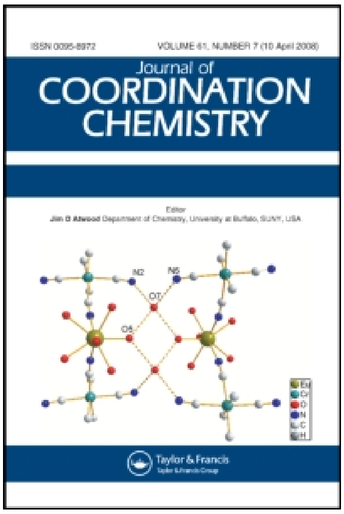

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Garnovskii, Alexander D. , Kharisov, Boris I. , Blanco, Leonor M. , Garnovskii, Dmitry A. , Burlov, Anatoly S. , Vasilchenko, Igor S. and Bondarenko, Gennady I.(1999) 'SOME ASPECTS OF COMPETITIVE COORDINATION OF β-DIKETONES AND NITROGEN-CONTAINING LIGANDS', Journal of Coordination Chemistry, 46: 4, 365 — 395

To link to this Article: DOI: 10.1080/00958979908054903

URL: http://dx.doi.org/10.1080/00958979908054903

J. Coord. Chem., 1999, Vol. 46, pp. 365–395
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Printed in Malaysia.

Review

SOME ASPECTS OF COMPETITIVE COORDINATION OF β-DIKETONES AND NITROGEN-CONTAINING LIGANDS

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(Received 28 July 1997; Revised 14 October 1997; In final form 24 March 1998)

Different coordination modes for transition metal atoms with typical chelating ligands such as β-diketones, *o*-oxyazomethines, azoles and azines are reviewed. Factors influencing the coordination such as ligand structure, methods and conditions of the synthesis, nature of solvent and specific hard–soft interactions are emphasized.

Keywords: β-Diketones; *o*-oxyazomethinic ligands; non-traditional coordinations; chelates; adducts

0. INTRODUCTION

Chelate-forming ligands have an important role in modern coordination chemistry.[1–4] The main features of such ligand systems (types 1 and 2) are the presence of acidic XH-groups, which take part in the formation of an

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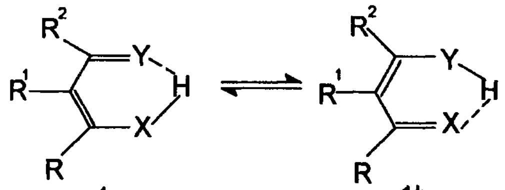
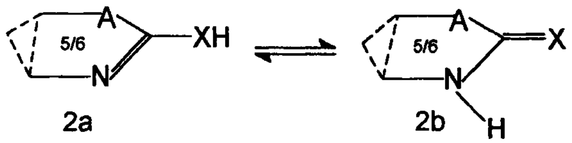
inner-molecular hydrogen bond,[5–7] and the existence of the prototropic tautomery (1a $\Longleftrightarrow$ 1b).[5–11]



1a 1b

X, Y = NR^3, O, S, Se

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

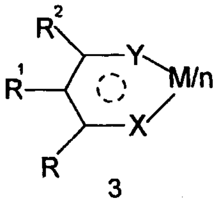


2a 2b

A = CR, N R = H, Alk, Ar

5/6 means five- or six-member heterocycle

It is accepted at present that only "inner-complex compounds" (chelates), formed as a result of substitution of the proton of the XH-group by the metal (for example, 3 and 4), could be obtained for chelating ligands.



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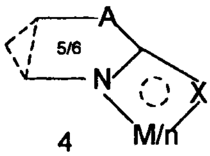

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Such coordination to metals is typical for chelate-forming anionic ligands. However, other (non-standard) ways of metal connection in complexes of the ligands of types 1 and 2 have been reported.

There are different classifications of metal chelates, one of them is the following:[4]

Molecular metal chelates where the metal ion is connected with the donor atoms of the chelate-forming ligand by donor–acceptor bonds (for example, metal complexes with ethylenediamine, 2,2′-bipyridine, or 1,10-phenanthroline);

Inner-complex compounds where bonding of the metal with one ligand takes place by both ionic and donor–acceptor bonds (metal complexes with β-diketones, *o*-hydroxyazomethines, aminoacids, *etc.*);

Macrocyclic complexes formed mostly by chelating ligands, whose donor centers provide bonding to the metal ion; in this case some metal cycles are formed (porphyrine, phthalocyanine and crown–ether complexes);

Metal chelates with π-bonds where the metal ion is connected with bi- and polydentate ligands containing two unsaturated fragments of the type C=C, C=X (X = N, P, As, O, S), C≡X (X = C, N), or one of these fragments and a functional group (*bis*-ethylene derivatives of metals, pyridine-ethylene complexes, *etc.*);

Polynuclear metal chelates including two and more metal atoms with a minimum of one metal part of a metallacycle (metal complexes of β,δ-triketones).

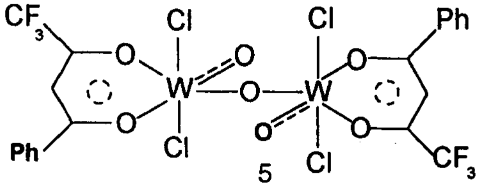
In each type of chelate, the complexes are divided on the nature of donor centers of the ligands, O,O-, N,O-, N,N-, N,S-, *etc.*

This review highlights complexes having standard and non-standard chelating ligands.

1. COMPLEX COMPOUNDS OF β-DIKETONES

Research shows that β-diketones 1 (X = Y = O)[4,5,12–16] and their thio- and seleno-analogs (1, X = O, Y = S; X = O, Y = Se; X = Y = S, Se)[17] form chelates of type 3 (X = Y = O, S, Se).

The existence of type 3 structures has been proven for β-diketone chelates by various physico-chemical methods, in particular on the basis of X-ray data.[4,5,13,14,18–37] Recent β-diketone structures of copper,[21–23,35–37] barium,[24,25] strontium,[24] yttrium,[25] the lanthanides,[26,27,32–34] and tungsten[29,30] are discussed in this paper. For tungsten, it is important to mention the binuclear structure of its dichloride complex 5 containing a W–O–W bridge.[30]



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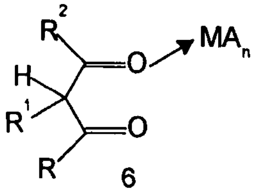
The β-diketone fragment of type 3 (X = Y = O) is a part of polynuclear clusters, for example of gadolinium $[Gd_4(\mu^3\text{-}OH)_4(\mu^2\text{-}H_2O)(H_2O)_4L_8]\cdot 2C_6H_6\cdot H_2O$, where L = 1,1,1,5,5,5-hexafluoropentan-2,4-dione.[27]

The η^2(O,O′)-coordination leads to different chelates, some forming rare polyhedra,[5,18–30] which are tabulated in a review.[5] The type 3 chelates are formed on the basis of monothio-β-diketones (X = O, Y = S) and dithio-β-diketones (X = Y = S),[17] although X-ray diffraction results have not confirmed the latter case.

The classical ideas about bonding of β-diketones with metals according to type 3 chelates were eliminated in the early 1960s, when X-ray diffraction demonstrated the possibility of non-standard coordination with participation of O- and even C-atoms of the given ligands.[38–40] Subsequently, the non-standard chelating and non-chelating types of coordination of β-diketones 6–19 have been established in a series of investigations and discussed in different reviews.[4,5,14,18,20,41,42]



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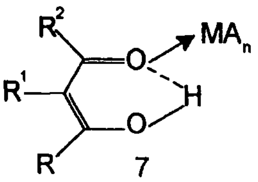

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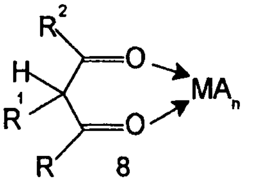

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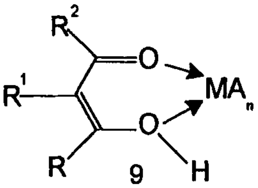

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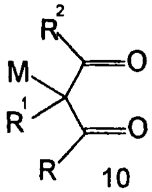

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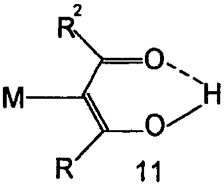

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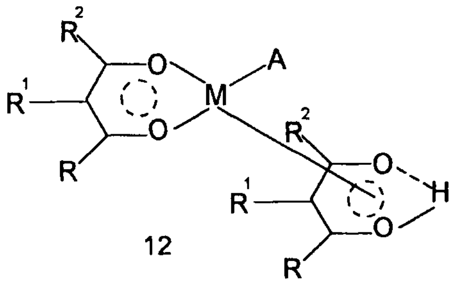

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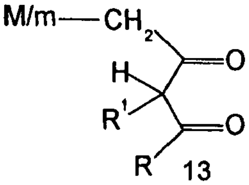
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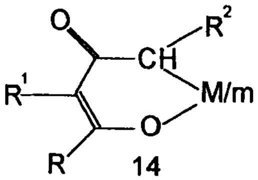
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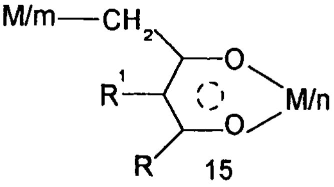
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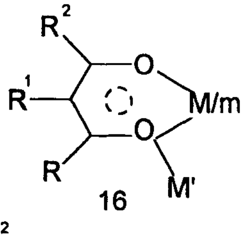
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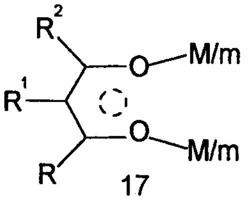
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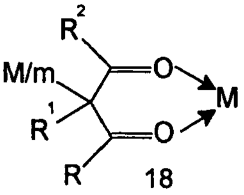
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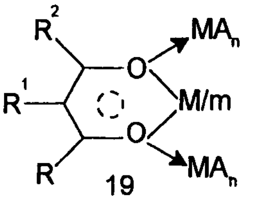
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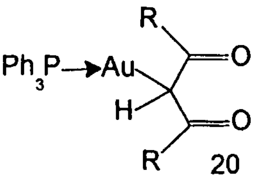
According to a review,[20] unusual monodentate O-coordination of type 7 exists in the complexes $[Mn(HAA)]Br_2$ and $Re(HBA)Cl(CO)_3$, where HAA is acetylacetone and HBA is benzoylacetone. The bidentate coordinated diketone form of acetylacetone 8 exists in the chelates $[Ni(HAA)_2]Br_2$ and $[Ni(HAA)_2(H_2O)_2](ClO_4)_2$.[20]

Among the mononuclear, C-coordinated β-diketone complexes, the recently obtained and structurally characterized compounds of univalent gold, 20,[43–46] have a structure of type 10.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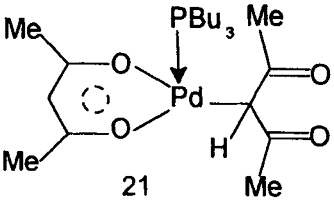
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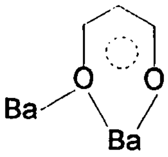
The interaction of palladium *bis*-acetylacetonate with organic phosphines leads to the C,O-coordinated complexes (for example 21), containing ionic forms of β-diketone ligands (see Ref. 47 and literature therein).

Complex compounds of β-diketones with additional O-coordination were discussed based on the example of di- and trinuclear barium complexes.[48,49] Coordination in these complexes is represented by formulae 22–25.



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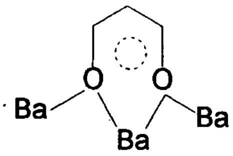

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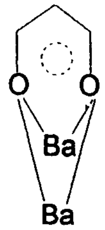

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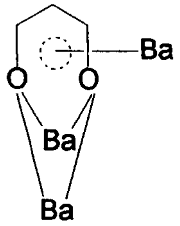

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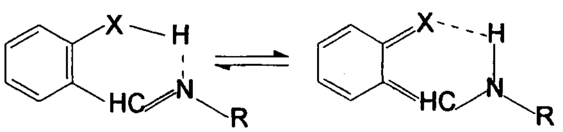
The β-diketone fragment behaves as a tridentate ligand in complex 22 and as a tetradentate ligand system in 23 and 24. In 24, a *bis*-chelate structure is formed.[50–53] This structure was proved by X-ray diffraction of the barium complex of dipivaloilmethane anion (DPM): $Ba_2(DPM)_4(NH_3)_4$,[50] $Ba(DPM)(Et_2O)$,[51] $Ba(DPM)_8$[48,52] and $Ba_2(DPM)_4(bipy)_2$.[53] The structure with the fragment 25 was discovered in the complex $Ba_5(DPM)_9H$-DPM and contains a pentadentate anion of dipivaloilmethane.[52] It is not excluded, that in this case one of the bonds is formed at the expense of the π-system of the β-diketone fragment.

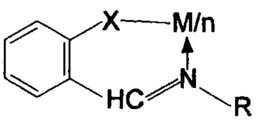
Structures similar to 6–25 have not been found in S,Se-analogs of β-diketones. This could be explained, obviously, by the absence of research on their programmed synthesis.

2. COMPLEX COMPOUNDS OF *O*-HYDROXYAZOMETHINES AND THEIR STRUCTURAL ANALOGS

Similar to the β-diketones, *o*-hydroxyazomethines 26 and their structural analogs 1 ($X = NR$; $Y = NR, O, S, Se$) form chelates of type 3 ($X, Y = O, S, Se, NR$), 27 and "molecular complexes" (adducts) 28, 29.



a 26 b



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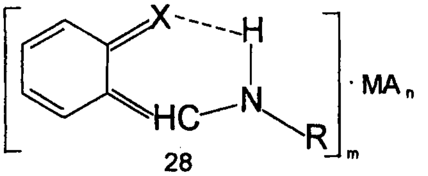

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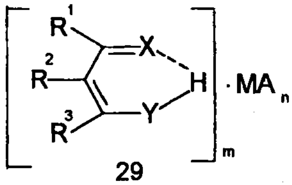

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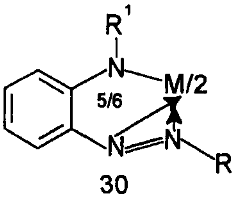
X = NR, O, S, Se; R = H, Alk, Ar
A = Hal, NO_2, NO_3, SO_3, SO_4, NCE (E = O, S, Se), *etc.*

Chelates of type 3 and 27 are primarily found in complexes of *o*-hydroxyazomethines and their analogs and contain bidentate anions of the ligand systems 1 and 26.[1,6,7,10,54–62] Chelates of type 3 (X = NR, Y = O) and 27 (X = O) are frequently found for 3*d*-metal complexes: cobalt,[7,58,59,63] nickel,[7,58,64–67] copper[7,58,68,69] and zinc.[7,70] In these chelate structures, the chelates with MN_2O_2 coordination, and the complexes with the ligand environment MN_4[7,55,60,61,71–73] and MN_2S_2[7,61,62,74] are common. Chelates containing MN_4 include the complexes obtained from β-aminovinylimines 3 (X = Y = NR),[7,61,73] Schiff bases of *o*-tosylaminobenzaldehyde 27 (X = NTs), azoamino compounds 30,[62,72] hydrazineimines 31[61,72] and phormazanes 32.[61,73,75,76]



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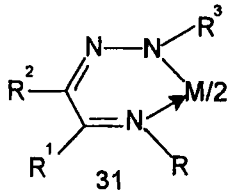

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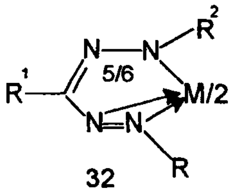


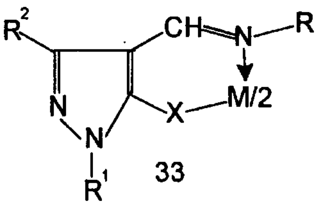
32

R = R¹ = R² = Alk, Ar, Het

Most six-member metallacycles 3, 27, 30, 31 exist in the type of chelates discussed above. Nevertheless, depending on the metal and the substituents R, five-membered coordination knots could be formed.[7,61] Five-membered metallacycles were detected by X-ray diffraction for nickel(II) and palladium(II) complexes with N-tosylaminoazo compounds 30[61,72] and for various chelates of hetarylphormazanes 32 (R = Het).[61,73]

A general structural characteristic for the chelates 3 (X = NR, Y = O) and 27 (X = O) with MN_2O_2 is the existence of *trans*-planar (M = Ni, Cu) or tetrahedral (M = Co, Ni) geometries.[7,18,19,61,77] For similar chelates, containing a 4N-ligand environment, the tetrahedral conformation is most common. These conformations become more planar with more nitrogen atoms in the cycles.[7,61]

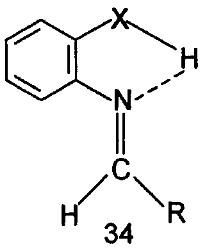
Considerable changes in the geometry for chelates of types 3 and 27 are observed when sulfur and selenium atoms are introduced instead of nitrogen and oxygen: practically all similar chelates of divalent d^8-metals (for example Ni and Pd) have a *cis*-planar structure.[7,61,74,78] This regularity, however, is only observed in chelates of aliphatic and aromatic azomethines and their analogs. In the case of addition of heterofragments to the metallacycle, formation of tetrahedral MN_2X_2 structures of the chelates takes place (see, for example, the structure of type 33), independent of the electronic configuration on the metal.[7,61,79]



33

X = O, S, Se

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

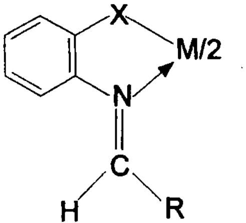


34

X = NTs, O, S

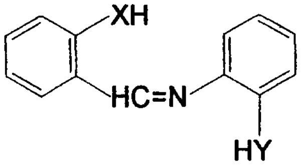
R = Ar, Het

The azomethinic ligands of type 34 play a significant role in modern coordination chemistry. A large group of chelates with five-member metallacycles MN_2X_2 (X = NTs, O, S, Se) 35 have been obtained on the basis of this ligand system.[7,61,80–87] It was shown that the complexes 35 (X = O) have a tetrahedral structure[7,61,88] or produce cluster structures,[89] while their thio analog 35 (X = S, M = Ni) have *cis*-planar configurations.[7,61,86,87,90]



35

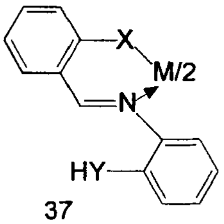
X = NTs, O, S
R = Ar, Het



36

X, Y = NTs, O, S

The tridentate azomethinic ligands of type 36 contain a combination of five- and six-membered cycles due to the existence of a hydrogen bond.[91] Based on structure 36 ($X = Y = O$) and the formulae 27 and 35, it is possible to propose structures 37–41 for complexes formed by ligand 36.



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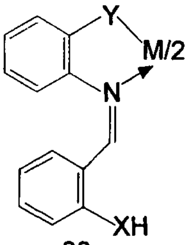

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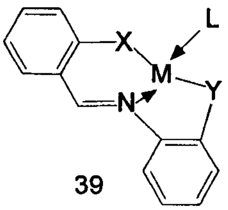

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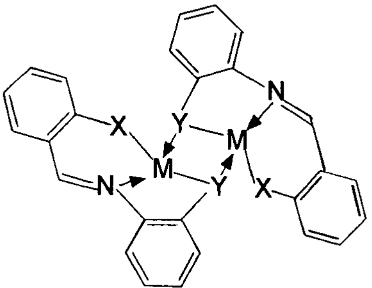

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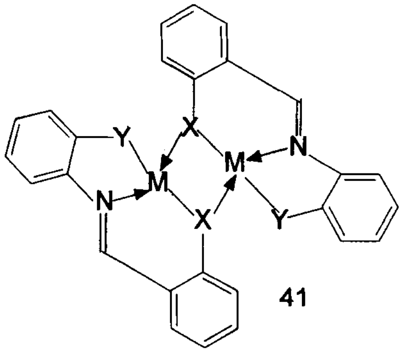


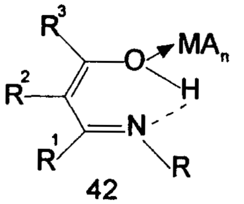
41

Complexes of types 37 and 38 have not been described; the existence of 39[92–97] and 40[98–100] were proven by X-ray diffraction. The possible formation of dimer 41 was suggested,[97] but, in our opinion, is not probable for two reasons. First, in all known structures of dimer complexes the bridge bond is formed at the expense of participation of the Y-donor center,[98–100] which is expressed by formula 40: Second, although for structures 40 and 41 an antiferromagnetic change should be observed, it should be stronger for a dimer with a M_2S_2-bridge than for M_2O_2-bridged structures.[101]

This was observed in magnetic properties of copper complexes 40 (X = NTs, Y = O; X = NTs, Y = S).[102]

Thus, coordination of *o*-hydroxyazomethinic ligands and their structural analogs is related to the presence of anionic bi- and tridentate ligand fragments in the inner sphere of chelates.

Non-standard adducts of types 28 and 29 (X = NR) are less known; the neutral azomethinic molecules participate as ligands.[7,61,103] Taking in account the tautomerism of type 1a, b and the presence of an intramolecular hydrogen bond, it is possible to propose structures 42–47 for molecular complexes of type 29 (X = NR, Y = O).



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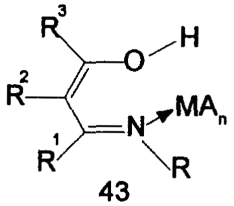

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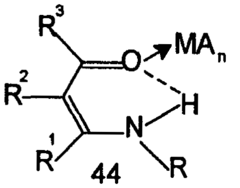

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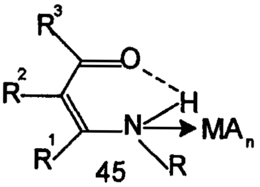

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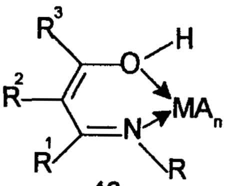

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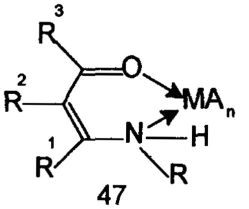
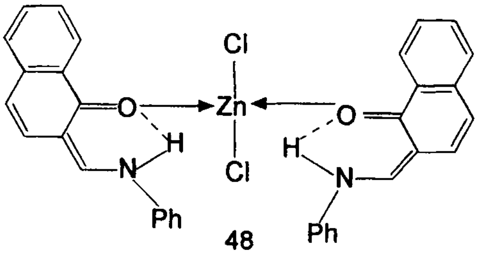


47

In the complex compounds 42–45 the ligands are monodentate, but have bidentate coordination in compounds 46 and 47.

Conclusions about coordination of the ligands in adducts of types 28 and 29 have been made by comparison of their IR-spectra with those of the corresponding ligands,[7,103] which is not sufficient. X-ray structural investigations showed that structure 44 is the only one of 42–47 that exists. This structure contains a monodentate azomethinic ligand in keto-imine tautomeric form while retaining the inner-molecular hydrogen bond. Existence of the hydrogen bond was established, for example, for complexes of zinc chloride with 2-hydroxy-1-naphtylidenaniline 48[104] and molybdenum dioxodichloride with β-aminovinylketones 49,[105,106] as well as for adducts of uranyl acetylacetonate with acetylacetonimine 50[20] and a manganese complex with *o*-hydroxyazomethines 51.[107]



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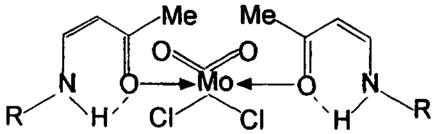

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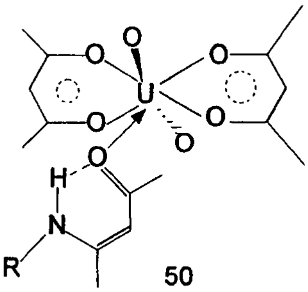

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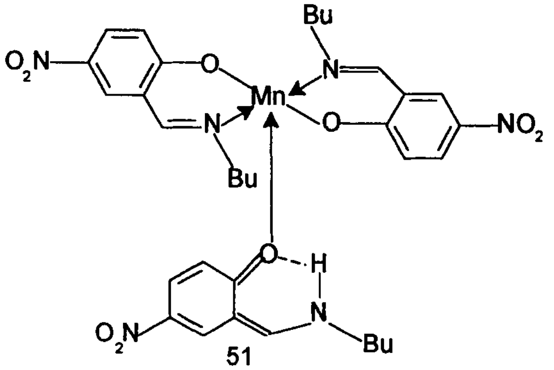
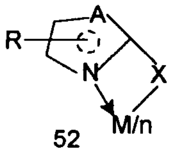


51

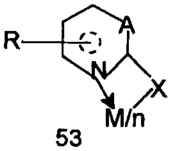
3. METAL COMPLEXES OF EXOCYCLIC DERIVATIVES OF AZOLES AND AZINES

A wide variety of structures is observed for the complex compounds obtained from ligand systems of type 2, containing O-, S- and Se-donor centers in the exocyclic substituent. The metal-cyclic (chelate) structures of type 52 and 53 are the most common.[108–110]



52

A = NR¹, O, S, Se; X = O, S, Se
R = H, Alk, Cyclo-C_4H_4
R¹ = H, Alk, Ar, Het



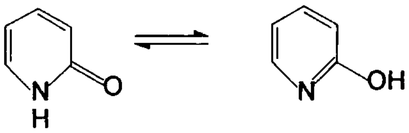
53

A = CH, N; X = O, S, Se
R = H, Alk, Ar, Hal, cyclo-C_4H_4, NO_2

3.1. Complexes of 2-hydroxy(oxo) Derivatives

Coordination chemistry of oxygen-containing ligands, represented by complexes of pyridinone 54, is discussed in detail in a review.[110]

The review[110] discussed mono- (55–57), di- (58–59) and tri- (60,61) nuclear bonding of metals and ligand 54, including tautomery of the type 54a ⟺ 54b.



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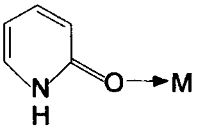

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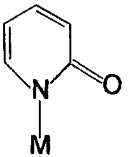

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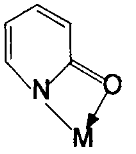

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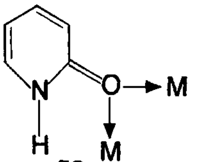

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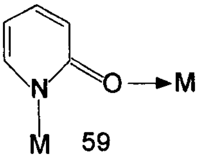

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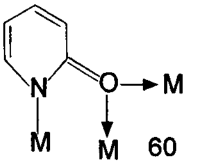

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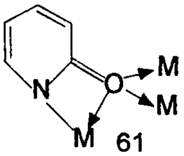
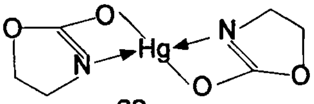


61

Special attention was devoted to bridging,[110] for ligands 54 in complexes with multiple "metal–metal" bonds. It was also mentioned earlier in monographs.[111,112]

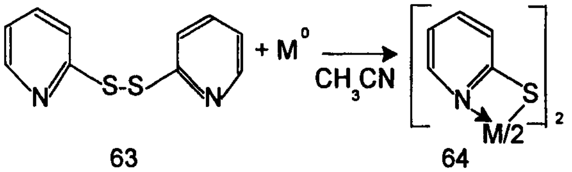


62

In addition, chelate structures of type 57 are frequently found in complexes 52, 53 with an oxygen atom as the endocyclic substituent (X = O). Structure 62 exists, for example, in the mercury complex with 1,3-oxazolidin-2-dione.[113]

3.2. Complexes of 2-S,Se Derivatives

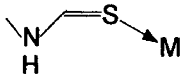
Chelate structures of the type 52 (X = S)[108,114–117] and 53 (X = S)[108–110,118–128] are frequently found in complexes of 2-mercapto derivatives. These compounds are primarily obtained by interaction of ligands of type 2 with metal salts,[108–110,114–117] as well as from disulfides and zero-valent metals in electrosynthesis.[119–125,127,128] For example, complexes 64 have been synthesized from the disulfide 63.



63 64

Complexes 64 and their adducts of the type $ML_2 \cdot nL^1$ (where LH are the mercapthoazoles or mercaptoazines, L^1 is *py*, *dipy*, *o-phen*, and other N-donors), are formed in the presence of different N-bases (L^1).[118,119,124,128] It was recently shown,[129] that a transformation of the type 63 ⇒ 64 could be carried out not only electrosynthetically, but also by chemical dissolution of zero-valent lanthanides (samarium, yttrium). The reaction is carried out in tetrahydrofuran in the presence of hexamethylphosphoramide.

In addition, the presence of N- and X-donor centers in the ligands and their prototropic tautomery lead to different structures of the mercaptoazoles and mercaptoazines, schematically represented by the formulae 65–70.



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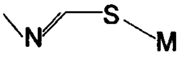

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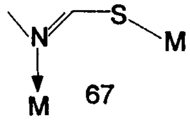

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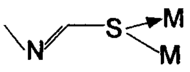

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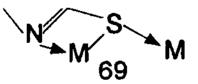

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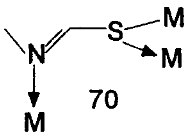
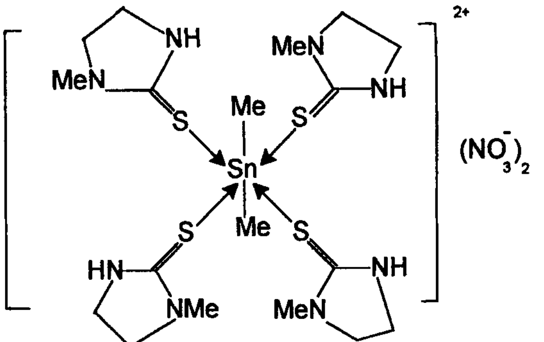


70

Structures of the type 65, where a mercapto derivative participates as a monodentate thionic ligand, are represented by a large group of complexes having the composition $(LH)_mMA_n$; they are discussed in a review[108] and subsequent papers (for example, Refs. 130–132). Similar complexes, from of 1-methyl-2(3H)-imidazolinthione 71,[130] quinoline-2-thione 72[131] and 4, 6-dimethylpyrimidine-2-thione 73,[132] have been characterized by X-ray diffraction.



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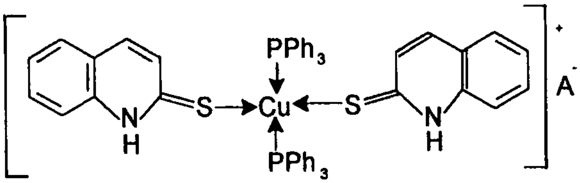
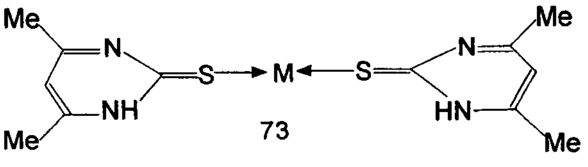


72

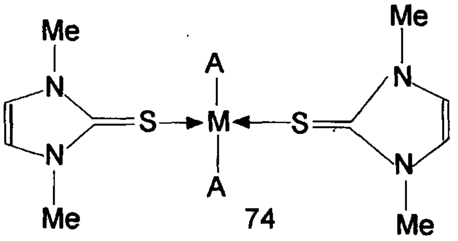
$A = NO_3, ClO_4$



73

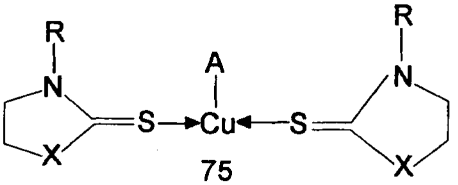
M = Zn, Cd

Metal complexes with fixed thionic ligands have S ⇒ M coordination: 74 with 1,3-dimethyl-2(3H)-imidazolthione,[133] 75 with N-alkylimidazolidin-2-thione ($A = NR^1$) or with thiazolidin-2-thione (A = S).[134]



74

M = Cd, Pb

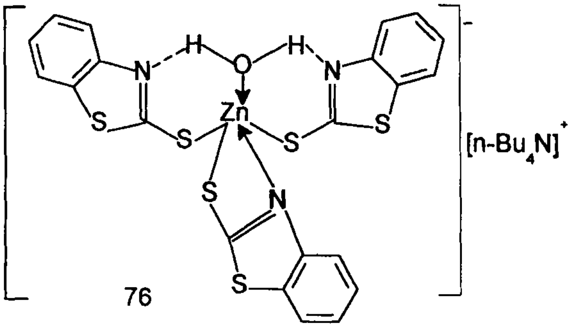


75

R = Alk; X = NR^1, S

R^1 = Me, Et, n-Pr; A = Cl, Br, I

Structures of type 66 have not been characterized to date. These complexes are especially interesting because the thiol form of the ligand, participating in their formation, does not lead to chelate structures. Such monodentate S-coordination is observed[108] in the anion of $[n\text{-}Bu_4N]^+[ZnL_3]^- \cdot H_2O$ (76) and in the cationic copper complex of the specific trisulfuric derivative 77, where the benzothiazol is a ligand.



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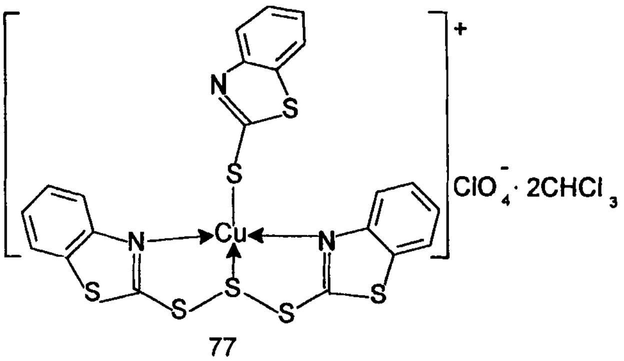
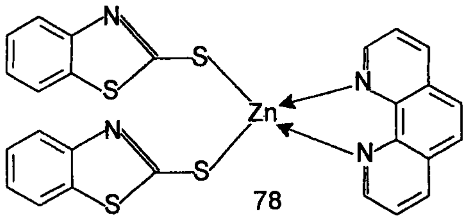


77

Mononuclear binding of the ligand, according to the X-ray data, is also typical for the adduct (78) of the zinc salt of 2-mercapthobenzothiazole with *o*-phenanthroline.[128]

The type of metal binding present in the η^1-S-monodentate coordination of 2-mercaptoazoles, also takes place in complexes of triphenylphosphinegold with 2-mercapto-1-methylimidazole 79,[135] with 8-mercaptotheophylline 80,[136] with 2-mercaptobenzoxazole 81[137] and with purine-6-thiole 82.[138]



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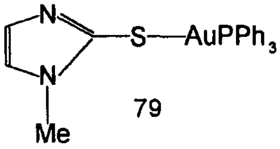

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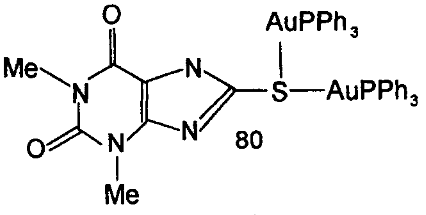

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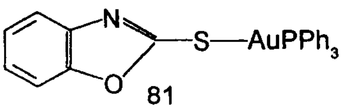

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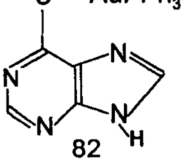
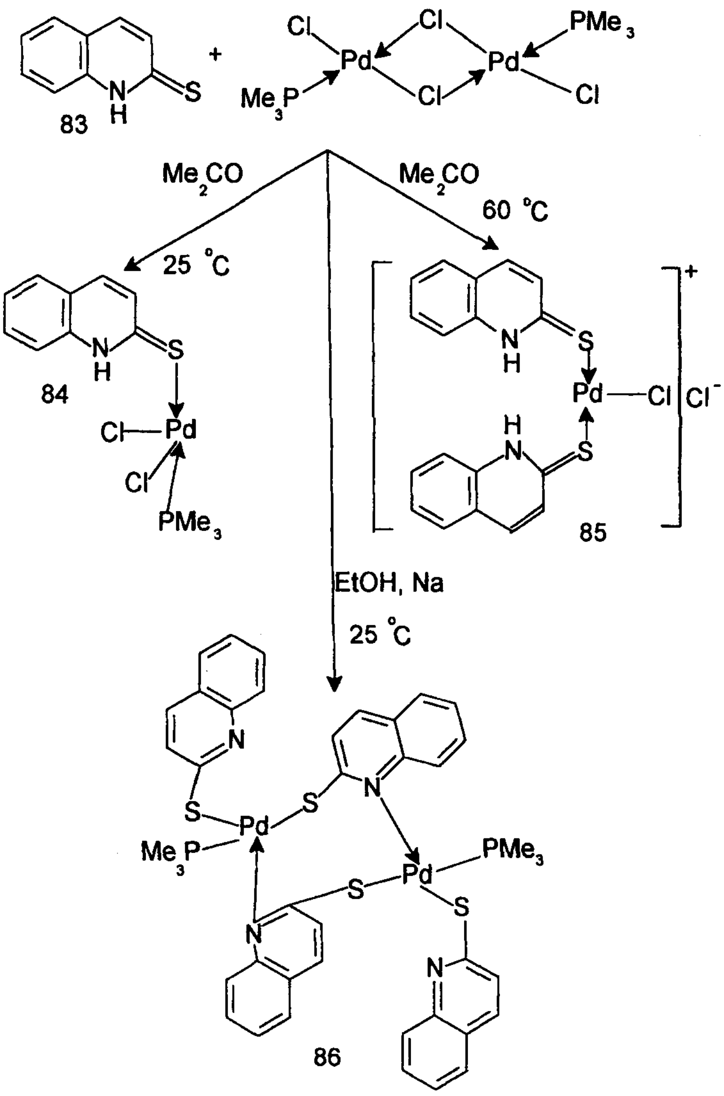
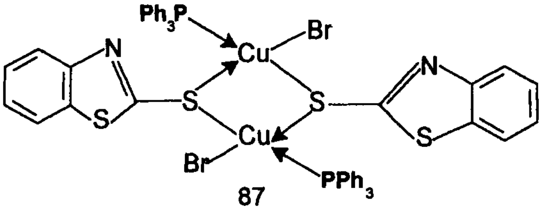


82

Structure 67 with a N,S-bridge is frequently found in binuclear complexes of heterocycles.[108,139–142] The influence of the synthetic conditions on the type of complexes formed is discussed in detail.[139,142] In particular, a scheme[139] is presented, which shows that, depending on the solvent, temperature and pH, different products could be obtained from the same ligands. For example, starting from ligand 83, the molecular mono-S-coordinated adducts 84, 85 could be obtained with the thionic tautomeric form of the ligand or the binuclear complex 86, where the thiol and N-bridge connections occur.

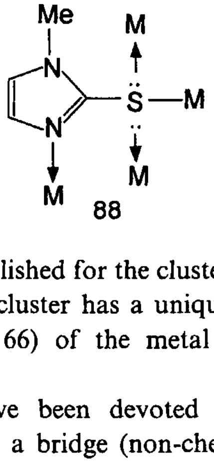


Coordination of type 68 was discovered in several complexes,[108,143,144] for example, in the benzothiazolic dimer of copper (87) with the S–Cu bond.[144]



87

The thiolic sulfur could participate simultaneously in coordination with three copper atoms in a dodeca-nuclear cluster $[Cu^I_2Cu^{II}_2(C_4H_5N_2S)_{12}(MeCN)_4]$, where $C_4H_5N_2S$ is 1-methyl-2-mercaptoimidazole.[145] In this case, a coordination of the type 88 occurs where the imidazole ligand behaves as a tetradentate bridge ligand[145].



88

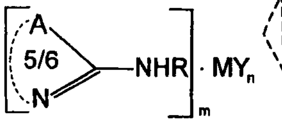
Similar bonding was established for the clusters $Ru_9L_3(CO)_{21}$.[146]

The polymeric cadmium cluster has a unique structure, where different types of connection (2, 65, 66) of the metal with 2-pyridineselenol are observed simultaneously.[147]

Some recent papers have been devoted to mononuclear[148,149] and cluster[150,151] structures with a bridge (non-chelate) N,S-metal bonding of mercaptoderivatives of heterocycles of type 67. Those rare chelates having the N_2S_2-ligand environment (of type 4) of manganese[152] and mixed-coordination (of types 4 and 66) rhenium complexes[153] have also been reported.

3.3. Complexes of 2-aminoderivatives

Unlike 2-hydroxy- and chalcogenhydride derivatives of nitrogen-containing heterocycles 2 (X = O, S, Se), the 2-amino-substituted azoles and azines 2 (X = NR; R = H, Alk, Ar), interact with metal salts to form mainly molecular complexes (adducts) of the type 89.[154,155]



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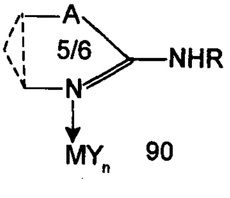

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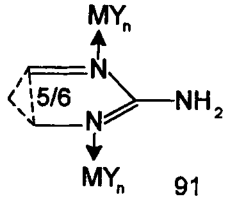


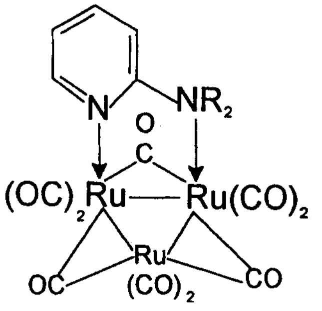
91

In spite of different proposals about possible coordination of the ligands in the complexes of aminoheterocycles, only one has been determined where the N-atom of pyridine (type 90) takes part in the bonding.[155] Localization of the bond has been established for many examples by X-ray diffraction (for example, Refs. 155–160); it has also been proved by quantum chemical calculations.[161–163] When donor pyridinic nitrogen atoms are present in nitrogen-containing heterocycles 91, a bridge N,N-metal bonding takes place.[155,164–166]

In addition, many publications on aminoheterocyclic complexes, where the ligand has a N,N-chelate or bridge function; show both pyridinic and aminic nitrogen atoms participate in the coordination. [111,112,155,167–180]

Coordination with simultaneous bonding of endocyclic η^2-μ-N-atom and N-atom of the amino group is observed, for example, in ruthenium cluster 92,[155] in the trinuclear complex adduct $[Ru^{III}Ru^{III}Ru^{II}OAc_6L_3]L^1_3$, where L = 2-aminopiperazine, L^1 = EDTA,[177] and in the complex of 9-methyladenine with platinum(II) nitrate and trimethylphosphine (93).[179]

Metal clusters with deprotonated amino groups of type 94 have also been described.[111,112,155] Both mono-[155,175,179] and polynuclear[155,167,176] complexes have been obtained. In particular, complexes of 2-methylamino- and 2(2′-pyridyl)aminopyridines (95) with halides and CF_3-substituted pentavalent phosphorus (here the phosphorus atom represents the role of metal) could be attributed to the mononuclear group.[175]



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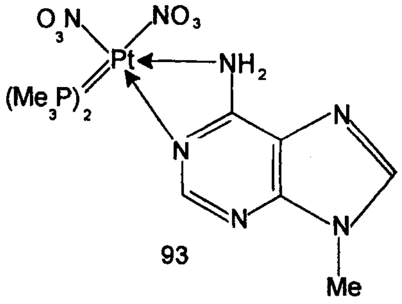
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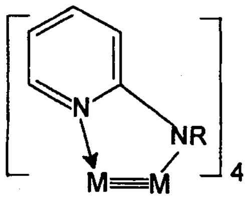
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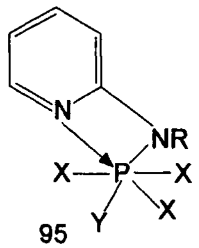
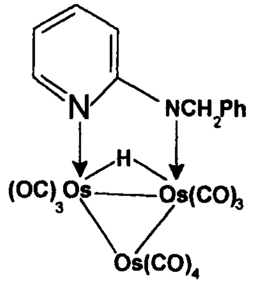
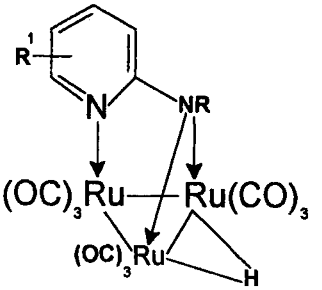

95

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


96

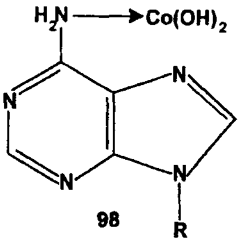

97

R = H, Me, Ph; R^1 = H, Me

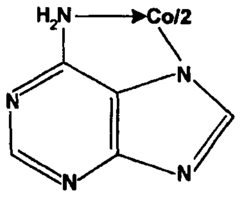
Cluster structures, for example 96, are discussed in a review.[155] The N-atom of the NR-fragment could take part in simultaneous bonding with two metal atoms, forming trinuclear clusters, which are frequently found in aminopyridine ruthenium complexes.[168–174] A general form of these cluster structures is represented by formula 97. It is known that substitution of the

H-atom of the NH_2-group by the metal take place in a series of other aminoheterocycles, for example in citozine[155] and 9-aminoacridine.[181]

Participation of both N-centers is typical for such aminoheterocycles, where the positions of pyridinic and aminic nitrogen atoms contribute to chelate structures. Such a structure was first proposed for the cobalt complexes of purine 98 and 99.[155]

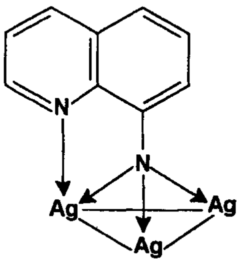


98

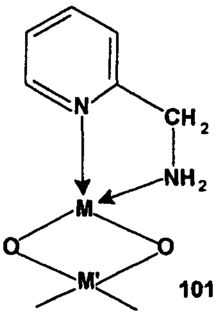


99

Later the existence of structures with N,N-five-membered metallocycles was proven for tri- and tetranuclear clusters of gold(I) with 8-aminoquinoline 100[182] and polymeric copper and rhodium acetate clusters 101.[183]



100



101

M = Cu, M' = Rh

4. FACTORS INFLUENCING COORDINATION OF CHELATE-FORMING LIGANDS

The following factors could affect the coordination of typical chelate-forming ligands: the structure of the ligand systems, the methods and conditions of synthesis of metal complexes and the specific interactions of the ligands and metals as well.

4.1. Thin Structure of the Ligand Systems

It was shown above that the prototropic tautomery of ligand systems and the presence of an inter-molecular hydrogen bond play a primary role in various types of complexes and of different types of coordination of chelate-forming ligands. Precisely for this reason, it is possible to obtain both the chelates and molecular complexes of β-diketones (Section 1), *o*-hydroxyazomethines (Section 2) and exocyclic derivatives of nitrogen heterocycles (Section 3) and their structural analogs.

Another peculiarity of the structure of some ligands examined above is that the presence of two electron pairs, belonging to the oxygen atoms (in particular in the β-diketone and in the hydroxyazomethine molecules and their analogs), leads to the participation of oxygen atoms in the coordination and to the existence of the structures 22–25, 44, 48–51, proven by X-ray diffraction.

4.2. Methods and Conditions of Synthesis

The presence of an acidic XH-group is necessary for formation of standard coordinated metal chelates with anionic ligands of the type ML_m. Direct interaction of the components (ligands LH and metal salts) are used to synthesize metal chelates:[7,14,61,184,185]

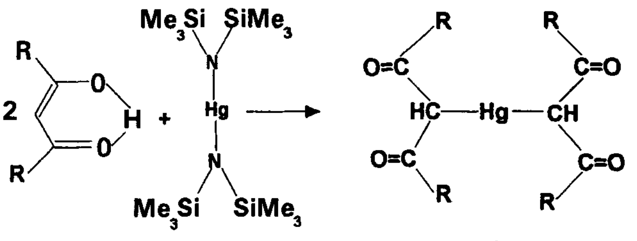
$$m\mathrm{LH} + \mathrm{MX}_m \longrightarrow \mathrm{ML}_m + m\mathrm{HX}$$

Direct synthesis using LH and zero-valent metals in gas-phase [128,186–190] and electrochemical[3,128,191–199] reactions or oxidative dissolution of metals in non-aqueous media[128,192,200–204] are very effective in preparation of chelates of types 3 and 4. Template reactions are also widely used, in which ligand systems are formed in the metal matrix.[7,128,185,205–207]

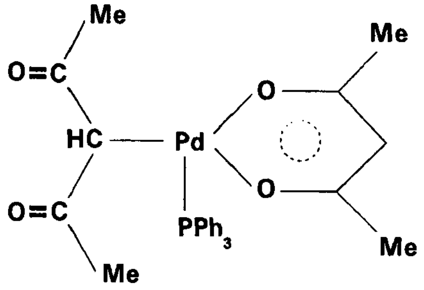
Metal exchange is frequently used to prepare chelates, especially β-diketonates (for example Refs. 14, 27). The method of ligand exchange is also useful in the synthesis of β-diketonates of barium,[24,25] strontium,[24] yttrium[25] and the lanthanides[26] starting from the adducts of ethylates of the mentioned metals with ethanol.

Direct interaction of the exchange components with the ligands is also used to prepare molecular complexes of β-diketonates of type 7,[20] *o*-hydroxyazomethines 28 (X = O) and β-aminovinyl-ketones 29 (X = O, Y = NR).[7,61,103]

Several methods of synthesis of C-metal-substituted β-diketones were proposed. Thus, the C–Hg derivative 104 of β-diketones was obtained in dry ether by reaction of acetylacetone 102 (R = Me) or dipivaloilmethane 102 (R = *t*-Bu) with bis(hexamethyldisilylamino)mercury 103.[208]



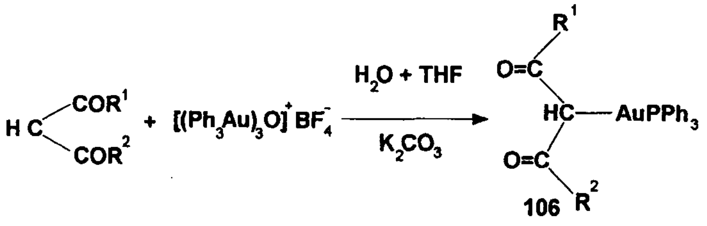
102 103 104



105

The palladium complex 105 with mixed-coordinated acetylacetone molecules (this coordination was proven by X-ray diffraction) was obtained by the reaction of triphenylphosphine with palladium acetylacetonate.[209]

The C-coordinated β-diketonates of univalent gold (106) were obtained as follows:[46]



106

R^1, R^2 = Me, Ph, *t*-Bu, $C_5H_5FeC_5H_4$

A correct choice of metal salts is very important in the synthesis of chelates and molecular complexes; the acetates are best to obtain complexes of the first type, whereas for complexes of the second type, the halides, pseudohalides or nitrates are the best precursors.[7,14,15,61,103,210] Metal β-diketonates 3 (X = Y = O) could also be obtained from nitrates in basic media.[37]

4.3. Nature of the Solvent

The solvent plays an important role in the programmed synthesis of complex compounds. Non-aqueous organic solvents are mainly used in modern coordination chemistry,[1,3,7,61,103] since many organic ligands are not soluble in water. Moreover, many ligand systems and metal salts undergo hydrolysis in water or water–organic media. The influence of the solvent on the reaction path in synthesis of coordination compounds is examined in detail in a review.[211] Metal chelates of the azomethinic and related chelate-forming ligands are usually formed in highly protic, polar solvents (mainly alcohols), while adducts are mainly obtained starting from the same ligand systems in aprotic solvents of low polarity (hydrocarbons and their halogenated derivatives).[211,214]

4.4. Specific Interactions

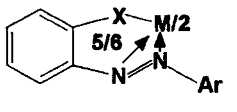
Other factors influencing the coordination of chelate-forming ligands are the specific hard–soft interactions,[4,212–214] As the data given above show, in general, a hard–hard interaction leads to formation of O-coordinated structures in a series of β-diketonate and *o*-hydroxyazomethinic ligands, while a soft–soft interaction contributes to formation of C–M bonds ($M = Hg, Au, Pd, Pt$). However, the use of the hard–soft and bases acids principles requires more detailed research, taking into account that specific synthetic methods are sometimes used to obtain C- and C,O-coordinated structures of β-diketones (see above).

5. CONCLUSIONS

This review gives an overview of the synthetic methods for formation of different types of metal complexes with typical chelate-forming ligands. It is necessary to take these data into consideration to evaluate the coordination possibilities of di- and polydentate ligands and to determine the procedure for selective synthesis of the complexes, i.e., the programmed formation of complex compounds with a given type of bonding of the metal with the ambidentate ligand system.

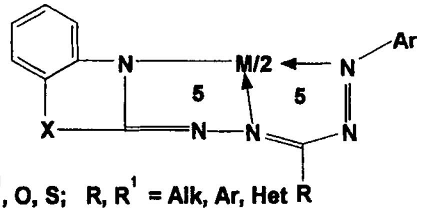
This review only covers a part of the topic of standard and non-standard coordination of typical polydentate ligand systems.[4,212,213] Other aspects of this topic are, for example, the usual $\eta^1(\sigma)$ and unusual $\eta^n(\pi)$-coordinations ($n = 5, 6$) of five- and six-member nitrogen heterocycles (general publications[4,212,213,215,216] are devoted to this issue), the possibility of different coordination in the various kinds of "direct synthesis" of metal chelates starting from zero-valent metals,[3,128,186-203,217-221] including the influence of oxide layer on the metal surface on coordination of a ligand.[200]

The problem of "inner-chelate competitive coordination" is also related.[61,222,223] In particular, the azocompounds 30, 107[61,72,222,224-227] and phormazanes 32, 108[61,73,76,228] could be used as examples of this.



X = O, S

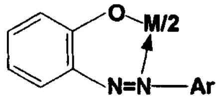
107



X = NR^1, O, S; R, R^1 = Alk, Ar, Het

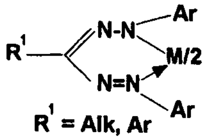
108

The structures containing two six-member metallocycles are standard for chelates of azocompounds. Thus, this structural type is typical for complexes of *o*-hydroxyazocompounds 109.[61,229] However, in the case of *o*-mercaptoazo derivatives (107: X = S), the complexes with two five- or five- and six-membered coordination shells (107) are formed.[61,224-227] The same situation is observed for chelates of the N-phenyl-[222] and N-tosyl-[72] azoderivatives (see 30, 107) (X = NR; R = NPh, Nts).



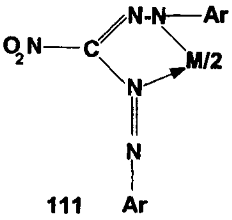
109

The aromatic azomethines form, in general, *bis*-chelates (110) containing six-membered metallocycles.[76] However, the examples of complexes with five-membered metallocycles 111[76,228] are also known for aromatic phormazanates. They are specially widely represented among metal chelates of hetaryl phormazanates 108.[76,228]



R^1 = Alk, Ar

110



111

Progress on competitive coordination of ligands is a perspective direction in the modern coordination chemistry.[214,230] The material, generalized in this manuscript, could be widely used in lecture courses on coordination chemistry, as well as in the preparation of manuals and monographs. Unfortunately, only standard coordination of chelates are presently discussed in manuals and textbooks on coordination chemistry.

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