.ru*

The best method for production of high purity hydrogen is separation via selective diffusion through metallic membranes palladium-based alloys. Lack of sufficient alloys significantly reduces the possibility to apply new membrane technology solutions to various industrial processes [1].

Our systematic and complex research of Pd-based membrane alloys with alloying elements in the solid-solution range allowed to develop effective Pd-In-Ru, Pd-Ru, Pd-Cu alloys for specific chemical technology processes and prepare thin foils with 30-50  $\mu\text{m}$  thickness.

Purpose of current work is to prepare leak-tight thin foils with 10-20  $\mu\text{m}$  thickness from tailored composition Pd-In-Ru, Pd-Ru, Pd-Cu alloys, research their membrane properties and catalytic reactivity and develop efficient membrane units with high hydrogen permeability and low Palladium content.



The strength properties, hydrogen permeability, structure, corrosion resistance and catalytic activity have been investigated on the obtained experimental foil samples of Pd-In-Ru, Pd-Ru and Pd-Cu alloys with 10 and 20  $\mu\text{m}$  thickness during working in different gas environments.

Our research group had developed a Membrane Element (ME). Developed ME is a membrane cell with 2.5 mm thickness. Cell consists of two plane walls. Walls' joints are sealed by diffusion and argon-arc welding in the absence of solders, pastes, etc., to ensure efficient sealing. A porous separator (wire netting) is placed between the walls. The membrane filtration element is a 'sandwichlike' assemblage of two walls in the form of disc membranes, made from a palladium-based alloy foil with different thicknesses and welded onto a stainless steel ring frame. After that, the frames are welded circularly with a branch pipe for the output of high purity hydrogen [2].

Welding modes have been developed to seal the membrane with 20 and 10  $\mu\text{m}$  thickness which consisted in increasing the temperature and specific pressure, as well as the selection of the thickness of nickel gaskets. Annealed membranes were used in welding.

Mode of obtaining vacuum-tight foils of 20 to 10  $\mu\text{m}$  thickness from Pd-In-Ru, Pd-Cu and Pd-Ru alloys is developed for the production of membranes, and complete set membrane characteristics, catalytic activity of membranes and structural materials were researched in gas medias.

*This work has been supported by grant 37P № AAAA-A18-118041990046-3*

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## **Influence of reducing agent content on the properties of molybdenum blue dispersion**

Harlamova D.V., Myachina M.A., Mikhalyuk V.A., Gavrilova N.N., Nazarov V.V.

*D. Mendeleev University of Chemical Technology of Russia, 125047, Moscow, Miusskaya sq. 9  
e-mail: dvharlamova@gmail.com*

Molybdenum blue dispersions are systems, which consist of polyoxometalate (POM) clusters with their deep-blue color, which originates from the partial reduction of  $\text{Mo}^{\text{VI}}$  to  $\text{Mo}^{\text{V}}$  giving a delocalized mixed valence state. The aim of this work was synthesis of molybdenum blue dispersion using ascorbic acid as reducing agent and investigation of its properties. It should be noticed, that there is the lack of such studies in the literature.

Depending on synthesis conditions different types of POM can be formed (such as wheel-shaped, spherical and “hedgehog”-shaped) [1]. But self-assembly process in dilute system is rather slow (approximately a few weeks) and therefore the optimum conditions of the synthesis should be chosen. Nowadays molybdenum oxide clusters are mostly used as catalyst and agent of targeted drug delivery.

The synthesis of molybdenum oxide clusters is achieved by the partial reduction of acidified solutions of molybdate. In our work we have been investigated systems with ascorbic acid/molybdenum molar ratios in the range of 0,6 – 2,0. Different amount of hydrochloride acid allowed to control the pH values of the dispersions in the range of 0,8 – 3,5.

Dynamic light scattering investigations showed that self-assembly began from the first day after reagents mixing. Regardless of various hydrochloride/molybdenum molar ratio and ascorbic acid/molybdenum molar ratio the average hydrodynamic radius of nanoclusters did not exceed 3 nm.

We have established that the synthesis of stable molybdenum blue dispersion did not required an excess of ascorbic acid. The most suitable ascorbic acid/molybdenum molar ratio should not be more than 1. In addition, the stable dispersion with the highest concentration of particles can be obtained in the range of pH 2,0 – 3,5.

Based on the results of spectrophotometric analysis we established that POM clusters are wheel-shaped, since the absorption peak of molybdenum blue dispersions is observed at 745 – 750 nm [2].

It should be noticed that concentration of particles in every system decreased with time. Also, in systems containing ascorbic acid/molybdenum molar ratio more than 1 aggregates of particles precipitated. Apparently, this phenomenon can be explained by competing redox processes that interfered with self-assembly of molybdenum oxide clusters. This assumption is confirmed by redox potential investigation of molybdenum blue dispersions.

*This work was supported by the Russian Foundation for Basic Research  
(grant № 18-33-00958)*

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## Synthesis of gold nanoclusters in the presence of DNA and guanosine monophosphate

Ivanova N.K., Aleksandrov Y.D., Lopatina L.I.

Lomonosov Moscow State University, 119991, Moscow, Lenin Hills, 1-3  
e-mail: n.ivanova1618@gmail.com

Over the recent decade, preparation of gold nanoparticles (AuNPs) has been widely investigated. DNA molecule as a matrices and stabilizer is one among the most attractive choices, due to efficient interaction between DNA and Au ions. The synthesis of AuNPs in the presence of DNA has been investigated in a series of researches and various reducing agent have been used, for example,  $\text{NaBH}_4$  [1], hydrazine [2] etc.

In our study, we investigated the possibility of obtaining gold nanoclusters using DNA molecule both as a stabilizer and a reducing agent. We suppose that the reduction may occur due to interaction of Au ions with guanine unit of DNA macromolecule. Therefore, the use of guanosine monophosphate (GMP) as a reducing agent was studied as well. We investigated the series of samples with  $\text{HAuCl}_4$  concentration 2.5 mM and 0.25 mM at different GMP: $\text{HAuCl}_4$  ratios (1:10 to 20:1) and series of samples DNA: Au (1:1, 1:10, 1:25,  $c_{\text{HAuCl}_4} = 0.5$  mM). All experiments were carried out at room temperature in phosphate-buffer saline (PBS) solution.

The change in absorption of spectrum at 400 nm indicate the formation of ultrasmall Au(0) nanoclusters. The increase in absorption at 400 nm in time was shown for both the DNA: Au fig.1(b), and for the GMP: Au fig.1(c). Interesting there is no plasmon absorption in all spectra, which indicates the formation of particles smaller then 2 nm. Formation of nanoclusters of 1 nm was also confirmed by transmission electron microscopy (TEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and *atomic force microscopy (AFM)*.

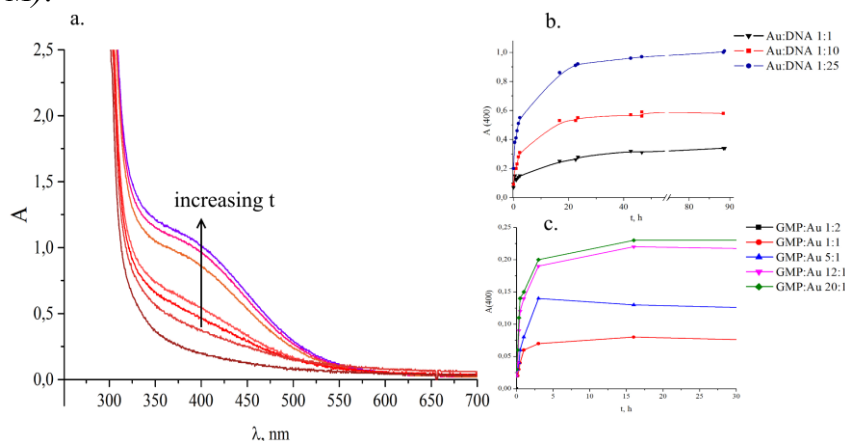


Fig.1. a – electronic absorption spectra of DNA–Au mixtures, b – absorbance of DNA–Au at 400 nm in time, b – absorbance of GMF–Au at 400 nm in time

*This study was financially supported by the Russian Foundation for Basic Research (grant no. 17-08-01087/17)*

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## **The zinc phthalocyanine's metal complex and an anti-cancer drug on the basis it**

Khromov A.V.<sup>1</sup>, Kogan B.Ya.<sup>2</sup>, Nikulin A.V.<sup>1</sup>

<sup>1</sup>*RUDN University, Moscow, Russia Miklukho –Maklaya str., 6;*

<sup>2</sup>*FSUE "SSC "NIOPIK", Moscow, B. Sadovaya str. 1, korp.4*

*e-mail: Arkadiy18@ya.ru*

Zinc phthalocyanine (Fig.1) - a metal complex heterocyclic pigment, practically insoluble in water. It can be obtained with condensation of o-phthalodinitrile with zinc acetate in an organic solvent with the formation of a grained crystal form. [1]

Compound of the nanoparticle zinc phthalocyanine is photosensibilizer. This complex is sensitive only to high-power pulsed laser radiation, to ordinary visible light and even continuous laser radiation, it is not sensitive. Therefore, in comparison with other photosensibilisers, it does not have phototoxicity for skin. At the same time, the molecular form of zinc phthalocyanine's complex is a powerful photosensitizer having strong fluorescence, possessing sensitive to continuous laser radiation, but zinc phthalocyanine's complex can be obtained in this form only with sublimation of zinc phthalocyanine's nanoparticles, for example, with a powerful laser pulse.

To obtain a drug on the basis zinc phthalocyanine's compound, it must be first converted into a nanoparticles form. A two-stage process was used for this.

At the first stage, technical zinc phthalocyanine's complex was subjected to plastic grinding in a paddle mixer using fine-crystalline inorganic salts as grinding media, as well as using diethylene glycol as a plasticizer.

After dispersion, the disperse salt and the plasticizer were completely washed with deionized water for extraction of all salts. Then, surfactant was added to the dispersion and repeated dispersion was obtained once again by ultrasonic disperser. The particle size in the dispersion process was controlled by laser scattering (Malvern Autosizer 2S).

Dispersion had carried out until an average particle size of 100-150 nm. Finally, the dispersion was diluted with a saline solution to a required concentration of zinc phthalocyanine's complex. It is drug-Nanosens®.

The drug-Nenosens® is a bright blue liquid which is stable dispersion of nanoparticles of complex of zinc phthalocyanine in physiological solution. The content of active substance in the drug is 2 mg/ml. Average size of the zinc phthalocyanine's nanoparticles is 150-250 nm [2].

Nanosens® is a drug intended for the treatment of skin cancer by an innovative method of Pulsed Laser Ablation of Nanoparticles (PLAN). The essence of the PLAN method is such: introduced nanoparticles of the drug into the tumor's cells are irradiated by powerful pulsed laser radiation, as a result-they are locally heated, and their micro-explosive ablation occurs, damaging the tumor tissues, as well as the capillaries feeding it. This leads to inhibition of the tumor's cells, suspension and suppression of its growth, regression, and in some cases to scarring. Thus, PLAN is a non-surgical method of treatment of superficial tumors. Nanosens® can also be used for treatment by PLAN combined with photodynamic therapy. In this case, the effects are made sequentially [3].

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## Peroxidation of substituted acetoacetic esters by hydrogen peroxide in heterogeneous conditions

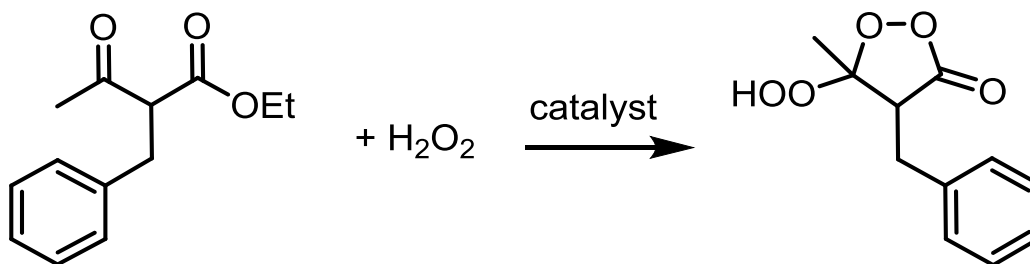
Khrustaleva A.N.<sup>1</sup>, Vil' V.A.<sup>2</sup>, Barsegyan Y.A.<sup>2</sup>, Cherednichenko A.G.<sup>1</sup>, Terent'ev A.O.<sup>2</sup>

<sup>1</sup> Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6

<sup>2</sup> N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,  
119991, Moscow, Leninsky prosp. 47  
e-mail: khrustaleva.anastasia@yandex.ru

The development of new approaches to the synthesis of cyclic organic peroxides is one of the central problems of modern organic and medical chemistry. Such interest is due to the fact that these compounds exhibit a wide spectrum of biological activity, in particular, antimalarial, fungicide and antiviral activities.

We have found that the treatment of  $\beta$ -ketoesters with hydrogen peroxide under acid catalysis conditions leads to the formation of  $\beta$ -hydroperoxy- $\beta$ -peroxylactones. The reaction proceeds selectively under mild conditions and allows to obtain the corresponding peroxides with good yields (30-96%) [1,2].



To get a deeper inside in the peroxidation of acetoacetic esters, we have studied the effect of acid type and its amount on the process. Thus, the reaction does not proceed in the presence of an equimolar amount of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . Contrariwise, raising the excess of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  to 10 equivalents leads to an increase of the target cyclic peroxide yield to 92%.

*The study was supported by Russian Science Foundation  
(Project 18-13-00027)*

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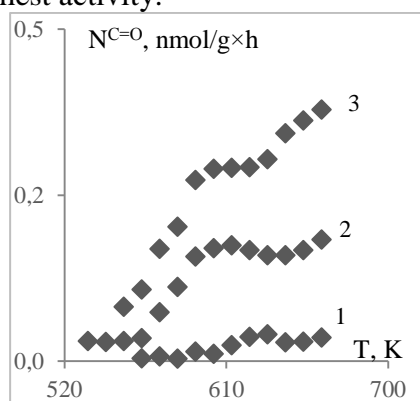
## Relationship between conductive properties and catalytic activity over perovskites of BIZRVOX family

Akhmedova L.S., Knyazeva E.I.

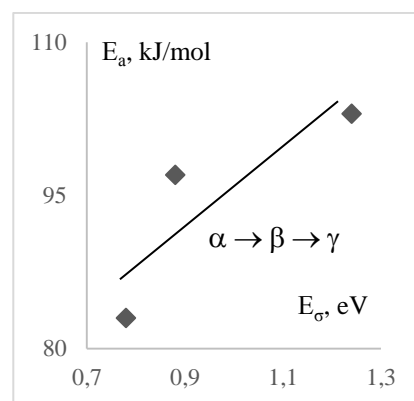
RUDN university, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: knyazeva-ei@rudn.ru

Solid electrolytes (SELs) with lamellar framework structure are of considerable interest for catalytic chemistry since the scope of these materials can be expanded by varying their composition by replacement of cations in the base compound with reactive dopant ions. Complex oxide materials belong to the SEL class with anionic (oxygen-ionic) conductivity type and have perovskite-like structures [1]. These oxides are based on the bismuth vanadate  $\text{Bi}_4\text{V}_2\text{O}_{11-\delta}$  which consists of alternating layers of  $(\text{B}_2\text{O}_2)_n^{n2+}$  and  $(\text{VO}_{3.5-y}\square_{0.5+y})_n^{n2-}$ , with  $\text{Bi}^{3+}$  cations being in square pyramidal coordination, while  $\text{V}^{5+}$  cations being in octahedral coordination with oxygen. Introduction dopant ions creates a large family of complex vanadate  $\text{Bi}_4\text{V}_{2-2x}\text{M}_{2x}\text{O}_{11-\delta}$  (BIMEVOX). The aim of this work was to study the catalytic activity of polymorphic BIZRVOX perovskites with the composition  $\text{Bi}_4\text{V}_{2-2x}\text{Zr}_{2x}\text{O}_{11-\delta}$  ( $x = 0.05-0.15$ ) in reactions of isobutanol.

Solid solutions were obtained solid-phase synthesis. All samples were studied in detail by means of DTA, XPA, and IR spectroscopy. In this work the catalytic characteristics of BIZRVOX were obtained at temperatures up to  $400^\circ\text{C}$  in flow regime with chromatography analysis. Alcohol dehydrogenation is the only reaction. The alcohol conversion  $W$ , % and the product yield increase with an increase in the content of the replacing ion, and the  $\gamma$ -phase has the highest activity.



**Fig. 1.** Temperature dependences of the yield of aldehyde on  $\text{Bi}_4\text{V}_{2-2x}\text{Zr}_{2x}\text{O}_{11-\delta}$  samples (1 - 0.05; 2 - 0.10; 3 - 0.15)



**Fig. 2.** Activation energy dependence of isobutanol dehydrogenation on the activation energy of  $\text{Bi}_4\text{V}_{2-2x}\text{Zr}_{2x}\text{O}_{11-\delta}$  conductivity

Temperature dependences of the aldehyde yield are S-shaped and resemble the temperature curve of conductivity (**Fig. 1**) [2]. The obtained form of curves in such systems may be due to a change in the conductive properties of the material with increasing temperature, i.e. a decrease in the activation energy of conductivity  $E_{a,\sigma}$  during transitions  $\alpha \rightarrow \beta \rightarrow \gamma$ . Thus, the results demonstrate a correlation between the content of the dopant-ion, the activation energy of conductivity the content of the dopant ion, the activation energy of conductivity  $E_a^{C=O}$  (**Fig. 2**).

*The reported study was funded by RFBR according to the research project №18-33-00928*

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## Chemosensory properties of negative amphiphilic spiropyran in solutions and at the air-water interface

Koryako N.E.<sup>1,2</sup>, Lyubimov A.V.<sup>3</sup>, Zaychenko N.L.<sup>3</sup>, Arslanov V.V.<sup>1</sup>, Rightman O.A.<sup>1</sup>

<sup>1</sup>*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6*

<sup>2</sup>*The Institute of Physical Chemistry and Electrochemistry RAS, 119071, Moscow, Leninsky Prospect, 31, 4*

<sup>3</sup>*N.N. Semenov Institute of Chemical Physics RAS, 119991, Moscow, Kosygin str. 4  
e-mail: pcss\_lab@mail.ru*

Chemosensors are the molecules capable of selectively and reversibly interacting with the substrate to be determined, resulting in changes in one or more properties of the sensory system. In most cases, the chemosensory molecule consists of the signal component, the receptor part, and the bridge between them. Depending on the type of signal component, it can be divided into three groups: chromogenic, fluorescent, and photo-switching. Photo-switched chemosensors are characterized by reversible “on-off” switching of sensory properties upon the of UV-vis light irradiation. Organic photochromic compounds attract a great interest due to the ability of reversible transformation between two forms with the different patterns of spectral absorption under electromagnetic irradiation. Optically active systems with a negative (reverse) photochromism, consisting of decolouration upon visible light exposure and colour restoration in the dark are of greater interest. Materials based on negative photochromes are used to create optically active recording media, visibility reduction systems, disguising coatings, optically controlled chemosensory systems, etc. However, due to certain difficulties in the synthesis of such systems, their number is not great, and the properties are still remain poorly investigated. In this work the results of the study of chemosensory properties of 1', 3'-dihydro-3', 3'-dimethyl-6-nitro-1'-octadecyl- [1-benzopyran-2,2'-indole] -8-methyl pyridine chloride (SP2) in organic solvents and at the air-/water interface are presented. It has been shown that the addition of the aluminum, iron (II), mercury and lead cations to the SP2 solution resulted in the formation of photochrome complexes with these metals, accompanied by bleaching of the system and, accordingly, a decrease in the absorption intensity of merocyanin. Besides, the interaction of negative spiropyran with copper (II) cations leads to a hypsochromic shift of the merocyanin absorption band by 35 nm. For the first time, monolayers of SP2 were formed and studied on the surface of water subphase. It has been established that negative spiropyran retained photosensitivity upon transition from a bulk phase to a two-dimensional ordered state. The study of the chemosensory properties of SP2 monolayers showed that upon addition of  $\text{Al}^{3+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  to the subphase, the isotherms were shifted towards larger mean molecular areas, which indicates the interaction of spiropyran with these metals at the interface and the formation of strong complexes. The results obtained open up broad prospects for the use of compounds of this class as working elements of molecular mechanisms and chemosensory systems.

## Quantum-chemical modeling of the molecular complexes of 2,4,7-trinitrophenanthrene-9,10-dione with polycyclic donors

Linko R.V., Ryabov M.A., Strashnov P.V.

Peoples' Friendship University of Russia (RUDN University),  
6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation  
e-mail: linko-rv@rudn.ru

The nitroderivatives of 9,10-phenanthrenequinone are known as electron-acceptor (**A**) components, which form with  $\pi$ -donor (**D**) charge transfer (**D-A**) molecular complexes. In the present work, molecular complexes (**I** – **VI**) formed by 2,4,7-trinitro-9,10-phenanthrenequinone (**TNPQ**) with a number of polycyclic hydrocarbons are considered: naphthalene (**NA**), phenanthrene (**PA**), anthracene (**ANT**), tetracene (**TET**), coronene (**COR**) as well as with tetrathiafulvalene (**TTF**). Electronic structure calculations of the molecular complexes were carried out in terms of density functional theory (DFT/B3LYP/def2-SV(P)) using the Firefly 8.2.G software package [1].

The following properties of the complexes **I** – **VI** were calculated and analyzed: the formation energies of molecular complexes  $\Delta E_f$  (kJ/mol), the average distances  $R$  (Å) between the **D** and **A** planes, the charge transfer from **D** to **A**  $q$  ( $\bar{e}$ ), the energies of the highest occupied and lowest free molecular orbitals  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  (eV), the energy difference  $\Delta E_{\text{MO}} = E_{\text{HOMO}} - E_{\text{LUMO}}$  (eV), and wavelengths  $\lambda$  (nm), corresponding to the energy difference  $\Delta E_{\text{MO}}$ . The results are summarized in the table 1. The molecular structure of complex **III** is shown in Fig.1.

Table 1. Results of calculations of molecular complexes.

Complex (D-A )	$\Delta E_f$	$R$	$q$	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E_{\text{MO}}$	$\lambda$
<b>I</b> (NA-TNPQ)	65,6	3,34	0,025	-6,6	-4,3	2,3	541
<b>II</b> (PA-TNPQ)	86,9	3,25	0,063	-6,7	-4,1	2,6	485
<b>III</b> (ANT-TNPQ)	91,1	3,29	0,091	-6,1	-4,1	2,0	632
<b>IV</b> (TET-TNPQ)	106,3	3,21	0,069	-5,6	-4,1	1,5	853
<b>V</b> (COR-TNPQ)	115,6	3,23	0,059	-6,2	-4,1	2,1	588
<b>VI</b> (TTF-TNPQ)	94,4	3,16	0,250	-5,6	-4,0	1,6	795

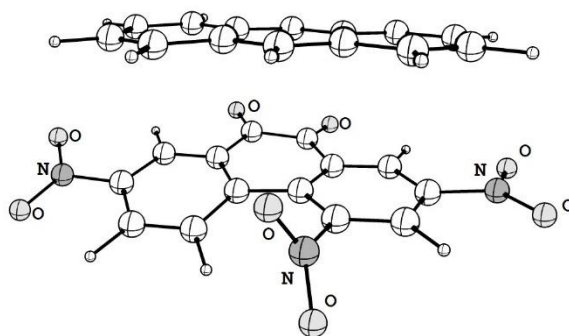


Fig.1. Molecular structure of complex **III**.

It can be seen that  $\Delta E_f$  increases with an increase in the number of cycles in the **I** – **V** series. The  $E_{\text{LUMO}}$  value in the complexes is slightly higher than the -4.5 eV value observed in **TNPQ**, and these changes are consistent with the charge transfer values found. The calculated values of  $\lambda$  are consistent with the experimental values of  $\lambda_{\text{max}}$  equal to 470 and 625 nm for complexes **II** and **III**, respectively.

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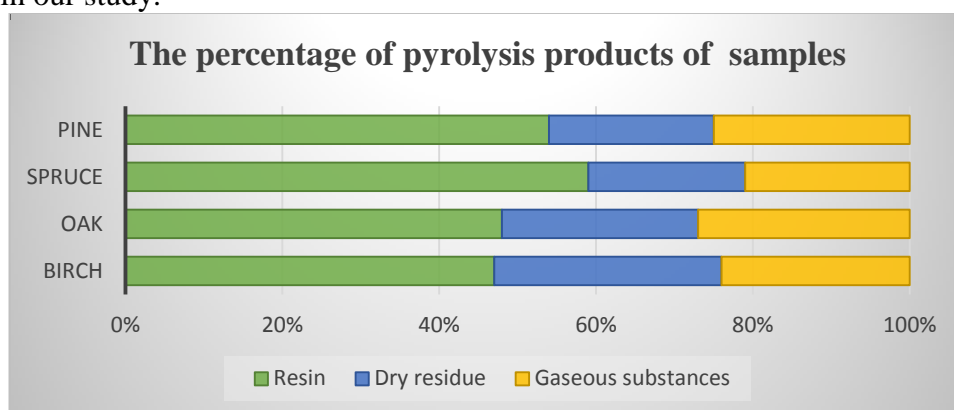
## Study of the pyrolysis process of different types of wood

Cherednichenko A.G., Markova E.B., Plyuschikov V.G., Morozova E.A., Kotareva M.P.

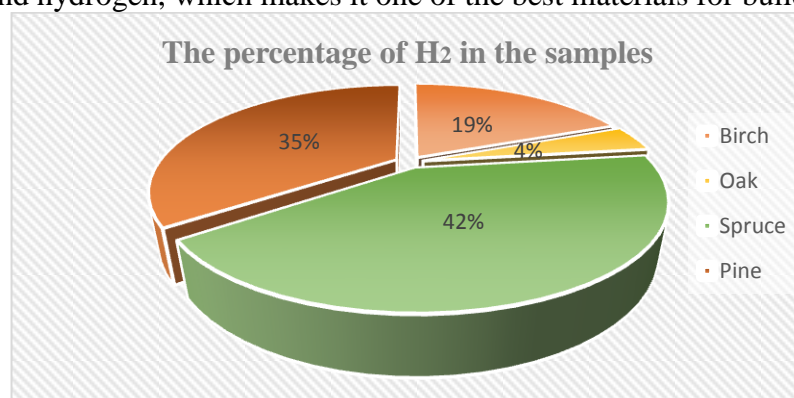
*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
e-mail: ebmarkova@gmail.com*

Wood pyrolysis is one of the ways to recycle it. It occurs at high temperatures without the presence of oxygen. The result of pyrolysis is the appearance of gaseous, liquid and solid fractions, as well as the release of hydrogen energy.

Many scientists in their articles describe this pyrolysis. Pyrolysis characteristics of oak are well described by Hyun Ju Park [1], or Jieun Kim [2]. Samples of spruce, pine, birch and oak were used in our study.



During heat treatment without oxygen access, spruce produces the greatest amount of carbon dioxide and hydrogen, which makes it one of the best materials for building.



The use of nanostructured catalytic systems based on rare earth elements promotes an increase in the gaseous fraction and a shift in the selectivity towards the target products.

*The publication has been prepared with the support of the «RUDN University Program 5-100»*

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## Synthesis of 2,6 -dimethylphenol and its chlorination in the electrochemical system

Muradov M.M., Huseynova İ.H., Murshudlu N.A., Hetemov M.M., Aghaev A.A.

*Sumgait State University, Sumgait, Republic of Azerbaijan  
e-mail: mailoglu@mail.ru*

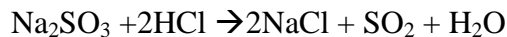
Chlorinated derivatives of 2,6 dimethyl phenol apply for production of bactericidal and disinfectant agents. Currently, it has been referred to a synthesis of these dimethyl homologs of phenol with one or two steps that were produced by coal tars before. On the other hand in contrast with classic chlorination methods selective producing of chlorinated derivatives of 2,6 dimethylphenol with the participation of sulfuryl chloride by electrochemical halogenation may have more importance.

In the report formation of 2,6 dimethylphenol by catalytic alkylation of 2-methylphenol and result of chlorination of 2,6 dimethylphenol with sulfuryl chloride in the electrochemical system are given.

Alkylation reaction of 2-methylphenol with methanol with the formation process of 2,6 dimethylphenol is realized by cobalt ferrite catalyst that modified by manganese and calculated yields of 2,6-xylene according to converted and initial o-cresol is 97.5% and 33.4% at defined reaction condition. Having the simple composition of alkylates that is obtained by process make easy their next processing and caused the high purity of (99.0%) obtained 2.6-dimethylphenol.

Chlorination of 2,6 dimethylphenol in the electrochemical system realizes by two steps. At first step sodium sulfite and 30% hydrochloric acid at 1:2 equimolar ratio that is required amount is added to the electrolysis device.

Sulfur (IV) oxide is obtained by the interaction of sodium sulfite with hydrogen chloride at 40-50°C temperature.



Current is given by constant current source and molecular chlorine ( $\text{Cl}_2$ ) is produced by electrolysis of hydrogen chloride. As a result of the reaction between this chlorine and sulfur (IV) oxide with the presence of activated coal catalyst is provided to obtain sulfuryl chloride. It must notice that formation of the alkaline environment ( $\text{pH} > 7$ ) which makes an opportunity to producing monochloride derivative of 2,6- dimethylphenol is obtained by electrolysis of sodium chloride that is producing by this process.

In the second step, it has been added 2,6- dimethyl phenol and  $\text{CCl}_4$  as a solvent. It has been obtained 2,6- dimethyl -4chlorophenol with ~ 75% and~ 60 % yield according to substance and current properly by chlorination of 2,6 dimethyl phenol with  $\text{SO}_2\text{Cl}_2$

Chlorination mechanism of sulfuryl chloride can be different by depending on condition. Sulfuryl chloride is considered as the source for molecular chlorine because of easy dissociation (like this:  $\text{SO}_2\text{Cl}_2 \leftrightarrow \text{SO}_2 + \text{Cl}_2$ ) without any catalyst. Decomposition is conditioned by reaction condition, nature of chlorinated substance, having the other additives that make easy to giving chlorine.

Though the sulfuryl chloride is one of the reagents that widely used for chlorinated phenol and its derivatives, doing chlorination by suggested method goes light and purposefully, more eased to control it.



**Thermodynamics of isopiestic binary solutions of hydrophilic non-electrolytes**

Nagovitsyna O.A., Ananyeva E.A., Rudakov A.M., Sergievskii V.V.

*National Research Nuclear University MEPhI, Moscow, 115409 Russia*  
*e-mail: OANagovitsyna@mephi.ru*

The non-ideality of many non-electrolytes aqueous solutions is mainly determined by their hydration, which leads to negative deviations from the Raoult's law. The dependences of the thermodynamic properties on concentration in such solutions, as established [1], are due to the formation of unstable hydrates, which have different stoichiometry. In this case, the dependence of water activity ( $a_w$ ) on the composition of the solution is described by the equation

$$a_w = x_w \exp(-h \cdot x^2)$$

where  $x_w$  and  $x$  - molar fractions of water and dissolved hydrophilic non-electrolyte,  $h$  - hydration number at  $a_w = 1$ .

For the isopiestic equilibrium of two binary solutions, in which the solvent activities in the compared solutions of different solutes are equal, taking into account (1) it is obvious that

$$x_1 + h_1^0 \cdot x_1^2 = x_2 + h_2^0 \cdot x_2^2, \quad (2)$$

where  $x_1$ ,  $x_2$  and  $h_1^0$ ,  $h_2^0$  - the mole fractions of nonelectrolytes and their hydration numbers at infinite dilution in the first and second isopiestic solutions, respectively. Simple transformations (2) lead to a relation equivalent to the well-known Zdanovskii equation [2], which underlies the substantiation of the Mikulin equation proposed by Mikulin [3] for describing the thermodynamic properties of mixed electrolyte solutions. The analysis of the restrictions of the Zdanovskii rule is carried out. It is shown that it is valid mainly for systems whose thermodynamic properties are determined by non-stoichiometric hydration of components (formation of clusters).

The results of the description of experimental data on water activity and the activity coefficients of components in binary and multicomponent solutions of hydrophilic non-electrolytes, as well as their mixtures with electrolytes, have been obtained and discussed. The results of the simulation of experimental data for the class of systems under discussion in isopiestic equilibrium indicate the adequacy of the developed model representations.

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## Synthesis and activation of mixed oxide catalysts for light alkane selective oxidation in sub- and supercritical water media

Ponomareva E.A.<sup>1</sup>, Gordienko Yu.A.<sup>1</sup>, Lomonosov V.I.<sup>1</sup>, Sinev M.Yu.<sup>1</sup>, Shashkin D.P.<sup>1</sup>,  
Fattakhova Z.T.<sup>1</sup>, Ivakin Yu.D.<sup>2</sup>

<sup>1</sup>*N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991, Moscow, Kosygin str., 4*

<sup>2</sup>*M.V. Lomonosov Moscow State University, Chemistry Department, 119991, Moscow, Leninskie Gory, 1, build. 3*  
*e-mail: katerinaii@inbox.ru*

The development of new technologies for efficient utilization of natural resources is associated with a search for new active and selective catalysts and methods of their synthesis. In this work the treatment of catalyst precursors and preliminary synthesized mixed oxides in sub- and supercritical water media was applied in order to achieve desired phase compositions of target systems and to improve their catalytic performance in light alkane (methane and its C<sub>2+</sub> homologues – the main components of natural and associated petroleum gases) transformation to light olefins via their reactions with molecular oxygen at high temperatures (>650°C). This group of reactions include oxidative coupling of methane (OCM), oxidative dehydrogenation of C<sub>2+</sub> alkanes (OD) and oxidative cracking of C<sub>3+</sub> alkanes (OC).

As a model system, the NaWMn/SiO<sub>2</sub> was chosen. It is highly selective in OCM and provides high olefin yields in OD and OC reactions. An optimum interaction between the support and active components can be achieved if silica is present in the form of cristobalite phase which usually is formed in the course of thermal treatment of mixed precursor containing amorphous silica and salts of Na, W and Mn. In this case, there is a probability of the inclusion of ions of supported component (Na, Mn) into the support phase, and it is difficult to conclude whether the catalytic action is related solely to the supported component, or can be attributed to the redox properties of Mn ions in silica matrix.

In this work, we have chosen a different synthetic strategy that includes a preliminary synthesis of cristobalite phase by the treatment of amorphous silica in water fluid at temperatures around the critical point of water (374°C). This material can be used as Na, Mn-free support.

It was demonstrated that the treatment of amorphous silica precursors in water fluid at sub- and supercritical temperatures leads to their fast crystallization. The rate of the latter strongly depends on the content of Na in the initial material: even trace amounts of sodium strongly accelerate the formation of multiple phases. However, the process of a single cristobalite phase formation can be optimized if high-purity silica is taken as a starting material and its processing consists of two steps: treatment in sub-critical water fluid and further thermal crystallization of hydrated material at relatively mild conditions.

Further deposition of sodium tungstate and manganese nitrate followed by calcination leads to the formation of the catalyst that possess a comparable activity and selectivity as the one obtained by a standard thermal treatment of the mixed precursor. Thus, the catalytic performance can be attributed to the supported component, and inclusion of them in the support phase does not play any significant role in catalysis.

A new effect of 10-fold increase of activity with no decrease in selectivity of the NaWMn/SiO<sub>2</sub> catalyst in the OCM reaction after its treatment in supercritical water was observed. According to the kinetic analysis, such effect is due to the increase of the number of active sites, but not to the modification of their properties in the course of the treatment.

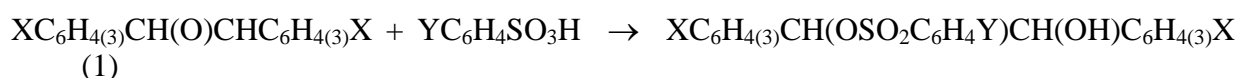
*This work was supported by the Russian Foundation for Basic Research  
(grants №№ 18-29-06055/18 and 18-33-00798)*

## Isoparametricity in reactions of trans-2,3-diaryloxiranes with arenesulfonic acids at different temperatures

Sadovaya I.V., Shpan'ko I.V.

Donetsk National University, Ukraine  
e-mail: sadovaya@bk.ru

The effect structure and temperature on the rate and free activation energy of reactions between X-substituted trans-2,3-diaryloxiranes ( $X = H, 3\text{-Br}, 4\text{-NO}_2, 3\text{-Br-5-NO}_2$ ) and Y-substituted arenesulfonic acids  $YC_6H_4SO_3H$  ( $Y = 4\text{-OCH}_3, 4\text{-CH}_3, H, 4\text{-Cl}, 3\text{-NO}_2$ ) in a mixture of dioxane with 1,2-dichloroethane (7:3) at 265, 281 and 298 K have been studied:



The reaction kinetics was examined using more than tenfold amounts of arenesulfonic acids (HA) with respect to the initial concentrations of trans-2,3-diaryloxiranes (S):  $[HA] \gg [S] = (2 \div 9) \cdot 10^{-3} \text{ mol dm}^{-3}$ . The reaction was found to exhibit the first order with respect to epoxide. At the same, linear relationships between  $k_1$  and  $[HA]^2$  were observed ( $r \geq 0.998$ ), which pass through the origin of coordinates. Thus, the kinetics of the reactions of interest is described by the equation:

$$-d[S]/dt = k_1 [S] = k_3 [S] [HA]^2, \quad (2)$$

where  $k_1$  ( $s^{-1}$ ) and  $k_3$  ( $\text{dm}^6 \text{ mol}^{-2} s^{-1}$ ) are pseudo-first-order and third-order rate constants, respectively.

Cross-correlation analysis of kinetic data was conducted. To estimate the joint effect substituents X, Y and temperature have on the rate of reactions (1), we used a cross-correlation equation for a three-parameter variant of principle of polylinearity:

$$\lg k_3 = \lg k_3^{st} + \rho_X^{st} \sigma_X' + \rho_Y^{st} \sigma_Y + B_T^{st}(1000/T) + q_{XY}^{st} \sigma_X' \sigma_Y + q_{XT}^{st} \sigma_X'(1000/T) + q_{YT}^{st} \sigma_Y(1000/T), \quad (3)$$

where  $k_3^{st}$  is the rate constant under standard conditions ( $\sigma_X' = \sigma_Y = 0, T = \infty \text{ K}$ ),  $\rho_X^{st}$ ,  $\rho_Y^{st}$  and  $B_T^{st}$  are the parameters of standard reactions at  $\sigma_Y = 0$  and  $T = \infty \text{ K}$ ,  $\sigma_X' = 0$  and  $T = \infty \text{ K}$ ,  $\sigma_X' = \sigma_Y = 0$ , respectively,  $q_{XY}^{st}$ ,  $q_{XT}^{st}$ ,  $q_{YT}^{st}$  are the coefficients of the second-order interactions under standard conditions ( $T = \infty \text{ K}$ ,  $\sigma_Y = 0$  and  $\sigma_X' = 0$ , respectively). The following polylinear regression was obtained in processing the kinetic data in accordance with equation (3):

$$\begin{aligned} \lg k_3 = & (5.8 \pm 0.4) + (1.1 \pm 0.1)\sigma_X' + (9.6 \pm 0.9)\sigma_Y + (-2.0 \pm 0.1)1000/T + (-0.32 \pm 0.03)\sigma_X' \sigma_Y + \\ & + (-0.56 \pm 0.04)\sigma_X' 1000/T + (-2.1 \pm 0.3)\sigma_Y 1000/T, \quad (4) \\ S = & 0.078; R = 0.998; F = 3159; n = 43. \end{aligned}$$

Due to non-additive effects of variable factors two-factor cross-reaction series exhibit isoparametric properties. Experimental evidence of the isoparametricity phenomenon was obtained. The critical values of the parameters of variable factors at which the corresponding terms disappear in the multilinear regressions were estimated.

## **CO+CO<sub>2</sub> hydrogenation: a comparison of olefin to paraffin ratios for GdBO<sub>3</sub> (B = Fe, Mn) based catalysts**

Sharaeva A.A.<sup>1</sup>, Sheshko T.F.<sup>1</sup>, O.K. Powell<sup>1</sup>, Bashkirova A.P.<sup>1</sup>, Serov Y.M.<sup>1</sup>, Chislova I.V.<sup>2</sup>, Yafarova L.V.<sup>2</sup>, Zvereva I.A.<sup>2</sup>

<sup>1</sup>*Peoples' Friendship University of Russia (RUDN University), Faculty of Science, Physical and Colloidal Chemistry Department, 6 Miklukho-Maklaya Street, Moscow, 117198, Russian Federation*

<sup>2</sup>*Saint-Petersburg State University, Petrodvorets, Universitetsky pr. 6, Saint-Petersburg, 198805, Russian Federation*  
*e-mail: alminasharaeva@gmail.com*

Fischer-Tropsch synthesis (FTS) is an important process for the hydrocarbons synthesis from CO and H<sub>2</sub>. Moreover, FTS provides us with pure products, being lower in sulfur and in heavy metals, as compared to those ones derived from crude oil. In recent years, perovskite catalysts with ABO<sub>3</sub>-type structure (A and B represent different metallic elements) have been investigated for carbon oxides hydrogenation. It is envisaged that their tailorable compositions and structures could be used to target on specific required products of the FTS reaction. GdBO<sub>3</sub> (B = Fe, Mn) perovskites were studied for the conversion of syngas to light hydrocarbons. The samples were prepared by sol-gel technology and characterized by set of the physical-chemical methods.

The catalytic activity of complex oxides (GdBO<sub>3</sub>, where B = Fe, Mn) was investigated under hydrogenation reaction of CO as well as a mixture of CO + CO<sub>2</sub>. During the experiment a correlation between CO / CO<sub>2</sub> and olefins / paraffins ratios was established. Thus, carrying out the reaction with carbon oxides mixture consist of 2:1 resulted in reduction the amount of olefins twofold compared with paraffins at 598 K. Approaching a stoichiometric value contributes to a significant improvement in all the catalyst characteristics. The saturated and unsaturated hydrocarbons ratio is no exception, it reached maximum. While with an increase in carbon dioxide content in the mixture to CO / CO<sub>2</sub>=0,5, this indicator for products sharply fell.

CO/CO<sub>2</sub> = 1 over GdMnO<sub>3</sub> in order to compare the effects of CO<sub>2</sub> - supplement on Fischer-Tropsch synthesis and to confirm the obtained data. The catalytic characteristics changed in the same way as when conducting the reaction on ferrite under the same conditions and composition of the gas mixture. It is worth noting, that the olefin selectivity was 35% at 708 K upon the process. To sum it all, CO hydrogenation in presence of CO<sub>2</sub> let us achieve an increased conversion of carbon monoxide and also product selectivity over the entire temperature range (523 - 708 K) and shift the ratio towards olefins.

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## The analysis of the cavitand effect on the spectral-luminescent properties of spiropyrans

Shestopyorova E.I.<sup>1</sup>, Lobova N.A.<sup>1,2</sup>, Venidiktova O.V.<sup>2</sup>

<sup>1</sup> *Moscow Institute of Physics and Technology, 141701, Dolgoprudniy, Institutskiy per. 9*

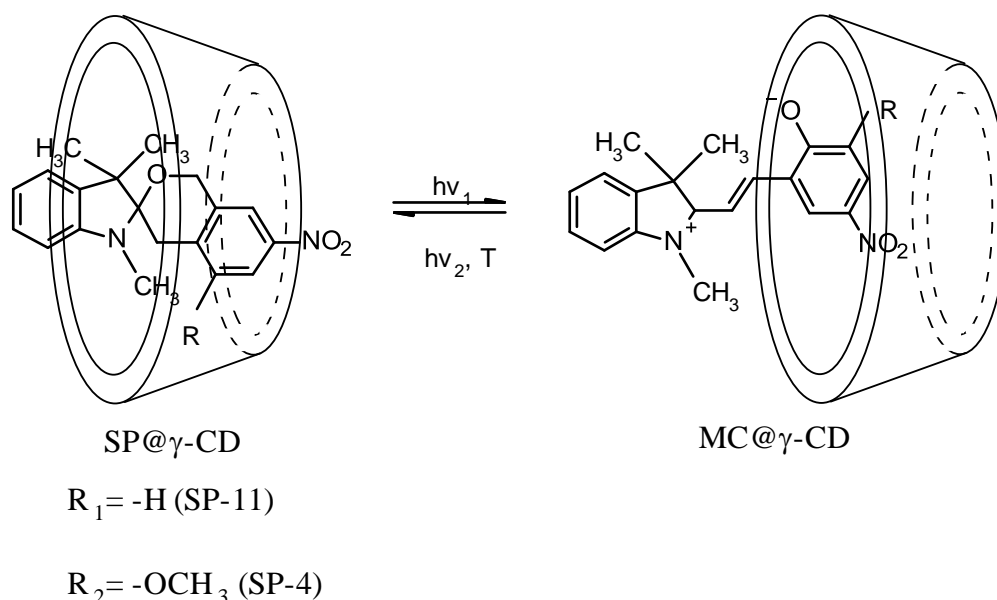
<sup>2</sup> *Photochemistry Center RAS FSRC "Crystallography and Photonics" RAS, 119421,*

*Novatorov str. 7A*

*e-mail: vish.max@yandex.ru*

Photochromic molecules can switch reversibly between two forms by excitation with the appropriate wavelength of light. The most popular class of such molecules are spiropyrans. They can exist in two forms: colorless closed (SP) and colored opened (MC) [1]. If the switching process can be effectively controlled, photochromic compounds could potentially be used as active components for molecular electronics, nanoscale machines or sensors [2].

In this study the effect of solvent nature on the properties of spiropyrans using molecules SP-4 and SP-11 was considered. The absorption and fluorescence spectra were measured in polar proton (ethanol, water), polar aprotic (acetonitrile) and non-polar (toluene, hexane) solvents.



**Fig. 1.** SP-MC possible transformation in the cyclodextrin cavity

There are some examples describing the formation of «host-guest» inclusion complexes between the photochromic dye and the water-soluble cavitand in the literature (Fig.1) [3]. Supramolecular complexes of photochromic dyes with  $\gamma$ -cyclodextrin were obtained to study the behavior of the «guest» molecule in the «host» molecule cavity and the stability of the complexes. It was found that the dye in the complex can withstand several cycles of staining-bleaching.

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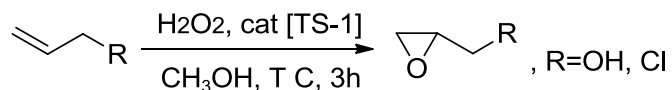
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## Kinetics and mechanism of olefins epoxidation with hydrogen peroxide on titanium silicalite (TS-1)

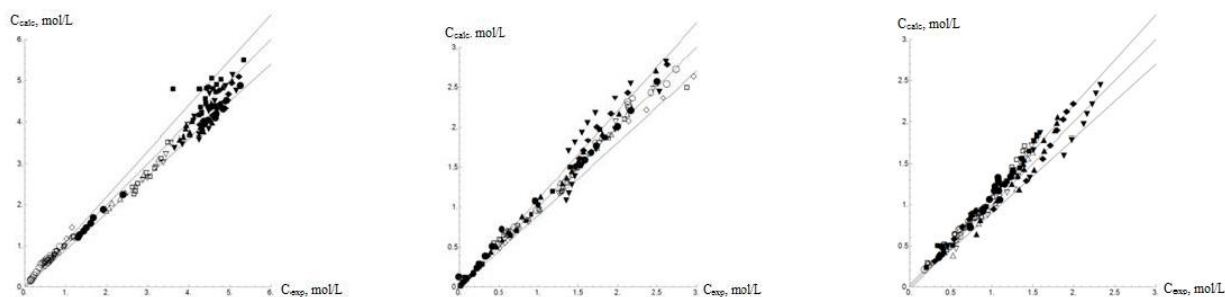
Sukhareva A.A., Levitin V.V., Vilkova I.S., Pastukhova Zh.Yu., Bruk L.G., Flid V.R.

MIREA - Russian Technological University, 119454, Moscow, Vernadsky Avenue, 78  
e-mail: SukharevaAA@yandex.ru

Currently, from the ecological and technological point of view, the most preferable method to obtain olefin oxides is by epoxidation of alkenes with hydrogen peroxide using a titanium-containing zeolite (TS-1) as a catalyst [1].



Although already exist production based on the epoxidation process using hydrogen peroxide, the mechanism and kinetics of this process are studied insufficiently. The aim of the work was to obtain a detailed kinetics and the process mechanism at the example of allyl alcohol and allyl chloride epoxidation to obtain glycidol and epichlorohydrin, respectively.



The mechanism of the allyl alcohol epoxidation process was studied at 40°C, allyl chloride epoxidation process - at 20°C. They were studied using the hypotheses nomination/discrimination procedure. Hypotheses were formulated based on the literature data and preliminary experiment data. Discrimination of hypothetical mechanisms was carried out based on the kinetic experiment results with variation of the reagents and the products concentrations (Fig.1). For each hypothesis the differential equations system was formulated and the rate constants was estimated.

**Fig. 1.** Consistency of the calculated and the experimental concentrations of allyl alcohol, hydrogen peroxide and glycidol for all experiments

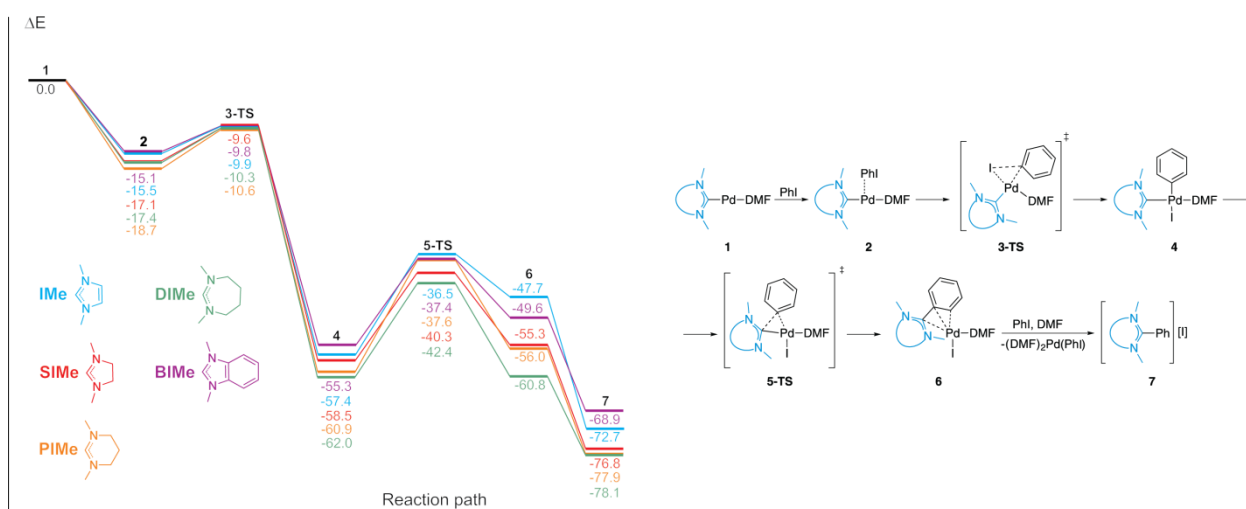
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*Zelinsky Institute of Organic Chemistry RAS, 119991, Leninsky pr. 47, Moscow, Russia*  
*e-mail: sushchenko@ioc.ac.ru*

In this work, 5-, 6- and 7-membered NHC rings with different substituents (2,4,6-trimethylphenyl or 2,6-diisopropylphenyl) were used for studying the dependence of NHC-Ph coupling on the NHC nature. The reaction was investigated by ESI-MS and quantum chemical calculations (Figure 1).



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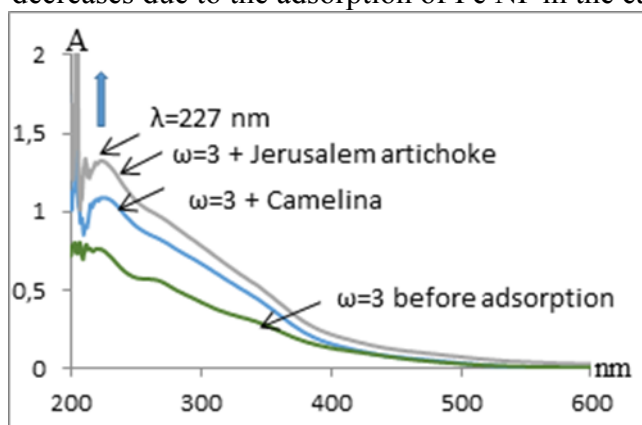
## The influence of iron nanoparticles doping into bio-based carbon sorbents on their behavior in propane dehydrogenation reaction

Terekhova I.A.<sup>1</sup>, Revina A.A.<sup>2</sup>, Markova E.B.<sup>1,2</sup>, Suvorova O.V.<sup>2</sup>.

*Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6  
Russian academy of sciences A.N. Frumkin Institute of Physical chemistry and Electrochemistry  
RAS, 119071, Moscow, Leninsky prospect str. 31  
e-mail: ebmarkova@gmail.com*

The work describes the synthesis of highly active biocarbon-based catalysts and their modification with Fe nanoparticles [1] for propane cracking reaction. A high catalytic activity of modified catalytic systems has been found; conversion reaches a maximum at 900 K.

With UV-Vis spectroscopy the changes in optical density spectrum of Fe nanoparticles solution ( $\omega=3,0$ ) were registered after 3-days contact with bio-based activated carbon. The present spectrum shows the increased intensity after contact with the surface of bio-based activated carbon. After 5÷6 days the optical density reaches saturation of the Fe NP solution, and then the optical density decreases due to the adsorption of Fe NP in the carbon pores.



The catalytic activity was studied by thermal cracking of propane. With natural carbons the formation of products starts from 773K, the conversion reaches 20% at 923K. With modified carbons the conversion increases to 35% at the same temperature point. The selectivity reaches 95% at maximum conversion. The stability of both biocarbon-based catalysts and modified with Fe NP biocarbon-based catalysts is rather high. In the temperature range up to 873K the operating time without activity changes was 400 h., and in the range 873-1023K was 150h.

*The publication has been prepared with the support of the  
«RUDN University Program 5-100»*

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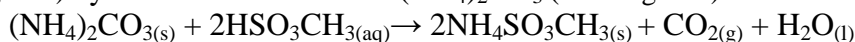
## Synthesis, phase behavior and thermodynamic properties of ammonium methanesulfonate

Tiflova L.A., Druzhinina A.I., Kosova D.A., Monayenkova A.S.

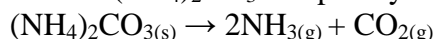
Moscow State University, Department of Chemistry, 119991, Moscow, Leninsky Gory 1  
e-mail: tiphlova@phys.chem.msu.ru

Investigation of the properties of methanesulfonic acid's salts is of interest from the fundamental point of view. Information on the properties of these salts is given partially in the literature, in spite of a widely application of methanesulfonic acid and its inorganic derivatives in various industries. In particular, it is important to research thermodynamic properties of ammonium methanesulfonate in the point of view the potential application of  $\text{NH}_4\text{SO}_3\text{CH}_3$  as an ionic liquid or additive in various technological liquids to lower their crystallization temperatures.

Ammonium methanesulfonate was synthesized by the neutralization of methanesulfonic acid ( $\geq 98$  weight %) by ammonium carbonate ( $\text{NH}_4)_2\text{CO}_3$  (99 weight %):



An excess of ammonium carbonate was gradually mixed with methanesulfonic acid in a ratio 2:1 ( $\text{NH}_4)_2\text{CO}_3:\text{HSO}_3\text{CH}_3$  with a constant stirring. The reaction was conducted in a water solution. The reaction vessel was placed in an ice bath to avoid overheating and boiling of the liquid. After mixing the excess of ammonium carbonate was removed from reaction medium by moderate heating at 333 – 338 K. During the heating ammonium carbonate decomposes to form ammonia and carbon dioxide, therefore  $(\text{NH}_4)_2\text{CO}_3$  completely leaves the reaction medium:



The completeness of the reaction was monitored using indicator paper. The excess solvent was evaporated, the crystals were recrystallized twice from water and dried first in air and then under vacuum ( $\sim 10^{-4}$  Pa). The moisture content in the sample was controlled by an ionization vacuum gauge and thermogravimetry. Obtained crystals of ammonium methanesulfonate was characterized by elemental analysis, X-ray diffraction method and TG-DSK.

Compound  $\text{NH}_4\text{SO}_3\text{CH}_3$  undergoes two endothermic processes in the temperature range 463-473 K which are not associated with the thermal decomposition of the substance (decomposition temperature is 520 K). The first peak on DSC curve is associated with the  $\text{NH}_4\text{SO}_3\text{CH}_3$  structural phase transition, and the second peak is associated with the melting of compound.

The thermodynamic properties of  $\text{NH}_4\text{SO}_3\text{CH}_3$  were investigated by methods of solution and adiabatic calorimetry. The enthalpy of solution of  $\text{NH}_4\text{SO}_3\text{CH}_3$  were measured in water at 298.15 K in hermetically sealed swinging calorimeter with an isothermal coat. The enthalpy of formation of  $\text{NH}_4\text{SO}_3\text{CH}_3$  at 298.15 K was calculated on the basis of the experimental data and  $\text{NH}_4^+(\text{aq})$  and  $\text{SO}_3\text{CH}_3^-(\text{aq})$  enthalpies of formation. The molar low-temperature heat capacity of the  $\text{NH}_4\text{SO}_3\text{CH}_3$  was measured with the help of an automated vacuum adiabatic calorimeter in the temperature range from 8 to 330 K. On the curve of temperature dependence of heat capacity of the  $\text{NH}_4\text{SO}_3\text{CH}_3$  thermal anomaly at  $T = 272.6$  K was observed. Smoothed values of heat capacity and entropy of  $\text{NH}_4\text{SO}_3\text{CH}_3$  were calculated from these data for the crystal state in the temperature interval studied. On the basis of experimental data, the standard entropy, enthalpy and Gibbs energy formation of  $\text{NH}_4\text{SO}_3\text{CH}_3$  at 298.15 K were calculated.

**Table.** Thermodynamic functions of  $\text{NH}_4\text{SO}_3\text{CH}_3$  (cr) at  $T = 298.15$  K

$C_p^0/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S_m^0/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f H_m^0(\text{cr})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f S_m^0(\text{cr})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f G_m^0(\text{cr})/\text{kJ}\cdot\text{mol}^{-1}$
156.11±0.5	174.3±1	-834.0±4	-724.4±1	-618.0±4

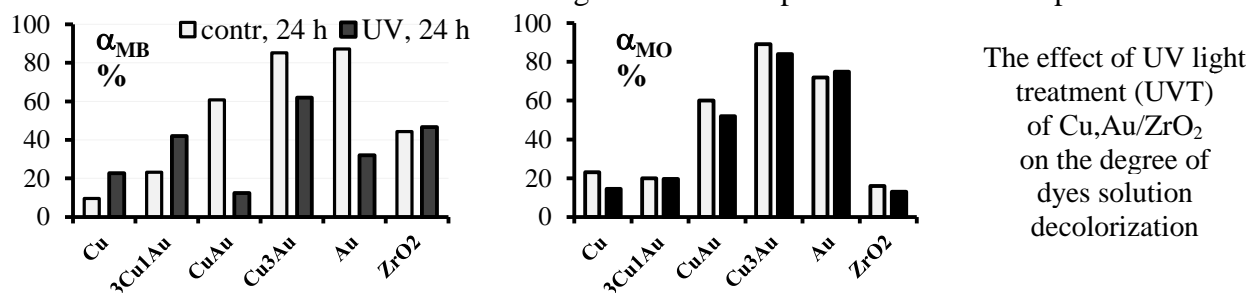
## Dyes and 4-nitrophenol adsorption on UV light activated CuAu/ZrO<sub>2</sub>

Cisse V. (Cote d'Ivoire), Mikhaleiko I.I.

Peoples Friendship University of Russia (RUDN-University) Moscow, Russia  
e-mail: mikhaleiko\_ii@pfur.ru

Organic pollutants cause several environmental problems to our environment. Adsorption technique is efficient method for the removal of toxic compounds. Activated carbon is well known as adsorbent for water and waste water treatment [1]. Oxides as adsorbents (aluminosilica commonly) may be used for the removal of dyes and pesticides from polluted water. Photoactive TiO<sub>2</sub> for adsorption application has been studied in our laboratory earlier [2] but activity of UV light exposed ZrO<sub>2</sub> studied not enough. Note, that hybrid titania-zirconia nanoparticles coated adsorbent is active for highly selective capture of nucleosides from human urine in physiological condition [3]. In present work the powders of zirconia supported copper and gold were studied for decolorization water solutions of methylene blue (MB), methylorange (MO) and 4-nitrophenol (4NP). The influence of UV light treatment of adsorbents in case of mono- and bicomponent surface additives in compare with "pure" support (commercial crystalline ZrO<sub>2</sub> m+t) has been studied by means of spectrophotometer (PE 5300B4, Ecros and Ecoview-1200, RF).

Adsorbents Cu,Au/ZrO<sub>2</sub> were prepared by impregnation method using chlorides salts as precursors, low temperature drying and calcination procedures. The sample ZrO<sub>2</sub> was treated the same mode in water. Figure "a" shows the activity for dyes decolorization in presence ZrO<sub>2</sub> with Au and binary surface additive in atomic ratio 1Cu-3Au were better than control sample ZrO<sub>2</sub>. The irradiation time was 10 min under UV light with broad spectra. Time of adsorption -24 h.



The result of doping effect and UV treatment on adsorption after 24 h contact time at room temperature is shown in diagrams. The degree of decolorization  $\alpha_{MB}$  % increases in row of control samples Cu < 3Cu1Au < CuAu ~ Au. The optimum activity for initial samples was obtained for gold enriched samples with  $\alpha_{MB}$  ~ 80-83% in compare with  $\alpha_{ZrO_2}$  ~50%. For MO and 4NP we obtained the similar results, but adsorption processes was complicated by supported Au<sup>+3</sup> reducing with Au nanoparticles formation. Plasmon spectra were revealed for liquid faze. Based on these facts, we conclude that (a) no effect of UV light treatment was found for ZrO<sub>2</sub>, (b) more active in adsorption Au enriched samples, (c) AuNPs formation is observed only in MO and 4NP solutions. Solid faze can adsorb AuNPs when contact time more than 24 h. Only for Cu enriched samples and MB or 4NP the enhancement of adsorptive ability after UVT was found. Values of Gibb's adsorption were calculated and compared for all adsorbents and substances.

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## Group hydrocarbon composition of petroleum of surakhani field in Azerbaijan

Yolchueva U.J., Abbasov V.M., Jafarova R.A., Aliyev B.M., Ibragimova R.A., Alieva A.Ə.

*Y.H.Mamedaliyev's Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan, Baku, AZ-1025, Khojaly Ave., 30,  
e-mail: ulviyya.yolcujeva@mail.ru*

The study of the physicochemical and structural group composition of oils is important from the point of view of the environmental problems of the Caspian region.

This paper presents the results of a quantitative analysis of the structural parameters of Surakhani native oil from well 1311 using UV and NMR spectroscopy. Petroleum from well No. 1311 has a depth of 685 meters and is the least studied among other operating wells of the Surakhani field. A distinctive feature of this oil is the predominance of branched alkanes over normal and low content of aromatic hydrocarbons in its composition (oil type A2).

UV spectroscopic study showed (JENWAY UV / VIS 6850 spectrophotometer) that aromatic hydrocarbons in molecules are mainly represented by benzene, naphthalene and phenanthrene structures, the total amount of which does not exceed 4%. Below are some physico-chemical characteristics of the oil studied.

Density at 200 °C, kg/m <sup>3</sup>	842
Pour point, °C	-40
Kinematic viscosity at 400 °C, mm <sup>2</sup> /s .....	6.33.
Sulfur content,% .....	0.78
Acid number, mgKOH/g .....	2.55
Flash point in a closed crucible, °C .....	-5...

Fractional composition (according to GOST 2177-99),% (vol.):

up to 180°C .....	15
up to 200°C .....	20
up to 300°C .....	48

Fragment composition of oil was also studied by NMR spectroscopy on <sup>1</sup>H nuclei. The spectra were recorded on a pulsed Fourier spectrometer of the Bruker company (Germany) at an operating frequency of 300, 18 MHz, in solutions of deuterated benzene at room temperature. Signal chemical shifts (in ppm) are relative to tetramethylsilane. Calculation of the relative content of protons in various structural fragments was carried out on the basis of peak areas in the corresponding spectral regions: for Har.- (6.6-8.0 ppm), H<sub>α</sub> - (2.0-3.0 ppm), H<sub>β</sub> - (1.1-2.0 ppm), H<sub>γ</sub> - (0.5-1.1 ppm).

It was found that in the studied oil the main amount of hydrogen (more than 90%) is concentrated in saturated structures (table): 11.5% in naphthenic, 49.1% in paraffin and 34.6% in terminal methyl groups H<sub>δ</sub>. In addition, the relative hydrogen content in aromatic structures is low (1.4%), which is consistent with its low degree of aromaticity (*f*<sub>a</sub> = 0.04). A large proportion of hydrogen atoms in the final methyl groups (about 35% of the total number of hydrogen atoms) indicates a high degree of branching of the paraffin chains (J) in the presence of several methyl groups on naphthenic rings.

Thus, the analysis of the experimental data shows that the composition of the studied oil is dominated by saturated (naphthenic-paraffin) hydrocarbons, which from an environmental point of view are the most favorable components for the environment of the Caspian region.

# Synthesis and research of dispersion based on poly-3-hydroxybutyrate with including of particles of hydroxyapatite

Fomichev V.A.<sup>1</sup>, Teleshev A.T.<sup>1</sup>, Gorshenev V.N.<sup>2</sup>, Lobanov A.V.<sup>1</sup>

*1 Moscow State Pedagogical University, 129164, Moscow, Kibalchicha str. 6*

*2 N.M. Emanuel Institute of Biochemical Physics RAS, 119334, Moscow, Kosygina str. 4*

*e-mail: fomichev.mpsu@gmail.com*

The problem of developing of composite materials for restoring the structure and properties of bone tissue is of great practical and scientific interest. Hydroxyapatite (HAP) is the main mineral component of bone tissue. Composition  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  and bacterial polyether poly-3-hydroxybutyrate (PHB)  $[\text{C}_4\text{H}_6\text{O}_2]_n$  with high pharmacological potential were selected for research [1].

The synthesis of the PHB-HAP composition under mechanoacoustic processing of the PHB suspension containing phosphate and calcium hydroxide [2] using an industrially significant rotary pulsation apparatus (RPA) [3] was carried out. Synthesis: at the included cooling turned on, 10 liters of distilled water were placed in the RPA loading tank, the engine speed of the apparatus was set ( $3000 \text{ min}^{-1}$ ), the temperature was set to not more than  $65^\circ\text{C}$  and the PHB powder was loaded in an amount of 200.0 g, calcium hydrogen phosphate 46.0 g and calcium hydroxide 11.0 g. The reaction mixture was processed in the operating mode of the apparatus for 2 minutes.

The dispersion of PHB-HAP after sedimentation has the following layers: «foam layer», «layer under foam», «layer above sediment» (not more than 5 cm) and «sediment layer». The layers were separated, diluted 10 times with distilled water and studied using dynamic light scattering. Dispersion of PHB-HAP is characterized by the following particle sizes of the dispersed phase in layers:  $5.2 \mu\text{m}$ ,  $0.075 \mu\text{m}$ ,  $0.5 \mu\text{m}$ ,  $4.5 \mu\text{m}$  as was established. Sample layers were dehydrated at  $110^\circ\text{C}$  and studied using IR spectroscopy. The formation of HAP is indicated by changes in the spectrum of PHB in the region of  $1025 \text{ cm}^{-1}$ , which is characteristic of the strong absorption of pure HAP [2]. The formation of the PHB-HAP composition occurs mainly in sediment and foam. The intermediate layer «under the foam» concentrates pure HAP, «above sediment» - mainly HAP with a small influence of PHB.

The prospect of using the PHB-HAP composition is associated with the introduction into its composition of medicines in order to create highly effective biomaterials suitable for replacing bone defects.

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