ESR spectra of spacered copper(II) dimers of 5-bromo-2-hydroxyacetophenone acyldihydrazones based on aliphatic dicarboxylic acids

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Binuclear copper(II) complexes with 5-bromo-2-hydroxyacetophenone acyldihydrazones (H_4L) with the composition $[Cu_2L \cdot nPy]$ where the coordination polyhedra are linked by polymethylene chains with different lengths (from one to five units) have been synthesized and studied. The ESR spectrum of a polycrystalline sample of a complex based on malonyldihydrazone contains a major signal ($g = 2.11$) together with a weak signal corresponding to the forbidden transition ($\Delta M_S = 2$, $g = 4.18$). At room temperature, ESR spectra of solutions of complexes of acyldihydrazones based on malonic, succinic, glutaric, and adipic acids contain seven HFS lines from two equivalent copper nuclei. These lines result from weak spin-spin exchange interaction between two unpaired electrons with the constant $(36—38) \cdot 10^{-4}$ cm^{-1}. An increase in the polymethylene chain length to five units prevents the exchange interactions, and the ESR spectrum of a complex of the acyldihydrazone based on pimelic acid contains a signal of four HFS lines ($a_{Cu} = 69.5 \cdot 10^{-4}$ cm^{-1}), which is common to the monomeric copper(II) compounds. In the parallel orientation, the ESR spectrum of a frozen solution of the complex of malonyldihydrazone contained the superposition of signals due to fine and hyperfine structures with similar constants ($D_{\parallel} = 0.0074$ cm^{-1}, $A_{\parallel} = 0.0070$ cm^{-1}, $g_{\parallel} = 2.089$, $g_{\perp} = 2.053$).

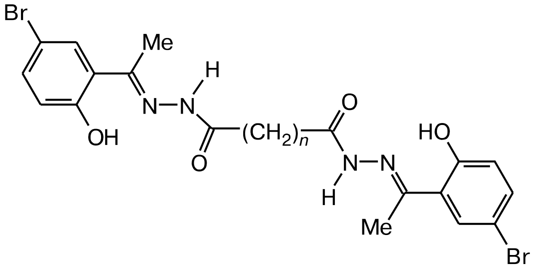
Kea words: 5-bromo-2-hydroxyacetophenone, acyldihydrazones, copper, dimers, ESR spectroscopy, hyperfine structure, spin-spin exchange interaction.

Recently, we have described[1] a number of new monomeric copper(II) binuclear complexes of 2-hydroxyacetophenone acyldihydrazones that contained polymethylene bridges of varied length (from one to five units). It was established[1] that the ESR spectra of these complexes were sensitive to the length of the polymethylene bridge (n). At room temperature, isotropic signals consisting of seven lines with the intensity ratio 1 : 2 : 3 : 4 : 3 : 2 : 1 and constant of $\sim 40 \cdot 10^{-4}$ cm^{-1} were observed in the spectra of liquid solutions of complexes with n = 1—4. The spectral pattern was interpreted to be due to coupling of unpaired electrons with two equivalent copper nuclei ($I = 3/2$). Earlier,[2,3] it has been shown that this kind of spectrum takes place when spin-spin exchange interaction has a value $|-2J| \gg 0.02$ cm^{-1}. An increase in the length of the polymethylene bridge results in the suppression of the exchange interactions. Hence, the ESR spectrum of a coordination compound with n = 5 represents a signal of four HFS lines ($a_{Cu} = 69.5 \cdot 10^{-4}$ cm^{-1}, $g = 2.113$), which is common to the monomeric copper(II) compounds.

Studies of ESR spectra of complexes based on 5-chloro- and 5-methyl-2-hydroxyacetophenone as well as 2-hydroxypropiophenone have shown that weak exchange interactions are not sensitive to the nature of substituents in both the benzene ring and the aliphatic chain of aliphatic-aromatic ketones.[4,5] For a more detailed study of the effect of the nature of substituents in the benzene ring of acyldihydrazones on weak exchange interactions, we synthesized and investigated binuclear copper(II) complexes with 5-bromo-2-hydroxyacetophenone acyldihydrazones. A series of complexes containing derivatives

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1752—1757, August, 2005.

of aliphatic acids (from malonic to pimelic, n = 1—5) have been studied.



Experimental

Coordination compounds were synthesized according to the procedure that has been developed earlier for the complexes with 2-hydroxyacetophenone acyldihydrazones.[1]

According to the data from elemental and thermal analysis, the composition of the complexes **1—5** corresponds to the formula $Cu_2L \cdot nPy \cdot mH_2O$ (H_4L is acyldihydrazone). The physicochemical parameters of these compounds are given in Table 1.

The content of copper was calculated with the use of data of trilonometric titration following thermal decomposition of the sample. The content of nitrogen was determined using the Dumas micromethod. The thermogravigrams were obtained on a Paulik—Paulik—Erdey Q-derivatograph in static atmosphere (air) at a heating rate of 10 °C min^{-1}. An open ceramic crucible was used as a sample holder with calcined aluminum oxide as a standard. IR spectra of the samples (KBr pellets) were recorded in the range of 4000—400 cm^{-1} on a Nicollet Fourier-transform spectrometer. The ESR spectra were recorded on an ADANI PS 100.X instrument in quartz tubes, which were free of the Fe^{3+} signal at low magnetic fields. The concentrations of the complexes were in the range of $(1—5) \cdot 10^{-3}$ mol L^{-1}. A mixture of pyridine with toluene (1 : 2, v/v) was used as a solvent. Theoretical simulation of the spectra was carried out with the use of a program package.[6] The ESR parameters were determined by comparing the experimental spectra with simulated ones constructed by summation of the line shapes of the individual transitions centered around the resonant field signal (H_p). The line shape function was fitted by the sum of Lorentzian and Gaussian profiles. According to the relaxation theory, the one-center contributions ($\Delta H_p(i)$) to the line widths were specified by the equation

$$\Delta H_p(i) = \alpha + \beta m_I + \gamma m_I^2,$$

where m_I is the projection of the nuclear spin and α, β, and γ are the parameters of the line width. Since the complexes containing polymethylene bridges are nonrigid stereochemically, we also took into account the contribution caused by the intramolecular mobility around the polymethylene bridge in the binuclear complex. As a result of this motion, the complexes polarize each other providing extra broadening of ESR lines:

$$\Delta H_p(1,2) = \delta(m_{Cu_1} - m_{Cu_2}).$$

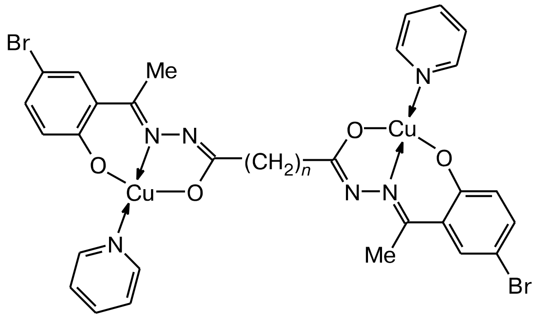
Results and Discussion

The interaction of 5-bromo-2-hydroxyacetophenone acyldihydrazones with copper(II) acetate proceeds according to a common scheme and results in polymeric complexes, in which the dimeric fragments Cu_2O_2 involving oxygen atoms of deprotonated phenolic groups are linked by polymethylene bridges.[1,4,5] Treatment of polymers with a large excess of pyridine at elevated temperature results in the cleavage of the phenoxy bridges and formation of binuclear complexes. In these complexes, the coordination polyhedra of copper(II) are linked by aliphatic bridges of different lengths. This allows us to consider the coordination compounds of this type as the spacered dimers.

The IR spectra of compounds **1—5** suggest the transition of ligand in the fourfold deprotonated imidol form. The band "amide-I", which is observed in the IR spectra of free acyldihydrazones in the range of 1670—1650 cm^{-1}, disappears but two new bands with absorption maxima at 1595—1580 cm^{-1} (stretching vibrations of the group >C=N—N=C<) and 1520—1505 cm^{-1} (stretching vibrations of the C—O bond of the fragment —N=C—O—) appear. The position of the band of stretching vibration of

Table 1. Physicochemical parameters of the compounds **1—5**

Compound	Found/Calculated (%) Cu	Found/Calculated (%) N	Molecular formula	IR spectrum, ν/cm^{-1}
$Cu_2L \cdot 2Py \cdot 2H_2O$ (**1**)	14.59 15.06	8.56 9.96	$C_{29}H_{28}Br_2Cu_2N_6O_6$	1595 (C=N); 1520 (N=C—O—); 1355 (CO_{phen})
$Cu_2L \cdot 2Py \cdot 2H_2O$ (**2**)	14.61 14.82	9.76 9.80	$C_{30}H_{30}Br_2Cu_2N_6O_6$	1580 (C=N); 1505 (N=C—O—); 1345 (CO_{phen})
$Cu_2L \cdot 2Py \cdot 4H_2O$ (**3**)	14.12 14.01	8.98 9.26	$C_{31}H_{36}Br_2Cu_2N_6O_8$	1595 (C=N); 1515 (N=C—O—); 1375 (CO_{phen})
$Cu_2L \cdot 2Py$ (**4**)	14.69 14.96	9.81 9.89	$C_{32}H_{30}Br_2Cu_2N_6O_4$	1590 (C=N); 1520 (N=C—O—); 1370 (CO_{phen})
$Cu_2L \cdot 4Py \cdot 2H_2O$ (**5**)	12.97 12.01	9.44 10.59	$C_{43}H_{46}Br_2Cu_2N_8O_6$	1585 (C=N); 1520 (N=C—O—); 1360 (CO_{phen})



1—5

Compound	**1**	**2**	**3**	**4**	**5**
n	1	2	3	4	5

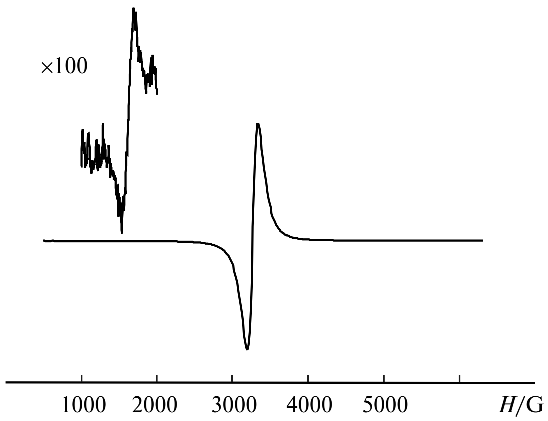


Fig. 1. The ESR spectrum of polycrystalline sample of complex **1** at 77 K.

the C—O bond of the phenoxy group within the range of 1375—1345 cm^{-1} is an indirect evidence of the cleavage of oxobridges[7] and formation of binuclear complexes **1—5**.

The results of X-ray diffraction analysis[5] of the complex of 2-hydroxypropiophenone adipoylhydrazone [$Cu_2L \cdot 4Py$] show that the copper cations in coordination compounds of this type are coordinated with two oxygen atoms of deprotonated phenoxy and imidol groups as well as nitrogen atom of the imino group. The fourth position in the coordination sphere is occupied by the nitrogen atom of a strongly coordinated pyridine molecule. In this type of complexes, an additional "weak" [4+1] coordination of a solvent molecule (pyridine, methanol, or water) with the formation of a tetragonal-pyramidal coordination polyhedron as well as insertion of a solvent molecule into the lattice cavity are often observed.[3,5]

According to the data from thermogravimetric analysis, removal of water molecules from complexes **1—3** takes place at rather low temperature (40—140 °C) and is accompanied by a weak endothermic effect with a minimum in the DTA curve in the range of 80—95 °C. Removal of a strongly coordinated pyridine molecule from complexes **1—4** starts at higher temperature (130—160 °C). This is accompanied by an *endo*-effect in the DTA curve with a minimum at 210—250 °C and is completed at 240—260 °C. At higher temperature, thermooxidative destruction of acylhydrazone takes place, which is accompanied by a sharp exothermic effect with a maximum in the DTA curve at 280—290 °C and later passes into burning out of the organic residue with one or two strong exothermic peaks with maxima within the range of 410—620 °C. The endmost region of decomposition is 710—770 °C. The thermogravigram of complex **5** reveals also well separated processes of removal of out-of-sphere water molecules as well as removal of weakly bound (40—90 °C, the *endo*-effect with a minimum at 90 °C) and strongly bound (110—210 °C, the *endo*-effect with a minimum at 180 °C) pyridine molecules.

At room temperature, the ESR spectrum of a polycrystalline sample of complex **1** contains intense exchange-narrowed line with a *g* factor equal to 2.11. A decrease in temperature down to 77 K results in a noticeable increase in absorption intensity with appearance, in a low-field region, of a very weak signal of the forbidden transition ($\Delta M_S = 2$) with $g = 4.18$ (Fig. 1), which is characteristic of dimeric copper(II) complexes. In the ESR spectra of polycrystalline samples of compounds **2—5**, the forbidden transition is not revealed and the only observed signal is the intense one corresponding to the allowed transition ($\Delta M_S = 1$) with *g* factor ~2.1.

In the ESR spectra of liquid solutions of complexes **1—4** (Fig. 2), isotropic signals with a well resolved HFS consisting of seven lines with the intensity ratio 1 : 2 : 3 : 4 : 3 : 2 : 1 and constant ~$40 \cdot 10^{-4}$ cm^{-1} are detected. This constant is about one half of the value typical of mononuclear complexes of acyldihydrazones (~$80 \cdot 10^{-4}$ cm^{-1}).[3] The solution of the spin Hamiltonian

$$\mathbf{H} = \beta \mathbf{S} g H + \mathbf{S}(A/2)(\mathbf{I}_1 + \mathbf{I}_2)$$

for dimeric complexes of cations with $S = 1/2$ gives half value of the HFS constant.[8,9]

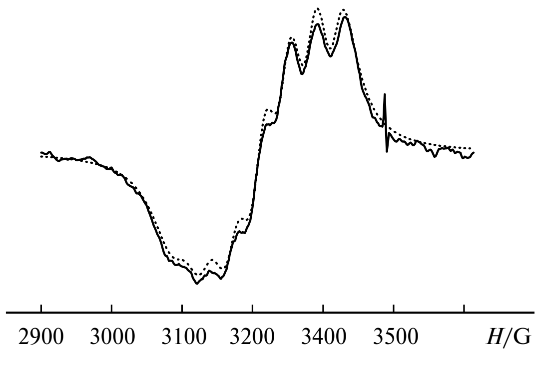


Fig. 2. The ESR spectrum of complex **1** in liquid solution (toluene—pyridine) at room temperature (solid line) and theoretical spectrum (dashed line).

Table 2. The parameters of ESR spectra of the spacered copper(II) dimers of 5-bromo-2-hydroxyacetophenone acyldihydrazones

Compound	g	$\alpha_{Cu}\cdot10^4$ /cm^{-1}	Parameters of line width/G				σ (%)	$g_\perp$	$g_\parallel$	$A_\parallel\cdot10^4$ /cm^{-1}
			α	β	γ	δ				
1	2.113	35.9	27.6	3.1	−0.53	2.00	2.5	2.053	2.089	70
2	2.115	37.8	32.8	9.1	−0.47	2.52	3.9	2.046	2.13	78
3	2.114	37.7	26.5	6.82	0.21	3.56	1.6	2.03	~2.16	~102
4	2.115	37.3	32.6	11.1	−0.24	6.96	2.4	2.02	2.22	~180
5	2.113	69.5	52.6	13.3	2.5	—	2.6	2.01	2.22	184

Simulation of the ESR spectra of complexes **1—4** gives similar values of the spin Hamiltonian parameters (Table 2) and the ratio of line width parameters ($\alpha \gg \beta > \gamma$) common to copper(II) complexes. The value of parameter δ, related to the conformational nonrigidity of the aliphatic spacer, increases systematically with the increase in the number of the methylene units from one to four.

Lengthening of the polymethylene spacer to $n = 5$ results in a dramatic change in the spectral pattern. The spectrum contains a signal consisting of four HFS lines with equal intensities and with the constant characteristic of one copper atom, which are common to monomeric copper(II) complexes (Fig. 3).

Earlier,[10,11] seven HFS lines have been observed in ESR spectra of frozen solutions of some spacered copper(II) dimers containing aromatic spacers. Due to low solubilities of this type of complexes in organic low-polar solvents, the HFS from two copper nuclei in liquid solutions at room temperature can be observed in rare cases.[11] The substitution of an aliphatic spacer for an aromatic one favors the solubility of complexes and allows one to observe the HFS consisting of seven lines in the ESR spectra of liquid solutions of a series of spacered copper(II) dimers based on acetylacetone[9,12,13] and trifluoroacetylacetone acyldihydrazones[14] as well as salicylic aldehyde[3,15—17] and 2-hydroxyacetophenone acyldihydrazones.[1,4,5] At the same time, the ESR spectra of frozen solutions of dimers with aliphatic spacers are much less informative as compared with the spectra of dimers with aromatic spacers. For the series under study, it is possible sometimes to observe more or less resolved HFS from two copper nuclei in the case of parallel orientation with the mono- or dimethylene spacer.[1,3,4]

The ESR spectrum of a frozen solution of complex **1** at 77 K exhibits a sufficiently well resolved signal with fine and hyperfine structures (Fig. 4). The spectrum contains nine lines, seven of which (in the low field) are assigned to HFS from two equivalent copper nuclei. The lines are nonequally spaced and the distance between them increases with an increase in the magnetic field strength and then becomes smaller again for two last components (2981, 3028, 3093, 3165, 3243, 3324, and 3392 G). The average distance between lines is 68.5 G. The calculation of the HFS constant with taking into account the Breit—Rabi rule[18] gives the value of $70\cdot10^{-4}$ cm^{-1}. It is known that the fine structure resulted from the primary splitting can be considered as partial superposition of two mirrored signal profiles.[6] The ESR spectrum of complex **1** at 77 K

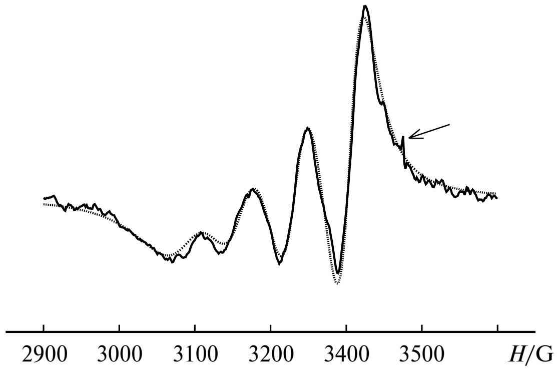


Fig. 3. The ESR spectrum of complex **5** in liquid solution (toluene—pyridine) at room temperature (solid line) and theoretical spectrum (dashed line). Here and then the arrow indicates the signal of diphenylpicrylhydrazyl.

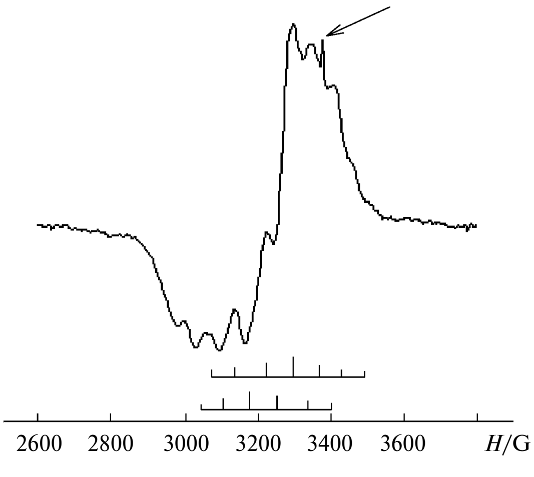


Fig. 4. The ESR spectrum of complex **1** in frozen solution (toluene—pyridine) at 77 K. Bar-diagram shows the approximate interpretation of HFS.

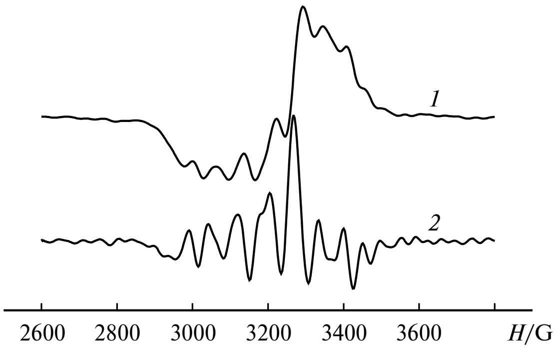


Fig. 5. The ESR spectrum of complex **1** in frozen solution (toluene—pyridine) at 77 K: first (*1*) and second (*2*) derivatives.

exhibits not only seven HFS lines superimposed on the signal with perpendicular orientation ($g = 2.053$) but also two weak lines in a high field at 3450 and 3495 G (Fig. 5, curve *1*). The use of the resonant field values for low-field components of the fine structure allowed us to calculate the positions of the rest HFS high-field lines (3086, 3154, 3235, 3313, 3385, 3450, and 3495 G). The fine structure becomes especially apparent in the second-derivative ESR spectrum of complex **1** (see Fig. 5, curve *2*). The positions of the central HFS lines (3175 and 3313 G) made it possible to calculate the fine structure constant $D_{\|}$ (74 G or 0.0074 cm^{-1}).

The tensor D can be represented as a sum of exchange (D_{exch}) and dipole-dipole (D_{dd}) contributions. Within the point dipole approximation,[8]

$$D_{dd} = -(g_{\|}^2 + 1/2g_{\perp}^2)\beta^2/r^3,$$

where r is the metal—metal distance. The optimization of the geometry of complex **1** by methods of molecular mechanics allowed us to estimate the distance between the copper atoms to be of ~6 Å. The calculation of D_{dd} with the use of the upper estimate gives the value $-128 \cdot 10^{-4}$ cm^{-1}. It is known that D_{dd} is always negative in sign,[8] whereas D can have both positive and negative values.[19] Therefore, D_{exch} can have one of the values: $202 \cdot 10^{-4}$ or $54 \cdot 10^{-4}$ cm^{-1}.

The value of D_{exch} can be estimated with the formula [19]:

$$D_{exch} \sim (\Delta g/g)^2(-2J'),$$

where Δg is a deviation of g factor value for a magnetic ion from purely spin number $g = 2.0023$, and $-2J'$ is a parameter of the exchange interaction for the excited state of a dimer. Substituting the values obtained above into the upper formula gives $-2J' \approx 6$ or 2 cm^{-1}. Although it is known that the magnitude of $-2J'$ can differ from the value of the exchange parameter for the ground state of a dimer substantially, the calculated value may be used as an approximate estimate for $-2J$.[20] The thus obtained value of $-2J$ (2—6 cm^{-1}) coincides in the order of magnitude with the earlier estimation of $-2J$ (1—3 cm^{-1}) made for the spacered dimer based on acetylacetone acyldihydrazone,[9] which is an analog of complex **1**, and with the experimental value ($-2J = 1.5$ cm^{-1}) calculated with the use of magnetochemical data for the spacered dimer, in which the coordination polyhedra of copper(II) are linked by a dimethylene spacer.[21]

Five of seven HFS lines due to two copper nuclei are seen also in the spectrum of a frozen solution of complex **2**, but the fine structure is not revealed in this case. The extension of the length of polymethylene spacer up to $n = 3$ and 4 results in disappearance of HFS consisting of seven lines. Instead, a poorly resolved HFS from one copper nucleus is observed in the parallel orientation (Fig. 6, *a*). Further lengthening of the polymethylene chain ($n = 5$) reduces the spin-spin exchange interactions down almost to zero, and the ESR spectrum in a parallel orientation at 77 K exhibits well resolved HFS from one copper atom, which is typical of mononuclear copper(II) complexes (Fig. 6, *b*). The increase in n is accompanied by a monotonic increase in HFS constant and magnitude of $g_{\|}$, whereas the value of perpendicular component of g factor decreases slightly (see Table 1).

The results of the present and previous studies[1,4] allow us to conclude that the introduction of substituents with positive mesomeric effect (Br, Cl, Me) into position 5 of

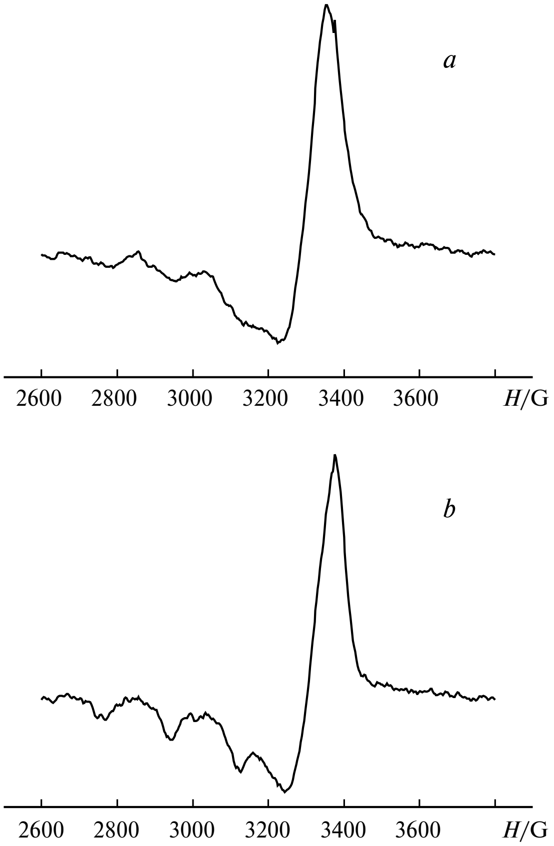


Fig. 6. The ESR spectra of complexes **4** (*a*) and **5** (*b*) in frozen solution (toluene—pyridine) at 77 K.

the benzene ring of 2-hydroxyacetophenone acyldihydrazones based on aliphatic dicarboxylic acids does not affect weak exchange interactions occuring in the spacered copper(II) dimers synthesized from these acylhydrazones.

This work was carried out with financial support from the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Grant 18/04).

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Received November 17, 2004;
in revised form March 23, 2005