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EPR spectra and structures of dinuclear copper(II) complexes with acyldihydrazones of benzenedicarboxylic acids

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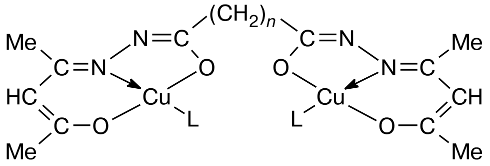
Spacer-armed dinuclear copper(II) complexes with condensation products of isophthalic and terephthalic acid dihydrazides with salicylaldehyde and 2-hydroxyacetophenone were synthesized and studied by EPR and X-ray diffraction. The compositions and structures of most of the complexes were determined by elemental analysis, thermogravimetric analysis, and IR spectroscopy. The structure of the copper(II) complex with acyldihydrazone of salicylaldehyde and 1,3-benzenedicarboxylic acid (H_4L) with the composition $[Cu_2L^1 \cdot 2morph \cdot MeOH]$ (morph is morpholine) was established by X-ray diffraction. The Cu^{II} atoms are spaced by 10.29 Å and are structurally nonequivalent. One copper cation has a square-planar coordination formed by donor atoms (2 N + O) of the doubly deprotonated acylhydrazine fragment and the N atom of the morpholine molecule. The second copper atom is additionally coordinated by a methanol molecule through the oxygen atom, so that this copper atom is in a tetragonal-pyramidal coordination with the oxygen atom in the axial position. The EPR spectra of liquid solutions of the complexes based on 1,4-benzenedicarboxylic acid acyldihydrazones and 1,3-benzenedicarboxylic acid bis(salicylidene)hydrazone at room temperature show a four-line hyperfine structure with the constant $a_{Cu} = 54.4—67.0 \cdot 10^{-4}$ cm^{-1} ($g = 2.105—2.147$), which is indicative of the independent behavior of the paramagnetic centers. The EPR spectrum of a solution of the complex based on isophthalic acid and 2-hydroxyacetophenone shows the seven-line hyperfine structure corresponding to two equivalent copper nuclei ($g = 2.11$, $a_{Cu} = 36.5 \cdot 10^{-4}$ cm^{-1}).

Key words: copper(II), dinuclear complexes, acylhydrazones, molecular and crystal structure, EPR, hyperfine structure, organic radicals.

The electron delocalization determines the electron density distribution in the molecule, which is responsible for the reactivity of these compounds, the character of metal—ligand bonds in d-metal coordination compounds with chelate ligands, the magnetic properties in the presence of unpaired electrons, *etc*. Earlier, it has been commonly accepted that the electron delocalization occurs only in the conjugated π system and cannot occur over σ bonds because the latter are orthogonal to each other (overlap integral is equal to zero). However, there is experimental evidence that the spin density of the unpaired electron of the central metal atom is located on atoms of chelate ligands coordinated to the metal atom by several σ bonds.

Earlier, it has been demonstrated[1,2] that the electron delocalization in d-metal chelate complexes, as opposed to organic compounds, can occur both in the conjugated π-bond system and in the σ-bond chain.

We have studied[1,3] dinuclear copper(II) complexes, in which two mononuclear copper(II) chelate complexes with tridentate bicyclic ligands are linked to each other by —$(CH_2)_n$ polymethylene bridges (spacers)



L is pyridine or piperidine

[†] Deceased.

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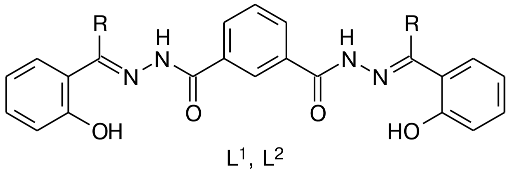
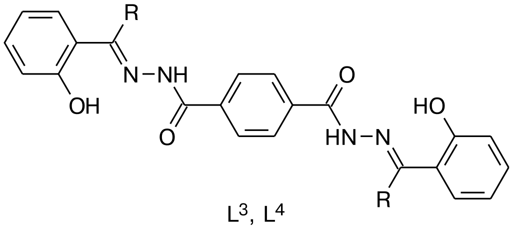
The EPR spectra of these complexes with $n = 1$, 2, or 4 in solution show the seven-line hyperfine structure corresponding to two equivalent copper atoms due to spin-spin exchange interactions between two copper(II) atoms. This exchange is attributed to the delocalization of the unpaired electrons of two copper atoms in the σ-bond chain of the polymethylene bridge. An increase in the chain length to $n = 8$ leads to the almost complete disappearance of exchange interactions.

Recent studies[4—7] of the factors influencing the electron delocalization in the σ-bond chain have shown that the delocalization depends mainly on the composition of the coordination sphere and the polymethylene chain length (largest distance between two copper atoms, which are linked *via* spin-spin exchange due to the electron delocalization in the σ-bond chain, is observed for $(CH_2)_4$ and is equal to 9.4 Å). We attributed the possibility of delocalization in the polymethylene chain to free rotation about σ bonds, due to which the p orbitals of the carbon atoms are no more orthogonal and can overlap with each other, thus providing the electron delocalization through the σ bonds.

In the present study, we investigated a new class of spacer-armed dinuclear copper(II) complexes, in which, in our opinion, the twisting about the hydrocarbon bridge cannot occur. For this purpose, we synthesized copper complexes with dihydrazide hydrazones of aromatic dicarboxylic acids and studied these complexes by the EPR method.



L^1, L^2



L^3, L^4

R = H (L^1, L^3), Me (L^2, L^4)

Experimental

Synthesis of ligands (general procedure). A carbonyl compound (0.022 mol) was added to a solution of dihydrazide of the corresponding acid (0.01 mol) in pyridine (50 mL), and the reaction mixture was refluxed for 8 h. After cooling, the product was precipitated with water, filtered off, washed with ethanol, and dried in air. The yield was 60—65%.

Synthesis of spacer-armed dinuclear copper(II) complexes (general procedure). Copper(II) acetate monohydrate (0.01 mol) was added to a solution of acyldihydrazone (L^1—L^4) (0.005 mol) in pyridine (30 mL), and the reaction mixture was magnetically stirred with heating for 5 h. Then the solution was filtered, and the target product was obtained by precipitation from the filtrate with water. The yield was 65—70%.

According to the results of elemental and thermal analysis, the compositions of the complexes correspond to the metal—ligand ratio of 2 : 1.

μ-[*N*,*N*′-Bis(2-hydroxybenzylidene)isophthaloyl(—4)dihydrazide]bis(pyridine)dicopper(II), solvate with pyridine and water, $[Cu_2L^1 \cdot 2Py] \cdot 2Py \cdot 2H_2O$ (1). Found (%): Cu, 14.79; N, 12.68. $C_{42}H_{38}Cu_2N_6O_6$. Calculated (%): Cu, 14.48; N, 12.77. IR, $\bar{\nu}_{max}/cm^{-1}$: ν(C=N) 1595, ν(N=C—O—) 1520.

μ-[*N*,*N*′-Bis(2-hydroxymethylbenzylidene)isophthaloyl(—4)dihydrazide]bis(pyridine)dicopper(II), solvate with pyridine and water, $[Cu_2L^2 \cdot 2Py] \cdot Py \cdot 2H_2O$ (2). Found (%): Cu, 15.24; N, 11.33. $C_{39}H_{37}Cu_2N_7O_6$. Calculated (%): Cu, 15.38; N, 11.86. IR, $\bar{\nu}_{max}/cm^{-1}$: ν(C=N) 1590, ν(N=C—O—) 1520.

μ-[*N*,*N*′-Bis(2-hydroxy-α-benzylidene)terephthaloyl(—4)dihydrazide]bis(pyridine)dicopper(II), solvate with water, $[Cu_2L^3 \cdot 2Py] \cdot 2H_2O$ (3). Found (%): Cu, 17.84; N, 11.64. $C_{32}H_{28}Cu_2N_6O_6$. Calculated (%): Cu, 17.66; N, 11.68. IR, $\bar{\nu}_{max}/cm^{-1}$: ν(C=N) 1590, ν(N=C—O—) 1515.

μ-[*N*,*N*′-Bis(2-hydroxy-α-methylbenzylidene)terephthaloyl(—4)dihydrazide]bis(pyridine)dicopper(II), solvate with pyridine and water, $[Cu_2L^4 \cdot 2Py] \cdot Py \cdot 4H_2O$ (4). Found (%): Cu, 14.70; N, 10.48. $C_{39}H_{41}Cu_2N_7O_8$. Calculated (%): Cu, 4.73; N, 11.37. IR, ν^{-}_{max}/cm^{-1}: ν(C=N) 1620, ν(N=C—O—) 1510.

μ-[*N*,*N*′-Bis(2-hydroxybenzylidene)isophthaloyl(—4)methanolbis(morpholine)dicopper(II), $[Cu_2L^1 \cdot 2morph \cdot MeOH]$ (5), was prepared by recrystallization of complex **1** from a 1 : 1 morpholine—methanol mixture.

Single-crystal X-ray diffraction study of compound **5**, $C_{31}H_{36}Cu_2N_6O_7$, the crystal with dimensions 0.38×0.25×0.15 mm, was performed at 293 K on an automated four-circle Enraf-Nonius CAD-4 diffractometer (MoKα radiation, $\lambda = 0.71073$ Å). A total of 5760 reflections were measured, of which 5714 reflections were symmetrically independent ($R_{int} = 0.0070$). The crystals are triclinic, $a = 9.814(2)$ Å, $b = 12.966(3)$ Å, $c = 13.411(3)$ Å, $\alpha = 106.40(2)°$, $\beta = 103.89(2)°$, $\gamma = 99.08(2)°$, space group $P\bar{1}$, $Z = 2$, $V = 1541.9(6)$ Å^3; M = 731.74, $d_{calc} = 1.576$ g cm^{-3}.

The structure of **5** was solved by direct methods and refined anisotropically by the full-matrix least-squares method using the SHELXS-97 and SHELXL-97 program packages.[8] The refinement was carried out with the use of 4079 reflections with $I > 4\sigma(I)$. The final *R* factors were $R = 0.0331$ and $R_w = 0.0937$; GOOF = 0.999. The maximum and minimum residual electron densities in the difference Fourier map were 0.726 and –0.370 e Å^{-3}, respectively. The complete X-ray diffraction data were deposited with the Cambridge Structural Database.

The copper content was calculated from the data from the titration with Trilon after the thermal decomposition of the weighted sample. Nitrogen was determined by the Dumas micromethod.[9,10] The thermogravimetric curves were recorded on a Paulik—Paulik—Erdey Q derivatograph in a static air atmosphere; the heating rate was 10 °C min^{-1}; samples were placed in a ceramic crucible without a lid; calcined aluminum oxide was used as the standard. The IR spectra (KBr pellets) were measured in the 4000—400 cm^{-1} region on a Nicollet Fourier-trans-form spectrophotometer. The X band EPR spectra were recorded on an ADANI PS 100.X instrument; the concentration of the complexes was $(1-5) \cdot 10^{-3}$ mol L^{-1}; a pyridine—toluene mixture (1 : 1, v/v) was used as the solvent.

The spectra were simulated with the use of the program package described in the monograph.[11] The EPR parameters were determined by comparing the experimental and theoretical spectra constructed by the summation of the line shapes of individual transitions centered at the resonance field (H_{res}). The line shapes were described by the sums of the Lorentz and Gaussian functions. According to the relaxation theory, the one-center contributions to the linewidths were specified by the equation

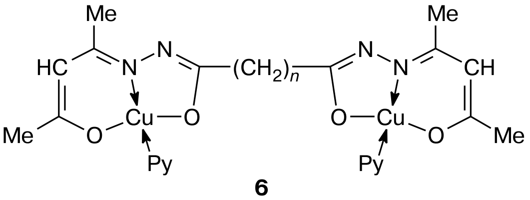
$$\Delta H_{res}(i) = \alpha + \beta m_I + \gamma m_I^2,$$

where m_I is the projection of the nuclear spin, and α, β, and γ are the linewidth parameters. Since the polymethylene-bridged complexes under study can be stereochemically nonrigid, we also took into account the contribution associated with intramolecular motions about the polymethylene bridge in the dinuclear complexes:

$$\Delta H_p(1,2) = \delta(m_1 - m_2)^2.$$

Results and Discussion

Recently, we have described three series of dinuclear copper(II) complexes synthesized starting from acyldihydrazones of β-diketones[1,3,5,11–13] (**6**), salicylaldehyde[14–16] (**7**), and alkylaromatic ketones[6,17–20] (**8**).



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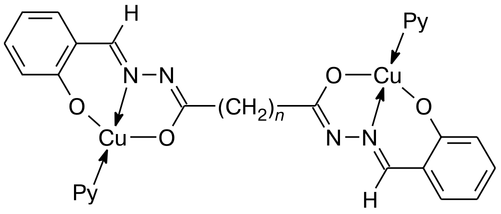

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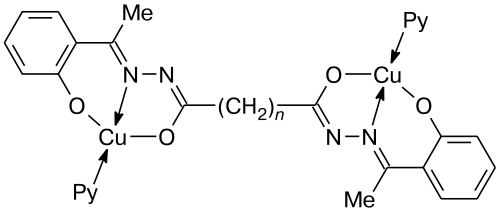

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The characteristic feature of the molecular structures of complexes **6**—**8** is that the coordination polyhedra in these complexes are linked by an aliphatic bridge (spacer). Hence, these compounds can be considered as spacer-armed dimers.

According to X-ray diffraction studies,[6,14,15,19] the distance between the copper atoms is as long as 8.2—9.2 Å for n = 3—4. Hence, the independent behavior of the paramagnetic centers would be expected. However, in spite of a large distance between the copper cations, the EPR spectra of spacer-armed complexes **5**—**7** containing short-length spacers (n = 1—4) show the following features characteristic of exchange dimers:[11,21,22]

1) signal of the forbidden transition ($\Delta M_S = 2$) at low field;

2) fine structure responsible for the splitting of the signal into two components in the EPR spectra of frozen solutions or magnetically dilute crystalline samples;

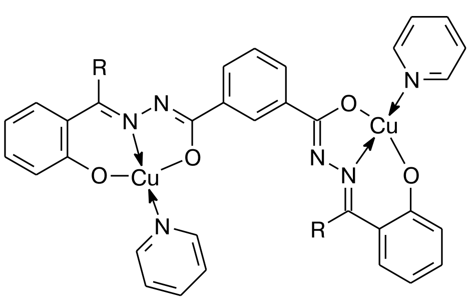
3) hyperfine structure consisting of seven lines with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 as a result of interactions between the unpaired electrons and two equivalent copper nuclei ($I = 3/2$).

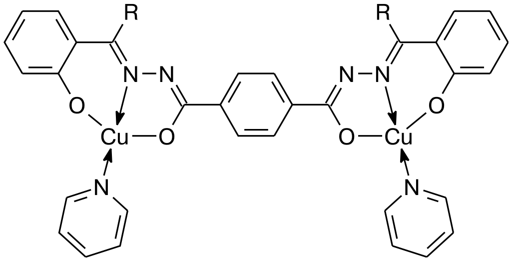
The latter feature of the EPR spectra of the spacer-armed complexes is observed for both frozen (77 K) and liquid solutions (~293 K). Earlier, the seven-line hyperfine structure corresponding to two equivalent copper nuclei has been observed in the EPR spectra of frozen solutions of spacer-armed complexes with an aromatic spacer.[23,24] The seven-line hyperfine structure was observed in a few EPR spectra of this type of dinuclear complexes in liquid solutions.[24]

An analysis of the IR spectra of coordination compounds **1**—**4** performed in the present study shows that the ligand is transformed into the quadruply deprotonated imidol form. Thus, a band, which is observed in the IR spectra of free acyldihydrazones in the 1650—1620 cm^{-1} region, disappears in the spectra of compounds **1**—**4**, and two new absorption bands with maxima at 1620—1590 cm^{-1} (stretching vibrations of the atoms of the >C=N—N=C< group) and 1520—1510 cm^{-1} (stretching vibrations of the —N=C—O— fragments)[25] are observed. The position of the C—O stretching band of the phenoxide group in the 1330—1370 cm^{-1} region is indicative of the absence of phenoxy bridges that link the copper atoms[26] to form the Cu_2O_2 dinuclear fragments.

According to the thermogravimetric analysis, the elimination of water solvent molecules that are present in complexes **1**—**4** proceeds at rather low temperature (40—100 °C) and is accompanied by noticeable thermal effects. The coordinated pyridine molecules are removed at higher temperature (140—280 °C). The process is endothermic and is characterized by a minimum in the DTA curve at 210—260 °C. At 300—360 °C, the thermooxidative destruction of acyldihydrazone starts, and this process is followed by the burning out of the organic residue. The decomposition is completed at 510—550 °C.

Based on the above-considered data, the following structures can be assigned to the complexes under consideration:





For all compounds, the copper cation would be expected to be additionally [4+1]- or [4+2]-coordinated by one or two pyridine molecules.

Earlier, the reactions of copper(II) acetate with dihydrazones of aliphatic dicarboxylic acids and salicylaldehyde or 2-hydroxyacetophenone have been shown to produce complexes, in which the Cu_2O_2 dinuclear fragments (see Ref. 25) are linked by aliphatic bridges with the involvement of the phenoxide oxygen atoms to form a polymeric chain.[27,28] The treatment of the polymers with excess pyridine leads to the cleavage of the phenoxide bridges and the formation of dinuclear complexes with an aliphatic spacer.[16,17] The reactions of copper(II) acetate with acyldihydrazones of benzenedicarboxylic acids in pyridine produce dinuclear complexes, in which the coordination polyhedra are linked by an aromatic spacer.

To unambiguously confirm the structures of the compounds under study, the crystal structure of the $[Cu_2L^1 \cdot 2morph \cdot MeOH]$ complex (**5**) was determined by X-ray diffraction. The X-ray diffraction study showed that compound **5** has a molecular structure. The overall view of the dinuclear molecule is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. The copper atoms are 0.29 Å apart and are structurally nonequivalent. The coordination environment of the Cu(2) atom can be described as a distorted square, whose vertices are occupied by the O(3), O(4), and N(4) atoms of the deprotonated hydrazone fragment and the nitrogen atom of the morpholine molecule. The Cu(1) atom is [4+1]-coordinated, and its nearest environment has a tetragonal-pyramidal geometry with a methanol molecule in the axial position. The Cu(1)O(1)O(2)N(1)N(5) bond system is virtually planar (deviations from the mean plane are less than 0.010 Å). The copper atom is shifted from the base of the pyramid by 0.027 Å toward the apical methanol molecule. The Cu(1)—O(1S) axial bond (2.567 Å) is substantially longer than the Cu(1)—O(1) and Cu(1)—O(2) bonds located in the equatorial plane

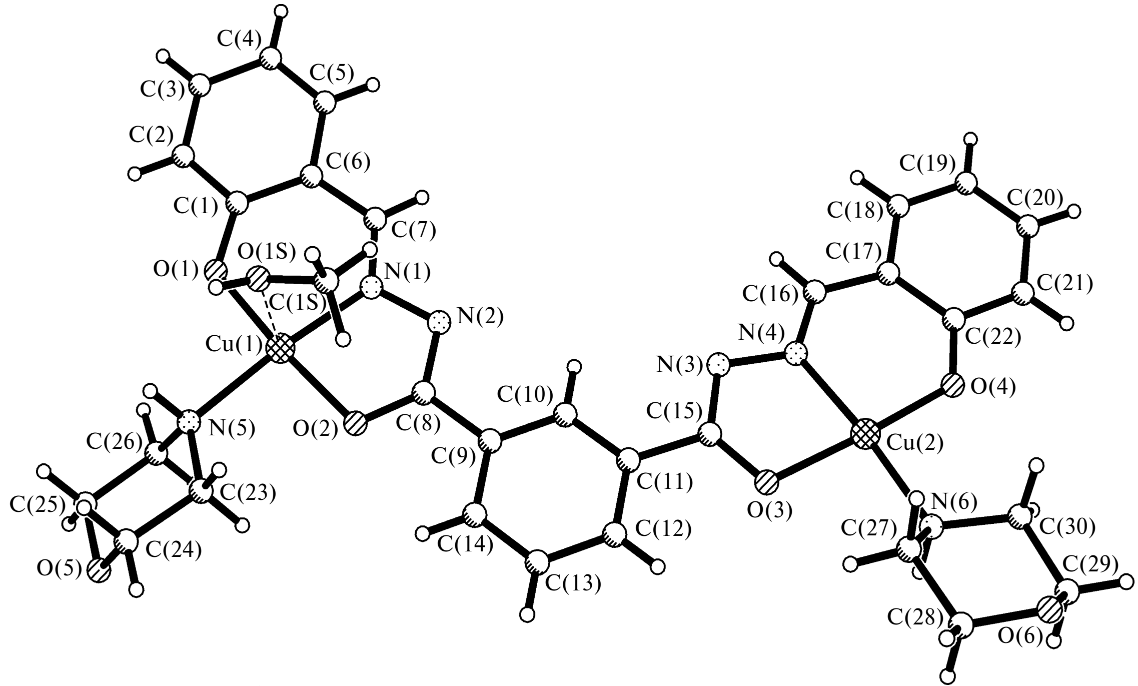


Fig. 1. Overall view of the $[Cu_2L^1 \cdot 2morph \cdot MeOH]$ molecule.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the [$Cu_2L^1 \cdot$ 2morph • MeOH] complex

Bond	*d*/Å	Angle	ω/deg
Cu(1)—O(1)	1.9143(19)	O(1)—Cu(1)—N(1)	93.99(9)
Cu(1)—N(1)	1.926(2)	O(1)—Cu(1)—O(2)	174.62(8)
Cu(1)—O(2)	1.9320(19)	N(1)—Cu(1)—O(2)	81.00(9)
Cu(1)—N(5)	2.022(2)	O(1)—Cu(1)—N(5)	90.85(9)
Cu(1)—O(1S)	2.567(2)	N(1)—Cu(1)—N(5)	175.01(9)
Cu(2)—O(4)	1.880(2)	O(2)—Cu(1)—N(5)	94.12(9)
Cu(2)—N(4)	1.911(2)	O(1)—Cu(1)—O(1S)	89.53(8)
Cu(2)—O(3)	1.939(2)	N(1)—Cu(1)—O(1S)	90.70(8)
Cu(2)—N(6)	2.019(2)	O(2)—Cu(1)—O(1S)	92.47(8)
O(1)—C(1)	1.325(3)	N(5)—Cu(1)—O(1S)	90.55(8)
O(2)—C(8)	1.284(3)	O(4)—Cu(2)—N(4)	93.91(10)
O(3)—C(15)	1.287(3)	O(4)—Cu(2)—O(3)	172.87(9)
O(4)—C(22)	1.304(3)	N(4)—Cu(2)—O(3)	80.93(9)
O(5)—C(25)	1.422(3)	O(4)—Cu(2)—N(6)	92.90(9)
O(5)—C(24)	1.424(4)	N(4)—Cu(2)—N(6)	172.87(10)
O(6)—C(29)	1.418(4)	O(3)—Cu(2)—N(6)	92.47(9)
O(6)—C(28)	1.418(4)	C(1)—O(1)—Cu(1)	126.20(17)
N(1)—C(7)	1.285(3)	C(8)—O(2)—Cu(1)	110.69(17)
N(1)—N(2)	1.389(3)	C(15)—O(3)—Cu(2)	110.33(17)
N(2)—C(8)	1.323(4)	C(22)—O(4)—Cu(2)	127.62(19)
N(3)—C(15)	1.317(4)	C(25)—O(5)—C(24)	109.7(2)
N(3)—N(4)	1.385(3)	C(29)—O(6)—C(28)	109.8(2)
N(4)—C(16)	1.303(4)	C(7)—N(1)—N(2)	117.6(2)
N(5)—C(23)	1.476(3)	C(7)—N(1)—Cu(1)	127.17(19)

Table 2. System of hydrogen bonds in the crystal structure of the [$Cu_2L^1 \cdot$ 2morph • MeOH] complex

Donor, (D—H)	*d*(D—H) /Å	Acceptor, (A)*	*d*(H—A) /Å	*d*(D...A) /Å	Angle DHA /deg
N(5)—H(5B)	0.910	O(1S)	2.270	3.068	146.26
O(1S)—H(1S)	0.820	O(1)	1.858	2.666	168.12

* The symmetry transformation for the acceptor: −*x* − 3, −*y* − 1, −*z* − 1.

(1.914 and 1.932 Å) respectively). The C(8)—O(2) (1.284 Å) and N(1)—N(2) (1.389 Å) bonds are substantially shorter than the corresponding single bonds, whereas the C(8)—N(2) (1.323 Å) and C(7)—N(1) (1.285 Å) bonds are somewhat longer than the typical double bonds, which may be indicative of a high degree of the double-bond delocalization in the chelate rings. The bond lengths and bond angles in the organic radicals of hydrazone and the morpholine molecule have typical values.[29]

An interesting feature of the crystal structure of compound **5** is that the benzene rings and the chelate rings of the adjacent molecules, whose planes are ~3.50 Å apart, are linked by nonbonded π—π interactions (Fig. 2). The interacting fragments are substantially shifted with respect to each other, the Cu(1) atoms form short contacts with the N(1b) (3.623 Å) and N(2b) (3.280 Å) atoms, and the Cu(2) atoms are in close proximity to the N(3a) (3.416 Å) and N(4a) (3.992 Å) atoms. The hydrogen bonds with the involvement of the methanol and morpholine molecules (Table 2) contribute to stabilization of the crystal structure.

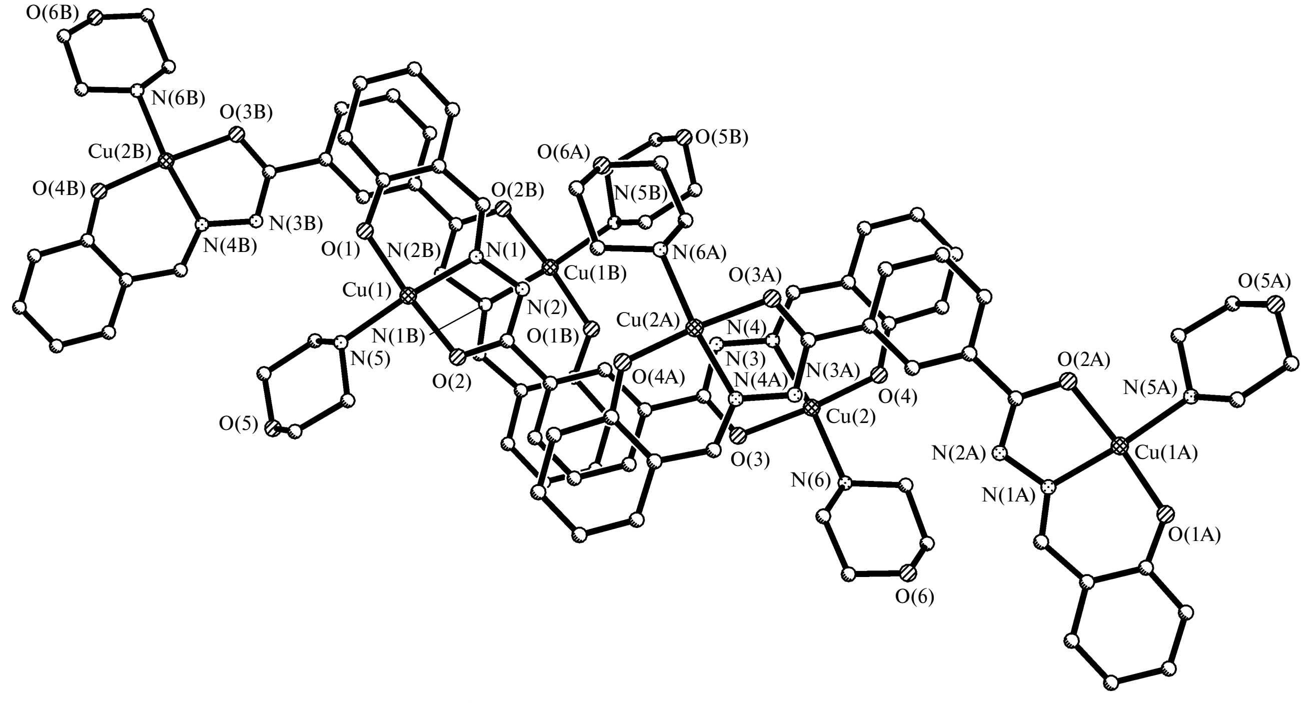


Fig. 2. Fragment of the crystal structure of [$Cu_2L^1 \cdot$ 2morph • MeOH]. The symmetry transformation for the molecule **A** is (1 − *x*, −*y*, −*z*); for the molecule **B**, (−1 − *x*, −1 − *y*, −1 − *z*). The methanol molecules are omitted.

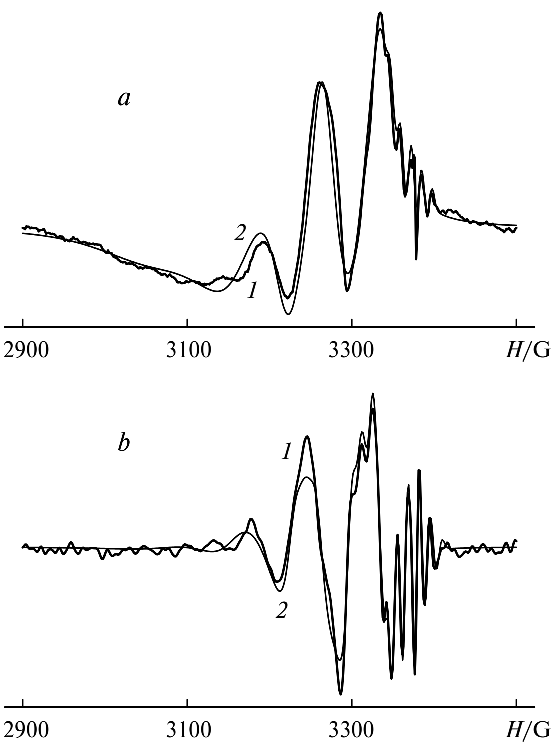


Fig. 3. Experimental (*1*) and theoretical (*2*) EPR spectra of a liquid solution of complex **2**: *a*, the first derivative; *b*, the second derivative.

In the EPR spectra of liquid solutions of complexes **1**, **3**, and **4**, the hyperfine structure consisting of four lines with equal intensities and the constant of about 54—65 G (Fig. 3) is resolved. The observed g factors (2.11—2.15) are typical of the oxygen-nitrogen environment of the central atom (Table 3). The spectral patterns are indicative of the complete absence of spin-spin exchange interactions between the unpaired electrons. The high-field region of the spectra of these compounds shows an additional five-line signal with $g = 2.008$ and $a_{(\mathrm{N})}$ = G corresponding to the organic radical, whose unpaired electron is delocalized on two equivalent nitrogen atoms (as was demonstrated by theoretical calculations). Interactions between the spin of the unpaired electron and the nuclei ($I_{\mathrm{N}} = 1$) of two nitrogen atoms give rise to the hyperfine structure consisting of five lines with an intensity ratio of 1 : 2 : 3 : 2 : 1. This is particularly clearly seen in the second derivative of the EPR spectrum (see Fig. 3, *b*). The EPR spectra of stable organic radicals in copper complexes with chelate ligands were observed many times, and several explanations were given for their appearance.[30—34] The intensity of the EPR spectra of radicals strongly depends, first, on the *meta* or *para* arrangement of the substituents and, second, on the nature of the substituents R.

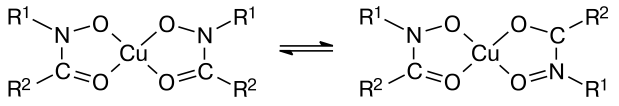
Table 3. EPR parameters for dinuclear complexes **1—4**

Compound	g	$a_{\mathrm{Cu}} \cdot 10^4$ /cm^{-1}	Linewidth parameters (G)				σ* (%)
			α	β	γ	δ	
1	2.116	65.5	37.1	20.3	7.5	—	3.3
2	2.111	66.5	33.2	21.2	11.5	—	5.2
3	2.109	36.5	39.5	12.4	−2.0	7.8	2.9
4	2.147	54.1	50.7	15.8	2.7	—	3.1

* The deviation of the theoretical spectrum from the experimental spectrum (R · 100).

This effect is generally attributed to the reversible charge transfer from the ligand to the metal atom accompanied by the partial reduction of the copper(II) cation, which appears as a result of conformational changes in the molecule or other reversible redox reactions. For example, the publications[30,31] were even titled "Transfer of Spin Density from Unpaired Electron to Eliminated Ligands." In these studies, it was stated that pH-dependent reversible redox reactions proceed in Ni$^{\mathrm{II}}$, Cu$^{\mathrm{II}}$, and Pd$^{\mathrm{II}}$ complexes with dithiozonates $[\mathrm{Ph_2N_4CSH}]^-$. These reactions involve the electron transfer from the ligand to the metal atoms as pH increases, the elimination of the ligand from the metal atom giving rise to a stable radical, and the reduction of the metal atoms to the oxidation state +1. The radical gives the EPR spectrum with the hyperfine structure corresponding to four equivalent nitrogen atoms.

It should be noted that the *cis—trans* isomerization is observed for copper(II) complexes with hydroxamic acids.[32,33]



A **B**

When coordinated to metals, hydroxamic acids behave as monobasic bidentate ligands and form four-coordinate complexes with the copper(II) atom with 2 : 1 the composition. In these complexes, the coordination sphere of copper is formed solely by oxygen atoms. However, the geometry of two chelate ligands with respect to each other taking into account the ligands, which are not directly bound to the copper atom, can be either *cis* or *trans*. In the former case, the nitrogen (or carbon) atoms involved in the second coordination sphere of two chelate ligands are on the same side with respect to the copper atom (form **A**). In the latter case, these atoms are in the N—Cu—N line (form **B**).

Actually, the EPR spectra of these compounds show signals corresponding to two different copper(II) complexes and a signal of the radical. The copper(II) atom in the square-planar environment with the coordination number 4 has a very stable configuration, and, consequently, the *cis—trans* isomerization is seemingly impossible for these complexes.

However, based on the results of quantum chemical calculations, the following sequence of molecular orbitals (MOs) in the copper(II) complex with $R^1 = R^2 = H$ was determined: $d^2{}_{xz}$, $d^2{}_{yz}$, $d^2{}_{z^2}$, $d^2{}_{xy}$, $\psi(L^1)^2$, $\psi(L^2)^2$, $d^1{}_{x^2-y^2}$, where $\psi(L^1)^2$ and $\psi(L^2)^2$ are occupied MOs located primarily on the ligands. A weakening of at least one metal—ligand bond leads to a lowering of the energy of the $|d_{x^2-y^2}>$ orbital due to which the $\psi(L^{1(2)})$ orbital can become the highest half-filled MO. In this case, the central Cu^{II} atom is reduced to Cu^I, and the weakly coordinated ligand loses an electron and is transformed into the radical. Since Cu^I can have the coordination number 2, one Cu—O bond is cleaved, which is accompanied by the twisting about another Cu—O bond by 180° and the formation of a new Cu—O bond. Copper(I) is oxidized to copper(II), resulting in the transformation from the *cis* configuration to the *trans* configuration or *vice versa*.[34]

The question as to which conformational process proceeds in the copper(II) complexes with acylhydrazones of benzoyldicarboxylic acids remains open.

The high-field component of the hyperfine structure of the copper atom is additionally split into a triplet with an intensity ratio of 1 : 1 : 1 (see Fig. 3, *b*), which is assigned to an interaction between the spin of the unpaired electron and the nuclear spin of one nitrogen atom. It was demonstrated[1,3,11] that an additional hyperfine structure in spacer-armed dinuclear complexes of Cu^{II} having the N_2O_2 coordination sphere is observed only for one nitrogen atom belonging to the tridentate chelate ligand, and is absent for the second nitrogen atom, which forms a donor-acceptor bond with the copper atom (pyridine, piperidine, ammonia, *etc.*).

The unusual result was obtained for compound **2**. The EPR spectrum of complex **2** shows the seven-line hyperfine structure with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 and the constant of 37.6 G (Fig. 4). Since this spectral pattern cannot be a consequence of an additional hyperfine interaction with the nitrogen nuclei (additional hyperfine coupling constant is approximately equal to 15 G), this spectrum was interpreted as the result of exchange interactions between the unpaired electrons and two equivalent copper nuclei.

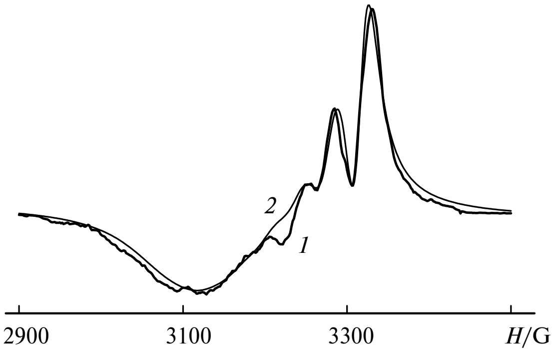


Fig. 4. Experimental (*1*) and theoretical (*2*) EPR spectra of a liquid solution of complex **3**.

The observation of the seven-line hyperfine structure corresponding to two equivalent copper nuclei is possible due to formation of exchange channels in the case of π-stacking interactions between the planar chelate rings of the monomeric complexes in crystalline samples at helium temperatures[35] and in concentrated solutions frozen at 110 K. A decrease in the concentration leads to destruction of intermolecular associates and the appearance of the hyperfine structure consisting of four lines with equal intensities in the EPR spectrum.[36] Since the spectral pattern of complex **2** remains unchanged upon dilution, the π—π interactions observed in the crystal structure (see Fig. 2) can be excluded from the factors facilitating the formation of intermolecular superexchange channels.

Due to a low concentration of the complex and a large excess of pyridine, the formation of exchange channels as a result of formation of the Cu_2O_2 dinuclear fragments involving the phenoxy bridges is highly improbable. Generally, such complexes are characterized by a short metal—metal distance (<3 Å) and strong antiferromagnetic interactions ($-2J > 100$ cm^{-1}), which makes it impossible to observe EPR spectra in solution.

Therefore, the superexchange through the aromatic spacer within a single molecule is the most probable mechanism of exchange interactions between the copper atoms in complex **2**. Exchange interactions through an aromatic spacer were observed in some nitrogen-containing biradicals. In the latter case, the EPR spectra were interpreted in the context of the mechanism of the spin density transfer through the *para*-substituted benzene ring resulting from the conjugation effects.[5]

The EPR spectra of chelate compounds based on acyldihydrazones of 1,4-benzenedicarboxylic acid show that this mechanism is inefficient for spacer-armed dinuclear copper(II) complexes. Presumably, the exchange interactions in complex **2** occur through the σ-bond system of the benzene ring due to the spin polarization effects rather than through the aromatic system of the spacer. Apparently, the positive inductive effect of the Me group is an important factor facilitating the exchange interactions through this channel in complex **2**. The replacement of the Me group with the hydrogen atom (complex **1**) decreases the electron density accumulation in the coordination polyhedron with the result that the superexchange channel through the σ-bond system becomes inefficient.

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