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ESR spectra of copper(II) complexes with 2-hydroxy-5-methyl- and 5-chloro-2-hydroxyacetophenone acyldihydrazones

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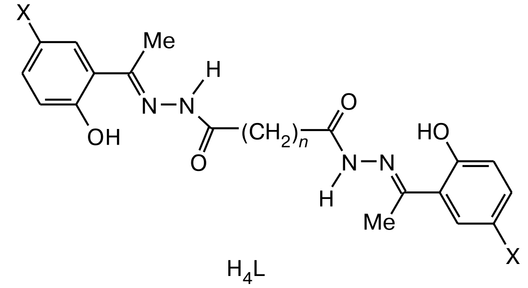
ESR spectra of binuclear copper(II) complexes with 2-hydroxy-5-methyl- and 5-chloro-2-hydroxyacetophenone acyldihydrazones (H_4L) [$Cu_2L \cdot 2Py$], in which the coordination polyhedra are linked by the polymethylene chain with different lengths (from one to five units), were studied. The spectra of the complexes based on acyldihydrazones of malonic, succinic, glutaric, and adipic acids exhibit weak exchange interactions between the paramagnetic sites. These interactions induce seven HFS lines from two equivalent copper nuclei with the constant ~$40 \cdot 10^{-4}$ cm^{-1} in the ESR spectra of liquid solutions. An increase in the polymethylene chain length to five units prevents the exchange interactions, and the ESR spectrum of the complex based on heptadioic acyldihydrazone contains the signal of four HFS lines with the constant ~$72 \cdot 10^{-4}$ cm^{-1}, which is common for the copper(II) monomeric compounds.

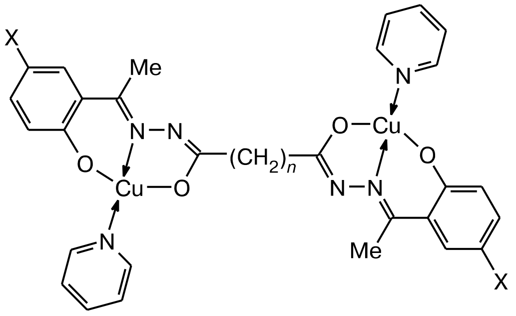
Key words: 2-hydroxyacetophenone acyldihydrazones, copper(II) binuclear complexes, hyperfine structure, spin-spin exchange interactions, ESR spectroscopy.

Several types of copper(II) binuclear complexes, whose spectra demonstrate weak exchange interactions between the paramagnetic centers through the chain of σ-bonds containing up to five units, have been described.[1—9] Such an interaction is most strikingly exhibited by the presence of seven HFS lines from two equivalent copper nuclei ($I = 3/2$) in the ESR spectra of liquid solutions. It has been shown[8,9] for the coordination compounds of salicylaldehyde and fluorinated β-diketones that exchange interactions of this type are sensitive to both the polymethylene chain length and the nature of substituents in the non-chelatophoric moiety of the binucleating organic ligand.



H_4L

X = Me, Cl; n = 1—5



1a—e, **2a—e**

X = Me (**1**), Cl (**2**)
n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**)

We have recently[10] described a new type of complexes with weak exchange interaction through the system of σ-bonds, *viz.*, the copper(II) coordination compounds with 2-hydroxyacetophenone acyldihydrazones. It was of interest to reveal the influence of substituents in the benzene ring of acyldihydrazones on the intensity of exchange interactions in complexes of this type. For this purpose we synthesized and studied the coordination compounds of copper(II) 2-hydroxy-5-methyl- and 5-chloro-2-hydroxyacetophenone acyldihydrazones. The series of complexes

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1a—e and **2a—e** based on hydrazones of malonic, succinic, glutaric, and heptadioic acids (H_4L) was studied.

Experimental

Copper(II) coordination compounds were synthesized using a procedure developed previously for the complexes of 2-hydroxyacetophenone acyldihydrazones.[10] The corresponding acetophenone (10 mmol) and AcOH (0.5 mL) as catalyst were added to a suspension of dicarboxylic acid dihydrazide (5 mmol) in MeOH (50 mL). The mixture was refluxed with magnetic stirring until dihydrazide was completely dissolved (1—2 h). The resulting solution was cooled to ~20 °C, copper(II) acetate monohydrate (10 mmol) was added, and the solution was stirred until crystals of the salt disappeared (3—5 h). The precipitate was filtered off, washed with water and EtOH, and dried in air. The product obtained was dissolved in Py (25—30 mL), and the solution was stored for 1 day, filtered off, and precipitated with water. The precipitate formed was filtered off, washed with water and EtOH, and dried in air. The target fine-crystalline gray-green or gray-sand-colored substance was obtained in 45—70% yield.

According to elemental and thermal analyses, the composition of complexes **1a—e** and **2a—e** corresponds to the formula $[Cu_2L \cdot 2Py] \cdot n$MeOH.

Complex $[Cu_2L \cdot 2Py \cdot MeOH]$ (1a). Found (%): Cu, 17.91; N, 12.01. $C_{32}H_{34}Cu_2N_6O_5$. Calculated (%): Cu, 17.92; N, 11.84. IR, ν/cm^{-1}: 1590 (C=N); 1515 (N=C—O—); 1360 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py \cdot 4MeOH]$ (1b). Found (%): Cu, 16.05; N, 11.07. $C_{36}H_{48}Cu_2N_6O_8$. Calculated (%): Cu, 15.51; N, 10.24. IR, ν/cm^{-1}: 1595 (C=N); 1515 (N=C—O—); 1360 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py]$ (1c). Found (%): Cu, 17.27; N, 11.05. $C_{33}H_{34}Cu_2N_6O_4$. Calculated (%): Cu, 18.03; N, 11.90. IR, ν/cm^{-1}: 1590 (C=N); 1515 (N=C—O—); 1360 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py \cdot MeOH]$ (1d). Found (%): Cu, 16.56; N, 11.36. $C_{35}H_{40}Cu_2N_6O_5$. Calculated (%): Cu, 16.89; N, 11.17. IR, ν/cm^{-1}: 1590 (C=N); 1515 (N=C—O—); 1360 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py \cdot MeOH]$ (1e). Found (%): Cu, 16.96; N, 10.42. $C_{36}H_{40}Cu_2N_6O_5$. Calculated (%): Cu, 16.59; N, 10.96. IR, ν/cm^{-1}: 1590 (C=N); 1525 (N=C—O—); 1370 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py \cdot MeOH]$ (2a). Found (%): Cu, 17.38; N, 11.28. $C_{30}H_{28}Cu_2Cl_2N_6O_5$. Calculated (%): Cu, 16.94; N, 11.18. IR, ν/cm^{-1}: 1590 (C=N); 1525 (N=C—O—); 1345 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py]$ (2b). Found (%): Cu, 17.05; N, 11.22. $C_{30}H_{26}Cu_2Cl_2N_6O_4$. Calculated (%): Cu, 17.36; N, 11.47. IR, ν/cm^{-1}: 1590 (C=N); 1525 (N=C—O—); 1345 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py \cdot MeOH]$ (2c). Found (%): Cu, 16.52; N, 10.65. $C_{32}H_{32}Cu_2Cl_2N_6O_5$. Calculated (%): Cu, 16.33; N, 10.79. IR, ν/cm^{-1}: 1590 (C=N); 1525 (N=C—O—); 1345 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py]$ (2d). Found (%): Cu, 16.53; N, 11.96. $C_{32}H_{30}Cu_2Cl_2N_6O_4$. Calculated (%): Cu, 16.72; N, 11.05. IR, ν/cm^{-1}: 1585 (C=N); 1525 (N=C—O—); 1345 (CO_{phen}).

Complex $[Cu_2L \cdot 2Py \cdot MeOH]$ (2e). Found (%): Cu, 16.01; N, 10.02. $C_{34}H_{36}Cu_2Cl_2N_6O_4$. Calculated (%): Cu, 15.76; N, 10.42. IR, ν/cm^{-1}: 1590 (C=N); 1515 (N=C—O—); 1350 (CO_{phen}).

The percentage of copper was calculated from the trilonometric titration data after the specimens were decomposed. The percentage of nitrogen was determined by the Dumas micromethod. Thermogravimetric analyses were performed on a Paulik-Paulik-Erdey Q derivatograph in a static air atmosphere using a heating velocity of 10 °C min^{-1}, an open ceramic crucible for the sample, and calcined alumina as reference. IR spectra of the samples molded with KBr were recorded in the 4000—400 cm^{-1} interval on a Nicollet FTIR spectrophotometer. ESR spectra were recorded on a PS 100X instrument in the X interval using a concentration of the complexes of $(1-5) \cdot 10^{-3}$ mol L^{-1}. A mixture of pyridine with toluene (1 : 1 vol/vol) was used as solvent.

The spectra were simulated using a program package described previously.[11] Parameters of ESR spectra were determined by a comparison of the experimental spectra with the spectra calculated by the summation of functions of the line shape of individual transitions centered around the resonance field (H_r). The sum of the Lorentz and Gauss functions was used as a function of the line shape. According to the relaxation theory, the one-center contributions to the linewidth were specified by the expression

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

where m_I is the projection of the nuclear spin; and α, β, and γ are the parameters of the linewidth.[8] Since complexes with the polymethylene bridges can manifest a stoichiometric nonrigidity, the contribution from intramolecular motions in the binuclear complex around the polymethylene bridge was also taken into account

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

Results and Discussion

The study of the products of the reactions of copper(II) acetate with acyldihydrazones of dicarboxylic acids and 2-hydroxyacetophenone 5-substituted derivatives shows that the interaction produces polymeric complexes containing the Cu_2O_2 nuclear fragments. This is typical of the coordination compounds of carboxylic salicylidenehydrazones.[12] Treatment of the latters with pyridine excess affords binuclear complexes **1** and **2** in which the coordination polyhedra are linked through the polymethylene chain.

Analysis of the IR spectra of the coordination compounds confirms the assumption about transformation of the ligand into the fourfold deprotonated imidole form. The spectra of complexes **1** and **2** demonstrate the disappearance of the "amide-I" band, which is observed in the IR spectra of free 2-hydroxyacetophenone acyldihydrazones at 1600 cm^{-1}, and the appearance of two new absorption bands with maxima in the regions of 1595—1585 cm^{-1} (stretching vibrations of >C=N—N=C<) and 1525—1515 cm^{-1} (stretching vibrations of the C—O bond in the —N=C—O— fragment). It is noteworthy that the band of C—O stretching vibrations in the phenoxide group shifts from 1290—1240 cm^{-1} in the spectra of the polymeric complexes to 1360—1345 cm^{-1} in the IR spectra of compounds **1** and **2**. This shift indirectly proves the cleavage of the oxo bridges and the formation of monomeric complexes in which each copper cation is coordinated by two O atoms of the deprotonated phenoxide and imidole groups and the imine N atom.[12] The fourth site in the coordination sphere is occupied by the N atom of the strongly coordinated pyridine molecule. In this case, the most probable geometry of the coordination polyhedron is a strongly distorted square. Several complexes exhibit an additional weak [4+1]-coordination of the O atom in the MeOH molecule by one or two copper cations to form a tetragonal pyramidal polyhedron. Two of four MeOH molecules in complex **1b** are likely weakly [4+2]-coordinated or occupy the out-of-sphere position. A possibility of the weak coordination of MeOH molecules in similar complexes has previously[6,7] been shown by X-ray diffraction analysis.

According to thermogravimetric analysis, the MeOH molecules are removed from some complexes at a relatively low temperature (40—170 °C) without any remarkable thermal effects. The strongly coordinated pyridine molecules are removed at higher temperatures (185—280 °C). The process is accompanied by an endotherm with a minimum in the DTA curve at 190—270 °C. At 300—360 °C the thermooxidative destruction of the acyldihydrazone molecule begins and is transformed into the burning-out of the organic residue. The latter process is accompanied by strong exotherms with maxima in the region of 310—630 °C.

The ESR spectra of liquid solutions of complexes **1a—d** and **2a—d** exhibit an isotropic signal with a well resolved HFS of seven lines with the ratio of intensities 1 : 2 : 3 : 4 : 3 : 2 : 1 (Fig. 1) and constant ~$40 \cdot 10^{-4}$ cm^{-1} (Table 1). This signal is induced by the exchange interaction of an unpaired electron with two equivalent copper nuclei. The HFS of seven lines has previously been observed[13,14] for forbidden transitions in the ESR spectra of polycrystalline samples of some copper dimers with the short metal—metal distance (~3 Å), favoring strong antiferromagnetic exchange interaction ($-2J$ of an order of several hundreds of inverse centimeters). In the binuclear complexes under study, the distance between the paramagnetic centers achieves 10 Å,[6,7] which prevents the magnetic orbitals from direct overlapping. Hence, the most probable mechanism of the spin-spin interaction becomes indirect exchange *via* the chain of σ-bonds of the polymethylene bridge. A simple theoretical analysis shows that $a_{\mathrm{Cu}} \ll |-2J|$ is the condition sufficient for HFS from two copper nuclei.[1] In this case, each unpaired electron interacts with two nuclear spins, and the ESR spectrum exhibits HFS from two equivalent copper nuclei as seven lines with the halved a_{Cu} constant.

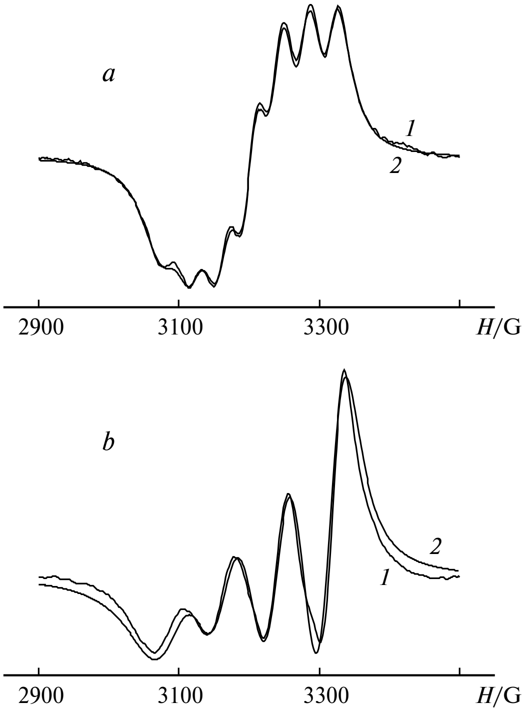

Fig. 1. Experimental (*1*) and theoretical (*2*) ESR spectra of liquid solutions of complexes **2a** (*a*) and **2e** (*b*) at 298 K.

The data obtained indicate a low sensitivity of the exchange interactions under study to the nature of substitu-

Table 1. Parameters of the ESR spectra of the Cu$^{\mathrm{II}}$ binuclear complexes with 2-hydroxy-5-methyl- and 5-chloro-2-hydroxyacetophenone acyldihydrazones

Compound	g	$a_{\mathrm{Cu}} \cdot 10^4$ /cm^{-1}	Parameters of linewidths/G				σ* (%)	$g_\perp$	$g_\parallel$	<A>/G
			α	β	γ	δ				
1a	2.111	37.2	31.4	6.3	−0.7	3.4	2.8	2.09	—	—
1b	2.112	38.1	29.7	6.9	−0.4	2.2	2.1	2.05	2.24	64
1c	2.113	38.2	28.8	7.9	−0.2	3.7	2.9	2.05	2.21	177
1d	2.114	39.0	35.2	10.7	−0.1	7.0	3.2	2.03	2.22	180
1e	2.110	72.1	50.6	11.4	1.8	—	2.2	2.01	2.23	185
2a	2.112	37.1	26.9	2.7	−0.6	1.8	1.2	2.06	2.14	68
2b	2.115	36.5	34.5	8.8	−1.8	2.7	3.0	2.04	—	—
2c	2.112	39.4	29.1	5.5	−1.9	4.1	3.1	2.06	—	—
2d	2.116	36.9	33.2	11.4	0.02	7.0	2.6	2.03	2.22	185
2e	2.109	71.8	49.7	10.4	2.0	—	3.0	2.02	2.23	180

* The error characterizing the deviation of the theoretical spectrum from the experimental one ($R \cdot 100$).

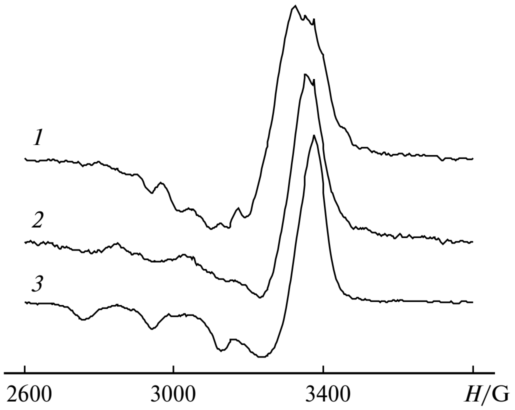

Fig. 2. ESR spectra of solutions of complexes **1b** (*1*), **1d** (*2*), and **1e** (*3*) frozen at 77 K.

ents in the benzene ring of 2-hydroxyacetophenone acyldihydrazones. For the copper(II) complexes with dicarboxylic salicylidenehydrazones, the introduction of different substituents (5-Br, 4-OH, 5,6-C_4H_4) into the benzene ring decreases the conductivity boundary of the spin density through the polymethylene chain to three units.[8] This difference in the behavior of the complexes with very similar molecular structures can be explained by the pronounced positive inductive effect of the Me group, which pumps the electron density to the alkylidene radical and favors the electron density transfer through the polymethylene chain.

An increase in the length of the polymethylene chain dividing the coordination polyhedra to five units decreases considerably the $-2J$ value, and the isotropic signal of four HFS lines from one copper nucleus with the standard value of the constant appears in the ESR spectra of complexes **1e** and **2e**. This signal is common for monomeric complexes.

The increase in the polymethylene chain length results in interesting changes in the ESR spectra of solutions frozen at 77 K. For example, the spectra of frozen solutions of compounds **1a** and **2b** exhibit an anisotropic signal with the g factor of 2.04—2.09, whereas HFS is not seen. At the same time, the spectra of complexes **1b** and **2a** contain the anisotropic signal typical of the systems with the axially symmetrical g factor ($g_\perp$ = 2.05—2.06, $g_\parallel$ = 2.14—2.24). The well resolved HFS from two equivalent copper nuclei with the constant 64—68 G is observed in the parallel orientation (Fig. 2). The increase in the length of the polymethylene chain to three or four units results in the appearance of the poorly resolved HFS from one copper nucleus with the constant 180—185 G. The spectra of frozen solutions of the complexes based on heptadioic acyldihydrazones (n = 5) exhibit the pronounced HFS from one copper nucleus in the parallel orientation, and the spectra become typical of the monomeric copper(II) complexes with the axial symmetry.[11] This indicates that weak exchange interactions between the copper cations through the polymethylene chain are also observed in frozen solutions but the distance of their influence is much shorter. The temperature dependence of the weak exchange interactions through the system of σ-bonds indicates the important role of dynamic effects in this phenomenon.

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