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Guest Editorial: Main Group Chemistry in Russia

Dear Colleagues!
This special issue of *Heteroatom Chemistry* is dedicated to the latest investigations in the heteroatom chemistry field being undertaken in Russia.

Included are some of the best current contributions of Russian chemists to the study of main group chemistry and the work of all key institutes in different regions of Russia.

As a result, the issue reviews works carried out at Moscow (M. V. Lomonosov Moscow State University and D. I. Mendeleev University of Chemical Technology), Chernogolovka (Institute of Physiologically Active Compounds of the Russian Academy of Sciences), Nizhny Novgorod (G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences), Kazan (A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Center of the Russian Academy of Sciences and A. M. Butlerov Chemical Institute at the Kazan State University), Rostov-on-Don (Institute of Physical and Organic Chemistry at the Rostov State University and Southern Research Center of the Russian Academy of Sciences), Ekaterinburg (Urals State Technical University and I. Ya. Postovsky Institute of Organic Synthesis of the Ural Branch of the Russian Academy of Science), and Irkutsk (A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences).

The reviews feature some principal directions that are being developed by the leading Russian specialists.

At the end of 1970s, Academician of RAS Mikhail G. Voronkov (Irkutsk Institute of Chemistry, Siberian Branch of RAS) discovered a new class of stable pentacoordinate organosilicon compounds having $O \rightarrow Si$ intramolecular bond. The compounds were called dragonoids because their structure is the famous alchemists' symbol, namely, a dragon devouring his tail. The synthesis, structure, and reactivity of compounds having the $OCSiF_3$ coordinate framework have been extensively studied and reviewed. Recently, a first representative of dragonoids, *N*-(trifluorosilylmethyl), a derivative of phthalimide having two donating carbonyl group, was prepared. X-ray electron diffraction analysis supported the existence of the intramolecular $O \rightarrow Si$ hypervalent bond between the silicon atom and only one of the two carbonyl oxygen atoms. The review article "Pentacoordinate Organosilicon Compounds. Molecular Structure and Stereodynamic Behavior of (Trifluorosilylmethyl) Succinimide and (Trifluorosilylmethyl) glutarimide" by M. G. Voronkov and coauthors includes the synthesis and study of the structure of new related compounds to elucidate the effect of the donor—the carbonyl group of the imides—on their ability to form $O \rightarrow Si$ bonds.

The study in the field of bioinorganic chemistry is conducted at the Organic Chemistry Department of the M. V. Lomonosov Moscow State University ("Organotins-promoted Peroxidation of Unsaturated Fatty Acids: A New Antioxidative Scavenger for Promoters" by Prof. Elena R. Milaeva and coauthors). It is oriented toward the interpretation of biomolecular mechanisms of organometallics-mediated oxidative stress in living organisms. The principal idea is the excessive free radical formation due to the hemolytic cleavage of C—M bond, which is implicated as one of the various causative factors responsible for the toxic cell damage associated with organotin compounds R_nSnX_{4-n}. The experiments also focus on the application of antioxidants inhibiting the pro-oxidative activity of organotins. A new efficient route to prevent the pro-oxidative impact of organotins is proposed, using the free base porphyrin-containing antioxidative phenolic groups [*meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl) porphyrin] as an antioxidative scavenger for metal.

Academician of RAS Gleb A. Abakumov and his colleagues (Nizhny Novgorod, G. A Razuvaev Institute of Organometallic Chemistry of RAS) in the review "The Reaction of 3,6-Di-*tert*-butyl-*O*-Benzoquinone with Tin Amalgam. Synthesis and Structure of Tin Catecholato Complexes" report the synthesis of various tin catecholate complexes $Cat_2Sn{\cdot}L_n$ (Cat = 3,6-di-*tert*-butylcatechol, L = different donor ligands, $n = 1,2$) by the direct reaction between tin amalgam and 3,6-di-*tert*-butyl-*O*-benzoquinone (3,6-Q) in different solvents and following ligand exchange. The chemistry of metal complexes containing redox-active ligands is a perspective line of investigation in modern coordination and organometallic chemistry. *o*-Quinones, *o*-iminoquinones, and α-diimines are the most abundant redox-active ligands. Nontrasition metals can form complexes with different reduced types of above-mentioned ligands, and these ligands once bound to the metal can receive and release electrons and protons, giving rise to a quite specific reactivity of such complexes toward inorganic and organic substrates (radicals, alkyl halides, nitriles, ketones, molecular oxygen, and so on). The paper is given up to the synthesis of tin complexes on the base of sterically hindered catecholate ligand.

The review "Solvent-Free Alkali and Alkaline Earth Metal Complexes of Diimine Ligands" by Prof. Igor L. Fedushkin and coauthors, who also are working at the G. A Razuvaev Institute of Organometallic Chemistry of RAS, concerns earth metal complexes. Main group metal complexes with ligands possessing a variable "oxidation state" might be a new class of reagents for organic synthesis. Such ligands may act as neutral, radical-anionic, dianionic etc. in the metal complexes and may change their "oxidation state" under attack from different substrates; thus, they act either as an electron sink or as a tank. However, it is required, that these ligands stay coordinated to metal under electron transfer.

Chemistry of phosphorus and its organic and organoelemental compounds as the basis for the development of new substances, materials, and technologies is the oldest research field in Russia and is considered as a particularly traditional research direction at the Kazan State University and the A. E. Arbuzov Institute of Kazan Scientific Center of RAS. Indeed, organometallic chemistry is quickly developing into a new direction at the A. E. Arbuzov Institute. Unusual poly- and heteropolynuclear compounds, as well as paramagnetic complexes of transition metals with free-radical fragments, are synthesized here. Coordination compounds with unusual geometry of transition metal environment are obtained; compounds with phosphorus-metal labile "bent" bonds and optically active metal complexes with chiral ligands are synthesized.

The paper "Synthesis, Structure and Transition Metal Complexes of Amphiphilic 1,5-Diaza-3,7-diphosphacyclooctanes" by Prof. Andrey A. Karasik and coauthors (A. E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Center of RAS) explains the synthesis, molecular structure, and transition metal complexes of a number of novel water-soluble cyclic bisphosphines with bulky substituents on the phosphorus atoms based on the condensation reaction of 5-aminoisophthalic acid or the sodium salt of sulfanilic acid with bis(hydroxymethyl)arylphosphines (aryl = phenyl (Ph), mesityl (Mes), and 2,4,6-triisopropylphenyl (Tipp)).

On the basis of systematic investigations, the main regularities concerning synthesis, structure, and reactivity of carboxylate phosphabetaines—phosphorus analogs of organic amino acids—are considered and analyzed in the paper "The Main Regularities in Synthesis, Structure, and Reactivity of Carboxylate Phosphabetaines and Their Derivatives" by Prof. Valery I. Galkin and coworkers (A. M. Butlerov Chemical Institute at Kazan State University). A wide series of phosphabetaines has been obtained in reactions of tertiary phosphines with unsaturated mono- and dicarboxylic acids, and also with their derivatives—esters and amides. By a complex of experimental and theoretical methods, it is shown that the thermodynamic stability of carboxylate phosphabetaines in an essential degree depends on the structure of initial phosphine and carboxylic acid. In some cases, the reaction between them carries the expressed equilibrium character. On the other hand, for a number of synthesized betaines, it is reliably established that they exist in equilibrium with isomeric phosphoranes. The extremely important condition for stabilization of phosphabetaine structures is the presence of protonodonor reagents, which are included in their crystal lattice. In a series of symmetrically substituted derivatives, the interesting phenomenon of phosphorotropy of phosphonium group is established. The reactivity of phosphabetaines in reactions with electrofilic reagents (haloid alkyls, acyls, isocyanates, and corbodiimides) has been investigated. The majority of key structures are confirmed by the direct X-ray method.

The review "Phosphonoallenes for Building organophosphorus derivatives" by Prof. Valery K. Brel (Institute of Physiologically Active Compounds of RAS, Chernogolovka) deals with new approaches to polyfunctional phosphonoallennes as well as synthetically useful reactions of this class of phosphororganic compounds for design of various heterocyclic phosphonate, new phosphonolipids, and phosphononucleotides.

A new approach to the synthesis of unsaturated and high unsaturated organylchalcogenides developed on the basis of divinylsulfide, divinylselenide, and divinyltelluride was discussed in the review "Synthesis and Reactivity of Alkyl, Aromatic, and Heteroaromatic Polyfunctional Vinylsulfides on the Basis of Divinylsulfide—A Promising Vinylthiogroup Synthone" by Dr. Galina M. Gavrilova and Prof. Svetlana V. Amosova (A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of RAS). This promising approach has made possible the preparation of polyfunctional vinylsulfanyl derivatives of perfluoro(chloro)benzenes, which are applied for the design of functionalized N-, O-, and S-containing heterocyclic systems. The structures of the new compounds were confirmed by IR, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

The review "Fluorinated Benzazoles and Benzazines" prepared by the Ural group of organic chemists headed by Academician of RAS Valery N. Charushin (I. Ya. Postovsky Institute of Organic Synthesis of the Ural Branch of RAS) is dedicated to the chemistry of fluorinated benzazoles and benzazines. Heterocyclic compounds and fluorine chemistry are two topics that have traditionally been the focus of attention of the Ural chemists for many decades, and the review reflects their recent results in this promising area of heteroatom chemistry. The authors outline synthetic approaches to a variety of derivatives in the series of benzimidazoles, benzofuroxanes, benzotriazoles, quinolines, quinoxalines, quinozolines, and other heterocyclic systems bearing one, two, or several fluorine atoms. Different features of tautomerism, cyclization, and ring transformation reactions, as well as the displacement of fluorine atoms by action of nucleophiles, are considered in this review. These are also of interest to organic chemists who are working in both academic and pharmaceutical research fields.

The organic chemistry of polyvalent iodine compounds has unprecedented explosive development during the last few years. The review "Polyvalent Iodine in Organic Chemistry (Recent Developments 2002–2005)" by Nikolay S Zefirov of M. V. Lomonosov Moscow State University, Academician of RAS, covers the recent developments during the period from 2002 to 2005. It consists of eight parts: (1) hypervalent iodine reagents as mild oxidants, (2) the addition of hypervalent iodine compounds to alkenes, (3) fluorination of organic compounds by hypervalent iodine compounds, (4) some new reaction of nucleophilic substitution of hypervalent iodine moiety, (5) iodine(III) compounds as a source of nitrene and carbene moiety, (6) novel and new iodine(III) compounds and methods of their preparation, (7) polyvalent iodine compounds in the synthesis of natural compounds, and (8) miscellaneous.

Quantum chemistry methods for the investigation of heteroatom chemistry objects are being actively used in Russia. The striking example of such kind of research is the paper "Sandwich Compounds with Central Hypercoordinate Carbon, Nitrogen, and Oxygen: A Quantum-Chemical Study" by Academician of RAS Vladimir I. Minkin and coauthors (Institute of Physical and Organic Chemistry at the Rostov State University, Southern Research Center of RAS). They report about calculations predicting stable structures of sandwich compounds with central carbon, nitrogen, and oxygen atoms surrounding lithium counter ions between three-membered $(BH)_3$ rings. The lithium counterions play a crucial role in the stabilization of these systems. The topological Bader analysis performed for these sandwich systems demonstrates that the central atom is linked to the ligands by nine bond paths and, consequently, should be regarded as a nine-coordinated atom. Such a coordination number of carbon is the highest for all known main-group organoelement compounds.

Quantitative analysis of bonding in the P_4 clusters was performed by the corresponding member of RAS Nataliya P. Tarasova and coauthors (D. I. Mendeleev University of Chemical Technology of Russia). Results are reported in"Quantitative Analysis of Bonding in the P_4 Clusters." Quantum-topological analysis based on the nonempirical quantum-chemical calculations of equilibrium P_4 clusters in different electronic states was performed, and changes in the geometric parameters at different electronic states of the equilibrium clusters of phosphorus and structures with the disrupting connection are traced. The P—P bond was quantitatively described.

I am grateful to my Russian colleagues for presenting their work for publication and sincerely appreciate the hard work of the Editorial Board. I hope that this issue will serve as an advertisement highlighting Russians' contributions to heteroatom chemistry and the promises they hold.

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