Russian Chemical Reviews **64** (3) 201 – 221 (1995) ©1995 Russian Academy of Sciences and Turpion Ltd

UDC 541.64:678.044

Direct synthesis of coordination compounds from zerovalent metals and organic ligands

A D Garnovskii, B I Kharisov, G Gojon-Zorrilla, D A Garnovskii

Contents

I.	Introduction	201
II.	Gas – phase synthesis	201
III.	Liquid – phase synthesis	206
IV.	Electrosynthesis of coordination compounds	211
V.	Other methods for the direct synthesis of coordination compounds	216
VI.	Conclusion	217

Abstract. Data on the direct synthesis of coordination compounds from zerovalent metals and organic ligands are surveyed and described systematically. The preparation of metal complexes in the gas and liquid phases is considered. It is shown that the direct syntheses are single-stage processes and make it possible to obtain all types of coordination compounds — molecular and π-complexes, metal chelates, and dinuclear and polynuclear structures. Problems of competitive reactions in the course of the direct synthesis of complexes of ambident ligand systems are discussed. The bibliography includes 289 references.

I. Introduction

A wide variety of methods are used nowadays to synthesise coordination compounds.[1-5] Metal complexes are obtained mainly by the direct interaction of the components (the ligands and a source of the complex-forming metal),[1-7] as a result of ligand[6-8] and metal[6] exchange, and under the conditions of template synthesis,[7-10] which includes also the method of nascent reagents.† In the reactions listed above, the source of the metal is either its salts or carbonyls.‡ At the same time, it has long been known that coordination compounds may be obtained as a result of direct synthesis from zerovalent metals. The possibility of employing compact metals for the synthesis of coordination compounds was first demonstrated by Gerdes[11] and Chugaev,[12] who obtained metal complexes during electrolysis. Methods for the synthesis of complex compounds under the conditions of gas-phase reactions,[13-15] oxidative dissolution of zerovalent metals in nonaqueous media,[16,17] and in the solid phase[18,19] were developed subsequently. These methods became the basis of a new field in synthetic chemistry — the direct synthesis of coordination compounds and organometallic compounds from zerovalent metals. Particular aspects of this problem have been described in a series of reviews.[13-17,20-25] and monographs.[4,26-28] However, on the whole the direct synthesis of metal complexes has not been dealt with in the review and monograph publications on coordination chemistry.[2-5]

The aim of the authors of the present review was therefore to survey the current data on the direct synthesis of coordination compounds from zerovalent metals and organic ligands. Attention was concentrated on the types of ligand systems and the complexes formed during these reactions.

In describing the data, we adhered to the classification of coordination compounds put forward in a previous review.[29] According to this classification, metal complexes are divided into molecular complexes, chelate complexes, π-complexes and polynuclear structures. Such a classification does not conflict with the subdivision of the complexes employed in modern coordination chemistry (see, for example, Kostromina et al.[5]).

In describing the problems of the direct synthesis of coordination compounds from zerovalent metals and organic ligands, we decided to employ individual postulates and references from earlier reviews[13-15] and monographs.[26]

† The formation of ligands under the conditions of formation of a complex from the components on a metal matrix.

‡ The modification of the complexes is widely carried out in the template syntheses.[7-10]

A D Garnovskii, D A Garnovskii Department of Coordination Chemistry, Institute of Physical and Organic Chemistry, Rostov State University, prosp. Stachki 194/3, 344104, Rostov-on-Don, Russian Federation. Fax (7-863) 228 56 67
B I Kharisov Department of Radiochemistry, Faculty of Chemistry, Lomonosov Moscow State University, Leninskie gory, 119899 Moscow. Russian Federation. Fax (7-095) 932 88 46.
G Gojon-Zorrilla Universidad Autonoma de Neuvo Leon, Departamento de Quimica Organica, Apartado 1864, Monterrey, Neuvo Leone, 64 000 Mexico. Fax (52-83)72 3309 Tel. (52-83)76 5375

Received 13 October 1994
Uspekhi Khimii **64** (3) 215 – 236 (1995); translated by A K Grzybowski

II. Gas-phase synthesis

1. Methods, conditions, apparatus, and reagents

Coordination compounds are obtained in the gas phase in a vacuum apparatus via the direct interaction of the vapour-phase atomic metals and ligands.[14,15,20,21,26,30-36] However, these reactions are restricted by the stability of the complexes in a high-temperature medium: they are frequently accompanied by the decomposition of the coordination compounds and reactions of the ligand systems (see, for example, Domrachev and Zinov'ev's review[15]). For this reason, greatest effectiveness is attained in gas-phase synthesis when metal and ligand vapours are condensed at low temperatures (cryosynthesis).[13-15,25,26,30,31] The range of working temperatures is usually from 10 to 273 K although in isolated instances both high (295 – 325 K)[37-39] and low (~4 K)[40] temperatures have been used.

Cryosynthetic reactions have been considered in reviews[25,41] and in a monograph.[42] It has been emphasised[41] that cryosynthesis involving gaseous metals is an irreversible process, since extremely high supersaturations of the vapour phase with respect to the metal are employed in it. The metal vapour obtained at high temperatures (2000–2500 K) is transported in vacuo as a stream of atoms which react at low temperatures with the condensed ligand phase.

The mechanism of the co-condensation of atomic metals with ligand systems has been considered in relation to the direct synthesis and decomposition of dibenzenechromium.[15] It was shown that the reactions occurring with formation of dibenzenechromium from gaseous chromium and solid, liquid, or gaseous benzene at 77, 298, and 1000 K respectively are thermodynamically allowed. The elementary steps in the synthesis–decomposition reactions of diarene complexes have been considered in two publications.[43,44]

The apparatus for the direct synthesis of metal complexes in the gas phase is on the whole simple in design, since it comprises the usual high vaccum systems.[15,45,46] Different versions of the apparatus differ as regards different solutions of the problem of the evaporation of the metal and of the supply of the ligand to the reaction chamber.

The technology of the vaporisation of metals has been developed quite satisfactorily. This process is achieved mainly by four methods:[15] (1) from a resistively heated evaporator; (2) as a result of the induction heating of the container with the metal; (3) by electron bombardment; (4) by exposing the metal specimen to a laser beam. The advantages and disadvantages of each of the above methods of preparation of metal vapours and the procedures for the supply of ligands to the reaction chamber and for the isolation of the coordination compounds formed in the direct syntheses have been considered.[15] The vaporisation methods indicated make it possible to obtain virtually all the metals of the Periodic System,[13–15,26] including refractory metals (chromium, molybdenum, and tungsten),[14,15,30,31,34,47–50] in the vapour phase.

Organic systems, mainly unsaturated, aromatic, and heteroaromatic compounds and their derivatives, are used as the ligands in the gas-phase synthesis. Taking into account the maximum possible number of electrons which a ligand of the unsaturated hydrocarbon type can give up to the metal, it is useful to differentiate among such ligands monoalkenes,[14,15,26,37–40] dialkenes,[14,15,26,30,51–54] and cyclic dienes[13–15,26,51,55–57] and trienes.[57] Ethyne and its derivatives are also used as ligand systems.[14,15,20,26,37,53,54] Aromatic hydrocarbons, especially benzene and its derivatives,[14,15,47–49,58–62] as well as heteroaromatic ligand systems such as thiophene[26] and pyridine[15,17,26,30,63] are most widely used among the ligands for the gas-phase synthesis of coordination compounds.

Apart from the compounds listed above, oxygen-containing organic derivatives are used as ligands — ethers,[26] ketones (especially acetone),[53,64] β-diketones,[15,35,36] organic acids,[15] and their anhydrides[15] and chlorides.[14]

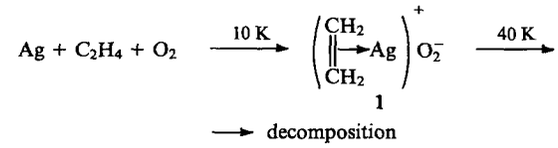
Two types of reactions occurring in the gas phase with formation of metal complexes have been differentiated[15] — reactions involving the addition of metal atoms and reactions involving the insertion of metal atoms in a C–X bond (X = H or a halogen).[15] The first embrace a wide range of the ligands listed above and comprise reactions leading mainly to the formation of π-complexes. Reactions of the second type are accompanied by the formation of organometallic compounds with metal–carbon σ-bonds.[15,25,26,31,32,65]

2. Coordination compounds

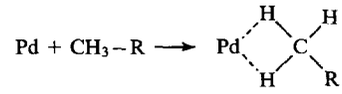
a. Gas-phase synthesis of π-complexes

The metal complex compounds obtained by gas-phase synthesis comprise mainly two types: π-complexes and metal chelates.

The simplest π-complexes have been synthesised by the reaction of metal vapours with alkenes (monoalkenes). The co-condensation of silver and ethene vapours in the presence of oxygen at 10 K leads to an unstable ethenesilver complex **1**, which decomposes on heating to 40 K.[26]

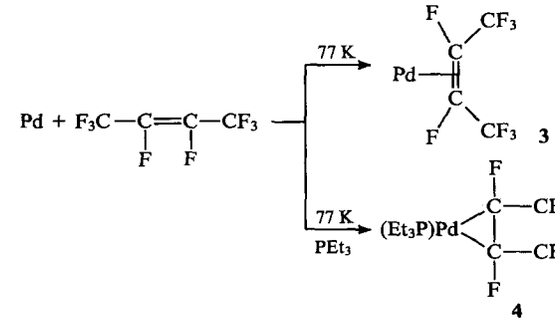


The ethene complexes of copper (argon, 295 and 325 K, pressure 50–600 Torr),[37] nickel (helium),[40] and palladium (helium, 300 ± 5 K, 0.5–0.8 Torr)[38] have been described. The kinetics of the gas-phase reactions of neutral transition metal atoms with alkenes have been investigated in relation to interactions of yttrium, molybdenum, zirconium, and niobium with ethene, propene, butene, and isobutene.[39] The effective rate constants for the above reactions have been found (helium, 300 K, 0.5–0.8 Torr) and it has been shown that under these conditions yttrium, zirconium, and niobium react rapidly with the above alkenes, while molybdenum reacts slowly.[39] Kinetic data indicating the interaction of monoalkenes with 3*d* and 4*d* metals have been published.[38,40,53] Thus the syntheses of scandium, titanium, vanadium, and nickel complexes of alkenes have been reported.[38] The same communications give the effective rate constants for the interaction of nickel and palladium with ethene, propene, and but-1-ene at a pressure of 0.5–0.8 Torr in helium. The formation of stable adducts of palladium with alkanes, to which the structure of the donor–acceptor π-complexes **2** has been attributed, is especially emphasised. These complexes do not fit within the framework of the ideas concerning the usual π-complexes.

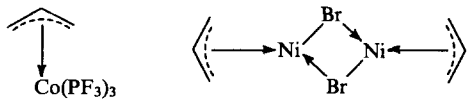


2

The interaction of ethene with iron results in the formation of 1 : 1 adducts,[53] while its interaction with copper affords 1 : 2 adduces.[37] The copper complex has been characterised thermodynamically. It is noteworthy that there are no X-ray diffraction data in the literature for the metal complexes with alkenes obtained by gas-phase synthesis. Therefore the ideas developed by Caroll et al.[39] and the schematic donor–acceptor model of the metal–alkene bond put forward by them are useful for the understanding of the mode of coordination of the metal in the alkene complexes. The σ-interaction makes a significant contribution to this bond. The interactions, not only with alkenes but also with their halo-derivatives, lead to π-complexes. Thus a reaction in which the coordination compound **3** is formed from perfluorobutene has been described in a monograph.[26] The same process in the presence of triethylphosphine leads to the σ-complex **4**.[14,15] However, the structures of complexes **3** and **4** cannot be regarded as rigorously demonstrated.

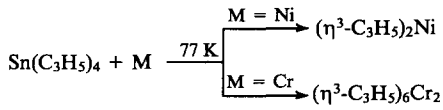


Gas-phase reactions of alkenes and haloalkenes with metals, accompanied by the formation of π-allyl complexes, are known. In particular, the interaction (at 77 K) of propene with atomic cobalt in the presence of phosphorus trifluoride results in the formation of the π-allyl complex **5**.[26,30] The reaction of bromopropene with atomic nickel at 77 and 298 K leads to the bisallyl derivative **6**.[26]



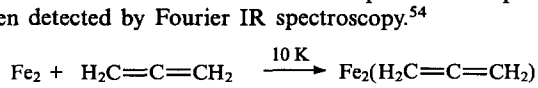
5 **6**

Organometallic compounds can serve as sources of the allyl ligand, which is indicated by the formation reactions of the π-allyl complexes of nickel and chromium.[15,26]

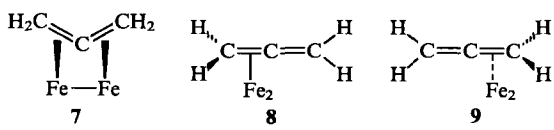


Acyclic diene hydrocarbons form in the gas phase a series of π-complexes in which the unsaturated ligands function predominantly as η^4-donor molecules.[14,15,17,26,30,51-53,66] The main bulk of these complexes have been synthesised from buta-1,3-diene, for which five types of coordination compounds have been differentiated. These have the compositions with metal : diene ratios of 1 : 1, 1 : 2, and 1 : 3 and also metal : diene : another ligand (L) = 1 : 1 : L_n and 1 : 2 : L_n, where L = CO, PF_3, or PR_3. According to Mitchell and Hackett's data,[53] the 1 : 1 complexes are formed in the reaction of buta-1,3-diene with iron at room temperature and a pressure of 100 Torr, while the 1 : 1 : L_n complexes are produced in the reaction of the above diene and trimethyl phosphite.[15] For cobalt and iron, there is a possibility of the formation of 1 : 2 coordination compounds.[15,26] The commonest type of the 1 : 2 : L_n complexes includes those of iron,[14,15,51] cobalt,[15,66] chromium,[14,67] and ruthenium.[52] In particular, ruthenium forms the stable adducts $Ru(\eta^4\text{-}C_4H_6)_2L$, where L = PF_3, CO, and Bu^tNC.[52] The 1 : 3 complexes (M = Mo, W)[15,66] have been characterised by X-ray diffraction. These data indicate equal distances between the molybdenum and tungsten atoms and all the carbon atoms of the butadiene ligand.

The photochemical cryosynthesis of iron complexes with allene in solid argon (10 K) takes place in an unusual manner.[54] The formation of dinuclear iron π-complexes in this process has been detected by Fourier IR spectroscopy.[54]

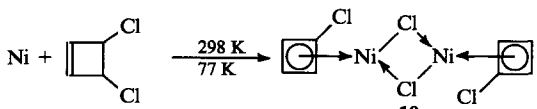


A structure described by formulae **7**–**9** has been proposed for these π-complexes.



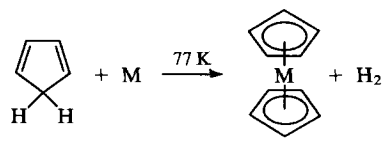
7 **8** **9**

The complexes of cycloalkenes occupy an important place among the coordination compounds synthesised in the gas phase from atomic metals.[14,15,26,50,55,57] The cyclobutadiene complexes are represented by compound **10**, which has been obtained as a result of the following reaction:[26]



10

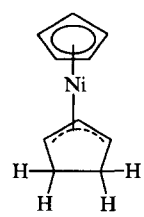
The greatest number of η^5-coordinated complexes having the general formula **11** have been synthesised from cyclopentadiene and its substituted derivatives.[14,15,20,50,55,57,68] During the reaction, the hydrogen atoms are substituted by the metal and the ligand system is aromatised.



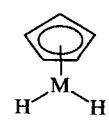
11

M = Co, Fe, Cr, Mo, W.

When atomic nickel is introduced into the process under consideration, the cyclopentadienyl ligand rings undergo intramolecular dehydrogenation-hydrogenation, the product of which is complex **12**.



12

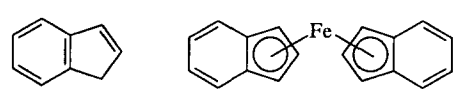


13

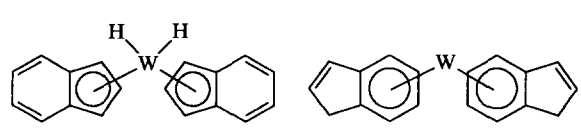
M = Cr, Mo, W.

When cyclopentadiene interacts with atomic chromium, molybdenum, or tungsten, the monocyclopentadienylmetal hydride complexes **13** are formed.[14]

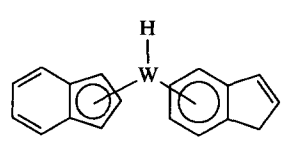
The reactions of indene **14** with iron and tungsten lead to complexes **15**–**18**, a characteristic feature of which is unusual bond isomerism due to the involvement of the cyclopentadienyl and benzene rings in coordination.[26]



14 **15**



16 **17**



18

This interesting phenomenon has been considered in relation to a limited number of systems and its causes are still not clear.

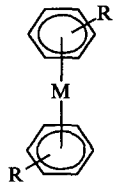
Mixed-ligand carbonylcyclopentadienyl $[C_5H_5M(CO)_2]$, cyclopentadienylpentamethylcyclopentadienyl $(C_5H_5MC_5Me_5)$, and cyclopentadienylethyne $[C_5H_5M(C_2H_2)_2]$ complexes of rhodium and iridium are known.[56]

The π-complexes of cyclohexa-1,3-diene (CHD) and cycloocta-1,3- and 1,5-dienes (COD) have been obtained by gas-phase synthesis with participation of atomic metals.[15,26,57] The complexes formed in these reactions have the compositions MLL'_n, ML_2, ML_2L', where L = diene, L' = H, CO, PF_3, PR_3, $Ph_2PCH_2CH_2PPh_2$, or BuNC, and M = Fe, Cr, or Mn.

The complex $Mn(\eta^4\text{-}1,3\text{-}CHD)_2CO$ has been obtained by condensing atomic manganese with cyclohexa-1,3-diene at 77 K and subsequent heating of the condensate to 293 K.[57] Its structure was demonstrated by X-ray diffraction and is therefore not open to doubt.[57] The manganese complexes of cycloocta-1,3-diene $Mn(\eta^5\text{-}C_8H_{11})(CO)_3$ and $Mn(\eta^3\text{-}C_8H_{13})(CO)_4$, in which the ligand system has undergone dehydrogenation-hydrogenation, have been synthesised under the same conditions.[57] The cocondensation reactions of cycloocta-1,3-diene and cycloocta-1,5-diene with metals have been considered in detail in a review[15] and in a monograph.[26] (New publications concerning ligands of this type have not appeared.) Among the results quoted in the above review,[15] the fact that cycloocta-1,3-diene isomerises, on formation of a complex with chromium, to the 1,5-diene ligand system is of greatest interest. X-Ray diffraction showed that the structure of the complex $C_8H_{11}Cr(PF_3)_3H$ is the same as that of (η^4-cyclooctadienyl)hydridotris(trifluorophosphine)chromium.

There are relatively few data on the gas-phase synthesis of π-complexes of cyclotrienes. However, there are no obstacles to such synthesis being achieved: the complexes $[Mn(\eta^4\text{-}C_7H_8)_2CO]$ and $[Mn(\eta^5\text{-}C_7H_9)(CO)_3]$ have been obtained (cryosynthesis at 77 K) from cycloheptatriene (C_7H_8), although the yield was low (5%–8%).[57]

The use of the aromatic benzene system (formally the hexatriene) system, benzene homologues, and substituted benzene derivatives as the ligands has led to extensive possibilities for the gas-phase synthesis of various arene π-complexes. At the present time, arene π-complexes, the structure of which is described predominantly by formula **19**, have been obtained under the conditions of gas-phase synthesis with virtually all transition metals and a wide variety of aromatic η^6-ligand systems.



19

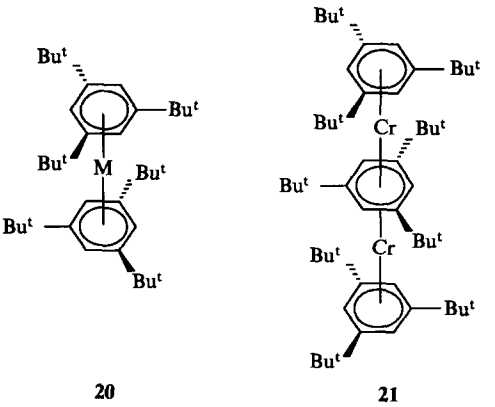
Early publications on the gas-phase synthesis, properties, and structures of type **19** complexes have been surveyed in reviews[13–15,30,47] and in a monograph.[26] Special mention should be made of communication ref. 48 in which 38 diarene sandwich complexes of type **19** (R = F, Cl, CF_3, Alk, OAlk, $NAlk_2$, COOAlk), obtained by the co-condensation of the metal and the ligands at 77 K and a pressure of 5×10^{-4} Torr, have been described. The complexes have been characterised by ^{13}C NMR spectroscopy and their comparative thermal stabilities have been estimated.

A large number of diarenechromium complexes, including those containing fragments coordinatively active in relation to the metal indicated (the phosphorus atom and the C≡C and C≡N bonds) as well as polynuclear aromatic compounds, have been described in a review.[47]

A series of π-complexes containing substituents such as ferrocenyl (yield 1%),[69] PrCO (4%), CH_2Ph (48%), and CH_2CH_2OH (5%) [70] have been obtained.

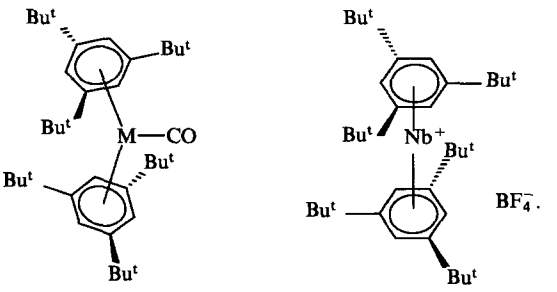
When the vapours of atomic yttrium, titanium, hafnium, niobium, chromium, molybdenum, and tungsten were heated with 1,3,5-tri-*tert*-butylbenzene, the diarene complexes $M[\eta^6\text{-}C_6H_3Bu^t_3]_2$ **20** were obtained.[59–61] The reactions take place at 77 K and the product yields are 20% (M = W), 30% (M = Cr, Mo), and 40% (M = Y, Ti, Zr, Hf).

In the case of chromium, the triple-decker complex **21** $Cr_2[\eta^6\text{-}C_6H_3Bu^t_3]_2[\mu\text{-}\eta^6 : \eta^6\text{-}C_6H_3Bu^t_3]$ is formed together with the diarene compounds **20** (yield 2%).[61] Reactions of zirconium and hafnium in the presence of carbon monoxide lead to the



20 **21**

stable 18-electron zirconium adduct **22** and the analogous relatively unstable hafnium complex. The reaction of complex **20** (M = Nb) with $AgBF_4$ in toluene is accompanied by the formation of a tetrafluoroborate complex containing the stable 16-electron cation **23**.



22 (M = Zr, Hf) **23**

The structures of complexes **20**–**23** have been demonstrated by mass spectrometry and ^1H NMR spectroscopy.[61] The yttrium complex **20** is interesting because it is paramagnetic ($\mu_{ef} = 1.74\ \mu_B$ at room temperature) and gives rise to clear-cut EPR signals in methylcyclohexane solution at 77 K; $g_{\|} = 2.085$ (doublet), $g_{\perp} = 2.005$, and $A = 3.0$ mT for ^{89}Y. X-Ray diffraction studies showed that the complex contains parallel benzene rings and is the first representative of η^6-coordination compounds of zerovalent yttrium.[60]

The chromium complex **19** with a dialkylamino-substituent (R = NMe_2) has been known for more than 20 years[15,48] and its structure has been demonstrated by X-ray diffraction.[71] However, the analogous complex with aniline could not be obtained for a long time. The complex **19** [R = $N(SiMe_3)_2$] has been obtained recently[49] by the co-condensation of chromium with bis(trimethylsilyl)aminobenzene at 77 K. After treatment with tetrabutylammonium fluoride trihydrate in tetrahydrofuran (THF) at 298 K, it affords the dianilinechromium complex **19** (R = NH_2). The reaction described proceeds in accordance with the following scheme:

$$Cr + 2\,PhN(SiMe_3)_2 \xrightarrow[\text{co-condensation}]{77\ K} \longrightarrow \mathbf{19}\,[R = N(SiMe_3)_2] \xrightarrow{Bu_4NF \cdot 3\,H_2O} \mathbf{19}\,(R = NH_2).$$

Complex **19** (R = NH_2) with $T_m = 501$ K has been characterised by elemental analysis, ^1H and ^{13}C NMR, and mass spectrometry and its reduction potential and Brønsted basicity have been investigated. It is striking that, in the interaction of di(π-aniline)chromium and its π-*N*,*N*-dimethylaniline analogue with HBF_4 in ether, the nitrogen atoms are protonated.

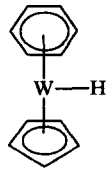
Diarenemetal π-complexes which had not been introduced previously into the reactions of the type considered, in particular those of titanium, have been synthesised.[49,72] Thus complex **19** (M = Ti, R = Et) has been obtained in ~100% yield by the reaction with ethylbenzene at 77 K in vacuo.[72] The study of the properties of η^6-naphthalenechromium complexes showed that a series of coordination compounds having the general formula (η^6-arene)CrL_3, where arene = $C_{10}H_8$, $C_{10}H_7Me$, or $C_{10}H_6Me_2$ and L = CO, PMe_3, $P(OMe)_3$, or PF_3, have been obtained, in addition to di(η^6-naphthalene)chromium(0), on co-condensation of the metal and naphthalene or its methyl derivatives (L) at 193 K. The complexes have been characterised by ^1H NMR. It is emphasised that atomic chromium interacts with 1,4-dimethylnaphthalene stereospecifically, forming predominantly (up to 95%) the isomer in which the metal is bound to the unsubstituted aromatic ring.

Numerous studies have been devoted to the stabilities, physicochemical properties, and structures of the diarene complexes obtained by gas-phase synthesis (see, for example, Refs 13–15, 26, 30, 49, and 71). The synthesis and decomposition of the diarene complexes have been considered in two investigations.[74,75] The possibility of employing the additivity method to calculate the ΔH for the vapours of the diarene complexes has been demonstrated.[76] Electronic[77,78] and fluorescence[79] spectra of the molybdenum complexes have been obtained and interpreted. The oxidation–reduction properties of the diarene derivatives of zerovalent metals have been investigated.[80]

Apart from the diarene compounds of types **19**, **20**, **22**, and **23**, the monoarene complexes **24** and the cyclopentadienylarene complex **25** have been obtained by gas-phase synthesis.[14,15]

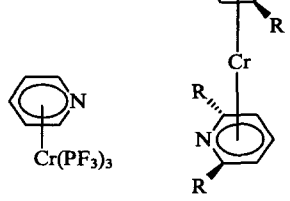


24 (L = PF_3)



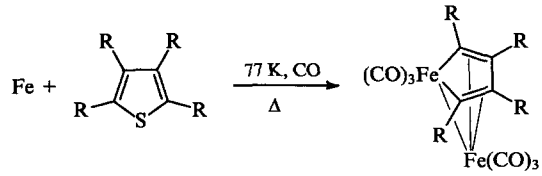
25

Complexes of heteroaromatic systems, obtained by gas-phase synthesis, are represented by the π-complexes of pyridine and its *C*-methyl substituted derivatives. The possibility of the involvement of the heteroaromatic π-system of the pyridine ring in coordination was demonstrated for the first time in relation to the cocondensation of chromium with pyridine in the presence of phosphorus trifluoride and the π-complex **26** was obtained.[30]



The low-temperature interaction of atomic chromium and 2,6-dimethylpyridine led to the sandwich π-complex bis(2,6-dimethylpyridine)chromium **27** (R = Me).[63] Its structure was demonstrated by X-ray diffraction.[81] When trimethylsilylpyridine derivatives were used in the same synthesis, it was possible to obtain di(η^6-pyridine)chromium **27** (R = H).[82] We emphasise that none of the di(η^6-pyridine)metal complexes can be obtained in the usual way.[83,84]

It has been shown in a review[85] that thiophene does not react with zerovalent metals, but a reaction accompanied by the desulfurisation of the heterocycle is known.[26]



This finding indicates a radical rearrangement of the thiophene system during the complex formation reaction. It must be taken into account in the further studies of the gas-phase syntheses of metal complexes with participation of heteroaromatic systems, the π-donor activity of which is not open to doubt.[85–87]

It has been shown in a review[15] that the gas-phase synthesis with participation of zerovalent metals and alkynes leads mainly to the trimerisation of the ligand systems with formation of benzene and its substituted derivatives. This is also confirmed by the data compiled in a monograph.[26] At the same time, a reaction indicating the formation of metal complexes with alkynes is presented in the same communication.

$$Fe + Me_3Si-C\equiv C-SiMe_3 \xrightarrow{77\ K} Fe(Me_3Si-C\equiv C-SiMe_3)$$

The possibility of obtaining the metal complexes of alkynes in atomic syntheses has been confirmed also in subsequent publications.[20,37,53,54,88] When nickel,[88] iron,[53] and copper[37,88] are co-condensed with ethyne at 10 K, the complexes $M(\pi\text{-}C_2H_2)_n$, where $n = 1, 2$, are formed. It is striking that the iron complex with methylethyne having the same composition has been obtained in the reaction of allene with iron at 10 K (argon, irradiation with visible light).[54] The reaction takes place in accordance with the following scheme:

$$Fe + H_2C{=}C{=}CH_2 \xrightarrow{h\nu} Fe(HC\equiv C-CH_3).$$

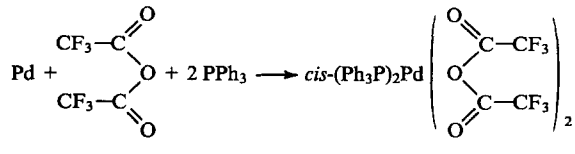
The last compound is converted into the σ-complexes $H-Fe-C\equiv C-CH_3$ and $H_3C-Fe-C\equiv CH$ on irradiation with UV light.[54]

It was shown above that the mixed-ligand complex $C_5H_5Mn(HC\equiv CH)_2$ is formed on interaction of ethyne, cyclopentadiene, and manganese under the conditions of cryosynthesis.[56]

The complexes obtained in gas-phase syntheses from atomic metals and oxygen-containing ligands are represented by a relatively small number of examples. Aromatic alcohols, ethers, ketones, and acids behave as the usual η^6-arene ligands, forming substituted di(η^6-arene)metal complexes of type **19** (R = CH_2CH_2OH,[70] OAlk,[14,15] COAlk,[70] or COOAlk,[15] where Alk = Me or Pr). Alcohols form metal alkoxides in the gas-phase synthesis. Stable complexes giving rise to colloidal systems in nonaqueous solutions with a particle size of ~8 nm have been obtained from acetone and atomic palladium. It has been suggested[64] that the following reaction involving the addition of the metal to the ketone takes place:

$$n\,Pd + x\,Me-\overset{\overset{O}{\|}}{C}-Me \xrightarrow{77\ K} Pd_n(Me-\overset{\overset{O}{\|}}{C}-Me)_x.$$

However, the structures of the reaction products formed have not been studied in detail. An addition reaction also takes place between palladium and trifluoroacetic acid anhydride in the presence of triphenylphosphine.[15]



At the same time, it is known[14] that the interaction of carboxylic acid chlorides with atomic palladium in the gas phase leads to insertion products of the metal in the C–Hal bond.

An example of such a reaction is presented below:

$$Pd + RCOCl \longrightarrow RCOPdCl$$

$R = CF_3$, C_3F_7.

The data presented in this section indicate the extensive possibilities of gas-phase synthesis in the preparation of diverse metal π-complexes.

b. Gas-phase synthesis of metal chelates

The metal chelates synthesised in the gas phase belong mainly to a single class of complexes — transition and nontransition metal β-diketonates. This is due to the high stability of β-diketones and β-diketonates under the conditions of the gas-phase synthesis.[15,36]

The gas-phase syntheses of metal acetylacetonates having the general formulae $M(acac)_2$ (M = Mn, Fe, Ni, Pd, Cu, Zn, Sn) and $M(acac)_3$ (M = Cr, Fe, Dy, Ho, Er) were described in early communications (see, for example, Domrachev and Zinov'ev[15]). The yields of the complexes obtained by the co-condensation of the vapours of acetylacetone and the atomic metals indicated varied in the range from 10% to 32% under the conditions of cryosynthesis. However, it was later possible to obtain (see, for example, Mazurenko and coworkers[36]) a series of β-diketonates at temperatures in the range 363 – 543 K (M = Co, Ni, Cu, Cr, Fe, Ti, Hf, Zr) in nearly quantitative yields (90% – 100%). It was emphasised[36] that the direct synthesis is the most promising method for the industrial preparation of β-diketonates. The productivity of the apparatus for the synthesis of the complexes increases sharply when the ligands are employed in the form of aerosols, which makes it possible to introduce appreciable amounts of β-diketones into the reaction zone with the simultaneous regulation of their concentration. Among other studies on these lines, mention should be made of the cryosynthesis of coordination compounds containing radionuclides, in particular ^{63}Ni acetylacetonate.[89]

The possibility of using the gas-synthesis for the preparation of various metal chelates is of interest.[90]

Analysis of the data presented in this section indicates extensive possibilities of the gas-phase synthesis for the preparation of π-complexes with alkene and aromatic ligands. At the same time, examples of the employment of heteroaromatic and chelating ligands in such syntheses are extremely limited and so far do not permit conclusions concerning the prospects for the preparation of metal complexes of heterocycles and inner-complex compounds in gas-phase reactions.

III. Liquid-phase synthesis

The syntheses of coordination compounds from zerovalent metals in the liquid phase comprise reactions of three types — direct interaction of the zerovalent metals and ligands, oxidative dissolution of compact metals in nonaqueous media, and electrosynthesis. Such reactions lead to the formation of predominantly molecular adducts and inner complexes as well as individual π-complexes and polynuclear clusters.

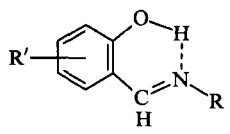
1. Synthesis of complexes by the direct interaction of zerovalent metals and ligands

In contrast to the gas-phase syntheses, this method of direct interaction of metals with ligands does not require special apparatus — the reactions take place under the usual conditions.

The method is used widely for the synthesis of individual types of π-complexes and metal chelates, although it is also possible to obtain other types of coordination compounds. As stated in a review,[17] the method of direct interaction of metals and ligands has been used successfully for the preparation of π-allylpalladium complexes (reaction between bromopropene and palladium at 353 K under a nitrogen atmosphere), the praseodymium complex of cycloocta-1,5-diene (in THF), and cyclopentadienyl derivatives of europium and ytterbium (in liquid ammonia).

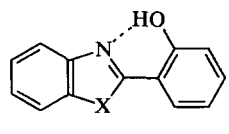
The formation of inner complexes in the syntheses under consideration is difficult mainly due to the chemical inertness of the *d* and *f* metals behaving as complex-forming agents in reactions involving the substitution of hydrogen atoms in the chelating ligands.[3] However, it has been possible to isolate metal chelates in satisfactory yields for individual ligand systems and zerovalent metals. Thus the interaction of acetylacetone with a series of *d* metals (Ti, Mn, Cr, Fe, Co, Ni, Cu, Mo, and Pd) has been investigated and it has been shown that iron forms bis- and tris-acetylacetonates, whereas the remaining metals are passive under an inert atmosphere.

Ligands containing the OH group in the *ortho*-position relative to the C=N group interact extremely effectively with zerovalent metals. Such ligands include salicylaldoxime **28** (R = OH),[17,91] salicylidene-*o*-aminophenol **28** (R = C_6H_4OH-*o*),[92] 2-*o*-hydroxyphenylbenzazoles **29**,[93] 3-hydroxyphenyl-5-R-1,2,4-oxadiazoles **30** (R = Me, Ph, $PhCH_2$),[92,94] 3-*o*-hydroxyphenyl-1,2,4-triazoles **31** (X = NH, NPh), and 3,5-di(*o*-hydroxyphenyl)-oxadiazole **32**.[95]



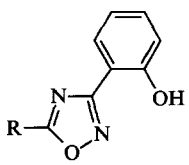
28

R = OH, C_6H_4OH-*o*, Py; R′ = H, OMe



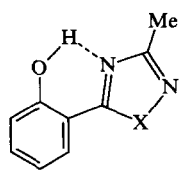
29

X = NH, NR′, O, S



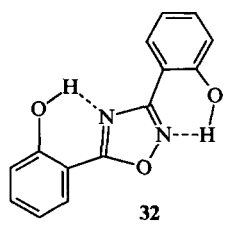
30

R = Me, Ph, CH=CH_2



31

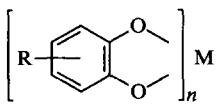
X = NH, NPh



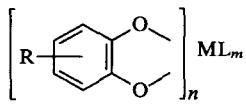
32

The solvents employed in these syntheses were ether, phenol, phenetole, acetylacetone, and dimethylformamide (DMF). The yields of the complexes vary in the range 80% – 100%. The complexes described have the compositions ML_2 [**28**(R = OH) – **31**] and ML [**28**(R = C_6H_4OH-*o*) and **32**] depending on the basicity of the ligands (LH or LH_2). The complexes ML are interesting because they have a dimeric structure (for the ligand **28**) or an oligomeric structure (for the ligand **32**) and are representatives of polynuclear compounds.[29,96,97] The polymeric nature of the complexes from the ligand **32** has been confirmed by magnetochemical[98] and EPR spectroscopic measurements: they indicate the presence in the copper(II) and cobalt(II) complexes considered of exchange-linked ions forming part of the composition of the polymeric coordination structure of the type $LH(ML)_nLH$ ($n = 1, 2, \ldots, \infty$).[95] In the copper complexes investigated, there is an exchange interaction of the antiferromagnetic type with an exchange integral $J \approx -100\ cm^{-1}$, whereas in the cobalt coordination polymers ferromagnetic exchange is observed with $J \approx 20 - 30\ cm^{-1}$.[95]

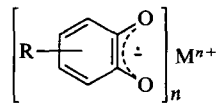
o-Quinones are extremely reactive ligands,[17,99-112] especially those containing *tert*-butyl substituents. Complexes of *o*-benzoquinones, *o*-semiquinones, and catechols of this kind have been obtained. They are radical in nature and play an important role in coordination chemistry.[106-108] In nonaqueous solvents (hexane, dimethoxyethane, toluene, THF, and chloroform), mainly the formation of complexes of types **33**–**36** (R = 3,5- or 3,6-Bu^t_2) has been observed by EPR.



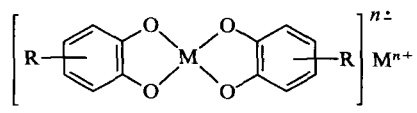
33



34



35



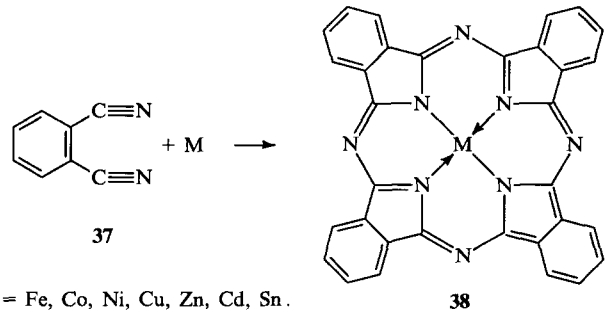
36

The formation of radical *o*-semiquinolates of type **33** has been detected for thallium,[109] indium,[102] zinc,[100,103,110] cadmium,[100,103,110] magnesium,[103] barium,[103] aluminium,[100] gallium,[105] and tin.[99] The adducts **34** are characteristic of copper and silver (L = PPh_3, $m = 2$, $n = 1$)[17] and also of indium (L = phen, m, $n = 1$).[102] Data on the radical-anion salts of types **35** and **36** have been presented in a review[17] and other publications.[99,110] Metal complexes of catechols can be obtained also from tetrahalo-*o*-quinones, for example $Sn(X_4C_6O_2)_2$ (X = Cl, Br).[102]

The data of Ozarowski et al.[103] and Adams et al.[105] are of greatest interest for the study of the properties and structures of type **33** complexes. Magnesium, barium, zinc, and cadmium complexes of 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone (L) and their adducts with pyridine, 2,2′-bipyridyl, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine(L′), having the compositions ML_2 and $ML_2 \cdot nL'$ ($n = 1, 2$), were isolated preparatively and characterised in the first of these studies. Complexes **33** and their adducts with L′ have been obtained by the reaction of the above zerovalent metals and ligands in toluene; detailed EPR spectroscopic studies confirmed their biradical nature and made it possible to establish the conformations of the biradical ligands. The study of Adams et al.[105] was devoted to the triradical gallium complex of 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone **33** ($n = 3$). This compound was obtained by heating gallium and the ligand in boiling toluene (under an argon atmosphere) and was characterised by X-ray diffraction. The complex has the form of a three-blade propeller with the gallium atom in the centre: the length of the C–C bond between the chelating oxygen atoms is 1.439(12) Å, which indicates the semiquinone nature of the ligands. It is striking that the above value differs little from the length of the same bond (1.433 Å) in the chromium analogue, the structure of which had been characterised previously.[112] The gallium complex **33** ($n = 3$) exhibits ferromagnetic properties; its magnetic moment is 2.95 μ_B at 320 K and 3.58 μ_B at 9 K; it then again decreases and is 3.26 μ_B at 2 K.

Thus direct evidence for the formation of radical complexes in the reactions of zerovalent metals with *o*-diquinones was obtained in the studies quoted above, methods were developed for the synthesis of these coordination compounds, and the characteristics of their structure and their physicochemical properties were established.

In a number of instances, the interaction of zerovalent metals with the ligand is accompanied by a template reaction, which yields macrocyclic chelates. The template reaction involving the direct synthesis of the macrocyclic phthalocyanine complexes **38** from zerovalent metals and *o*-phthalodinitrile (1,2-dicyanobenzene) **37**, which has long been known, has now become a classical reaction.[9,10,17,113,114]



37 **38**

M = Fe, Co, Ni, Cu, Zn, Cd, Sn.

The phthalocyanine complexes **38** are formed in high-boiling solvents — α-methyl- and α-chloro-naphthalene, *o*-dichloronitro- and trichloro-benzene, and quinoline. Apart from the ligand **37**, *o*-cyanobenzamide, phthalimide, and diiminoisoindoline have been introduced into this reaction.[17,113]

In conclusion of this section, we may note that molecular complexes are formed on direct interaction of metals and ligands.[17] Such complexes have been obtained, for example, between alcohols and carboxylic acids, on the one hand, and bases (pyridine, bipyridyl, and phenanthroline), on the other.[115-117]

2. Synthesis of complexes on oxidative dissolution of metals

In contrast to the direct synthesis methods considered above, the oxidative dissolution of metals in the liquid phase, accompanied by the formation of coordination compounds, proceeds in the presence of oxidants.[14,16,17,118-153] The simplest mechanism of this reaction may be as follows:[16]

$$M^0 + Ox \xrightarrow[-ne]{mL} L_mM^{n+} + Red + P,$$

where M is the metal, Ox the oxidant, L the complex-forming agent (ligand), Red the reduced form of the oxidant, and P the products of the interaction of the components of the medium.

The halogens were used as the oxidants in the old investigations (see the literature in the review of Gernovskii et al.[17] and also Kurskov[130]). Later, hydrogen halides[17,126,129,132,138,148-150] and halohydrocarbons[118-120,124-127,131,133,137,148,150] began to be employed widely. This change is not fortuitous — the synthesis of coordination compounds with the aid of hydrogen halides and especially halohydrocarbons takes place in donor–acceptor nonaqueous solvents under mild conditions without the use of corrosive media and special apparatus. Apart from the oxidants investigated, the sulfates, perchlorates, bromates, and chromates of certain metals,[17] mercury chloride,[4] and nontraditional oxidants[4,128] — nitrosonium (NO^+X^-), arenediazonium ($ArN_2^+X^-$), and triphenylcarbenium ($Ph_3C^+X^-$, X = BF_4, ClO_4, PF_6) salts — began to be used in individual syntheses.

Ammonium salts are extremely effective reagents in the synthesis of coordination compounds by the oxidative dissolution of metals.[153-171] A simple and readily applicable method of synthesis of metal complexes based on the following reaction has been developed:[153,156,166,169]

$$M^0 + m\,NH_4X + n\,L + \tfrac{1}{2}p\,O_2 \longrightarrow MX_mL_n + m\,NH_3 + p\,H_2O.$$

We may note that metal oxides also enter readily into this reaction.[153,168,169,172-176]

Cobalt,[16,17,119,120,130,155,156,158] nickel,[16,17,120,160,161,164] iron,[16,17,118,120,130,134,145] zinc,[153,159,166,169] and copper[16,17,118,121,123,127,134,135,137,141,142,146,153,159,166,169] are most frequently employed in liquid-phase syntheses. Many studies have been devoted to the dissolution of platinum group metals and the formation in these syntheses of palladium,[16,17,124,129,131,133,134,136,143] platinum,[129,131,133,134] and rhodium[129,131] complexes. Much attention has been devoted to the preparation of gold[132,134,138,148,150] and silver[138,139] complexes in oxidising donor–acceptor media. The preparation of titanium,[119] chromium,[125,134] manganese,[119] cadmium,[163] niobium,[126] tantalum,[126] and europium[128] complexes has been described in individual publications. It has been suggested[117] that lanthanide (Ln) complexes may be formed in the $Ln-PBu_3-CCl_4$ system, but their synthesis has not been described.

Solvents which in the majority of cases are also ligands are represented mainly by compounds with N and O donor atoms such as acetonitrile (AN),[16,17,118,128,129,146] benzonitrile (BN),[130] aliphatic amines (AM),[130,164,166,167,169] pyridine (Py),[16,17,133,178] dimethyl sulfoxide (DMSO),[16,17,118,120,130,138,139,143,146,148–150] dimethylformamide (DMF),[16,17,118,119,124,126,137,146,155,164] formamide (FA), monomethylformamide (MFA), dimethylacetamide (DMA),[121,123,141,145] alcohols,[157,160] and propylene carbonate (PC).[142] Apart from the compounds listed above, azoles,[137] 2,2′-bipyridyl (Bipy),[16,17,121,123,130,142] 1,10-phenanthroline (Phen),[123,131] and adenine[137] function as N donors and urea,[125] pyridine *N*-oxide,[120,133,178] triphenylphosphine oxide,[120,178] dimethylglyoxime,[130,179] and β-diketones[130,151,152,179] function as O donors. Triphenylphosphine has been used as a ligand with a phosphorus donor atom.[130]

The complexes obtained as a result of the oxidative dissolution of zerovalent metals include all types of complexes,[17] but their proportions are very different.

A single example of a π-complex, obtained by the oxidative dissolution of zerovalent copper in the 1,5-COD–DMF–CCl_4 system, is known. In the complex $[Cu(COD)Cl]_2$ synthesised, copper is stabilised in the lowest oxidation state (+1) by the soft cyclooctadiene ligand system, which is confirmed by the diamagnetism of the complex considered.[16,179] This result agrees with the familiar postulate that, within the framework of the principle of hard and soft acids and bases (HSAB), soft bases (ligands) stabilise the lowest oxidation states of the complex-forming agents.[180]

There have also been only a few dinuclear and polynuclear complexes synthesised in oxidative systems.[16,17,118,123,141,171,181]

The main bulk of the complexes obtained by the method considered are molecular complexes and metal chelates.

a. Synthesis of molecular complexes

In conformity with the approach proposed in the review of Lavrent'ev and Khidekel',[16] it is possible to differentiate two types of compounds among molecular complexes — neutral and ionic. The former include, for example, adducts having the general formula MX_mL_n, where M = Co,[16,178] Cr,[125] Ni,[16,178] Fe,[118,178] Cu,[16,118,137,146,178] Pd,[131,133,146] Pt,[131] Rh,[131] Zn,[159,166,169] Cd,[163] Au,[132,148,150] Ag,[138] MoO_2,[16] WO_2,[16] and Eu,[128] L = DMSO,[16,17,118,146,148–150] DMF,[16,17,118,137,146] DMA,[16] AN,[16,17,118,128,146] Py,[133,177] Py–O,[133,178] and Ph_3PO,[177] X = Cl, Br, NCS, and BF_4, and *m*, *n* = 1–3. Coordination compounds of the second type are represented by complexes of the following metals: iron complexes[16,17,118] — *cis,trans*-$[Fe^{III}(DMF)_nCl_2].[Fe^{III}Cl_4]$, (*n* = 3, 4), *cis*-$[Fe^{III}(DMSO)_4Cl_2]Cl$, *cis*-$[Fe^{III}(DMSO)_4Cl_2][FeCl_4]$, $[Fe^{III}(DMSO)_5Cl][FeCl_4]_2$, $[Fe^{III}.(DMSO)_5Cl][Fe_2Cl_6O]$, $[Fe^{II}(AN)_6][Fe^{III}Cl_4]_2$, and $[Fe^{II}.(BN)_6][Fe^{III}Cl_4]_2$; copper complexes[146] — $[Cu^{I}(AN)_4]BF_4$, $[Cu^{I}(Me_3S)_3]I_4$, $[Cu^{II}(DMSO)_5](BF_4)_2$, $[Cu^{II}(DMSO)_4(AN)_2].(BF_4)_2$, $[Cu^{II}(DMSO)_4DMF{\cdot}AN](BF_4)_2$, and $[Cu^{II}(DMSO)_4.AN{\cdot}H_2O](BF_4)_2$; cobalt complex[16] — $[Co^{II}(DMSO)_6][Co^{II}Cl_4]$; chromium complex[125] — $[NH_2Me_2][CrCl_6]Cl$; palladium complexes — $[NH_4]_2[PdCl_4]$,[129] $[NH_2Me_2]_2[PdBr_4]$,[124] $[NH_2Bz_2]_2.[PdBr_4]$,[124] $[NHMe_3]_2[PdBr_4]$,[133] $[Me_3NOH]_2[PdBr_4]$,[133] $[(PyO)_2H]_2[Pd_2Cl_6]$,[133] and $[PdL_2Br_2][PdBr_4]$ (where L = Ph_3BuP);[131] platinum complexes[129] — $[NH_2Me_2]_2[PtCl_6]$ and $[PtLBr_2][PtBr_4]$; rhodium complexes — $[NH_2Me_2]_4.[RhCl_6]Cl$,[129] $[PyH][RhPy_2Br_4]$, $[Ph_3BuP][Rh(CO)_5Br_4]$,[131] and $[Ph_3BuP][Rh(CO)Br_4(EtOH)]$;[131] titanium complex[126] — $[NH_2Me_2]_4[TiOF_4][TiF_6]{\cdot}HF{\cdot}H_2O$; zirconium complex[126] — $[NH_2Me_2]_2[ZrOF_4]{\cdot}2HF$; niobium complex[126] — $[NH_2Me_2]_2.[NbOF_5][NH_2Me_2F]{\cdot}4HF$; tantalum complex — $[NH_2Me_2].[TaOF_5][NH_2Me_2]{\cdot}HF$; gold complexes[148,150] — $[Me_3S].[AuBr_4]$, $[Me_3S][AuBr_4(Me_2S)]{\cdot}H_2O$, $[Me_3SO][AuBr_4]{\cdot}H_2O$, $[Me_2BuSO][AuBr_4]{\cdot}H_2O$, $[Me_3S]_2[Au_2Br_8]{\cdot}2DMSO{\cdot}H_2O$, and $[Me_3S][Au_2Br_7(Me_2S)]{\cdot}3H_2O$; silver complex[139] — $[Me_2S^{+}CH_2.COR][AgX_2]^{-}$.

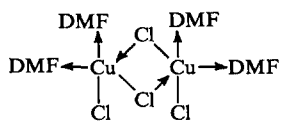
The structures of the dimethyl sulfoxide complexes indicated above have been investigated by X-ray diffraction (see the references in the paper of Lavrentiev et al.[118]).

The above complexes are interesting not only because of their unusual composition but also because in some of them the complex-forming agents are in different oxidation states (for example, in the iron complexes). Another characteristic feature of the complexes obtained in donor–acceptor oxidative systems is the stabilisation in them of uncharacteristic oxidation states of the metals. Thus, together with the usual oxidation states of the metals, in particular +1 and +2 for copper, diamagnetic § Cu(+3) complexes are formed in the Cu–DMSO–CCl_4–TU system (TU = tetramethylthiuram disulfide) according to Shirshova et al.[142]

It is believed[143] that the use of the same system in the case of palladium leads to intermediate univalent palladium complexes. Oxidation of zerovalent gold by hydrogen chloride or bromide in DMSO led to the isolation of univalent and trivalent gold complexes — $[(Me_2S)AuBr]$ and $[(Me_2S)AuBr_3]$.[132,148,150] We emphasise that trivalent copper and gold complexes as well as univalent palladium complexes are encountered comparatively rarely.

It has been emphasised in a review[16] that the complexes considered can contain as ligands both the components of the reaction mixture (solvents, additional ligand systems) and the products of the reactions of these components. This postulate was clearly confirmed when amides[16,118,123,141,179] and sulfoxides[132,144,148–150] were employed as the ligands. Diverse complexes are formed in M^0–amide–Ox systems, the nature of which is determined by the nature of the amide ligand, the metal, and the oxidant. It has been shown in the above review[16] (see the references therein) that complexes with transformed ligand fragments — $[(Me_2NCH)_2CH].[Fe^{III}(DMF)_6][Fe^{III}Cl_4]_4$ and $[MeNH_3]_4[Fe^{II}Cl_6]{\cdot}H_2O$ — have been isolated from the DMF–Fe–CCl_4 system and characterised. The reaction proceeds with dissociation of the bonds in the DMF molecule: N–CH_3, NC–O, and N–CHO.

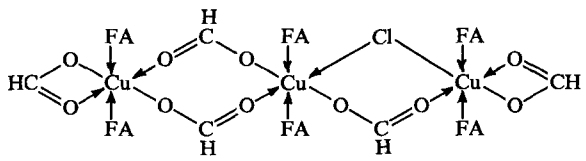
Amides behave similarly in the oxidative system containing copper and CCl_4: apart from the isolation and structural characterisation of complex **39** with the unchanged DMF ligand, complexes with a significantly modified ligand system are formed.



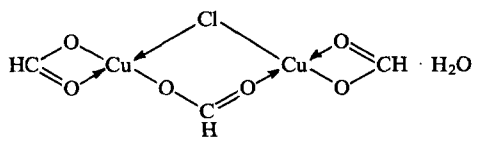
39

§ However, diamagnetism does not constitute incontrovertible proof of the oxidation state of copper, since there are quite a few paramagnetic compounds among trivalent copper complexes.[3] The Cu^{3+} ion has the d^8 electronic configuration, like Ni^{2+}.

For example, formamide (FA) gives rise to three types of complexes in the same system:[141] $[Cu(HCOO)_2(FA)_2]$, $[Cu_3Cl.(HCOO)_5(FA)_6]$, and $[Cu_2Cl(HCOO)_3].H_2O$, while methylformamide[141] gives rise to the tetrameric cluster $[(MeNH_3).Cu(HCOO)_3]_4$. The complex $[Cu(HCOO)_2(FA)_2]$ has also been obtained by dissolving copper in formamide in the presence of atmospheric oxygen and α,α′-bipyridyl.[123] On the basis of X-ray diffraction data, a polymeric structure was attributed to it and it was demonstrated that it belongs to the class of network carboxylates. The copper atom, which occupies the centre of inversion, coordinates the oxygen atoms of two formamide molecules and four formate groups. The coordination polyhedron is a tetragonal bipyramid. In the formate group and in the formamide molecule, the bond lengths are close to the standard values. In the tetrameric compound $[(MeNH_3)Cu(HCOO)_3]_4$, the individual formatocuprate anionic fragments are linked by NH...O hydrogen bonds to the methylammonium cations.[141] The N...O distance is 2.81 Å. The structures of the complexes $[Cu_3Cl(HCOO)_5(FA)_6]$ and $[Cu_2Cl(HCOO)_3]\cdot H_2O$ can be represented by formulae **40** and **41** respectively.



40



41

The formation of copper formate complexes in the Cu–FA(or MFA)–CCl_4 systems has been accounted for by the hydrolysis of formamide and methylformamide under the copper oxidation conditions in the presence of CCl_4.[141]

Analysis of the data presented shows that the compositions of the complexes formed on oxidation of zerovalent copper in the CCl_4–amide system are determined mainly by the nature of the amide ligand: complexes of the type $[Cu_nCl_{2n}(DMF)_m]$ are formed in the case of DMF, whereas FA and MFA hydrolyse and the products of their hydrolysis behave as ligands. Furthermore, the compositions and structures of the complexes formed in the Cu^0–CCl_4–DMF system are influenced by the component ratios:[179] the complex $[CuCl_2(DMF)_2]_2$ was isolated for $[CCl_4]=[DMF] \gg [Cu^0]$, whereas in the case where $[CCl_4] \approx [DMF] \approx [Cu^0]$ the complexes $[Cu_3Cl_6(DMF)_2]$ and $[Cu_4OCl_6(DMF)_6]$ were isolated.

In the DMA–Fe–CCl_4 system, dimethylacetamide gives rise[145] to the complex $[Fe^{II}Fe^{III}_2Cl_8(DMA)_6]$ with an unaltered ligand system. X-Ray diffraction showed that the iron atoms in the crystals of this complex are in typical octahedral and tetrahedral environments in proportions of 1:2. DMA is coordinated via the oxygen atoms. This mode of coordination of the ligand considered follows also from IR spectroscopic data: an appreciable decrease [in the frequency?] of the stretching vibrations of the carbonyl group in the complex (~1600 cm^{-1}) is observed compared with the analogous absorption of free DMA (1655 cm^{-1}). Dimethylformamide undergoes even more prolonged changes in the DMF–Pd–$PhCH_2Br$,[16] DMF–Pt–HCl,[129] and DMF–Rh–HCl[129] systems. Ionic ammonium halide complexes were isolated in all cases—$[Me_2N(PhCH_2)_2][PdBr_4]$, $[H_2NMe_2]_2[PtCl_6]$, and $[H_2NMe_2]_4[RhCl_6]Cl$ respectively. The structures of the complexes described have been demonstrated[129] by X-ray diffraction for the platinum complex and by X-ray diffraction, magnetic susceptibility, and electronic and photoelectron spectroscopic methods for the rhodium complex.

Like DMF, dimethyl sulfoxide forms complexes containing as the ligand system a DMSO molecule[16,17,118,130] and the products of the reaction of this ligand and the oxidant.[132,138,139,143,148–150] As stated above,[16,17,118,130] molecular adducts of DMSO have been obtained in the DMSO–M^0–CCl_4 systems, where M = Fe or Co. In the case of Pd, Au, and Ag, the sulfoxide molecule is deoxygenated and sulfide complexes are formed. The oxidation of palladium in the presence of DMSO and HBr involves the formation of the complex $(Me_2S)PdBr_2$;[16] when CI_4 is used as the oxidant, the complex PdI(MeS).H_2O is obtained.[143] The oxidation of zerovalent gold in the DMSO–RX system (R = H, Bu; X = Cl, Br) is accompanied by the formation of a series of the dimethyl sulfide complexes examined above.[132,148,150] One of the processes occurring in this case is described by the scheme[132]

$$Au^0 + Me_2SO + HBr \xrightarrow[293\ K,\ 72\ h]{333\ K,\ 4\ h} \underset{\mathbf{A}}{[(Me_2S)AuBr]} + [(Me_2S)AuBr_3](solution) \xrightarrow{H_2O} \underset{\mathbf{B}}{[(Me_2S)AuBr_3]}.$$

The structures of complexes **A** and **B** have been established by X-ray diffraction. It was shown that the crystals of complex **A** contain intermolecular Au...Au chain contacts and intermolecular Au...Br contacts, which build up the square-planar coordination of the gold atoms to a distorted bipyramidal coordination. At the same time, a complex with an unaltered ligand system has been obtained in the DMSO–Au^0–BuBr system—the butyldimethyloxosulfonium salt $[Me_2SO(Bu)].[AuBr_4]$.[148,150] Together with a deoxygenated molecule of the sulfur-containing ligand, the mixed compound $\{[Me_3S]_2[Au_2Br_8].2DMSO\cdot H_2O\}$ contains also DMSO.[148,150]

Silver forms in the same systems the trimethylsulfonium salts $[Me_3S]AgBr_2$ and $[Me_3S]Ag_2X_3$, where X = Br or I.[138] When ketones were added to the reaction mixture, the ionic complexes $[R_2\overset{+}{S}-CH_2COR][AgX_2^-]$ (R = Me, Ph) were synthesised. These are carbonyl-containing sulfonium salts of silver halides. It has been suggested[139] that the above complexes are formed as a result of the condensation of DMSO with the ketones in an acid medium in the presence of silver halides in accordance with the scheme

$$Me_2SO + R'-CH_2COR \xrightarrow[-R'OH]{HAgX_2} [Me_2S^+-CH_2COR][AgX_2^-].$$

The condensation occurred when silver was dissolved in a DMSO–HBr mixture at 333 K for 3 h or after being allowed to stand for two days with subsequent addition of ketones (acetone or acetophenone). Similar complexes, containing iodine as the ligand X, have been obtained in the reaction of $Me_2S.I_2$ with acetone to which AgI and a mixture of hydriodic acid and alcohol had been added or on dissolution of the complex $[Me_3S]Ag_2I_3$ in a DMSO–HI mixture on heating with addition of an alcoholic solution of acetone.[138] The structure of the carbonyl-containing complexes has been demonstrated by X-ray diffraction.

The isostructural compounds with X = Br or I and R = Me contain a chain of the tetrahedral anions $[AgX_4]^-$, in which small differences are observed between the Ag–X bond lengths together with appreciable angular distortions (up to 20°). The structure of the analogous complex with R = Ph and X = Br is made up of the tetrahedral anions $[AgBr_4]^-$ joined together via the common edges of the tetrahedra to give an infinite chain.[139] The proposed mechanisms of the interaction of sulfoxides with

zerovalent transition metals in donor–acceptor media are based on the literature data concerning the chemistry of sulfoxides and the results of studies on the oxidation processes considered.[148–150]

An attempt has been made to describe the mechanism of the oxidative dissolution of metals.[16,17,140,146] It was initially suggested (see the bibliography in the relevant reviews[16,17]) that these processes proceed via the intermediate formation of reactive complexes between the oxidant and the solvent, which possess an enhanced ability to bind the electrons of the metal, facilitating thereby its oxidation. The mechanism of such a process has been tentatively represented as follows:

$$S + A \rightleftharpoons S\cdot A \rightleftharpoons [S^{\delta+}\cdot A^{\delta-}] + M^0 \rightleftharpoons$$
$$\rightleftharpoons M^0[S^{\delta+}\cdot A^{\delta-}] \rightleftharpoons M^+[S\cdot A^-] \rightleftharpoons M^+ + [SA^-] \rightleftharpoons \ldots$$

where S is the solvent and A the oxidant (electron acceptor). The role of the metals and oxygen in the oxidation processes considered has been discussed.[16,17] However, the evidence for the above mechanism is so far inadequate.

The concept of donor–acceptor electron-transport systems (DAETS) is therefore more attractive.[140,146] According to these ideas, dipolar onium compounds, simulating the intermediate products of the DAETS interaction, are formed in oxidising media. The interaction of onium compounds of the type $[Me_2Et\overset{+}{S}=O][BF_4^-]$, $[Me_2N\overset{+}{C}H-OEt][BF_4^-]$, and $[Me_3\overset{+}{S}=O]I^-$ with metallic copper has been investigated to demonstrate the oxidation of metals in nonaqueous media with formation of DAETS.[146] This led to the isolation of a series of complexes containing the metal in the +1 oxidation state—$[Cu^I(AN)_4]\cdot[BF_4]$, $Cu^I[Me_3S^+]_3I_4$, and Cu^IIPy—and in the +2 oxidation state—$[Cu^{II}(DMSO)_5][BF_4]_2$, $[Cu^{II}(DMSO)_4(AN)_2][BF_4]_2$, $[Cu^{II}(DMSO)_4\cdot AN\cdot H_2O][BF_4]_2$, and $[Cu^{II}(DMSO)_2\cdot AN\cdot DMF][BF_4]_2$. Mixed-ligand complexes containing DMSO, DMFA, and AN molecules simultaneously have been obtained from a solution of the $[Me_2Et\overset{+}{S}=O][BF_4^-]$–$Cu^0$DMSO DAETS system to which a mixture of DMFA and AN had been added. It is striking that some of the above complexes can be obtained also under the usual conditions involving the oxidative dissolution of copper. The structure of the complex $[Cu^I(AN)_4][BF_4]$ has been established by X-ray diffraction.

The complexes containing DMSO as a ligand are interesting because, as suggested by Epel'baum et al.[146] on the basis of IR spectroscopic data, three types of bonding of the DMSO molecule to divalent copper occur in them—via the oxygen and sulfur atoms and with participation of both donor centres. Since the commonest bonding between Cu^{II} and DMSO involves the coordination of the metal to an oxygen atom,[180] the above results[146] require additional evidence, in particular X-ray diffraction studies of the structures of divalent copper complexes of DMSO.

b. Synthesis of metal chelates

The inner complexes obtained in oxidative donor–acceptor systems in the presence of chelating ligand systems are represented by transition metal acetylacetonates,[16,130,151,179] carboxylates,[152] dimethylglyoximates,[142,143] 8-hydroxyquinolinates,[16,179] and dithiocarbamates.[142,143] The acetylacetonates $Co(acac)_2$ and $Fe(acac)_3$ are formed in the acacH–DMSO–BN oxidative system (where BN = benzonitrile) under a nitrogen atmosphere.[130] Atmospheric oxygen accelerates not only the dissolution of cobalt but also the formation of $Co(acac)_3$. The same complex has been isolated in the presence of triethylamine, which is not coordinated to the metal of the acetylacetonate considered. On the other hand, N donors such as pyridine and α,α′-bipyridyl (L) form with the acetylacetonate the adducts $M(acac)_2\cdot nL$, where M = Co or Fe and $n = 1, 2$. The complex $Cu(acac)_2$, obtained in an oxidative system incorporating a hydrogen halide, has been described.[16,179] The oxidative dissolution of yttrium in systems containing acetylacetone as the main component as well as acetone, ether, dioxane, acetonitrile, pyridine, α,α′-bipyridyl, DMSO, DMF, 2-pyrrolidinone, and acetic acid (AcOH) has been investigated recently.[151] Complexes having the same composition $Y(acac)_3\cdot 2H_2O$ have been isolated from Y–acac–Me_2CO (ether, dioxane, acetonitrile) mixtures. The complexes $Y(acac)_3\cdot H_2O\cdot Py$, $Y(acac)_3\cdot H_2O\cdot\frac{1}{2}Bipy$, $Y(acac)_3\cdot H_2O\cdot DMSO$, $Y(acac)_3\cdot\frac{5}{3}H_2O\cdot\frac{1}{3}DMF$, $Y(acac)_3\cdot\frac{5}{3}H_2O\cdot\frac{1}{3}PC$, and $Y(OAc)_3\cdot 2H_2O$ are formed in the acac–Py (α,α′-Bipy, DMSO, DMFA, PC, and AcOH) systems respectively.

Direct dissolution of zerovalent bismuth and antimony in the presence of an oxidant has been used to obtain the carboxylates of the above metals.[152] The reaction proceeds in accordance with the scheme

$$2M + 6HL + 3[O] \longrightarrow 2ML_3 + 3H_2O.$$

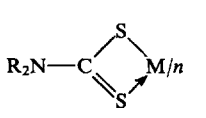
Bismuth formate and acetate (in the presence of atmospheric oxygen or H_2O_2 as oxidants) and antimony acetate and trifluoroacetate (in the presence of nitric acid, acetyl peroxide, or acyl nitrates) have been obtained in this way.

Coordination compounds are readily synthesised in oxidative metal donor–acceptor systems when dimethylglyoxime is used as the ligand.[16,17,130,179,182] Dimethylglyoxime is a classical chelating ligand.[3,12] Inner complexes of the type ML_2, where LH = dimethylglyoxime (DGl) have been obtained from it. However, the use of the method involving the oxidative dissolution of metals makes it possible to obtain not only the complexes ML_2, but also $MX_n(LH)_m$ and $MX_{n-p}(LH)_mL_p$. In addition, the mixed-ligand complexes $MX_n(LH)_m\cdot p$Solv, where Solv = DMSO or DMF, are known. A complex of the first type is formed in the Ni^0–LH–AN–CCl_4 system.[179] Coordination compounds of the second type are represented by the complexes [CuCl.LH] obtained in the Cu^0–LH–EtOH–CCl_4 system;[17,179] compounds of the third type comprise the complexes $[CoX_2(LH)L]$, where X = Cl, Br, or I.[130,179,182] Their formulae have been expressed in the form $H[CoX_2L_2]$. One of the complexes of this type described (X = Cl) is diamagnetic,[179] which indicates that it contains cobalt in the +3 oxidation state.

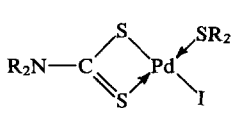
Solvated complexes include a series of compounds, for example $[CuCl_2(LH)_2DMSO]$[179] and $[NiCl_2(LH)_2]_n\cdot DMF$.[17,130] The preparation of complexes with a fully preserved ligand system (LH) is of fundamental importance for the coordination chemistry of chelating ligands incorporating an acid EH group, to which much attention has been devoted recently.[7,183]

Copper[142] and palladium[143] dimethyldithiocarbamates have been synthesised in oxidative systems containing FA, DMF, and DMSO or PC, CI_4, and tetramethylthiuram (or its cation). A series of copper complexes containing apparently both copper(II) and copper(III)—$[CuI(Me_2NCS_2)_2]CHI_3$, $[Cu_2I(Me_2NCS_2)]$, $[Cu_2I_4(Me_2NCS_2)_3]$, $Cu_2SCN(Me_2NCS_2)_2\cdot H_2O$, $[Me_2NH_2]\cdot[CuCO_3(Me_2NCS_2)]\cdot Cu_2S$, and $[Cu_3I_2(Me_2NCS_2)_5]$—and palladium complexes—$PdI[Me_2NCS_2]$, $Pd[Me_2NCS_2][Me_2S]$, and $Pd_3I_3[Me_2NCS_2]_3[Me_2S]$—have been obtained.

The presence of the dimethyldithiocarbamate fragment in the complexes considered has been demonstrated by IR spectroscopy and, in the case of the coordination compounds **42** (M = Cu^{2+}, $n = 2$)¶ and **43**, by X-ray diffraction.[142,143]



42



43

R = Me, Et.

¶ Complex **42** has been obtained on slow sublimation of the compound $[Cu_3I_2(Me_2NCS_2)_5]$ at 473–493 K.

The data presented in this section indicate the possibility, in principle, of synthesising inner complexes by the oxidative dissolution of metals in donor–acceptor media. However, few chelating ligand systems are known for this type of the direct synthesis of metal complexes.[3,6,7,9,10,182]

c. Synthesis of dinuclear and polynuclear complexes

The polynuclear complexes synthesised as a result of the oxidative dissolution of zerovalent metals in donor–acceptor systems are of undoubted interest from the standpoint of the chemistry of dimetallic and polymetallic coordination compounds.[29,97,184–186] The dinuclear and trinuclear copper compounds **39–41** as well as ionic iron, palladium, gold, and silver compounds containing several metal atoms in the molecule may be assigned to complexes of this type.

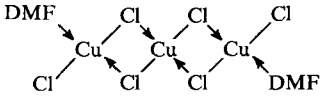
The advantage of direct synthesis is the possibility of the specific preparation of complexes with different contents of metal atoms. Thus, by varying the component ratios in the Cu^0–DMF–CCl_4 system, di-, tri-, and tetra-nuclear cluster structures have been obtained.[181] The reactions are described by the following scheme:

$$Cu^0 + DMFA + CCl_4 \xrightarrow{[DMFA]\approx[CCl_4]\gg[Cu]} [Cu_2Cl_2(DMFA)_4]_4 \quad \mathbf{39}$$

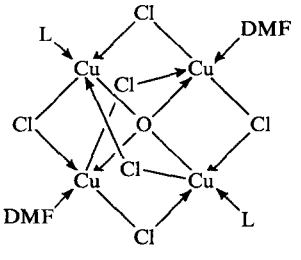
$$Cu^0 + DMFA + CCl_4 \xrightarrow{[DMFA]\approx[CCl_4]\approx[Cu]} [Cu_3Cl_6(DMFA)_2] \quad \mathbf{44}$$

$$Cu^0 + DMFA + CCl_4 \xrightarrow{[Cu]\ll[DMFA]\ll[CCl_4]} [Cu_4OCl_6(DMFA)_2] \quad \mathbf{45}$$

The structures of complexes **39**, **44**, and **45** have been demonstrated by X-ray diffraction.[118,181]



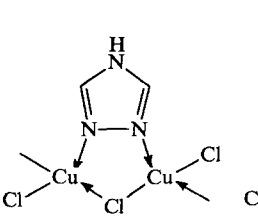
44



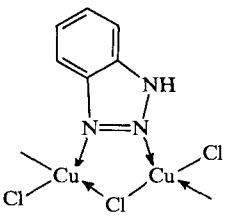
45, L = DMF,[181] Me_2NH[171]

Clusters with the same metal core and a structure similar to that of complex **45** have been described.[171] Their general formula is $Cu_4OCl_6 \cdot n(CH_3)_2NH \cdot m$Solv, where $n = 4$, $m = 0–2$, and Solv = MeOH or DMSO.

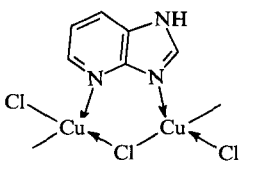
The bimetallic compounds **46–48** with two copper atoms are formed in the Cu^0–DMF–L system, where L represents nitrogen-containing heterocycles: 1,2,4-triazole, benzotriazole, and adenine.[137] We emphasise that the authors[137] attributed an erroneous formula to complex **48**, having included in the coordination the nitrogen atom of the NH-pyrrole fragment, which is known[29,187–190] to lack donor properties almost completely.



46



47



48

However there is no doubt about the bridging function of the triazole ligand in complexes **46** and **47**: this mode of coordination of triazoles and their derivatives has been unambiguously demonstrated by X-ray diffraction (see the bibliography in the review of Garnovskii et al.[190])

In conclusion we may point out that the physicochemical properties and the structures of the coordination compounds described here have been relatively little investigated. This remark applies particularly to the fact that the magnetic properties of dinuclear and polynuclear complexes, many of which (for example, complexes **39–41**, **44**, and **45**) are of undoubted interest as magnetic-exchange clusters, have been scarcely studied at all.

IV. Electrosynthesis of coordination compounds

Electrosynthesis is not only the oldest[11,12] but also one of the easiest preparative methods of synthesis of coordination compounds.[4,17,22–24,27,191–194] Electrosyntheses are carried out using dissolving anodes or cathodes, reactions involving the former type of electrodes being particularly widely used. The essential feature of the electrosyntheses of complexes are described by the simple scheme[22]

$$M^+ + L + e^- \longrightarrow [M...L].$$

If the ligands LH with an acid EH group (E = NR, O, S, Se) participate in the process, the following reactions take place:[17]

$$M \xrightarrow[-ne]{} M^{n+},$$

$$LH \longrightarrow L^- + H^+,$$

$$M^{n+} + nL^- \longrightarrow ML_n.$$

In the last case, the mechanism presupposes the anodic dissolution of the metal with subsequent complex formation.[4,24]

$$\text{Anode: } nL^- + M \longrightarrow ML_n + ne,$$

$$\text{Cathode: } nHL + ne \longrightarrow nL^- + \tfrac{1}{2}nH_2.$$

Thus the electrochemical reactions do not require the use of oxidants or reductants. This makes them definitely attractive.[4] Other important advantages of the electrosynthesis of coordination compounds over the usual synthetic methods consist in the possibility of regulating them, in the preparation of compounds otherwise difficult to synthesise, and in carrying out the processes under mild conditions with high yields.[17,27] Alcohols, THF,

DMF, DMSO, acetonitrile, pyridine, propylene carbonate, sulfolane, diglyme, and hexamethylphosphoramide (HMDA) are most widely used as solvents in electrosyntheses. All types of coordination compounds can be obtained with the aid of electrosynthesis, but the method is most widely applied at the present time in the synthesis of molecular and inner complexes.

a. Electrosynthesis of molecular complexes

The molecular complexes obtained by electrosynthesis are represented by diverse adducts of organic N, P, and O donors with metal halides (pseudohalides) and organometallic halides.[4,23,24,27,195-199] The former have the general formula $MX_n \cdot pL$ and the latter have the formula $R_mMX_{n-m} \cdot pL$, where M are Group I (Cu, Ag, Au),[27,197] Group II (Zn, Cd),[23,27,199] Group III (Ga, In),[23,27] Group IV (Sn, Pb, Ti, Zr, Hf),[23,24,195] Group V (V),[23] Group VI (Cr),[23,196] Group VII (Mn),[24] and Group VIII (Co, Ni, Pd)[23,27,198] metals, L = acetonitrile, pyridine, bipyridyl, *o*-phenanthroline, ethylenediamine (En), imidazole, PR_3, $R_2PCH_2CH_2PR_2$,[23,27] DMSO, dioxane, or urea,[23,27] R = alkyl or aryl, X = OH,[199] halogen,[23,27] CN,[23] NCO,[197] or ClO_4,[197,198] and m, n, $p = 1-3$.

Under the conditions of electrosynthesis with anodic dissolution of cadmium in acetonitrile solution containing *N*-(hydroxyethyl)salicylideneimine and phenanthroline, the adduct $Cd(OH)_2 \cdot (Phen)_2$ was obtained[199] instead of the azomethine chelate.[200] The structure of this molecular complex was demonstrated by X-ray diffraction: it was an octahedral structure with the CdN_4O_2 coordination unit.[199] Ionic complexes of the cationic[4,23,24,195,197,198] and anionic[23,24,195,196] type can be assigned to the same type of coordination compounds. The cationic complexes are represented by a fairly wide range of compounds[23,27] synthesised by the anodic dissolution of metals in organic solvents containing strong inorganic acids — HBF_4 or $HClO_4$. Ammonium salts of perchloric acid also serve as a source of perchlorate anions (see, for example, McAuliffe and coworkers[197,198]).

A series of cationic complexes with the general formula $[ML_n][BF_4]_m$, where L = acetonitrile or DMSO, $n = 4$, 6, and $m = 2$, 3, have been obtained by the electrolytic dissolution of metals (Zn, Cd, In, Ti, V, Cr, Co, Ni, Fe) in acetonitrile or DMSO solution in the presence of HBF_4.[23,27] The electrochemical dissolution of the copper anode in acetonitrile in the presence of 2,2′-bipyridyl, 2(1*H*)-pyridone, and tetramethylammonium perchlorate leads to isocyanatobis(2,2′-bipyridyl)copper(II) perchlorate $[Cu(C_{10}H_8N_2)_2(NCO)]ClO_4$. According to X-ray diffraction data,[197] the cation of the complex considered is a square pyramid with the isocyanate group at the apex. The latter is coordinated to copper via the nitrogen atom, which is of interest for the consideration of the ambident binding of pseudohalide ions.[180,201] Electrosynthesis with a cobalt anode under the same conditions in the presence of 1,10-phenanthroline promotes the formation of the complex $[Co(CO_3)(Phen)_2] \cdot ClO_4$.[198] According to X-ray diffraction data, the cation of this complex has an octahedral structure as a result of the bidentate binding of the phenanthroline ligand (N,N-coordination) and the carbonate ion (O,O)-coordination.[198]

Among the anionic complexes, compounds of the type $[Et_4N]_m[MBr_4]$, formed during electrosynthesis with participation of zerovalent metals, bromine, and tetraethylammonium bromide in solution in a benzene–methanol mixture, have been described.[23,24] The metals employed were Au, Cd, In, Sn, Ti, Hf, Th, Co, Ni, and Fe. The adducts of metal thiolates with N, P, and S donor ligands may be assigned to molecular complexes.[202-205] Thus electrolysis at a copper anode in acetonitrile solution with Et_4NCl as the supporting electrolyte in the presence of *o*-methylthiophenol and 1,10-phenanthroline leads to the formation of the complex $[Cu(SC_6H_4Me\text{-}o)(Phen)]_2 \cdot AN$, the structure of which has been demonstrated by X-ray diffraction.[203] Under the conditions of galvanostatic electrolysis in acetone or acetonitrile, a series of complexes having the general formula $M(SR)_2L_2$, where M = Co or Ni, R = Ph, 2,3,5,6-F_4C_6H, 3-MeC_6H_4, or 2-$C_{10}H_7$, and L = *o*-Phen or Bipy have been obtained.[204] Magnetochemical measurements {μ_{ef} = 2.70 μ_B for the complex $[Co(SPh)_2(Phen)_2]$ and μ_{ef} = 3.30 μ_B for the nickel analogue} and the compositions of the complexes indicate an octahedral configuration. The occurrence of the latter has been unambiguously demonstrated by X-ray diffraction for the cation of the complex $[Co^{III}(SPh)_2(Phen)_2]ClO_4$.[204] Adducts having the general formula $CuSR \cdot nL$, where R = Ph, *o*-, *m*-, or *p*-MeC_6H_4, or 2,3,5,6-F_4C_6H, L = $Me_2NCH_2CH_2NMe_2$, PhNCS, Bu^tNCS, or PPh_3, and $n = 0.5$, 1.5, 2, have been synthesised[205] by the electrochemical dissolution of copper in acetonitrile solutions of the thiols and the ligands (L).

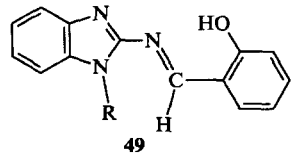
b. Electrosynthesis of π-complexes

Compilations of data on the electrochemical synthesis of transition metal π-complexes have been published.[4,22,24,27] They cover the electrosyntheses of metal complexes of cycloalkenes [for example, the copper complex of cyclooctadiene $Cu(COD)_2ClO_4$,[27] the nickel derivative of cyclooctatetraene Ni(COT),[22] and the bis(η^5-cyclopentadienyl) metal derivatives of type **11** (M = Fe, Mn, Ni,[4,22,27])]. Ferrocene **11** (M = Fe) was first obtained electrochemically by the dissolution of an iron anode in a dimethylformamide solution of cyclopentadienylthallium.[4] The analogous manganese and nickel complexes have been synthesised by the electrolysis of the lithium, sodium, or cadmium salts of cyclopentadiene in solution in THF.[4] However, it was subsequently demonstrated that the metallocene complexes can be obtained directly from cyclopentadiene and its derivatives.[206,207] The electrosynthesis of the type **11** and **15** metallocene complexes from CH acids having the general formula RH, where R = cyclo-C_5H_5, MeC_5H_4, 2,4-$Me_2C_5H_3$, C_5Me_5, indenyl, or fluorenyl, is therefore of special interest.[207] It has been shown that the π-complexes R_2M [207] (R = C_5H_5 or 2,4-$Me_2C_5H_3$ and M = Fe, Ni, Co, or Zn; R = MeC_5H_4 or fluorenyl and M = Fe or Ni; R = indenyl and M = Fe) may be obtained by electrolysis at soluble anodes (M = Fe, Co, Ni, Cu, Zn) and a platinum cathode in solutions in acetonitrile (AN–$MeOCH_2CH_2OMe$ and AN–THF with Bu_4NBr as the supporting electrolyte). In addition, the cyclopentadienyl π-complexes $(C_5H_5)CuPPh_3$, $[Co(C_5H_5)_2]Br$, $[Co(C_5H_5)_2(CoCl_4)]$, and $[Co(C_5H_5)_2(CoBF_4)]$ have been synthesised.

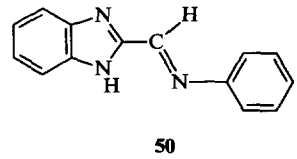
The above examples of electrosynthesis indicate the limited applicability of this method in the preparation of metal π-complexes and this situation has persisted to this day.

c. Electrosynthesis of metal chelates

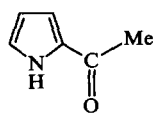
Only individual chelating ligands have been used in the electrosynthesis of inner complexes until quite recently: dimethylglyoxime,[4,12,17,27] β-diketones,[17,23,27] Schiff bases **49** and **50**,[4,17,24,27] azoles,[4,17,27] *o*-hydroxyphenylazoles and benzazoles **29**,[17,27] 2-acetylpyrrole **51**,[23] and 3-hydroxy-4-pyrone **52**.[23]



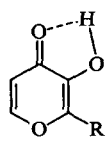
49



50



51

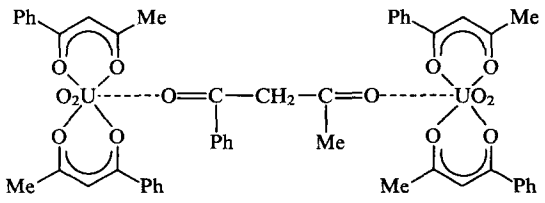


52

Electrosyntheses of inner complexes comprising metallocycles with different numbers of members [ring atoms] and with different ligand environments (N, O, S) have now been achieved.

Among chelates with a six-membered metallocycle, mention should be made of the complexes of β-diketones [36,195,209-211] and azomethines [200,212-223] which have been obtained electrochemically. Thus the electrosynthesis of cadmium,[209] thorium,[195] and dysprosium [210] β-diketonates has been described. The structure of the adduct $Cd(acac)_2$.Phen has been demonstrated by X-ray diffraction.[209] Systematic studies[36] have shown that β-diketonates having the compositions ML_2 (M = Ni), ML_3 (M = Al, In, Co, Fe, Ti, Zr), ML_4 (M = Zr, Hf), ML_2·Solv (M = Ni, Fe), ML_3Cl (M = Ti, Zr), $TiL_2(OMe)_2$, and ZrL_3OMe are formed in satisfactory yields from a wide variety of β-diketones and their fluoro-derivatives under the conditions of electrosynthesis. These chelates have been synthesised from liquid β-diketones or their 15%-20% solutions in methanol, ethanol, acetonitrile, and DMF with LiCl, LiBr, NH_4Cl, or Bu_4NBF_4 as the supporting electrolytes.

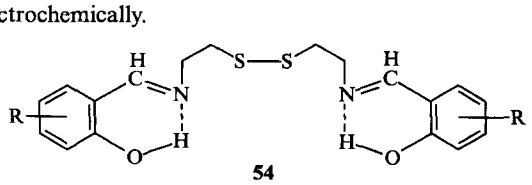
The electrochemical oxidation of uranium leads to chelates of the type UL_4 and UO_2L_2 (LH = β-diketone).[211] Apart from these complexes, the compound $UO_2L_2(HL)_{0.5}$ was isolated and the structure **53** was attributed to it. It was justified by IR spectroscopic data,[211] but in our view this requires more rigorous evidence.



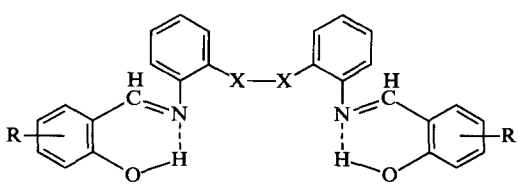
53

The inner complexes of Schiff bases have been obtained by electrosynthesis in an acetonitrile solution of the ligands using a platinum electrode (cathode) and an anode consisting of the complex-forming metal.

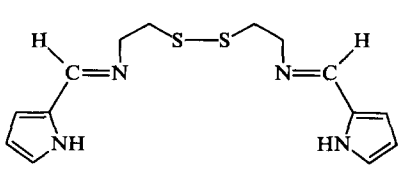
Together with the complexes containing alkyl or aryl substituents at the nitrogen atom of the azomethine group (R = Pr^i, Bu, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$),[200] a large number of *o*-hydroxyazomethines containing the coordinatively active fragments **28** (R = 2-Py,[212,214] CH_2CH_2Py-2,[213,215] $CH_2CH_2NMe_2$ [213]), **54**,[217] **55** (X = S,[218,220,223] Se [222]), **56**,[216] and **57** [216] at the above nitrogen atom have been synthesised electrochemically.



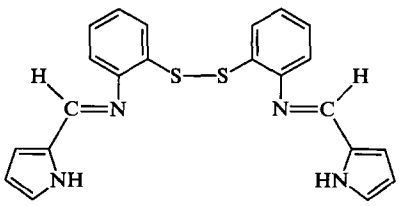
54



55 (X = S, Se)



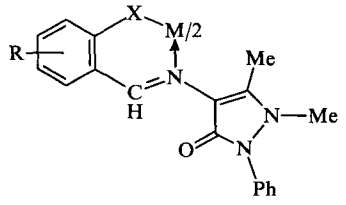
56



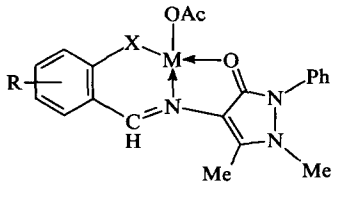
57

Analysis of X-ray diffraction data shows[214] that the nitrogen atom of the pyridine ring in the copper complex of the ligand **28** (R = 2-Py-3-Me, R′ = 5-OMe) is not involved in the coordination, i.e. this formally tridentate ligand system behaves as a bidentate system and the metallocycles MN_2O_2 involving the phenolic oxygen and the azomethine nitrogen are formed in the complexes described. This situation is characteristic of the copper complex obtained from the ligand **28** [R = CH_2CH_2Py, R′ = 4,6-$(OMe)_2$]. The complex has a square-planar structure with a non-coordinated nitrogen atom of the pyridine ring.[213] At the same time, X-ray diffraction data indicate the involvement in the coordination of the pyridine ring in the nickel complex of *N*-(2-pyridylethyl)salicylideneamine **28** (R = CH_2CH_2Py), which leads to the NiN_4O_2 octahedron.[215] The results described are of undoubted value for the understanding of the problem of competitive coordination in a series of formally tridentate ligand systems — different ways of binding the latter depending on the electronic configuration of the metals and the structure of the complexes formed by them.[7,208,224-226]

Azomethines containing an antipyrine fragment at the nitrogen atom can be assigned to the same class of ambident ligand systems.[219] Inner complexes of type **58** (X = O) having the composition ML_2 have been obtained from them by the electrochemical method.[219] Both the involvement[227] and the lack of such involvement of the oxygen atom of the carbonyl group[219,227] in coordination, apart from the phenolic oxygen and the azomethine nitrogen, have been postulated in such inner complexes. In this case, the electrochemical method has the advantage that, when it is employed, complexes **58** with the composition ML_2 alone are formed, whereas under the usual conditions involving the use of the metal acetates coordination compounds of two types were isolated: ML_2 (compounds **58**) and MLAcO (compounds **59**).[227]



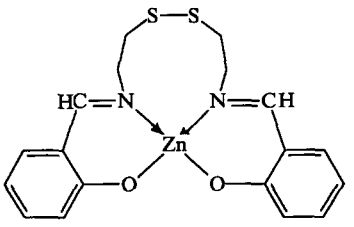
58



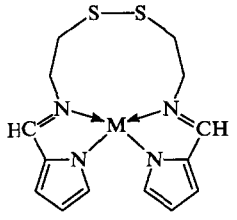
59

The formally hexadentate ligand systems **54**-**57** behave in an unusual manner under the conditions of electrosynthesis. The disulfide structure of the ligand **54** remains unaltered in the complex formation reaction.[217] The structure **60** has been proposed for the complex. The coordination polyhedron is a tetrahedron formed with participation of the phenolic oxygen atoms and azomethine nitrogen atoms.[217]

The complexes ML **61**, obtained from the ligands **56** and **57**, evidently have a similar structure without the involvement of sulfur atoms in the coordination.[216] In the remaining cases, the dissociation of the X–X (X = S, Se) bonds and the formation of a complex with a comparatively rarely encountered N,X- or N,O,X-ligand environment are observed under the conditions of electrolysis.[7,208]

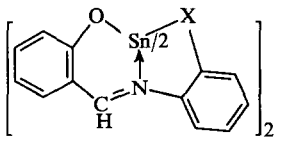


60

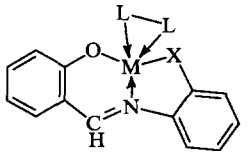


61 (M = Ni, Cu, Zn, Cd)

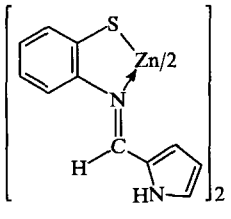
It has been demonstrated by X-ray diffraction that two types of complexes are formed from compound **55**—complexes **62** (X = S,[218] Se[222]) and **63** (M = Zn, L–L = 2,2′-Bipy;[220] M = Co, L–L = *o*-Phen[223]).



62



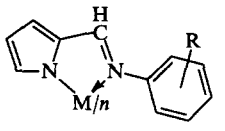
63



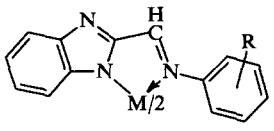
64

The dissociation of the disulfide bond in the ligand **57** (LH_2) results in the formation of the complex $Zn(LH)_2$ **64**, which is, according to X-ray diffraction data, a complex of pyrrolemethylidene-*o*-aminothiophenol, in which the pyrrole fragments are not involved in coordination.[216] The results described expand the possibilities for the synthesis of coordination compounds containing in the coordination units the N and S(Se) donor atoms, in which considerable interest has been shown recently.[7,208,224–227] In this connection, we may note that complexes of type **64**, containing the five-membered coordination units MN_2X_2 (X = S, Se), have been synthesised fairly long ago using metal salts or were obtained by template synthesis.[7,208]

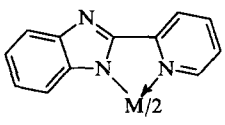
Coordination compounds of another type (compounds **65**–**67**) with the five-membered metallocycle MN_4 have been obtained by electrolysis from azomethines derived from the aldehydes of five-membered nitrogen heterocycles—pyrrole-2-aldehyde[228–237] (complex **65**), benzimidazole-2-aldehyde[4,24] (complex **66**), and 2-(2′-pyridyl)benzimidazole[4,24,27] (complex **67**).



65

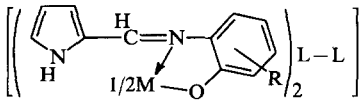


66



67

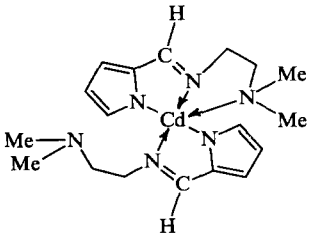
Complexes **65** are classical,[7,208,238–240] but the application of electrosynthesis not only made it possible to expand the range of such compounds but also helped to refine their structures and to elucidate questions concerning the competitive reactions of azole ligand systems with zerovalent metals. X-Ray diffraction data for the pyrrolealdiminates **65**, obtained under the conditions of electrosynthesis (solution in acetonitrile), indicate that the copper complex **65** ($M = Cu^{2+}$, R = *p*-Me, $n = 2$) contains the tetrahedrally distorted metallocycle CuN_4,[229] while the trivalent cobalt chelate **65** ($M = Co^{3+}$, R = *o*-Me, $n = 3$) is an octahedron with the CoN_6 coordination unit.[229] X-Ray diffraction data has shown that an analogous ligand environment MN_6 is characteristic of the adducts of the nickel chelate **65** (M = Ni, R = H, $n = 2$) and the cadmium chelate **65** (M = Cd, R = 2-OMe, $n = 2$) with bipyridyl.[231] Competitive coordination and the formation of three types of structures are characteristic of the ambident ligand systems of the pyrrolealdimine type: with participation of the iminophenol fragment (complex **68**),[232,235,237] with participation of all the nitrogen donor atoms (complex **69**),[233] and with participation of the iminoamine group (complex **70**).[236]



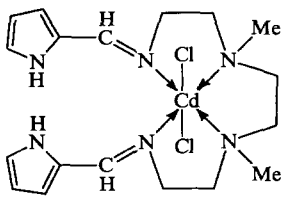
68

R = H, 4-Me, 5-Me, 5-Cl, 3,5-Me_2;

M = Co, Ni, Zn; L–L = acetonitrile, Bipy, *o*-Phen



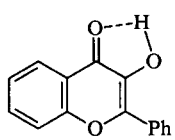
69



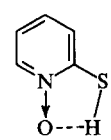
70

We emphasise that the pyrrole fragment in complexes **68** and **70** is not involved in coordination. This may be associated with the electrosynthesis being carried out in solution in acetonitrile and with the presence in the reaction medium of powerful chelating N-donors such as 2,2′-bipyridyl, 1,10-phenanthroline, or a macrocyclic fragment. A definite confirmation of this hypothesis is provided by the finding that, when the electrochemical synthesis is carried out with participation of ligands of the azole series having a lower NH acidity than pyrrole in an alcoholic medium,[241] the *N*-metal-substituted complexes **66** and **67** are formed.[4,24,27,242] A characteristic feature is that *N*-metal substitution is observed in the electrochemical synthesis in methanol (ethanol) and for the azoles themselves.[27,242]

Among other metal chelates with a five-membered metallocycle, one may mention complexes synthesised electrochemically from bidentate oxygen-containing donor ligands **52** (R = Me)[243] and **71**,[244] as well as pyridine-2-thiol *N*-oxide **72**.[245] The presence of five-membered metallocycles of type MO_4 and MO_2S_2 in these complexes has been demonstrated by X-ray diffraction.[243-245]

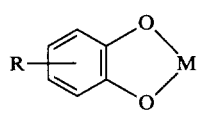


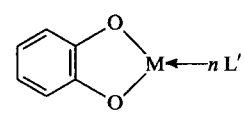
71



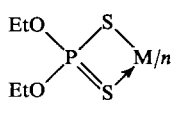
72

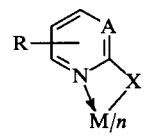
The electrochemically synthesised inner complexes with four-membered chelate units are represented by complexes of catechols (complexes **73**)[246-248] and their adducts with N- and O-bases (complexes **74**),[246-248] dialkylthiocarbamates (complexes **42**),[249] dialkyl phosphorodithioates (complexes **75**).[249] 2-pyridinol [complex **76** (X = O, A = CH)],[250-252] pyridine-2-thiol [complex **76** (X = S, A = CH)], pyrimidine-2-thiol [complex **76** (X = S, A = N)],[255-258] and their molecular adducts with azines and bisazines (complexes **77**).[256-258]

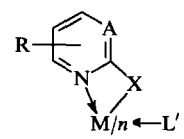




73 (R = H, cyclo-C_4H_4, 3,4,5,6-Br_4) **74**





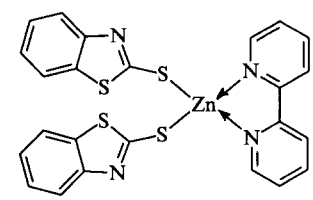


75 **76** **77**

A = CH, N; X = O, S

Complexes **73** and **74**, having the compositions ML and ML·*n*L′ respectively (M = Zn,[246] Cd,[246] Sn;[247] LH_2 = catechols; L′ = Bipy, Phen, Py, DMSO; *n* = 1, 2), have been obtained in acetone with the above metals as the anode. In the case of the indium anode, the complex [In(LH)], in which only one of the two phenolic hydrogen atoms of 1,2-dihydroxybenzene is substituted by the metal, is formed under the same conditions.[248] The electrosyntheses of the complexes of dialkyldithiocarbamates [complexes **42** (R = Me, Et)] and diethyl phosphorodithioates (complexes **75**) have been carried in solution in acetonitrile with silver, zinc, cadmium, indium, thallium, cobalt, nickel and iron anodes.[249] When 1,10-phenanthroline (L′) was added to the reaction mixture, the adducts ML_n·Phen (M = Ga, V, Mn, Co, Fe) were obtained. The complexes were characterised by elemental analysis, the results of which indicated[249] the formation of the inner complexes ML_2 **42** and **75** (*n* = 2), ML **42** (M = Ag, Tl; *n* = 1) and **75** (M = Cu, Tl, Ga; *n* = 1), and ML_3 **42** (M = Fe, In, Tl; *n* = 3) and **75** (M = Co; *n* = 3). The ^{31}P NMR spectra of compound **75** were also obtained. Metal chelates of divalent iron, copper,[250] zinc and cadmium,[251] and cobalt and nickel[252] have been obtained from 2-pyridinone under the conditions of electrosynthesis and isolated. In our view, the results of magnetochemical measurements for complexes **76** and **77** (X = O, A = CH) are of greatest interest. In particular, the values of μ_{ef} for the copper complexes $[CuL_2]\cdot 3H_2O$ and $[CuL_2\cdot Phen]\cdot 3H_2O$ are 1.5 and 2.4 μ_B respectively[250] and may be associated with exchange interactions of the antiferromagnetic and ferromagnetic types.[98]

The heteroarene-2-one and heteroarene-2-thione ligands are known to form several types of complexes.[253,255,256,258,259] X-Ray diffraction data have shown that structures in which the MN_2S_2 metallocycle is a fragment are characteristic of the adducts of pyridine-2-thiol [complexes **77** (A = CH, X = S: M = Ni,[253] L′ = Bipy, R = H, *n* = 2; M = Zn,[254] L′ = Phen, R = H, *n* = 2)] and pyrimidine-2-thiol [complexes **77** (A = N, X = S: M = Ni,[255] L′ = Bipy, R = H, *n* = 2; M = Cd,[256] L′ = Phen, R = H, *n* = 2; M = Zn,[257] L′ = Py, R = 4,6-Me_2, *n* = 2; M = Ni, Cd,[258] L′=Bipy, Phen, *n* = 1)]. The metallocycle is formed via the endocyclic nitrogen atom of the pyridine type and the thiol sulfur atom. The adduct-forming ligand (L′) lead to octahedral (Bipy, Phen)[253-256,258] or trigonal bipyramidal (Py)[257] configurations. On the basis of magnetochemical data, an octahedral structure has been attributed to the adduct of the nickel complex of benzothiazole-2-thione with 2,2′-bipyridyl (μ_{ef} = 3.4 μ_B) and 1,10-phenantholine (μ_{ef} = 2.9 μ_B).[259] However, the magnetic criterion can hardly be used for an unambiguous choice between octahedral and a tetrahedral coordination. The occurrence of the latter for the adducts of benzothiazole-2-thiolates is entirely probable when account is taken of the results of X-ray diffraction studies on the tetrahedral complex **78**.[259]



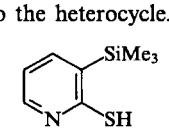
78

The structure of compound **78** is interesting also because it does not involve the formation of a four-membered metallocycle of type MN_2S_2 characteristic of all the complexes of 2-azinols and azine-2-thiols described above.

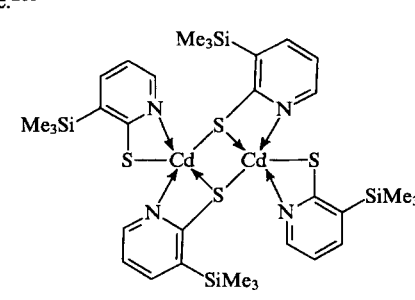
b. Electrosynthesis of bimetallic and polymetallic complexes

The few existing examples of the electrosynthesis of polymetallic complexes show that this method is promising.

A cadmium complex CdL_2 has been obtained under the conditions of the electrolysis (acetonitrile, Et_4NClO_4) of pyridine-2-thiol **79** with a trimethylsilyl substituent attached to the heterocycle.[260]



79



80

According to X-ray diffraction data and in contrast to the inner complexes **76–78**, this compound has the dimeric structure $[CdL_2]_2$ **80**, in which the cadmium atoms involved in a trigonal bipyramidal coordination are linked by sulfide bridges.[260] One cannot rule out the possibility that the nickel and zinc complexes of pyridine-2-thiol **79** have similar structures.[260] The tetranuclear complex $[Cu_4(\mu\text{-}C_5H_{11}S)_4(Ph_2PCH_2PPh_2)_2]$ has been synthesised by the reaction of copper with pentyl sulfide and bis-(diphenylphosphino)methane under the conditions of electrolysis (acetonitrile, Et_4NClO_4).[261] According to X-ray diffraction data, a new type of eight-membered cyclic structure Cu_4S_4, in which the copper atoms are linked by sulfide bridges, is formed in this complex.[261]

Complexes $[Et_3NH]^+[M_4(SPh)_{10}]^-$ with the tetranuclear anions, where M = Zn or Cd, have been obtained by direct electrochemical synthesis with participation of zinc (or cadmium), thiophenol, and triethylamine in acetonitrile with Et_4NClO_4 as the supporting electrolyte.[262] A bicyclic structure with terminal coordination of zinc and with the bridging SPh fragments is produced in the anion with M = Zn.[262] X-Ray diffraction studies have shown that the electrochemical synthesis makes it possible to create two types of hexanuclear cluster structures on the basis of 4,6-dimethylpyrimidine-2-thione: for Cu_6L_6, an octahedral cluster with six Cu atoms, each of which is trigonally coordinated to one N atom and two S atoms of three different ligands,[263] and for Cd_6L_6 a cyclic system with six cadmium atoms linked by sulfide bridges.[258] Since the electrosyntheses of both clusters considered were carried out under the same conditions (acetonitrile, Et_4NClO_4), one may postulate that the decisive factor in the creation of the structures indicated is the ability of the complex forming species (Cu^+, Cd^{2+}) to form different polyhedra.

The possibility of obtaining clusters from the complexes synthesised electrochemically is of undoubted interest. Thus the octanuclear cluster $[Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_{11}]$ has been synthesised from the univalent copper complex of pentyl sulfide obtained under the conditions of electrosynthesis in acetonitrile using a copper anode[203] and carbon disulfide.[264] The interaction of the electrochemically synthesised adduct of the cadmium complex of pyrimidine-2-thione with 1,10-phenanthroline [complex **77** (M = Cd, A = N, L′ = Phen, R = H, n = 2)] and divalent copper hexafluoroacetylacetonate (F_6acac) in acetonitrile leads to the tetraheteronuclear complex $[Cu_2(Phen).(\mu^3\text{-}L)_2Cd_2(F_6acac)_2]\cdot 2AN$,[265] where L = the trianion of 1,3,5-tris(trifluoromethyl)cyclohexane-1,3,5-triol.

V. Other methods for the direct synthesis of coordination compounds

Special mention should be made of the synthesis of complexes from zerovalent metals in a melt[10,17,113] and under the conditions of boundary friction of the metals (tribochemical reactions).[17–19,266–279] These methods were segregated in a separate section because syntheses in the melt and tribochemical reactions may be regarded as solid-phase processes accompanied by transition to the liquid phase or (and this cannot be ruled out) may be regarded as processes occurring in a plasma.

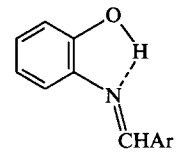
Virtually all the complexes obtained by these methods are inner complexes. Copper, nickel, cobalt, and zinc react exceptionally vigorously with fused salicylidene-*o*-aminophenol **28** (R = C_6H_4OH-*o*, R′ = H), *o*-hydroxyphenyl-1,2,4-oxadiazoles **30**, and 8-hydroxyquinoline.[17] The yields of the inner complexes in these syntheses are fairly high (up to 60%–70%). Benzoylacetone and acetoxime react with copper in the fused state, but the reactions are slow and afford low yields of the metal chelates. Macrocyclic complexes, for example metal-phthalocyanines **38**, have been synthesised in a melt of a mixture of solid reagents (the metal, *o*-phthalodinitrile or phthalimide, as well as certain other derivatives).[10]

The tribochemical method of synthesis of coordination compounds is based on the preparation of inner complexes under the conditions of boundary friction in a reactor which is a modification of the end-face friction machine.[17–19] The friction couple is made from the complex-forming metal (M^1 = specimen) and its alloy (M^2 = counterbody). The tribochemical reactions are described as follows:[19]

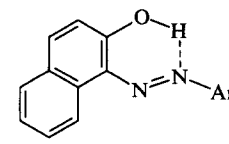
$$M^1 + n\,LH \xrightarrow[\text{friction}]{M^1/M^2} M^1L_n + \tfrac{1}{2}nH_2\,.$$

A scheme has been proposed for the formation of complexes under the conditions of boundary friction via chemisorption processes in which an electron is transferred from the metal atom to the ligand and the adsorbed molecules are rearranged in conformity with the geometry of the complex.[17–19] Another important factor governing the successful tribosynthesis of coordination compounds is the appearance in the region of the friction contact of zones with local temperatures in excess of 1273 K. This leads to the formation of a triboplasma in the microvolumes in which the complex formation reactions take place.[19,267]

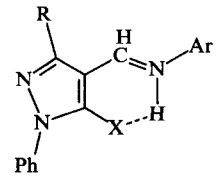
Ideas concerning tribocoordination and the influence of external conditions on the latter have been developed in a number of studies.[19,272,274,277–279] It has been established that a necessary condition for tribocoordination is the presence of acid HX groups (X = NR, O, S) in the molecules of the organic compounds used as ligands.[19] By virtue of their presence, the tribosynthesis of inner complexes has been achieved with participation of salicylideneaniline and its derivatives **28**,[17–19,267,273,276] arylidene-*o*-aminophenols **81**,[17–19] arylazonaphthols **82**,[17–19,266] azomethines **83**,[17–19] and azo-derivatives of the pyrazole series **84**.[17–19]



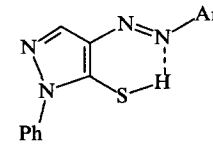
81



82

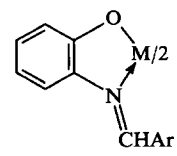


83 (X = S, Se)

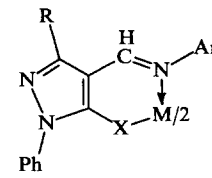


84

Among the complexes obtained from the ligand systems **81–84**, the arylidene-*o*-aminophenoxides **85**, which are formed readily under the conditions of tribosynthesis, require special consideration.[17–19] Under the usual conditions, they are obtained from metal salts with fairly considerable difficulty owing to the hydrolysis of the azomethine linkage.[7,280]



85



86

The successful tribosynthesis of the metal chelates **86** from the ligands **83**, in which a constant interest has been shown in connection with the detailed characteristics of their

stereochemistry and stereodynamics, may be noted.[7,208,281] Inner complexes of other classes of ligand systems have also been obtained under the conditions of boundary friction. Thus the tribosyntheses of metal β-diketonate chelates, in particular the complexes of 3,3,3-trifluoro-1-thienoylacetone, have been described.[270,275]

The tribochemical method has definite advantages, since it makes it possible to obtain complexes over a wide temperature range in polar and nonpolar media. At the same time, the low yields of the final products (see, for example, Kuzharov et al.[18]) are its significant disadvantage. Because of this, the prospects for the application of the tribochemical method in modern synthetic coordination chemistry are obscure.

Definite advances have been made using ultrasound for the synthesis of complexes from zerovalent metals.[282–284] The inner complexes of 3*d* transition metals with salicylideneanilines of type **28** have been obtained with the aid of ultrasound.[282–284] However, much work still remains to be done on the improvement of this type of activation of zerovalent metals before a preparative method of synthesis of coordination compounds can be created on its basis.

VI. Conclusion

In assessing the data presented in the present review from the standpoint of modern coordination chemistry,[3–5,7,29,281] the following features must be emphasised.

First, the direct synthesis from zerovalent metals makes it possible to obtain all types of coordination compounds. In this connection, the gas-phase reactions are carried out mainly in order to obtain π-complexes, while the liquid-phase synthesis is designed predominantly for the preparation of molecular adducts and metal chelates.

Second, diverse organic ligand systems, forming molecular complexes, π-complexes, metal chelates, and clusters may participate in the direct synthesis. This factor permits the specific synthesis of complexes with a specified geometry and a specified location of their coordinate bond (see, for example, Refs 153, 169, 216, 229–238, 253–258, and 263).

Third, under the conditions of the direct synthesis of coordination compounds, it is possible to employ the metals of virtually all the Groups of the Periodic System and to regulate the oxidation states of the complex-forming metals by selecting the ligands. The preparation by this method of gold, silver, and lanthanide complexes is especially promising. Definite progress in regulating the oxidation states of the metals may be attained by means of a correct selection of ligand systems taking into account the principle of hard and soft acids and bases,[180,285,286] namely low oxidation states of the metals should be stabilised by soft bases (P, As, S, and Se donors), while high oxidation states should be stabilised by hard bases (N and O donors).

Fourth, despite the wide-scale employment of direct synthesis for the preparation of metal complexes, individual methods require improvement in order to bring them up to preparative application (gas-phase synthesis and tribosynthesis). For the application of certain methods, it is desirable to expand the range of ligand systems: chelating ligands in the gas-phase synthesis and compounds forming π-complexes and cluster structures in the liquid-phase synthesis.

Extensive possibilities for the study of the products of the direct synthesis arise from the use of ion-cyclotron resonance.[287,288]

All the features described above demonstrate the likely usefulness of the direct synthesis of metal complexes and give rise to the hope for the extensive employment of this method in coordination chemistry. This is also indicated by a review[289] devoted to the electrosynthesis of coordination compounds.

This review has been written with the financial support of the Russian Fundamental Research Fund (project 94-03-09731).

References

1. I I Chernyaev (Ed.) *Sintez Kompleksnykh Soedinenii Metallov Platinovoi Gruppy* (Synthesis of Complex Compounds of Platinum Group Metals) (Moscow: Nauka, 1964)
2. G Brauer (Ed.) *Handbuch der Präparativen Anorganischen Chemie* Vols 5, 6 (Translated into Russian; Moscow: Mir, 1985–1986)
3. G Wilkinson (Ed.) *Comprehensive Coordination Chemistry. The Synthesis Reactions Properties* Vol. 3–5 (Oxford: Pergamon Press, 1987)
4. V Yu Kukushkin, Yu N Kukushkin *Teoriya i Praktika Sinteza Koordinatsionnykh Soedinenii* (Theory and Practice in the Synthesis of Coordination Compounds) (Leningrad: Nauka, 1990)
5. N A Kostromina, V N Kumok, N A Skorik, in *Khimiya Koordinatsionnykh Soedinenii* (Chemistry of Coordination Compounds) (Moscow: Vysshaya Shkola, 1990) p. 395
6. J F Martin, in *Preparative Inorganic Reactions* Vol. 1 (Ed. W L Jolli) (Translated into Russian; Moscow: Mir, 1966) p. 70
7. A D Garnovskii, A L Nivorozhkin, V I Minkin *Coord. Chem. Rev.* **126** 1 (1993)
8. J P Candlin, K A Taylor, D T Thompson *Reactions of Transition Metal-Complexes* (Translated into Russian; Moscow: Mir, 1970)
9. N V Gerbeleu *Reaktsii na Matritsakh* (Reactions on Matrices) (Kishinev: Shtiintsa, 1980)
10. N V Gerbeleu, V B Arion *Templatnyi Sintez Makrotsiklicheskikh Soedinenii* (Template Synthesis of Macrocyclic Compounds) (Kishinev: Shtiintsa, 1990)
11. B Gerdes *J. Prakt. Chem.* **26** 257 (1882)
12. V M Zamyatkina, Yu N Kukushkin, A A Makarenya *Lev Aleksandrovich Chugaev* (Moscow: Nauka, 1973)
13. P L Timms *Adv. Inorg. Chem. Radiochem.* **14** 121 (1972)
14. K J Klabunde *Acc. Chem. Res.* **8** 393 (1975); *Angew. Chem.* **87** 309 (1975)
15. G A Domrachev, V D Zinov'ev *Usp. Khim.* **47** 679 (1978) [*Russ. Chem. Rev.* **47** 354 (1978)]
16. I P Lavrent'ev, M A Khidekel' *Usp. Khim.* **52** 596 (1983) [*Russ. Chem. Rev.* **52** 337 (1983)]
17. A D Garnovskii, Yu I Ryabukhin, A S Kuzharov *Koord. Khim.* **10** 1011 (1984)
18. A S Kuzharov, A D Garnovskii, A A Kut'kov *Zh. Obshch. Khim.* **49** 861 (1979)
19. A S Kuzharov, Doctoral Thesis in Technical Sciences, Rostov Institute of Agricultural Machine Building, Rostov-on-Don, 1991
20. R W Zoeller, R J Klabunde *Chem. Rev.* **84** 545 (1984)
21. P L Timms *Acc. Chem. Res.* **6** 118 (1973)
22. H Lehmkuhl *Synthesis* 377 (1973)
23. D G Tuck *Pure Appl. Chem.* **51** 2005 (1979)
24. V A Konev, V Yu Kukushkin, Yu N Kukushkin *Zh. Neorg. Khim.* **31** 1466 (1986)
25. G B Sergeev *Zh. Vses. Khim. O-va im. D I Mendeleeva* **35** 566 (1990)
26. J R Blackborow, D Young *Metal Vapour Synthesis in Organometallic Chemistry* (Berlin: Springer-Verlag Chemie, 1979)
27. A P Tomilov, I N Chernykh, Yu N Kargin *Elektrokhimiya Elementoorganicheskikh Soedinenii. Elementy I, II, III Grupp Periodicheskoi Sistemy i Perekhodnye Metally* (Electrochemistry of Organoelement Compounds. Group I, II, and III Elements and Transition Metals) (Moscow: Nauka, 1985)
28. D H Russel (Ed.) *Gas Phase Inorganic Chemistry* (New York: Plenum Press, 1989)
29. A D Garnovskii *Koord. Khim.* **14** 579 (1988)
30. P L Timms *Angew. Chem.* **87** 295 (1975); *Angew. Chem., Int. Ed. Engl.* **14** 273 (1975)
31. W J Power, G A Ozin *Adv. Inorg. Chem. Radiochem.* **23** 80 (1980)
32. T S Pochekutova, V K Khamylov, G A Domrachev, B V Zhuk *Zh. Org. Khim.* **23** 2156 (1987)
33. P L Timms *J. Chem. Soc., Chem. Commun.* 158 (1988)
34. S W Buckner, B S Freiser *Polyhedron* **7** 1583 (1988)
35. E A Mazurenko, G N Novitskaya, Zh N Bublik, S V Volkov *Ukr. Khim. Zh.* **50** 227 (1984)
36. E A Mazurenko, Doctoral Thesis in Chemical Sciences, Institute of General and Inorganic Chemistry, Academy of Sciences Ukr. SSR, Kiev, 1987
37. M A Blitz, S A Mitchell, P A Hackett *J. Phys. Chem.* **95** 8719 (1991)

38. J J Caroll, J C Weisshaar *J. Am. Chem. Soc.* **115** 800 (1993)
39. J J Caroll, K L Hang, J C Weisshaar *J. Am. Chem. Soc.* **115** 6962 (1993)
40. D Ritter, J C Weisshaar *J. Am. Chem. Soc.* **112** 6425 (1990)
41. G A Domrachev, L N Zakharov, Yu A Shevelev *Usp. Khim.* **54** 1260 (1985) [*Russ. Chem. Rev.* **54** 739 (1985)]
42. M Moskovits, G A Ozin (Ed.) *Cryochemistry* (Translated into Russian; Moscow: Mir, 1979)
43. G A Domrachev, L N Zakharov, Yu A Shevelev, in *Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov* (Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials) (Moscow: Nauka, 1986) p. 5
44. G A Domrachev, L N Zakharov, Yu A Shevelev, G A Razuvaev *Zh. Strukt. Khim.* **27** 14 (1986)
45. G A Domrachev, G I Andreev, Yu A Shevelev, B E Nemtsov *Zh. Prikl. Khim.* **57** 1266 (1984)
46. Yu A Shevelev, in *Tez. Dokl. 4-i Vsesoyuz. Konf. po Khimii Nizkikh Temperatur* (Abstracts of Reports at the Fourth All-Union Conference on the Chemistry of Low Temperatures) (Moscow: Nauka, 1988) p. 210
47. L P Yur'eva, N N Zaitsev, I A Uralets, S I Peregudova, D N Kravtsov, A Yu Vasil'kov, V A Sergeev *Metalloorg. Khim.* **3** 783 (1990)
48. V Graves, J J Lagowski *Inorg. Chem.* **15** 577 (1976)
49. C Elshenbroich, S Hoppe, B Mertz *Chem. Ber.* **126** 399 (1993)
50. P L Timms *J. Chem. Soc., Chem. Commun.* 1033 (1969)
51. E A K von Gustoff, O Janicke, O Wolfbeis, C R Eady *Angew. Chem.* **87** 300 (1975)
52. M Domenico, P L Timms *J. Organomet. Chem.* **258** 12 (1983)
53. S A Mitchell, P A Hackett *J. Chem. Phys.* **93** 7822 (1990)
54. D W Ball, R G Pong, H Kafafi *J. Am. Chem. Soc.* **115** 2864 (1993)
55. J R Blackborow, U Feldhoff, F-W Grevels *J. Organomet. Chem.* **173** 253 (1979)
56. G A Ozin, D M Haddleton, C J Gill *J. Phys. Chem.* **93** 6710 (1989)
57. E P Kündig, P L Timms, B A Kelly, P Woodward *J. Chem. Soc., Dalton Trans.* 901 (1983)
58. F G N Cloke, M L H Green *J. Chem. Soc., Dalton Trans.* 1938 (1981)
59. F G N Cloke, M F Lappert, G A Lawless, A C Swain *J. Chem. Soc., Chem. Commun.* 1667 (1987)
60. J C Brean, F G N Cloke, A A Sameh, A Salkin *J. Chem. Soc., Chem. Commun.* 1668 (1987)
61. F G N Cloke, K E A Courtney, A A Sameh, A C Swain *Polyhedron* **8** 1641 (1989)
62. H Brunner, H Koch *Chem. Ber.* **115** 65 (1982)
63. A H Simmons, P E Rilley, R F Davies, J J Lagowski *J. Am. Chem. Soc.* **98** 1044 (1976)
64. G Gardenas-Trivino, K J Klabunde, E B Dale *Langmuir* **3** 986 (1987)
65. K B Starowiewski, K J Klabunde *Appl. Organomet. Chem.* **3** 219 (1989)
66. P S Skell, M J McGlinchey *Angew. Chem.* **87** 215 (1975)
67. E A K von Gustoff, O Janicke, O E Polansky *Angew. Chem.* **84** 547 (1972)
68. F G N Cloke, J P Day *J. Chem. Soc., Chem. Commun.* 967 (1985)
69. Yu A Shevelev, M V Dodonov, L P Yur'eva, G A Domrachev, N I Zaitseva *Izv. Akad. Nauk SSSR, Ser. Khim.* 1414 (1981)
70. Yu A Shevelev, V L Cherepnov, G A Domrachev, V K Smirnov, P G Semen'kov, Yu A Silkin, Yu N Il'in, A A Nikonov, O M Zherelova *Dokl. Akad. Nauk SSSR* **289** 640 (1986)
71. V M Lynch, M O Joon, J J Lagowsky, B E Davis *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **46** 1094 (1990)
72. G A Domrachev, Yu A Shevelev, I G Andreev, N P Makarenko, in *Khimiya Elementoorganicheskikh Soedinenii* (Chemistry of Organoelement Compounds) (Gor'kii: Nauka, 1987) p. 15
73. E P Kündig, P L Timms *J. Chem. Soc., Dalton Trans.* 991 (1980)
74. G A Domrachev *Problemy Ustoichivosti Metalloorganicheskikh Soedinenii v Protsessakh Ikh Sinteza i Raspada* (Problems of the Stability of Organometallic Compounds during Their Synthesis and Decomposition) (Moscow: Nauka, 1985) p. 138
75. I G Andreev, A G Bazyakin, I L Vasilevskaya, G A Domrachev, B S Kaverin, in *Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov (Tez. Dokl. VI Vsesoyuz. Soveshch., Nizhnii Novgorod, 1991)* (Abstracts of Reports at the Sixth All-Union Conference on the Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials) (Moscow: Nauka, 1991) Part 1, p. 103
76. N T Kuznetsov, V G Sevast'yanov, I Yu Filatov, L N Zakharov, G A Domrachev *Vysokochist. Veshch.* 42 (1989)
77. S Yu Ketkov, G A Domrachev *Opt. Spektrosk.* **67** 475 (1989)
78. S Yu Ketkov, G A Domrachev, in *Tez. Dokl. Vsesoyuz. Chugaevskogo Soveshch. po Khimii Kompleksnykh Soedinenii, Belorus. Gos. Univ., Minsk, 1990* (Abstracts of Reports at the All-Union Chugaev Conference on the Chemistry of Complex Compounds, Belorussian State University, Minsk, 1990) Part 3, p. 484
79. S Yu Ketkov, G A Domrachev *Metalloorg. Khim.* **3** 957 (1990)
80. G A Domrachev, S Yu Ketkov, Yu A Shevelev, B I Petrov, A M Slushkov, G A Razuvaev *Metalloorg. Khim.* **3** 827 (1990)
81. P E Riley, R E Davis *Inorg. Chem.* **15** 2735 (1976)
82. C Elschenbroich, J Koch, J Kroker, M Wünsch, W Massa, G Baum, G Stork *Chem. Ber.* **121** 1983 (1988)
83. E O Fischer, K Öfele *Z. Naturforsch. B* **14** 736 (1959)
84. E O Fischer, K Öfele *J. Organomet. Chem.* **44** 353 (1972)
85. G M Bogdanov, Yu G Bundel' *Khim. Geterotsikl. Soedin.* 1155 (1983)
86. A P Sadimenko, A D Garnovskii, O A Osipov, V N Sheinker *Khim. Geterotsikl. Soedin.* 1299 (1983)
87. A P Sadimenko, A D Garnovskii, N Retta *Coord. Chem. Rev.* **126** 237 (1993)
88. G A Ozin, D F McIntosh, W J Power, R P Messmer *Inorg. Chem.* **20** 1782 (1981)
89. Yu A Ryukhin, G A Fokin, in *Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov* (Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials) (Moscow: Nauka, 1983) p. 195
90. A S Kuzharov, A A Kut'kov, V V Suchkov *Koord. Khim.* **6** 1123 (1980)
91. G N Dorofeenko, Yu I Ryabukhin *Zh. Obshch. Khim.* **48** 1168 (1978)
92. Yu I Ryabukhin, G N Dorofeenko, N V Shibaeva, in *Tez. Dokl. IV Vsesoyuz. Konf. "Sintez i Issledovanie Neorganicheskikh Soedinenii v Nevodnykh Sredakh", Ivanov. Khim.-Tekhnol. Inst., Ivanovo, 1980* (Abstracts of Reports at the Fourth All-Union Conference "Synthesis and Investigation of Inorganic Compounds in Nonaqueous Media", Ivanovo Chemical Technology Institute, Ivanovo) Part 1, p. 196
93. Yu I Ryabukhin, A S Kuzharov, N V Shibaeva, A D Garnovskii, in *Tez. Dokl. III Vsesoyuz. Konf. po Khimii Azotistykh Geterotsiklov* (Abstracts of Reports at the Third All-Union Conference on the Chemistry of Nitrogen Heterocycles) (Rostov-on-Don: Izd. Rostovsk. Gos. Univ., 1983) p. 188
94. Yu I Ryabukhin, L N Faleeva, T V Kovaleva, in *Nukleofil'nye Reaktsii Karbonil'nykh Soedinenii* (Nucleophilic Reactions of Carbonyl Compounds) (Saratov: Izd. Saratovsk. Univ., 1982) p. 120
95. Yu I Ryabukhin, N V Shibaeva, A S Kuzharov, V G Korobkova, A V Khokhlov, A D Garnovskii *Koord. Khim.* **13** 869 (1987)
96. I E Uflyand, A D Pomogailo *Usp. Khim.* **60** 1532 (1991) [*Russ. Chem. Rev.* **60** 773 (1991)]
97. A D Pomogailo, I E Uflyand *Makromolekulyarnye Metall-khelaty* (Macromolecular Metal Chelates) (Moscow: Khimiya, 1991)
98. V T Kalinnikov, Yu V Rakitin, in *Vvedenie v Magnetokhimiyu. Metod Statisticheskoi Magnitnoi Vospriimchivosti v Khimii* (Introduction to Magnetochemistry. The Method of Statistical Magnetic Susceptibility in Chemistry) (Moscow: Nauka, 1980) p. 255
99. A I Prokof'ev, T I Prokof'eva, N N Bubnov, S P Solodovnikov, I S Belostotskaya, V V Ershov, M I Kabachnik *Dokl. Akad. Nauk SSSR* **245** 1393 (1979)
100. V B Vol'eva, A I Prokof'ev, T I Prokof'eva, E V Ivanova, V A Zhorin, V V Ershov, N S Enikolopyan *Izv. Akad. Nauk SSSR, Ser. Khim.* 2800 (1986)

101. T A Annan, D H McConville, B R McGarvey, A Ozarowski, D G Tuck *Inorg. Chem.* **28** 1644 (1989)
102. T A Annan, D G Tuck *Can. J. Chem.* **67** 1807 (1989)
103. A Ozarowski, B R McGarvey, C Peppe, D G Tuck *J. Am. Chem. Soc.* **113** 3288 (1991)
104. A Ceneschi, A Dei, D Gatteschi *J. Chem. Soc., Chem. Commun.* 630 (1992)
105. D M Adams, A L Reingold, A Dei, D N Hendrickson *Angew. Chem.* **105** 434 (1993)
106. C G Pierpont, R M Buchnan *Coord. Chem. Rev.* **38** 45 (1981)
107. W Kaim *Coord. Chem. Rev.* **76** 187 (1987)
108. C G Pierpont, S K Larsen, S R Bose *Pure Appl. Chem.* **60** 1331 (1988)
109. V A Muraev, G A Abakumov, G A Razuvaev *Dokl. Akad. Nauk SSSR* **217** 1083 (1974)
110. V A Muraev, G A Abakumov, G A Razuvaev *Dokl. Akad. Nauk SSSR* **236** 3 (1977)
111. G I Prokof'ev, N A Malyshev, N N Bubnov, S P Solodovnikov, M I Kabachnik *Dokl. Akad. Nauk SSSR* **252** 370 (1980)
112. R S Sofen, D C Ware, S R Copper, K N Raymond *Inorg. Chem.* **18** 234 (1979)
113. B D Berezin *Koordinatsionnye Soedineniya Porfirinov i Ftalotsianinov* (Coordination Compounds of Porphyrins and Phthalocyanines) (Moscow: Nauka, 1978)
114. K Kasuda, M Tsutsui *Coord. Chem. Rev.* **32** 67 (1980)
115. V V Skopenko, V N Kokozei, M D Nevesenko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* (9) 56 (1980)
116. V V Skopenko, V N Kokozei *Dokl. Akad. Nauk Ukr. SSR, Ser. B* 740 (1979)
117. V V Skopenko, V N Kokozei *Ukr. Khim. Zh.* **46** 3 (1980)
118. I P Lavrentiev, L G Korableva, E A Lavrentieva, G A Nifontova, M L Khidekel', J G Gusakovskaya, T I Larkina, L D Arutyunian, O S Filipenko, V A Ponomarev, L O Atovmyan *Transition Met. Chem.* **5** 193 (1980)
119. I E Konstantinova, I P Lavrent'ev, E A Grigor'yan, A I Sukhova, M L Khidekel', V Ya Baskakov *Zh. Fiz. Khim.* **57** 929 (1983)
120. V A Letuchii, I P Lavrentiev, M L Khidekel' *Oxid. Commun.* **6** 285 (1984)
121. A K Chulkevich, I P Lavrent'ev, M L Khidekel', in *Materialy 6-go Vsesoyuz. Soveshch. po Probleme Kompleksov s Perenosom Zaryada i Ionradikal'nykh Solei* (Proceedings of the Sixth All-Union Conference on Problems of Charge-Transfer Complexes and Radical-ion Salts) (Moscow: Nauka, 1984) p. 250
122. I P Lavrent'ev, M L Khidekel', in *Tez. Dokl. V Vsesoyuz. Soveshch. po Khimii Nevodnykh Rastvorov* (Abstracts of Reports at the Fifth All-Union Conference on the Chemistry of Nonaqueous Solutions) (Rostov-on-Don: Izd. Rostovsk. Gos. Univ. 1985) p. 47
123. A K Chulkevich, I P Lavrent'ev, A P Moravskii, M L Khidekel', V I Ponomarev, O S Filipenko, L O Atovmyan *Koord. Khim.* **12** 470 (1986)
124. D D Makitov, L G Korableva, O N Krasochka, I P Lavrent'ev, L O Atovmyan, M L Khidekel' *Koord. Khim.* **12** 1262 (1986)
125. A K Chulkevich, L G Korableva, I P Lavrent'ev, V I Ponomarev, M L Khidekel' *Izv. Akad. Nauk SSSR, Ser. Khim.* 667 (1986)
126. A K Chulkevich, E V Smolina, I P Lavrent'ev, M L Khidekel' *Izv. Akad. Nauk SSSR, Ser. Khim.* 1896 (1986)
127. A K Chulkevich, I P Lavrent'ev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2130 (1986)
128. R R Thomas, V Chebolu, A Sen *J. Am. Chem. Soc.* **108** 4096 (1986)
129. D D Makitov, O N Krasochka, L O Atovmyan, I P Lavrent'ev, Yu M Shul'ga, L V Revenko, M L Khidekel' *Koord. Khim.* **13** 383 (1987)
130. S N Kurskov *Koord. Khim.* **13** 1082 (1987)
131. D D Makitov, O N Krasochka, L O Atovmyan, Ya A Letuchii, O S Roshchupkina, I P Lavrent'ev, M L Khidekel' *Koord. Khim.* **13** 1650 (1987)
132. G A Nifontova, O N Krasochka, I P Lavrent'ev, D D Makitov, L O Atovmyan, M L Khidekel' *Izv. Akad. Nauk SSSR, Ser. Khim.* 450 (1988)
133. D D Makitov, O S Roshchupkina, I P Lavrent'ev, L O Atovmyan, M L Khidekel' *Koord. Khim.* **14** 394 (1988)
134. A K Chulkevich, I P Lavrent'ev *Koord. Khim.* **14** 1434 (1988)
135. I P Lavrent'ev, V I Ponomarev, L O Atovmyan, M L Khidekel', in *Difraktsionnye Metody v Khimii (Tez. Dokl. Vsesoyuz. Soveshch., Suzdal', 1988)* (Abstracts of Reports at the All-Union Conference on Diffraction Methods in Chemistry, Suzdal', 1988) Part 1, p. 19
136. L V Shirshova, L G Kovaleva, I P Lavrent'ev, V I Ponomarev, in *Difraktsionnye Metody v Khimii (Tez. Dokl. Vsesoyuz. Soveshch., Suzdal', 1988)* (Abstracts of Reports at the All-Union Conference on Diffraction Methods in Chemistry, Suzdal', 1988) Part 2, p. 202
137. G A Nifontova, M G Kaplunov, I P Lavrent'ev *Koord. Khim.* **15** 32 (1989)
138. L V Shirshova, I P Lavrent'ev, V I Ponomarev *Koord. Khim.* **15** 1048 (1989)
139. L V Shirshova, I P Lavrent'ev, M L Khidekel', O N Krasochka, V I Ponomarev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1894 (1989)
140. I P Lavrent'ev *Tez. Dokl. 14-go Vsesoyuz. Chernyaevskogo Soveshch. po Khimii, Analizu i Tekhnologii Platinovykh Metallov* (Abstracts of Reports at the XIVth All-Union Chernyaev Conference on the Chemistry, Analysis and Technology of Platinum Metals) (Novosibirsk: Inst. Inorg. Chem. Sib. Div. Acad. Sci. USSR, 1989) Vol. 1, p. 26
141. G A Nifontova, O S Filipenko, A S Astakhova, I P Lavrent'ev, L O Atovmyan *Koord. Khim.* **16** 218 (1990)
142. L V Shirshova, L G Korableva, A S Astakhova, I P Lavrent'ev, V I Ponomarev *Koord. Khim.* **16** 348 (1990)
143. L V Shirshova, V I Ponomarev, L G Korableva, I P Lavrent'ev *Koord. Khim.* **16** 1118 (1990)
144. L V Shirshova, I P Lavrent'ev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2625 (1990)
145. E A Lavrent'eva, V I Ponomarev, I P Lavrent'ev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2794 (1990)
146. E T Epel'baum, V I Ponomarev, I P Lavrent'ev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1325 (1991)
147. V Ya Khentov, L N Velikanova, I P Lavrent'ev *Zh. Fiz. Khim.* **65** 1986 (1991)
148. G A Nifontova, I P Lavrent'ev *Izv. Akad. Nauk SSSR, Ser. Khim.* 498 (1992)
149. L V Shirshova, I P Lavrent'ev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1929 (1992)
150. G A Nifontova, I P Lavrentiev *Transition Met. Chem.* **18** 27 (1993)
151. S N Kurskov, N V Varlamov, V I Labunskaya, O E Koblova, A F Bol'shakov *Koord. Khim.* **20** 70 (1994)
152. A P Pisarevskii, L I Martynenko *Koord. Khim.* **20** 324 (1994)
153. V N Kokozei, Doctoral Thesis in Chemical Sciences, Kiev State University, Kiev, 1994
154. V A Pavlenko, V V Skopenko, V N Kokozei *Dokl. Akad. Nauk Ukr. SSR, Ser. B* (7) 47 (1983)
155. V N Kokozei, N D Nevesenko, V V Skopenko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* (4) 31 (1984)
156. V A Pavlenko, V N Kokozei, V V Skopenko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* (7) 42 (1985)
157. N D Nevesenko, V N Kokozei *Ukr. Khim. Zh.* **52** 1129 (1986)
158. N D Nevesenko, V V Skopenko, V N Kokozei *Zh. Neorg. Khim.* **31** 2062 (1986)
159. V N Kokozei, N D Nevesenko, V V Skopenko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* 42 (1987)
160. N D Nevesenko, V N Kokozei, V I Shvachko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* (9) 51 (1987)
161. O Yu Vasil'eva, N D Nevesenko, V N Kokozei, V V Skopenko, Yu S Gerasimenko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* (3) 38 (1988)
162. V A Pavlenko, V N Kokozei, V V Skopenko *Dokl. Akad. Nauk Ukr. SSR, Ser. B* (6) 48 (1989)
163. V A Pavlenko, V N Kokozei *Zh. Prikl. Khim.* **63** 216 (1990)
164. Yu A Simonov, V V Skopenko, V N Kokozei, S R Petrusenko, A A Dvorkin *Zh. Neorg. Khim.* **36** 625 (1991)
165. V R Polyakov, V N Kokozei, V A Pavlenko *Ukr. Khim. Zh.* **57** 127 (1991)
166. V N Kokozei, A A Dvorkin, O Yu Vasil'eva, A V Sinkevich, O N Rebrova *Zh. Neorg. Khim.* **36** 1446 (1991)
167. O Yu Vasil'eva, V N Kokozei *Koord. Khim.* **17** 968 (1991)
168. N M Dudarenko, V N Kokozei, V A Pavlenko *Ukr. Khim. Zh.* **58** 721 (1992)
169. V V Skopenko, V N Kokozei, V A Pavlenko *Ukr. Khim. Zh.* **59** 485 (1993)

170. O Yu Vasil'eva, V N Kokozei *Ukr. Khim. Zh.* **59** 1249 (1993)
171. V Pavlenko, V N Kokozay, O Babich *Z. Naturforsch., B Chem. Sci.* **48** 1321 (1993)
172. V N Kokozay, V R Polyakov, Yu A Simonov *J. Coord. Chem.* **28** 191 (1993)
173. V N Kokozay, A Sienkiewicz *J. Coord. Chem.* **30** 245 (1993)
174. V N Kokozay, A Sienkiewicz *Polyhedron* **12** 2421 (1993)
175. V V Skopenko, V N Kokozay, V R Polyakov, A Sienkiewicz *Polyhedron* **13** 15 (1994)
176. S R Petrusenko, V N Kokozei, Yu A Simonov *Zh. Neorg. Khim.* **39** 81 (1994)
177. A E Morozov, V P Seleznev, I P Sokolov *Zh. Neorg. Khim.* **38** 53 (1993)
178. Ya A Letuchii, I P Lavrent'ev, M L Khidekel' *Koord. Khim.* **8** 1477 (1982)
179. S N Kurskov, I N Ivleva, I P Lavrent'ev, M L Khidekel' *Izv. Akad. Nauk SSSR, Ser. Khim.* 1708 (1977)
180. A D Garnovskii, A P Sadimenko, O A Osipov, G V Tsintsadze *Zhestko–Myagkie Vzaimodeistviya v Koordinatsionnoi Khimii* (Hard–Soft Interactions in Coordination Chemistry) (Rostov-on-Don: Izd. Rostovsk. Gos. Univ., 1986)
181. G A Nifontova, I P Lavrent'ev, V I Ponomarev, O S Filipenko, O N Krasochka, L O Atovmyan, M L Khidekel' *Izv. Akad. Nauk SSSR, Ser. Khim.* 1691 (1982)
182. S N Kurskov, I N Ivleva, I P Lavrent'ev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1961 (1974)
183. A D Garnovskii *Koord. Khim.* **18** 675 (1992)
184. B F G Jonson (Ed.) *Transition Metal Clusters* (Chichester: Wiley, 1980)
185. S P Gubin *Koord. Khim.* **20** 403 (1994)
186. S P Gubin *Khimiya Klasterov. Osnovy Klassifikatsii i Stroenie* (Chemistry of Clusters. Fundamental Classification and Structure) (Moscow: Nauka, 1987)
187. A D Garnovskii, O A Osipov, L I Kuznetsova, N N Bogdashev *Usp. Khim.* **42** 177 (1973) [*Russ. Chem. Rev.* **42** 89 (1973)]
188. A D Garnovskii, O A Osipov, V N Sheinker *Koord. Khim.* **6** 3 (1980)
189. S S Kukalenko, B A Bovykin, S I Shestopalova, A M Omel'chenko *Usp. Khim.* **54** 1152 (1985) [*Russ. Chem. Rev.* **54** 676 (1985)]
190. D A Garnovskii, A D Garnovskii, A P Sadimenko, S G Sigeikin *Koord. Khim.* **20** 83 (1994)
191. B L Laube, C D Schulbach *Prog. Inorg. Chem.* **14** 65 (1971)
192. G A Tedoradze *J. Organomet. Chem.* **88** 1 (1975)
193. H Lemcul, in *Sytheses of Organometallic Compounds. Electrochemistry of Organic Compounds* (Ed. M Bazer) (Translated into Russian; Moscow: Mir, 1976) p. 442
194. M O Lebers, N J Coville *Coord. Chem. Rev.* **53** 227 (1984)
195. N Kumar, D G Tuck *Can. J. Chem.* **60** 2579 (1982); *Inorg. Chem.* **22** 211 (1983)
196. N Kumar, D G Tuck *Inorg. Chim. Acta* **95** 211 (1984)
197. C A McAuliffe, R G Pritchard, M R Bermejo, J A Garcia-Vazquez, A Maccias, J Sanmartin, J Romero, A Sousa *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **48** 1316 (1992)
198. C A McAuliffe, R G Pritchard, M R Bermejo, J A Garcia-Vazquez, A Maccias, J Sanmartin, J Romero, A Sousa *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **48** 1841 (1992)
199. E Labisbal, J Romero, J A Garcia-Vazquez, A Sousa, A Castineiras *J. Crystallogr. Spectrosc. Res.* **23** 895 (1993)
200. T Sogo, J Romero, A Sousa, A de Blas, M L Duran *Z. Naturforsch., B Chem. Sci.* **43** 611 (1988)
201. A M Golub, H Cöler, V V Skopenko (Eds) *Khimiya Pseudogalogenidov* (Kiev: Izd. Kievsk. Gos. Univ., 1981); *The Chemistry of Pseudohalides* (Amsterdam: Elsevier, 1986)
202. J L Hencher, M Khan, F F Said, R Sieler, D G Tuck *Inorg. Chem.* **21** 2787 (1982)
203. R K Chadha, R Kumar, D G Tuck *Can. J. Chem.* **65** 1336 (1987)
204. R K Chadha, R Kumar, J R Lopez-Grado, D G Tuck *Can. J. Chem.* **66** 2151 (1988)
205. R Kumar, D G Tuck *Inorg. Chem.* **29** 1444 (1990)
206. H Lemkuhl *Chem.-Ing.-Tech.* **54** 690 (1982)
207. A T Casey, A M Vecchio *Appl. Organomet. Chem.* **4** 513 (1990)
208. A D Garnovskii *Koord. Khim.* **19** 394 (1993)
209. L Bustos, J H Green, J L Heucher, M A Khan, D G Tuck *Can. J. Chem.* **61** 2141 (1983)
210. N N Kostyuk, V L Shirokii, T A Dik, I I Vinokurov, D S Umreiko *Koord. Khim.* **17** 1573 (1991)
211. N N Kostyuk, T A Kovalevich, V L Shirokii, D S Umreiko *Koord. Khim.* **15** 1704 (1989)
212. C Alvarino, J Romero, A Sousa, M L Duran *Z. Anorg. Allg. Chem.* **556** 223 (1988)
213. N M Atherton, D E Fenton, G J Hewson, C H McLean, R Bastida, J Romero, A Sousa, E E Castelleno *J. Chem. Soc., Dalton Trans.* 1059 (1988)
214. A Castineiras, J A Castro, M L Duran, J A Garcia-Vazquez, A Macias, J Romero, A Sousa *Polyhedron* **8** 2543 (1989)
215. M L Duran, J A Garcia-Vazquez, A Macias, J Romero, A Sousa *Z. Anorg. Allg. Chem.* **573** 215 (1989)
216. J A Castro, J Romero, J A Garcia-Vazquez, M L Duran, A Castineiras, A Sousa, D E Fenton *J. Chem. Soc., Dalton Trans.* 3255 (1990)
217. E Labisbal, J Romero, A De Blas, J A Garcia-Vazquez, M L Duran, A Castineiras, A Sousa, D E Fenton *Polyhedron* **11** 53 (1992)
218. E Labisbal, A De Blas, J A Garcia-Vazquez, J Romero, M L Duran, A Sousa, N A Bailey, D E Fenton, P B Leeson, R V Parish *Polyhedron* **11** 227 (1992)
219. M Gaber, H E Mabrouk, A A Ba-Issa, M M Ayad *Monatsh. Chem.* **123** 1089 (1992)
220. E Labisbal, J A Garcia-Vazquez, A Macias, J Romero, A Sousa, U Englett, D E Fenton *Inorg. Chim. Acta* **203** 67 (1993)
221. C A McAuliffe, R G Pritchard, L Luaces, J A Garcia-Vazquez, J Romero, M R Bermejo, A Sousa *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **49** 587 (1993)
222. E Labisbal, J Romero, M L Duran, J A Garcia-Vazquez, A Sousa, U Russo, R G Pritchard, M Renson *J. Chem. Soc., Dalton Trans.* 755 (1993)
223. E Labisbal, J Romero, J A Garcia-Vazquez, C Gomez, A Sousa *Polyhedron* **13** 1735 (1994)
224. A E Mistryukov, I S Vasil'chenko, V S Sergienko, A L Nivorozhkin, S G Kochin, M A Porai-Koshits, L E Nivorozhkin, A D Garnovskii *Mendeleev Commun.* 30 (1992)
225. A S Antsyshkina, M A Porai-Koshits, I S Vasil'chenko, A L Nivorozhkin, A D Garnovskii *Dokl. Akad. Nauk SSSR* **330** 54 (1993)
226. A D Garnovskii, A S Antsyshkina, I S Vasil'chenko, V S Sergienko, S G Kochin, A L Nivorozhkin, A E Mistryukov, A I Uraev, D A Garnovskii, G G Sadikov, M A Porai-Koshits *Zh. Neorg. Khim.* **40** 67 (1995)
227. A D Garnovskii, A S Burlov, T A Yusman, V G Zaletov *Koord. Khim.* **20** 62 (1995)
228. J A Castro, J A Vilasandes, J Romero, J A Garcia-Vazquez, M L Duran, A Sousa, F E Castellano, J Zukerman-Schpector *Z. Anorg. Allg. Chem.* **612** 83 (1992)
229. J A Castro, J Romero, J A Garcia-Vazquez, A Castineiras, M L Duran, A Sousa *Z. Anorg. Allg. Chem.* **615** 155 (1992)
230. J A Castro, J Romero, J A Garcia-Vazquez, M L Duran, A Sousa, F E Castellano, J Zukerman-Schpector *Polyhedron* **11** 235 (1992)
231. J A Castro, J Romero, J A Garcia-Vazquez, A Sousa, F E Castellano, J Zukerman-Schpector *Polyhedron* **12** 31 (1993)
232. J A Castro, J Romero, J A Garcia-Vazquez, A Castineiras, A Sousa *Z. Anorg. Allg. Chem.* **619** 601 (1993)
233. J A Castro, J Romero, J A Garcia-Vazquez, A Sousa, F E Castellano, J Zukerman-Schpector *J. Coord. Chem.* **28** 125 (1993)
234. J A Castro, J Romero, J A Garcia-Vazquez, A Sousa, F E Castellano, J Zukerman-Schpector *J. Coord. Chem.* **30** 165 (1993)
235. J A Castro, J Romero, J A Garcia-Vazquez, A Macias, A Sousa, U Englert *Polyhedron* **12** 1391 (1993)
236. J A Castro, J Romero, J A Garcia-Vazquez, A Macias, A Sousa, U Englert *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **50** 369 (1994)
237. J A Castro, J Romero, J A Garcia-Vazquez, A Castineiras, A Sousa *Transition Met. Chem.* **19** 343 (1994)
238. H Hennig *Z. Chem.* **11** 81 (1971)

239. G V Panova, N K Vikulova, V M Potapov *Usp. Khim.* **49** 1234 (1980) [*Russ. Chem. Rev.* **49** 655 (1980)]
240. A D Garnovskii, V A Alekseenko, A S Burlov, V S Nedzvetskii *Zh. Neorg. Khim.* **36** 886 (1991)
241. V I Ivanskii *Khimiya Geterotsiklicheskikh Soedinenii* (Chemistry of Heterocyclic Compounds) (Moscow: Vysshaya Shkola, 1978)
242. N N Bogdashev, A D Garnovskii, O A Osipov, V P Grigor'ev, N M Gontmakher *Zh. Obshch. Khimii* **46** 675 (1976)
243. T A Annan, C Peppe, D G Tuck *Can. J. Chem.* **68** 1598 (1990)
244. T A Annan, C Peppe, D G Tuck *Can. J. Chem.* **68** 423 (1990)
245. J Sanmartin, M R Bermejo, J Romero, J A Garcia-Vazquez, A Sousa, A Brodbeck, A Castineiras, W Hiller, J Strähle *Z. Naturforsch., B Chem. Sci.* **43** 431 (1993); *Transition Met. Chem.* **18** 187 (1993)
246. H E Mabrouk, D G Tuck, M A Khan *Inorg. Chim. Acta* **129** 75 (1987)
247. H E Mabrouk, D G Tuck *J. Chem. Soc., Dalton Trans.* 2539 (1988)
248. H E Mabrouk, D G Tuck *Can. J. Chem.* **67** 746 (1989)
249. C Geloso, R Kumar, J Lopez-Grado, D E Tuck *Can. J. Chem.* **65** 928 (1987)
250. J Sanmartin, M R Bermejo, J A Garcia-Vazquez, J Romero, A Sousa *Transition Met. Chem.* **18** 528 (1993)
251. J Sanmartin, M R Bermejo, J A Garcia-Vazquez, J Romero, A Sousa *Synth. React. Inorg. Metal-Org. Chem.* **23** 1259 (1993)
252. J Sanmartin, M R Bermejo, J A Garcia-Vazquez, J Romero, A Sousa *Transition Met. Chem.* **19** 209 (1994)
253. R Castro, M L Duran, J A Garcia-Vazquez, J Romero, A Sousa, A Castineiras, W Hiller, J Strähle *J. Chem. Soc., Dalton Trans.* 531 (1990)
254. M L Duran, J Romero, J A Garcia-Vazquez, R Castro, A Castineiras, A Sousa *Polyhedron* **10** 197 (1991)
255. R Castro, M L Duran, J A Garcia-Vazquez, J Romero, A Sousa, A Castineiras, W Hiller, J Strähle *Z. Naturforsch., B Chem. Sci.* **45** 1632 (1990)
256. R Castro, M L Duran, J A Garcia-Vazquez, J Romero, A Sousa, A Castineiras, W Hiller, J Strähle *Z. Naturforsch., B Chem. Sci.* **47** 1067 (1992)
257. R Castro, J A Garcia-Vazquez, J Romero, A Sousa, W Hiller, J Strähle *Polyhedron* **13** 273 (1994)
258. R Castro, J A Garcia-Vazquez, J Romero, A Sousa, R Pritchard, C A McAuliffe *J. Chem. Soc., Dalton Trans.* 1115 (1994)
259. R Castro, J A Garcia-Vazquez, J Romero, A Sousa, C A McAuliffe, R Pritchard *Polyhedron* **12** 2241 (1993)
260. R Castro, J A Garcia-Vazquez, J Romero, A Sousa, A Castineiras, W Hiller, J Strähle *Inorg. Chim. Acta* **211** 47 (1993)
261. M A Khan, R Kumar, D G Tuck *Polyhedron* **7** 49 (1988)
262. J L Hencher, M A Khan, F F Said, D G Tuck *Polyhedron* **4** 1263 (1985)
263. J A Castro, M L Duran, J A Garcia-Vazquez, J Romero, A Sousa, F E Castellano, J Zukerman-Schpector *J. Chem. Soc., Dalton Trans.* 2559 (1992)
264. R Chandha, K Kumar, D G Tuck *J. Chem. Soc., Chem. Commun.* 188 (1986); *Polyhedron* **7** 1121 (1988)
265. R Castro, M L Duran, J A Garcia-Vazquez, J Romero, A Sousa, A Castineiras, W Hiller, J Strähle *Polyhedron* **11** 1195 (1992)
266. A S Kuzharov, V S Bolotnikov *Zh. Fiz. Khim.* **53** 2639 (1979)
267. A S Kuzharov, V V Suchkov *Zh. Fiz. Khim.* **54** 3114 (1980)
268. A S Kuzharov, V V Suchkov, L A Vlasenko *Zh. Fiz. Khim.* **55** 2588 (1981)
269. N Yu Onishchuk, A S Kuzharov, A A Kut'kov *Trenie Iznos* **2** 625 (1981)
270. A S Kuzharov, V V Suchkov, L A Komarchuk *Zh. Fiz. Khim.* **57** 1748 (1983)
271. A S Kuzharov, N Yu Onishchuk *Svoistva i Primenenie Metalloplakiruyushchikh Smazok* (Properties and Application of Metal-Coating Lubricants) (Moscow: Izd. ONIITEneftekhim, 1985)
272. A S Kuzharov, in *Tez. Dokl. X Yubileinogo Vsesoyuz. Simp. po Mekhanokhimii i Mekhanoemissii Tverdykh Tel, Rostovsk. Inst. S-Kh. Mashinostroeniya, Rostov-na-Donu, 1986* (Abstracts of Reports at the Jubilee All-Union Symposium on Mechanochemistry and Mechanoemission, Rostov Institute of Agricultural Machine Building, Rostov-on-Don, 1986) p. 158
273. A S Kuzharov, N Yu Onishchuk *Trenie Iznos* **8** 1106 (1987)
274. A S Kuzharov, in *Abstracts of Papers XXV International Conference on Coordination Chemistry, Nanjing, China, 1987* p. 792
275. A S Kuzharov, V V Suchkov, A T Kozakov *Trenie Iznos* **10** 1031 (1989)
276. G G Chigarenko, A G Ponomarenko, V S Bolotnikov, V A Alekseev, A S Burlov, A D Garnovskii, G P Barchan *Trenie Iznos* **10** 1050 (1989)
277. A S Kuzharov *Vestn. Mashinostroen.* 27 (1990)
278. A S Kuzharov, in *Abstracts of Posters XXVII International Conference on Coordination Chemistry, Gera, DDR, 1990* p. 6184
279. A S Kuzharov, Yu I Ryabukhin *Trenie Iznos* **12** 99 (1991)
280. A D Garnovskii, L V Orlova, O A Osipov, O A Raevskii *Zh. Obshch. Khim.* **37** 308 (1967)
281. V I Minkin, L E Nivorozhkin, M S Korobov *Usp. Khim.* **63** 303 (1994) [*Russ. Chem. Rev.* **63** 289 (1994)]
282. A S Kuzharov, V V Suchkov, L A Vlasenko *Zh. Fiz. Khim.* **53** 2064 (1979)
283. A S Kuzharov, V Ya Khentov *Koord. Khim.* **5** 601 (1979)
284. A S Kuzharov, L A Vlasenko, V V Suchkov *Zh. Fiz. Khim.* **58** 894 (1984)
285. A D Garnovskii, O A Osipov, S B Bulgarevich *Usp. Khim.* **41** 648 (1972) [*Russ. Chem. Rev.* **41** 341 (1972)]
286. A D Garnovskii *Koord. Khim.* **6** 1779 (1980)
287. K Eller, H Schwarz *Chem. Rev.* **91** 1121 (1991)
288. K Eller *Coord. Chem. Rev.* **126** 93 (1993)
289. M C Chakravorti, G V P Subrahmaniam *Coord. Chem. Rev.* **135/136** 65 (1994)