Russian Chemical Bulletin, International Edition, Vol. 50, No. 5, pp. 812—819, May, 2001

EPR study of weak exchange interactions in binuclear copper(II) complexes with salicylaldehyde acyldihydrazones

G. M. Larin,[a] V. F. Shul'gin,[b] E. A. Sarnit,[b] and Yu. V. Rakitin[c]★

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: lagema@igic.ras.ru
[b]*V. I. Vernadskii Taurida National University,*
4 ul. Yalta, 95007 Simferopol, Ukraine.
Fax: (065 2) 23 2310. E-mail: vshul@ccssu.crimea.ua
[c]*I. V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials*
of Kola Science Centre, Russian Academy of Sciences,
26 A ul. Fersmana, 184200 Apatity, Murmansk reg., Russian Federation.
Fax: +7 (881 555) 76 425. E-mail: rakitin@chemy.kolasc.net.ru

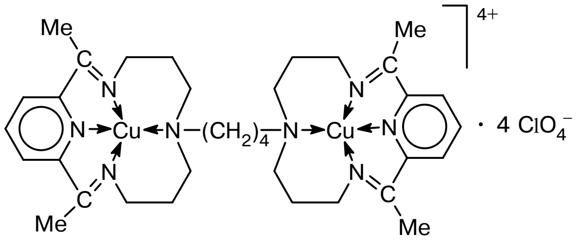
The binuclear Cu^{II} complexes with bis(salicylidene)hydrazones of dicarboxylic acids and their analogs (H_4L) of composition [$Cu_2L \cdot 2Py$] in which the coordination polyhedra are linked by a polymethylene chain containing from one to eight CH_2 units were studied by EPR spectroscopy. Weak antiferromagnetic spin-spin exchange interactions between two Cu^{II} atoms were found in the complexes based on hydrazones of malonic, succinic, glutaric, and adipic acids. These exchange interactions are manifested in the EPR spectra of liquid solutions as seven-line hyperfine signals from two equivalent Cu^{II} atoms with the hyperfine coupling constant $a_{Cu} \approx 40 \cdot 10^{-4}$ cm^{-1}. The exchange ceases as the length of the polymetylene chain increases to five—eight units and the EPR spectra show a four-line signal with $a_{Cu} \approx 80 \cdot 10^{-4}$ cm^{-1} typical of mononuclear complexes.

Key words: binuclear copper(II) complexes, bis(salicylidene)hydrazones of dicarboxylic acids, EPR, hyperfine structure, spin-spin exchange interactions.

Recently, studies of magnetic exchange between paramagnetic metal atoms separated by distances larger than >3 Å have attracted considerable attention.[1—5] This line of investigation is promising from both the theoretical and practical standpoints because it opens up possibilities for the construction of new magnetic materials[6,7] and can give an idea of the mechanism of high-temperature superconductivity.[3,4] Studies of the exchange between paramagnetic centers can also provide an insight into the mechanism of long-range electron transfer (>10 Å) in biochemical processes.[1,2] Theoretical fundamentals of this phenomenon are lacking because of scarcity of the experimental data.

Oxalate complexes of Cu^{II} possessing strong antiferromagnetic exchange between the paramagnetic centers ($-2J$ = 385.4 cm^{-1}; the distance between the copper ions r(Cu...Cu) is 5.15 Å) and binuclear Cu^{II} and Co^{II} complexes based on terephthalic acid for which exchange interactions are manifested at distances larger than 10 Å ($-2J$ = 70 cm^{-1} for r(Cu...Cu) = 11.252 Å and $-2J$ = 16 cm^{-1} for r(Co...Co) = 10.310 Å) were described in the literature.[1,2,6]

The data on only two complexes for which long-range exchange interactions were studied in solutions are available in the literature. Thus, the Cu^{II} coordination compound in which the exchange interaction between the paramagnetic centers occurs through a chain consisting of seven σ-bonds was reported.[8] The composition of the compound corresponds to the formula $[Cu_2B](ClO_4)_4 \cdot 1.5\ H_2O$ (**1**), where B is an octadentate organic Lewis base formed by condensation of 2,6-diacetylpyridine with N,N,N',N'-tetra(3-aminopropyl)-1,4-diaminobutane.



1

Compound **1** was prepared by the reaction of an aqueous-alcoholic solution of copper(II) perchlorate with an alcoholic solution of 2,6-diacetylpyridine and N,N,N',N'-tetra(3-aminopropyl)-1,4-diaminobutane taken in a ratio of 2 : 2 : 1. An analogous reaction with $NiCl_2$ in the presence of $HClO_4$ and $NaClO_4$ afforded the $[Ni_2B](ClO_4)_4 \cdot H_2O$ complex. According to the data

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 777—783, May, 2001.

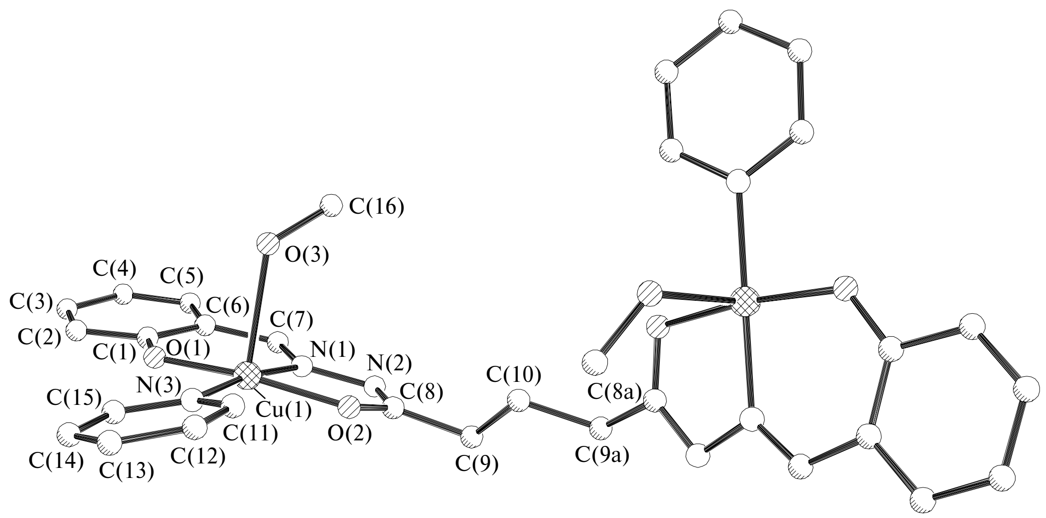
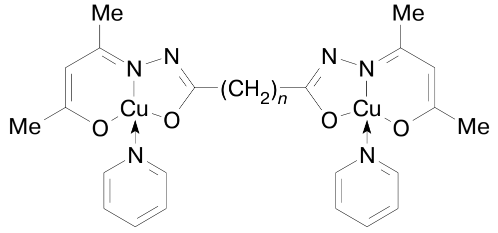


Fig. 1. Overall view of the [$Cu_2L(C_5H_5N)_2(MeOH)_2$] molecule based on the X-ray diffraction data.[10,11]

of X-ray diffraction analysis, the Ni^{II} atom in the complex is in a distorted planar-square environment and r(Ni...Ni) is equal to 9.130 Å. This complex is isostructural to the Cu^{II} complex. The EPR spectrum of a polycrystalline sample of the copper complex introduced into a diamagnetic matrix of its nickel analog has seven parallel hyperfine lines, which are indicative of interactions between the unpaired electrons and two Cu^{II} nuclei (I_{Cu} = 3/2).

Simultaneously with the above-mentioned investigation,[8] we have independently found the exchange interaction between the copper(II) atoms separated by a polymethylene chain in the EPR spectral study of solutions of coordination compounds with acetylacetone acyldihydrazones (**2**).[4]

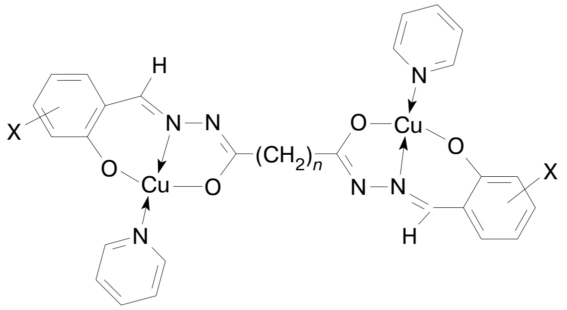


2

n = 0—2, 4, 8

The EPR spectra of complexes **2** based on acyldihydrazones of malonic, succinic, and adipic acids have a seven-line hyperfine signal from two equivalent Cu^{II} atoms. Based on the data obtained previously,[4,8] the mechanism of interaction (superexchange) between the Cu^{II} ions through a chain of σ-bonds in the polymethylene bridge was proposed.

In the present work, the binuclear copper(II) complexes with salicylaldehyde acyldihydrazones and its analogs **3—6** in which the coordination polyhedra are linked by polymethylene chains of different length were studied by EPR spectroscopy.



X = H (**3**), 5-Br (**4**), 4-OH (**5**), 5,6-C_4H_4 (**6**)

Experimental

The procedure for the synthesis of complexes of type **3** and the results of their studies by elemental and thermal analysis and IR spectroscopy have been reported previously.[9] According to the data of X-ray diffraction analysis,[10,11] the Cu^{II} complex with bis(salicylidene)hydrazone of glutaric acid [$Cu_2L(C_5H_5N)_2(MeOH)_2$] $\cdot$ $2H_2O$ has a binuclear structure (Fig. 1). The coordination polyhedron about the copper cations is a distorted tetragonal pyramid whose base is formed by the N atom and two O atoms of the doubly deprotonated form of salicylidene hydrazone and by the N atom of the pyridine molecule. The vertex of the pyramid is occupied by the methanol molecule. The distance between the Cu atoms is 9.182 Å.*

The EPR spectra of liquid and frozen solutions in a chloroform—pyridine mixture (10 : 1 v/v) or in pyridine were measured on an ADANI PS100X instrument (Belarus) at the concentration of the complexes of (1—5) $\cdot$ 10^{-3} mol L^{-1}. Theoretical simulation of the spectra was carried out using a program package described previously.[5] The experimental spectra

---

* The results of the structure solution have been reported in detail previously.[10,11]

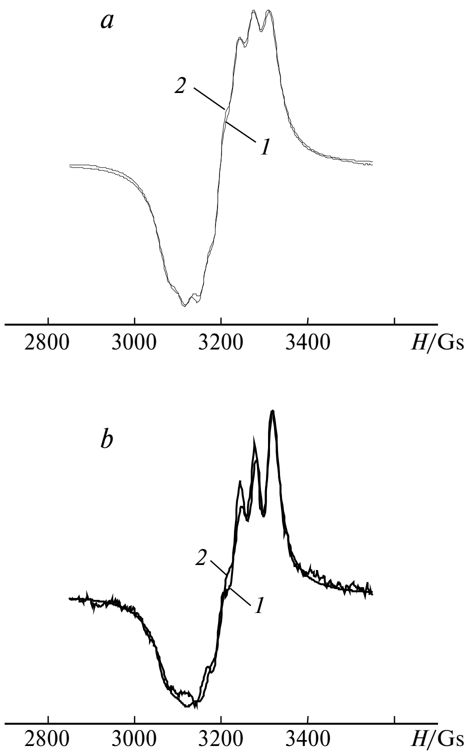


Fig. 2. Experimental (*1*) and theoretical (*2*) EPR spectra of liquid solutions of complexes **3**.1* (*a*) and **3**.2 (*b*).

were processed on a computer by the method of best approximation of the experimental spectra by the theoretical data with minimization of the error functional

$$R = \Sigma_i (I_i^{\mathrm{obs}} - I_i^{\mathrm{t}})^2/N,$$

where I_i^{obs} are experimental intensities of the EPR signal processed on a computer as a file of points with a constant step along the magnetic field H; I_i^{t} are theoretical intensities at the same H values calculated as the sum of derivatives of the Lorentz and Gaussian functions centered at the resonance values of H; and N is the number of points.

The g factors, the hyperfine structure splitting from the copper nuclei, and the widths of the resonance lines were varied in the course of minimization. The line width was specified by the equation

$$\Delta H = \alpha + \beta m_I + \gamma m_I^2,$$

where α is the term accounting for broadening effects identical for all hyperfine lines; m_I is the projection of the nuclear spin onto the direction of the external magnetic field; the β coefficient is determined by the product of the g tensor and the tensor of hyperfine coupling; and the γ coefficient is determined by anisotropy of hyperfine coupling and depends on the correlation time of rotational motion of the paramagnetic species in the liquid. Since the complexes containing polymethylene bridges can be stereochemically nonrigid, we also took into account the contribution

$$\Delta H_{(1,2)} = \delta(m_1 - m_2)^2,$$

associated with intramolecular motions of one copper(II) complex (m_1) with respect to another one (m_2) about the polymethylene bridge in the binuclear complex. The theoretical parameters (g, a_{Cu}, α, β, γ, and δ) were varied until the minimum of the error functional was attained. The minimization was terminated when R reached the value at which the theoretical spectrum agreed well with the experimental data and further iterations did not lead to changes in the values of R (the amplitude of the spectrum was normalized to unity). Generally, this was achieved at $R < 0.03$ (Fig. 2).

Results and Discussion

The isotropic EPR spectra of liquid solutions of compounds **3**.1—**3**.4 differ somewhat from those of their acetylacetone analogs.[4] However, the former also have an isotropic signal consisting of seven hyperfine lines (see Fig. 2). The spectra of compounds **3**.3 and **3**.4 are similar to that of compound **3**.2. The hyperfine coupling constant (a_{Cu}) (Table 1) is several times as large as the typical value for the N nucleus (10—14 Gs), *i.e.*, the observed spectrum is not associated with splitting of the signal due to additional hyperfine coupling of the unpaired electron with the N nuclei. The spectrum can be interpreted as a result of coupling of the unpaired electron with two equivalent Cu nuclei. The solution of the spin-Hamiltonian for this system demonstrated that the hyperfine coupling constant in this case should be half as large as that for the monomeric complex, *i.e.*, ~40 Gs.[12]

Table 1. Parameters of the EPR spectra of the Cu$^{\mathrm{II}}$ complexes with bis(salicylidene)hydrazones of dicarboxylic acids

Compound	n^a	g	$a_{\mathrm{Cu}} \cdot 10^4$ ^{b} /cm^{-1}	Parameters of the line width/Gs				σ^c (%)
				α	β	γ	δ	
3.1	7	2.111	33.1	31.6	1.9	−1.3	−1.8	1.4
3.2	7	2.112	36.0	32.0	7.8	−3.3	−1.8	1.8
3.3	7	2.106	39.9	28.1	5.8	−0.3	3.6	2.3
3.4	7	2.105	39.3	32.1	6.9	−1.2	6.4	2.0
3.5	4	2.104	71.5, 76.6	51.8	10.9	2.8	—	1.9
3.6	4	2.110	71.4, 76.5	46.3	13.0	2.6	—	1.8
3.7	4	2.103	77.2, 82.7	42.4	9.1	2.2	—	2.2
3.8	4	2.105	76.8, 82.3	40.8	9.7	2.1	—	3.2

[a] The number of hyperfine lines.

[b] For compounds **3**.5—**3**.8, the first and second values correspond to the ^{63}Cu and ^{65}Cu isotopes, respectively.

[c] The error characterizing the difference between the theoretical and experimental spectra ($R \cdot 100$).

---

* Hereinafter, the second figure in the numbers of the compounds indicates the number of CH_2 units in the polymethylene chain.

In some cases, the seven-line hyperfine structure is resolved for the forbidden transition ($\Delta m_I = \pm 2$) in the EPR spectra of polycrystalline specimens of dimeric copper(II) complexes[12,13] in which the Cu^{II} ions are linked by the methylene bridge and are separated by a distance of ~3 Å.[4] In addition, seven parallel hyperfine lines are observed in the anisotropic EPR spectra of some heterovalent copper(II, I) complexes with the metal—metal distance of ~2.4 Å, which is indicative of the covalent interaction between the copper atoms.[14,15]

Planar dimeric fragments of the Cu_2O_2 type have been found previously[16] in studies of the Cu^{II} complexes with salicylidene hydrazones of some substituted monocarboxylic acids. However, the crystal structure of the $[Cu_2L(C_5H_5N)_2(MeOH)_2] \cdot 2H_2O$ complex excludes exchange interactions.[11] Moreover, the EPR spectra were measured for solutions containing a large excess of pyridine, which generally causes the cleavage of the phenoxide bonds to form monomeric complexes.[3,4]

An increase in the length of the polymethylene chain to five—eight units (10—13 σ-bonds between the Cu atoms) leads to weakening of interactions between the paramagnetic centers, and hence, the EPR spectra of solutions of compounds **3**.5—**3**.8 have a four-line hyperfine signal from one Cu nucleus with the hyperfine coupling constant $a_{Cu} \approx 80 \cdot 10^{-4}$ cm^{-1} (Fig. 3) typical of mononuclear complexes. The parameters of the spin-Hamiltonian (g and a_{Cu}), which were obtained by theoretical simulation of the spectra, are given in Table 1. The spectra were simulated taking into account the signals from two copper isotopes, *viz.*, ^{63}Cu (natural content was 69.1%) and ^{65}Cu (content was 30.9%).

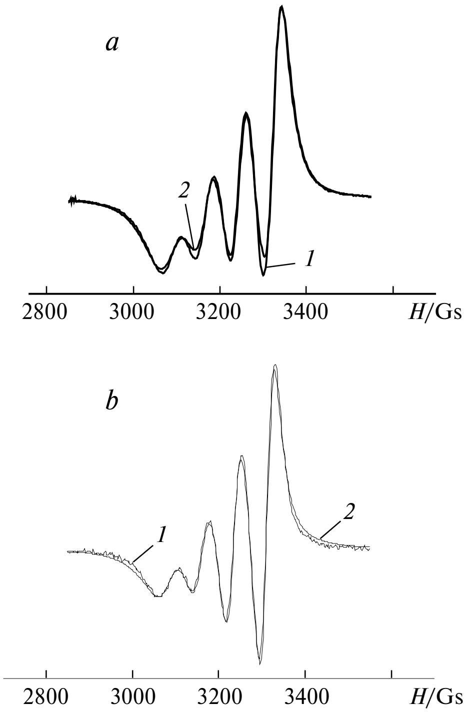


Fig. 3. Experimental (*1*) and theoretical (*2*) EPR spectra of liquid solutions of complexes **3**.5 (*a*) and **3**.6 (*b*).

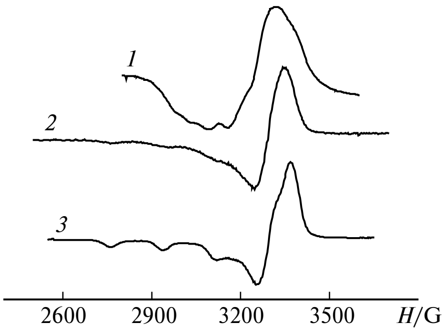


Fig. 4. EPR spectra of solutions of complexes **3**.1 (*1*), **3**.4 (*2*), and **3**.5 (*3*) frozen at 77 K.

Interesting changes are observed in the EPR spectra of solutions of complexes **3** frozen at 77 K as the length of the polymethylene chain increases. The spectral patterns are typical of systems with the axial symmetry, but the character of hyperfine coupling, which is generally manifested in the parallel orientation, changes on going from compound **3**.1 to compound **3**.5 (Fig. 4). Thus, the poorly resolved parallel hyperfine signal with one-half the constant (about 60 Gs) is observed in the spectrum of compound **3**.1. Unfortunately, only five hyperfine lines instead of seven lines expected for coupling of the unpaired electron with two equivalent Cu^{II} atoms are observed due to overlapping of the parallel and perpendicular signals (see Fig. 4, curve *1*). However, the hyperfine coupling constant and the character of absorption are indicative of exchange interaction between two copper(II) atoms. It should be noted that the hyperfine structure of this type has been observed previously[8] in the EPR spectra of frozen solutions and magnetically dilute polycrystalline specimens of binuclear copper complexes with tetraazamacrocyclic ligands.

The parallel hyperfine lines disappear as the length of the polymethylene (CH_2=) chain increases from one to two units, and this structure appears again only in the spectra of compounds **3**.3 and **3**.4, but just as a poorly resolved four-line hyperfine signal with the hyperfine coupling constant of ~160 Gs (see Fig. 4, curve *2*) typical of monomeric complexes. Finally, the anisotropic EPR spectrum of a frozen solution of complex **3**.5 (n = 5) has three well-resolved parallel hyperfine lines from one Cu nucleus with the constant of 180 Gs (the fourth line overlaps with the perpendicular signal, see Fig. 4, curve *3*). A further increase in the length of the aliphatic bridge does not lead to a change in the character of absorption, and the EPR spectra of complexes **3**.6—**3**.8 at 77 K are analogous to the spectrum of compound **3**.5.

These data indicate that weak exchange interactions between two copper atoms are also manifested in low intensity signals in the spectra of frozen solutions. This is indirect evidence in favor of the fact that dynamic effects are of importance in the mechanisms of spin-density transfer through the aliphatic bridge.

The results of the EPR spectral studies of the copper(II) complexes with bis(salicylidene)hydrazones of dicarboxylic acids made it possible to extend the range of compounds for which weak exchange interactions between the Cu atoms occur through the aliphatic bridge. In this connection, it was of interest to elucidate the effect of the substituent in the carbonyl fragment of acyldihydrazone on the character of the exchange interaction between the paramagnetic centers. For this purpose, we studied the binuclear copper(II) complexes with acyldihydrazones of 5-bromosalicylaldehyde, 4-oxylsalicylaldehyde, and 2-oxynaphthalene-1-carbaldehyde. Our results (Table 2) are somewhat different from those obtained in the studies of the complexes with acetylacetone bis(salicylidene)hydrazones and acyldihydrazones.

Table 2. Parameters of the EPR spectra of the binuclear Cu^{II} complexes with derivatives of bis(salicylidene)hydrazones of dicarboxylic acids

Compound	n[a]	g	$a_{Cu}\cdot10^4$ [b] /cm^{-1}	Parameters of the line width/Gs				σ[c] (%)
				α	β	γ	δ	
Complexes with bis(5-bromosalicylidene)hydrazones								
4.1	7	2.116	35.6	31.7	3.9	−0.9	1.9	2.3
4.2	7	2.115	35.1	30.4	8.6	0.6	−0.4	1.9
4.3	7	2.112	36.2	28.9	9.7	2.0	0.0	4.3
4.4	4	2.109	68.3, 73.2	45.2	16.9	3.8	—	6.4
4.5	4	2.106	71.5, 76.6	52.3	12.3	3.2	—	1.4
4.6	4	2.107	66.5, 71.3	55.6	20.9	9.3	—	3.2
4.7	4	2.107	73.1, 78.3	44.1	11.9	3.1	—	2.4
4.8	4	2.110	72.4, 77.7	47.1	11.7	3.6	—	3.4
Complexes with bis(4-oxysalicylidene)hydrazones								
5.1	7	2.113	33.1	34.8	2.8	−3.7	2.9	2.2
5.2	7	2.111	32.5	37.3	2.5	−3.6	3.0	2.3
5.3	7	2.111	35.5	29.8	8.6	8.2	−1.3	4.4
5.4	4	2.103	70.7, 75.8	49.6	15.2	4.8	—	4.3
5.5	4	2.106	71.1, 76.2	58.5	16.0	3.8	—	2.3
5.6	4	2.045	66.7, 71.5	53.5	20.9	9.3	—	3.6
5.7	4	2.100	75.5, 80.9	49.6	14.9	10.3	—	5.7
5.8	4	2.107	70.2, 75.2	53.3	18.1	4.0	—	2.2
Complexes with bis(2-oxynaphthylidene)hydrazones								
6.1	7	2.116	36.2	37.0	7.7	−2.1	2.3	5.5
6.2	7	2.115	37.6	34.1	10.1	0.5	0	2.7
6.3	7	2.115	38.7	31.4	10.9	2.2	1.6	3.1
6.4	4	2.105	61.2, 65.2	67.4	−1.8	8.0	—	4.8
6.5	4	2.106	68.4, 73.4	58.1	16.1	1.9	—	5.0
6.6	4	2.045	66.5, 71.2	52.3	16.5	2.0	—	3.3
6.7	4	2.100	76.0, 81.4	49.2	12.2	4.2	—	1.8
6.8	4	2.107	71.7, 76.8	51.3	15.8	3.5	—	2.3

[a] The number of hyperfine lines.

[b] For compounds **4**.4—**4**.8, **5**.4—**5**.8, and **6**.4—**6**.8, the first and second values correspond to the ^{63}Cu and ^{65}Cu isotopes, respectively.

[c] The error characterizing the difference between the theoretical and experimental spectra ($R\cdot100$).

Thus, the isotropic EPR spectra of liquid solutions of the complexes with bis(5-bromosalicylidene)hydrazones of malonic, succinic, or glutaric acids have a seven-line hyperfine signal (Fig. 5, curves *1—3*). The character of absorption changes as the number of σ-bonds separating the paramagnetic centers increases due to insertion of one more methylene group (n = 4). The EPR spectrum of a solution of the complex with bis(5-bromosalicylidene)hydrazone of adipic acid has a four-line hyperfine signal, which is indicative of substantial weakening of exchange interaction between the paramagnetic centers. The EPR spectra of the complexes with bis(5-bromosalicylidene)hydrazones of adipic, pimelic, suberic, azelaic, or sebacic acids are similar to those of compounds **3**.5 and **3**.6 (see Fig. 3). The character of absorption and the a_{Cu} values are indicative of the absence of exchange interactions between the copper(II) atoms.

The EPR spectra of liquid solutions of the complexes with bis(4-oxysalicylidene)- or bis(2-oxynaphthylsalicylidene)hydrazones are analogous to those of bis(5-bromosalicylidene)hydrazones (see Table 2). The signal in the EPR spectra of liquid solutions of the complexes with acyldihydrazones of malonic, succinic, or glutaric acids consists of seven hyperfine lines, whereas the spectra of solutions of the complexes containing the polymetylene chain of larger length (n = 4—8) have four hyperfine lines from one copper atom. In the latter case, exchange interactions between the paramagnetic centers are also absent.

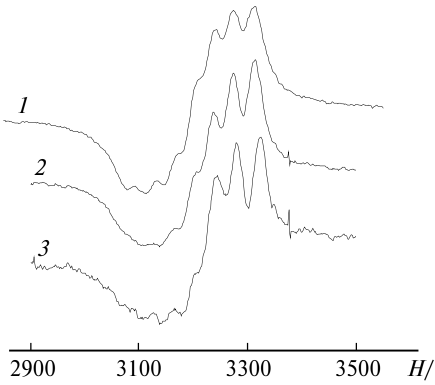


Fig. 5. EPR spectra of liquid solutions of complexes **4**.1 (*1*), **4**.2 (*2*), and **4**.3 (*3*) at 293 K.

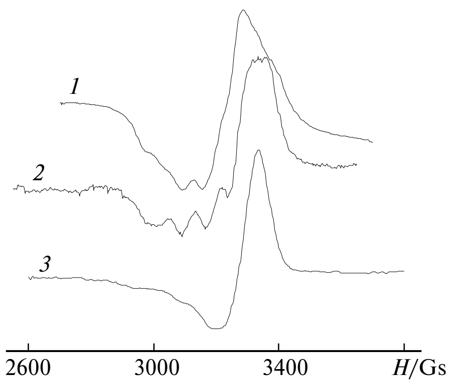


Fig. 6. EPR spectra of solutions of complexes **4**.1 (*1*), **4**.2 (*2*), and **4**.3 (*3*) frozen at 77 K.

The EPR spectra of frozen solutions (77 K) of complexes **4** are similar to those of salicylidene compounds with axial symmetry. The EPR spectra of compounds **4**.1 and **4**.2 have a poorly resolved parallel hyperfine signal from two equivalent copper atoms. Only five or six lines are observed instead of the expected seven lines due to overlapping of the parallel and perpendicular hyperfine signals (Fig. 6, curves *1* and *2*). When the length of the chain increases to $n = 3$, the parallel hyperfine structure disappears (see Fig. 6, curve *3*). This structure appears only in the spectra of compounds with $n = 4$, but as a poorly resolved four-line hyperfine signal with the hyperfine coupling constant typical of mononuclear complexes. A further increase in the length of the polymethylene bridge does not lead to a change in the character of absorption, the parallel hyperfine signals being more pronounced.

The results of EPR spectral studies of the chelate copper(II) complexes with acetylacetone acyldihydrazone, salilcylaldehyde acyldihydrazone, or analogs of the latter are unambiguously indicative of the presence of weak exchange interactions between the paramagnetic centers. This interaction is most clearly manifested in the fact that the EPR spectra of solutions of these compounds have an isotropic signal consisting of seven hyperfine lines, which appear as a result of coupling of the unpaired electron with two equivalent copper nuclei. Recall that the seven-line hyperfine signal has been observed previously[12,13] for forbidden transitions in the EPR spectra of polycrystalline specimens of some copper dimers with short metal—metal distances (~3 Å) and strong antiferromagnetic exchange interactions. In the molecular systems considered in the present study, the distance between the paramagnetic centers reaches 10 Å due to which direct overlapping of the orbitals with the unpaired electrons is impossible. This is evidence in favor of indirect exchange mechanisms.

Based on the available experimental data, several mechanisms of exchange interactions between the Cu^{II} atoms in the binuclear complexes with acyldihydrazones of dicarboxylic acids can be proposed.

1. The formation of oxo bridges between the copper(II) atoms giving rise to the intra- or intermolecular dimeric Cu_2O_2 fragments.
2. The formation of intra- or intermolecular associates involving coordinated pyridine molecules through nonbonded π—π-interactions between the aromatic systems (stacking).
3. Stacking interaction between the pseudoaromatic systems formed due to delocalization of the double bonds in the chelate rings of the coordination sphere.
4. Superexchange through the system of σ-bonds in the aliphatic bridge of acyldihydrazone.

Taking into account the conditions under which the EPR spectra were recorded, the first of the above-mentioned mechanism should be excluded because intermolecular interactions cannot occur due to low concentrations of the complexes in solutions ($(1—5) \cdot 10^{-3}$ mol L^{-1}), whereas the presence of a large excess of pyridine leads to the cleavage of the oxo bridges between the copper atoms.[3,4] An excess of pyridine also hinders the formation of intramolecular associates. In additions, the formation of intramolecular associates through interactions between the coordination spheres of Cu^{II} is sterically hindered for the first members of the series of the complexes under consideration.

From the above reasoning, we synthesized and studied the chelate copper(II) complexes with salicylidene hydrazones of monocarboxylic acids. The series of Cu^{II} compounds involved derivatives of pentanoic and octanoic acids and a complex based on cyclohexanecarboxylic acid. It appeared that the EPR spectra of liquid solutions of the above-mentioned complexes have an isotropic signal consisting of four hyperfine lines with the parameters $g = 2.106—2.107$ and $a_{Cu} = (77.5—78.5) \cdot 10^{-4}$ cm^{-1}, which is typical of mononuclear copper(II) complexes, regardless of the nature and the length of the aliphatic fragment. Hence it follows that dimeric structures involving phenoxide bridges cannot be formed.

To elucidate the question of whether stacking interactions between the pyridine molecules can serve as a channel of exchange interactions between the paramagnetic centers, we studied the effect of the solvent on the parameters of the EPR spectra. In addition to pyridine, we used morpholine as the solvent whose molecules, like Py molecules, can form a coordination bond through the lone electron pair of the N atom. However, morpholine molecules, unlike Py molecules, cannot be involved in staking interactions due to the aliphatic nature of the heterocycle. It was found that the EPR spectra of morpholine adducts for the complexes with $n = 3$ and 4 have a seven-line hyperfine signal with the parameters $g = 2.106$, $a_{Cu} = 42.3 \cdot 10^{-4}$, and $40.9 \cdot 10^{-4}$ cm^{-1}, respectively, regardless of the nature of the carbonyl fragment of acyldihydrazone. This indicates that exchange interactions are retained on going from pyridine to morpholine. An insignificant decrease in the hyperfine coupling constants compared to those in the spectra of the Py complexes may be associated with a change in the mode of bonding of the Cu atom with the terminal ligand because morpholine, unlike pyridine, cannot be involved in π-dative interaction with the d orbitals of the central copper(II) atom.[17]

Stacking interactions between the pseudoaromatic systems of the chelate rings have been found previously[16] in the X-ray diffraction study of the crystal structures of the copper complexes with salicylidene hydrazones of aryloxycarboxylic acids. The crystal structure of the $[Cu_2L(C_5H_5N)_2(MeOH)_2]$ complex prepared based on compound **3**.3[11] completely excludes such interaction. In addition, as mentioned above, the conditions under which the spectra were recorded hinder the formation of intermolecular associates in solutions.

Therefore, the polymethylene chain is the only possible channel of interactions between the Cu^{II} atoms in the binuclear complexes with acyldihydrazones. This suggestion is supported by the fact that this interaction depends strongly on the length of the aliphatic bridge. For complexes based on acyldihydrazones of acetylacetone or salicylaldehyde, the exchange is observed only at $n \leq 4$. Apparently, a decrease in the critical length of the polymethylene chain to three units on introduction of substituents into the salicylidene fragment is associated with the spin-density withdraw from the coordination polyhedron through the σ-bonds (the negative inductive effect) or due to conjugation (the negative mesomeric effect).

The energies of exchange interactions in the complexes under study can be theoretically evaluated based on the general concepts of the EPR theory, which is well elaborated for organic biradicals.[18] According to this theory, the Hamiltonian for two electron spins S_1 and S_2 involved in coupling with the nuclear spins I_1 and I_2 can be written as follows:

$$\mathbf{H} = g\beta H(S_{1z} + S_{2z}) + A(S_{1z}I_{1z} + S_{2z}I_{2z}) - 2JS_1S_2 + S_1DS_2.$$

The first term in this equation accounts for the Zeeman interactions of electron spins with the external magnetic field, the second term describes the hyperfine coupling between electron spins and nuclear spins, the third term corresponds to intramolecular exchange interactions between electron spins, and the fourth term accounts for magnetic dipole-dipole interactions between unpaired electrons. Since the energy of the dipole-dipole interaction is inversely proportional to the cube of the distance between the unpaired electrons, it can be ignored. Moreover, dipole-dipole interactions generally affect the EPR spectral parameters of polycrystalline specimens, but are insignificant in studies of liquid solutions.[5]

In the case under consideration, the EPR spectrum is determined by the ratio between A and $-2J$. Three following situations are theoretically possible.

1. $A \gg |-2J|$. Each unpaired electron is localized on its own nucleus and the EPR spectrum has a four-line hyperfine signal with the normal constant, which is typical of mononuclear Cu^{II} complexes.

2. $A \ll |-2J|$. Each unpaired electron interacts with two nuclear spins and the EPR spectrum shows a seven-line hyperfine signal from two copper nuclei with half the constant.

3. $A \approx |-2J|$. The spectrum is more complicated and its interpretation requires special simulation.

In the case of the maximum values of the hyperfine coupling constants observed for the parallel orientation of the anisotropic spectra of solutions frozen at 77 K, the exchange integral $|-2J|$ should be $\gg 0.02$ cm^{-1}.

Two mechanisms of spin-density transfer through the system of σ-bonds of the aliphatic bridge are possible. One of them is associated with superconjugation. However, analysis of the data published in recent years demonstrated that the phenomena, which have previously been attributed to superconjugation effects, are presently interpreted in another way.[19] An alternative mechanism associated with spin polarization of the chain of σ-bonds[20] seems to be most plausible. The fact that the minimum length of the aliphatic bridge performing spin polarization decreases on going from liquid solutions to glasses (frozen solutions) is indicative of the important role of the dynamic effects in this mechanism.

In the present study, we did not consider the mechanism of spin exchange due to intramolecular collisions (encounters), which sometimes manifests itself as one of the mechanisms of spin exchange in long-chain ($(-CH_2-)_n$, where n = 8—10) biradicals (see the handbook,[18] p. 93). First, no such exchanges have been observed in coordination compounds of d-block elements. Second, we have found no exchange interactions in the previous study[21] of the monomeric copper(II) complexes with tridentate ligands based on tridentate hydrazones. Analogous data for the monomeric copper complexes were considered above. Apparently, if this exchange mechanism was realized in the copper complexes, it would be more efficient in monomeric complexes (due to the fact that diffusion in the latter compounds occurs more readily) than in bulkier dimers with larger molecular weights. Third, the mechanisms of spin exchange in biradicals and copper(II) dimers linked by polyethylene bridges are radically different. In biradicals, the mechanism of spin exchange through intramolecular collisions of two radicals is realized only if the length of the polymethylene bridge n = 8—10. This is quite evident because the longer the bridge the easier the encounter of two radicals. Finally, spin exchange in the copper(II) dimers under study is observed in the case of short polymethylene bridges. Depending on the nature of the chelate hydrazone ligand, this exchange ceases at n = 3 or n = 4 when the mechanism of intramolecular collisions cannot be realized.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32817).

References

1. P. Chaudhuri, K. Oder, and K. Wighardt, *J. Am. Chem. Soc.*, 1988, **110**, 3657.
2. K. Heinze, G. Huttner, and P. Schober, *Eur. J. Inorg. Chem.*, 1988, 183.
3. G. M. Larin, *Koord. Khim.,* 1992, **18**, 699 [*Russ. J. Coord. Chem.,* 1992, 598 (Engl. Transl.)].
4. G. M. Larin, B. B. Umarov, V. V. Minin, Yu. V. Rakitin, V. G. Yusupov, N. A. Parpiev, and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR,* 1988, **303**, 139 [*Dokl. Chem.*, 1988 (Engl. Transl.)].
5. Yu. V. Rakitin, G. M. Larin, and V. V. Minin, *Interpretatsiya spektrov EPR koordinatsionnykh soedinenii* [*Interpretation of EPR Spectra of Coordination Compounds*], Nauka, Moscow, 1993, 399 pp. (in Russian).
6. O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **97**, 837.
7. L. Dulong and J. S. Kim, *Angew. Chem., Int. Ed. Engl.*, 1990, **102**, 403.
8. K. A. Foster, D. R. Brown, M. D. Timken, D. G. Van Derveer, R. L. Belford, and E. K. Barefield, *J. Coord. Chem.*, 1988, **19**, 123.
9. V. F. Shul′gin, E. A. Sarnit, and G. M. Larin, *Koord. Khim.,* 1998, **24**, 222 [*Russ. J. Coord. Chem.,* 1998, **24**, 207 (Engl. Transl.)].
10. G. M. Larin, V. F. Schul′gin, and E. A. Sarnit, *Mendeleev Commun.*, 1999, 129.
11. G. M. Larin, V. F. Shul′gin, and E. A. Sarnit, *Zh. Neorg. Khim.,* 2000, **45**, 1007 [*Russ. J. Inorg. Chem.*, 2000, **45**, 909 (Engl. Transl.)].
12. T. D. Smith and I. R. Pilbrow, *Coord. Chem. Rev.*, 1974, **13**, 173.
13. Yu. V. Rakitin, *Koord. Khim.,* 1981, **7**, 1311 [*Sov. J. Coord. Chem.,* 1981, **7** (Engl. Transl.)].
14. M. E. Barr, P. H. Smith, W. E. Antholine, and B. J. Spencer, *J. Chem. Soc., Chem. Commun.*, 1993, 1652.
15. F. Neese, *Electronic Structure and Spectroscopy of Novel Copper Chromophores in Biology*, Dr. Sc. (Nat. Sci.), Konstanz, Univ. Germany, 1996, 257 pp.
16. V. F. Shul′gin, O. V. Konnik, K. V. Rabotyagov, V. M. Novotortsev, O. G. Ellert, V. M. Shcherbakova, I. L. Eremenko, S. E. Nefedov, and Yu. T. Struchkov, *Zh. Neorg. Khim.,* 1994, **39**, 1486 [*Russ. J. Inorg. Chem.*, 1994, **39** (Engl. Transl.)].
17. Yu. N. Kukushkin, *Khimiya koordinatsionnykh soedinenii* [*Chemistry of Coordination Compounds*], Vysshaya Shkola, Moscow, 1985, 144 pp. (in Russian).
18. V. N. Parmon, A. I. Kokorin, and G. M. Zhidomirov, *Stabil′nye biradikaly* [*Stable Biradicals*], Nauka, Moscow, 1980, 240 pp. (in Russian).
19. J. March, *Advanced Organic Chemistry. Reaction, Mechanism and Structure*, McGraw-Hill, New York—Toronto—London, 1985, **1**.
20. R. S. Drago, *Physical Methods in Inorganic Chemistry*, W. B. Saunders Co., New York—London, 1965, **1**.
21. G. M. Larin, Z. M. Musaev, O. F. Khodzhaev, S. D. Nasirdinov, V. G. Yusupov, and N. A. Parpiev, *Koord. Khim.,* 1983, **9**, 175 [*Sov. J. Coord. Chem.,* 1983, **9** (Engl. Transl.)].

Received July 1, 2000;
in revised form January 4, 2001