RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

February 1973

U.D.C. 541.8;547.324

Advances in the Coordination Chemistry of Azoles

A.D.Garnovskii, O.A.Osipov, L.I.Kuznetsova, and N.N.Bogdashev

A systematic account and review of the literature on complexes of azoles is given. Particular attention has been devoted to the problem of the location of the coordinate bond in the azole molecule, competitive coordination in ambident azole-containing systems, elementotropism in a series of *N*-element derivatives of azoles, and the polyhedral forms of chelate complexes in the azole series.
The bibliography includes 508 references.

CONTENTS

I. Introduction	89
II. Molecular complexes of azoles	89
III. *N*-metal and *N*-element derivatives of azoles	97
IV. Chelate complexes in the azole series	99

I. INTRODUCTION

In 1958 Dorothy Hodgkin's group summarised[1] the results of almost ten years work on the elucidation of the structure of vitamin B_{12} for which the Nobel Prize was subsequently awarded. The authors established that, in contrast to nucleic acid nucleotides, in the B_{12} nucleotide the base (skeleton) is not a purine or pyrimidine but the cobalt complex of 5,6-dimethylbenzimidazole[2,3]. More than anything else, this discovery[4] and also earlier data concerning the involvement of azole systems in the biochemical binding of metals (haemoglobin, cytochromes, etc.)[5] served as a powerful stimulus for the development of synthetic, physicochemical, and structural studies on metal complexes of azoles and their derivatives. This idea is confirmed by the finding that, whereas up to the end of the 1950's occasional synthetic or analytical studies were made on azole complexes[6-8], in the 1960's and the 1970's azole-containing systems began to occupy leading positions among nitrogen-containing ligands[9].

In the present review, a systematic account is given of data for different types of complexes formed by azole-containing ligands: (1) molecular complexes; (2) *N*-metal and *N*-element derivatives of azoles; (3) chelate complexes.

The review does not claim to give an exhaustive coverage of all data on azole complexes but it does include the main advances in the synthetic and structural chemistry of complexes of azole-containing systems during the last decade (1961–1971 and partly 1972).

II. MOLECULAR COMPLEXES OF AZOLES

The presence of several heteratoms in the quasiaromatic π system suggests that azoles can behave as polydentate ligands. Therefore the most important problem in the chemistry of the complexes of azole-containing systems is the site of the coordinate bond (competitive coordination[10]). Hitherto, this problem has not been unambiguously solved.

It is believed that, depending on the type of azole, metal, and reaction conditions, the coordinate bond may be located at the pyridine-type nitrogen atom [4,5,9-27], the oxygen or sulphur heteroatom [28-31], or the π system [32-36]. On the other hand, analysis of numerous literature data suggests that azoles are monodentate ligands† with a single centre where the coordinate bond is located—the nitrogen atom of the pyridine type. This conclusion has been justified not only theoretically [9] (by the finding of the maximum π-electronic charge at the pyridine nitrogen atom) but also by direct X-ray diffraction studies [36-40] and by NMR, [41] infrared [18,22,42-44], and ultraviolet [24] spectroscopy. The conclusion that transition metals may be coordinated to the oxygen atom of the oxazole ring [29,30], reached by Duff on the basis of infrared spectroscopic and magnetochemical studies of benzoxazole complexes, has little evidence to support it. Pyl's attempts [28] to account for the unusual properties of thiazolylformazan by the coordination of the metal to the sulphur atom of the thiazole ring is also unconvincing. Finally there is no rigorous evidence for the possibility of complex formation involving the π system of the azole rings: even typical π-complex forming agents, such as metal carbonyls, form with azoles predominantly σ complexes and not π complexes [9,34,35,45-48].

1. COMPLEXES OF AZOLES WITH GROUP I, II, VII, AND VIII BIVALENT METALS

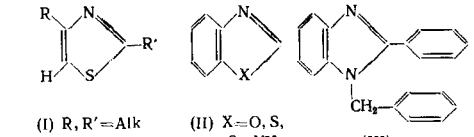
The greatest number of studies have been made on the physicochemical properties and structures of the coordination compounds of monodentate azoles with metal (II) salts‡. In most cases complexes of this type are synthesised by heating the components in ethanol [49-66]. Sometimes methanol [25,26,67-69] and acetone [27,50,63,70] are used for this purpose or the azoles are fused together with metal halides [20]. However, these procedures yielded complexes containing a large number of ligand molecules. Therefore, to synthesise complexes with a low coordination number (C.N.) of the metal, the above complexes were decomposed *in vacuo* at 90–140°C. [31,55,64] The composition of the complexes varies from $MX_2.L$ to $MX_2.6L$ and depends mainly on the stoichiometry of the reactants.

The basicity (pK_a) of azoles has almost no influence on the coordination number of the metal: coordination compounds with compositions ranging from $MX_2.L$ to $MX_2.6L$ may be obtained both for imidazole ($pK_a = 7$) [9,71] and for tetrazole ($pK_a \simeq 0$). [72] Similarly in the series of *C*- and *N*-alkyl substituted pyrazoles, complexes with the composition $MX_2.nL$ ($n = 2-4$) have been obtained [23] regardless of the basicity (the pK_a varied from 4.12 to −1.96). However, in the series of benzazoles the effect of basicity on composition is fairly clear: complexes of the type $MX_2.4L$ are readily obtained for benzimidazole ($pK_a = 5.53$), [9] the less basic benzothiazole ($pK_a \simeq 2.0$) [9] forms coordination compounds having the above composition only with a limited number of metals and anions, and benzoxazole ($pK_a \simeq 1$) [9] forms complexes which do not contain more than two ligand molecules.

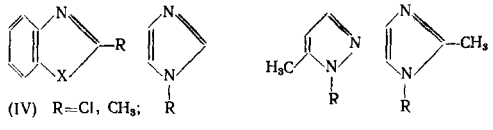
The metal has also little influence on the composition. Coordination compounds with the composition $CuX_2.6L$ cannot be isolated in most cases only for copper salts, although such complexes are known for imidazole [49] and its 4(5)-bromo-derivative [73].

The effect of anions and steric factors, which depend on the steric effectiveness of the ligand structure, on the composition of the coordination compounds is much more significant. Metals linked to ClO_4^- and BF_4^- show the greatest coordination capacity (complexes $MX_2.4L$ are formed), while NO_3 and NCY (Y = O, S, or Se) reduce the coordination number of the metal owing to their largely bidentate properties.

The introduction of bulky substituents into the ligand molecule reduces the number of coordinated azoles. Thus the complexes $MX_2.2L$ have been described [57,74] for alkyl-substituted thiazole (I). Benzo-analogues of azoles (II) form complexes which do not contain more than four ligand molecules even in the presence of the perchlorate anion [59,63]. On further increase of the complexity of the ligand, coordination compounds containing not more than two azole molecules are obtained, for example with 1-benzyl-2-phenylbenzimidazole (III). [75] In most cases other complexes, obtained with ligands containing in the 2-position of the azole ring substituents less bulky than the phenyl group [compounds (IV)], have the same composition [25,26,29,67,76,77].



(I) R, R′=Alk (II) X=O, S, Se, NH (III)



(IV) R=Cl, CH_3; X=O,S, NH (V) R=CH_3, n-C_4H_9 (VI) (VII) R=H, CH_3.

The above considerations concern only *C*-alkyl or *C*-aryl substituted derivatives in which the substituent gives rise to steric hindrance at the reaction centre (the pyridine-type nitrogen atom). On the other hand if the substituents are remote from the centre where the coordinate bond is located, the composition of the complexes is similar for substituted and unsubstituted azoles. This is probably the explanation of the finding that *N*-alkyl-substituted imidazoles (V) form $MX_2.6L$ complexes even in the presence of the bulky butyl substituent [44,78], while 5-methylpyrazole (VI) forms in addition [79] a complex with seven ligand molecules§. On the other hand, coordination compounds not containing more than four azole molecules have been described for 2-methylimidazole (VII, R = H) [73] and 1,2-dimethylimidazole (VII, R = CH_3). [70,80].

The type of polyhedra formed by azole complexes depends mainly on the coordination number of this metal and its electronic configuration, the nature of the anion and the ligand, and in many cases on the state of aggregation of the system. The complexes $MX_2.4L$ and $MX_2.6L$ have an octahedral structure with some distortion along the tetragonal axes due to the specific influence of the ligand and the anion.

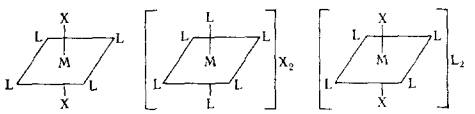
† Azoles containing in the heterocyclic nucleus several sp^2-hybridised nitrogen atoms behave as bridge-type bidentate ligands (see below).

‡ Data for complexes of the most important azole-containing systems have been tabulated [9].

§ In the complex $MX_2.7L$ [L = (VI)], one of the ligand molecules is partly linked as a solvating species [79].

Usually, but not necessarily, coordination compounds of the type $MX_2.4L$ have a *trans*-octahedral structure (VIII). Distortion of the latter can lead to an elongated or shortened tetragonal bipyramid [81,82] and also to a tetrahedral configuration with weakly bound anions located along the tetragonal axes [68]. On the other hand, planar square polyhedra are also encountered among complexes of this type. These are characteristic of nickel [49,58,83] coordination compounds with I^-, ClO_4^-, BF_4^-, and NCS^- anions and of palladium [31] complexes with Cl^-, I^-, and NO_3^-.

The fundamental problem concerning the $MX_2.6L$ complexes is that of the octahedron formed: $[ML_6]_2X_2$ (IX) or $[MX_2L_4]L_2$ (X): [49]



X-Ray diffraction [39,84] and spectroscopic [16,24,49,86] studies led to an unambiguous solution in favour of structure (IX) in which the metal is surrounded by six atoms of pyridine-type nitrogen. The polyhedral forms of the complexes $MX_2.2L$ are much more varied.

The electronic configuration of the metal in this type of coordination compound frequently plays a decisive role: mainly tetrahedral complexes are formed by Co^{II} (d^7) and Zn^{II} (d^{10}), planar and octahedral complexes are formed by Ni^{II} (d^8) and Cu^{II} (d^9), and only planar complexes are formed by Pd^{II} (d^8). However, this postulate cannot be regarded as valid without exception since among cobalt and zinc complexes coordination complexes are encountered with an octahedral structure [27,55] and there are tetrahedral copper and nickel complexes [19,58]. These deviations are associated primarily with the nature of the anions among which mention should be made of I, NCY (Y = O, S, or Se), and NO_3, which exhibit specific effects. When chlorine and bromine in the nickel complexes of imidazole [20], its 5-bromo-derivative [73], and benzoxazole [19] of the type $NiX_2.2L$ (X = Cl or Br) are replaced by iodine, there is a change from an octahedral to a tetrahedral coordination. On the other hand, in the 2-methylimidazole complexes the octahedron → tetrahedron transition is observed not only for nickel iodide but also for the bromide.

The replacement of chlorine and bromine by iodine frequently leads to a flattening of the tetrahedral configuration. The tetrahedron → planar square transition is characteristic of complexes of nickel halides with 1-benzyl-2-phenylbenzimidazole [75] and 2-aminobenzothiazole [86]. The structural characteristics of such complexes can be accounted for by the different degrees of polarisability of the halogens (I > Br > Cl) and their different sequence in terms of their effective contribution to the metal–ligand π-dative bond [87].

The specific effect of the NO_3^- and NCY^- groups is due to the fact that the nitrate ion frequently behaves as a bidentate ligand [88-91] and pseudohalide anions form bridge-type structures [9,10,92-95]. As a result, both anions increase the coordination number of the metal in the complexes $MX_2.2L$ to six and promote the formation of octahedral structures. The transition from tetrahedral and planar configurations to the octahedral configuration, which is frequently observed [19,50,64,81,96,97], was discussed in detail by Duff and coworkers for benzothiazole and benzoxazole complexes of transition metal nitrates [65]. The infrared and Raman spectra of these complexes show M–O bond vibration frequencies in the low-frequency region (at 270–350 cm^{-1}), which vary with the nature of the metal and the ligand. On the other hand, there have been a number of studies where it has been shown convincingly that the NO_3^- anion can also behave as a monodentate ligand. In this case, when complexes are formed with nitrate, the type of polyhedra formed by the $MX_2.2L$ coordination compounds remains the same [4,27]. Pseudohalide ions behave in the same way, since among the complexes $MX_2.2L$ containing the NCY^- anions not only bridge-type octahedral but also planar [75,76,98,99] and tetrahedral [27,63,77,100] structures are encountered. In the latter case the question of the mode of coordination of the pseudohalide ion is usually discussed and a decision in favour of the M–N bond is made for the azole complexes [27,44,63,76,77,98-100] on the basis of the generally accepted tests [9,10,92-94,101].

For the same composition, metal, and anion, it is possible to follow the influence of the fine structure of the ligand on the structure of the coordination compound. Thus, in contrast to the planar complexes of nickel thiocyanate with 2-methylbenzimidazole [76], the analogous benzimidazole complexes are octahedral [102]. Nickel chloride complexes of the type $MX_2.2L$ are tetrahedral with benzimidazole [60], while those with benzothiazole [63] and benzoxazole [19] are octahedral.

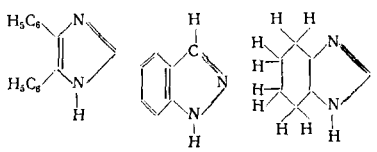
The amount of data available for the interpretation of the structures of the azole complexes of the type $MX_2.L$ and $MX_2.3L$ is much less. Depending on the electronic structure of the metal, planar (copper [31,55,63]), octahedral (nickel [20,31,61,63] and cobalt [20,55]), or tetrahedral (cobalt [20,31] and zinc [31]) configurations are attributed to complexes of the first type. Trigonal-bipyramidal [70] or polymeric-octahedral [29,57] configurations are postulated for $MX_2.3L$ coordination compounds. Rigorous proof has been obtained only for the 1,2-dimethylimidazole complex of copper(II) chloride: X-ray diffraction analysis definitely indicates a *cis*-trigonal bipyramidal structure [103]. Bearing in mind that in many cases the configuration of the complexes may alter in solution [9,104,105], the data quoted in this section must be treated with some caution. Whereas one can hardly expect a change in the form of the polyhedron on dissolution of coordination compounds of the type $MX_2.6L$ and $MX_2.4L$, the changes in the polyhedral forms of certain azole complexes of the type $MX_2.2L$ are very significant (as already shown above) [19,27,99].

The stability of the azole complexes of the type discussed above has not been the subject of systematic studies. Most data are available for the stabilities of the complexes of imidazole [106-114] and some of its derivatives [115,116]. Sklenskaya and Karapet'yants [114] determined the thermodynamic functions for the formation of complexes by bivalent copper, nickel, and cobalt ions with imidazole in aqueous solutions from measurements of the temperature variation of the instability constants in the range 10–50°C. They established that the instability constants of the imidazole complexes and the ΔH_1 vary in the sequence Cu > Ni > Co, which is the same as the Irving–Williams stability series generally adopted for nitrogen-containing ligands [117]. The ΔH_1 agree with the values found calorimetrically (7.6 kcal $mole^{-1}$ for copper and 5.8 kcal $mole^{-1}$ for nickel), the values for the imidazole complexes being significantly higher than for the ammines (5.6 kcal $mole^{-1}$ for copper and 4 kcal $mole^{-1}$ for nickel) [118].

2. COMPLEXES OF AZOLES WITH THE HALIDES AND TRIALKYL DERIVATIVE OF GROUP III ELEMENTS

With the exception of scandium coordination compounds, complexes of azoles with MX_3 (M = B, Al, Ga, In, Tl, or Sc and X = Cl, Br, I, or CH_3) are synthesised in aprotic absolute solvents [9,119-125]. The comparatively high stability of scandium halides and their complexes makes it possible to synthesise the latter in ethanol [121]. The trihalides of boron [119,126], aluminium [120,121], and gallium [9,119] and their trimethyl derivatives [119,122] form mainly 1 : 1 complexes with azoles, while the compositions $MX_3.2L$ and $MX_3.3L$ are more characteristic of the corresponding indium [9,119,123,124], thallium [125], and scandium [121] coordination compounds. This result is apparently due to the fact that a tetrahedral structure with an sp^3-hybridised metal atom is most characteristic of the boron, aluminium, and gallium complexes, while an octahedral or a trigonal-bipyramidal structure (with d^2sp^3 and sp^3d-hybridisation respectively) is typical for indium, thallium, and scandium coordination compounds [9,104,127-129].

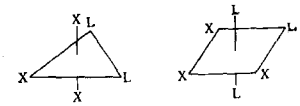
As for the azole coordination compounds with bivalent metals, the compositions of complexes of azole ligands with MX_3 depends more on the bulk than on the basicity of the ligand. Thus, whereas up to 4 (indium chloride [123]), 5 (aluminium bromide [120] and indium iodide [123]), and 6 (aluminium chloride [119,121] and scandium chloride [121]) molecules of imidazole(V), which has a relatively small bulk and a high basicity, combine with the metal halides, the number of coordinated molecules of the bulky 4,5-diphenylimidazole (XI), which has a similar pK_a, does not exceed unity for AlX_3 [9,119-121] or two for InX_3. [119,123] In the series of benzimidazole, pyrazole, and indazole (XII) derivatives, the basicity decreases while the composition remains unchanged ($InX_3.3L$). [123]



(XI) (XII) (XIII)

On the other hand, the increase of the basicity of certain imidazole derivatives with analogous structures is accompanied by an increase of the number of coordinated ligand molecules in the complex. Depending on the reactant ratio, aluminium bromide [120] and chloride [121] and scandium chloride [121] can combine with up to five molecules of tetrahydrobenzimidazole (XIII), while in the complexes with benzimidazole (IV, X = NH, R = H) the maximum number of coordinated molecules does not exceed three. Similarly indium trichloride and tri-iodide form complexes having the composition $InX_3.4L$ with (XIII) and $InX_3.3L$ with (IV, X = NH, R = H).

In order to obtain information about the structures of coordination compounds, studies have been made [9,119-123] on the infrared absorption spectra of the complexes and their dipole moments have been determined; infrared, Raman, and ESR spectra have been studied by Cotton and Gibson [124], mass spectrometric, NMR, and vibration spectra by Lee [125], and NMR spectra by Fratiello [126]. The stretching vibration frequencies of the azole rings were found to increase in the infrared spectra of complexes of the type $MX_3.nL$ ($n = 1-6$) which suggested [9,119-123] that the coordinate bond is located at the pyridine-type nitrogen atom of the heterocycle. In addition to this frequency increase, the infrared spectra of the coordination compounds $MX_3.nL$ (M = Al or B, $n > 1$; M = In or Sc, $n > 3$) showed bands due to non-coordinated ligands. On this basis, a solvate structure of the type $[MX_3.(n-m)L]mL$ was attributed to these coordination compounds [9,119-121,123]. One cannot rule out the possibility of the formation of solvates also in the case of gallium complexes of the type $GaCl_3.2L$, although the coordination capacity of this metal is consistent with the formation of trigonal-bipyramidal coordination compounds (sp^3d hybridisation). On the basis of the infrared spectra and the dipole moments, which vary in the range 4–7 D, a *cis*-trigonal-bipyramidal configuration (XIV) was attributed to the complexes $InX_3.2L$ and a *cis*-structure with C_{2v} symmetry (XV) was attributed to octahedral coordination compounds of the type $InX_3.3L$:



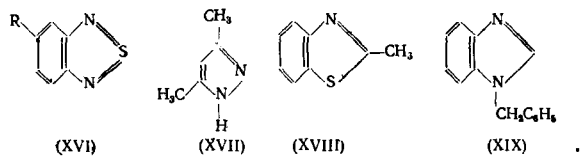
(XIV) (XV) 9,119,123

A comparative estimate of the stabilities of the complexes was made from the frequency shifts of the stretching vibrations of the azole rings ($\Delta\gamma$). It was found that the $\Delta\gamma$ for the MX_3 complexes of the same composition and structure are satisfactorily correlated with the basicities of the azole ligands [9].

The conclusions based on the infrared spectroscopic studies have been confirmed in a few cases also by measurements of the dipole moments [9,119].

3. COMPLEXES OF THE AZOLES WITH THE TETRAHALIDES OF GROUP IV ELEMENTS

The azole complexes with MX_4 (M = Sn, Ge, Ti, Zr, Hf, or Th; X = Cl, Br, or I) known hitherto are confined mainly to complexes of imidazole-containing systems [9,130-132]. Only in the case of tin tetrachloride have complexes been obtained also with benzo-2,1,3-thiadiazole (XVI, R = H) and its 5-methyl derivative (XVI, R = CH_3), [133,134] and germanium tetrachloride was found to form complexes with 3,5-dimethylpyrazole (XVII) and 2-methylbenzothiazole (XVIII). [9]



(XVI) (XVII) (XVIII) (XIX)

The azole complexes with Group IV metal tetrachlorides were synthesised by mixing in the cold the benzene or chloroform solutions of the ligands with MX_4 solutions in benzene (M = Sn, Ti, or Ge) [9,130,132] or ether (M = Zr, Hf, or Th). [9,131,132]

As for the coordination compounds of other oxygen- and nitrogen-containing ligands [9,104,132-135], the compositions of complexes of this type are fairly rigorously correlated with the properties of the MX_4. [9,132] Regardless of the reactant ratio and the bulk and basicity of the ligand, tin [9,130,133], zirconium [131], and hafnium tetrahalides [131] form coordination compounds of the type $MX_4.2L$. The complexes $MX_4.3L$ are most characteristic of germanium tetrachloride although (XVII) forms the complex $GeCl_4.L$

and imidazole even $GeCl_4.5L$.[9] Depending on the reactant ratio, titanium tetrachloride was found to form the coordination compounds $TiCl_4.2L$ and $TiCl_4.L$.[9,130,132] Thorium tetrachloride complexes of definite composition could be obtained only with ligands containing bulky substituents in the azole rings [for example (XIX) and the 1-(α-phenylethyl), 1-(α-naphthylmethyl), and diphenylmethyl derivatives resembling it][131]. Thorium tetrachloride forms with imidazole, benzimidazole, and their *CN*-alkyl(aryl) derivatives coordination compounds having the composition $ThCl_4.2L.n(C_2H_5)_2O$ in which n varies from 6 to 14 depending on the bulk of the ligand[132].

The study of the structure of the coordination compounds of MX_4 with azoles led to the conclusion that the only complex-formation centre in the imidazole ring is the pyridine-type nitrogen atom[130]. The conclusion was based on the increase of the stretching vibration frequencies in the imidazole ring (1550–1570 cm^{-1}) on complex formation and the similarity of a number of chemical and physical properties (spectroscopic behaviour on coordination) of imidazole-containing systems and pyridine[9,130]. Subsequently this test was widely used to demonstrate that coordination involves the pyridine-type nitrogen atom of the azole ligand[9,99,119-121,130-132,136-138].

It was also established that the stretching vibration shifts $\Delta\gamma$ of the imidazole ring on coordination interaction with MX_4 are correlated with the basicity of the ligand[9,130-132].

The structure of the complexes $MX_4.2L$ with azoles was not studied in detail owing to their extremely low solubility and ready hydrolysability. However, low-frequency vibration spectra show that the $SnCl_4$ and $TiCl_4$ complexes with benzimidazole as well as a number of other nitrogen-containing ligands[139] have the *cis*-octahedral configuration in the crystalline phase[9].

4. COMPLEXES OF AZOLES WITH GROUP V METALS

Complexes of azoles with niobium pentachloride[140,141] and niobium oxide trichloride[142-144] have been isolated on a preparative scale and partly investigated. The complexes of both niobium derivatives were obtained by the interaction of the ether compound of the pentachloride[140,141] or the chloride trioxide[142-144] with azoles in benzene solutions.

The composition of the coordination compound of $NbCl_5$ depends significantly on the basicity of the azoles and in many cases also on the reactant ratio and on the solvent. For azoles with a comparatively high basicity imidazole, benzimidazole, 2-methylbenzimidazole), the complexes $NbCl_5.nL$ with n = 1, 2, or 3 may be obtained for different reactant ratios[140,141]. As the basicity decreases (3,5-dimethylpyrazole and benzothiazole), the complexes $NbCl_5.L$ are formed[140,141]. When benzene is replaced by acetonitrile, the complex $NbCl_5.L.CH_3CN$ may be isolated[141].

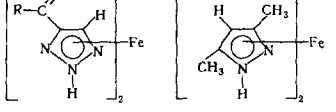
In contrast to the $NbCl_5$ complexes, the composition $NbOCl_3.L$ is most characteristic of the $NbOCl_3$ coordination compounds[142-144]. However, it is difficult to reach final conclusions concerning the dependence of the composition of the $NbOCl_3$ complexes with azoles on structural factors and conditions of synthesis owing to the narrow range of azole-containing systems which have been introduced into the reaction with niobium oxide trichloride[142-144].

The properties of the $NbCl_5$ and $NbOCl_3$ coordination compounds have been investigated by magnetochemical and infrared spectroscopic methods. It has been shown[140,141] that, when $NbCl_5$ interacts with azoles, niobium is not reduced to the quadrivalent state¶: all the complexes synthesised, except $NbCl_5.2L.CH_3CN$, are diamagnetic. On the other hand, the weak paramagnetism ($\mu_{eff} \simeq 0.7$ Bohr magneton) of the complex containing an acetonitrile molecule has been explained[141] by the coordination of CH_3CN to $NbCl_5$ (the complex $NbCl_5.CH_3CN$ is also weakly paramagnetic—μ_{eff} = 0.6 Bohr magneton).[148]

In view of the increase of the vibration frequencies of the azole ring in the complexes $NbCl_5.nL$[140,141] and $NbOCl_3.L$,[142-144] it was concluded that the coordinate bond involves the pyridine-type nitrogen atom of the azole ring. It was also established that the interaction of $NbOCl_3$ with azoles entails a decrease of absorption due to the NbO bond by 30–65 cm^{-1} (in the range 700–800 cm^{-1}). On this basis, it has been suggested that the frequency shifts of the bond stretching vibrations can serve as a kind of measure of the stability of the donor–acceptor bond between the ligand and niobium oxide trichloride[143,144].

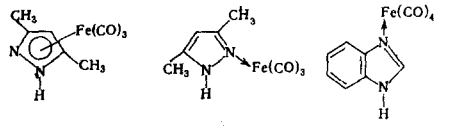
5. GROUP VI–VIII METAL CARBONYL COMPLEXES OF AZOLES

The synthesis and the study of the properties of the metal carbonyl complexes of azoles were undertaken mainly to investigate the possibility of the formation of π complexes in the azole series. On the basis of the available data concerning the successful synthesis of azoferrocene[149-152] and the similarity of a number of properties of azoles and pyrrole, Nesmeyanov et al.[33] allowed 4-butyryl(benzoyl)-1,2,3-triazoles and 3,5-dimethylpyrazole to react with iron nonacarbonyl. Elemental analysis, molecular weight measurements, and infrared spectra led the authors[33] to the hypothesis that the compounds (XX) and (XXI) obtained have the π-complex structure:



(XX), R = C_3H_7, C_6H_5 (XXI)

Later similar considerations were adduced concerning the structure (XXII) of azole complexes having the composition $LFe(CO)_3$[34-35] but σ-complex structures (XXIII) and (XXIV) were attributed to complexes of the type $LFe(CO)_4$ on the basis of mass spectrometric, infrared spectroscopic, and NMR studies[35,37]:

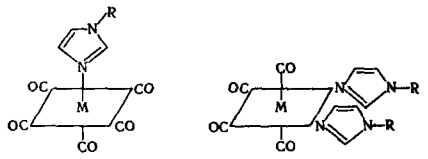


(XXII) (XXIII) (XXIV)

Complexes of a large group of azoles and their benzoanalogues with chromium, molybdenum, and tungsten hexacarbonyls were obtained by Beck et al.[41] and independently by Garnovskii and coworkers[46,48]. Elemental analysis [composition $LM(CO)_5$ or $L_2M(CO)_4$], infrared spectroscopy, dipole moment[46,48], and ^{14}N NMR measurements[41] suggested that all these compounds have the

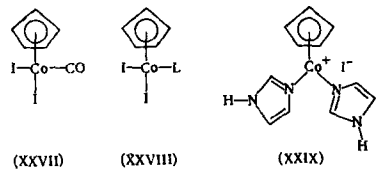
¶ Earlier it was stated that, when $NbCl_5$ interacts with nitrogen-containing organic compounds, paramagnetic coordination compounds of the type $NbCl_4.nL$ are formed[145-147].

σ-complex structure with an M ← N bond involving the pyridine-type nitrogen atom of the heterocyclic ring, for example (XXV) and (XXVI):



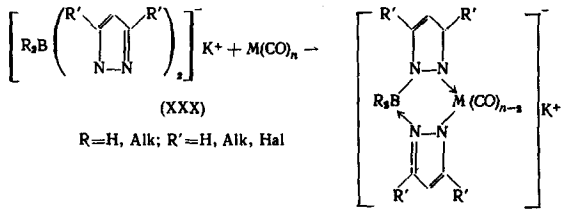
(XXV) (XXVI)

The reaction of cyclopentadienylcobalt di-iodide (XXVII) with imidazole, benzimidazole, indazole, and benzotriazole led to the synthesis of the complexes (XXVIII) and (XXIX) with a Co–N σ bond[153]:



(XXVII) (XXVIII) (XXIX)

Alkali metal polypyrazolylborates (XXX) react with molybdenum hexacarbonyl[154,155] and bromomanganese pentacarbonyl or dimanganese decacarbonyl[156] to form anions with a σ-linked metal carbonyl residue (XXXI):

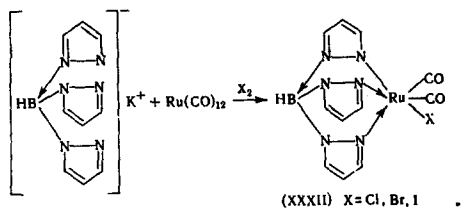


(XXX)

R=H, Alk; R′=H, Alk, Hal

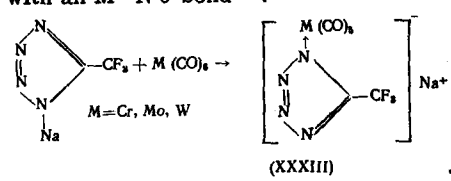
(XXXI)

The reaction of potassium tripyrazolylborate with $Ru_3(CO)_{12}$ in the presence of a halogen (Cl_2, Br_2, I_2) yields the metal carbonyl derivatives (XXXII) in which an Ru–N σ bond is formed[157]:



(XXXII) X=Cl, Br, I

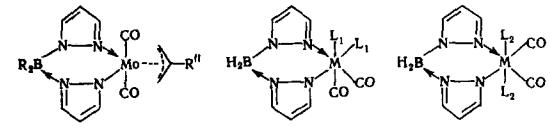
The anion (XXXIII), formed in the reaction of sodium 5-trifluoromethylpyrazolide with $M(CO)_6$, also has a structure with an M–N σ bond[158]:



M=Cr, Mo, W

(XXXIII)

The reactions of the above anions with unsaturated compounds[154] or phosphines (phosphites)[156] can yield the coordination compounds (XXXIV)–(XXXVI) respectively. In the case of phosphines, the ligands (L_1) occupy the *cis*-positions relative to one another [as in compound (XXXV)] and in the case of the phosphites (L_2) the complex has the *trans*-configuration (XXXVI):[156]



(XXXIV) (XXXV) (XXXVI)

Thus the data presented clearly demonstrate the preferential formation by azoles of σ and not π complexes even with powerful π acceptors such as metal carbonyls. We believe that the difficulty of obtaining π complexes in the series of azoles, in contrast to pyrrole[149–152,159,160] and other five-membered systems with one heteroatom[161,162], can be explained[9,48] by the combination in the azole molecule of a π-electron sextet with the unsaturated pyridine-type nitrogen atom, the electron-donating activity of which greatly exceeds that of the π-electron system†.

The study of the polar properties of complexes of the type $LM(CO)_5$ showed that the stability of the coordination compounds varies in parallel with the basicity of ligands of a similar type[9,46,48]: imidazole > benzimidazole > pyrazole > tetrazole. However, the stabilities of azole complexes containing oxygen or sulphur atoms in the heterocyclic ring (benzoxazole, benzothiazole) do not fit in the above sequence[9,46,48].

The considerable polarity (μ = 10 D) of azole complexes of the type $L_2M(CO)_4$ demonstrate their *cis*-octahedral configuration in solution[46,48]. According to infrared spectroscopic data, the complexes have the same structure in the crystalline phase too[41,46,48] (four bands in the range 1800–2000 cm^{-1}).

To conclude our discussion on coordination compounds with monodentate azoles, note that we have not discussed data for the coordination compounds of *N*-substituted tetrazoles, since a fairly complete review on this subject is available[72]. On the other hand, one must emphasise that, according to the latest X-ray diffraction data[165], the tetrazole ring can be coordinated not only via the $N_{(4)}$ atom[72] but also via the $N_{(3)}$ atom[166]. Together with the azole complexes discussed above, the coordination compounds of 2-methylbenzoselenazole[100], isothiazole[167,168], thia- and selena-diazoles[169–171], and also a number of azole solvates with the general formula $MX_2.2L.2H_2O$ (the latter have an octahedral configuration)[172] have also been investigated, albeit in less detail. Finally, in addition to the metals mentioned above, azole complexes of ruthenium[173,174], rhenium[175], and rhodium[171] have been synthesised.

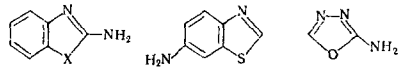
6. COMPLEXES OF AMBIDENT AZOLE-CONTAINING SYSTEMS

Azole ligands with several electron-donating atoms combined into a single conjugated system (ambident compounds[10,93]) are of considerable interest for the problem of competitive coordination in the chemistry of their complexes[9,10]; for this problem, it is useful to arrange the ligands of the azole series systematically in terms of the possible bonding atoms.

† The suggestion that π complexes are formed in the pyridine series[163] proved to be erroneous[164].

a. Azole-containing Ligands with Electron-donating Nitrogen Atoms

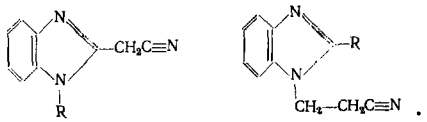
Amino-derivatives of azoles [(XXXVII)–(XXXIX)] containing two electron-donating nitrogen atoms hybridised in different ways are mainly monodentate ligands and form with transition metal salts [86,98,176-180] and the halides of Group I, [180] III, [9,119] IV, [9,132,181] and V [140-144] complexes in which the coordinate bond involves mainly the pyridine-type ring nitrogen atom:



(XXXVII) (XXXVIII) (XXXIX)

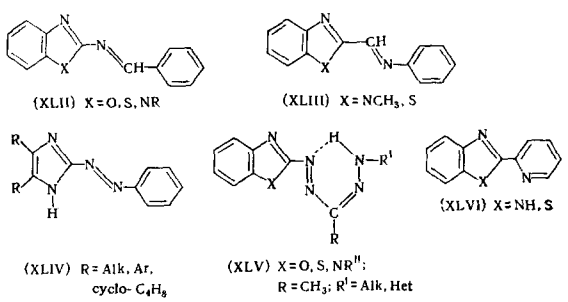
X = O, S, NR; R = H, Alk, Ar

Only in a few cases has it been claimed that the complex may be formed with participation of both electron-donating centres [9,140,141] and, in the case of compounds (XXXVII) [180] and (XXXIX), [178] with participation of the amino-nitrogen. In amino-derivatives of azoles, coordinating attack is directed to the nitrogen heteroatom with the highest π-electronic charge (the X atom and the amino-nitrogen are positively charged) [9,181]. Although this result, which follows from infrared spectroscopic [9,132,140-144] and ultraviolet spectroscopic [86,176,177,180] studies, conflicts with Pauling's postulate that the electron-donating capacity of nucleophilic atoms increases with the amount of p-character of the hybrid orbitals [182], it is consistent with data showing that the coordinate bond involves the electron-donating centre with the maximum negative potential [183] and hence with the maximum negative π-electronic charge [10,184]. Similarly the coordinate bond in the cyano-derivatives of the azole series (XL) and (XLI) involves the nitrogen atom of the heterocyclic ring [9,185]:



(XL) (XLI)

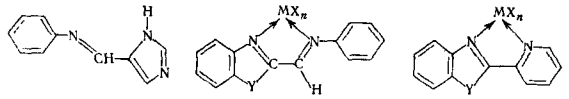
Similarly complexes are formed via the nitrogen atom with the maximum negative π-electronic charge in the series of azole-containing systems with equally hybridised nitrogen atoms: the anils (XLII) and (XLIII) via the azomethine nitrogen atom [9,10,181] and the azo-compounds (XLIV) [9,186] and formazans (XLV) [187,188] via the pyridine-type heterocyclic nitrogen atom:



(XLII) X = O, S, NR (XLIII) X = NCH$_3$, S

(XLIV) R = Alk, Ar, cyclo-C$_4$H$_8$ (XLV) X = O, S, NR$''$; R = CH$_3$; R$'$ = Alk, Het (XLVI) X = NH, S

At the same time, the ligands (XLIII), (XLIV), and (XLVI) [185,186,189-208] as well as (XLVII), [209] containing electron-donating nitrogen atoms in positions favouring the formation of cyclic structures, give rise to chelate complexes (XLVIII) and (XLIX):



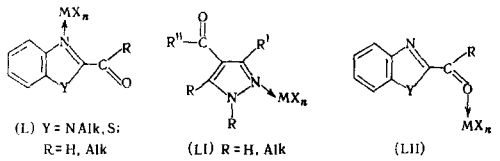
(XLVII) (XLVIII) (XLIX)

The composition and structure of complexes of ambident nitrogen-containing systems depend on the same factors as the complexes of monodentate azoles. 2-Aminobenzazoles (XXXVII) form mainly complexes of type $MX_2.2L$. [86,176,177] However, the coordination compounds of 2-aminobenzothiazole (XXXVII, X = S) with the composition $Co(ClO_4).3L$ may be isolated [176] and synthesis in a hydrochloric acid medium yields the complexes $MX_2.L$ (M = Cu, Co, or Hg). [179] Depending on the reactant ratio, 2-amino-1,3,4-oxadiazole (XXXIX) forms the coordination compounds $MX_2.nL$ (n = 2–6). [178] The type of polyhedra formed is determined by the electronic structure of the metal (the cobalt complexes are mainly tetrahedral [86,176,177]) but it depends also on the anion [86].

The bulky ligands (XLII)–(XLVI) tend to decrease the coordination number of the metal and to form mainly the complexes $MX_m.L$, [9] while the coordination compounds of bisazole systems (XLVI) give rise to planar or polymeric-octahedral structures [199,202,205].

b. Oxygen- and Sulphur-containing Derivatives of Azoles

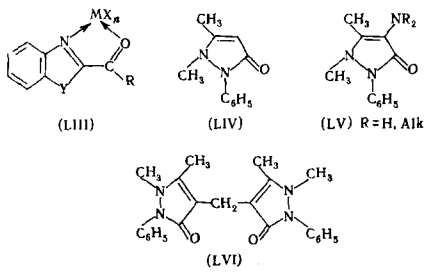
Infrared spectroscopic studies demonstrate fairly clearly that, in complexes of *C*-carbonyl derivatives of the azole series [(L) and (LI)], the coordinate bond involves mainly the nitrogen atom of the heterocyclic ring [9,119,210].



(L) Y = NAlk, S; R = H, Alk (LI) R = H, Alk (LII)

Only the "hardest" [10] Lewis acids $AlCl_3$ and $AlBr_3$ form complexes via the oxygen atom: (LII) and (LIII). [9,210]

Antipyrine (LIV) and its derivatives (LV) and (LVI) form two types of complexes depending on the conditions of synthesis: $MX_m.nL$ in neutral or weakly acid media [9,132,211-226] and ionic association complexes of the antipyrinium cation in acid solutions [212,223,226-230].

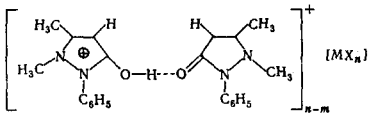


(LIII) (LIV) (LV) R = H, Alk

(LVI)

Regardless of the nature of MX_m, the formation of the complexes $MX_m.nL$ involves exclusively the exocyclic oxygen atom [9,132,211-230], which is consistent with the high

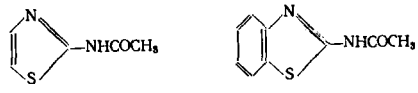
negative π-electronic charge of the oxygen atom [9,132,225,231,232]. In the ionic association complexes (LVII), the proton adds to the same electron-donating centre [226-230].



(LVII)

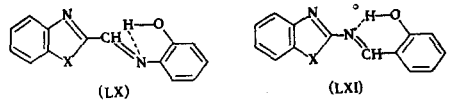
A cyclic structure with the metal coordinated to exocyclic oxygen and nitrogen atoms has been attributed [233-235] to 4-aminoantipyrine (LV, R = H) and its *N*-dimethylamino-derivative (LV, R = CH_3). Complexes of ligands of this type have an octahedral structure regardless of the metal and the anion [236].

2-Acetamidothiazole (LVIII) and its benzo-analogue (LIX) are ambident systems whose complexes with different MX_2 may be formed in three ways: (1) via the nitrogen atom in the thiazole ring ($CuCl_2$), (2) via the amide oxygen atom and the heterocyclic nitrogen atom (NiX_2, X = Cl, Br, or I; $CuBr_2$), and (3) via the amide and ring nitrogen atoms [CuX_2, X = NO_3 or ClO_4; $Ni(NO_3)_2$]. [237]

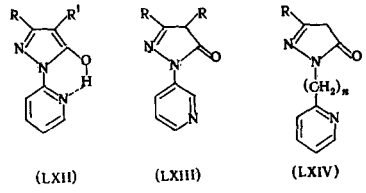


(LVIII) (LIX)

o-Hydroxyanils of the azole series (LX) and (LXI) [9,132,189] and the 5-hydroxy derivatives of 1-pyridylpyrazole (LXII)–(LXIV) [186,204] are unusual ambident nitrogen- and oxygen-containing ligands.



(LX) (LXI)

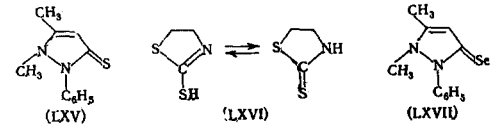


(LXII) (LXIII) (LXIV)

Compounds (LX)–(LXII) form complexes via the azomethine [compounds (LX) and (LXI)] [9,132,189] or pyridine-type nitrogen atoms [186,204]. However, for ligands with a preferential oxo-form [(LXIII) and (LXIV)], [9,185,204,238] the coordinate bond involves the oxygen atom of the carbonyl group [185,204].

There are comparatively few data concerning the nature of the polyhedral forms of these complexes. Antipyrine complexes of the type $CuCl_2.2L$ and $CuBr_2.2L$ are known to be pseudotetrahedral and the complexes $Cu(NO_3)_2.2L$ are planar or have a distorted octahedral structure [214]. The complex $Cu(ClO_4)_2.5L$ has a pentacoordinate copper atom [215] and the copper complexes with acetate or arenecarboxylate anions have tetragonally distorted octahedral structures [224]. The octahedral configuration is characteristic of antipyrine complexes of the type $M(ClO_4)_2.6L$. [239]

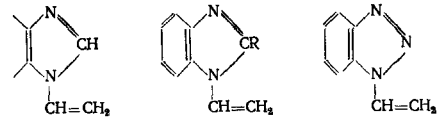
Thiopyrine (LXV) [217] and thiazolidenethione (LXVI) [240] must be classified as sulphur- and nitrogen-containing ambident systems.



(LXV) (LXVI) (LXVII)

In the coordination compounds of both ligands, the coordinate bond involves the exocyclic sulphur atom. Similarly, the coordination interaction [9] of selenapyrine (LXVII) involves the exocyclic selenium atom. The complexes of thiazolidine-2-thione (LXVI) have been investigated in fair detail [240]. Magnetic and spectroscopic (ultraviolet and infrared) studies established that the complexes $MX_2.2L$ are tetrahedral (M = Co, X = Cl, Br, or I; M = Ni; X = I) or octahedral (M = Ni, X = Cl or Br). [240]

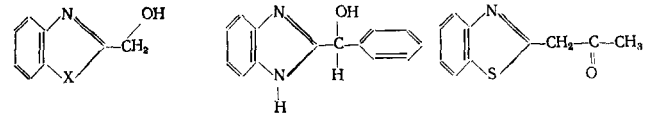
Apart from the ambident systems mentioned above, *N*-vinyl derivatives of azoles (LXVIII)–(LXX) have been used to form complexes with metal salts [137,138,241,242]:



(LXVIII) (LXIX) (LXX)

The study of the interaction of tin and nickel chlorides with the ligands (LXVIII)–(LXX) showed that in this case too the composition of the complexes depends on the reactant ratio and on the nature of the ligand and the solvent [241,242]. Infrared, ultraviolet, and NMR spectroscopic studies showed unambiguously that the coordinate bond involves the pyridine-type nitrogen atom of the azole ring. [137,138,241] A similar conclusion was reached concerning the structure of the cobalt complexes of *N*-vinylbenzimidazole and a number of its 2-alkyl(arylalkyl) derivatives (XIX). [242]

Together with the complexes of the amibdent systems, those of a number of azole ligands with isolated electron-donating centres have been obtained: 2-hydroxymethyl derivatives of benzimidazole (XXI) [68,81,243-247] and benzothiazole (LXXII), [26,96,248] 2-(α-hydroxybenzyl)benzimidazole (LXXIII), [249] and 2-acetonylbenzothiazole (LXXIV): [26]



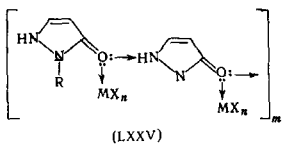
(LXXI) X=NH
(LXXII) X=S (LXXIII) (LXXIV)

The ligands (LXXI)–(LXXIV) are bidentate; the complexes are formed via the pyridine-type nitrogen atom of the azole ring and the hydroxyl oxygen, as a result of which they have a chelate structure with an octahedral configuration. Apparently the ligand (LXXIV) also occupies two coordination sites in the coordination compound [26]. However, in order to reach a final conclusion concerning the mode of its coordination, it is necessary to make a detailed infrared spectroscopic study of the stretching vibration frequencies of the carbonyl group on complex formation.

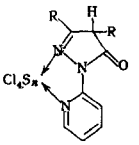
7. STABILISATION OF TAUTOMERS AND CONFORMERS OF AZOLE-CONTAINING COMPOUNDS AS A RESULT OF COMPLEX FORMATION

It is believed [250] that the formation of chelate complexes results in the stabilisation of specific tautomeric forms of the ligands (for example the enol and thiol forms in the metal chelates of acetylacetone [251] and its thio-analogues [252-254]). However, these examples of the stabilisation of one of the tautomeric forms as a result of complex formation are not altogether correct. In the coordinated ligand of a chelate complex, the bonds are known to be partly equivalent (acetylacetonates) and therefore it is difficult to speak of the stabilisation of a particular tautomeric form as a result of the formation of the chelate. On the other hand, it has been shown [9,255] that the hypothesis of the stabilisation of one of the tautomeric forms of the ligand as a result of complex formation is valid for molecular complexes in which the ligand [bonding] system is fully retained.

The infrared spectra of the complexes of pyrazolones as well as of the coordination compounds of antipyrine (LIV) show bands due to the NH group (2400–3300 cm^{-1}) and the protonated antipyrine ring (1550–1600 cm^{-1}). Moreover, frequencies characteristic of the complexes of MX_n with 3,4,4-trimethylpyrazolone-5-one do not occur in the region of 1700 cm^{-1}. These data suggest that in the pyrazolone complexes the antipyrine structure is stabilised and the complexes have the structure of coordination polymers (LXXV):



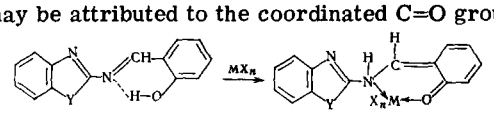
(LXXV)



(LXXVI) R = H, Alk

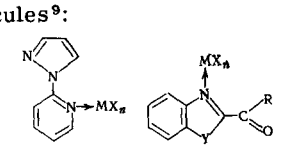
In the complexes of 1-(α-pyridyl)pyrazolones (LXII), the pyrazolone tautomeric form (LXXVI) is stabilised: the infrared spectra of the complex of (LXII) with $SnCl_4$ show absorption due to the free carbonyl group (1710 to 1715 cm^{-1}). [204]

A study of the infrared spectra of complexes of MX_n with o-hydroxyanils of the benzazole series led to the view [9] that the quinonoid form (LXXVII), which is "uncharacteristic" of o-hydroxyazomethines, is stabilised by complex formation: at 1650 cm^{-1} a band was observed, which may be attributed to the coordinated C=O group:



(LXXVII)

It has been established that not only tautomers but also conformers of compounds of the azole series may be stabilised by complex formation [9]. This may involve the retention or an alteration of the configuration of the ligand compared with the form of the non-coordinated azole molecule. In their complexes with MX_n, 1-(α-pyridyl)-pyrazoles [204] and 2-formylbenzazoles [210] retain the *S-trans*-configurations (LXXVIII) and (LXXIX) characteristic of free azole molecules [9]:



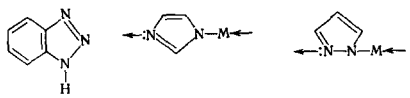
(LXXVIII) (LXXIX)

Only the complexes of carbonylazoles with AlX_3 (X = Cl or Br) form cyclic structures (LIII) in which the ligands assume the *S-cis*-form [9]. A similar conversion of the *S-trans-trans*-form into the *S-cis-trans*-configuration (XLVIII) is observed when anils of 2-formylbenzazoles (XLIII) react with MX_n. [9,189] It has been concluded [9] that the stabilisation of one of the conformers need not necessarily be due solely to the structure of the ligand system as is usually postulated for a whole series of bisheterocyclic systems (bipyridyl): the properties of the complex-forming agent (MX_n) play an extremely important role in this process.

III. *N*-METAL AND *N*-ELEMENT DERIVATIVES OF AZOLES

Azoles with an unsubstituted NH-group exhibit acid properties on interaction with metals. The acidity constants of tetrazole and its derivatives ($pK_b = 5$), which are the most acid of the azoles, are close to those of acetic acid ($pK_b = 4.76$), while imidazole, which is least acidic, has $pK_b = 14.52$. Despite the comparatively low pK_b values of azoles, *N*-metal-substituted derivatives of imidazole [13,16,49,50,122,172,256-263], pyrazole [113,264,265], triazoles [261,266-268], tetrazole [269-277], benzimidazole [4,57,278], and benzotriazole (LXXX) [261,279-285] are now known.

In contrast to the molecular complexes discussed in section II, *N*-metal-substituted azoles contain covalent M–N σ bonds and electron-donating (sp^2-hybridised nitrogen) and electron-accepting (metal atom) centres not involved in coordination interaction [compounds (LXXXI) and (LXXXII)]:



(LXXX) (LXXXI) (LXXXII)

Therefore molecules of types (LXXXI) and (LXXXII) tend to undergo self-association and to form polymeric structures [9,50,125,258-262,270]. Metal-containing polymers of the azole series have anomalous magnetic properties (the μ_{eff} are lower than the spin-only values), which is attributed to a metal–metal exchange interaction via the π-electron system of the azole rings [4,9,261,262,268] or to a metal–metal bond [50].

The study of the magnetic properties [4,50,57,258,259] and reflection spectra [4,50,57] leads to the conclusion that the type of polyhedra formed in the crystalline phase by *N*-metal-substituted azoles depends primarily on the nature of the metal [50]. Copper complexes of imidazole and benzimidazole [57] have distorted tetrahedral (almost planar) structures, cobalt and zinc coordination compounds have tetrahedral structures regardless of the type of ligand [4,49,50,113], and nickel complexes have predominantly planar structures [16,50,258,259].

The capacity of azoles with an unsubstituted NH group to form *N*-element-substituted compounds was observed in the 1960's by several independent groups of investigators [9]. Birkofer developed a method for the synthesis of *N*-silyl derivatives of azoles [286,287], which proved to be exceptionally reactive in the synthesis of numerous *N*-substituted azole derivatives [286-291]. Systematic studies on *N*-trialkylmetal derivatives of azole-containing systems have been made by Van der Kerk and coworkers [292-305].

The development of the chemistry of pyrazole derivatives of boron is associated mainly with studies by

Trofimenko [154,155,265,302-306]. Other investigations in this field have also been made [125,307-311].

The choice of conditions for the synthesis of *N*-element-substituted derivatives depends on the acidity of the NH group of azoles, the reactivity of the metallating agents, and the resistance of the complexes obtained to hydrolysis. Tetrazole reacts with trimethylsilane under exceptionally mild conditions (benzene, 10°C), [287] while the synthesis of *N*-trimethylsilyl-substituted derivatives of other azoles requires heating of the azole system with hexamethyldisilazane for many hours [286]. The trimethyl derivatives of the majority of Group III elements react even with imidazole, the least acid compound of this series, in benzene or hexane in the cold [9,122], but BR_3 derivatives react only under comparatively severe conditions [9,119,302,305].

The majority of *N*-metal derivatives of the azole series are readily hydrolysed, but tin-, [297,299-301] germanium-, [296] and lead-substituted [298] compounds are comparatively stable. Therefore *N*-trimethylmetal derivatives can be obtained from the oxides [297] and hydroxides [293,298,308] of the corresponding elements:

$$(R_3M)_2O + 2HN\!\!\rangle \rightarrow 2R_3M{-}N\!\!\rangle + H_2O\ ,$$

$$R_3MOH + HN\!\!\rangle \rightarrow R_3M{-}N\!\!\rangle + H_2O\ .$$

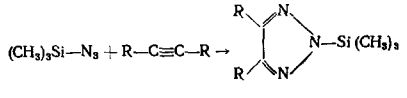
N-Element-substituted derivatives are obtained with the aid of the above reactions for a number of azoles and benzazoles and also purines [308]. *N*-Phenylmercury derivatives of imidazole, benzimidazole [312], and pyrazole [313] systems are obtained in the same way.

N-Metal carbonyl derivatives of the azole series are successfully synthesised by methods based on the interaction of alkali metal salts of azoles with metal carbonyl halides [154] or their π-cyclopentadienyl derivatives [34,35,45,314,315]:

$$\rangle N{-}M + X\,(CO)_2FeC_5H_5{\cdot}\pi \rightarrow \rangle N{-}Fe\,(CO)_2C_5H_5{\cdot}\pi\ ,$$

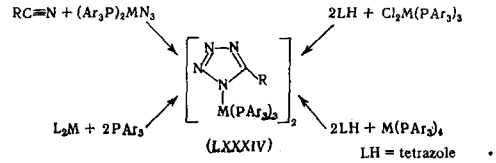
where M = Na or K, X = Cl, Br, or I, and $\rangle N$ is a heterocyclic group. This reaction was first widely employed by Seel to prepared a series of σ-complexes of azoles with π-cyclopentadienyliron dicarbonyl [45,314]. Subsequently the analogous benzotriazole derivatives [34,35,315] and rhodium dicarbonyl complexes of pyrazoles [154] were synthesised in the same way. The reaction serves as a basis for the synthesis of rhodium and palladium complexes of pyrazole and its derivatives linked by π bonds to olefins [154,155].

N-Element-substituted derivatives of azoles can be obtained not only directly from the heterocycles but also by an indirect method. Thus Birkofer [287,289] employed the 1,3-cycloaddition of trimethylsilyl azides to synthesise *N*-trimethylsilyl derivatives of 1,2,3-triazoles (LXXXIII):



(LXXXIII)

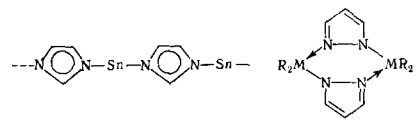
The synthesis of bis[tetrazolyltris(triphenylphosphine)-metal] complexes (LXXXIV) [8,90] in which the metal is copper, palladium, platinum, and ruthenium has been achieved on the same basis although other methods for the synthesis of complexes of this class from tetrazole or its *N*-metal derivatives have been developed [277,316]:



(LXXXIV) LH = tetrazole .

N-Element-substituted derivatives of azoles, like the *N*-metal-substituted derivatives discussed above, are mainly coordination-saturated oligomers or polymers [296-301,312,317]. Comparative viscometric studies showed that organotin polymers contain association complexes with much higher molecular weights than the organogermanium polymers [296].

The structure of *N*-element-substituted derivatives of azoles has so far been very little investigated. It has been postulated, albeit without insufficient justification, that trialkyltin derivatives of imidazoles have a linear coordination-saturated structure (LXXXV) with a pentacoordinate tin atom and equivalent bonds [297,317]:

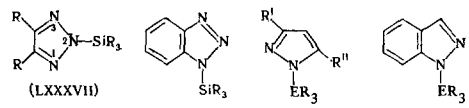


(LXXXV) (LXXXVI) M = B, Al .

According to NMR spectroscopic data, *N*-phenylmercury derivatives of 4,5-dichloro-2-methylimidazole have a similar configuration [312], *N*-dialkylmetal derivatives of azoles [9,119,122,265,303,306], *N*-trimethylsilylazoles [287,291], and *N*-phenylmercury derivatives of imidazole [312] and pyrazole [313] have been most thoroughly investigated among compounds of this class.

Cryoscopic (ebullioscopic) studies, NMR spectroscopy, and determinations of dipole moments showed [9,119,122] that the type of oligomers of the alkyl derivatives of Group III elements under consideration depends on the nature of the ligand (the distribution of nitrogen atoms in the heterocyclic ring) and on the properties of the ER_n substituent, where E is an element and R an organic group. *N*-Trialkyl-boron- [155,265,303] and -aluminium-substituted [9,122] pyrazoles are highly symmetrical dimers (LXXXVI), while the complexes of imidazole, benzimidazole, and tetrahydrobenzimidazole with the same substituents are probably linear polymers [9,119,122]. *N*-Dimethyl-gallium and -indium derivatives form cyclic tetramers or hexamers in solution regardless of the type of azole [9,122].

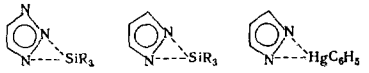
N-Trimethylsilyl(germyl)-substituted triazoles [289], pyrazoles [291,309], and indazoles [309] have been investigated mainly in connection with the determination of the position of the ER_n substituent in the azole ring [289,309] and of the elementotropic mobility of the ER_3 group [289,291]. Measurements of the dipole moments of a series of $NSiR_3$-substituted 1,2,3-triazoles showed that these complexes have the structure (LXXXVII) with the substituent in the 2-position of the triazole ring [289]. However, the analogous benzotriazole derivative (LXXXVII) contains the SiR_3 substituents in the 1-position [289]:



(LXXXVII) R = CH_3 (LXXXVIII) (LXXXIX) (XC) .

Elguero et al.[309] determined from NMR spectroscopic data the position of the ER_3 substituent (E = Si or Ge; R = CH_3 or C_2H_5) in pyrazoles (LXXXIX) and in indazole (XC).

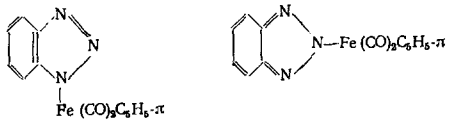
In 1966 Birkofer[289] suggested that the SiR_3 group may migrate readily between the nitrogen atoms of the triazole ring (XCI):



(XCI) (XCII) (XCIII)

Subsequently this elementotropic mobility of the *N*-substituent was observed for methylsilyl derivatives of pyrazole (XCII)[304] and was demonstrated almost unambiguously in a series of *N*-phenylmercury derivatives of the same heterocycle (XCIII).[313]

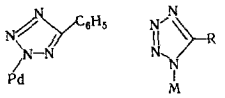
The situation is different with the coordination-saturated *N*-substituted derivative of benzotriazole containing a substituent with a relatively low mobility—π-cyclopentadienyliron carbonyl[315]. In this case, it is possible to isolate two isomers in which the substituent is linked to different nitrogen atoms of the triazole ring [(XCIV) and (XCV)].[315]



(XCIV) (XCV)

Thus even a limited number of examples demonstrate that not only is it possible to observe elementotropism in azole *N*-substituted derivatives of the elements but also one can isolate stable isomers involving different positions of the substituent relative to the nitrogen atoms of the heterocyclic ring. Nesmeyanov et al.[315] noted that the formation of similar isomers could probably be expected also for *N*-metal-substituted benzotriazole systems. We believe that, when the substituents and temperature conditions are suitably chosen, elementotropism may be observed or stable isomers isolated also for other *N*-element- and possibly *N*-metal-substituted triazole and tetrazole systems.

In this connection it is interesting to note that X-ray diffraction studies led to the discovery of a 2-palladium-substituted 5-phenyltetrazole derivative (XCVI),[277] while 1-metal-substituted structures (XCVII) have been postulated for other metals[269-277]:



(XCVI) (XCVII)

In conclusion we may note that the reaction of alkali metal borohydrides with pyrazole yielded polypyrazolylborates[154,302,303,305], which are exceptionally interesting ligands for the synthesis of metal chelates[155,265] and π complexes[154-157,306].

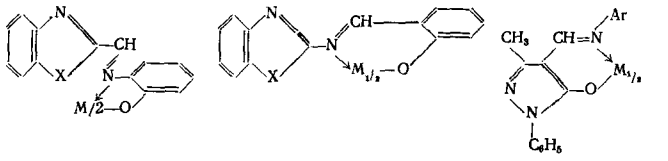
IV. CHELATE COMPLEXES IN THE AZOLE SERIES

Numerous chelate complexes synthesised from azole ligands‡ and containing chelate groups of the types MO_2N_2, MS_2N_2, MSe_2N_2, and MN_4, which are of greatest importance for coordination chemistry, are now known. In considering the methods of synthesis, the physicochemical properties, and the structures of complexes of this class, it is useful to arrange them systematically in terms of different types of coordination units.

‡ Azole-containing systems with chelating groups occupy an outstanding place among analytical reagents, metallochromic indicators, and extractants[6-9,318-338].

1. METAL CHELATES WITH AN MO_2N_2 COORDINATION UNIT

The hydroxyazomethines (LX)[9,339,340] and (LXI)[9,339] and 4-aminomethylene derivatives of pyrazolones[9] interact with bivalent metals salts to form chelates with five-membered [compounds (XCVIII)][9,340-344] and six-membered [compounds (XCIX) and (C)][9,189,344,345] metal-containing rings:



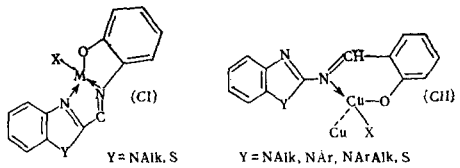
(XCVIII) (XCIX) (C)

The most typical composition of the chelates is ML_2, where LH are the ligands (XCVIII)–(C).[9,341-345] However, the anils (XCIX) form the complexes $ML.COOCH_3$ with copper(II), manganese(II), cadmium(II), lead(II), and $U^{II}O_2$.[341-344] Copper complexes of a similar type were obtained also for the azomethines (XCIX).[9,189] On the other hand, zinc and cadmium complexes with the composition ML_2 can be synthesised by refluxing the *o*-aminophenoxides of the above metals and the corresponding 2-formylbenzazoles in dioxan[344].

The chelate structure of the above complexes was established by comparing the infrared spectra of the coordination compound and the ligand: the hydrogen atoms of the hydroxy-group are found to be substituted [the bands corresponding to the OH stretching vibrations in the range 3400–3450 cm^{-1} for compound (LX)[339] and 3000–4000 cm^{-1} for compound (LXI)[9,189]] and the stretching vibration frequencies of the azomethine linkage increase[342,344]. Magnetic measurements showed that, as for the chelates of aromatic azomethines with a five-membered metal-containing ring[104,346-351], the complexes of the *o*-hydroxyanils (LX) have a tetrahedral or polymeric-octahedral configuration in the crystalline phase[343,344]. In contrast to the chelates of aromatic *o*-hydroxyazomethines with a six-membered metal chelate unit[104,352], coordination compounds of types (XCIX) and (C) have a polymeric-octahedral structure in the solid phase and a tetrahedral structure in solution regardless of the complex-forming metal[9,344,345]. These differences were explained[9,344] by the additional coordination of the metal to the pyridine-type nitrogen atom of the azole ring, which leads to an increase of the number of binding sites of the ligand actually employed (octahedron) or stabilises the tetrahedral configuration in solution.

Copper chelates with the acetate anion have unusual magnetic properties: while the chelates of the azomethine (XCVIII) have effective magnetic moments (μeff) corresponding to one unpaired electron (1.8–1.9 Bohr magnetons) the complexes of the *o*-hydroxyanils (XCIV) and (C) have the anomalous values μeff = 1.47–1.62 Bohr magnetons[9,344]. This result is attributed[9,344,351] to the formation in the first case of the coordination-saturated structure (CI) and metal–metal exchange interaction, while in the second

case the structure (CII) is believed to be formed via a Cu–Cu linkage or an acetate bridge [353,354]:

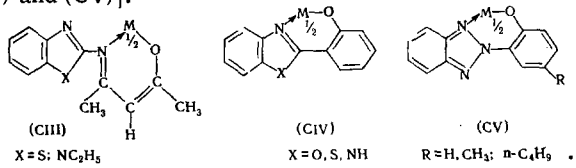


(CI) (CII)

Y = NAlk, S Y = NAlk, NAr, NArAlk, S

X = $OCOCH_3$

The six-membered metal chelate unit MN_2O_2 is also formed in the chelates of β-aminovinylketones [compounds (CIII)] [9] and 2-(*o*-hydroxyphenyl)benzazoles [compounds (CIV) and (CV)]. [9,14,191,355–361]

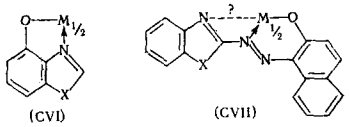


(CIII) (CIV) (CV)

X = S; NC_2H_5 X = O, S, NH R = H, CH_3; n-C_4H_9 .

The synthesis of the chelates (CIII) was achieved by the reaction of the metal acetylacetonates with 2-aminobenzazoles [9] and compounds (CIV) and (CV) were obtained by direct interaction of metal salts (the acetates are best) [358,359] with 2-(*o*-hydroxyphenyl)benzazoles. In the crystalline phase, all these complexes apparently have a polymeric-octahedral structure [9,361]. The initial hypothesis of a tetrahedral configuration of the metal chelates (CIV) [359] was shown to be erroneous by X-ray diffraction studies [361] §: in the copper and palladium complexes the metal is located in the plane of the coordination unit, but, as a result of the intermolecular (axial) coordination of copper(II) or palladium(II) to the oxygen atom of an adjacent metal-containing ring, a polymeric-octahedral configuration is produced [361].

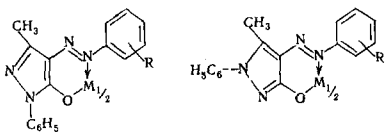
The 4-hydroxybenzazole complexes (CVI) were investigated [363–366] only in order to compare their stability with that of the chelates of the very important analytical reagent 8-hydroxyquinoline. It was found that, with the exception of the zinc complexes, the stability of the chelates fits the Irving–Williams series and is lower than that of the 8-hydroxyquinoline complexes [363–366]:



(CVI) (CVII)

X = O, S, NH X = O, S, NR; R = H, Alk .

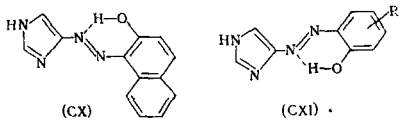
Hydroxyazo-derivatives of benzazoles (CVII) [9,344,367] and pyrazolones [compounds (CVIII) and CIX)] [368–370] yielded chelates with a six-membered metal chelate unit MO_2N_2, which in the crystalline phase has mainly an octahedral structure [9,370,371,373] and in solution mainly a tetrahedral structure [9,373].



(CVIII) R = H; *o*, *m*, *p*-CH_3; OCH_3; SCH_3; Hal; NO_2 (CIX) .

The tetrahedral configuration of chelates of type (CVII) precludes the intramolecular coordination of the metal to the nitrogen atom of the heterocyclic ring [344,367] and was adopted *a priori* for complexes of pyridylazonaphthol and related heterocyclic compounds [374–377], including benzothiazolylazonaphthol [375,376].

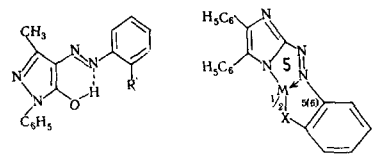
Snavely and coworkers have carried systematic determinations of the stability constants of chelates of types (CVIII) and (CIX). [369,370,372,378] The studies of Yamayichi et al. [379] of the properties of *o*-(4-hydroxyaryl)azoimidazole complexes (CX) and (CXI) had the same aim¶. However, thermodynamic data were not obtained in any of these investigations and therefore the conclusions arrived at must be treated with a certain amount of caution:



(CX) (CXI)

R = *p*-OCH_3, *m*-$N(CH_3)_2$.

Schetty's studies on the structures of the chromium chelate complexes of the tridentate azopyrazolone systems of type (CXII) need not be specially considered, since they have been reviewed by the author himself [380]:

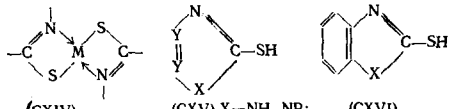


(CXII): R = OH, COOH (CXIII): X = O^-, COO^- .

We shall mention only that, after the publication of his review, a number of reports by the same author appeared, in which are described stereoisomeric chromium chelates of azopyrazolone derivatives (CXII, R = COOH) [381] and also complexes of 2-(*o*-hydroxyphenyl)-4,5-diphenylimidazoles with 5/5- or 5/6-metal-containing rings [382].

2. CHELATES OF TYPES MS_2N_2 AND MSe_2N_2

Complexes of 2-mercaptoazoles (CXV) [383–385] and 2-mercaptobenzazoles (CXVI) [386–393] with a five-membered metal-containing ring of type MN_2S_2 [structure (CXIV)] have been investigated. The majority of the studies were directed towards the analytical applications of compounds (CXV) and (CXVI) for a quantitative determination of platinum group metals [338,384–386,389,394,395].



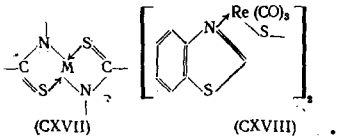
(CXIV) (CXV) X = NH, NR; Y = CR; Y = N (CXVI) X = NH, S .

However, in some of the investigations data have been obtained for the structures of the chelates synthesised from mercaptoazoles [387,392,393,396]. It is believed [392] that

§ In constructing a model of the metal chelate unit, Verkhovedova et al. [359] employed the usual [362] M–O bond lengths of 1.8–1.9 Å. However, in chelates of type (CIV) they actually exceed 2 Å.

¶ They described [379] the metal chelate (CXI–LH) with the composition LCuBr, in which according to infrared spectroscopy the hydrogen atom of the OH group and not the NH group is substituted by the metal.

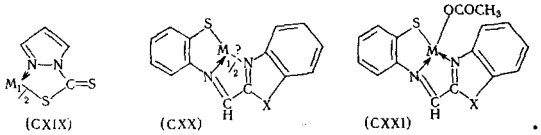
the bis(azathio)chelate unit (CXIV) is most probably formed rather than the thione configuration (CXVII):



(CXVII) (CXVIII)

The chelates of 2-mercapto-1-phenyltetrazoles (CXV, X = NH, Y = N) of type RuL_3 have an octahedral structure and those of types PtL_2 and $(RhL_2)_2$ have a planar structure [390]. The same derivatives of tetrazole with $Rh(PAr_3)_3Cl$ form mixed triphenylphosphine complexes of rhodium in which an Rh–S bond (300 cm^{-1}) and a metal chelate unit with a square planar configuration were found [396]. The dimeric octahedral complex (CXVIII) of 2-mercaptobenzothiazole with rhenium tricarbonyl is of undoubted interest [397].

A five-membered metal chelate unit of the type under consideration is formed in 1-pyrazolyldithiocarboxylates (CXIX) [398] and in the chelates of *o*-mercaptoanils of 2-formylbenzazoles [compounds (CXX) and (CXXI)]. [9,343,344,399]

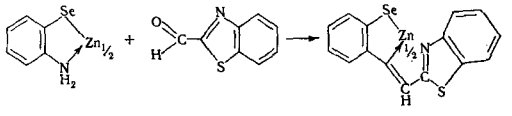


(CXIX) (CXX) (CXXI)

X = NCH_3, S

The complexes (CXX) and (CXXI) were shown to be metal chelates by infrared spectroscopy [9,343,399]. Magnetochemical studies make it possible to ascribe to the chelates (CXX) a polymeric-octahedral or tetrahedral configuration in the crystalline phase [9,343,399]. Intramolecular coordination of the metal to the nitrogen atom of the heterocyclic ring appears to be very probable in the complexes (CXXI), which have a normal magnetic moment [399].

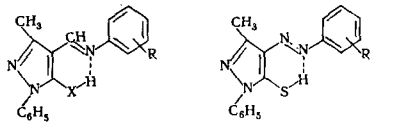
Recently an azomethine complex (CXXII) of the azole series containing a five-membered metal chelate unit with nitrogen and selenium atoms was synthesised [9,400]:



(CXXII)

As was to be expected [104], the zinc complex (CXXII) was found to have a tetrahedral structure in solution [400]. On the other hand, the pathways followed in the synthesis of this chelate with transition metals are still obscure†.

4-Phenylaminomethylene derivatives of thio- and selenopyrazol-5-one (CXXIII) [402] form chelates containing the six-membered coordination units MN_2S_2 [9,345,407] and MN_2Se_2, [9] which are rarely encountered with aromatic ligands [403–406]:



(CXXIII): R = H, *o*, *m*, *p*-CH_3, Hal, NO_2, OCH_3, $N(CH_3)_2$; X = S, Se

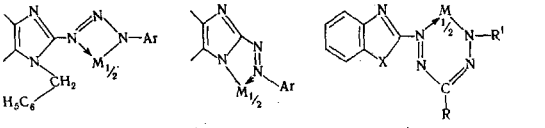
(CXXIV): R = H, *o*, *m*, *p*-CH_3, Hal, NO_2, OCH_3, SCH_3, $N(CH_3)_2$

The nickel complexes of the ligands (CXXIII) have unusual magnetic properties in the crystalline phase: in contrast to the mainly diamagnetic (planar) metal chelates containing nitrogen and sulphur atoms in the coordination unit [362,408,409], these chelate complexes have intermediate effective magnetic moments varying in the range 1.3–1.8 Bohr magnetons [9,345,407]. This result is attributed to the formation in the solid phase of a mixture of square planar (diamagnetic) and polymeric-octahedral (paramagnetic) forms [345,407]. On the other hand, in solution the nickel, cobalt, and zinc chelates of (CXXIII) are tetrahedral [9,345,407] according to their dipole (Ni^{2+}, Co^{2+}, Zn^{2+}) and magnetic (Ni^{2+}, Co^{2+}) moments. The cobalt and zinc chelates apparently have the same configuration in the crystalline phase [9,345]. The nickel‡ metal chelates of thioazopyrazolones (CXXIV), synthesised for the first time by Snavely [368,369,410,411], have the same properties in the solid phase [373,410] as their azomethine analogues (CXXIII). However, in solution the chelates (CXXIV) assume the diamagnetic and polar ($\mu = 3$ D) tetragonal-pyramidal configuration with the metal atom raised above the plane of the metal-containing ring [373,412].

3. CHELATES WITH MN_4 UNITS

In his review, Hennig [207] described fairly completely the studies on chelates based on ligands with an acid NH group, including those of the azole series with an MN_4 coordination unit. Therefore we shall consider only some of the fundamental characteristics introduced by the azole moiety into the configuration of the complexes in which the metal is linked to the nitrogen atoms.

In contrast to the usually planar chelates of aromatic compounds with an MN_4 coordination unit [362,408,409], the analogous metal chelates of azole-containing systems have in the crystalline phase mainly a polymeric-octahedral structure and in solution a tetrahedral structure. This difference between the configurations of the metal chelate units was observed in a study of the magnetic and polar properties of the chelates of the azole series with four-membered [the triazene complexes [9,413] (CXXV)], five-membered [complexes of azo-compounds [9,186,414–416] (CXXVI)], and six-membered [complexes of formazans [9,28,132,416–429] (CXXVII)] metal-containing rings.



(CXXV): Ar = C_6H_4X; X = H, *p*-Alk, *p*-Cl

(CXXVI): Ar = C_6H_5, $C_6H_4CH_3$

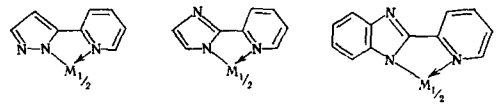
(CXXVII): R = Alk, Ar; R' = Ar, Het

There is no doubt that the formation of polymeric-octahedral structures in the crystalline phase can be accounted for by the coordination of the metal to the nitrogen atom of the azole ring of an adjacent molecule (the monomeric units of such chelates are coordination-unsaturated) [9,418,422,424,425]. The only study in which intramolecular coordination of the metal to the sulphur atom of the thiazole ring in the nickel and cobalt complexes of *N*-thiazolylformazan [28] was postulated does not withstand criticism, since the above heteroatom virtually lacks electron-donating properties (see above). On the

† Selenium-containing azomethines are unstable. On the other hand, a reaction similar to that indicated above proceeds only with seleno- and thio-phenoxides of non-transition metals [400,401].

‡ The chelates of thioazopyrazolones with other metals have been described and their stabilities have been determined [410,411].

other hand, planar polyhedra are encountered among chelates of the azole series with MN_4 metal chelate [207]. The latter include the nickel complexes (CXXVII) of pyridylpyrazoles, the planar structure of which has been demonstrated not only by magnetochemical [430] but also by X-ray diffraction [431] studies:



(CXXVIII) (CXXIX) (CXXX)

Possibly the above anomaly is associated with the comparatively low basicity of pyrazole. However, final conclusions will become possible only after detailed physicochemical and X-ray diffraction studies of the chelates of 2-pyridylimidazole (CXXIX) and its benzo-analogue (CXXX). [207,432]

ADDENDUM

During the preparation of the manuscript for the press, new data were published on the synthesis and structure of molecular complexes of azoles with transition metals [433-459] and complexes of polypyrazolyl borate ligands [460-462]§. Competitive coordination in the following ambident azole systems was considered: benzothiazole [445], benzoselenazole [457], *N*-vinylimidazole [439,440], 2-aminobenzazoles [463], pyridylmethylene-2-aminobenzothiazole [464], oligoheterocycles [465-470], and dinuclear copper complexes of 2-formylbenzimidazole aldoximes [471]. The structures and magnetic properties of complexes of the antipyrine series [472-483] and of acetamidothiazole [484] have been investigated.

Studies have been made on the physicochemical properties of *N*-metal-substituted 5-chloro- and 5-methoxyphenyltetrazoles [485], and 1-borylimidazole [486] and on the possible synthetic applications of silver and chloromercury salts of benzotriazole [487].

New metal chelates of *o*-hydroxyazo- [488] and *o*-hydroxyazomethine [489] derivatives of isoxazoles have been obtained. An electrochemical method has been developed [490] for the synthesis of chelates of types (XCVIII), (XCIX), (CIV), and (CV). Chelate complexes of copper(I) with 2-mercaptobenzothiazole [491] and of lanthanides with tetrazole-5-thione [492] have been synthesised.

Comparison of the properties of the chelates obtained [489,493] from pyrazole [(compounds (CXXIII)] [402] and pyrrole [494] mercaptoaldimines led to the conclusion that the heterocyclic moiety promotes a tetrahedral structure of the complexes with an MS_2N_2 coordination unit not only in solution [9,345,407] but also in the crystalline phase [489,493].

The ESR spectra of the copper complex (CXXVIII) of pyridylpyrazole have been investigated [495]. There has been a growth of interest in *C*-metal- and *C*-element-substituted derivatives of azoles [496-506]. *C*-Metal-substituted azoles have a polymeric-octahedral structure [496].

REFERENCES

1. D. C. Hodgkin, J. Kamper, J. Lindsey, M. Mackay, J. Rickworth, J. H. Robertson, C. B. Shoemaker, J. G. White, R. J. Prosen, and K. N. Trueblood, Proc. Roy. Soc. A, 242, 228 (1958); D. Crowfoot-Hodgkin, Angew. Chem., 77, 954 (1965).
2. E. Lester Smith, "Vitamin B12" (Translated into Russian), Inostr. Lit., Moscow, 1962, pp. 42, 57.
3. V. M. Berezovskii, Uspekhi Khim., 27, 551 (1958).
4. M. Goodgame and F. A. Cotton, J. Amer. Chem. Soc., 84, 1543 (1962).
5. G. Eichhorn, in "The Chemistry of the Coordination Compounds" (Edited by J. C. Bailar and D. H. Busch) (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 587.
6. R. C. Elderfield (Editor), "Heterocyclic Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1961, Vol. 5.
7. R. C. Elderfield (Editor), "Heterocyclic Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1965, Vol. 7.
8. R. C. Elderfield (Editor), "Heterocyclic Compounds" (Translated into Russian), Izd. Mir, Moscow, 1969, Vol. 8.
9. A. D. Garnovskii, Doctoral Thesis, Rostov-on-Don State University, 1972.
10. A. D. Garnovskii, O. A. Osipov, and S. B. Bulgarevich, Uspekhi Khim., 41, 648 (1972) [Russ. Chem. Rev., No. 4 (1972)].
11. N. C. Li, J. M. White, and F. Doody, J. Amer. Chem. Soc., 76, 6219 (1954).
12. I. Weitzel and A. M. Fretzdorf, Z. physiol. Chem., 305, 1 (1956).
13. I. Weitzel and A. M. Fretzdorf, Z. physiol. Chem., 307, 14 (1957).
14. T. J. Lane, J. Nakagawa, J. L. Walter, and A. J. Kandatiel, Inorg. Chem., 1, 267 (1962).
15. A. D. Garnovskii, O. A. Osipov, V. T. Panyushkin, and A. F. Pozharskii, Zhur. Obshch. Khim., 36, 1063 (1966).
16. W. J. Eilbeck, F. Holmes, and A. E. Underhill, J. Chem. Soc. (A), 757 (1967).
17. R. Driver and W. R. Walker, Austral. J. Chem., 21, 672 (1968).
18. G. A. Nelson and R. Nuttal, J. Molal. Struct., 1, 405 (1968).
19. E. Duff and M. N. Hughes, J. Chem. Soc. (A), 2144 (1968).
20. C. E. Taylor and A. E. Underhill, J. Chem. Soc. (A), 368 (1969).
21. C. Perchard and A. Novak, J. Chim. phys. et phys.-chim. Biol., 65, 1964 (1968).
22. J. Reedijk, Rec. Trav. chim., 88, 1451 (1969).
23. J. Reedijk, J. C. A. Windhorst, N. R. M. Van Ham, and W. L. Groeneveld, Rec. Trav. chim., 90, 234 (1971).
24. C. W. Reimann, J. Phys. Chem., 74, 561 (1970).
25. M. V. Artemenko, E. A. Chistyakova, and K. F. Slyusarenko, Zhur. Neorg. Khim., 14, 1847 (1969) [Russ. J. Inorg. Chem., No. 7 (1969)].
26. M. V. Artemenko, E. A. Chistyakova, P. A. Suprunenko, and G. I. Kal'naya, Zhur. Neorg. Khim., 16, 2448 (1971) [Russ. J. Inorg. Chem., No. 9 (1971)].
27. W. J. Davis and J. Smith, J. Chem. Soc. (A), 317 (1971).
28. T. Pyl and P. Meyer, Z. Chem., 6, 264 (1966).
29. E. J. Duff and M. N. Hughes, J. Chem. Soc. (A), 447 (1969).
30. E. J. Duff, J. Inorg. Nuclear Chem., 32, 3103 (1970).
31. P. Ghosh and L. K. Mishra, J. Indian Chem. Soc., 47, 1153 (1970).
33. A. N. Nesmeyanov, M. M. Rybinskaya, N. S. Kochetkova, V. N. Babin, and G. B. Shul'pin, Dokl. Akad. Nauk SSSR, 181, 1397 (1968).

§ See also the Editor's comments in Ref. 155.

34. V.N.Babin, L.A.Fedorov, N.S.Kochetkova, and Yu.A.Belousov, "Tezisy Dokladov V Mezhdunarodnogo Kongressa po Metalloorganicheskoi Khimii" (Abstracts of Reports at the Fifth International Congress of Organometallic Chemistry), Moscow, 1971, Vol.2, p.429.
35. V.N.Babin, Candidate's Thesis, Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow, 1971.
36. C.W.Reimann, A.D.Mighell, and F.A.Mauer, Acta Cryst., B 23, 135 (1967).
37. F.Akhtar, D.M.L.Goodgame, M.Goodgame, J.W. Rayner-Canham, and A.C.Scapski, Chem.Comm., 1389 (1968).
38. C.W.Reimann and A.Santoro, Acta Cryst., B25, 595 (1969).
39. A.Santoro, A.D.Mighell, M.Zocchi, and C.W. Reimann, Acta Cryst., B25, 842 (1969).
40. A.Cadet, Compt.rend., 272C, 1299 (1971).
41. W.Beck, J.C.Weiss, and J.Wieczirek, J.Organomet.Chem., 30, 89 (1971); Ber., 105, 3202 (1972).
42. J.Reedijk, Inorg.Chim.Acta, 3, 517 (1969).
43. J.Reedijk, Rec.Trav.chim., 90, 117 (1971).
44. J.Reedijk, Rec.Trav.chim., 90, 1249 (1971).
45. F.Seel and V.Sperber, J.Organomet.Chem., 14, 405 (1969).
46. A.D.Garnovskii, N.E.Kolobova, I.B.Zlotina, G.K.Mitina, K.N.Anisimov, and O.A.Osipov, "Tezisy Dokladov V Mezhdunarodnogo Kongressa po Metalloorganicheskoi Khimii" (Abstracts of Reports at the Fifth International Congress of Organometallic Chemistry), Moscow, 1971, Vol.I, p.108; Izv.Akad.Nauk SSSR, Ser.Khim., 629 (1972).
47. A.N.Nesmeyanov, V.N.Babin, N.S.Kochetkova, and Yu.S.Nekrasov, Dokl.Akad.Nauk SSSR, 200, 601 (1971).
48. A.D.Garnovskii, N.E.Kolobova, O.A.Osipov, K.N.Anisimov, I.B.Zlotina, G.K.Mitina, and Yu.V.Kolodyazhnyi, Zhur.Obshch.Khim., 42, 929 (1972).
49. D.M.L.Goodgame, M.Goodgame, P.J.Hayward, and C.W.Rayner-Canham, Inorg.Chem., 7, 2447 (1968).
50. W.J.Eilbeck, F.Holmes, C.E.Taylor, and A.E. Underhill, J.Chem.Soc.(A), 128 (1968).
51. C.D.Burbidge and D.M.L.Goodgame, Inorg.Chim. Acta, 4, 231 (1970).
52. N.A.Daugherty and J.H.Swister, Inorg.Chem., 7, 165 (1968).
53. D.Nichols and B.A.Warburton, J.Inorg.Nuclear Chem., 32, 3871 (1970).
54. M.J.Badley, D.Nichols, and B.A.Warburton, J. Chem.Soc.(A), 2694 (1970).
55. M.N.Hughes and R.J.Rutt, J.Chem.Soc.(A), 3015 (1970).
56. J.A.Weaver, P.Hambright, P.T.Talbert, E.Kang, and A.N.Thorpe, Inorg.Chem., 9, 268 (1970).
57. M.Goodgame and L.J.B.Heines, J.Chem.Soc.(A), 174 (1966).
58. K.Bose, B.Sharma, and C.C.Patel, J.Inorg. Nuclear Chem., 32, 1742 (1970).
59. D.M.L.Goodgame, M.Goodgame, and J.M.Weeks, J.Chem.Soc.(A), 1125 (1967).
60. D.M.L.Goodgame and M.Goodgame, Inorg.Chem., 4, 139 (1965).
61. D.M.L.Goodgame, M.Goodgame, and J.M.Weeks, J.Chem.Soc.(A), 5194 (1964).
62. D.M.L.Goodgame, M.Goodgame, and J.M.Weeks, J.Chem.Soc.(A), 1676 (1967).
63. E.J.Duff, M.N.Hughes, and K.J.Rutt, J.Chem. Soc.(A), 2354 (1968).
64. R.A.Ford, G.Halkyard, and A.E.Underhill, Inorg.Nuclear Chem.Letters, 7, 507 (1968).
65. E.Duff, M.N.Hughes, and K.J.Rutt, J.Chem.Soc. (A), 2126 (1969).
66. M.M.J.Chan, M.Goodgame, and J.M.Weeks, J. Chem.Soc.(A), 2499 (1968).
67. M.V.Artemenko and K.F.Slyusarenko, Ukrain. Khim.Zhur., 32, 136 (1966).
68. M.V.Artemenko and E.A.Chistyakova, Zhur. Neorg.Khim., 15, 2423 (1970) [Russ.J.Inorg. Chem., No.9 (1970)].
69. E.A.Chistyakova, Candidate's Thesis, The State University, Kiev, 1972.
70. D.M.L.Goodgame, M.Goodgame, and C.W. Rayner-Canham, J.Chem.Soc.(A), 1923 (1971).
71. V.I.Minkin, V.A.Bren', A.D.Garnovskii, and R.I.Nikitina, Khim.Geterotsikl.Soed., 552 (1972).
72. A.I.Popov, Coord.Chem.Rev., 4, 463 (1969).
73. W.J.Eilbeck, F.Holmes, C.E.Taylor, and A.E. Underhill, J.Chem.Soc.(A), 1189 (1968).
74. P.T.Talbert, J.A.Weaver, and P.Hambright, J. Inorg.Nuclear Chem., 32, 2147 (1970).
75. K.S.Bose and C.C.Patel, J.Inorg.Nuclear Chem., 33, 755 (1971).
76. M.Goodgame and J.M.Weeks, J.Chem.Soc.(A), 1156 (1966).
77. E.Duff, M.N.Hughes, and K.J.Rutt, J.Chem.Soc. (A), 2102 (1969).
78. J.Reedijk, J.Inorg.Nuclear Chem., 33, 179 (1971).
79. J.Reedijk, Rec.Trav.chim., 90, 605 (1970).
80. D.M.L.Goodgame, M.Goodgame, and C.W. Rayner-Canham, Inorg.Chim.Acta, 3, 399, 406 (1968).
81. M.V.Artemenko and K.F.Slyusarenko, Zhur. Neorg.Khim., 12, 974 (1967) [Russ.J.Inorg.Chem., No.4 (1967)].
82. M.V.Artemenko and K.F.Slyusarenko, Zhur. Neorg.Khim., 16, 2163 (1971) [Russ.J.Inorg. Chem., No.8 (1971)].
83. F.Heins and M.Zimmermann, Naturwiss., 43, 468 (1956).
84. C.Sandmark and C.J.Brändén, Acta Chem.Scand., 21, 993 (1967).
85. S.Hataeyama and C.Sato, Sci.Rept.Hirosaki Univ., 71, 7 (1970).
86. M.J.M.Campbell, D.W.Gard, and R.Grzeskowiak, Inorg.Nuclear Chem.Letters, 5, 39 (1969).
87. R.King, N.Koros, and G.Nelson, J.Chem.Soc.(A), 5549 (1963).
88. C.C.Addison and N.Loran, Adv.Inorg.Chem. Radiochem., 6, 71 (1964).
89. B.O.Field and C.J.Hardy, Quart.Rev., 18, 361 (1964).
90. C.C.Addison and D.Sutton, Progr.Inorg.Chem., 8, 195 (1967).
91. C.C.Addison, N.Logan, and S.C.Wallwork, Quart. Rev., 25, 289 (1971).
92. M.A.Porai-Koshits and G.V.Tsintsadze, Symposium, "Kristallokhimiya. 'Itogi Nauki'" (Crystal Chemistry, "Advances in Science"), Izd.VINITI, Akad.Nauk SSSR, Moscow, 1967, p.196.
93. A.H.Norbury and A.J.P.Sinha, Quart.Rev., 24, 69 (1970).

94. "Kolebatel'nye Spektry v Neorganicheskoi Khimii" (Vibrational Spectra in Inorganic Chemistry), Moscow, 1971, p. 139.
95. A. H. Norbury, J. Chem. Soc. (A), 1089 (1971).
96. M. V. Artemenko and K. F. Slyusarenko, Zhur. Neorg. Khim., 15, 106 (1970) [Russ. J. Inorg. Chem., No. 1 (1970)].
97. N. S. Elder, Y. A. Nelson, and D. R. Busch, Inorg. Chem., 5, 1309 (1966).
98. M. V. Artemenko, E. A. Chistyakova, P. A. Suprunenko, and G. I. Kal'naya, Zhur. Neorg. Khim., 16, 1082 (1971) [Russ. J. Inorg. Chem., No. 4 (1971)].
99. M. V. Artemenko, E. A. Chistyakova, P. A. Suprunenko, and G. I. Kal'naya, Zhur. Neorg. Khim., 16, 1932 (1971) [Russ. J. Inorg. Chem., No. 7 (1971)].
100. M. V. Artemenko, E. A. Chistyakova, P. A. Suprunenko, and G. I. Kal'naya, Zhur. Neorg. Khim., 17, 713 (1972) [Russ. J. Inorg. Chem., No. 3 (1972)].
101. K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds" (Translated into Russian), Izd. Mir, Moscow, 1966.
102. A. D. Garnovskii, E. V. Skopenko, T. D. Artyukhovich, O. A. Osipov, M. I. Knyazhanskii, and P. V. Gilyanovskii, Zhur. Obshch. Khim., 42, 2068 (1972).
103. F. Hug and A. C. Scapski, J. Chem. Soc. (A), 1923 (1971).
104. O. A. Osipov, A. D. Garnovskii, and V. I. Minkin, Zhur. Strukt. Khim., 8, 913 (1967).
105. A. D. Garnovskii, O. A. Osipov, and V. I. Minkin, Uspekhi Khim., 37, 1782 (1968) [Russ. Chem. Rev., No. 10 (1968)].
106. J. T. Edsall, G. Felsenfeld, D. S. Goodman, and F. N. R. Gurd, J. Amer. Chem. Soc., 76, 3054 (1954).
107. R. L. Mickel and A. C. Andrews, J. Amer. Chem. Soc., 77, 5291 (1955).
108. M. R. Bruce and J. T. Edsall, J. Amer. Chem. Soc., 80, 5033 (1958).
109. R. Mathur and H. Lal, J. Phys. Chem., 63, 439 (1959).
110. A. Taurins and W. G. Schneider, Canad. J. Chem., 38, 1237 (1960).
111. F. Schneider and W. Schlag, Z. Physiol. Chem., 327, 74 (1962).
112. A. C. Andrews and R. J. Kirk, Trans. Kansas Acad. Sci., 67, 630 (1964).
113. J. E. Baumann and J. C. Wang, Inorg. Chem., 3, 368 (1964).
114. E. V. Sklenskaya and M. Kh. Karapet'yants, Zhur. Neorg. Khim., 11, 2061 (1966) [Russ. J. Inorg. Chem., No. 9 (1966)].
115. N. Yasuhiko, F. N. R. Gurd, R. F. Chen, and J. T. Edsall, J. Amer. Chem. Soc., 79, 2123 (1957).
116. T. Kaden and A. Zuberbiller, Helv. Chim. Acta, 49, 2189 (1966).
117. J. Lewis and R. G. Wilkins, (Editors), "Modern Coordination Chemistry. Principles and Methods" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 51.
118. K. B. Yatsimirskii and V. P. Vasil'ev, "Konstanty Nestoikosti Kompleksnykh Soedinenii" (Instability Constants of Complex Compounds), Izd. Akad. Nauk SSSR, Moscow, 1959.
119. K. M. Yunusov, Candidate's Thesis, The State University, Rostov-on-Don, 1971.
120. K. M. Yunusov, A. D. Garnovskii, O. A. Osipov, and N. D. Vitkevich, Zhur. Neorg. Khim., 15, 1802 (1970) [Russ. J. Inorg. Chem., No. 7 (1970)].
121. K. M. Yunusov, N. L. Firsova, A. D. Garnovskii, Yu. V. Kolodyazhnyi, and O. A. Osipov, Zhur. Obshch. Khim., 41, 1128 (1971).
122. A. D. Garnovskii, O. Yu. Okhlobystin, O. A. Osipov, K. M. Yunusov, Yu. V. Kolodyazhnyi, L. M. Golubinskaya, and V. I. Svergun, see Ref. 34, p. 376; Zhur. Obshch. Khim., 42, 920 (1972).
123. K. M. Yunusov, A. D. Garnovskii, O. A. Osipov, and Yu. V. Kolodyazhnyi, Zhur. Obshch. Khim., 41, 1320 (1971).
124. F. A. Cotton and J. F. Gibson, J. Chem. Soc. (A), 1696 (1971).
125. A. G. Lee, J. Chem. Soc. (A), 880 (1971).
126. A. Fratiello, Inorg. Chem., 7, 1581 (1968).
127. E. N. Gur'yanova, Uspekhi Khim., 37, 1981 (1968) [Russ. Chem. Rev., No. 11 (1968)].
128. A. J. Carty, Coord. Chem. Rev., 4, 29 (1969).
129. E. N. Gur'yanova, I. G. Gol'dshtein, and I. P. Romm, "Donorno-aktseptornaya Svyaz'" (The Donor-acceptor Bond), Izd. Khimiya, Moscow, 1973.
130. A. D. Garnovskii, O. A. Osipov, V. T. Panyushkin, and A. F. Pozharskii, Zhur. Obshch. Khim., 36, 1063 (1966).
131. V. T. Panyushkin, A. D. Garnovskii, O. A. Osipov, A. L. Sinyavin, and A. F. Pozharskii, Zhur. Obshch. Khim., 37, 312 (1967).
132. V. T. Panyushkin, Candidate's Thesis, The State University, Rostov-on-Don, 1967.
133. V. G. Pesin and E. K. D'yachenko, Khim. Geterotsikl. Soed., 1048 (1967).
134. V. G. Pesin, Uspekhi Khim., 39, 1972 (1970) [Russ. Chem. Rev., 11 (1970)].
135. O. A. Osipov, "Polyarnye Svoistva Koordinatsionnykh Soedinenii i Rastvorov" (The Polar Properties of Coordination Compounds and Solutions), Izd. Rostov. Gos. Univ., Rostov-on-Don, 1963.
136. M. V. Artemenko and K. F. Slyusarenko, Zhur. Neorg. Khim., 15, 3103 (1970 [Russ. J. Inorg. Chem., No. 11 (1970)].
137. E. S. Domnina, Yu. N. Ivlev, N. I. Shergina, N. N. Chipanina, L. V. Belousova, Yu. L. Frolov, and G. G. Skvortsova, Zhur. Obshch. Khim., 41, 1102 (1971).
138. G. G. Skvortsova, E. S. Domnina, Yu. V. Yevlev, N. N. Chapanina, V. I. Skorobogatova, and Yu. A. Myachin, Zhur. Obshch. Khim., 42, 596, 2199 (1972).
139. D. M. Adams, "Metal-ligand and Related Vibrations", London, 1967.
140. L. V. Surpina, Candidate's Thesis, The State University, Rostov-on-Don, 1971.
141. L. V. Surpina, A. D. Garnovskii, Yu. V. Kolodyazhnyi, and O. A. Osipov, Zhur. Obshch. Khim., 41, 2279 (1971).
142. A. V. Leshchenko, V. T. Panyushkin, A. D. Garnovskii, and O. A. Osipov, Zhur. Neorg. Khim., 11, 2156 (1966) [Russ. J. Inorg. Chem., No. 9 (1966)].
143. A. V. Leshchenko, V. T. Panyushkin, A. D. Garnovskii, and O. A. Osipov, Zhur. Obshch. Khim., 37, 1069 (1967).
144. L. V. Leshchenko, Candidate's Thesis, The State University, Rostov-on-Don, 1967.
145. M. Allbut, K. Feenan, and G. W. A. Fowles, J. Less Common Metals, 6, 299 (1964).
146. R. E. McCarley and B. A. Torp, Inorg. Chem., 2, 540 (1963).
147. G. W. A. Fowles, D. J. Tidmarsh, and R. A. Walton, J. Chem. Soc. (A), 1546 (1969).

148. D. L. Kepert and R. S. Nyholm, J. Chem. Soc. (A), 2871 (1965).
149. K. K. Joishi and P. L. Pauson, Proc. Chem. Soc., 326 (1962).
150. K. K. Joishi, P. L. Pauson, A. B. Qasi, and W. H. Stobbs, J. Organomet. Chem., 1, 47 (1964).
151. P. L. Pauson and A. R. Qasi, J. Organomet. Chem., 7, 321 (1967).
152. R. B. King and M. B. Bisnette, Inorg. Chem., 3, 796 (1964).
153. D. J. O'Sullivan and E. J. Labor, J. Organomet. Chem., 25, 180 (1970).
154. S. Trofimenko, Inorg. Chem., 10, 1372 (1971).
155. S. Trofimenko, Accounts Chem. Res., 4, 17 (1971).
156. A. Bond and M. Green, J. Chem. Soc. (A), 682 (1971).
157. M. I. Bruce, D. N. Sharrocks, and F. G. A. Stone, J. Organomet. Chem., 31, 269 (1971).
158. W. Beck, K. Bürger, and E. Schier, "Proceedings of the XIIIth International Conference on Coordination Chemistry, Poland", 1970, Vol. I, p. 270.
159. B. L. King and A. Efrady, J. Organomet. Chem., 20, 264 (1969).
160. K. Öfele and E. Dotzauer, J. Organomet. Chem., 30, 215 (1971).
161. K. Öfele, Ber., 99, 1732 (1966); J. Organomet. Chem., 42, c 87 (1972).
162. H. Lumbroso and B. Roques, see Ref. 34, p. 260.
163. E. O. Fischer and K. Öfele, Z. Naturforsch., 14b, 736 (1959); 93, 1156 (1960).
164. E. O. Fischer and K. Öfele, J. Organomet. Chem., 8, 5 (1967).
165. N. C. Baenziger and R. L. Schatz, Inorg. Chem., 10, 661 (1971).
166. D. M. Bewers, R. H. Erlich, S. Policec, and A. I. Popov, J. Inorg. Nuclear Chem., 33, 81 (1971).
167. M. E. Reach and K. K. Ramaswamy, Inorg. Chim. Acta, 5, 445 (1971).
168. R. Rivest and A. Weiss, Canad. J. Chem., 49, 1750 (1971).
169. R. H. Hanson and C. E. Meloan, Inorg. Nuclear Chem. Letters, 7, 461 (1971).
170. R. H. Hanson and C. E. Meloan, Inorg. Nuclear Chem. Letters, 7, 467 (1971).
171. Yu. N. Kukushkin, S. A. Simanova, V. K. Krylov, S. A. D'yachenko, and V. P. Alkashevich, Zhur. Obshch. Khim., 42, 592 (1972).
172. E. Baraniak, H. C. Freeman, J. M. James, and C. E. Nickols, J. Chem. Soc. (A), 2558 (1970).
173. E. Kralik and J. Vrestal, Coll. Czech. Chem. Comm., 26, 1293, 1298 (1961).
174. E. Kralik and J. Vrestal, Coll. Czech. Chem. Comm., 27, 1651 (1962).
175. D. G. Tisley and R. A. Walton, Inorg. Nuclear Chem. Letters, 6, 479 (1970).
176. M. J. M. Campbell, D. W. Gard, M. Goldstein, and R. Grzeskowiak, J. Chem. Soc. (A), 672 (1970).
177. M. J. M. Campbell, G. W. Gard, and M. Goldstein, J. Inorg. Nuclear Chem., 32, 3843 (1970).
178. H. Gehlen and H. Waeschke, J. Prakt. Chem., 312, 408 (1970).
179. W. C. Malik, P. K. Srivastava, and S. C. Mehra, J. Indian. Chem. Soc., 46, 486 (1969).
180. M. V. Artemenko, E. A. Chistyakova, K. F. Slyusarenko, and O. B. Pritula, Ukrain. Khim. Zhur., 38, 137 (1972).
181. A. D. Garnovskii, V. T. Panyushkin, L. I. Kuznetsova, O. A. Osipov, V. I. Minkin, and V. I. Martynov, Zhur. Obshch. Khim., 38, 1858 (1968).
182. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow, 1947; L. Pauling, "The Nature of the Chemical Bond", 3rd Edition, New York, 1960.
183. J. O. Edwards and R. G. Pearson, J. Amer. Chem. Soc., 84, 16 (1962).
184. A. D. Garnovskii, V. I. Minkin, O. A. Osipov, V. T. Panyushkin, L. K. Isaeva, and M. I. Knyazhanskii, Zhur. Neorg. Khim., 12, 2443 (1967) [Russ. J. Inorg. Chem., No. 9 (1967)].
185. S. A. Alieva, Candidate's Thesis, The State University, Rostov-on-Don, 1970.
186. A. D. Garnovskii, L. I. Kuznetsova, Yu. P. Andreichikov, O. A. Osipov, Yu. V. Kolodyazhnyi, V. I. Minkin, V. A. Bren', A. M. Simonov, and N. I. Avdonina, Zhur. Obshch. Khim., 41, 1899 (1971).
187. V. T. Panyushkin, A. D. Garnovskii, O. A. Osipov, N. P. Bednyagina, and R. I. Nikitina, Zhur. Obshch. Khim., 38, 1161 (1968).
188. R. I. Ogloblina, N. P. Bednyagina, and A. D. Garnovskii, Zhur. Obshch. Khim., 40, 367 (1970).
189. L. I. Kuznetsova, A. D. Garnovskii, O. A. Osipov, Yu. V. Kolodyazhnyi, and N. N. Viranovskaya, Zhur. Obshch. Khim., 42, 566 (1972).
190. J. L. Walter and H. Freiser, Anal. Chem., 26, 217 (1954).
191. T. R. Harkins, J. L. Walter, O. E. Harris, and H. Freiser, J. Amer. Chem. Soc., 78, 260 (1956).
192. T. R. Harkins and H. Freiser, J. Amer. Chem. Soc., 78, 1143 (1956).
193. F. Holmes, K. M. Jones, and E. G. Torrible, J. Chem. Soc. (A), 4790 (1961).
194. G. J. Hanania and D. H. Irving, J. Chem. Soc., 2750 (1962).
195. B. Chiswell, F. Lions, and H. S. Morris, Inorg. Chem., 3, 110 (1964).
196. H. A. Goodwin, Austral. J. Chem., 17, 1366 (1964).
197. J. Wang and J. E. Bauman, Inorg. Chem., 4, 1613 (1965).
198. H. A. Goodwin and R. N. Sylva, Austral. J. Chem., 21, 2881 (1968).
199. P. S. K. Chia and S. E. Livingstone, Inorg. Chim. Acta, 2, 427 (1968).
200. W. J. Eilbeck, F. Holmes, T. W. Thomas, and G. Williams, J. Chem. Soc. (A), 2348 (1968).
201. R. J. Dosser, W. J. Eilbeck, A. E. Underhill, P. R. Edwards, and C. E. Johnson, J. Chem. Soc. (A), 810 (1968).
202. A. D. Mighel, C. W. Reimann, and F. A. Mauer, Acta Cryst., 25B, 60 (1969).
203. P. W. Ball and A. B. Blake, J. Chem. Soc. (A), 1415 (1969).
204. A. D. Garnovskii, Yu. V. Kolodyazhnyi, S. A. Alieva, N. F. Krokhina, I. I. Grandberg, O. A. Osipova, and T. M. Presnyakova, Zhur. Obshch. Khim., 40, 1114 (1970).
205. R. J. Dosser and A. E. Underhill, J. Chem. Soc. (A), 88 (1970).
206. E. D. MacKenzie, Coord. Chem. Rev., 6, 212 (1971).
207. H. Hennig, Z. Chem., 11, 81 (1971).
208. H. Hennig, M. Benedix, and R. Benedix, Z. Chem., 11, 188 (1971).
209. O. Yamayichi, H. Tanaka, and T. Uno, Chem. Pharm. Bull., 15, 1453 (1967).
210. A. D. Garnovskii, Yu. V. Kolodyazhnyi, S. A. Alieva, K. M. Yunusov, I. I. Popov, O. A. Osipov, V. I. Minkin, A. M. Simonov, and I. I. Grandberg, Zhur. Obshch. Khim., 41, 352 (1971).

211. M. Vijayan and M. R. Viswamitra, Acta Cryst., 21, 522 (1966).
212. V. K. Akimov, A. I. Busev, B. E. Zaitsev, and B. P. Zhivopistsev, Zhur. Obshch. Khim., 37, 658 (1967).
213. D. N. Sathyanargiana and C. C. Patel, Indian J. Chem., 5, 260 (1967).
214. D. N. Sathyanargiana and C. C. Patel, Indian J. Chem., 5, 364 (1967).
215. D. Gopalakrishnan, A. Ravi, and C. C. Patel, Bull. Chem. Soc. Japan, 40, 791 (1967).
216. M. Blazekova and H. L. Schlafer, Z. anorg. Chem., 360, 169 (1968).
217. V. T. Panyushkin, A. D. Garnovskii, I. I. Grandberg, O. A. Osipov, V. I. Minkin, V. S. Troitskaya, and V. G. Vinokurov, Zhur. Obshch. Khim., 38, 1154 (1968).
218. A. K. Babko, N. P. Evtushenko, and M. M. Tananaiko, Ukrain. Khim. Zhur., 34, 1156 (1968).
219. G. V. Tsintsadze, Doctoral Thesis, The State University, Tbilisi, 1970.
220. V. V. Skopenko, Ukrain. Khim. Zhur., 38, 1196 (1972).
221. Yu. G. Eremin and V. S. Katochkin, Zhur. Neorg. Khim., 15, 972 (1970).
222. D. Gracinescu, A. I. Fruma, and G. Chirvi, Inorg. Chim. Acta, 4, 305 (1970).
223. A. I. Busev, V. K. Akimov, and S. A. Saber, Zhur. Anal. Khim., 25, 918 (1970).
224. J. Krätsmar-Smogrovic, J. Kohout, and K. Staiger, Z. Chem., 11, 26 (1971).
225. B. E. Zaitsev, B. N. Ivanov-Emin, R. K. Gridasov, and G. Val'karsel', Teor. Eksper. Khim., 7, 266 (1971).
226. A. I. Busev, V. K. Akimov, B. E. Zaitsev, and I. A. Emel'yanova, "Materialy III Vsesoyuznoi Konferentsii Organicheskie Reagenty v Analiticheskoi Khimii" (Proceedings of the Third All-Union Conference on Organic Reagents in Analytical Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1971, p. 8.
227. A. I. Busev, B. E. Zaitsev, and V. K. Akimov, Zhur. Obshch. Khim., 35, 1548 (1965).
228. V. K. Akimov, B. E. Zaitsev, A. I. Busev, and I. A. Emel'yanova, Zhur. Obshch. Khim., 38, 2759 (1968).
229. V. K. Akimov, A. E. Busev, and I. A. Emel'yanova, Zhur. Anal. Khim., 25, 918 (1970).
230. V. K. Akimov, B. E. Zaitsev, A. I. Busev, and I. A. Emel'yanova, Zhur. Obshch. Khim., 40, 2711 (1970).
231. A. D. Garnovskii, V. I. Minkin, I. I. Grandberg, and T. A. Ivanova, Khim. Geterotsikl. Soed., Symposium No. 1, 74 (1967).
232. B. E. Zaitsev, B. N. Ivanov-Emin, and R. K. Gridasov, "Tezisy Dokladov X Vsesoyuznogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Reports at the Tenth All-Union Conference on the Chemistry of Complex Compounds), Izd. Naukova Dumka, Kiev, 1969, p. 17.
233. J. Dick, R. Bagaloglu, and A. Maurer, Rev. Roumaine. Chim., 12, 607, 617, 629 (1967).
234. J. Dick and A. Maurer, Rev. Roumaine. Chim., 14, 1603 (1969).
235. J. Dick, Rev. Roumaine. Chim., 15, 103, 917 (1970).
236. R. A. Bailey and T. R. Peterson, Canad. J. Chem., 47, 1681 (1969).
237. M. Hughes and K. J. Rutt, Inorg. Nuclear Chem. Letters, 7, 1049 (1971).
238. Yu. V. Kolodyazhnyi, A. D. Garnovskii, S. A. Alieva, and O. A. Osipov, Khim. Geterotsikl. Soed., 1556 (1970).
239. A. Ravi, J. Gopalakrishnan, and C. C. Patel, Indian J. Chem., 5, 356 (1967).
240. D. De Filippo and C. Preti, J. Chem. Soc. (A), 1904 (1970).
241. G. G. Skvortsova, Doctoral Thesis, The State University, Irkutsk, 1970.
242. S. V. Koroleva, Candidate's Thesis, The State University, Voronezh, 1971.
243. M. V. Artemenko and K. F. Slyusarenko, Ukrain Khim. Zhur., 32, 560 (1966).
244. M. V. Artemenko and K. F. Slyusarenko, Zhur. Neorg. Khim., 12, 2449 (1967) [Russ. J. Inorg. Chem., No. 9 (1967)].
245. M. V. Artemenko and K. F. Slyusarenko, Ukrain. Khim. Zhur., 37, 753 (1971).
246. M. V. Artemenko and K. F. Slyusarenko, Ukrain. Khim. Zhur., 37, 859 (1971).
247. M. V. Artemenko, K. F. Slyusarenko, and D. A. Stakhov, Ukrain. Khim. Zhur., 38, 227 (1971).
248. M. V. Artemenko, K. F. Slyusarenko, and D. A. Stakhov, Zhur. Neorg. Khim., 9, 2547 (1964) [Russ. J. Inorg. Chem., No. 11 (1964)].
249. M. Goodgame and B. Pigott, J. Chem. Soc. (A), 826 (1971).
250. J. P. Candlin, K. A. Taylor, and D. C. Thompson, "Reactions of Transition-Metal Complexes" (Translated into Russian), Izd. Mir, Moscow, 1970, p. 6.
251. I. L. Burmeister, Coord. Chem. Rev., 3, 471 (1968). [This is a review by E. König (Ed. of Translation).]
252. R. Uhlemann, H. Müller, and P. Thomas, Z. Chem., 11, 401 (1971).
253. M. Cox and I. Darken, Coord. Chem. Rev., 7, 29 (1971).
254. S. E. Livingstone, Coord. Chem. Rev., 7, 59 (1971).
255. V. A. Koptyug, T. A. Andreeva, and V. I. Mamatyuk, Izv. Akad. Nauk SSSR, Ser. Khim., 2845 (1968).
256. S. Hatem-Champy, Compt. rend., 253, 2791 (1961).
257. P. Brooks and D. N. Davidson, J. Amer. Chem. Soc., 82, 2118 (1960).
258. J. A. J. Jarvis and A. F. Wells, Acta Cryst., 13, 1027 (1960).
259. J. Brigande and D. Colaitis, Compt. rend., 256, 5574 (1963).
260. G. P. Brown and S. Aftergut, J. Polymer Sci., (A), 2, 1839 (1964).
261. M. Inoue, M. Kishita, and M. Kubo, Inorg. Chem., 4, 626 (1965).
262. M. Inoue, M. Kishita, and M. Kubo, Bull. Chem. Soc. Japan, 39, 1352 (1966).
263. F. Seel and J. Rodian, J. Organomet. Chem., 16, 479 (1969).
264. L. Harzel and F. R. Benson, J. Amer. Chem. Soc., 76, 667 (1954).
265. S. Trofimenko, Chem. Rev., 72, 497 (1972).
266. A. N. Nesmeyanov, Yu. N. Sheinker, N. S. Kochetkova, M. I. Rybinskaya, L. B. Sinyavina, and R. B. Materikova, Zhur. Org. Khim., 3, 403 (1967).
267. See Ref. 7, pp. 347, 349.
268. M. Inoue and M. Kubo, Inorg. Chem., 5, 70 (1966).
269. See Ref. 8, pp. 12, 13.
270. N. A. Daugherty and C. H. Brubaker, J. Amer. Chem. Soc., 83, 3779 (1961).
271. L. L. Garber, L. B. Sims, and C. H. Brubaker, J. Amer. Chem. Soc., 90, 2518 (1963).
272. H. B. Jonassen, J. D. Terry, and A. D. Harris, J. Inorg. Nuclear Chem., 25, 1239 (1963).
273. C. L. Gilbert and C. H. Brubaker, Inorg. Chem., 2, 1216 (1963).

274. A. D. Harris, H. B. Jonassen, and R. D. Archer, Inorg. Chem., 4, 147 (1965).
275. L. M. Vallarino, W. E. Hill, and J. V. Quagliano, Inorg. Chem., 4, 1598 (1965).
276. B. D. Holm and P. L. Donelly, J. Inorg. Nuclear Chem., 28, 1887 (1966).
277. W. Beek, W. P. Fehlhammer, H. Bock, and M. Bauder, Ber., 102, 3637 (1969).
278. S. P. Ghosh, J. Indian. Chem. Soc., 28, 710 (1951).
279. N. I. Tarasevich, Vestnik Moskov. Gos. Univ., 3, No. 10, 161 (1948).
280. L. Canonica, R. De Leone, and C. Bersano, Rend. Ist Lombardo Sci. Lettere, Classe Sci. Mat. Natur., 87, 376 (1954).
281. K. L. Cheng, Anal. Chem., 26, 1038 (1954).
282. A. Cambi, L. Canonica, and L. Sironi, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 18, 583 (1955).
283. R. F. Wilson and L. E. Wilson, J. Amer. Chem. Soc., 77, 6204 (1955).
284. L. N. Lomakina and I. P. Alimarin, Zhur. Neorg. Khim., 12, 409 (1967) [Russ. J. Inorg. Chem., No. 2 (1967)].
285. E. Müller and H. Meier, Annalen, 716, 11 (1968).
286. L. Birkofer, P. Richter, and A. Ritter, Ber., 93, 2804 (1960).
287. L. Birkofer, P. Richter, and A. Ritter, Ber., 96, 2750 (1963).
288. L. Birkofer, W. Gilden, and A. Ritter, Angew. Chem., 73, 143 (1961).
289. L. Birkofer and P. Werner, Ber., 99, 2512 (1966).
290. See Ref. 8, p. 45.
291. D. H. O'Brien and Chang Po-Hrung, J. Organomet. Chem., 27, 185 (1971).
292. G. J. M. Van der Kerk, J. G. A. Luijten, and M. J. Yanssen, Chimia (Switz.), 16, 10 (1962).
293. J. G. A. Luijten, M. J. Yanssen, and G. J. M. Van der Kerk, Rec. Trav. Chim., 81, 2021 (1962).
294. J. G. A. Luijten and G. J. M. Van der Kerk, Rec. Trav. Chim., 82, 1181 (1963).
295. J. G. A. Luijten and G. J. M. Van der Kerk, Rec. Trav. Chim., 83, 295 (1964).
296. F. Rijkes and G. J. M. Van der Kerk, "Investigations of Organogermanium Chemistry", Utrecht, 1964, pp. 45, 51.
297. J. G. A. Luijten, F. Rijkens, and G. J. M. Van der Kerk, "Advances in Organometallic Chemistry" (Edited by F. Stone), Vol. 3, 1965.
298. L. C. Willemsen and G. J. M. Van der Kerk, "Investigations of Organolead Chemistry", Utrecht, 1965, p. 69.
299. W. P. Neuman, "Die organische Chemie", Ferdinand Enke Verlag, Stuttgart, 1967, p. 155.
300. W. P. Neuman, "Advances in Organometallic Chemistry", 1968, Vol. 7.
301. R. C. Poller, "The Chemistry of Organotin Compounds", Logos Press Limited, London, 1970, p. 94.
302. S. Trofimenko, J. Amer. Chem. Soc., 88, 1842 (1966).
303. S. Trofimenko, J. Amer. Chem. Soc., 89, 3165 (1967).
304. S. Trofimenko, J. Amer. Chem. Soc., 89, 4948 (1967).
305. S. Trofimenko, Inorg. Chem., 8, 1714 (1969).
306. J. P. Jesson, S. Trofimenko, and D. R. Eaton, J. Amer. Chem. Soc., 89, 3148 (1967).
307. P. Dunn and D. Oldfield, Austral. J. Chem., 24, 645 (1971).
308. H. Corth and M. C. Henry, J. Organomet. Chem., 9, 117 (1967).
309. M. J. Elguero, M. Riviere-Baudet, and M. J. Satge, Compt. rend., 266C, 41 (1968).
310. E. J. Kupchik and E. F. Yucrney, J. Organomet. Chem., 11, 291 (1968).
311. A. Finch, J. B. Leach, and Y. H. Morris, Organomet. Chem. Rev., 4, 1 (1969).
312. A. N. Nesmeyanov, D. N. Kravtsov, A. P. Zhukov, P. M. Kochergin, and G. K. Semin, Dokl. Akad. Nauk SSSR, 179, 102 (1968).
313. D. N. Kravtsov, L. A. Fedorov, A. S. Peregudov, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 196, 110 (1971).
314. F. Seel and V. Sperber, Angew. Chem., 80, 38 (1968).
315. A. N. Nesmeyanov, V. N. Babin, N. S. Kochetkova, E. I. Mysov, Yu. A. Belousov, and L. A. Fedorov, Dokl. Akad. Nauk SSSR, 200, 1112 (1971).
316. J. H. Nelson, D. L. Schmitt, R. A. Henry, D. W. Moore, and H. B. Jonassen, Inorg. Chem., 9, 2678 (1970).
317. M. Y. Yansen, G. J. A. Luijten, and G. J. M. Van der Kerk, J. Organomet. Chem., 1, 286 (1964).
318. H. Zollinger, "Azo and Diazo Chemistry: Aromatic and Aliphatic Compounds" (Translated into Russian), Izd. Khimiya, Leningrad, 1960.
319. D. D. Perrin, "Organic Complexing Reagents: Structures, Behaviour, and Application to Inorganic Analysis" (Translated into Russian), Izd. Mir, Moscow, 1967.
320. "Azometiny" (Azomethines), Izd. Rostov. Gos. Univ., Rostov-on-Don, 1967, pp. 6, 273.
321. L. Sommer and V. M. Ivanov, Talanta, 14, 171, 329 (1967).
322. A. I. Busev, V. M. Ivanov, and L. S. Krysina, Vestnik Moskov. Gos. Univ., No. 1, 80 (1968); No. 1, 103 (1969).
323. L. Sommer, T. Sepel, and V. M. Ivanov, Talanta, 15, 949 (1968).
324. A. I. Busev, V. M. Ivanov, and V. G. Gresl', Zhur. Anal. Khim., 23, 1580 (1968).
325. A. I. Busev, V. M. Ivanov, and L. I. Bogdanovich, Zhur. Anal. Khim., 24, 1273 (1969).
326. V. M. Ivanov, A. I. Busev, Zh. I. Nemtseva, and L. I. Smirnova, Zavod. Lab., 35, 1042 (1969).
327. V. M. Ivanov, A. I. Busev, L. V. Popova, and L. I. Bogdanovich, Zhur. Anal. Khim., 24, 1064 (1969).
328. A. I. Busev, V. M. Ivanov, and Zh. I. Nemtseva, Zhur. Anal. Khim., 24, 414 (1969).
329. V. G. Gresl', Candidate's Thesis, Moscow State University, Moscow, 1968.
330. L. S. Krysina, Candidate's Thesis, Moscow State University, Moscow, 1968.
331. Zh. I. Nemtseva, Candidate's Thesis, Moscow State University, Moscow, 1969.
332. L. I. Bogdanovich, Candidate's Thesis, Moscow State University, Moscow, 1969.
333. Usama Khaled el Dbik, Candidate's Thesis, Moscow State University, Moscow, 1969.
334. V. M. Ivanov, A. I. Busev, and Usama el Dbik, Vestnik Moskov. Gos. Univ., No. 1, 88 (1970).
335. G. Schwarzenbach and H. Flaschka, "Complexometric Titrations" (Translated into Russian), Izd. Khimiya, Moscow, 1970.
336. O. Navratil and R. W. Frei, Canad. J. Chem., 49, 173 (1971).
337. "Organicheskie Reagenty v Analiticheskoi Khimii. Tret'ya Vsesoyuznaya Konferentsiya, Moskva,

1971" (Organic Reagents in Analytical Chemistry. The Third All-Union Conference, Moscow, 1971).
338. F. I. Welcher, "Organic Analytical Reagents", Van Norstrand, Vol. IV, 1965.
339. V. I. Minkin, Yu. A. Zhdanov, A. D. Granovskii, and I. D. Sadekov, Zhur. Fiz. Khim., 40, 675 (1966) [Russ. J. Phys. Chem., No. 3 (1966)].
340. A. D. Garnovskii, B. A. Tertov, V. I. Minkin, M. A. Kazanbieva, F. T. Pozharskii, and O. A. Raevskii, Zhur. Obshch. Khim., 36, 328 (1966).
341. M. Seyhan, Ber., 85, 436 (1952); 86, 889 (1953).
342. A. D. Garnovskii, O. A. Osipov, D. D. Dalgatov, A. M. Simonov, V. I. Minkin, Zhur. Obshch. Khim., 34, 3407 (1964).
343. A. D. Garnovskii, V. A. Kogan, O. A. Osipov, S. G. Kochin, L. I. Kuznetsova, and G. K. Mitina, Zhur. Obshch. Khim., 41, 1370 (1971).
344. A. D. Garnovskii, O. A. Osipov, V. A. Kogan, M. V. Gorelik, L. I. Kuznetsova, S. G. Kochin, T. Kh. Gladysheva, and G. K. Mitina, Dokl. Akad. Nauk SSSR, 198, 341 (1971).
345. A. D. Garnovskii, V. P. Kurbatov, B. A. Porai-Koshits, O. A. Osipov, I. Ya. Kvitko, L. S. Minkina, E. M. Sof'ina, and A. F. Soloshko-Doroshenko, Zhur. Obshch. Khim., 40, 2338 (1970).
346. A. D. Garnovskii, O. A. Osipov, L. V. Orlova, and V. I. Minkin, Zhur. Neorg. Khim., 10, 2821 (1965) [Russ. J. Inorg. Chem., No. 12 (1965)].
347. A. D. Garnovskii, L. V. Orlova, O. A. Osipov, and O. A. Raevskii, Zhur. Obshch. Khim., 37, 308 (1967).
348. L. V. Orlova, A. D. Garnovskii, O. A. Osipov, and V. I. Minkin, Zhur. Obshch. Khim., 37, 1783 (1967).
349. L. V. Orlova, A. D. Garnovskii, O. A. Osipov, and V. I. Minkin, Zhur. Obshch. Khim., 38, 1167 (1968).
350. L. V. Orlova, A. D. Garnovskii, O. A. Osipov, V. I. Minkin, and I. I. Kukushkina, Zhur. Obshch. Khim., 38, 1845 (1968).
351. A. D. Garnovskii, O. A. Osipov, V. I. Minkin, L. V. Orlova, and L. I. Kuznetsova, Dokl. Akad. Nauk SSSR, 178, 598 (1968).
352. R. H. Holm, G. W. Everett, and A. Chakravorty, "Progress in Inorganic Chemistry", New York–London, 1966, Vol. 7, p. 1.
353. M. Kato, H. B. Jonassen, and J. G. Farring, Chem. Rev., 64, 99 (1964).
354. A. S. Kudryavtsev, I. A. Savich, and Vikt. I. Spitsyn, Dokl. Akad. Nauk SSSR, 165, 864 (1965).
355. H. Freiser, Analyst, 77, 830 (1952).
356. L. Müslin, W. Roth, and H. Erlenmeyer, Helv. Chim. Acta, 36, 886 (1953).
357. R. G. Charles and H. Freiser, Analyt. Chim. Acta, 11, 1 (1954).
358. T. E. McDermott, Austral. J. Chem., 19, 2181 (1966).
359. D. Sh. Verkhovedova, N. R. Kal'nitskii, V. I. Minkin, A. D. Garnovskii, and O. A. Osipov, Zhur. Neorg. Khim., 12, 3385 (1967) [Russ. J. Inorg. Chem., No. 12 (1967)].
360. K. S. Murray and B. O. West, Inorg. Nuclear Chem. Letters, 4, 439 (1968).
361. P. Stenson, Acta Chem. Scand., 23, 1514 (1969).
362. A. E. Shugam and L. M. Shkol'nikova, in "Kristallokhimiya, 1965, 'Itogi Nauki'" (Crystal Chemistry, 1965, "Advances in Science"), Izd. VINITI, Akad. Nauk SSSR, 1967, p. 62.
363. P. K. Feng and Q. Fernando, J. Amer. Chem. Soc., 82, 2115 (1960).
364. T. J. Lane and A. Sam, J. Amer. Chem. Soc., 82, 4462 (1960).
365. P. K. Feng and Q. Fernando, Inorg. Chem., 1, 426 (1962).
366. P. K. Feng and Q. Fernando, Analyt. Chim. Acta, 24, 548 (1961).
367. T. A. Zhuchenko, L. I. Kuznetsova, V. A. Kogan, A. D. Garnovskii, O. A. Osipov, M. V. Gorelik, T. Kh. Gladysheva, V. A. Alekseenko, and T. A. Zayakina, Zhur. Neorg. Khim., 16, 2169 (1971) [Russ. J. Inorg. Chem., No. 8 (1971)].
368. F. A. Snavely and F. H. Suygam, J. Org. Chem., 24, 2039 (1959).
369. F. A. Snavely, Inorg. Chem., 2, 708 (1963).
370. F. A. Snavely, Inorg. Chem., 6, 1222 (1967).
371. F. A. Snavely, D. A. Sweigert, J. Hay, and J. Farrel, Inorg. Chem., 10, 1180 (1971).
372. F. A. Snavely, N. M. Rosenblum, P. S. Danielson, and R. R. Rill, J. Inorg. Nuclear Chem., 33, 455 (1971).
373. A. D. Garnovskii, O. A. Osipov, N. F. Krokhina, T. A. Zayakina, and L. I. Kuznetsova, "Tezisy Dokladov IV Vsesoyuznogo Soveshchaniya po Primeneniyu Noveishikh Metodov k Issledovaniyu Koordinatsionnykh Soedinenii" (Abstracts of Reports at the Fourth All-Union Conference on the Application of the Latest Methods to the Study of Coordination Compounds), Izd. ShTIINTSA, Kishinev, 1971, p. 27.
374. A. I. Busev and V. M. Ivanov, Zhur. Anal. Khim., 19, 1250 (1964).
375. R. Anderson and G. Nickless, Analyt. Chim. Acta, 39, 413 (1967).
376. R. Anderson and G. Nickless, Analyst, 92, 207 (1967).
377. A. T. Pilipenko and L. I. Savranskii, Dokl. Akad. Nauk SSSR, 195, 614 (1970).
378. F. A. Snavely and D. A. Sweigart, Inorg. Chem., 8, 1659 (1969).
379. O. Yamayichi, H. Tanaka, and T. Uno, Talanta, 15, 177 (1968).
380. G. Schetty, Chimia (Switz.), 18, 244 (1964).
381. G. Schetty, Helv. Chim. Acta, 50, 15 (1967); 51, 77 (1968).
382. G. Schetty, Helv. Chim. Acta, 51, 505, 509 (1968).
383. U. Agarwala, V. A. Narayan, and S. K. Dikchit, Canad. J. Chem., 12, 1061 (1967).
384. M. I. Mikhailenko, K. V. Tserkasevich, and P. O. Knizhko, Ukrain. Khim. Zhur., 36, 326 (1970).
385. M. I. Mikhailenko, K. V. Tserkasevich, and P. O. Knizhko, Zhur. Neorg. Khim., 14, 3039 (1969) [Russ. J. Inorg. Chem., No. 11 (1969)].
386. B. C. Bera and M. N. Chakravorty, Talanta, 13, 1086 (1966).
387. R. F. Wilson and P. Merchant, J. Inorg. Nuclear Chem., 29, 1993 (1967).
388. L. N. Lomakina and I. P. Alimarin, Zhur. Neorg. Khim., 12, 409 (1967) [Russ. J. Inorg. Chem., No. 2 (1967)].
389. L. N. Lomakina and E. K. Yanovskaya, Zhur. Anal. Khim., 24, 1176 (1969).
390. U. Agarwala and B. Singh, J. Inorg. Nuclear Chem., 31, 2515 (1969).
391. I. P. Alimarin, L. N. Lomakina, and G. V. Andreeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1459 (1970).
392. A. P. Terent'ev, I. G. Il'ina, E. G. Rukhadze, and I. G. Vorontsova, Zhur. Obshch. Khim., 40, 1516 (1970).
393. V. M. Shul'man and T. V. Zagorskaya, Zhur. Neorg. Khim., 16, 1361 (1971) [Russ. J. Inorg. Chem., No. 5 (1971)].

394. O. Navratil and J. Ziska, Coll. Czech. Chem. Comm., 33, 987 (1968).
395. C. S. Johar and U. Agarwala, Talanta, 17, 355 (1970).
396. U. Agarwala and B. Singh, J. Inorg. Nuclear Chem., 33, 598 (1971).
397. W. Lieber and W. Rohm, Ber., 102, 2787 (1969).
398. S. Trofimenko, J. Org. Chem., 33, 890 (1968).
399. A. D. Garnovskii, V. A. Kogan, O. A. Osipov, S. G. Kochin, L. I. Kuznetsova, and G. K. Mitina, Zhur. Neorg. Khim., 15, 2010 (1970) [Russ. J. Inorg. Chem., No. 7 (1970)].
400. A. D. Garnovskii, L. S. Minkina, L. V. Sakhashchik, V. P. Kurbatov, and O. A. Osipov, Zhur. Obshch. Khim., 41, 1884 (1971).
401. S. G. Kochin, A. D. Garnovskii, V. A. Kogan, O. A. Osipov, and T. G. Sushko, Zhur. Neorg. Khim., 14, 1428 (1969) [Russ. J. Inorg. Chem., No. 5 (1969)].
402. I. Ya. Kvitko and B. A. Porai-Koshits, Zhur. Org. Khim., 5, 1685 (1969).
403. E. Höyer and B. Lorent, Z. Chem., 6, 28 (1968).
404. L. P. Olekhnevich, V. P. Kurbatov, O. A. Osipov, L. S. Minkina, and V. I. Minkin, Zhur. Obshch. Khim., 308, 2593 (1968).
405. L. S. Minkina, V. P. Kurbatov, O. A. Osipov, V. I. Minkin, and L. E. Nivorozhkin, Zhur. Neorg. Khim., 16, 1075 (1971) [Russ. J. Inorg. Chem., No. 4 (1971)].
406. L. E. Nivorozhkin, V. P. Kurbatov, L. S. Minkina, M. S. Korobov, L. P. Olekhnovich, O. A. Osipov, and V. I. Minkin, Zhur. Obshch. Khim., 41, 2726 (1971).
407. O. A. Osipov, L. S. Minkina, A. D. Garnovskii, V. P. Kurbatov, I. Ya. Kvitko, and E. M. Sof'ina, Zhur. Obshch. Khim., 42, 926 (1972).
408. M. A. Porai-Koshits and E. A. Gilinskaya, in "Kristallokhimiya. 'Itogi Nauki'" (Crystal Chemistry, "Advances in Science"), Izd. VINITI, Akad. Nauk SSSR, Moscow, 1966, p. 182.
409. A. B. Naiding, in "Magnetokhimiya. 'Itogi Nauki'" (Magnetochemistry. "Advances in Science"), Izd. VINITI, Akad. Nauk SSSR, Moscow, 1970.
410. F. Snavely, W. S. Trahanowsky, and T. H. Suygam, J. Org. Chem., 27, 994 (1962).
411. E. Snavely, W. S. Trahanowsky, and T. H. Suygam, Inorg. Chem., 3, 123 (1964).
412. A. D. Garnovskii, N. F. Krokhina, and T. A. Zayakina, Zhur. Neorg. Khim., 17, 2302 (1972) [Russ. J. Inorg. Chem., No. 8 (1972)].
413. A. D. Garnovskii, B. A. Tertov, O. A. Osipov, V. V. Burykin, and L. S. Kostromina, Zhur. Strukt. Khim., 10, 339 (1969).
414. A. D. Garnovskii, L. I. Kuznetsova, Yu. P. Andreichikov, O. A. Osipov, A. M. Simonov, V. I. Zvonareva, V. P. Kurbatov, and N. I. Avdyunina, Zhur. Obshch. Khim., 40, 710 (1970).
415. L. I. Kuznetsova, Candidate's Thesis, The State University, Rostov-on-Don, 1970.
416. Yu. S. Varshavskii, T. G. Cherkasova, O. A. Osipov, N. P. Bednyagina, A. D. Garnovskii, R. N. Ogloblina, G. K. Mitina, and G. N. Lipunova, Zhur. Neorg. Khim., 17, 1401 (1972) [Russ. J. Inorg. Chem., No. 5 (1972)].
417. N. P. Bednyagina and Yu. A. Rybakova, Khim. Geterotsikl. Soed., 425 (1965).
418. A. D. Garnovskii, V. T. Panyushkin, N. P. Bednyagina, and O. A. Osipov, Zhur. Strukt. Khim., 8, 247 (1967).
419. E. N. Yurchenko, V. I. Avdeev, and I. I. Kalinichenko, Teor. Eksper. Khim., 552 (1967).
420. G. N. Lyapunova, K. V. Aglitskaya, and N. P. Bednyagina, Izv. Sibir. Otd. Akad. Nauk SSSR, No. 4, 50 (1967).
421. A. P. Novikova, N. P. Bednyagina, and I. Ya. Postovskii, Khim. Geterotsikl. Soed., Symposium 1, 196 (1967).
422. N. P. Bednyagina, Doctoral Thesis, The Urals Polytechnic Institute, Sverdlovsk, 1968.
423. N. P. Bednyagina, G. M. Petrova, and K. V. Aglitskaya, Zhur. Obshch. Khim., 38, 529 (1968).
424. A. D. Garnovskii, O. A. Osipov, N. P. Bednyagina, L. I. Kuznetsova, A. S. Kostromina, V. P. Kurbatov, V. T. Panyushkin, R. I. Ogloblina, and N. V. Serebryakova, Dokl. Akad. Nauk SSSR, 184, 1132 (1969).
425. A. D. Garnovskii, O. A. Osipov, N. P. Bednyagina, L. I. Kuznetsova, A. S. Kostromina, V. P. Kurbatov, V. T. Panyushkin, R. I. Ogloblina, and N. V. Serebryakova, Zhur. Obshch. Khim., 39, 1622 (1969).
426. G. N. Lipunova, E. I. Krylov, N. P. Bednyagina, and V. P. Sharov, Zhur. Obshch. Khim., 39, 1293 (1969).
427. M. Seyhan, Ber., 88, 646 (1955).
428. M. Seyhan, Ber., 99, 2072 (1966).
429. L. P. Sidorova, E. P. Darienko, L. P. Davydenkova, and N. P. Bednyagina, Zhur. Obshch. Khim., 42, 571, 2547 (1972).
430. H. Henning, J. prakt. Chem., 34, 64 (1966).
431. J. Sieler and H. Hennig, Z. anorg. Chem., 381, 219 (1971).
432. I. A. Rastrepina, Candidate's Thesis, The State University, Kharkov, 1972.
433. J. Reedijk, B. A. Stork-Blaisse, and G. V. Verschoor, Inorg. Chem., 10, 2594 (1971).
434. C. W. Reiman and M. Zocchi, Acta Cryst., B27, 682 (1971).
435. A. D. Mighel and A. Santoro, Acta Cryst., B27, 2089 (1971).
436. R. Strauberg and B. K. S. Lundberg, Acta Chem. Scand., 25, 1767 (1971).
437. F. Akhtar, F. Hug, and A. C. Skapski, J. Chem. Soc. (Dalton Trans.), 1353 (1972).
438. J. W. Carmichael, N. Chan, A. W. Cordes, C. K. Fair, and D. A. Johnson, Inorg. Chem., 11, 1117 (1972).
439. V. K. Voronov, Yu. N. Ivlev, E. S. Domnina, and G. G. Skvortsova, Khim. Geterotsikl. Soed., 1416 (1971).
440. V. K. Voronov, Yu. N. Ivlev, E. S. Domnina, and G. G. Skvortsova, Khim. Geterotsikl. Soed., 994 (1972).
441. M. Tsutsui, D. Ostfeld, and L. M. Hoffmann, J. Amer. Chem. Soc., 93, 1820 (1971).
442. A. Fratiello, R. H. Schuster, and M. Geisel, Inorg. Chem., 11, 11 (1972).
443. M. V. Artemenko, K. F. Slyusarenko, P. A. Suprunenko, E. I. Kal'naya, and A. G. Mazurenko, Zhur. Neorg. Khim., 17, 1638 (1972).
444. M. V. Artemenko and E. A. Chistyakova, Ukrain. Khim. Zhur., 37, 975 (1972).
445. V. M. Shul'man, T. V. Zagorskaya, I. M. Cheremisina, G. K. Parygina, and E. A. Kravtsova, Zhur. Neorg. Khim., 17, 2498 (1972) [Russ. J. Inorg. Chem., No. 9 (1972)].
446. A. K. Das, V. Rao, and Ramana, Indian J. Chem., 7, 480 (1971).
447. M. V. Artemenko, K. F. Slyusarenko, and D. A. Strakhov, Zhur. Neorg. Khim., 17, 164 (1972) [Russ. J. Inorg. Chem., No. 1 (1972)].

448. J. Reedijk, Rec. Trav. chim., 90, 1285 (1971).
449. J. Reedijk, Rec. Trav. chim., 91, 507 (1972).
450. J. Reedijk and B. Nieuwenhuijse, Rec. Trav. chim., 91, 533 (1972).
451. P. S. Gonun and A. E. Underhill, J. Inorg. Nuclear Chem., 34, 1879 (1972).
452. D. Nicholls and B. A. Warburton, J. Inorg. Nuclear Chem., 33, 1041 (1971).
453. R. D. Dowsing, B. A. Niewenhuijse, and J. Reedijk, Inorg. Chim. Acta, 5, 301 (1971).
454. J. Reedijk and J. A. Smit, Rec. Trav. chim., 90, 1135 (1971).
455. J. Reedijk and D. W. Engelfriet, Rec. Trav. chim., 91, 883 (1972).
456. R. M. Biefied and B. L. Gilbert, J. Inorg. Nuclear Chem., 33, 3947 (1971).
457. M. V. Artemenko, T. I. Kal'naya, S. M. Karel'nik, A. V. Koval', and P. A. Suprunenko, Zhur. Neorg. Khim., 17, 1006 (1972) [Russ. J. Inorg. Chem., No. 4 (1972)].
458. S. P. Crosh and A. Misha, J. Inorg. Nuclear Chem., 33, 4199 (1971).
459. A. W. Addison, K. Dawson, R. D. Gillard, B. T. Heaton, and H. Shaw, J. Chem. Soc. (Dalton Trans.), 589 (1972).
460. A. J. Carty, Organomet. Chem. Rev., A7, 191 (1972).
461. J. L. Calderon, F. A. Cotton, and A. Shaver, J. Organomet. Chem., 38, 105 (1972).
462. J. L. Calderon, F. A. Cotton, and A. Shaver, J. Organomet. Chem., 37. 127; 42, 419 (1972).
463. M. J. M. Campbell, D. W. Gard, R. Grzeskowiak, and M. Goldstein, J. Chem. Soc. (Dalton Trans.), 1687 (1972).
464. A. Montenero and C. Pellizzi, Inorg. Chim. Acta, 6, 88 (1972).
465. H. Hennig, R. Kirmse, and J. Tauchnitz, Z. Chem., 11, 115 (1971).
466. M. L. Goodgame, Bull. Soc. chim. France, 3 (1972).
467. M. L. Goodgame and A. A. S. C. Machado, Inorg. Chim. Acta, 6, 317 (1972).
468. R. J. Drosser and A. E. Underhill, J. Chem. Soc. (Dalton Trans.), 611 (1972).
469. S. E. Livingstone and J. D. Nolan, J. Chem. Soc. (Dalton Trans.), 218 (1972).
470. H. A. Goodwin and D. W. Mather, Austral. J. Chem., 25, 715 (1972).
471. V. A. Kogan, O. A. Osipov, N. K. Chub, A. D. Garnovskii, A. S. Burlov, E. B. Tsupak, and A. A. Polunin, Zhur. Obshch. Khim., 42, 581 (1972).
472. M. B. Cinci, C. Guastini, A. Musatti, and M. Nardalli, Acta Cryst., 28B, 667 (1972).
473. E. P. Klimenko and S. Ya. Shnaiderman, Zhur. Neorg. Khim., 17, 2442 (1972) [Russ. J. Inorg. Chem., No. 9 (1972)].
474. V. V. Zelentsov, N. A. Subbotina, V. I. Spitsyn, I. A. Emel'yanova, A. I. Busev, and V. K. Akimov, Dokl. Akad. Nauk SSSR, 205, 1124 (1972).
475. M. Gerloch and D. J. Mackey, J. Chem. Soc. (A), 3030 (1970).
476. M. Gerloch and D. J. Mackey, J. Chem. Soc. (A), 3040 (1970).
477. M. Gerloch and D. J. Mackey, J. Chem. Soc. (A), 2605 (1971).
478. M. Gerloch and D. J. Mackey, J. Chem. Soc. (A), 2612 (1971).
479. M. Gerloch and D. J. Mackey, J. Chem. Soc. (A), 3372 (1971).
480. M. Gerloch and D. J. Mackey, J. Chem. Soc. (Dalton Trans.), 37 (1972).
481. M. Gerloch and D. J. Mackey, J. Chem. Soc. (Dalton Trans.), 42 (1972).
482. M. Gerloch and D. J. Mackey, J. Chem. Soc. (Dalton Trans.), 410 (1972).
483. M. Gerloch and D. J. Mackey, J. Chem. Soc. (Dalton Trans.), 415 (1972).
484. M. N. Hughes and K. J. Rutt, J. Chem. Soc. (Dalton Trans.), 1311 (1972).
485. P. Labine and C. H. Brubaker, J. Inorg. Nuclear Chem., 33, 3383 (1971).
486. S. Trofimenko, J. Amer. Chem. Soc., 89, 3903 (1967).
487. V. P. Chernetskii, E. E. Rengevich, L. S. Usenko, and I. F. Franchuk, Khim. Geterotsikl. Soed., 1429 (1971).
488. F. A. Snavely and C. H. Yoder, J. Inorg. Nuclear Chem., 33, 2699 (1971).
489. L. S. Minkina, A. D. Garnovskii, I. Ya. Kvitko, V. P. Kurbatov, and O. A. Osipov, Zhur. Obshch. Khim. (in the press).
490. N. N. Bogdashev, A. D. Garnovskii, O. A. Osipov, and V. P. Grigor'ev, Zhur. Obshch. Khim. (in the press).
491. M. M. Khan and A. U. Malik, J. Inorg. Nuclear Chem., 34, 1847 (1972).
492. L. Agarwala and U. Agarwala, J. Inorg. Nuclear Chem., 34, 2255 (1972).
493. L. S. Minkina, Candidate's Thesis, The State University, Rostov-on-Don, 1972.
494. I. Ya. Kvitko and N. B. Sokolova, Khim. Geterotsikl. Soed., 791 (1972).
495. H. Henning and R. Kirsme, Z. anorg. Chem., 388, 238 (1972).
496. L. L. Garber and C. H. Brubaker, J. Amer. Chem. Soc., 88, 4266 (1966); 90, 309 (1968).
497. F. H. Pinkerton and S. F. Thames, J. Heterocycl. Chem., 8, 257 (1971).
498. F. H. Pinkerton and S. F. Thames, J. Heterocycl. Chem., 9, 67 (1972).
499. P. Jutzi and H. J. Hoffmann, J. Organomet. Chem., 40, C61 (1972).
450. L. Birkofer and M. Franz, Ber., 100, 2681 (1967); 104, 3062 (1971).
501. A. N. Nesmeyanov, I. B. Zlotina, N. E. Kolobova, and K. N. Anisimov, Izv. Akad. Nauk SSSR, Ser. Khim., 2127 (1968).
502. N. S. Nametkin, G. A. Shvekhgeimer, V. D. Tyurin, A. I. Tutubalina, and T. N. Kosheleva, Izv. Akad. Nauk SSSR, Ser. Khim., 1567 (1970).
503. V. D. Tyurin, N. S. Nametkin, G. A. Shvekhgeimer, and Kh. M. Khasan, Izv. Akad. Nauk SSSR, Ser. Khim., 2645 (1970).
504. D. Seyferth and T. C. Flood, J. Organomet. Chem., 29, C25 (1971).
505. N. S. Nametkin, G. A. Shvekhgeimer, V. D. Tyurin, Kh. M. Khasan, and V. I. Ivanov, Izv. Akad. Nauk SSSR, Ser. Khim., 478 (1972).
506. W. Beck, K. Burger, and W. P. Fehlhammer, Ber., 104, 1861 (1971).
507. V. S. Zavgorodnii, A. I. Maleeva, and A. A. Petrov, Zhur. Obshch. Khim., 41, 2230 (1971).
508. W. P. Fehlhammer and L. F. Dahl, J. Amer. Chem. Soc., 94, 3370 (1972).

The State University,
Rostov-on-Don