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Dinuclear and Polynuclear Complexes with Azomethine Ligands and Their Magnetic Properties

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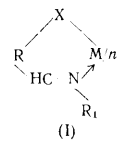
The review deals with di- and poly-nuclear metal complexes of Schiff bases whose magnetic properties are interpreted, within the framework of the exchange mechanism, as due to an exchange interaction between paramagnetic centres. The principal types of di- and poly-nuclear complexes with azomethine ligands and the factors influencing the strength and nature of the exchange interaction (the nature of the bridge groups and the stereochemistry of the coordination units) are examined. The problems of the specific selection of ligands for the synthesis of the above complexes are discussed.
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I. INTRODUCTION

Metal complexes of type (I) with azomethine ligands (Schiff bases) have been vigorously investigated since the 1930s.[1]



(I)

The experimental data accumulated hitherto[2-4] make it possible to deduce definite correlations between the electronic and molecular structures of these compounds, on the one hand, and their physicochemical properties, on the other. A detailed study of the structure–property relation is possible if one can vary (a) the ligand fragments R and R_1 in (I) while keeping constant the immediate environment of the metal atom, (b) the electron-donating atoms X (O, N, S, or Se) for the same R and R_1, and (c) the central atom M while keeping constant R, R_1, and X. Comparison of systematic series of complexes with a regular variation of particular physicochemical properties makes it possible to discover which structural factors are responsible for these changes[5,6].

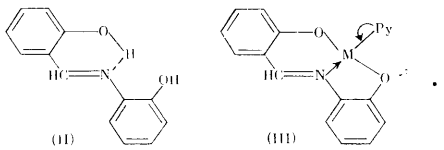
The wide variety of types of monomeric chelates becomes appreciably greater when di- and poly-nuclear compounds are formed from tri- and poly-dentate azomethine ligands or inner complexes of type (I). Compounds in which exchange interactions between paramagnetic centres are manifested are of greatest interest.

The use of azomethine compounds as ligands in order to obtain the so-called exchange-bound clusters makes it possible to follow the influence of stereochemical and electronic factors on the extent and nature of exchange interactions when substituents in the ligands and the ligands themselves are varied. The exchange properties of the complexes are determined by the structure of the ligand and the nature of the bridge groups.

This review deals with studies which illustrate most fully these characteristic features of di- and poly-nuclear complexes with azomethine ligands. The principal types of di- and polynuclear complexes with exchange interactions and factors which determine the specific selection of ligands in order to obtain these compounds are considered.

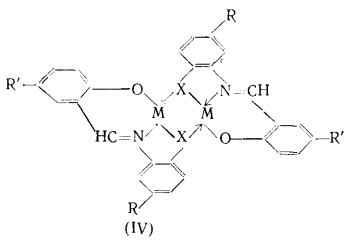
II. COMPLEXES WITH TRIDENTATE AND SIMILAR LIGANDS

The ability to form dimeric and polymeric complexes is always manifested when organic compounds with an appropriate structure, giving rise on interaction with the metal to coordination-unsaturated complexes in the monomeric state, are used. One of the most common types of compounds of this kind are complexes of 3*d* metals obtained on the basis of salicylidene-*o*-aminophenol (II):

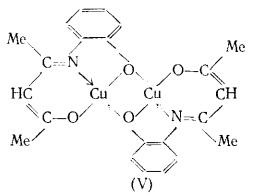


(II) (III)

If monomeric complexes (III) are formed, in which the fourth coordination site is occupied by a solvent molecule [in the present case pyridine (Py)], then they have effective magnetic moments μ_{eff} corresponding to a single unpaired electron (for example, with $M=Cu^{II}$).[7-9] If the monomers are coordination saturated by interaction with one another, dimeric complexes of types IV and V are formed:



(IV)



(V)

Here two paramagnetic centres are fairly close to one another and exchange interaction takes place between them. This was established for the first time for complexes of type (IV) (with M = Cu and X = O, [7-9] with M = VO and X = O, [10,11] and with M = Ni [12]) on the basis of the decrease of μeff relative to the "spin only" value. An analogous phenomenon was observed for complexes of type (V). [7,11-14] An X-ray diffraction study confirmed the dimeric structure of (V) in which the Cu–Cu distance is 2.99 Å, the temperature dependence of the magnetic measurement indicating the antiferromagnetic nature of this exchange interaction[13,14]. Cu^{II} and VO^{II} complexes of types (V) [11,17] and (IV) [15-22] with various substituents have been investigated particularly thoroughly[23]. Careful analysis of the temperature dependence of the magnetic susceptibilities of complexes of type (V) (μeff = 1.39–1.00 μB at 203–88 K) showed that it does not obey the Bleany–Bowers equation[24]†

$$\chi = \frac{Ng^2\beta^2}{3kT}[1 + 1/3\exp(2J/kT)]^{-1} + N\alpha, \qquad (1)$$

which takes into account only the exchange interaction between the paramagnetic ions in the dimeric molecule[17]. An additional interaction of the dimeric fragments with one another has been established for this compound as well as a number of other Cu^{II} and VO^{II} complexes of type (IV). [22,25]

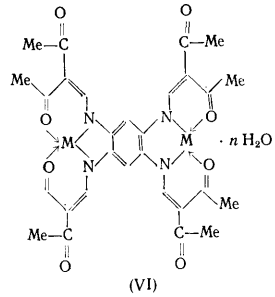
The study of complexes of types (IV) and (V) showed that the model taking into account only the direct metal–metal interaction, as a result of the partial overlap of the *d* orbitals of the metal atoms, cannot adequately account for the paramagnetism; ideas postulating an indirect exchange interaction via bridge groups X have been developed[10,11,14-17]. This was convincingly confirmed also by studies of the influence of the substituents R and R′ in (IV, N = Cu, X = O) on the strength of the exchange interaction in the dimeric molecules (Table 1)[15].

Table 1. The effective magnetic moments, *g*-factors, and exchange integrals for complexes of type (IV, M = Cu, X = O).

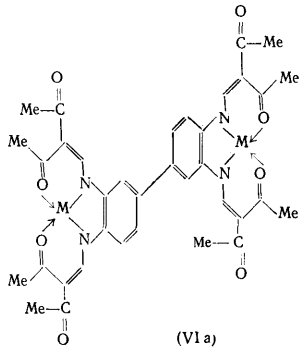
R	R′	*T*, K	μeff, μB	*g*	$-2J$, cm^{-1}
H	H	45—292	0.10—1.31	1.97±0.1	289±10
H	Me	47—296	0.11—1.47	2.10±0.1	245±10
H	Cl	43.2—296	0.15—1.25	2.16±0.1	371±25
H	Br	40—300	0.11—1.28	2.13±0.1	341±20
H	NO_2	20.7—294	0.17—1.25	—	—
Cl	H	4.95—295	0.10—1.60	1.86±0.1	46±20
NO_2	H	35—294	0.30—1.55	1.97±0.1	125±5
Cl	Cl	6.3—299	0.22—1.60	1.88±0.1	39±20
NO_2	NO_2	47—295	0.10—1.30	2.05±0.1	307±10

It has been shown that electron-accepting groups in the R′ position tend to increase the extent of the antiferromagnetic interaction, while the same groups in the R position tend to decrease it. From the standpoint of the mechanism[26] postulating that the indirect exchange is determined by the antibonding *d* orbitals of the metal and the hybrid *sp* orbitals of the ligand atoms, the different effects of the substituents R and R′ can be explained by the fact that electron-accepting substituents in the R′ position influence the non-bridging oxygen and nitrogen atoms, while those in the R position influence the bridging oxygen atom.

The use of complexes with azomethine ligands as models made it possible subsequently to obtain unambiguous evidence showing that the exchange interaction can be only indirect. Thus the magnetic properties of complexes (VI) and (VIa) were compared[27]:



(VI)



(VIa)

M=Cu^{II}, Ni^{II}, or VO^{II}.

A direct copper–copper exchange is ruled out in complex (VI), but, despite this, an antiferromagnetic interaction is observed between the copper ions with $2J = 12.2$ cm^{-1} (μeff = 1.8–0.42 μB at 216–4.2 K). It was assumed that the interaction is due to the polarisation of the spins of the unpaired electron of the copper atom and the electrons of the nitrogen atom, which is then distributed via the π-electron system of the benzene ring to the second copper atom. The presence of the C–C single bond in complex (VIa) prevents such delocalisation and an antiferromagnetic interaction is not observed (μeff = 1.83–1.69 μB at 241–4.2 K). [27]

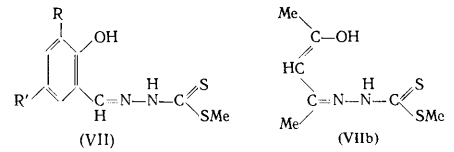
Sulphur-containing ligands also form di- and polynuclear complexes with exchange interaction[17,28,29]. As for complex (III), the addition of a pyridine molecule in these compounds promotes the formation of a complex with a normal magnetic moment[29]. When the bridging O atom is replaced by S, the magnetic properties of the complexes change.

The effective magnetic moments of complexes of type (IV, X = S, M = Cu) are almost independent of temperature (μeff = 1.73–1.85 μB at 291–80 K), [17] which was explained by the increase of the copper–copper distance and the change of the angles in the bridge fragment.

The copper complexes (VIIa) and (VIIb), obtained by the interaction of *S*-methyldithiocarbazide with salicylaldehyde (VII) and acetylacetone (VIIb), [28-32] as well as complexes with the thiosemicarbazones of *o*-hydroxyaldehydes (VIId) [30,31] and with tridentate ligands (VIIe), obtained by the condensation of diacetyl monoxime and its *O*-methyl

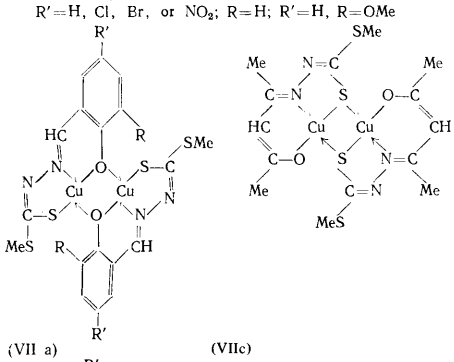
† Here *N* is the Avogadro number, $2J$ the exchange integral, μB the Bohr magneton, *k* the Boltzmann constant, *T* the absolute temperature, and $N\alpha$ the temperature-independent paramagnetism.

ether with methyl hydrazinethiocarboxylate (VIIf) have been investigated:

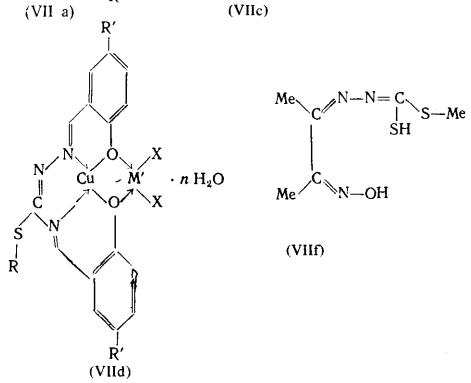


(VII) (VIIb)

R′=H, Cl, Br, or NO_2; R=H; R′=H, R=OMe



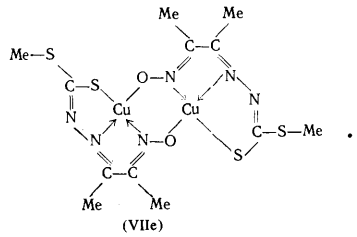
(VII a) (VIIc)



(VIIf)

(VIId)

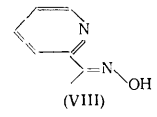
M′=Cu^{II}, Fe^{II}, or Zn^{II}; R=Me, or Et; R′=H, or Me; X=Cl, or Br



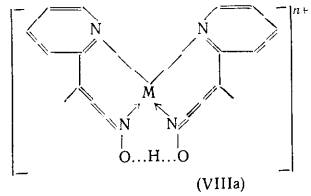
(VIIe)

Complexes (VIIe) are characterised by anomalous magnetic properties characteristic of exchange-bound clusters[32]; the compounds retain a similar structure when the sulphur atom is replaced by oxygen.

It has been found that complexes (VIIa) can manifest exchange interactions of both antiferromagnetic and ferromagnetic types depending on the nature of the substituents R and R′ (Table 2). An exchange interaction of the ferromagnetic type has also been observed for complex (VIIc) (μ_{eff} = 1.59–1.81 μ_B at 333–83 K). It has been suggested[29] that the indirect electronic influence of the substituents R and R′ and ultimately the change in the nature of the packing in the unit cell of the crystal have an effect here. Whereas complexes with an antiferromagnetic exchange interaction have a dimeric planar structure, complexes with a ferromagnetic exchange interaction consists of tetranuclear clusters in which copper atoms occupy the vertices of a distorted tetrahedron. The antiferromagnetic exchange interaction in complexes (VIId) depends on the nature of the substituents at the sulphur atom and in the benzene ring[30,31].



(VIII)



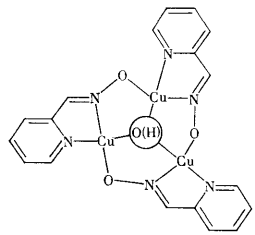
(VIIIa)

Table 2. Magnetic properties of copper complexes of types (VIIa) and (VIId).

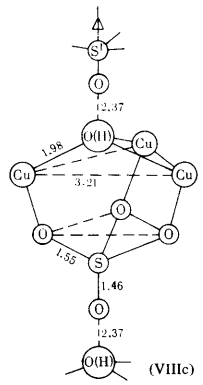
Type of complex	R′	R	X	T, K	μ_{eff}, μ_B
(VIIa)*	NO_2	H	—	333—83	2.02—2.43
(VIIa)	H	H	—	313—93	1.09—0.60
(VIIa)	H	OMe	—	373—193	1.01—0.40
(VIIa)	Cl	H	—	289	0.77
(VIIa)	Br	H	—	293	0.79
(VIId)	H	Me	—	288—78.8	1.60—0.67
(VIId)	H	Et	—	291.4—78.8	1.61—0.71
(VIId)	H	Me	Cl	288.3—78.8	1.60—0.67
(VIId)	H	Et	Cl	291.4—78.8	1.61—0.71
(VIId)	H	n-Bu	Cl	297.6—78.8	1.65—0.80
(VIId)	H	iso-Bu	Cl	297.6—78.2	1.62—0.99

* Ferromagnetic interaction; in the remaining cases the interaction is antiferromagnetic.

Depending on the method of synthesis of the complex, pyridinealdoxime (VIII) (HLig) can behave either as a bidentate ligand forming monomeric paramagnetic complexes[33] (VIIIa) or as a tridentate ligand forming coordination-unsaturated monomeric complexes, which are combined in the course of the reaction into trimeric molecules (VIIIb).



(VIIIb)



(VIIIc)

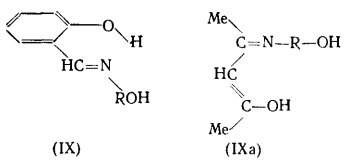
Several trinuclear copper complexes of this kind have been obtained: $[Cu_3Lig_3OH]X_2.H_2O$, where X = $\frac{1}{2}SO_4^{2-}$, I^-, NO_3^-, ClO_4^-, or OH^-; they all have anomalously low magnetic moments[34-37]. The study of the temperature dependence

of the magnetic susceptibility[37] as well as structural studies[36,37] confirmed the hypothesis that compounds of type (VIIIb) are trinuclear clusters in which copper ions are bound by an antiferromagnetic exchange interaction.

A cluster structure of the cation has been established for the complex $[Cu_3(C_6H_5N_3O_3)OH]SO_4.16H_2O$. The copper atoms are located at the corners of an equilateral triangle and the oxygen atom of the hydroxy-group is suspended over its centre at a distance of 0.71 Å. Each of the symmetrically linked aldoxime groups is a bridge group linking adjacent copper atoms. An interesting structural feature of this trimer is the fact that the three oxygen atoms of the sulphate ion augment the coordination polyhedron of each of the three copper atoms in the cluster to form a square pyramid. The trinuclear clusters are linked to one another via hydrogen bonds between the proton of the hydroxyl of one trimer and a non-coordinated oxygen atom in the sulpho-group of a neighbouring cluster.

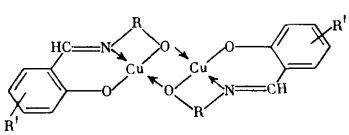
Similar trinuclear clusters with an antiferromagnetic exchange interaction have been obtained and investigated also with other analogous tridentate azomethine ligands[38-43].

The use of tridentate ligands of another type for the synthesis of complexes via the condensation of amino-alcohols with salicylaldehyde (IX) and acetylacetone (IXa),

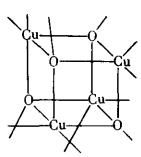


(IX) (IXa)

made it possible to follow clearly the influence on the nature of the exchange interaction in complexes (IXb) of the structural factor determined by the length and branching of the hydrocarbon group R.[43-47] It was found that only one compound among those investigated [R = $(CH_2)_3$] exhibits an exchange interaction of the antiferromagnetic type.

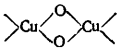


(IXb)



(IXc)

The other compounds exhibit an exchange interaction of the ferromagnetic type (Table 3)[46].

A study of a complex of type (IXb) with R = $(CH_2)_3$ established tentatively its dimeric structure[45] and, in view of the influence of the transmission of the electronic effects of the substituents on the strength of the exchange interaction, it was postulated that the oxygen atoms of the alcohol and not the phenol are involved as bridge groups in the dimeric fragment .[43] An X-ray diffraction study of the analogous copper complex (IXa), obtained from acetylacetone and having a very low magnetic moment (0.41 μ_B at room temperature) showed that this complex has a dimeric structure where the oxygen atoms of the alcohols function as the bridge groups[47]. In structures (IXa) and (IXb) the planes formed by the tetracoordinate environment of the copper ion and the tricoordinate environment of the oxygen bridge atoms are coplanar. It is suggested that this structural feature in fact accounts for the strong antiferromagnetic interaction [$-2J$ = 884 cm^{-1} and g = 2.20 were obtained for (IXb)] [46] via an indirect exchange interaction π-mechanism [$Cu(3d_{xz})$ – $O(2p_\pi)$ – $Cu(3d_{yz})$], involving the d_{xz} and d_{yz} orbitals of the copper ion[47], rather than via the expected exchange via a σ-mechanism

$$\{Cu\,(3d_{x^2-y^2}) - O\,(2p_\sigma) - Cu\,(3d_{x^2-y^2})\}\ .$$

A decrease of the length of the hydrocarbon group to R = $(CH_2)_2$ leads to the formation of tetrameric exchange-bound clusters (IXc).[47] This structure explains the ferromagnetic nature of the exchange in complexes (IXb) (Table 3).

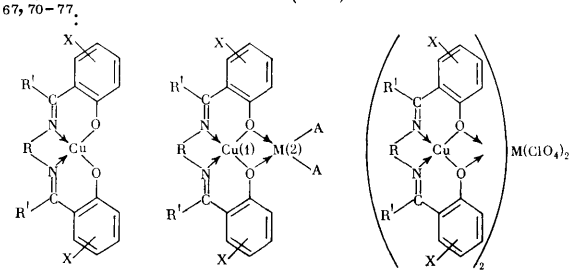
Table 3. Magnetic properties of complexes of type (IXb).

R	T, K	μ_{eff}, μ_B
$-CH_2-CH_2-CH_2$ *	295.7—150.1	0.43—0.07
$-CH_2-CH_2-$	291.4—76.4	1.88—2.09
$-CH_2-CH(Me)$	289.3—76.4	1.84—2.00
$-C(Me)_3$	286.1—76.4	2.09—2.41

* Antiferromagnetic interaction; in the remaining cases the interaction is ferromagnetic.

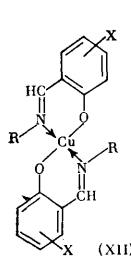
III. DI- AND POLY-NUCLEAR COMPLEXES BASED ON CHELATES WITH SCHIFF BASES AS LIGANDS

One of the commonest types of di- and poly-nuclear complexes with exchange interaction comprises compounds obtained by the insertion of a paramagnetic centre in the coordination unit of a chelate with a paramagnetic metal ion. These compounds are usually obtained either by the interaction of metal salts with chelates of tetradentate Schiff bases (X), whereupon di- and tri-nuclear complexes with a *cis*-structure (XI, a and b) are formed[48-66], or by the interaction of metal salts with the chelate (XII) formed by bidentate ligands, whereupon di- or poly-nuclear complexes with a *trans*-structure (XIII) are formed[44,49-51,53,54,57,59-67,70-77].



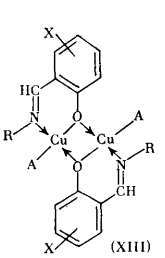
(X) (XIa) (XIb)

R = $(CH_2)_n$, n = 2, 3; R' = H, or Me; A = Cl, Br, or NO_3; X = H, 5-Cl, 5-Br, or 5,6-C_4H_4; M = Cu^{II}, Ni^{II}, Co^{II}, $Fe^{II,III}$, or Mn^{II}



(XII)

R = Alk or Ar



(XIII)

X = H, 5-Cl, 5-Br, 5,6-C_4H_4, or 3-OMe; A = Cl or Br

Chelates with tridentate Schiff bases behave as neutral bidentate ligands coordinated to the metal atom of the MX_2 molecule via the two phenolic oxygen atoms, which is confirmed by the change in the vibration frequency of the Ph–O bond in the infrared spectra[53,54,67,77,83,85]. Dinuclear complexes of type (XIa, $n = 2$, M = Cu, A = Cl) are formed, the temperature dependence of the magnetic susceptibility of which obeys the Bleany–Bowers equation with $J < 0$. The exchange intergrals ($-2J$) and the g-factors are presented in Table 4.[52,61]

Table 4. The exchange integrals and g-factors for copper complexes of type (XIa).

X	R	R′	m*	A	$-2J$, cm^{-1}	g
H	$(CH_2)_2$	H	1	Cl	166	2.11
H	$(CH_2)_3$	H	0	Cl	49	2.14
H	CH_2-CH(Me)	H	0	Cl	106	2.15
H	o-C_6H_4	H	1	Cl	97	2.07
H	4-Me-C_6H_3	Me	1	Cl	91	2.08
H	$(CH_2)_2$	Me	0	Cl	236	2.35
H	$(CH_2)_3$	H	1	Cl	140	2.05
H	o-C_6H_4	H	1.2	Br	194	2.28
H	o-C_6H_4	H	1	Br	95	2.09
H	$(CH_2)_6$	H	0	Cl	139	2.29
5-Cl	$(CH_2)_2$	H	0	Cl	105	2.14
5,6-C_4H_4	$(CH_2)_2$	H	0	Cl	155	2.18
5-Cl	$(CH_2)_3$	H	0	Cl	204	2.35
5-Br	$(CH_2)_3$	H	0	Cl	195	2.35
H**	$(CH_2)_3$	H	1	Cl	55	1.87
H***	$(CH_2)_3$	H	2	Cl	24	1.92

* m is the number of water molecules.
** M = Fe^{III}.
*** M = Mn^{II}.

It has been noted in a number of studies[49,53,54,78,80] that the two metal atoms Cu(1) and M(2) in dinuclear complexes of type (XIa) are in different environments: Cu(1) in a square-planar environment and M(2) in a pseudotetrahedral environment (Fig. 1). The symmetry of the M(2) coordination unit depends significantly on the number of R = $(CH_2)_n$ bridge groups[75]. In complexes (XIa) with $n = 2$ the M(2) unit has the structure of a distorted tetragonal pyramid (as a result of the additional coordination of chlorine from a neighbouring molecule); for complexes with $n = 3$, M(2) has a pseudotetrahedral stereochemistry. The magnetic properties of complexes (XIb), forming trinuclear compounds, have been interpreted on the assumption that the metal atoms are located at the vertices of an equilateral triangle[50], the antiferromagnetic properties increasing in the sequence Co < Ni < Cu.[51] The relative stability of complexes (XIb) and the energy of d–d transitions were found to vary in parallel with the extent of the antiferromagnetic interaction, which can be accounted for by the successive increase of the tetragonal distortion of the M(2) coordination unit in many copper, nickel, and cobalt complexes (Fig. 1),[49,53,54]. However, one must bear in mind that this explanation is not always correct owing to the possibility of an increase of the coordination number of Cu(2) to five, and M(2) can partly displace copper from the "planar" complex.

It has been shown[60,62,66] that the interaction of complexes [X, R = $(CH_2)_2$, M = Cu^{II}, Ni^{II}, Co^{II}, or $FeIII$] with the Lewis acids SnX_2, SnX_4, $TiCl_4$, SbX_5, $InCl_3$, $CaCl_2$, PCl_3, and $AsCl_3$ (where X = Cl or Bi) leads to the formation of dinuclear complexes in which the initial chelate with a tetradentate Schiff base can exchange the metal with the Lewis acid, forming various structures. Only when cyclic polymeric-tetrahedral adducts (XIa, M = Co or Cu) and polymeric-octahedral adducts (XIa, M = Ni^{II}) are formed with PCl_3 and $AsCl_3$, is the non-linearity of the temperature dependence of the reciprocal of the magnetic susceptibility attributed to the antiferromagnetic interaction. For the compound with PCl_3, a satisfactory agreement is observed between the experimental susceptibility and the value calculated using the linear chain model ($g = 2.11$, $2J = -55$ cm^{-1}).[65]

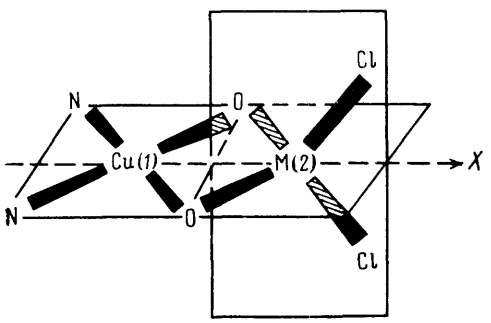


Figure 1. A fragment of the structure of a dinuclear complex of type (XIa).

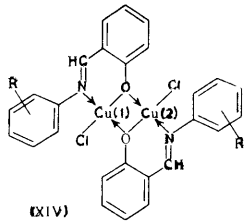
In dinuclear complexes (XIa, M = Ni), containing a water molecule, the exchange interaction can exhibit ferromagnetic features[72].

When Lewis acids interact with copper(II), cobalt(II), and nickel(II) complexes of type (XII), there is a possibility, judging from the changes in the infrared and electronic spectra, of the cleavage of the metal chelate ring in the initial chelate, which leads to the formation of complex dinuclear structures[83–86]. The effective magnetic moments of the above compounds, calculated per atom of the paramagnetic metal, have normal values. However, the coordination-unsaturated compounds formed as a result of the cleavage of the metal-chelate ring interact with one another and not with the Lewis acid and give rise to insignificant amounts of compounds with exchange-bound [electron] pairs as impurities in the main product, as shown by the appearance of a broad absorption band in the EPR spectra of the copper complexes in the region corresponding to weak fields.

Dinuclear copper complexes based on chelates with bidentate ligands (XIII) also manifest an appreciable exchange interaction of the antiferromagnetic type. The exchange integrals ($-2J$) and average g-factors of some of these are presented in Table 5.

In the dinuclear ecomplexes (XIa) and (XIII) the Cu–Cu distance is ~3 Å,[78–81] as in the copper complex of N-(2-hydroxyphenyl)acetylacetoneimine[13,14]. In the dimeric copper complex of the tetradentate N,N'-bis-(2-hydroxyethyl)acetylacetonediimine the Cu–Cu distance increases to 4.99 Å and the exchange integral is $2J = -94$ cm^{-1}.[82] In the trinuclear complexes $(NiL_2)_2.Ni(NO_3)_2$ there is a weak ferromagnetic interaction[71].

Systematic studies of dinuclear complexes of type (XIV)



(XIV)

showed[69,70,75-77] that, as in the analogous dinuclear complexes of copper halides with pyridine *N*-oxides[73,74], the substituents R have a weak influence on the energy of the *d–d* transitions and the effective magnetic moments. Nevertheless the bands corresponding to the *d–d* transitions in dimeric complexes with *ortho*-substituents are shown at shorter wavelengths than for the corresponding complexes with *meta*- and *para*-substituents (Fig. 2), which is believed to correspond to a decrease of μeff in dinuclear complexes with *ortho*-substituents compared with complexes having *meta*- and *para*-substituents[69,75,76].

Table 5. The exchange integrals ($-2J$) and g-factors for complexes of type (XIII).

R	X	A	$-2J$, cm^{-1}	g	Refs.
Me	H	Cl	149	2.17	55
CH_2Me	H	Cl	240	2.18	55
$(CH_2)_2Me$	H	Cl	255	2.08	55
$(CH_2)_3Me$	H	Cl	205	2.14	55
$(CH_2)_5Me$	H	Cl	188	2.12	55
$(CH_2)_7Me$	H	Cl	180	2.14	55
$CH_2CH(Me)_2$	H	Cl	245	2.12	55
$CH(Me)_2$	H	Cl	145	2.17	55
$CH(Me)CH_2Me$	H	Cl	155	2.11	55
C_6H_{11}	H	Cl	220	2.18	55
Ph	H	Cl	180	2.16	55
CH_2Me	5-Cl	Cl	140	2.14	57
$(CH_2)_2Me$	5-Cl	Cl	188	2.35	57
$CH(Me)_2$	5-Cl	Cl	136	2.38	57
Me	5-Br	Cl	220	2.23	57
CH_2Me	5-Br	Cl	200	2.30	57
$CH(Me)_2$	5-Br	Cl	195	2.22	57
Me	5,6-C_4H_4	Br	175	2.20	57
Me	5-Cl	Br	146	2.20	57
Me	5-Br	Br	140	2.35	57
Me	5-Cl	Cl	280	2.15	57
Me	5,6-C_4H_4	Cl	173	2.14	57
Me	H	NO_3	280	2.12	71
CH_2Me	H	NO_3	83	2.14	71
$(CH_2)_2Me$	H	NO_3	350	2.20	71
$(CH_2)_3Me$	H	NO_3	191	2.18	71
C_6H_{11}	H	NO_3	208	2.12	71
CH_2Ph	H	NO_3	120	2.08	71
Me	3-OMe	NO_3	43	2.17	71
C_6H_{11}	5,6-C_4H_4	Cl	130	2.10	57
C_6H_{11}	5-Cl	Cl	250	2.20	57
C_6H_{11}	5-Br	Cl	215	2.32	57
C_5H_9	5,6-C_4H_4	Cl	160	2.20	57
C_5H_9	5-Cl	Cl	132	2.28	57
C_5H_9	5-Br	Cl	210	2.38	57
$CH(Me)_2$	5,6-C_4H_4	Cl	97	2.30	57
$(CH_2)_2(Me)$	5-Br	Cl	180	2.26	57

There is a linear relation between the magnetic moment and the position of the band due to the *d–d* transition (Fig. 3)[75]. The same type of relation has been found also for dinuclear complexes of copper with tetradentate Schiff bases of type (XIa).[53,54] It has been suggested[77] that this type of linear relation indicates a transition from a distorted pseudotetrahedral configuration to a planar configuration when *ortho*-substituents are introduced. An increasing degree of planarity leads to a hypsochromic shift of the *d–d* band and to a decrease of the magnetic moment owing to the appreciable overlap of the metal atom orbitals with the orbitals of the bridging oxygen atoms. A similar effect involving the "flattening" of the coordination unit following the introduction of *ortho*-substituents has been observed for monomeric copper complexes of salicylidenearylamines[6] and can be accounted for by the steric conditions arising after the introduction of *ortho*-substituents, since the benzene rings both in copper complexes of salicylideneaniline derivatives and in the dinuclear complexes investigated are located at an angle of 60° relative to the plane of the coordination unit.

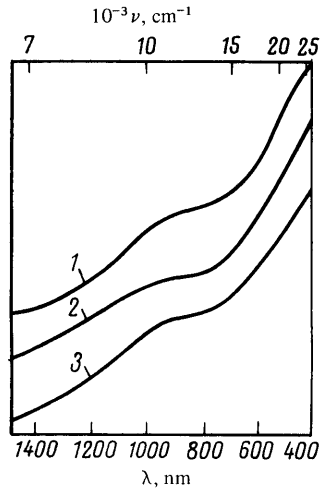


Figure 2. Diffuse reflection spectra of complexes (XIV); R: 1) 2-Me; 2) 3-Me; 3) 4-Me.

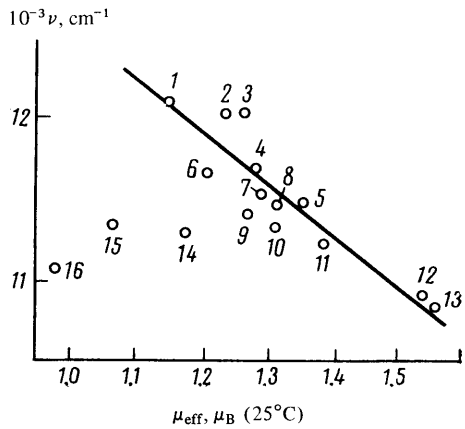


Figure 3. Dependence of the position of the *d–d* transition bands and μeff (at 25°C) on the substituent R for complexes of type (XIV); R: 1) 2-Cl; 2) 2-Me; 3) 3-Cl; 4) 2,4-Me_2; 5) 2,6-Me_2; 6) 2,6-Cl_2; 7) 3,4-Cl_2; 8) 4-Me; 9) 3,5-Cl_2; 10) 4-Cl; 11) H; 12) 3-NO_2; 13) 3-Me; 14) 2,5-Cl_2; 15) 2-NO_2; 16) 4-NO_2.

An analogous relation has been established for dinuclear complexes (XIII, R = alkyl) with alkyl substituents. As for mononuclear chelates, the replacement of a straight-chain alkyl group by a bulky branched group (for example, the replacement of n-C_3H_7 by iso-C_3H_7 or of n-C_4H_9 by t-C_4H_9) leads, with rare exceptions (R = Me), [81] to a tetrahedral distortion of the geometry and to a corresponding increase of μ_{eff} and a decrease of the frequency of the d–d transition[77].

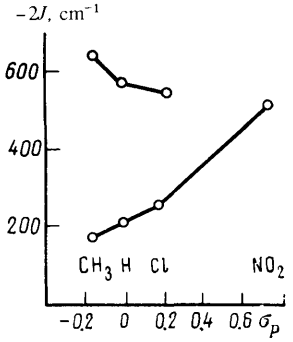


Figure 4. Dependence of the exchange integral on the Hammett constants σ_p for complexes of type (XIXa).

Thus there is a direct relation between the degree of tetrahedral distortion of the coordination unit in dinuclear complexes of type (XIII) and the decrease of the antiferromagnetic interaction between pairs of copper atoms[81]. The dihedral angles τ between the planes in which the copper atoms of the two halves of the dimeric molecules of (XIII) are located have been compared[81] with the integrals $-2J$. The values of τ are respectively 33.1°, 35.7°, 35.5°, and 39.3° for complexes with the following substituents: A = Cl, X = H, and R = Et; A = Br, X = H, and R = Et; A = Br, R = n-C_4H_9, and X = 5-Cl; A = Cl, X = H, and R = Me; the corresponding values of $-2J$ are 240, 205, 220, and 146 cm^{-1}.

If the structure of the complexes differs from the pseudotetrahedral structure, a linear relation is not observed between μ_{eff} and the d–d transition frequency. Depending on the conditions of synthesis and the nature of the alkyl substituent introduced into the aldehyde ring of the liquid, complexes (XIII) with different stereochemistries of the coordination units can be obtained[77]. The above compounds have been classified on the basis of the results: (1) type B—pseudotetrahedron; (2) type YG—square pyramid with a weak distortion in the direction of a trigonal-pyramidal configuration; (3) type Y—trigonal bipyramid with a weak distortion in the direction of a square-pyramidal configuration; (4) type Y'—trigonal bipyramid with a large distortion in the direction of a square-pyramidal configuration.

Naturally, for different stereochemical configurations, the dependence of μ_{eff} on the d–d transition frequency is different[77]. For regular square-pyramidal dinuclear structures, antiferromagnetic exchange via oxygen bridges should take place, as for planar complexes:

$$3d_{x^2-y^2}\,[\mathrm{Cu}\,(1)] - p_\sigma\,(\mathrm{O}) - 3d_{x^2-y^2}\,[\mathrm{Cu}\,(2)] \quad \sigma\text{-mechanism};$$
$$3d_{xz}\,[\mathrm{Cu}\,(1)] - p_\pi\,(\mathrm{O}) - 3d_{yz}\,[\mathrm{Cu}\,(2)] \quad \pi\text{-mechanism}.$$

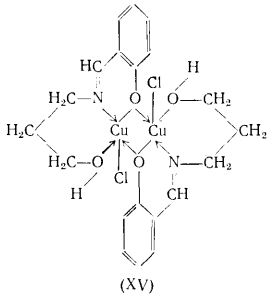
For regular trigonal-bipyramidal structures, antiferromagnetic exchange takes place as follows:

$$3d_{x^2-y^2}\,[\mathrm{Cu}\,(1)] - p_\sigma\,(\mathrm{O}) - 3d_{z^2}\,[\mathrm{Cu}\,(2)] \quad \sigma\text{-mechanism},$$
$$3d_{xy}\,[\mathrm{Cu}\,(1)] - p_\pi\,(\mathrm{O}) - 3d_{yz}\,[\mathrm{Cu}\,(2)] \quad \pi\text{-mechanism}.$$

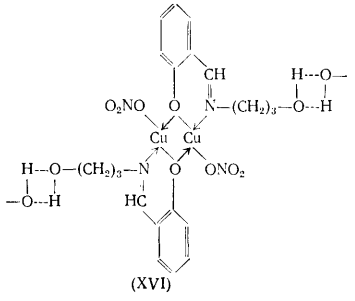
This approach makes it possible to infer the nature of the antiferromagnetic interaction and the symmetry of the coordination unit on the basis of the study of the dependence of the d–d transition energy on the effective magnetic moment in systematically selected series of complexes.

The complexes Cu(SalNROH)X (X = Cl, NO_3, or ClO_4), which are obtained by the interaction of copper salts and copper chelates with N-hydroxyalkylsalicylideneamines (IX), can have different compositions, structures, and magnetic properties depending on the method of synthesis, the nature of the anion, and the steric conditions (determined by the length and degree of branching of the hydroxyalkyl group)[46,87,88].

Whereas antiferromagnetic interactions of different strengths are observed for complexes with R = $(CH_2)_2$, $(CH_2)_3$, or CH_2–CH(Me) and X = Cl or ClO_4, when a nitro-group is introduced into the aldehyde ring of the ligand [for the complex with R = $(CH_2)_2$ and X = Cl] and with increase of the degree of branching of the group [R = Me–CH(Me), X = Cl or NO_2], these complexes behave as the usual paramagnetic materials[88]. It is suggested that the nature of the exchange interaction in the dimeric compounds (XV) is associated with the different degrees of distortion of the coordination unit as a function of R. For compounds with R = $-(CH_2)_3-$ and X = Cl, X-ray diffraction analysis revealed a distorted trigonal-pyramidal structure (XV):[89,90]



(XV)



(XVI)

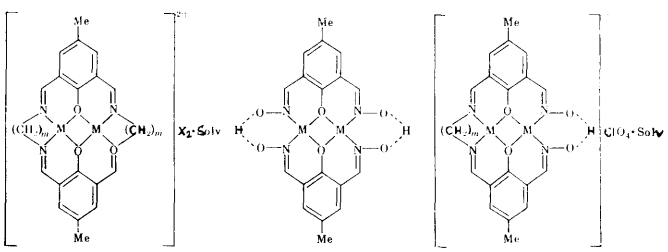
These are thus complexes of the second type, obtained on the basis of 3-hydroxy-N-propylsalicyclideneamines [the first type is a dimer (IXb) with a strong exchange interaction]. It has been shown[87] that these two types of complexes can undergo an interconversion under certain conditions. It has been suggested[87] that interaction with copper nitrate gives rise to compound (XVI), in which the alcoholic group is not deprotonated and is not coordinated to the metal, but forms a polymer chain via hydrogen bonding. An antiferromagnetic type of exchange is also

characteristic of complex (XVI), but its magnetic properties cannot be interpreted unambiguously[87,91].

The influence of the structural factor on the magnetic properties of copper compounds with *N*-hydroxyethyl-5-R-salicylaldimines of type (XV, R = H, Me, Cl, or NO_2) has been investigated[88]. A dinuclear structure with chloride bridges has been established for $[Cu(5\text{-}RSaL.NEtOH)Cl]_2$ with R = H or Me; a dinuclear structure with a phenolic oxygen as the bridge has been found for Cu-(5-MeSal. .NEtOH)Br.0.1 DMF (DMF = dimethylformamide); a linear trinuclear structure (also with the phenolic oxygen as the bridge) has been determined for $Cu_3(Sal.N.EtOH)_2Cl_4$. .2EtOH. The magnetic properties of these complexes are presented in Table 6. The form of the temperature dependence of the magnetic susceptibility permits a polymeric chain structure of $Cu_2(5\text{-}MeSalNEtOH)Cl_3.0.5H_2O$. For other complexes of this type, the structural data have also been correlated with their magnetic properties (Table 6).

IV. DINUCLEAR COMPLEXES WITH POLYDENTATE DIMERISING LIGANDS

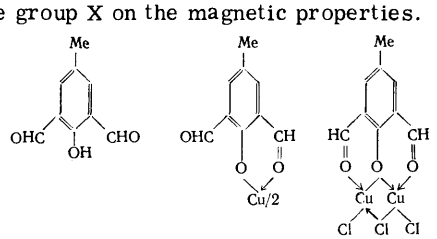
The azomethine derivatives (XVIII) and (XIX), obtained on the basis of 3-formyl-5-methylsalicylaldehyde (XVII), are typical dimerising ligands[92,93].



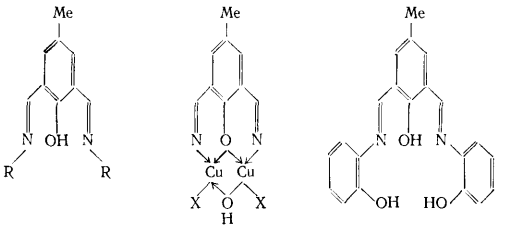
(XXa) (XXb) (XXc)

M = Cu, Ni, or Co; X = Cl or ClO_4; Solv = H_2O; m = 2, 3 . M = Cu or Ni M = Cu or Ni; Solv = DMF or H_2O

The effective magnetic moments of the mononuclear complex (XVIIa) and the dinuclear complex (XVIIb) are respectively 1.81 and 1.58 μ_B, while the μ_{eff} for dinuclear azomethine complexes of type (XVIIIa) are 0.8–1.29 μ_B at room temperature, depending on the substituent R.[93] Hence one may conclude that azomethine ligands give rise to dinuclear complexes (XVIIIa) with a stronger exchange interaction than complexes (XVIIb). These compounds were described for the first time by Robson[92], who investigated complexes (XIXa) with the ligand (XIX). The structure of (XIXa) has been confirmed by X-ray diffraction[92]. Several types of complexes (XXIa) have been synthesised by condensing (XVII) with various amines and investigated[92,94–97]. Comparison of complexes of type (XIXa) with different bridge groups but with identical Z (nos. 1–7, Table 7) reveals the influence of the nature of the bridge group X on the magnetic properties.

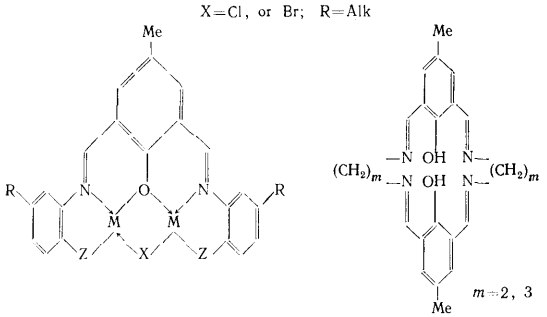


(XVII) (XVIIa) (XVIIb)



(XVIII) (XVIIIa) (XIX)

X=Cl, or Br; R=Alk



(XIXa) (XX)

X: $1/2O_2$, OMe, OEt, OH, N_3, $OCH_2C_6H_5$, $C_3H_3N_2$, Cl or (OCH_2CH_2OMe); Z = O or S; M = Cu or VO; R = H, Cl, Me, or NO_2.

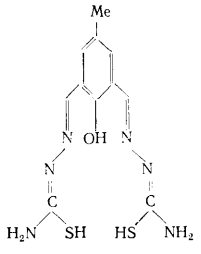
Table 6. The exchange integrals ($-2J$), magnetic moments (μ_{eff}), and g-factors for the complexes $Cu_n(5R'.SalNROH)_m.X.Solv$.

n	m	R¹	X	R	Solv	T, K	μ_{eff}, μ_B	$-2J$, cm^{-1}	g	Refs.
1	1	H	Cl	$(CH_2)_2$	—	76.4—289.7	1.0—1.63	124	2.10	46
						118.3—309.4	1.79—1.82	10	2.06	87
1	1	NO_2	Cl	$(CH_2)_2$	—	76.2—291.8	1.79—1.80	—	—	46
1	1	H	Cl	$CH_2CH(Me)$	H_2O	76.2—299.7	1.82—1.83	—	—	46
1	1	H	Cl	$(CH_2)_3$	—	96.3—309.6	0.04—1.05	504	2.20	46
1	1	H	Cl	$(CH_2)_3OMe$ *	—	76.3—287.7	0.07—1.00	491	2.18	46
1	1	H	NO_3	$(CH_2)_2$	—	81.0—300.5	1.81—1.80	—	—	46
						86.0—320.5	1.66—1.85	30	—	87
1	1	H	NO_3	$CH_2CH(Me)$	—	76.4—298.1	1.80—1.83	—	—	46
1	1	H	NO_3	$(CH_2)_3$	—	76.4—301.3	1.80—1.81	—	—	46
1	1	H	ClO_4	$(CH_2)_2$	H_2O	76.4—292.0	0.16—1.27	332	2.10	46
1	1	H	ClO_4	$(CH_2)_2$	2DMF	76.2—290.5	1.86—1.86	—	—	46
1	1	H	ClO_4	$CH_2CH(Me)$	EtOH	76.2—294.8	0.07—1.18	403	2.15	46
1	1	H	ClO_4	$CH_2CH(Me)$	2DMF	76.2—291.2	1.82—1.81	—	—	46
2	2	H	$2NO_3$	$(CH_2)_3$	—	114.0—345.3	0.47—1.36	320	2.08	87
2	2	H	2Cl	$(CH_2)_3$	—	138.0—387.5	0.30—1.20	470	2.09	87
1	1	Cl	NO_3	(CH_2)	—	79.0—345.3	1.25—1.59	—	—	87
1	1	Cl	Cl	(CH_2)		77.0—381.5	1.74—1.80	10	2.06	87
3	2	H	4Cl	$(CH_2)_2$	2EtOH	76.3—299.9	1.20—1.68	60	2.18	88
1	1	H	Br	$(CH_2)_2$	—	76.3—289.6	1.76—1.78	—	—	88
1	1	Me	Cl	$(CH_2)_2$	—	76.3—286.1	1.09—1.64	55	2.06	88
1	1	Me	Cl	$(CH_2)_2$	1/2·EtOH	76.4—286.0	1.79—1.82	—	—	88
2	1	Me	3Cl	$(CH_2)_2$	1/2 H_2O	76.4—287.4	0.84—1.49	83	2.13	88
1	1	Me	Br	$(CH_2)_2$	1/2 H_2O	76.3—286.5	1.71—1.76	—	—	88
1	1	Me	Br	$(CH_2)_2$	0.1DMF	76.3—288.7	0.16—0.83	290	2.20	88
1	1	Cl	Cl	$(CH_2)_2$	—	76.3—287.5	1.75—1.79	—	—	88
1	1	Cl	Br	$(CH_2)_2$	—	76.4—286.5	1.73—1.76	—	—	88
1	1	NO_2	Br	$(CH_2)_2$	—	76.3—286.5	1.72—1.76	—	—	88

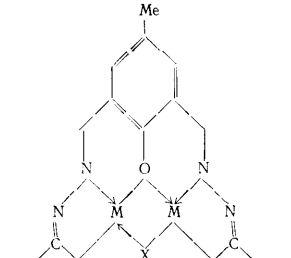
* Compound having the general formula $Cu_n(5\text{-}R'.Sal.N.ROMe)_m.X.Solv$.

On the other hand, when complexes with the same group but different Z are compared (Nos. 2 and 8, Table 7), the enhancement of the exchange interaction following the replacement of oxygen by sulphur in the coordination unit is clearly manifested, and the ligand residue does not apparently have a significant influence in these complexes

on the nature of the exchange interaction, as shown by a comparison of the properties of complexes of different types [(XIXa) and (XXIa)] but with the same bridge groups X and identical Z (Nos. 8 and 9 and 10 and 11, Table 7).



(XXI)



(XXIa)

M=Cu^{II} or Ni^{II}; X=$C_3H_3N_2$, N_3 or Cl .

Table 7. The values of μ^*_{eff}, exchange integrals, and g-factors for complexes.

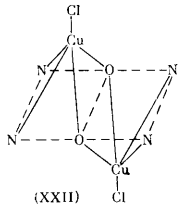
No.	Type of complex	M	Z	R	X	μ_{eff}, μ_B	$-2J$, cm^{-1}	g	Refs.
1	(XIX)	Cu	0	H	OMe	0.97	385	2.1	92
2	(XIXa)	Cu	0	H	$C_3H_3N_2$	1.40	230	2.1	92
3	(XIXa)	Cu	0	H	OEt	0.85	—	—	94
4	(XIXa)	Cu	0	H	OCH_2CH_2OMe	0.77	—	—	94
5	(XIXa)	Cu	0	H	OCH_2Ph	0.60	—	—	94
6	(XIXa)	Cu	0	H	OH	1.17	—	—	94
7	(XIXa)	Cu	0	H	OH	0.98	—	—	94
8	(XIXa)	Cu	S	H	$C_3H_3N_2$	1.20	372	2.0	95
9	(XIXa)	Cu	S	H	N_3	0.70	—	—	95
10	(XXIa)	Cu	—	—	$C_3H_3N_2$	1.20	414	2.2	95
11	(XXIa)	Cu	—		N_3	1.00	472	2.0	95
12	(XXIa)	Cu	—		Cl	1.20	430	2.3	95
13	(XIXa)	VO	0	Me	OMe	1.46	180	1.87	98
14	(XIXa)	VO	0	H	OMe	1.37	230	1.86	98
15	(XIXa)	VO	0	Cl	OMe	1.25	280	1.81	98
16	(XIXa)	VO	0	NO_2	OMe	0.85	545	1.95	98
17	(XIXa)	Cu	0	Me	OMe	0.70	655	2.15	98
18	(XIXa)	Cu	0	H	OMe	0.88	570	2.15	98
19	(XIXa)	Cu	0	Cl	OMe	1.04	555	2.15	98
20	(XIXa)	Cu	0	NO_2	OMe	1.18	—	—	98
21**	(XXa)	Cu	—	—	Cl	0.70—0.04	—	—	96
22***	(XXa)	Cu	—	—	ClO_4	0.58—0.10	—	—	96

* At room temperature.
** In the range 351–89 K.
*** In the range 286–90 K.

According to a hypothesis[95], confirmed by X-ray diffraction analysis of analogous complexes[97], compounds (XIXa) have a tetrameric structure and the change in magnetic properties is to a large extent determined by the distortion of the coordination unit on formation of the tetramers.

It is of interest to compare the behaviour of dinuclear complexes of type (XIXa) having identical Z and X (Z = O, X = OMe) but variable R. [98] A certain correspondence between the electronic influence of the substituents R (Hammett σ_p constants) and the quantity $-2J$ (Fig. 4 and Nos. 13–20 in Table 7) has been explained[98] by the fact that the overlap of the d_{xy} orbitals in the vanadyl complexes increases in the sequence R = Me < H < Cl in parallel with the deviation of the vanadium atom from the plane of the coordination unit. On the other hand, $-2J$ for tetragonal copper complexes is influenced to the greatest extent by the change in the equatorial bonds involved in the exchange. This is why $-2J$ decreases with enhancement of the electron-accepting properties of the substituent R, leading to the combination of electron density at the phenolic oxygen bridge. Complexes (XIXa) with R = NO_2 for which a polymeric structure has been established, constitute a special case.

A strong antiferromagnetic interaction has been observed for complexes (XXa) (Nos. 13 and 14, Table 8). The square-pyramidal structure (XXII)



(XXII)

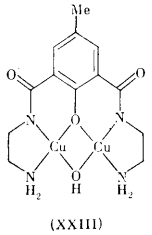
was assigned to them on the basis of X-ray diffraction studies of similar compounds[96].

Table 8. The values of μ_{eff}, exchange integrals, and g-factors for complexes.

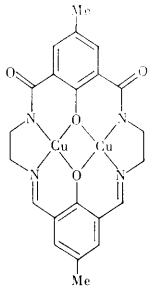
No.	Type of complex	m	R	X	M^{2+}	T, K	μ_{eff}, μ_B	$-2J$, cm^{-1}	g	Refs.
1	(XXIV)	—	H	OH	Cu	76.2—283.0	0.07—1.05	447	2.16	103
2	(XXIV)	—	H	Cl	Cu	76.2—289.8	1.52—1.71	—	—	103
3	(XXIV)	—	H	Br	Cu	76.2—288.3	1.70—1.76	—	—	103
4	(XXIV)	—	Me	Cl	Cu	76.3—285.3	1.45—1.72	—	—	103
5	(XXV)	—	Me	Cl	Cu	299.3	1.61	143	2.10	104
6	(XXV)	—	Me	Br	Cu	301.1	1.61	155	2.10	104
7	(XXV)	—	Me	OH	Cu	291.8	1.29	330	2.11	104
8	(XXV)	—	Et	Cl	Cu	302.6	1.66	123	2.10	104
9	(XXV)	—	Et	Br	Cu	291.6	1.68	125	2.16	104
10	(XXV)	—	Et	OH	Cu	303.4	0.49	865	2.15	104
11	(XXb)	—	—	—	Cu	room	0.59	—	—	106
12	(XXb)	—	—	—	Ni	room	2.87	—	—	106
13	(XXc)		—	—	Cu	room	0.59	—	—	106
14	(XXc)		—	—	Cu	room	0.61	725	2.10	106
15	(XXc)*	—	—	—	Cu	room	2.25	—	—	106
16	(XXIIIb)	—	Me	—	Cu	297.7	0.68	720	2.20	99
17	(XXIIIb)	—	Et	—	Cu	291.6	0.66	715	2.20	99
18	(XXIIIb)	—	C_2H_4OH	—	Cu	297.7	0.54	820	2.20	99
19	(XXIIIb)	—	n-Pr	—	Cu	294.2	0.66	725	2.20	99
20	(XXIIIb)	—	n-Bu	—	Cu	296.6	0.71	705	2.20	99
21	(XXIIIb)	—	iso-Bu	—	Cu	294.1	0.63	735	2.17	99
22	(XXIIIb)	—	s-Bu	—	Cu	295.4	0.63	750	2.20	99
23	(XXIIIb)	—	Me	—	Ni	198.7—87.0	3.14—2.76	—	—	99
24	(XXIIIb)	—	Et	—	Ni	293.0—77.5	3.10—2.64	—	—	99
25	(XXIIIb)	—	C_2H_4OH	—	Ni	291.7—83.5	3.06—2.74	—	—	99
26	(XXIIIb)	—	n-Bu	—	Ni	296.6—87.1	3.17—2.72	—	—	99
27	(XXV)	—	Me	NCS	Cu	298.0	1.57	—	2.18	105
28	(XXV)	—	Et	NCS	Cu	297.0	1.62	—	2.17	105

* The value of μeff was found on the assumption that one nickel atom is diamagnetic.

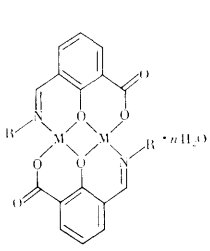
Dinuclear complexes (XXIIIa) with analogous ligands (XXIII) have been synthesised[100]:



(XXIII)



(XXIIIa)

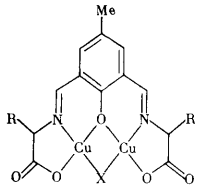


(XXIIIb)

M = Cu^{II}, or Ni^{II}; R = Alk .

It has been shown that the exchange interaction is greatly intensified on passing from (XXIII) (μ_{eff} = 1.14 μ_B at T_{room}) to (XXIIIa) (μ_{eff} = 0.79 μ_B at T_{room}), because the system is more rigid and because of the introduction of the conjugated azomethine fragment. At the same time, dimeric complexes (XXIIIb) have been obtained on the basis of 3-formylsalicylic acid[99]; the parameters characterising the exchange interaction in (XXIIIb) were compared with the values for the analogous complexes (XIII). The authors[99] emphasise that the substituents R in compounds (XXIIIb) have a weaker steric influence than in (XIII).

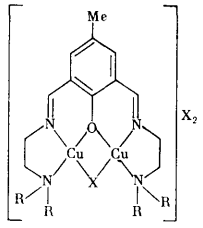
Complexes (XXb) and (XXIV) have been synthesised and investigated[101-103]:



(XXIV)

R = Me, X = Cl;

R = H, X = Cl, Br, or OH



(XXV)

R = Me, Et, or H;

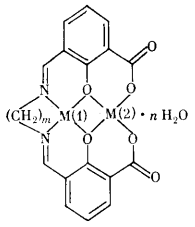
X = Cl, Br, OH, or NSC

A significant change in their magnetic properties was demonstrated on varying the bridge group X [101-103] (Table 8): for X = OH, a strong antiferromagnetic interaction is observed, while for X = Cl or Br, it is significantly less intense[101-103]. Since the Cu–Cu distance in a dimeric molecule is 3.4 Å, an indirect exchange interaction via the bridge groups is observed. It is suggested that this change in magnetic properties indicates a change in the extent of the indirect interaction of the bridge groups in the sequence OH $\gtrsim$ Cl $\simeq$ Br. At the same time the authors[103] assume that the high effective magnetic moments of compound Nos. 5, 6, and 7 in Table 8 can be due to the distortion of the plane of the coordination unit.

An analogous effect of bridge groups was investigated in greater detail in relation to complexes of type (XXV).[104] It was shown on the basis of the temperature variation of the magnetic susceptibility that the antiferromagnetic exchange interaction between two copper atoms diminishes in the sequence OH $\geqslant$ Br > Cl for the same contribution of the phenolic oxygen to the indirect exchange. However, one must bear in mind (Nos. 8–10, Table 8)[104] the role of the geometrical factor. It has been postulated[104] that the above complexes with a chloride anion have a tetragonal-pyramidal structure and, judging from the electronic spectra, complexes (XXV) with X = OH have a structure different to that of complexes with X = Cl or Br. Indeed the introduction of the group X = SCN leads[105] to the formation of tetrameric structures in which two dimers are linked to form a tetramer via intermolecular S...Cu bonds. The Cu–Cu interaction in the dimers remains antiferromagnetic.

A strong exchange interaction has been observed also for complexes of type (XX, b and c) (Nos. 11–15, Table 8)[106]. A tetragonal-pyramidal structure was also attributed to them. The enhancement of the exchange interaction between them is explained by a more rigid matrix due to the ligand.

Polydentate ligands based on 3-formylsalicylaldehyde[107,108] have been used to obtain di- and poly-nuclear complexes whose molecules contain two different metals (Cu and Ni).[107,111] Bimetallic complexes of type (XXa), each molecule of which contains Co^{II} and Co^{III},[110] as well as complexes of type (XXVI) based on 3-formylsalicylic acid[110-112] have been synthesised.



M(1) = Cu, m = 3, M(1) = Cu, n = 1;

m = 2, M(2) = Co, Fe, Mn, Ni, UO_2, or Th/2; n = 0–3.

(XXVI)

It is noteworthy that the possibilities of complexes of this series have been by no means exhausted and, on the basis of studies carried out hitherto[92-111], it is difficult to make general conclusions concerning the correlation between the structure, the nature of the bridge groups, and the exchange interaction. This is because the structures of these compounds have been inadequately elucidated and the conclusion that the complexes have the same structures, reached when a systematic comparison is made of series of such complexes, are mainly based on the analogy with the known structural data for other similar systems.

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