Molecular structures and ESR spectra of copper(II) complexes with 2-hydroxypropiophenone acyldihydrazones

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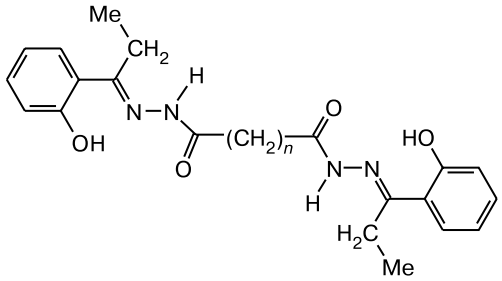
The dinuclear copper(II) complexes with 2-hydroxypropiophenone acyldihydrazones (H_4L) having the composition $[Cu_2L \cdot mPy]$, where the L ligand contains the polymethylene chain with different lengths (from two to five units), were synthesized and studied. The crystal and molecular structures of the 2-hydroxypropiophenone adipoylhydrazone complex $[Cu_2L \cdot 4Py] \cdot Py$ were established by X-ray diffraction analysis. Copper atoms are 8.212 Å distant from each other, and their nearest environment has the tetragonal pyramidal geometry. The ESR spectra of solutions of the complexes based on acyldihydrazones of succinic, glutaric, and adipic acids contain seven HFS lines with the constant $\sim 40 \cdot 10^{-4}$ cm^{-1} from two equivalent copper atoms. The spectra were interpreted as a result of the spin-spin exchange interaction of two unpaired electrons. An increase in the polymethylene chain length to five units prevents exchange interactions. The ESR spectrum of the complex with acyldihydrazone of pimelic acid contains a signal of four HFS lines with $a_{Cu} = 73.4 \cdot 10^{-4}$ cm^{-1}, which is typical of mononuclear copper(II) complexes.

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

Several classes of complexes, whose ESR spectra exhibit weak exchange interactions between paramagnetic centers through a polymethylene chain, are known.[1—9] We have recently[10,11] synthesized and studied a new type of copper(II) coordination compounds with an exchange interaction through the system of σ-bonds, *viz.*, complexes based on acyldihydrazones of 2-hydroxyacetophenone and its aryl-substituted derivatives. It is established[11] that, unlike the bissalicylidenehydrazones, exchange interactions in the 2-hydroxyacetophenone complexes are insensitive to the nature of substituent in the benzene ring. This result was explained by the positive inductive effect of the methyl group of the ketone aliphatic fragment. It was of interest to check a change in the conductivity of weak exchange interactions through the polymethylene chain $(CH_2)_n$ due to the further increase in the electron-releasing character of the aliphatic radical. For this purpose, we synthesized coordination compounds of copper(II) with dihydrazones of 2-hydroxypropiophenone and lower dicarboxylic acids (from succinic to pimelic acid, n = 2—5).



We failed to synthesize a similar complex based on acyldihydrazone of malonic acid (n = 1), although several attempts were made.

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Experimental

The coordination compounds were synthesized using a procedure developed previously for the complexes of 2-hydroxyacetophenone acyldihydrazones.[10]

The percentage of copper was calculated from the trilonometric titration data after the weighed samples were thermally decomposed. The percentage of nitrogen was determined by the Dumas micromethod. Thermogravimetric curves were obtained on a Paulik—Paulik—Erdey Q derivatograph in a static air atmosphere with a heating rate of 10 °C min^{-1}, using an open ceramic crucible as the sample holder and calcined alumina as reference. IR spectra were recorded in the 4000—400 cm^{-1} interval on a Nicollet FTIR spectrophotometer (KBr pellets). ESR spectra were recorded on a PS 100.X instrument in the X interval using a concentration of the complexes of $1—5 \cdot 10^{-3}$ mol L^{-1}. A pyridine—toluene (1 : 1 vol/vol) mixture was used as solvent. The spectra were simulated by a program package described in the monograph.[12]

According to the elemental and thermal analyses data, the composition of the complexes corresponds to the common formula $Cu_2L \cdot m$Py$\cdot k$MeOH.

Complex $Cu_2L \cdot 2Py \cdot 3MeOH$ (**1**, $n = 2$). Found (%): Cu, 16.01; N, 10.14. $C_{35}H_{44}Cu_2N_6O_7$. Calculated (%): Cu, 16.14; N, 10.67. IR, ν/cm^{-1}: 1590 (C=N); 1525 (N=C—O—); 1345 (CO_{phen}).

Complex $Cu_2L \cdot 2Py \cdot 3MeOH$ (**2**, $n = 3$). Found (%): Cu, 17.54; N, 11.01. $C_{34}H_{38}Cu_2N_6O_5$. Calculated (%): Cu, 17.23; N, 11.39. IR, ν/cm^{-1}: 1585 (C=N); 1525 (N=C—O—); 1345 (CO_{phen}).

Complex $Cu_2L \cdot 2Py \cdot 4MeOH$ (**3**, $n = 4$). Found (%): Cu, 14.49; N, 9.90. $C_{38}H_{52}Cu_2N_6O_8$. Calculated (%): Cu, 15.27; N, 10.67. IR, ν/cm^{-1}: 1585 (C=N); 1525 (N=C—O—); 1345 (CO_{phen}).

Complex $Cu_2L \cdot 2Py \cdot MeOH$ (**4**, $n = 5$). Found (%): Cu, 16.29; N, 10.55. $C_{36}H_{42}Cu_2N_6O_5$. Calculated (%): Cu, 16.60; N, 10.97. IR, ν/cm^{-1}: 1590 (C=N); 1515 (N=C—O—); 1350 (CO_{phen}).

Single crystals of the $[Cu_2L \cdot 4Py] \cdot Py$ complex were obtained by recrystallization of compound **3** from pyridine. Crystals of $C_{44}H_{46}Cu_2N_8O_4 \cdot NC_5H_5$ are monoclinic with the linear sizes 0.22×0.28×0.49 mm. Space group is $P2_1/n$, $a = 10.807(3)$, $b = 15.823(3)$, $c = 14.028(5)$ Å, $\beta = 101.97(2)°$, $V = 2347(1)$ $Å^3$, $M = 957.1$, $Z = 2$, $d_{calc} = 1.35$ g cm^{-3}, $\mu = 9.55$ cm^{-1}, $F(000) = 997.16$. X-ray diffraction analysis was carried out at ~20 °C on an Enraf—Nonius CAD-4 automated four-circle diffractometer using Mo-Kα radiation ($\lambda = 0.71069$ Å), $\theta_{max} = 30°$. During X-ray analysis 4262 reflections were collected, of which 3707 reflections were symmetrically independent (averaging R factor 0.055). Absorption in crystal was applied by the azimuth scan-angle method.[13] The structure (Fig. 1) was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation using the CRYSTALS program complex.[14] The C(23), C(24), C(25), and N(5) atoms of the disordered solvate pyridine molecule were refined isotropically. The positions of H atoms were calculated geometrically and refined isotropically with fixed positional and thermal parameters. The refinement used 1371 reflections with $I > 2\sigma(I)$ (274 refined parameters, number of reflections per parameter 5.0). The refinement was performed using the Chebyshev weighing scheme[15] with the parameters 1.030, 0.916, and 0.701. The final divergence factors were $R = 0.074$ and $R_w = 0.073$, GOOF = 1.159. The residual electron density from the difference Fourier synthesis was 0.38 and 0.32 e $Å^{-3}$. The main bond lengths and bond angles are presented in Table 1.

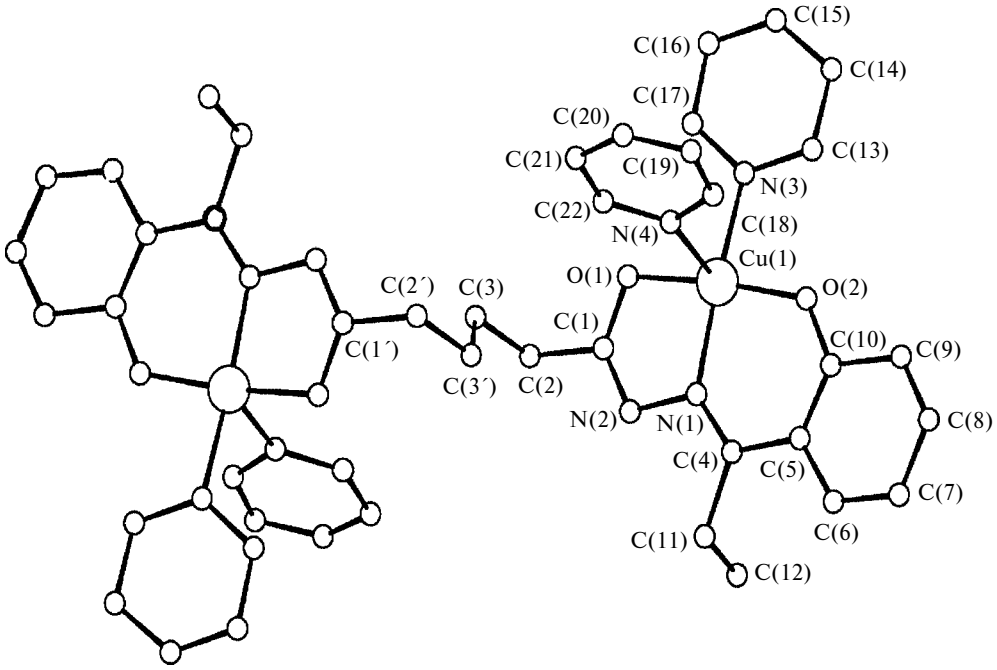


Fig. 1. Molecular structure of the copper(II) complex with 2-hydroxypropiophenone adipoylhydrazone (**3**).

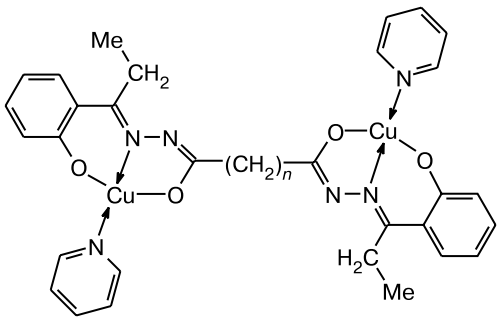
Table 1. Main bond lengths (*d*) and bond angles (ω) in the copper(II) complex with 2-hydroxypropiophenone adipoylhydrazone (**3**)

Bond	*d*/Å	Angle	ω/deg
Cu(1)—O(1)	1.958(6)	O(1)—Cu(1)—O(2)	172.2(3)
Cu(1)—O(2)	1.897(8)	O(1)—Cu(1)—N(1)	81.2(4)
Cu(1)—N(1)	1.936(8)	O(2)—Cu(1)—N(1)	92.7(4)
Cu(1)—N(3)	2.041(8)	O(1)—Cu(1)—N(3)	93.5(4)
Cu(1)—N(4)	2.343(9)	O(2)—Cu(1)—N(3)	90.9(4)
O(1)—C(1)	1.294(11)	N(1)—Cu(1)—N(3)	162.4(3)
O(2)—C(10)	1.316(13)	O(1)—Cu(1)—N(4)	91.5(3)
N(1)—N(2)	1.41(1)	O(2)—Cu(1)—N(4)	95.1(4)
N(1)—C(4)	1.295(12)	N(1)—Cu(1)—N(4)	109.1(3)
N(2)—C(1)	1.283(12)	N(3)—Cu(1)—N(4)	87.7(3)
N(3)—C(13)	1.349(12)	Cu(1)—O(1)—C(1)	109.9(7)
N(3)—C(17)	1.334(14)	Cu(1)—O(2)—C(10)	125.8(7)
N(4)—C(18)	1.336(15)	Cu(1)—N(1)—N(2)	113.4(7)
N(4)—C(22)	1.336(13)	Cu(1)—N(1)—C(4)	129.3(8)
C(1)—C(2)	1.504(14)	N(2)—N(1)—C(4)	117.3(8)
C(2)—C(3)	1.493(14)	N(1)—N(2)— C(1)	110.3(9)
C(3)—C´(3)	1.500(19)	Cu(1)—N(3)—C(13)	123.2(9)
C(4)—C(5)	1.459(14)	Cu(1)—N(3)—C(17)	119.8(8)
C(4)—C(11)	1.512(14)	C(13)—N(3)—C(17)	116.9(9)
C(5)—C(6)	1.414(14)	Cu(1)—N(4)—C(18)	121.7(9)
C(5)—C(10)	1.365(14)	Cu(1)—N(4)—C(22)	122.2(8)
C(6)—C(7)	1.379(15)	C(18)—N(4)—C(22)	115.2(10)
C(7)—C(8)	1.339(15)	O(1)—C(1)—N(2)	125.2(10)
C(8)—C(9)	1.393(16)	O(1)—C(1)—C(2)	115.8(11)
C(9)—C(10)	1.416(15)	N(2)—C(1)—C(2)	119.0(11)
C(11)—C(12)	1.514(14)		

The complete set of X-ray diffraction data is deposited with the Cambridge Structural Data Bank (No. CCDC196802).

Results and Discussion

The results of studying the reactions of copper(II) acetate with the products of condensation of dihydrazides of aliphatic dicarboxylic acids with 2-hydroxybenzaldehydes and 2-hydroxyacetophenones indicate that these reactions proceed *via* the same scheme and afford dinuclear complexes.[4—11] Copper acetate reacts similarly with 2-hydroxyphenone acyldihydrazone to produce Cu^{II} complexes **1—4**, in which the ligand contains a polymethylene chain with different lengths (n = 2—5).



Complex formation is accompanied by the transformation of acyldihydrazones into the fourfold deprotonated species, which fact is confirmed by the IR spectra demonstrating the disappearance of the "amide-I" band (~1600 cm^{-1} in the spectrum of free acyldihydrazone) and the appearance of two new bands with absorption maxima at 1590—1585 cm^{-1} (stretching vibrations of the group >C=N—N=C<) and 1525—1515 cm^{-1} (stretching vibrations of the C—O bond in the —N=C—O— fragment).[16]

According to the data of thermogravimetric analysis, the methanol molecules are removed from the complexes at a low temperature (40—140 °C) without noticeable thermal effects. Strongly coordinated pyridine molecules are removed at a higher temperature (140—280 °C). The process is accompanied by the endotherm with a minimum in the DTA curve at 170—230 °C. The further temperature increase results in the thermooxidative destruction of acyldihydrazone followed by burning out of the organic residue. These processes are accompanied by a series of strong exothermics with maxima in the DTA curve at 300—390 and 430—600 °C.

To confirm the structures of the compounds, we performed the X-ray diffraction analysis for the copper(II) complex with 2-hydroxypropiophenone adipoylhydrazone. It was established that the $[Cu_2L \cdot 4Py] \cdot Py$ complex has the molecular structure and its crystal contains a solvate pyridine molecule. The coordination sphere of the Cu(1) atom is of the [4+1] type[17] and has the tetragonal pyramidal geometry with the N(4)C(18)—C(22) pyridine molecule in the axial position. The equatorial plane is formed by the O(1), O(2), and N(1) atoms of the doubly deprotonated chelatophoric group of acyldihydrazone and the N(3) atom of the second pyridine molecule. The Cu(1)O(1)O(2)N(1)N(2)C(1)C(4)—C(10) fragment is virtually planar (deviations of the atoms from the root-mean-square plane do not exceed 0.09 Å). The Cu atom shifts from the plane of the base to the pyramid center by 0.196 Å. The Cu(1)—N(4) apical bond (2.343(9) Å) is noticeably elongated compared to the Cu(1)—N(1) and Cu(1)—N(3) bonds lying in the equatorial plane (1.936(8) and 2.041(8) Å). The bond lengths and bond angles of the organic ligands are close to standard values.[18,19] The Cu atoms are separated by a chain of nine σ-bonds and are 8.212 Å apart.

The ESR spectra of solutions of complexes **1—3** contain an isotropic signal with the well resolved HFS of seven lines with the ratio of intensities 1 : 2 : 3 : 4 : 3 : 2 : 1 (Fig. 2) and the constant ~40 Oe (Table 2). This signal is generated by the exchange interaction of an unpaired electron with nuclei of two equivalent Cu atoms.

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

Compound	n^a	g^b	$a_{Cu}{}^c \cdot 10^4/cm^{-1}$	Linewidth parameters^d/G				σ^e (%)
				α	β	γ	δ	
1	2	2.112	38.0	27.6	6.6	−0.04	2.09	2.3
2	3	2.112	39.4	28.8	5.8	−1.82	4.05	3.5
3	4	2.112	39.1	34.1	10.1	−1.12	6.64	2.8
4	5	2.109	73.5	48.1	11.4	2.8	—	2.9

[a] Number of units of the polymethylene chain.
[b] Determination error ±0.003.
[c] Determination error ±0.5 cm^{-1}.
[d] Determination error ±0.5 G.
[e] Error characterizing the deviation between the simulated and experimental spectra ($R \cdot 100$).

A similar signal has previously been observed in the ESR spectra of the mixed-valence copper(I)—copper(II) complexes containing the metal—metal covalent bond.[20] Seven HFS lines are sometimes resolved on signals of forbidden transitions of dimeric copper complexes with a short metal—metal distance (~3 Å) and a strong antiferromagnetic interaction.[21,22] The molecular structure of the complexes under study excludes the direct overlap of magnetic orbitals of the copper atoms, *i.e.*, orbitals containing unpaired electrons. Therefore, the indirect exchange through the system of σ-bonds of the polymethylene chain containing up to four units seems, in our opinion, most probable.

An increase in the length of the polymethylene chain of the ligand to five units strongly decreases the $-2J$ value, and a usual (for mononuclear complexes) isotropic signal of four HFS lines from one Cu nucleus with the normal constant value was detected in the ESR spectrum of complex **4** (see Table 2). This indicates that an increase in the electron-releasing ability of the aliphatic radical on going from 2-hydroxyacetophenone acyldihydrazones to 2-hydroxypropiophenone acyldihydrazones does not increase the conductivity of spin-spin exchange interactions through the polymethylene chain. It can be assumed that the pentamethylene chain has a critical length preventing weak exchange interactions between the copper(II) cations.

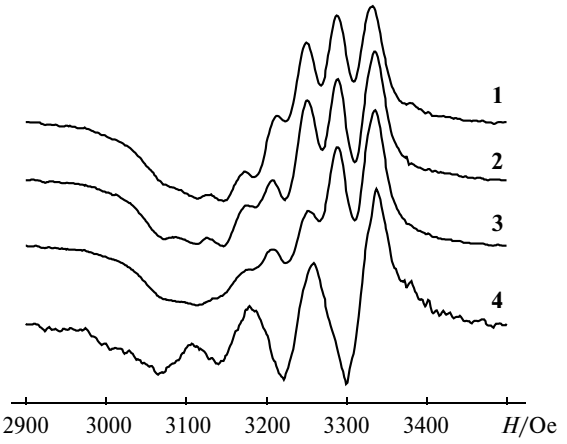


Fig. 2. Experimental ESR spectra of solutions of complexes **1**—**4** at 298 K.

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