The conference is dedicated to the memory of
Prof. Yuri T. Struchkov

The 2nd STRUCHKOV MEETING

International Workshop
on Chemical Crystallography
and Structural Biology

Book of abstracts

13–16 November 2018

Moscow, RUDN University

Moscow
Peoples’ Friendship University of Russia
2018
The event was financially supported by the RUDN University Program “5-100” and the Russian Foundation for Basic Research (grant 18-03-20113_g)

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Secretary
Dr. Ekaterina K. Kultyshkina


The book of abstracts of The International Workshop on Chemical Crystallography and Structural Biology “The 2nd Struchkov Meeting” which was held from 13 to 16 November 2018 based on chemical departments of Faculty of Science of RUDN University includes abstracts of lectures of plenary speakers, invited and oral reports and Struchkov prize 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 978-5-209-08888-2 © Коллектив авторов, 2018
© Российский университет дружбы народов, 2018
Dear Colleagues,

Today we are welcoming participants of International Workshop on Chemical Crystallography and Structural Biology, dedicated to the memory of Prof. Yuri Struchkov. This is the first time we are holding this workshop here in Moscow on the premises of the RUDN University. However, this conference features the continuation of a tradition, which was established more than 10 years ago, when the students and former colleagues of Prof. Struchkov first met to share their new and inspirational scientific achievements and, at times, their old and precious memories. Today we are very happy to play the host for their second reunion.

Prof. Struchkov was famous among the world crystallographers for the encyclopedic coverage of his structural results, which touch upon almost all areas of organic, inorganic, and organometallic chemistry. He was also famous among the Soviet and Russian chemists for the first time bringing single crystal X-ray diffraction results to almost every chemical research institution in our country. He was famous among scientific publishers, as a workaholic, who in the decade of 1980-1990 published more papers, than any other scientist in the world. Yet, it could be even more important than all these impressive accomplishments, that Prof. Struchkov and his X-ray laboratory were at the source of a great scholarly community, and its numerous representatives are now actively working in Russia, in countries of Former Soviet Union and in the universities and scientific laboratories all around the world. We are very happy that many of them assembled this week here in Moscow to present at our Workshop their results in the diverse fields ranging from studies of conformational dynamics in biomolecular systems to elucidation of structural principles of minerals, from structure determinations of giant supramolecules at atomic resolutions to assessing the effects of ultrasound on click reactions in chitosan chemistry. We are very grateful to some of Prof. Struchkov’s former students, who agreed to share their insights and professional experiences in master classes featuring the latest technologies in structure solution and panel discussions surveying the recent advances in the analysis of structural results. We are also honored to hold the first special session including the talks of the laureates of Struchkov Prize, which, since 1997, is being annually awarded for the best research in the field of crystallography contributed by the young scientist.

It is quite expected for most scientific conference participants to share many common interests related to the subject of their research. We are now present at such special forum, where most of the participants share with each other not only the latest scientific developments, but also many common memories of various events both in their professional and personal lives. Let me wish to all of us, that this Workshop would become one more memorable occasion to be remembered and cherished by this community in years to come.

Workshop Chairman,
Rector of RUDN University

Vladimir M. Filippov
# SCIENTIFIC PROGRAM

## Monday November 12, 2018

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<td>9 00–18 00</td>
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<td>10 00–14 00</td>
<td><strong>Master Class on OLEX2</strong> <em>(Computer Class)</em></td>
<td><em>(Ordzhonikidze Street, 3)</em></td>
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<tr>
<td></td>
<td>“A complete structure solution and analysis program”</td>
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<tr>
<td></td>
<td><em>Iliia A. Guzei</em></td>
<td>University of Wisconsin-Madison (USA)</td>
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<td>14 00–15 00</td>
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<td><em>(Ordzhonikidze Street, 3)</em></td>
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<tr>
<td></td>
<td>“Advances in the modern X-ray structural analysis”</td>
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<tr>
<td></td>
<td><em>Sergey V. Lindeman</em></td>
<td>Marquette University (USA)</td>
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## Tuesday November 13, 2018

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<td>9 40–9 50</td>
<td><em>Igor L. Eremenko</em> <em>(Co-Chair of Program Committee)</em></td>
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<td>9 50–9 55</td>
<td><em>Mikhail V. Kovalchuk</em> <em>(Co-Chair of Program Committee)</em></td>
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<tr>
<td>9 55–10 00</td>
<td><em>Tatiana V. Timofeeva</em> <em>(Member of Program Committee)</em></td>
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<td>10 00–10 45</td>
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<td><em>Igor L. Eremenko</em> <em>(Co-Chair of Program Committee)</em></td>
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<tr>
<td></td>
<td><em>Yu.T. Struchkov and his role in the development of organic crystals in the territory of the former Soviet Union</em></td>
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<td><em>Igor A. Litvinov</em></td>
<td>Arbuzov Institute of Organic and Physical Chemistry RAS (Kazan, Russia)</td>
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<td><em>The Struchkov Group and Crystallographic Instrumentation Development</em></td>
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<td><em>Susan Byram</em></td>
<td>Bruker (USA)</td>
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<td></td>
<td><em>How conformational dynamics can relate structure and function in biomolecular systems</em></td>
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<td><em>Petra Imhof</em></td>
<td>Freie University Berlin (Germany)</td>
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<td><em>How conformational dynamics descriptors may help in remodelling of allosteric regulation in proteins</em></td>
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<td><em>Luba Tchertanov</em></td>
<td>Centre Mathématiques et leurs Applications (CMLA) – ENS Cachan (France)</td>
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<td></td>
<td><em>Structural chemistry of cyanoximes and their metal complexes</em></td>
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<td><em>Nikolay N. Gerasimchuk</em></td>
<td>Missouri State University (USA)</td>
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<td><strong>Ganna B. Lyashenko</strong></td>
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<td>Chemistry – A European Journal, Wiley-VCH (Germany)</td>
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<td>16 00–16 30</td>
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<td>16 30–17 15</td>
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<td></td>
<td><strong>Model study of the structure of supramolecular complexes of glycyrrhizic acid and its monoammonium salt (glycyrham)</strong></td>
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<td></td>
<td><strong>Bolot K. Sadybakasov</strong></td>
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<td>Kyrgyz-Russian Slavonic University (Kyrgyzstan)</td>
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<td>17 15–18 00</td>
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<td><strong>Crystal structure of some iron(II,III) sulfate solid solutions and forbidden by symmetry X-ray reflections</strong></td>
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<td><strong>Vakhob K. Sabirov</strong></td>
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<td>Auezov South-Kazakhstan State University (Kazakhstan)</td>
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<tr>
<td>18 30–20 30</td>
<td>Welcome Cocktail</td>
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**Wednesday November 14, 2018** (Ordzhonikidze Street, 3, Science Faculty Club)

**Session C** | Session Chairs: Igor S. Antipin (Russia), Sergey V. Lindeman (USA)

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<td></td>
<td><strong>X-ray Crystallography: Azaborines; From a molecule to a device; On the way from benzene to carbon nanotubes</strong></td>
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<td><strong>Lev N. Zakharov</strong></td>
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<td>CAMCOR – The Center for Advanced Materials Characterization in Oregon, University of Oregon (USA)</td>
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<td>10 45–11 30</td>
<td>Plenary</td>
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<td><strong>Observing mechanisms of nanochemistry through a keyhole of molecular models</strong></td>
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<td><strong>Vadim Kessler</strong></td>
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<td>Swedish University of Agricultural Sciences (Sweden)</td>
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<td>11 30–12 00</td>
<td>Coffee Break</td>
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<td>12 00–12 45</td>
<td>Plenary</td>
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<td></td>
<td><strong>Effect of wax crystallinity on oil production</strong></td>
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<td><strong>Olga E. Lindeman</strong></td>
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<td>Ecolab, Energy Services Department (USA)</td>
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<td>12 45–13 30</td>
<td>Plenary</td>
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<td><strong>A step to predictive structural biochemistry: QM/MM &amp; QTAIM approach</strong></td>
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<td><strong>Maria G. Khrenova</strong></td>
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<td>Federal Research Center of Biotechnology RAS (Moscow, Russia)</td>
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<tr>
<td>13 30–14 30</td>
<td>Lunch</td>
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**Session D** | Session Chairs: Vladimir G. Tsirelson (Russia), Vadim Kessler (Sweden)

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<td>14 30–15 15</td>
<td>Plenary</td>
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<td><strong>Click reactions + ultrasound = a new aurora of chitosan chemistry</strong></td>
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<tr>
<td></td>
<td><strong>Andrei S. Kritchenkov</strong></td>
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<td></td>
<td>Institute of Technical Acoustics, National Academy of Sciences of Belarus (Belarus)</td>
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<td>15 15–16 00</td>
<td>Plenary</td>
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<td><strong>Coordination chemistry of diazenium diolates. Structure-spectral overview</strong></td>
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<td><strong>Olga V. Kovalchukova</strong></td>
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<td>RUDN University (Moscow, Russia)</td>
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<td>Time</td>
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<td>16 00–16 30</td>
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<td>16 30–17 00</td>
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<td>17 00–17 20</td>
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<td>17 20–17 35</td>
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<td>18 05–18 20</td>
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**Thursday November 15, 2018 (Ordzhonikidze Street, 3, Science Faculty Club)**

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<th>Type</th>
<th>Title</th>
<th>Speaker</th>
<th>Institution</th>
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<td>Struchkov Prize Session</td>
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<tr>
<td>10 00–10 30</td>
<td>Invited Giant supramolecules at atomic resolution: how far away is the horizon?</td>
<td>Alexander V. Virovets, The First Struchkov Prize Laureate of 1997</td>
<td>University of Regensburg (Germany), Nikolaev Institute of Inorganic Chemistry SB RAS (Novosibirsk, Russia)</td>
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<tr>
<td>10 30–11 00</td>
<td>Invited Giant pentaphosphaferrocene-based supramolecules</td>
<td>Eugenia V. Peresypkina, The 2008 Struchkov Prize Laureate</td>
<td>University of Regensburg (Germany), Nikolaev Institute of Inorganic Chemistry SB RAS (Novosibirsk, Russia)</td>
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<td>11 00–11 30</td>
<td>Invited Hydrocerussite-related minerals and materials: structural principles</td>
<td>Oleg I. Siidra, The 2010 Struchkov Prize Laureate</td>
<td>Saint-Petersburg State University (Russia)</td>
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<td>11 30–12 00</td>
<td>Coffee Break</td>
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<tr>
<td>Time</td>
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<td>12 00–12 30</td>
<td>Invited</td>
<td><strong>Evolution of structural and topological complexity in uranyl sulfates and selenates</strong></td>
<td>Vladislav V. Gurzhiy, The 2015 Struchkov Prize Laureate</td>
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<td>12 30–12 50</td>
<td>Oral</td>
<td><strong>Protonic metal-based ionic liquids: DEAHFeCl₄, (DEAH)₂CoCl₄, DEAHMnCl₃</strong></td>
<td>Maksim A. Zakharov, The 2001 Struchkov Prize Laureate</td>
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<td>12 50–13 10</td>
<td>Oral</td>
<td><strong>Development and application of the Debye scattering equation method for a full-profile analysis of X-ray diffraction patterns for the structural diagnostics of powder nanomaterials</strong></td>
<td>Dmitriy A. Yatsenko, The 2013 Struchkov Prize Laureate</td>
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<td>13 10–13 30</td>
<td>Oral</td>
<td><strong>Serial crystallography studies of 7-TM membrane proteins</strong></td>
<td>Valentin I. Borshchevskiy, The 2015 Struchkov Prize Laureate</td>
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<td>13 30–14 30</td>
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<td>14 30–15 00</td>
<td>Invited</td>
<td><strong>Crucial role of water in the reactivity of a chiral NNO type copper(II) coordination polymers in the asymmetric Henry reaction</strong></td>
<td>Vladimir A. Larionov</td>
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<td>15 00–15 20</td>
<td>Oral</td>
<td><strong>Relationships between crystal structure and electrochemical properties in fluoride-phosphate-based cathode materials for rechargeable batteries</strong></td>
<td>Stanislav S. Fedotov, The 2017 Struchkov Prize Laureate</td>
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<td>15 20–15 40</td>
<td>Oral</td>
<td><strong>In situ XRD study of mixed Mn-containing oxide catalysts</strong></td>
<td>Olga A. Bulavchenko, The 2016 Struchkov Prize Laureate</td>
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<td>15 40–15 55</td>
<td>Oral</td>
<td><strong>Rotation of molecules in crystals: the influence of crystallographic symmetry</strong></td>
<td>Daut R. Islamov, The 2016 Struchkov Prize Laureate</td>
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<td>15 55–16 10</td>
<td>Oral</td>
<td><strong>Combined experimental and theoretical studies of non-covalent interactions using X-ray diffraction analysis and quantum chemical calculations</strong></td>
<td>Alexander S. Novikov, The 2017 Struchkov Prize Laureate</td>
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<td>16 10–16 40</td>
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<td>16:40–17:00</td>
<td>Oral</td>
<td>Intermolecular complexes of macrocyclic copper(I) and silver(I) pyrazolates with Lewis bases: comparison of structures in the solution and in the crystal</td>
<td>Alexey A. Titov</td>
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<td>17:00–17:15</td>
<td>Oral</td>
<td>Dehydrogenation of propane on catalytic systems based vanadium salts</td>
<td>Ekaterina B. Markova</td>
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<td>17:15–17:30</td>
<td>Oral</td>
<td>Substituents effect on the crystal packing and solid state transformations of phosphorylated acetothiosemicarbazides</td>
<td>Aida I. Samigullina</td>
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<td>17:30–17:45</td>
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<td>The effect of Fe$^{3+}$ and Zr$^{4+}$ on the structural and catalytic properties of BIMEVOX</td>
<td>Elena I. Knyazeva</td>
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<td>Oral</td>
<td>New approaches for the reductive formation of C-N bond</td>
<td>Alexey A. Tsygankov</td>
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**Friday November 16, 2018** (Ordzhonikidze Street, 3, Science Faculty Club)

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<th>Affiliation</th>
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<tr>
<td>10:45–11:30</td>
<td>Plenary</td>
<td>“A graveyard of experimental errors”? What lies behind thermal ellipsoids</td>
<td>Sergey V. Lindeman</td>
<td>Marquette University (USA)</td>
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<td>11:30–12:00</td>
<td>Coffee Break</td>
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<tr>
<td>12:00–12:45</td>
<td>Plenary</td>
<td>Crystal chemistry of functionally substituted cyclic phosphines</td>
<td>Igor A. Litvinov</td>
<td>Arbuzov Institute of Organic and Physical Chemistry RAS (Kazan, Russia)</td>
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<tr>
<td>12:45–13:30</td>
<td>Plenary</td>
<td>Substituents effect on structure and properties of pincer-ligated (PXCXP)IrH(Cl) complexes</td>
<td>Natalia V. Belkova</td>
<td>Nesmeyanov Institute of Organoelement Compounds RAS (Moscow, Russia)</td>
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<td>13:30–14:30</td>
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<tr>
<td>14:30–15:15</td>
<td>Plenary</td>
<td>Structural chemistry of organometallosiloxanes at INEOS RAS. History and prospects.</td>
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<tr>
<td>15:15–16:00</td>
<td>Plenary</td>
<td>3,7-Diazabicyclo[3.3.1]nonanes as unique platform for studying the supramolecular interactions and as a building block for organic synthesis.</td>
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<tr>
<td>16:00–16:30</td>
<td>Coffee Break</td>
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<td>16:30–17:00</td>
<td>Oral</td>
<td>Quantum chemical investigations of Cr$_2$O$_n$ and Cr$_2$O$_n^-$ series (n = 1-14)</td>
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<td>16:50–17:05</td>
<td>Oral</td>
<td>The evaluation of nanostructured Perovskite-type oxides SrFeO$_{(3-\delta)}$, GdFeO$_3$, GdSrFeO$_4$ and Gd$<em>2$xSr$</em>{1+x}$Fe$_2$O$_7$ in catalytic processes.</td>
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<td>17:05–17:20</td>
<td>Oral</td>
<td>Co(Ni)–Zr-Phosphates modified by plasma treatments: physico-chemical properties and catalytic activity.</td>
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<td>17:20–18:00</td>
<td>Awarding</td>
<td>Awarding the Winners for the best presentation from the <em>Chemistry – A European Journal</em>.</td>
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<td>Closing</td>
<td>Concluding remarks of the Rector of RUDN University, Chairmen and Members of the Program and Organizing Committees.</td>
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*Notes:*
- Session Chairs: Igor A. Litvinov (Russia), Nikolay N. Gerasimchuk (USA)
- RUDN University (Moscow, Russia)
Plenary Speakers
Yu.T. Struchkov and his role in the development of organic crystallochemistry in the territory of the former Soviet Union

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The report is dedicated to the memory of the remarkable Teacher, a corresponding member of the Russian Academy of Sciences, Yuri Timofeevich Struchkov.

The report outlines the system of training and education of specialists, developed and implemented in the RSA laboratory by Yuri Timofeevich. This system was extended to both laboratory staff and seconded from other organizations trainees and post-graduate students. The process of education is described from the point of view of one of such trainees, who worked in the laboratory for three years - from November 1979 to March 1983.

After a preliminary conversation, Yu.T. appointed a trainee or postgraduate curator ("micro-chef") from the laboratory staff, who had to teach the sponsored basics of the experiment - from searching of a crystal, preparing it for setting on a diffractometer, setting of the experiment, solving and refining the structure. But teaching experimental work was not the main thing in the learning process. The main thing was the very atmosphere of the laboratory, the rules and relations established between the employees and their attitude to work. Of particular importance in the training process were the weekly colloquiums of the laboratory. At the colloquium, discussions were held on topics, the distribution of the instrumental time and the order of the experiments, the results of the research were reported, articles and reports of staff at the conferences were discussed. Each employee, including interns and graduate students, was assigned a specific topic, which he periodically reported at the colloquium.

All the employees were registered by the VINITI's referee on the section "Crystal chemistry and crystallography". When Yu.T. made the decision that the trainee was "ripe", he began to give him a review of articles sent from magazines.

Special attention Yu.T. paid for the preparation of publications. He demanded from the first days not to delay the publication of completed studies, while constantly "raising the bar" of the quality of descriptions. He read, edited the texts of the articles, forced them to rewrite until a worthy description of the research was obtained. High demands were made on both the content and the form of publication, including the logic of the presentation, the clarity of the wording, the terminology and literacy of the text. Also very carefully edited and texts prepared by trainees and graduate students of dissertations. The result of such training and education was the production of highly qualified specialists able to perform the X-ray structural study of the most complex compounds independently and to organize the effective work of the X-ray group in their organizations.

Another equally important result of the internship of specialists from organizations and institutions from many cities of the Soviet Union was the conviction of the leaders of these organizations that scientific research is impossible without a high-level X-ray. And in many organizations, in the following years, there appeared their own diffractometers, groups and
Plenary Speakers

laboratories of the X-ray were established, many of which are successfully working now. In particular, laboratories organized by Yu.T. students work in the A.E.Arbuzov Institute RAS (Kazan), Institute of Organic Chemistry of the National Academy of Sciences of Ukraine (Kiev), Institute of Crystal Growth (Kharkov), IMOKh RAS (Nizhny Novgorod), Yerevan, Tashkent, Baku, Alma-Ata, etc. Many students Yu.T. for various reasons, left Russia and are now successfully working in the institutes and universities of foreign countries.
It is an honor to be asked to participate in the Second Struchkov Meeting in Moscow in 2018. I was fortunate to meet Professor Yuri Struchkov when he first visited our predecessor company, Syntex Analytical Instruments, in the 1970’s. I was a young software developer, contributing to the new P21 single crystal diffractometer and the first XTL minicomputer-based structure solution and refinement software. Professor Struchkov came to our development and manufacturing site in Cupertino, CA, where we discussed crystallography, science and the world. He was a visionary scientist and a great person.

The P21 diffractometer with its XTL structure determination suite was soon installed at the Institute of Organoelement Compounds in Moscow, and we were very proud that these and later instruments contributed to the outstanding record of 2,745 Cambridge Structural Database (CSD) entries authored by Yuri Struchkov – which meant that he was the top author in the CSD for over twenty years.

Our company maintained close ties with the group over many decades. From time to time I met Professor Struchkov at international crystallographic meetings. I remember particularly the 1986 IUCr-sponsored Symposium on Small Molecules in Beijing, China, where we were asked to bring our first two-dimensional area detector for crystallography. A special group of outstanding crystallographers gathered from all over the world to meet their Chinese counterparts. We met again at the IUCr meeting in 1990 in Bordeaux, France, where he was elected to the IUCr Executive Committee.

After Professor Struchkov’s far too early death in 1995, we maintained close ties with Professor Mikhail Antipin, facilitating parts and upgrades during times when new instrumentation was not possible. I saw Professor Antipin and Professor Tatiana Timofeeva more frequently in the USA as they established group collaborations between Russia and the USA, culminating in a very special Struchkov Symposium in August 2007, held in Chicago with an excursion to our company’s home base in Madison, Wisconsin. In 2010 I was able to visit INEOS in Moscow and see the original P21 and its successor instruments, all still working – and the huge set of printed publications from this group.

During this time span, single crystal diffraction instrumentation in the home laboratory progressed from point detectors to two dimensional CCD detectors to fast readout CMOS and CPAD detectors, from sealed x-ray tubes to high brightness microfocus sources, and from paper tape controlled instruments to rapid structure determination and structure validation on powerful personal computers. Data collection in 1970 took a few days to weeks and there were approximately 8,300 structures in the CSD at the beginning of that year. Today, data collection may take a few minutes to hours, with over 900,000 structures deposited in the CSD to date.
How conformational dynamics can relate structure and function in biomolecular systems

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At finite, e.g. physiological temperature, molecules are not static entities with a fixed geometry but rather exhibit dynamics, occupying and interchanging between several conformational and configurational states. Often, only a few of those states render the molecule functional, such as the folded form of a protein, or a open/closed complex. And even so often, the transition between states is associated with function such as the switching in a signalling protein, or the chemical reaction catalysed by an enzyme. Both, the intrinsic probability to populate different states as well as the probabilities for transitions between them are influenced by the physical conditions and the molecules' interactions with their environment.

In this contribution, we present examples of how molecular simulations reveal the interplay of dynamics, interaction, and reactivity in biological molecules and their complexes. The first two examples deal with DNA-processing proteins and the role conformational dynamics play in recognition and specificity. In the first example, the intrinsic propensity of a certain DNA-sequence to bend is exploited by a restriction enzyme, EcoRV, specifically cleaving that particular sequence [1,2]. In the second example, a mismatch in the DNA leads to a different conformational behaviour than intact DNA, giving rise to an additional, slightly deformed, conformational state [3]. The repair protein Thymine DNA Glycosylase, further stabilised this distorted state upon binding [4], thereby facilitating the extrusion of the mispaired base out of the DNA helix and into the enzyme’s active site – a necessary pre-requisite for the chemical step of the repair process [5] to take place. Further discrimination is achieved by the substrate base being better accommodated in the active site than non-cognate bases [4,5].

In the membrane protein Cytochrome c Oxidase (CcO) proton transport, hydration and conformational dynamics are closely linked. Our analyses of molecular dynamics simulations of CcO show an auto-regulation of proton transport through one of the protein’s proton-conducting channels which is furthermore controlled by the protonation state of the second channel [6,7].

This work was supported by the German Research Foundation (grant № IM141/1 and project C5 in the CRC1078 “Protonation dynamics in protein function”).

References
How conformational dynamics descriptors may help in remodelling of allosteric regulation in proteins

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Allostery controls nearly all biological processes, and it has been declared by Jacques Monod to be “the second secrete of life” after the genome. This universal phenomenon in nature represents a protein perturbation induced by an effector (non-covalent binding of molecule, environmental change or point mutation) leading to a functional change at the protein’s binding site(s) through alteration of the structure and/or dynamics. Such an event can be described in terms of a large-scale transmission of information (communication), which takes place through a dynamic coupling between residues. This concept is the cornerstone of the MOdular NETwork Analysis (MONETA), which allows localizing and ‘visualizing’ the communication through the network of residues of a protein, built from the molecular dynamics (MD) simulation [1-2]. Using inter-residue cross-correlations computed from conformational dynamics and topological description of a protein, MONETA builds a modular network representation composed of clusters of residues (dynamic segments) that are linked by chains of residues (communication pathways, CP).

With MONETA, we described the CPs in different proteins [1-10], delivering a key information in identification of residues controlling protein activation. The rigorous analysis of molecular dynamics of the native and mutated (missense mutations) receptor tyrosine kinases (RTKs), controlling cell signaling, yielded the mechanisms of their activation and delivered the novel targets for in silico drug design [1-7]. The intramolecular CPs at proximity of surface pockets were identified in the cell signaling proteins STAT5 by using dynamical components and their interdependence built with the Principal Features Decomposition (PFD) [8]. Focusing on the understanding of the allosteric mechanisms of receptors regulation, we investigated the human NMDA-type glutamate receptor (hNMDAR), the voltage-dependent and ligand-gated ion channels that contribute to excitatory neurotransmission in the central nervous system and very important for controlling synaptic plasticity and memory. The MD simulations of 3D models of hNMDAR in two states, unbound and bound with the functional agonist ligands. The careful statistical analysis of DM data evidenced the ligand-induced global reduction of molecular flexibility and a higher cooperative regularity of moving. We evidenced that the ligand-induced synchronization of motion, identified on all structural levels of the modular hNMDAR, is a fundamental factor in channel gating [9].

The most probable intermediate states of an allosterically regulated protein may be predicted with Configurational Scanning (ConfigScan), a new method that allows estimation of the population (density) of conformations in the reduced space [10]. From MD simulations, we represented the low-dimensional data while keeping a maximum of information, and then we detected the transient and stable portions of path using different physical quantities (e.g., energy) characterizing the stability of a state through the underlying stochastic dynamics.

Our methodological development is intimately coupled to a study of the concrete
clinically relevant proteins for elucidation of their function- or dysfunction-related features. The yielded characteristics – the allosteric binding sites of the intermediate conformations – may constitute valid targets for the development of modulators, able to regulate the function-related communication properties of a protein. This communication-inspired and communication-targeted modulation may selectively block several activation or post-transduction processes in the cells.

**References**


Incredible diversity of structural chemistry of cyanoximes and their metal complexes

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During the last two decades my research interests were dedicated to the new class of weak organic acids – cyanoximes – that have general formula:

\[
\begin{align*}
R = & \text{CN, C(O)NX}_2, \text{C(S)NX}_2 [X=H, \text{CH}_3], \text{C(O)NHNH}_2, \\
& \text{C(O)OY} [X=\text{CH}_3, \text{C}_2\text{H}_5], \text{C(O)C}_6\text{H}_5, \text{C(O)C(CH}_3)_3, \\
& \text{2-heteroary1 (pyridyl, quinolyl, benziazolyl, thiazolyl, benzimidazolyl, benzoaxazolyl), substituted aryl groups}
\end{align*}
\]

where R is an electron-withdrawing group specified above. These low molecular weight organic molecules represent series of new amplydentate ligands for coordination, organometallic and bioinorganic chemistry as explained in Figure 1 below [1]. Both unbound to metal free ligands, their Na\(^+\) and K\(^+\) salts and other metal complexes show a large spectrum of biological activity from growth regulation in plants to in vitro and in vivo cytotoxicity. Currently 42 cyanoximes are known and more than two hundreds cyanoxime complexes synthesized and studied using a variety of different spectroscopic methods and the X-ray analysis. Stereochemistry of cyanoxime ligands [2], structures and properties of the most interesting coordinations compounds are reviewed in this presentation [3,4]. A broad spectrum of applications of both cyanoximes and their metal complexes is outlined in this lecture as well [5-23].

Figure 1. Possible binding modes for one of the simplest cyanoxime – 2-oximino-2-cyanoacetamide anion (commonly known as ACO- ligand) with those confirmed by the X-ray analysis indicated with red stars.
Work on this large project throughout the years received multiple funding from local sources as well as the ACS PRF, the Research Corporation, the NSF and NIH, and was reflected in 105 papers and 8 patents.

References

Insider tips for successful submissions: editorial advice for authors

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This lecture provides an overview on the editor's daily responsibilities, as well as the peer-review and publishing process, to the scientific community. In particular, the presentation is interesting for young scientists, because of the numerous tips and tricks, which are given in order to avoid problems when submitting a paper. The importance of a clear structure of a paper and relevant research content is emphasized, as well as benefits of a good cover letter to explain to the editor what makes the article worth being published in the journal are elucidated. Another part of the talk includes an overview on scientific misconduct, what to avoid and why, wrapping up with tips on how to improve the readability and presentation of an article.

Moreover, the role of ChemPubSoc Europe, the family of journals of the Wiley-VCH in-house editorial offices, is explained. Additionally, the advantages of the cascade system for transferring manuscripts between journals, such as saving time in submitting from scratch to another journal, are explained.
Plenary Speakers

Model study of the structure of supramolecular complexes of glycyrrhizic acid and its monoammonium salt (glycyram)

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The huge interest to supramolecular systems is caused by the fact that they have a new, unique properties different from the original components. The formation of supramolecular complexes of active pharmaceutical ingredients is one of the most well-known methods to improve drug resistance, bioavailability and reduce toxicity. From this point of view, a glycoside of different types of licorice \textit{Glycyrrhiza} – L-18ß-glycyrrhizic acid (GA) and its monoammonium salt glycyram (GC) \cite{1} are considered as promising complexing compounds for use in the pharmaceutical industry. Recently a great attention is paid to complexes on the basis of glycyram and \(\alpha\)-hederine with amino acids \cite{2}, in which the formation of the complexes increases the useful properties of both components.

We investigated the spatial structure of such complexes using quantum chemical methods of calculation on the basis of considerations of donor-acceptor nature of the interaction between components of complexes. For the description of intermolecular interactions there were estimated molecular electrostatic potential (MESP), affinity of aminoacids, and the energies of boundary orbitals, which have not described the complex as a whole, but its individual components. To describe the structure of the complex of glycyram and amino acids using the method of PM3 method from the program complex GW03 \cite{3}, we used a super-molecule method \cite{4}.

We have selected for calculations such a representatives of amino acids in the complexes as glycine (neutral), lysine (basic), and glutamic acid (acidic) amino acids. There are considered complexes, which are the new drugs designed by clathrating the farmakons by natural glycosides on the principle of "host-guest" proposed by Russian scientists \cite{1}. The nature of the amino acids plays a significant role in the formation of supramolecular systems with glycyram, and it affects the strength of formed complexes. Molecule of glycyram has been designed with a positive charge on the ammonium nitrogen atom and negative charge on the oxygen atoms of the carbonyl group of glycyram. The mutual arrangement of the components of the complexes in their most energetically favorable form for the different amino acids are shown in the figures below. The most strong complex of all the amino acids is formed by the lysine, because of its basic nature and forming the largest number of hydrogen bonds with a molecule of glycyram.

Molecules of monoammonium salt of glycyrrhizic acid (glycyram) (a), glycine (b), lysine (c), and glutamic acid (d) are taken as a model. The choice of these amino acids is due to the fact that glycine is a neutral amino acid, arginine is the main amino acid and glutamic acid exhibits acidic properties, which plays an important role in the formation of a supramolecular system with glyceram, and that affects the strength of the formation of the complex.
The predominance interactions depends on the nature of the components involved in the formation of the supramolecular system, and to evaluate separately the role of each of these components of the interaction is a difficult task. Construction of the surface of the potential energy of SMS is a complex computational task, and for polyatomic molecules, even in a rough approximation is used very rarely. We used an approach that allows to estimate in one parameter four values (electrostatic interactions, van der Waals forces, donor-acceptor interactions, the formation of hydrogen bonds) for molecules – an approach called the molecular electrostatic potential (MESP) method [5].

The coordinates of the minimum MESP values on the contour maps correspond to stable or quasi-stable equilibrium points of two parts of the system: the studied molecule and the "test" charge. The physical analogue of such a "test" charge is a proton, i.e. the nucleus of a hydrogen atom. Therefore, the MESP method is particularly effective in the analysis of protonation reaction, hydrogen bond formation, polar interactions.

To determine the likely locations of amino acids relative to glycyram, we estimated the MESP of glycyram, glycine, lysine, glutamic acid and compared it with their zwitter ions. All probable locations of amino acids relative to glycyram, where hydrogen bonds can occur, are presented in [6]. To calculate supermolecules of glycyram and amino acid molecules, we used the non-empirical quantum chemical method MP2/6-311++G (d,p), which allowed us to calculate the dispersion interactions between molecules and provides attraction between molecules. The basic set of atomic orbitals used in the calculations includes diffusion functions on all atoms, which makes it possible to more fully take into account the dispersion interactions of molecules at large distances. Before calculating the interaction energy of glycyram molecules and amino acids, the energy of individual molecules was previously minimized using the semi-empirical PM6 method, then the energy of the complex was minimized.

Based on the calculations, it can be concluded that steric difficulties play more significant role in the formation of complexes than electrostatic characteristics. It can also be concluded that there is formation of only one complex of glycyram molecules with amino acid molecules; judging by the values of the formation energies of the studied models of complexes, there is a distribution of complexes by the formation energies.

References

Crystal structure of some iron(II,III) sulfate solid solutions and forbidden by symmetry X-ray reflections

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This work discusses the results of the single crystal XRD analysis of sulfate solid solution crystals of compositions \((\text{Fe}_{x}\text{Mg}_{1-x})\text{SO}_4\cdot7\text{H}_2\text{O}\) \((x=0.93, \text{I})\), \((x=0.87, \text{II})\), \(\text{NH}_4\text{Al}_{0.43}\text{Fe}_{0.57}(\text{SO}_4)_2\cdot2\text{H}_2\text{O}\) (III), \(\text{NH}_4\text{Al}_{1.4}\text{Cr}_{1.4}(\text{SO}_4)_2\cdot12\text{H}_2\text{O}\) (IV) [1] and two voltaite crystals containing \(\text{Fe}^{2+}\), \(\text{Fe}^{3+}\) and \(\text{Mg}\) atoms [2]. These substances have been used for different practical applications. In particular, crystals I and II are a paramagnetic materials and used as magnetic materials for adiabatic demagnetization in ultra-low temperature physics. They show also the nonlinear optical properties: abnormal double refraction and the optical second harmonic generation.

The X-ray experimental reflection data for these solid solution crystals contain a few forbidden reflections in the space groups of the homogeneous crystals. The appearance of these reflections may be related to the generation the superstructure by replacing one type atom by other.

Crystal structures of I and II are isomorphic to melanterite and consist of \([\text{M}(\text{H}_2\text{O})_6]^{2+}\) octahedra \([\text{M}=\text{xFe}^3+(1-x)\text{Mg}]\), distributed on two crystallographically distinct sites \(\text{M}(1)\) and \(\text{M}(2)\) (Wyckoff positions \(2a\) and \(2d\) with symmetry \(\overline{1}\)), the \(\text{SO}_4^{2+}\) tetrahedron and one crystallization water in common positions. The number of forbidden reflection for these crystals is directly proportional to the content of purity atoms of \(\text{Mg}\) in crystals. The site population of the atom \(\text{Mg}\) in the position \(\text{M}(2)\) is more than in the position \(\text{M}(2)\).

Symmetry-forbidden reflections that were present in the X-ray diffraction dates for crystals of III and IV suggest the crystal lattice symmetry to be lowered from space group \(\text{Pa}\overline{3}\) to space group \(\text{P}1\) in the series of maximal subgroups \(\text{Pa}\overline{3} > \text{R}3\overline{1} > \text{P}1\overline{1} > \text{P}1\). In the centrosymmetric models under consideration, all sulfate groups are oppositely oriented with respect to each other. In non-centrosymmetric space group \(\text{P}1\), four of the eight sulfate groups have the same orientation, whereas the other four groups are oriented in an opposite direction. The second harmonic generation is observed when a train of chirped optical pulses of ytterbium diode pumped solid state laser passes through the crystal of III.

The voltaite crystals of the compositions \([\text{K}_{0.88}(\text{NH}_4)_{0.12}]\text{Fe}_{6.20}\text{Mg}_{1.82}\text{Al}_{0.98}(\text{SO}_4)_{12}\cdot18.9\text{H}_2\text{O}\) (V) and \([\text{K}_{0.15}(\text{NH}_4)_{0.85}]\text{Fe}_{6.74}\text{Mg}_{1.26}\text{Al}(\text{SO}_4)_{12}\cdot18.3\text{H}_2\text{O}\) (VI) are formed of joined \(\text{M}(1)\text{O}_6\) \([\text{M}(1)=(\text{Fe}^{3+},\text{Mg})], \text{M}(2)\text{O}_4(\text{H}_2\text{O})_2\) \([\text{M}(2)=(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})]\) octahedra and \((\text{K}^+,\text{NH}_4^+)\text{O}_{12}\) 12-vertex polyhedra arranged in a three-dimensional framework due to the bridging function of the tetrahedral \(\text{SO}_4^{2-}\) ion. In the voids of the framework, \([\text{Fe},\text{Al})(\text{H}_2\text{O})_6]^{3+}\) cations with strongly disordered aqua ligands are located. These crystals contain two different valence iron cations and other one and two valence cations. Owing to this possibility voltaite crystals are potential a new type magnetic materials and can be used in processing of the new magnetic materials.

References
X-ray Crystallography: azaborines; from a molecule to a device; on the way from benzene to carbon nanotubes

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**Azaborines.** After decades 1,2-dihydro-1,2-azaborine and many other compounds with N,B-hetero-cycle were synthesized in the Prof. Shih-Yuan Liu group (University of Oregon, Eugene OR, USA). Single crystal X-ray diffraction methods were deeply involved in this work and provided crystal clear evidence for electron delocalization in 1,2-dihydro-1,2-azaborines. For the first time the structures of a complex of 1,2-dihydro-1,2-azaborines with transition metal, 1,3-Dihydro-1,3-azaborine products, 1,2-BN Cyclohexane, the parent “fused” BN indole and other compounds with B,N-cycle have been determined. X-ray crystallography was used to confirm structures of different intermediate compounds in creating stable liquid hydrogen storage materials based on azaborines.

![X-ray Crystallography: azaborines; from a molecule to a device; on the way from benzene to carbon nanotubes](image)

**From a molecule to a device.** As a part of systematic work (together with the Prof. D. Johnson, Prof. M. Haley and Prof. M. Pluth groups, University of Oregon, Eugene OR, USA) on design and synthesis organic receptors that selectively bind and sense anions (Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), H\(_2\)PO\(_4\)\(^{-}\), HSO\(_4\)\(^{-}\), SH and others) crystal structures of different types of receptors have been determined. It will be shown that the found crystal structures provided a lot of useful information about electrostatic attractions, hydrogen bond interactions and attractions with electron-deficient arenes (anion-\(\pi\), CH•••X\(^{-}\) hydrogen bonds).

![From a molecule to a device](image)

Work on such receptors has led to a successful start-up company, SupraSensor Technologies (http://www.nsf.gov/news/special_reports/science_nation/suprasensor.jsp).

A new heterometallic gallium–indium cluster, \([\text{Ga}_7\text{In}_6(\mu_3-\text{OH})_{6}(\mu-\text{OH})_{18}(\text{H}_2\text{O})_{27}(\text{NO}_3)_{15}]\) (“flat” \(\text{Ga}_7\text{In}_6\)), was synthesized and its crystal structure was determined. Due to the large indium fraction in this cluster and the excellent performance of \(\text{In}_2\text{O}_3\)-based semiconductors this cluster was recognized as potential oxide precursor in printed microelectronics. It was shown this cluster can be used as a precursor for getting thin-film transistors (TFTs) from a spin-coated aqueous solution. A device with a TFT with an amorphous \(\text{In}_{0.92}\text{Ga}_{1.08}\text{O}_3\) (IGO) semiconductor
derived obtained in this way has nice characteristics for materials obtained by the direct deposition. This work was carried out together with the groups of Prof. D. Keszler (Oregon State University, Corvallis OR, USA) and Prof. D. Johnson (University of Oregon, Eugene OR, USA).

On the way from benzene to carbon nanotubes. Such carbon materials as C\textsubscript{60}, carbon nanotubes and graphene are well known. Chemists try to find a way how to get carbon nanotubes via traditional chemical synthesis. Results of using X-ray crystallography in such work done together with the Prof. Ramesh Jasti group (University of Oregon, Eugene OR, USA) will be presented.
Observing mechanisms of nano chemistry through a keyhole of molecular models

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Nanoparticles and nanostructures of metal oxides and silica have been during the last decades attracting tremendous attention due to extremely broad application spectrum for these materials. They are employed as chemical and photo catalysts, protective and functional coatings, electrodes in alkali metal ion batteries and solar cells, adsorbents for advanced water purification and hydrometallurgy and as materials for diverse applications in agriculture and biomedicine. Gaining insights into the molecular structure and reactivity of the oxide surfaces is a tremendously exciting challenge, capable to provide keys to rational design of future nanomaterials.

Oligonuclear metal complexes bearing O-donor ligands, forming in non-aqueous media, are, along with oxo-metallates obtained from aqueous solutions, providing attractive models for understanding of how oxide nanoparticles are formed in solutions and reacting with molecules on their surface. An important common feature of these complexes is that their structures follow general principles for inorganic salts, featuring dense packing of cations and anions that can be rationalized in the terms of Goldschmidt-Pauling rules in theory of inorganic solids [1]. Using these rules it is possible to design structures of complexes possessing potentially enhanced thermal and chemical stability, attractive for applications in Metal-Organic Chemical Vapor Deposition.

The structures of complexes with O-donor ligands with increased size are reminding closely those of the related oxides which permits to conclude that nucleation of solid oxides in hydrolytic and thermolytic processes, where these complexes are emerging as intermediates, proceeds also through species possessing oxo-metallate types of structures. These species are in their own products of coordination equilibria [2]. Understanding of this principle permits to predict and design optimized condition for production of stable nanoparticle dispersions or, alternatively, of porous nanostructures with controlled morphology and topology.

It is important also to keep in mind that changing the conditions in the medium where the oligonuclear complexes are formed results in their restructuring into new complexes and, ultimately, into nanoparticles and nanostructures. In the absence of metal-metal bonding the oligonuclear O-donor ligand complexes are not clusters and do not feature cluster behavior [3].

This work was supported by the Swedish Research Council (grants № 2001-3352, 2005-3435, 2008-3857, 2011-3718, 2012-6205, 2014-3938).

References

Effect of wax crystallinity on oil production

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Ability of a substance to form crystals is a highly desirable feature for a crystallographer, allowing to investigate its exact molecule structure and supramolecular organization. However, for practical purposes, the tendency to crystalize can cause severe complications in many industrial processes, particularly – in oil production. Hydrocarbons of a various alkane composition represent a major part of any oil or crude condensate. Usually they exist in a form of a relatively stable solution or a colloid within other oil components. However, during commercial oil production, some sudden temperature and pressure changes are a common occurrence. The resulting thermodynamical instability may cause crystallization of normal alkenes and growth of wax deposits. Essentially paraffin crystallization event carries a serious risk of blocking the transport lines and stopping the oil production.

Crystallization of normal paraffins is an important technical parameter of oils controlled by several methods. The beginning of wax crystallization is attributed to the highest temperature of the crystal formation, which is called WAT (Wax Appearance Temperature) or cloud point. The most reliable techniques of determination of WAT are measuring of crystallization flux by DSC (Differential Scanning Calorimetry) as well as optical detection of wax crystals in polarized light – CPM (Cross Polarized Microscopy). Here are the typical images of the measurements:

We attempted to monitor the process of wax crystal formation by an X-ray powder diffraction technique. The experiments were done in thin-walled glass capillaries by slow cooling the samples from room temperature to 200K. However, much clearer results were obtained using a MiTeGen micromesh sample holder. The appearance and growth of wax diffraction peaks gave an indication of the crystallization process. The experiment also suggested an identical composition of crystalline wax residue for two different samples of oil:
Proactively control wax formation and precipitation is an important engineering task in the oil industry. Usually, some polymer compounds – paraffin inhibitors – are applied to change the crystallization pattern of the wax formation and assure an uninterrupted oil flow:

Developing of the paraffin inhibitors is based on a concept of combination of long-chain alkyls with polar or sterically bulky fragments in a polymer molecule to increase steric hindrances for wax agglomerations. Several approaches to such polymers’ design will be presented. Crystallinity of different inhibitors was evaluated by X-ray diffraction for effectiveness prediction and ranking purpose.

Successful oil production is strongly dependent on expertise with fundamental phenomena of crystal organization and prevention of crystal formation. The presentation highlights a few examples of wax crystallization control by specifically designed chemical treatment and implemented various testing techniques.

References
A step to predictive structural biochemistry: QM/MM & QTAIM approach

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This talk presents new applications of advanced molecular modeling approach in structural biology. It includes combined method of quantum mechanics/molecular mechanics (QM/MM), molecular dynamics with classical or QM/MM potentials complemented with quantum theory of atoms in molecules (QTAIM). Experimental methods of structural studies, such as X-ray diffraction or NMR serve with the information of the 3D structures of apo-proteins or stable protein-ligand complexes. However, these methods can be now hardly used for studies of the structures of the transient intermediates of the biochemical processes. In this respect molecular modeling is complementary to the experimental studies and can deepen the knowledge of 3D structures. In particular, QM/MM method does successfully trap the reaction intermediates in enzymatic reactions and light-induced biological processes. In this report we present the next step in development of the precise analysis of the 3D structures and in prediction of new compounds or proteins with the desired properties.

Our idea assumes detailed study of electron density in the active sites of proteins and relevant conclusions on the particular system based on its analysis. First, we consider metallo-β-lactamases, the proteins responsible for the bacterial drug resistance due to the hydrolysis of the β-lactam moiety of many antibiotics. We demonstrate that analysis of the electron-density features of the transition state protein-antibiotic complex, corresponding to the limiting stage of the hydrolysis reaction allows to predict the reaction rate constant of the particular antibiotic. Then we apply QTAIM to find the bond critical points (BCP) in the active sites and to calculate their properties. We demonstrate that properties of particular BCPs are correlated with the macroscopic parameter of the system, i.e. catalytic rate constant k_{cat}, and can be further applied to predict this value for the novel compounds. Another example covers the red fluorescent proteins. Using the same computational scheme, we found parameters of the electron density of the chromophore-binding pocket that can be correlated with the absorption and fluorescent band maxima that allow suggesting new variants of fluorescence proteins and test them in silico.

To sum up, we make a next step to predictive structural biochemistry: propose new protocol of prediction of properties of biological systems on the basis of analysis of the electron density in the reactive part of the system using a combination of QM/MM and QTAIM approaches and demonstrate its power.

This work is supported by the Russian Science Foundation (project # 18-74-10056).
Click reactions + ultrasound = a new aurora of chitosan chemistry

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Involvement of ultrasonic methods in chitosan chemistry in the past few years resulted in enhancement of scope of polymeric systems with attractive physico-chemical and biological properties (chiral biocompatible hydrogels, drug and gene delivery systems, stimuli responsive polymers etc.) [1]. Moreover, ultrasonic approach often leads to high selective chemical modification of chitosan, including fragmentation of the polymer and its derivatives[2]. On the one hand, ultrasound dramatically affects reactivity of chitosan via modification of its supramolecular structure [3]. On the other hand, ultrasonic irradiation can affect also reactants and solvents due to different mechanisms including free radical formation. This, in turn, results in various organic transformations of chitosan, which are not feasible under ultrasound-free conditions [4].

Other outstanding and powerful tool for chitosan modification is click chemistry. Application of the modern click chemistry methods for chitosan derivatization opened up simple ways for controlled, selective, and technically convenient synthesis of biocompatible and biodegradable polymers with specified structures and properties [5]. Click reactions using chitosan that are presented in the literature focus on (i) copper-catalyzed azide-alkyne dipolar cycloadditions, (ii) metal-free cycloadditions of azides to highly dipolarophilic systems, and (iii) metal-free thiol-ene additions.

In some instances, click-reactions can be efficiently mediated by ultrasonic irradiation. This report is an attempt of critical review in the field of ultrasonic assisted click reaction in chitosan and other polysaccharide chemistry, and the results of our group and colleagues will be presented herein.

References
Compounds containing N-nitrosohydroxylamine fragments are nowadays of a wide interest. They occur in natural antibiotics, such as alanosine and dopastin, and also were recently discovered in certain microorganisms and mushrooms. A variety of synthetic analogues containing nitrosohydroxylamine groups were isolated and their biological activities such as vasodilating, sedative, analgetic antineoplastic, antiviral and other were reported.

It was recently shown that the biological activity of the above substances correlates with their ability to release nitrogen monoxide both \textit{in vitro} and \textit{in vivo} (Fig. 1) as well as with complex formation with the metal cations.

![Figure 1](image1.png)

**Figure 1.** NO release in one electron oxidation of para-substituted nitrosohydroxylamines.

N-Nitrosohydroxylamine containing compounds also find their application as analytical reagents, for metal extraction, precipitation and separation. Recently they were proposed as effective precursors for the synthesis of inorganic nano-dimensional materials.

The tautomerism of N-notrosohydroxylamino-group is related to the position of a proton (Fig. 2).

![Figure 2](image2.png)

**Figure 2.** Tautomeric and anionic forms of the N-nitrosohydroxylamine functional group (syn-\textit{anti} isomerism is avoided).

At ionization or at complex formation, anionic forms of N-notrosohydroxylamines are formed which are characterized by the almost full equalizing of NO bonds so the functional group becomes better of the diazenium diolate character.

The presented review of diazenium diolate fragments containing compounds is focused on the features of their molecular, crystal, and electronic structures, as well as spectral criteria of coordination and ionization.

The multiple crystallographic data indicates three possible coordination modes of diazenium diolate containing compounds. They include bidentate chelating (monometallic biconnective, O$^1$O$^2$-\(\eta^2\)) coordination (Fig. 3a), bidentate bridging (\(\mu\)-O$^1$O$^2$) coordination (Fig. 3b), and bimetallic triconnective (O$^1$O$^2$-\(\eta^2\), O$^2$-\(\eta^1\)) bridging (Fig. 3c).
The overview of a plenty of available information indicated that the structural characteristics of the chelating center do not significantly depend either on the substituent at the diazenium diolate fragment or on the origin of the metal cation. The conjugation of the functional group with an aromatic substituent does not affect the structure of the chelate ring.

Although majority of the reviewed diazenium diolate metal complexes are crystallized in the monoclinic space group, they cannot be considered as isostructural. The major role in the shape of the lattice is played by steric factors due to the nature of the substituent at the diazenium diolate fragment.

Despite the structural characteristics of diazenium diolate metal complexes seem to be rather close, the shifts in the absorption bands in IR and UV-VIS spectra of the organic molecules at complexation differ significantly depending on the nature of the metallic cation. The theoretical DFT modeling of non-coordinated organic molecules and their metal complexes indicated that the shift of the absorption bands at complexation correlates with the calculated effective charges on the metal cations. Thus, the position of the absorption bands in the IR and UV-VIS regions depends not on the structural parameters and coordination modes of the complexes but mainly on the degree of covalency of metal-to-ligand chemical bonds which may change in wide ranges.

The publication has been prepared with the support of the «RUDN University Program 5-100». 
Revolution in technology, software development and incredible computing performance resulted in the new generation of the sensitive zero-noise detectors, powerful maintenance-free X-ray sources and software packages, which are able to obtain relevant results without deep understanding of the method. At specialized crystallographic facilities, the majority of everyday crystallographic work may be more likely considered as scientific service. Those tendencies led to major change in the status of the scientist who perform analysis which reflected in a modern title for this position – “Service Crystallographer” (AKA “Director of X-Ray Lab”, “Manager of X-Ray Lab”).

**Data collection.** All special techniques (unstable samples, low temperature, high-pressure experiments etc.) have been established many years ago. You need few minutes to evaluate the quality of your crystal. You do not need even to find out if your crystal may cause you problems, what are the cell parameters and symmetry. Full sphere data collection with desired redundancy, longer exposure and increased crystal-to-detector distance will cover everything. Universal fool-proof strategy “Shoot first. Collect everything. Find out consequences later” will work just fine. Typical experiment will last just few hours.

**Structure Solution/Refinement.** “Black-box” software (like Bruker EXPRESSO) can obtain good results for simple samples automatically. However, now we are able to retrieve a very important information from low quality, poorly diffracted crystals, twins and co-crystal. Even 10 years ago, such samples were definitely of no use. As an example, giant spherical keplerate cluster structures containing \{Mo_{72}V_{30}\} require many restrains to model the disorder during the refinement to hold outer and inner ligands at reasonable positions and with acceptable temperature factors. The expected concomitant difficulties- split positions for metal core, huge voids filled with diffused water solvent, uncertainties in the valence state of metals and occupancy factors/positions of counter-ions. Where is the limit of data “massaging” and “fixing” on the way of supporting our model of choice? Where should we stop?

Majority of customers use X-Ray structure determination for the qualitative and quantitative analysis, which means they are fully satisfied with the connectivity table to assure the synthetic path and the proof of obtaining the target substance. How far should we go with such structures? The refinement for the simple metallo-organic complex can illustrate how stepwise split of disordered benzene solvent position influences the geometrical and thermal parameters of the main cluster.

**Publication.** Can we trust old X-ray structural results even though they can hardly pass the new strict requirements for publication? How many different expert opinions can we have on one simple structure like \[\text{[Cr}_3(\text{C}_3\text{H}_5\text{O}_2)_6\text{O(\text{H}_2\text{O})}_3]\text{NO}_3 \times 0.5 \text{H}_2\text{O}\] and what is wrong with publishing questionable (or even unintentionally wrong) results? Should we still describe the structure in a paper if we must supply CIF with all intensity/refinement data in advance? Why one might still consider service crystallographer as a valuable co-author of publication? Let us try to get a consensus on those and some other actual questions.
“A graveyard of experimental errors”? What is hidden in thermal ellipsoids

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Thermal motion of atoms has a significant detrimental effect on X-ray diffraction. Since the very beginning of X-ray studies, it was recognized as a substantial nuisance, and big efforts have been done to (a) reduce amount of the thermal motion by cooling crystals, and (b) mathematically compensate for its effects by introducing anisotropic model of individual atomic harmonic vibrations.

This brought us to the paradoxical situation when in the modern X-ray structure analysis almost 2/3 of experimentally determined parameters (Uij) are used to describe thermal motion of atoms and only remaining 1/3 (XYZ) contain information about molecular geometry and intermolecular separations. The latter third of the data is of utmost importance, but what use is for the other two thirds?

In the overwhelming majority of X-ray studies, the anisotropic thermal parameters of the atoms (ATPs) are only used as an indicator of experimental errors including unresolved disorder and mistakes in data processing (absorption etc.). And of course, they are a source to produce “professionally looking” ORTEP pictures with thermal ellipsoids.

So, are the ATP values just mere fitting parameters in least-square refinements, introduced with a solo purpose to reduce R-factor or they contain a useful information?

It was recognized very early [1] that ATP values of individual atoms in crystal structures are not independent, especially for rigid moieties in molecular crystals. In many cases, molecules in crystals move as a whole. This motion can be described in terms of three TLS tensors (translation-libration-screw motions) with individual ATPs derived from them. At that time, this was considered beneficial in terms to reduce the number of independent parameters in the structural refinement.

With development of low-temperature techniques in X-ray crystallography, it was found [2] that TLS model does not work well at lower temperatures (~100K and below), and it was proposed that the deviations correspond to some “internal” molecular movements and “anharmonic” vibrations. The authors apparently neglected the knowledge that the “internal” movements also must be temperature-dependent and “anharmonicity” must vanish at the lower temperatures.

Nevertheless, relatively recently, there was an attempt [3] to separate temperature-dependent ATP values from “temperature-independent” values using multi-temperature X-ray diffraction experiments. The difference was attributed to internal vibrational frequencies of the molecules.

We studied a series of rigid donor (octamethylanthracene – OMA, and octamethylbiphenylene – OMB) and acceptor (chloranil – CA, tetracyanoethylene – TCNE, tetracianoquinodimethane – TCNQ) molecules as well as their binary donor-acceptor complexes at various temperatures (100-250K). An advanced procedure was developed within Olex2 software [4] to calculate TLS tensors of the molecules and subtract corresponding “calculated”
ADPs from experimental values. The resulting “difference” ADPs can be graphically visualized.

From analysis of the data, we came to a firm conclusion that the observed at low temperatures deviations of individual ATPs from the values dictated by TLS model occur because of “contamination” of ATPs by deformation electron density – the thermal ellipsoids attempt to compensate for asphericity of chemically bonded atoms. Particularly, they appear to increase along chemical bonds and in the direction of pi-electron clouds. Because of the different symmetry of ATPs and atomic bonding orbitals, the ATPs absorb only a fraction of the deformation density. However, the “difference” ATPs give a very clear overall picture of electron density redistribution within the molecules, for a fraction of computational costs as compared to multipole refinement. Moreover, the difference ATPs gave as an estimate of the inter-molecular electron transfer in the various donor-acceptor complexes. The relative values are in a good agreement with the oxidation potentials and electron affinities of the components.

We conclude that the “difference” ATPs are a cheap and efficient alternative to more sophisticated methods of calculating deformation electron density when it comes to intra-molecular charge polarization, and they have an advantage when it comes to inter-molecular charge re-distribution.

References
Crystal chemistry of functionally substituted cyclic phosphines

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Work on the molecular and crystalline structure of cyclic functionally substituted phosphines was initiated at the Laboratory of the X-Ray of the INEOS RAS under the leadership of Yury Timofeevich Struchkov.

In the 1980s, crystals of 1,3,5-dioxaphosphorinanes, which are still the only structures with heterocycles of this type, were investigated. At present, 1,3,5-dioxaphosphorinanes have not been studied further. The structures of 33 substituted 2-boro-1,3,5-dioxaphosphorinanes were investigated by us, the first of which was taken in the laboratory of Yu.T. Struchkov and published in 1981. Structures with three- and four-coordinated atoms of phosphorus and boron were established, and one structure of the complex with dichloroplatinum was established. It is shown that the metal atom is coordinated only by the phosphorus atoms of these heterocycles, neither oxygen atoms nor boron atoms in coordination with the metal participate.

The next large group of compounds studied are cyclic aminomethylphosphine ligands. Of the 6-membered heterocycles, the structure of 1,3,5-diazaphosphorinanes has been studied. The results of the study of the first structure were published by us in 1981, and the structure of the platinum complexes with these ligands was published by us in 1993. Later, we (1993 - 1996) and foreign researchers (2009-2012) published several structures with diazaphosphorinanes ligands. In all structures, these ligands coordinate the atoms of the metal only by phosphorus atoms.

A new type of phosphorus-containing heterocycles - 1,5-diaza-3,7-diphosphacyclooctane, was established by us in 1980. In subsequent years, compounds of this class with various substituents at phosphorus and nitrogen atoms were investigated, in 1994 the study of the first complex of copper(I) with these heterocycles was published, and in 1995 - complexes with platinum. In these complexes, the 8-membered heterocycle is a chelate ligand, coordinating the metal atoms only by the phosphorus atoms.

In the 1990s and in the "zero" years of the 21st century, this topic was developed mainly by the synthetics of our institute. During these years, 8-membered heterocycles with various substituents at phosphorus and nitrogen atoms were synthesized and investigated, including chiral substituents, heterocyclic systems, ferrocene substituents, and functionally substituted aromatic systems. Metallocomplexes with these ligands were also obtained. In the same years, macrocycles were synthesized and studied, including 8-membered heterocycles, and their complexes with monovalent copper.

The revival of interest in 1,5-diaza-3,7-diphosphacyclooctanes and their metal complexes occurred in the first years of the 21st century, and after the publication of M.R. DuBois, D.L. DuBois, JACS. 128 (2006) 358, the catalytic properties of the nickel complex with 1,5-diaza-3,7-diphosphacyclooctane ligands show increase in the number of studies on the synthesis and study of the structure of such systems. Complexes of various metals with one and two 1,5-diaza-3,7-diphosphacyclooctane ligands were synthesized, among which promising complexes of
nickel with good catalytic properties were found. In recent years, 8-membered heterocycles with ethylpyridine substituents at phosphorus atoms have been synthesized and studied. It is shown that, due to a longer and more flexible chain, pyridine rings can act as additional coordinating centers. As a result, the ligand can act as a tetradeutate chelate, coordinating the metal atom with phosphorus atoms of a heterocycle and nitrogen atoms of pyridine-containing substituents, and bridging, coordinating various metal atoms. Among the complexes of univalent copper with such ligands, binuclear complexes with luminescent properties,

![Fig.1. Scheme of synthesis of the binuclear complex.](image1)

and the hexanuclear complex, which in the crystalline phase exhibits white luminescence.

![Fig.2. Scheme for the synthesis of a hexanuclear complex that exhibits white light luminescence.](image2)

7-Membered heterocycles - 1-aza-3,6-diphosphacycloheptanes, as well as their metal complexes - were synthesized and studied at our institute for the first time. In them, the lability of the P-C bonds, which leads to equilibrium of the isomers of these compounds, is discovered and isomerization during crystallization. They also demonstrated the possibility of formation of 14-membered "dimeric" macrocycles and their reverse transition to 7-membered heterocycles.

In the synthesis of 18-membered macrocycles, 5-membered phospholanes with pyridine substituents at the phosphorus atom were obtained. It turned out that they are able to act as monodentate ligands that coordinate the metal atoms only by phosphorus atoms and bridged bidentate ligands that coordinate the atoms of the metal and the phosphorus atom and the nitrogen atom of the pyridine substituent. In this case, binuclear complexes and coordination polymers can be obtained.
Substituents effect on structure and properties of pincer-ligated (PXCXP)IrH(Cl) complexes

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Complexes of transition metals supported by benzene-based pincer ligands are known to be effective catalysts for various processes. Among them, iridium systems are preferred for transfer dehydrogenation and acceptorless dehydrogenation catalysis [1]. In this lecture we will discuss the results of our recent experimental and computational studies on a series of pincer ligated Ir(tBuPXCXP) complexes 1-3, where C is a 2,6-disubstituted phenyl ring with X = O or CH₂ (Scheme). The combined variable temperature spectroscopic (NMR, IR- and UV-vis) measurements of the interaction of 1-3 with bases (pyridines, nitriles, isonitrile) revealed the formation of two types of hexacoordinated complexes [2-3] and allowed to experimentally access their thermodynamic parameters. The single crystal X-ray data together with comprehensive DFT study gave an insight into the electronic and structural peculiarities of the complexes 1-3 and to structural changes induced by the sixth ligand coordination. These data allow deducing some trends and explaining the reactivity observed in dependence on the (PXCXP) ligand. Combined with the experimental data on the amine-boranes dehydrogenation catalyzed by [Ir(tBuPXCXP)] this investigation resulted in the detailed mechanistic proposals on both the pre-catalyst activation and the catalytic cycle itself [4].

Some parts of this work were supported by the Russian Science Foundation (grant № 14-13-00801).

References
Structural chemistry of organometallosiloxanes at INEOS RAS.
History and prospects

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Metallosiloxanes are compounds containing alkali and/or transition metals in conjunction with organosilicon macrocyclic ligands. Initially, the research of their crystal and molecular structures was started by Yu.T. Struchkov’s laboratory of X-ray studies using single crystal samples obtained in laboratory of organosilicon compounds headed by A.A. Zhdanov at Nesmeyanov Institute of Organoelement compounds Russian Academy of Sciences (INEOS RAS). The proposed report is dedicated to the short overview of progress in the structural chemistry of metallosiloxanes during past decades and analysis of their structural peculiarities to establish the path to variety of potential application of these compounds.

The extensive structural studies of metallosiloxanes in INEOS RAS began in the middle of 1980s starting from cluster cobaltphenylsiloxane. In 1990s the most successful studies were related to metallosiloxanes of sandwich and globular types with a wide range of transition or rare earth metals (oxidation states (II) and (III)), respectively) in their cluster frameworks. In this period pioneering studies of their magnetic and catalytic properties first began. Later, in 2000s first representatives of metallosiloxanes containing Fe(III) ion were synthesized. At the same time, continuous efforts to construct hybrid system containing both organic and organometallic ligands bounded with transition metals were undertaken. As consequence, the analysis of geometry of metallosiloxane frameworks allowed one to solve several tasks:

1. Reveal the factors governs the shape of metallosiloxane units and the number of transition metals.
2. Discovering the factors favorable for the construction of coordination polymers from metallosiloxane units.

It was demonstrated that shape of globular coppersiloxanes can be controlled by variation of the ionic radii of alkali metal bounded to metallosiloxane framework. Analogously, the shape of sandwich metallosiloxanes can be distorted by the induction of chelate ligand, thus giving the structures of skewed sandwich. The exchange of sodium atoms to rubidium and cesium one led to formation of coordination polymers.

The main prospects of structural chemistry are related to the establishing of correlation between the structure and the type of metallosiloxane units to their magnetic and catalytic properties. Especial attention is payed to the investigation of porosity of metallosiloxanes and nanocomposites obtained by their thermal decomposition.

The work was supported by the Russian Foundation for Basic Research (projects 16-29-05180 and 16-03-00206). Author is grateful to Dr. Y. V. Zubavichus (Kurchatov Centre for synchrotron radiation and nanotechnology) for help in single-crystal synchrotron X-ray studies.
3,7-diazabicyclo[3.3.1]nonanes as unique platform for studying the supramolecular interarctions and as a building block for organic synthesis

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Recently, we have introduced a concept of “stereochemical chameleon”, i.e., a functional group, which could exhibit ether donor or acceptor behavior depending on its surrounding and conformation\(^1,2\). One of the most exciting examples of such groups is the amide group widespread in nature and extremely important synthetically. The typical and acknowledged property of amide moiety is its planarity, which is a result of N-CO conjugation; in some cases, this planarity causes the existence of stereoisomeric \(E\)- and \(Z\)-forms. Under some conditions, the amide group could undergo inversion of its configuration, which could be stable under other conditions. When we have two amide functionalities in one molecule, they could influence each other, provided they are spatially aligned in a close proximity. Bispidine scaffold seems to be highly useful platform in this respect since \(N,N'\)-bis-amides could exist in either \textit{anti}- or \textit{syn}-isomers.

In the frames of our studies on bispidine-type ligands for \(^{64}\text{Cu}\)-based PET applications\(^3\), we focus our effort on two groups of bispidine bis-amides, namely, derivatives of ferrocene, which is interesting for producing electro- and photochemical sensor molecules, and pyrazoles, which are promising in designing novel multidentate ligands.

This work was supported by RSF (grant 16-13-00114).

References

Current, there is a consistent transition of the search for medicinal substances (MS) from the empirical to the target. Changing the chemical structure of the prototype molecule (the structure-leader), which is the basis of the search, is one of the key options for the rational creation of MSs, including semi-synthetic analogues of antibiotics, hormones, antitumor drugs, cardiovascular and other agents. The principle of modification of the prototype is the basis for the described studies, in which the molecule of diphenylmethylpiperazine, which is part of the widely used and widely used in medical practice, drugs cinnarizine (stugeron) and flunarizine (sibelium) is selected as the base synthon [1]. They serve as blockers of slow calcium channels (antagonists of calcium ions) in the treatment of cerebral vascular pathologies, have antihistaminic, antiarrhythmic, anticonvulsant activity, anti-vasoconstrictive and anti-ischemic action, reduce the excitability of the vestibular apparatus. In addition, the diphenylmethylpiperazine molecule serves as a common structural fragment and for the drug cetirizine (trade names: Zirtek, Zodak, Parlazin, Cetrin) is a competitive histamine antagonist, a hydroxyzine metabolite, and a H1-histamine receptor blocker [1].

Purposeful design of the molecule from the point of view of its biological properties also includes the introduction of additional fragments, which in the future will lead to an increase in the basic pharmacological activity or the appearance of a new one. It is already known that the introduction of a phenoxyalkyl moiety in a molecule positively influences the growth of its pharmacological activity [2]. At the same time, the "limiting" requirement for the structure of the planned molecules was their sufficient simplicity. We synthesized a number of new derivatives of basic synthon - 1-(diphenylmethyl)piperazine, in the present work - with aromatic (phenoxy (ethyl- [3], propyl- or butyl-) bromides with the formation of the corresponding phenoxyalkyl derivatives of benzhydrylpiperazine:

The optimal reaction conditions were: room temperature, presence of powdered potassium hydroxide and solvent - dimethylformamide. However, the yield of the products did not exceed more than 60%, the reaction time from 6 hours to several days, and the formation of a by-product of the reaction of phenoxyalkyl bromide with DMF.

To prove the formation of 1-phenoxyalkyl-4- (diphenylmethyl) pyperazin and by-
products, 13C and N1 NMR spectroscopy is involved, the data of which are consistent with the proposed structure.

For the bioscreening of novel 1-phenoxyalkyl-4-(diphenylmethyl)piperazin (n = 3,4), it is expedient to obtain their inclusion complexes with β-cyclodextrin due to the entry into the sugar cavity, most likely the phenoxyalkyl fragment. On the basis of X-ray diffraction analysis it was found that piperazine cycles in both structures have chair conformations with the equatorial orientation of diphenylmethyl and phenoxyalkyl substituents. The bond lengths and valence angles have common values for similar compounds. In this case, the β-atom of alkoxy substituents is in the trans position to one of the α-carbon atoms and in the gosh-conformation to another piperazine ring. Alkyl (propyl- and butyl-) substituents have transoide conformations close to planar ones, in which the phenoxyalkyl group is actually located:

![Diagram](image)

Thus, the molecule 1-(diphenylmethyl)piperazine is a promising synthon for the preparation of new low-toxic biologically active substances with a variety of pharmacological properties. However, in order to increase the yield, shorten the time of the process, reject DMF as a solvent and other technological issues, it is necessary to carry out additional studies involving microwave and/or ultrasound promotion technologies, interphase transfer catalysis, medium-ionic liquid, etc.

*Research was supported by the Committee of Science of the MES of the Republic of Kazakhstan for scientific and technical program No. BR05234667*

**References**


Invited and Oral reports
Electron density distribution in catecholate, amidophenolate and acrylate complexes of triphenylantimony

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Interest to study catecholate and amidophenolate complexes is caused by reversible binding of molecular oxygen to them (Fig. 1). Our investigations [1-3] have shown that the combined use of electronic [-5.09 eV (inert) > \(E_{\text{HOMO}}\), \(E_{\text{HOMO}}\) >-5.06 eV (active); ] and steric (G-parameter <90%) criteria allow for a rational interpretation of the reversible binding of molecular oxygen to catecholate and amidophenolate complexes of Sb(V). In addition, these criteria can be used for the activity search of new complexes of antimony (V) (or related complexes of other non-transition metals) towards \(O_2\).

Interest to study acrylate complexes of triphenylantimony is caused by phase transitions (\(\text{Ph}_3\text{Sb(O}_2\text{C(Me)}=\text{CH}_2\text{)}\cdot\text{C}_6\text{H}_6\) and \(\text{Ph}_3\text{Sb(O}_2\text{CCH}_2\text{CH}=\text{CH}_2\text{)}\) (Fig.2), realization of \(\pi...\pi\) interactions in \(\text{Ph}_3\text{Sb(O}_2\text{CH}=\text{CH}_2\text{)}\) [4] (Fig.3) and also absence of expected critical points (3,-1) between atom of antimony and carbonyl atom of oxygen in some complexes.

This work was supported by the Russian Foundation for Basic Research (grant № 17-03-01257).

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Quantum chemical investigations of Cr$_2$O$_n$ and Cr$_2$O$_n^-$ series (n=1-14)

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The geometrical and electronic structures of the Cr$_2$O$_n$ and Cr$_2$O$_n^-$ clusters are computed using density functional theory with a generalized gradient approximation in the range of 1 ≤ n ≤ 14. Local total spin magnetic moments, polarizabilities, binding energies per atom, and energies of abstraction of O and O$_2$ are computed for both series along with electron affinities of the neutrals and vertical detachment energies of the anions. In the lowest total energies states of Cr$_2$O$_2$, Cr$_2$O$_3$, Cr$_2$O$_4$, Cr$_2$O$_{14}$, Cr$_2$O$_3^-$, Cr$_2$O$_4^-$, and Cr$_2$O$_{14}^-$, total spin magnetic moments of the Cr atoms are quite large and antiferromagnetically coupled. In the rest of the series, at least one of the Cr atoms has no spin-magnetic moment at all. The computed vertical electron-detachment energies of the Cr$_2$O$_n^-$ are in good agreement with experimental values obtained in the 1 ≤ n ≤ 7 range. All neutral Cr$_2$O$_n$ possess electron affinities larger than the electron affinities of halogen atoms when n > 6 and are thus superhalogens. It is found that the neutrals and anions are stable with respect to the abstraction of an O atom in the whole range of n considered, whereas both neutrals and anions became unstable toward the loss of O$_2$ for n > 7. The polarizability per atom decreases sharply when n moves from one to four and then remains nearly constant for larger n values in both series. The largest members in both series, Cr$_2$O$_{14}$ and Cr$_2$O$_{14}^-$, possess the geometrical structures of the Cr$_2$(O$_2$)$_7$ type by analogy with monochromium Cr(O$_2$)$_4$.

It was found that the lowest total energy states of Cr$_2$O$_n$ and Cr$_2$O$_n^-$ are ferromagnetic or antiferromagnetic for n = 1–4, and we computed magnetic exchange coupling constants $J_{12}$ in this n range. The Cr atoms in Cr$_2$O$_n$ and Cr$_2$O$_n^-$ for larger n carry either no or small local spin magnetic moments except for Cr$_2$O$_{14}$ and Cr$_2$O$_{14}^-$. In the case of the lowest total energy state of Cr$_2$O$_{14}$, the local spin magnetic moments are ±0.9 μB; i.e., the moments are coupled antiferromagnetically. In the Cr$_2$O$_{14}^-$ anion the local spin magnetic moments are also antiferromagnetically coupled but with different absolute values (-1.1μB and +0.4μB, respectively).
Relationship "structure-conductivity-activity" in alcohols conversions over solid electrolyte catalysts

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Ternary oxides (perovskites-like vismuth vanadates Bi$_4$V$_{2-2x}$M$_{2x}$O$_{11-\delta}$ of BIMEVOX family) and ternary phosphates Na(Cs)$_{1-2x}$M$_x$Zr$_2$(PO$_4$)$_3$ (NASICON-family) represent solid electrolytes (SE) with anionic and cationic conductivity respectively. The structural and electro physical characteristics of these ceramic materials were well defined, but their catalytic properties are studied insufficiently [1-5]. When analyzing the influence of the structure and conductivity of a solid electrolyte on its catalytic activity and the nature of active sites, it is reasonable to use the reactions of aliphatic alcohols because two routes are possible: dehydrogenation (1) and dehydration (2) of alcohol, which occur by the redox and acid mechanisms, respectively. It was found that several particularities in conduction properties of these materials are of a great importance in proceeding the reactions 1 and 2 for isopropanol and butanols over SE-catalysts’ surface in the temperature range 200-400 °C.

In our work for SE-catalysts characterization the methods XRD, XPS, IR, UVS, SEM, TEM, acidity/basicity surface titration were used.

Complex bismuth vanadates in which the V$^{5+}$ ion is partially replaced by 3$d$ metal cations (M = Cu$^{2+}$, Fe$^{3+}$, Zr$^{4+}$) form Aurivillius phases: $\alpha$ and $\beta$ modifications with low M contents, and highly conductive tetragonal $\gamma$ modification at increased cation concentrations. The most active in catalysis is anion deficit $\gamma$ phase. For the BIMEVOX series, the conductivity increases for BICUVOX and BIZRVOX compared with that of binary vanadate Bi$_4$V$_2$O$_{11-\delta}$ and considerably decreases in case of BIFEVOX. The observed step-wise Arrhenius dependences for isobutanol dehydrogenation reaction are related to changes in the conducting properties of the catalyst. The apparent activation energy $E_a$ (1) decreases linear with phase transformation when Cu$^{2+}$ or Zr$^{4+}$ content increases, but, on the contrary, for BIFEVOX catalysts the $E_a$ value increases. In the $\gamma$-BIMEVOX series in row Cu$^{2+}$ → Fe$^{3+}$ → Zr$^{4+}$ activation energy of conductivity $E_a$,σ increases and in the same consequence value $E_a,1$ augments too (fig.1a). The influence of the charge of the dopant cation on conducting and catalytic properties demonstrates fig.1b.

![Fig.1](image_url)

**Fig.1.** Correlation between activation energy of isobutanol dehydrogenating reaction and activation energy of conductivity (a) and charge of dopant cation (b) for $\gamma$-BIMEVOX catalysts

For most active Cu sites the redox mechanism of C4 alcohol dehydrogenation may be written by two stages with alkoxide anion formation and reoxidation of copper active site (rate...
invited and oral reports

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determining step): 1/. \( \text{Cu}^{2+} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{Cu}^0 + 2\text{H}^+ + 2\text{C}_2\text{H}_5\text{O}^- \); 2/. \( 2\text{H}^+ + \text{Cu}^0 \rightarrow \text{H}_2 + \text{Cu}^{2+} \).

In \( \alpha \)-phase the complex active site includes vanadium ion in linkage [V-O-M]. In the surface layer BIMEVOX catalysts the initial charges of M ions are changed and \( \text{Cu}^+ \) or \( \text{Cu}^0 \), \( \text{Fe}^{2+} \) or \( \text{Fe}^0 \), \( \text{Zr}^{3+} \) or \( \text{Zr}^0 \) as well as \( V^{4+} \) form that confirm XPS spectra of the samples before/after catalysis, so the relationship \( \text{Ea}(1) \) vs standard potential of \( M^{m+} \) reduction takes place.

For Na-M-Zr-Phosphates (Na-M-ZP) prepared as BIMEVOX by solid phase method the linear correlation between activation energy for isopropanol dehydrogenation reaction and ionic radius of substituting ions \( M = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+} \) was found. When temperature rises, the change in position \( M \) in conductive channel occurs and \( \text{Ea} \) value of alcohol dehydrogenation reaction diminishes (see fig.2). In isopropanol dehydrogenation over NASICON with general formula \( \text{Na}_{(1-2x)}\text{M}_x\text{Zr}_2(\text{PO}_4)_3 \), where \( x = 0.125 \) и 0.25, the nature and location \( M \) are more significant.

Fig.2. Velocity of acetone formation at 400 °C (a) and the influence of ionic crystalline radius \( M^{2+} \) dopant on apparent activation energy of isopropanol dehydrogenation reaction (b)

It was found that Cs-M-Zr-phosphates catalysts prepared by sol-gel procedure showed high selectivity in isobutanol dehydration reaction. More active and selective ternary phosphates with Co and Ni, substituting partially conducting Cs\(^+\) ion (cooperative effect), crystallized in rhombohedra modification, but binary Ni-Zr and Co-Zr phosphates were of monoclinic form. It was evident the correlation between drops of volume of elementary unit and surface acidity with transfer Cs-Ni-ZP, Cs-Co-ZP to Ni-ZP and Co-ZP catalysts.

So, we find many examples indicating the role of bulk general characteristics of conducting materials in surface processes (heterogeneous catalysis and adsorption of substrate on active site), which tightly connect with the structure of cationic and anionic solid electrolytes.

References


The evaluation of nanostructured perovskite-type oxides \( \text{SrFeO}_{3-\delta}, \text{GdFeO}_3, \text{GdSrFeO}_4 \) and \( \text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7 \) in catalytic processes

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Catalytic systems based on complex perovskite-type oxides of gadolinium and strontium were synthesized and further investigated in the hydrogenation of carbon oxides at atmospheric pressure. Perovskite oxides \( \text{SrFeO}_3, \text{GdFeO}_3, \text{GdSrFeO}_4, \text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7 \) \((x = 0, 1; 0.2; 0.3; 0.4)\) were prepared by the sol-gel method and by ceramic technology and characterized by X-ray diffraction, scanning electron microscopy, photon correlation spectroscopy, Mössbauer spectroscopy and low-temperature nitrogen desorption. The presence of one phase with a perovskite-type laminate structure was established for all samples. It should also be noted that oxides synthesized with the use of the ceramic technology are in microcrystalline one magnetically ordered state of \( \text{Fe}^{3+} \), and the ones obtained by the sol-gel method are in the nanocrystalline and heterovalent state of \( \text{Fe}^{3+}, \text{Fe}^{4+} \) with a porous structure and a number of oxygen vacancies.

The results of physical and chemical analyses confirmed that the sol-gel method makes it possible to obtain samples with better catalytic characteristics in comparison with ceramic systems. The correlation between the number of perovskite layers \((n = 1, 2, ..., \infty)\) in the laminate oxide structure and the olefin selectivity was observed in the series \( \text{SrFeO}_{3-x}, \text{GdSrFeO}_4, \text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7, \text{GdFeO}_3 \). The nonizovalent substitution of \( \text{Gd}^{3+} \) by \( \text{Sr}^{2+} \) leads to a distortion of the complex oxide structure and results in the appearance of a heterovalent state of iron atoms \( \text{Fe}^{3+}, \text{Fe}^{4+} \), which has influence on the values of conversion of reactants and selectivities for the target products.

**Figure 1.** Diffractograms of complex oxide \( \text{Gd}_2\text{SrFe}_2\text{O}_7 \) synthesized by sol-gel method before the catalytic process; after the process of CO hydrogenation; after the process of dry reforming of methane.
Figure 2. Mossbauer spectrum of complex oxide Gd$_2$SrFe$_2$O$_7$, synthesized by sol-gel method a) before the catalytic process; b) after the CO hydrogenation.

All investigated ferrites showed high stability. It has been established that the phase composition of all ferrites remains steady after catalytic reactions. Partial decomposition of catalysts under the action of the reaction medium does not occur. However, the formation of Gd$_3$O$_2$CO$_3$ on GdFeO$_3$ takes place. It is supposed that formation of carbonate complexes passes on Gd$^{3+}$ ions (A-site), and transition metal ions in B-site are responsible for the formation of atomic hydrogen. During the catalytic reactions, no significant changes in the morphology of the samples were detected. Under the action of the reaction medium, the reduction of Fe$^{3+}$ to Fe$^{2+}$ was observed. There is a carbon presence on the surface of the catalysts after the process, but since the activity of the catalysts does not change and persists for a long time, and $\Delta n_C$, which characterizes the amount of carbon on the surface, reached a peak with increasing temperature, it can be assumed that this surface carbon is more active. For samples obtained by the sol-gel method, the formation of inactive carbon is minimal.

Figure 3. A microphotography (a) and EDX (b) of the complex laminate oxide Gd$_2$SrFe$_2$O$_7$ after the CO hydrogenation.

This work was supported by the Russian Foundation for Basic Research (grant № 17-03-00647). This paper was financially supported by the Ministry of Education and Science of Russian Federation on the program to improve the competitiveness of Peoples’ Friendship University of Russia (RUDN University) among the world’s leading research and education centers in the 2016-2020.
Co (Ni) - Zr - Phosphates modified by plasma treatments: physico-chemical properties and catalytic activity

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Plasma treatment of catalysts produces a significant effect on their activity. Investigation of the plasma effect on solids provides a basis for developing new plasma chemical technologies. In addition, plasma treatment changes the structure and chemical composition of the surface through the action of reactive species forming in the plasma and through plasma radiation.

In the conversion of butanols, particularly in isobutanol conversion, the most desirable product is isobutene, a product of alcohol dehydration occurring on acid sites. Its subsequent polymerization affords valuable products, such as high molecular weight polyisobutylene, which is widely employed in various industries.

The purpose of this study was to elucidate the effect of hydrogen and argon radio-frequency (RF) plasma treatments of the NASICON-type nickel and cobalt zirconium phosphate \( \text{Cs}_{1-2x}\text{Co(Ni)}_x\text{Zr}_2(\text{PO}_4)_3 \) with \( x=0,15; 0,25; 0,50 \) on \( \text{CO}_2 \) adsorption characteristics and its catalytic activity in vapor phase reactions of isobutanol.

Zirconium phosphates \( \text{Cs}_{1-2x}\text{Co(Ni)}_x\text{Zr}_2(\text{PO}_4)_3 \) were prepared by sol-gel method [1], characterized by physical-chemistry methods (X-ray diffraction XRD, X-ray photoelectron spectroscopy XPS, UV-, IR-spectroscopy, TEM) and tested in decomposition of butanol-2.

The X-ray diffraction data substantiated the structure of CZP. The XPS data showed that the composition of the surface layer differed from the stoichiometric: for example, the concentration of Co\(^{2+} \) on surface of \( \text{Co}_{0,5}\text{Zr}_2(\text{PO}_4)_3 \) was overrated by a factor of \( \sim 2.5 \).

The main reaction of butanol transformation was dehydration. The triple phosphates samples (\( x=0,15; 0,25 \)) exhibited the highest activity than double one (\( x=0,5 \)). The process of butanol 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. The plasma treatment effects are due to the activation of the phosphate surface through an increase in the number of adsorption and catalysis sites and in their accessibility to the alcohol molecules undergoing adsorption and chemical reactions.

This work was supported by the Russian Foundation for Basic Research (grant № 18-33-20101).

References
The Struchkov Prize session
(laureates and young scientists)
Giant supramolecules at atomic resolution: how far away is the horizon?

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One of the ultimate goals of the single crystal X-ray structure analysis (SC-XRD) is to obtain structure of a crystalline compound as accurate and detailed as possible. For small molecules, not only precise geometrical characteristics but also charge density distribution can be obtained from high-angle diffraction experiment. On the other hand, for biological macromolecules as proteins or DNA the resolution reachable in SC-XRD is usually significantly lower, revealing smeared-out image of a giant molecule with approximate positions of its parts.

However, these two extreme cases, small molecules and biological macromolecules, do not limit all possible objects for X-ray diffraction study. During the last decades, various approaches were developed to control the formation of giant supramolecules, like e.g. metal complexes with bridging organic ligands (Fig. a), polyoxometallates (Fig. b), metallic or metal-chalcogenide nanoparticles surrounded by organic ligands (Fig. c,d) and pentaphosphaferrocene-based superspheres (Fig. e) [1-7].

These molecules can be very large, up to 8.2 nm in diameter (Fig. a), or heavy up to 79.9 kDa (Fig. b) [1,2]. Their crystal structures consisting of hundreds of heavy atoms formally still fall into the class of ‘small molecules’ and, therefore must fulfil the corresponding quality criteria originally developed for the structures solved at atomic resolution. Unfortunately, the problematics of SC-XRD applied to the supramolecules and the giant clusters is rather less-debated. The following questions arise: What is the best strategy of the diffraction experiment? How high-resolution data help in understanding of the chemical aspects of the self-assembly process? How can information from other physical methods and knowledge of structural chemistry help to verify and to improve a structural model? Which information can be obtained from low-angle diffraction data of poorly scattering single crystals? To answer these questions, we will summarize a knowledge from the literature as well as our own experience on the crystal structure determination of giant, up to 4.2 nm in size, spherical supramolecules obtained by the a reaction of pentaphosphaferrocene \([\text{Cp}^R\text{Fe}(\eta^5-P_5)]\) (\(\text{Cp}^R = \eta^5-C_5R_5, R = \text{Me, CH}_2\text{Ph, PhC}_4\text{H}_9\)) with various copper(I) and silver(I) salts [5-7].

We thank ERC grant AdG339072-SELFPHOS for support. The research was partly done at the light source PETRA III at DESY.
References

Protonic metal-based ionic liquids: DEAHFeCl₄, (DEAH)₂CoCl₄, DEAHMnCl₃

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Due to different unique properties (low melting point, ionic structure, negligible vapor pressure, electrochemical and thermal stability, ionic conductivity etc.) ionic liquids (IL) have not only fundamental scientific interest, but the applied significance as well. Highly perspective feature is to design desirable properties by functional group embedding to cation and anion selection [1].

The present work deals with ionic liquids with diethanolammonium cation and metal-halogenide anions. Diethanolammonium (HOCH₂CH₂)₂NH²⁺ has acidic protons (OH and NH₂⁺ groups) and IL could have protonic conductivity potentially. The metal-based anion in IL is often responsible for magnetic, catalytic and electrochemical properties [2].

The syntheses of these ILs consisted of two stages: on the first stage the salt of diethanolamine (DEA) and hydrochloric acid was produced; the second stage included reaction between the salt made on 1st stage (DEAHCl) and corresponding water free metal chloride (FeCl₃, CoCl₂, MnCl₂). The resulting compounds were drying in desiccator over P₄O₁₀. All of them were characterized by single crystal XRD, thermal analyses (DTA-TG, DSC), IR spectroscopy.

Thermal properties are shown in Table 1.

Table 1. Thermal properties of ILs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point, °C</th>
<th>Decomposition temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEAHFeCl₄</td>
<td>31.0</td>
<td>128-486</td>
</tr>
<tr>
<td>(DEAH)₂CoCl₄</td>
<td>48.7</td>
<td>210-525</td>
</tr>
<tr>
<td>DEAHMnCl₃</td>
<td>162.4</td>
<td>269-272</td>
</tr>
</tbody>
</table>

Crystal structures of ILs DEAHFeCl₄ and (DEAH)₂CoCl₄ at room temperature are composed of cations DEAH and anions MCl₄, whereas in DEAHMnCl₃ cation DEAH is connected to manganese atom by coordination bond through oxygen atom of OH group (Fig. 1). This fact causes melting point to increase (see Table 1).
Hydrogen bonding systems in all three structures are different. In DEAHFeCl₄ cations DEAH are combined by O–H···O hydrogen bonds to tetramers (Fig. 2) which are connected to corrugated layers. Protonic conductivity could be found along these layers. Layers of cations are joined by anions to 2D structure, therefore DEAHFeCl₄ is layer structure. In (DEAH)₂CoCl₄ cations are linked to chains through N–H···O hydrogen bonds, skew cation chains are connected with anions to 3D structure. Finally there are disordering hydrogen system in DEAHMnCl₃ structure (Fig. 3). Blue dashed lines are the first hydrogen bonding system occurring simultaneously O₁–H₁₁···O₂₁, O₂₁–H₂₂···O₂₂, O₂₂–H₂₁···Cl₃ and O₁–H₁₂···Cl₃. The second hydrogen bonding system is shown by magenta dashed lines in Fig. 3. This system is symmetry equivalent to blue one and both systems arrange in crystal statistically. Manganese atom has 5 chlorine atoms in closed environment and one oxygen atom from cation DEAH, whereas 4 chlorine atoms are bridge. Thus the chain from Mn and Cl is formed with adjoined cations DEAH. These chains are connected to 3D structure through hydrogen bonding.

In conclusion, the structure of ionic liquid is dramatically depended on the kind of metal in metal-chloride anion, iron produces low melting ionic liquid with layered structure and disordering hydrogen bond system, cobalt gives moderate melting ionic liquid with 3D structure and chain-like hydrogen bonding system, manganese yields 3D structure with disordering hydrogen bonding system, extended (MnCl₃)ₙ-chains with coordinated DEAH and, as consequence, high melting point.

This work was supported in part by M.V. Lomonosov Moscow State University Program of Development.

References
Giant pentaphosphaferrocene-based supramolecules

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Since 2003, we have been investigating the use of pentaphosphaferrocene \([\text{Cp}^R\text{Fe}(\eta^5-P_5)]\) \((\text{Cp}^R = \eta^5-C_5R_5, R = \text{Me}, \text{CH}_2\text{Ph}, \text{PhC}_4\text{H}_9)\) as versatile building block in supramolecular chemistry. Due to the presence of the planar P_5-ring it possesses intrinsic fivefold symmetry. The self-assembly of these building blocks with \(d^{10}\)-metal cations \((M^+ = \text{Cu}^+ \text{and Ag}^+)\) results in spherical supramolecules or superspheres of more than 15 basic types revealing fullerene or fullerene-like topologies and beyond them [1-5]. With the size up 4.6 nm [2] (Fig. a), some supramolecules provide a central cavity of 0.8 – 1 nm in diameter [3] (Fig. b). It makes them useful as molecular containers for various small molecules. For example we succeeded in the encapsulation of metallocenes such as \(\text{Cp}_2\text{Fe} [4]\) or \(\text{Cp}_2\text{Co}^+ [5]\) as well as of metastable guest molecules such as the tetrahedral molecules of white phosphorus, \(\text{P}_4\), and yellow arsenic, \(\text{As}_4 [6]\).

All pentaphosphaferrocene-based supramolecules consist of a central inorganic core built from \(M^+\) cations, cyclo-P_5 moieties and halides (Cl\(^-\), Br\(^-\), I\(^-\)) or triflates (O_3SCF_3\(^-\)) as bridging ligands and counteranions. The central core is surrounded by organic \(\text{Cp}^R\) groups defining the outer size of the superspheres. The structure of individual supramolecule can be controlled by changing the nature of \(M^+, R\) and the counterion [1, 3] as well as by using various guest molecules as templates [4, 5].

Recently we succeeded in obtaining the first series of coordination polymers, where pentaphosphaferrocene-based supramolecules play a role of nodes. The successful strategy lies in the usage of weakly coordinating SbF_6\(^-\) anion in combination with Ag\(^+\) and flexible ditopic linkers N≡C(CH_2)_nC≡N \((L^n, n = 7-10)\). The coordination of Ag\(^+\) cations to the cyclo-P_5 results in the formation of supramolecules in situ (Fig. c), while the additional coordination of Ag\(^+\) to N-donor atoms of \(L^n\) in turn leads to 1D, 2D and 3D coordination polymers in an one-pot reactions (Fig. d). The composition and structure of the supramolecules as well as the dimensionality of the polymer can be controlled by changing the reaction stoichiometry or by adding the guest molecules as e.g. white phosphorus, \(\text{P}_4\).

In the course of our structural studies, it was shown that the molecular structure of the supramolecules quite often manifests structural variations owing to occasionally arising multi-choice alternatives during the self-assembly process. These structurally diverse, but generally similar supramolecules co-crystallize and give solid solutions of different isomers and forms. In the diffraction patterns these structural effects sometimes reveal themselves in diffuse scattering signifying disorder, superstructural or non-Bragg satellite reflections giving evidence to
commensurate or incommensurate ordering, respectively.

*This work was supported by the SELFPHOS grant ERC-2013-AdG-339072. Parts of these investigations were carried out at the PETRA III synchrotron source at DESY, a member of the Helmholtz Association (HGF).*

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Hydrocerussite-related minerals and materials: structural principles

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‘White lead’ or basic lead carbonate, ‘2PbCO₃·Pb(OH)₂’, the synthetic analogue of hydrocerussite Pb₃(OH)₂(CO₃)₂, has been known since antiquity as the most frequently used white paint. In modern times, the hydrocerussite to cerussite ratio in paints is used for the identification and characterization of the age and geographical origin of paintings. Another white pigment, but with ‘pearlescent’ or ‘nacreous’ appearance, is known as ‘modern white lead’, the synthetic analogue of the mineral plumbonacrite. The modern method for the production of white lead was developed only in the 1940s and thus finding this type of white pigment on a painting, indicates that it cannot have been done before that date, at least in principle. However, care must be taken, because in some cases a synthetic analogue of plumbonacrite has been found on much older paintings, as reported recently for van Gogh paintings [1]. Very likely that the phase composition of some of ‘white lead’-based pigments is more complex and a detailed knowledge of XRD patterns of different phases after evaluation of structural architectures may help in various aspects from identification to restoration of paintings.

Hydrocerussite, Pb₃(OH)₂(CO₃)₂, has been known for 140 years. This secondary mineral is usually found in oxidized lead ore deposits and has been reported from more than one hundred different localities all over the world. Surprisingly, till recently [2], there were no published single crystal diffraction data for the crystal structure of hydrocerussite, neither from synthetic nor from natural samples.

In this contribution, I give a review of general structural principles of the rapidly growing family of hydrocerussite-related minerals and synthetic materials. Only structures containing a hydroxo- and/or oxo-component, i.e. which are compositionally directly related with hydrocerussite and ‘white lead’, are reviewed in detail. An essential structural feature of all the considered phases is the presence of electroneutral [PbCO₃]⁰ cerussite-type layers or sheets.

This work was supported by the Russian President grant MD-5229.2018.5. Technical support by the X-Ray Diffraction Resource Centre of Saint-Petersburg State University is gratefully acknowledged.

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Development and application of the Debye scattering equation method for a full-profile analysis of X-ray diffraction patterns for the structural diagnostics of powder nanomaterials

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It is known that the physical and chemical properties of nanomaterials are defined by features of the atomic structure and morphology. It can be both individual nanoparticles and organized nanostructures. X-ray diffraction method has considerable potential for structural research. For nanoparticles, diffraction effects caused by small dimensions or an anisotropic shape of particles appear. Scattering from nanostructures can provide information about the size of blocks, their defectiveness and relative spatial arrangement. Standard X-ray diffraction techniques used for bulk materials with periodic structures are often not applicable in this case.

For nano-sized Debye Function Analysis (DFA) method [1] based on Debye scattering equation (DSE) [2] can be used. It is full-profile method which is applicable for any an arbitrary atoms collection, and therefore can be used for crystalline objects, non-crystalline materials or nanostructures. The method is the most general and does not require artificial corrections.

Possibilities of modelling diffraction patterns by the DFA by our software [3] will be shown for examples of various nanocrystalline materials: hydroxides of magnesium and tungsten, layered structures, metastable forms of aluminum oxide, ultradispersed iron oxides et al. [4-8]. It is public-domain software available on the website: www.sourceforge.net/projects/dianna.

This work was supported by the framework of the budget project AAAA-A17-117041710079-8 for Boreskov Institute of Catalysis.

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On morphotropic transition in apatite-structured compounds

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Apatite is a large class of inorganic compounds, the general formula of which can be represented as $\text{M}_{10}(\text{AO}_4)_6\text{X}_2$, where $\text{M}$ - metals and metalloids in oxidation states +1, +2, +3 and +4; $\text{A}$ - most often P, Si, V, Mn, As, Cr; $\text{X}$ - halogens, OH - group, etc. Apatites crystallize in the hexagonal system with the space group $\text{P6}_3/m$. It is known that the structural type of apatite can tolerate significant iso- and heterovalent substitutions both in cationic and anionic positions of the structure. Most often, the isomorphism is observed among the M atoms, due to the presence of two crystallographic positions of the cation with different coordination environments.

One of the most topical field of using apatite materials is in biomaterials applications because substituted hydroxyapatite (idealized formula $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is the main mineral component of natural bones and teeth of mammals. Nowadays, hydroxyapatite-based materials are existing in different forms: from powders to ceramics. To improve biological activity of apatite-based materials chemical substitutions can be utilized. Such examples can be derived by the incorporation of bismuth and antimony in apatite structure, which are well known as antimicrobial agents. The interest is not only in obtaining and properties of these materials, but also in their behavior after introduction into the body, especially when poisoning with heavy metals (Cd, Pb) or radioactive isotopes (Sr-90). In this work, we present the results of studying solid solutions formed on the basis of the antimicrobial biocompatible Bi-apatite $\text{Ca}_8\text{Bi}_2(\text{PO}_4)_6\text{O}_2$ upon the incorporation of lead ions in them.

Powdered samples of compounds of the composition $\text{Ca}_{8-2x}\text{Bi}_2\text{Pb}_{2x}(\text{PO}_4)_6\text{O}_2$ ($x = 0, 1, 2, 3, 4$) were obtained by the reaction in the solid phase. Compounds of the composition $\text{Ca}_2\text{BiPb}_6(\text{PO}_4)_6\text{O}_2$, $\text{Ca}_4\text{Bi}_2\text{Pb}_4(\text{PO}_4)_6\text{O}_2$, $\text{Ca}_6\text{Bi}_2\text{Pb}_2(\text{PO}_4)_6\text{O}_2$ were obtained and identified for the first time. A sample of a compound of the composition $\text{Bi}_2\text{Pb}_8(\text{PO}_4)_6\text{O}_2$ under the indicated conditions has a diffraction pattern that is substantially different from the other compounds of the series. As follows from the literature data, this compound, despite its isoformality, crystallizes in the Pnma space group of orthorhombic system. Thus, the phenomenon of morphotropy is observed - a sharp change in the crystal structure in a regular series of chemical compounds while maintaining a quantitative ratio of structural units. In order to detect the cation ratio ($\text{Ca}^{2+}/\text{Pb}^{2+}$) at which a hexagonal to orthorhombic structure changes, attempts have been made to synthesize compounds of $\text{Ca}_{8-2x}\text{Bi}_2\text{Pb}_{2x}(\text{PO}_4)_6\text{O}_2$ compounds at $x = 3.25; 3.5; 3.75$. As it follows from XRD data, no individual substance was obtained. The change in temperature conditions and synthesis time also did not lead to the production of the desired product. Using TOPAS 3.0 software, a qualitative and quantitative phase analysis of the resulting mixture was carried out, which showed that in this case the process takes place to form a mixture of $\text{Bi}_2\text{Pb}_6(\text{PO}_4)_6\text{O}_2$ and $\text{Ca}_2\text{Bi}_2\text{Pb}_6(\text{PO}_4)_6\text{O}_2$ compounds and the process can be described by the following reaction equation:
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\[
1.5 \text{Ca(NO}_3\text{)}_2\cdot 4\text{H}_2\text{O} + 2 \text{Bi(NO}_3\text{)}_3\cdot 5\text{H}_2\text{O} + 6 \text{(NH}_4\text{)}_2\text{HPO}_4 + 6.5 \text{Pb(NO}_3\text{)}_2 \rightarrow \\
\rightarrow 0.25 \text{Bi}_2\text{Pb}_8(\text{PO}_4)_6\text{O}_2 + 0.75 \text{Ca}_2\text{Bi}_2\text{Pb}_6(\text{PO}_4)_6\text{O}_2 + 23 \text{NO}_2 + 11 \text{NH}_3 + 3.75 \text{O}_2 + \\
+ 26.5 \text{H}_2\text{O}
\]

Further attempts to obtain monophasic samples of compounds of the \(\text{Ca}_8\text{Bi}_2\text{Pb}_{2x}(\text{PO}_4)_6\text{O}_2\) composition at \(3<x<4\) also resulted in a mixture of \(\text{Bi}_2\text{Pb}_8(\text{PO}_4)_6\text{O}_2\) and \(\text{Ca}_2\text{Bi}_2\text{Pb}_6(\text{PO}_4)_6\text{O}_2\) phases of different composition (Fig. 1).

![Figure 1. Areas of existence of different structural types in a system of \(\text{Ca}_8\text{Bi}_2\text{Pb}_{2x}(\text{PO}_4)_6\text{O}_2\) solid solutions](image)

In order to determine the features of the crystalline structure of the obtained substances, an analysis of their structure by the Rietveld method was made on the basis of powder X-ray diffraction data. In the \(\text{Ca}_8\text{Bi}_2(\text{PO}_4)_6\text{O}_2\) compound, the calcium and bismuth ions are distributed between two crystallographic positions for the cations - 4f and 6h. Moreover, it should be noted that bismuth is located mainly in position 6h, which is characterized by lower coordination numbers (7) compared to position 4f (9), which is more typical for bismuth. At the same time, the introduction of lead atoms into the crystal structure leads to the fact that bismuth is completely localized only at positions 6h. In addition, an analysis of the distortion of cation polyhedra occupying position 4f, based on the calculation of their twist angle, confirms the untypicality of large coordination numbers for bismuth atoms: the distortion of polyhedra decreases in the case when only the atoms of calcium and lead occupy this position. The calculated average deviation of the bond length from the mean value in the coordination polyhedra formed by the cations in positions 4f and 6h increases with an increase in the proportion of lead in the compounds. Perhaps this is due to its less deformable electronic shell.

*The work was performed with the financial support of the Russian Foundation for Basic Research (Project Number 16-33-601721 мол_а_ок).*
The first microporous framework structures containing uranium and chromium have been synthesized and characterized. Rb2[(UO2)2(CrO4)3(H2O)2](H2O)3 (1) was crystallized from uranyl chromate solution by evaporation. Further evaporation led to increased viscosity of the solution and overgrowing of Rb2[(UO2)2(CrO4)3(H2O)](H2O) (2) on the crystals of 1. With respect to 1, the framework of 2 is partially dehydrated. Both frameworks differ compositionally by only one water molecule, but this seemingly small difference affects significantly the pore size and overall structural topology of the frameworks, which present very different flexibility of the U-O-Cr links. These are rigid in the pillared framework of 1, in contrast to 2 where the U-O-Cr angles range from 126.3° to 168.2°, reflecting the substantial flexibility of Cr-O-U connections which make them comparable to the corresponding Mo-O-U links in uranyl molybdates.

A new organically templated uranyl sulfate, (pyrH+)2[(UO2)6(SO4)7(H2O)2] (3) was obtained by slow evaporating from the solution containing uranyl nitrate, sulfuric acid and pyridine. The crystals of 3, within two weeks, in the mother liquor gradually disappeared, followed by the simultaneous crystallization of framework (pyrH+)(H3O)2[(UO2)3(SO4)4(H2O)2](H2O) (4) and layered (pyrH+)2[(UO2)2(SO4)3] (5). The frameworks, in the structures 3 and 4, contain channel systems with sizes 12.4×10.2 and 12.9×10.8 Å, respectively. Change of frameworks densities and structural complexity after the recrystallization is discussed.

In the crystal structures of Na2(SO3OH)(mfaH+)[(UO2)(SO4)2] (6) and Na(mfaH+)2[(UO2)2(SeO4)3(H2O)](H2O)2 (7) uranyl-sulphate and uranyl-selenate units are interconnected via sodium complexes with mfa into metal-organic frameworks. Both frameworks contain the channels of 10.2×9.8 and 12.8×5.4 Å in 6 and 7, respectively.

Until recently, crystal structures of uranyl compounds containing inorganic nanotubes were known only for uranyl-selenate systems. There are three known topological types of nanotubes with internal diameters of ~7 Å and ~15 Å. Uranyl sulfate Na(phgH+)7[(UO2)6(SO4)10](H2O)3.5 (8) was obtained at room temperature by evaporation from aqueous solution. Its structure contains unique uranyl sulfate [(UO2)6(SO4)10]8-nanotubules templated by protonated N-phenylglycine (C6H5NH2CH2COOH)+. Their internal diameter is 14 Å. A comparative crystal chemical analysis of new and previously described micro- and mesoporous framework uranyl compounds will be discussed.

This work was financially supported by the Russian Science Foundation through the grant 16-17-10085. Technical support by the SPbSU X-ray Diffraction Resource Centre is gratefully acknowledged.
Evolution of structural and topological complexity in uranyl sulfates and selenates

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Uranyl sulfates and selenates are the most remarkable groups of U⁶⁺-containing compounds due to their mineralogical importance and fascinating variety of structural topologies and topological isomers. The unique diversity of these materials can be explained by the high topological and structural adaptability of uranyl-based structural units to the charge and shape of organic and/or inorganic complexes that compensate for the negative charge of the uranyl complexes. Due to the small energetic differences between distinct topologies with the same overall composition, the structures of uranyl-based units may adapt to a particular template through topological and geometrical variations, thus demonstrating considerable structural flexibility. The interesting problem that appears in this regard is how complexity of a particular topological structure is related to the shape and complexity of templating ions.

Within the conceptual framework of the information-based approach recently developed in [1], uranyl-containing 1D and 2D units have been investigated using topological approach and information-based complexity measures demonstrating that very complex structures may form as transitional architectures between phases with relatively small amounts of structural information [2], wherein the overall trend shows that complexities of structures formed on the latter stages of crystallization are higher than those for the phases growing on the primary stages [3-4]. In addition, it was found that complex topologies form more rare than their simplest counterparts, which is a response of the crystal structure to changes of chemical conditions within the system [5].

This work was supported by St. Petersburg State University and Russian Science Foundation (grant № 18-17-00018).

References
Serial crystallography studies of 7-TM membrane proteins

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7-transmembrane (TM) α-helices proteins form a large and important superfamiliy represented in all kingdoms of life. Examples of proteins containing the 7α-helix motif include variety of receptors, channels and transmembrane transporters.

Included in 7α-helices family are G-protein coupled receptors (GPCRs) which detect most of hormones and signaling molecules in human body [1]. GPCRs constitute the largest human membrane protein family with over 800 members. They reside in cell membranes mediating cell signaling and regulate virtually every physiological process, making them successful targets of over 30-40% of current drugs.

Another example of 7α-helices proteins are microbial rhodopsins (MR) – a large family of photoactive membrane proteins, found in bacteria, archaea, eukaryota and viruses [2]. Among MRs are light-driven proton and ion pumps, light-gated channels, and photoreceptors. The recent interest to MRs relies on optogenetics – an approach which allows for spatially and temporally control of defined events in biological systems with the most important example in neuroscience [3].

Structural studies of both GPCRs and MRs made a tremendous impact to the field and were enabled by multiple breakthroughs in technology of high-throughput nanovolume crystallization in a native-like lipidic cubic phase matrix and micro-crystallography. Despite the enormous progress achieved in structural biology of 7α-helices proteins, obtaining structures of new members is still a challenge. In addition, the mechanisms of protein functioning remains hindered for current approaches.

Here, we discuss the current progress in the field of structural studies [4–13] of GPCRs and MRs. The particular attention is given to recently emerged techniques of serial crystallography using synchrotrons and X-ray free-electron lasers (XFELs).

This work was supported by RSF project no. 16-14-10273.

References


The development of modern in situ technologies of X-ray diffraction brings a wide application for study of different materials. For example, to create a new generation of catalysts, it is necessary to understand the state of catalyst under different stages of preparation and utilizing. Modern in situ methods make it possible to monitor the state of the catalyst directly during the real conditions of catalyst synthesis, activation and catalytic reaction. In particular, in situ X-ray diffraction can be used to investigate chemical and phase transformations, the formation of stable phases and intermediate compounds, the presence of point and planar defects and the formation of nanostructured states.

In this work, we used in situ XRD to study the effect of thermoactivation of Mn-containing oxide catalyst for total oxidation of hydrocarbons, CO and VOCs. The effect of thermoactivation was observed when the increase in the calcination temperature to 950–1000°C leads to the growth of catalytic activity. In situ XRD studies of MnO$_x$-Al$_2$O$_3$ catalysts shown that active component of the catalysts was formed via decomposition of the high-temperature precursor (cubic spinel Mn$_{3-x}$Al$_x$O$_4$) followed by the appearance of aggregates consisting of imperfect Mn$_3$O$_{4+\delta}$ oxide and amorphous Mn-Al-O phase. The decomposition was accompanied by the formation of weakly bound oxygen which appears to be active in oxidation reactions. The structure of the active component was directly related to the composition of the high-temperature precursor - the higher the concentration of manganese cations are in the Mn$_3$-xAl$_x$O$_4$ cubic spinel, the more Mn$_3$O$_4$ and weakly bound oxygen appear in the decomposition product. When Al is replaced by Ga, a significant decrease in catalytic activity is observed.

To understand the origin of active component of Mn-containing catalysts, detailed mechanism of high-temperature precursor decomposition was investigated on the model systems – singlephase spinels Mn$_{3-x}$Al$_x$O$_4$ and Mn$_{3-x}$Ga$_x$O$_4$. In situ XRD analysis indicates that during heating and cooling in the air both spinels decompose at the temperatures range of 400–800°C. This process is accompanied by partially oxidation of Mn$^{2+}$ to Mn$^{3+}$ and cation vacancies formation in the spinel structure that leads to decomposition of initial spinel into two spinel-type phases. Under heating Mn$_{3-x}$Al$_x$O$_4$ oxide decomposes according to nucleation and growth mechanism due to the diffusion of Mn cations toward the surface and its segregation into nanoparticles of $\beta$-Mn$_3$O$_4$. Spinodal decomposition of initial spinel occurs during cooling caused by Mn$^{3+}$ clustering. For Mn$_{3-x}$Ga$_x$O$_4$ spinel, products of decomposition are different during cooling and heating. Decomposition of Mn$_{3-x}$Ga$_x$O$_4$ leads to formation of two spinel structures with the similar Mn/Ga ratio but different oxygen content. In situ XRD study shown that difference in catalytic activity in CO oxidation in MnO$_x$-Al$_2$O$_3$ and MnO$_x$-Ga$_2$O$_3$ catalysts is due to different mechanism of precursor decomposition.
Rotation of molecules in crystals: the influence of crystallographic symmetry

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Crystal design is becoming one of the fastest growing fields in chemistry and physics today. In these fields, rotation of molecules in crystals has long attracted the attention of researchers. The rotation of molecules in crystals is investigated, in particular, for the creation of molecular rotors. Chemists who envisioned and built machines on the molecular scale have won the 2016 Nobel Prize in Chemistry. It is well known that controlled molecular motion is the heart of the molecular rotor and is a decisive parameter in the operation of molecular machines which are capable of tuning the bulk physical properties of materials. Consequently, this requirement prompted us to explore correlation between the rotation of molecules and symmetry.

Our work showed that rotational mobility of molecules in crystals is affected by the symmetry of their surroundings [1, 2]. A hypothesis was proposed for the discovered correlation. Three cases are possible for the location of the molecules with respect to the crystallographic symmetry elements: I – the location in a general position; II – the location in special positions without symmetry disordering; III – the location in special positions with symmetry disordering. According to the experimental data, the rotation barrier heights at the location of the molecules in cases I and III are lower than in case II. This fact is explained by the amplitude and phase shifts of the rotational energy profiles of two parts of the molecule in case I and by increasing the number of minima on the rotation barrier profile at disordering the molecules by symmetry in case III. The way is proposed for lowering the rotational barrier of molecules in crystals.

The work was performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

References
Relationships between crystal structure and electrochemical properties in fluoride-phosphate-based cathode materials for rechargeable batteries

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During two past decades, numerous cathode materials for rechargeable batteries with complex polyanionic crystal structure beyond simple layered oxides have been discovered. This offered a large playground for designing new cathode candidates and tailoring their electrochemical properties.

Recently we obtained a novel series of KTiOPO4-(KTP)-type vanadium-based AVPO4F (A = Li–Rb) cathode materials using different soft-chemistry approaches including hydrothermal and freeze-drying techniques [1-3]. The peculiarities of the KTP-type “VPO4F” framework enabled excellent rate capability particularly demonstrated in Li-ion cells. The material exhibited retention of more than 75% of the initial specific capacity in Li-ion cells at 40C and showed an average potential of 4.0 V vs Li/Li+ with maximal theoretical energy density of more than 650 mWh/g.

The material also maintains reversible intercalation of Na+, K+ and even Rb+ ions preserving the parent structure, though the electrochemical and transport properties drastically differ for Li+, Na+, K+ and Rb+ ions including the topology and dimensionality of ion migration pathways, energy barriers and alkali ion diffusion coefficients. The diffusion coefficients measured by PITT were lowest for Li+ (10^-12–10^-14 cm^2/s) and highest for K+ (10^-11–10^-12 cm^2/s) [2]. The energy barriers for K+ and Rb+ diffusion, calculated using DFT methodology, appeared to be extremely low, less than 0.15 and 0.2 eV for K+ and Rb+, respectively [3]. Moreover, the full de/intercalation of K+ in KVPO4F occurs at the highest potential among Li+, Na+ and Rb+, exceeding 4.6 V vs K/K+, which sets up KVPO4F as the highest voltage cathode material for K-ion batteries known so far.

In this report, we will focus on our recent advancement on KTP-type fluoride-phosphates and highlight important structure-property relationships for this promising class of cathode materials for rechargeable batteries.

This work was supported by the Russian Science Foundation (grant № 18-73-00313).

References
Combined experimental and theoretical studies of non-covalent interactions using X-ray diffraction analysis and quantum chemical calculations

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Hydrogen, halogen and chalcogen bonds, π-stacking, anagostic, cation-/anion-π and metallophilic interactions are innovative topics in modern chemistry, drug design, polymers and material science [1]. These non-covalent interactions are efficiently used as a tool in crystal engineering and in supramolecular organization.

Our research group (http://www.chem.spbu.ru/ptchem.html) applied combined experimental (e.g., XRD, NMR, IR) and theoretical (e.g., QTAIM, NBO, CDA) techniques for systematic study of various types of non-covalent interactions in different supramolecular systems based on organic, inorganic, and organometallic compounds. We are performing a quantitative estimation of appropriate bonding energies and elucidating influence of crystal packing effects on the geometric parameters of these systems. In addition, we are studying the relative stability of different isomers, composition and energies of molecular orbitals, charge distribution, vibrational frequencies, conformational transitions and rotation barriers of functional groups, elementary reaction steps and their driving forces, thermodynamic and kinetic factors. We are searching various correlations between theoretically calculated and experimentally observed parameters (e.g., bonds lengths, luminescence, conductivity, magnetism, and stability).

The obtained results are potentially useful for biochemistry (understanding the nature of proteins folding), medicine (synthesis of antibacterial, antiviral, and antitumor drugs), chemical industry and technology (catalysis of cross-coupling and multicomponent reactions), materials science (design of smart materials with valuable electronic, thermal, magnetic and optical parameters).

For recent representative publication of our research group, see [2–5].

I am grateful to the Russian Foundation for Basic Research for supporting my research within the framework of Project 16-33-60063.

References
Crucial role of water in the reactivity of a chiral NNO type copper(II) coordination polymers in the asymmetric Henry reaction

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To date the copper(II) coordination polymers (CPs) are very attractive class of heterogeneous catalysts.1 Chiral copper(II) CPs were also used as catalysts for asymmetric reactions.1 In seminal works it was shown that the addition of some amount of water is crucial for the reactivity of the catalyst, however there was no clear explanation about the role of water in the reaction.2

Herein we report the synthesis and characterization of chiral copper(II) CPs based on Schiff bases of (S)-2-aminomethylpyrrolidine and salicylaldehyde derivatives including both Lewis and Bronsted acid/basic functions (Figure). In addition, their application as catalysts in enantioselective Henry reaction was detailed (Figure).3 It was demonstrated that the water molecules play a crucial role in the reactivity of CPs in the enantioselective Henry reaction with up to 82% ee. The mechanism of the reaction was kinetically studied and shown to involve two Cu-complexes, acting in concert with both Cu-ions and NH-centers activating the substrates. The bridging OAc-ion functioned as the basic group, deprotonating nitromethane molecules. The step was found to be the rate-limiting in the reaction with the observed kinetic isotope effect equal (KIE) 6.4.4 We have showed that, at least, some copper(II) complexes derived from tridentate complexes become real catalysts only in the presence of water in solution. Their activity may vary within several orders of magnitude and water presence may become a crucial feature of the catalysis by copper(II) complexes.

Figure. The X-ray structure of chiral copper(II) CP and Henry reaction.

This work was supported by the Russian Science Foundation (RSF grant 18-73-00257).

References
Intermolecular complexes of macrocyclic copper(I) and silver(I) pyrazolates with Lewis bases: comparison of structures in the solution and in the crystal

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Complexes of coinage metal ions with fluorinated pyrazolates and their chemistry has recently attracted strong attention because of their interesting luminescence properties, acid/base chemistry and ability to form supramolecular aggregates through metallophilic interactions. The trinuclear metal pyrazolates are studied most often due to their planar structure that determines their photophysical properties, which, in turn, depend on temperature and solvent.

Our contribution to the chemistry of the trinuclear macrocyclic copper(I) and silver(I) pyrazolates is the investigation of their intermolecular interactions with bases of different nature in solution and succeeding transition to the solid state. Here we will analyze the data acquired on the host-guest complexes between the copper(I) and silver(I) macrocyclic pyrazolates and a wide range of organic and organometallic bases possessing hydride, halide, carbonyl and p-electronic ligands. Investigations of complexes compositions and their thermodynamic parameters (formation constants, $\Delta H^\circ$, $\Delta S^\circ$) in solution were carried out using IR, NMR, UV–vis spectroscopy in a wide range of temperature (200–290 K). These studies also take into account a competition between different basic sites of the guest and selectivity of the macrocycles complexation with basic centers of certain types.

Peculiar features of crystal packing are deduced for intermolecular adducts involving cyclic trinuclear metal pyrazolates and bases of different types. The influence of complexes formation and their crystal packing on the macrocycles properties will be discussed. This analysis shows how the information on the complexes structure and stability in solution can be used to predict and control the supramolecular architecture in the solid state.

This work was partially supported by Russian Science Foundation (grant № 17-73-10369) and “RUDN University Program 5-100”.

References
Non-covalent interactions in the reactions of catalytic olefination

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In our previous studies, by the reaction of the catalytic olefination of N-substituted hydrazones of a series of aldehydes with CCl\textsubscript{4} in the presence of CuCl, the corresponding derivatives of 4,4-dichloro-1,2-diazobuta-1,3-diene were obtained in one step [1]. Given the above, catalytic olefination reactions based on hydrazones, obtained by reaction of 4-(dimethylamine)benzaldehyde with 4-methylphenyl hydrazine and 4-cyano-phenylhydrazine were carried out.

\[ \text{H}_3\text{C}-\text{N}^+\text{C}(\text{CH}_3)=\text{N}^+\text{C}(\text{CH}_3)-\text{R} \quad \text{CCl}_4, \text{CuCl} (1\%) \quad \text{TMEDA} (2.5 \text{ eq.}) \quad \text{DMSO, rt.} \]

It was found that, when COR of (E)-4-(2-(4(dimethylamine)benzylidene)hydrazinyl)benzonitrile, obtained on the basis of 4-cyano-phenylhydrazine, along with the product of catalytic olefination 2 (10\%) - (E)-4-((2,2-dichloro-1-(4-(dimethylamine)phenyl)vinyl)diazenyl) benzonitrile, the compound 3 (65\%) - ((E)-4-(((1-(4-cyanophenyl)-1)-2-(4-(dimethylamino)benzyl)hydrazinyl)4-(dimethylamino)phenyl)methyl)diazenyl)benzonitrile was obtained. The structure of compounds was confirmed by X-ray diffraction.

In contrast to previous reactions based on phenylhydrazone, the reason for the formation of dimerization product 3 is probably due to the difference in electron density in the benzene rings of (E) -4-(2-(4-(dimethylamine)benzylidene)hydrazinyl)benzonitrile. Thus, as a result of non-covalent interactions between benzene rings, intermolecular distances decrease, which creates the prerequisites for crosslinking of hydrazone molecules. Thus, the variation in the p-positions of benzene rings by electron-donor or electron-acceptor substitutions significantly expands the synthetic capabilities of the COR.
The Struchkov Prize session (laureates and young scientists)

Structure and properties of new push-pull molecules

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For several decades attention to structure and properties of push-pull systems with donor and acceptor groups connected with pi-conjugated bridge was attracted due to their potential nonlinear optical properties [1-3] and corresponding applications such as terahertz (THz) generation and detection [4] and microresonator filters and modulators [5]. Relatively recently emerged several publications devoted to biological applications of push-pull molecules as near infrared (NIR) probes for non-invasive detection of accumulation of beta-amyloid plaques in the brain related to Alzheimer disease [6].

Here we present structural studies of two series of push-pull molecules: homologues of 4-(4-dimethylamino)-dicyanovinylbenzene and organic chromophores with (3-cyano-5,5-dimethyl-2(5H)-furanylidene)malononitrile (so called tricyanofuran, TCF) as an acceptor group with the polyene bridges containing 1-5 -C=C- bonds (Scheme 1).

Properties of these materials are discussed based on information obtained on their structure, results of quantum chemical computations and spectroscopic data.

References
Substituents effect on the crystal packing and solid state transformations of phosphorylated acetothiosemicarbazides

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Polymorphism of crystals is a common phenomenon among the crystals of organic compounds and defined of the conformational flexibility of molecular fragments, different packing in the crystals and the type of interaction of origin compound with solvent molecules during crystallization. The behavior of the molecule during crystallization can not always be predicted, but in rare cases of "smart" crystallization or co-crystallization, the geometry of the molecule can change significantly to adjusting to external conditions. Examples of such "smart" behavior among small organic molecules can be considered by the example of a new class of compounds - derivatives of fosenazide, a known drug.

Diphenylphosphorylacetic acid thiosemicarbazides were obtained by modification of fosenazid (diphenylphosphorylacetic acid hydrazide) by insertion of pharmacophore fragments, such as thiosemicarbazide moiety, that allows to expand the pharmacological properties [1].

![Diagram 1](image1)

Compound 1 is thiosemicarbazide with a symmetric terminal amine group. Individual crystalline forms of this compound and its solvates (with DMSO, methanol, ethanol, acetone) were obtained. It was established that the molecule of the compound 1 essentially changes its conformation and adjusts it for the corresponding solvate molecule to achieve optimal crystal packing and packing density. However, the single crystal and polycrystalline solvates obtained are not sufficiently stable and within a few days a solid-phase transition to the original crystalline form takes place, and the conformation of the molecule returns to its original state. For all substances the “solid-solid” transitions were observed and confirmed by the X-Ray powder diffraction method and by time-resolved experiments for some of them. It was found that these transformations are reversible and the saturation of the polycrystalline unsolvated form with solvent vapors leads to the solid-state transition and to the corresponding crystals formation. This conformational flexibility of the molecule 1, which is observed in crystalline solvates, allows to hope for the possibility of obtaining new polymorphs with a change in temperature. These opportunities are discussed.

The geometry of the molecule of compound 2 in the crystal is due to two factors - a
phenyl substituent, as an “anchor”, and an intramolecular hydrogen bond that stabilizes this conformation. As a result, the molecule keeps its geometry, regardless of influence of solvent molecules. The only change in the geometry of the molecule is the possibility of rotation of the phenyl substituents. These rotations introduce insignificant changes in the geometry of the molecule itself, but, as was founded, give the possibility to obtain polymorphic modifications with different unit cell symmetry and volumes. For this compound two polymorphic modifications and two solvates (with DMSO and methanol) were obtained. There is no strong changes in the geometry of the molecule are observed in the case of the formation of crystal solvates. Solvates have the similar type localization in the crystals – in the 0D-voids and this prevents the solid-state phase transformations.

Thus, variation of the type of the substituent in the thiosemicarbazide moiety of the molecule of title compound makes it possible meaningly obtain molecular systems capable of programatically uptake and isolation of solvent molecules.

This work was supported by the Russian Foundation for Basic Research (grant № 18-33-00228).

References
The effect of Fe\(^{3+}\) and Zr\(^{4+}\) on the structural and catalytic properties of BIMEVOX


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Complex oxide materials belong to the Solid electrolytes (SELs) class with anionic (oxygen-ionic) conductivity type and have perovskite-like structures (Fig.) [1,2]. These oxides are based on the bismuth vanadate \(\text{Bi}_4\text{V}_2\text{O}_{11-\delta}\) which consists of alternating layers of \((\text{B}_{2}\text{O}_2)_{n}^{2+}\) and \((\text{VO}_{3.5-0.5+y})_{n}^{2-}\), with Bi\(^{3+}\) cations in square pyramidal coordination, while V\(^{5+}\) cations in octahedral coordination with oxygen. The incorporation of vacancies in the vanadate layer may decrease coordination numbers of vanadium cations from 6 to 4 or 5. It is well known that replacement of vanadium anions affects the structural type of perovskite and the formation of structural defects responsible for oxygen mobility in the crystal lattice, which is reflected in their transport properties [3]. The \(\gamma\)-phase stabilized by doping ions has high conductivity and the value of activation energy of conduction is the lowest. Introduction of dopant ions creates a large family of complex vanadate \(\text{Bi}_4\text{V}_{2-2x}\text{M}_{2x}\text{O}_{11-\delta}\) (BIMEVOX) [4]. The possibility of modification in the perovskite structure of bismuth vanadate by 3d-metal ions allows their usage as heterogeneous catalysts in the acid-base and redox reactions.

The aim of this work is to study the effect of Fe\(^{3+}\) and Zr\(^{4+}\) cations on the structural and catalytic properties of BIMEVOX.

<table>
<thead>
<tr>
<th>(\text{M}^{n+})</th>
<th>(\text{N}_\text{M})</th>
<th>Unit-cell parameters (a, \text{Å})</th>
<th>(b, \text{Å})</th>
<th>(c, \text{Å})</th>
<th>(V, \text{Å}^3)</th>
<th>(E_{\sigma}, \text{eV})</th>
<th>(E_{\text{a}}^{\text{eoin}}, \text{kJ/mol})</th>
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<tbody>
<tr>
<td>Fe(^{3+})</td>
<td>1</td>
<td>5.51</td>
<td>5.58</td>
<td>15.28</td>
<td>469.0</td>
<td>0.96</td>
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<tr>
<td></td>
<td>2</td>
<td>5.59</td>
<td>5.55</td>
<td>15.40</td>
<td>473.5</td>
<td>0.79</td>
<td>32</td>
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<tr>
<td></td>
<td>3</td>
<td>5.53</td>
<td>15.43</td>
<td>471.9</td>
<td>0.68</td>
<td>45</td>
<td></td>
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<tr>
<td>Zr(^{4+})</td>
<td>4</td>
<td>5.54</td>
<td>5.60</td>
<td>15.34</td>
<td>475.9</td>
<td>1.24</td>
<td>103</td>
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<td>5</td>
<td>5.55</td>
<td>5.59</td>
<td>15.42</td>
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<td>0.78</td>
<td>97</td>
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<tr>
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<td>6</td>
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<td>5.59</td>
<td>15.44</td>
<td>479.9</td>
<td>0.80</td>
<td>83</td>
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</table>

Ceramic solid solutions \(\text{Bi}_4\text{V}_{2-2x}\text{M}_{2x}\text{O}_{11-\delta}\), where \(x_M = 0.04\) (1), 0.10 (2), or 0.15 (3) (BIFEVOX) and 0.05 (4), 0.10 (5), or 0.15 (6) (BIZRVOX), were obtained by solid phase synthesis and characterized in detail [4]. X-Ray diffraction analysis (XRD) was used to determine the phase composition and crystal lattice parameters. Single-phase samples were obtained for the entire BIMEVOX line: sample 1, 4 represented the monoclinic modification (\(\alpha\)-phase), sample 2, 5 – rhombic modification (\(\beta\)-phase), and sample 3, 6 – tetragonal modification (\(\gamma\)-phase). The unit cell volume increases in all solid solutions in accordance with the ionic radius of the dopant cations. The results agree well with that published for BIZRVOX and BIFEVOX compositions [5].
The catalytic conversions of isobutanol were studied in the temperature range of 250–400°C in a flow-through unit coupled with a chromatographic analyzer (helium as the carrier gas, a flame ionization detector, a column with Porapak Q).

According to Table, the relationship between the dopant ion content and the activation energy of alcohol dehydrogenation is linear for all series of samples. The value activation energies for aldehyde formation increase linearly with an increase in Fe³⁺ content and decrease in Zr⁴⁺ content, hence 3d-metal ions is involved in the catalytically active site where an metal ions can be coordinated with a vanadium ion through oxygen, M–O–V. The substrate–catalyst bond strengths depends on the state of metal ion in M–O–V. As x in Bi₄V₂₋ₓM₂ₓO₁₁−δ increases, the coordination number of ions in the vanadium(+5) sublattice decreases and oxygen deficiency increases.

The correlations between $E_a^{\text{C=O}}$ with the charge of the incorporated ion Fe(3+) → Zr(4+) and the activation energy of conductivity $E_a^{\sigma}$ are linear for the highly conductive γ modification of all the catalysts. This result can be explained by the change in the state of oxygen as a result of the decrease in the dopant ion charge in the series Zr⁴⁺→Fe³⁺. For redox reactions, a decrease in the charge of the M³⁺ cation increases the chemical potential of electrons and facilitates their donation and hence the reoxidation stage of the active ion, as indicated by the decreased activation energy of dehydrogenation. In addition, the reduction of M³⁺ under the action of the reaction medium during alcohol dehydrogenation leads to an increase in the catalytic activity.

Thus, iron- and zirconium-containing bismuth vanadates showed high activity of the tetragonal phase in catalytic conversion of isobutanol and sensitivity of reactions to changes in the conductive properties of perovskite. It should be noted that the value of the reaction activation energy on the content of the incorporated ion have different directions for Fe- and Zr-containing bismuth vanadates.

The reported study was funded by RFBR according to the research project №18-33-00928

References
Dehydrogenation of propane on catalytic systems based vanadium salts

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Petrochemical industry is of great importance in the life of modern man. Every day we are confronted with goods, the production of which is somehow connected with oil and its components. For example, after processing and purifying natural gas, gases are obtained, including propane, which is actively used in various spheres of human life. Based on this, an analysis was made of the relevance of propane dehydrogenation, in order to ensure that interest in these areas increases every year. In comparison with the 90th years, at the time of 2017, the relevance of dehydrogenation processes has increased significantly.

Investigations of catalytic activity were conducted at atmospheric pressure in catalytic fluid cracking unit with a quartz reactor, loading of the catalyst was equal to 0.05 g. As initial raw materials propane of high purity (99.98 mass%) was used. Flow velocity was equal to 1.25 ml/s. Analysis of the reaction products was carried out by means of a chromatograph Crystal 2000M.

The parameters of the porous structure of the samples were determined from nitrogen vapors adsorption isotherms at 77 K, measured by means of a high-vacuum volumetric equipment ASAP-2020 MP Micromeritics USA. (Table 1).

<table>
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<tr>
<th>Assay</th>
<th>BET</th>
<th>( W_{\text{BJH}} ) cm(^3)/g des/ads</th>
<th>( 2_{\text{B}} ) ( \text{nm} ) des/ads</th>
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<td>LaVO(_3)</td>
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<td>0,047/0,045</td>
<td>13,2/13,3</td>
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<td>LuVO(_3)</td>
<td>2,3</td>
<td>0,047/0,045</td>
<td>15,2/15,3</td>
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</table>

Figure 1. Dependence of selectivity on temperature

Catalytic systems in which vanadium is in the oxidation state of +5 and +3 were considered.
In the case of a perovskite-like structure, the dehydrogenation reaction with the desired product is predominantly propylene (Figure 1).

Simultaneous fall in the formation of industrially important products, not a decrease in education, but also an increase in activity - is very strange. Therefore, for the study of heavier hydrocarbons, an analysis of the reaction products was carried out using the chromatography mass spectrometry assay.

Indeed, the drop in the yield of ethylene and propylene causes the formats from carbon steel from C₁₂ to C₁₇, but excluding C₁₄, C₁₆. In this case, the use of lutetium vanadite leads to the formation of predominantly hydrocarbons of the ethylene homologous series.

At the same time, during the analysis, a different degree of carbon-carbon content of the samples from vanadites of the REM was observed.

The catalytic activity of the vanadites catalyst was quite stable. Namely, at temperatures up to 873 K, the catalyst exhibited the activity during ~ 150 hours. In the temperature range of 873-1023 K, the complete loss of activity occurred after 100 hours; above 1023 K the activity disappeared after 50 hours.

References
New approaches for the reductive formation of the C-N bond

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Development of new approaches for the formation of C-N bonds is of great importance since many nitrogen containing compounds have interesting and diverse biological activities. Despite great advancements in the field, discovering new atom-economic and selective processes is required. Apart from that it is highly desirable to develop methods that are based on the use of cheap and easily available reagents.

Carbon monoxide is produced as side product in steel manufacturing process and requires utilization. Normally, to prevent its release to the atmosphere, carbon monoxide is oxidized further to carbon dioxide. But carbon monoxide is very powerful reducing agent and instead of simple combustion it can be used in synthetically valuable processes. It was previously shown by our group that carbon monoxide can be used as reducing agent in the reductive amination [1]. Important feature of this protocol is the lack of external hydrogen source in the system, which leads to the unique selectivity since many functional groups that are sensible to hydrogen and hydrides, should be stable under this conditions.

In attempt of demonstration of the practical importance of this approach we were able to synthesize family of organocatalysts based on 1,2-cyclohexanediamine. These compounds proved to be active catalysts for enantioselective synthesis of alcohols[2].

![Reductive formation of C-N bond](image)

We also investigated reductive addition of amines to cyclopropyl ketones. It was shown that main products of these reactions are cyclopropyl amine and pyrrolidine. As the result of this study orthogonal methods of synthesis of both products was developed [3].

![Reductive addition of amines to cyclopropyl ketones](image)
Amides are known for their low nucleophilicity. Still we have shown that at certain conditions they can be employed in reductive addition to carbonyl group.

\[ R^1\text{H} + R^2\text{CONH}_2 \xrightarrow{1 \text{ mol} \% \text{Rh/C}_{\text{matrix}} 5 \text{ wt} \%} \text{CO (40 bar)} \rightarrow R^2\text{NH}_2\text{COR}^1 \]

On of the disadvantages of the method based on the use of carbon monoxide is relatively harsh conditions (30-90 bar of CO and 130-180°C). But recently we were able to develop new catalytic system based on the cyclobutadiene rhodium complex which allowed to carry out this reaction in considerably milder conditions [4].

\[ \text{Et} \begin{array}{c} \text{Et} \\ \text{Et} \\ \text{Rh} \\ \text{Et} \end{array} + R^1\text{H} + R^2\text{NH}_2 + \text{CO (1-3 bar)} \xrightarrow{(1-2 \text{ mol} \%)} \text{EtOH, 90 °C, 12-24 h} \rightarrow R^3\text{NR}^4 + \text{CO}_2 \]

This work was supported by the Grant for Young Scientists (No. MK-520.2017.3) and RUDN University Program “5-100”.

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Научное издание

II СТРУЧКОВСКИЕ ЧТЕНИЯ

МЕЖДУНАРОДНАЯ КОНФЕРЕНЦИЯ
ПО КРИСТАЛЛОХИМИИ
И СТРУКТУРНОЙ БИОЛОГИИ

Издание подготовлено в авторской редакции

Технический редактор Н.А. Ясько
Дизайн обложки Ю.Н. Ефремова
About Project "5-100"

Project of Competitiveness Enhancement of Leading Russian Universities among Global Research and Education Centers

The goal of Project 5-100 is to maximize the competitive position of a group of leading Russian universities in the global research and education market. The work on the project, scheduled for 7 years, started in May 2013 in accordance with the provisions of the Decree № 599 of the President of the Russian Federation "On measures to implement the state policy in education and science." Institutions of higher education to receive the state support will be determined on a competitive basis.

**RUDN University in the Project "5-100"**

In 2015, Peoples' Friendship University of Russia (PFUR - RUDN University) was among the competition winners to receive the state support within the 5-100 Project framework.

The University presented its Action Plan (Roadmap) for implementing the RUDN competitiveness enhancement program at the meeting of the Council on Competitiveness Enhancement of Leading Russian Universities among Global Research and Education Centers on 18 March, 2016.

The University has embarked on a major shift to a research-oriented model and considers as its high priorities boosting international cooperation, building scientific capacity, training PhD students and postdoctoral fellows (including the continuing professional development framework) for the world developing and emerging economies through advanced science achievements and technologies. The RUDN unique profile is determined by the international exposure of its research and education activities, as well as by the RUDN focus on countries with developing and emerging economies in all regions of the world.
General information about RFBR

INTRODUCTION

Russian Foundation for Basic Research (RFBR) was created by decree #426 of the President of the Russian Federation “On urgent measures for preserving scientific and technological potential of the Russian Federation” and is a self-governed state nonprofit organisation in the form of a federal organisation controlled by the Government of the Russian Federation. Being a representative of the state, the Foundation provides targeted diversified support to leading groups of scientists regardless of the organisation they represent. Support of initiative scientific research in all the principal directions of fundamental science is carried out strictly on a competition basis after a comprehensive evaluation. Decisions on whether to support or to decline projects by RFBR are taken by the scientific community itself represented by the most authoritative and actively working scientists – members of the Foundation expert panels. This is a completely new organisational form for Russian science, which has opened to scientists broader possibilities for creative self-expression and allowed them to choose the subjects of research on their own, create research groups and concentrate funds in the most promising research directions. The Foundation carries out its activities in accordance with the Constitution of the Russian Federation, federal laws, decrees and directives of the President of the Russian Federation, decrees and directives of the Government of the Russian Federation, and its charter. In its chartered activities RFBR relies on the following principles:
- openness - announcements of competitions and their results, the Foundation's decisions on financing projects and events, and also other materials are published in paper editions and online;
- targeted financing of groups of scientists (and not organisations as a whole), which perform projects approved by the Foundation experts;
- giving the scientists freedom of choice of subjects in all fields of natural sciences and humanities, of methods of conducting fundamental research, and of creating research groups.

The Foundation sees its mission in developing the powerful intellectual potential of our country, which is becoming a key element in the development of Russia.

RFBR COMPETITIONS

The main task of the Foundation is to select on the basis of competitions the best scientific projects among those that were submitted to the Foundation by scientists in an initiative order and subsequently to support the selected projects organisationally and financially. Scientific directions supported by the Foundation are:
- mathematics, mechanics, and information technology;
- physics and astronomy;
- chemistry and studies of materials;
- biology and medical science;
- Earth science;
- humanities and social sciences;
- information technology and computer systems;
- fundamental basics of engineering sciences.

Overall during the year the Foundation financed 15 types of competitions and two programs:
- competition for initiative scientific projects carried out by small (up to ten persons) groups of scientists or individual researchers;
- competition for projects of writing analytical reviews;
- competition for projects of developing the material and technical base of scientific research;
- competition for projects of organising Russian and international scientific events on Russian territory;
- competition for publishing projects;
- competition for projects of participation of Russian scientists in international scientific events abroad;
- competition for projects of organising expeditions (and field trips);
- competitions for international projects;
- competition for projects in the program “Mobility of young scientists”;
- competition for projects of oriented fundamental research on interdisciplinary subjects of current interest;
- competition for projects of oriented fundamental research;
- joint competition with RF organisations;
- competition for regional projects;
- competitions for projects with CIS countries;
- competition for popular scientific articles by RFBR grant holders;
- competition for projects of urgent research support;
- program “Electronic Scientific Library”.

EXPERTISE
Expertise is a principal element of the Foundation's activity. All RFBR decisions to support projects are made only as a result of expertise. RFBR became the first organisation in Russia using this practice. Each application to RFBR goes through an independent multistage expert evaluation in every field of knowledge.

Each year the Foundation engages about 3,000 experts who conduct 65-70 thousand evaluations. RFBR uses modern information technology widely, which allows to conduct 75 to 100% of expert evaluations online. This has allowed to increase the number of experts from the regions of Russia significantly. RFBR is an active participant in international scientific cooperation.

RFBR FINANCING
According to the Government's decision, beginning with 1997, 6% of funding in the federal budget assigned to financing fundamental research and facilitating scientific and technical progress is sent to RFBR each year.

RFBR grants are given as subsidies to legal entities for targeted use without the need to return the funds.

The allocation of funds between different kinds of RFBR activities is approved each year by the Foundation Board. The principal part of the Foundation's funds (over 70%) is directed towards financing initiative scientific projects performed by small groups of scientists (up to ten persons) or individual scientists. An initiative project can be financed for three years at most.

More information you can find here  http://www.rfbr.ru/rffi/eng
Chemistry—A European Journal is a truly international journal with top quality contributions (2017 ISI Impact Factor: 5.16). It publishes a wide range of outstanding Reviews, Minireviews, Concepts, Full Papers, and Communications from all areas of chemistry and related fields.

Based in Europe, Chemistry—A European Journal provides an excellent platform for increasing the visibility of European chemistry, as well as for featuring the best research from authors from around the world. All manuscripts are peer-reviewed, and electronic processing ensures accurate reproduction of text and data, plus short publication times. The Concepts section provides nonspecialist readers with a useful conceptual guide to unfamiliar areas and experts with new angles on familiar problems.


Chemistry—A European Journal is a multicultural team consisting of 13 editors, each of which has a PhD in chemistry. Haymo Ross, PhD (Editor) studied chemistry at the Technische Universität Braunschweig and the Universität Kiel where he received a doctoral degree in organic chemistry in 1997. In the same year, he joined Wiley-VCH as a member of the Angewandte Chemie editorial team. From 2000 to 2017, he was a Deputy Editor of Angewandte Chemie and from 2003 to 2017 he was the Editor-in-Chief of the European Journal of Organic Chemistry (EurJOC). He joined Chemistry—A European Journal as Neville Compton's successor in October 2017. Ganna Lyashenko, PhD (Senior Associate Editor) will be giving a plenary lecture on Chemistry—A European Journal editorial standards on Tuesday, November 13th. In this lecture, Ganna will describe what goes on in the editorial office; give advice on how to make your submission successful; explain the peer-review process, referee selection, and decision making; and give useful advice on how to improve your writing skills. Ganna studied chemistry at the National Taras Shevchenko University (Kiev, Ukraine) and obtained her PhD in bioinorganic chemistry in 2008 from the Karl-Franzens-Universität Graz (Austria). Subsequently, she undertook postdoctoral research at the University of California in Riverside. She joined Chemistry—A European Journal team in August 2011.