ESR study of weak exchange interactions in binuclear copper(II) complexes with 2-hydroxyacetophenone acyldihydrazones

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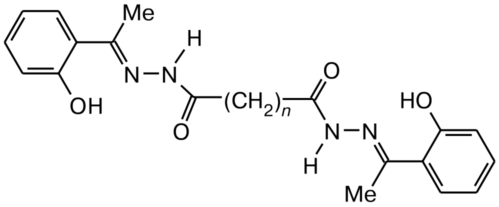
The binuclear copper(II) complexes with 2-hydroxyacetophenone acyldihydrazones (H_4L) $Cu_2L \cdot 2Py$ were studied by ESR spectroscopy. In these complexes, the coordination polyhedra are linked *via* the polymethylene chain containing from one to five units. In the complexes based on acyldihydrazones of malonic, succinic, glutaric, and adipic acids, weak spin-spin exchange interactions occur between the paramagnetic centers. An increase in the length of the polymethylene chain to five units hinders exchange interactions, and the ESR spectrum of the corresponding complex has a signal typical of monomeric copper(II) complexes.

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

Three types of binuclear copper(II) complexes were described in the literature, in which weak exchange interactions between the paramagnetic centers occur through the polymethylene chain.[1—7] The majority of these complexes (molecular paramagnetics exhibiting weak antiferromagnetism) were synthesized based on acyldihydrazones of acetylacetone[2—4] or salicylaldehyde.[5—7] In the present study, we synthesized binuclear copper(II) complexes with 2-hydroxyacetophenone acyldihydrazones and investigated weak exchange interactions between the copper cations in these complexes by ESR spectroscopy.



H_4L^1 (n = 1), H_4L^2 (n = 2), H_4L^3 (n = 3), H_4L^4 (n = 4), H_4L^5 (n = 5)

Experimental

The coordination compounds were synthesized as follows. 2-Hydroxyacetophenone (10 mmol) and AcOH (0.5 mL) as the catalyst were added to a suspension containing dihydrazide of the corresponding dicarboxylic acid (from malonic to pimelic) (5 mmol) in MeOH (50 mL). The reaction mixture was refluxed with magnetical stirring until the dihydrazide was completely dissolved (1—3 h). The resulting solution was cooled to ~20 °C, copper(II) acetate monohydrate (10 mmol) was added, and the reaction mixture was stirred until crystals of copper acetate disappeared (3—5 h). The precipitate that formed was filtered off, washed with water and EtOH, and dried in air. The resulting product was dissolved in pyridine (5—10 mL), kept for one day, filtered off, and precipitated with water. The precipitate that formed was filtered off, washed with water and EtOH, and dried in air. Gray-green or gray-sand-colored finely crystalline powders were obtained in yields of 1.6—2.5 g (50—80%).

According to the results of elemental and thermogravimetric analyses, the compositions of the complexes correspond to the general formula $Cu_2L \cdot 2Py$.

[$Cu_2L^1 \cdot 2Py$]$\cdot H_2O$ (1). Found (%): Cu, 19.37; N, 13.11. $C_{29}H_{28}Cu_2N_6O_5$. Calculated (%): Cu, 19.03; N, 12.58. IR, ν/cm^{-1}: 1575 (ν(C=N)); 1515 (ν(N=C—O—)); 1350 (ν(CO_{phen})).

[$Cu_2L^2 \cdot 2Py$]$\cdot MeOH \cdot H_2O$ (2). Found (%): Cu, 18.63; N, 12.91. $C_{31}H_{34}Cu_2N_6O_6$. Calculated (%): Cu, 17.80; N, 11.78. IR, ν/cm^{-1}: 1575 (ν(C=N)); 1510 (ν(N=C—O—)); 1360 (ν(CO_{phen})).

[$Cu_2L^3 \cdot 2Py$] (3). Found (%): Cu, 18.04; N, 12.88. $C_{31}H_{30}Cu_2N_6O_4$. Calculated (%): Cu, 18.75; N, 12.40.

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IR, ν/cm^{-1}: 1570 (ν(C=N)); 1500 (ν(N=C—O—)); 1360 (ν(CO$_{phen}$)).

[Cu$_2$L^4·2Py] (4). Found (%): Cu, 18.16; N, 12.87. $C_{32}H_{32}Cu_2N_6O_4$. Calculated (%): Cu, 18.37; N, 12.15. IR, ν/cm^{-1}: 1585 (ν(C=N)); 1515 (ν(N=C—O—)); 1365 (ν(CO$_{phen}$)).

[Cu$_2$L^5·2Py] (5). Found (%): Cu, 18.38; N, 12.87. $C_{33}H_{34}Cu_2N_6O_4$. Calculated (%): Cu, 18.01; N, 11.91. IR, ν/cm^{-1}: 1580 (ν(C=N)); 1510 ((N=C—O—)); 1375 (ν(CO$_{phen}$)).

The copper percentage was calculated from the results of trilonometric titration after thermal decomposition of a weighed sample. The nitrogen percentage was determined by the Duma micromethod. The thermogravimetric curves were obtained on a Paulik—Paulik—Erdey Q derivatograph in a static air atmosphere; the rate of heating 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 of samples (KBr pellets) were measured in the range of 4000—400 cm^{-1} on a Specord IR-75 spectrophotometer. The ESR spectra were recorded on an ADANI PS 100X (9.45 Hz) radiospectrometer in a CHCl$_3$—pyridine mixture (10 : 1, v/v). Because of the poor solubility of the complexes (the concentrations of the complexes were $5 \cdot 10^{-4}$ mol L^{-1}), the spectra with a lower noise level could not be recorded. The magnetic field was monitored on a nuclear magnetometer using the diphenylpicrylhydrazyl (DPPH) radical as the standard. The experimental spectra were processed on a computer by the method of the best approximation of the experimental spectra by the theoretical spectra with minimization of the error functional

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

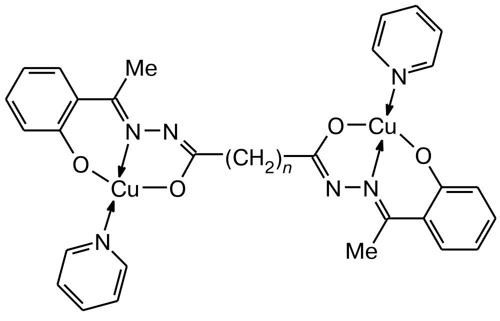
where I_i^{obs} are the experimental intensities of the ESR signal processed on a computer as a file of points with a constant step along the magnetic field H; I_i^{t} are the theoretical intensities at the same H values calculated as the sum of derivatives of the Lorentz and Gaussian functions centered at the resonance values of H; and N is the number of points. The g factors, the constants of hyperfine structure from the nuclei of the copper isotopes, 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 m_I is the projection of the nuclear spin onto the direction of the external magnetic field; and α, β, and γ are the parameters of the line width. Since complexes containing polymethylene bridges can be geometrically flexible, we also took into account the contribution $\Delta H_{\mathrm{p}}(1,2) = \delta(m_1 - m_2)^2$ associated with the influence of stereochemical nonrigidity on the isotropic exchange through intramolecular motions about the polymethylene bridge.[3]

Results and Discussion

Previously,[5] it has been demonstrated that the reactions of copper(II) acetate with salicylaldehyde acyldihydrazones afforded polymeric complexes. These complexes contain the dimeric Cu_2O_2 fragments linked *via* the polymethylene chain. Treatment of these complexes with an excess of pyridine led to the cleavage of the phenoxide bridges to form binuclear complexes. We demonstrated that the reactions of copper(II) acetate with 2-hydroxyacetophenone acyldihydrazones proceeded according to an analogous scheme to give binuclear complexes **1—5** in which the coordination polyhedra are separated by polymethylene chains of different lengths.



1—5

n = 1 (**1**), 2 (**2**), 3 (**3**), 4 (**4**), 5 (**5**)

Analysis of the IR spectra of compounds **1—5** confirmed the assumption that the ligand is transformed into the tetraprotonated imidol form because the spectra of the complexes have no amide I band, which is observed in the IR spectra of free 2-hydroxyacetophenone acyldihydrazones at ~1600 cm^{-1}, whereas the spectra show two new absorption bands with maxima in the regions of 1585—1570 cm^{-1} (stretching vibrations of the

Table 1. Results of thermogravimetric analysis of the copper(II) complexes with 2-hydroxyacetophenone acyldihydrazones

Compound	ΔT [a]	T [b]	Δm [c] (%)	Process
	°C			
1	40—90	—	3	$-H_2O$
	90—260	200 (–)	26	–2 Py
	260—570	340, 540 (+)	80	Decomposition
2	40—130	110 (–)	6	$-H_2O$, MeOH
	170—240	230 (–)	33	–2 Py
	300—520	340, 410 (+)	78	Decomposition
3	130—200	150, 170 (–)	26	–2 Py
	300—640	400 (+)	80	Decomposition
4	110—190	170 (–)	25	–2 Py
	280—420	330, 370 (+)	78	Decomposition
5	100—190	150, 170 (–)	25	–2 Py
	300—730	390, 540 (+)	82	Decomposition

[a] The temperature range according to the thermogravimetric data.

[b] The extremum in the DTA curve, the endothermic (–) and exothermic (+) effects are indicated.

[c] The weight loss.

>C=N—N=C< group) and 1515—1500 cm^{-1} (C—O stretching vibrations of the —N=C—O— fragment).

It should be noted that the C—O stretching band of the phenoxide group in the spectra of compounds **1—5** is shifted (to 1375—1350 cm^{-1}) as compared to that in the IR spectra of the polymeric complexes (1320—1290 cm^{-1}). This is indirect evidence for the cleavage of the oxo bridges[9] and the formation of monomeric complexes in which each copper cation is coordinated by two O atoms of the deprotonated phenoxide and imidol groups and also by the imine N atom. The fourth site in the coordination sphere is occupied by the N atom of the strongly coordinated pyridine molecule. It is most probable that the coordination polyhedron is a strongly distorted square. In complexes **1** and **2**, the water or MeOH molecule is, apparently, involved in a weak additional coordination bond to form a [4+1]-type polyhedron, *viz.*, a tetragonal pyramid.

The binuclear structures of the copper(II) complexes with acyldihydrazones of oxalic acid and 2-hydroxyacetophenone were confirmed[10] by X-ray diffraction analysis. According to the X-ray diffraction data, the copper(II) complex prepared based on bis(salicylidene) hydrazone of glutaric acid has an analogous structure.[6,7]

According to the results of thermogravimetric analysis (Table 1), the elimination of the solvent molecules involved in complexes **1** and **2** occurred at 40—130 °C and was not accompanied by noticeable thermal effects. The pyridine molecule that is ivolved in a strong coordination bond was eliminated at higher temperature (90—260 °C). The process was accompanied by the *endo* effect with a minimum in the DTA curve at 150—230 °C. At 260—300 °C, the acyldihydrazone molecule underwent thermooxidative destruction grading into burning-out of the organic residue. The latter process was characterized by a strong exothermic effect.

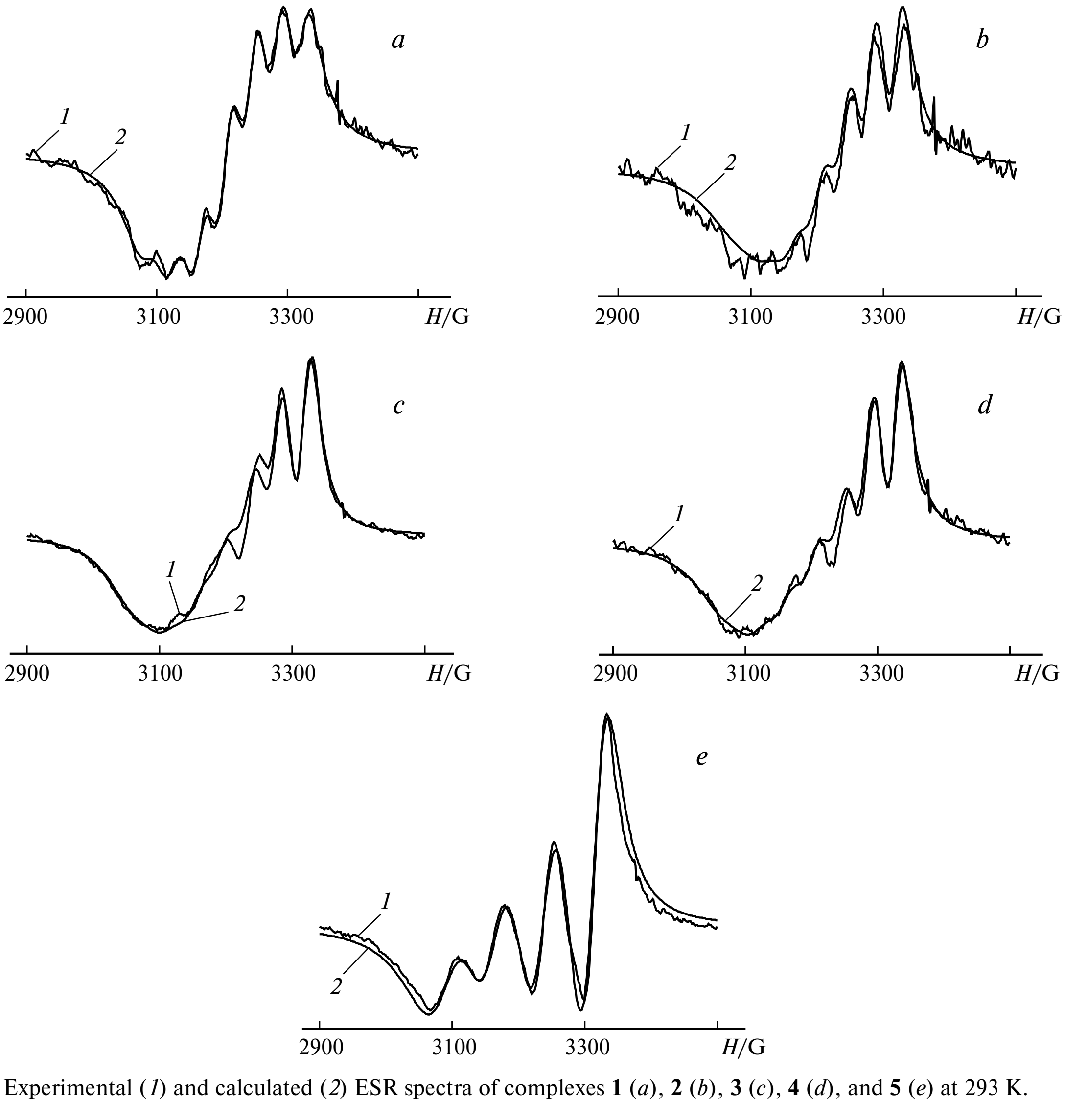


Fig. 1. Experimental (*1*) and calculated (*2*) ESR spectra of complexes **1** (*a*), **2** (*b*), **3** (*c*), **4** (*d*), and **5** (*e*) at 293 K.

Table 2. Parameters of the ESR spectra of the copper(II) complexes with 2-hydroxyacetophenone acyldihydrazones

Compound	g	$a_{Cu} \cdot 10^4$ /cm^{-1}	Parameters of the line width/G				σ (%)	$g_{\perp}$	$g_{\parallel}$	$A_{\parallel}$ /G
			α	β	γ	δ				
1	2.110	38.2	29.5	3.0	−0.5	2.1	2.0	2.05	2.14	68
2	2.112	38.1	32.2	9.5	1.0	3.4	5.3	2.04	2.15	61
3	2.117	39.8	32.0	7.6	−1.1	5.3	3.1	2.03	2.24	144
4	2.112	40.3	32.6	8.9	−0.3	7.5	2.9	2.02	2.34	155
5	2.110	72.1	50.6	10.0	1.1	—	2.5	2.01	2.23	185

The ESR spectra of solutions of complexes **1—4** (Fig. 1, *a—d*) have an isotropic signals with a well-resolved seven-line hyperfine structure with the coupling constant of ~40 G (Table 2), which is caused[2—8] by the exchange coupling between the unpaired electron and two equivalent copper nuclei ($I = 3/2$). Previously,[11,12] a seven-line hyperfine structure was observed for forbidden transitions in the ESR spectra of polycrystalline samples of some binuclear copper(II) complexes with short metal—metal distances (~3 Å) favorable for a strong antiferromagnetic exchange interaction ($-2J$ is about several hundreds of reciprocal centimeters). In the binuclear complexes under study, the direct overlapping of the magnetic orbitals is impossible because of a large distance between the paramagnetic centers (up to 10 Å), and the most probable mechanism of spin-spin coupling involves the indirect exchange through the chain of σ bonds of the polymethylene bridge.

Theoretical analysis[1] demonstrated that the sufficient condition for a hyperfine structure from two copper nuclei to occur is $A_{Cu} \ll |-2J|$ or $|-2J| \gg 0.02$ cm^{-1}. In this case, each unpaired electron interacts with two nuclear spins and the ESR spectrum shows a seven-line hyperfine structure from two copper nuclei with one-half the constant. A more rigorous treatment showed[3] that in complexes characterized by a weak exchange interaction through the polymethylene chain with n = 1—4, the exchange integral is 1—3 cm^{-1}.

An increase in the length of the polymethylene chain, which separates the coordination polyhedra, to five units leads to a substantial decrease in $-2J$. As a result, the ESR spectrum of complex **5** has an isotropic signal with a four-line hyperfine structure from one nucleus having the "normal" value of the coupling constant, which is typical of monomeric copper(II) complexes (Fig. 1, *e*).

An increase in the length of the polymethylene bridge leads to interesting changes in the ESR spectra of solutions frozen at 77 K. Thus, the spectra of complexes **1** and **2** show an anisotropic signal typical of systems with the axially symmetrical g factor ($g_{\perp}$ = 2.04—2.05, $g_{\parallel}$ = 2.14—2.15). In these spectra, a well-resolved seven-line hyperfine structure from two equivalent copper nuclei with the constant of 61—68 G is observed in the parallel orientation (Fig. 2, *a*). When the length of the polymethylene chain is increased to three—four units, a seven-line hyperfine structure disappears and a poorly

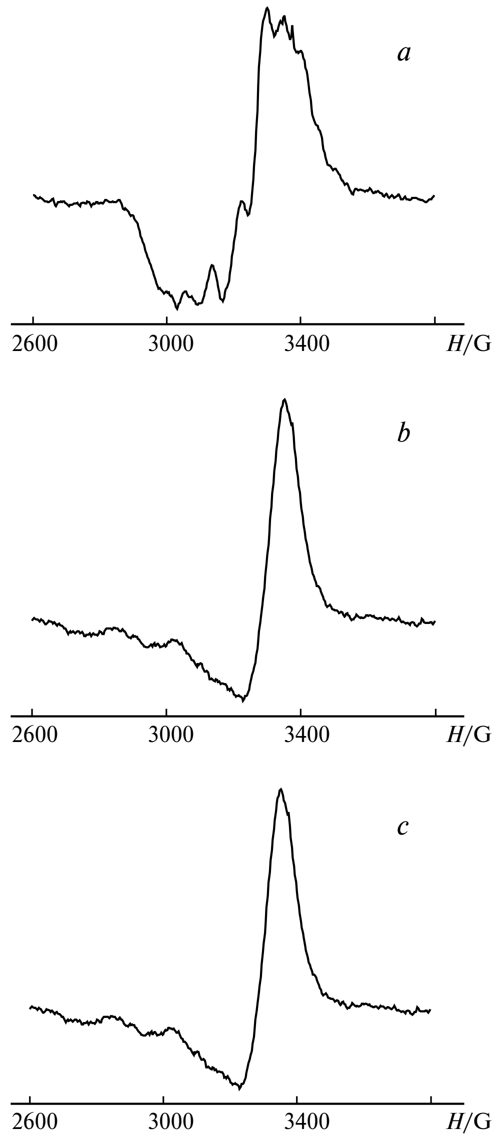


Fig. 2. ESR spectra of solutions of complexes **1** (*a*), **4** (*b*), and **5** (*c*) at 77 K.

resolved hyperfine structure from one copper nuclei with the constant of 144—145 G is observed (Fig. 2, *b*). The ESR spectrum of a frozen solution of the complex based on acyldihydrazone of pimelic acid ($n = 5$) has a pronounced hyperfine structure from one copper nucleus in the parallel orientation (Fig. 2, *c*), and the constant of the hyperfine structure increases to 185 G. This indicates that weak exchange interactions between the copper cations through the polymethylene chain are retained in frozen solutions, but these interactions act at substantially smaller distances.

References

1. K. A. Forster, D. R. Brown, M. D. Timken, D. G. Van Derveer, R. L. Belford, and E. K. Barefield, *J. Coord. Chem.*, 1988, **19**, 123.
2. G. M. Larin, B. B. Umarov, V. V. Minin, Yu. V. Rakitin, V. G. Yusupov, N. A. Parpiev, and Yu. V. Buslaev, *Dokl. Akad. Nauk SSSR,* 1988, **303**, 139 [*Dokl. Chem.*, 1988 (Engl. Transl.)].
3. G. M. Larin, V. V. Minin, and Yu. V. Rakitin, *Neorg. Mater.,* 1994, **30**, 1424 [*Inorg. Mater.*, 1994, **30** (Engl. Transl.)].
4. G. M. Larin, V. F. Shul´gin, E. A. Sarnit, and Yu. V. Rakitin, *Koord. Khim.,* 1999, **25**, 356 [*Russ. J. Coord. Chem.*, 1999, **25** (Engl. Transl.)].
5. V. F. Shul´gin, E. A. Sarnit, and G. M. Larin, *Koord. Khim.,* 1998, **24**, 222 [*Russ. J. Coord. Chem.*, 1998, **24** (Engl. Transl.)].
6. G. M. Larin, V. F. Shul´gin, and E. A. Sarnit, *Mendeleev Commun.*, 1999, 129.
7. G. M. Larin, V. F. Shul´gin, and E. A. Sarnit, *Zh. Neorg. Khim.,* 2000, **45**, 1010 [*Russ. J. Inorg. Chem.*, 2000, **4** (Engl. Transl.)].
8. 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).
9. V. A. Kogan, V. V. Zelentsov, G. M. Larin, and V. V. Lukov, *Kompleksy perekhodnykh metallov s gidrazonami. Fiziko-khimicheskie svoistva i stroenie* [*Transition Metal Complexes with Hydrazones. Physicochemical Properties and Structure*], Nauka, Moscow, 1990, 112 pp. (in Russian).
10. M. T. Toshev, V. G. Yusupov, Z. T. Karimov, Kh. B. Dustov, B. B. Umarov, N. A. Parpiev, and G. G. Aleksandrov, *Koord. Khim.,* 1990, **16**, 1092 [*Sov. J. Coord. Chem.*, 1990, **16** (Engl. Transl.)].
11. T. D. Smith and Y. R. Pilbrow, *Coord. Chem. Rev.*, 1974, **13**, 173.
12. Yu. V. Rakitin, *Koord. Khim.,* 1981, **7**, 1311 [*Sov. J. Coord. Chem.*, 1981, **7** (Engl. Transl.)].

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