Spacered dinuclear copper(II) complexes with acyldihydrazones of aliphatic dicarboxylic acids and 2-hydroxy-5-nitroacetophenone

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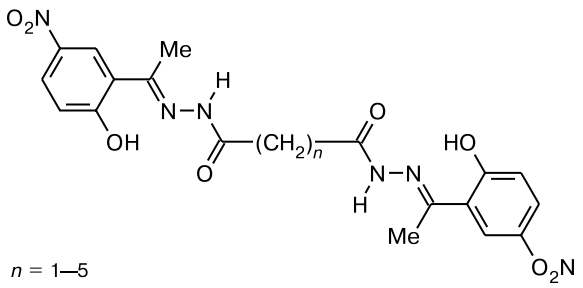
Dinuclear copper(II) complexes with acyldihydrazones of 2-hydroxy-5-nitroacetophenone (H_4L) of the composition $Cu_2(Py)_xL \cdot m$EtOH were synthesized and characterized. In these complexes, the coordination polyhedra of the copper atoms are linked to each other by a polymethylene chain of different lengths, from one to five monomer units. The structure of the $[Cu_2L \cdot 4Mrf]$ complex (Mrf is morpholine) based on acyldihydrazone of malonic acid was established by X-ray diffraction. The copper(II) atoms in this complex are [4+1]-coordinated and are spaced by 6.94 Å. At room temperature, the signal in the ESR spectra of solutions of the complexes based on acyldihydrazones of malonic, succinic, glutaric, and adipic acids has a seven-line hyperfine structure with the constant of $(35.3—38.8) \cdot 10^{-4}$ cm^{-1} ($g = 2.109—2.112$) due to exchange interactions between unpaired electrons and two equivalent copper nuclei. An increase in the length of the polymethylene chain to five monomer units hinders exchange interactions, and the ESR signal of the complex based on acyldihydrazone of pimelic acid has a four-line hyperfine structure with $a_{Cu} = 72.7 \cdot 10^{-4}$ cm^{-1} typical of mononuclear copper(II) complexes.

Key words: 2-hydroxy-5-nitroacetophenone, acyldihydrazones, dinuclear copper(II) complexes, electron paramagnetic resonance, superexchange.

Studies of dinuclear copper(II) complexes based on acyldihydrazones of aliphatic dicarboxylic acids[1—8] have demonstrated that an aliphatic spacer containing from one to four methylene groups can provide spin-spin exchange interactions between paramagnetic centers. As a result, the ESR signals of liquid solutions of these complexes show a seven-line hyperfine structure with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 and have half the hyperfine coupling constant ($A_{Cu} \approx 40$ G). The theoretical analysis demonstrated[8,9] that the exchange parameter $|-2J| \gg 0.02$ cm^{-1} is a condition sufficient for the observation of this spectrum.

Recently, we have described[10] a new type of spacered dinuclear copper(II) complexes containing acyldihydrazones of aliphatic dicarboxylic acids and 2-hydroxyacetophenone as bidentate ligands. The introduction of substituents with a positive mesomeric effect (5-Cl or 5-Me) into the benzene ring and the use of acyldihydrazones of 2-hydroxypropiophenone were demonstrated[11,12] to have no effect on the spin density transfer through an aliphatic bridge.

It was of interest to reveal the effect of electron-withdrawing substituents on this interaction. For this purpose, we synthesized and studied coordination copper(II) compounds with acyldihydrazones of aliphatic dicarboxylic acids ($n = 1—5$) and 2-hydroxy-5-nitroacetophenone.



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Experimental

Coordination copper(II) compounds were synthesized according to a procedure developed earlier[10] for the synthesis of complexes with acyldihydrazones of 2-hydroxyacetophenone. Elemental analysis and thermal analysis demonstrated that the composition of the complexes corresponds to the formula $Cu_2(Py)_xL \cdot m$EtOH (H_4L^n is the corresponding acyldihydrazone); the compound number is equal to the number of the monomer units in the polymethylene chain.

μ-[*N*,*N*′-Bis(2-hydroxy-5-nitromethylbenzylidene)malonodihydrazinato(−4)]pyridinedicopper(+2), solvate with ethanol, $Cu_2(Py)_3L^1 \cdot 2EtOH$ (1). Found (%): C, 50.10; H, 4.87. $C_{38}H_{41}Cu_2N_9O_{10}$. Calculated (%): C, 50.11; H, 4.51. IR, ν/cm^{-1}: 1600 (C=N); 1525 (N=C—O—).

μ-[*N*,*N*′-Bis(2-hydroxy-5-nitromethylbenzylidene)succinodihydrazinato(−4)]pyridinedicopper(+2), $Cu_2(Py)_3L^2$ (2). Found (%): C, 50.34; H, 4.71. $C_{35}H_{31}Cu_2N_9O_8$. Calculated (%): C, 50.48; H, 3.75. IR, ν/cm^{-1}: 1595 (C=N); 1525 (N=C—O—).

μ-[*N*,*N*′-Bis(2-hydroxy-5-nitromethylbenzylidene)glutarodihydrazinato(−4)]pyridinedicopper(+2), solvate with ethanol, $Cu_2(Py)_2L^3 \cdot 3EtOH$ (3). Found (%): C, 49.85; H, 4.95. $C_{37}H_{46}Cu_2N_8O_{11}$. Calculated (%): C, 49.06; H, 5.08. IR, ν/cm^{-1}: 1600 (C=N); 1520 (N=C—O—).

μ-[*N*,*N*′-Bis(2-hydroxy-5-nitromethylbenzylidene)adipodihydrazinato(−4)]pyridinedicopper(+2), $Cu_2(Py)_2L^4$ (4). Found (%): C, 50.10; H, 4.36. $C_{32}H_{30}Cu_2N_8O_8$. Calculated (%): C, 49.17; H, 3.89. IR, ν/cm^{-1}: 1605 (C=N); 1525 (N=C—O—).

μ-[*N*,*N*′-Bis(2-hydroxy-5-nitromethylbenzylidene)pimelinodihydrazinato(−4)]pyridinedicopper(+2), solvate with ethanol, $Cu_2(Py)_2L^5 \cdot 3EtOH$ (5). Found (%): C, 50.19; H, 4.99. $C_{39}H_{50}Cu_2N_8O_{11}$. Calculated (%): C, 50.16; H, 5.35. IR, ν/cm^{-1}: 1600 (C=N); 1525 (N=C—O—).

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 were measured in the 4000—400 cm^{-1} range on a Nicollet Fourier-transform spectrophotometer in KBr pellets. The X band ESR spectra were recorded on an ADANI PS 100.X instrument; the concentration of the complexes was $(1—5) \cdot 10^{-3}$ mol L^{-1}. Since the complexes are virtually insoluble in pyridine and pyridine-based mixed solvents, we used a mixture of morpholine and toluene (1 : 5, v/v). The spectra were simulated using a program package described in the monograph.[13] The spin-Hamiltonian 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 line widths 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 line-width parameters. Since complexes with polymethylene bridges can be stereochemically nonrigid, we also took into account the contribution

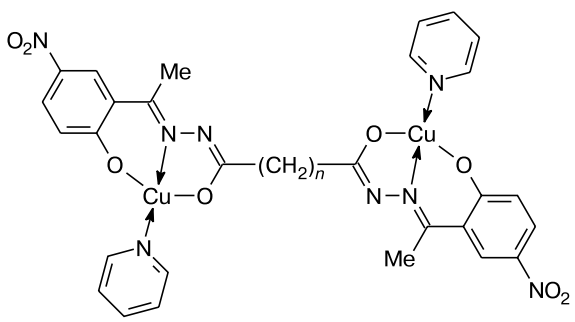
$$\Delta H_{res}(1, 2) = \delta(m_1 - m_2)^2$$

associated with intramolecular motions of one copper(II) complex (m_1) relative to another one (m_2) in the dinuclear complex.

Single-crystal X-ray diffraction study of $[Cu_2L^1 \cdot 4Mrf]$ (Mrf is morpholine) (6) was performed at room temperature using a crystal of linear dimensions 0.19×0.29×0.31 mm, which was grown by recrystallization of complex **1** from morpholine, on an automated four-circle Enraf—Nonius CAD-4 diffractometer (Cu-Kα radiation, λ = 1.54178 Å, the scan rate ratio $2\theta/\omega = 1.2$, $\theta_{max} = 65°$, the segment of the sphere $0 \le h \le 14$, $0 \le k \le 17$, $-26 \le l \le 24$). A total of 4441 reflections were collected, of which 3380 reflections were symmetrically independent ($R_{int} = 0.023$). The crystals are monoclinic, $a = 12.317(2)$ Å, $b = 14.680(3)$ Å, $c = 22.193(4)$ Å, β = 91.26(2)°, $V = 4012(1)$ Å^3, M = 953.96, $Z = 4$, $d_{calc} = 1.58$ g cm^{-3}, μ = 19.62 cm^{-1}, $F(000) = 1920.0$, space group $C2/c$ (No. 15). The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms using the CRYSTALS program package.[14] The refinement was performed based on 2098 reflections with $I > 3\sigma(I)$ (267 parameters were refined, 7.9 reflections per parameter). About 50% hydrogen atoms were located in difference electron density maps. The other H atoms were positioned geometrically. All hydrogen atoms were refined isotropically. The Chebyshev weighting scheme[15] with the parameters 1.83, −0.72, 0.61, −0.62, and −0.55 was used in the refinement. The final R factors were as follows: $R = 0.063$ and $R_w = 0.068$, GOF 1.087. The positive and negative residual electron densities in the difference Fourier map were 0.49 and −0.64 e Å^{-3}, respectively. The absorption correction was applied using the azimuthal scan method.[16] The complete X-ray structural data for compound **6** were deposited with the Cambridge Structural Database (CCDC 271 501).

Results and Discussion

Elemental analysis and the thermogravimetric data[8,10,11] provide evidence that the reactions of acyldihydrazones of 2-hydroxy-5-nitroacetophenone with copper(II) acetate in the presence of pyridine produce dinuclear complexes, in which the coordination polyhedra of the copper(II) atoms are linked to each other by an aliphatic spacer.



n = 1—5

The IR spectra of coordination compounds **1**—**5** are indicative of the transformation of the ligands into the fourfold deprotonated imidol form. In the spectra of the complexes, the amide I band, which is observed in the IR spectra of free acyldihydrazones at ~1650 cm^{-1}, is absent, and two new bands with absorption maxima at 1595—1600 cm^{-1} (stretching vibrations of the >C=N—N=C< group) and 1530—1520 cm^{-1} (stretching vibrations of the carbon—oxygen bond of the —N=C—O— fragment) appear.

The TGA data showed that the ethanol molecules involved in complexes **1** and **3** are eliminated at low temperature (30—100 °C), which is accompanied by a weak endothermic effect with a minimum in the DTA curve at 70 °C. Ethanol involved in compound **5** is removed at higher temperature (100—140 °C, the endothermic effect with a minimum in the DTA curve at 140 °C). Elimination of the pyridine molecules from complexes **1**—**5** starts at 200—250 °C, is accompanied by an endotherm with a minimum in the DTA curve at 250—270 °C, and is completed at 270—300 °C. Explosive decomposition of the compound accompanied by a throw out of the substance from the crucible was observed immediately after desolvation of the complex.

To reliably confirm the structures of these compounds, the crystal structure of complex **6**, which was prepared by recrystallization of compound **1** from morpholine, was studied by X-ray diffraction. Compound **6** has a dinuclear structure, in which two mononuclear subunits are related by a twofold axis. The overall view of molecule **6** is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 1. The copper atom is [4+1]-coordinated and has a slightly distorted square-pyramidal geometry of the

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **6**

Bond	*d*/Å	Angle	ω/deg
Cu(1)—O(1)	1.867(4)	O(1)—Cu(1)—O(2)	174.74(17)
Cu(1)—O(2)	1.912(3)	O(1)—Cu(1)—N(1)	94.02(16)
Cu(1)—N(1)	1.943(4)	O(2)—Cu(1)—N(1)	82.43(15)
Cu(1)—N(4)	2.037(4)	O(1)—Cu(1)—N(4)	93.55(18)
Cu(1)—N(5)	2.550(5)	O(2)—Cu(1)—N(4)	89.08(17)
O(1)—C(1)	1.304(6)	N(1)—Cu(1)—N(4)	165.3(2)
O(2)—C(8)	1.290(6)	O(1)—Cu(1)—N(5)	91.84(19)
N(1)—N(2)	1.404(6)	O(2)—Cu(1)—N(5)	92.23(16)
N(2)—C(8)	1.303(6)	N(1)—Cu(1)—N(5)	93.05(17)
C(8)—C(10)	1.507(6)	N(4)—Cu(1)—N(5)	99.28(18)
		Cu(1)—O(1)—C(1)	126.7(3)
		Cu(1)—O(2)—C(8)	109.6(3)
		Cu(1)—N(1)—N(2)	112.6(3)
		Cu(1)—N(1)—C(7)	129.4(3)

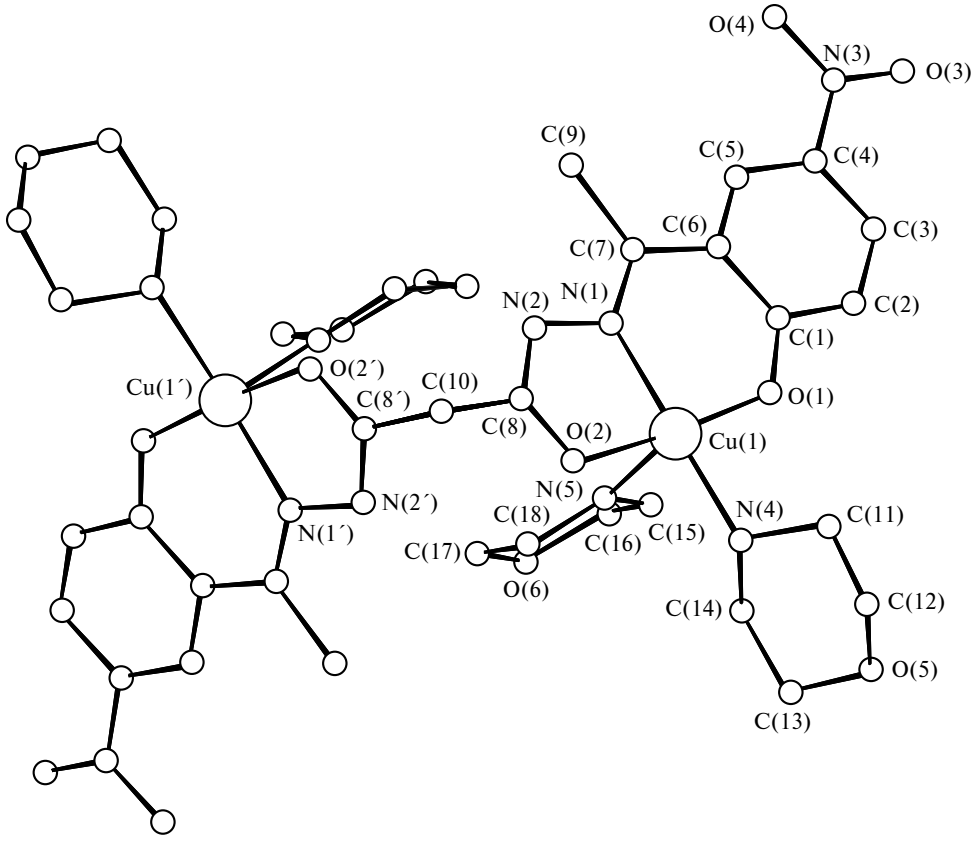


Fig. 1. Overall view of molecule **6** (H atoms are omitted). The primed atoms are related to the unprimed atoms by a twofold axis.

coordination polyhedron (the deviations of the bond angles at the Cu(1) atom from the ideal values are as large as 14.7(2)°). The base of the pyramid is formed by the O(1), O(2), and N(1) atoms of the bidentate acyldihydrazone ligand and the N(4) atom of the strongly coordinated morpholine molecule. The N(5) atom of the second weakly coordinated morpholine molecule occupies the apical position. The Cu(1) atom is shifted by 0.141 Å from the basal plane toward the apical morpholine ligand. The apical Cu(1)—N(5) bond is substantially elongated (2.550(5) Å) compared to the equatorial Cu(1)—N(1) (1.943(4) Å) and Cu(1)—N(4) (2.037(4) Å) bonds. The tricyclic system Cu(1)O(1)O(2)N(1)N(2)C(1)—C(8) is planar (within 0.044 Å). The nitro group N(3)O(3)O(4) is virtually coplanar with this system; the corresponding dihedral angle is 4.9°. The dihedral angle between the symmetrically related Cu(1)O(1)O(2)N(1)N(2)C(1)—C(8) and Cu(1′)O(1′)O(2′)N(1′)N(2′)C(1′)—C(8′) fragments is 76.0°. The distance between the copper atoms in complex **6** is 6.94 Å.

An interesting feature of the crystal structure of compound **6** is that the 5-nitro-substituted benzene rings of the ligand and the chelate rings of the adjacent molecule, which are located at a distance of 3.5 Å, form stacks *via* nonbonded π—π stacking interactions (Fig. 2). This confirms the earlier assumption[7] of the pseudoaromatic nature of the conjugated chelate rings in this type of complexes.

The ESR spectra of dinuclear copper(II) compounds, including some spacered complexes,[17,18] generally have three characteristic features: a signal corresponding to a forbidden transition ($\Delta M_S = 2$) at low field ($g \approx 4$), a hyperfine structure due to dipole-dipole and exchange interactions between the copper cations, resulting in splitting of absorption bands by 2 D, and a seven-line hyperfine structure with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 due to interactions between the unpaired electrons and two equivalent copper nuclei ($I = 3/2$).

The signal of the forbidden transition is generally observed in the ESR spectra of polycrystalline samples, and its intensity is proportional to the exchange interaction parameter ($-2J$). The ESR spectra of polycrystalline samples of complexes **1**—**4** show an intense virtually symmetrical signal with $g \approx 2.1$. The ESR spectrum of complex **5** clearly shows axial anisotropy with the g factors characteristic of the copper(II) cation in the ground state $d_{x^2-y^2}$ ($g_\parallel = 2.21$; $g_\perp = 2.05$). In all cases, the signal of the forbidden transition is absent, which is indicative of the small exchange parameter $-2J$.

In the ESR spectrum of a solution of complex **1** frozen at 77 K in the parallel orientation, the hyperfine structure of two copper nuclei is resolved (Fig. 3). Of the expected seven lines, only four lines are clearly observed, whereas the other three lines overlap with the intense line in the perpendicular orientation. However, the hyperfine coupling constant (105 G) is equal to approximately one half of $A_\parallel$ characteristic of mononuclear complexes containing the copper(II) cation in an analogous environment.[10—12]

An increase in the length of the polymethylene spacer to $n = 3$ or 4 leads to the disappearance of the seven-line hyperfine structure; instead, a poorly resolved hyperfine structure of one copper nucleus is observed in the parallel orientation. A further increase in the length of the polymethylene chain to $n = 5$ gives rise to a well-resolved hyperfine structure in the parallel orientation typical of mononuclear copper(II) complexes with axial symmetry ($g_\perp = 2.035$; $g_\parallel = 2.228$; $A_\parallel = 195$ G).

A seven-line hyperfine structure has been observed earlier[17,18] in the ESR spectra of frozen solutions of spacered dinuclear copper complexes containing a rigid aromatic spacer. In the ESR spectra of liquid solutions of

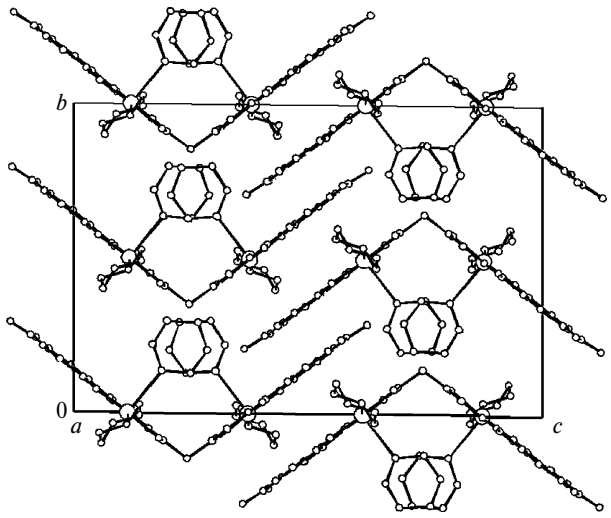


Fig. 2. Crystal structure of compound **6** projected onto the *bc* plane.

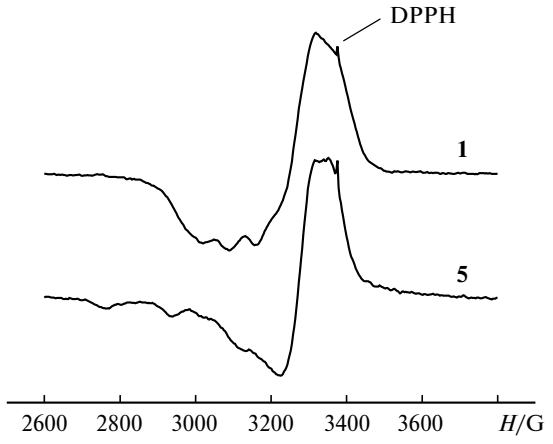


Fig. 3. ESR spectra of complexes **1** and **5** in frozen solutions (toluene—morpholine, 77 K); DPPH is diphenylpicrylhydrazyl.

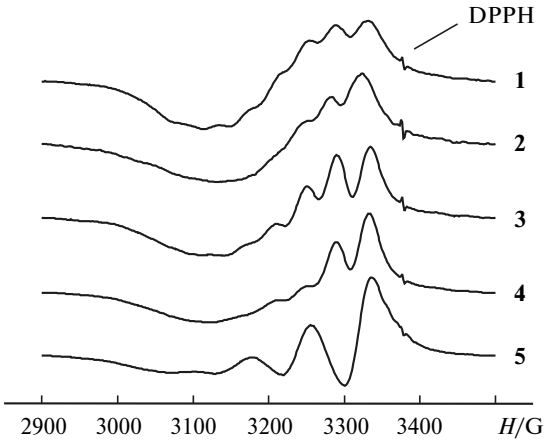


Fig. 4. ESR spectra of liquid solutions of complexes **1**—**5** (toluene—morpholine, 293 K).

this type of complexes, a seven-line hyperfine structure is rarely observed.[18] By contrast, spacered copper(II) complexes containing a flexible aliphatic bridge are characterized by a signal having a seven-line hyperfine structure.[1—8,10—12] Complexes **1**—**4** are no exception. The ESR spectra of these complexes in solution show a well-resolved signal having a seven-line hyperfine structure (Fig. 4) with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 and half the hyperfine coupling constant (Table 2). The observed ratio of the line-width parameters ($\alpha > \beta > \gamma$) is typical of copper complexes. The parameter δ, which takes into account the conformational flexibility of the aliphatic bridge, increases with increasing length of the polymethylene chain. The ESR spectrum of complex **5** exhibits a signal with the "normal value" of the hyperfine constant (see Fig. 4 and Table 2) typical of monomeric copper(II) complexes.

Earlier, it has been demonstrated that a seven-line hyperfine structure can occur due to interactions between the copper(II) atoms in the case when mononuclear complexes are packed to form dimeric stacks (stacking) both in the crystalline state[19] and in solution.[20] In the latter case, the spectral pattern strongly changes with varying concentration of the complexes. In concentrated solutions, a seven-line hyperfine structure is seen, whereas a four-line hyperfine structure is observed in dilute solutions due to dissociation of dinuclear complexes.[20] The ESR spectra of complexes **1**—**4** are invariant with respect to the concentration. This is evidence that the formation of an exchange channel *via* intermolecular stacking interactions is hardly probable in this case. The formation of the dinuclear Cu_2O_2 fragments involving the phenoxy bridges, which are typical of acyldihydrazones of salicylaldehyde and 2-hydroxyacetophenone,[21] in solution is also unlikely because a large excess of morpholine having high coordination ability should lead to decomposition of such dimers. Therefore, it is evident that only intramolecular exchange channels can be involved in weak exchange interactions between the copper(II) atoms in spacered complexes based on acyldihydrazones of aliphatic dicarboxylic acids. The polymethylene chain is the most probable exchange channel because the ESR spectra are very sensitive to its length. Moreover, the formation of other channels *via* intramolecular interactions (stacking or phenoxy bridges) is sterically impossible for the first two representatives of the homologous series.

The results of the present and earlier studies[10—12] allow the conclusion that the ESR spectra of the spacered dinuclear copper(II) complexes based acyldihydrazones of 2-hydroxyacetophenone are insensitive to the nature of substituents in the benzene ring of the bidentate ligand. This is probably due to the strongly pronounced positive induction effect of the Me group because the introduction of substituents of different nature into the benzene ring of the spacered complexes with on acyldihydrazones of salicylaldehyde studied earlier[8] decreases the limit of weak exchange interactions between the paramagnetic centers through a σ-bond system of the polymethylene bridge.

Table 2. ESR parameters of spacered dinuclear copper(II) complexes **1**—**5**

Compound	g	$a_{Cu} \cdot 10^4$ /cm^{-1}	Line-width parameters/G				σ* (%)
			α	β	γ	δ	
1	2.112	38.3	33.0	5.3	−0.47	2.80	1.2
2	2.112	35.3	43.3	13.9	−0.06	1.76	1.6
3	2.111	38.8	31.7	9.11	−0.14	3.68	2.3
4	2.109	37.1	38.3	13.6	−0.14	7.78	2.1
5	2.109	72.7	56.1	15.3	2.43	—	2.5

* The error characterizing the deviation of the theoretical spectrum from the experimental data.

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