MINISTRY OF EDUCATION AND SCIENCE OF RUSSIAN FEDERATION
RUDN UNIVERSITY

The conference is dedicated to the memory of
Prof. N.S. Prostakov
on the 100th anniversary of his birth

ADVANCES IN SYNTHESIS AND COMPLEXING

Book of abstracts
The Fourth International Scientific Conference

In Two Parts

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

24–28 April 2017
Moscow, RUDN University

Moscow
Peoples' Friendship University of Russia
2017

УДК 54(063)
ББК 24
У78

The event was financially supported by the Ministry of Education and Science of the Russian Federation
(the Agreement № 02.A03.21.0008)
and the Russian Foundation for Basic Research (grant 17-03-20137)

У78 **Успехи синтеза и комплексообразования = Advances in synthesis and complexing** : сборник тезисов четвертой международной научной конференции : в 2 ч. Москва, РУДН, 24–28 апреля 2017 г. – Москва : РУДН, 2017.
ISBN 978-5-209-07930-9
Ч. 2 : Секции «Неорганическая и координационная химия», «Физическая и коллоидная химия». – 127 с. : ил.
ISBN 978-5-209-07932-3 (ч. 2)

The book of abstracts of the Fourth International Scientific Conference: «Advances in Synthesis and Complexing» which was held from 24 to 28 April 2017 based on chemical departments of Faculty of Science of RUDN University includes abstracts of lectures of plenary and key-note speakers, oral reports and poster session.
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.

ISBN 978-5-209-07932-3 (ч. 2)
ISBN 978-5-209-07930-9

Dear Colleagues,

It is our pleasure to extend a very warm welcome to the honorable scientists and young researchers participating in the 4-th International conference "Advances in Synthesis and Complexing" (RUDN University, Moscow, Russia).

This series of conferences has attracted many leading scientists.

The 4-th International conference "Advances in Synthesis and Complexing" is dedicated to the memory of **Prof. N.S. Prostakov** and 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.

We hope that you will find your participation in the 4-th International conference "Advances in Synthesis and Complexing" intellectually stimulating and socially enjoyable.

Chair of the organizing committee

Prof. Dr. Leonid G. Voskressensky

Plenary
and
Key-note Speakers

AeroNanoToxicology project

Matveeva M.D., Voskressensky L.G., Sablin V.V., Slavyansky V.M.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
Vyatka State University, 610000, Kirov, Kirovskaya oblast', Moskovskaya ul., 36
e-mail: nauka@alphananotech.com

In the 21st century - nanotechnology is seen as one of the key technologies. The previous industrial revolution has taught us that rapid technological change impacts on society in a variety of ways. Nanotechnology offers on the one hand various new properties and opportunities and on the other hand - brings new risks and uncertainties.

Sources of nanoparticles can be classified as natural or intentional and unintentional anthropogenic activities. Major natural processes that release nanoparticles in the atmosphere are forest fires, volcanic activities, weathering, formation from clay minerals, soil erosion by wind and water, or dust storms from desert. Man-made nanoparticles are released in the environment during various industrial and mechanical processes. The unfiltered exhaust gases from diesel engines contain large quantities of potentially harmful nanoparticles from the incomplete combustion of fuel. In the fireplace at home, fullerenes like buckyballs or buckytubes are formed when wood is burned. In industrial processes, coal, oil, and gas boilers release tons of nanoparticles unintentionally.

"AeroNanoToxicology" is a project which is intended to develop and introduce new cost-effective physical principles in large-scale production of the control devices and the use of nanoecology in the residential, office, laboratory and production facilities. The cooperation of the Peoples' Friendship University of Russia and the Vyatka State University has led to the elaborating of a new approach for determining the level of potential danger of nanoobjects using "Atmospheric modeling complex".

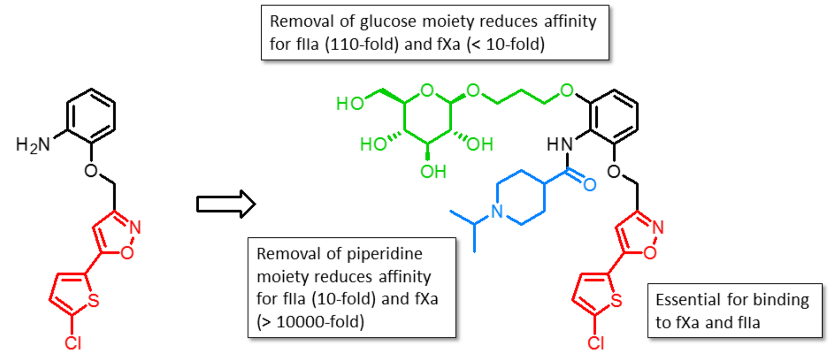
Fragment-based approach to the optimization of glycosidic inhibitors of blood coagulation proteases: deconstruction, superadditivity, and selectivity

Altomare C.D.,[1] de Candia M.,[1] Zaetta G.,[1] Cellamare S.,[1] Belviso B.D.,[2] Caliandro R.[2]

[1]Department of Pharmacy-Drug Sciences, University of Bari Aldo Moro, Via E. Orabona 4, 70125 Bari, Italy; [2]Institute of Crystallography, Consiglio Nazionale delle Ricerche, Via Amendola 122/o, 70126, Bari, Italy
e-mail: cosimodamiano.altomare@uniba.it

The principle of thermodynamic additivity does not fully apply in complex noncovalent systems, in which the energetics of individual components are not truly independent of each other. Molecular recognition in protein-ligand complexes predominantly occurs through multiple noncovalent interactions, and often Δ*G* of linked fragments is significantly greater than the sum of Δ*G* increments from each fragment ('superadditivity' or synergy).

Here we explore Δ*G* additivity in a fragment-based study of inhibitors of factor Xa (fXa) and thrombin (fIIa), two well-characterized anticoagulant targets. Recently, we reported the β-D-glucose-containing compound **2** as highly potent inhibitor of fXa (K_i = 0.090 nM) and fIIa (K_i = 100 nM), with good anticoagulant and profibrinolytic activities [1,2]. As seen previously for fXa, the chlorothiophene moiety (red) is essential for binding. Removing the glucose moiety (green) reduced affinity for fXa by less than ten-fold and for fIIa by more than two orders of magnitude, whereas removing the piperidine moiety (blue) reduced affinity to fXa by several orders of magnitude. Experimental deconstruction of **2** into smaller fragments revealed a binding cooperativity of the piperidine and propylene-linked β-D-glucose fragments, stronger in fIIa (15.5 kJ·mol^{-1}) than in fXa (2.8 kJ·mol^{-1}).



Removal of glucose moiety reduces affinity for fIIa (110-fold) and fXa (< 10-fold)

Removal of piperidine moiety reduces affinity for fIIa (10-fold) and fXa (> 10000-fold)

Essential for binding to fXa and fIIa

1

fXa: K_i = 11600 nM
fIIa: K_i = 31000 nM

2

fXa: K_i = 0.09 nM
fIIa: K_i = 100 nM

The crystal structure of **2** bound to fIIa revealed several hydrogen bond interactions between the glucose moiety and basic residues (R221a and K224) implicated in allosteric activation of the protease. In order to extend the exploration of the SARs, the glucose moiety and the piperidine group were modified. A fragment screening through surface plasmon resonance (SPR) and docking calculations provided information useful for designing and optimizing new inhibitors of blood coagulation proteases.

References

[1]. Lopopolo, G.; de Candia, M.; Panza, L.; Romano, M.R.; Lograno, M.D.; Campagna, F.: Altomare, C. *ChemMedChem* **2012**, *7*, 1669.

[2]. Belviso, B.D.; Caliandro, R.; de Candia, M.; Zaetta, G.; Lopopolo, G.; Incampo, F.; Colucci, M.; Altomare, C. *J. Med. Chem.* **2014**, *57*, 8563.

Dynamic phenomena in catalytic transformations: influence on efficiency and selectivity

Ananikov V. P.

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospekt 47, Moscow, 119991, Russia; http://AnanikovLab.ru;
e-mail: val@ioc.ac.ru

Catalysis is a tremendously developing area of modern chemistry with fascinating recent achievements and conceptual progress (Figure 1) [1].

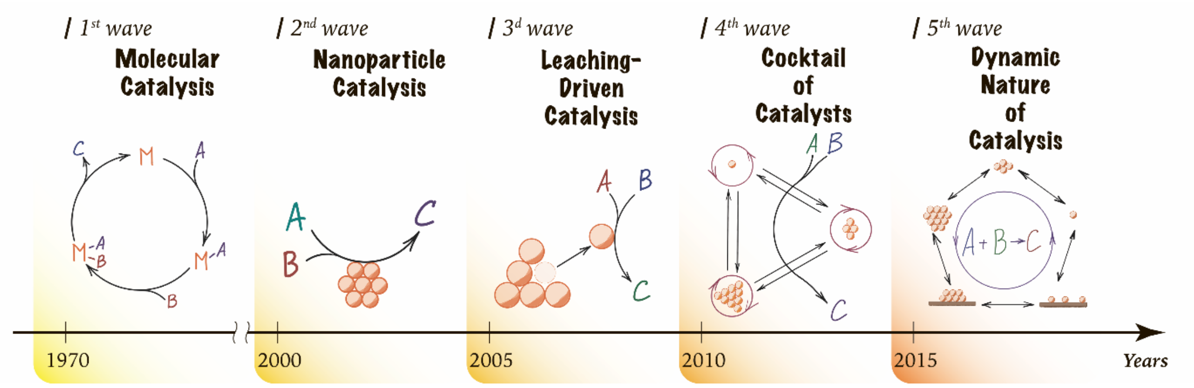


Figure 1. Different "waves" in the development of catalytic reactions [1].

Dynamic behavior of catalytic systems (Figure 2), influence on activity and selectivity, ecological profiles and application in sustainable development will be presented and discussed based on our recent findings [1-4].

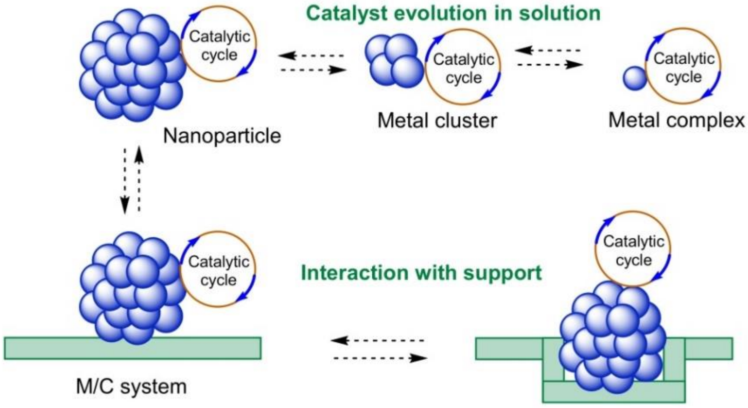


Figure 2. Catalyst dynamics in solution and on the surface of supported systems.

References

[1]. Eremin D.B., Ananikov V. P., *Coord. Chem. Rev.*, **2017**, doi: 10.1016/j.ccr.2016.12.021.

[2]. Egorova K.S., Ananikov V. P., *Angew. Chem. Int. Ed.*, **2016**, 55, 12150, doi: 10.1002/anie.201603777.

[3]. Galkin K.I., Krivodaeva E.A., Romashov L.V., Zalesskiy S.S., Kachala V.V., Burykina J.V., Ananikov V. P., *Angew. Chem. Int. Ed.*, **2016**, 55, 8338, doi: 10.1002/anie.201602883.

[4]. Kashin A.S., Galkin K.I., Khokhlova E.A., Ananikov V. P., *Angew. Chem. Int. Ed.*, **2016**, 55, 2161, doi: 10.1002/anie.201510090.

Advances in heterocycle synthesis

Antonchick A.P.

Max-Planck-Institut für Molekulare Physiologie, Otto-Hahn-Strasse 11, 44227 Dortmund, Germany
Technische Universität Dortmund, Otto-Hahn-Strasse 4a, 44227 Dortmund, Germany
e-mail: andrey.antonchick@mpi-dortmund.mpg.de

Heterocyclic compounds constitute the majority of organic compounds. Nitrogen-containing heterocycles are present in many natural compounds, biological probes, chemicals and materials. However, the chemical space which can be occupied by relatively simple bicyclic heteroaromatic compounds has not been fully explored and hundreds of novel molecules still remain to be synthesized. A considerable amount of novel ring systems successfully enter drug space annually. Therefore, the development of novel efficient methods of heterocycle synthesis is highly desired and represents a field of intense investigations.

This lecture is dedicated to recent developments in synthesis and functionalization of heterocycles.[1-9]

References

[1]. Manna S., Antonchick A. P., *Angew. Chem., Int. Ed.* **2014**, *53*, 7324.
[2]. Manna S., Matcha K., Antonchick A. P., *Angew. Chem., Int. Ed.* **2014**, *53*, 8163.
[3]. Matcha K., Antonchick A. P., *Angew. Chem., Int. Ed.* **2014**, *53*, 11960.
[4]. Manna S., Narayan R., Golz C., Strohmann C., Antonchick A. P. *Chem. Commun.*, **2015**, *51*, 6119.
[5]. Manna S., Antonchick A. P. *Angew. Chem., Int. Ed.* **2015**, *54*, 14845.
[6]. Bering L., Antonchick A. P. *Org. Lett.*, **2015**, *17*, 3134.
[7]. Manna S., Antonchick A. P. *Org. Lett.*, **2015**, *17*, 4300.
[8]. Manna S., Serebrennikova P.O., Utepova I.A., Antonchick A.P., Chupakhin O.N. *Org. Lett.*, **2015**, *17*, 4588.
[9]. Caporaso R., Manna S., Zinken S., Kochnev A.R.,Lukyanenko E.R., Kurkin A.V., Antonchick A. P. *Chem. Commun.*, **2016**, *52*, 12486.

Natural products: an opportunity for discovery

Jef K. De Brabander

Department of Biochemistry and Harold C. Simmons Comprehensive Cancer Center, The University of Texas Southwestern Medical Center at Dallas, Dallas, TX 75390-9038, USA.
e-mail: jef.debrabander@utsouthwestern.edu

Our laboratory focuses on the synthesis of complex molecular architectures, including both designed and naturally occurring substances with novel structural features and interesting biological function. To facilitate the execution of efficient and practical syntheses, we also develop novel methodology relevant to medicinal chemistry and complex natural products synthesis. We take advantage of the collaborative, multi-disciplinary research environment at UTSW, and have significantly fortified our chemistry program with molecular pharmacology, biochemistry, and discovery biology.

I will present our rationale for the development of novel methodology relevant to the synthesis of natural products, medicinal chemistry, and ligand design. We developed gold and platinum catalyzed reactions that enable the synthesis of novel oxazole-based dipeptide mimetics, spiroketals, morpholines, dioxanes, and other heterocycles. I will provide examples related to the synthesis of various complex polyketide natural products. Our practical synthetic solutions to natural products have enabled us to access analog collections for meaningful structure-function and mode-of-action studies to investigate their biological effects in vitro and in vivo, and for optimization of potency and pharmacological properties.

Development of novel C–H functionalization methodologies

Vladimir N. Gevorgyan

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 convertable 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.

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

Mechanochemistry : a powerful sustainable approach in organic and organometallic synthesis

Lamaty F.

Institut des Biomolécules Max Mousseron, UMR 5247 CNRS-Université de Montpellier-ENSCM,
Green Chemistry and Enabling Technologies Team, Place Eugène Bataillon, 34095 Montpellier
Cedex 5, France
e-mail: frederic.lamaty@umontpellier.fr

A major concern for the development of a sustainable chemical synthesis is the use of organic solvents. These solvents are very often toxic and volatile, the halogenated ones creating major damages to the environment. One of the solutions so far has been to treat and recycle the solvents or to use them as fuel after employing them in a chemical process. A major research effort is now being made to find alternatives to the use of these organic solvents. The challenging approach that we have chosen is to develop organic reactions in the absence of solvent by mechanochemistry.

Mechanochemical activation can be a useful tool for solvent-free organic synthesis. Designed at the beginning for crushing inorganic matter, apparatus such as ball-mills proved their efficacy in some organic chemistry reactions and can be applied on an industrial scale. We have shown that this kind of activation is applicable to the synthesis of important organic molecules, including amino acid derivatives and peptides [1]. In the last years, we have developed this methodology and applied it to peptides such as aspartame or enkephalin or heterocycles such as hydantoins [2]. More recently, in connection with other projects dedicated to green chemistry in our group, we have investigated mechanochemistry in palladium-catalyzed reactions and in the preparation of organometallic complexes [3]. We have shown that mechanochemistry is a sustainable synthetic method avoiding the use of solvents but also a very powerful approach to prepare unprecedented structures.

This work was supported by the CNRS and the University of Montpellier.

References

[1]. a. T.-X. Métro, E. Colacino, J. Martinez, F. Lamaty « Amino acids and Peptides in Ball-milling» in Ball Milling Towards Green Synthesis: Applications, Projects, Challenges RSC Green Chemistry Series 2015 p. 114-150. b. Declerck, V. ; Nun, P.; Martinez, J.; Lamaty, F. *Angew. Chem. Int. Ed.* **2009**, *48*, 9318-9321. c. Bonnamour, J.; Métro, T.-X.; Martinez, J.; Lamaty, F. *Green Chem.* **2013**, *15*, 1116-1120. d. Métro, T.-X.; Bonnamour, J.; Reidon, T.; Duprez, A.; Sarpoulet, J.; Martinez, J.; Lamaty, F. *Chem. Eur. J.* **2015**, *21,* 12787-12796. e. V. Porte, M. Thioloy, T. Pigoux, T.-X. Métro, J. Martinez, F. Lamaty *Eur. J. Org. Chem.* **2016,** 3505-3508

[2]. a. L. Konnert, B. Reneaud, R. Marcia de Figuereido, J.-M. Campagne, F. Lamaty, J. Martinez, E. Colacino, *J. Org. Chem.* **2014,** *79,* 10132-10142. b. Konnert, L.; Gonnet, L.; Halasz, I.; Suppo, J.-S.; Marcia de Figuereido, R.; Campagne, J.-M.; Lamaty, F.; Martinez, J.; Colacino, E. *J. Org. Chem.* **2016,** *81*, 9802-9809.

[3]. a. V. Declerck, E. Colacino, X. Bantreil, J. Martinez, F. Lamaty, *Chem. Commun.* **2012**, *48*, 11778–11780. b. Beillard, A.; Golliard, E.; Gillet, V.; Bantreil, X.; Métro, T.-X.; Martinez, J.; Lamaty, F. *Chem. Eur. J.* **2015**, *21,* 17614-17617 c. Beillard, A.; Bantreil, X.; Métro, T.-X.; Martinez, J.; Lamaty, F. *Dalton Trans.* **2016, 45,** 17859-17866. d. Beillard, A.; Bantreil, X.; Métro, T.-X.; Martinez, J.; Lamaty, F. *Chem. Sci.* **2017**, in print DOI : 10.1039/C6SC03182J.

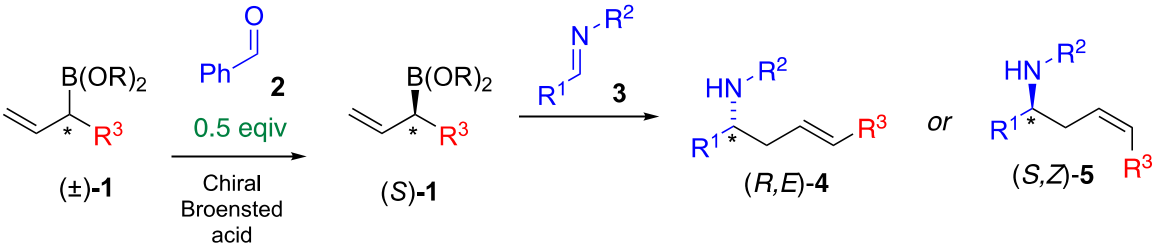
Catalytic stereoselective formation of C-C and C-N bonds in target-oriented synthesis.

Laura Villar,[b] Orlov N.,[a] Kondratyev N.,[a] José L. Vicario,[b] Malkov A.V. *,[a,c]

[a]*Department of Chemistry, Loughborough University, Loughborough, Leics, LE11 3TU, UK*
[b]*Department of Organic Chemistry II, Faculty of Science of Technology, University of the Basque Country (UPV/EHU), P.O. Box 644, 48080 Bilbao, Spain.*
[c]*Department of Organic Chemistry, RUDN, Moscow 117198, Russia*

Chiral amines are powerful pharmacophore groups due to their favourable physico-chemical properties that include inherent capability of hydrogen bonding and a wealth of relevant, well-understood structural information. Homochiral amines and their derivatives belong to the class of strategic building blocks for pharmaceutical, agrochemical and fine chemical development.[1]

Scheme



Herein, we present a novel solution to attaining high stereoselectivity in the allylation of imines with secondary allylboronates (Scheme). The method is based on our recently developed kinetic resolution of chiral racemic allylboronates (±)-**1**,[2] which are readily synthesised from simple precursors.[3,4] Conditions of the kinetic resolution catalysed by chiral Brønsted acid TRIP were optimised to afford highly enantioenriched boronates (*S*)-**1**. DFT calculations at TPSSh/cc-pvtz//B3LYP/6-31g(d,p) level of theory were performed on the system to elucidate the origin of the stereodifferentiation.[2] In developing allylation of imines **3** with allylboronates (*S*)-**1**, it was important to ensure that the reaction is stereoselective, i.e. that chirality of the reagent is efficiently transferred into the product and that its selectivity is controlled with respect to the alkene geometry to give either **4** or **5**. In the case of aldehydes, the factors governing stereoselectivity of this process are reasonably well understood. In imines, substitution on the nitrogen brings an additional element of complexity – the steric size of the substituent. Therefore, the method is focused on the allylation of the in situ generated NH imines **3** (R^2 = H),[5] where the steric arrangement of the transition state should resemble that of aldehydes. Details of the development of stereoselective addition of (*S*)-**1** to imines to furnish selectively (*S,Z*)-**5** will be presented.

References:

[1]. T. Nugent, in *Process Chemistry in the Pharmaceutical Industry, Volume 2*, CRC Press, 2007, pp. 137–156.

[2]. C. A. Incerti-Pradillos, M. A. Kabeshov, A.V. Malkov, *Angew. Chem. Int. Ed.* **2013**, *52*, 5338–5341.

[3]. M. W. Andersen, B. Hildebrandt, G. Köster, R. W. Hoffmann, *Chem. Ber.*, **1989**, *122*, 1777–1782.

[4]. W. Clary, T. J. Rettenmaier, R. Snelling, W. Bryks, J. Banwell, W. T. Wipke, B. Singaram, *J. Org. Chem.*, **2011**, *76*, 9602–9610.

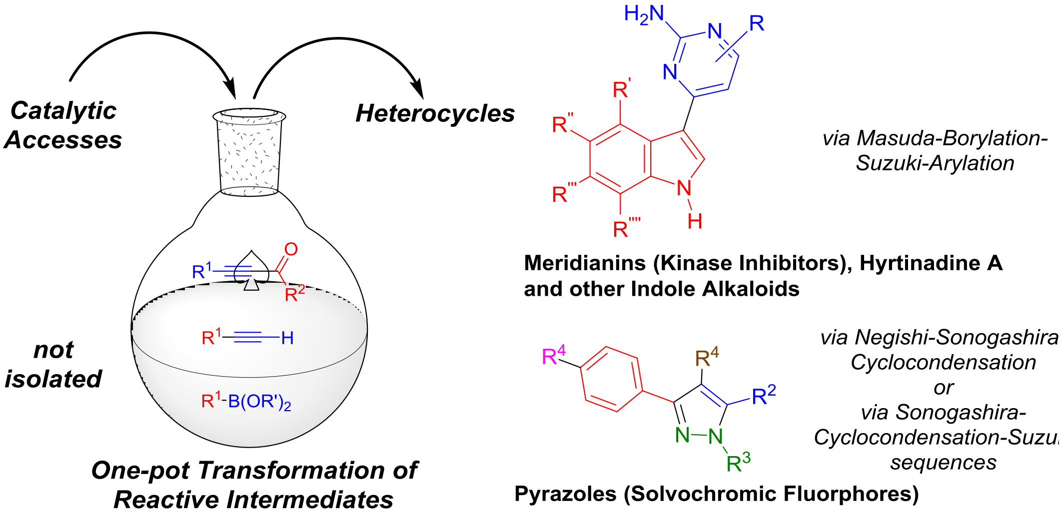
[5]. M. Sugiura, K. Hirano and S. Kobayashi, *J. Am. Chem. Soc.*, **2004**, *126*, 7182–7183.

Sequentially Pd-catalyzed one-pot syntheses of functional heterocycles

Müller T. J. J.

Institut für Organische Chemie und Makromolekulare Chemie, Universität Düsseldorf,
Universitätsstrasse 1, D-40225 Düsseldorf, Germany
e-mail: ThomasJJ.Mueller@uni-duesseldorf.de

Multi-component and domino reactions are efficient and effective methods in the rapid and diversity-oriented synthesis of heterocycles. In particular, transition metal catalyzed multi-component sequences have recently gained a considerable interest.[1] Most interestingly, in sequentially Pd-catalyzed processes[2] the same catalyst source is operative a second time without further catalyst addition. This one-pot methodological concept is most elegantly applied to the syntheses of highly luminescent pyrazoles[3] and to concise syntheses of marine alkaloids and kinase inhibitors, the latter by applying a Masuda-borylation-Suzuki-arylation sequence.[4]



This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and Merck Serono.

References

[1]. D'Souza, D. M.; Müller, T. J. J. *Chem. Soc. Rev.,* **2007**, *36*, 1095.

[2]. a) Müller, T. J. J. *Top. Organomet. Chem.,* **2006**, *19*, 149. b) Müller, T. J. J. In *Molecular Catalysts: Structure and Functional Design*, Gade, L. H.; Hofmann, P., Eds., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2014**, 255. c) Lessing, T.; Müller, T. J. J. *Appl. Sci.,* **2015**, *5*, 1803.

[3]. a) Götzinger, A. C.; Theßeling, F. A.; Hoppe, C.; Müller, T. J. J. *J. Org. Chem.,* **2016**, *81*, 10328. b) Denißen, M.; Nordmann, J.; Dziambor, J.; Mayer, B.; Frank, W.; Müller, T. J. J. *RSC Advances,* **2015**, *5*, 33838-33854. c) Willy, B.; Müller, T. J. J. *Org. Lett.,* **2011**, *13*, 2082.

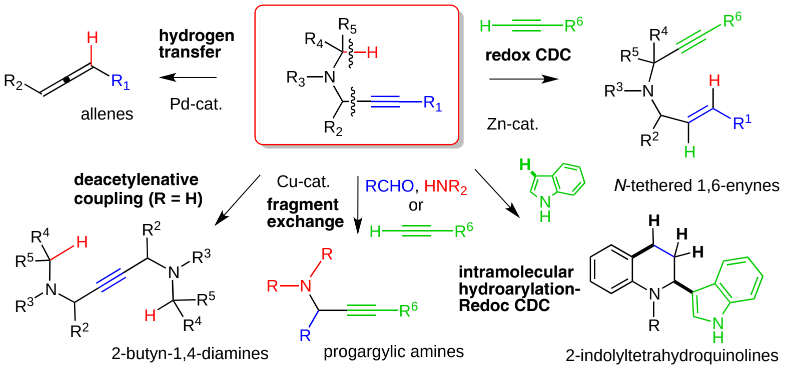
[4]. a) Merkul, E.; Schäfer, E.; Müller, T. J. J. *Org. Biomol. Chem.,* **2011**, *9*, 3139. b) Merkul, E.; Klukas, F.; Dorsch, D.; Grädler, U.; Greiner, H. E.; Müller, T. J. J. *Org. Biomol. Chem.,* **2011**, *9*, 5129. c) Tasch, B. O. A.; Merkul, E.; Müller, T. J. J. *Eur. J. Org. Chem.,* **2011**, 4532. d) Tasch, B. O. A.; Antovic, D.; Merkul, E.; Müller, T. J. J. *Eur. J. Org. Chem.,* **2013**, 4564. e) Tasch, B. O. A.; Bensch, L.; Antovic, D.; Müller, T. J. J. *Org. Biomol. Chem.,* **2013**, *11*, 6113. f) Wucherer-Plietker, M.; Merkul, E.; Müller, T. J. J.; Esdar, C.; Knöchel, T.; Heinrich, T.; Buchstaller, H.-P.; Greiner, H.; Dorsch, D.; Finsinger, D.; Calderini, M.; Bruge, D. *Bioorg. Med. Chem. Lett.,* **2016**, *26*, 3073.

C-H versus C-C in activation of propargylic amines under transition-metal catalysis

Hiroyuki Nakamura

Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, 226-8503, Japan.
e-mail: hiro@res.titech.ac.jp

The strategy for the transition metal-catalyzed C-H bond activations has attracted greatest interest in an environmentally friendly process for organic synthesis. In particular, the C(sp^3)-H activation alpha to nitrogen has shown a variety of transformations. We found that propargylic amines undergo the C(sp^3)-C(sp) activation in the presence of Cu(II) catalysts or the C(sp^3)-H activation in the presence of Pd or Zn(II) catalysts (Scheme 1). Propargylic amines underwent the C(sp3)-H activation in the presence of palladium catalysts to form allenes.[1] In contrast, the C(sp3)-C(sp) activation was observed in the presence of copper catalysts to generate the corresponding iminium intermediates and copper acetylides, that reacted with another equivalent of the starting material (R^1 = H) to give the deacetylenative coupling products, 2-butyn-1,4-diamines, in the absence of bases,[2] or reacted with aldehydes, amines and/or 1-alkynes to give the fragment exchanged propargylic amines.[3] Moreover, the propargylic amines underwent the C(sp^3)-H activation by zinc catalysts to afford the hydrogen-migrated vinyl zinc species that reacted with 1-alkynes to give the corresponding N-tethered 1,6-enynes.[4] In this case, a coupling between the C(sp^3)-H of the propargylic amines and the C(sp)-H of 1-alkynes took place and the generated two hydrogen atoms were trapped by the internal alkyne. As a result, redox CDC proceeded during the reaction, and additional oxidants were not necessary for this coupling. Furthermore, intramolecular hydroarylation-redox CDC of N-propargylic anilines with indoles was also catalyzed by zinc(II) to give 2-indolyltetrahydroquinolines.[5] In this transformation, three C–H bonds (two sp^2 and one sp^3) are activated in one shot and these hydrogen atoms are trapped by a propargylic triple bond in the molecule. In this paper, our recent results of propargylic amine-based transformations induced by the transition metal-catalyzed C(sp^3)-H activations[6] will be presented.



Scheme 1. Overview of the C-H and C-C activation-based transformations of propargylic amines

References

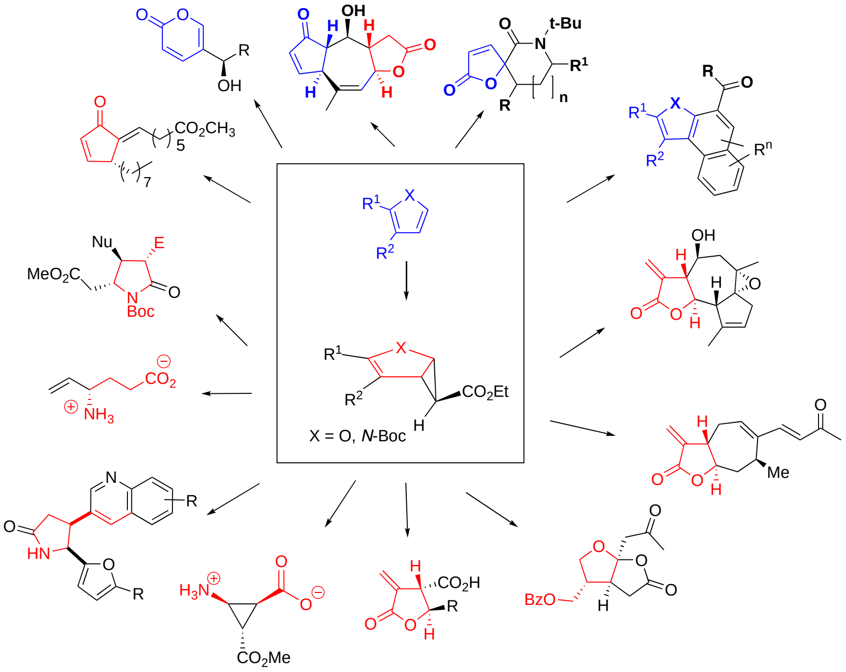
[1]. H. Nakamura, T. Kamakura, M. Ishikura, J-F. Biellmann, J. Am. Chem. Soc. 2004, 126, 5958.
[2]. Y. Kim, H. Nakamura, Chem. Eur. J. **2011,** 17, 12561.
[3]. T. Sugiishi, A. Kimura, H. Nakamura, J. Am. Chem. Soc. **2010,** 132, 5332.
[4]. T. Sugiishi, H. Nakamura, J. Am. Chem. Soc. **2012**, 134, 2504.
[5]. G. Li and H. Nakamura, Angew. Chem. Int. Ed. **2016,** 55, 6758.
[6]. H. Nakamura, Synlett, **2015,** 26, 1649-1664.

Converting hay to gold with modern spinning wheels: non-edible, renewable resources as starting materials for the synthesis of fine chemicals utilizing light, flow and mag(net)ic catalysts

Reiser O.

Institute of Organic Chemistry, University of Regensburg, Universitätsstr. 31
93053 Regensburg, Germany
e-mail: oliver.reiser@chemie.uni-regensburg.de

Pyrroles and furans represent readily available bulk chemicals derived from non-edible, renewable resources. Focusing on asymmetric transition metal and visible light photoredox catalysis, we are developing strategies to rapidly convert such starting materials into novel heterocyclic and carbocyclic scaffolds related to natural products or drugs.



References

(for a complete list of publications see http://www-oc.chemie.uni-regensburg.de/reiser/publikat/index.php)

[1]. O.Reiser, *Acc. Chem. Res.* **2016**, *49*, 1990-1996

[2]. O. Reiser, *Isr. J. Chem.* **2016**, *56*, 531-539

[3]. D. Rackl, P. Kreitmeier, O. Reiser, *Green Chem.* **2016**, *18*, 214-219;

[4]. C. M. Eichenseer, B. Kastl, M. Pericas, P. R. Hanson, O. Reiser, *ACS Sus. Chem. Eng.* **2016**, *4*, 2698-2705;

[5]. D. Dobler, O. Reiser, *J. Org. Chem.* **2016**, *81*, 10357-10365;

[6]. N. Arisetti, O. Reiser, *Org. Lett.* **2015**, *17*, 94-97;

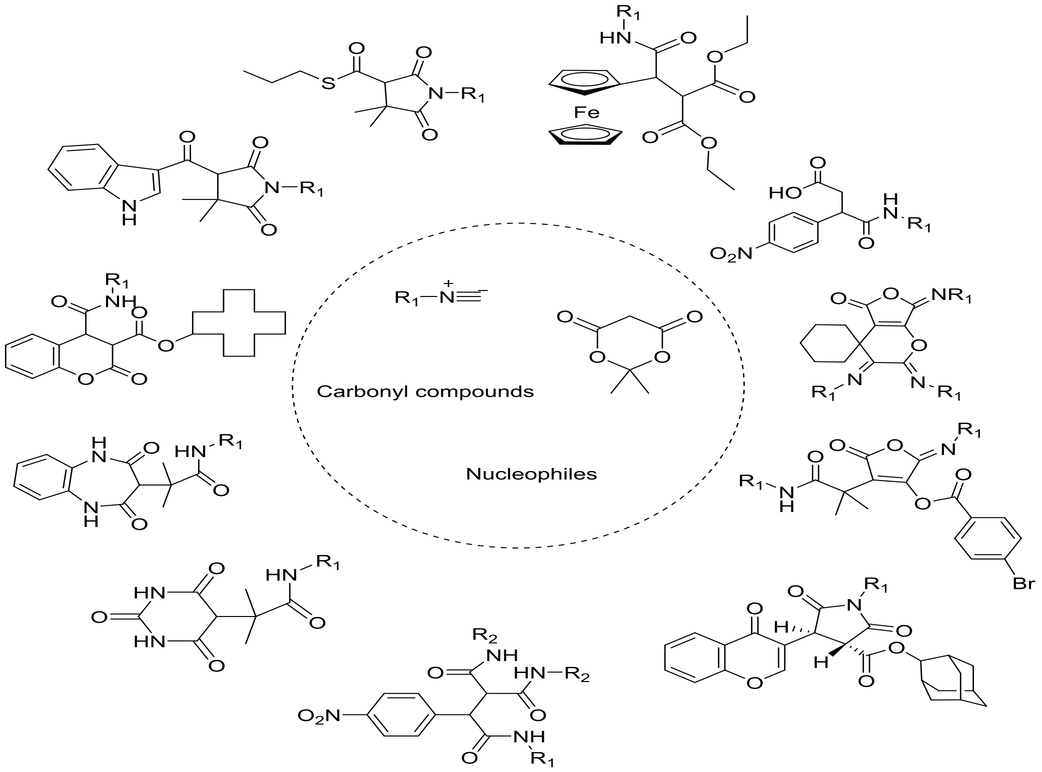
[7]. D. B. Bagal, G. Kachkovskyi, M. Knorn, T. Rawner, B. M. Bhanage, O. Reiser, *Angew. Chem. Int. Ed.* **2015**, *54*, 6999-7002; *Angew. Chem.* **2015**, *127*, 7105-7108;

[8]. Q. M. Kainz, O. Reiser, *Acc. Chem. Res.* **2014**, *47*, 667-677.

The status of isocyanide based multicomponent reactions in Iran

Shaabani A.

Department of Chemistry, Shahid Beheshti University, P. O. Box 19396-4716, Tehran, Iran
E-mail: a-shaabani@sbu.ac.ir



Design and discovery of novel multicomponent reactions which are able to generate useful chemical products may be regarded as a prominent topic in organic chemistry. In this context, isocyanide based multicomponent reactions (IMCRs) are special subclasses of the multicomponent reactions. In this presentation, an overview of the contributions and recent advances made by Iranian scientists in the field of IMCRs between 1999 and 2017 have been reported. With over 400 publications during this period, Iranians are responsible for approximately 8 % of all publications in the world involving IMCRs. Some attractive features of these IMCRs are synthesis of numerous classes of pharmaceutically and industrially valuable heterocyclic and acyclic organic compounds in a one pot manner, carrying out reactions in green reaction mediums like water or ethanol, high atom economies, mild reaction conditions, high yields and catalyst-free processes.

References

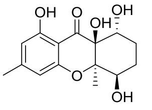
[1]. Shaabani, A., Maleki, A., Rezayan, A. H., & Sarvary, A. (2011). Mol. Divers., 15(1), 41-68.
[2]. Shaabani, A., Hooshmand, S. E. (2016). RSC Adv., 6(63), 58142-58159.
[3]. Shaabani, A., Soleimani, E., Rezayan, A. H., Sarvary, A., & Khavasi, H. R. (2008). Org. Lett., 10(12), 2581-2584.
[4]. Shaabani, A., Ghadari, R., Sarvary, A., & Rezayan, A. H. (2009). J. Org. Chem., 74(11), 4372-4374.

Domino reactions. The green and economical art of chemical synthesis

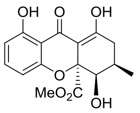
Lutz F. Tietze

Institute of Organic and Biomolecular Chemistry, Georg-August-University Göttingen,
Tammannstr. 2, D-37077 Göttingen, Germany,
e-mail: ltietze@gwdg.de

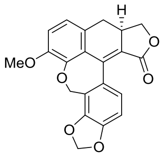
The efficient synthesis of natural products, drugs, agrochemicals and materials is a very important aspect in academia and industry. To allow an ecologically and economically favourable approach in a green fashion the former stepwise procedures must be replaced by domino reactions which allow the preparation of complex molecules starting from simple substrates in a straight forward way. Domino reactions[1] allow the reduction of the amount of waste being formed and the preservation of our resources. Moreover, they are also favourable in an economical way since they consume less time.



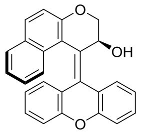
Diversonol



(-)-Blenolid A



Linoxepin



Molecular Switches

The usefulness of the domino concept is demonstrated with the syntheses of the fungal metabolites diversonol[2], blennolide A[3a], blennolide C[3b] and gonytolide[3b] as well as other natural products of the dimeric tetrahydroxanthenone type[4] using an enantioselective domino-Wacker/carbonylation/methoxylation reaction and of the natural aryldihydronaphthalene lignan linoxepine[4] employing a domino-carbopalladation/Heck reaction. The approach has also been applied for the synthesis of novel materials such as molecular switches[5a-d] and fluorescence dyes[5e,f] using a domino-Sonogashira/carbopalladation/CH-activation reaction.

References

[1]. a) Domino Reactions: Concepts for Efficient Organic Synthesis", Ed.: L. F. Tietze, Wiley-VCH, Weinheim, **2014**; b) L.F. Tietze, Chem Rev. **1996**, *96*, 115-136.

[2]. a) L. F. Tietze, D. A. Spiegl, F. Stecker, J. Major, C. Raith, C. Grosse, *Chem. Eur. J.* **2008**, *14*, 8956-8963; b) L. F. Tietze, S. Jackenkroll, C. Raith, D. A. Spiegl, J. R. Reiner, M. C. Ochoa Campos, *Chem. Eur. J.* **2013**, *19*, 4876-4882.

[3]. a) L. F. Tietze, L. Ma, J.R. Reiner, S. Jackenkroll, S. Heidemann, *Chem. Eur. J.* **2013**, *19*, 8610-8614; b) L. F. Tietze, S. Jackenkroll, J. Hierold, L. Ma, B. Waldecker, *Chem. Eur. J.* **2014**, *20*, 8628-8635.

[4]. a) D. Ganapathy, J.R. Reiner, G. Valdomir,S. Senthilkumar, L.F. Tietze *Chem. Eur. J.* **2017**, accepted; b) D. Ganapathy, J.R. Reiner, L.E. Löffler, L. Ma, B. Gnanaprakasam, B. Niepötter, I. Koehne, L.F. Tietze *Chem. Eur. J.* **2015**, *21*, 16807-16810

[5]. a) L. F. Tietze, S.-C. Duefert, J. Clerc, M. Bischoff, C. Maaß, D. Stalke, *Angew. Chem.* **2013**, *125*, 3273-3276; b) L. F. Tietze, J. Clerc, S. Biller, S.-C. Duefert, M. Bischoff *Chem. Eur. J.* **2014**, *20*, 17119–17124.

[6]. a) L. F. Tietze, M. A. Düfert, F. Lotz, L. Sölter, K. Oum, T. Lenzer, T. Beck, R. Herbst-Irmer, *J. Am. Chem. Soc.* **2009**, *131*, 17879-17884; b) L. F. Tietze, M. A. Düfert, T. Hungerland, K. Oum, T. Lenzer, *Chem. Eur. J.* **2011**, *17*, 8452-8461; c) L. F. Tietze, T. Hungerland, M. A. Düfert, I. Objartel, D. Stalke. *Chem. Eur. J.* **2012**, *18*, 3286-3291; d) L. F. Tietze, T. Hungerland, C. Eichhorst, A. Düfert, C. Maaß, D. Stalke, *Angew. Chem., Int. Ed.* **2013**, *52*, 3668-3671; e) L. F. Tietze, C. Eichhorst, T. Hungerland, M. Steinert, *Chem. Eur. J.* **2014**, *20*, 12553-12448; f) L. F. Tietze, C. Eichhorst, *Heterocycles* **2015**, *90*, 919-27.

Structural tuniong of luminescent and magnetic properties of porous metal organic frameworks

Timofeeva T., Carlos Ordonez, Taoguang Qu, Jennifer Lindlina, Michael Pertonis, Quiang Wei

Deparment of Chemistry, New Mexico Highlands University, Las Vegas, NM 87701, USA
e-mail: tvtimofeeva@nmhu.edu

Two large series of metal organic frameworks (MOFs) were synthesised and structurally characterized. The first series represents anionic frameworks constructed from Zn^{2+} with 1,3,5-benzenetricarboxylate (BTC) anions and amino-cations. An influence of various cations such as NH_4+, $MeNH_3$+, Me_2NH_2+, Et_3NH+, and n-Bu_4N+ was manifested by the structural changes of the anionic Zn-BTC connectivity within the frameworks, and the fluorescence of the corresponding MOFs. The 13 Zn-BTC MOFs with 1, 2 and 3 dimensional structures were obtained and it was clearly demonstrated that cations are acting as structure directing agents. The second series represents MOFs based on the same cationic-anionic structure {Zn-BTC}{ Me_2NH_2+} that was doped with different metals (Co, Cu, Ni, Mn, Ca, Mg and Gd). Obtained materrials have significant differences in their magnetic behavier depending on the nature of the dopant metal atoms. The X-ray diffraction studies did not reveal strutural differences between doped materials, however their luminescent properties were found to be different that might lead to their potential practical applications.

Bridging chemistry and biology through metal catalysis

Jing Zhao,[a]

[a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical
Engineering, Nanjing University, Nanjing 210093, China.;
e-mail: jingzhao@nju.edu.cn

We first studied a heavy metal-detoxification protein GolB, a gold-specific binding protein. GolB was recently identified, providing a unique opportunity for the study of the Au-S bond at the molecular level. We measured the rupture force of the Au-S bond to be 165 pN, much lower than Au-S bonds measured on different gold surfaces (~1000 pN). We further solved the structures of apo-GolB and Au(I)-GolB complex using X-ray crystallography.[1] The interaction between silver ions and the CXXC in GolB and copper chaperone Atx1 and GolB revealed that the conserved CXXC metal-binding motif (MBD) coordinated a unique tetrasilver cluster.

Next, inspired by these results from metalloproteins, we designed small-molecule ligands to overcome the copper cytotoxicity of Cu(I) ions, enabling the biocompatible Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC). The CuAAC reaction could occur on the cell surface, directly visualizing of the dynamics of the biosynthesis of sialylated glycans at the intact heart level.[2a,2b] Application of the biocompatible CuAAC reaction for intracellular modification of proteins realized protein labelling within the cytoplasm of *Escherichia coli*.[2c]

Lastly, by mimicking O_2-enzymes' intermediate M-O-O structure (M=Fe, Cu), we developed new metal-catalyzed C–H activation reaction cascades to access structurally diverse polycyclic phenols in one pot.[3a,3b]

References

[1]. Wei, W.; Sun, Y.; Liu, X.; Sun, P.; Wang, F.; Gui, Q.; Meng, W.; Cao, Y.; Zhao, J., *J. Am. Chem. Soc.* **2015**, 15358.

[2]. (a) Feng, L.; Hong, S.; Rong, J.; You, Q.; Dai, P.; Huang, R.; Tan, Y.; Hong, W.; Xie, C.; Zhao, J. and Chen, X., *J. Am. Chem. Soc.* **2013**, 9244. (b) Rong, J.; Han, J.; Dong, L.; Tan, Y.; Yang, H.; Feng, L.; Wang, Q. W.; Meng, R.; Zhao, J.; Wang, S. Q.; Chen, X., *J. Am. Chem. Soc.* **2014**, 17468. (c) Yang, M.; Jalloh, A. S.; Wei, W.; Zhao, J.; Wu, P.; Chen, P. R., *Nature Commun.* **2014**, 5, 4981.

[3]. (a) Chen, Y.; Wang, D.; Duan, P.; Ben, R.; Dai, L.; Shao, X.; Hong, M.; Zhao, J.; Huang, Y., *Nature Commun.* **2014**, 4610. (b) Wu, Q.; Chen, Y.; Yan, D.; Zhang, M.; Lu, Y.; Sun, W.; Zhao, J. *Chem. Sci.*, **2017**, 169.

Inorganic and Coordination Chemistry Section

Oral Reports (20-40 min)

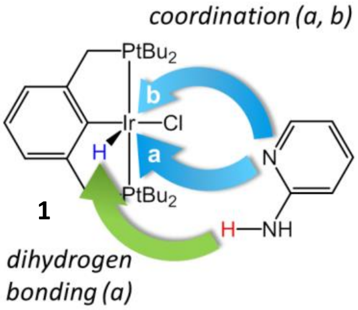
Coordination chemistry and reactivity of iridium pincer hydrides

Belkova N.V., Osipova E.A., Titova E.M., Filippov O.A.

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences
Vavilov Str. 28, Moscow, 119991 Russia
nataliabelk@ineos.ac.ru

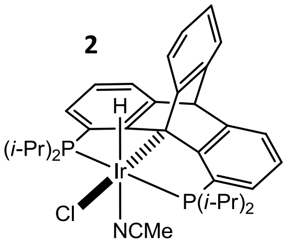
Transition metal hydrides constitute an important class of organometallic compounds involved in various stoichiometric and catalytic transformations of organic molecules. The particular type of hydride reactivity is obviously determined by metal nature, its ligand environment and by partner reagents (reaction conditions) [1]. Over the last decades κ^3-PCP-pincer-ligands have been extensively studied since they are robust and still amenable to structural and electronic modifications [2]. It is generally accepted that pincer ligands enforce meridional geometry at the metal center and control over vacant coordination sites via bulky substituents on the donor atoms. So far, the most popular scaffold used to design pincer ligands relies on an aromatic moiety (PC(sp^2)P). The reports on the chemistry and practical applications of the aliphatic C(sp^3)-metalated pincer complexes are far less common [2].

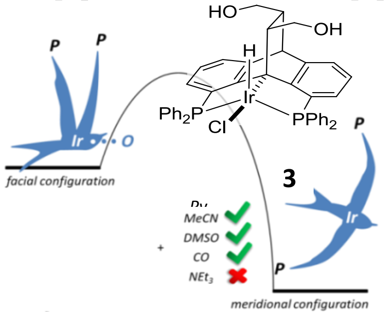
In this contribution we will analyze the results of our recent studies on the reactivity of iridium(III) hydride complexes supported by benzene-based $^{t\mathrm{Bu}}$PC(sp^2)P (**1**), and dibenzobarrelene-based ^{R}PC(sp^3)P (**2, 3**) pincer ligands. The detailed spectroscopic study of **3** unveiled the flexibility of the dibenzobarrelene-based scaffold unprecedented for aromatic pincers like **1** [3]. The results obtained for the complexes **1-3** interaction with Lewis bases (CH_3CN, (amino)pyridines, DMSO, CO, Et_3N) and acids [3-6] allow discussing the fundamental aspects of the coordination chemistry of this class of compounds. These findings were employed in the mechanistic studies of catalytic dehydrogenation of alcohols [6] and amine-boranes [7].



1

2





3

This work was supported by the Russian Science Foundation (grant № 14-13-00801).

References

[1]. Belkova, N.V.; Epstein, L.M.; Filippov, O.A.; Shubina, E.S. *Chem. Rev.* **2016**, *116*, 8545.

[2]. van Koten, G.; Milstein, D. (Eds.) *Organometallic Pincer Chemistry,* in *Topics in Organometallic Chemistry, Vol. 40*, Springer Berlin Heidelberg, **2013**, 356 pp.

[3]. Silantyev, G. A.; Filippov, O. A.; Musa, S.; Gelman, D.; Belkova, N. V.; Weisz, K.; Epstein, L. M.; Shubina, E. S. *Organometallics*, **2014**, *33*, 5964.

[4]. Titova, E. M.; Silantyev, G. A.; Filippov, O. A.; Gulyaeva, E. S.; Gutsul, E. I.; Dolgushin, F. M.; Belkova, N. V. *Eur. J. Inorg. Chem.* **2016**, 56.

[5]. Titova, E.M.; Osipova, E.S.; Gulyaeva, E.S.; Torocheshnikov, V.N.; Pavlov, A.A.; Silantyev, G. A.; Filippov, O. A.; Shubina, E. S.; Belkova, N. V. *J. Organomet. Chem.* **2017**, *827*, 86.

[6]. Silantyev, G. A.; Titova, E. M.; Filippov, O. A.; Gutsul, E. I.; Gelman, D.; Belkova, N. V. *Russ. Chem. Bull.* **2015**, 2806.

[7]. Titova, E. M.; Osipova, E. S.; Pavlov, A. A.; Filippov, O. A.; Safronov, S. V.; Shubina, E. S.; Belkova, N. V. *ACS Catal* **2017**, ASAP. doi: 10.1021/acscatal.6b03207

Granular structures based on manganese arsenide inclusions embedded in $A^{II}B^{IV}C^{V}_2$ semiconductors host

Fedorchenko I.V., Izotov A.D., Marenkin S.F.

Kurnakov Institute of General and Inorganic Chemistry RAS, 119991, Moscow, Leninsky pr.31
e-mail: irina@igic.ras.ru

There are two main directions in the researches of new materials for spintronics applications. The first direction is the supperlattices based on non-magnetic and ferromagnetic materials [1] and the second is the composites or granular structures based on ferromagnetic inclusions embedded in nonmagnetic host [2, 3].The composite materials have the variety of the technological advantages.

In the comparison with metals and insulators, the semiconductors are the promising materials for the host of the magnetic inclusions. The main advantages of the semiconductors are what they have high mobility and relative large mean free path of the carriers. The phase equlibria of the semiconductor-ferromagnetic systems have typically eutectic type. The eutectic point has regular composition and structure which is valuable for the granular structures [4].

In this work, we present phase equlibria in the $A^{II}B^{IV}C^{V}_2$-MnAs systems (A-Zn, Cd; B-Si,Ge, Sn; C-As) and magnetic properties of the granular structures based on these materials. $A^{II}B^{IV}C^{V}_2$ is well known nonlinear optic application material. MnAs is a well known ferromagnetic with Curie point exceed room temperature. The magnetic properties of all composites are due to the magnetic inclusions of manganese arsenide. Regardless, the magnetic properties of the composites based on MnAs have dramatic differences. On the isostructural composites in the similar concentrations positive and negative magnetoresistance was observed and significant difference in magnetic saturation. The size of the magnetic inclusions makes a big difference of the magnetic properties of the composite. Such behavior of MnAs in different hosts can be explained by the different type of interaction between semiconductor matrix and MnAs precipitates, such as form, size and internal stress of the inclusions. Results in Ref. [5] support our suggestions. In this paper, authors described that Curie point of MnAs can be shifted from 320 to 400 K as a result of the lattice deformation.

References

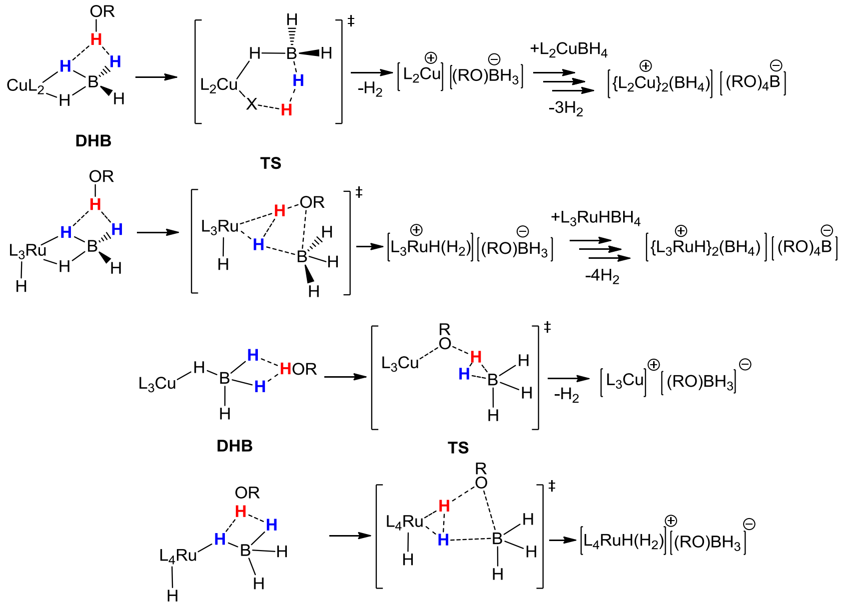
[1]. G. Li, M. Li, J. Wang, J. Du, K. Wang, Q. Wang, *J. Magn. Magn. Mater*, V. 423, **2017**, PP. 353-358
[2]. J. Garcia-Torres, E. Valles, E. Gomez, *J. Magn. Magn. Mater*., 322 **2010**, pp. 3186–3191
[3]. C.J. Won, R.C. Kambale, N. Hur, *J. Alloy. Compd.*, 509 (24) **2011**, pp. 6969–6972
[4]. I.V. Fedorchenko, L. Kilanski, I. Zakharchukb and et., *J. Alloy. Compd.*, V.650, **2015**, PP. 277–284
[5]. J.H. Song, Y. Cui, J.B. Ketterson, *J. Appl. Phys*., 111 (**2012**), p. 07E125

Proton-Hydride Transfer and BH/XH Activation in Metal Tetrahydroborates Alcoholysis

Golub I.E.[1,2], , Filippov O.A.[2], Shubina E.S.[2]

[1]Inorganic Chemistry Department, Peoples' Friendship University of Russia (RUDN University), 117198, 6 Miklukho-Maklay St, Moscow, Russia
[2]A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991, 28 Vavilova St, Moscow, Russia
e-mail: seraph347@gmail.com

The non-covalent intra- and intermolecular interactions (e.g. hydrogen, dihydrogen bonds) are known to have a great impact on reactivity of boron hydrides in reactions with proton transfer and hydrogen evolution. Herein we present comprehensive investigation of the reactivity [BH$_4$]$^-$ [1] and transition metals (Cu, Ru) tetrahydroborate and hydrido-tetrahydroborate complexes with in alcoholysis reactions [2-4]. 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.



This work was supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.21.0008), the Russian-Italian bilateral project CNR-RFBR №15-53-78027 and RFBR projects № 16-03-00324 and 16-33-01070.

References

[1]. Golub, I. E.; Filippov, O. A.; Gulyaeva, E. S.; Gutsul, E. I.; Belkova, N. V., Inorg. Chim. Acta 2017, 456, 113-119.

[2]. Golub, I. E.; Filippov, O. A.; Belkova, N. V.; Epstein, L. M.; Rossin, A.; Peruzzini, M.; Shubina, E. S., Dalton Trans. 2016, 45, 9127-9135.

[3]. Belkova, N. V.; Bakhmutova-Albert, E. V.; Gutsul, E. I.; Bakhmutov, V. I.; Golub, I. E.; Filippov, O. A.; Epstein, L. M.; Peruzzini, M.; Rossin, A.; Zanobini, F.; Shubina, E. S., Inorg. Chem. 2014, 53, 1080-1090.

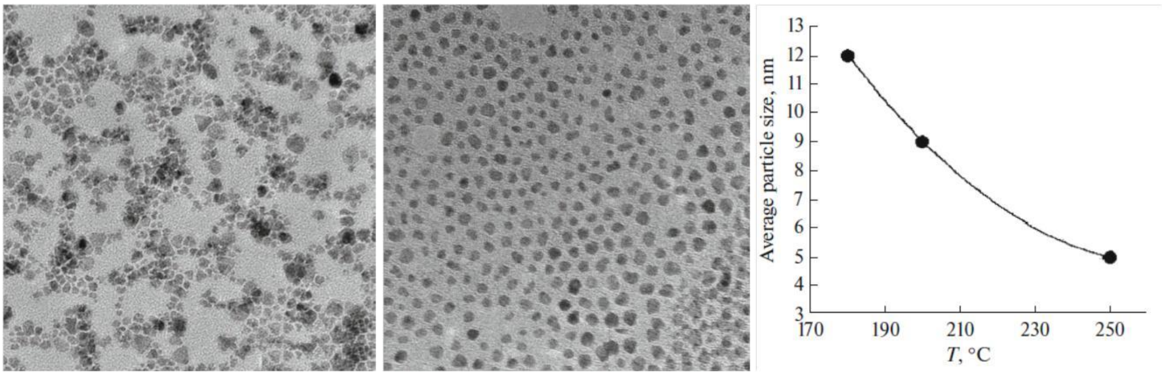
[4]. Golub, I. E.; Filippov, O. A.; Gutsul, E. I.; Belkova, N. V.; Epstein, L. M.; Rossin, A.; Peruzzini, M.; Shubina, E. S., Inorg. Chem. 2012, 51, 6486-6497.

The formation features of nanosized iron(III) oxide

Lyadov A.S., Kochubeev A.A., Khadzhiev S.N.

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991,
29 Leninsky prospect, Moscow
e-mail: lyadov@ips.ac.ru

The synthesis of iron oxide nanoparticles was performed by thermolysis of iron(III) acetylacetonate using diphenyl ether as a dispersion medium. Figure 1 displays the TEM-image of nanosized iron oxide particles obtained in the absence of surfactant. It is seen that at low-temperature of thermolysis (180°C, Fig. 1a) the particles differ in form, there is a trend to form particles of triangle shape; the average size is 12–15 nm. Increase in thermolysis temperature leads not only to decrease of average particle size but also formation of particles of uniform shape (Fig. 1b). Increase in thermolysis temperature from 180 to 250°C provides more than twofold decrease of average size of iron(III) oxide particles (Fig. 1c).



(A) (B) (C)

Fig. 1. TEM images of nano-Fe_2O_3: (a) thermolysis at 180°C, (b) thermolysis at 250°C, dependence of particle size on thermolysis temperature (c).

The introduction of surfactant into dispersion medium also leads to decrease of the average size of particles down to 4 nm. The features of reduction of obtained nano-Fe_2O_3 were studied. The TPR profile of nanosized iron oxide (Fig. 2) has three peaks of hydrogen consumption (I peak: $Fe_2O_3 \rightarrow Fe_3O_4$, II peak: $Fe_3O_4 \rightarrow Fe_{1-x}O$, III peak: $Fe_{1-x}O \rightarrow Fe$). The activation energies of the reduction processes were determined by the Kissinger method.

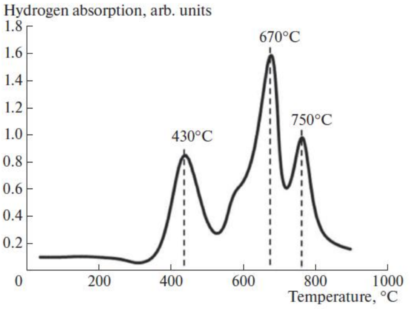


Fig.2. TPR-profile of nano-Fe_2O_3

Nano-Fe_2O_3 was tested as a catalyst in the decomposition of oxidized sulphur compounds (second step of oxidative desulfurization process) of model oil (dibenzothiophene in hexadecane), crude oil and diesel fuels with different sulphur concentrations. It was shown that nano-Fe_2O_3 is active and effective catalyst for decomposition of oxidized sulphur compounds.

This work was supported by the Presidium of the Russian Academy of Sciences (program no. 25 “Fundamental Aspects of the Chemistry of Carbon Power Engineering,” project “Research on the Development of a Technology for the Oxidative Desulfurization of Crude Oil and Petrochemicals in the Presence of Nanosized Oxide Catalyst Systems”).

Volatile iridium (I) β-diketone derivatives for MOCVD application: synthesis, structure, thermal properties

Vikulova E.S.[1], Karakovskaya K.I.[1,2], Iliyn I.Yu.[1], Piryazev D.A.[1,2], Morozova N.B.[1]

[1]Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Novosibirsk, Acad. Lavrentive ave. 3
[2]Novosibirsk State University, 630090, Novosibirsk, Pirogova str. 2
e-mail: lazorevka@mail.ru

Ir-containing film materials are used in several essential applications such as in catalysts, spark plugs, protective anti-oxidizing coatings, implanted electrodes for neuro- and cardio surgery et. al. Metal-Organic Chemical Vapor Deposition (MOCVD) and its modifications seems to be ones of the most preferable technique to obtain refractory Ir-containing coatings with required characteristics [1]. However, using MOCVD and related methods, it should be appreciated that the morphology, structure and composition of coatings obtained are strongly dependent on the thermochemical properties of the precursor used. So, the establishment of relationships between structure and thermal properties of volatile compounds has the great importance because it creates the platform to choose the best precursor for material with specified characteristics. Recently, mixed-ligand mononuclear complexes of iridium(I) have caused the growing interest because of high volatility and relatively easy synthesis [1]. β-Diketonates and their derivatives $R^1C(X^1)CHC(X^2)R^2$ are promising as the ligands to create the effective MOCVD precursors due to the possibility to manage thermal properties of the complexes by varying of terminal substituents R^i, donor groups X^i, etc.

So, the present work deals with the investigation of influence of the ligands on the structure and thermal properties of Ir(I) β-diketone derivatives [Ir(Q)n(L)] with 1,5-cycalooctadiene (cod, n = 1) or carbolyls (n = 2) as neutral ligands Q. The β-diketonate ligands L ($X^1 = X^2 = O$) were varied to explore the influence of steric effect and terminal substituent types as follows: $R^1 = R^2 =$ Me (*acac*), ^{t}Bu (*thd*), CF_3 (*hfac*); $R^1 = CF_3$, $R^2 =$ Me (*tfac*); ^{t}Bu (*ptac*), Ph (*btfac*), $R^1 = {}^t$Bu, $R^2 = Me_2OMe$ (*zis*). Also, some β-iminoketonates L ($X^1 = NR^3$, $X^2 = O$) were used to evaluate the donor group influence: R^1 = Me, R^2 = Me, R^3 = H (*i-acac*), R^3 = Me (*Mei-acac*), $R^1 = CF_3$, R^3 = Me (*Mei-tfac*).

As a result, the series of 16 iridium(I) mixed-ligand complexes including 9 new compounds were synthesized and characterized by elemental and powder X-ray diffraction analysis, IR- and NMR-spectroscopy. The structures of 11 complexes were determined by single-crystal X-ray diffraction. All compounds are molecular complexes4 the H-type interactions are presented in the crystal packing of complexes with *zis* and *i-acac* ligands.

The thermal properties of complexes were investigated by thermogravimetry, differential scanning calorimetry, tensiometry and *in situ* high temperature mass-spectrometry methods. Using the data obtained, the thermodynamic parameters of melting and vaporization were calculated and relative volatility and stability rows were determined. It was shown that complexes with carbonyl ligands are more volatile than corresponding cod-analogs. The volatility row of the complexes is following: L = *hfac* > *tfac* > *ptac* > *acac*> *thd* > *i-acac* > *Mei-acac* > *btfac*. The vapors of complexes with *thd* ligand is characterized by the highest thermal stability due to the steric effects caused the presence of bulky ^{t}Bu-groups in β-diketonate ligand.

The work was partially financially supported by the Council on the Grants from the President of the Russian Federation (SP-3215.2016.4).

References

[1]. Vasilyev, V.Y., Morozova, N.B., Basova, T.V., Igumenov, I.K., Hassan, A.. *RSC Adv.*, **2015**, *5*, 32034.

Oral Reports
(10 min)

Modification of surfaces of aluminum alloys for controlling functional properties

Bezbomnikov A.A.[1,2], Saifutdinova A.R.[1,2], Emelyanenko K.A.[2], Savinkina E.V.[1]

[1] *Moscow Technological University (MITHT), 119571, Moscow,*
Vernadsky Prospekt, 86
[2] *A.N. Frumkin Institute of Physical chemistry and Electrochemistry RAS, 119991, Moscow,*
Leninsky Prospect, 31
e-mail: jlexarus@ya.ru

Aluminum alloys are very significant constructional materials. Improvement of their corrosion resistance can reduce operating costs and expand field of their application. Great resources are wasted for control of corrosion and its *consequences. These expenses are hard to analyze; however, several experts evaluate them as 2–4% of gross domestic product [1].*

To solve this problem, we decided to use passive protection – modification by anodizing followed by chemical hydrophobization. This method allows improving barrier properties of alloys and makes their surface superhydrophobic. It inhibits corrosion on the contact with an electrolyte due to synergetic action of various mechanisms [2] including decrease of the area contacting with aggressive environment.

To evaluate the resulting anticorrosion properties, electrochemical study was carried out. The impedance spectra were recorded and polarization curves were obtained. Dynamics of wetting angles of the surfaces of superhydrophobic samples was also studied.

References

[1]. Koch, G.H, Brongers, MPH, Thomson, NG, Virmani, YP, Payer, JH, *“Corrosion Cost and Preventive Strategies in the United States.” Mater. Perform.,* **2002**, 65, 1.
[2]. L.B. Boinovich, A.M. Emelyanenko, A.D. Modestov, et al., *Corrosion Science*, **2016**, 112, 517–527.

Synthesis, structure and biological activity of Cu(II) coordination compounds with heterocyclic polynitrogen ligands

Dyukova I.I.[a,b], Komarov V.Y.[a,b], Vorontsova E.V.[c], Lavrenova L.G.[a,b]

[a] *Institute of Inorganic Chemistry, Siberian Division of RAS, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090, Russia*
[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090, Russia*
[c] *Institute of Molecular Biology and Biophysics, Novosibirsk, 630117, Russia*
e-mail: ira.dukova.94@mail.ru

Complexes of 3*d* metals with heterocyclic polynitrogen ligands are of great interest to scientists, since such compounds have a significant biological activity and/or nontrivial magnetic properties. In particular, 1,2,4-triazolo[1,5-a]benzimidazoles and pyrimidines represent a promising class of ligands for the synthesis of copper(II) coordination compounds which exhibit a wide range of pharmacological properties [1-2].

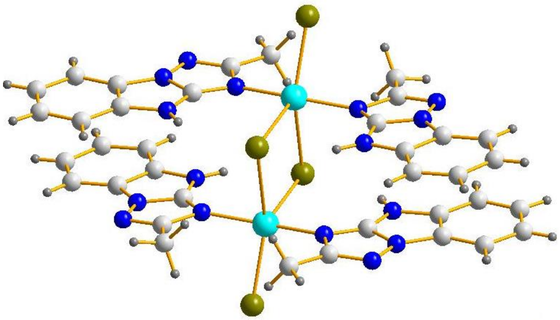


Fig. 1. Structure of $Cu_2(L^1)_4(\mu\text{-}Br)_2Br_2$

Copper(II) coordination compounds with 2-methyl- and 2,4-dimethyl-1,2,4-triazolo[1,5-a] benzimidazoles (L^1, L^2) presented as $Cu_2(L^1)_4(\mu\text{-}Br)_2Br_2$ (I), $Cu(L^2)Hal_2$ (Hal=Cl (II); Hal=Br (III)), and halides of copper(II) with 2-N-acetylaminopyrimidine presented as $Cu(L^3)_2Cl_2 \cdot nH_2O$ (Hal=Cl, n=1 (IV); Hal=Br, n=0 (V)) have been synthesized. The compounds have been studied using elemental analysis, IR and UV/Vis spectroscopy, and powder X-ray diffraction. The crystal and molecular structures of I and II have been determined using a single crystal X-ray diffraction technique (Fig. 1).

The cytotoxicity of ligands L^1, L^2, L^3 and complexes I-V with respect to *human laryngeal cancer cell line* (Hep-2) has been tested by using High Content Analysis. This method involves the use of two types of fluorescent dyes (Hoechst and Propidium Iodide), which allow to identify living, apoptotic and dead cells. The results show that the ligands have a little cytotoxic effect leading to the death of less than 10 % of cancer cells only. However, the complexation of Cu(II) with the mentioned ligands allows one to obtain much more efficient compounds as to compare with free organic ligands. The effect of the complexes leads to a significant cell death to occur (for I and IV at concentration > 5 μM). Thus, the study of the synthesized Cu(II) complexes as potential antitumor drugs is a promising direction of research.

The further study of this class of compounds should include an extended range of biological targets and studying the magnetic properties of the mentioned substances.

This work was supported by the Russian Foundation for Basic Research (grant № 16-53-00020).

References

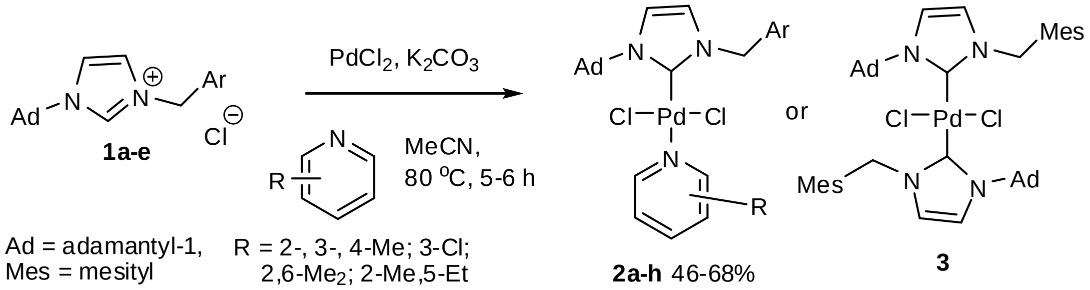
[1]. Roopashree B., Gayathri V., Mukund H. *J. Coord. Chem.*, **2012**, *65*, 1354-1355.
[2]. Jain K. S., Chitre T. S., Miniyar P. B., Kathiravan M. K., Bendre V. S, Veer V. S., Shahane S. R., Shishoo C. J. *Current Science*, **2006**, *90*, 793-802.

Synthesis and studies on catalytic performance of new NHC-Pd(II) peppsi-type complexes

Glushkov V.A. [1,2], Denisov M.S. [1], Gorbunov A.A. [2], Dmitriev M.V. [1]

[1]*Institute of Technical Chemistry, Ural`s Branch, Russian Academy of Sciences, 3 Acad.
Koroleva St., 614013, Perm, Russian Federation*
[2]*Perm State University, 15 Bukireva St., 614990, Perm, Russian Federation*
e-mail: glusha55@gmail.com

Unsymmetrical N-heterocyclic carbene ligands represent some new trend in research. Starting from adamantyl-substituted imidazolium salts **1a-e**, a series of Pd(II) PEPPSI-type complexes **2a-h** were synthesized (PEPPSI = Pyridine Enhanced Precatalysts: Preparation, Stabilisation and Initiation) [1]. In the absence of pyridine binuclear complex **3** was obtained.



Ad = adamantyl-1, R = 2-, 3-, 4-Me; 3-Cl; 2,6-Me_2; 2-Me,5-Et
Mes = mesityl

1: **a** Ar = Ph; **b** Ar = 3,5-$Me_2C_6H_3$; **c** Ar =2,4,6-$Me_3C_6H_2$,
d Ar = 2,3,5,6-Me_4C_6H

Complexes **2** and **3** were studied by single-crystal X-ray diffraction analysis; they all have *trans*-configuration, according to literary data.

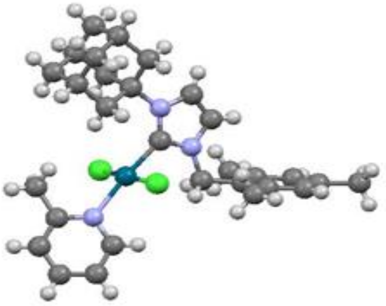


Fig. 1. Structure of compound **2c**

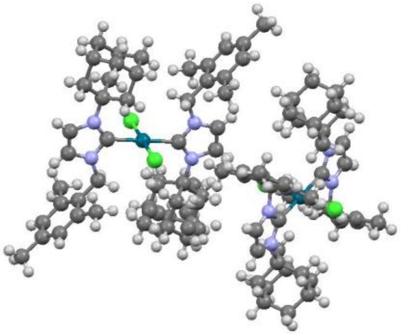


Fig. 2. Two molecules of **3**

Complexes **2a-h** are efficient precatalysts for Suzuki coupling of phenylboronic acid with 4-bromotoluene (5 mol% of Pd-cat., propanol-2, 2h, 80°, yields 75-98%) or with 4-chlorotoluene (5 mol% of Pd-cat., neat water, microwave activation, 10 min, 120°, yields 53-73%). Compounds **2,3** were also successfully tested in Heck and Sonogashira reactions.

This work was supported by Russian Foundation of Basic Research (Grant No. 17-03-00456).

References

[1]. C.J. O`Brien, E.A.B. Kantchev, C. Valente, N. Nadei, G.A. Chass, A. Lough, A.C. Hopkinson, M.G. Organ, *Chem. Eur. J.*, **2006**, *12*, 4743-4748.

Application of the method of electrometric titration for determination of oxidation level of atoms of manganese in the synthesized manganese oxides

Godunov E.B. [1,2], Izotov A.D. [2], Gorichev I.G. [1,3]

[1]Moscow Polytechnic University, B.Semenovskaya street, 38, Moscow, 107023, Russian Federation.
[2]Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31, Leninsky prospekt, Moscow,119991, Russian Federation.
[3]Moscow State Pedagogical University, 1, Malaya Pirogovskaya street, Moscow, 119992, Russian Federation.
e-mail: gen225@mail.ru

For studying of kinetic processes of dissolution of the received oxides of manganese and of change of composition of oxide of manganese in the course of dissolution it is necessary to know exact structure of the studied oxide sample. In work the potentiometric method of definition of structure consisting in the following stages is offered and checked.

Stage 1. Determination of content of atoms of oxygen in oxide.

The hinge plate of oxide of manganese weighing 300 mg was dissolved in 1 M the H_2SO_4 solution containing 0.01 mol of $FeSO_4$ when hashing on a magnetic mixer before full dissolution of oxide. The received solution of a titrated of 0.01 M $KMnO_4$ solution by an electrometric method before obtaining equivalent volume of $KMnO_4$ (V_1, ml).

Process of restoration can be described the reaction equation:

$$MnO_x + (2x-2)Fe^{2+} + 2xH^+ = Mn^{2+} + (2x-2)Fe^{3+} + xH_2O.$$

Counted volume $KMnO_4$ which has gone for definition of concentration of atoms of oxygen on a formula: $V_{ox} = V_0 - V_1$,

where V_0 — $KMnO_4$ volume which has gone for titration of initial quantity of $FeSO_4$, ml;

V_1 — $KMnO_4$ volume which has gone for titration of ions of Fe(II) of the ions of Fe(II) which have remained after restoration, ml.

Determination of the general content of initial iron (V_0, ml) based on reaction course:

$$5Fe^{2+} + MnO_4^- + 8H^+ = 5Fe^{3+} + Mn^{2+} + 4H_2O.$$

Stage 2. Definition of concentration of atoms of manganese in oxide.

The result obtained in step 1 was added and continued $Na_2H_2P_4O_7$ titrated 0.01 M solution of $KMnO_4$ (V_2, ml). In the titration of chemical reactions:

$$4Mn^{2+} + MnO_4^- + 8H^+ + 15H_2P_2O_7^{2-} = 5[Mn(H_2P_2O_7)_3]^{3-} + 4H_2O.$$

The general concentration of atoms of manganese in a sample of oxide of manganese was calculated by a formula:

$$V_{Mn} = V_2 - 0.25\cdot V_1,$$

From the relation of volumes:

$$V_{ox}/V_{Mn} = 0{,}8\cdot(2x-2).$$

counted composition of oxide of manganese (x = O/Mn) taking into account volumes of $KMnO_4$ which has gone for titration of oxide on a formula:

$$x = 1 + 0.625\cdot(V_{ox}/V_{Mn}).$$

On the example of oxide of manganese(IV) it is shown that its structure corresponds to a formula $MnO_{1.980}$, and when keeping in solution (pH 3.54, C(Mn^{2+}) = 0.005 M and 298 K), passes into oxide of structure $MnO_{1.865}$. This method is perspective for definition of composition of oxide of manganese in the absence of the expensive equipment.

Heteroligand metal complexes of alkoxi-β-diketonate species as prospective precursors for functional nanomaterials

Gorobtsov Ph.Yu., Ivanova V.M., Simonenko N.P., Simonenko E.P., Sevastyanov V.G., Kuznetsov N.T.

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

The sol-gel method for synthesizing materials attracts much interest nowadays. It is caused by the fact that this technology is quite versatile, allowing to prepare diverse types of nanomaterials, such as powder, thin films and 3D-materials (composites and ceramics). The choice of reactants has a large impact on the possibility of obtaining the product and on its properties. Some of the particularly prospective precursors for sol-gel synthesis are heteroligand metal complexes belonging to the alkoxi-β-diketonate class. By varying the composition of the coordination sphere of heteroligand complex, one can control the process of sol-gel synthesis and tune the necessary properties of the final products [1-5].

In this work the processes for preparing heteroligand metal complexes belonging to the isoamylacetylacetonate species were studied. Nickel, yttrium, aluminium, iron and europium cations were used as the central atoms for these compounds. The change of rheological properties of the solutions of the said complexes under hydrolysis has been studied utilizing the rotational viscometer. Methods of IR- and UV-spectroscopy and refractometry were also used in the study.

This research was carried out with partial support by the Russian Foundation for Basic Research (projects №15-03-07568 A and №15-29-01213 ofi_m).

References

[1]. Egorova T.L., Kalinina M.V., Simonenko E.P., Simonenko N.P., Shilova O.A., Sevastyanov V.G., Kuznetsov N.T., *Russ. J. Inorg. Chem.*, **2016**, *v. 61*, p. 1061.

[2]. Simonenko N.P., Nikolaev V.A., Simonenko E.P., Generalova N.B., Sevastyanov V.G., Kuznetsov N.T., *Russ. J. Inorg. Chem.*, **2016**, *v. 61*, p. 1505.

[3]. Simonenko N.P., Simonenko E.P., Sevastyanov V.G., Kuznetsov N.T., *Russ. J. Inorg. Chem.*, **2016**, *v. 61*, p. 667.

[4]. Simonenko N.P., Simonenko E.P., Sevastyanov V.G., Kuznetsov N.T., *Russ. J. Inorg. Chem.*, **2016**, *v. 61*, p. 805.

[5]. Simonenko N.P., Simonenko E.P., Sevastyanov V.G., Kuznetsov N.T., *Russ. J. Inorg. Chem.*, **2015**, *v. 60*, p. 795.

Binding properties of some of fluorine-containing aryl-*β*-diketones: biological activity and luminescent properties of metal complexes

Khamidullina L.A.[1,2], Pestov A.V.[2], Slepukhin P.A.[2], Khrustalev V.N.[3], Dorovatovskii P.V.[4], Shatunova S.A.[1], Puzyrev I.S.[1,2].

[1]*Ural Federal University, 620002, Ekaterinburg, 19 Mira Str.*
[2]*I. Ya. Postovsky Institute of Organic Synthesis UB RAS, 620990, Ekaterinburg, 22 Sofia Kovalevskaya Str.*
[3]*RUDN University, Russia, 117198, Moscow, 6 Miklukho-Maklay Str.*
[4] *National Research Centre «Kurchatov Institute», 123182, Moscow, 1 Acad. Kurchatov Sq.*
e-mail: lili.khamidullina@gmail.com

β-Diketones are promising multi-donor ligands for metal coordination and recognition which are valued for pharmaceutical and material science applications. They have been shown to exhibit antitumor, antiviral, antibacterial, antifungal, insecticidal and antioxidant activities. In some structure-activity relationship studies, the biological activity of such compounds is attributed to the presence of a *β*-diketone moiety. The presence of aryl ring in the molecular structure has a great effect on the antibacterial activity of the compound. Also fluorine and fluorine-containing substituents have an impact on biological properties of organic compounds. Furthermore, ability of *β*-diketones to form metal complexes may also play an important role in biological functions of the compounds.

Metal complexes of *β*-dicarbonyl ligands possess a variety of applications in the biological, analytical, clinical, and industrial areas. Transition metal complexes of *β*-diketone ligands have gained considerable attention, not only due to their spectroscopic properties and applications but also due to their remarkable antifungal, antibacterial and antitumor activities. With respect to the biological activity and desirable physicochemical, stereochemical, electrochemical, structural and catalytic properties of *β*-dicarbonyl metal complexes, their values have attracted significant attention.

In view of these facts, we decided to study the binding properties of a series of *β*-diketone derivatives and evaluate the biological activity and luminescent properties of their metal complexes.

Protolytic equilibria of the compounds in solutions were studied [1]. The binding properties of the ligands towards transition metal ions were studied using spectrophotometric method. The stoichiometric composition of the complexes in solutions was determined by the molar ratio and Job's methods, as well as Starik-Barbanel relative yield method. The formation of 1:2, 1:1 and 2:2 metal–ligand complexes was observed. X-ray analysis gives evidence the formation of complexes in which the ratio metal to ligand can be 1:2 and 2:2. Similar to *β*-triketones some of the studied ligands tend to formation of binuclear complexes with transition metal ions. Biological activity of the ligands and their metal complexes was evaluated. Aluminum [2] and boron complexes of some of the ligands were obtained and their luminescent properties were studied.

References

[1]. Pestov, A.V.; Khamidullina, L.A.; Sosnovskikh, V.Y.; Slepukhin, P.A.; Puzyrev, I.S. *Polyhedron*, **2016**, *106*, 75.

[2]. Khamidullina, L.A.; Obydennov, K.L.; Slepukhin, P.A.; Puzyrev, I.S. *J. Mol. Struc.*, **2016**, *1125*, 550.

Oxidation of ethylenediaminetetraacetate, diethylentriaminepentaacetate and their complexes with the metals of immobilized bacterial cells of *Chelativorans oligotrophicus* VKM B-2395

[1]Kuvichkina T.N., [1]Kaparullina E.N., [2]Safonov A.V., [2]Doronina N.V., [1]Reshetilov A.N.

[1]Federal Agency of Scientific Organizations Federal State Budgetary Institution of Science G.K.Skryabin Institute of Biochemistry and Physiology of Microorganisms, Russian Academy of Sciences 142290 Pushchino, Moscow region, prospekt Nauki, 5
[2]Federal Agency of Scientific Organizations Federal State Budgetary Institution of Science A.M.Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow,Obruchev str.,bld. 1
e-mail:kuv@ibpm.pushchino.ru

Complexons (such as polyaminopolyacetic acids) are referred to as polydentate chelate-forming ligands and these ligands are often called chelating agents and complexes comprising chelating agents are chelates. Sexidentate ethylenediaminetetraacetate (EDTA) and eightdentate diethylentriaminepentaacetate (DTPA) can be considered to be optimal as universally acting complexons. These complexons are used to remove interfering metal cation and, vica versa, to introduce the metals into a certain system. DTPA, due to its ability to form water-soluble complexes with bi- and trivalent metals, can be used in deactivation of nuclear reactors [1, 2]. Titrimetric method and high-performance liquid chromatography (HPLC) are conventional methods for detection of EDTA and DTPA, these methods are rather effective but expensive. It was previously shown that there exist some aerobic bacteria *Chelativorans oligotrophicus* VKM B-2395 that are able to oxidize tetraacetate (EDTA) using molecular oxygen. This property of bacteria was taken into account when creating an amperometric biosensor for detection of EDTA and complexes with ions Ba^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}[3] and developing a biosensor for determination of DTPA and its complexes with ions Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}[4]. The low limit of detection for EDTA was 0,125 mM; long-time stability was 14 days The low limit of determination for DTPA was 0,5 mM; long-time stability was 3 days. In future bacterial degradation of the DTPA complexes with metals by *Chelativorans oligotrophicus* VKM B-2395 has the potential to solve waste-disposal issues (deactivation of nuclear installations) and waste-recycling issues (establishments of nuclear fuel cycles).

References

[1]. Melentev, A.B.; Mashkin, A.N.; Tugarina, O.V.; Kolupaev, D.N.; German, K.E.; Tananaev, I.G. *Radiochemistry*, **2011**, *53*, № 2, 150-154.

[2]. German, K.E.; Melentev, A.B.; Zubavichus, Ya. V.; Kalmykov, S.N.; Shiryaev, A.A.; Tananaev, I.G., *Radiochemistry,* **2011**, *53*, № 2, 155-161.

[3]. Kuvichkina, T.N.; Kaparullina, E.N.; Doronina, N.V.; Trotsenko, Yu.A.; Reshetilov, A.N. *Applied biochemistry and microbiology,* **2012**, *48*, № 6, 626-630.

[4]. Kuvichkina, T.N.; Safonov, A.V.; Kaparullina, E.N.; Reshetilov A.N. *National association of scientists*, Yekaterinburg. **2015**, Part *2,* № 5 (10), 134-137.

Study of the electronic structure of the methacrylate components of Eu(III) using x-ray spectroscopy and the density functional theory

Mikhailenko E.V., Korochencev V.V., Vovna V.I.

Far Eastern Federal University, 690920, Vladivostok, Ajax
e-mail: elric2009@gmail.com

Organic acids RC(O)OH has been found wide application in the synthesis of mononuclear M(O2CR)n and binuclear M2(O2CR)n complexes of transition metals. The ability of the oxygen atoms of the carboxyl groups act as bridging allowed us to synthesis of macromolecular systems. The macromolecular system of the lanthanides are used as luminophores.

Quantum-chemical calculations were performed using the software package FireFly 8.1 using the functionality B3LYP5. For atoms H, C, O were used basis 6-311**G and ECP52MWB_GUESS for the Eu, developed by the Stuttgart/Cologne. X-ray spectra were obtained in ultrahigh vacuum photoelectron spectrometer of the company Omicron (Germany) with MgKα radiation source 1253,6 eV.

Spectra of methacrylate components have been received and processed: Eu(marc)3, Eu(macr)2(dbm), Eu(dbm)2(macr). Correlation diagram of the valence electronic levels were built using the calculated data. The calculation of the three methacrylate components of Eu(III) allowed us to obtain data on the geometrical structure and to analyze the electronic structure mapping of the x-ray spectrum with the Kohn-Sham's molecular orbitals. The research will allow to plan the synthesis of compounds with the required photochemical properties.

It was discovered that substitution of the macr-ligands to the dbm-ligands increases the metal-ligand ionic binding (if the charge difference between the ligands and the metal ion is increased, therefore the ion binding is increased too) due to the redistribution of charge on the carbons of the dbm-ligands in the study of the Mulliken's charges, which are shown in the table 1. Also there is a destabilization of the valence electronic levels and the mixing of orbitals macr and dbm in the study of the correlation diagram. Then it was produced a comparison of the theoretically calculated bands with x-ray spectra. In region 2-4 eV is the peak O2p, in the region 6-8 eV is peak C2p, and at 21-23 eV - Eu5p, and theoretically calculated extreme strip level of the Eu5p level is shifted at 0,30/0,50 eV to the lowest energies.

Table 1. Mulliken's charges of methacrylate components of Eu(III)

	Eu(macr)3	Eu(macr)2(dbm)	Eu(macr)(dbm)2
N	q(Mull)	q(Mull)	q(Mull)
Eu	1,56	1,64	1,73
macr	-0,52	-0,53	-0,55
2O(macr)	-1,09	-1,08	-1,08
dbm		-0,57	-0,59
2O(dbm)		-1,31	-1,29

Enhancing the cytotoxic activity of anticancer Pt(IV) complexes by introduction of glycolysis inhibitor as an axial ligand

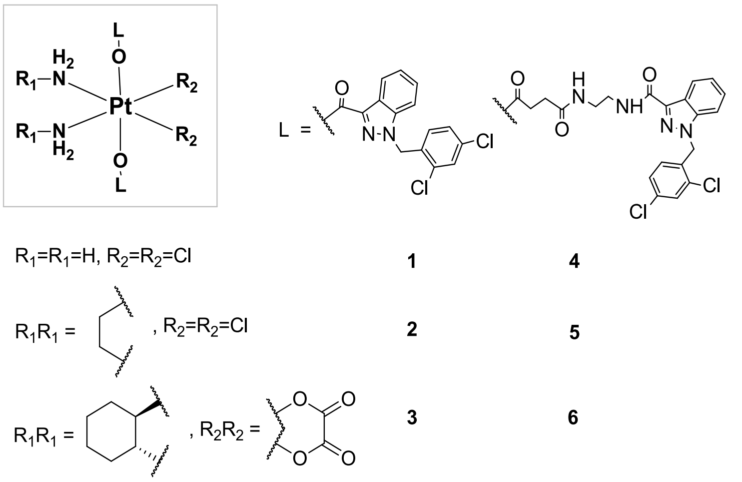
Nosova Y.N.[a], Zenin I.V. [a], Zadorozhnaya O.I. [b], Fetisov T.I. [b], Kirsanov K.I. [b], Milaeva E.R.[a],
Nazarov A.A. [a]

[a] M.V.Lomonosov Moscow State University, Faculty of Chemistry, 119991, Russia, Moscow,
Leninskie gory 1/3 e-mail: nosovayulia@yahoo.com
[b] N.N.Blokhin Cancer Research Center RAMS, Moscow, Russia.

Anticancer Pt(IV) complexes have recently considerable interest due to their kinetical inertness and specific reactivity in the reducing milieu of the cancer cell (activation by reduction), lower general toxicity, and possibility of oral administration. In cancer chemotherapy, drug combinations are widely applied, and therefore incorporation of a bioactive ligand can increase the activity or selectivity of new complexes and realize the controlled release of an active organic molecule. One of the synthetic advantages of Pt(IV) complexes is the possibility to covalently link biologically active ligands at the respective axial positions.

In this work, by attaching glycolysis inhibitor lonidamine to cisplatin or oxaliplatin metal center, the novel complexes with specific mode of action were obtained.

All synthetized compounds were characterized by NMR (^{1}H, ^{13}C, ^{195}Pt) spectroscopy, ESI-MS and elemental analysis [1]. The structure of oxaliplatin-based compound was established by X-ray analysis. The antiproliferative activity of the Pt(IV) complexes was investigated against several cancer cell lines (A549, SW480, MCF7). All complexes showed higher in vitro activity in comparison to the lonidamine and cisplatin.



Compounds	IC$_{50}$, µM MCF-7
1	0.45±0.3
2	0.03±0.008
3	0.5±0.2
Lonidamine	8.5±2.1
Cisplatin	16±4.8

This work was supported by the Russian Foundation for Basic Research (grant № 16-03-00743).

References

[1]. Nosova Y. N.; Foteeva L. S.; Zenin I. V.; Fetisov T. I.; Kirsanov K. I.; Yakubovskaya M. G.; Antonenko T. A. ; Tafeenko V. A. ; Aslanov L. A.; Lobas A. A.; Gorshkov M. V.; Galanski M.; Keppler, B. K.; Timerbaev A. R.; Milaeva E. R. and Nazarov A. A. *Eur. J. Inorg. Chem.,* **2016**, doi:10.1002/ejic.201600857

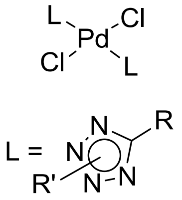
DNA/protein binding and gel electrophoresis studies of novel water soluble palladium(II) complexes featuring tetrazolylacetic acids and their esters

Protas A.V., Popova E.A., Mikolaichuk O.V., Mukhametshina A.V., Ovsepyan G.K.,
Volkov K.V., Suslonov V.V., Alekseev G.V., Kasyanenko N.A. and Trifonov R.E.

Saint Petersburg State University, 199034, Saint Petersburg, Universitetskaya emb. 7/9
e-mail: aleksandra.protas@mail.ru

It is known that some palladium(II) complexes with heterocyclic ligands exhibit comparatively high anti-tumor activity [1, 2].

Here water soluble palladium(II) complexes containing tetrazolylacetic acids and their esters derivatives as ligands were synthesized and characterized by means of HRESI-MS, ^{1}H and ^{13}C{^{1}H} NMR, IR spectroscopies, and DSC/TG analysis. The structure of the complexes obtained established by X-ray diffraction analysis.



R: CH_3, COOH, COOEt
R': ^{i}Pr, ^{t}Bu

Calf-thymus DNA and an abundant plasma protein have been taken as models for the two major targets for metallodrug interactions by CD, UV/VIS and fluorescence spectroscopy. The effect of the compounds on pBR322 plasmid DNA was studied by gel-electrophoretic mobility measurements. The studies have shown that the complexes effectively bind with calf thymus DNA (CT DNA) through electrostatic interactions. In addition, these complexes cause static quenching of the bovine serum albumin fluorophore.

The authors acknowledge Russian Foundation for Basic Research for financial support of a joint project (grants 16-53-00047 Bel_a) and St.Petersburg State University (Grant 12.38.428.2015).

References

[1]. Brown, S.D.; Trotter, K.D.; Sutcliffe, O.B.; Plumb, J.A.; Waddell, B.; Briggsa, N.E.B.; Wheate, N.J. *Dalton Trans.*, **2012**, *41*, 11330.

[2]. Ulukaya, E.; Ari, F.; Dimas, K.; Ikitimur, E.I.; Guney, E.; Yilmaz, V.T. *Europ. J Med. Chem.*, **2011**, *46*, 4957.

The use of metal polyolates in synthesis of metal oxides and composites

Puzyrev I.S.[a], Andreikov E.I.[a], Zakharova G.S.[b]

[a] *Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, 620990, Ekaterinburg, Sofia Kovalevskaya str. 22*
[b] *Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences, 620990, Ekaterinburg, Pervomaiskaya str. 91*
e-mail: igor.puzyrev@mail.ru

The demands for high-power are led to the extensive research efforts on the development of electrode materials with low cost, high capacity, chemical stability, and environmental friendliness [1]. For this purpose the composites transition metal oxide/carbon are successfully applied. Moreover, the composites have found applications in a great number of areas such as catalysis, sorption etc. The synthesis of such materials based on employment of metal alkoxides and other solid precursors has such advantages as the ease of fabrication and high yields [2,3].

While preparation of metal oxides from solid alkoxides the morphology of precursors remains for target products. However metal alkoxides are expensive and easy hydrolysable. Moreover, this consistent pattern has not yet been demonstrated to be true as applied to metal oxide composites.

In this work, we studied the transformation of metal polyolates into one-dimensional metal oxides (TiO_2, ZrO_2, HfO_2) as well as we developed the effective methods for the synthesis of the composites TiO_2/C and ZnO/C. In case of composites synthesis the main stage is the thermal treatment of metal/glycerol complexes (TiGly and ZnGly) in inert atmosphere at variable temperatures, for which purpose we originally tested the behavior of TiGly and ZnGly in air and Ar flow by using the thermogravimetric analysis. Based on the results the conditions of composites synthesis were chosen. During the process, the products retain the morphology of precursors in the same manner as it is observed for metal oxides [2]. The obtained composites were characterized by TGA, FT-IR and Raman spectroscopy, XRD analysis, and nitrogen adsorption.

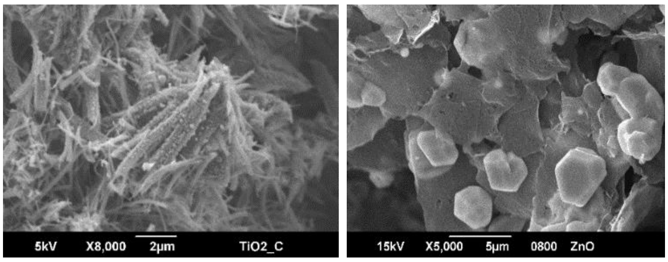


Fig. 1. Examples of morphologies of TiO_2/C and ZnO/C composites.

In summary, a facile synthesis method of titanium oxide/carbon rod-like composites has been developed through a titanium glycerolate carbonization in inert atmosphere. Also it was shown that zinc glycerolates were successfully used to obtain of zinc oxide/carbon composites. The obtained materials are of interest for different applications.

This work was supported by the Presidium of Russian Academy of Sciences (project 15-21-3-6).

References

[1]. Dahl, M.; Liu, Y.; Yin, Y. *Chem. Rev*, **2014**, *114(19)*, 9853.
[2]. Zhao, J.; Liu, Y.; Fan, M.; Yuana, L.; Zou, X. *Inorg. Chem. Front.*, **2015**, *2*, 198.
[3]. Lian, S.; Huang, H.; Zhang, J.; Kang, Z.; Liu, Y. *Solid State Commun.*, **2013**, *155*, 53.

Electronic structure of adducts of Eu(III) β-diketonates complexes

Shurygin A.V., Korochentsev V.V., Vovna V.I.

Far Eastern Federal University, Vladivostok, Russia
shurygin.av@dvfu.ru

Lanthanide complexes with organic ligands are widely used in various areas of science and technology and in biomedicine as light transforming materials, luminescent light sources, and photochemical sensors. Luminescence excitation in the visible and near IR ranges considerably depends on the ligands and can change by two to three orders of magnitude. The luminescence quantum yield is determined by the efficiency of non-radiative transitions, which depends on the energy gap between the lowest triplet state of the ligands and the excited state of *f*-electrons and on the localization of excitation on functional groups of the ligands.

Among the chemical compounds of rare earth elements which are of interest for the development of light-transforming materials includes a broad class of adducts of tris-β-diketonates with the general formula $Ln(OC_{\beta}(R_1)C_{\gamma}HC_{\beta}(R_2)O)_3 \cdot L$.

The influence of ligands, including β-diketonate ligands, on the luminescence properties of europium has recently been considered using Eu^{3+} as an example. An analysis of the dependence of spectral luminescence properties of the complexes on their electronic structure and orbital nature of the chemical bonds makes it possible to plan the synthesis of new compounds with desired optical properties.

Coordinative unsaturation of the most part of lanthanide tris(β-diketonates) predetermines the wide use of their adducts as luminescent materials with such neutral ligands as Phen (1,10-phenantroline), TPPO (triphenylphosphineoxide), HMPA (hexamethylphosphoramide), and Dip (dipyridyl). Instrumental possibilities of an X-ray spectrometer do not allow one to carry out the detailed analysis of the highest occupied levels involved in luminescence excitation. The UPS spectra of the sublimation products in the spectrometer of these complexes at 200°C clearly illustrate the change in the structure of the valent MOs (including the 2p orbitals of fluorine in a range of 16 - 18 eV) with the introduction of additional ligands into the coordination sphere of Eu.

In this work we use experimental X-Ray spectroscopy (MgKα) and density functional theory methods (DFT/TDDFT/B3LYP5/ECP52MWB/6-311G*) to investigate adducts of tris-β-diketonates (Acac – acetylacetonate; Hfac – hexafluoroacetylacetonate) of Eu(III) and Lu(III) with 1,10-phenantroline. Quantum chemical calculations have shown that the geometry of the coordination sphere LnO_6N_2 close to the square antiprism. Geometrical structure of 1,10-phenanthroline is almost independent of the chemical environment. The value of destabilization MO tris-chelate complexes with adducting an average of 0.7 eV. From the analysis the obtained data we see that the orbital 1,10-phenanthroline are involved in the mixing only with the orbitals, the energy of which is from 8 to 10 eV. With the data of theoretical calculations agree with experimental, we assume that the addition of 1,10-phenanthroline to the tris-β-diketonates complexes Eu and Lu is destabilized complex levels and stabilizing levels of 1,10-phenanthroline.

The distribution of charges for the three adducts evidence of the presence of polarization tris-chelate rings with a neutral ligand 1,10-phenanthroline and ion-dipole interaction between chelate fragment and 1,10-phenanthroline. Addition of 1,10-phenanthroline shifts the position of the excitation band in the red region thus reducing energy transition break with orbitals of the ligand to the metal and increasing the probability of transition.

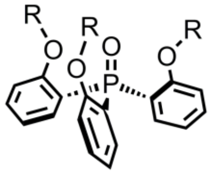
As a result of research it was shown the applicability of the chosen calculation method to the interpretation of the photoelectron spectra with sufficiently accurate results, allowing to analyze and identify features of electronic effects after adducting.

Novel type of preorganized C3-symmetrical triarylphosphine oxide tripodal kigands: synthesis, coordination and extraction properties

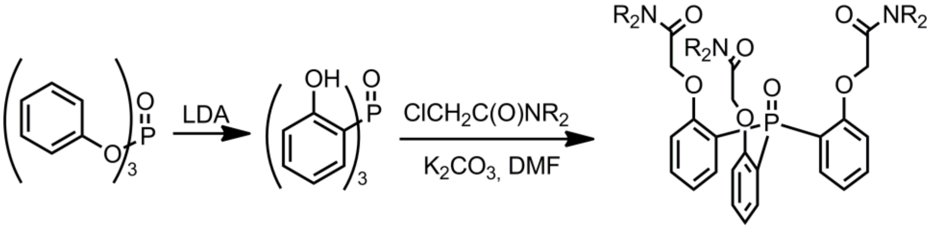
Sukat G.Ya. [1], Tsyplenkova A.V. [1,2], Kudryavtsev I.Yu. [1], Baulina T.V. [1], Matveeva A.G. [1],
Vologzhanina A.V. [1], Turanov A.N. [3]

[1]Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia
e-mail: zaq@ineos.ac.ru
[2]Higher Chemistry College of Russian Academy of Sciences, Mendeleev University of
Chemical Technology of Russia, Miusskaya pl. 9, 125047 Russia
[3]Institute of Solid State Physics, Russian Academy of Sciences, ul. Academica Osipyana
2, Chernogolovka, Moscow oblast, 142432 Russia

Ortho-substituted triarylphosphine oxides adopt the most stable conformation as an unsymmetrical propeller where the substituents in the ortho positions are oriented to the same direction as the phosphoryl group. This conformational feature provides a possibility to design a new type of polydentate tripodal ligands on this basis by introduction of various donor groups into the substituents. The concerted orientation of side donor atoms and the phosphoryl group produces a preorganized tripodal ligand, which may be applied for artificial receptors design as well as for extraction of metals from aqueous solutions.



Potentially tetradentate tripodal ligands **1a-c** with carbamoyl side arms have been synthesized in two steps from tris(2-hydroxyphenyl)phosphine oxide. Compounds obtained have been studied by means of elemental analysis, X-ray diffraction, IR and multinuclear NMR spectroscopy.



1a-c

R = Me (**a**), Bu (**b**), C_6H_{11} (**c**)

Complexes of compounds **1a-c** with lanthanide (La, Nd, Lu) nitrates have been obtained and characterized using elemental analysis, IR and multinuclear NMR spectroscopy. Complex of ligand **1a** with neodymium nitrate has also been studied by means of X-ray diffraction. Extraction properties of ligands **1a-c** toward a series of rare earth elements have been investigated. Compounds **1b** and **1c** proved to be efficient extractants.

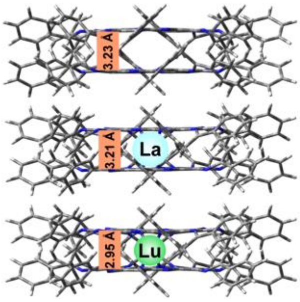
Structural features of sandwich-type tetradiazepinoporphyrazine lanthanide complexes

Tarakanova E.N.,[1] Simakov A.O.,[2] Tarakanov P.A.,[1] Dorovatovskii P.V.,[3] Zubavichus Y.V.,[3]
Khrustalev V.N.,[4] Pushkarev V.E.,[1] Tomilova L.G.[1]

[1]*Institute of Physiologically Active Compounds, RAS, Chernogolovka, Russian Federation*
e-mail: tarakanova.ek.nik@gmail.com
[2]*University of Oslo, Oslo, Norway*
[3]*National Research Centre “Kurchatov Institute”, Moscow, Russian Federation*
[4]*Peoples’ Friendship University of Russia, Moscow, Russian Federation*

Recently, we have reported the preparation of a series of sandwich double-decker tetradiazepinoporphyrazine-based lanthanide complexes [1-4]. The formation of sandwich-type complexes took place under relatively mild reaction conditions. Moreover, the corresponding early lanthanide double-deckers demonstrated high stability towards dissociation as compared with phthalocyanine (Pc) counterparts [3].

To gain insight into the structural features of this type of compounds, we analyzed the structure of the free-base ligand and the double-deckers obtained using two-dimensional NMR techniques combined with quantum chemical calculations [4]. A combination of experimental and theoretical studies revealed the presence of two types of hydrogen bonding interactions in the metal-free porphyrazine and the corresponding sandwich complexes, namely, interligand C–$H^{ax}\cdots N^{meso}$ hydrogen bonding and O–$H\cdots N^{Dz}$ ligand–water interaction [4]. Thus, the presence of interligand hydrogen bonding facilitates the formation of tetradiazepinoporphyrazine double-deckers compared to lanthanide bis(Pcs) and stabilizes the corresponding early lanthanide double-decker complexes towards dissociation.



Very recently, we have succeeded in crystal structure determination of 1,4-diazepinoporphyrazine compound using synchrotron radiation X-ray diffraction analysis. To our knowledge, this is the first example of the crystal structure of diazepine-containing macroheterocycle. The structural data completely agree with the results of quantum-chemical studies [4], which provides a unified understanding of the nature of specific interactions in 1,4-diazepinoporphyrazine compounds.

This work was supported by RFBR (Grant Nos. 16-33-00097, 15-03-05890), the Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grant MD-2991.2017.3) and the Ministry of Education and Science of the Russian Federation (Agreement 02.a03.21.0008).

References

[1]. Tarakanova E.N.; Tarakanov P.A.; Pushkarev V.E.; Tomilova L.G. *J. Porphyrins Phthalocyanines*, **2014**, *18*, 149–154.

[2]. Tarakanova E.N.; Levitskiy O.A.; Magdesieva T.V.; Tarakanov P.A.; Pushkarev V. E.; Tomilova L.G. *New J. Chem.*, **2015**, *39*, 5797–5804.

[3]. Tarakanova E.N.; Trashin S.A.; Tarakanov P.A.; Pushkarev V.E.; Tomilova L.G. *Dyes Pigm.*, **2015**, *117*, 61–63.

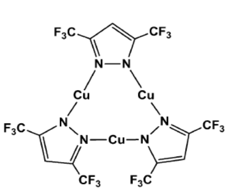
[4]. Tarakanova E.N.; Trashin S.A.; Simakov A.O.; Furuyama T.; Dzuban A.V.; Inasaridze L.N.; Tarakanov P.A.; Troshin P.A.; Pushkarev V.E.; Kobayashi N.; Tomilova L.G. *Dalton Trans.*, **2016**, *45*, 12041–12052.

Complexes formed by trimeric copper(I) and silver(I) pyrazolates with phosphorus containing compounds

Titov A.A.[1,2], Filippov O.A.[2], Guseva E.A.[2], Tunik S.P.[3], Shubina E.S.[2]

[1]Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
[2]INEOS RAS, 119991 Moscow, Vavilov str. 28
[3]Saint-Petersburg State University, Institute of Chemistry, 198504, Saint Petersburg, Petergof, Universitetskii pr. 2
e-mail: tit@ineos.ac.ru

Complexes of d^{10} metals with nitrogen-containing donor ligands has recently attracted strong attention because of their interesting properties for fundamental researches and practical application aspects. There are great interest to the chemistry of d^{10} transition metals pyrazolates. Investigations show that coinage metals form with pyrazole the macrocyclic compounds in general formula $[M(Pz)]_n$ (n=3, Scheme 1), where n depends on the type of substituents in the pyrazolate ligand and a metal atom. Cu(I) and Ag(I) macrocyclic pyrazolates displaying interesting luminescence properties and ability to form supramolecular aggregates due to π-acid/π-base or metallophilic interaction [1]. Here we report study of strong complex formation of $[CuL]_3$ with $[Cp^*Fe(\eta^5\text{-}P_5)]$. In this complex macrocycle plane folded along the Cu···Cu axis to 89°. Folding of the macrocycle results in new, high-energy orbital interactions that are otherwise impossible. Copper atoms were shown to play the role of both Lewis acid and Lewis base [3].



Scheme 1

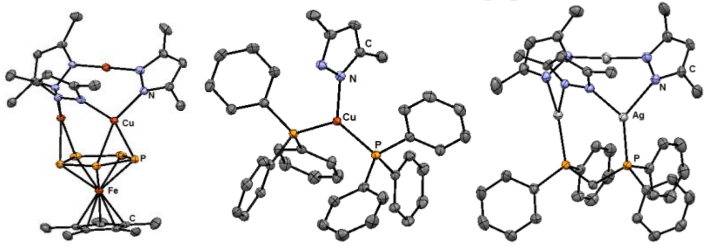


Figure 1. Structures of complexes $[ML]_3$ with $[Cp^*Fe(\eta^5\text{-}P_5)]$, PPh_3 and dppm.

The study of complexation of trinuclear d10 metals pyrazolates with phosphorus-containing compounds will be discussed. XRD indicates phosphorus coordination to metals in macrocycles, which leads to the bending of macrocycles planes. Complexes show green-blue luminescence in solution of CH_2Cl_2 and solid state at RT and 77K.

This work was financially supported by Ministry of Education and Science of the Russian Federation (the agreement № 02.a03.21.0008), Russian Foundation for Basic Research (projects № 15-03-08017, 16-33-50280).

References

[1]. H.V.R. Dias, H.V.K. Diyabalanage, M.A. Rawashdeh-Omary, M.A. Franzman, M.A. Omary, *J. Am. Chem. Soc*., 125, 12072.

[2]. V. N. Tsupreva, A. A. Titov, O. A. Filippov, A. N. Bilyachenko, A. F. Smol'yakov, F. M. Dolgushin, D. V. Agapkin, I. A. Godovikov, L. M. Epstein, E. S. Shubina, *Inorg. Chem*., **2011**, 50, 3325.

[3]. O. A. Filippov, A. A. Titov, E. A. Guseva, D. A. Loginov, A. F. Smol'yakov, F. M. Dolgushin, N.V. Belkova, L. M. Epstein, and E. S. Shubina *Chem. Eur. J.* **2015**, 21, 13176.

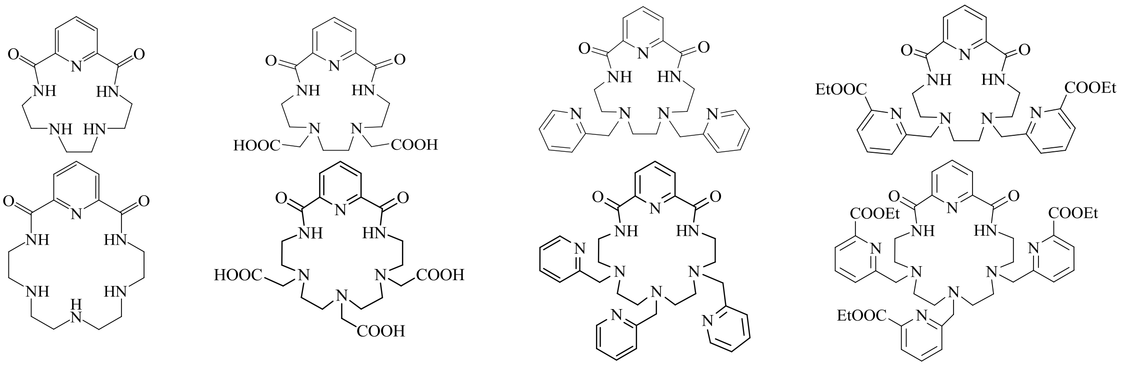
Synthesis and complex formation of pyridine-azacrown macrocycles with heavy and rare earth metal ions in aqueous solution

Zubenko A.D.[1], Egorova B.V.[2], Fedorova O.A.[1], Fedorov Yu.V.[1], Kalmykov S.N.[2]

[1]A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia
[2]Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow, Russia
e-mail: nastya.mutasik@rambler.ru

Recent biomedical applications of metal complexes have a growing interest in the synthesis and study of new chelators that form highly stable and kinetically inert complexes with various ions. Today, only complexes based upon DOTA (tetraazacyclododecanetetraacetatic acid) and DTPA (diethylenetriaminepentaacetic acid) have been widely used in biomedicine. Unfortunately complexes of DTPA are kinetically labile, and DOTA has low complex formation rate with metal ions. Thereby the goal of our work is development of novel chelators for metal ions that have more favorable formation kinetics and remain inert toward dissociation.

In the present research a series of pyridine-containing 15- and 18-membered azacrown macrocycles with two or three pendant arms (carboxylate and pyridine) have been synthesized. The coordination properties of their complexes with heavy and rare earth metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Y^{3+}, Eu^{3+}, Lu^{3+}, Bi^{3+}) in aqueous solutions, as well as cytotoxicity and radiolysis resistance were investigated.



It was demonstrated that both the size of the cavity and its heteroatom composition were important factors influencing on complex formation with the metal ions. The introducing of additional coordination groups improves the binding properties of pyridine-azacrown macrocycles. The greatest impact on the stability of the complexes provides the presence and amount of carboxyl substituents in macrocycles. Along with an increase in stability of complexes the reduction of selectivity of complex formation is observed. Also it was shown that pyridine-crown macrocycle with three carboxylic pendant arms is attractive ligand for binding of Cu^{2+} and Bi^{3+} ions applicable for synthesis of radiopharmaceuticals due to fast complex formation. X-ray diffraction analysis and potentiometric data showed that in ligands N-amide atoms do not participate in coordination with protons or metal cations. Nevertheless the rigid structure of pyridine-2,6-dicarbamide fragment and an open macrocyclic cavity provide a possibility to fast kinetics of complex formation. Thereby developed chelators based on azacrown compounds are promising for use in biomecicine.

We thank the RSF grant № 16-13-10226 and grant RAS № P-8 for financial support.

Poster Session

Concentrating lead(II) with chelating sorbent

[1]Aliyeva R.A., [2]Huseynova N.S., [1]Abilova U.M., [1]Chiragov F.M.

1. *Baku State University, 1148, Baku, Z. Khalilov str. 23, Azerbaijan*
2. *Azerbaijan Medical University, 1048, Baku, A. Bakuxanov str. 21, Azerbaijan*

e-mail: u.abilova@mail.ru

One of the important ecological problem is control of heavy metals in natural and industrial objects on level their limit permissible concentration and below. Therefore arise a necessity in elaboration new methods of collection heavy metals with following determination different methods. For the extraction of heavy metals and lead are used complexing sorbents containing functional analytical groups of atoms of nitrogen and sulfur [1-3]. In this paper, was obtained by a new polymeric sorbent containing fragment of sulfadimezini.

This invention censers to derivatives of copolymer of malein anhydride-styrene and can be used in analytical chemistry and hydrometallurgy for extraction of lead(II) and its concentration.

Essence of the invention is concluded in that copolymer of malein anhydride-styrene modification with sulfadimezini. The Reaction is conducted on sand bath, under unceasing mixing. Whereas, reaction is conducted in water phase anhydride groups consist in copolymer hydrolyzes. In system from interaction phormaldehide and amine is formed unstable carbonylamin, which interacts with carbocsyl group consist in macromolecule with the result that amino fragment falls into macromolecule. The Announced sorbent possesses high sorption characteristic to lead(II). As follows, sorption capacity to lead ion in water solution 463 mg /g and degree of sorbtion -99,6%.

The composition of obtained sorbent has been studied by the IR-spectroscopy method. In static condition has been researched influence pH an ionic strength liquid phase to sorption ion Pb(II) by the synthesized sorbent. This sorbent adsorb Pb(II) at pH 6 and the install time, sorption equilibrium does not exceed 180 minutes. Lead content in solution was determined by photometric method. Number of adsorbed lead was determined by the difference of the metal content before and after sorption. The effect of pH on the preconcentration of the ions Pb(II) in static conditions in the chelating sorbent in the pH range 1-8. At low pH of the liquid phase (pH 1.4), the low degree of extraction may be associated with protonation of functional groups present in the sorbent phase and a low degree of swelling of the polymer. With increasing pH of the liquid phase (pH 5-6) the degree of swelling of polymer sorbents increases.

It has been influence sorption processes from concentration of ion Pb(II) and time. It has been research influence equally capacity and concentration of acid $HClO_4$, H_2SO_4, HCl, HNO_3, H_3PO_4 on desorption sorbed ion Pb(II) from polymer sorbent. The experiment shows that H_2SO_4 desorbs Pb(II) ion from the polymer adsorbent better than others. The study of increasing of the concentration of H_2SO_4 shows that the desorption process increases till 2mol/l concentration of H_2SO_4. Above this concentration desorption degree does not increase. It may be concerned with the arrangement and stability of remaining xelat cycles.

Adsorption and desorption processes has been taken place in static condition.

References

[1]. Lyapunov S.M.; Sereqina İ.F. and etc. *Environment and Natural Resources: Review inform.* **1998**. № 11. p. 219-224.
[2]. Cepalev S.V. *Abstract of the thesis for the degree of Candidate of Chemical Sciences*, **2011**
[3]. Polyanskiy N.Q. Analytical chemistry of elements. lead *M.: Nauka*, **1986** . 357 c.

Synthesis, characterization and thermal decomposition of hexamethylenetetramine complexes with cobalt(II) and nickel(II) bromides and iodides

Al-gburi M.F., Savinkina E.V., Davydova M.N.

Moscow Technological University, Institute of Fine Chemical Technologies, prospekt Vernadskogo 86, Moscow, 119571, Russia
e-mail: misskorea60@yahoo.com

There has been some considerable and renewed interest in the synthesis and characterization of metal complexes of hexamethylenetetramine (HMTA) [1], e.g. hexamethylenetetramine complexes of cobalt(II) and nickel(II) forming three-dimensional networks [2]. Hexamethylenetetramine as a ligand can bind either in a monodentate manner to a metal, acting as bridging ligand linking two, three, or four metals, or bind to metal-containing species through the formation of hydrogen bonding. The combination of both covalent and hydrogen bonding in certain complexes of hexamethylenetetramine leads to the formation of three-dimensional structures that easily decompose by thermal treatment to give thin films of metal oxides [3].

We have synthesized and studied the complexes of the $MX_2 \cdot 2HMTA \cdot 10H_2O$ composition, where M = Co, Ni; X = Br, I. Composition of the compounds is confirmed by elemental analysis. X-ray diffraction patterns of the complexes show that they are isostructural to the earlier reported complex $[Ni(H_2O)_6]Cl_2 \cdot 2HMTA \cdot 4H_2O$ [4]. The central atom is bonded to six aqua ligands giving an octahedral geometry.

Infrared spectra were obtained in the range of 400–4000 cm^{-1} at room temperature. We can see bands at 3440–3443 cm^{-1}, ν(OH) (water); at 2922–3123 cm^{-1}, $\nu_{as}(CH_2)$; at 1457–1465 cm^{-1}, $\nu_{scissor}(CH_2)$ (HMTA); at 1203–1240 cm^{-1}, $\nu_{rock}(CH_2)$, C–N (HMTA); at 1009–1055 cm^{-1}, ν(C–N) (HMTA); at 812–817 cm^{-1}, ν(C–N) (HMTA), at 629–672 cm^{-1}), δ(NCN) (HMTA). The bands of HMTA do not shift on complex formation indicating its position on the outer spheres of the complex compounds.

Thermal studies show decomposition patterns corresponding to the loss of the uncoordinated and coordinated water molecules, followed by loss of HMTA and halide ions. Decomposition of the complexes begins at 68–82°C with the loss of 1–2 H_2O molecules; at 155–170°C all other H_2O molecules are removed; at 263–282°C the compounds lose one HMTA molecule; over 400°C bromide, iodide ions and HMTA ligand are removed in the form of a mixture of gases.

References

[1]. Yufanyi, D.M.; Tendo, J.F.; Ondoh, A.M.; Mbadcam J.K. *J. Mater. Sci. Res.*, **2014**, *3*, no. 3, 1.
[2]. Mbonu, I.J.; Okpalaezinne N.P. *Chem. Mat. Res.*, **2015**, *7*, no. 2, 52.
[3]. Prabhu, Y.T.; Rao, K.V.; Kumar, V.S.S.; Kumari B.S. *Adv. Nanoparticles*, **2013**, *2*, 45.
[4]. Agwara, M.O.; Ndifon, P.T.; Yufanyi, M.D.; Foba Tendo, J.N.; Atamba, M.A.; Awawou, P.G.; Galindo, A., Álvarez E. *Rasayan J. Chem.*, **2010**, *3*, 207.

Recyclable micellar catalysts for hydrogenation of ketones in water

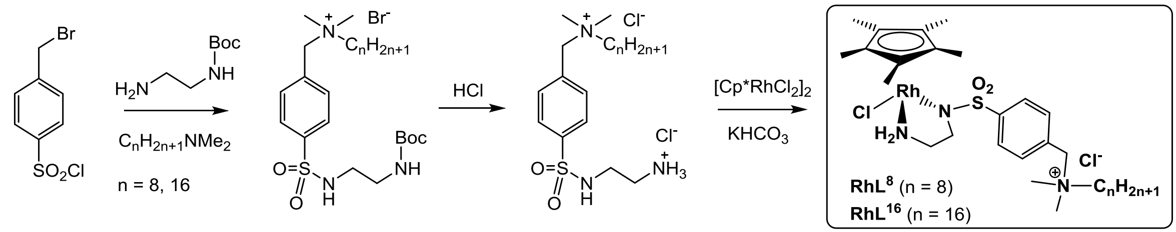
Antonova A.S.[1,2], Peganova T.A.[2], Kalsin A.M.[2]

[1] *Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6.*
[2] *A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), 119991 GSP-1, V-334, Moscow, 28 Vavilova str.*

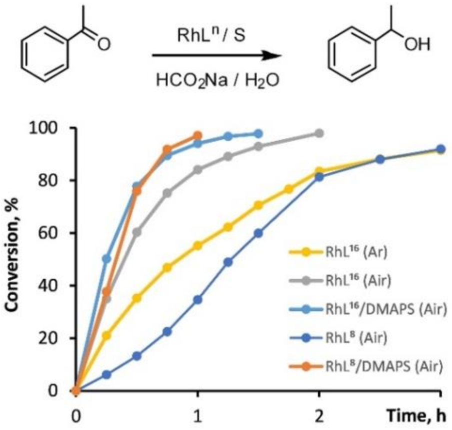
Modern chemical industry is experiencing a spectacular increase of the use of hetero- and homogeneous catalysts in producing different chemicals. Replacement of classical processes with other based on more effective / selective catalysts is an important target as it can significantly reduce industrial wastes [1]. Transfer hydrogenation of ketones in water by formates is a versatile and "green" method of preparing secondary alcohols with high atom-economy, however until early 2000s it was limited mostly to (partially) water-soluble substrates.

Recently we have developed a convenient method for the synthesis of surface-active ruthenium complexes [(*p*-Cym)RuCl(**L^n**)] (**RuL^n**) with a diamine ligand **L^n** functionalized with a quaternary ammonium group bearing long alkyls C_nH_{2n+1} (n = 8,16) [2]. These catalysts are highly active for transfer hydrogenation of (hydrophobic) ketones in water and can be reused after catalytic cycle multiple times. Unlike **RuL^{16}**, the complex with shorter alkyl "tail" **RuL^8** does not leach to the organic solvent phase during extraction of the product and thus can be used as a recyclable catalyst. We have shown that **RuL^8**-based catalytic system can be used at least 10 cycles, however its strict protection from air is mandatory.

Here we report the development of a recyclable micellar catalytic system based on novel surface-active complexes **RhL^n** for reduction of ketones in water that is *tolerant to air*.



The complexes **RhL^8**, **RhL^{16}** were fully characterized spectroscopically, by ESI-MS and elemental analysis. The catalytic study showed that **RhL^n** are highly active in hydrogenation of model ketone (acetophenone) in water, moreover their activity can be greatly improved by the addition of zwitter-ionic surfactant $C_{14}H_{29}NMe_2^+(CH_2)_3SO_3^-$ (DMAPS). Interestingly, these catalysts are stable and even more active on air and thus satisfy the initial objective. We demonstrated that **RhL^8**-based catalytic systems can perform at least 6 cycles on air without significant activity decay. Further tests with hydrophobic substrates are in progress.



This work was supported by the Russian Science Foundation (grant № 14-13-00801).

References

[1]. P.T.Anastas, J.C.Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.

[2]. A.M. Kalsin, T.A. Peganova, V.V. Novikov, A.I. Zhamoitina, L. Gonsalvi, M. Peruzzini, *Chem. Eur. J.* **2014**, *20*, 846.

An influence of the basicity ligand on the behavior of chromium-pyrrole catalytic systems

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

Irkutsk State University, 664003, Irkutsk, K. Marksa str. 1
e-mail: legatt112@yandex.ru

A literature review [1] shows in recent years the number of papers devoted to the selective tri- and tetramerization processes has become more and more. In different years, homogeneous chrome-pyrrole catalytic systems have been studied by many foreign researchers of oil refining companies. Successfully implemented elaborations industrial processes include catalytic systems such as chromium(III) / organoaluminum cocatalyst / L / modifier, L are N-donor stabilizing ligands of the pyrrole series.

Despite the existence of literature devoted to the study of chrome-pyrrole catalytic systems with various substituted pyrroles (in most cases there are two-substituted pyrroles having substituents in the 2 and 5 positions), papers dealing directly with the study of the effect of substituents into the pyrrole ring and on the nitrogen atom, in the literature is not available. Acid-basic properties of pyrrole ligands can be carried out by theoretical calculations using the methods of quantum chemistry [2]. Mentioning the successful prediction of catalytic properties on the basis of quantum-mechanical calculations there are in the literature. As a result of the DFT calculations, the authors [3] predicted 6 new PNP ligands, in a highly selective ethylene trimerization on chromium-containing catalytic systems.

For this reason, in [4] the pyrrole series ligands influence was evaluated by comparing the quantum-chemical calculations results of their basicity with the experimental data of the catalytic investigations obtained under identical conditions. As shown the research, lowering the basic properties in the series: pyrrole, 2-phenylpyrrole, 2-formylpyrrole leads to decrease activity and selectivity of ethylene trimerization catalytic systems.

Table. Selectivity dependence on the pyrrole ligands ΔpKa.

	ΔpK_a	Hexen-1 selectivity, wt.%		
		$Cr(EH)_3$	$Cr(acac)_3$	$CrCl_3(THF)_3$
pyrrole	0,0	76	73	73
2-phenylpyrrole	-4,4	69	53	61
2-formilpyrrole	-8,4	26	43	57

The authors thank V.B. Kobychev (Laboratory of Quantum Chemistry, Irkutsk State University) for assistance in quantum-chemical calculations and discussion of the results.

References

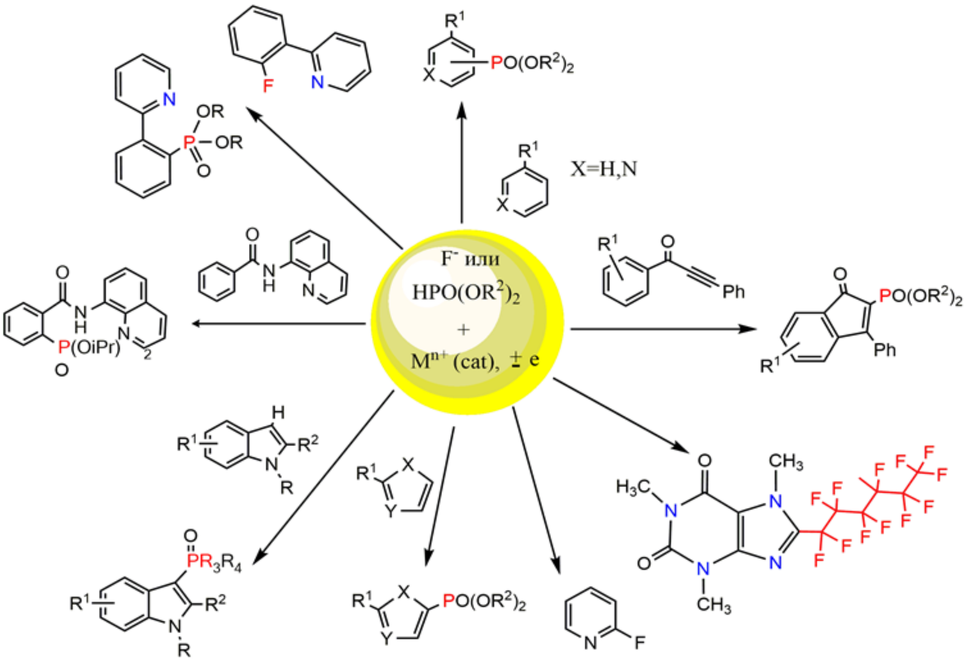
[1]. Alferov, K.A., Babenko, I.A., Belov, G.P. *Petroleum chemistry*, **2017**, *57*, 1.
[2]. Gianola, A.J., Ichino, T., Hoenigman, R.L., Kato, S., Bierbaum, V.M., Lineberger, W.C. *J. Phys. Chem. A.* **2004**, *108*, 10326.
[3]. Tang, S., Liu, Z., Zhan, X., Cheng, R., He, X., Liu, B. *J. Mol. Model.* **2014**, *20*, 2129.
[4]. Vilms, A.I., Babenko, I.A., Bezborodov, V.A., Ivanov, A.V., Belov, G.P. *Petroleum chemistry*, **2017**, *57*, 244.

Metal catalysed electrochemical functionalisation of aromatic C-H bonds

Budnikova Y. H.

A.E.Arbuzov Institute of Organic and Physical Chemistry, KSC of RAS, Kazan, Russia
e-mail: yulia@iopc.ru

New methods that allow for the incorporation of fluorous or phosphorous synthons into a molecule at late synthesis stage are desperately needed. Metal-catalyzed coupling procedures would greatly facilitate the construction of fluoro- or phosphorous organic molecules; however they have been slow to develop. Achieving site selectivity in C–H functionalization reactions is a significant challenge. We propose a one-step catalytic method for introduction of fluorine- and phosphorus-containing functional groups to different compounds with C(sp^2)-H bonds assisted by electrochemical reduction or oxidation of metal complexes under mild conditions. The catalytically active form of metal complexes (Ni^{III} or Pd^{III}, Fe^{II}, etc.) is generated and regenerated on the electrode without specially added reducing agents (or oxidants). We aimed to develop a mild method for the functionalization of simple arenes and more complicated substrates (for example, caffeine) and to utilize relatively inexpensive perfluoroalkyl iodides as RF precursors and dialkylphosphites as P-precursors and rarely used accessible, reasonable and nontoxic iron and silver compounds as catalysts. Key organometallic intermediates are isolated and characterized. Possibilities and advantages of directed metal-induced aromatic C-H-fluoroalkylation, phosphorylations etc. are demonstrated.



M=Ni, Co, Pd, Mn, Fe, etc.

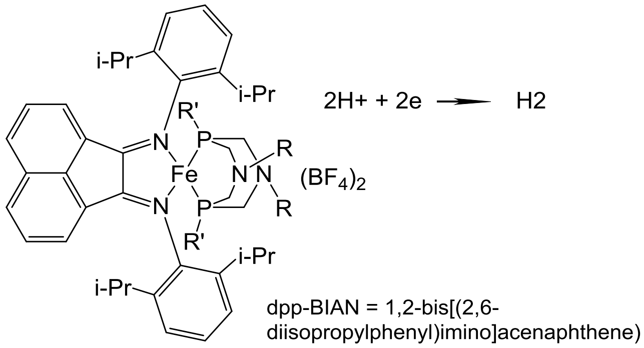
This work was supported by Russian Science Foundation (grant № 14-23-00016).

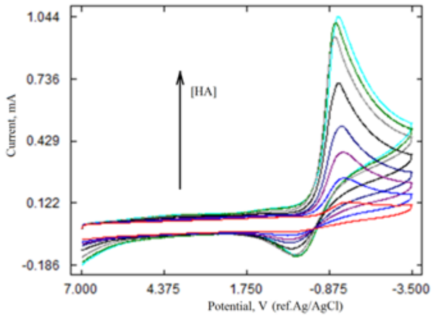
Iron or nickel complexes bearing diphosphine and BIAN ligands as electrocatalysts for the H_2 evolution

Budnikova Y.H. [a*], Khrizanforova V.V. [a], Fedushkin I.L. [b], Karasik A.A. [a]

[a]*A.E.Arbuzov Institute of Organic and Physical Chemistry, KSC of RAS, Kazan, Russia*
[b]*G.A. Razuvaev Institute of Organometallic Chemistry, RAS, Nizhny Novgorod, Russia*
e-mail: yulia@iopc.ru

Over the past several years, much effort has been undertaken to construct artificial systems, and to understand the mechanism of proton reduction by [FeFe]-H2ase mimics. Nevertheless, the activity of the artificial systems for H_2 evolution is still low. The classical Fe^IFe^I organometallic complexes $[(\mu\text{-xdt})Fe_2(CO)_6]$ (xdt = dithiolate linkers) highly resemble the active site of [FeFe] hydrogenases so they have been used as biomimetic model complexes for mechanistic studies of H_2 evolution. Among hundreds Fe_2 complexes, the most common derivatives contain phosphine ligands, which substitute one or more COs. Upon phosphine substitution, the reduction of the Fe_2 complexes shifts toward more negative potentials. Unfortunately, most of the phosphine-substituted derivatives are unstable after redox events. It was reported that $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$ complexes are highly active catalysts for H_2 production and oxidation, and bidirectional catalysts active for both H_2 production and oxidation, where $P^R{}_2N^{R'}{}_2$ is a cyclic 1,5-diaza-3,7-diphosphacyclooctane ligand. Unfortunately, similar iron complexes do not exhibit catalytic activity under the conditions studied. We assumed it would be possible to involve the iron complexes with diazadiphosphocyclooctane ligands in hydrogen catalysis by entering the additional redox active ligand into the iron coordination sphere. Iron complexes bearing diphosphine ligands with positioned pendant amines along with non-innocent dpp-BIAN ligand have been investigated by cyclic voltammetry, which is the usual way to demonstrate electrocatalytic ability for hydrogen evolution. Cyclic voltammograms (CVs) in CH_3CN have been recorded in the presence of increasing amounts of acids (Figure 1). The catalytic reactivity of these new mixed ligands iron complexes at low overpotential was demonstrated. Catalysis potential for all complexes is around -0.5V ref Fc^+/Fc in THF, so it is very low overpotential of hydrogen evolution.





This work was supported by RFBR (grant № 16-03-00195).

Conformational isomerism of chelate ring in $[\eta^2$ - $Ph_2P(O)(CH_2)_2C(O)NMe_2]TiF_4$ single crystal

Danilov V.V.[a], Il'in E.G. [a], Parshakov A. S.[a], Aleksandrov G. G.[a], Yarzhemskii V. G. [a], Bodrin G. V.[b], Goryunov E. I.[b], Kurilkin V.V.[c], Nifantev E. E.[b]

[a] Kurnakov Institute of General and Inorganic Chemistry, 119991, Moscow, Leninskii pr. 31
[b] Nesmeyanov Institute of Organoelement Compounds, 119991, Moscow, ul. Vavilova 28
[c] Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: vsevoloddanilov@hotmail.com

By the example of TiF4 complex formation with the simplest diphenyl[2-(N,N-dialkylcarbamoyl)ethyl]phosphine oxide we have shown for the first time that these functionalized phosphine oxides can produce original complexes with stable seven-membered chelate heterocycles.

The composition and structure of TiF_4 complexes with $Ph_2P(O)(CH_2)_2C(O)N_2$ (L) in CH_2Cl_2 was studied recently by ^{19}F and ^{31}P NMR [1]. It was shown that the elongation of the hydrocarbon bridge between the donor P=O and C=O groups in ω-carbamoylalkylphosphine oxides from –CH2– to $(–CH_2–)_2$ does not decrease the chelating ability of the ligand, while the composition of resultant complexes in solution is determined by the component ratio. Chelated tetrafluorocomplex is present mostly in equimolar solutions.

Studying the temperature dependence of ^{19}F and ^{31}P NMR spectra of this chelate we observed at 228 K appearans of the same group of signals which were assigned to possible conformational isomerism of the TiOPCCCO chelated ring.

X-ray diffraction study of $[\eta^2$ - $Ph_2P(O)(CH_2)_2C(O)NMe_2]TiF_4$ single crystal showed that this compound contains four crystallographically independent complex molecules of similar structure which have only slightly different bond distances between the ligands and the central Ti ion and noticeably different geometries of the seven-membered chelated rings. The results of quantum-chemical optimization for the experimental parameters of all four molecular structures led to one theoretical structure practically coinciding with structures 1-2.

Table

Selected bond lengths and bond angles according to the X-ray diffraction study and quantum chemical calculations

Bond lengths, Å and bond angles, deg	Conformational isomers				
	$(\eta^2$-$)TiF_4$**(1)**	$(\eta^2$-L$)TiF_4$ **(2)**	$(\eta^2$-L$)TiF_4$ **(3)**	$(\eta^2$-L$)TiF_4$ **(4)**	Theoretical structure
Ti - F^1 (tr. to F)	1,817(7) 1,828(6)	1,804(6) 1,811(6)	1,806(5) 1,846(5)	1,823(5) 1,851(5)	1,853 1,839
Ti-F^2(tr. to OP)	1,820(7)	1,779(7)	1,782	1,807(5)	1,800
Ti-F^3(tr. to OC)	1,759(7)	1,811(7)	1,791	1,797(5)	1,785
Ti-OP…L	2,029(7)	2,043(7)	2,049(7)	2,017(7)	2,185
Ti-OC…L	2,093(7)	2,022(8)	2,053(6)	2,049(6)	2,307
O-Ti-O	83,8	85,7(3)	85,0(3)	86,4(3)	
F^1-Ti-F^1	167,1	170,1(3)	168,6(3)	172,3(3)	156,6

This work was supported by the Federal Agency of Scientific Organizations.

References

[1]. Il'in E.G., Parshakov A.S., Privalov V.I, Yarzhemskii V. G., Bodrin G. V., Goryunov E. I., Nifantev E. E., Dokl.Chem., 2016, V. 467, 2, P. 122–125.

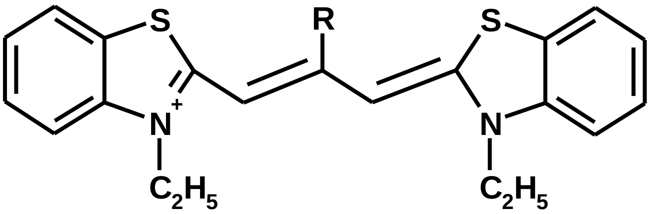
The effect of cucurbit[8]uril on the photophysical properties of 3,3'-diethylthiacarbocyanine and its 9-methyl substituted

Fedotova T.V.[1,2], Zakharova G.V.[2], Chibisov A.K.[1,2]

[1]*Moscow Institute of Physics and Technology (State University), Moscow, Russia,*
[2]*Photochemistry Centre RAS FSRC "Crystallography and Photonics" RAS, Moscow, Russia,*
e-mail: tatyana.fedotova@phystech.edu

Cucurbit[n]uril is a relatively new class of macrocyclic compounds, actively studied in recent years. They are molecular containers made of glycouril monomers linked by methylene bridges. Of particular interest is the ability of cucurbiturils to form stable complexes "host-guest" with metal cations, as well as with the positively charged organic molecules due to the large negative charge on the carbonyl portals.

As the "guest molecules" it is interesting to consider cationic polymethine dyes [1-3] containing in its composition the conjugate structure of an odd number of methine groups between the two nitrogen atoms with delocalized charge. It has been previously demonstrated [4] that the dye **1** in aqueous solution is present as *trans*-form, while the dye **2** is predominantly in *cis*-form, as indicated by the relative position of their absorption peaks in the spectra.



Dye	R
1	H
2	C_2H_5

Fig.1. The structural formula of 3,3'-diethylthiacarbocyanine (**1**) and its 9-methyl substituted (**2**)

It is shown that the interaction of the dyes with cucurbit[8]uril results in the formation of stable inclusion complexes with the composition of 2:2, which is accompanied by the change in spectral-luminescent properties of the dyes. The resulting dimeric complexes demonstrate luminesce, the dimeric complex of the dye **1** exhibits both fast and delayed fluorescence, whereas the dimeric complex of the dye **2** is phosphorescent. Intensively luminescent complexes of polymethine dyes with cucurbiturils can be used as fluorescent labels in biologically-active media.

References

[1]. Edited by MV Alfimova Photochemistry Center, Russian Academy of Sciences. Basic and Applied Research. M .: OOO "CPI" Mask"" 2013. 566 p.

[2]. Zakharova G.V., Zhizhimov D.A. etc. Photoprocesses of alkyl meso-thiacarbocyanine dyes in the presense of cucurbit [7] uril // Journal of Photochemistry and Photobiology. 2015, P. 69-77.

[3]. Zakharova G.V., Avakian V.G., Markelov V.P. etc. Effect of Cucurbituril for Primary Photoprocesses of Thiacarbocyanine Dyes in water // High Energy Chemistry, 2015, Vol. 6. No. 49, P. 1-8.

[4]. Vladimirova K.G., Freidzon A.Ya., Bagatur'yants A.A., Zakharova G.V.,Chibisov A. K., and Alfimov M. V. Modeling the Structure, Absorption Spectra, and Cis–Trans Isomerization of Thiacarbocyanine Dyes // High Energy Chemistry, 2008, Vol. 42, No. 4, P. 275–282.

Synthesis and investigation of $MgAl_2O_4$: Eu^{3+} nanopowders

Golyeva E.V., Kolesnikov I.E., Mikhailov M.D.

Scientific and Technological Institute of Optical Material Science, VNTs S.I. Vavilov State
Optical Institute, 192171, St. Petersburg, Babushkina 36/1
e-mail: lenysik_net@mail.ru

Nowadays, nanophosphors doped with rare earth elements attract considerable scientific and technological interest due to their excellent physico-chemical and luminescent properties. The most popular are the double and triple compounds consisting mainly of highly stable refractory components, for example the magnesium aluminum spinel (MAS, $MgAl_2O_4$). Spinel has a cubic crystal structure, thus optically isotropic and, besides its high melting point, excellent mechanical properties and corrosion resistance, it shows an outstanding transparency up the near-infrared frequency range even in the polycrystalline state.

It is also known that structure, chemical and phase purity and luminescent properties of nanophosphors are strongly related to synthesis conditions. The determination of optimal parameters for obtaining mono-phased $MgAl_2O_4$:Eu^{3+} nanoparticles with high luminescence intensity is a pressing and complex scientific and technical task.

Nanocrystalline magnesium aluminate spinel doped with Eu^{3+} ions was prepared by modified Pechini method which allows obtaining weakly agglomerated nanoparticles. Such modification of standard Pechini technique has already been used to synthesize various Eu^{3+} and Nd^{3+} doped oxides [1]. The using of two-step heat treatment and molten salt in the second calcination provides low agglomerated synthesized nanopowders.

The complex structural analysis with XRD diffraction and Rietveld methods showed that all samples have cubic spinel phase without any structural impurities. According to the SEM and SLS analysis, prepared samples are weakly agglomerated and consist of near-spherical nanoparticles with average size of ~50 nm. The effect of synthesis conditions (calcination temperatures and durations) on structural, morphological and luminescence properties of $MgAl_2O_4$:Eu^{3+} nanopowders was studied The minimal first calcination temperature (T_1) required for burning out of the organic components was defined as 600 °C/1.5h using the DTG analysis. It was found that the increase of the second calcination temperature leads to more perfect crystalline structure of the samples but reduces luminescence intensity. Dependence of calcination temperature on luminescence intensity was the same regardless of the excitation mechanism. Strong changes in the structure and luminescent properties of $MgAl_2O_4$:Eu^{3+} occur when the T_2 is near 2/3 of $MgAl_2O_4$ melting temperature (T_2=1200 °C). In this condition the spinel structure reaches an equilibrium state and the europium ions are displaced on the $MgAl_2O_4$ surface, which leads to the abrupt decrease of luminescence intensity and observed $^5D_0$ level lifetime. Radiative and nonradiative decay rates and Judd-Ofelt intensity parameters of $MgAl_2O_4$:Eu^{3+} powders were calculated using 4f–4f intensity theory. The optimal synthesis conditions of nanopowders with high luminescence intensity were defined as T_1 = 600°C/1.5h T_2 = 850°C/2h.

Experimental investigations were carried out in "Center for Optical and Laser materials research", "Research Centre for X-ray Diffraction Studies", "Innovative Technologies of Composite Nanomaterials", "Thermogravimetric and Calorimetric Research Centre" (St. Petersburg State University).

References

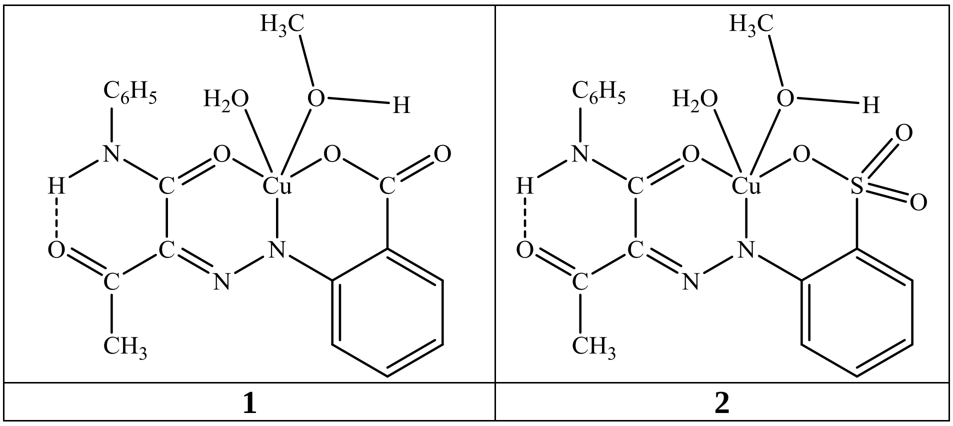
[1]. Kolesnikov, I.E.; Golyeva, E.V.; Kurochkin, A.V.; Mikhailov M.D. *J. Alloys Compd*. **2016**, *654*, 32.

Copper(II) complexes of arylhydrazones of acetoacetanilide as catalysts for the cyanosilylation of aldehydes

Gurbanov A.V.[a,b,c], Maharramov A.M.[a], Huseynov F.E.[a,b], Zubkov I.V.[b], Mammadova G.Z.[a], Mahmudov K.T.[a,b,c], Pombeiro A.J.L.[c]

[a]Baku State University, Z. Khalilov str. 23, AZ 1148 Baku, Azerbaijan,
[b]RUDN University, 6 Miklukho-Maklaya str., Moscow 117198, Russian Federation
[c]CQE,, IST, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisbon, Portugal
e-mail: organik10@hotmail.com

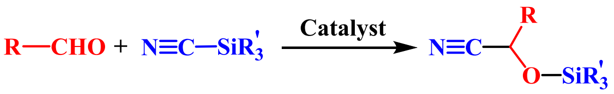
The new copper(II) complexes [Cu(HL^1)(H_2O)(CH_3OH)] (**1**, H_3L^1 = (Z)-2-(2-(1,3-dioxo-1-(phenyl-amino)butan-2-ylidene)hydrazinyl)benzoic acid) and [Cu(HL^2)(H_2O)(CH_3OH)] (**2**, NaH_2L^2 = sodium (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl) benzene-sulfonate) were synthesized and characterized by IR and ESI-MS spectroscopies, elemental and X-ray crystal structural analyses (Scheme 1) [1]. The coordination environment of the central copper(II) has a square pyramidal geometry, three sites being occupied by $(HL^{1,2})^{2-}$, which chelates in the O,N,O fashion, while the two other sites are filled with the water and methanol ligands. Multiple intra- and intermolecular non-covalent interactions between the $(HL^{1,2})^{2-}$, water and methanol ligands lead to supramolecular network.



1 **2**

Scheme 1. Schematic representation of **1** and **2**.

Both compounds **1** and **2** act as homogenous catalysts for the cyanosilylation reaction of a variety of both aromatic and aliphatic aldehydes with trimethylsilyl cyanide affording the corresponding cyanohydrin trimethylsilyl ethers in high yields (up to 90 %) and at room temperature (Scheme 2).



Scheme 2. Cyanosilylation of aldehydes.

This work was supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.21.0008) and Baku State University.

References

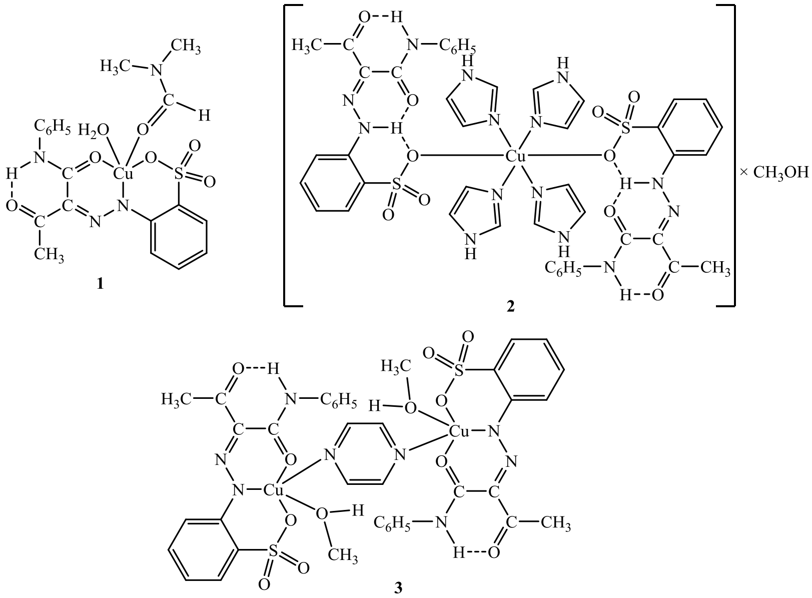
[1]. Gurbanov, A.V.; Mahmudov, K.T.; Sutradhar, M.; Guedes da Silva, M.F.C.; Mahmudov T.A.; Guseinov, F.I.; Zubkov, F.I.; Maharramov, A.M.; Pombeiro A.J.L. *Journal of Organometallic Chemistry*, **2017**, *834*, 22-27.

Copper(II) complexes of arylhydrazones of acetoacetanilide as catalysts for the henry reaction in water

Gurbanov A.V.[a,b,c], Maharramov A.M.[a], Mammadova G.Z.[a],Huseynov F.E.[a,b], Zubkov I.V.[b], Mahmudov K.T.[a,b,c], Pombeiro A.J.L.[c]

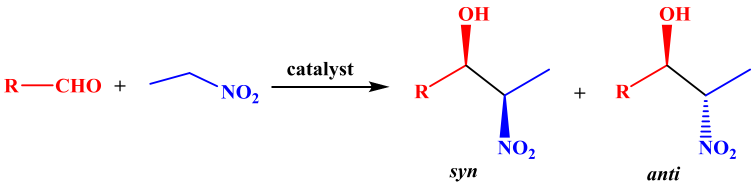
[a]Baku State University, Z. Khalilov str. 23, AZ 1148 Baku, Azerbaijan,
[b]RUDN University, 6 Miklukho-Maklaya str., Moscow 117198, Russian Federation
[c]CQE, IST, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisbon, Portugal
e-mail: organik10@hotmail.com

Three new water-soluble copper(II) complexes $[Cu(HL)(H_2O)\{(CH_3)_2NCHO\}]$ (**1**), $[Cu(H_2L)_2(im)_4]\cdot CH_3OH$ (**2**) and $[Cu(HL)(CH_3OH)]_2(\mu_2\text{-py})$ (**3**) were synthesized from copper(II) nitrate and sodium (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzene-sulfonate (NaH_2L), in the absence (for **1**) and presence of imidazole (im) (for **2**) or pyrazine (py) (for **3**), and fully characterized by IR and ESI-MS spectroscopies, elemental and X-ray crystal structural analyses (Scheme 1) [1].



Scheme 1. Schematic representation of **1**−**3**.

All complexes **1**−**3** have been tested as stereoselective C−H activating catalysts for the model nitroaldol (Henry) condensation of nitroethane with various aldehydes in water (Scheme 2). **1** was the most active catalyst affording 64−87% yields with *syn/anti* diasteroselectivities up to 77:23.



Scheme 2. Cyanosilylation of aldehydes.

This work was supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.21.0008) and Baku State University.

References

[1]. Ma Z.; Gurbanov, A.V.; Maharramov, A.M. et al. *J. Mol. Catal. A: Chem.* **2017**, *426*, 526.

Influence of annealing conditions on the structure and luminescent properties of $KGd_{1-x}Eu_x(MoO_4)_2(0<x<1)$ solid solutions

Gushchina I.I., Morozov V.A.

Faculty of science materials, Moscow State University, Moscow, Russia
Iriska.gu@gmail.com

The present work is devoted to a research of the influence of preparation conditions and Eu^{3+} concentration on the structure and luminescent properties of $KGd_{1-x}Eu_x(MoO_4)_2$ ($0 \le x \le 1$) solid solutions.

White light-emitting diodes (WLEDs) are a promising solid-state lighting source (SSL) bound to replace conventional incandescent and fluorescent lamps. They have attracted a lot of attention due to their high reliability, long lifetime, low energy consumption and environment friendly characteristics. Rare earth elements doped molybdates and tungstates with the scheelite-type ($CaWO_4$) structure have a large potential for use in WLEDs. Molybdate and tungstate phosphors have broad and intense absorption bands due to charge transfer (CT) from oxygen to metal in the near-UV region. Some scheelite-type compounds, such as $PbMoO_4$, $KGd(WO_4)_2$, $NaBi(WO_4)_2$ and MWO_4 (M = Pb, Cd, Ca) are well known and used while other materials with Eu^{3+} cations are often proposed as potential red-phosphors for WLEDs.

α-$KGd_{1-x}Eu_x(MoO_4)_2$ (α-KGEMO) solid solutions were synthesized from stoichiometric amounts of Gd_2O_3, Eu_2O_3, K_2CO_3 and MoO_3 by a routine ceramic technique in alumina crucible at 923 K for 20 h in air followed by slow cooling (SC) in the furnace from 923 K to room temperature (T_R). Powder X-ray diffraction (PXRD) patterns of all α-KGEMO are similar to the pattern of anorthic $P\bar{1}$ α-$KEu(MoO_4)_2$. Substitution Gd^{3+} (r_{VIII} = 1.053Å) by Eu^{3+} (r_{VIII} = 1.066Å) leads to an increase of unit cell volume. The broad features of the photoluminescence excitation spectra (PLE) spectra for the Eu^{3+} emission in α-KGEMO ($0.1 \le x \le 1$) are in general linked to host related mechanisms like charge transfer (CT) states and point to an energy transfer between the host matrix and the luminescent ion.

The changing of the Eu^{3+} concentration did not change significantly peak positions and peak shape on photoluminescence emission spectra (PL), but the $^5D_0 \rightarrow {}^7F_J$ (J = 0–2) emission intensities depended on x reaching maxima for $x = 0.5$ after excitation at the CT band (300 nm) and at the $^7F_0 \rightarrow {}^5L_6$ transition (395 nm). The polycrystalline α-$KEu(MoO_4)_2$ was used as a reference. At the same time, the change in the excitation from 395 nm to 300 nm for the α-KGEMO leads to a significant increase in the luminescence intensity. Thus, the revealed change in the luminescence intensity in the range of the $^5D_0 - {}^7F_2$ transition for α-KGEMO with a change of λ_{ex} from 395 to 300 nm shows that, for the $0.1 \le x < 1$, the luminescence excitation mechanism involving charge transfer to luminescent centers (Eu^{3+}) is more efficient than direct excitation of luminescent centers, as is the case for α-$KEu(MoO_4)_2$ phase.

Annealing of α-KGEMO at 1073 K in air followed by SC from 1073 K to T_R leads to a mixture of solid solutions with the anorthic $P\bar{1}$ and monoclinic $I2/b(\alpha\beta0)00$ structures for x=0.8 and x=0.9 while PXRD patterns for $0 \le x \le 0.7$ practically do not change. Higher annealing temperature leads to strong changes in the PLE and PL spectra. The transformation of $KEu(MoO_4)_2$ from a low temperature anorthic α-phase to a monoclinic high temperature β–phase with an incommensurately modulated structure is accompanied by decreasing of the $^5D_0 - {}^7F_2$ luminescence intensity. The CT band intensity drastic decreases and thus the direct excitation mechanism is a most efficient as compared to the charge transfer mechanism between the host matrix and the luminescent ion.

Crystal structure and solid state luminescence of alkali metal 2-acyl-1,1,3,3-tetracyanopropenides

Karpov S.V., Kaukov Ya.S., Grigor'ev A.A., Karpova I.V.

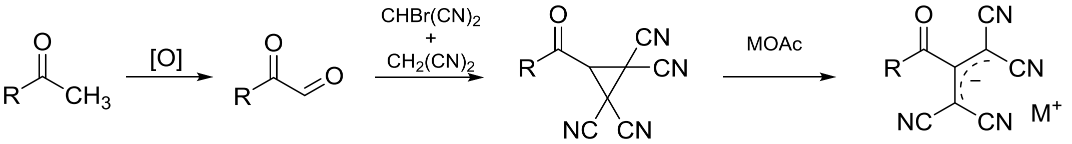
I. N. Ul'yanov Chuvash State University, Russia, 428015, Cheboksary, Moskovskii Prospekt 15,
e-mail: serg31.chem@mail.ru

Currently, a salts containing tetracyanoallyl (TCA) anion have received considerable attention. TCA salts can be applied for creating materials with potentially useful properties, such as magnetic, thermo- and photochromic, semiconducting and photomagnetic.

A new representatives of TCA salts - 2-acyl-1,1,3,3-tetracyanopropenides (ATCN) have systematically studied by our research group. These compounds can be easily obtained from readily available methylketones, malononitrile, bromine, and metal acetates [1].

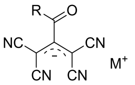
We investigated the crystal structure and luminescent properties of 20 ATCN salts, containing Li-Cs as cation and Ph, 4-MePh, 4-MeOPh or 4-BrPh group in acyl fragment.

Single crystal X-ray diffraction reveals that there are eight crystal packing types, most of them are 2D layered. Some salts were obtained as two crystal polymorphs (α modification is thermodynamically stable, β is metastable) with different structure.



ATCN

Type of crystal packing and λ_{max} (NL = non luminescient, λ_{ex} = 430 nm) for ATCN

	Substitutients in acyl fragment			
	Ph	4-MePh	4-MeOPh	4-BrPh
Li^+	**1a** (type 6), 1D chain struct., λ_{max} 513 nm	**1b** (type 1), NL	**1c** (type 2), λ_{max} 518 nm	**1d** (type 3), 2D layered struct., λ_{max} 528 nm
Na^+	**α-2a** (type 5), 2D layered struct., λ_{max} 519 nm	**α-2b** (type 5), NL	**2c** (type 1), λ_{max} 495 nm	**2d** (type 7), 3D struct., NL
	β-2a (type 1), 2D layered struct.	**β-2b** (type 3), λ_{max} 518 nm		
K^+	**α-3a** (type 5), NL	**3b** (type 2), 2D layered struct., λ_{max} 522 nm	**α-3c** (type 1), NL	**α-3d** (type 1), NL
	β-3a (type 1), λ_{max} 471 nm		**β-3c** (type 2), λ_{max} 529 nm	**β-3d** (type 2), λ_{max} 525 nm
Rb^+	**4a** (type 4), 3D struct., NL	**4b** (type 2), λ_{max} 495 nm	**4c** (type 2), λ_{max} 525 nm	**4d** (type 4), NL
Cs^+	**5a** (type 4), NL	**5b** (type 2), λ_{max} 507 nm	**5c** (type 5), λ_{max} 486 nm	**5d** (type 8), 3D struct., NL

This work was supported by the Russian Foundation for Basic Research (grant № 16-33-60135 mol_a_dk).

References

[1]. Sergey V. Karpov, Arthur A. Grigor'ev, Yakov S. Kayukov, Irina V. Karpova, Oleg E. Nasakin, Victor A. Tafeenko. *J. Org. Chem.* **2016**, *81*, 6402 − 6408.

Structural variety and properties of transition metal cymantrenecarboxylates

Koroteev P.S., Ilyukhin A.B., Gavrikov A.V., Efimov A.V., Dobrokhotova Zh.V., Novotortsev V.M.

N.S. Kurnakov Institute of General and Inorganic Chemistry, RAS,
Leninsky prosp. 31, GSP-1, 119991 Moscow, Russian Federation
e-mail: pskoroteev@list.ru

Heterometallic carboxylates containing one of the metal atoms as a part of organometallic ligand represent a poorly studied type of compounds. In recent years we have obtained Mn-Ln-heterometallic complexes containing cymantrenecarboxylate ligand $CymCO_2^-$ (Cym = (η^5-C_5H_4)Mn(CO)$_3$); their structures and physicochemical properties were studied [1-4].

It was found that in aqua-organic media, in which the lanthanides form coordination polymers [1, 3], the transition metals give rise to the isostructural complexes $[M(H_2O)_6](CymCO_2)_2\cdot 4H_2O$ (M = Co (**1**), Ni (**2**), Zn(**3**)) built of the isolated ions. In presence of various organic ligands in different organic media the complexes $[Co(CymCO_2)_2(bpy)_2]\cdot 2PhMe$ (**4**), $[Co(CymCO_2)_2(imidazole)_2]$ (**5**), $[Ni(CymCO_2)(bpy)_2(H_2O)][CymCO_2]\cdot 0.5MePh\cdot 2H_2O$ (**6**), $[Cu(CymCO_2)_2(imidazole)_2]$ (**7**), $[Cu(CymCO_2)_2(bpy)(H_2O)]$ (**8**), $[Fe_3(CymCO_2)_6(bpy)_2]\cdot 2PhMe$ (**9**), and $[HNEt_3][(VO)_6(SO_4)O(CymCO_2)_3(MeO)_6(MeOH)_2]\cdot 5H_2O$ (**10**) showing structural diversity were obtained (Figs. 1, 2). Complexes **5** and **6** display the properties of field-induced single molecule magnets. Thermolysis of the complexes **1-8** in air brings about the spinels MMn_2O_4 which are valuable magnetic materials.

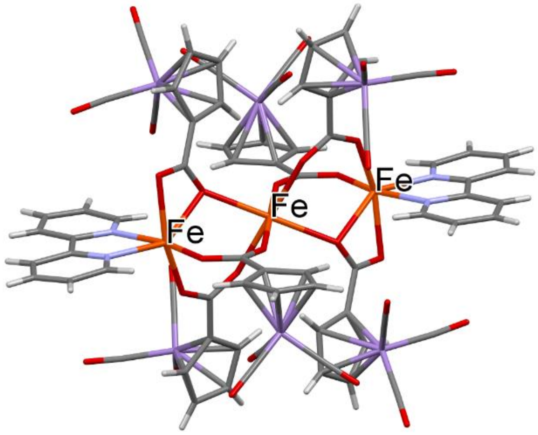


Fig. 1. Molecular structure of **9**.

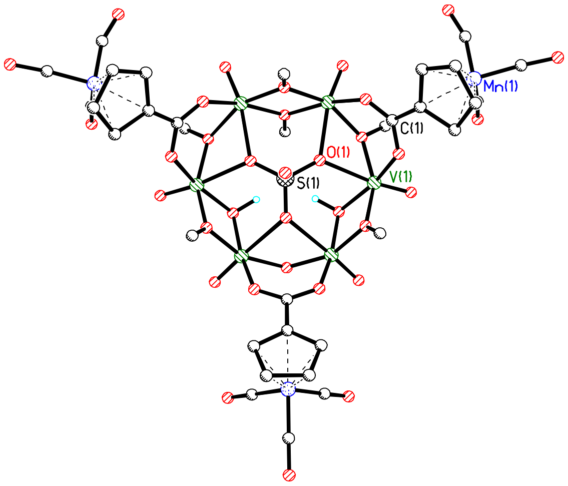


Fig. 2. Structure of the anion in **10**.

The work was supported by the Presidium of the Russian Academy of Sciences.

References

[1]. Koroteev P.S.; Dobrokhotova Zh.V.; Ilyukhin A.B.; Efimov N.N.; Gavrikov A.V.; Novotortsev V.M. *Russ. J. Coord. Chem.*, **2016**, *42(9)*, 591.

[2]. Efimov N.N.; Koroteev P.S.; Gavrikov A.V.; Ilyukhin A.B.; Dobrokhotova Zh.V.; Novotortsev V.M. *Magnetochemistry*, **2016**, *2(4)*, 38; doi:10.3390/magnetochemistry2040038.

[3]. Koroteev P.S.; Dobrokhotova Zh.V.; Ilyukhin A.B.; Efimov N.N.; Kirdyankin D.I.; Tyurin A.V.; Gavrikov A.V.; Novotortsev V.M.; *Polyhedron*, **2015**, *85*, 941.

[4]. Koroteev P.S.; Kiskin M.A.; Dobrokhotova Zh.V.; Bogomyakov A.S.; Efimov N.N.; Novotortsev V.M. *Polyhedron*, **2011**, *30*, 2523.

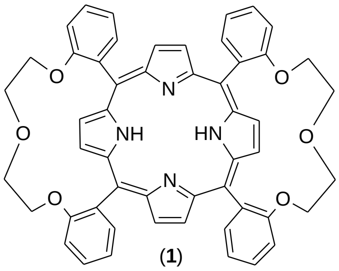
Quantum chemical studies of some crown-tetraphenylporphyrinates

Kotsuba V.E.[a], Freidzon A. Ya.[b,c]., Kolyadina N.M.[a]

[a]*RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6*
[b]*Photochemistry center, Russian Academy of Sciences, 119421, Moscow, ul. Novatorov 7A*
[c]*National Research Nuclear University (Moscow Engineering Physics Institute),*
115409, Moscow, Kashirskoe sh. 31
email: vasilyk@yandex.ru

Macroheterocyclic ligands with both tetrapyrrolic and crown ether subunits present considerable interest both for fundamental coordination chemistry and for practical applications. They can be used as chemical sensors, in self-assembly processes, in modelling of enzymatic processes, etc.

Our group studies crown-fused tetraphenylporphyrins: **1** and analogs with larger crown cavities. These promising ligands can form multi-nuclear complexes with d-metals bound to the tetrapyrrolic core and alkaline/alkaline earth metals – to oxygen atoms of the crown subunits.

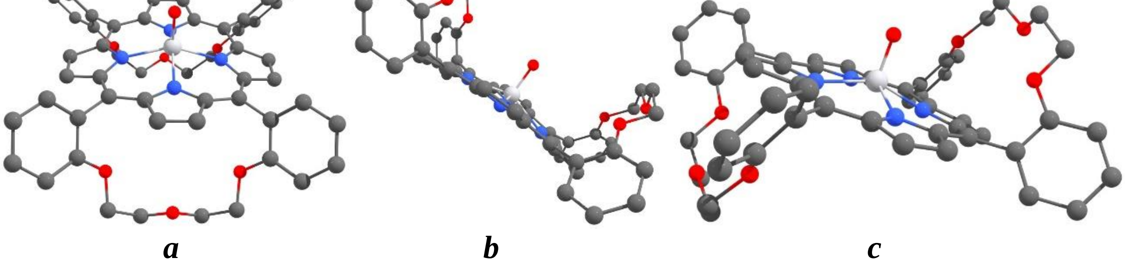


(**1**)

However, the yields of the ligands are quite low (≤11%). We have found that the addition of vanadyl sulfate improves the yields. Other metal cations, such as Zn^{2+}, did not give such results. We performed quantum chemical calculations (Priroda, DFT PBE/3z) to evaluate the energy of the tetrapyrrolic core distortion in **1** and its vanadyl porphyrinate (the energies of the corresponding dianions were calculated). When vanadyl is inserted in the core, its total energy is lowered (and stability increased) by 0.34 kcal/mol.

Several geometrical isomers are possible for such a porphyrinate (**Fig 2a-c**). We isolated a VO^{2+} complex and determined its structure by X-ray analysis. The isolated crystals possess the structural type of **2a**. However, calculations show that structure **2b** is most stable of the 3 types, probably due to CH…O=V interactions. The energy difference between **2b** and **2a** is 0.73 kcal/mol. The transoid structure **2c** is the least favorable (by 1.92 kcal/mol compared to **2a**). When VO^{2+} is replaced by Zn^{2+}, the corresponding cisoid molecules have virtually the same calculated energy, while the transoid one is 1.5 kcal/mol less favorable.

We are currently improving our calculations using various solvation models.



a ***b*** ***c***

Fig 2. Models of VO-porphyrinates. Hydrogen atoms are not shown for clarity.

Equipment of the Shared Research and Educational Center of Physico-Chemical Studies of New Materials, Substances and Catalytic Systems, Peoples' Friendship University of Russia, was used in the current study.

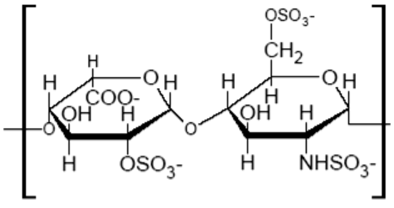
Study of heparin interactions with zinc cation(II) and amino acid (proline)

Kryukov T.V., Skobin M.I., Feofanova M.A.

Tver State University, Tver, 170100 Sadovyi per. 33
e-mail: p528491@yandex.ru

The aim of this work was to study the complexation of Zn(II) ions with high molecular weight heparin and amino acid (proline) in a molar ratio of 1: 1: 1 using pH titration (background electrolyte 0,15 M NaCl; temperature 37 °C) and methods of mathematical modeling of chemical equilibria (algorithms New DALSFEK, AUTOEQUIL and HYPERQUAD 2008).

It was considered that the high molecular weight heparin forms monoligand and polyligand complexes with Zn(II) ions (caused by a number of factors: the conformation of the polymer chain, steric factors) monomer unit of heparin in this case acts as tetradentate ligand.



Monomer disaccharide unit of heparin

As the result, after processing of titration curves using methods of mathematical modeling of ternary systems: metal ions – heparin – amino acids were obtained equilibria models, including the most likely possible forms. Equilibriums, forms and the corresponding stability constants are shown in the table below:

Equilibrium	lgβ
$Hep^{4-} + Pro^{-} + Zn^{2+} \leftrightarrow ZnHepPro^{3-}$	9.54 ± 0.29
$Hep^{4-} + H^{+} + Pro^{-} + Zn^{2+} \leftrightarrow ZnHepHPro^{2-}$	16.26 ± 0.31

All efforts demonstrated in this paper are focused on complex ion-molecule equilibria, which involve Zn(II) ion, high molecular weight heparin, as well as amino acid (proline). Particular interest for us is the synthesis and structural identification of ternary metal complexes due to possibility of their use in medicine.

Spectrophotometric determination of copper(II) with 2, 6-dithiol-4-ethylphenol and hydrophobic amine

Kuliev K. A., Mamedova Sh. A.

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

2, 6-dithiol-4-ethylphenol (DTEP) in the presence hydrofobic amins gave instantaneous and stable blue colour with Copper(II) in the pH range 6.2 to 7.7. As hydrophobic amine phenantroline (Phen), batophenantroline (BPhen) and dipiridile (Dip) were used.

Cu(II) reacts with DTEP and gives a yellow colored complexes. These complexes are insoluble in non-polar solvents. When hidrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

The extraction of the complex has been tried with several solvents: chloroform, 1, 2-dichloroethane, tetrachloromethane, dichloromethane, benzene, chlorobenzene, toluene, xylol, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, 1-butanol, isoamyl acetate and their mixes. Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with chloroform, 97,8-98,5% of copper was extracted as an ion associate (in a case the dichloroethane and carbontetrachloride was removed 95,6 - 96,6% of Copper).

The absorption spectrum of Cu(II): DTEP in chloroform shows the maximum absorption at 475 nm. Maximum absorbance of MLC is observed at 534-540 nm. Molar coefficients of absorption make $(3.61 - 4.82) \cdot 10^4$ dm $^3 \cdot$ mol$^{-1} \cdot$ cm^{-1}.

For the formation and extraction of MLC, a 10-15-fold excess of complexing reagents is required; for example, theoptimal conditions for formation and extraction of these compounds are provided by $0.8\text{x}10^{-3}$ M DTEP and $1.0\ \text{x}10^{-3}$ M Am.

Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods were employed to elucidate the composition of the complex. It shows that the composition of Cu(II) : DTEP : Am complex is 1:1:1.

The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3460 sm^{-1} observed in the spectrum of DTEP, 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 sm^{-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 1360 cm^{-1} indicates the presence of a coordinated phenantroline.

It was found using the Nazarenko method that Cu(II) in the complexes was present in the form of Cu^{2+}. The number of protons replaced by cobalt in one DP molecule appeared to be one.

The stability constant of Cu(II)-DTEP-Am complexes was calculated and found to be $\lg\beta = 10.52$-10.96 at room temperature. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 1.04 - 1.09$).

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Cu(II) may be determined in the range 0.05-3.8 μg/ml.

The proposed method was successfully applied for the determination of copper from various pharmaceutical, food and in plant sample.

Crystal structure model of a new Ni(II) complex with carboethoxy-substituted bis(benzo)aza-14-crown-4 ether

Kolyadina N.M.[1], Kvartalov V.B.[1,2], Antipin A.M.[2], Davydov V.V.[1], Drogova G.M.[1]

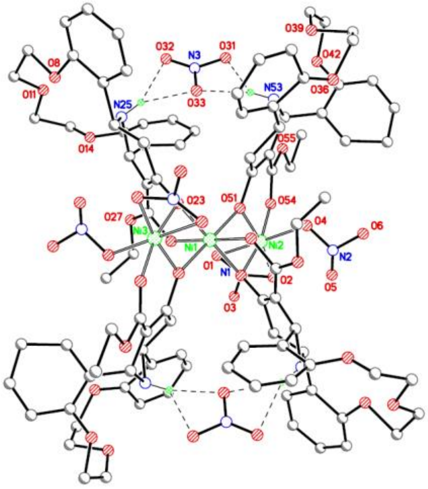
[1]RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6
[2]National Research Center Kurchatov Institute, 123182, Moscow 1, Akademika Kurchatova pl.

e-mail: kvartalov@gmail.com

This work continues our studies [1,2] devoted to the synthesis and study of physical and chemical properties of new complex compounds based on dibenzoazapiperidino-14-crown-4-ethers with biologically important metal salts.

Recently we obtained new complexes of lithium nitrate, zinc chloride and nickel nitrate with carboethoxy-substituted 14-crown-4 ethers. Coordination compounds were isolated by co-crystallization from organic solvents as powders in case of lithium and zinc ions and single crystals in case of nickel(II). Our attempt to synthesize the corresponding calcium complex was unsuccessful, but the presence of calcium cations in the solution allowed to isolate single crystals of the ligand.

The substances were identified by elemental analysis (EuroEA Elemental Analyzer), infrared spectroscopy (FT 801), and AES data (Cary 50). Precise information about the elementary cells parameters of the ligand and its complex compounds was obtained by powder diffraction analysis (Miniflex600). Complex studies of single crystals of carboethoxy-azacrown ether and its complex compound with Ni(II) cations were carried out using synchrotron radiation at "Belok" and "RKFM" stations in NRC «Kurchatov institute». The structures of the organic ligand containing carboethoxy subunit and the nickel complex compound ($[Ni_3(NO_3)_4L_4]2{\cdot}NO_3$) were solved using the data of the X-ray diffraction pattern. This allowed to evaluate the structural features of the ligand and its changes in the process of complexation. The presence of the nickel atoms in the complex compound was confirmed by X-ray fluorescence analysis.



Pic 1. Crystal structure model of complex compound of Ni(II) cation with carboethoxy-azacrown ether.

References

[1]. Polyakova I.N., Sergienko V.S., Sokol V.I., Kvartalov V.B., Kolyadina N.M. Russian Journal of Inorganic Chemistry. **2016.** T. 61. № 2. C. 168-173..

[2]. Sokol V.I., Sergienko V.S., Kolyadina N.M., Kvartalov V.B., Soldatenkov A.T., Davydov V.V. Russian Chemical Bulletin. **2011**. T. 60. № 10. C. 2124-2127.

Synthesis and acid-base characteristics of L-forms of N-(carboxymethyl)aspartic acid

Loginova E.S., Nikolskiy V.M.

Tver state University, 170100, Tver, Zhelyabova str. 33
e-mail: jeniatver@inbox.ru

Natural amino acids exhibit optical activity, i.e. are in the form as D- and L-isomers, the vast majority of them belong to L-series. It is known that in the human body are digested and are involved in biochemical processes only L-isomers amino acids [1].

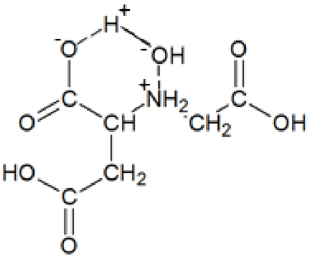
It is interesting to study chemical properties demanded by the nature of the L-isomers of N-(carboxymethyl)aspartic acid (L-CMA) in comparison with chemical properties of the racemate. This was carried out the synthesis of L - CMA by heating in a water bath solution containing L-aspartic acid, chloroacetic acid, and lithium hydroxide. The solution was then cooled and acidified using was acidified with HCl to a pH of 2-2.5 for precipitation.

Table. The negative logarithms of the concentration and speed of acid dissociation constants of D,L- CMA, L- CMA I=0,1 (KNO_3), T=25°C.

	pk_1	pk_2	pk_3
D,L- CMA [2]	2.58±0.04	3.85±0.06	9.65±0.04
L- CMA	3.32±0.02	4.40±0.03	10.42±0.03

The table shows the logarithms of the concentration step acid dissociation constants L-CMA and D,L- CMA.

It should be noted the high basic nitrogen atom of L- CMA (pK_4 = 10.42), which can probably be explained by the fact that the separation of the betaine hydrogen from the amino group of L-isomer in the titration, you must first break the loop formed by the ionized α-carboxyl group and a protonated amine group with a water molecule, included in this cycle by hydrogen bonds:



The CMA is an environmentally friendly chelating agent, derivatives of succinic acid possessing biologically active properties. Complexes metals can be used as microelement fertilizer, as catalysts of reactions of a metabolism, as stabilizers unusual oxidation states of metals, as a vehicle of physiologically important molecules, atoms and cations through the membranes of cells, and the L-isomer has found application as a sorbent for dissymmetrical splitting racemates method legendable chromatography [3].

References

[1]. Kovalev G.I., Firstova Y.Y., Abaimov D.A. *Journal of neurology and psychiatry*, **2012**, *3*, 39.

[2]. Gorelov I. P.; Nikolskiy V.M.; Kapustnikov A.I. *Russian Journal of General chemistry*, **1978,** *11*, 2596.

[3]. Rogozhin S.V.; Yamskov I.A.; Pushkin A.S. and others, *Izv. Chemical Bulletin*, **1976**, *10*, 2378.

Crystal and molecular structure of [$C_8H_{30}CuN_6O_8$]

[1]Maharramov A.M., [1]Aliyeva R.A., [1]Mardanova V.I. [1]Chyragov F.M.,
[1]Gurbanov A.V., [2]Potekhin K.A.

[1]Baku State University, Baku, Azerbaijan
[2]Vladimirsky State University for the Humanities
vusala_chem@mail.ru

The extractability of a metal chelate in the solvent extraction is often enhanced by the addition of a neutral ligand such as amine, dimethyl sulfoxide, organophosphorus or heteroeyclic compound. Copper(II) was chosen as an acceptor matrix, because he formed stable complexes with these amines. First, the complex should be mononuclear (monomeric) because polynuclear species are usually not highly volatile. To tackle this problem, we have developed hydrogen-bond driven assembly of metal complexes [1,2].

Synthesized complex copper (II) with ethylenediamine (L) and studied by X-ray crystal structure. Coordination nickel atom environment (II) is formed by four nitrogen atoms of two ethylenediamine ligands in the equatorial positions and two atoms of oxygen in the water in axial positions. Coordination polyhedron of Cu- distorted octahedron. The crystal structure consists of isolated mononuclear complexes of composition [$\mathbf{C_8H_{30}CuN_6O_8}$]. Between the complexes are observed only vander Waals contacts.

Synthesis. To a solution of 0.20 g (0.001 mol) $Cu(CH_3COO)_2\ 2{\cdot}H_2O$ in 50 ml of water was added a solution of 0.12 g (0.002 mole) L in 40 mL of ethanol. The resulting blue colored solution was heated in air at room temperature for a week. The precipitated green crystals was filtered, washed with water and then dried on the air. Yield 70%. X-ray diffraction study of compound was performed on diffractometer Bruker APEX II CCD (T = 293 the K, MoKα radiation, graphite monochromator, φ- and ω- scans 2Θmax = 56 °)

For anal $\mathbf{C_8H_{30}CuN_6O_8}$ calcd., %: C, 23.88; H, 7.46; N, 20.90; O, 31.84.
Found, %: C, 23.97; H, 7.51; N, 20.98; F, 31.92.

Table 1. Crystal data and structure refinement for [$\mathbf{C_8H_{30}CuN_6O_8}$].

Crystal data	structure refinement
Formula weight	401.92
Temperature, K	293
Crystal system	monoclinic
Space group	*C 2/c*
Unit cell dimensions, Å	*a = 19.3225(9), b = 9.6965(5) , c = 10.1761(5)*
β	113.6980^0
Z	4
Volume, $Å^3$	1745.83(15)
μ, мм	0,95
Crystal size, мм	0.32 x 0.30 x 0.29
R-faktor (to all)	R1 = 0.0254, wR2 = 0.0699
GOOF to F^2	1.000

Fiq.The structure of the complex and the numbering of the atoms

[1]. L. Bao-Long, L Jian-Ping, C.Jing, Z.Yong and Z.Li-Min *Chin.J.Chem*, 2003. ,21, 520
[2]. I.Yeltsov, V.Ovcharenko, V.Ikorskii, G.Romanenko and S.Vasilevsky *Polyhedron* 2001, 20, 1215–1222.

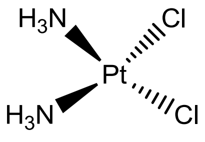
Novel binuclear Cu(II) and Pt(II) - containing coordination compounds as potential antitumor therapeutic agents

Mazhuga M.P., Plodukhin A.Yu., Makarov M.M., Krasnovskaya O.O., Zyk N.V., Beloglazkina E.K., Majouga A.G.

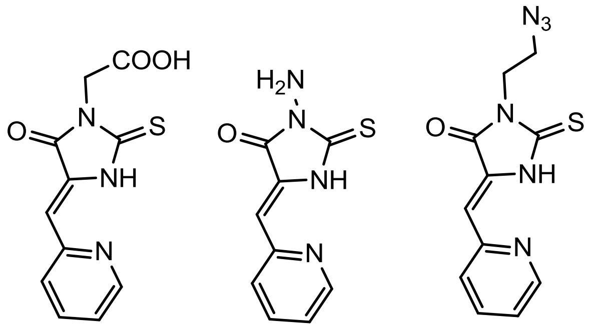
Lomonosov Moscow State University, Chemistry department, 119991, Moscow, Leninskie gory str. 1-3
e-mail: mashamaj@gmail.com

The discovery of cisplatin in 1965 was outbreak of wide-ranging application of the metal-containing drugs effective for the cancer treatment. However, there are several disadvantages in platinum drugs therapy due to its high toxicity. Despite their success, cisplatin-based therapies suffer from intrinsic and acquired resistance mechanisms appearing after repeated administrations of the drug [1]. The majority of studies have been reported focused on the Cu(II) [2] and Pt(II) complexes and their interaction with DNA being a potential anticancer drug [3]. In those researches, bifunctional ligands were observed in order to increase the activity of the DNA cleavage complex as compared with the Cu(II) complexes. Cisplatin enter cells by passive diffusion or using transporters (CTR1) – a significant one being the copper transporter. To account for all mentioned above, the study of Cu(II) and Pt(II) binuclear complexes draws a lot of attention nowadays.

2-Thiohydantoins are promising class of heterocycles compounds and their Cu(II) complexes are known to be potent as anticancer drugs. Recently, our laboratory synthesised Cu(II), Cu(I) complexes that are currently under preclinical developments as molecules for treatment of triple negative breast cancer [4]. In this research, taking into account cytotoxicity of Pt - drugs, we aimed to design novel binuclear Cu(II) – Pt(II) containing coordination compounds of 2-thiohydontoins. We have already synthesised 3 novel ligands, containing carboxylic, amine or azide exocyclic functional groups for further functionalization with Pt salts:



cisplatin



Cu(II) - Pt(II) compounds represent the novel class of metal-based anticancer drugs. They are expected to have the comparable or better antitumor activity of known Pt drugs. Detailed results of biological study will be presented.

This work was supported by the Russian Foundation for Basic Research (grant № 16-33-60166).

References

[1]. E. Wong, C. M. Giandomenico. Chemical Review **1999**, 99, 2451−2466.
[2]. C. Santini, M. Pellei, V. Gandin, etc., Chemical Review, **2014**, 114, 815–862 .
[3]. E. E. Aranda, T. A. Matias, K. Araki, etc. Journal of Inorganic Biochemistry **2016**, 165,108–118.
[4]. A. G. Majouga, M. I. Zvereva, M. P. Rubtsova, etc., Journal of Medicinal Chemistry **2014**, 57, 6252−6258.

The search of the complex sulfide in system BaS – MnS – Tb_2S_3

Monina L.N., Vasileva I.I., Ignatyeva A.A., Yakubin A.A.

Tyumen State University, 625003, Tyumen, Russia, Semakova str. 10
e-mail: monina83@yandex.ru

According to published data is known the formation of complex sulfides of composition $BaLn_2MnS_5$ (Ln = La - Nd) [1-5]. The data of the existence of phase at a ratio of initial components $1BaS:1Ln_2S_3:1MnS$ for series of rare earth elements Sm - Lu not detected. $BaSm_2MnS_5$ $BaGd_2MnS_5$ compounds and are not formed that is reported at works [6, 7]. The configuration of the valence shells of atoms of terbium 4f95d06s2 and terbium appears immediately 2 additional electron on the 4f sublevel compared with gadolinium atom. The aim of this work is a study of a sample containing 33.3(3) mol.% BaS-33.3(3) mol.% Tb_2S_3-33.3(3) mol.% MnS, obtained at different time-temperature conditions. Learning the sample belongs to quasi-binary section MnS - $BaTb_2S_4$ ternary BaS – MnS – Tb_2S_3 system. At the diffraction pattern of the sample cooled from the melt, there are only characteristic peaks of MnS for (structural type (ST) NaCl) and $BaTb_2S_4$ rhombic structure (ST $CaFe_2S_4$). At the microstructure of the prepared surface of sample is contains 2 phases. The most part occupy oval-round primary crystallized $BaSm_2S_4$ grains, traces of the eutectic mixture between the grains are found. Annealing of the cast sample pieces for 1 hour at a temperature of 1470 K and 1270 K at 2250 h did not lead to a change in the phase composition. The diffraction patterns of the samples are qualitatively similar to the diffraction pattern of the sample cooled from the melt: were identified reflexes characteristic $BaSm_2S_4$ and MnS (Figure 1). The samples that annealed are heterogeneous according to the microstructural analysis. Research of the sample 1 $BaS:1Tb_2S_3:1MnS$ by X-ray and microstructural analysis showed the absence of a complex of sulfide $BaTb_2MnS_5$ when cooled from the melt and annealing at 1470 K and 1270 K.

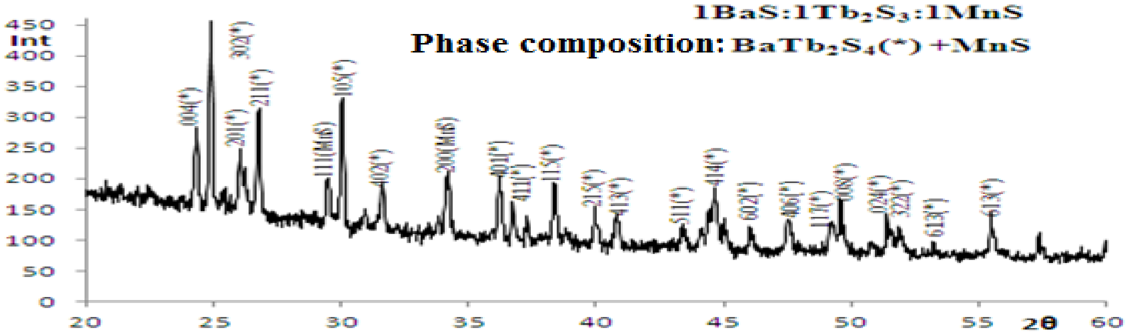


Fig.1. Diffraction pattern of the sample composition 1BaS: $1Tb_2S_3$: 1MnS, annealed at 1270 K during 2250 hours. Conditions: CuKα radiation (λ1 = 1.5406 Å), Ni-filter

References

[1]. Masuda, H.; Fujino, T.; Sato, N.; Yamada, K. J. Solid State Chem., **1999**, *146*, 336.

[2]. Wakeshima, M.; Hinatsu, Y.; Oikawa, K.; Shimojo, Y.; Morii, Y. J. Materials Chem., **2000**, *10*, 2183.

[3]. Wakeshima, M.**;** Hinatsu**,** Y. J. Solid State Chem., **2000,**153, 330.

[4]. Wakeshima, M.; Hinatsu, Y. J. Solid State Chem., **2001**, *159*, 163.

[5]. Koo, H.-J.; Whangbo, M.-H.; Lee, K.-S. J. Solid State Chem., **2002**, *169*, 143.

[6]. Monina, L.N.; Yakubin, A.A. Materials of All-Russian scientific conference with international participation «II materials science Baikal Forum», **2015**, *2*, 87.

[7]. Monina, L.N.; Yakubin, A.A. Proceedings of the IX International scientific conference «Kinetics and mechanism of crystallization. Crystallization and materials of the future», **2016**, 36.

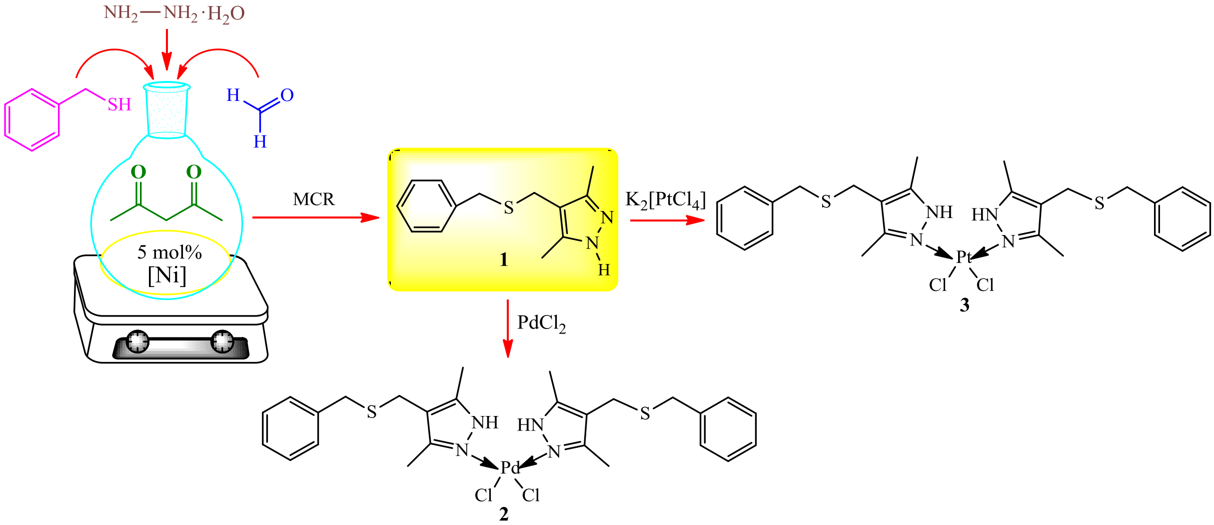
Synthesis of new Pd(II) and Pt(II) *N*-complexes with 3,5-dimethyl-4-((benzylsulfanyl)methyl)-1*H*-pyrazole ligand

Akhmadiev N.S.,[1] Nurtdinova G.M.,[2] Akhmetova V.R.,[1] Ibragimov A.G.[1]

[1]*Institute of Petrochemistry and Catalysis, RAS, 450075, Ufa, Prospekt Oktyabrya 141*
[2]*Ufa State Petroleum Technological University, 450062, Ufa, Kosmonavtov str. 1*
e-mail: vnirara@mail.ru

Pyrazole-containing compounds have a wide range of useful properties [1]: substituted pyrazoles are components of the some drugs (Celecoxib, Aminophenazone, Antipyrin) or exhibit fungicidal activity. Recently it was discovered that the palladium and platinum complexes with ligands pyrazole demonstrate significant anticancer and specific catalytic properties [2,3].

We have proposed a new effective method of synthesis of sulfur-containing ligand - 3,5-dimethyl-4-((benzylsulfanyl)methyl)-1*H*-pyrazole **1** through multicomponent reaction of 2,4-pentanedione, formaldehyde, benzylthiol and hydrazine hydrate.



Interaction between the palladium and platinum salts is implemented with the reagent **1** with the selective formation of N-complexes **2** and **3**, the structures of which were set on the basis of ^{1}H NMR, ^{13}C, ^{15}N, and elemental analysis. In the IR spectra of the complexes **2,3** there are the absorption bands in region 477 (Pd-N) and 476 (Pt-N) cm^{-1} that confirm the metal coordination to the pyrazole ring nitrogen atoms between the two molecules of **1**. It was found that the obtained compounds have a low toxicity and products **1-3** are of interest as antiinflammatory and antitumor agents (*in silico* calculations).

This work was supported by the Russian Foundation for Basic Research (grant № 14-03-00240_A, 14-03-97023 r_ Povolzhie_a).

References

[1]. Shokol, T.W.; Gorbulenko, N.V.; Turov, A.V.; Khilya, V.P. *Chem. Heterocycl. Compd.*, **2013**, *2*, 351.

[2]. Abu-Surrah, A.S.; Safieh, K.A.A.; Ahmad, I.M.; Abdalla, M.Y.; Ayoub, M.T.; Qaroush, A.K.; Abu-Mahtheieh A.M. *Eur. J. Med. Chem.*, **2010**, *2*, 471.

[3]. Peral, D.; Gomez-Villarraga, F. ; Sala, X.; Pons, J.; Bayon, J.C.; Ros, J.; Guerrero, M.; Vendier, L.; Lecante, P.; Garcia-Anton, J.; Philippot. K. *Catal. Sci. Technol.*, **2013**, *3*, 475.

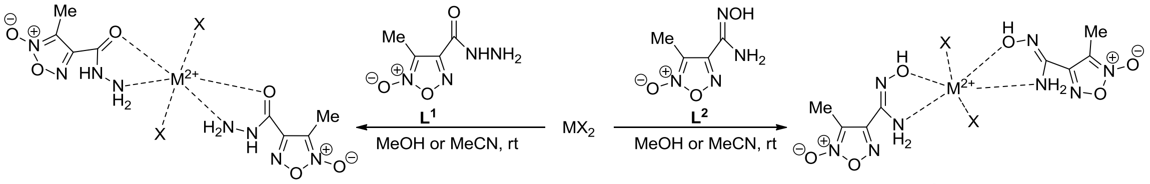
Synthesis of novel furoxan-based complex structures

Radzhabov M.R., Fershtat L.L., Makhova N.N.

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky prosp., 119991, Moscow, Russian Federation
e-mail: ethanol181@gmail.com

An effective approach to the creation of new drug candidates with improved pharmacokinetic profiles is the design of new structures by molecular hybridization of compounds of various classes. In recent years, the 1,2,5-oxadiazole-2-oxide (furoxan) motif has been the subject of increased attention owing to the ability of furoxans to release nitric oxide (NO). A family of hybrid hetarylfuroxan structures representing a combination of various pharmacologically active compounds with furoxan ring in one molecule was synthesized [1]. However, the utilization of furoxan derivatives as complexating agents is rather neglected.

In our study we have synthesized a series of novel furoxan complex structures **1-7** based on the complexation of pre-functionalized furoxan unit **L^1** or **L^2** with an appropriate d-element (Cd or Ni). The ratio of ligand : metal was found to be 2:1 irrespective of the ligand and transition-metal character.



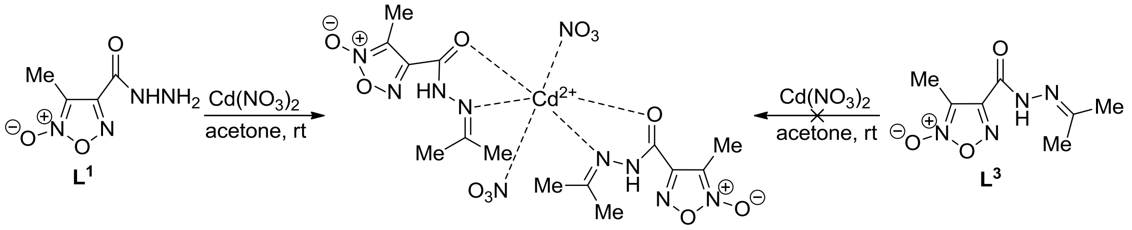
1-3 (58-66%)

1: M = Ni, X = NO_3
2: M = Cd, X = Cl
3: M = Cd, X = NO_3

4-7 (29-89%)

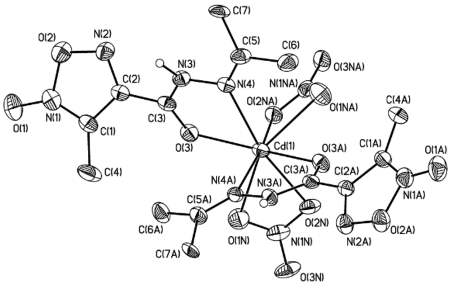
4: M = Ni, X = NO_3
5: M = Ni, X = ClO_4
6: M = Cd, X = Cl
7: M = Cd, X = NO_3

Interestingly, complexation of furoxan **L^1** with $Cd(NO_3)_2$ in acetone afforded complex **8** containing hydrazone units linked to the furoxan cycle as a result of condensation of amino groups in initial ligand with acetone. Surprisingly, complexation of hydrazone **L^3** with $Cd(NO_3)_2$ did not result in complex **8** formation.



8 (69%)

The structure of complex **8** was unambiguously determined by X-ray diffraction study. According to X-ray data, Cd atom is in pseudo-octahedron surrounding consisting of NO_3-anions and N and O atoms of hydrazone moieties as neutral ligands.



This work was supported by the Russian Foundation for Basic Research (grant № 16-33-00564).

References

[1]. Fershtat, L.L.; Makhova, N.N. *Russ. Chem. Rev.*, **2016**, *85*, 1097.

The study of complexes of osmium(IV): $[H(dmso)_2][OsX_5(dmso)]$ (X=Cl, Br)

Tereshina T.A., Dobrokhotova E.V., Kultyshkina E.K., Rudnitskaya O.V.,
Khrustalev V.N.
RUDN university
dobrokhotova_ev@rudn.university

Dimethyl sulfoxide complexes attract attention of researchers in recent decades because they are of interest for both pure and applied chemistry. The complexes can be used as homogeneous catalysts or precursors of various compounds. Osmium compounds are relatively poorly studied among dimethyl sulfoxide complexes of platinum-group metals.

This abstract presents the results of the study of osmium complexes: $[H(dmso)_2][OsCl_5(dmso)]$ (**1**) [1], $[H(dmso)_2][OsBr_5(dmso)]$ (**2**). The synthesized complexes were characterized by IR, UV/Vis and NMR spectroscopy and X-ray diffraction.

The ATR IR spectra of compounds **1** and **2** exhibit wide bands absorption of cations ν(S=O…H...O=S) at 722 and 724 cm^{-1} and ν(SO) of O-coordinated DMSO at 878 and 890 cm^{-1}, respectively, and vibrations of CH_3-groups $\rho(CH_3)$ at 1029, 1034 cm^{-1}, δ(CH3) at 1422 cm^{-1}; in FIR spectra ν(Os-Cl) is observed at 312 and ν(Os-Br) at 215 cm^{-1}.

Behavior of complexes **1** and **2** in various solvents was studied by UV/Vis spectroscopy.

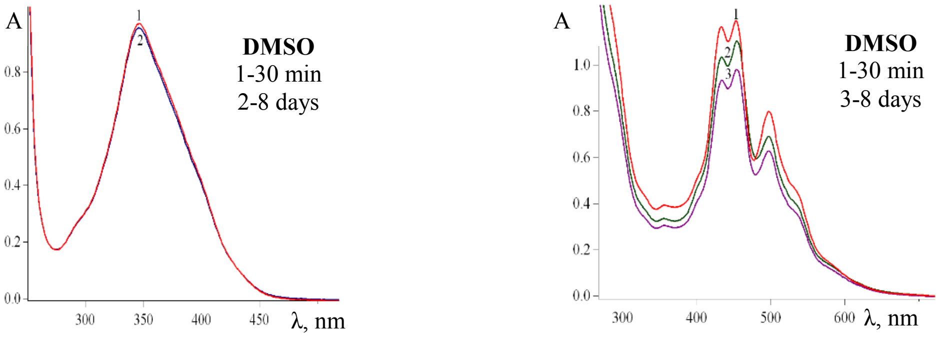


Fig. 1. UV/Vis spectra of solutions of 1 and 2 in DMSO.

The target compounds are well soluble in DMSO, water, ethanol, acetone, DMF have similar spectra and differ than that of $[OsX_6]^{2-}$ ions. Complex **1** is quite stable in these solvents, even after 8 days noticeable changes in the electronic spectra not observed. Compound **2**, in contrast, is labile in solution. (fig.1).

NMR ^1H spectra in DMSO-d_6 contain singlets at 2.54 ppm of free DMSO and 3.87 (**1**) and 3.49 (**2**) ppm of O-coordinated DMSO, which agrees well with the ^{13}C spectra, which contain signals of free DMSO at 40.43 ppm, and signals at 87.8 ppm (**1**) and 93.2 (**2**) ppm is related to dmso-O, these shifts are associated with the presence of the compound of osmium in the oxidation state +4.

According to X-ray diffraction analysis crystals belong to orthorhombic space group $Pca2_1$ (**1**) and Pbca (**2**). The complexes are composed of a cation $[H(dmso)_2]^+$ and anions $[OsCl_5(dmso)]^-$ $[OsBr_5(dmso)]^-$. In the complexes the coordination of DMSO molecules to the metal through the oxygen atom. The structure of the cation $[H(dmso)_2]^+$ is symmetric. The difference is that in the case of the chloride complex of sulfur atoms are located in cis-position relative to the line strong O...H...O hydrogen bonds, bromidem same complex they are in trans-position.

References

[1]. O. V. Rudnitskaya, T. M. Buslaeva, and M. M. Lyalina // Zh. Neorg. Khim. 1994. 39. p. 922.

Polyhedral rearrangements in the complexes of rhodium and iridium with isomeric carborane anions [7,8-Me_2-X-SMe_2-7,8-*nido*-$C_2B_9H_8$]$^-$ (X = 9; 10)

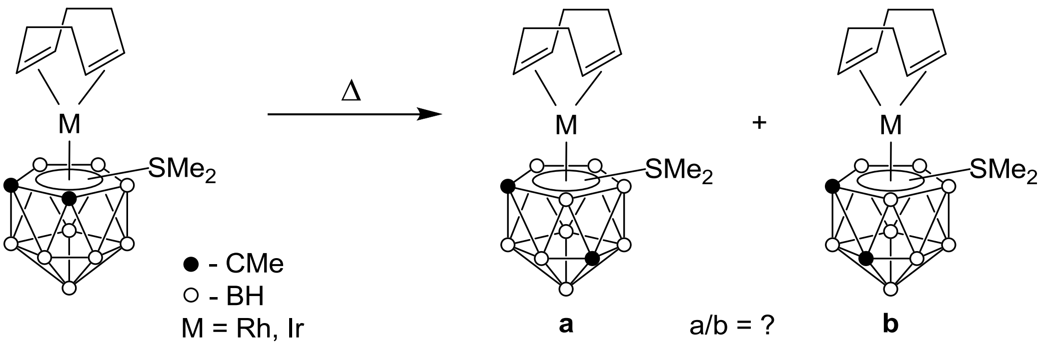
Vinogradov M.M., Nelyubina Y.V., Pavlov A.A., Novikov V.V., Kudinov A.R.

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
119991, Moscow, Vavilova str. 28, Fax: +7 499 135 5085,

e-mail: vmm@ineos.ac.ru

Icosahedral carboranes are an interesting class of exceptionally stable boron-rich clusters that can be linked with three-dimensional (3D) aromatic character of such compounds. Unique chemical and physical properties of carborane species, such as rigidity, high stability to air and moisture allowed to incorporate these molecules into a variety of materials, such as biologically active molecules, ceramics and polymers, light-emitting materials, electricity sources, and to access a set of properties not normally available in carbon chemistry.

The remarkable feature of the *o*-carborane (1,2-*closo*-$C_2B_{10}H_{12}$) is an ability to undergo polyhedral rearrangement (at 450 °C) which has been of the interest for many years since the first report of *ortho* to *meta*-carborane transformation [1]. Coordination of metals to carboranes appears to lower the rearrangement barrier and thereby allows investigating cage isomerizations at RT or even at lower temperatures [2]. Although numerous metallacarborane rearrangements were reported, this information has a fragmentary character that makes its systematization unavailable due to the different organometallic fragments and carborane ligands used.



We report the synthesis of new complexes of relative charge-compensated carborane anions with common organometallic fragments and their thermo-induced isomerization reactions. The temperature at which synthesized complexes undergo isomerization depends on the nature of metal atom, its oxidation state and emplacement of SMe_2 moiety in carborane ligand. Moreover, rearrangement may lead to the exclusive formation of type **a** complex (1,2→1,7 carbon atoms isomerization scheme) or to the mixture of type **a** and type **b** (1,2→1,2 scheme) products. A new mechanism of 1,2→1,2 isomerization was proposed on the basis of DFT calculations.

This work was supported by the Russian Foundation for Basic Research (grant № 16-33-00166).

References

[1]. Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128.

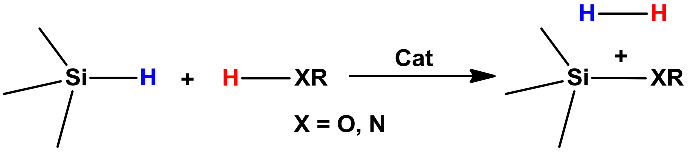
[2]. Tutusaus, O.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Teixidor, F. *Chem. Commun.* **2003**, 2458.

Dihydrogen bonding with silanes and its role in dehydrocoupling

Voronova E. D., Golub I.E., Filippov O.A., Shubina E.S., Belkova N.V.

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

Dehydrogenative coupling reactions forming E–E' bond are central to the development of many areas of main group chemistry. These reactions have a wide range of important applications in terms of both the main group element products formed and the H_2 gas released [1]. Dehydrocoupling to form Si–E bonds (Scheme 1) is an area of significant interest given the diversity of applications of compounds such as silicones and silazanes ranging from construction materials through to elastomers and medical applications. Thus the catalytic formation of silicon–element bonds represents a rapidly developing area [2,3]. Most of the modern studies rely on the use of Lewis acids, whereas a series of earlier works reports the use of organic bases as a dehydrocoupling catalyst [4,5].



Scheme 1

The intermediacy of dihydrogen bonds, E-H···H-X, in H_2 from transition-metals and main-group elements hydrides is well established [6]. In this work we present the results of our studies of dihydrogen bonding and other intermolecular interactions involving phenylsilanes Ph_nSiH_{4-n} (n = 1-3) as well as their role in amine-catalyzed dehydrocoupling. The experimental study was performed using variable temperature (190-298 K) IR and NMR (^{1}H and ^{29}Si) spectroscopy in non-polar solvents (hexane, toluene) in combination with quantum chemical calculations. The results obtained allow suggesting the detailed reaction mechanism taking into account various intermolecular interactions.

This work was partially supported by the Russian Foundation for Basic Research (grant № 16-03-00324*).*

References

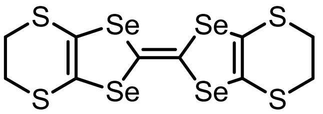
[1]. Melen, R. L. Chem. Soc. Rev. **2016**, 45, 775.
[2]. Bellini, C.; Dorcet, V.; Carpentier, J.-F.; Tobisch, S.; Sarazin, Y. Chem. Eur. J. **2016**, 22, 4564.
[3]. Dunne, J. F.; Neal, S. R.; Engelkemier, J.; Ellern, A.; Sadow, A. D. J. Am. Chem. Soc. **2011**, 133, 16782.
[4]. Lukevics, E.; Dzintara, M. J. Organomet. Chem. **1984**, 271, 307.
[5]. Lukevics, E.; Dzintara, M. J. Organomet. Chem. **1985**, 295, 265.
[6]. Belkova, N. V.; Epstein, L. M.; Filippov, O. A.; Shubina, E. S. Chem. Rev. **2016**, 116, 8545.

Halogenocadmiates of tetrathiafulvalenes - layered organic conductors

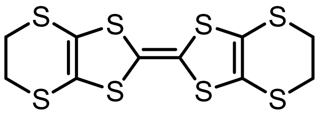
Zhilyaeva E.I., Flakina A.M., Lyubovskaya R.N.

Institute of Problems of Chemical Physics RAS, Russia, 142432, Chernogolovka, Academician Semenov avenue 1
e-mail: zhilya@icp.ac.ru

Hybrid layered compounds have been prepared in which conducting organic layers composed of π-donors of the tetrathiafulvlene family alternate with nonconducting inorganic layers formed by cadmium halides anions. Bis(ethylenedithio)tetraselenafulvalene (BETS) and bis(ethylenedithio)tetrathiafulvalene (ET) were used in syntheses.



BETS



ET

The products were synthesized by electrochemical oxidaion of appropriate tetrathiafulvalene in the presence of $[Bu_4N]CdI_3$, $[Bu_4N]CdBr_3$ and $[Bu_4N]_2CdBr_4$ as supporting electrolytes. Iodocadmiates of the tetrathiafulvalenes were prepared in 1,1,2-trichloroethane, the compounds of $(BETS)_3Cd_2I_5$, $(ET)_4Cd_5I_{12}$ and $(ET)_2CdI_3$ composition being isolated. Bromocadmiates of the tetrathiafulvalenes were synthesized in chloro, bromo- and fluorobenzenes, o-dichlorobenzene, chlorocyclohexane, and 2-halogenotoluenes as solvents. $(BETS)_3Cd_2Br_7(H_2O)_x$, $(BETS)_4CdBr_4(C_6H_4Cl_2)$, $(ET)_3CdBr_4$ and a series of isostructural compounds $(ET)_4CdBr_4$(solvent) (solvent = C_6H_5F, C_6H_5Cl, C_6H_5Br, C_7H_7Cl and C_7H_7Br) were prepared.

The compounds obtained have layered structures. Conducting organic layers are built of stacks of ET or BETS molecules. Nonconducting inorganic layers in $(ET)_4Cd_5I_{12}$ are formed by CdI_6 octahedra and CdI_4 tetrahedra interlinked in a two-dimensional anionic network. This compound can be attributed to layered perovskite-like structures. Nonconducting inorganic layers in $(ET)_2CdI_3$ are built of $[Cd_2I_6]$ dimeric anions with tetrahedral configuration of cadmium atom bonds. In $(BETS)_4CdBr_4(C_6H_4Cl_2)$ and $(ET)_4CdBr_4$(solvent), nonconducting inorganic layers are built of $[CdBr_4]$ anions of tetrahedral geometry and solvent molecules, and in $(ET)_3CdBr_4$ they built of $[CdBr_4]$ anions only.

Electrical resistivity measurements showed that BETS-based compounds and $(ET)_4CdBr_4$(solvent) behave as metals with decreasing temperature showing different metal-insulator transition temperatures. $(ET)_4Cd_5I_{12}$, $(ET)_2CdI_3$, and $(ET)_3CdBr_4$ are semiconductors.

The combination of conducting organic layers and anionic layers with perovskite-like structure in the single lattice can provide new properties in such materials. Hybrid organic-inorganic compounds with perovskite-like structure and potential photovoltaic properties are intensely studied now as materials of photoactive layers for solar cells [1,2].

The work was supported by the Russian Foundation for Basic Research (grant № 16-03-01103).

References

[1]. Kojima, A.: Teshima, K.; Shirai, Y.; Miyasaka T. *J. Am. Chem. Soc.*, **2009**, *131*, 6050.
[2]. Jeng, J.-Y.; Chiang, Y.-F.; Lee, M.-H.; Peng, S.-R.; Guo, T.-F.; Chen, P.; Wen, T.-C. *Adv. Mater.*, **2013**, *25*, 3727.

New α-diimine nickel complexes - synthesis and catalysis of alkene oligomerization reactions

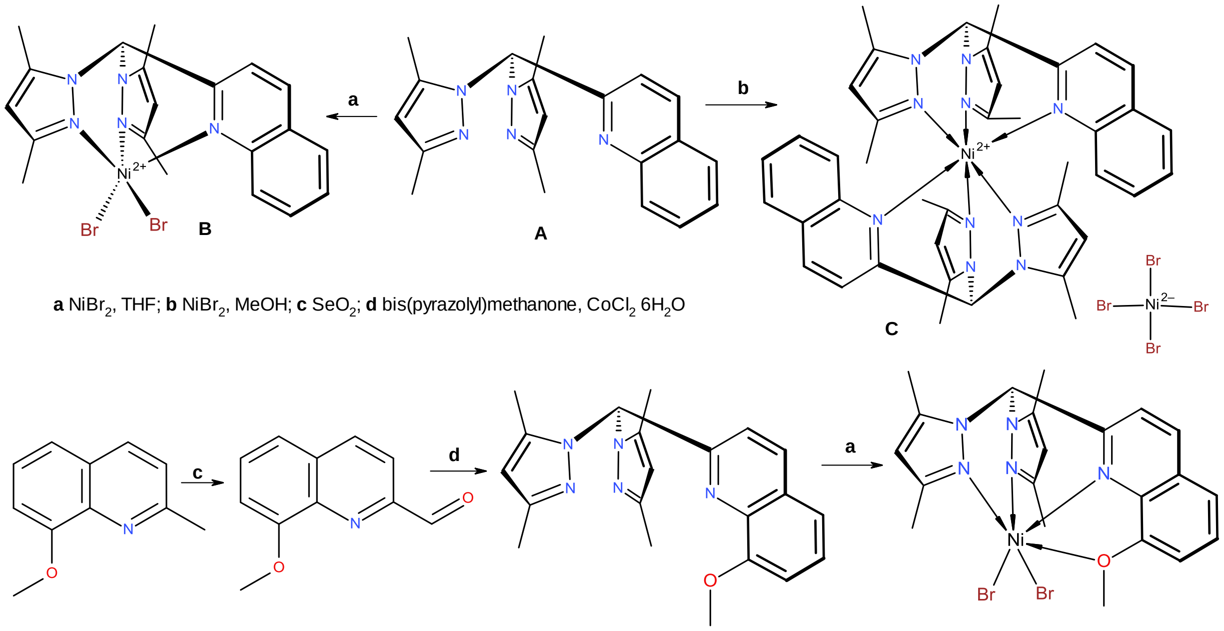
Zubkevich S.V.[a], Gagieva S.C.[a], Tuskaev V.A.[a], Sabanov V.K.[b], Bulychev B.M.[a]

[a]Lomonosov Moscow State University, Department of Chemistry, 1 Leninskie Gory, Moscow, 119992, Russia
e-mail: zubkevich.sergey@gmail.com
[b] Innovative technological materials science centre, ul. Nicolaeva 4, Vladikavkaz 362011, Russia

Heteroscorpionate ligands have been demonstrated as attractive ancillary ligands for the synthesis of transition metal complexes. Their reactions with Ni(II) salts can, in principle, give half-sandwich (structure B, kinetic control) or full-sandwich (structure C, thermodynamic control) complexes through the tripodal coordination of one or two scorpionates via the pyrazolyl ring's nitrogen atom. The coordinatively saturated complexes **C** showed a very moderate activity in alkene oligomerization reactions.

The selective synthesis of coordination compounds type B – is a challenging task. To overcome these problems various synthetic approaches were used, including slow addition of the ligand solution to the solution of the starting nickel complex, an exception to prolonged heating of the reaction mixture or the use of rather exotic metal sources, such as tetrahalonickelate(II) ion in nitromethane.

In this paper, for the stabilization the half -sandwich complexes were applied a tetradentate heteroscorpionate ligand, synthesized by Peterson rearrangement from 8-methoxyquinoline-2-carboxaldexyde and bis(3,5-dimethylpyrazolyl)methanone.



a $NiBr_2$, THF; **b** $NiBr_2$, MeOH; **c** SeO_2; **d** bis(pyrazolyl)methanone, $CoCl_2$ $6H_2O$

A structural study of the obtained complexes and the study of their catalytic activity in the reaction of ethylene oligomerization are ongoing.

This work was financially supported by the Russian Foundation for Basic Research – Russia (Project Nos. 14-43-01014), republican budget of the Republic of North Ossetia-Alania.

Physical and Colloidal Chemistry Section

Oral Reports

Synthesis TiO_2 and modified TiO_2 by salt metal to prepare $CoTiO_3$ under thermal decomposition of titanium butoxide (IV)

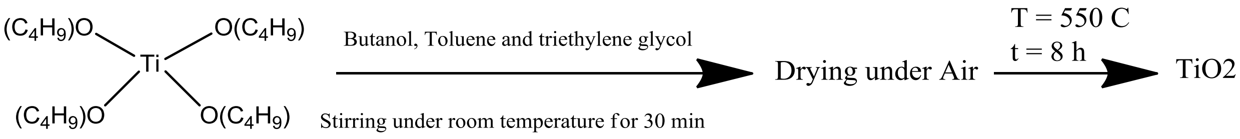
Yahya Absalan, Olga Kovalchukova

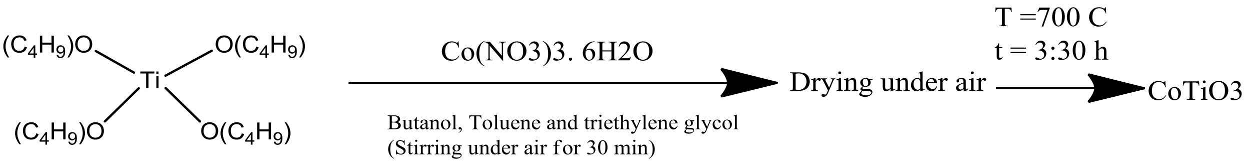
Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: Yahya_absalan@rudn.university

Nano-materials have been considered in recent times because of many valuable features such as high activity, singular optical and magnetic valuables [1].These properties come from unique features of nanoparticles due to their large surface and surface activity compared with material's bulk phase [2].

In this study TiO_2 nanoparticle in Degussa phase has been synthesized by a new method using Butanol, Toluene and triethylene glycol as solvent at 550 C for 8 hours. To modify TiO_2, doping has been done by transition metal and $CoTiO_3$ has been synthesized. Pure $CoTiO_3$ nanoparticle has been formed when the precursor was heat-treated at 700 °C for 410 min.

Characterizing the new additions has been done by X-ray diffraction (XRD), FT-IR spectroscopy, UV-Vis spectroscopy, Scanning electron microscope (SEM) image and Transmission electron microscopy (TEM) picture. According to the reaction, while Titanium (IV) butoxide as a precursor was being reacted with the metal, the energy band gap was decreased markedly. To show existing bond of Titanium and metal, FT-IR has been used so as to investigate the obtained addition and SEM image has been used to investigate better their morphology. Obtained $CoTiO_3$ by this method can be used in variety areas especially as a catalyst to degrade harmful substance under UV and Vis light and also it can be used as humidity sensor.





Reference

[1]. V. Arabali, M. Ebrahimi, M. Abbasghorbani, V.K. Gupta, M. Farsi, M.R. Ganjali, F. Karimi, Electrochemical determination of cysteamine in the presence of guanine and adenine using a carbon paste electrode modified with N-(4-hydroxyphenyl)-3,5-dinitrobenzamide and magnesium oxide nanoparticles J. Mol. Liq, 213 (**2016**).

[2]. E. Khosravifarda, M. Salavati-Niasari, M. Dadkhah, G. Sodeifiana, Synthesis and Characterization of TiO2-CNTs Nanocomposite and Investigation of Viscosity and Thermal Conductivity of a New Nanofluid J Nanostruct, 2 (**2012**) 191-197.

The analysis of chemical bonding in benzene, cyclobutadiene and cyclopentadienyl ions. The test for the presence of conflicting aromaticity

Baranov N.I. [1], Bozhenko K.V. [1], Popov I.A. [2], Boldyrev A.I. [2]

[1]*Physical and colloidal chemistry department, Peoples' Friendship university of Russia, Moscow 117198, Russian Federation*
[2]*Department of chemistry and biochemistry, Utah State University, Logan, Utah 84322, USA*
e-mail: lurtum2@gmail.com

The main purpose of research is to investigate the chemical bonding picture in aromatic molecules during transitions to ionic states. In most cases forming ions are systems with open shells. Thus, it is possible to detect conflicting aromaticity (the simultaneous presence of aromaticity by α-electrons and antiaromaticity by β- ones or vice versa) in these species.

The aims of the research are deep analysis of geometrical and electronic structure of the benzene, cyclobutadiene molecules, cyclopentadienyl radical and their ions and conducting the chemical bonding analysis with the usage of the Adaptive Natural Density Partitioning algorithm(AdNDP).

The geometry optimization and normal-mode analysis for the studied systems were carried out using PBE1PBE functionalwith 6-311++G** basis set as implemented in Gaussian 09. The density matrix used and natural atomic orbital basis sets were generated at the PBE1PBE/6-31G.

These findings make it possible to conclude that in the current form AdNDP method is able to detect various delocalized patterns in chemical systems with open shells.

Furthermore, π-conflicting aromaticity has been detected and analyzed for following structures: C_5H_5, $C_6H_6^+$, $C_6H_6^-$.The detailed analysis of chemical bonding in aromatic molecules and ions are able to explain the stability of triplet cyclopentadienyl cation (aromatic by α- as well as β-electrons, what form highly symmetric structure) as well as the instability of the cyclobutadiene in the triplet state (only one 4c-2e MO, while two leftover π, α-electrons are detected as lone pairs between opposite carbon atoms).

References

[1]. Zubarev Dmitry Yu. and Boldyrev Alexander I. Developing paradigms of chemical bonding: adaptive natural density partitioning // Physical chemistry chemical physics. 2008.10. P. 5207-5210. DOI: 10.1039/b804083d

[2]. Bully Thomas. Cyclobutadiene: the antiaromatic paradigm? // Angewandte chemie international edition. 2006. 45(60).P. 6616-6619

[3]. Zubarev Dmitry Yu. and Boldyrev Alexander I. Revealing intuitively chemical bonding patterns in organic molecules via adaptive natural density partitioning // Journal of organic chemistry. 2008.73. P. 9251-9258. DOI:10.1021/jo801407e

Synthesis of (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))

Belyankova Y.O.[a], Tursynbekova M.M.[b], Rafikova K. S.[a,b], Zazybin A.G.[a], Aydemir M.[c], Meric N.[c], Duygu E.K.[d], Askerov A.K.[a], Doskumbay M.[a] and Tokenova Zh. [a]

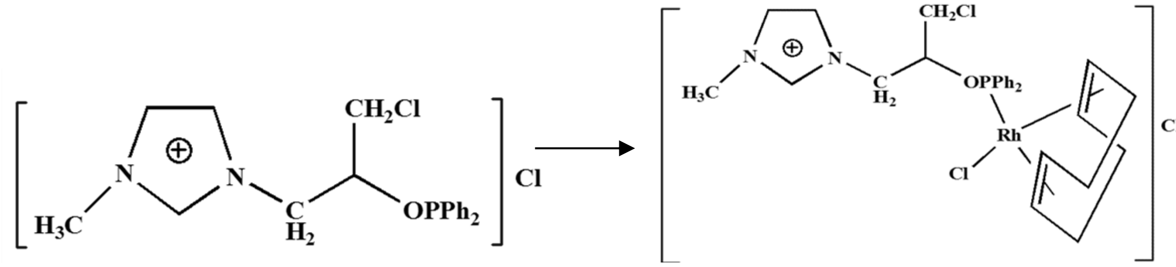
[a] *Kazakh-British Technical University Kazakhstan, 050000, Almaty, Tole bi str. 59*
[b] *Kazakh-National Research Technical University Kazakhstan, 050013, Almaty, Satpayev str. 22*
[c] *University of Dicle Turkey, 21280, Diyarbakir, Kıtılbıl Mahallesi.*
[d] *, Siirt University, Turkey, 56100, Siirt, Güreş Cad.*
e-mail: belyankovae@gmail.com

Transition metal complexes are powerful catalysts for organic transformations and when the suitable ligands are associated with the metal center, they can offer chemo-, regio- or stereo-selectivity under mild conditions [1]. A number of transition metal complexes are known to be effective catalysts for hydrogen atom transfer from an alcohol to a ketone, known as transfer hydrogenation (TH) [2].

Metal-containing ionic liquids are regarded as promising new materials that combine the properties of ionic liquids with additional intrinsic magnetic, spectroscopic, or catalytic properties, depending on the incorporated metal ion [3].

The synthesis of 1-(3-chloro-2-(hydroxypropyl)-3-methyl-imidazolium chloride, $[C_7H_{12}N_2OCl]Cl$, was accomplished in one step from the reaction of 1-methylimidazole and epichlorohydrin in ethanol at room temperature. Phosphinite ligand $[(Ph_2PO)\text{-}C_7H_{11}N_2Cl]Cl$, was synthesized from the starting material PPh_2Cl, in CH_2Cl_2 solution. The progress of this reaction was conveniently followed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

Reactions of $[Rh(\square\text{-}Cl)(cod)]_2$ with $[(Ph_2PO)\text{-}C_7H_{11}N_2Cl]Cl$ in CH_2Cl_2 in a ratio of 1/2:1 at room temperature for 1 h gave micro-crystalline precipitate of complex (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yldiphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))].



The synthesized rhodium complex was applied as a catalyst in the TH of ketones using alcohols as a source of hydrogen and appeared to be very promising catalyst of TH, giving high yield (up to 99%) of product.

This work was supported in part by the Ministry of Education and Science of the Republic of Kazakhstan, Grant 1318/GF4, 1752/GF4.

References

[1]. Noyori, R.; Takaya H. *Acc. Chem. Res.* **1990,** *23*, 345-350.
[2]. Pamies O.; Backvall J.E. *Chem. Eur. J.* **2001**, *23*, 5052-5058.
[3]. Chiappe C.; Pomelli C.S.; Bardi U.; Caporali S. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5045-5051.

Quantum-chemical modeling of exchange coupling in the magnetic sublattice of bifunctional compounds

Bozhenko K.V. [1,2], Aldoshin S.M. [1,2], Utenishev A.N. [1]

[1] *Institute of Problems of Chemical Physics, Russian Academy of Sciences,1, Acad. Semenov av., Chernogolovka 142432, Moscow Region, Russia.*
[2] *Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6*
e-mail: kbogenko@mail.ru

For modeling of the magnetic sublattice of bifunctional compounds, quantum-chemical calculations of complexes $[(L)_2M1^{III}(L)M2^{II}(L)_2]^{5-}$ (I) have been performed ($M1^{III}$ and $M2^{II}$ are tri- and divalent atoms of 3d and 4d transition metals M_1 (Cr, Fe) and M_2 (Ni, Co, Pd), L is dithiooxamide or oxalate). We suggested that transfer from 3d to 4d transition metals is accompanied by an increase of the exchange coupling constant J between metals $M1^{III}$ and $M2^{II}$.

Calculations of the complexes' geometric structure were performed by using the GAUSSIAN-03 [1] program (the B3LYP/LANL2DZ level of theory) and of J constants by using the ORCA program [2] (the B3LYP/TZV level of theory). The replacement of a divalent atom of 3d metal by a divalent atom of 4d metal leads to J increase, whereas replacement of a trivalent atom of 3d metal by a trivalent metal atom of 4d metal does not change the constant value. It has been found out that there was the correlation of J with the total change of the spin density on the M1 and M2 metals in the complex structures compared to the $M1^{3+}$ and $M2^{2+}$ isolated cations.

References

[1]. Licence to Use Agreement: Gaussian, Inc., 340 Quinnipiac Street, Building 40, Wallingford, CT 6492.

[2]. F. Neese, ORCA-An ab initio, DFT, and Semiempirical Program Package 2.7–00, Universität Bonn, Bonn, 2009.

Direct formation of diethyl ether from ethanol conversion on complex ZrO_2-Al_2O_3 oxide catalytic systems

Chuklina S.G., Akhmedova L.S., Maslenkova S.A., Pylinina A.I.

Peoples' Friendship Universityof Russia, 117198, Moscow,Miklukho-Maklaya str. 6
e-mail: sofyaogan@gmail.com

Alumina and zirconia mixed oxide systems are attracting reasonable interest in various catalytic processes. There are numerous literature articles on converting ethanol isobutene over supported complex oxide catalyststo higher alcohols and other valuable compounds, such as ethylene,hydrogen and butadiene[1-3].

Complex oxides Al_2O_3-(CeO_2-ZrO_2)with different composition of Al_2O_3(5 to 75%) were obtained by the sol-gel method, using the simultaneous precipitation of the components with a solution of ammonia in the presence of isobutanol. The effect of the heat treatment temperature on the dispersion, morphology, agglomeration of xerogels and powders of the Al_2O_3-CeO_2-ZrO_2 system was investigated.The surface area of the catalysts decreased with increasing Zr/Al molar ratio.

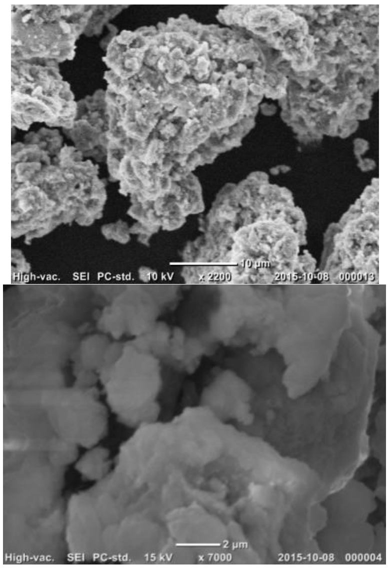


Fig.1The SEM pictures of surface of the calcinated sample with 50% content of Al_2O_3

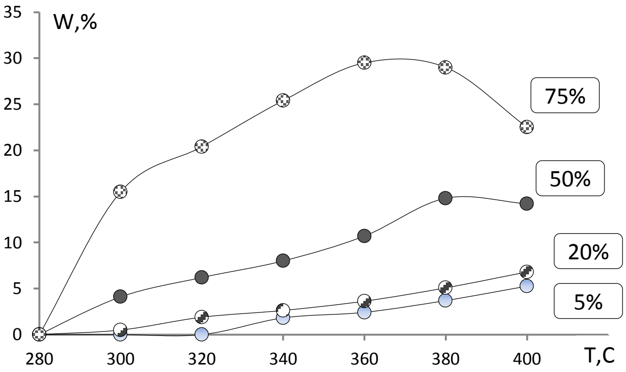


Fig 2. The dependency of the ethanol conversion to DEE on the %Al_2O_3 content in calcinatedat 500°C samples.

Synthesis temperature affects the selectivity and activity of ethanol conversion to diethyl ether (DEE) as well as the sample composition. For calcinated samples the DEE formation activity and selectivity increase with increasing of alumina content (Fig.2)[4].

The publication was financially supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.008).

References

[1]. N. Hebbena, C. Diehma, O. Deutschmanna Catalytic partial oxidation of ethanol on alumina-supported rhodium catalysts: An experimental studyApplCatal A: General V.388, I.1–2, **2010**, P. 225–231

[2]. ChangjunLiua, JunmingSuna, Colin Smitha, A study of ZnxZryOz mixed oxides for direct conversion of ethanol to isobutene ApplCatal A: General**2013**, 467, P.91–97

[3]. E. Kraleva, M.-M. Pohl, A. Jürgensen, H. Ehrich Hydrogen production by bioethanol partial oxidation over Ni based catalysts ApplCatal B Environ, 179 **2015**, pp. 509–520

[4]. Sofia Chuklina, Svetlana Maslenkova, Anna Pylinina, LujdmilaPodzorova, AllaIly'icheva, IOP Conf. Series: Materials Science and Engineering 175 **2017** 012031

Synthesis and characterization of new complex Co-Zr-phosphates in catalytic transformations of isobutanol

Chernyshova M.N., Pylinina A.I., Povarova E.I., Lobanov N.N., Coleva L.D.

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

Zirconium phosphates of the NASICON (NZP) type with the basic composition $NaZr_2(PO_4)_3$arouse interestas catalysts for theprocessesof alcohols dehydration and dehydrogenation due to the unique physical and chemical properties, such as high-temperature superconductivity, high ionic and mixed ionic-electronic conductivity.Feature NZP - is the ability to replace the structure-forming cations on ions of different charge and the radius with the retaining frame geometry, this allows to change the number and strength of acidic and basic sites of the catalyst, and the direction of alcohol conversion (aldehyde / ketone or olefin) depends on the ratio of the acid-base and redox surface properties [1, 2].

Zirconium phosphates $Cs_{1-2x}Co_xZr_2(PO_4)_3$ with x=0,15; 0,25; 0,50 were prepared by sol-gel method[3], characterized by physical-chemistry methods (x-ray diffraction XRD, x-ray photoelectronspectroscopy XPS, UV-, IR-spectroscopy, TEM) and tested in decomposition of isobutanol.

The main reaction of isobutanol transformation was dehydration into isobutylen. The triple phosphates samples (x=0,15; 0,25) exhibited the highest activity than double one (x=0,5). The process of isobutanol dehydration on framework phosphates takes place through the mechanism of acid catalysis. It was shown correlation of yield of olefins and number of acidic center.

As a result of the work, it was found that partial replacement of the cesium ion for cobalt leadsto a linear decreaseof the parameters of the crystal lattice, and complete substitution leads to a change of crystal lattice type with a sharp decrease of the parameters of the crystal lattice.Thus, the cesium-cobalt-zirconium phosphates are promising catalyst of isobutylen production from isobutanol.

References

[1]. Ivanov-Shits A.K., Murin I.V. // *Ionica of a solid*. SPbGU, **2000**.616.

[2]. Povarova E.I. // *Catalytic transformations of C_3-C_4 alcohols on solid electrolytes of the BIMEVOX and NZP families with dopant ions Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Zr^{4+}*.Diss…PhD in Chemistry. RUDN, **2016**. 161.

[3]. ChernyshovaM.N.,Pylinina, A.I., Kasatkin E.M.// *Theoretical and experimental chemistry*, **2017**.T 53.46–50.

Ethanol transformations overγ-Al_2O_3 and TiO_2-anatase with Cu, Ag, Au

Do Thuy Mai, Pylinina A.I., Mikhalenko I.I.
Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: mikhalenko_ii@pfur.ru

Alumina and titania arethe most wide spreading oxides to prepare supported catalysts. The most important products of alcohol conversions are H_2, acetaldehyde, ethyleneanddiethyl ether DE. Hydrogenproduction from bioethanol may be exploited as renewable energy resource. Some results for $M^{+n}/TiO_2$where M^{+n} =Ag, Cu, Au [1] andAuCu/Al_2O_3[2] we reported earlier.

This work focuses on the role of oxide support nature (commercial γ-Al_2O_3or TiO_2)in ethanoldehydrogenation vs. dehydration reactions over supported copper, silver, gold catalysts.The specific surface area of anataseTiO_2andγ-$Al_2O_3$was about 100and ~200 m^2g^{-1} respectively. All samplesafter impregnation were dried and calcined. For "pure" and supported oxides (30 mg) heated in flow diffusion free reactor from 200^0step by step up to 400^0 C the total Etconversions (α%) and selectivity (S%) were calculated from chromatograph analysis data. For characterization of the catalysts` IR spectra and XRay profiles were studied.

The alcohol conversion increases but its aldehyde selectivity *S* decreases with temperature rise, except Al_2O_3withstrongacidic surfaceproperties when only dehydration reactions occur (table).

Supporting on aluminaCu,Ag,Aubecome the centers of Et dehydrogenation. Its different nature in *redox* mechanism of aldehyde formationas well as in *acidic* mechanism of ethylene and DE formation shows the different activation energy values Ea.

The total conversions and *selectivityof dehydrogenation* (in %) at several temperatures and apparent activation energy (kJ/mole) of organic products` formation

Образец	250^0	300^0	350^0	400^0	**Ea(1)** aldehyde	**Ea (2)** ethylene	**Ea (3)** ether
Al_2O_3	59 *0*	80 *0*	93 *0*	100 *0*	no	**107**	**121**
Cu/Al_2O_3	28 *35*	52 *41*	64 *42*	68 *17*	**61**	**82**	**141**
Ag/Al_2O_3	37 *56*	68 *29*	91 *17*	79 *0*	**91**	**133**	**115**
Au/Al_2O_3	46 *30*	68 *27*	75 *26*	68 *16*	**123**	**75**	**116**
TiO_2	3100	989	1570	2542	**47**	**141**	**81**
Cu/TiO_2	9100	21 *100*	2484	2565	**92**	**144**	**132**
Ag/TiO_2	592	1191	1877	1953	**48**	**139**	**51**
Au/TiO_2	6100	1191	1786	1882	**26**	**81**	**80**

Due to Cu,Ag,Au additives the centers of dehydrogenation on aluminaappear. Aldehyde selectivity $S^{C=O}$ augments in arow Ag/Al_2O_3< Au/Al_2O_3<Cu/Al_2O_3(350 ^{0}C).Above 350^0 the values$S^{C=O}$ decreases. The catalystCu/Al_2O_3has the lowest Ea(1). The total ethanol conversion on titania is not too much but the selectivity $S^{C=O}$is about 100%. The different values of Ea(1) as well as Ea for other products forming on M^{+n}/oxide demonstrate the influence of M^{+n} and support nature. Namely, for Ea(1) the divergence Δ= Ea (alumina) –Ea (titania) is –31 (Cu), +43 (Ag) and +97 (Au) kJ/mole. For Ea(2) the consequence is –34 (pure oxide), –62 (Cu), ~0 (Ag) and ~0 (Au). It is necessary to note that pure oxide was treated in water with the same modeling precipitation and thermal procedures as in case of supported oxides`preparation.

References

[1]. Mai Do Tkhyui, Mikhalenko I I., Pylinina, A.I.//Russian J.Phys.Chem.2014,V.88. P. 1637.

[2]. До Тхюи Май, Пылинина А.И., Михаленко И.И. //Межд. науч. конф. «Полифункциональные химические материалы и технологии», 21-22 мая 2015 г, Томск,ТГУ,Т.3, С.100.

Zeolites as nano-reactores - Alkylation of phenol derivatives with methanol

Einemann M., Schröter F., Roessner F.

Industrial Chemistry II, Carl von Ossietzky University Oldenburg, D-26122 Oldenburg, Germany, Ammerländer Heerstraße 114-118, e-mail: frank.roessner@uni-oldenburg.de

Zeolites have, because of their diversity, a high potential as selective heterogeneous catalyst. The alkylation of phenol derivatives towards 2,3,5-trimethylphenol is of great industrial interest, due to the fact, that it is one of the key products in the (all-rac)-α-Tocopherol (vitamin E) synthesis.[1] Starting from *m*-cresol 2,3,5-trimethylphenol could be obtained through the alkylation with methanol. Unfortunately, the number of byproducts, as dimethylphenols (DMP), trimethylphenols (TMP), tetramethylphenols (Tetra) or anisoles, is very high. Catalyst for this reaction can be zeolites with a well-defined structure as well as other acidic oxidic materials. Different catalyst and reaction conditions were applied in this work to evaluate the influence of the structural and chemical differences of the catalysts. The gas-phase reaction was carried out in a micro reactor equipped with an on-line gas chromatograph.

Results show the difficulty of the alkylation in the kinetically un-favored meta position, which is necessary for the formation of 2,3,5-trimethylphenol starting from *m*-cresol. Typically, multiple alkylation of one molecule is unlikely. This can be overcome with higher reaction temperatures. Therefore, *m*-cresol was substituted by 2,3-dimehylphenol as the starting material. Figure 2 shows the conversion and yields for the different catalysts. Surprisingly, *t*-ZrO_2 catalyst are more promising than zeolites like the H-Beta, *i.e.* expected form selective properties of zeolites do not dominate the reaction. This observation was also made for the conversion of *m*-cresol. Interestingly, Al_2O_3 has the highest measured conversion at 270 °C, as well as the highest selectivity (84.3%) towards 2,3,5-trimethylphenol at 220 °C. Al_2O_3 catalyzes the *ortho*-alkylation stronger than the alkylation in other positions. All tested catalysts deactivate very slowly.

Summarizing the results, the synthesis route to 2,3,5-trimethylphenole, as precursor for tocopherol, via alkylation of alkylphenols seems to be an promising approach for usage of cheaper feed.

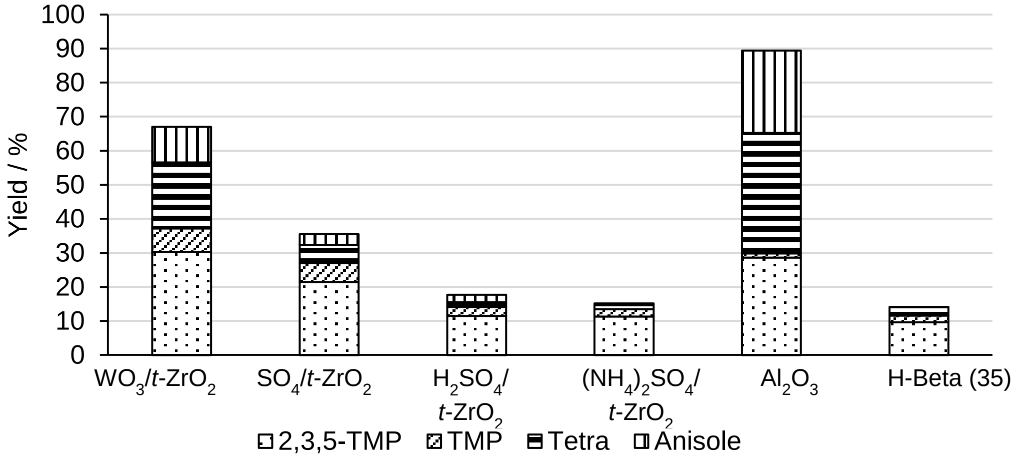


Figure 2: Comparison of different catalysts for the 3,5-DMP conversion, T= 270 °C, molar ratio 3,5-DMP:methanol 1:3

References

[1]. Eggersdorfer, M.; Laudert, D.; Létinois, U.; McClymont, T.; Medlock, J.; Netscher, T.; Bonrath, W. *Angew.Chem.* **2012**, *124*, 13134-13165.

Efficient photoluminescence attenuation of zinc oxide by DNA complexes with gadolinium or yttrium complex oxides

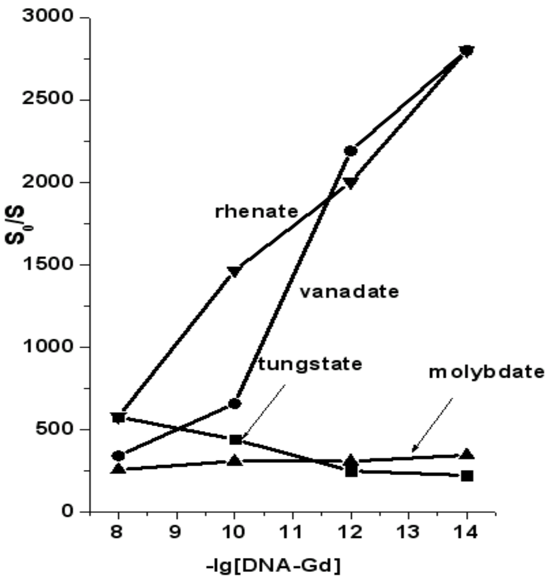
Hayrullina I.A.[a], Shulga A.A.[a], Butusov L.A.[a,b], Kurilkin V.V.[a], Chudinova G.C.[b,c]

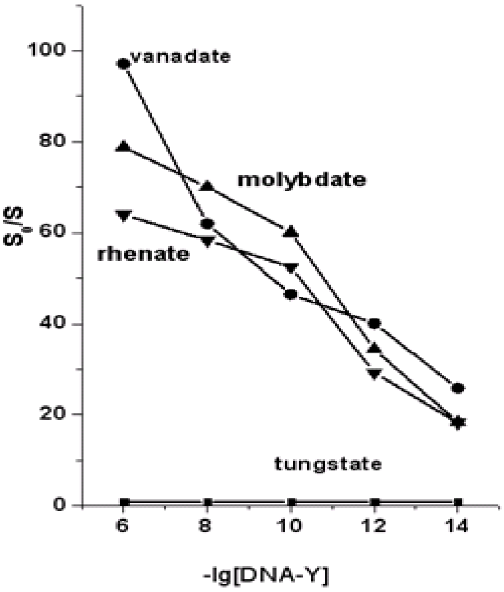
[a] *Peoples' Friendship University of Russia*
[b] *Natural Science Center of General Physics Institute RAS*
[c] *National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)*
**e-mail: spaldingtm@mail.ru*

In the following work, the nanocrystals of inorganic luminophores [1] were used to create supramolecular systems, based on DNA biopolymer for the first time. The optical properties of the given films, as well as the received complexes of DNA – inorganic luminophores on zinc oxide substrates [2], were also researched.

Creating a sensitive, selective biosensor device, in this given case, is difficult, therefore the main objective was to determine the compounds, which can influence the photoluminescence of zinc oxide, either by the formation of new peaks of fluorescence varying in their maxima, or by causing the shift of photoluminescence band, or by its suppression. Inorganic luminophores – complex oxides of vanadium, rhenium, molybdenum, tungsten with gadolinium oxide or yttrium oxide in conjunction with DNA, were chosen for such purposes.

The relationship of attenuation efficiency of zinc oxide's photoluminescence vs the concentration of a hybrid material based on gadolinium and yttrium, is shown on the graphs.





References

[1]. Yang, H.K.; Chung, J.W.; Moon B.K.; Choi B.C.; Jeong, J.H.; Kim J.H. Synthesis and luminescence properties behavior of Eu(3+)-doped nanocrystalline and bulk GdVO4 phosphors by high-energy ball milling and solid state reaction *J. Nanosci Nanotechnol* **2011**,*11*(*1*): 474-8.

[2]. Ma, L.; Liu, B.; Huang, P.J.; Zhang, X.; Liu. J. DNA Adsorption by ZnO Nanoparticles near Its Solubility Limit: Implications for DNA Fluorescence Quenching and DNAzyme Activity Assays *Langmuir* **2016**, *32*(*22*), 5672-5680.

Adsorption of methylene blue by activated carbons depending on timeoperating

Kasatkin E.M., Romanova Y.A., Sokolova Y.S., Lebedeva T.A., Pylinina A.I.

Peoples' Friendship Universityof Russia, 117198, Moscow,Miklukho-Maklaya str. 6
e-mail: kasatkin.1991@list.ru

Currently a lot of attention is paid to the methods of air cleaning from foul-smelling substances (FSS). In connection with it, some regulations regarding odor emissions have been developed in the EU countries and in the Russian Federation: the European Standard EN 13725 and the Russian Standard 32676-2014 [1,2].

The aim of this work is to test the applicability of the methylene blue adsorption method to control the activated carbons adsorption capacity.

The dependence of the AG-3 and AddSorb®VA12NG carbons adsorption capacity recession from its operation time is presented on the Fig. 1.

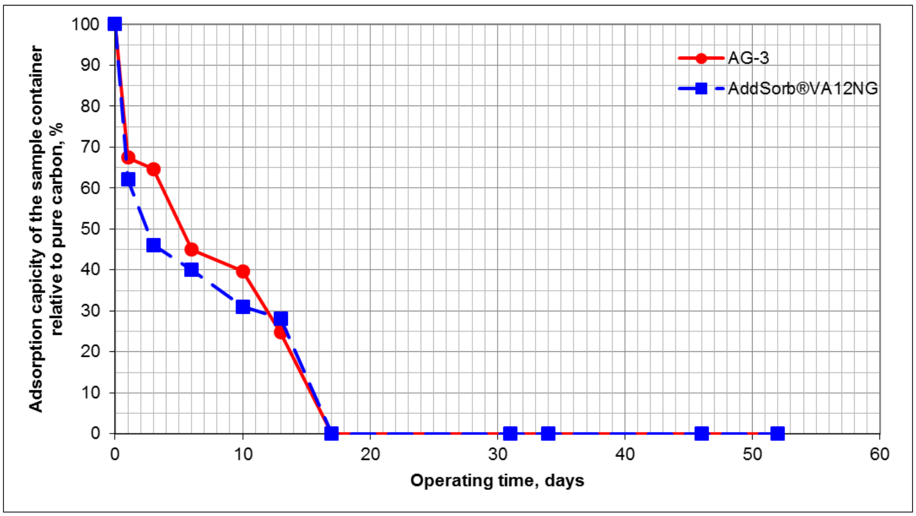


Fig. 1. The dependence of carbon adsorption capacity recession from its operation time

Fig. 1 shows that carbon capacity decreased in 2 times comparing with its initial numbers on the fifth day of operation time, and it was equal to zero on the seventeenth day. Continued usage of carbon (from 17 to 30 days) led to accumulation of FSS and its interaction products only on carbon granules surface. Because of the fact that the AC contamination degree affects on the cleaning time and on the water consumption, it is advisable to clean the carbon before it becomes completely dirty.

To summarize all, due to the simplicity and efficiency of methylene blue adsorption method, it can be applied to the monitoring of various AC adsorption capacity for determination of the operation time during which the contaminated carbon can be cleaned with a minimal amount of time and resource.

References

[1]. EN 13725:2003(E). Air quality – Determination of odour concentration by dynamic olfactometry. Brussels, March 2003.

[2]. GOST 32673-2014. Rules for establishing standards for controlling emissions of foul-smelling substances into the atmosphere. Enter. 2015 - 07 - 01. Moscow: Standartinform, 2014. - 18 p.

Multifunctional magnetic iron-containing nanocomposites based on natural polysaccharide arabinogalactan

Khutsishvili S.S., Tikhonov N.I., Vakul’skaya T.I., Aleksandrova G.P., Sukhov B.G.

A.E.Favorsky Irkutsk Institute of Chemistry of the Siberian Branch of the Russian Academy of Sciences, 664033, Irkutsk, Favorsky str. 1
e-mail: khutsishvili_sp@yahoo.com

Magnetic nanocomposite materials with metal particles are widely used in modern electronics, solar cell production, in biology, the preparation of catalysts, medicines and others. Among received nanosubstances special interest biocompatible nanocomposites based on a variety of polysaccharides, and in particular, arabinogalactan (AG), received from siberian larch, with a complex of catalytic, magnetic, optical and biological - antimicrobial, immunomodulatory and cytotoxic properties. Unusual magnetic, in particular paramagnetic, and thermostable properties of the nanocomposites largely determine their uniqueness and wide application.

It was made the study of thermal stability of multifunctional iron composite based on the natural polysaccharide AG and iron oxides and their paramagnetic properties change with temperature. We have shown that the magnetite nanoparticles of Fe_3O_4, being coated with a shell of natural high molecular polymer, form aggregate stability of magnetic nanomaterials. Nanocomposites study was performed in a linear temperature rise process by the methods of synchronous thermal analysis to 1000°C, and by EPR to 400°C. The results indicate that the nanocomposites have a temperature resistance up to 180-200°C. EPR method shows that all composites to some extent possess ferromagnetic properties at room temperature, which was confirmed by measurements of their magnetization. The similar nature of the FMR spectra investigated nanocomposites, which are asymmetric broad absorption lines, shows small changes in size and shape of the resulting nanoparticles with varying iron content in the nanocomposite from 1 to 12%. Trends destruction ferroarabinogalactan observed directly in the EPR spectrometer resonator. The EPR characteristics of change of *g*-factor and linewidth signal showed the presence of critical points on reaching 200°C – thermal degradation of the nanocomposite. Introduction of magnetite nanoparticles in polysaccharide matrix greatly lowers the activation energy of thermal degradation process, thereby reducing the degradation of the nanocomposite temperature range compared to the initial polysaccharide. On exotherm effect in ranging 220-290°C due to the thermal degradation of AG, superimposed very intense effect in the temperature interval 250-400°C, due to oxidation of iron oxide (II), which is part of the magnetite. Thus, this process lead to obtaining of the novel nanosystems with controlled magnetic properties. Prolonged storage nanocomposites bounded by external impact has shown that metal nanoparticles exist stably in the matrix, at least for one year, while maintaining the unchanged EPR characteristics.

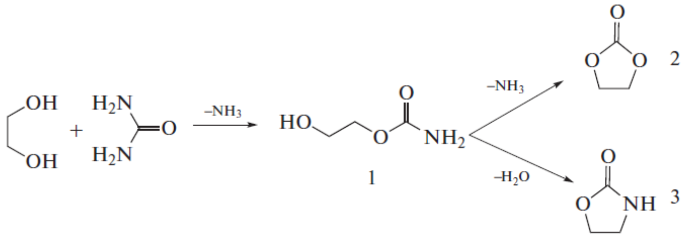
Synthesis of ethylene carbonate from ethylene glycol and urea in the presence of cobalt oxide nanoparticles

Kochubeev A.A., Lyadov A.S.

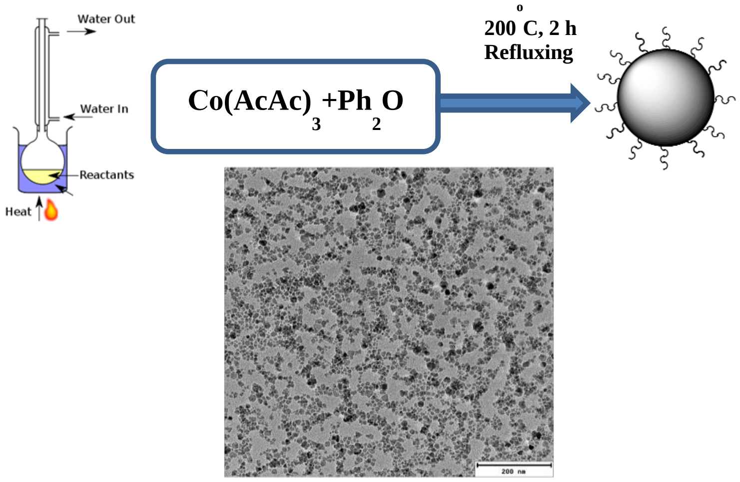
A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991, 29 Leninsky prospect, Moscow
e-mail: a.kochubeev@ips.ac.ru

Ethylene carbonate (EC) is an ester of ethylene glycol and carbonic acid; EC is commonly used as a polar solvent because it has a molecular dipole moment of 4.9 D. In the liquid state, EC is capable of dissolving many polymers, polyester fibers, and resins. It is a good solvent for acrylonitrile polymers and copolymers and is used in the production of polyacrylonitrile fiber.

The cyclocondensation of dihydric alcohols and urea is one of the most convenient and environmentally safe methods for producing cyclic carbonates. At the first stage, ethylene glycol and urea react to form 2-hydroxyethyl carbamate (1), which undergoes further cyclization to form the desired product EC (2) and 2-oxazolidone (3):



The effective nanocatalyst with average particle size 10-12 nm for ethylene carbonate synthesis were obtained by thermolysis of cobalt acetylacetonate using diphenyl ether as a dispersion medium:



Particle size– 10-12 нм

It was found that nanosized cobalt oxide is very active and selective catalyst in this process. The effect of reaction conditions (temperature, pressure, contact time, and catalyst concentration) on the main parameters of catalytic conversion has been studied.

This work was supported by grant 15-33-70018 from the Russian Foundation for Basic Research and Moscow Government.

The effect of acrylic acid on the properties of Ag nanoparticles in thin films

Kononova E.A., Belko E.G., Mikhalenko I.I.

Peoples' Friendship University of Russia, 117198, Moscow ,Miklukho-Maklaya str. 6
e-mail: kononova_ea@list.ru, imikhalenko@pfur.ru

Ag-nanoparticles (AgNPs) located on substrates of different nature, including AgNPs in thin islands films, due to their unique optical, electronic and adsorption properties are the promising material for sensory detectors nanocatalysts and materials for medicine with antibacterial properties. Combination AgNPs with polymers extends the functionality and stability of such systems and permit to obtain hybrid metal-polymer materials. So, the analysis of interaction of AgNPs with acrylic acid (AA) as a monomer of poly-AA takes of some interest.

The aim of this study was to determine the influence of acrylic acid on spectral and electrical characteristics of islands thin Ag-films, evaporated on glass substrate.

Films were prepared by electric sublimation of Ag wire (99,99%) in vacuum on 'Pyrex' glass as well as glass treatment in boiling Ag-Hydrosol. AgNPs were characterized by plazmon absorption spectra. Observed maximum position near 450 nm indicated to presence of aggregated AgNPs, including NPs chains. If you increase the duration of AA contact with film the spectrum shape is changed (Fig.1). The increase in optical density range in maximum and its "red" shift indicates a change of NPs surface properties, their size and arrangement.

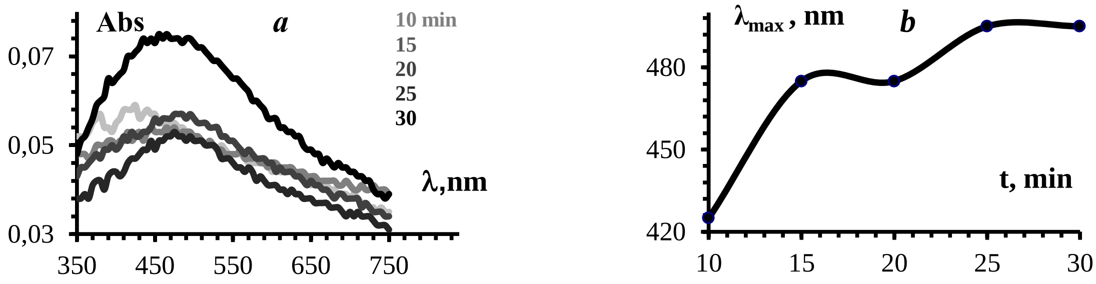


Fig. 1 a. Absorption spectra of AgNPs of Ag thin films; b. Shift of absorption maximum in plasmon spectra vs. increasing duration of film exposure in acrylic acid (AA) vapor.

To compare the activation energy of electrical conductivity (φ) before and after AA treatment we can determine the polarization sign of AA adsorbed molecules, both in chemisorbed (undesorbed under pumping) and reversibly adsorbed forms (Fig.2).

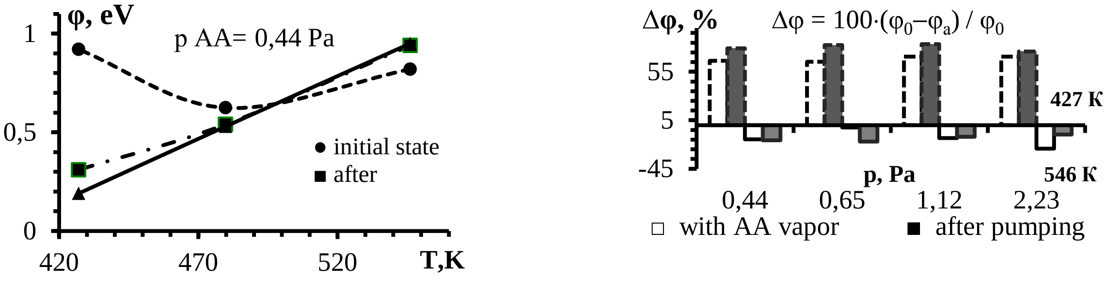


Fig.2. **a**. The effect of temperature on the φ values before and after contact of AgNPs with AA vapor;
b. The effect of AA vapor pressure on the relative change of φ value at 427 K and 546 K.

With temperature rise the change of AgNPs surface charge is observed and it is connected with different polarization of adsorbed AA molecules – positive sign below 473 K and a weak negative charge above 473 K. Note, that T=473 K is close to Tamman temperature.

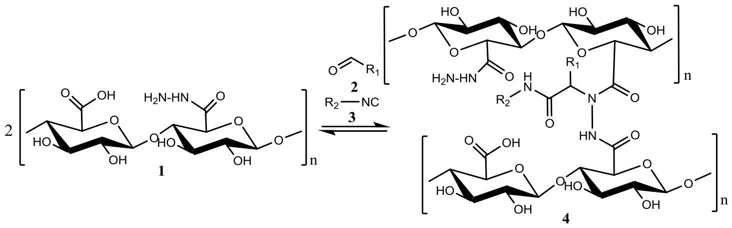
Synthesis of nanosized mucoadhesive pectinic hydrogel for local anesthesia

Kozhikhova K.V., Tolstykh D.A., Schulepov I.D., Mironov M.A.

Ural Federal University, 620002, Ekaterinburg, Mira str. 19
e-mail: k.v.kozhikhova@gmail.com

The dental treatment usually requires preoperative anesthetic and postoperative analgesic, so to prevent dental pain in effective and light way is an actual task for modern dentistry, especially in pediatric case [1]. The current advances in carbohydrate science have resulted in a novel type of drug delivery systems based on cross-linked biopolymers. They conjoin the advantages of natural materials, such as biocompatibility, low toxicity, biodegradability and market availability, with positive properties of synthetic polymers, such as workability, stability and reproducibility [2]. The aim of this investigation was to design a patient-friendly transmucosal drug delivery system based on natural polysaccharide nanoscaled hydrogel loaded with novocaine.

We chose high-methoxyl apple pectin (Herbstreith & Fox GmbH) with the 62 mol % degree of esterification due to already displayed mucoadhesive properties [3]. For further process natural polymer was modified by hydrazide groups and purified from low-molecular additives. Using original approach developed our research group and based on the Ugi multicomponent condensation (U-4CR) in diluted colloidal suspensions (0.1 m/v %) [4]. The wide range of cross-linked polysaccharide derivatives were synthesized according to reaction scheme. Various isocyanides (aliphatic, alicyclic and aromatic) and aldehydes with short aliphatic chains were used here.



The structures of the products were confirmed by the ^{1}H NMR-spectroscopy. The size distributions and polydispersity indexes of particles were determined by dynamic light scattering with the meaning 90-350 nm. Mucoadhesive properties of the hydrogels were evaluated by mucin adsorption method [5]. The derivative with basic properties showed extremely high level of mucosa affinity in 92 % that is comparable with the best known mucoadhesive carriers. The cytotoxicity of the modified polysaccharides was determined against HeLa cells by the MTT assay where they were evaluated as non-cytotoxic (cell viability near 80 %) with statistical significance. Three of the synthesized carriers were loaded with novocaine. The drug entrapment efficiency and rate of drug release were investigated by dialysis with UV-detection. The results of 84-92 % active compound loading and consistent release rate during 4 hours allows considering the developed form as a potential medicine for local anesthesia.

References

[1]. Nidhi, M.; Patro, M.N.; Kusumvalli, S.; Kusumdevi V. *Int. J. Nanomedicine*, **2016**, 11, 2901–2920.

[2]. Villanova, J.C.O.; Ayres, E.; Orefice, R.L. *Carbohydr. Polym.*, **2015**, 121, 372–381.

[3]. Thirawong, N.; Nunthanid, J.; Puttipipatkhachorn, S.; Sriamornsak P. *Eur. J. Pharm. Biopharm.*, **2007**, 67, 132–140.

[4]. Mironov, M.A.; Shulepov, I.D.; Ponomarev, V.S.; Bakulev, V.A. *Colloid. Polym. Sci.*, **2013**, 291, 1683-1691.

[5]. Qiang, F.; Shin, H.J.; Lee, B.J.; Han, H.K. *Int. J. Pharm.*, **2012**, 430, 161-166.

Synthesis, physical and chemical and catalytic properties of manganese-containing layered oxides

Kryuchkova T.A.[1], Sheshko T.F.[1], Zimina V.D.[1], Serov Y.M.[1], Zvereva I.A.[2], Yafarova L.V.[2]

1 – RUDN University, Faculty of Science, Physical and Colloidal Chemistry Department, Russia
2 – Saint-Petersburg State University, Petrodvorets, Russia
sheshko_tf@rudn.university

Nowadays, complex oxides due to its high stability and activity have been used as catalysts for high temperature processes. The purpose of this work was to study and comparison the catalytic properties of nanostructured perovskite manganites or ferrites of gadolinium, obtained by sol-gel method, in terms of dry (carbon dioxide) reforming of methane (DRM).
Perovskite-type layered oxides $GdMnO_3$, $GdMn_xFe_{1-x}O_3$ (x=0,01; 0,05; 0,5) and $GdFeO_3$ were synthesized by sol-gel technology and were characterized using different techniques to study structure and morphology. The catalytic activity were studied in a flow apparatus at atmospheric pressure in the temperature range of 773-1223 K and flow rates of 0.5-1.0 l/h. Experiments were carried out with feeding a mixture of gases in a ratio of components $[CH_4:CO_2] = 1:1$ for the DRM reaction. Analyses of the products were performed by chromatography.

The complex of physical and chemical methods of investigation showed that the samples showed were present in the nanocrystalline state and a porous structure. Comparison of the perovskite-type oxides properties under conditions of dry reforming of methane showed that the use of manganites reduces the deposition of carbon was almost twice compared to ferrites. However, partial or complete replacement of the iron to manganese in the anion sublattice several inhibited the catalytic activity of the complex oxides. The conversion of methane and carbon dioxide were respectively comparable over $GdFeO_3$ and $GdMn_{0,01}Fe_{0,99}O_3$, and were observed minimum values of conversions over $GdMnO_3$. Thus, the catalytic activity increased in the row:

$$GdMnO_3 < GdMn_{0,5}Fe_{0,5}O_3 < GdMn_{0,05}Fe_{0,95}O_3 < GdFeO_3 \approx GdMn_{0,01}Fe_{0,99}O_3$$

And hydrogen selectivity determination in this process showed it to increase per the proportion of manganese in the following sequence:

$$GdMnO_3 < GdMn_{0,5}Fe_{0,5}O_3 < GdMn_{0,01}Fe_{0,99}O_3 < GdFeO_3 < GdMn_{0,05}Fe_{0,95}O_3$$

The complex of physical and chemical data showed that all investigated oxides after catalysis preserved their perovskite structure. And data Energy-dispersive X-ray spectroscopy (EDX) for the investigated samples after the catalytic reaction were shown the carbon presence on the sample surface (estimated about 5%).

This work was supported by Russian Foundation for Basic Research, research projects No. 16-33-00971 mol_a.
The reported study was supported by Fund of assistance small forms of enterprises in scientific and technical sphere.

Preparation of novel nanoscaled delivery system based on proliposomes

Kuznetsova D.O., Kozhikhova K.V., Mironov M.A.

Ural Federal University, 620002, Ekaterinburg, Mira str. 19
e-mail: d.kuznetsova95@mail.ru

The development of drug delivery systems is an innovative approach towards solving pharmaceutical tough issues associated with medicine toxicity and low therapeutic efficiency. Lipid-based nanomedicine has already proved their capability to improve bioavailability of encapsulated active compounds both hydrophilic and hydrophobic nature. However there are a number of clinical limitations for liquid liposomal forms due to poor physical and chemical stability related to leakage, sedimentation, aggregation, fusion and degradation reactions such as oxidation and hydrolysis. In order to overcome the stability problems a novel method to prepare liposome using the concept of proliposome was introduced. Proliposomes are defined as dry, free-flowing powders that immediately form liposomal vesicles when contact with aqueous phase [1]. Because of the solid properties, long-term stability of liposome can be achieved simultaneously with high entrapment efficiency, narrow size distribution and protective properties.

This study reports an improved design and a comparison of proliposomes obtained with various micronized species [2], such as sucrose, lactose and cellulose. The specified amounts of phosphatidylcholine, lecithin, cholesterol and additives were dissolved in chloroform. This solution was adsorbed onto micro-carriers (sieved crushed sucrose, lactose Pharmatose 100 M, microcrystalline cellulose Pharmacel 101), and the excess solvent was removed to obtain dry powder. Following hydration and size reduction using sonication led to stable nano-vesicles. These proliposomes were compared with conventional liposomes prepared by thin-lipid film technique with following extrusion in terms of liposome size, zeta potential and drug entrapment efficiency using rimantadine as a model drug.

Comparison of two approaches has shown that proliposome formation technique tended to yield liposomes smaller than the corresponding vesicles downsized via extrusion (ultrafiltration membrane 100 nm). In the first case all size measurements were in the range of 93.8–112.9 nm and pdI 0.205-0.285, meanwhile for the common liposomes the hydrodynamic diameters were 158.9-192.3 nm and pdI 0.125-0.223 for the same lipid mixtures. Obtained liposomes had positive or negative surface charge depending on their composition. The data indicate that the investigated technique of proliposomes was appropriate to obtain nanoscaled vesicles for different lipid types. Moreover the rimantadine entrapment efficiency in proliposomes was found to increase in comparison with thin-lipid film method that allows reaching the high drug entrapment efficiency (96.7±0.5%) for rehydrated liposomes.

In general, we have reported a reliable production method of nano-liposomes based on widely applicable industrial technologies such as micronized base coating, hydration and sonication. Moreover, sucrose and lactose can perform as a carrier in the proliposome formulations and as a cryoprotectant during future freeze-drying.

References

[1]. Deshpande, P.B.; Gurram, A.K.; Deshpande, A.; Shavi, G.V.; Musmade, P.; Arumugam, K.; Averineni, R.K.; Mutalik, S.; Reddy, M.S.; Udupa, N. *Life Sciences*, **2016**, 162, 125–137.

[2]. Silva, G.S.; Jange, C.G.; Rocha, J.S.S.; Chaves, M.A.; Pinho, S.C. *International Journal of Food Science and Technology*, **2017**, 52, 772–780.

Thermochemical properties of biphenyls and diPHenyl-oxides. Energy characteristics of their radicals and bonds

Pashchenko L.L. [1], Miroshnichenko E.A. [2]

[1] *Department of Chemistry, Lomonosov Moscow State University, Lewinski Gory 1,*
bl.3, Moscow, 119991, Russia
[2]*Semenov Institute of Chemical Physics RAS, Kosygin str. 4, Moscow, 119991, Russia*
e-mail: eamir02@mail.ru

Aromatic nitro compounds, including 4-nitrobiphenyl and others, are important industrial chemicals with a broad range of applications. This class of compounds is widely used in the synthesis of many diverse products, including drugs, dyes, polymers, pesticides and explosives. Some aromatic nitro compounds are highly explosive, especially when the compound contains more than one nitro group. To investigate the stability and performance of these chemicals, knowledge of the enthalpy of formation ($\Delta_f H^o{}_{298}$) is an essential requirement. Other thermo-chemical properties, such as enthalpy of vaporization ($\Delta_{vap} H^o{}_{298}$) and enthalpy of sublimation ($\Delta_{sub} H^o{}_{298}$), are needed for the characterization of the chemical degradation pathways of aromatic nitro compounds.

Despite the extensive studies of aromatic nitro compounds, available thermo-chemical experimental information is often scarce and frequently shows significant discrepancy among published results. The enthalpies of formation of 4-nitrobiphenyl and 1, 1'-biphenyl were calculated using their enthalpies of sublimation. In this work, the standard $\Delta_{sub} H^o{}_{298}$ were determined on micro-calorimeter Calvet over the temperature range from (323 to 373) K with an estimated accuracy of < 1 per cent. We have used these experimental results for correlating the enthalpies of sublimation of 4-nitrobiphenyl and 1, 1'-biphenyl with the temperature in order to test internal consistency of the experimental data. The average values of the standard enthalpies of vaporization were adjusted to 298.15 K.

On the base of "double the difference" method the novel scheme for formation enthalpies of aromatic radicals calculations have been suggested. Using fundamental equations of the chemical physics, the new calculation method is offered to determine the energies of reorganization of molecules fragments into radicals. Formation enthalpies of radicals a namely biphenyl, biphenyl-oxide and phenyl-oxide are determined, using their enthalpies of formation [1]. Reorganization energies of these radicals and bond dissociation energies are calculated.
Energy of reorganization of phenyl radical gives way to calculate median thermo-chemical energies of bonds in benzene: E (C – H) = 472, 8 kJ· mol^{-1} and E (C – C) = 448, 1 kJ· mol^{-1}.

Table 1. Power properties of biphenyls and enthalpy of formation of biphenyl-4-yl, kJ· mol^{-1}

Compound	$\Delta_f H^o{}_{(g)}$ (298.15K)	$\Delta_f H_{BP\bullet}$ (NO$_2$)	$\Delta_f H_{BP\bullet}$ (H)	$\Delta_{vap} H_{exp}$ (298.15K)
Biphenyl (BP)	179.9 ± 2.9	432.6	–	81.5 ± 0.8
4-nitroBP	154.4 ± 7.1	–	425.9	108.4 ± 0.9
4-methylBP	143.3 ± 1.3	429.7	429.7	69.7 ± 0.7
4-*iso*-propylBP	97.2 ± 2.5	430.1	430.1	76.6 ± 0.5
4-*tert*-butylBP	72.0 ± 2.8	431.8	431.8	79.6± 0.8

References

[1]. Druzhinina, A.I.; Pimenova, S.M.; Tarasanov, S.V.; Nesterova, T.N.; Varushchenko, R.M. *J.Chem. Therm.*, **2015**, *87*, 69.

Activation of ammonia on Fischer-Tropsch-catalysts

Frank Roessner

Carl von Ossietzky University of Oldenburg, Institute of Chemistry,
Industrial Chemistry II, D-26111 Oldenburg, Germany
e-mail: frank.roessner@uni-oldenburg.de

The Fischer-Tropsch (FT) synthesis is a polymerization reaction between carbon monoxide and hydrogen to generate products such as paraffins, olefins and oxygenated compounds including aldehydes, alcohols, ketones and carboxylic acids on iron, cobalt or ruthenium catalysts. The addition of ammonia to the synthesis gas (CO, H_2) leads to an extended product spectrum. Beside the typical Fischer-Tropsch products, it is feasible to obtain valuable organic N-containing compounds such as amines, nitriles and amides [1-3].

Based on these results it is important to understand the mechanisms and the principle of the interaction of ammonia during the Fischer-Tropsch process as this could present a new pathway for the production of nitrogen-containing chemical compounds using a different feedstock than crude oil.

The experiments with ammonia-containing synthesis gas were conducted in a fixed-bed and slurry reactor at pressures between 4-5 bar using cobalt and potassium promoted iron catalysts. The catalytic performance was studied as function of reaction temperature, synthesis gas composition, residence time and ammonia concentration.

Additional co-feeding experiments with oxygenates and N-containing compounds were carried out in order to get an insight onto the reaction behaviour during the formation of N-containing products. The product stream was analyzed online and offline using different gas chromatographic techniques. Organic compounds were identified by means of one- and two-dimensional gas chromatography equipped with mass spectrometers (GC-MS, GCxGC-TOF).

In the absence of ammonia, the formation of conventional FT products such as paraffins, olefins and oxygenated compounds was observed. The addition of ammonia leads to the formation of nitrogen-containing compounds including amines, nitriles and amides. It was noted that the formation of alcohols, aldehydes and carboxylic acids was suppressed upon ammonia co-feeding.

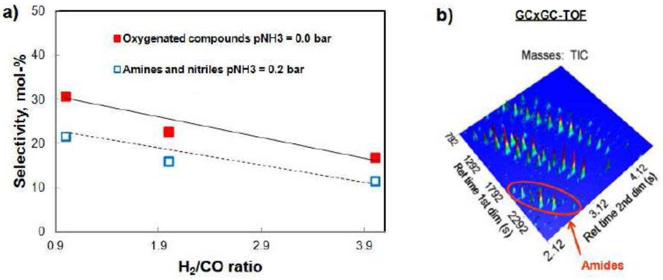


Fig.:
a) Selectivity to oxygenated compounds, amines and nitriles.

b) Amides analyzed by means of GCxGC-TOF.

Moreover, while terminal amines and nitriles were obtained during the experiments in a fixed-bed reactor, N-alkylated amines were predominant using a slurry reactor. In addition, it was feasible to control the selectivity to amines and nitriles with different reaction temperatures, synthesis gas compositions, residence times, ammonia concentrations and reactor types during the experiments. However, the mechanism of formation of N-containing products is still under discussions, since an un-catalyzed reaction of O-containing compounds with ammonia cannot excluded at the actual state of investigation.

References

[1]. Rottig, W., *U.S. Patent No. 2821537, 1958.*
[2]. Olivé, C., *U.S. Patent No. 4179462, 1979.*
[3]. Sango, T., Claeys, M., van Steen, E., Roessner, F., *U.S. Patent 0092728, 2009.*

Peculiarities of interaction of hydrogen with two-layer clusters of iron and manganese

Rozhnov A.V., Bozhenko K.V., Sheshko T.F., Serov Y.M.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: toha_26@mail.ru

Studying of adsorption of hydrogenium on the surface of iron plays an important role as iron is often used in a catalysis. The comprehension of interaction between the surface of the transitional metal and, in particular, iron with prime molecules is important for effective management of technological processes of synthesis of hydrocarbons and alcohols from mix of hydrogenium and carbon oxide (Fischer-Tropsh's catalysts), synthesis of ammonia from hydrogenium and nitrogen, etc.

The purpose of this work is modeling of the mechanism of adsorption of particles of H, H_2, H^-, H_2^+, H_2^- on the hydrogenated and pure surface of iron and manganese crystals.

For the solution of the problem non-empirical quantum chemical calculations are executed of adsorption energy (ΔE) of the listed particles on these crystals for various places of adsorption. Calculations are executed by Gamess US program [1] in approach of B3LYP/LANL2DZ.

It is showed that for the correct description of adsorption the two-layer cluster of iron whose each layer consists of 9 atoms of metal is optimum. At the same time it is found that on a surface of a manganese cluster adsorption is absent. It is established that ΔE for hydrogen atom on a surface of an iron cluster changes from -56,2 to -69,6 kcal/mol. Similarly,

ΔE for H^- : from -164,9 to 175, 2 kcal/mol.
ΔE for H_2: from -9,2 to -17,8 kcal/mol.
ΔE for H_2^+: from -228,3 to -236,1 kcal/mol.
ΔE for H_2^-: from -144,4 to 159,2 kcal/mol.

The received results are well coordinated with experimental data on adsorption of hydrogen and hydrogenation of carbon oxides on catalytic systems based on iron and manganese [2]. It has been showed that on the surface of manganese catalysts hydrogen is not practically adsorbed, and on a surface of ferriferous samples existence of two forms of chemisorbed hydrogen is possible: H_I - loosely coupled and H_{II} - strongly adsorbed. Selectivity of process by olefins is defined by H_I:H_{II} ratio on the surfaces of the catalyst. Apparently, increase of concentration of hydrogen in the form of H_{II} increases an exit of olefins. Distinctions in catalytic activity of samples can be connected with various speed of diffusion of loosely coupled hydrogen (H_I) on the surface of catalysts through contact borders between Fe particles (spillover effect) [2].

References

[1]. http://www.msg.ameslab.gov/gamess/download.html
[2]. Sheshko T. F., Serov Yu. M. // Russ. J. Phys. Chem. A. – 2012. - Vol. 86. - No. 2. - P. 283–288.

The influence of adsorbed surfactants on the wettability of syperhydrophobic coatings by water

Sayfutdinova A.R.[1,2], Boinovich L.B.[2].

[1] *Moscow Technological University (MITHT), 119571, Moscow,*
Vernadsky Prospekt, 86
[2] *A.N. Frumkin Institute of Physical chemistry and Electrochemistry RAS, 119991, Moscow,*
Leninsky Prospect, 31
e-mail: sayfutdinova@gmail.com

As a majority of superhydrophobic materials created for aviation, shipbuilding, electric power and other areas of the economy operated in the environmental conditions the adsorption processes including air-borne surfactants adsorption take place on these coatings. So our aim in this study is to investigate the impact of adsorbed surfactants on the wettability of syperhydrophobic coatings by water.

Four different types of the experiment were performed to analyze the impact of short-term and long-term contact of superhydrophobic coatings with surfactantsAnodized or laser textured superhydrophobic aluminium alloys were used as the substrates, while dodecanol and hexadecanol were used to model the air-borne surfactants. The experiments were performed in the conditions of saturated water vapors.

We used digital video images processing of sessile drop to analyze the water droplet shape parameters. This setup allows to determine droplet parameters such as surface tension, contact angle, contact diameter, drop surface, volume by using the Laplace curve fitting routine[1].

It was shown that the impact of short-term contact of superhydrophobic surface with surfactants does not cause the breakdown of superhydrophobic state. Long-term contact of superhydrophobic surface with surfactants which results in the filling of porous structure with surfactant leads to the transition of wetting regime of surface from heterogeneous to homogeneous one and to the partial degradation of protective properties of coating. For the latter case, the self-restoration of superhydrophobic properties of surfactant contaminated coating takes place upon prolonged contact of such coatings with water.

References

[1]. L.B. Boinovich, A.M. Emelyanenko, K.A. Emelyanenko. *Journal of Physical Chemistry C.* **2015**, 119 (16), 8718-8724.

Li-rich layered oxide cathodes for next-generation li-ion batteries

Shvetsov A.O., Mikhalenko I.I.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: sashashvetsov3@gmail.com

For the past several years, rechargeable lithium ion battery (LIB) technology has been the most widely used energy storage method for powering consumer electronics and power tools. layered oxide materials having the chemical formula $LiCoO_2$ have been extensively utilized and studied. However, because of their limited capacity, limited energy density, and safety concerns, these cathode materials fail to meet the necessary demands for LIBs to power electric vehicles. Creation and testing of the complex oxide $Li_{1-a}Ni_bMn_cCo_dO_2$ $(-0{,}2 \leq a \leq 0{,}1, 0{,}1 \leq b \leq 0{,}6, 0 \leq c \leq 0{,}5, 0 \leq d \leq 0{,}4)$[1] as a positive electrode was a promising way to increase workers LIB characteristics.

This paper presents a method of obtaining highly-capacitive cathode nanomaterials $Li_{1,1}(LiNi_{0,7}Mn_{0,2}Co_{0,1})$. It has been experimentally established that when the lithium concentration increases by 10%, the capacitance increases by a factor of 1.5, this can be attributed to the suppression of anti-structural defects in lithium positions (Ni / Li substitution), which has a positive effect on lithium transport, especially at high Discharge rates. It is assumed that the excess amount of lithium ions occupies the positions of transition metals, which is accompanied by the formation of oxygen vacancies. In parallel with this, the reduction of manganese ions to Mn^{3+} occurs [2].

As a result of the electrochemical test CM vs. lithium metal as the anode and the reference electrode, the sample showed a high discharge capacity 258 mAh / g at the current C / 10 in the voltage range 3.0-4.6 V. Moreover capacity drop after 50 cycles was about 6.9 % relative to the initial (Figure 1).

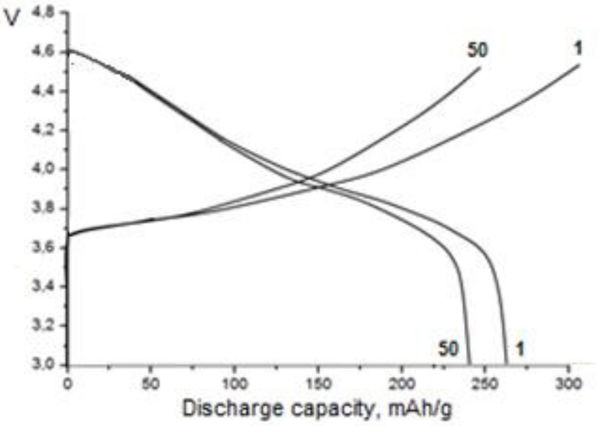


Figure 1. The charge / discharge curves of the first and 50th cycles of CM $Li_{1,1}(LiNi_{0,7}Mn_{0,2}Co_{0,1})$

References

[1]. Wang F., Zhang Y., Zou J. The structural mechanism of the improved electrochemical performances resulted from sintering atmosphere for $LiNi_{0,5}Mn_{0,3}Co_{0,2}$ cathode material. J. of Alloys and Compounds. 2013. V. 558. P. 172.

[2]. Voronov V.A., Shvetsov A.O., Gubin S.P. Influence of cathode material producing method $LiNi_{0,33}Mn_{0,33}Co_{0,33}$on the electrochemical characteristics of lithium-ion battery. Journal of Inorganic Chemistry, 2016, V.61 (9), pp. 1211-1217.

Modified Mesoporous Silica as Basic Hybrid Materials

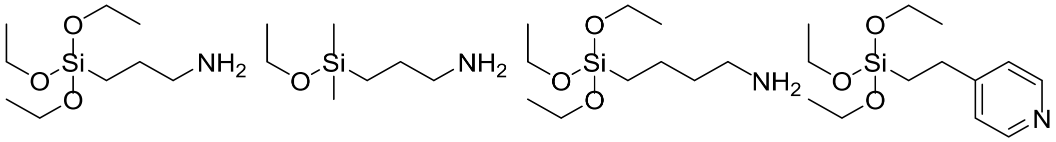
Thomé A.G., Roessner F.

Industrial Chemistry II, Carl von Ossietzky University Oldenburg, D-26122, Oldenburg,
Germany, Ammerländer Heerstraße 114-118,
e-mail: frank.roessner@uni-oldenburg.de

Porous materials with defined porosity and basicity are desirable for applications in heterogeneous catalysis and adsorption. An effective route to synthesize ordered mesoporous materials with a narrow pore size distribution is a surfactant templated synthesis. Using different surfactants and reaction conditions, the pore size as well as the three dimensional order of the pores can be tailored.

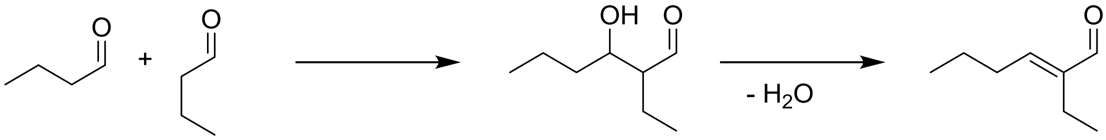
The corresponding silica-based ordered mesoporous materials are amorphous and contain silanol groups on their surfaces. These silanol groups offer the possibility for chemical modification *via* grafting with suitable organosilicon compounds.

This approach has been used to modify said porous silica materials of two different pore sizes (MCM-41 and SBA-15) with four different organic precursors comprising different types of basic functionalities.



Nitrogen adsorption measurements and XRD prove the high amount of ordered pores as well as the narrow pore size distribution both of calcined and modified materials. TGA and XPS measurements confirm the successful modification of nitrogen containing organic entities and give insight into their thermal stability.

Selected modified samples have been tested in the aldol condensation of *n*-butanal. Apart from the desired product 2-ethylhexenal, various byproducts, such as Tishchenko- or Cannizzaro-products can be observed. The aim of this study is to minimize all byproducts while obtaining a high yield of 2-ethylhexenal.



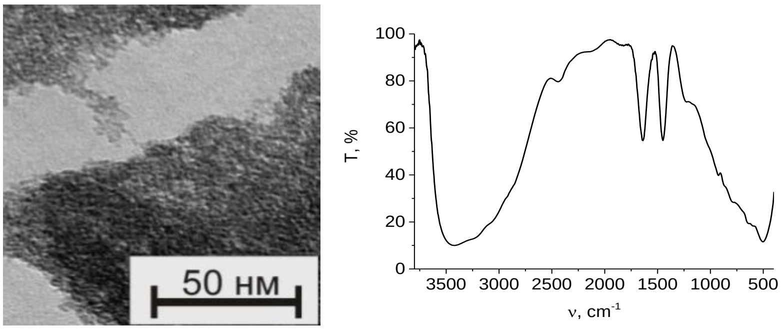
This work was supported by the German academic exchange service
(grant № 57212311).

Composition and microstructure of nanoparticles in SnO_2 sol used in medicine diagnostics and in processec of metal electroplating

Konakov A. O.[1], Maltanova H. M.[2], Vorobyova T. N.[1,2]

[1]*Belarusian State University , 220030, Minsk, Leningradskaya str. 14*
[2]*Research Institute for Physical Chemical Problems of the BSU, Minsk, Leningradskaja str. 14*
e-mail: vorobyovatn@gmail.com

SnO_2 sol was synthesised by $SnCl_4{\cdot}5H_2O$ hydrolysis in ammonium solution by method described in [1]. According to XRD data the powder obtained by sol coagulation and the precipitate drying at room temperature is amorphous. After its calcination at 350 ^{o}C 1 h the crystalline SnO_2 phase is formed. According to TEM data nanoparticles in the initial sol are about 2 nm in size (Fig. *a*). IR study has shown that sol nanoparticles consist of SnO_2 core and $SnO_{2-x}(OH)_{2x}$ shell that follows from the next peculiarities in IR spectra (Fig. *b*). There are broad absorbance bands in the region 2900–3400 cm^{-1} corresponding to vibrations of OH groups which are bound to the surface of tin dioxide particles by hydrogen bonds. A narrow peak at 1639 cm^{-1} assigned to deformation vibrations of HOH in water molecules is present in IR spectrum. There are peaks at 1230, 1173, 1053 и 924 cm^{-1} attributed to stretching vibrations of terminal OH groups [2]. The absorbance bands with maximums at 794, 645, 594 и 504 cm^{-1} present the response of O−Sn−O and Sn–O valency vibrations in SnO_2. The appearance of extra bands in the region 870–3300 см$^{-1}$ and a strong shift of the peaks at 636 и 778 cm^{-1} to large wavenumbers can be explained by the presence of large quantity of water molecules and hydroxyl groups.



a *b*

TEM photo of SnO_2 nanoparticles in sol (*a*) and IR spectrum of this sol (*b*)

Conditions of photocatalytic $HAuCl_4$ reduction on SnO_2 nanoparticles with the formation of structures including amorphous $SnO_2{\cdot}nH_2O$ (core) – crystalline gold nanoparticles (shell) were revealed which were able to be conjugated with biopolymers such as rabbits antibodies against immunoglobulins and *Shigella sonnei* antibodies. As it is shown in [1] these structures can be applied for the express detection of antigens in immunochemical analysis.

The effect of SnO_2 sol addition into diphosphate copper plating solution on the peculiarities of coatings deposition on steel, aluminium, zink and Zn–Al alloy, microstructure and protective ability of coatings has been studied. A strong effect of sol additive on peculiarities of metal nuclei formation, on copper coatings microstructure and properties has been found although SnO_2 content in coatings does not exceed 1 at. %. The coatings are dense, fine grained, have an increased protective ability. Corrosion of metal substrate in copper plating solution at the initial stages of metal plating is diminished owing to sol adsorption on the growing surface [3].

References

[1]. *Maltanava H.M., Vorobyova T.N., Poznyak S.K.* // Sviridov Readings. Iss. 9. Minsk, 2013. P. 104.
[2]. *Orel B., Lavrenčič-Štankgar U., Crnjak-Orel Z. [et al.* // J. Non-Cryst. Solids. 1994. V. 167. P. 272.
[3]. *Konakov A.O., Vorobyova T.N., Nasonova D.I.* // Sviridov Readings. Iss. 12. Minsk, 2016. P. 76–88.

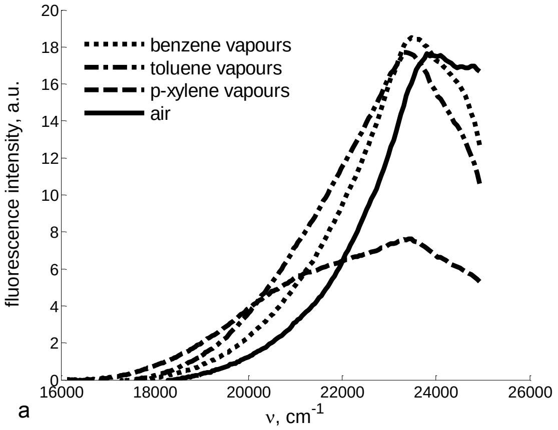
Ink-jet printed chemosensing layers based on surface-functionalized silica nanoparticles

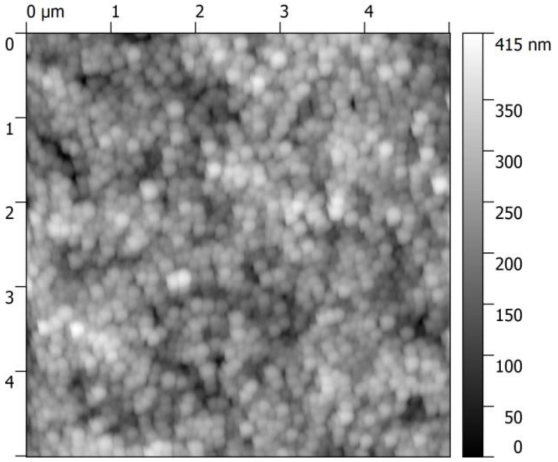
Yurasik G.A., Ionov D.S., Kononevich Yu.N., Surin N.M., Svidchenko E.A., Sazhnikov V.A.,
Muzafarov A.M., Alfimov M.V.

*Photochemictry Research Center, Russian Academy of Sciences, ul. Novatorov 7A/1, Moscow,
119421 Russia*
e-mail: yurasik.georgy@yandex.ru

The fluorescence properties of the $DBMBF_2$/methylbenzene exciplexes strongly depend on the nature of aromatic moieties and can be used to achieve their selective detection. The high sensitivity to benzene, toluene and xylene vapors has been previously demonstrated with materials based on $DBMBF_2$ [1]. On the other hand nanoparticles with immobilized photoactive organic dyes are of great scientific interest in terms of their potential applications as fluorescent labels, molecular sensors, as components in optoelectronic devices and devices for the conversion and storage of solar energy and other [2].

Dichloroethane suspensions of synthesized silica nanoparticles (SNPs) with a mean diameter of 100 nm and surface modified with covalently-linked dibenzoylmethanatoboron difluoride ($DBMBF_2$) were used as ink to print sensitive layers with micro-valve ink-jet technology. It was demonstrated that deposited SNP-based thin films are sensitive for methylbenzene vapors and could be a good candidate as a printed sensor. The fluorescence spectra (λ_{exit} = 340 nm) of printed SNPs coating before exposure and after exposure to methylbenzenes saturated vapors for 10 minutes are represented on the left. AFM image of the printed sample is represented on the right. Responses of sensing films to methylbenzene vapors were analyzed using multivariate nonlinear regression method.





This work was supported by the Russian Science Foundation
(projects no. 15-13-00163 and no. 14-23-00231).

References

[1]. Ionov D.S. et al. Model of the formation of dibenzoylmethanatoboron difluoride exciplexes with aromatic hydrocarbons on silica surface, High Energy Chem. 49 (2015) P. 183–188

[2]. Crowley K. et al. Fabrication of an ammonia gas sensor using inkjet-printed polyaniline nanoparticles // Talanta. 2008. Vol. 77, № 2. P. 710–717.

Photostimulated adsorption of dyes on TiO_2 with Au and Cu

Zaev D.A., Mikhalenko I.I., Trofimov N.S., Chechlova T.K.

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

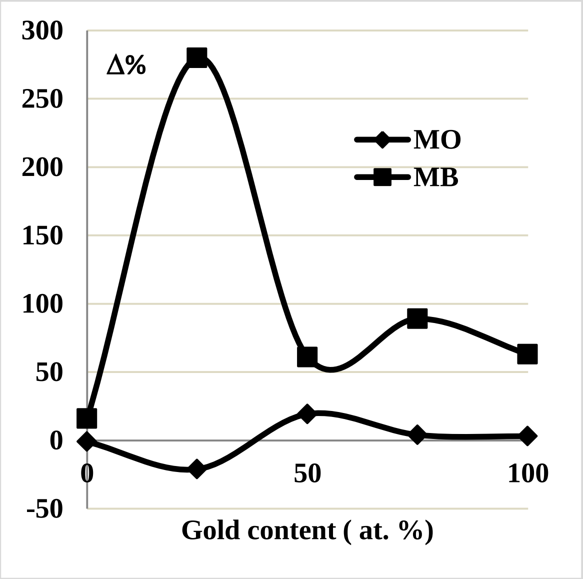
Titanium dioxide is one of the most intensely studied metal oxides due to its application in many fields, such as catalysis, optoelectronics, gas sensors, functional coatings in self-cleaning, antifogging, and in medicine and pharmacy. TiO_2 has received much attention as a well-known photocatalytic material [1,2]. In this work TiO_2 was synthesized by gel technology mode. Organogel prepared from titanium butoxide and triethylenglycol in butanol media was treated by heating in air at 120^0C during 3 h. and then gold and copper (precursors – chloride salts) were added by precipitation and calcination procedures. The dopants were mono Au or Cu and binary AuCu which content was verified by X-ray fluorescence analysis. The state of initial TiO_2 support in form of powder was analyzed by AFM-Raman method.

The aim of this work was to compare the influence of the previous ultraviolet irradiation of TiO_2, Au/TiO_2, Au/TiO_2 and $AuCu/TiO_2$ on its adsorption ability for cationic and anionic dyes in aqueous solutions. The values of adsorption were obtained by photometric method.

Dyes Gibbs adsorption in µmol/g
(MO - Methyl orange, MB - Methylene blue)
for the TiO_2 with dopants for samples without
(1) and with (2) UV exposure 10 minutes

	Adsorption duration			
	16 hours		5 days	
	MO	MB	MO	MB
No dopant 1	15	42	7	480
2	0	**113**	0	179
Au_{100} 1	444	505	447	636
2	459	**822**	471	**852**
$Au_{75}Cu_{25}$ 1	444	447	446	600
2	461	**843**	459	**863**
$Au_{50}Cu_{50}$ 1	374	401	400	483
2	446	**646**	459	**713**
$Au_{25}Cu_{75}$ 1	453	107	453	635
2	355	**412**	410	556
Cu_{100} 1	27	51	33	248
2	0	59	0	167

The relative changes of dyes adsorption (after 16 h) due to UV treatment TiO_2 samples with supported Au and Cu



The data of the table show that in gold presence the adsorption of cationic dye (MB) greatly increases including mixed AuCu dopants with 75 and 50% Au. Pure copper is inactive dopant. The results indicate that only in case of cationic dye MB the enhancement of adsorption due to UV treatments may be obtained. The greater UV increase of MB adsorption is for $Au_{25}Cu_{75}/TiO_2$ – in 4 times or 280% relatively after 16 h of adsorption, as it can be seen from the figuer.

References

[1]. Mai Do Tkhyui, Mikhalenko I I., Pylinina, A.I. // Russian J. Phys.Chem. 2014,V.88. P. 1637.

[2]. Neaţu Ş., Maciá-Agulló J.A. et al. // *J. Am. Chem. Soc.* 2014. V.136 (45). P.15969.

Poster Session

Influence of acoustic vibrations on the kinetics and the mechanism of chemical reactions of first order in the nano-structured liquid phase

Chegodaev N.A., Kulagina T.P., Smirnov L.P.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: tan@icp.ac.ru

It is experimentally shown that vibration acoustic vibrations influence a kinetics of chemical reactions [1,2]. When studying action of acoustic waves on melts and polymer blends on a kinetics of polymerization noticeable physical and chemical and chemical effects are found with frequencies about 10-100 Hz.

The purpose of the real work is theoretical studying of the mechanism of impact of vibration acoustic vibrations on reaction rate of the first or second order.

Model operation for prime kinetic schemes (reaction of the first or second order, consecutive reversible tests) taking into account formation of associates is carried out.

The mathematical model of influence of association of reagents on a kinetics of multistage reactions is offered [1]. In the analysis of the kinetic equations only formation of dimers and tetramers was taken into account. . For example, the reaction of first order with formation one product B at monomers A_1 and dimmers A_2 are take part is considered as:

$A_1 \rightarrow B$, k_1 (1)
$A_2 \rightarrow B + A_1$, k_2 (2)
$2A_1 \leftrightarrow A_2$, K , (3)

where k_1, k_2 are the constants of reaction rates (1) and (2), K is the equilibrium constant.
Reaction rate has view:
$w = k_{ef}[A] = K^{-1}k_1[(0.0625 + 0.5K[A])^{0.5} - 0.25] ++ K^{-1}k_2[(0.0625 + 0.5K[A])^{0.5} - 0.25]^2$.
The influence of acoustic vibrations on the equilibrium constant K is:

$K = K_0 \exp[-aP_0 \sin(2\pi\upsilon t)]$

Connection of chemical reaction rate and concentration of reagents with parameters of wave mechanical influence (amplitude, oscillation frequency) depending on the kinetic scheme of reaction and the nature of the supra-molecular structure of reagents (quantity of types and type of associates) is established.

References

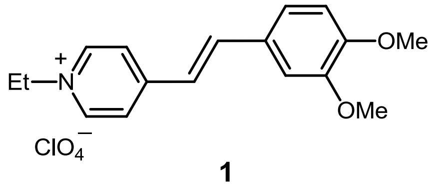
[1]. Kulagina, T. P., Smirnov, L. P. *Kinetiks and Catalisis* **2011**, *52*, 177.

An ultrafast stage of the [2 + 2] photocycloaddition of styryl dyes mediated by cucurbit[8]urils

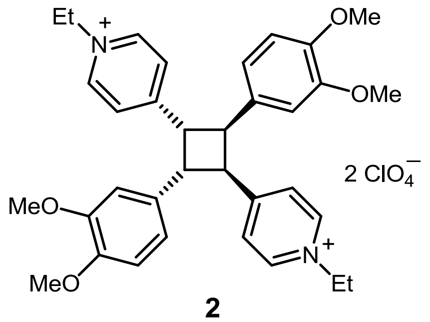
Ivanov D.A.[1], Shandarov Yu.A.[1], Kryukov I.V. [1], Svirida A.D. [2], Avakyan V.G. [1], Petrov N.Kh. [1,2], Alfimov M.V. [1,2], Gromov S.P. [1,2]

[1]*Photochemistry Center of the Russian Academy of Sciences, ul. Novatorov 7A, 119421 Moscow, Russia*
[2]*Moscow Institute of Physics and Technology (State University), Institutsky per. 9, 141707, Dolgoprudny, Russia*
e-mail: ivanovd@photonics.ru

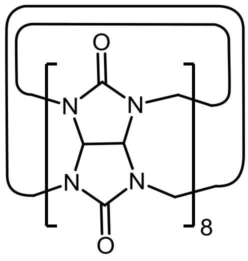
The [2 + 2] photocycloaddition of styryl dye, 4-[(E)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate (**1**), mediated by 1:2 host-guest complexes with cucurbit[8]urils (CB[8]), was studied by means of fluorescence upconversion techniques. The quenching of florescence has been observed that leads to cyclobutane (**2**). The lifetime of 14.5 ps for excited **1** in aqueous solution and 3.8 ps for that in the presence of 0.5 equiv. of CB[8] were extracted from the fluorescence decay curves. The rate constant of such a quenching that was estimated by the classical Stern-Volmer formula is close to the diffusion control limit for bimolecular reactions.



1



2



CB[8]

The results of quantum-chemical calculations confirmed that in the ground state the geometry of reactants inside the cavity does not fit the topochemical principles and it requires a marked displacement to get a reaction-ready structure. The pre-organisation motion of excited **1** along a direction almost parallel to cucurbituril's axis was suggested on the basis of the measurements of time-resolved fluorescence anisotropy in the range of 1-5 ps.

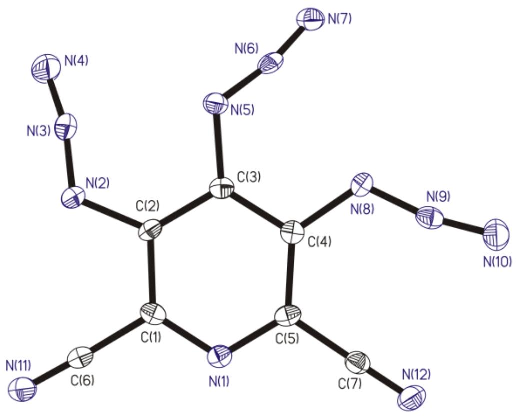
The work was supported by the Russian Scientific Foundation (project no. 14-13-00751) and (in part) by the Russian Foundation for Basic Research (project no. 15-03-01883).

Structure and properties of polyazidopyridines with adjacent azido groups

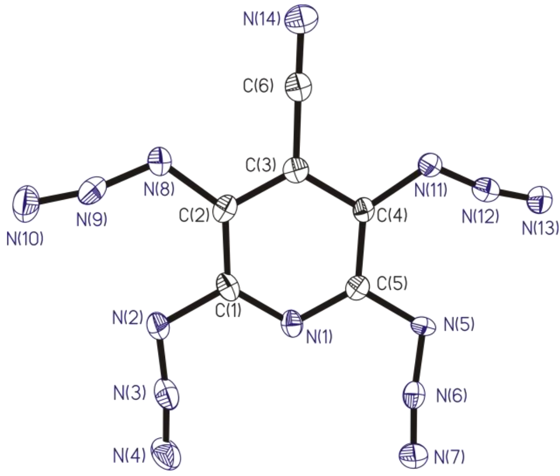
Korchagin D.V.[a,b], Aldoshin S.M.[a] and Chapyshev S.V.[a]

[a] Institute of Problems of Chemical Physics RAS, 142432, Chernogolovka, Ac.Semenov av. 1
[b] RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: korden@icp.ac.ru

To the moment, there are known 26 six-membered aromatic triazides, and, in all of them, the azido groups are located in the *meta*-positions relative to each other [1]. In this work we report on the x-ray structure and properties of two novel polyazides: 3,4,5-triazidopyridine-2,6-dicarbonitrile (**1**) and tetraazidopyridine-4-carbonitrile (**2**) representing first examples of heteroaromatic polyazides with adjacent azido groups in the ring.



1



2

The x-ray structure information of these compounds for the first time possible to analyze the structural parameters of the azido group located in β-positions of the pyridine ring. β-azido groups in comparison with the α-azido groups have significantly smaller N_α–N_β–N_γ and larger C–N_α–N_β bond angles, as well as slightly shorter N_α–N_β bond lengths (as in the case of γ-azido groups of 3,5-substituted 2,4,6-triazidopyridines [2]). Such structural parameters, according to the literature [1] point to the relatively low activation energy of β-azido group in the reactions of 1,3-dipolar cycloaddition, reduction and phosphorylation by Staudinger, thermolysis, and photolysis, where the transition states have the N_α–N_β–N_γ bond angles reduced to 125–130º. Unlike tetrazide **2** in which α- and β-azido groups have structural differences and, as a consequence, their reactions must be selective, in triazides **1** the all three azido groups are structurally almost identical that indicates an absence of selectivity in their reactions.

These polyazides have high positive heats of formation and may be of interest as a component of high-energy materials as well as source compounds in organic chemistry.

This work was supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.21.0008), FASO (the theme "Creating of high-energy materials") and the Presidium of RAS ("Fundamental principles of dual-use technologies in the interests of national security").

References

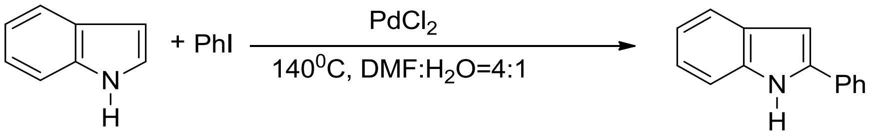
[1]. Chapyshev, S. V. *Molecules*, **2015**, *20*, 19142.
[2]. Korchagin, D. V.; Aldoshin, S. M.; Chapyshev, S. V. *J. Struct. Chem*. **2016**, *57(6)*, 1255.

Formation of $[PdX_4]^{2-}$ complexes as a result of a catalyst deactivation in the direct arylation of indole by iodobenzene

Larina E.V., Lagoda N.A., Yarosh E.V., Sharipova D.A., Kurokhtina A.A., Schmidt A.F.

Irkutsk State University, Russia, 664003, Irkutsk, K. Marx str. 1
e-mail: kurokhtina@chem.isu.ru

The formation of $[PdI_4]^{2-}$ was detected by UV-vis spectroscopy in the investigations of the direct arylation of indole by iodobenzene using ligand-free catalytic systems under real catalytic conditions. Operando kinetic studies of the reaction were carried out to obtain information about the role of the observed complexes in catalysis. It was found that in the reaction beginning concentration of $[PdI_4]^{2-}$ increased to achieve about 25%, following its decreasing to complete disappearance coincided with the drop in catalytic activity and full conversion of iodobenzene resulted from side reaction of biphenyl formation. The dependence of $[PdI_4]^{2-}$ concentration on the rate of 2-phenyl indole formation was found to have the extensive section exhibiting negative dependences. The formation of such complexes is known to result from the homocoupling of iodobenzene to produce biphenyl [1]. Taking into account the results of kinetic modeling being the simulation of [species amount]–[catalytic reaction rate] dependences for catalyst species playing different roles in the catalytic conversion of substrate to product, these results indicated that $[PdI_4]^{2-}$ is inactive species and is formed in a side reaction (biphenyl formation) but not in the reaction leading to main product (2-phenylindole) formation.



The plotting the $[PdI_4]^{2-}$ concentration versus that of 2-phenylindole for the experiments with various catalyst precursor concentrations indicated that they have clearly marked maxima and matched leads. In accordance with the results of kinetic modeling, this indicated that the deactivation of active species to $[PdI_4]^{2-}$ was irreversible but these species could be reactivated through a consequence of steps.

This work was supported by the Russian Foundation for Basic Research
(grant № 16-29-10731).

References

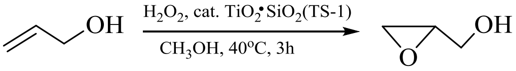
[1]. Schmidt A. F.; Smirnov V. V.; Al-Halaiga A. *Kinet. Catal.*, **2007**, *48*, 390.

Kinetics and mechanism of allyl alcohol epoxidation to glycidol with hydrogen peroxide at titanium silicalite

Zh.Yu. Pastukhova, M.V. Marchenko, L.G. Bruk, V.R. Flid

Moscow technological university (Institute of Fine Chemical Technologies),
119571, Moscow, Vernadsky Avenue,78
e-mail: mmarchenkomsk@mail.com

Oxygen-containing heterocyclic compounds (oxides olefins, cyclic acetals, etc.) are important products and intermediates of the basic and fine organic synthesis [1]. Great practical interest is the glycidol oxide of allyl alcohol. It is a valuable intermediate product in the manufacture of surfactants, plasticizers, textile dyes, photographic chemicals, drugs, pesticides, some rubbers, paints, thermosetting resins and plastics [2]. One of the most promising methods for producing glycidol is the epoxidation of allyl alcohol by hydrogen peroxide on the titanium-containing catalyst.



It was studied the epoxidation mechanism of allyl alcohol using titanosilicate zeolite (TS-1) at 40°C by means of procedures for the nomination and discrimination of mechanism hypotheses.

The hypotheses were carried out using the literature data and the preliminary experiment results. Discrimination hypothetical mechanisms implemented on the basis of the univariate results of the kinetic experiment, varying concentrations of allyl alcohol, hydrogen peroxide and glycidol.

The most probable mechanism involves the hydrogen peroxide and allyl alcohol adsorption at the catalyst active centers and the glycidol formation at a reversible stage in the interaction of the adsorbed molecules of the reactants. Considered hypotheses include a different sequence of interaction of the reactants with active catalyst centre. In addition, hypotheses take into account the formation of intermediate compounds as well as inactive products of the interaction of substances present in the reaction system, with the active centers on the silicalite surface. For each hypothesis, it was formulated the corresponding system of differential equations and carried out the estimation of the rate constants. The quality of the experimental data description was judged by the residual sums of squared deviations and correlation coefficients.

The best results are obtained for the hypothesis involving the hydrogen peroxide and allyl alcohol adsorption at the two active catalyst centers with subsequent interaction of the resultant intermediates between them, with the formation of glycidol adsorbed on one center, free catalyst centre and molecule of water. Formation of free glycidol occurs at a reversible stage. A significant part of the active centers of the catalyst increasing the concentration of glycidol is associated with it. This is the main reason for the decrease of the reaction rate, apart from reducing the concentration of the reactants.

References

[1]. Kozlovskiy, R.A., Shvets, V.F., Kozlovskiy, I.A., Makarov, M.G., Suchkov, J.P., Koustov, A.V. *Organic Process. Research & Development*, **2002**, *6*, 660–664.

[2]. Timofeev, V. C., Serafimov, L. A. Principles of technology of basic organic and petrochemical synthesis,: proc. the manual for high schools. M.: *Higher school*, **2003**, 536.

Combined effects of structure and temperature on kinetics of reactions between 4-nitrophenyloxirane and arenesulfinic acids

I. V. Sadovaya, I. V Shpan'ko

Donetsk National University, Ukraine
e-mail: sadovaya@bk.ru

The effect structure and temperature on the rate and free activation energy of reactions between 4-nitrophenyloxirane and Y-substituted arenesulfinic acids $YC_6H_4SO_2H$ (Y = 4-CH_3, H, 4-Cl) in dioxane at 298, 308, and 323 K have been studied:

$$4\text{-}NO_2C_6H_4CH(O)CH_2 + YC_6H_4SO_2H \rightarrow 4\text{-}NO_2C_6H_4CH(OSOC_6H_4Y)CH_2OH \qquad (1)$$

The reaction kinetics was examined using more than tenfold amounts of arenesulfinic acids (HA) with respect to the initial concentrations of 4-nitrophenyloxirane (S): $[HA] >> [S] = (4 \div 8)\ 10^{-3}$ 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:

$$- d[S]/dt = k_1 [S] = k_3 [S] [HA]^2, \qquad (2)$$

where k_1 (s^{-1}) and k_3 (dm^6 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 Y and temperature have on the rate of reactions (1), we used a cross correlation equation for a two-parameter variant of principle of polylinearity:

$$\lg k_3 = \lg k_3^{st} + \rho_Y^{st}\sigma_Y + B_T^{st}(1000/T) + q_{YT}\sigma_Y(1000/T), \qquad (3)$$

where k_3^{st} is the rate constant under standard conditions ($\sigma_Y = 0$, $T = \infty$ K), ρ_Y^{st} and B_T^{st} are the parameters of standard reactions at $T = \infty$ K and $\sigma_Y = 0$, respectively, and q_{YT} is the cross interaction coefficient. The following polylinear regression was obtained in processing the kinetic data in accordance with equation (3):

$$\lg k_3 = (9.3 \pm 0.2) + (-9 \pm 1)\sigma_Y + (-3.38 \pm 0.07)\cdot 1000/T + (3.3 \pm 0.4)\sigma_Y\cdot 1000/T, \quad (4)$$
$$s = 0.022;\ R = 0.999;\ F = 1368,\ n = 9.$$

It is found that as a result of the nonadditivity of the joint effect of substituents Y and temperature, the cross reaction series exhibits isoparametric properties, the quantitative characteristics of which are isoparametrical points with respect to the constant of substituents Y ($\sigma_Y^{IP} = 1.02$) and to temperature ($T^{IP} = 367$ K). At the isoparametrical point $\sigma_Y^{IP} = 1.02$, the rate of the process should not depend on temperature. At the isoparametric temperature the rate of the process should not depend on the effects of substituents Y ($\lg k_3$ = const, $\rho_Y^T = 0$). All these isoparametrical points fall outside experimental attainability.

Electrophoretic concentration of TiO_2 nanoparticles in AOT microemulsions

Shaparenko N.O., Demidova M.G., Bulavchenko A.I.

Nikolayev Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, pr. Academika Lavrent'eva 3, Novosibirsk, Novosibirsk State University, Pirogova, 2,
Novosibirsk, 630090 Russia
e-mail: nikshapar@mail.ru

Stable and highly concentrated organo- and hydrosols of nanoparticles of metals, oxides and salts are of great interest for nanochemistry and nanotechnology. They are promising as inks for printers, microcircuits, fluid heat sink. Nanoparticles are "free" in sols, i.e. are not bound with each other by coagulation and coagulation-crystallization (phase) contacts. As a result, their application for the formation of nanomaterials provides a uniform distribution of nanoparticles in the bulk phase or in the film of the composite. A great number of published works are devoted to the synthesis of TiO_2 nanoparticles. The interest arises from the prospects of production of new nanomaterials for catalysis, photovoltaics, biosensorics and delivery of medicine.

One of the most widespread and popular techniques for the production of organosols and ultra-dispersed powders is micellar (microemulsions) synthesis. It allows production of organosols with qualitative nanoparticles with a specified size and a narrow distribution function. However, significant and, at times, insuperable disadvantages of micellar synthesis are the low mass concentration of produced organosols and enormous concentration of surfactant-stabilizers (typically about 10 and more mass %). The problems are due to the low solubilization capacity of reversed microemulsions relative to initial reagents (1-5 vol.%). As a result, to obtain concentrated organosols in micellar synthesis, it is necessary to introduce additional concentration and purification stages.

A promising method of separation and concentration of nanoparticles is electrophoresis. In spite of the low electric conductivity, reversed microemulsions are widely used as the medium for separating various substances.

The aim of this work is to study the possibility of application of nonaqueous electrophoresis in a **capacitor**-type cell to concentrate and separate TiO_2 nanoparticles and to separate them from the excess of AOT and reaction by-products.

Stable organosols of TiO_2 nanoparticles were prepared, using the hydrolysis of titanium tetraisopropoxide (TTIP) in the microemulsions of sodium bis(2-ethylhexyl)sulfoxynate (AOT) in decane by increasing the content of water pseudophase from 0.15 to 0.85 vol.%. The hydrodynamic diameter of nanoparticles increased with water content increasing from 10 до 225 nm, and ξ-potential, from -6 to 18 mV (recharge of TiO_2 nanoparticles surface was registered at 0.45 vol.%).

Using nonaqueous electrophoresis in an electrophoretic cell of capacity-type, we succeeded to concentrate nanoparticles with a diameter from 60 to 225 nm (enrichment factor was 10), to separate 20 and 225 nm particles and by an order of magnitude to reduce the content of AOT in organosol. Laser and spectrophotometric scanning of interelectrode space in situ showed that during electrophoresis a sharp boundary formed between raffinate and the layer of moving nanoparticles.

The work was financially supported by the Russian Scientific Foundation
(project № 15-13-00080).

References

[1]. Nooney, R., O'Conell, C., Shibsekhar, R. etal., Sens. Actuators, B **2015**, 221, 470.
[2]. Hollamby, M.J., Hudson, L., Adv. Colloid Interface Sci. **2006**, 5-15, 128–130.

Complex formation with charge transfer in the ionic liquid - cellulose acetate - penetrant system in the crystal matrix

Grinvald I.I., Kalagaev I.Yu., Spirin I.A., Petukhov A.N., Vorotyntsev I.V., Kapustin R.V., Grushevskaya A.I.

Nizhny Novgorod Technical State University n.a. R.E. Alekseev,
603950, Minin St., 24, Nizhny Novgorod
email: ivan.sn.92@mail.ru

Ionic liquids are used currently for the modification of the polymeric membrane, in particular cellulose acetate, for the improvement of the separation quality at the production of high purity components. This effect is determined by the appearance in a polymeric material of active ionic centers providing the complex formation in the system. Infrared spectroscopy is the most informative method for studying the structure of similar complexes as well as the mechanism of their binding. However, the strong absorption of the polymeric materials leads to the serious difficulties at spectral observation of these intermediates. We have proposed a method of sample preparation in crystalline matrix allowing to solve this problem [1]. In the present work there were considered model systems, consisting: 1-butyl-3-methylimidazole chloride (IL1) or 1-butyl-3-methyl-imidazole hexaflurophosphate (IL2) as well as cellulose acetate (AC), water or ammonia.

In the spectrum of the potassium bromide matrix containing cellulose acetate, modified by IL1, at saturation by water vapour the new bands at 3397 and 2108 cm^{-1} appear, which were assigned to stretching vibration of water in a complex. For the system (cellulose acetate - IL2 – water) the new bands at 3631, 3567 and 3424 cm^{-1} were observed. They can be interpreted as the bands of stretching vibrations of adsorbed (the first two bands) and complex bounded (the last one) water molecules.

In the system (cellulose acetate – IL1 – ammonia) the new bands at 1668 and 1457 cm^{-1} were detected. The band at 1668 cm^{-1} belongs undoubtedly to the bending vibration of ammonia, and the band at 1457 cm^{-1} assigns to vibrations of the ammonium ($NH4^+$), which can form in the complex by hydrogen atom transfer at presence of water.

In the matrix, including cellulose acetate, methyl iodide and ammonia the new bands at 3200 cm^{-1} and 1670 cm^{-1} were shown. The first band assigns to the stretching vibration of ammonia in the intermediate, and the second one to the bending vibration of ammonia. The input of methyl iodide in the system provides the charge transfer into the polymeric matter.

The mechanism of complex formation is considered by *ab initio* calculations in terms of DFT. It is shown that the molecules of alkali metal play the role of a stabilization component in the structure of the complexes. There was estimated that both the nature of metal and halogen atoms affect the structure of the complexes. The interaction of alkali salts with the system components increases in the row Li >Na>K and F >Cl >Br.

This work was supported by the Russian Foundation for Basic Research (grant № 14-08-05494-a).

References

[1]. I.V. Vorotyntsev, I.I. Grinvald, I. Yu. Kalagaev, etc.//Russ. J. Phys. Chem. A, 2014, **88**, 625-628.

Synthesis and thermodynamical properties of calcium-ammonium nitrate decahydrate

Tiflova L.A., Druzhinina A.I., Grishchenko R.O., Monayenkova A.S.

Moscow State University, Department of Chemistry, 119991, Moscow, Leninsky Gory 1
e-mail: tiphlova@phys.chem.msu.ru

This work is a part of systematic studies of new functional materials which is carried out at Luginin's Thermochemistry and Chemical Thermodynamics Laboratories. It is devoted to the study of thermodynamical properties of $5Ca(NO_3)_2{\cdot}NH_4NO_3{\cdot}10H_2O$ (CAN). The choice of object of research is caused by its application as components of calcium nitrogen fertilizations. There are no literature thermodynamical data for CAN.

CAN was synthesized by crystallization from a supersaturated solution. $Ca(NO_3)_2{\cdot}4H_2O$ (99.0%) and NH_4NO_3 (99.5%) and distilled water were reagents for synthesis. The synthesized sample was checked by X-ray, TG-DSK, IR and chemical analysis.

The thermodynamical properties of CAN were investigated by methods of calorimetry of solution and of vacuum adiabatic.

The enthalpy of solution of CAN was measured in water at 298.15 K in hermetically sealed swinging calorimeter with an isothermal coat. Temperature rise in each run was measured by platinum resistance thermometer. Thermometric sensitivity was $3{\cdot}10^{-5}$ K. The energy equivalent of the calorimeter was determined by electric technique. The enthalpy of formation of CAN at 298.15 K was calculated on the basis of the experimental data and enthalpies of dilution of aqueous solution of calcium and ammonium nitrates and Ca^{2+}(aq) and NO^{3-}(aq) enthalpies of formation.

The low-temperature heat capacities of CAN was measured by vacuum adiabatic calorimetry in the temperature range (7 to 338) K. The errors in the determination of heat capacities are on average 0.2-0.3 %. The curve of heat capacity exhibits solid-to-solid transition. The temperature of the transition, $T_{tr} = 323.7 \pm 0.3$ K, and the jump of heat capacity, $\Delta C_{p,m} = 91.7 \pm 0.2$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$, were determined. The standard thermodynamic functions (changes of the enthalpy, entropy, and Gibbs energy) were obtained for the crystal state in the temperature interval studied. The standard thermodynamic functions for CAN in the crystal state at T = 298.15 K are presented in Table 1.

Table 1. Standard thermodynamic functions for CAN in the crystal state at T = 298.15 K

$C_{p,m}$ / $J{\cdot}K^{-1}{\cdot}mol^{-1}$	$H^0_m(0) - H^0_m(T)$ / $kJ{\cdot}mol^{-1}$	$S^0_m(T)$ / $J{\cdot}K^{-1}{\cdot}mol^{-1}$	$[G^0_m(0) - G^0_m(T)]$ / $kJ{\cdot}mol^{-1}$
1822.6±3.4	309.6±1.5	2050±1	-301±3

Table 2. Thermodynamic functions of formation for CAN in the crystal state at T= 298.15 K

$\Delta_f H^0_m(cr)$ / $kJ{\cdot}mol^{-1}$	$\Delta_f S^0_m(cr)$ / $J{\cdot}K^{-1}{\cdot}mol^{-1}$	$\Delta_f G^0_m(cr)$ / $kJ{\cdot}mol^{-1}$
–8070±7	-5282±2	-6495±7

The functions of the formation $\Delta_f H^0_m(298)$, $\Delta_f S^0_m(298)$ and $\Delta_f G^0_m(298)$ were calculated for the crystal state on the basis of the obtained experimental data (Table 2).

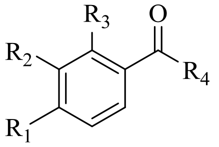
Unprecedented effect of aryl alkyl ketones as a hydrogen peroxide stabilizers

Pastukhova Zh.Yu., Vilkova I.S., Sukhareva A.A., Kaliya O.L., Bruk L.G.

Moscow technological university (Institute of Fine Chemical Technologies), 119571, Moscow,
Vernadsky Avenue,78
e-mail: ira_vilkova123@mail.ru

Hydrogen peroxide is one of large-scale products highly demanded in industry and laboratory chemistry. Scientific research related to hydrogen peroxide involves the following three areas of the study: preparation, application, and stabilization. A considerable progress has been achieved in the former two areas [1]. Less advances have been made in investigations concerning then stabilization of hydrogen peroxide, which still remains one of the key problems. Hydrogen peroxide decomposes on storage when exposed to light or high temperatures, and on contact with organic impurities and salts of metals of variable valence [2].

In the present work, when studying the synthesis of organic peroxides from carbonyl compounds and hydrogen peroxide, we unexpectedly found that aryl alkyl ketones would efficiently stabilize aqueous solutions of hydrogen peroxide. We tested aryl alkyl ketones **1–15** with σ-electron-donating, π-electron-withdrawing, and π -electron-donating substituents for the stabilization of hydrogen peroxide [3].



1: R_1 = H, R_2 = H, R_3 = H, R_4 = Me;
2: R_1 = *t*-Bu, R_2 = H, R_3 = H, R_4 = Et;
3: R_1 = Me; R_2 = H, R_3 = H, R_4 = Me;
4: R_1 = C(O)Me, R_2 = H, R_3 = H, R_4 = Me;
5: R_1 = H, R_2 = H, R_3 = COOH, R_4 = Me;
6: R_1 = OMe, R_2 = H, R_3 = H, R_4 = Me;
7: R_1 = OH, R_2 = H, R_3 = H, R_4 = Me;
8: R_1 = H, R_2 = H, R_3 = OH, R_4 = Me;
9: R_1 = OH, R_2 = H, R_3 = OH, R_4 = Me;
10: R_1 = H, R_2 = H, R_3 = Cl, R_4 = Me;
11: R_1 = Cl, R_2 = H, R_3 = H, R_4 = Me;
12: R_1 = Cl, R_2 = H, R_3 = Cl, R_4 = Me;
13: R_1 = H, R_2 = Br, R_3 = H, R_4 = Me;
14: R_1 = Br, R_2 = H, R_3 = H, R_4 = Me;
15: R_1 = OMe, R_2 = Br, R_3 = H, R_4 = Me.

Aryl alkyl ketones are proposed as new stabilizers of aqueous solutions of hydrogen peroxide. The efficient stabilizing effect is observed within 16–24 months for 33–37% H_2O_2 in the presence of a stabilizer in an amount of 0.005–0.5 wt% of the weight of the solution. Taking into account the large scale of application of hydrogen peroxide, as well as the commercial availability and low toxicity of aryl alkyl ketones, the results of the present study can find use in industry.

This work was supported by the Russian Foundation for Basic Research
(grant № 16-33-00555).

References

[1]. Campos-Martin, J.M., Blanco-Brieva, G., Fierro, J.L. *Angew. Chem. Int. Ed.*, **2006**, *45*, 6962.
[2]. Hug, S., Leupin, O. *Environ. Sci. Technol.*, **2003**, *37*, 2734.
[3]. Terent'ev, A.O., Pastukhova, Zh.Yu., Yaremenko, I.A., Bruk, L.G., Nikishin, G.I. *Mendeleev Communication,* **2016,** *26*, 4, 329-331.

Author Index

Contents

Научное издание

УСПЕХИ СИНТЕЗА И КОМПЛЕКСООБРАЗОВАНИЯ

В двух частях

Часть 2
Секции
«Неорганическая и координационная химия»
«Физическая и коллоидная химия»

На английском языке

Издание подготовлено в авторской редакции

Дизайн обложки *Ю.Н. Ефремова*

Подписано в печать 17.04.2017 г. Формат 60×84/8.
Бумага офсетная. Печать офсетная. Гарнитура Таймс.
Усл. печ. л. 16,0. Тираж 150 экз. Заказ 630

Российский университет дружбы народов
115419, ГСП-1, г. Москва, ул. Орджоникидзе, д. 3

Типография РУДН
115419, ГСП-1, г. Москва, ул. Орджоникидзе, д. 3, тел. 952-04-41