

## VISITING SESSION OF THE ACADEMY OF SCIENCES OF THE USSR

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A visiting session of the scientific counsels on inorganic chemistry of the Academy of Sciences of the USSR (AS USSR) and the Academy of Sciences of the Ukrainian SSR (AS Ukr. SSR) devoted to problems of bioinorganic chemistry was held at Kuban University (Krasnodar, September 19-24, 1976). The achievements were discussed, and future pathways for the development of bioinorganic chemistry in the USSR, which briefly can be reduced to the following, were projected: creation of models of biological systems and processes that model the action of metalloenzymes, vitamins, ionophores, substances that irreversibly add, transport, and activate oxygen and other gaseous molecules and ions; the synthesis of new bioinorganic (coordination and organometallic) preparations with expected chemotherapeutic action, particularly antitumor agents; the comprehensive physicochemical and medicobiological study of the properties of metal-containing biologically active natural substances and their synthetic analogs in order to establish the relationship between the fine (stereochemical and electronic) structure of bioinorganic systems and their physiological activity and the specific creation, on the basis of this, of new medicinal preparations, ionophoric compounds, and inhibitors of diverse physiological and industrial chemical-biological processes; the solution of applied problems of bioinorganic chemistry, particularly in connection with the problems of the protection of the environment from the action of harmful metals, the struggle with diseases of animal and plant organisms caused by disruption of metallometabolism, the utilization of the metal resources of the ocean, and the specific approach to new catalytic systems and biochemical processes (chemical bionics) that are of fundamental significance for the national economy.

Papers presented at the session showed that principal attention is being directed to heterocyclic compounds in the execution of research in all of the directions indicated above.

In a plenary paper the president of the organizing committee Academician K. B. Yatsimirskii ("Chemical models in bioinorganic chemistry") showed that mixed cobalt(II) complexes with imidazole or histidine and aliphatic amino acids model substances that add, transport, and activate molecular oxygen in aqueous solutions. It follows from a communication by D. M. Palade (Donetsk) that the phenanthroline-oxygen complex of divalent cobalt is an oxygen carrier. Imidazole systems, as well as pyridine and phenanthroline systems, play a most important role as components of metal complex catalysts that regulate the metabolism of active forms of folic acid and in autoxidative processes with the participation of dihydro- and tetrahydrofolic acids (M. E. Vol'pin, Moscow, Institute of Heteroorganic Compounds of the AS USSR). A study of these processes enabled Vol'pin and co-workers to create a model of the respiratory network and to show that the most effective catalysts in the indicated processes are square cobalt and copper metal chelates with axially coordinated heterocyclic bases (phenanthroline and dipyriddy).

Modeling of Biological processes with the participation of catalysts obtained on the basis of heterocyclic ligands was the subject of communications entitled "Complexes that model the active center of serine proteinases" (Institute of Organic Chemistry, AS USSR, Moscow) and "Modeling of processes involving the transfer of electrons from a substrate to oxygen in systems containing iron ion" (Moscow State University, Moscow). The authors (T. N. Filantova and Yu. I. Khurgin) of the first of these papers created, on the basis of imidazole complexes, a "proton-relay" model that models the proton shifts typical for the active center of  $\alpha$ -chymotrypsin; the role of dipyriddy complexes of iron in the redox reactions of the biocatalytic plan was discussed in detail in the second communication (A. N. Astanin and co-workers). Analogous reactions with the participation of 2,2-dipyriddy and 1,10-phenanthroline complexes of iron and manganese were studied in detail by Ya. D. Tiginyanu (Kishinev Medical Institute).

Important information for the direct approach to biocatalytic metal-containing systems was presented in a plenary paper by B. D. Berezin (Ivanovo, Chemical-Engineering Institute) entitled "Extracoordination in

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metalloporphyrins and its role in biological processes." The author demonstrated by means of comprehensive experimental data that the biocatalytic action of metalloporphyrins is in many respects associated with their ability to additionally coordinate various heterocyclic ligands (extracoordination) along the axial axes. Moreover, the nature of the extraligands and the character of the coordination interactions determine the activity of this most important natural biocatalytic system.

Metal derivatives of porphyrins, corrins, phthalocyanines, and other macrocyclic systems with nitrogen heterocycles were the subject of a detailed discussion in a number of communications of a group of researchers from the Institute of Physics of the Academy of Sciences of the Belorussian SSR (K. N. Solov'ev, M. P. Tsvirko, V. A. Kuz'menskii, et al.). The authors used the Pariser-Parr-Pople method to calculate the molecules of porphyrin and its magnesium derivative, studied processes involving energy transfer with the participation of the state of the ligand field of the metalloporphyrin molecules, and investigated the electronic structures of metalloporphyrins by electron vibrational spectroscopy, resonance Raman spectroscopy with the application of laser technique, polarization luminescence, and circular dichromism. This series of studies contains important data for an understanding of the relationship between the fine structure of metalloporphyrin systems and their biocatalytic activity. A paper by A. M. Yurkevich (Moscow) entitled "Nonenzymatic reactions of cobalamines that model the mechanism of cobamide-dependent enzymatic transformations" is directly related to the same subject matter.

Heterocyclic ligand systems occupied a central position in communications regarding complexing in biologically active compounds. Methods for the synthesis of and the properties and structures of physiologically active complexes obtained from amides and hydrazides of nicotinic, isonicotinic, and pyrazinic acids, amidopyrene, theophylline, and other medicinal preparations were discussed in papers by G. V. Tsinzadze, (Tbilisi, Georgian Polytechnic Institute), Kh. Kh. Khakimov, T. A. Azizova (Tashkent), M. A. Pora-Koshits (Moscow, Institute of General and Inorganic Chemistry, AS USSR) and co-workers. The authors, on the basis of IR spectral data and, in individual cases, data from x-ray diffraction analysis, established the mode of localization of the coordinate bond; this is of fundamental importance for an understanding of the character of the bonding of a metal in biologically active systems.

A number of communications contained data on the structures and physicochemical and chemotherapeutic properties of metal complexes created with the participation of hetarylcarbohydrates (Yu. A. Zhdanov, O. A. Osipov, and co-workers, Rostov University), heterocyclic derivatives with sulfamido substituents (V. N. Shafranskii, and P. K. Galetskii, Kishinev, Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev Medical Institute; O. A. Osipov and co-workers, Rostov State University, Rostov-on-Don), and o-hydroxyphenyl derivatives of azoles that fragment terphenylporphyrin systems (G. N. Dorofeenko and co-workers, Scientific Research Institute of Physical and Organic Chemistry, Rostov-on-Don).

Research on the Synthesis and study of the properties of platinum and palladium derivatives of heterocyclic amines intensified sharply after the discovery of antitumor activity in Pt and Pd complexes of nitrogen-containing substances (particularly cis-dichlorodiamineplatinums). A number of communications on the antitumor properties of Pt(II) and Pd(II) compounds with biologically active ligands, among which complexes of the indicated metals with purine bases (R. E. Kavetskii, K. B. Yatsimirskii, and co-workers, Kiev Institutes of the Problems of Oncology and Physical Chemistry, AS Ukr. SSR; A. I. Stetsenko, Leningrad (Pharmaceutical-Chemistry Institute) are of undoubted interest, were devoted to this subject area.

The above-indicated applied aspects of bioinorganic chemistry were discussed in a report paper by V. Ya. Temkina (Moscow, All-Union Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Substances), and the author demonstrated that the examination of these aspects is unthinkable without extensive recourse to data from the chemistry of heterocyclic compounds that constitute the foundation of the most important biological objects and processes.

The session afforded much that was novel and useful for the improvement of research in the area of bioinorganic chemistry and the solution of the most important problems of this young and extremely promising trend in chemical science. It graphically demonstrated the need for the more extensive involvement of specialists in the chemistry of heterocyclic compounds in the solution of the problems of bioinorganic chemistry.