# HETEROCYCLES IN COORDINATION CHEMISTRY

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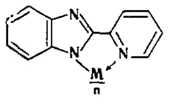
UDC 547.7

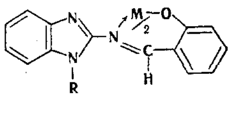
Heterocyclic compounds are playing an increasingly significant role as complexing ligands. This is distinctly attested to by the topics of papers presented at the Third All Union Conference "Synthesis and Study of Inorganic Compounds in Nonaqueous Media" held in Rostov-on-Don from June 1 to June 3, 1976. The conference was attended by scientists from practically all of the largest chemical schools of the country engaged in the synthesis and study of inorganic compounds and complexes in nonaqueous media.

The interest in heterocycles as ligands is due to the prominent role played by heterocyclic compounds in various biological specimens and processes, being essentially the principal ligand system in modern bioinorganic chemistry. It is precisely for this reason that a number of the papers presented at the conference contained data on the synthesis and study of the properties of complexes of porphyrins (B. D. Berezin and coworkers, Ivanovo), corrins (V. M. Berezovskii, Moscow), phthalocyanines (N. I. Bundina, Moscow) and other macroheterocyclic complexes (V. M. Dziomko, Moscow) that model the most important biocatalytic systems. The synthesis and study of the properties of complexes of hetaryl carbohydrates (Yu. A. Zhdanov, O. A. Osipov, and Yu. E. Alekseev, Rostov-on-Don), morpholine (V. Sh. Teplyakova, Kiev), nicotinamide and pyridinecarboxylic acids (M. K. Alyaviya and M. A. Azizov, Tashkent), and numerous coordination compounds of pyridines and azoles, particularly those with an $MN_4$ chelate node (A. D. Garnovskii and O. A. Osipov, Rostov-on-Don; I. Ya. Postovskii and N. P. Bednyagina, Sverdlovsk; V. M. Dziomko, Moscow) involve a direct approach to biologically active metal-containing systems. The bioinorganic aspects lie at the foundation of the study of the axial bonding of heterocyclic systems by metal chelates and also at the foundation of the study of the kinetics and therodynamics of adduct formation with "life metal" complexes (D. G. Batyr, Kishinev; I. N. Marov and O. M. Petrukhin, Moscow; V. N. Sheinker and V. A. Chetverikova, Rostov-on-Don).

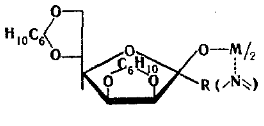
New methods for synthesis in nonaqueous media, both electrochemical (N. N. Bogdashev and V. P. Grigor'ev, Rostov-on-Don) and direct, based on the oxidation of zero-valent metals (M. L. Khidekel', Chernogolovka), have proved to be extremely effective for the preparation of difficult-to-obtain complexes: 2-pyridylbenzimidazole (I), salicylal-2-amino-1-alkylbenzimidazole (II), C-hetaryl derivatives of carbohydrates (III), and adducts of platinum metals and nickel or cobalt acetylacetonates with dipyridyl.



I



II



III

I M=Cu, Ni, Co, Fe; n=2—3; II M=Cu, Ni, Co, Zn; R=Alk, Ar, ArAlk; III R= 2-benzothiazolyl; 2-picolyl; 4-picolyl; etc.

Heteroaromatic systems have been found to be extremely convenient subjects for the discussion of the mode of localization of the coordinate bond in ambident systems with several donor centers (competitive coordination). In this connection, complexing with azoles and their derivatives (Rostov-on-Don; E. S. Domnina and G. G. Skvortsov, Irkutsk; N. V. Artemenko, N. N. Mushkalo, and V. V. Skopenko, Kiev), pyridines (V. N. Shafranskii, Kishinev; A. A. Pasynskii, Moscow; Samoilenko, Kiev; G. V. Tsintsadze, Tbilisi), phenanthroline

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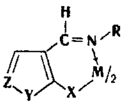
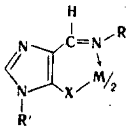
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 132-133, January, 1977.

(A. A. Kuznetsova and N. M. Dyatlova, Moscow), and a number of related mono- and bicyclic polyfunctional systems (E. N. Gur'yanova, I. P. Gol'dshtein, and A. V. Ivashchenko, Moscow; N. I. Pirtskhalava, Tbilisi) were discussed in a number of papers. It has been shown by diverse physical methods that the metal in all of the indicated systems is coordinated with the N atom of the pyridine type. However, the possibility of p and π complexing in N-heteroaromatic systems was discussed in a paper by I. P. Roma and V. N. Sheinker (Moscow, Rostov-on-Don).

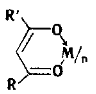
The directed synthesis of complexes with predesignated properties – a problem of exceptional importance in modern coordination chemistry – is successfully resolved by means of heterocyclic ligands. The introduction of such fragments makes it possible to obtain tetrahedral and polymeric octahedral structures for complexes with $MN_{4-6}$ and $MN_2S_2(Se_2)$ coordination nodes, which in the aromatic series are usually planar. This is the fundamental conclusion from a series of papers from scientists of Rostov University (A. D. Garnovskii, O. A. Osipov, V. I. Minkin, and V. A. Kogan), Lensovet Leningrad Technological Institute (I. Ya. Kvitko and A. V. El'tsov), and Ural Polytechnic Institute (I. Ya. Postovksii and N. P. Bednyagina). In these papers and in a series of other communications [V. M. Dziomko, All-Union Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Substances, Moscow (IREA); I. Ya. Postovskii and K. I. Pashkevich, S. M. Kirov Ural Polytechnic Institute (UPI), Sverdlovsk] it is shown that ligands for the synthesis of complexes with difficult-to-obtain $MN_2S_2$ and $MN_2Se_2$ chelate ligands (IV, V) or having increased solubility (VI) as compared with the analogous aromatic systems can be obtained from heterocycles; this opens up extensive possibilities for their investigation in nonaqueous media.



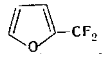
IV



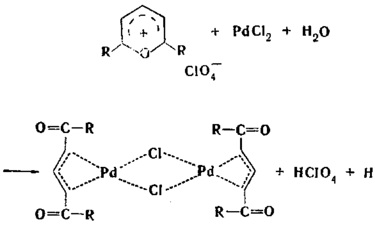
V



VI

IV X=S, Se; Y=O, S, NR′, Z=CR′, N; R, R′=H, Alk, Ar; V X=S, Se; R=Alk, Ar; R′=H, Alk; IV—V M=Cu, Ni, Co, Zn, Pd, Pt; VI R=Alk, Ar; R′=  M=Cu, Ni, Co, Mn, Fe; n=2—3.

Several interesting transformations were discovered during the study of complexing. Thus binuclear 1,3-bis-π-allyl complexes of palladium were obtained by reaction of 2,6-disubstituted pyrylium salts with $PdCl_2$ in an organic solvent (L. Yu. Ukhin, Rostov University):



The thermodynamic and kinetic parameters of a fast reversible ligand exchange of the $ML_1^2 + ML_2^2 = 2ML_1L_2$ type (where $L_1$ and $L_2$ are ligands – hydroxy, thio, and seleno derivatives of the pyrazole series – IV: X=O, S, Se; Y=N–Ar, Alk, Z=N) were determined by PMR spectroscopy (V. I. Minkin, Rostov-on-Don). Regularities in the rates for Ni→Zn→Cd→Pb metal complexes and for various heteroatoms were revealed. The thermodynamic characteristics of the formation of adducts with copper (II) chelates with pyridine were estimated by an ESR method (I. N. Marov and O. M. Petrukhin, V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Moscow). Magnetochemical, dielcometric, and ESR and NMR spectroscopic measurements made it possible to form an opinion regarding the structures and conformational equilibria of metal chelates, among which complexes of heteroaromatic ligands occupy an important position (O. A. Osipov and coworkers, Rostov-on-Don).

The solution of the problem of the site of localization of the coordinate bond in the heteroring is directly associated with the evaluation of the most-nucleophilic center of a heterocyclic system (A. D. Garnovskii, Rostov University). The use of shift reagents (complexing with salts of the rare earth elements) in the NMR spectroscopy of C- and N-acetyl derivatives of azoles made it possible to establish the conformation of a number of heterocycles (V. N. Sheinker, Rostov-on-Don). The Fourier $C^{13}$ $(H^1)$ spectra of zinc, cadmium, and mercury complexes were used to study the conformational behavior of isomeric dipyridyls (M. K. Alyaviya, Tashkent).

The investigation of the complexing of heterocyclic compounds promotes their extensive practical applications – this idea was repeatedly emphasized in a number of communications. The detailed development of methods for the synthesis of complexes of heterocycles and a knowledge of their physicochemical properties and structures make it possible to use heterocyclic compounds as extractants for the isolation and separation of metals (Yu. A. Zolotov and V. M. Dziomko, Moscow; I. N. Kremenskaya, Chernogolovka, etc.), medicinal preparations (V. M. Berezovskii, Moscow; M. A. Azizov, Tashkent), photochromic and thermochromic substances (M. I. Knyazhanskii, Rostov-on-Don; A. V. El'tsov, Leningrad), and dyes (N. N. Mushkalo, Kiev).

The conference made it apparent that the various aspects of coordination chemistry are undergoing active development in the largest heterocyclic schools of the country (UPI and the Ural Branch of the Academy of Sciences of the USSR; Kiev, Rostov, and Moscow Universities; Lensovet Leningrad Technological Institite; IREA and the All Union Vitamin Institute, Moscow; etc.), demonstrated the ever increasing interest of heterocyclic chemists in the problems of complexing with metals, and projected pathways of the subsequent application of heterocycles as ligands.

In addition, the need for the more extensive utilization of macroheterocyclic systems as ligands was emphasized, since without this type of complexing one cannot conduct investigations in modern bioinorganic chemistry and create new medicinal preparations, extractants, and complexes with predesignated properties.

The next such conference was planned to be held in 1979, but its location has not been accurately determined – applications have been submitted by Tbilisi, Ivanovo, Kiev, Odessa, and Donetsk.