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Competitive coordination: ambident ligands in the modern chemistry of metal complexes

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Abstract. Data on the problem of competitive coordination, obtained mainly during the last 10 years, are surveyed and treated systematically. The competitive binding of metals in complexes of bi- and poly-dentate ligand systems — simple diatomic and triatomic compounds (N_2, O_2, CO, CO_2, CS_2, *etc.*), ambident anions (CN^-, NCX^-, NO_2^-, SO_3^{2-}, *etc.*), and neutral aliphatic, aromatic, and heterocyclic compounds, including chelating organic ligands — is examined. Attention is specially concentrated on non-traditional ways in which typical ligand systems are coordinated and on regioselective synthesis as a method for the specific synthesis of metal complexes with a specified location of the coordinate bond. The bibliography includes 575 references.

I. Introduction

Competitive coordination is the term applied to the ability of bidentate and polydentate ligands to react with metal atoms at different donor (nucleophilic) centres. Investigators encountered the problem of competitive coordination for the first time a quarter of a century ago.[1,2] Review publications[2–24] have been devoted to individual aspects of this problem. They include reviews on the coordination of nitrogen,[4,7,8] oxygen,[9,10] carbon monoxide,[11–13] and carbon dioxide[14,15] molecules. The interest in the problem under consideration can be accounted for by the fact that it embraces problems of donor–acceptor interaction,[18,25,26] bond isomerism,[3,5,6,17,18,27–32] and the synthesis of complexes of a particular type (stereoselective synthesis)[4,22,31–34] and with a specified location of the coordinate bond (regioselective synthesis)[17,22,33–35] and specific coordination of metals in biologically important systems.[35–39]

In order to account for the different ways in which bidentate and polydentate ligands are coordinated, Pearson's principle of hard and soft acids and bases (HSAB) was applied.[40–42] In relation to competitive coordination,[2] it is formulated as follows: in polydentate ligand systems, it is possible to identify hard (mainly N and O) and soft (P, As, Sb; S, Se, Te; π,σ-donors) reaction centres, and the HSAB principle itself indicates in this instance[2] the preferential binding of hard Pearson acids (metal salts) to hard donor centres and of soft acids to soft nucleophilic atoms or π-donor groups of ligands.†

The concepts of the 'hardness' and 'softness' of acids and bases have been examined many times.[2,3,18,25–27,40–42,45,46] The collective nature of these concepts, embracing characteristics of the reactants such as polarisability, electronegativity, and ion size, were emphasised in this connection.[2,3,18] Nowadays attempts are being made to develop the quantitative aspects of the HSAB concept (see, for example, Pearson[45]). Pearson's attempts[45] to estimate hardness and softness theoretically merit special attention. According to Pearson[45], the future developments of these studies will involve the establishment of the relation between the difference in the energies of the highest occupied and lowest unoccupied molecular orbitals and the hardness of the system. In a later study, Datta[46] emphasises that, although hardness is an important reactivity index and has been estimated quantitatively, a full theoretical justification of the HSAB principle, *i.e.* the principle that 'hard likes hard' and 'soft likes soft', has not yet been achieved. In a study of the thermodynamics of exchange reactions of the type

$$AB + CD \rightleftharpoons AC + BD$$

with participation of lithium hydrides and halides, hydrogen halides, monohalo-derivatives of methane and silane, and other reagents,[46] he concluded that the formation of the hardest of the possible compounds is the driving force of the exchange reaction and that the average hardness of the products becomes greater than that of the initial compounds.

It is noteworthy that, although bidentate and polydentate ligand systems with soft and hard donor centres include a wide range of compounds, they do not embrace the entire series of ligands. Thus they do not include molecules which contain only hard or only soft nucleophilic centres and are capable of binding to the metal in different ways.

Evidently the HSAB approach reduces the number of ligand systems which could be considered within the framework of the problem of the competitive coordination of bidentate and polydentate ligands.

In the present review,we tried to examine all the possible ways in which the coordinate bond can be located in complexes with the

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† The possibility of employing the HSAB concept to explain the different ways in which ligands are bound to metals in complexes was first demonstrated in relation to complexes of pseudohalide anions.[43,44]

most familiar ligands — both with simple inorganic molecules and with complicated organic compounds having several donor atoms and groups. Attention is concentrated on the nontraditional ways in which typical ligands are coordinated and on regioselective synthesis. Mainly the literature of the last 10 years has been used in the review.

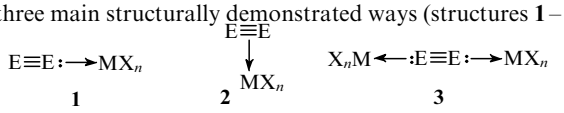
II. Types of competitively reacting ligands

For a correct understanding and assessment of the regioselectivity of complex formation reactions, it is necessary to consider only thermodynamically stable products (complexes) formed under the conditions of kinetic control.[3,47] In other words, one is dealing with the thermodynamic stability of the products of the initial attack by the metal (complex-forming agent) on the nucleophilic centre of the ligand. This postulate is extremely significant, since in many cases complexes in which the ligands are prone to tautomerism undergo various metallotropic processes.[48–56] The latter are frequently accompanied by a change in the centre where the coordinate bond is located in relation to the expected location.

Ligand systems forming bond isomers comprise bidentate and polydentate and homogeneous and heterogeneous inorganic compounds, ambident ‡ anions,[1] and diverse organic compounds.

1. Inorganic molecules

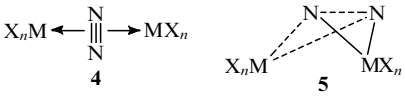
The homoatomic nitrogen,[4,8,57–66] phosphorus,[67–69] and arsenic[69,70] molecules in coordination compounds of metals function as monodentate or bidentate ligands and are coordinated in three main structurally demonstrated ways (structures **1**–**3**).



1 **2** **3**

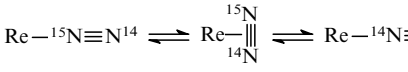
E = N, P, As.

Apart from the structures indicated, complexes described by formulae **4**,[8,71] and **5**[8] (see also the footnote below §) have been noted.

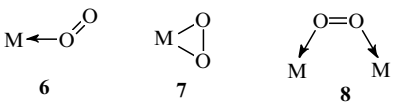


4 **5**

The bond isomers of the nitrogen complexes **1** and **2** may be in equilibrium. Thus exchange described by the following equilibrium reaction has been detected for the compound $[(\eta^5\text{-}C_5Me_5)Re(CO)_2N_2]$ by ^{15}N NMR.[62]

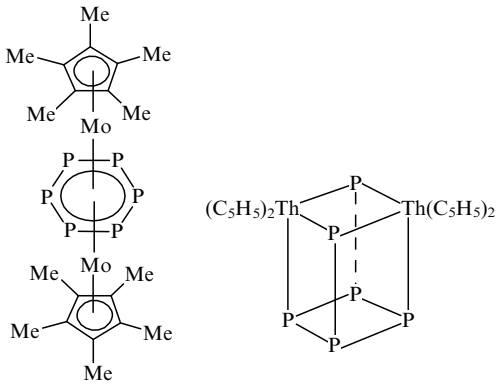


Bond isomers similar to complexes **1**–**3** are characteristic also of the complexes formed by diatomic oxygen (structures **6**–**8**),[9,10,72] sulfur,[73–75] selenium,[76,77] and tellurium[77–82] molecules.



6 **7** **8**

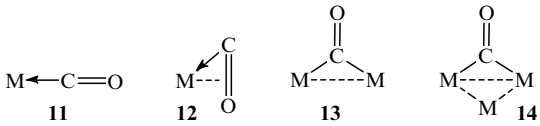
Among inorganic homoelement ligands, compounds containing three and more atoms are encountered. This is particularly characteristic of phosphorus, for which metal complexes based on trimeric,[82] tetrameric,[83] pentameric,[84] and hexameric[85–87] phosphorus-containing ligand systems with different locations of the coordinate bond have been obtained. It is striking that the P_6 molecule can behave not only as a η^6-coordinated ligand (for example, in the triple-deck complex **9**),[76] but also as a η^3,η^3-binding ligand system (complex **10**).[87]



9 **10**

Different types of coordination of Se_n and Te_n molecules have been considered in a review.[82]

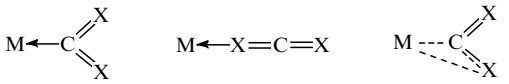
The heteroelement diatomic CO,[4,11–13,27,28,69,88–90] CS,[69,91–93] and NO[69,94–96] molecules also behave as monodentate and bidentate ligands and can function as both terminal and bridging ligands. For example, the formation of the following structures has been demonstrated for carbon monoxide:



11 **12** **13** **14**

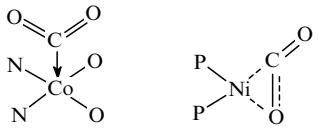
Similar types of coordination are characteristic of carbon monosulfide[91–93] and nitrogen monoxide.[94–96]

There are various types of coordination of heteroelement triatomic molecules: CO_2,[14,15,69,97] COS,[15] CS_2,[15,98–100] and SO_2.[5,69,101–105] The formation of three types of metal — ligand bonds (compounds **15**–**17**) has been demonstrated[15,97] for carbon dioxide complexes with the aid of X-ray diffraction (XRD) data.



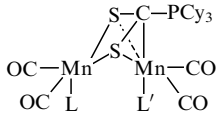
15 **16** **17**

The type **15** (X = O) structure is characteristic of the cobalt complex **18**,[97] while structure **17** (X = O) occurs in the nickel complex **19**.[15]



18 **19**

Like CO_2, carbon disulfide is bound to the metal in different ways.[15] For example, in the dinuclear complex $[Mn_2(CO)_9(CS_2)PPh_3]$[100] the above ligand behaves as a S-monodentate species, while in the manganese complexes **20** and **21** (Cy = cyclohexyl) the same ligand system behaves as a C–S bridge.[100]



20: L = L′ = CO;
21: L – L′ = $Ph_2PCH_2PPh_2$.

20, **21**

‡ Ambident systems are inorganic and organic molecules and ions with conjugated donor atoms.

§ R J Deeth, S A Laygtord *J. Chem. Soc., Dalton Trans.* 1 (1995); N Desmangles, H Jenkins, K B Ruppa, S Gamborotta. *Inorg. Chim. Acta* **250** 1 (1996)

Five modes of coordination (compounds **22**–**26**) are characteristic of sulfur dioxide complexes,[69, 101–105] two of the compounds (**22** and **23**) being stereoisomeric.



22 (η^1-planar)



23 (η^1-pyramidal)



24 (η^2-O, S-pyramidal)



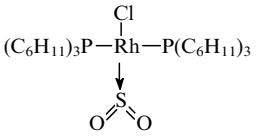
25 (η^2-S-bridging)



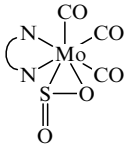
26 (η^2-O, S-bridging)

In particular, it has been demonstrated by X-ray diffraction [101] that structure **27** with a cis-planar dioxide fragment (type **22**) occurs in the complex $[RhCl(PCy_3)_2(\eta^1\text{-}SO_2)]$.

The pyramidal O,S-binding of the SO_2 group is characteristic of the complexes $[Mo(CO)_3(Bipy)(\eta^2\text{-}SO_2)]$ and $[Mo(CO)_3(o\text{-}Phen)(\eta^2\text{-}SO_2)]$ with the same fragment (structures **28** and **29**, type **24**).



27



28:  Bipy

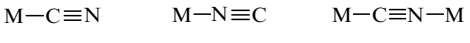
29: *o*-Phen

Bond isomers of metal complexes of heteroelement ligands, the molecules of which incorporate four (N_2S_2),[106] six (N_2S_4),[107] and eight (N_4S_4) [108] heteroatoms, have been described.

2. Ambident inorganic anions

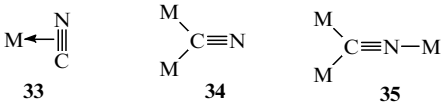
Among ambident anions, the following have been most thoroughly investigated as competitively reacting ligands: cyanide [5, 16, 27, 28, 109–113] nitrite,[3, 5, 18, 27, 28, 114–119] sulfite,[5, 18, 103, 117, 118, 120] and triatomic pseudohalides.[2–5, 17, 18, 31, 32, 43, 44, 121–125]

The formation of structures of three types (**30**–**32**) has been demonstrated for the cyanide anion.[5, 16, 27, 112]

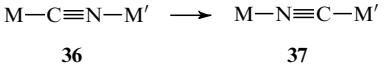


30 **31** **32**

In addition, the coordination types **33**–**37** are possible [16, 27] (the last two types of coordination correspond to the two stereoisomers **36** and **37**).

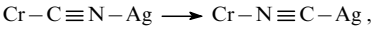


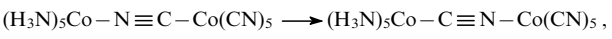
33 **34** **35**

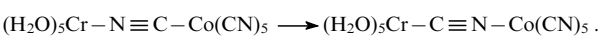


36 **37**

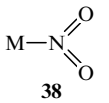
The above C,N-isomerisation has been observed in the following bimetallic complexes: Cr, Ag; Co, Co; Cr, Co.



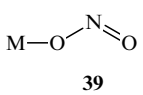




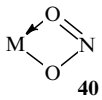
Eight types of bond isomers (**38**–**45**) have been proposed for complexes of nitrite anions.[5, 27, 114, 119]



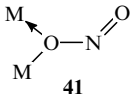
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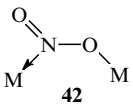
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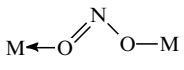
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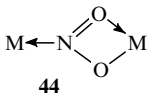
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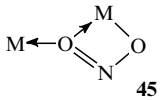
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43

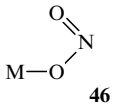


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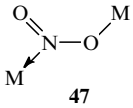


45

The stereoisomers of anionic metal nitrite complexes have also been described:[5] angular (**46**) and *trans*-planar (**47**).



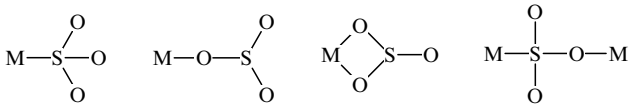
46



47

Numerous specific examples of nitrite complexes have been presented in a review.[5]

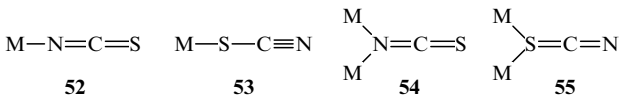
The complexes of the sulfite anion are represented by bond isomers in which the SO_3^{2-} fragment behaves as S- (**48**),[2, 3, 5, 103, 118] O- (**49**),[5, 18, 103] and O,O-chelate (**50**) [5, 103] ligands or an O,S-bridging ligand (**51**).[103, 117, 118]



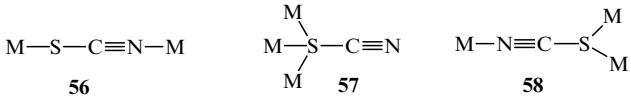
48 **49** **50** **51**

Other variants of coordination have also been put forward for dinuclear and polynuclear complexes of the SO_3^{2-} anion.[103] In the majority of these complexes the location of the coordinate bond has been established from vibrational spectroscopic data and the results of kinetic studies.[5, 103] Definite progress has been achieved in the study of the structures of sulfite complexes by NMR spectroscopy involving different nuclei.[117, 118, 125, 126] It has been established by X-ray diffraction [118, 125] that the three cobalt atoms in the trinuclear anion of the complex $Na_4[Co_3(NH_3)_6(SO_3)_6]$ are linked by the bridging SO_3 group. The SO_3 groups are bound to two cobalt atoms via sulfur atoms and to the third cobalt atom *via* an oxygen atom.[118, 125] The metal atoms are coordinated *via* oxygen and chalcogen atoms in complexes of the selenite [5, 118, 125] and tellurite [118, 125] anions. On the other hand, the sulfate anion is usually bound to the metal atoms *via* an oxygen atom and performs mainly a bridging function.[127–130]

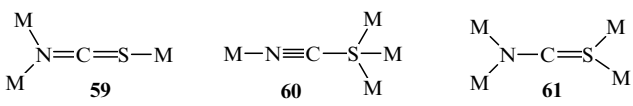
For complexes of pseudohalide anions (NCX, where X = O, S, or Se), the structures with ten modes of coordination (**52**–**61**) of the NCS anion as an example have been proposed.[4, 5, 17, 18, 43, 44, 124]



52 **53** **54** **55**



56 **57** **58**

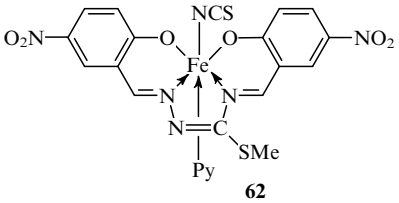


59 **60** **61**

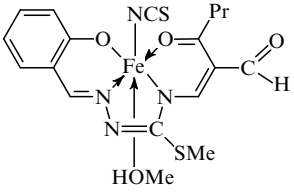
Extensive compilations of X-ray diffraction data for different modes of coordination of NCX anions are available in monographs [17, 44] and reviews.[5, 124] The greatest number of complexes contain the M–N=C=X fragment (**52**). This type of coordina-

tion is characteristic of, for example, gallium,[131] indium,[132] tin,[133, 134] iron,[135–137] cobalt,[138, 139] manganese,[140, 141] nickel,[142, 143] and copper[144–149] complexes.

An analogous M–NCS coordination has been observed also in chelate complexes, for example complexes **62**[150] and **63**.[151]



62



63

The Fe–NCS coordination in the adducts **62** and **63** was demonstrated by X-ray diffraction. The number of structures of the pseudohalide complexes in which the M–X–C≡N coordination (**53**) occurs is significantly smaller. Such structures are observed mainly in complexes of soft metals.[2–5, 17, 18, 43, 44, 124, 152, 153] It is striking that there are virtually no descriptions of structures with a pure M–SCN bond in the literature of recent years, although in certain cases (see, for example, Maurya *et al.*,[154]) its occurrence has been postulated.

Complexes with a bridging M–NCS–M′ bond occupy an important place among the coordination compounds of pseudohalides. Early information about such structures is available in reviews[5, 34, 44, 122, 124, 152] and monographs.[4, 17, 18] Among the studies in recent years, we shall mention those devoted to the structures of bismuth(III),[155] antimony(III),[156] molybdenum(IV)[157] nickel(II),[158, 159] copper,[160, 161] and ruthenium(IV)[162] pseudohalide complexes as well as the heterodinuclear lanthanum — mercury complex.[163] Soft–hard Hg–SCN bonding and hard–hard La–CNS bonding are observed in the La–Hg complex. The latter type of bonding is characteristic also of the mononuclear lanthanum thiocyanate compound $La(NCS)_3 \cdot 2(Me_2N)_3PO$.[164]

The structure of the complex AgLSCN·0.25L (L = α,α-bipyridyl),[165] in which the rarely encountered type **55** coordination occurs, is of undoubted interest.

The data presented above on the competitive reactions of pseudohalide ions refer mainly to soft–hard interactions,[2, 3, 5, 18] *i.e.* they take into account the nature of the donor N,X atoms on the complex-forming metals. At the same time, one should bear in mind that the nature of other ligands and the conditions in the synthesis of the pseudohalide complex exert an extremely significant influence on the nature of the binding of NCX anions to metals. Extensive data, partly published in Refs 4, 17, 122, 124, 153, 165, and 166, have accumulated on these problems. Bond isomerism of the type MNCS⇄MSCN is quite frequently observed in complexes of this type.[4, 123, 167]

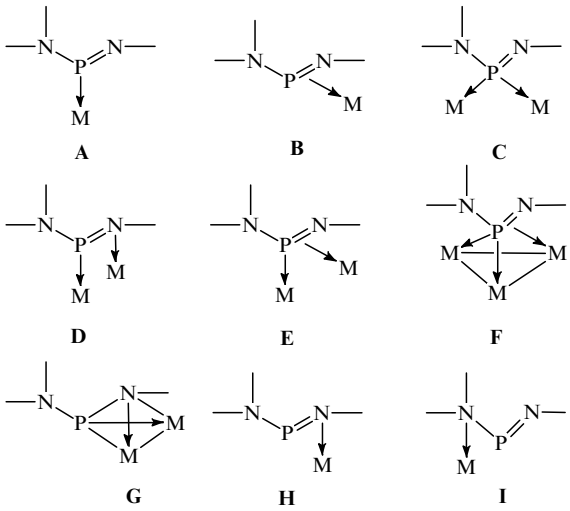
It is noteworthy that the results of a recent *ab initio* quantum-chemical calculation for pseudohalide ions[168] indicate the possibility of the chelation of the NCX groups. However, there are as yet no experimental data confirming this conclusion.

There are data on various modes of coordination of other ambident anions also: CNO^- (see, for example, Refs 5 and 17), CNS^-,[5] $[C(CN)_3]^-$,[17] NO_3^-,[27, 28, 169, 170] NSO^-,[5, 169] SNO^-,[5] NSO_2^-,[169] $S_2O_3^{2-}$,[3, 5, 18, 103, 117, 118, 171] $S_2CO_3^{2-}$,[5] $OSNH^-$,[5] and NS_3^-.[169]

3. Organic bidentate and polydentate ligand systems with donor atoms — the elements of the main Group V and VI subgroups

Extensive data on the competitive coordination of organic bidentate and polydentate ligands have been collected in reviews[2, 3, 5, 6, 29, 30] and monographs.[4, 17, 18, 25, 26] In the present review, the fundamental results in this field achieved in recent years will be considered.

Two reviews[172, 173] contain compilations of data on ligands with N,P-donor atoms and the complexes obtained from them. It had been shown earlier that mainly the phosphorus atom participates in the coordinate bond formed in complexes of these ligands. However, when the disposition of the nucleophilic centres is favourable for the formation of a bridge or chelation, metallocyclic structures with participation of N and P atoms are obtained regardless of the hardness or softness of the metal salts. Thus the formation of at least seven types of transition metal complexes (**A**–**G**) is possible for the amides of the imidophosphonous acid $R^1R^2N-P=NR^3$.[172]



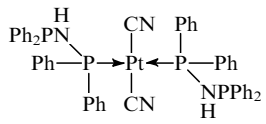
A **B** **C**

D **E** **F**

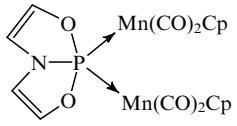
G **H** **I**

The possible structures **H** and **I**, in which coordination is achieved *via* the nitrogen atom, were not considered in the above study[172] for reasons which are not clear.

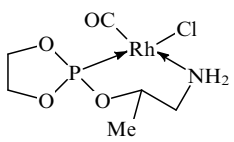
A similar situation is characteristic also of ligands containing a donor oxygen atom (compounds **65**,[175] **66**[176, 177] **67**, and **68**[173, 178]) apart from the N,P atoms (compound **64**[174]).



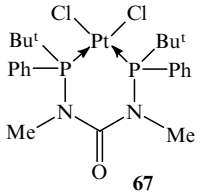
64



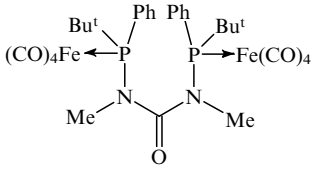
65



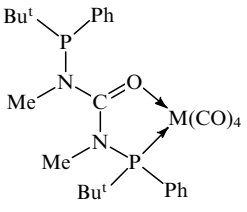
66



67



68

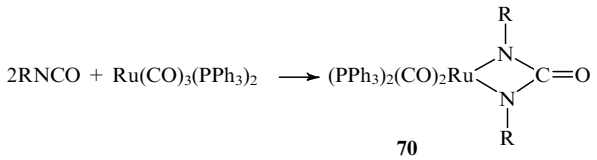


69 (M = Cr, Mo, W)

An increase in the electron-donating activity of the carbonyl oxygen compared with the ester oxygen (structure **65**) and a disposition of the donor centres suitable for chelation lead to the chelate structure **69**.[178]

Phosphazenes, the coordination chemistry of which involves a series of complexes with hard (N) and soft (P) coordination, are N,P-donor ligands.[18, 179] Several examples of complexes obtained from N,As(Sb)-containing ligands are known,[18, 175] but these do not allow a discussion of the characteristic features of their competitive reactions.

There are comparatively few new data on the competitive coordination of N,O-donors. The study of the structures of the complexes $SnCl_4$ and $EtSnCl_3$ with tetramethylurea confirmed [2] that the latter is a predominantly monodentate O-donor ligand.[180, 181] Thus an O—Sn bond is formed in the complex between 1,3-dimethylurea and $SnCl_4$. This conclusion was reached on the basis of IR and Mössbauer spectroscopic data.[181] We may note that reliable information about the possibility of the involvement of the urea nitrogen atoms in coordination is lacking in the studies published previously. Complexes with N-coordinated urea **70**, obtained as a result of the reaction [182]

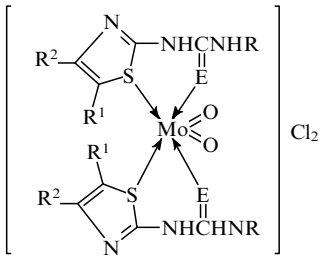


70

are therefore of undoubted interest.

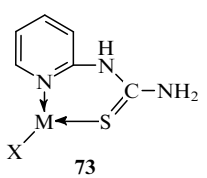
The coordination chemistry of organopseudohalides of the type RNCX (X = O, S, Se, Te) has been examined in a review.[182] It is remarkable that the interaction of ligands of this type with metal salts and carbonyls is accompanied not only by the formation of the adducts $(RNCX)_m \cdot RX_n$ but also by chemical reactions of the ligand systems.[182]

Among the ligands containing N- and S-donor centres, thiourea (L) and its derivatives are widely represented. Thus complexes between thiourea and ruthenium(III) trifluorosulfonate [183] and copper(II) bis(dimethylglyoximate),[184] between 1,3-dimethylurea and tin chloride,[181] between 1,3-diphenylurea and rhodium(I) chloride,[185] and between ethylenethiourea and copper(I) sulfate [186] have been obtained. It has been suggested that S—N coordination obtains in the chelate complexes **71**.[187] **72**,[187] **73**,[188] and **74**.[188]

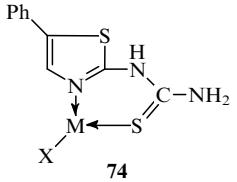


71 (E = O), **72** (E = S)

R = H, Alk, Ar; R^1, R^2 = Alk, Ar;



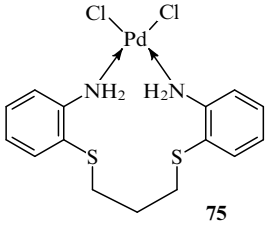
73



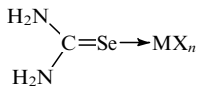
74

M = Cu(I), Ag(I); X = Cl, Br.

Whereas the occurrence of structures **73** and **74** is not open to serious objections, the possibility of the involvement of S and not N atoms of the thiazole ring (structures **71** and **72**) is hardly realistic.[189, 190] The chelate structure **75** is believed probable for the complex between a diaminodithioether and palladium chloride.[191]



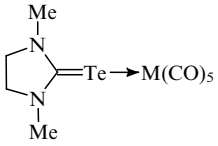
75



76

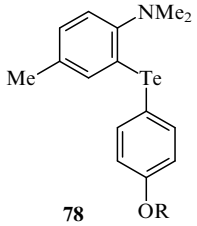
Coordination compounds of N,Se-containing ligands are mainly represented [2, 18, 192–194] by selenourea complexes in which the Se—M bond is formed (compound **76**). In particular, such a bond has been found (on the basis of XRD data) in the complex of selenourea with triphenylphosphinegold(I) chloride **76** ($MX_n = Ph_3PAuCl$).[194]

The interest in complexes containing N,Te-donor ligands has increased recently, although individual examples of such compounds had been examined also in earlier investigations.[18, 81, 193, 195–197] A series of studies [198–211] (among them a review [204]) devoted to complexes of ligands with N,Te-donor centres have been published during the last six years. However, the problem of competitive coordination was not discussed in these publications. In our view, this can be explained by the fact that in most other investigations conditions were created for the monodentate M—Te coordination of the ligands considered or for the formation of N—M—Te metallocycles. Thus, owing to the high donor activity of the chalcogen atom and the steric effects preventing the occurrence of M—N coordination, the ligand behaves as a monodentate Te-donor in the tellurourea complex **77**,[195] as in the thio- and seleno-analogues examined above.



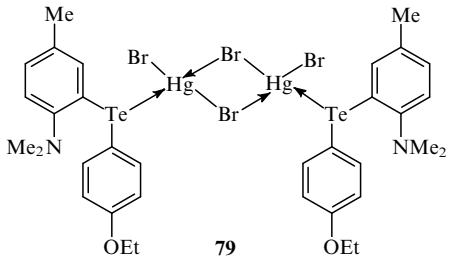
77

The steric effect apparently prevents the involvement in chelation of the potentially bidentate ligand **78**, the mercury bromide complex of which has the structure **79** according to X-ray diffraction data.[201]



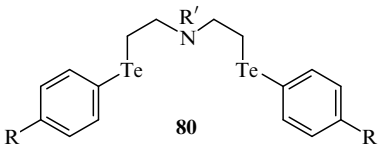
78

R = Me, Et;



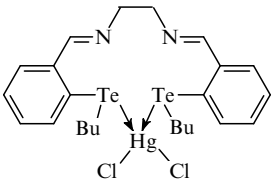
79

At the same time, it is believed [203] that ligands **78** and **80** form with rhodium(I) and rhodium(III) chlorides chelate structures having N,Te-coordination.

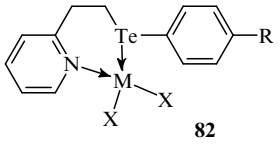


80

The formation of the chelate structure **81** has been demonstrated by X-ray diffraction.[212] A similar structure is characteristic also of type **82** complexes.[207, 209]



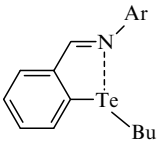
81



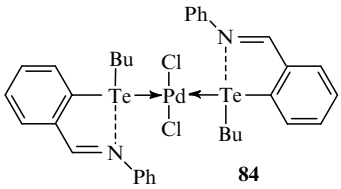
82

R = H, OMe, OEt;
M = Pd, Pt, Co, Cu;
X = Cl, Br.

The tellurium-containing azomethines **83** must also be regarded as potential N,Te-chelating ligands.[213] However, the ligand system in the palladium dichloride complexes obtained from them behaves as a Te-monodentate system, forming,in particular, complex L_2PdCl_2 with structure **84**.[210]

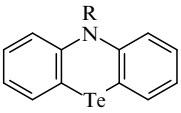


83

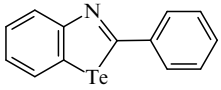


84

Although the location of the coordinate bond in complex **84** is justified from the standpoint of the HSAB principle, one cannot rule out that the decrease in the denticity of ligand **83** can be accounted for by the formation of the intramolecular Te···N bond,[212, 217] which virtually deprives the azomethine nitrogen atom of the possibility of becoming coordinated to the metal. Ligands **85**[18, 218] and **86**[211] are free from the above disadvantages.

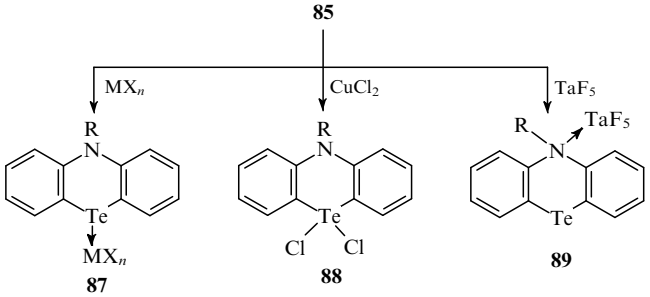


85



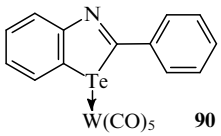
86

A cycle of reactions of *N*-alkyltellurazines **85** has been achieved with Pearson acids: soft (MX_n = rhodium carbonyl chlorides, palladium, silver, and mercury halides) (with formation of complexes **87**), intermediate ($CuCl_2$) (with formation of complex **88**), and hard (TaF_5) (with formation of complexes **89**).[18, 219]



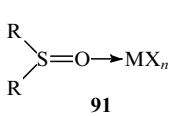
87 **88** **89**

The structures of the products formed have been justified by IR and NMR spectroscopic data and by studying their chemical behaviour.[18, 196] In conformity with the HSAB principle,[18] ligand **86** (L) interacts with chromium, molybdenum, and tungsten (M) hexacarbonyls to form complexes of the type $LM(CO)_5$ with a M—Te bond, which has been rigorously demonstrated[211] by X-ray diffraction in relation to complex **90**.

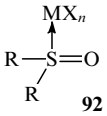


90

Fairly numerous publications have been devoted to complexes with ambident ligands containing O, S-donor centres.[2, 18, 103] Those devoted to the competitive reaction of organosulfoxides, especially dialkyl(aryl) sulfoxides forming O-bonded (compounds **91**)[220–227] and S-bonded (compounds **92**)[228–239] isomers are outstanding among them.



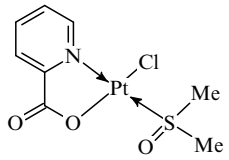
91



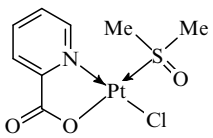
92

The occurrence of O→M coordination **91** has been demonstrated by X-ray diffraction in relation to complexes of dimethyl sulfoxide (DMSO) with trichlorodipheny-lantimony(V)[220] and zirconium tetrachloride,[222] ionic complexes of osmium,[223] and heterometallic compounds.[224–227]

It also follows from X-ray diffraction data that S→M bonding is characteristic[228] of the isomeric adducts of DMSO and the platinum chelate complexes of pyridine-α-carboxylic acid **93** and **94**.



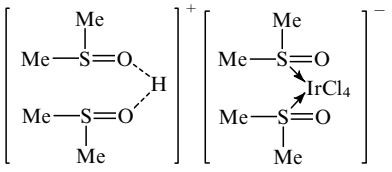
93



94

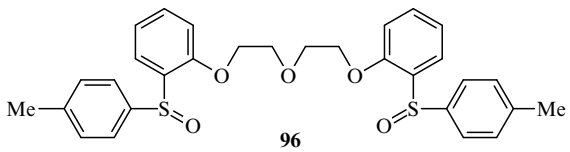
The same type of coordination is observed in the complexes $\{[Pt(NH_3)_4][PtCl_3(DMSO)]_2\}$,[229] $\{[PtCl_3(DMSO)_2L]DMSO\}$,[230] $[Pt(DMSO)(CH_3CN)Cl_2]$,[231] $[Pt(DMSO)(Py)Cl_2]$,[232] $\{K[Pt.(Et_2SO)Br_3]\}$,[233] $[RuCl_2(DMSO)_3(NH_3)]$, $\{[Ru(DMSO)_2.(NH_3)_2]H_2O\}$,[234] $\{[H(DMSO)_2]^+[RuCl_4(DMSO)_2]^-\}$,[235] $\{[H(DMSO)_2]^+[OsNO(DMSO)Cl_4]^-\}$.[236]

We may note that the structure containing the $[H(DMSO)_2]^+$ cation had been described earlier for the complex between iridium chloride and DMSO.[237]



95

S,S-Coordination has also been observed in the complex between palladium chloride and the podand **96**.[238]



96

It has been suggested that several types of coordination of the ligand (O-, S-, or bridging O,S-coordination) may occur simultaneously in the DMSO complexes. It is believed[239] that such a situation is observed in complexes of dibenzyl and tetramethylene sulfoxides of the type $[PtL_2Cl_2]$ and $[ML_3Cl_3]$, where M = Ru(III), Rh(III), and Ir(III). Finally, we may draw attention to the

extremely unexpected result obtained in a study [240] of the structure of the complex {[$EuL_3Phen(H_2O)_2$]DMSO}, where $L = C_5H_4NCO_2^-$ is the anion of nicotinic acid. In this complex, the DMSO molecule is not involved in coordination with the metal but forms a hydrogen bond with the oxygen atom of one of the coordinated water molecules.

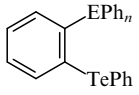
Analysis of the data presented shows that in virtually all cases DMSO is coordinated in accordance with the HSAB principle: hard Pearson acids are bound to the oxygen atom and soft acids are bound to the sulfur atom.

There are comparatively few examples of complexes containing O,Se- or O,Te-donor atoms.[18, 204] It is believed that the M—O bond is mainly formed in dimethyl selenoxide complexes.[18] It is so far difficult to discuss competitive coordination in the series of O,Te-containing compounds presented,[204, 216, 241–243] since there are no structural data for the few available O,Te-containing ligands which have not been used to obtain complexes.[18, 204, 241, 244, 245]

In conclusion of this section we may note that the review of Singh and Srivastava [204] contains data on the complexes of a series of ligands containing the N-, P-, S- and Se-donor atoms in addition to tellurium, for example, compounds **97** and **98**.

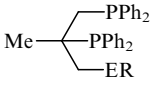


97

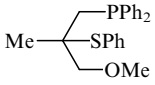


98 (E = N, P, S, Se)

Ligands **99** and **100**, containing three donor atoms, are not without interest in connection with the problem of competitive coordination under discussion.[246]



99 (E = O, S; R = Me, Ph)



100

4. Heteroaromatic compounds and their derivatives

Heteroaromatic compounds belong to ambident σ,σ′-, σ,π-, and π,π′-ligand systems,[247–249] which interact with metals or their salts and also with organometallic derivatives to form complexes in which these ligands are bound to the metal atom either *via* the heteroatom or *via* the π-system.[2, 18–21] When competitive coordination is considered, the ligands of this type can be usefully divided into two varieties:[19–21] π-excess and π-deficient ligands. According to the literature,[250, 251] five-membered heterocyclic compounds of type **101**, in which the number of π electrons exceeds the number of atoms in the ring, belong to ligands of the first variety. These are pyrrole (**101**: A = NR; R = H, Alk, Ar), phosphole (**101**: A = PR), arsole (**101**: A = AsR), stibole (**101**: A = SbR), furan (**101**: A = O), thiophene (**101**: A = S), selenophene (**101**: A = Se), and tellurophene (**101**: A = Te) ligand systems. The ligands of the second type include pyridine (**l02**) and other six-membered nitrogen-containing heterocycles (azines) with one or,several heteroatoms (**103**). The azoles **104** can be formally [250, 251] assigned to π-excess systems.



101



102



103

A = NR, PR, AsR, SbR, O, S, Se, Te.



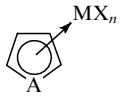
104a



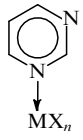
104b

A = NR′, O, S, Se, Te; R = H, Alk, Ar, benzo.

It has been shown in numerous investigations that the π-excess ligand systems form mainly type **105** η^5(π)-complexes, while π-deficient ligands give rise to η^1(N)-metallo-derivatives of type **l06**.



105



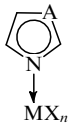
106

A = NR, PR, AsR, SbR,O, S, Se, Te.

The azole ligands behave in complex formation reactions as π-deficient species (complexes **107a**, **b**).



107a



107b

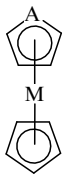
A = NR, O, S, Se.

It will be shown below that, although these rules hold for numerous examples of complexes of heteroaromatic ligand systems, there are quite a few complexes of type **101** and **102** ligands with a non-traditional location of the coordinate bond.

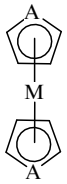
a. Complexes of five-membered heterocycles containing one heteroatom

Reviews[19, 20, 84, 252] and other publications [18, 253] contain numerous examples indicating the formation of type **105** η^5(π)-complexes based on pyrrole (A = NR), phosphole (A = PR), arsole (A = AsR), stibole (A = SbR), thiophene (A = S), selenophene (A = Se), and tellurophene (A = Te). Fragments of metal carbonyls, mainly $Mn(CO)_3$ and $Cr(CO)_3$, usually serve as the Lewis acids MX_n.

In addition to complexes of this type, sandwich structures of type **108** and **109** are quite widely represented among η^5-coordinated systems.



108



109

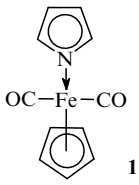


110

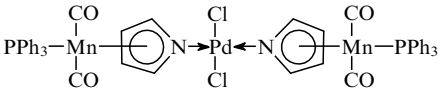


111

The η^1(σ)-coordinated structures **110** and **111** have been obtained mainly from pyrroles (**105**: A = NR, R = H, Alk, Ar) and phospholes (**105**: A = PR, R = H, Alk, Ar). Apart from the *N*-metal-substituted compounds **110** (see, for example, Refs 253 and 254), the organometallic compounds **112** and **113** have been described [20] among the N-coordinated pyrrole complexes.

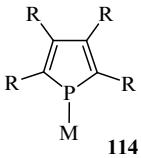


112

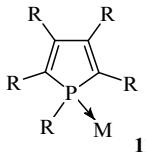


113

The P-coordinated phosphorus complexes are represented,[20, 84, 255, 256] by structures of two types (**114** and **115**), structure **114** being more common than structure **115**.



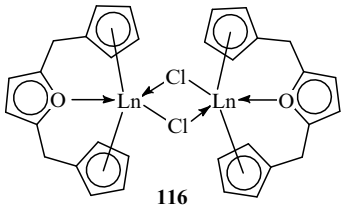
114



115

We are not aware of type **110** and **111** complexes in the arsole (A = As), stibole (A = Sb), and bismuthole (A = Bi) series.

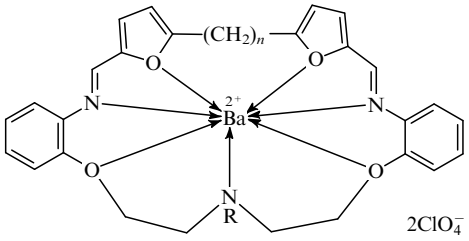
The question of the possibility of the involvement in coordination of the furan ring oxygen atom remains unelucidated. We may note in this connection a recently published communication [257] in which the hitherto unique example of a complex with a O—M coordinate bond is described (complex **116**).



116

In the absence of X-ray diffraction data, the structure of compound **116**, described on the basis of IR and ^{1}H NMR spectroscopic studies,[247] gives rise to doubt.

The involvement in coordination of the furan ring oxygen atom forming part of the composition of macrocyclic ligands, for example compound **117**, is more realistic.[258]

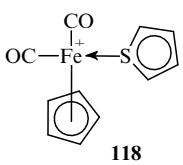


117

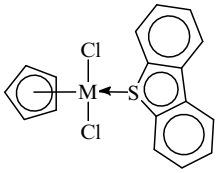
R = Alk, CH_2CH_2OAlk.

The stabilisation of structures **116** and **117** is apparently associated with chelate and macrocyclic effects.[259] We may also note that an organometallic compound with a M—C bond may be formed from furan (see, for example, Selna and Merob [260]).

In contrast to furan complexes, thiophene complexes with the sulfur-centred coordinate bond are represented by a large set of structures.[20, 261] In particular, such coordination has been observed in the ionic complex **118**.[20]



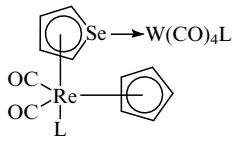
118



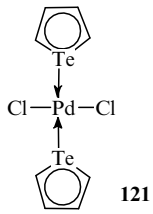
119 (M = Rh, Ir)

η^1(S)-Coordination is also characteristic of the dibenzothiophene complexes **119**.[262]

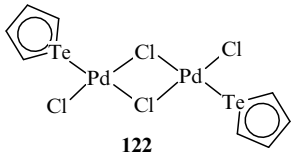
An example of the involvement in coordination of the selenophene Se atom (complex **120**) is known.[263]



120



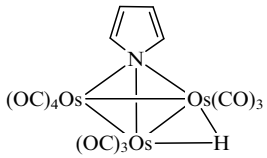
121



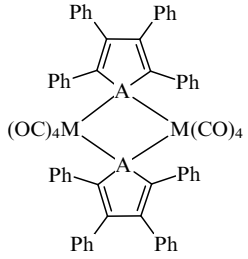
122

η^1(Te)-Coordinated tellurophene complexes are represented by the palladium chloride compounds **121** and **122**, the structures of which have been frequently considered, for example in reviews.[81, 193, 195] A similar coordination has apparently been observed in complexes of tellurium-containing heterocycles with univalent and trivalent rhodium chlorides and carbonyl chlorides.[264]

In a number of instances, type **101** ligand systems behave as bidentate and even tridentate ligands.[20] Complexes have been formed in which A(σ)- or A(σ), π-metal bonds are formed. Such nonstandard η^3(N,σ)-coordination has been observed in the pyrrole cluster **123**.[20]



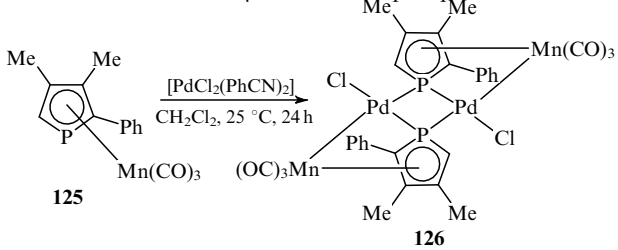
123



124

M = MN, Re; A = P, As.

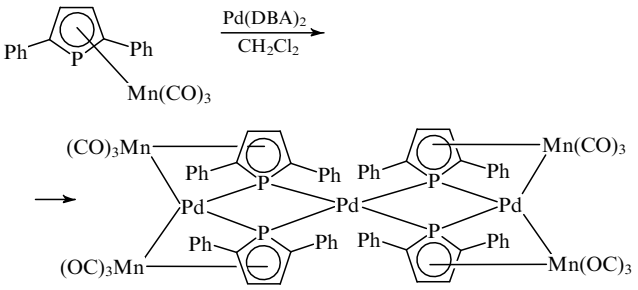
Complexes with η^2-coordinated phosphorus are particularly widely represented in the series of phosphole and its derivatives.[20] In particular, such coordination has been observed in the manganese and rhenium dimers **124**.[20] The reaction of 3,4-dimethyl-2-phenylphosphocymantrene **125** with the benzonitrile complex of palladium dichloride in methylene chloride afforded the dinuclear palladium cluster **126** with η^2-coordinated phosphorus.[265]



125

126

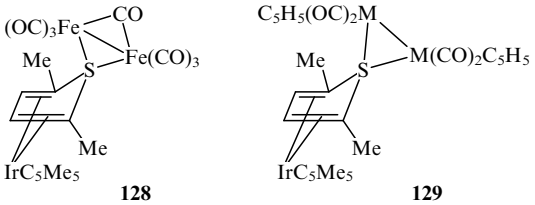
The same type of coordination of phosphorus occurs in the trinuclear cluster **127** obtained in the course of the following reaction:[265]



127

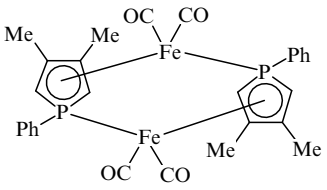
DBA = dibenzylideneacetonate anion.

η^2-Bonding is observed also in the analogous arsole complexes **124** (A = As) [20] and also in the thiophene complexes **128** [266] and **129**.[267]



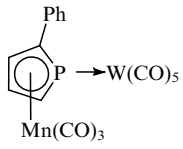
128 **129**

In this connection, we may mention the polymeric iron complex of pyrrole in which the heterocycle is involved in coordination of the $\eta^1(\sigma)$- and $\eta^5(\pi)$-types.[20,268] The same coordination is characteristic [20] of phosphole complexes, for example compound **130**.



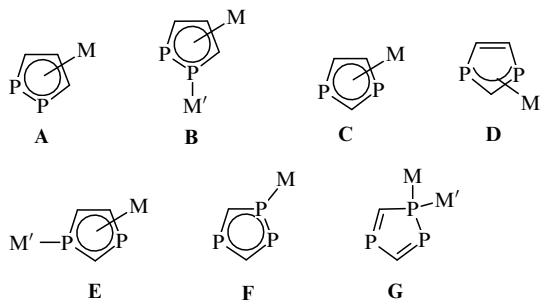
130

A heteronuclear complex of *C*-phenylphosphocymantrene with tungsten pentacarbonyl (compound **131**), in which phosphole also behaves as a σ,π-donor ligand system, has been described.[269]

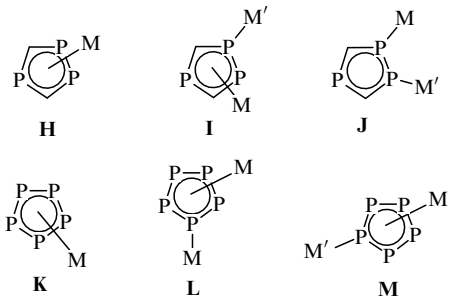


131

The complexes of phospholes containing several phosphorus atoms in the heterocycle are quite widely represented.[84] The possible variants of their bonding to metals are presented below (structures **A**–**M**).[84]



A **B** **C** **D** **E** **F** **G**



H **I** **J** **K** **L** **M**

Other examples of complexes with heterocycles **101** bound to the metal in different ways have been described in reviews [20,270] and other communications.[271–274]

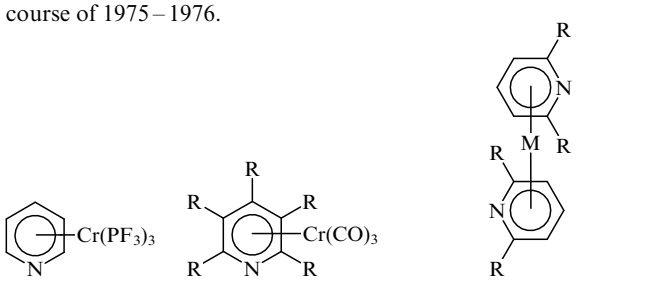
b. Complexes of azines

The commonest and well known mode of coordination of pyridine and other six-membered nitrogen-containing heterocycles is N(σ)-bonding to the metal, which is indicated by the early reviews.[18,19,275–277] Among the studies published in recent years, we shall mention data concerning the complexes of N-coordinated pyridine with BH_2CN [278] and the ruthenium-cyclopentadienyl fragment [279] and a series of publications by Italian investigators [280–284] devoted to the properties and structures of the adducts of pyridine and chelates modelling the fragments of biologically important systems (in particular vitamin B_{12}) and the corrole complex of iron.[285]

The structure of the adduct of pyridine and copper(II) acetate, in which N–Cu coordination also occurs, has been revised.[286]

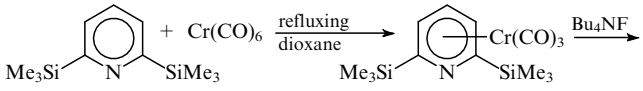
Studies in which the metal is coordinated to several pyridine molecules with formation of the complexes MPy_n are of interest.[287,288] The η^1(N)-coordination of pyridine in the dinuclear rhodium complexes $[Rh_2(MeCOO)_3Py_4]CF_3SO_3$ and $[Rh_2(MeCOO)_2Py_6](CF_3SO_3)_2$ has been demonstrated by X-ray diffraction.[289]

The η^1(N)-coordination of azines was believed to be the only one possible up to the middle of the 1970s, to a considerable extent as a result of the unsuccessful attempt to obtain $\eta^6(\pi)$-coordinated pyridine complexes by Fischer — a Nobel Laureate.[290] However, the unusual $\eta^6(\pi)$-complexes of pyridine **132**,[291] **133**,[292,293] and **134** [294–296] were synthesised in independent investigations in the course of 1975–1976.

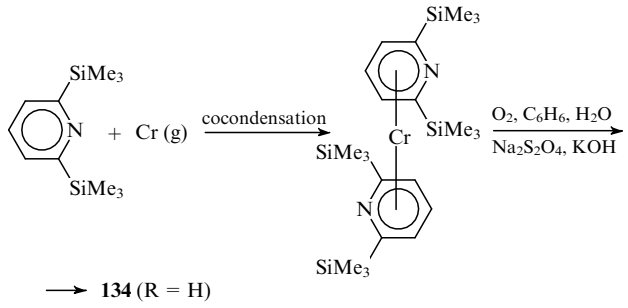


132 **133** (R = H, Me, $SiMe_3$) **134** (R = H, Me; M = Cr, Mo, Ti, V)

Complexes of types **133** [297] and **134** [298] with unsubstituted pyridine (R = H) were later obtained and in both cases trimethylsilylpyridine derivatives served as the starting compounds.



→ **133** (R = H);

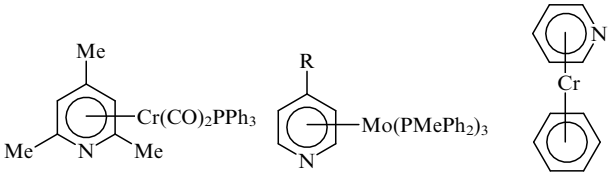


134 (R = H)

We may note that the direct gas-phase synthesis of the type **132** and **134** π-complexes of pyridine from the zerovalent metals played a decisive role.[299, 300]

The η^6-2,4,6-collidine(triphenylphosphine)chromium dicarbonyl complex **135** has been synthesised [301] and characterised by X-ray diffraction.[302]

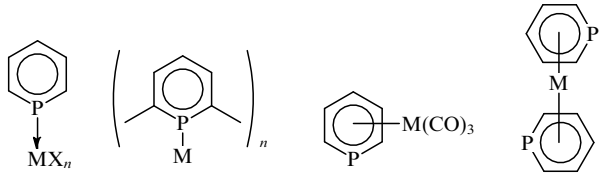
Complexes similar to complex **132** have also been obtained from molybdenum (complex **136** [303]).



135 **136** (R = H, Me) **137**

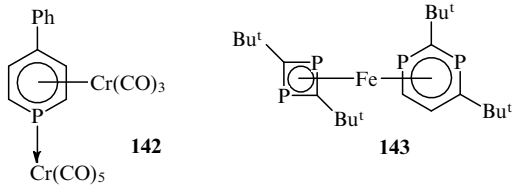
The mixed-ligand complex **137** has been obtained by the gas-phase cocondensation of three components — pyridine, benzene, and zerovalent chromium.[298]

The complexes of the phosphorus analogue of pyridine — phosphabenzene — (compounds **138**–**141**) are represented by a fairly wide range of compounds. Among them, the coordination compounds **138** [304, 305] and **139** [306–309] are $\eta^1(\sigma)$-coordinated, while compounds **140** [304, 310] and **141** [304, 311, 312] are $\eta^6(\pi)$-coordinated.



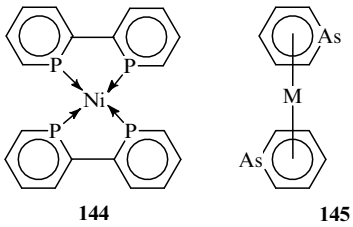
138 **139** **140** **141**

Complex **142**, in which mixed $\eta^1(\sigma)$- and $\eta^6(\pi)$-coordination of 4-phenylphosphabenzene occurs,[304] and the heteroligand sandwich complex of four- and six-membered diphosphorus heterocycles **143** [274] are also of undoubted interest.



142 **143**

α,α′-Diphosphaphenyl (the phosphorus analogue of α,α′-bipyridyl) is bound to nickel in a way similar to that in compound **139** [313] with formation of complex **144**.

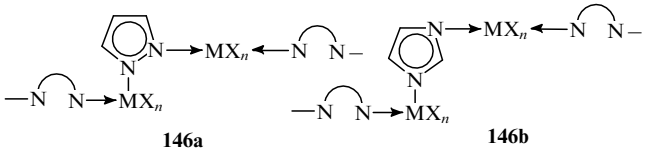


144 **145**

Complexes of $\eta^6(\pi)$-coordinated arsabenzene **145** (M = Cr,[314] Ti,[314] and V [315]) have been described.

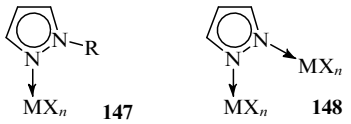
c. Coordination compounds of azoles

Until recently, it was believed that, in contrast to the heterocycles **101** and the azines **102** and **103**, azoles form only complexes in which the ligands are bound to the metal *via* the N atom of the pyridine ring. The ligand systems then behave as monodentate species (**107**) [1–3, 18, 21, 189, 276, 316–318] or perform a bridging function (**146**).[21, 139, 276, 319–323]



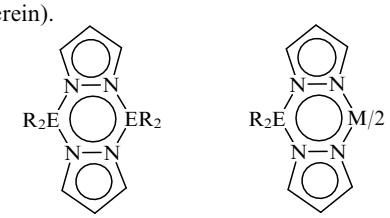
146a **146b**

$\eta^1(\sigma,N)$-Bonding to the metal has been observed in the pyrazole complexes **147** [21, 189, 317, 318, 324, 325] and **148**.[41, 319–323, 326–330]



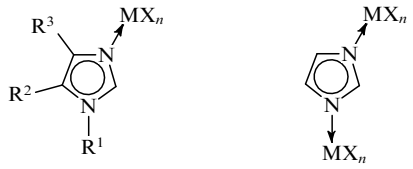
147 **148**

Type **149** organoelement derivatives of pyrazoles [1, 21, 139] and numerous complexes [150] obtained from them are of special interest (see the relevant reviews [21, 321–323] and the literature quoted therein).



149 (E = B, Al, Ga) **150** (E = B, Ga)

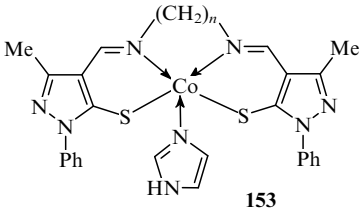
Like the pyrazole complexes, the imidazole complexes are represented by structures **151** (monodentate coordination of the ligand) [1–3, 318, 331–339] and **152** (bridging coordination).[1, 2, 340–342]



151 (R^1, R^2, R^3 = H, Alk, Ar) **152**

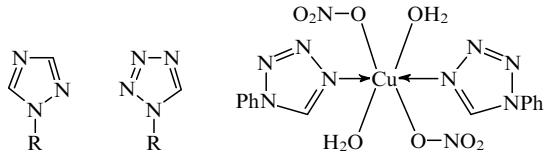
Among the studies devoted to imidazole (L) complexes, we shall mention the following: the unexpected formation of the monomeric copper acetate complex $CuAc_2L_2$,[334] the synthesis of

previously unknown complexes ZnS_6L_2 and $ZnSe_4L_2$,[333] and also the isolation of the imidazole adduct of the chelate pyrazole complex **153**.[339]



153

σ(N)-Coordination is characteristic also of 1,2,4-triazoles **154**[343] and tetrazoles **155**.[344, 345]

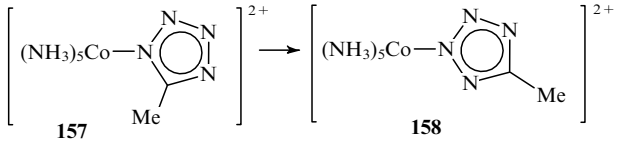


154 **155** **156**

We emphasise that the tetrazole fragment in the dinitrodiaquobis(phenyltetrazole)copper(II) complex is coordinated *via* the N(4) atom of the heterocycle (complex **156**).[344]

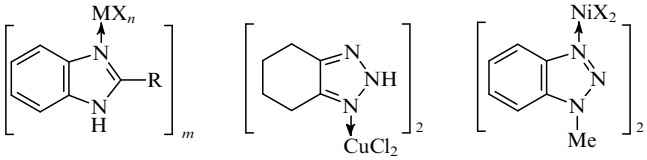
1-Ethyltetrazole **155** (R = Et) is bound to the metal *via* the same donor centre in the complex with copper dinitrate.[345]

The bond isomerisation (**157**→**158**) observed in the cations of 5-methyltetrazole complexes of pentamminecobalt(III) is of undoubted interest in connection with the problem of competitive coordination.[346–348]



157 **158**

As in the case of azoles, the metal complexes of the benzoanalogues of azoles are N-coordinated compounds. For example, such coordination is characteristic of 2-substituted derivatives of benzimidazole **159**,[1, 189, 317, 349] tetrahydrobenzotriazole **160**,[350] and 1-methylbenzotriazole **161**,[351] *i.e.*



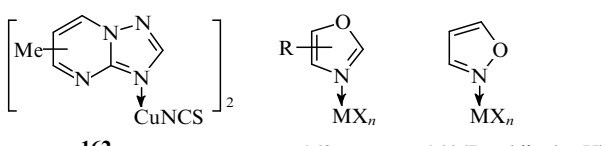
159 (R = H, Et, Pr, Pr^i, Bu; M = Co, Ni; X = NCS, ClO_4; *m* = 2, 3)

160

161 (X = Cl, Br, NCS, NO_3)

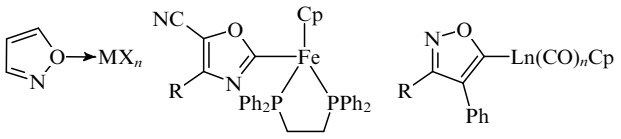
The η^1(N)-coordination in complexes **160**[350] and **161**[351] (X = NO_3) has been demonstrated by X-ray diffraction.

A type of binding of the metal analogous to that in complex **160** occurs in the copper complex of 5(6)-methyl-1,2,4-triazolo[1,5*a*]pyrimidine **162**.[144]



162 **163** **164** (R = Alk, Ar, H)

The N–M coordination also occurs in oxazole and isoxazole complexes[352, 353] (complexes **163** and **164**). At the same time, the possibility of the involvement of the O atom of the oxazole ring (complex **165**) has been discussed.[353] In our view, this donor atom can hardly compete with powerful nucleophilic centres such as the N atom.



165 **166** (R = H, Alk) **167**

C-Organometallic derivatives of oxazole **166**[354] and isoxazole **167**[355] are of undoubted interest.

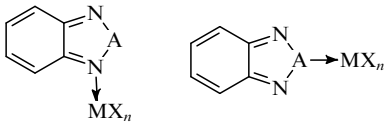
The complexes of chalcogen-containing azoles, for example complex **168**, N–M and benzazoles, for example complex **169**, contain mainly N–M bonds.[1, 2, 189, 336, 356–364]



168 **169**

A = CH, N; B = O, S, Se.

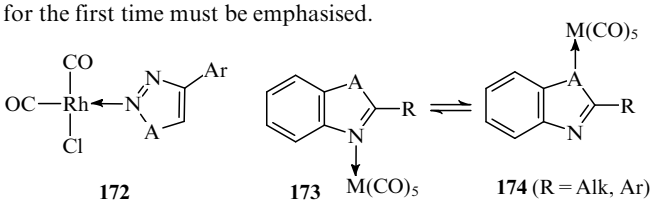
The location of the coordinate bond in the complexes of benzo-2,1,3-thiadiazole and of its selenium analogue (coordination types **170** and **171**) has aroused an especially great deal of controversy.



170 **171**

A = S, Se.

At the same time, X-ray diffraction studies indicate unambiguously[359, 360] that only type **170** N–M coordination occurs in the coordination compounds under consideration. The same mode of coordination is characteristic of the rhodium chloride dicarbonyl complexes of 1,2,3-thiadiazole and 1,2,3-selenodiazole (coordination type **172**).[361] In connection with the data under discussion, the X-ray diffraction studies[211, 365] in which direct evidence for the possibility of the involvement of the tellurium atom of benzotellurazole in coordination to the metal (complex **90**) was obtained for the first time must be emphasised.

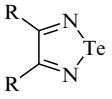


172 **173** **174** (R = Alk, Ar)

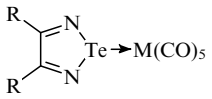
A = S, Se, Te.

This type of coordination can probably be accounted for by the high electron-donating activity of the tellurium atom in the complexes of N,Te-containing ligands, which were considered previously in the present review.

In connection with the problem of the competitive reaction of chalcogenazoles with metals, it appears important to carry out X-ray diffraction studies on a series of metal carbonyl complexes of benzothiazole **173** (A = S) and benzoselenazole **173** (A = Se), for which the equilibrium **173**⇄**174** exists in solution according to ^{1}H NMR data.[366] Furthermore, it appears important to carry out specific studies on the complex formation reactions of other tellurium-containing azole ligands for the same purpose.[196, 367, 368] In particular, the deliberately synthesised tellurodiazole **175**, from which complexes **176** with a Te–M bond, hitherto unknown in the series of chalcogeondiazoles (*cf.* complexes **170** and **171**), may be obtained with a high degree of probability, is of undoubted interest.



175

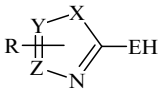


176 (M = Cr, Mo, W)

d. Complexes of exocyclic substituted heteroaromatic ligands

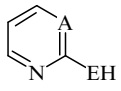
The complex formation reactions of heteroaromatic ligands with coordination-active groups result in the formation, apart from the metal derivatives of types **106** and **107** examined above, also of complexes involving exocyclic groups and also bimetallic complexes involving two donor centres.

Particularly numerous data indicating the occurrence of these types of coordination of heteroaromatic ligand systems with coordination-active side substituents have been obtained in relation to complexes of amino- and hydroxy(chalcogen hydride)-derivatives of five- and six- membered heterocycles of types **177** and **178**.



177

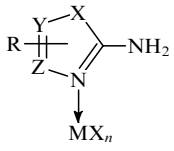
X = NR′, O, S, Se;
Y, Z = CR, N;
R = H, Alk, Ar, benzo;
E = NH, O, S, Se, Te.



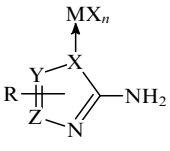
178

A = CH, N;
E = NH, O, S, Se, Te.

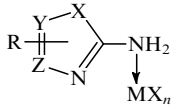
Aminoazoles **177** and aminoazines **178** (E = NH) are involved in both monodentate (**179**–**183**) and bidentate bridging (**184** and **185**) binding of the metal.[1–3, 35]



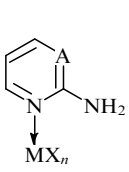
179



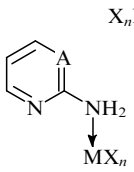
180



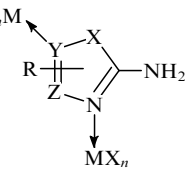
181



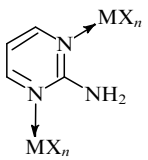
182



183



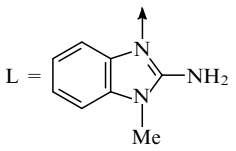
184

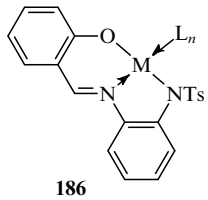


185

The coordination types **179** and **182** are the most common.[35] Apart from the extensive compilation of data presented by Garnovskii *et al.*[35], there are data on the type **179** structure obtained by X-ray diffraction for the 2-aminoimidazole complexes of copper dichloride[369] and dibromide[370] and of the 2-aminothiazole complex of zinc dichloride.[371] The same type of location of the coordinate bond arises from the quantum-chemical interpretation of the regioselective coordination in the series of metal complexes of 2-aminoazoles.[372–374] In contrast to earlier calculations,[374] Garnovskii and coworkers[372, 373] determined the relative theromodynamic stabilities of the bond isomers **179**–**181**[372] and their geometry.[373] The preferential N-coordination (type **179**) of the proton and BH_3 arises also from the results of quantum-chemical calculations[375] by the MNDO method.

The location of the coordinate bond at the N atom (type **179**) is also characteristic[376] of more involved complexes, for example of the adducts of 2-amino-1-methylbenzimidazole (L) with the chelate complexes of tridentate Schiff bases (complex **186**).



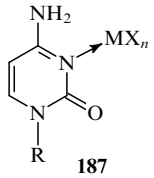


186

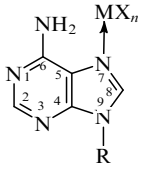
M = Cu, Co; *n* = 1, 2.

These complex adducts are of interest because they have been obtained electrochemically.[376, 377] Complexes of aminoazoles with a bridging function of type **184** have been described.[35, 141, 378–380]

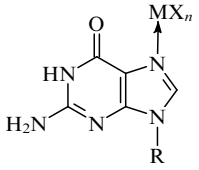
The complexes of aminopyridines **182** (A = CH),[35, 381–384] pyrimidines **182** and **185** (A = N),[35, 130, 382, 385–390] and fragments of biologically important systems (amino-derivatives of pyridine)–cytosine **187**,[35, 38, 381, 391–396] adenine **188**,[35, 38, 381, 397, 398] and guanine **189**[399, 400] — are represented by a wide range of structures in which metal salts are coordinated *via* endocyclic N atoms of the pyridine type.



187

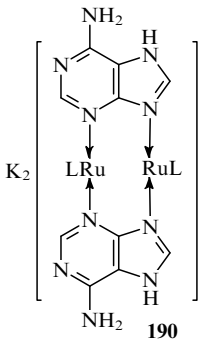


188



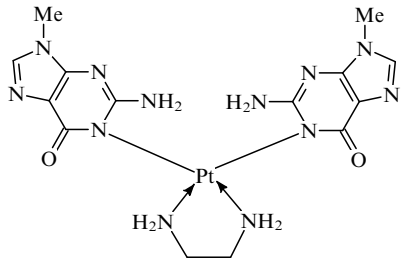
189

Apart from complex **188**, the formation of the dimeric ruthenium complex **190** involving the N(3) and N(9) atoms has been postulated[401] for adenine **188** (R = H) on the basis of ^{1}H NMR data. According to X-ray diffraction data, the bridging type of binding of this ligand with deprotonation of the NH group of the imidazole ring and the formation of a tetranuclear η^6-benzeneruthenium(II) cluster is also possible.[402]



190

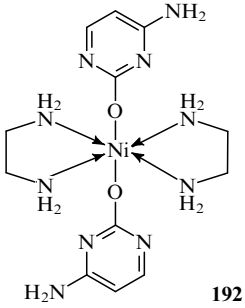
L = EDTA anion.



191

Coordination of type **189** is mainly characteristic of guanine.[35, 38, 381, 399] At the same time, complexes in which guanine is coordinated *via* the N(1) atoms and also *via* the N(1) and N(7) atoms are known.[403] Thus the complex of 9-methylguanine with ethylenediamineplatinum(II) has the structure **191**.[403]

We may note[404] the very unexpected O-coordination of cytosine in complex **192**. In this case, the ligand is coordinated in the enolic tautomeric form.

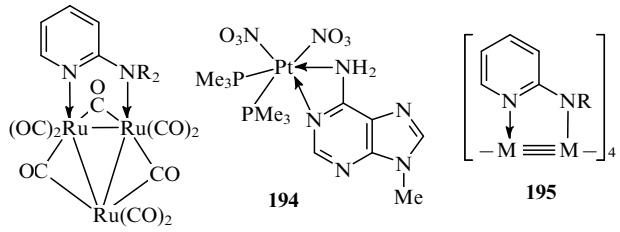


192

In the series of complexes of aminoazoles and aminoazines, there is virtually no direct evidence for the formation of structures **181** and **183** with a coordinated NH_2 group, although in individual instances such types of coordination have not been ruled out from consideration.[35, 353]

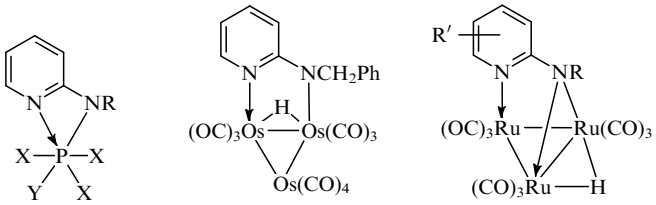
Numerous studies have been devoted to heterocyclic aminocomplexes in which the ligand is bound *via* two donor centres: nitrogen atoms of the pyridine type and an unaltered or deprotonated amino-group. The interest in this type of complex arose a fairly long time ago,[35, 405] mainly in connection with the formation in the latter of multiple metal – metal bonds,[405, 406] but the greatest number of complexes with this type of coordinate bonds have been obtained recently.[35, 406 – 418]

η^2,μ-Coordination with the simultaneous binding of an endocyclic nitrogen atom and the nitrogen atom of an amino-group occurs in the following complexes: for example, in the ruthenium cluster **193**,[35] in the trinuclear complex adduct $\{[Ru(III)Ru(III)Ru(II)OAc_6L_3]L'_3\}$, where L = 2-aminopiperazine and L′ = EDTA,[416] in the platinum(II) nitrate complex of 9-methyladenine and trimethylphosphine **194**,[418, 419] and in the silver complex $[Ag_3(Py-NH_2)_4(NO_3)_4]$.[419]



193 **194** **195**

The structure of metal clusters of type **195** with a deprotonated amino-group has been discussed in a number of publications.[35, 405, 406] Both mononuclear[35, 414, 418] and polynuclear[35, 407, 415] complexes have been noted among complexes with a deprotonated NHR group. In particular, complexes of 2-methylamino- and 2-(2′-pyridyl)aminopyridines **196** with pentavalent phosphorus halides and CF_3-substituted derivatives may be assigned to the former.[414]



196 **197** **198**

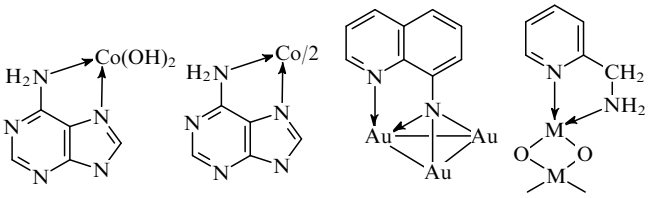
R = Me, 2-Py; X = F, Cl; Y = F, Cl, CF_3.

R = H, Me, Ph; R′ = H, Me.

Cluster structures of the type considered, for example **197**, have been discussed in a review.[35] The nitrogen atom of the NR fragment may participate in the simultaneous bonding to two metal atoms, forming trinuclear clusters which are very common among aminopyridine complexes of ruthenium (complexes **198**).[408 – 413]

Instances of substitution of a hydrogen atom of the NH_2 group by a metal atom are also known in the series of other aminoheterocycles, for example in cytosine[35] and in 9-aminoacridine.[420]

In conclusion, we may note that the involvement of both nucleophilic N centres in coordination is characteristic of aminoheterocycles where the disposition of the pyridine and amine nitrogen atoms promotes the formation of chelate structures. Such a structure was first proposed for cobalt complexes of adenine **199** and **200**.[35]



199 **200** **201** **202** (M = Cu, Rh)

The formation of structures with a N,N′-five-membered metallocycle was later demonstrated in relation to trinuclear and tetranuclear gold(I) clusters with 8-aminoquinoline **201**[421] and polymeric copper and rhodium acetate clusters **202**.[422]

A wide variety of structures is characteristic of complexes obtained from type **177** and **178** ligand systems containing O, S, and Se donor centres in the exocyclic substituent. Metallocyclic (chelate) structures of types **203** and **204** (E = O, S, Se) are most common among them.[423 – 425]

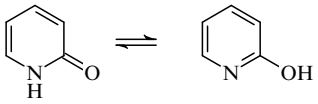


203 **204**

A = NR′, O, S, Se; R = H, Alk, Ar.

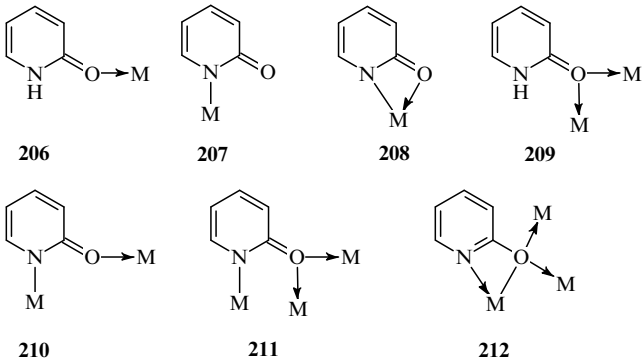
A = CH, N; R = H, Alk, Ar, benzo, Hal, NO_2, *etc.*

The coordination chemistry of oxygen-containing ligands, represented mainly by the pyridinone **205** complexes, has been examined in another review[425] and will not be discussed in detail here.



205a **205b**

Rawson and Winpenny[425] examined the mononuclear (**206 – 208**), dinuclear (**209** and **210**), and trinuclear (**211** and **212**) binding of metals by the ligand **205**, taking into account tautomerism of the type **205a** ⇄ **205b**.

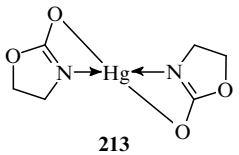


206 **207** **208** **209**

210 **211** **212**

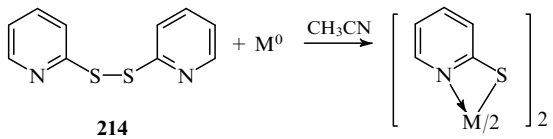
They paid particular attention[425] to the bridging function performed by the ligands **205** in complexes with multiple metal – metal bonds.

It is noteworthy that chelate structures of type **208** are fairly common among complexes **203** and **204** with an endocyclic oxygen substituent (E = O). A metallocyclic structure **213** of this type occurs, for example, in the mercury complex of 1,3-oxazolidin-2-one.[426]



213

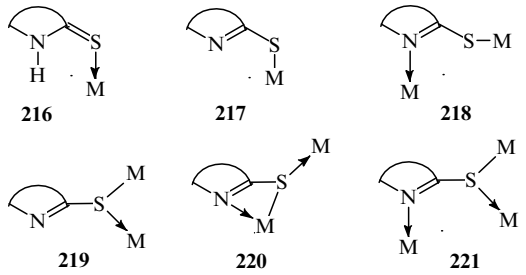
Chelate structures of types **203** (E = S)[423,424–430] and **204**[423–425,431–441] are quite widely represented among complexes of 2-mercapto-derivatives. These compounds are obtained preferentially in the interaction of type **177** and **178** ligands with metal salts[423–425,427–430] and also from disulfides (for example, compound **214**) and zerovalent metals under the conditions of electrosynthesis.[432–437,440]



214 **215**

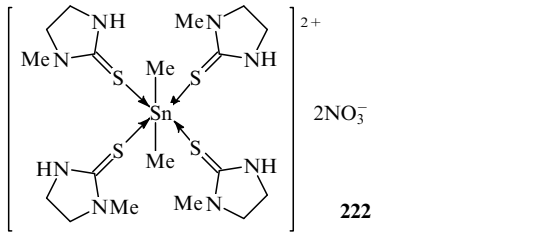
Apart from complexes **215**, adducts of the type $ML_2 \cdot nL'$ are formed in the presence of various N-bases (L′), where LH = mercaptoazoles or mercaptoazines and L′ = Py, Bipy, *o*-Phen and other N-donors.[299,431,432,437,438] It has been shown recently[441] that a transformation of the type **214**→**215** can be achieved not only under the conditions of electrosynthesis but also in chemical syntheses carried out for zerovalent lanthanides (samarium and yttrium) in tetrahydrofuran (THF) in the presence of hexamethylphosphoramide.

The presence of N- and E-donor centres in the ligands considered and also prototropic tautomerism lead to the occurrence of various structures of the complexes of mercaptoazoles and mercaptoazines, which can be represented by the following types:

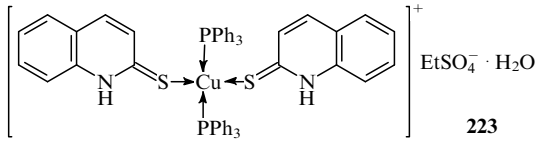


216 **217** **218** **219** **220** **221**

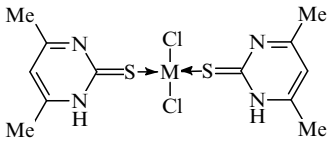
Compounds **216**, which behave as monodentate thione ligands (LH), are represented by a fairly large series of complexes having the composition $(LH)_mMA_n$ (see the relevant review[423] and the subsequent publications, for example, Refs 442–444). Complexes obtained from 1-methyl-2(3*H*)-imidazolinethione **222**,[442] quinoline-2-thione **223**,[443] and 4,6-dimethylpyrimidine-2-thione **224**[444] have been characterised structurally among them.



222

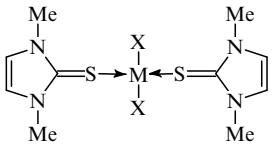


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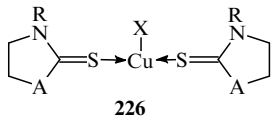


224 (M = Zn, Cd)

Naturally the =S→M coordination is observed in metal complexes with fixed thione forms of the ligand — in the complexes of 1,3-dimethyl-2(3*H*)-imidazolinethione **225**,[445] *N*-alkylimidazolidine-2-thione **226** (A = NR′),[446] and thiazolidine-2-thione **226** (A = S).[446]



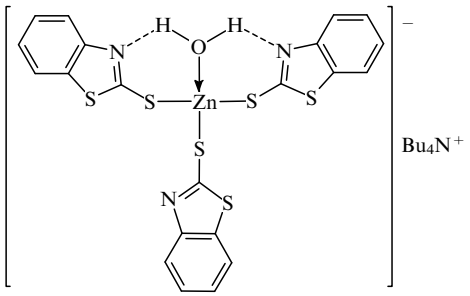
225 (M = Cd, Pb)



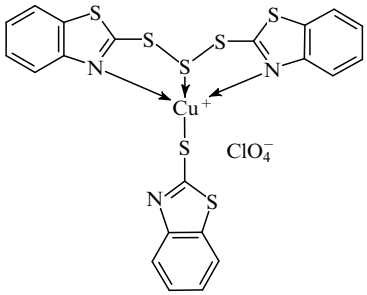
226

R = Alk; A = NR′ (R′ = Me, Et, Pr^n), S; X = Cl, Br, I.

The number of structurally characterised complexes of type **217** with the thiol form of the ligand, which is of interest because chelate structures are not formed with its participation, is significantly smaller. Such monodentate S-coordination has been observed in the anion of the complex $\{[Bu_4N]^+[ZnL_3]^- \cdot H_2O\}$ **227**[423] and in the cationic complex of an unusual trisulfide derivative of benzothiazole **228**.

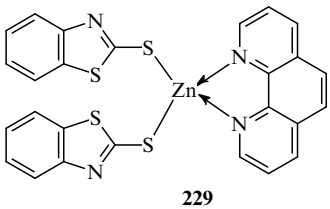


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228

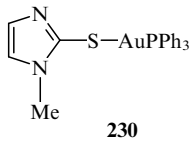
X-Ray diffraction data have shown[440] that such mononuclear binding of the ligand is characteristic also of the adduct of the zinc salt of 2-mercapto-benzothiazole with *o*-phenanthroline (compound **229**).



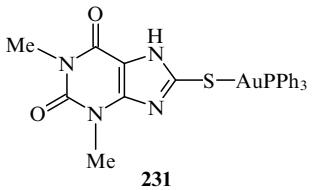
229

In connection with the η^1(S)-monodentate coordination of 2-mercaptoazoles being discussed, we may note that the same type of binding of the metal is observed in complexes of triphenylphos-

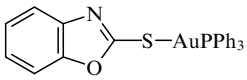
phinegold with 2-mercapto-1-methylimidazole **230**,[447] 8-mercaptotheophylline **231**,[448] 2-mercaptobenzoxazole **232**,[449] and purine-6-thiol **233**.[450]



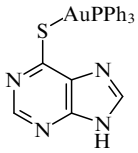
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231

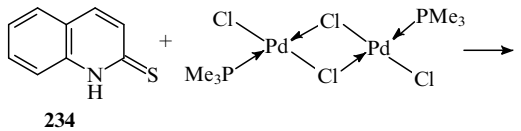


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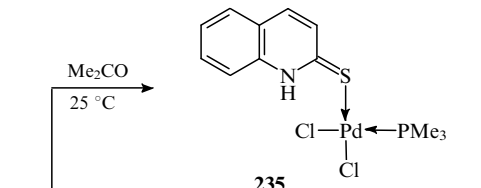


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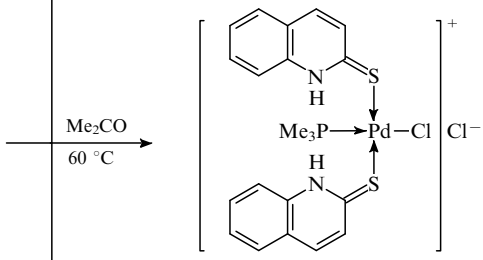
Structures **218** with bridging N,S-coordination are quite common for the dinuclear complexes of the heterocycles considered.[423, 451–454] Studies [451, 454] in which the detailed influence of the complex formation reaction conditions on the type of complexes formed was detected are of special interest. In particular, a scheme has been published [451] showing that molecular mono-S-coordinated adducts **235** and **236** with the thione tautomeric form of the ligand and the dinuclear complex **237** in which the thiol and bridging binding of the ligand system occur simultaneously may be obtained for the same ligands, for example compound **234**, depending on the nature of the solvent, temperature, and the pH of the medium.



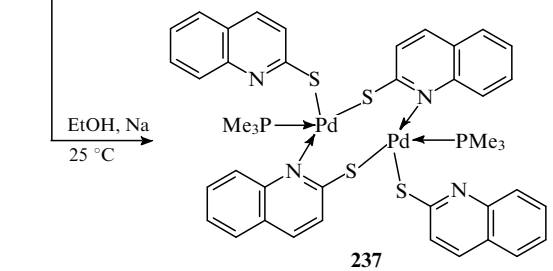
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235

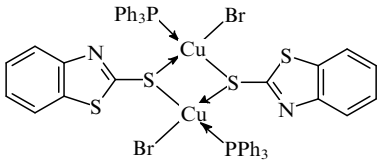


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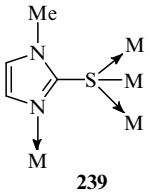
237

Coordination of type **219** has been observed in a series of complexes,[423, 455, 456] for example in the recently described dimeric copper complex of benzothiazole **238**.[456]



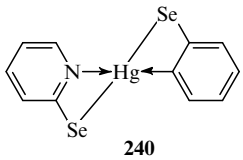
238

In this connection, we may point out that, in the dodecanuclear cluster $[Cu^{I}_{10}Cu^{II}_{2}(C_4H_5N_2S)_{12}(MeCM)_4]$, where $C_4H_5N_2S$ = 2-mercapto-1-methylimidazole, the thiol sulfur can participate simultaneously in coordination with three copper atoms.[457] The coordination of type **239**, not considered previously, in which the above imidazole derivative behaves as a tetradentate bridging ligand, occurs in this instance.

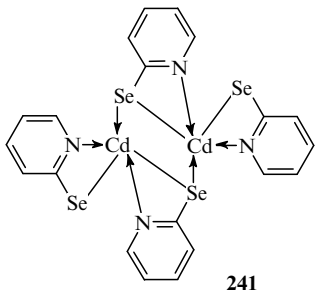


239

The same type of bonding has been established [458] for the clusters $Ru_9H_3(Py)(CO)_{21}$. The complexes of the selenium-containing analogues **203** and **204** (E = Se) are represented by single investigations. For example, it has been demonstrated by X-ray diffraction [459] that the mercury complex of pyridine-2-selenol has the structure **240**, whereas the chelate and bridging configurations occur simultaneously in the cadmium dimer **241** obtained from the same ligand.

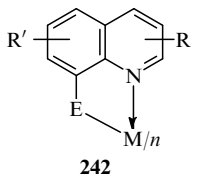


240



241

When the disposition of the donor centres is favourable for the formation of the metallocycle, the hydroxy-, mercapto-, and hydroseleno-derivatives form chelate structures like the amino-substituted nitrogen heterocycles examined above. They are represented particularly widely among complexes of 8-hydroxy- and 8-mercapto-quinolines **242** (E = O [424, 460, 461] and E = S [424, 462–467]). Thus the chelate complexes **242** (E = O; R = H, Alk; n = 3) of trivalent indium, gallium, thallium, cobalt, antimony,[460] osmium, ruthenium, and rhodium [461] have been synthesised from 8-hydroxy-quinoline and its substituted derivatives (LH) and characterised structurally. The complexes have an octahedral structure and contain the C_2H_5OH (In, Ga, Co), H_2O (Te), and $CHCl_3$ (Os, Ru, Rh) molecules as additional ligands. The antimony complex does not contain other molecules and has the composition SbL_3.



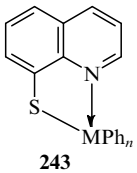
242

E = O, S.

Data on the structures of nickel, cobalt, copper, zinc, and cadmium bishydroxyquinolinates (type **242**, n = 2) are presented in a review [424]. The structures of nickel,[462] indium,[463] palladium,[465] rhodium,[464, 466] and iridium [467] 8-mercaptoquinolinates

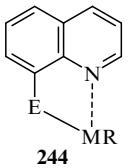
were described subsequently. We may note the synthesis and the rigorous demonstration of the structures of two heterovalent complexes between vanadyl and 8-mercaptoquinoline (LH):[468] in one of them, having the composition $(VL_3)^-(PPh_4)^+$, the vanadium entering into the composition of the anion has a oxidation state of two, whilst in the other, neutral complex having the composition VL_3, the oxidation state of vanadium is three. The above oxidation states of vanadium have been confirmed by magnetochemical measurements: the experimental magnetic moment is 3.73 B.M. for the first of the above complexes and 2.78 B.M. for the second.

Organometallic derivatives of 8-hydroxyquinoline [469–473] and 8-mercaptoquinoline [470, 474–477] are of special interest. Judging from the literature data,[424, 470–477] the question of the denticity and the modes of coordination of 8-mercaptoquinoline in mercury,[469, 471, 473] gold,[472, 474–476] tin,[470] lead,[470] and antimony [477] complexes is controversial. It has been suggested [470, 477] that the chelate structure **243**, which is standard for 8-mercaptoquinoline, occurs in these complexes.



243

M = Sn, Pb, Sb; n = 2, 3.

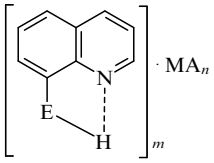


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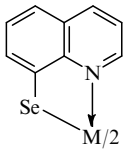
M = Hg, Au; R = Ph, PPh_3; E = O, S.

At the same time, a non-standard coordination interaction has been proposed for complexes of 8-hydroxy- and 8-mercaptoquinolines with phenylmercury and triphenylphosphinegold fragments (complex **244**): the presence of only one covalent E–M bond and the formation of a secondary N···M bond.[471–473, 474–476]

Apparently the coordination in the molecules of the adducts of 8-hydroxy- and 8-mercapto-quinolines with Lewis acids (complex **245**) should also be non-standard. However, although their synthesis has in fact been achieved,[22] we are not aware of data on the structures of these complexes.



245



246

By analogy with molecular complexes of *o*-hydroxyazomethines,[22, 23] the remaining option is to assume that the coordinate bond in the adducts **245** can be located on the donor atom E. The structures of complexes of 8-hydroselenoquinoline are not clear either, although the chelates **246** themselves have been known for a fairly long time.[182]

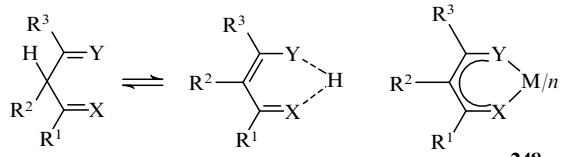
So far as we are aware,[76, 193, 195, 368] the complexes of telluroderivatives of types **203** and **204** (E = Te) have not been described.

5. Competitive coordination of chelating ligands

Competitive coordination in the series of chelating ligands leads to the formation of structures of several types and to intrachelate isomerism involving the closure of metallocycles with different numbers of 'members'. This aspect of competitive coordination has been most clearly investigated in relation to complexes of β-diketones, *o*-hydroxyazomethines, and their structural analogues.

a. Complexes of chelating ligands

It is well known that β-diketones and their thio- and selenoanalogues **247** give rise to metal chelates of type **248** on interaction with metal salts[4, 103, 478, 482] and under the conditions of gas-phase synthesis or electrosynthesis.[299, 483]

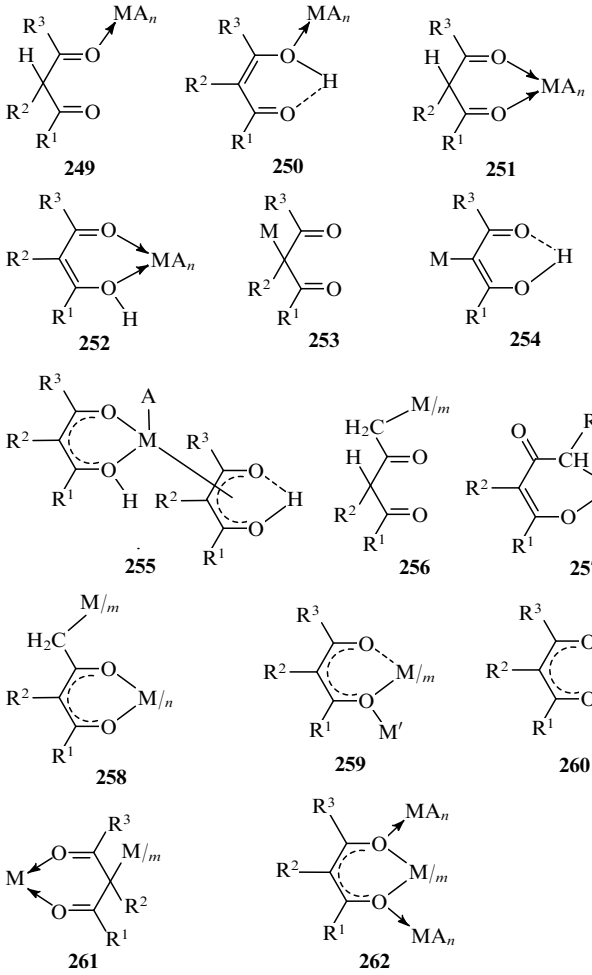


247 (X, Y = O, S, Se)

248

The structure of type **248** β-diketonates (X = Y = O) has been demonstrated by X-ray diffraction.[478, 481, 484–501] The structures of copper,[485–487, 499–501] tungsten,[493, 494] yttrium,[489, 496] and lanthanides [490, 491, 496–498] β-diketonates have been investigated. Type **248** (X = O, Y = S) metal chelates are formed [103] also in the case of monothio-β-diketones. It has been suggested that chelate complexes of dithio-β-diketones **248** (X = Y = S) have a structure similar to that of the β-diketonates.[103]

Together with the above mode of coordination, other (chelate and nonchelate) types of binding of the ligands have been observed for complexes of β-diketones. Coordination can be achieved with participation of the oxygen atom as well as the carbon atom or with participation of both donor centres. Similar types of coordination (**249**–**262**) have been frequently discussed in a number of publications.[4, 24, 31, 481, 484, 502, 503]



249 **250** **251**

252 **253** **254**

255 **256** **257**

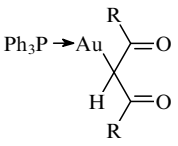
258 **259** **260**

261 **262**

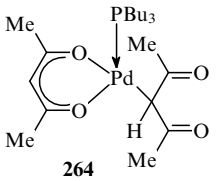
It follows from the data presented in a review [484] that an unusual monodentate type **250** O-coordination occurs in the complexes $Mn(HAA)Br_2$ and $Re(HBA)Cl(CO)_3$, where HAA = acetylacetone and HBA = benzoylacetone, while the diketone form of acetylacetone **251**, coordinated as a bidentate species, is encountered in the chelates $\{[(Ni(HAA)_2]Br_2\}$ and $\{[Ni(HAA)_2(H_2O)_2](ClO_4)_2\}$.[484]

Among the mononuclear β-diketone C-coordinated complexes, we shall differentiate univalent gold compounds **263**,

having a structure of type **253**, which have been recently obtained and characterised structurally.[504–507]



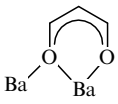
263



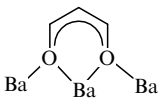
264

It has been suggested[508] that a structure with acetylacetone fragments of type **255** coordinated in different ways is characteristic of complex **264**, but rigorous evidence for its occurrence is lacking.

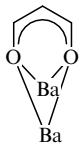
The complexes of β-diketones with additional O-coordinations have been discussed in relation to dinuclear and trinuclear barium complexes.[509, 510] Their coordination units can be represented by formulae **265**–**268**.



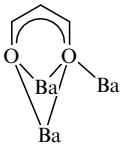
265



266



267

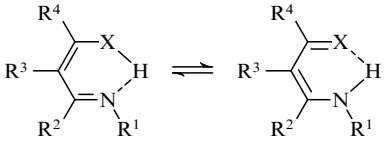


268

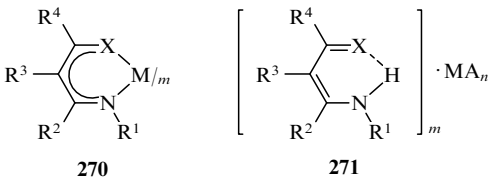
We emphasise that the β-diketone fragment behaves as a tridentate ligand in complex **265** and as a tetradentate ligand in complexes **266** and **267**. However, in contrast to complex **266**, a bischelate structure occurs in complex **267**.[511–514] Structure **267** has been detected by X-ray diffraction in the barium complexes of the dipivaloylmethane anion (DPM): $Ba_2(DPM)_4(NH_3)_4$,[511] $Ba(DPM)Et_2O$,[512] $Ba_4(DPM)_8$,[509, 513] and $Ba_2(DPM)_4(Bipy)_2$.[514] The structure with the fragment **268** has been noted in the complex $Ba_5(DPM)_9H$ — DPM. According to Drozdov and Trojanov[513], it contains a pentadentate dipivaloylmethane anion.

According to the information available to us, structures similar to **249**–**268** are unknown in the series of chalcogen-containing analogues of β-diketones. Such complexes have apparently not been obtained.

A situation similar to that described above for the β-diketone complexes observed also for *o*-hydroxyazomethines and their structural analogue **269** (see the relevant reviews[22, 23, 33, 34, 503] and the literature quoted therein).



269a **269b**

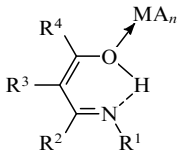


270 **271**

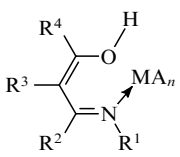
X = NR^5 (R^5 = H, Alk, Ar, Het, Ts), O, S, Se.

The accumulated literature data show that type **269a**,**b** ligands form mainly type **270** chelate compounds ML_m (m = 1–4). The chelates obtained from ligands **269a**,**b** (X = O) and 3*d* metals — cobalt,[23, 515] nickel,[23, 516–519] copper,[23, 520, 521] and zinc[23, 522] — are the most common.

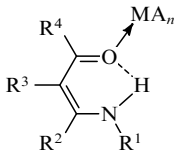
The complexes in which the ligands **269** are involved in type **271** bonding are less well known. In this case, neutral azomethine molecules function as the ligands.[22, 23, 34] Taking into account the tautomerism of ligands **269a**,**b** (X = O)[23, 33] and intramolecular hydrogen bonding,[23] structures with non-standard formation of a coordinate bond were attributed to these complexes.



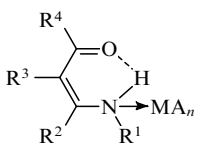
272



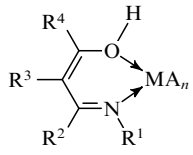
273



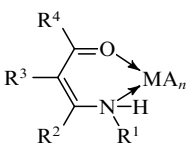
274



275



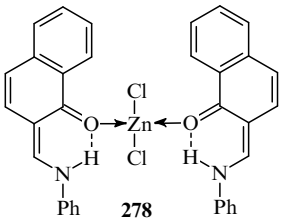
276



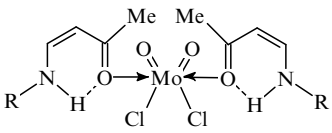
277

In complexes **272**–**275**, *o*-hydroxyazomethines **269** (X = O) and their structural analogues (X = NR^4, S) behave as monodentate ligands, whereas they are involved in bidentate coordination in complexes **276** and **277**.

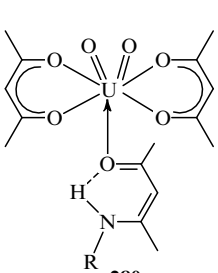
Conclusions concerning the modes of coordination of the ligands in type **271** adducts indicated above have been reached mainly on the basis of data obtained in comparative studies of the IR spectra of these complexes and the corresponding ligands **269**, which is not sufficiently rigorous.[22] X-Ray diffraction studies have demonstrated unambiguously that, out of the six structures **272**–**277**, only one (**274**), containing the monodentate azomethine ligand in the ketoamine tautomeric form and having an intramolecular hydrogen bond, is actually formed. This situation has been established, for example, for the zinc chloride complex of 2-oxo-1-naphthylideneaniline (complex **278**)[523] and the molybdenum dioxide chloride complexes of β-aminovinyl ketones (complexes **279**)[524, 525] and also in the case of adducts of uranyl acetylacetonates with acetylacetone imine **280**[484] and the type **281** manganese complexes of salicylaldimines.[526]



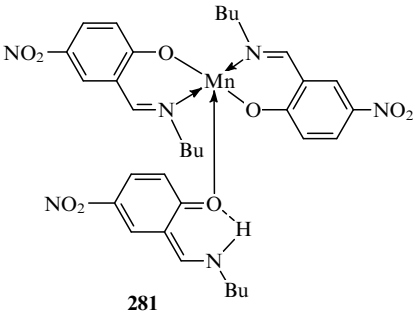
278



279 (R = C_7H_{13}, Ph)



280

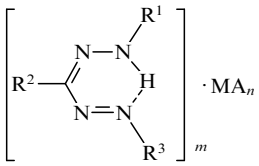


281

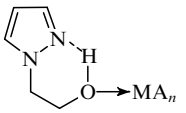
The coordination of salicylaldimines *via* the oxygen atom in type **281** complexes has been confirmed by the O-binding of these ligands to various metal salts.[527]

The molecular complexes **271** of structural analogues of β-aminovinyl ketones — β-aminovinylimines **269** (X = NR^4) and β-aminovinyl thiones **269** (X = S) — have been described.[22, 23] However, the structures of these molecular complexes have not been investigated by X-ray diffraction, so that the location of the coordinate bond in them remains obscure.

Molecular complexes are also formed by other chelating ligands, for example by formazans **282** and *S*-hydroxy- and *S*-mercapto-quinolines **245** (X = Y = S).[22]



282 (R^1, R^2, R^3 = H, Alk, Ar, Het)

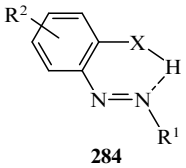


283

Interesting results have been obtained in a study [528] in which a molecular complex of 1-ethylenehydroxypyrazole **283** was described and characterised structurally.

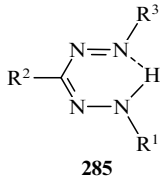
b. Intrachelate isomerism

In the presence of several donor atoms in the chelating unit of the ligand, the possibility of their competitive reaction and of the closure of metallocycles with different numbers of members arises. This type of competitive coordination is particularly characteristic of the azo-compounds **284** and the formazans **285**.



284

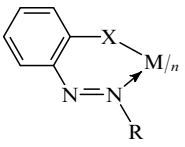
X = NR^3 (R^3 = H, Alk, Ar, Ts), O, S;
R^1 = Ar, Het;
R^2 = H, Alk, Ar, benzo, Hal, NMe_2, *etc.*



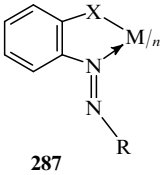
285

R^1, R^2, R^3 = H, Alk, Ar, Het.

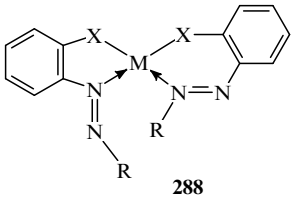
It is well known that six-membered metallocycles **286** (X = O) are produced in chelate complexes of *o*-hydroxyazobenzenes.[34, 529]



286 (X = O)



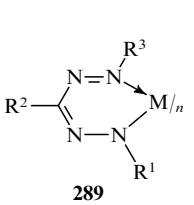
287



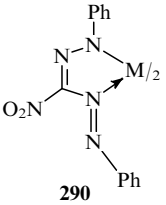
288

At the same time, when X = NR or S, five-membered chelates are formed together with six-membered ones.[23, 34, 530, 531] The number of members in type **287** chelate compounds is determined by the nature of not only the donor atom X but also of the metal. Thus, according to X-ray diffraction data, when X = S five-membered metallocycles are formed in the nickel and zinc complexes, whereas five- and six-membered chelate units are produced in the palladium complexes **288** (see the relevant review [34] and the literature therein).

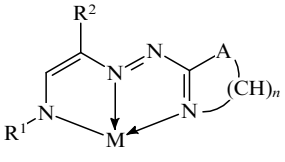
A similar situation is characteristic of complexes formed by type **285** formazan ligands, which afford chelate complexes of type **289**–**291** depending on the nature of the substituents R and the metal (see the relevant reviews,[37, 532] a communication,[531] and the literature therein).



289



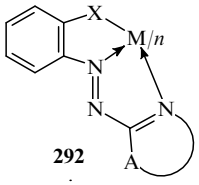
290



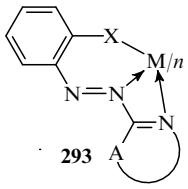
291

A = NR^3, O, S; *n* = 3, 4.

Another type of intrachelate isomerism is associated with the formation of metallocycles, differing in the number of members in complexes of heteroarylamino(hydroxy)azo-compounds.[531] In the case of ligands of this type, one has to expect, apart from type **286**–**288** coordination (R = Het), the involvement of the N atoms of the hetero-fragments in additional bonding to the metal with formation of complexes **292** or **293** (see Garnovskii *et al.* [531] and the literature quoted therein).



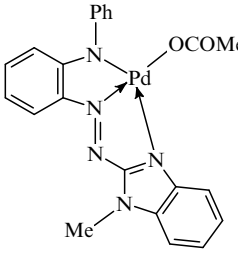
292



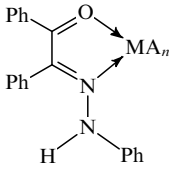
293

X = NR, O; A = CH, N.

The controversy, extending over a period of many years, concerning the formation of five-membered (complexes **292**) or six-membered and four-membered (complexes **293**) metallocycles has been recently resolved in favour of the first combination by solving the structure of the palladium complex **294**.[531]

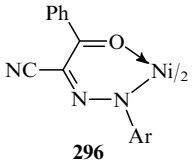


294



295

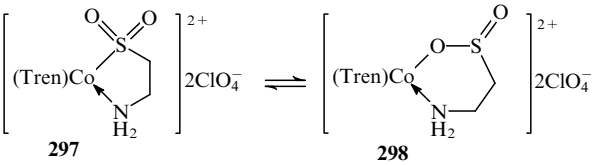
M = Mn, Cu;
A = Cl, NCS



296

Bond isomerism involving different ring sizes has been observed also in the case of the monohydrazones of β-dicarbonyl compounds. Thus complex **295**, with a five-membered metallocycle, has been described in a monograph,[533] while the structure of the six-membered hydrazone metal chelate **296** was established in another study.[534]

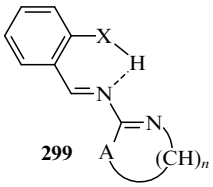
An interesting instance of chelate isomerism **297**→**298** has been observed in cobalt complexes of aminoethanesulfinates.[535] Not only the ring size in the coordination unit but also the ligand environment changes in these complexes.



297 **298**

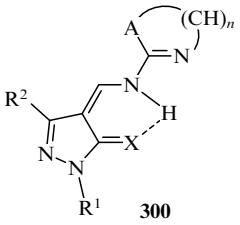
Tren = tri(2-aminoethyl)amine.

The competitive coordination of bidentate and polydentate chelating ligands occupies an important place in modern coordination chemistry.[536] With the aid of these ligands, it is possible to vary the number and nature of the donor centres involved in bonding with the metal. The potentially tridentate ligands of type **299**–**301** are convenient models for the study of competitive coordination of this type.



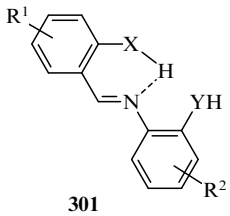
299

X = NTs, O;
A = N, O, S, *n* = 3, 4.



300

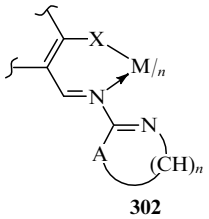
X = NTs, O, S, Se;
R^1, R^2 = H, Alk, Ar, Het;
A = N, O, S; n = 3, 4.



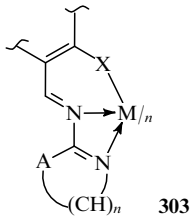
301

X, Y = NTs, O, S;
R^1, R^2 = H, Alk, Ar.

Analysis of published data (see the relevant reviews [23, 34]) shows that the denticity of type **299** and **300** ligands depends on the structure of the chelates which they form: bidentate coordination without the involvement of the nitrogen atom of the heterocycle in the binding of the metal is characteristic of planar complexes (complex **302**), whereas additional coordination to the nitrogen atom of the heterocycle is observed in tetrahedral structures (complex **303**).



302

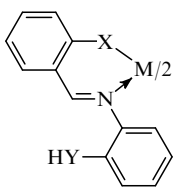


303

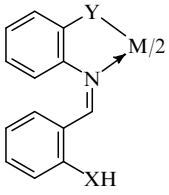


= Ar, Het, n = 3, 4.

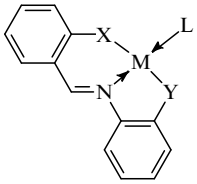
Structures **304**–**308** may be attributed to the complexes of ligands **301** on the basis of the structure of the latter (X = Y = O) [537] and data [23, 34] indicating the formation of six-membered and five-membered metallocycles by azomethine ligands.



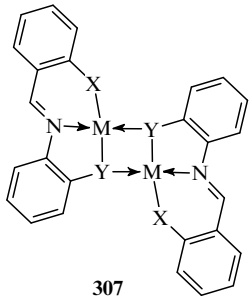
304



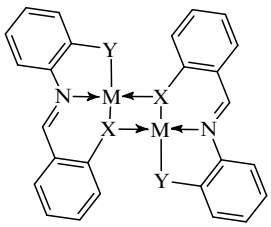
305



306



307



308

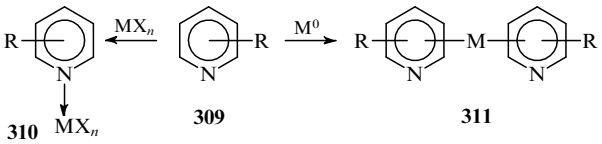
So far as we are aware, the mononuclear complexes **304** and **305** have not so far been described. The formation of structures **306** [538–544] **307**,[545, 546] and **308** [547] has been unambiguously demonstrated by X-ray diffraction. Comparison of structures **307** and **308** revealed an intrachelate bond isomerism due to the ability of type **301** ligands to form metal-bridge fragments involving various donor atoms (X in compounds **308** or Y in compounds **307**).[546, 548]

The dimeric complexes **307** possess antiferromagnetic properties (see, for example, Refs 541, 542, and 549). The magnetic behaviour of the dimeric compounds **308** should evidently be similar. However, structures similar to that of compounds **308** have not been described for paramagnetic metals.

III. Regioselective synthesis. C-Metal-coordinated ligand systems

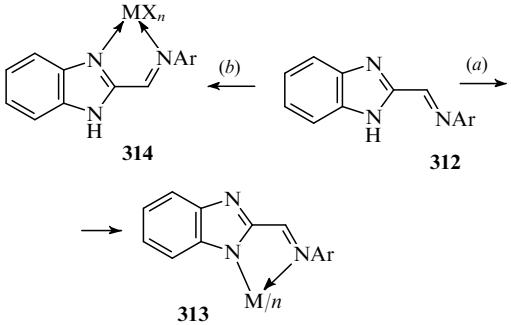
We consider regioselective synthesis from the standpoint of competitive coordination as a method for the preparation of complexes with a specified site (region) where the metal is bound to the ligand. Such synthesis may be based on allowance for the specificity of the soft–hard interactions.[1–3, 18] Thus hard and intermediate Pearson acids are used for the synthesis of complexes of the N-coordinated NCX group (X = S, Se),[2, 18] whereas complexes with the M–XCN fragment may be obtained mainly with participation of soft Pearson acids.[2, 18] A similar situation is observed also in the case of regioselective syntheses with participation of other ligands containing donor centres differing in hardness and softness: N, P; N, As; N, S; N, Se; N, Te; O, S; O, Se; O, Te.[2, 18]

Specific regioselective complex formation is in many respects determined by the methods of synthesis of the coordination compounds. Thus, under the conditions of chemical synthesis from substituted pyridine derivatives **309**, the molecular adducts **310** are produced, whereas gas-phase synthesis [299, 300, 550] opens a path to the π-complexes **311** of these ligands, which are difficult to obtain.



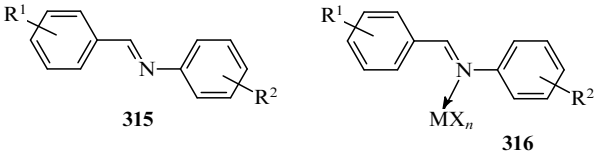
310 **309** **311**

The use of electrosynthesis (path *a*) [299, 551] makes it possible to obtain the chelate complexes **313** from chelating ligands with weakly acid NH groups (for example, the azomethines **312**), whereas complexes **314** are formed [1] in the usual chemical syntheses (path *b*) (*cf.* Teom *et al.*[552]).

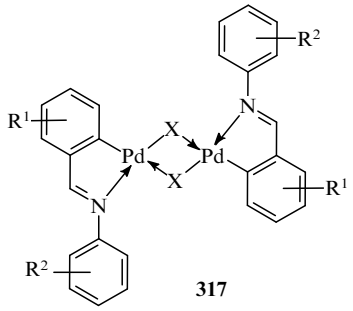


314 **312** **313**

The cyclometallation [553–558] and 1,3-dipolar cycloaddition [559, 560] reactions are used widely for the synthesis of metal complexes of azomethines, azo-compounds, and nitrogen-containing heterocycles with non-standard C-bonding of the ligands. Thus type **315** monodentate azomethines, which usually form η^1(N)-molecular adducts **316** with Lewis acids (MX_n), exhibit the properties of bidentate η^2(C,N)-chelating ligands under the conditions of the cyclopalladation reaction and lead to chelate compounds,[558, 561] for example to compounds **317**.



315 **316**

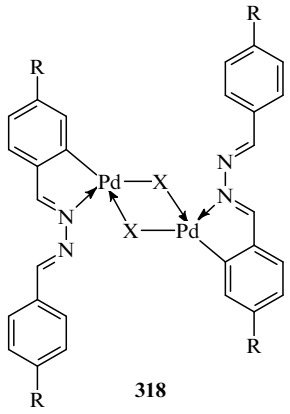


317

X = Cl, Br, SCN;
R^1, R^2 = H, Alk, OAlk, OCOAlk, Hal, CN, NO_2.

The formation of complex **317** (R^1 = 4-OMe, R^2 = 4-OBu) has been demonstrated by X-ray diffraction.[561]

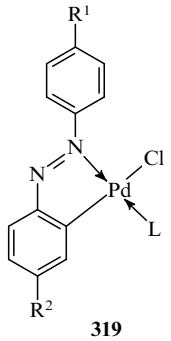
Cyclometallation, leading to a new Pd_4 cluster, is observed also in the acetolysis of bis(salicylaldiminato)palladium.[562] When the cyclometallation reaction is carried out with a series of aldazines,[553, 555, 558, 563] chelates with C,N-coordinated ligands, for example complex **318**, are formed, as in the case of the azomethines considered above.



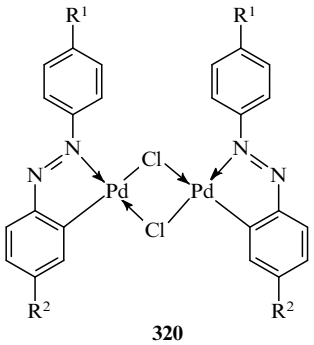
318

X = Cl, Br, NCS.

The same non-standard type of C,N-chelation occurs in cyclometallation reactions involving azo-compounds,[358, 555, 556, 564] whereupon complexes **319** and **320** are formed.



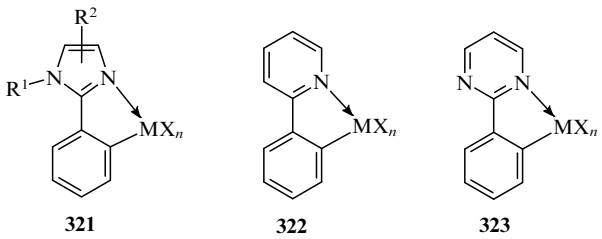
319



320

R^1, R^2 = Alk, OCOAlk; L = Py, quinoline.

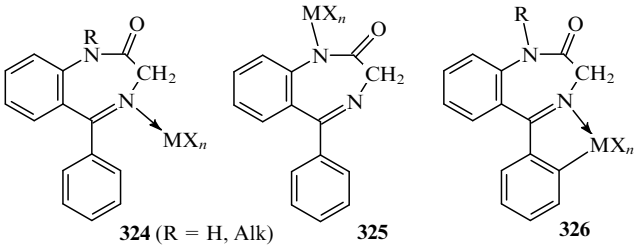
We may also note the increase in denticity in the cyclometallation reactions of nitrogen-containing heterocycles: azoles, benzazoles (for example, compounds **321**),[565, 566] and azines (for example, compounds **322** and **323**).[553–558, 567–569]



321 **322** **323**

R^1 = H, Alk, Ar; R^2 = H, Alk, Ar, benzo.

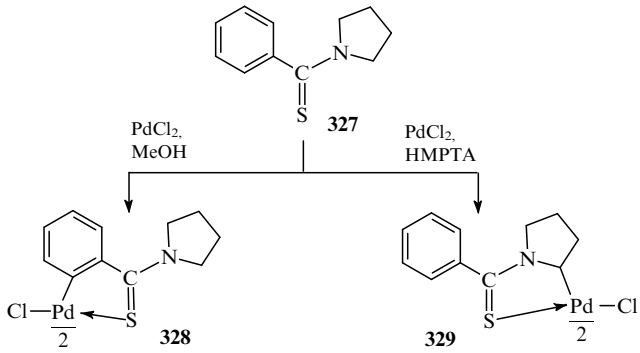
Cyclometallation alters the location of the coordinate bond also in the series of complexes of more involved nitrogen-containing heterocycles, for example dibenzodiazepine derivatives (see Stoccoro *et al.*[570] and the literature quoted therein). Thus 1,4-benzodiazepin-2-one usually affords adducts of types **324** and **325** on interaction with metal salts and organometallic compounds, whereas cyclometallation leads to the C,N-metal chelates **326**.[570]



324 (R = H, Alk) **325** **326**

In a number of instances, the direction of coordination attack in regioselective synthesis is determined by the type of solvent. When aprotic solvents are employed, molecular adducts with a fully preserved ligand system may be obtained from typical chelating ligands (complexes **249**–**252** and **274**).[22, 23, 503]

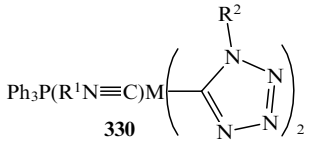
Other examples of the regulation of regioselective coordination by the type of solvent have been quoted in a review.[556] In this connection, we may note the reaction



327

This regioselective synthesis, occurring in methanol or hexamethylphosphoramide (HMPA) with participation of N-thiobenzoylpyrrolidine **327**, is accompanied by the formation of two complexes, **328** and **329**, in which different cyclic systems are coordinated to the palladium atom. It is interesting because it demonstrates the possibility of the involvement in coordination of the S-donor ligand centre and of the saturated (and not aromatic or heterocyclic) CH fragment. We emphasise that the cyclometallation reactions can involve not only the C–H but also the C–Hal bonds.

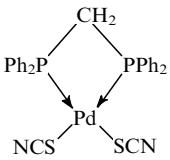
Dipolar 1,3-cycloaddition[16, 559] is interesting as regards the specific regioselective synthesis of a series of C-metal derivatives of nitrogen-containing heterocycles. The tetrazole derivatives **330** may be assigned to the latter.[559]



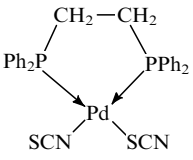
330

M = Hg, Pt, Pd.

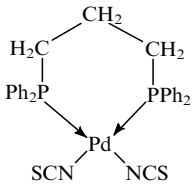
The mode of the reactions in the regioselective synthesis depends on the fine structure of the ligand system, which has been demonstrated in relation to different types of coordination of the NCX group in palladium complexes of diphosphines with different lengths of the alkyl chain (complexes **331** – **333**).[4, 31]



331



332



333

However, there are so far few examples of such regioselective reactions.

IV. Conclusion

The use of the concept of competitive coordination enabled us to survey extensive modern data concerning the regioselective binding of metals in complexes of bidentate and polydentate ligands. It is noteworthy that, in the majority of the publications which we have examined, only a particular mode of coordination was elucidated fairly reliably without analysis of the causes which would account for its regioselectivity. Nor is the situation saved by the application of the HSAB principle, since the latter can be used only for a limited range of ligands with soft and hard donor centres.

We believe that the main task in the development of the competitive coordination method is, firstly, the identification of the factors determining the centres at which the coordinate bond is located in complexes of bidentate and polydentate ligand systems. The solution of this problem will permit the specific regioselective synthesis of coordination compounds and will assist in studies devoted to the specific features of the binding of metals in biologically important systems.

The second task is the specific selection of ambident ligand systems with nitrogen – phosphorus and nitrogen – selenium (tellurium) donor centres and the synthesis from them of new metal complexes, the establishment of the structures of the latter, and the discovery of the causes of the regioselective coordination in these complexes. Despite the fact that continued interest has been shown in ligands of this type and the complexes obtained from them,[77, 571 – 575] they still remain the least investigated objects in coordination chemistry.

In conclusion, one would wish to note that members of the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, the 80th Anniversary of which occurs next year, have made a major contribution to the development of the problem of the binding of metals in complexes of ambident ligands.

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