ESR study of weak exchange interactions in binuclear copper(II) complexes with acyldihydrazones of fluorinated β-diketones

G. M. Larin,[a] V. F. Shul´gin,[b] E. D. Mel´nikova,[b] V. Ya. Zub,[c] and Yu. V. Rakitin[d]*

[a]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 954 1279. E-mail: lagema@igic.ras.ru
[b]V. I. Vernadskii Taurida National University, 4 ul. Yaltinskaya, 95007 Simferopol, Ukraine. Fax: (065 2) 23 2310. E-mail: vshul@ccssu.crimea.ua
[c]Taras Shevchenko Kiev State University, 60 ul. Vladimirskaya, 01033 Kiev, Ukraine, E-mail: vera@anorgchemie.univ.kiev.ua
[d]I. V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Kola Science Center, Russian Academy of Sciences, 26 A ul. Fersmana, 184200 Apatity, Murmansk oblast´, Russian Federation. Fax: +7 (881 555) 76 425. E-mail: rakitin@chemy.kolasc.net.ru

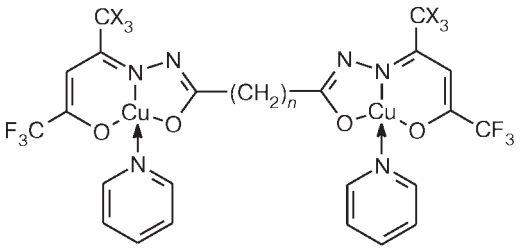
A series of binuclear copper(II) complexes with acyldihydrazones of aliphatic dicarboxylic acids (from malonic to adipic) and fluorinated β-diketones (trifluoro- and hexafluoroacetylacetone) of composition $Cu_2L \cdot 2Py$ (H_4L is acyldihydrazone) were studied by ESR spectroscopy. The ESR spectra of solutions of complexes with trifluoroacetylacetone acyldihydrazones have an isotropic signal with a seven-line hyperfine structure from two equivalent copper nuclei ($g = 2.112$, $a_{Cu} = (39—40) \cdot 10^{-4}$ cm^{-1}), which is indicative of weak exchange interactions between the paramagnetic centers due to spin density delocalization through a chain of the σ-bonds of the polymethylene bridge. On going to hexafluoroacetylacetone derivatives, the coupling is suppressed and the ESR spectra of solutions of such complexes show a signal with a four-line hyperfine structure ($g = 2.121—2.131$, $a_{Cu} = (55—63) \cdot 10^{-4}$ cm^{-1}) typical of mononuclear copper complexes.

Key words: ESR spectra, hyperfine structure, spin-spin exchange interactions, binuclear copper(II) complexes, hydrazones of β-diketones and dicarboxylic acids.

In recent years, studies of exchange interactions between paramagnetic cations separated by distances longer than 3 Å have attracted considerable attention.[1—11] These investigations are promising from both the theoretical and practical standpoints because they open up possibilities for the construction of new magnetic materials (molecular paramagnetics exhibiting weak antiferromagnetism) and provide prerequisites for an explanation of the mechanism of high-Tc superconductivity.[7] Studies of weak exchange interactions between paramagnetic centers are also of importance for elucidating the mechanisms of long-range (for distances larger than 10 Å) electron transfer in biochemical processes.[1]

The main information on this problem was obtained in studies of static magnetic susceptibilities of crystalline samples.[1—5] The data on weak exchange interactions in solutions are scarce and refer primarily to copper(II) complexes with acetylacetone acyldihydrazones[6—9] and salicylaldehyde acyldihydrazones.[10—13]

In the present study, solutions of binuclear copper(II) complexes with trifluoro- and hexafluoroacetylacetone acyldihydrazones **1** and **2** were examined by ESR spectroscopy.



1, **2**

X = H (**1**); F = (**2**)

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Table 1. Compositions of the copper(II) compounds and the data from elemental analysis

Compound*	Found / Calculated (%)		Molecular formula
	N	Cu	
$Cu_2L \cdot Py \cdot H_2O$	10.27	19.83	$C_{18}H_{18}Cu_2F_6N_5O_5$
(**1**, $n = 1$)	11.22	20.34	
$Cu_2L \cdot 2Py$	11.30	17.76	$C_{24}H_{22}Cu_2F_6N_6O_4$
(**1**, $n = 2$)	12.00	18.20	
$Cu_2L \cdot 2Py$	11.80	17.20	$C_{25}H_{24}Cu_2F_6N_6O_4$
(**1**, $n = 3$)	11.80	17.80	
$Cu_2L \cdot 2Py$	10.80	17.33	$C_{26}H_{26}Cu_2F_6N_6O_4$
(**1**, $n = 4$)	11.54	17.45	
$Cu_2L \cdot 4Py$	11.60	13.88	$C_{33}H_{24}Cu_2F_{12}N_8O_4$
(**2**, $n = 1$)	11.78	13.36	
$Cu_2L \cdot 2Py$	11.20	15.59	$C_{24}H_{16}Cu_2F_{12}N_6O_4$
(**2**, $n = 2$)	10.41	15.75	
$Cu_2L \cdot 3Py$	9.90	14.05	$C_{30}H_{23}Cu_2F_{12}N_7O_4$
(**2**, $n = 3$)	10.89	14.12	
$Cu_2L \cdot 4Py$	12.10	12.17	$C_{36}H_{30}Cu_2F_{12}N_8O_4$
(**2**, $n = 4$)	11.28	12.80	

* Hereinafter, *n* indicates the length of the polymethylene chain in the acyldihydrazone molecule.

Experimental

Complexes based on trifluoroacetylacetone acyldihydrazones were synthesized according to the procedure,[7] which has been developed previously for acetylacetone. Trifluoroacetylacetone (20 mmol) was added to a suspension of dihydrazide (10 mmol) in MeOH (50 mL). The reaction mixture was magnetically stirred until the dihydrazide was dissolved and then kept for 48 h. A solution of copper(II) acetate (20 mmol) in a minimum amount of concentrated aqueous ammonia was added to the reaction solution. The precipitate that formed was kept over the mother liquor for 24 h, filtered off, washed with water and 95% EtOH, and finally dried in air and in a desiccator over $CaCl_2$. Complexes with pyridine were prepared by isothermal evaporation of a pyridine solution of the ammonia adducts.

Taking into account that hexafluoroacetylacetone is highly prone to adding proton-donor reagents, its acyldihydrazones were prepared according to a special procedure. A mixture containing dihydrazide of the corresponding acid (6 mmol), hexafluoroacetylacetone (14 mmol), and benzene (50 mL) was refluxed for 2 h. The solvent and an excess of β-diketone were distilled off and the addition product was dehydrated by heating at 120—140 °C *in vacuo* for 30 min.

The complexes were obtained as finely crystalline dark-lilac (**1**) or dark-green (**2**) compounds in 70—80% yields with respect to the theoretical values. The elemental analysis data are given in Table 1.

The ESR spectra were recorded on an ADANI PS100X instrument (Belarus) in a $CHCl_3$—pyridine mixture (10 : 1, v/v) at the concentrations of the complex of $(1—5) \cdot 10^{-3}$ mol L^{-1}. The magnetic field was measured on a nuclear magnetometer using the diphenylpicrylhydrazyl radical as the standard. Theoretical simulation of the spectra was carried out using a program package described previously.[14] The ESR parameters were determined by comparing the experimental spectra with the theoretical spectra constructed by summation of the line shapes of the individual transitions centered at the resonance field (H_{res}). The line shapes were described as the sums of the Lorentz and Gaussian fitting curves. According to the relaxation theory, the one-center contributions to the line widths ($\Delta H_{res}(i)$) were specified by the equation

$$\Delta H_{res}(i) = \alpha + \beta m_I + \gamma m_I^2, \quad (1)$$

where m_I is the projection of the nuclear spin, and α, β, and γ are the parameters of the line width. Since complexes containing polymethylene bridges are stereochemically nonrigid, we also took into account the contribution

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

associated with intramolecular motions about the polymethylene bridge in the binuclear complex,[15] which influence the ex-

Table 2. Parameters of the ESR spectra of complexes **1** and **2**

Compound	Number of lines	*g*	$a_{Cu} \cdot 10^4$ /cm^{-1}	Parameters of the line width /G				σ (%)
				α	β	γ	δ	
1 ($n = 1$)	7	2.110	38.5	26.6	3.50	−1.60	3.6	2.6
1 ($n = 2$)	7	2.110	39.6	31.5	1.90	−3.5	3.9	5.9
1 ($n = 3$)	7	2.110	40.0	29.7	4.60	−2.6	4.0	4.7
1 ($n = 4$)	7	2.110	40.5	30.6	8.50	0.30	7.10	3.2
2 ($n = 1$)	4	2.144	57.0	50.0	4.60	2.00	—	1.6
2 ($n = 2$)[a]	4	2.141	51.1	60.0	6.20	1.1	—	1.8
2 ($n = 3$)[a]	4	2.118	62.1	26.7	9.4	6.5	17.0	6.5
2 ($n = 4$)[a]	4	2.117	60.1	23.3	8.10	6.4	17.1	6.1
2 ($n = 4$)[b]	4	2.117	65.4	29.4	16.2	3.1	13.0	4.2

[a] The spectra were simulatied taking into account an additional hyperfine structure from one nitrogen atom. [b] The second derivative of the ESR spectrum.

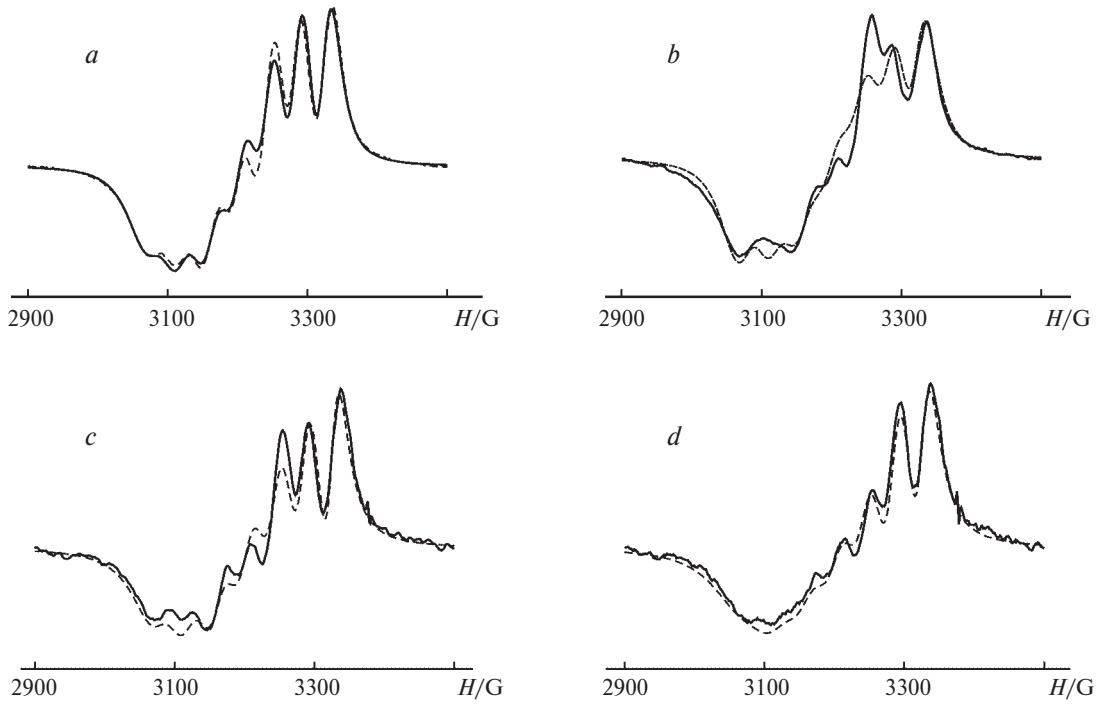

Fig. 1. Experimental (solid curve) and theoretical (dashed curve) ESR spectra of complexes **1** (n = 1) (*a*), **1** (n = 2) (*b*), **1** (n = 3) (*c*), and **1** (n = 4) (*d*).

change. The g_0, a_{Cu}, α, β, and γ parameters were varied until the minimum of the error functional was attained

$$\sigma = \frac{1}{N}\left[\sum_{i=1}^{N}(Y_i^{exp} - Y_i^{th}\right],$$

where Y_i^{exp} and Y_i^{th} are the experimental and theoretical values of the amplitude of the ESR signal at N discrete points of the spectra, respectively. The reliability of the results was achieved by using a large number of experimental points ($N \approx 400$) and was provided by small residual values of σ. The parameters of the best approximation at the minimum residual σ values are given in Table 2. The agreement between the experimental and theoretical ESR spectra is illustrated by Fig. 1.

Results and Discussion

Previously,[7—9] solutions of copper(II) complexes with acetylacetone acyldihydrazones containing polymethylene bridges of the length from one to four units have been studied by ESR spectroscopy, which revealed an isotropic signal with a seven-line hyperfine structure and with the intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1, g = 2.092—2.097 and $a_{Cu} = 44.3 \cdot 10^{-4}$ cm^{-1}. The signal was accounted for coupling of the unpaired electron with two equivalent copper nuclei (I = 3/2). It was demonstrated[5,13] that weak exchange interaction between copper cations at $|-2J| \gg a_{Cu}$ is sufficient for the manifestation of this spectrum for copper(II) dimers linked *via* a polymethylene bridge.

The isotropic signals in the ESR spectra of the copper(II) complexes with trifluoroacetylacetone acyldihydrazones (**1**) under consideration also consist of seven lines with a hyperfine structure (see Fig. 1) characterized by the close spin-Hamiltonian parameters and line widths (see Table 2). The usual order of the arrangement of the lines (α ≫ β > γ) is retained. The δ value increases as n is increased, which is attributable to an increase in the conformational lability of the polymethylene chain.

Hence, the replacement of one methyl group in acetylacetone acyldihydrazones by the trifluoromethyl group is not accompanied by a change in the overall pattern and the parameters of the ESR spectra of their complexes with copper(II) cations. This fact is indicative of the retention of weak spin-spin exchange interactions between the paramagnetic centers. In the case of complexes based on hexafluoroacetylacetone acyldihydrazones, the intensities of exchange interactions are decreased resulting in $|-2J| \ll a_{Cu}$ due to which the ESR spectra of complexes **2** have an isotropic signal with a four-line hyperfine structure from one of the copper nuclei with the intensity ratio of 1 : 1 : 1 : 1. However, an increase in the length of the polymethylene chain in this series of complexes leads to substantial changes in the overall spectral pattern, the spin-Hamiltonian parameters, and the line widths. The ESR spectra of the complexes of acyldihydrazones of malonic and succinic acids have a poorly resolved signal with g = 2.130, $a_{Cu} \approx 50$ cm^{-1}

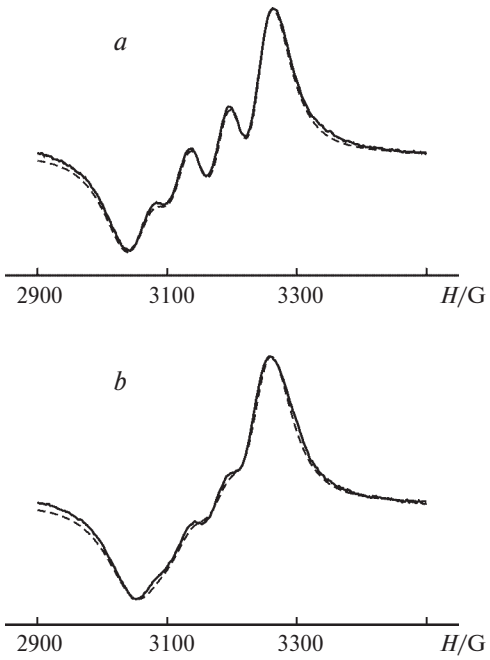

Fig. 2. Experimental (solid curve) and theoretical (dashed curve) ESR spectra of complexes **2** (n = 1) (*a*) and **2** (n = 2) (*b*).

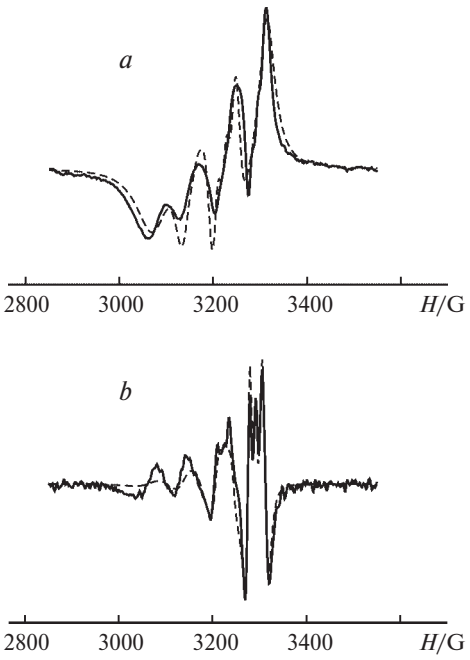

Fig. 3. Experimental (solid curve) and theoretical (dashed curve) ESR spectra of complexes **2** (n = 4). The first (*a*) and second (*b*) derivatives.

(Fig. 2), and the anomalously large α value (see Table 2). This may be associated with residual very weak interactions between the paramagnetic centers.

An increase in the length of the polymethylene chain to three or four units results in complete suppression of exchange interactions, and the ESR spectra of the complexes based on acyldihydrazones of glutaric and adipic acids have a signal with a four-line hyperfine structure typical of monomeric copper(II) complexes (g = 2.119—2.120; $a_{Cu} = (62—63)\cdot 10^{-4}$ cm^{-1}) and also show evidence of an additional hyperfine structure from one nitrogen nucleus with the constant of about 16 Gs (Fig. 3). The high-field line of the hyperfine structure from the copper nucleus, which is the narrowest line in the ESR spectra of copper(II) complexes, is weakly split. The measurement of the second derivative of the ESR spectra of these compounds demonstrated that splitting is an additional three-line hyperfine structure with the intensity ratio of 1 : 1 : 1 from one nitrogen atom (Fig. 3, *b*). However, a large discrepancy between the experimental and theoretical spectra (see Table 2) (latter spectrum was calculated without considering weak exchange interactions) indicates that weak spin-spin exchange interactions in the ESR spectra of copper complexes with hydrazones of hexafluoroacetylacetonate and dicarboxylic acids are not completely suppressed and have a nonzero exchange integral. This is manifested in a more complex dependence of the line widths in the ESR spectra of complexes **2** (n = 1)—**2** (n = 4) as compared to Eq. (1).

Suppression of weak exchange interactions between the copper(II) cations in complexes **2** is attributable to a decrease in the spin density in the coordination polyhedron due to the pronounced negative inductive effect of the trifluoromethyl group.

The ESR spectra of frozen (77 K) solutions of complexes **1** (n = 2)—**1** (n = 4) have an anisotropic signal characteristic of systems with an axial symmetry ($g_\perp$ = 2.05 and $g_\parallel$ = 2.25), the hyperfine structure from one copper atom with the constant A = 170—180 G being observed in the parallel orientation. This is indicative of suppression of exchange interactions between the paramagnetic centers. However, the spectrum of complex **1** (n = 1) shows no hyperfine structure from the copper nucleus in the parallel orientation. It should also be noted that the spectrum becomes more pronounced as the length of the polymethylene chain is increased, which may be associated with weak lower-energy exchange interactions between the copper(II) cations. This assumption was confirmed by the manifestation of a pronounced hyperfine structure in the parallel orientation of the ESR spectra of **2** regardless of the length of the polymethylene chain ($g_\perp$ = 2.04—2.05 and $g_\parallel$ = 2.25—2.30; A = 160—180 G) (Fig. 4).

Previously,[13] we have found that the introduction of different electron-withdrawing substituents (5-bromo-, 2,4-dioxy-, or 5,6-C_4H_4-) into the aromatic ring of salicylidene hydrazone led to a decrease in the limit of conductivity of exchange interactions through the polymethylene chain from four to three units. In the

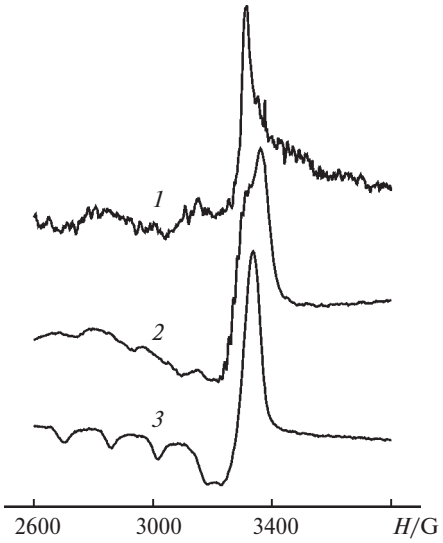

Fig. 4. ESR spectra of complexes **1** (n = 1) (*1*), **1** (n = 2) (*2*), and **1** (n = 3) (*3*) at 77 K.

present study, we demonstrated that further enhancement of electron-withdrawing properties of the peripheral substituents in the chelate ligand of hydrazone (12 fluorine atoms) led to virtually complete suppression of spin-spin exchange interactions through the polymethylene bridge.

Hence, the studies of copper(II) dimers with acylhydrazones of aliphatic dicarboxylic acids (from oxalic to adipic HOOC—$(CH_2)_n$—COOH, where n = 0—8) and chelates of different nature revealed the following facts.[7—14]

1. According to the ESR spectra and the data on the magnetic susceptibilities, antiferromagnetic exchange with the exchange integral $-2J$ = 80 cm^{-1} occurs in solid compounds deprived of the polymethylene bridge (n = 0). The spectra of solutions of these compounds have a broad line due to dipole-dipole interactions, which are weakened proportionally to r^{-3}. Hence, in the presence of the polymethylene chain ($n \geq 1$), the Cu—Cu distance is increased, dipole-dipole interactions are weakened, the line is narrowed, and the hyperfine structure from the copper atoms becomes resolved.[7,8,14]

2. In the solid state, copper(II) dimers with polymethylene bridges (n = 1—4) behave as monomers in which Cu—Cu spin-spin exchange interactions are absent.[7,8,14] The effective magnetic moments are close to purely spin moments and are independent of the temperature. The ESR spectra of solutions of these compounds show a seven-line hyperfine structure from two equivalent copper atoms associated with spin-spin exchange interactions between these atoms.

3. The seven-line ESR spectra of some copper dimers (n = 1, 2, or 4) differ in the shape because the molecules containing polymethylene bridges with n = 1 or 2 are rotated as a unit, whereas intramolecular motion takes place in the molecule with n = 4, *i.e.*, two chelates in the same molecule are independently rotated around the polymethylene bridge with respect to one another. This excludes the formation of the oxo bridges between the copper(II) atoms, which could give rise to the intra- or intermolecular Cu_2O_2 dimeric fragments, whereas the exchange is retained.

4. At $n > 4$, the behavior of binuclear complexes is very similar to that of mononuclear complexes as evidenced by the hyperfine structure from one copper nucleus. At the same time, their ESR spectra differ from the spectra of mononuclear complexes because the distances between the components of the hyperfine structure from the copper nucleus do not obey the Breit—Rabi law as apparent from the occurrence of very weak exchange interactions. In the case of the replacement of one copper atom by a nickel atom, the usual ESR spectrum typical of monomers is observed.

5. In the ESR spectra of dimers, the hyperfine interaction constant from the copper nucleus is half as large as that in the spectra of monomers. It was demonstrated[5,13] that the sufficient condition for antiferromagnetic exchange interactions to occur through a chain of σ bonds is the exchange integral $|-2J| \gg 0.02$ cm^{-1}. We cannot precisely determine the exchange integral in the region of very weak spin-spin exchange interactions comparable with hyperfine splitting.

6. The strength of spin-spin exchange interactions depends primarily on the length of the polymethylene bridge. Spin-spin exchange interactions are weakened as the length of the bridge is increased.

7. Spin-spin exchange interactions are substantially influenced by the electronic structure of the metal-chelate ring. Spin-spin exchange interactions through the polymethylene bridge can reduce to zero when the electron density of the unpaired electron is accepted in the metal-chelate ring.

8. In inorganic compounds, delocalization over the σ bonds can occur.

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