Russian Chemical Reviews **78** (7) 643 – 658 (2009)

DOI 10.1070/RC2009v078n07ABEH003890

Metal complexes with polyfunctional ligands based of bis(hydrazones) of dicarbonyl compounds

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Contents

Abstract. Data on the metal complexes with bis(hydrazones) obtained from various classes of dicarbonyl compounds are generalized and described systematically. The structures and complexing properties of bis(hydrazones) are considered and the factors influencing structures of the metal complexes are analyzed. The relationships between the structures and physicochemical properties of the considered compounds are discussed. The bibliography includes 240 references.

I. Introduction

Hydrazones are the condensation products of hydrazine derivatives with carbonyl compounds, they contain an acyclic group $>C{=}N-N<$. It is long since hydrazones and their derivatives, due to their high complexing ability, have attracted the attention of scientists. Depending on various factors (the nature of the hydrazone and the metal atom, reaction conditions, the ratio of reactants *etc.*) hydrazones form either mono- or polynuclear coordination compounds with metal atoms. These complexes have found applications in different areas of science and technology, *e.g.*, in homogeneous catalysis, in bioinorganic chemistry (as models of metalloenzymes and oxygen activators), in magnetochemistry (for the investigation of the exchange interaction and the design of new magnetic materials), in medicinal chemistry and agricultural chemistry, in materials science (for the preparation of materials with predetermined properties).

The beginning of the investigations into the complexing ability of hydrazones was connected with their wide use in analytical chemistry (as effective extractants, chromogenic reagents, selective sensors) and also in electrochemistry (in the investigation of the corrosion processes, for the formation of different metal-containing coatings). In the recent years, metal complexes with hydrazones have found application in supramolecular chemistry due to their ability to form supramolecular structures in crystal. This opens the possibilities for the tailor-made design of substances with the predictable properties.

From the theoretical point of view, hydrazones and their metal complexes are of interest for the investigation of different tautomeric (isomeric) forms and their interconversions, for the establishing the structure – property relationships and the mechanisms of the complexing reactions and also for the investigation of different aspects of the reactivity of metal complexes.

At present, vast experimental material has been collected on the polyfunctional Schiff bases and monohydrazones as well as their complexes, these data are generalized in a number of reviews and monographs (see, *e.g.*, Refs 1 – 7); however, no reviews on complexes based on bis(hydrazones) are available. Some data on these compounds can be found in monographs [6,7] and reviews,[4,5,8–12] but all of them have fragmentary character.

In the present review, the literature data on the coordination derivatives of bis(hydrazones), bis(semicarbazones) and bis(thiosemicarbazones) of dicarbonyl compounds published mainly over the past two decades are generalized for the first time. The primary attention is paid to the derivatives that contain substituents with functional groups capable of complexing, since such structures are of greatest interest as possible ligands. We do not consider metal complexes with the so-called 'inverse' bis(hydrazones), which are the condensation products of monocarbonyl derivatives with dicarbohydrazides or carbo(thiocarbo)hydrazide. Abundant data are also accumulated on this class of compounds, their generalization can become the topic of a separate review.

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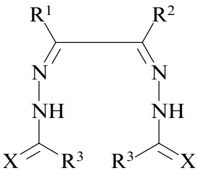
Received 11 February 2009
Uspekhi Khimii **78** (7) 697 – 713 (2009); translated by I V Glukhov

It was not our task to describe in detail all the aspects of the coordination chemistry of bis(hydrazones), but we rather tried to reflect the general state of investigations in this area of coordination chemistry. In the present review, the metal complexes with bis(hydrazones) are considered in the order of complication of their structures.

II. Bis(hydrazones) of α-, β-and γ-dicarbonyl compounds and their metal complexes

Bis(hydrazones) **1**, *i.e.*, the 1 : 2 condensation products of symmetrical or non-symmetrical derivatives of α-diketones (glyoxal, diacetyl, benzil) with hydrazides, are the simplest complexing polyfunctional systems containing bis(hydrazone) groups.



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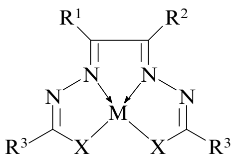


2

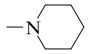
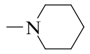
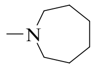
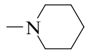
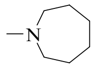
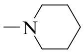
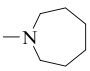
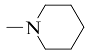
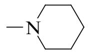
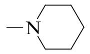
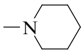
X = O, S, NR; R^1, R^2 = H, Me, Ph, Het; R^3 = Ar, Alk;
M = Ni, Cu, Co, Zn, Cd, Pt, *etc.*

Bis(hydrazones) of type **1** usually have chain structures, but sometimes, as in the case of diacetyl bis(thiobenzoylhydrazone), they are cyclic.[6,7]

Bis(hydrazones) **1** interact with metal ions to form mononuclear complexes **2**, which contain three fused five-membered metallacycles. In these complexes, bis(hydrazones) **1** usually act as tridentate chelating systems. Table 1 lists metal complexes **2** that were investigated by X-ray diffraction analysis and other physicochemical methods (IR, NMR, EPR spectroscopy). In some cases, the formation of dimeric metal chelates is possible through the additional coordination of the sulfur atoms of the thiosemicarbazide fragments to the metal atom[15–17,24,37] or through the formation of H-bonds between the mononuclear complexes with the formation of supramolecular structures.[15]

Analysis of the literature data has shown that metal chelates **2** possess similar structures: the ligands in complexes are in the enol doubly deprotonated form. Metallacycles in the majority of complexes **2** have planar structures with slight deviations. For example, the Ni(II) complex with diacetyl bis(*p*-methoxybenzoylhydrazone) has a mononuclear structure[14] with *cis*-arrangement of the donor nitrogen and oxygen atoms. The coordination fragment MN_2O_2 is a virtually planar square. The diamagnetic character of the complex as well as the d – d-transition band in the region

Table 1. Metal complexes **2** with bis(hydrazone) ligands of the type **1** with known structure.

M(II)	X	R^1	R^2	R^3	Ref.	M(II)	X	R^1	R^2	R^3	Ref.
Ni	O	Me	Me	Ph	13	Cu	S	Ph	Ph		31
	O	Me	Me	C_6H_4OMe-*p*	14						
	S	Me	Me	NHMe	15		S	Et	Et		32
	S	Me	Me	Ph	16						
	S	Me	Me	Bn	17		S	Et	Et		32
	S	Me	Me	NPhMe	18						
	S	H	Ph	NEt_2	19, 20		S	2-Py	2-Py		33
	S	Me	H	NEt_2	21						
	S	Me	H	NHMe	21		S	2-Py	2-Py		33
	S	Me	Me	Bn	22						
							S	2-Py	2-Py	NEt_2	33
	S	2-Py	2-Py		23						
						Zn	S	H	CHMe(OEt)	NH_2	34
							S	Me	Me	SMe	35, 36
	S	2-Py	2-Py		23, 24		S	H	H	SMe	37
	S	2-Py	2-Py	NEt_2	23		S	H	Ph		38
	S	2-Py	2-Py	NPr_2	23						
	NH	Ph	Ph	SEt	25	Cd	S	H	Ph		38
Cu	S	H	H	NH_2	15		S	Ph	Ph	NH_2	39
	S	H	H	NHMe	15						
	S	Me	H	NH_2	15	Pd	S	H	Ph	NEt_2	19
	S	Me	Me	NHMe	15, 26	Co[a]	O	Me	Me	C_6H_4OMe-*p*	40
	S	Me	Me	NMe_2	15						
	S	Me	Et	NH_2	15	Pt	S	H	Ph		38
	S	Et	Et	NH_2	15						
	S	Ph	Ph	NH_2	27, 28		S	2-Py	2-Py	NPr_2	41
	S	H	CHMe(OEt)	NH_2	29, 30						
	S	H	Ph	NEt_2	19	UO_2	S	Me	Me	Ph	42
							S	H	CHMe(OEt)	NH_2	43
	S	Me	Ph		31						
						Nd[a]	O	Ph	Ph	NH_2	44

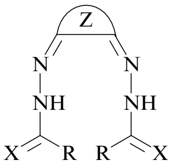
[a] M(III).

of 580 nm in the UV spectra also point to the planar structure of the coordinating unit. The M−O and M−N bond lengths are equal to 1.894 and 1.795 Å, respectively, and are close to the values in analogous metal complexes.

In contrast to the considered Ni(II)complex, Cu(II) complexes of type **2** are paramagnetic;[11,27] the values of the magnetic moments are in the range of the 'normal' values (1.75−1.9 μ_B) and virtually do not change with the decrease in temperature down to 77.4 K, which suggests the mononuclear structure of the copper complexes. The EPR spectra of the copper complexes **2** with X = O at 110 K are typical of the complexes with the axial symmetry ($g_{\|} \approx 2.11$, $g_{\perp} \approx 2.02$, $A_{\|} \approx 185-193$ Gs) and consist of four lines of different intensity and width. An additional hyperfine structure (AHFS) consisting of five lines is observed in solutions, which corresponds to the coordination of both azomethine nitrogen atoms to the metal, while the value of the *g*-factor indicates their relative *cis*-orientation. With the substitution of the sulfur atom for oxygen, the value of the *g*-factor decreases, while the HFS and AHFS constants increase. This is, most probably, caused by the increase in the extent of the covalent nature of the S−Cu bond compared to the O−Cu bond. Studies of the effect of the substituents R^1 and R^2 on the structures and properties of copper(II) complexes with bis (thiosemicarbazones) showed[15] that the introduction of substituents results in the elongation of the C−C bond allowing the metal to fit better into the ligand cavity with shorter Cu−S bonds.

The Zn(II) and Cd(II) complexes, as a rule, have octahedral structure of the chelate unit due to the additional coordination of the solvent molecules or acid residues to the metal atom,[34, 38, 39] while the increase in the coordination number up to eleven is typical of the complexes with rare-earth metals.[44] Complexes containing acid residues as ligands are non-electrolytes, which suggests the intra-sphere covalent binding character of these ligands to the metal atom.

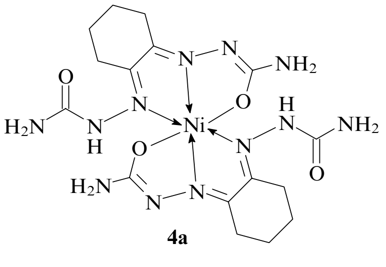
Both carbonyl groups of cyclic 1,2-diketones (benzoquinone, acenaphthoquinone, phenanthrenequinone) also react with hydrazides to form bis(hydrazones) (compounds **3**).



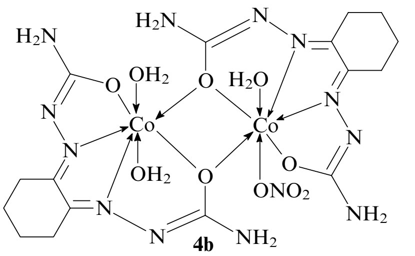
3

Z = Ar, Naph, Antryl.

The structures of the nickel and cobalt complexes with such ligands were studied. [45,46]It was found that cyclohexane-1,2-dione bis(semicarbazone) can act as tri- or tetradentate ligand with respect to the metal atom; either mono- (**4a**) or binuclear (**4b**) complexes are formed.[46]



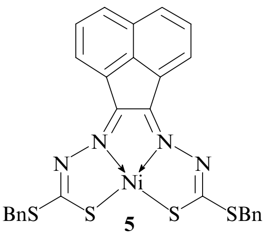
4a



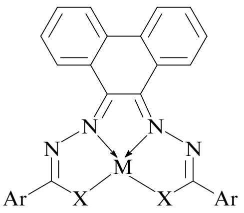
4b

Bis[cyclohexane-1,2-bis(2-pyridylhydrazonato)]dinickel(II)[45] has an unusual dimeric structure in which two nickel atoms are bound to three nitrogen atoms of one ligand and one nitrogen atom of the pyridyl substituent of the other ligand.

The structure of nickel complex **5** was studied[47] by X-ray diffraction analysis. The X-ray structural data on the chelates of type **6** are absent due to their extremely low solubility in organic solvents, so the structures of copper(II), nickel(II) and cobalt(II) complexes of type **6** were studied by indirect methods (IR, UV, EPR spectroscopy, diffuse scattering spectroscopy, magnetochemistry).[48]



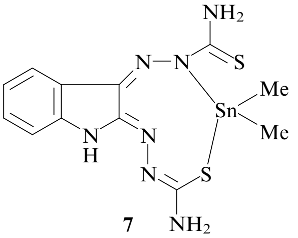
5



6

M = Cu(II), Ni(II), Co(II);
X = S, O.

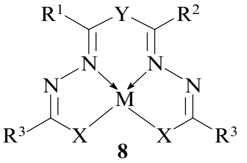
The bis(thiosemicarbazone) prepared from non-symmetrical α-diketone isatin and thiosemicarbazide reacted with Me_2SnO to afford complex **7**.[49]



7

Its unusual coordination type is, most probably, caused by the non-equivalence of the thiosemicarbazone fragments linked with the indole moiety.

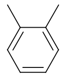
The beginning of the investigations of the bis(hydrazone) complexes based on β- and γ-diketones dates back to the 1980s.[50] Chelates **8** with bis(hydrazonate) ligands based on β- and γ-diketones, for which the molecular structures were established, are listed in Table 2.



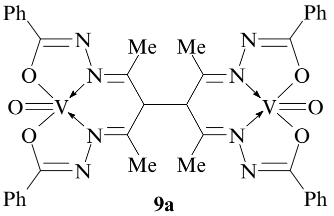
8

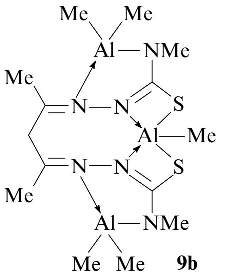
In addition to mononuclear coordination compounds of type **8**, di- and trinuclear metal organic compounds [M = Al(III), In(III) and VO(IV)] were synthesized with bis(thiosemicarbazonate)[59, 60] and bis(benzoylhydrazo-

Table 2. Metal complexes **8** with bis(hydrazone) ligands based on β- and γ-diketones.

M	X	R^1	R^2	R^3	Y	Ref.
$\mathrm{Ni^{II}}$	O	Me	Me	Ph	CH_2	51
	S	Me	Me	Me	CH_2	52
	S	Me	Me	Me	C(O)	52
	S	Me	Me	C_6H_4OH-*o*	C(O)	53
	S	Me	Me	NHPh	$(CH_2)_2$	54
	S	Me	Me	NHMe	$(CH_2)_2$	55
	S	H	H	NHMe		55
	NH	Me	Me	SMe	CH_2	56
$\mathrm{Co^{III}}$	NH	Me	Me	SMe	C(O)	57
$\mathrm{Fe^{III}}$	S	Me	Me	SEt	CH_2	58

nate)[61] ligands based on β-diketones (*e.g.*, acetylacetone). Vanadyl cross-linked macrocyclic binuclear complex (**9a**)[61] and aluminium trinuclear complex (**9b**)[59] can be given as examples.


9a

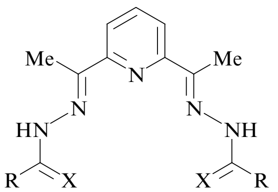

9b

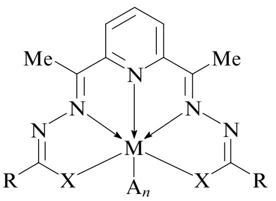
In contrast to the metal complexes with bis(hydrazones) of α-dicarbonyl compounds, which have planar structures of the coordination centres, metal complexes with bis(hydrazones) of β- and γ-dicarbonyl compounds have a distorted tetrahedral structure, which is connected with higher flexibility of one of the metallacycles due to the appearance of additional methylene units.

III. Bis(hydrazones) of dicarbonyl derivatives of heterocycles and their complexing ability

The introduction of a heterocyclic fragment (pyridine, furan, thiophene *etc.*) into the molecule of bis(hydrazone) allows increasing the denticity of the ligand systems formed due to the increase in the number of donor centres. This widens the possibility of the application of such ligands as effective complexing agents. 2,6-Diacetylpiridine bis(hydrazones) (compounds **10**) are studied in most details.

Reactions of bis(hydrazones) **10** with metal salts affords, as a rule, mononuclear symmetrical complexes with the composition $[M(H_2L)A_n]$ and structure **11**.


10 (H_2L)

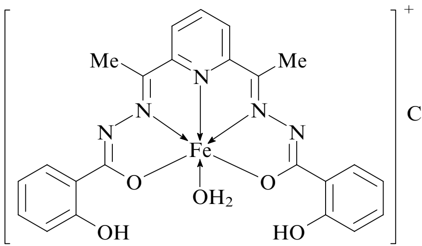

11

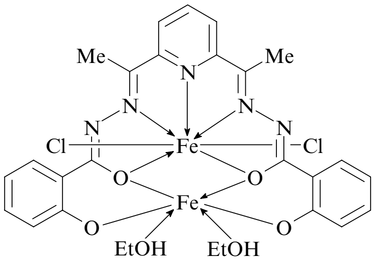
X = O, S, NH; R = Alk, Ar, Het; A are solvent molecules or acid residues.

Metal complexes of this type are numerous. Structural data on such complexes are partially considered.[6] The newer data obtained after this monograph was published are presented in Table 3.

Analysis of the literature data allows one to infer that the large majority of the coordination compounds of metals with 2,6-diacetylpiridine bis(hydrazones) have the structure of a distorted pentagonal bipyramid with the coordination number of the central metal atom equal to seven. The pyridine nitrogen atom, the azomethine nitrogen atoms and atoms X (X = O, S, NH) of the hydrazone fragment are involved in the metal coordination. All these atoms occupy the equatorial metal positions, while the solvent (water, alcohols) molecules or acid residues can be located in the axial positions.

Depending on the conditions of synthesis (stoichiometry, the nature of the metal atom and solvent, pH of the medium) 2,6-diacetylpyridine bis(hydrazones) can exist in the complex in both non-protonated (H_2L) and monodeprotonated (HL) and doubly deprotonated (L) forms. Thus metal halides form complexes with the composition $[M(H_2L)Y_2]\cdot n\,H_2O$ with bis(hydrazones) **10** at $pH \leqslant 7$, while metal acetates form chelate compounds with the composition $[ML_2]\cdot n\,H_2O$ in the basic medium. Moreover, one can pass from mononuclear complexes to binuclear complexes by varying the reaction conditions.[68, 81, 88, 112] Thus the reaction of iron(III) chloride with 2,6-diacetylpyridine bis(salicyloylhydrazone) (H_4daps) in ethanol yields the complex $[Fe(H_4daps)Cl_2]\cdot 0.5\,H_2O$, its treatment with a solution of sodium thiocyanate in ethanol leads to the mononuclear iron complex $[Fe(H_2daps)(OH_2)]NCS$ (**A**). Binuclear complex **B** is formed in the reaction of an excess of $FeCl_2$ in anhydrous ethanol with monosodium salt of H_4daps, which is prepared by treatment of a solution of H_4daps in chloroform with acetic anhydride in a 1 : 1 chloroform – acetonitrile mixture in the presence of solid sodium acetate.[112]

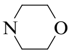
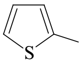
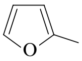
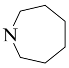
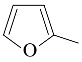
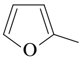
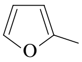
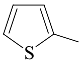
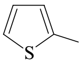
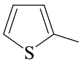
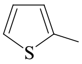
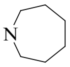

A


B

The ligand H_4daps in complex **A** is pentadentate and is doubly deprotonated, while in complex **B** it is heptadentate and tetradeprotonated. In complex **B**, both iron atoms have a formal oxidation state of 3+ but differ in the coordination environment.

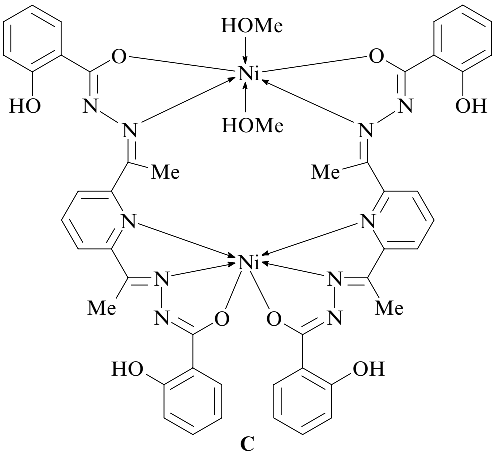
Complex **B** was also studied by Mössbauer spectroscopy.[112] The Mössbauer spectrum of this complex is a

Table 3. Metal complexes with macrocyclic ligands **10**.

M	X	R	Composition of the complex	Ref.
Ni^{II}	O	NH_2	$[Ni(HL)_2]\cdot 5H_2O$	62
	O	NH_2	$[Ni(H_2L)(H_2O)_2](NO_3)_2\cdot H_2O$	63
	O	Me	$[Ni(H_2L)(H_2O)_2](NO_3)_2$	64
	O	n-C_7H_{15}	$[Ni(H_2L)(H_2O)_2]Cl_2$	65
	O	CO_2H	$[Ni(H_2L)_2](ClO_4)_2$	66
	O	C_6H_4OH-*o*	$[Ni(H_2L)(H_2O)_2](NO_3)_2\cdot H_2O$	67
	O	C_6H_4OH-*o*	$[Ni_2L_2Py_2]\cdot CH_2Cl_2$	68
	O	CH(OH)Ph	$[Ni(H_2L)L]\cdot 13H_2O$	69
	S	NMe_2	$[NiL_2]$	70
	S		[NiL]	71
	S	SMe	[NiL(NCS)]	72
	S	SBn	$[NiL_2]\cdot 2H_2O$	73
	NH	SMe	[Ni(HL)I]	74
Cu^{II}	O	NH_2	$[Cu(H_2L)Cl(H_2O)]Cl\cdot 2H_2O$	75
	O	NH_2	$[Cu(H_2L)(H_2O)_2](NO_3)_2\cdot H_2O$	63
	O	Me	$[Cu(H_2L)(H_2O)_2](NO_3)_2\cdot H_2O$	76
	O	2-Py	$[Cu_2LBr]\cdot 2H_2O$	77
	O	$C(O)NH_2$	$[CuL(H_2O)]\cdot H_2O$	78
	O	$C(O)NH_2$	$[Cu(HL)(H_2O)]ClO_4$	79
	O	$CH_2C(O)OMe$	$[Cu(H_2L)Cl_2]\cdot H_2O$	80
	O	C_6H_4OH-*o*	$[Cu_2L_2(H_2O)]\cdot CNMe$	81
	O		$[CuL]_2$	82
	NH	NH_2	$[H_5L]\{CuCl_4]Cl\cdot H_2O$	83
Zn^{II}	O	NH_2	$[Zn(H_2L)(H_2O)_2](MeCOO)_2\cdot 5.5H_2O$	84
	O		$[Zn(H_2L)Cl(H_2O)]Cl\cdot 4H_2O$	85
	S	NH_2	$[Zn_2(H_2L)_2]$	86
	S	NH_2	$[Zn_2L_2]\cdot MeOH\cdot H_2O$	87
	S	NMe_2	$[Zn_2L_2]\cdot CNMe$	88
	S	SBn	$[Zn_2L_2]$	89
	S		$[ZnL]_2$	90
Co^{II}	O	NH_2	$[Co(H_2L)(H_2O)_2](MeCOO)_2\cdot 6H_2O$	62
	O	NH_2	$[Co(H_2L)(H_2O)_2](NO_3)_2\cdot H_2O$	62
	O	$C(O)NH_2$	$[CoL(H_2O)_2]\cdot 4H_2O$	91
	O	$C(O)NH_2$	$[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2$	92
	O	2-Py	$[Co(H_2L)(H_2O)_2]\cdot 4H_2O$	93
	O	Ph	$[Co(H_2L)(NO_3)(H_2O)]NO_3$	94
	O	C_6H_4OH-*o*	$[CoLPy_2]$	68
	O	C_6H_4OH-*o*	$[Co(H_2L)(H_2O)_2](NO_3)_2$	95
Mn^{II}	O	NH_2	$[Mn(H_2L)Cl_2]$	96
	O	NH_2	$[Mn(H_2L)(NCS)_2]$	97
	O	Me	$[Mn(H_2L)(H_2O)_2](NO_3)_2$	64
Mn^{II}	O	Ph	$[Mn(H_2L)Cl(H_2O)]Cl$	98
	O	C_6H_4OH-*o*	$[MnLPy_2]\cdot CH_2Cl_2$	68
	O	C_6H_4OH-*o*	$[MnL(EtOH)(H_2O)]$	99
	O	$C_6H_4NH_2$-*o*	$[Mn(H_2L)Cl(MeOH)]Cl\cdot H_2O$	100
	O	2-Py	$[MnL]\cdot 9H_2O$	101
	S	NH_2	$[Mn(H_2L)(H_2O)_2](ClO_4)_2$	102
	S	SMe	[MnL]	103
Cd^{II}	O		[CdLCl]Cl	104
	O	C_6H_4OH-*o*	$[Cd(H_2L)Cl_2]\cdot CHCl_3\cdot MeOH$	105
	O	C_6H_4OH-*o*	$[CdL(H_2O)_2]$	106
Hg^{II}	O		[HgLCl]Cl	104
Fe^{II}	O	NH_2	$[Fe(H_2L)Cl(H_2O)]Cl\cdot 2H_2O$	107
	O		$[Fe(H_2L)Cl]Cl$	108
Fe^{III}	O	NH_2	$[Fe(H_2L)Cl_2]Cl$	109
	O	CO_2H	$[FeL(H_2O)]_2O\cdot 3H_2O$	110
	O	$C(O)NH_2$	$[FeL(H_2O)_2]ClO_4\cdot H_2O$	111
	O	C_6H_4OH-*o*	$[Fe_2LCl_2(EtOH)_2]$	112
	S	NH_2	$[Fe(H_2L)(NCS)_2]\cdot 2H_2O$	113
	NH	SMe	$[FeL(N_3)_2]$	114
Cr^{III}	O	NH_2	$[Cr(HL)(H_2O)_2](NO_3)_3\cdot 2H_2O$	115
Bi^{III}	O		$[BiL(OH)]\cdot DMSO\cdot H_2O$	116
	O		$[Bi(HL)Cl_2]\cdot DMSO\cdot H_2O$, $[BiLCl]\cdot DMSO$	117
La^{III}	O	Ph	$[La(H_2L)(NO_3)_3]$	118
	O		$[La(HL)Cl_2(H_2O)_3]Cl$	119
Y^{III}	O	Me	$[Y(H_2L)(H_2O)_4](NO_3)_3$	120
Pr^{III}	O	NH_2	$[Pr(H_2L)(H_2O)_2]Cl_3$	121
Sc^{III}	O	NH_2	$[Sc(H_2L)(H_2O)_2]OH(NO_3)_2$	122
Sn^{IV}	O		$[Et_2SnL]$	123
	S	NH_2	$[Me(Ph)Sn(HL)]Cl\cdot 1.25MeOH$	124
	S	NH_2	$[Et(Ph)Sn(H_2L)]Cl_2\cdot MeOH\cdot H_2O$	124
	S		$[Bu^n_2SnL]$	90
V^{IV}	S	NH_2	$[\{VL(MeOH)\}_2O](ClO_4)_2$	125
U^{IV}	O	Ph	$[UO_2L(DMSO)]$	126
	O	NHPh	$[UO_2L]\cdot[UO_2L(DMSO)]\cdot DMSO\cdot H_2O$	126
Re^{III}	O	Ph	$[Re(H_2L)Cl(PPh_3)]$	127

symmetrical, well resolved doublet. The chemical shift values suggest the high-spin state of both Fe^{3+} atoms (δ = 0.459 and 0.494). However, high magnitudes of the quadruple splitting ($\Delta E_Q = 1.063$ and 2.076) contradict this conclusion. Nevertheless, it is believed that the iron atoms in this complex are in the high-spin state.

The interaction of 2,6-diacetylpyridine bis(salicyloylhydrazone) with the divalent nickel ion in methanol yields also binuclear complex **C**, but while in Fe(III) complex this ligand is tetradeprotonated, in Ni(II) complex it is doubly deprotonated. In complex **C**, both Ni(II) atoms coordinate two H_2daps^{2-} ligands. Such a coordination leads to the 'bending' of the ligand, which causes apparently violation of the conjugation of the hydrazone part of the molecule with the π-system of the pyridine fragment. Both nickel atoms in complex **C** have octahedral configuration.

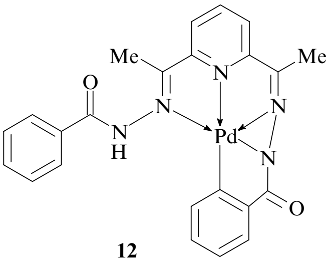


C

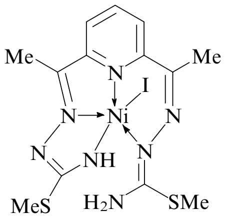
The same ligand with Mn(II) yields mononuclear complex, its structure is in general analogous to the structure of complex **A**. The geometry of the coordination centre of the Mn atom is the distorted pentagonal bipyramid.[99]

Magnetochemical measurements of Ni(II) and Mn(II) complexes suggest the high-spin character of the metal atoms [$\mu_{eff}(Ni^{II}) = 2.9\ \mu_B$, $\mu_{eff}(Mn^{II}) = 5.7\ \mu_B$].

Several examples of the metal complexes with 2,6-diacetylpyridine bis(hydrazone) with non-symmetrical structure are known. These are for example complexes **12** and **13**.[74,128]

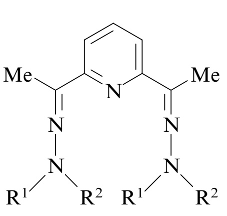


12



13

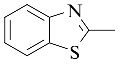
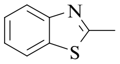
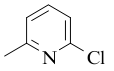
The ligands of type **14** with aromatic, aliphatic or heterocyclic hydrazine fragments are genetically similar to ligands of type **10**. Table 4 lists complexes based on bis(hydrazones) **14** for which the structure was established by X-ray diffraction analysis.



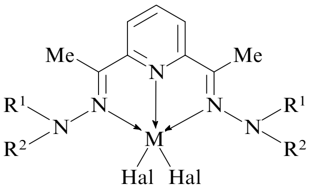
14

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

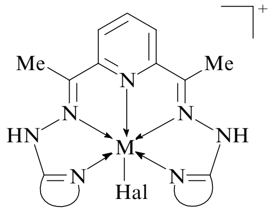
Table 4. Complexes based on bis(hydrazones) **14**.

M	R^1	R^2	Composition of the complex	Ref.
Cu^{II}, Co^{II}, Ni^{II}, Mn^{II}, Zn^{II}, Cd^{II}	H		$[M(H_2L)Cl]Cl \cdot H_2O$	129
VO^{II}	H		$[VO(H_2L)SO_4] \cdot H_2O$	129
Fe^{II}	Me	Me	$[Fe(H_2L)Cl_2]$	130
	Ph	Ph	$[Fe(H_2L)Cl_2] \cdot 0.5\,CH_2Cl_2$	130
	Ph	Me	$[Fe(H_2L)Cl_2] \cdot MeCN$	130
Co^{II}	Ph	Ph	$[Co(H_2L)Cl_2] \cdot 1.5\,CH_2Cl_2$	130
Hg^{II}	Me	2-Py	$[Hg(H_2L)Cl]_2 \cdot Hg_2Cl_6$	131
Mn^{II}	Ph	Me	$[Mn(H_2L)Cl_2] \cdot MeCN$	132
Ag^{II}	H		$[Ag_2(H_2L)_2]PF_6$	133

The reaction of bis(hydrazones) **14** (R^1, R^2 = Alk, Ar) with metal(II) salts affords complexes **A** with two five-membered chelate rings, while bis(hydrazones) with R^1, R^2 = Het afford complexes with four five-membered metallacycles due to the participation of the heteroatoms of the heterocyclic fragments in the coordination (compounds **B**).[129,131,133]



A



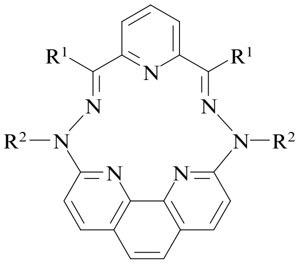
B

Thus the transition metal complexes of 2,6-diacetylpyridine bis(benzothiazolylhydrazone) were investigated by IR, UV, EPR and NMR spectroscopy, mass spectrometry, magnetochemistry and conductometry.[129] It was established that the complexes are 1 : 1 electrolytes and have mononuclear structure with the octahedral geometry of the coordination centre. The values of the effective magnetic moments of the paramagnetic chelates are close to the spin-only values. The EPR spectrum of the Cu(II) complex has a resolved fine structure ($g_{\parallel} = 2.19$, $g_{\perp} = 2.16$). A higher $g_{\parallel}$ value compared to $g_{\perp}$ points to the location of the unpaired electron in the $d_{x^2-y^2}$ orbital. Parameters of the EPR spectrum for the VO(II) complex ($g_{\perp} = 1.95$, $g_{\perp} = 2.04$, $g_0 = 2.01$, $A_0 = -52.61$ G) can be attributed to the slight distortion of the octahedral environment around the metal atom. The electronic spectra of the Ni(II), Co(II) and Mn(II) complexes combined with the data of the magnetochemical measurements indicate the high-spin state of the metal ion and the octahedral structure of the chelate unit.

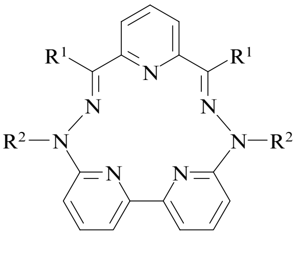
Macrocyclic pentadentate ligands based on 2,6-diformylpyridine or 2,6-diacetylpyridine and phenanthroline (ligand **15a**) or bipyridyl (ligand **15b**) belong to the bis(hydrazone) ligands of the closed type. These ligands have bulky cavities capable of chelating metals (Table 5).

Table 5. Metal complexes with macrocyclic ligands **15a** and **15b** (L).

Ligand	M	R^1	R^2	Composition of the complex	Ref.
15a	Mn^{II}	Me	Me	$[MnLCl]BF_4$	134
	Mn^{II}	Me	$(CH_2)_2OH$	$[MnLCl]Cl$	135
	Ni^{II}	Me	Me	$[NiL(H_2O)_2](BF_4)_2$	136
	Co^{II}	Me	Me	$[CoL(H_2O)_2](BF_4)_2$	137
	Co^{II}	Me	Me	$[CoL(MeOH)_2](BF_4)_2$	138
	Co^{II}	H	Me	$[CoL(H_2O)_2](SiF_6)_2 \cdot 6\,H_2O$	139
15b	Cr^{II}	H	$(CH_2)_2OH$	$[CrL(H_2O)_2]Cl_3 \cdot 2\,H_2O$	140
	Zn^{II}	Me	H	$[ZnL(H_2O)_2](NO_3)_2$	141
	Fe^{III}	Me	$(CH_2)_2OH$	$[FeLCl_2]Cl$	142
	Fe^{II}	Me	Me	$[FeL(H_2O)_2](BF_4)_2$	143
	Ag^{I}	H	$(CH_2)_2OH$	$[AgL]NO_3$	144



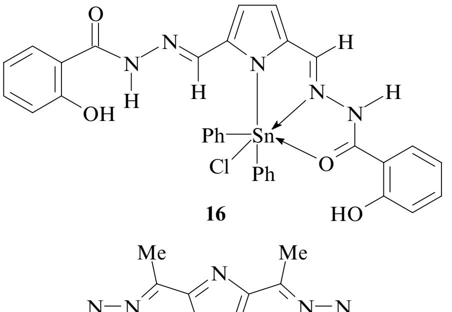
15a



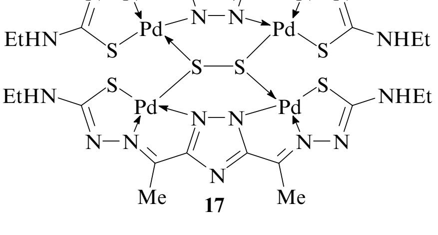
15b

Complexes based on macrocycles **15** have a mononuclear structure. Coordination to the metal is effected by five nitrogen atoms: two nitrogen atoms of the phenanthroline (or bipyridyl) core, the nitrogen atom of the pyridine fragment and one nitrogen atom in each of the hydrazine fragments. The environment of the metal atoms in such complexes is either a pentagonal bipyramid with two solvent molecules [136–139, 143] or a pentagonal pyramid with an acid residue involved in the coordination.[134, 135] In the former case, the MN_5 chelate centre has a planar structure, in the latter this is non-planar.

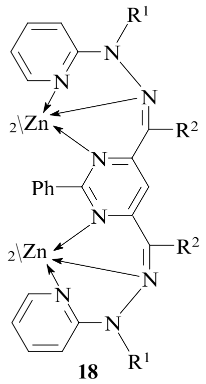
In addition to the bis(hydrazones) based on 2,6-diacetylpyridine, bis(hydrazones) of other nitrogen-containing heterocycles, such as, *e.g.*, pyrrole,[145] 1,2,4-triazole [146, 147] and pyrimidine[148] are known. These ligands were used for the synthesis of coordination compounds **16**–**18** for which the structures were unambiguously established by X-ray diffraction analysis.



16



17

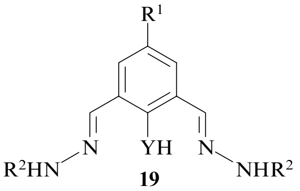


18 R^1, R^2 = H, Me.

Tetranuclear complex $(ZnL)_4$ (**18**) was prepared by a self-assembly process. Each metal atom has an octahedral coordination due to bonding with nitrogen atoms of the pyrimidine, pyridine and azomethine fragments of the two perpendicular ligands.[148]

IV. Metal complexes with 2,6-diformyl-4-R-phenol, -benzenethiol and -aniline bis(hydrazones)

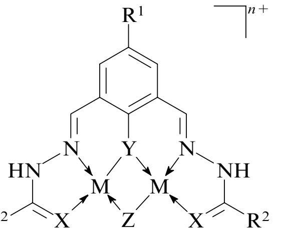
The introduction of an additional *ortho*-formyl group relative to the HY group (Y = O, S, NH) in salicylaldehyde (2-mercapto- or 2-aminobenzaldehyde) establishes the conditions for the preparation of bis(hydrazones) of type **19**, which are compartment ligands.



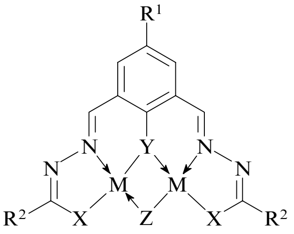
19

Y = O, S, NH; R^1 = Alk, Hal; R^2 = Het, $C(X)R^3$ (X = O, S, NH; R^3 = Ar, NH_2).

The ligand system **19** is different in principle from those considered above in that the HY group divides the inner cavity of the bis(hydrazone) into two symmetrical parts, which determines the predominant formation of binuclear coordination compounds. The geometry of the ligand system also favours the formation of the binuclear complexes. In metal complexes, ligand **19** with $R^2 = C(X)R^3$ can exist in either keto- (compounds **20**) or enol (compounds **21**) form. The presence of three labile protons and several donor centres in ligands **19** allows preparation of complexes with different structures and compositions therefrom.



20



21

The complexing properties of the ligand systems **19** were studied in detail. The first copper(II) and nickel(II) complexes based on 4-methyl-2,6-diformylphenol bis(thiosemicarbazone) with different bridging ligands (Z) were

Table 6. Metal complexes **20**, **21** with 2,6-diformyl-4-R-phenol and -benzenethiol bis(hydrazones) studied by X-ray diffraction method.

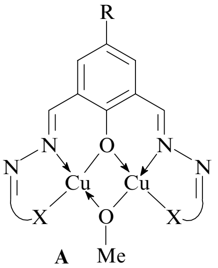
M	X	Y	Z	R^1	R^2	Composition of the complex	Ref.
Ni^{II}	S	O	EtO	Me	NH_2	$[Ni_2L(\mu\text{-OEt})]\cdot 2\,DMF$	149
Pd^{II}	O	S	primid [a]	Me	cyclo-C_6H_{11}	$[Pd_2L(\mu\text{-primid})]$	150
	O	S	MeCOO	Me	cyclo-C_6H_{11}	$[Pd_2L(\mu\text{-OAc})]\cdot 2\,CHCl_3$	151
	O	S	I	Me	cyclo-C_6H_{11}	$[Pd_2L(\mu\text{-I})]$	152
	O	S	maleimide	Me	cyclo-C_6H_{11}	$[Pd_2L(\mu\text{-}C_4H_2NO_2)]$	153
Pd^{II} (see [b])	O	S	–	Me	cyclo-C_6H_{11}	$[Pd_3L_2]$	154
Cu^{II}	O	O	MeO	Me	Ph	$[Cu_2L(\mu\text{-OMe})]\cdot DMF$	155
	O	S	pz [c]	Me	cyclo-C_6H_{11}	$[Cu_2L(\mu\text{-pz})]$	156
	O	O	EtO	Bu^t	cyclo-C_6H_{11}	$[Cu_2L(\mu\text{-OEt})(MeOH)](ClO_4)_2$	157
	NH	O	EtO	Me	SMe	$[Cu_2L(\mu\text{-OMe})]$	158
	O	O	MeO	Me	n-C_6H_{13}	$[Cu_2L(\mu\text{-OMe})(MeOH)_2]$	159
	O	O	MeO	Bu^t	Ph	$[Cu_2(HL)(\mu\text{-OMe})(ClO_4)]ClO_4\cdot EtOH$	160
	O	O	N_3	Me	Ph	$[Cu_2(HL)(\mu\text{-}N_3)(H_2O)(EtOH)(ClO_4)]$	161
Zn^{II}	S	O	OH	Me	NH_2	$[Zn_2L(\mu\text{-OH})(Py)_2]\cdot Py$	162
Ho^{III}	O	O	–	Me	4-Py	$[Ho_2L_3(H_2O)](NO_3)_2(OH)\cdot 3.5\,H_2O$	163
Li^{III}	O	O	–	Me	4-Py	$[Lu_2L_3](OH)_3$	163

[a] primid is 1-propylimidazole; [b] Pd(II) complex has a trinuclear structure; [c] pz is pyrazole.

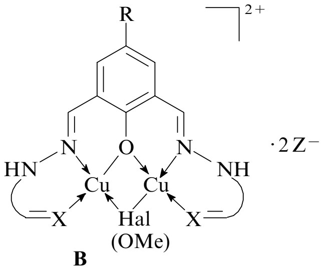
obtained and investigated back in 1972 by Hoskins *et al.*[149] Table 6 contains complexes of type **20** and **21** for which the structures were established by X-ray diffraction analysis, and Table 7 lists complexes for which the structures were established by indirect physicochemical methods.

In binuclear complexes **20** and **21**, the metal is coordinated to the oxygen (sulfur) atom of the phenol (benzenethiol) fragment, two azomethine nitrogen atoms and oxygen (sulfur) atoms of the C=O (C=S) groups of the hydrazide fragment. These groups can be coordinated in both the enol and keto forms, which depends on the conditions of synthesis of the complexes and on the nature of the metal atom. Studies [172] of the complexing properties of 2,6-diformyl-4-chlorophenol bis(aroylhydrazones) with respect to divalent copper, nickel, zinc and cobalt can be regarded as a classical proof of this fact. In particular, it was shown that coordination compounds of nickel(II) with bis(hydrazones) **19** with different degrees of deprotonation (mono, doubly or triply) can be obtained depending on pH of the medium.

The interest in different classes of binuclear metal complexes and, in particular, to the metal complexes with 2,6-diformyl-4-R-phenols bis(hydrazones) is determined, first of all, by their possible application for the design of new magnetoactive materials, which can be employed in different areas of technology. From the analysis of a great number of copper complexes with 2,6-diformyl-4-R-phenol bis(hydrazones), two structural types were revealed that differed in the magnetic properties; complexes **A** were prepared starting from copper acetate and complexes **B** were prepared starting from copper halides, nitrate or perchlorate.



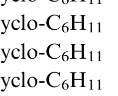
A



B

X = O, S; Z = Hal, NO_3, ClO_4.

The results of X-ray diffraction studies [155, 158, 159] have shown that compounds of type **A** are characterized by the almost planar structure of the exchange fragment

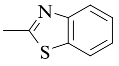
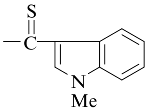
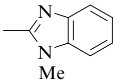
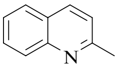
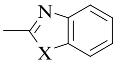
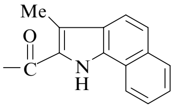
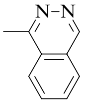


Such a structure of the coordination unit implies the effective overlap of the magnetic orbitals of copper(II) ions and, hence, the significant paramagnetic character of the complexes (the exchange interaction parameter $-2J = 300-1000\ cm^{-1}$). In compounds of the type **B**, the planarity of the exchange fragment is violated, which leads to the weakening of the antiferromagnetic character of these compounds ($-2J < 140\ cm^{-1}$).

It is well known that the magnetic exchange in copper(II) binuclear complexes (Cu^{2+} ions have only one magnetic orbital) depends on a great number of electronic and geometric factors,[182] in particular on the nature of the substituent R in the phenol fragment and on the nature of the heteroatom X. A comparative analysis of the exchange parameters [189, 190] made it possible to reveal and to rationalize the regular increase in the extent of the exchange interaction upon consecutive replacement of the oxygen atoms by the nitrogen and sulfur atoms in the chelating centre $Cu_2O_2N_2X_2$: $Cu_2O_2N_2O_2 \rightarrow Cu_2O_2N_4 \rightarrow Cu_2O_2N_2S_2$. The quantum chemical calculations of the $Cu_2O_2N_2X_2$ fragments with the application of the extended Hückel method showed parallel variation of the $2J$ and Δ^2 values (Δ is the value of the energetic splitting between the frontier orbitals HOMO and LUMO). Such a dependence allows suggesting that the electronic factor, which manifests itself in the interrelated variation of the electronegativity of atoms X and the Δ^2 value, exerts the decisive influence on the variation of the strength of the antiferromagnetic exchange interaction.

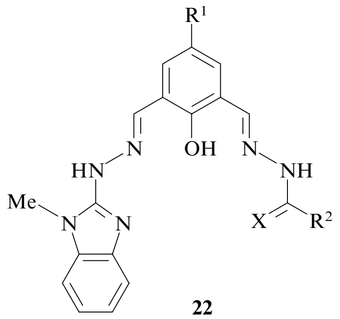
The EPR spectra of the copper(II) binuclear complexes of the type **20**, **21** recorded at room temperature[160, 162, 186] have standard shapes and are characterized by the *g* values

Table 7. Binuclear metal complexes of the types **20** and **21** (X = Y = O) the structures of which were established by indirect methods.

M	Z	R^1	R^2	Composition of the complex	Ref.
Fe^{II}, Ni^{II}, Cu^{II}	Cl	Me	$C(O)C_6H_4OH\text{-}o$	$[M_2L(\mu\text{-Cl})(H_2O)_4]\cdot n\,H_2O$ (n = 0, 1, 2)	164
V^{II}	CNO	Me	C(O)Py-4	$[(VO)_2(H_2L)(\mu\text{-CNO})]SO_4\cdot 3\,H_2O$	165
Mn^{II}	Cl	Me	C(O)Py-4	$[Mn_2(H_2L)(\mu\text{-Cl})Cl]Cl\cdot 3\,H_2O$	166
Yb^{III}	OH	Me	C(O)Py-4	$[Yb_2L_3](OH)_3$	167
Ln^{III} (Ln = La, Ce, Pr, Nd, Sm)	NO_3	Me	C(O)Py-4	$[Ln_2L_3(\mu\text{-NO}_3)]$	168
Cu^{II}	N_3	Me	C(O)Py-4	$[Cu_2L(\mu\text{-N}_3)]\cdot H_2O$	169
Cu^{II}, Ni^{II}, Pb^{II}, Cd^{II}	OEt	Bu^t	$C(S)NHC_6H_{13}\text{-}n$	$[M_2L(\mu\text{-OEt})]$	170
Cu^{II}	Cl, Br, NO_3	Me	$C(S)NH_2$, $C(Se)NH_2$	$[Cu_2(H_2L)(\mu\text{-Z})]Z_2\cdot n\,A$ (A = DMSO, H_2O)	171
Cu^{II}	Cl, Br, NO_3	Me	C(S)SMe, C(Se)SMe	$[Cu_2(H_2L)(\mu\text{-Z})]Z_2\cdot n\,A$ (A = DMSO, H_2O)	171
Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}	Cl, OH	Me	$C(O)C_6H_4R\text{-}p$	$[M_2(H_2L)(\mu\text{-Z})]$	172
Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}	Cl	Me		$[M_2L(\mu\text{-Cl})Cl_2]\cdot H_2O$	173
Ln^{III} (Ln = La, Nd, Sn, Gd, Dy, Pr, Eu, Yb)	NO_3	Me	$C(O)C_6H_4R\text{-}p$	$[M_2L_3(NO_3)_2]NO_3\cdot 3\,H_2O$	174
Cu^{II}, Ni^{II}	OMe, Cl, N_3	Me	$C(S)NH_2$	$[M_2L(\mu\text{-Z})]$	175
Zn^{II}	MeCOO	Me		$[Zn_2L(\mu\text{-MeCOO})]$	176
Cu^{II}, Ni^{II}, Co^{II}	Cl	Me	C(S)Ph	$[M_2L(\mu\text{-Cl})]$	177
Cu^{II}, Ni^{II}	Cl, Br	Me		$[M_2(H_2L)(\mu\text{-Z})Z_2]$	178
Ni^{II}	Cl	OAc	$C(O)C_6H_4NO_2\text{-}m$	$[Ni_2(H_2L)(\mu\text{-Cl})Cl_2]$	179
Ni^{II}	Cl	OAc	$P(O)Ph_2$	$[Ni_2(H_2L)(\mu\text{-Cl})Cl_2]$	179
Cu^{II}	Cl, Br	Me	$P(O)Ph_2$, $P(Se)Ph_2$	$[Cu_2L(\mu\text{-Cl})Cl_2]$	180
Cu^{II}	OMe	Me, OMe	C(O)Ph	$[Cu_2(H_2L)(\mu\text{-OMe})](NO_3)_2$	181
Cu^{II}	Cl	Me	C(S)NHPh	$[Cu_2(H_2L)(\mu\text{-Cl})]$	182
Cu^{II}	OMe, Cl	Me		$[Cu_2L(\mu\text{-OMe})]$, $[Cu_2(H_2L)(\mu\text{-Cl})Cl_2]$	183
Cu^{II}	Cl, Br	Me, Hal	COOMe	$[Cu_2LCl]$, $[Cu_2(H_2L)(\mu\text{-Z})Z_2]$	184
Cu^{II}	NO_3, ClO_4	Me		$[Cu_2(H_2L)(\mu\text{-OMe})]Z_2$	185
Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II}, Hg^{II}, Co^{II}, Mn^{II}, Fe^{II}, VO^{II}	Cl, OMe	Me		$[M_2(H_2L)(\mu\text{-Z})Z_2]\cdot n\,H_2O$ ($M \neq Cu$), $[Cu_2L(\mu\text{-OMe})]\cdot MeOH$	186
Cu^{II}, VO^{II}	Cl, Br, OMe	Me		$[M_2(H_2L)(\mu\text{-Z})Z_2]\cdot MeOH$	187
VO^{II}	OMe	Me	C(O)Ph	$[(VO)_2L(OMe)]$	188

lying in the range from 2.140 to 2.230 for $g_{||}$ and from 2.050 to 2.065 for $g_{\perp}$, while for all cases $g_{||} > g_{\perp} > g_e$ (2.0023), which allows inferring the localization of the unpaired electron in the x^2-y^2 orbital. This is in line with the square-pyramidal structure of the chelating centre in the complexes mentioned, which was also confirmed by the data from EPR spectroscopy. The EPR spectra represent a broadened signal, which agrees with the presence of the bridging atoms that bind the copper ions in complexes **20**, **21**. At low temperatures (140 K), the form of the spectrum changes.[160] It corresponds to that of the complexes with the exchange interaction of the antiferromagnetic type. Such an exchange interaction was also observed with the use of magnetochemical methods.

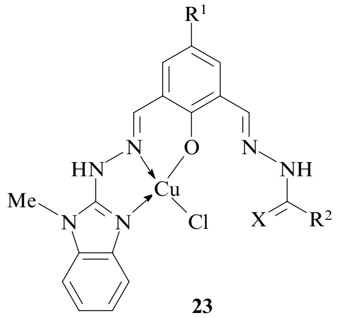
Non-symmetrical bis(hydrazones) of the type **22** were also synthesized in addition to symmetrical 2,6-diformyl-4-R-phenol bis(hydrazones) of the type **19**.



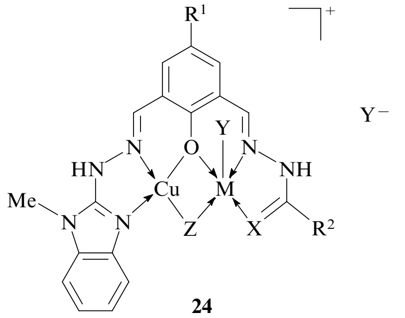
22

X = O, S; R^1 = Me, OMe, CO_2Et; R^2 = Me, Ar, NH_2.

The metal ions form mononuclear chelates **23** with these ligands as well as homo- and heterobinuclear complexes **24**.[191–195]



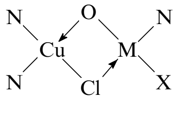
23



24

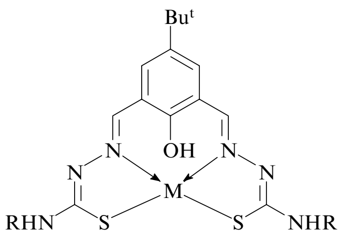
Z = Cl, OMe;
Y = Cl, NO_3;
M = Cu(II), Ni(II), VO(II), Mn(II).

The structure of complexes **23** and **24** was established based on the data from elemental analysis, IR spectroscopy, conductometry and low-temperature magnetochemistry. The effect of the geometric factor, which reflects structural features of the chelating centre and the complex as a whole, on the magnetic properties becomes stronger than that of the electronic factor on going from the symmetrical bis(hydrazone) complexes of the types **20**, **21** to non-symmetrical complexes **24**. The results of the quantum chemical calculations of the electronic structure of the exchange fragment



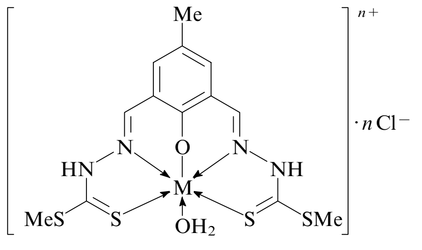
in the heterobinuclear complexes of the type **24** are in good agreement with this conclusion.[195]

Finally, mention can also be made of complexes **25a** and **25b** for which the mononuclear structures were unreasonably, in our opinion, suggested[196–198] judging by the data from elemental analysis, IR spectroscopy and thermogravimetry only.



25a

M = Co(II), MoO_2(II); R = C_6H_{13}, Ar.



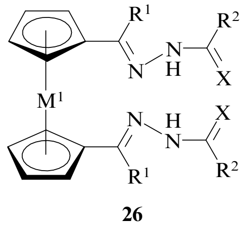
25b

M = Co(II), Ni(II), Cu(II), Cd(II), n = 1; M = Cr(III), n = 2.

We believe that these complexes are binuclear. Due to steric strain in the mononuclear metal chelates, they are energetically unfavourable and their implementation is hardly possible. Moreover, the geometrical features of the ligand system **19**, as was mentioned above, suggest that it is the binuclear complexes that should be formed. No X-ray data on the mononuclear complexes based on 2,6-diformylphenol bis(hydrazones) have been documented, which can also be regarded as an argument in favour of their binuclear structures.

V. Metal complexes containing bis(hydrazones) of metallocene dicarbonyl derivatives

Complex compounds based on the monohydrazones that contain ferrocene or another metallocene have been studied in sufficient detail.[199–207] In our opinion, however, the complexes based on metallocene-derived bis(hydrazones) (compounds **26**) deserve greater attention.



26

M^1 = Fe, Ru; X = O, S; R^1 = H, Me; R^2 = Alk, Ar, Het, NH_2.

The fact of the presence of chelatophore substituents in both cyclopentadienyl rings is remarkable itself as it allows tracing the dependence of the complex structure (and the sandwich fragment itself) on different factors, including the extension of the chelatophore (hydrazone) groups, the radius of the complex-forming metal, type of the chalcogenide atom and substituents in the hydrazone fragment and also on the radius and nature of the metal constituent of the metallocene moiety of the molecule. Of considerable interest is the structure of the sandwich fragment, which is geometrically labile and is subject to different kinds of defor-

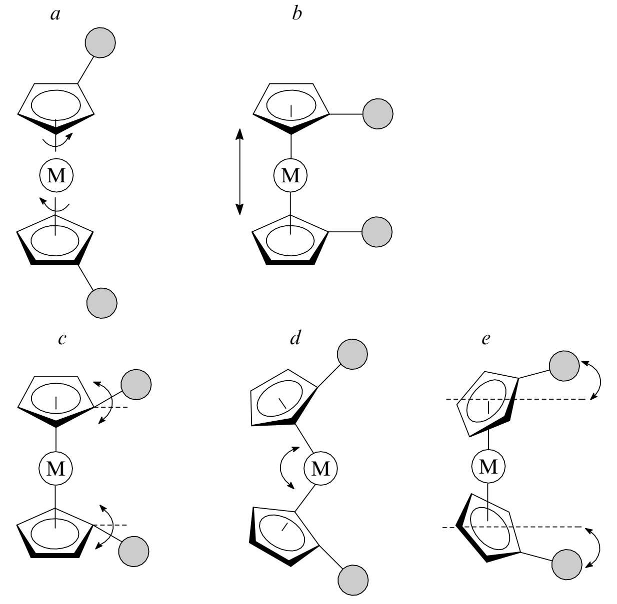


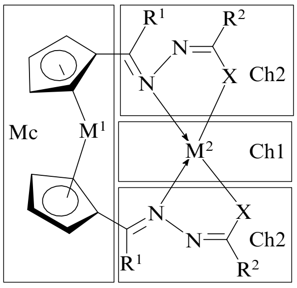
Figure 1. Types of metallocene deformation.
(*a*) Mutual rotation of the cyclopentadienyl rings; (*b*) increase in the $M-C_{Cp}$ distance (ring expansion); (*c*) deviation of substituents from the plane of the Cp rings; (*d*) violation of the parallelism of the Cp rings due to change in the CCp – M – CCp angle, (*e*) the same but with preservation of the CCp – M – CCp angle equal to 180°.

mation (Fig. 1). The overall deformation of the sandwich fragment is the sum of the deformations *a* + *b* + *c* + *d* + *e*.

Two types of the equilibrium states are typical of ligands **26**. One of them relates to the well-known tautomerism of hydrazones based on acid hydrazides,[208] which can exist in the solution in ene-imine and keto-imine forms. The second type of the equilibrium state has the conformational character and is connected with the low energy to rotation of the cyclopentadienyl rings around the fivefold axis.

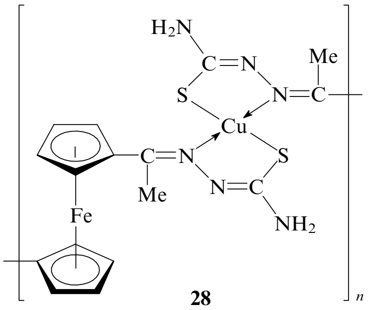
Both monomeric and polymeric structures can form upon the coordination of ligand **26** to the complexing metal; the concomitant conformational changes of the metallocene fragment are different in principle. Thus no deformation of the *b*–*e* type of the sandwich fragment is required for the formation of a polymeric structure. The metallocene fragment assumes the intermediate geometry between the prismatic and antiprismatic, while the rotation angle of the cyclopentadienyl substituents depends on the conditions of the formation of the crystal lattice.

As can be seen from the analysis of the geometric factors, the monomeric structure of complex **27** is sterically strained. The steric strains can be partially compensated by their even distribution over the three parts of the molecule: the metallocene fragment (Mc), chelating centre (Ch1) and chelating rings (Ch2). The radii of the metals M^1 and M^2 as well as the type of the chalcogenide atom X are the factors determining the extent of the distortion of each of these fragments.



27

The first complex based on bis(hydrazones) containing the ferrocene fragment and the structure of which was investigated by IR and UV spectroscopy was apparently the copper complex with 1,1′-diacetylferrocene bis(thiosemicarbazone).[209] No absorption bands of the stretching vibrations of the NH and thiocarbonyl groups are present in the IR spectrum of the complex in contrast to the spectrum of the free ligand, while the absorption band at 1606 cm^{-1}, which corresponds to the absorption band of the C=N group, is shifted to the long-wavelength region by 8 cm^{-1}. Despite such a small shift of this band, the authors made a conclusion of the coordination of the azomethine nitrogen atom of the hydrazone group to the copper atom and attributed structure **28** to this complex.

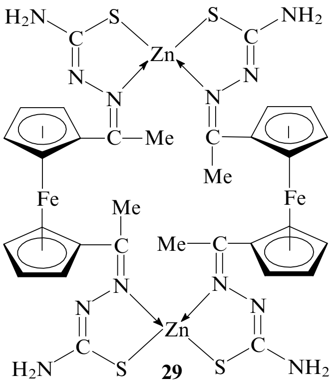


28

The structure of the complex was inferred only based on the data from elemental analysis and IR and UV spectroscopy. In our opinion, these data are insufficient to attribute the polymeric structure **28** to the copper complex with 1,1′-diacetylferrocene bis(thiosemicarbazone), since the molecular weight of the complex was not determined.

A detailed investigation of the complexing properties of the ligand **26** (X = S, $R^2 = NH_2$) to the zinc(II) ion was performed[210]. An X-ray diffraction study established that the configuration of the ferrocene fragment in the ligand is close to prismatic (the unsubstituted ferrocene has the antiprismatic configuration), the thiosemicarbazone substituents are in *cis*-position (the torsion angle is −10.8°) and are virtually coplanar with the cyclopentadienyl rings due probably to the conjugation. The bond lengths sulfur – carbon are 1.69 Å in the free ligand, those in the complex are 1.78 [range from 1.736(11) to 1.748(11) Å], indicating the thione tautomeric form of the ligand and the thiol tautomeric form in the complex.

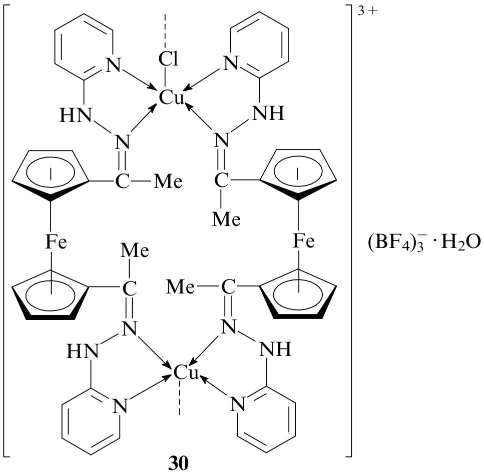
The data from X-ray diffraction analysis show that complex **29** is binuclear. Such a structure allows minimizing



29

steric strains in the complex, in particular the cyclopentadienyl rings of the ferrocene fragments are practically parallel. The strain is relieved through the distortion of the chelate centres Ch1.

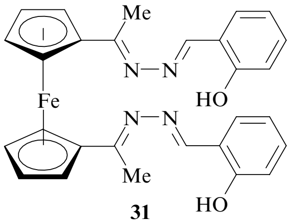
Copper(II) complex **30** has a similar structure, which was established by X-ray diffraction analysis.[211]



30

The mass spectrum of complex **30** shows a peak with m/z 1066.5, which corresponds to the cation $[Cu_2(LH)_2Cl]^+$. Data [from X-ray crystallography] and EPR spectroscopy suggest that the coordination polyhedron of the copper ion is intermediate between the tetragonal pyramid and the trigonal bipyramid. Due to the formation of the dimeric structure, the ferrocene fragments are not practically deformed. The Cu−Cu distance is 8.4 Å. The complex has a polymeric structure in the solid state due to the chloro-bridges, which coordinate to two copper centres. The structural unit of this polymer is the mixed-valence cyclic bis(ferrocene) structure **30**. The voltammetric measurements have shown the presence of two peaks with half-wave potentials ($E_{1/2}$) of 0.75 and 0.58 V, which correspond to two single-electron oxidation processes of the ferrocene moieties of the molecule. Peaks with $E_{1/2} = 0.29$ and 0.14 V were also found for the Cu^{II}/Cu^{I} reduction.

The complexing ability of ligands based on 1,1′-diacetylferrocene, hydrazine and salicylaldehyde (ligand **31**) or 2-formylpyridine (ligand **32**) was studied[212]. The introduction of an additional coordination centre (OH or N) into the hydrazone fragment of the ligand brings about the removal of the coordination center to the peripheral part of a molecule.



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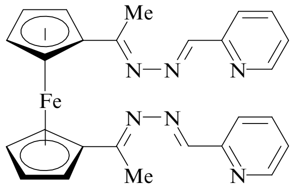
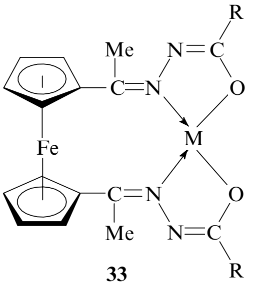


32

The removal of the coordination centre from the metallocene moiety upon complex formation with metal salts and the overall increase in the number of units in the atomic chain linking M^1 and M^2 should result in the decrease in the total structural rigidity of the molecule and in the release of the steric strains. In this case, one could expect the formation of a monomeric complex. Indeed, according to the data from X-ray diffraction, no wedge-like kink of the ferrocene moieties in these ligands is observed upon the coordination to the metal: the arrangement of the cyclopentadienyl rings is close to parallel, while the $Fe-C_{Cp}$ distances have common values. Nevertheless, the complex obtained in the reaction of bis(hydrazone) **31** with copper acetate has the dimeric structure.

Other metal complexes with bis(thiosemicarbazones) **26** (X = S, $R^2 = NH_2$) are also known.[213–215] In these complexes, the ligand exists in the doubly deprotonated enol form.

A number of metal complexes with ligands based on diacetylferrocene and aromatic or heterocyclic acid hydrazides was synthesized.[216–223] Unfortunately, no X-ray diffraction data for such complexes are available, which is connected with their low solubilities and the impossibility of obtaining single crystals (poor solubility of the complexes is most often caused by their polymeric structures). It is believed that these complexes have either the monomeric (complex **33**) or the polymeric structures (complex **34**).



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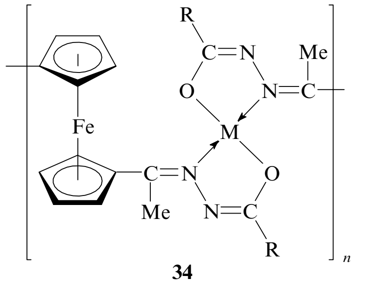
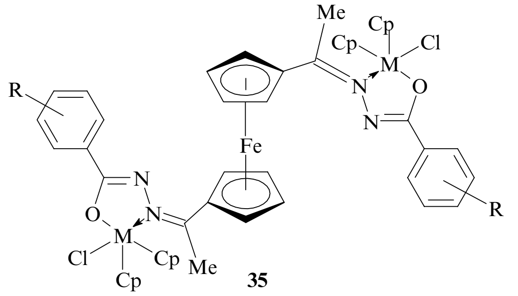


34

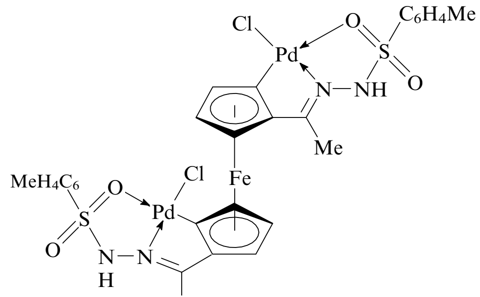
R = Ar, Het; M = Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Hg(II), Mn(II), Cr(II).

Monomeric trimetallic semi-chelate complexes **35** and **36** are documented.[220, 224]



35

R = H, Cl, NO_2, Me; M = Ti(IV), Zr(IV).



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Tentative structures of these complexes were proposed using spectroscopic methods (^{13}C and ^{1}H NMR, UV and IR) and conductometry.

VI. Conclusion

The material of the present review illustrates diversity of metal coordination compounds with polyfunctional bis(hydrazones).

This class of compounds is of great interest in both the theoretical and practical aspects. However, the detailed theoretical investigations into this class of compounds (tautomerism problems, relationships of the structure and physicochemical properties *etc.*) contrast the problems of their practical application including industrial and technological implementations, which are yet to be solved. In general, there are quite a few obstacles to the practical application of the bis(hydrazone) complexes.

Despite the large number of the synthesized bis(hydrazone) complexes, their properties are not yet fully investigated, which makes topical further studies of these subjects. Both bis(hydrazones) themselves and their complexes possess biological activity,[11, 225] including antitumour,[226–230] antimicrobial,[123, 184] antibacterial,[174, 231] antifungal[179] activities. The use of metal complexes of bis(hydrazones) as drugs necessitates, however, that they be water-soluble or oil-soluble. The targeted modification is required to impart solubility to these metal complexes (*e.g.*, the introduction of carboxylic or sulfonate groups to enhance the solubility in water or the introduction of lipophilic fragments to enhance the solubility in oils or fats).

The data on chromogenic,[232, 233] catalytic,[37, 234, 235] liquid-crystalline[236] and fluorescence[237, 238] properties of the bis(hydrazone) complexes are also available. Metal complexes with bis(hydrazones) are used as components of nanobiochips,[239] and also as the reagents for the positron-emission tomography (PET).[240] The availability and relatively low price of the bis(hydrazone) complexes are of great importance for their use as catalysts, motor oil and fuel additives.

The review was prepared with the financial support of the Federal Agency on Science and Innovations in the framework of the Federal Target Programme 'Scientific and Scientific-pedagogical Personnel of the Innovative Russia' for 2009 – 2013 (GK No. 02.740.11.0255), and also the grant of the Russian Foundation for Basic Research (08-03-91316-IND_a).

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