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Exchange interactions in binuclear copper(II) complexes with hydrazones based on saturated dicarbohydrazides

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Abstract. The results of studies of weak spin – spin exchange interactions in binuclear copper(II) complexes with hydrazones based on saturated dicarbohydrazides in which the coordination polyhedra are connected by polymethylene spacers are generalised and systematically described. The bibliography includes 51 references.

I. Introduction

One of the fundamental quantum chemistry ideas — the hypothesis of delocalisation of electrons in molecules — has made possible a new approach to the theory of the chemical bond. A number of experimental facts that did not agree with the classical theory were explained assuming partial delocalisation of electrons in molecules. However for a long time this fruitful idea remained just a concept, as it was not supported by experimental evidences. These were obtained by the investigation of a hyperfine structure (HFS) in EPR spectra of organic radicals [1] and an additional hyperfine structure of ligand atoms in the spectra of complex compounds.[2] Such structures were first recorded in 1953 in the EPR study of naphthalene radical anion $[C_{10}H_8]^{-\bullet}$ and complex anion $[IrCl_6]^{2-}$ doped into a single crystal of $Na_2[PtCl_6]$ (Ref. 2). The presence of HFS from eight hydrogen atoms in the spectrum of naphthalene radical anion and additional HFS from six chlorine atoms in the spectrum of $[IrCl_6]^{2-}$ is direct evidence for delocalisation of the unpaired electron over the atoms of a molecular species.

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The information about charge density distribution in a molecule may be obtained from the data on the extent of delocalisation of unpaired electrons in complex compounds because the additional HFS in the spectra originates from the interaction of a spin of unpaired electron with the spins of nuclei of the ligand atoms. From this information, the electronic structure of compounds may be derived, *i.e.*, the energy levels of molecular orbitals (MO) and the nature of a metal – ligand chemical bond, as well as the data about reactivity, catalytic properties and other physicochemical parameters of compounds.[3–9]

In this review, we shortly present the theory of hyperfine interactions, consider the problem of delocalisation of unpaired electrons in organic radicals and discuss possible mechanisms of the unpaired electron delocalisation in binuclear copper(II) complexes, where the coordination polyhedra are linked through hydrocarbon spacers.

II. Hyperfine interaction

The general theory of HFS in EPR spectra is described in numerous monographs (see, for example, Refs 3–9). The energy of hyperfine interaction is usually described by the following Hamiltonian:

$$\boldsymbol{H} = g_0 g_I \beta\beta_I \sum_k \left\{ \left[\frac{(\boldsymbol{l}_k - \boldsymbol{S}_k)\boldsymbol{I}_k}{\boldsymbol{r}^3} + \frac{3(\boldsymbol{r}_k \boldsymbol{S}_k)(\boldsymbol{r}_k \boldsymbol{I}_k)}{\boldsymbol{r}^5} \right] + \frac{8\pi}{3}\delta(r_k)(\boldsymbol{S}_k \boldsymbol{I}_k) \right\}, \quad (1)$$

where g_0 is the electron g-factor; g_I is the nuclear g-factor; β is the Bohr magneton; β_I is the nuclear magneton; $\boldsymbol{l}_k$ is the electron orbital angular moment operator; $\boldsymbol{S}_k$ is the electron spin operator; $\boldsymbol{I}_k$ is the nuclear spin operator; $\boldsymbol{r}$ is the radius-vector from nuclei to an electron; $\delta(r_k)$ is the Dirac delta-function normalised in three directions. The summation takes place over all k unpaired electrons.

The Hamiltonian (1) consists of two terms: the first one (in square brackets) describes the anisotropic (dipol – dipole)

interaction of nuclear magnetic moments with magnetic moments of unpaired electrons; the second one containing a δ-function corresponds to the isotropic (contact) interaction of unpaired electrons with nuclear spins. The anisotropic part of hyperfine interaction consists of two main components because the magnetic moment of electrons is determined partially by their orbital movement and partially by the spin of an electron. The term containing the product $l_k I_k$ describes the contribution of interaction of partially 'frozen' orbital angular moment of the electron with the nuclear spin. Other terms describe the interaction of nuclear magnetic moment with spin magnetisation of electrons out of the nucleus. The anisotropic interaction may be regarded as a classical dipole–dipole interaction between two magnets. A additional field H_d created by the magnetic moment of a nucleus in the vicinity of the unpaired electron can be obtained directly from the classical theory and for that reason this term of hyperfine splitting is not discussed here in details. Anisotropic HFS is readily resolved in spectra of magnetically doped single crystals and can often be observed in EPR spectra of glasses containing complexes of d elements. If a system possesses a continual series of H_d values due to the random orientation of molecular symmetry axes relative to the direction of magnetic field and such molecular motions as rotation or translation are also present, then anisotropic HFS cannot be resolved and appears only as the broadening of isotropic hyperfine components. The dipole–dipole interaction is equal to zero in systems with isotropic g-factors.

The hyperfine interaction determined by the Dirac delta-function $\delta(r_k)$ in Eqn (1) is caused by the appearance of isotropic (contact) hyperfine splitting. δ-Function has a non-zero value if the wave function of an unpaired electron in the position of a particular nucleus is not equal to zero. Thus, the finite probability of the location of an electron at the position of a nucleus is a prerequsite for the appearance of hyperfine interaction. Only the s-orbitals of spherically symmetrical atoms have non-zero density on the nucleus. The wave functions of p-, d- and f-electrons the shape of which resembles variously oriented petals, have a nod (zero density) at the nucleus position. Therefore, the electrons of these orbitals do not contribute to the isotropic hyperfine splitting. The isotropic hyperfine interaction is often named the contact Fermi interaction because it appears to be a result of the direct 'contact' of magnetic moments of an electron with a nucleus.

The interaction of the magnetic moment of an unpaired electron with the magnetic moment of a nucleus, resulting in HFS, may be considered in various ways:

— as an interaction of the nuclear magnetic moment with the magnetic field induced by an unpaired electron (the magnitude of this field is about $10^5 - 10^6$ G);

— as an interaction of the magnetic moment of an unpaired electron with the magnetic field induced by the nuclear magnetic moment.

Both concepts allow developing of a the consistent theory of hyperfine interactions. Simultaneous application of both approaches was discussed by Bleaney.[10]

Let us consider the second approach. Only some definite orientations of a magnetic moment are inherent in the external magnetic field (H) of a nucleus possessing a magnetic moment and a spin I, *i.e.* the nuclear magnetic moment is quantified over the directions of the external magnetic field H. The nuclear magnetic moment will possess $(2I+1)$ possible orientations in the magnetic field. The radio-frequency field causes transitions between electronic sub-levels but does not really affect the nuclear magnetic moments. The nuclear magnetic moment creates $(2I+1)$ values of the magnetic field H in the vicinity of an electron [corresponding to $(2I+1)$ possible projections of nuclear moment]. As the orientations of nuclear magnetic moments with respect to the external field do not change during the electronic transitions, the condition of resonance in the presence of hyperfine interaction may be expressed as follows:

$$h\nu = g\beta H_0 + \sum_i \Delta H_i m_i \,, \tag{2}$$

where H_0 is the resonance magnetic field without contribution of hyperfine interaction, ΔH_i is the magnetic field induced by the ith projection of the nuclear moment, m_i is the ith projection of the nuclear magnetic moment in the direction of field H.

Equation (2) may be more conveniently expressed through the intensities of the external magnetic field H_i, which correspond to the components of HFS

$$H_i = H_0 + \sum_i \frac{\Delta H_i}{g\beta} m_i = H_0 + \sum_i A_i m_i \,, \tag{3}$$

where A_i is the constant of hyperfine interaction of the magnetic nucleus i with the magnetic moment of spin of an unpaired electron.

In the case where an unpaired electron of the compound in an external magnetic field H is localised on the atom with the nuclear spin I and the corresponding magnetic moment, the Zeeman levels of unpaired electron split to $(2I+1)$ sub-levels as a result of the interaction of spin moments of the electron with the nucleus. The transitions between these sub-levels produce HFS in the EPR spectra (in the case of adequate resolution). In the first approximation, an EPR spectrum with HFS consists of $(2I+1)$ evenly spaced components of equal intensity with the distance A between them (Fig. 1). EPR

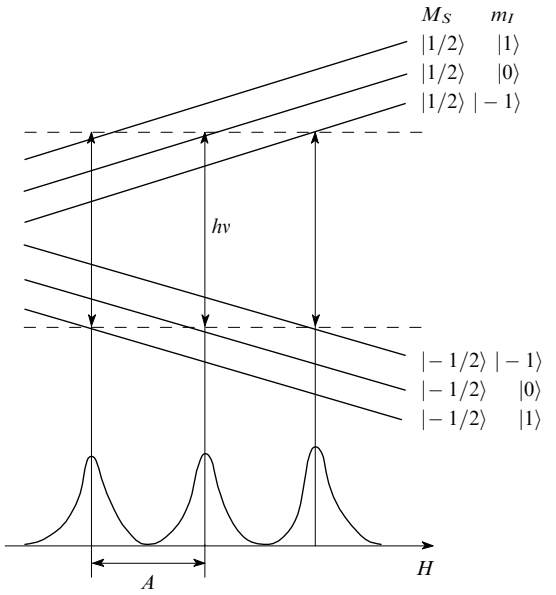
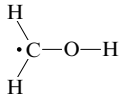


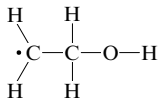
Figure 1. Scheme of hyperfine splitting caused by an interaction of spin magnetic moments of an electron and a nucleus in the ESR spectra for the case of $S = 1/2$ and $I = 1$ within the strong field limitation.
M_S is the spin magnetic moment, m_I is a projection of the nuclear spin on the direction of the external magnetic field.

spectra with evenly spaced HFS components are observed for all radicals and for some paramagnetic transition metal ions with small nuclear magnetic moments.

The mechanism of delocalisation of unpaired electrons in organic radicals was developed back in 1965.[11–14] It was found that the long-range delocalisation of an unpaired electron in an organic molecule can proceed only over a conjugated π-system. Here are some examples. The splitting from two protons of the methylene group CH_2

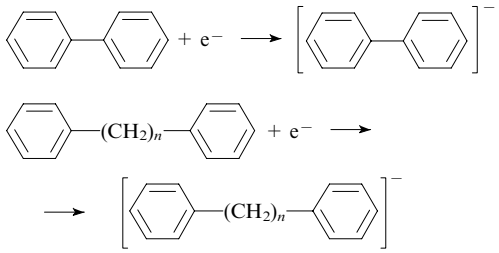


in the spectrum of a methanol radical is equal to 17.3 G, and that from the proton of the hydroxy group is 1.15 G. The splitting from two protons of the terminal methylene group in the EPR spectrum of ethanol



is equal to 15.3 G, that from two protons of the bridging methylene group, 12.5 G and that from the proton of the hydroxy group was not observed.[11]

Radical anions of binuclear aromatic hydrocarbons without bridges (biphenyl) and with bridges of one or several methylene units were used in later investigations of the features of unpaired electron delocalisation in organic molecules:



$n = 1, 2$.

The HFS of 23 signals from 10 protons of two phenyl rings was observed in the case of the biphenyl radical anion.

The authors of the first EPR studies of radical anions of diphenylmethane and diphenylethane arrived to the conclusion that the delocalisation of unpaired electron over two phenyl rings through CH_2 or CH_2-CH_2 bridges is possible. A detailed description of these results is given in a monograph.[5] However, further more thorough investigations revealed that unstable blue or blue-green coloured radical anions are formed initially.[12–14] They exist in the temperature range of the resonator from −90 °C to 80 °C and produce a quintet with splitting of ~5 G in the EPR spectra.

The shape of the EPR spectrum and splitting constants of the primary reduction product of diphenylmethane are similar to those of the EPR spectra of radical anions of alkyl derivatives of benzene.[15,16] In these spectra, the quintet with splitting of ~5 G is produced upon interaction of an unpaired electron with four approximately equivalent protons in *ortho*- and *meta*-positions of the benzene ring.

These results lead to the conclusion that in binuclear aromatic bridged radical anions (the initial reduction products) an unpaired electron is delocalised only over one benzene ring and its delocalisation through a CH_2 bridge and moreover through a $(CH_2)_2$ chain does not take place.

Characteristically, the radical anions of dibenzyl and 1,3-diphenylpropane are unstable and disappear at temperatures from −77 °C to −60 °C. The quintet spectrum of the diphenylmethane radical anion is transformed into a well resolved spectrum, containing 23 components of HFS, as low as at −80 °C. This spectrum is produced by a secondary radical anion in which an unpaired electron is delocalised over two benzene rings. This secondary radical anion (biphenyl) is formed at higher temperatures upon elimination of the methylene group or the polymethylene chain followed by the direct binding of two phenyl radicals into biphenyl.

Thus, the studies of delocalisation of unpaired electrons in organic radicals lead to the conclusion that a long-range delocalisation of these electrons may only occur over a conjugated π-system.

This point of view was predominant over a quarter of the century up to the first studies of binuclear copper(II) coordination compounds in which two chelate complexes were linked together by a polymethylene chain $(CH_2)_n$. Below we will discuss in detail the molecular structures and EPR spectra of binuclear copper(II) complexes in which the coordination polyhedra are linked by a saturated aliphatic bridge.

III. EPR spectra of binuclear copper(II) complexes

Dimeric copper(II) complexes attract attention of scientists for the following reasons:

— these dimers are the simplest subjects for theoretical investigations of cooperative magnetic effects;[17]

— the study of dimeric copper complexes has a potential in search for new catalytic systems and in modelling of active centres of copper-containing enzymes;[18]

— the method of electron paramagnetic resonance reveals its full potential in the studies of copper(II) coordination compounds.[3–9,19]

The overall spin of a dimer containing two unpaired electrons is equal to one. In the energy diagrams, it is represented by two levels with $S = 0$ and 1 and the difference in energy between them is equal to $-2J$ (Fig. 2). In the case of antiferromagnetic interaction, the level with $S = 0$ is the lowest. As the energies of levels with $M_S = 0$ and ± 1 are different due to the inter-electronic interaction, the level with $S = 1$ is split even in the absence of a magnetic field. The external magnetic field produces Zeeman's splitting of levels with $M_S = \pm 1$, which diverge linearly with the increase in the field intensity. Since the selection rule allows only transitions with $\Delta M_S = \pm 1$, the isotropic EPR spectrum should contain a hyperfine structure of two signals with a distance between them

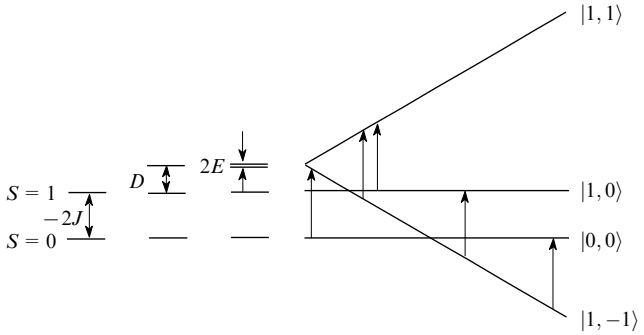
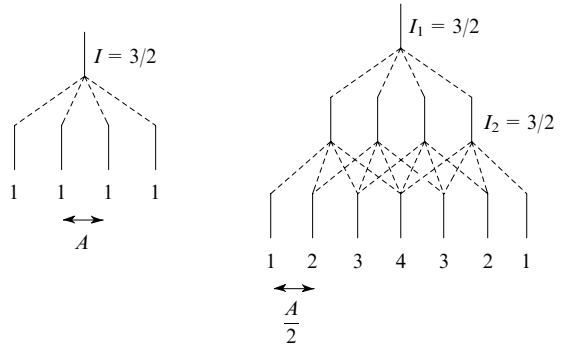


Figure 2. The energy diagram of a dimer containing two spin-connected copper(II) cations, the HFS is not taken into account.

equal to the doubled splitting parameter under zero external magnetic field ($2D$). The tetragonal distortion of a coordination polyhedron and the reduction of symmetry of the nearest environment of the copper(II) cation results in the shift of the levels by $2E$. Besides, the EPR spectra of dimeric copper(II) complexes often contain the signal of a forbidden transition with $\Delta M_S = \pm 2$ and the signals of forbidden singlet–triplet transitions. Taking into account the possibility of additional splitting of energy levels due to anisotropic effects and the absence of signals which are out of range of the spectrometer, it becomes understandable why EPR spectra of dimeric copper(II) complexes quite often are rather difficult to interpret.

Additionally, EPR spectra of copper(II) complexes become more complicated due to the interaction of the unpaired electron with the magnetic nucleus of central atom, resulting in the formation of hyperfine structure. As the unpaired electron of copper(II) cation is located in the 3d-orbital and only an s-orbital electron can interact with the magnetic moment of the nucleus, the concept of spin-polarisation of electron shells of the central atom is generally used for the explanation of the mechanism of HFS formation.

Copper contains two natural isotopes: ^{63}Cu (contents 69.09%) and ^{65}Cu (contents 30.91%). The nuclear spin of both of them is equal to 3/2. The signal splitting on one and two copper atoms can be represented as follows:



The scheme shows that hyperfine interaction of an unpaired electron with one copper nucleus results in splitting of the signal into four components of equal intensity and the distance between the components corresponds to the constant of the hyperfine structure. The interaction of an electron with two equivalent copper nuclei results in splitting of the signal into seven components with the ratio of intensities 1 : 2 : 3 : 4 : 3 : 2 : 1. The solution of the spin Hamiltonian

$$\boldsymbol{H} = g\beta H(S_1 + S_2) + \frac{A}{2}(S_1 I_1 + S_2 I_2) \qquad (4)$$

also shows that the constant of hyperfine structure of a dimer is equal to the half of the HFS constant of the monomeric complex.[19]

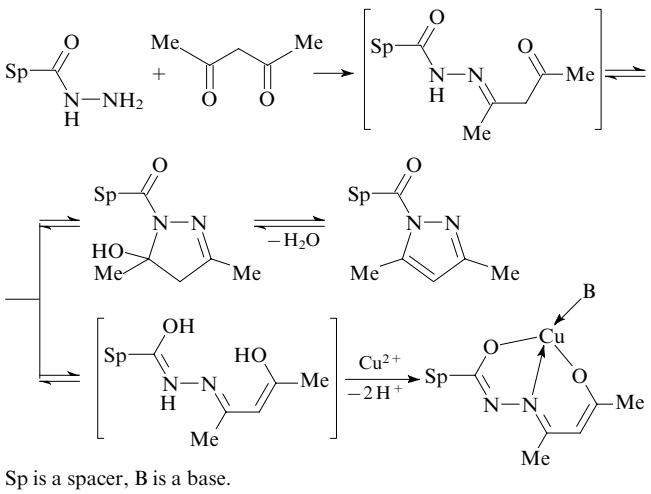
The signal containing seven HFS lines was observed in EPR spectra of mix-valence complexes Cu(I)–Cu(II) with a covalent metal–metal bond.[20] In this case, the so-called direct exchange takes place, *i.e.*, the exchange due to overlapping of 'magnetic orbitals' *i.e.*, the orbitals containing an unpaired electron. The indirect exchange in which the orbitals of bridging ligands are involved into the interaction takes place in dimers with bridges between paramagnetic centres. The theory of indirect exchange in binuclear complexes containing paramagnetic ions linked by monoatomic bridges or small bridging ligands, as well as examples of such copper(II) dimers are given in a number of publications, for instance in monograph.[17]

Recently, the dimers with a significant separation of paramagnetic centres have become a focus of attention for scientists. Quite often there is a spacer, *i.e.*, a long group not directly bound to the central ion atoms, between the coordination polyhedra in such complexes. Binuclear complexes containing aliphatic spacers between monomeric subunits, are the most interesting. The interest is caused by following factors. First, the length of the aliphatic spacer may be easily varied in a wide range by changing the number of links in the polymethylene chain. Second, the conformation flexibility of aliphatic spacers makes these complexes a favourable subject for studying the dynamic effects. Third, the dimers with aliphatic spacers are usually readily soluble in non-polar organic solvents and this makes possible the multi-temperature EPR studies of solutions of such dimers. In the case of dimeric copper(II) complexes, the EPR studies are usually conducted on crystals or frozen homogeneous solutions (isotropic glasses).[7, 19]

IV. Synthesis of binuclear copper(II) complexes with hydrazones based on aliphatic dicarbohydrazides

The simplest method of synthesis of the coordination compounds under study, namely, of binuclear copper(II) complexes with hydrazones based on aliphatic dicarbohydrazides and some bifunctional carbonyl compounds (β-diketones, salicylaldehyde, 2-hydroxyacetophenone and their derivatives), is the condensation of a dicarbohydrazide with the corresponding carbonyl compound in the presence of copper salts and a weak base (ammonia, pyridine, morpholine, piperidine). According to the study of reactions of dicarbohydrazides with acetylacetone,[21–24] the reaction proceeds in several steps (Scheme 1, the reaction with only one hydrazide fragment is shown). Initially, *N*-substituted 5-hydroxy-3,5-dimethyl-4,5-dihydropyrazole is formed, which undergoes dehydration yielding 3,5-dimethylpyrazole. Probably the reaction proceeds *via* the unstable open isomer of acylhydrazone. The addition of copper salts to the solution leads to the opening of the heterocycle and to the formation of complexes with doubly deprotonated open form of the hydrazone. The presence of a proton acceptor is required for deprotonation of the ligand.

Scheme 1



Sp is a spacer, B is a base.

The presence of vacancies in the coordination sphere of the copper cation makes possible an additional coordination of one or two molecules of a base or molecules of a base and a solvent, resulting in the formation of [4 + 1] type coordinated

copper. Some other β-diketones (trifluoroacetylacetone and hexafluoroacetylacetone,[25] benzoylacetone and 3-methylbenzoylacetone,[26] 3-methylacetylacetone and 6-propylundecane-5,7-dione [27]) behave similarly in this reaction. However, it should be noted that the reactions of carbohydrazides with unsymmetric β-diketones are significantly more complicated because of a possibility of involvement of different carbonyl groups in the condensation.

The binuclear copper(II) complexes based on acylhydrazones of salicylaldehyde [28–32] or 2-hydroxyacetophenone and their analogues [33–38] can be synthesised by one of the following methods:

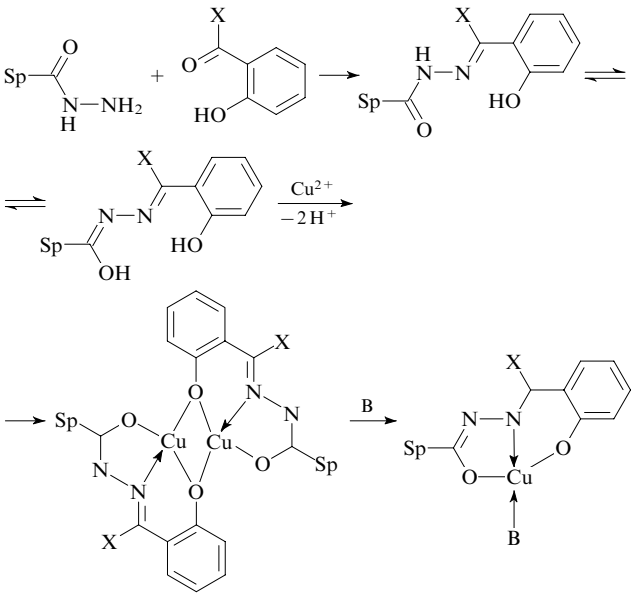
— by the reaction of the corresponding acyldihydrazone with copper salts in an ethanolic solution in the presence of a proton acceptor;

— by the reaction of a dicarbohydrazide with corresponding carbonyl compound and a copper salt, taken in the ratio of 1 : 2 : 2, followed by the treatment of the isolated product with an excess of a base, for example, of pyridine;

— by the reaction of a dicarbohydrazide with the corresponding carbonyl compound and a copper salt in the ratio of 1 : 2 : 2 in the presence of an excess of a base.

The intermediate products, namely, the polymeric complexes containing dimeric fragments Cu_2O_2 typical of copper phenolates (Scheme 2), are formed in these reactions. The treatment of the polymeric complex with an excess of a base (pyridine or morpholine) results in the cleavage of phenoxide bridges and yields monomeric binuclear complexes in which the coordination polyhedra are linked by a polymethylene spacer.

Scheme 2

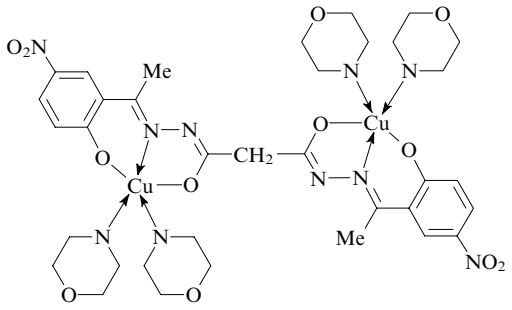


X = H, Me.

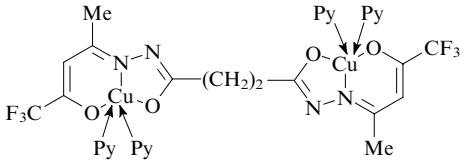
V. Structures of binuclear copper(II) complexes with methylene spacers

Single-crystal X-ray difraction analysis of the following compounds was carried out in order to confirm their structures and to determine structural features of binuclear copper(II) complexes.

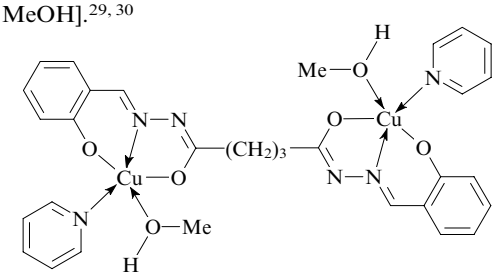
1. Copper(II) complex with dihydrazone derived from malonodihydrazide and 2-hydroxy-5-nitroacetophenone [$Cu_2L \cdot 4\,Mrf$] (Mrf is morpholine).[36]



2. Copper(II) complex with dihydrazone derived from succinodihydrazide and trifluoroacetone [$Cu_2L \cdot 4\,Py$] (Py is pyridine).[39]



3. Copper(II) complex with dihydrazone derived from glutarodihydrazide and salicylaldehyde [$Cu_2L \cdot 2\,Py \cdot 2\,MeOH$].[29, 30]



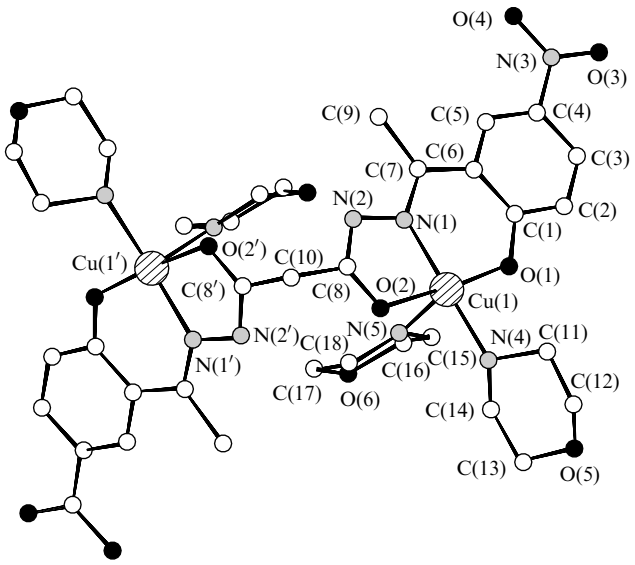
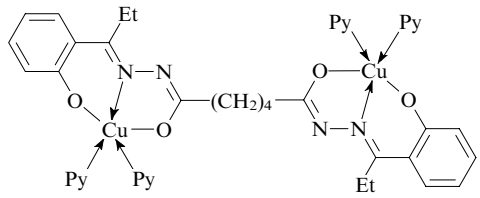


Figure 3. The structure of the complex [$Cu_2L \cdot 4\,Mrf$] (H_4L is malonyldihydrazone of 5-nitro-2-hydroxyacetophenone. Here, as well as in the Figs 5, 6, the H atoms are omitted).

Selected bond lengths /Å: Cu(1)–O(1) 1.867, Cu(1)–O(2) 1.912, Cu(1)–N(1) 1.943, Cu(1)–N(4) 2.037, Cu(1)–N(5) 2.550; bond angles /deg: O(1)–Cu(1)–O(2) 174.74, O(1)–Cu(1)–N(1) 94.02, O(2)–Cu(1)–N(1) 82.43, O(1)–Cu(1)–N(4) 93.55, O(2)–Cu(1)–N(4) 89.08, N(1)–Cu(1)–N(4) 165.3, O(1)–Cu(1)–N(5) 91.84, O(2)–Cu(1)–N(5) 92.23, N(1)–Cu(1)–N(5) 93.05.

4. Copper(II) complex with dihydrazone derived from adipodihydrazide and 2-hydroxypropiophenone $[Cu_2L \cdot 4\,Py]$.[37, 38]



The structures of studied complexes and the most important bond lengths and angles are shown in Fig. 3–6.

Summarising the results of X-ray structural studies of binuclear copper complexes with dihydrazones derived from aliphatic dicarbohydrazides several typical features can be distinguished.

1. The complexes contain two structurally equivalent copper cations.

2. The coordination polyhedron of the copper atom is of [4 + 1] type, has a shape of tetragonal pyramid and is formed by three donor atoms of acyldihydrazone and the nitrogen atom of strongly coordinated Lewis base molecule (pyridine or morpholine). The axial position is occupied by a donor atom of weakly coordinated molecule of a base or a solvent molecule (methanol).

3. Five- and six-membered chelate rings of coordination polyhedra are virtually co-planar. The values of bond lengths in these rings are an important argument in favour of the suggestion about delocalisation of double bonds and formation of a pseudo-aromatic system.

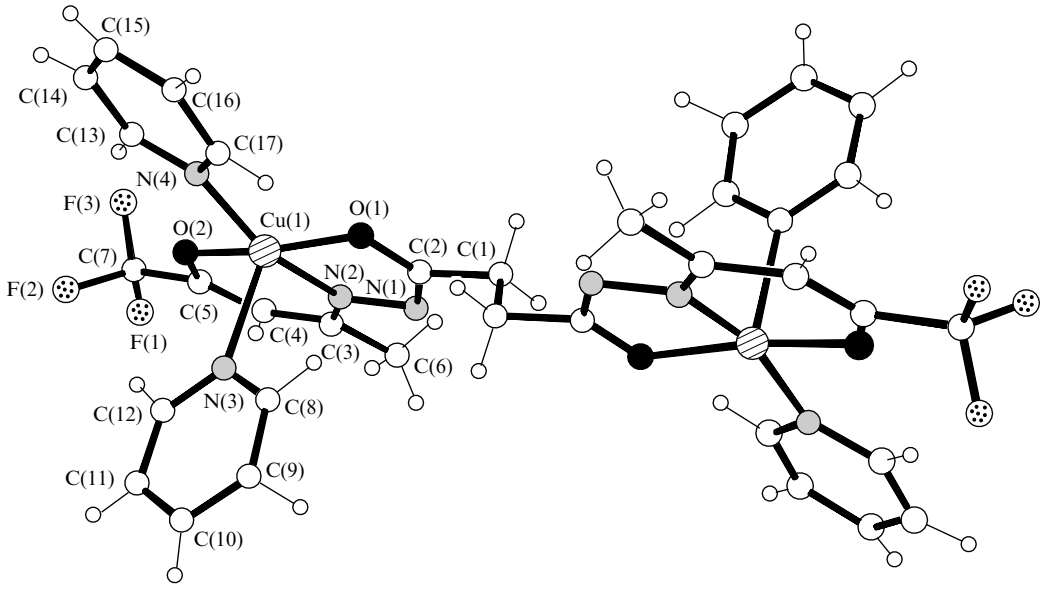


Figure 4. The structure of the complex $[Cu_2L \cdot 4\,Py]$ (H_4L is succinyldihydrazone of trifluoroacetone).
Selected bond lengths/Å: Cu(1)–O(2) 1.937, Cu(1)–N(2) 1.947, Cu(1)–O(1) 1.962, Cu(1)–N(4) 2.032, Cu(1)–N(3) 2.342; bond angles/deg: O(2)–Cu(1)–N(2) 93.25, O(2)–Cu(1)–O(1) 168.52, N(2)–Cu(1)–O(1) 80.78, O(2)–Cu(1)–N(4) 90.92, N(2)–Cu(1)–N(4) 165.30, O(1)–Cu(1)–N(4) 92.57, O(2)–Cu(1)–N(3) 97.68, N(2)–Cu(1)–N(3) 98.23, O(1)–Cu(1)–N(3) 92.90, N(4)–Cu(1)–N(3) 95.17.

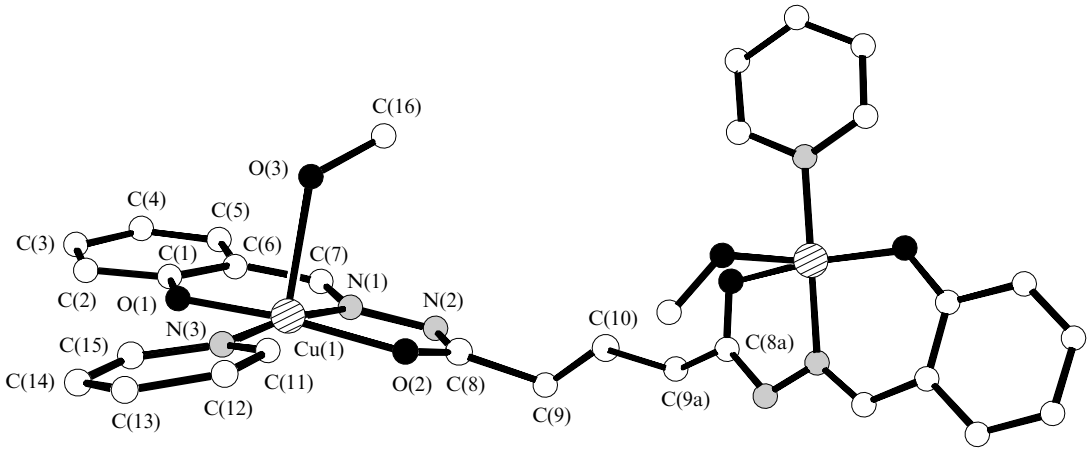


Figure 5. The structure of a copper complex with salicylidene hydrazone based on glutarohydrazide (H_4L) $[Cu_2L \cdot 2\,Py \cdot 2\,MeOH]$.
Selected bond lengths/Å: Cu(1)–O(1) 1.901, Cu(1)–O(2) 1.969, Cu(1)–O(3) 2.422, Cu(1)–N(1) 1.926, Cu(1)–N(3) 2.008; bond angles/deg: O(1)–Cu(1)–O(2) 170.49, O(1)–Cu(1)–O(3) 94.7, O(2)–Cu(1)–O(3) 92.9, O(1)–Cu(1)–N(1) 92.99, O(2)–Cu(1)–N(1) 80.78, O(3)–Cu(1)–N(1) 94.0, O(1)–Cu(1)–N(3) 90.88, O(2)–Cu(1)–N(3) 94.57, O(3)–Cu(1)–N(3) 91.8, N(1)–Cu(1)–N(3) 172.69.

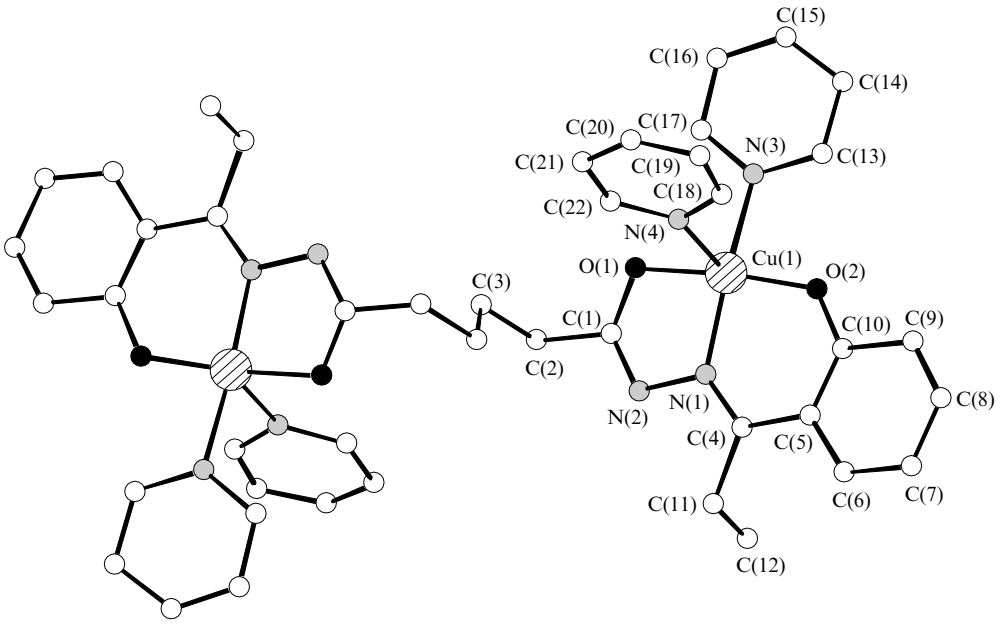


Figure 6. The structure of a binuclear copper(II) complex with adipoylhydrazone of 2-hydroxypropiophenone (H_4L) [$Cu_2L \cdot 4\,Py$].
Selected bond lengths/Å: Cu(1)–O(1) 1.958, Cu(1)–O(2) 1.897, Cu(1)–N(1) 1.936, Cu(1)–N(3) 2.041, Cu(1)–N(4) 2.343; bond angles/deg: O(1)–Cu(1)–O(2) 172.2, O(1)–Cu(1)–N(1) 81.2, O(2)–Cu(1)–N(1) 92.7, O(1)–Cu(1)–N(3) 93.5, O(2)–Cu(1)–N(3) 90.9, N(1)–Cu(1)–N(3) 162.4, O(1)–Cu(1)–N(4) 91.5, O(2)–Cu(1)–N(4) 95.1, N(1)–Cu(1)–N(4) 109.1, N(3)–Cu(1)–N(4) 87.7.

4. The Cu–Cu distance increases from 6.940 Å in the malonic acid-derived complex up to 9.182 Å in the glutaric acid-derived complex, but unexpectedly decreases to 8.212 Å in the adipic acid-derived complex. It can be explained by packing effects of this relatively bulky molecules in the crystal structure.

VI. Magnetic properties of binuclear copper(II) complexes

The method of measurement of static magnetic susceptibility and EPR spectroscopy were used for studying the magnetic properties of binuclear copper(II) complexes. The theoretical simulation of the spectra was performed with a program package described in a monograph.[9] In order to determine the parameters of EPR spectra the experimental spectra were fitted to the calculated ones by minimisation of the error functional

$$F = \frac{1}{N}\left[\sum_{i=1}^{N}\left(Y_i^{e} - Y_i^{t}\right)^2\right], \qquad (5)$$

where N is a number of the points, Y_i^{e} and Y_i^{t} are the experimental and theoretical values of absorption in the ith point of the spectrum.

The convolution products of Lorentz and Gauss functions were used as the line shape functions.[40] According to the relaxation theory, the one-centred contributions to the line width were represented by the following expression [41]

$$\Delta H = \alpha + \beta m_I + \gamma m_I^2, \qquad (6)$$

where α takes into account all broadening effects identical for all HFS lines; the coefficient β is determined by the product of the g-tensor and the hyperfine interaction (HFI) tensor; m_I is the projection of nuclear spin to the external magnetic field direction; the coefficient γ is determined by anisotropy of HFI and depends on the time of correlation of rotation of a paramagnetic species in a liquid.

As the complexes containing polymethylene spacers, are stereochemically flexible, the contribution of intramolecular motion in binuclear complexes around the polymethylene spacer was also taken into account,[42]

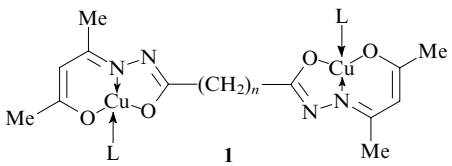
$$\Delta H_p(1,2) = \delta(m_{I_1} - m_{I_2})^2, \qquad (7)$$

where m_{I_1} and m_{I_2} are the projections of nuclear spins of the first (1) and the second (2) copper atoms, respectively.

The theoretical parameters g, a, α, β, γ and δ were varied according to the method described [43] until the minimum of the error functional (F) was reached.

The static magnetic susceptibility $\chi(T)$ of polycrystalline samples of some binuclear complexes was measured in the temperature range from 77 to 300 K by the relative Faraday method. The obtained values were corrected for temperature-independent paramagnetism and diamagnetism of the ligands.

Copper(II) compounds **1,** based on the condensation products of aliphatic dicarbohydrazides with acetylacetone [21,22] in which two chelate complexes with tridentate bicyclic ligands are linked by polymethylene spacers with $n = 0–2$, 4 and 8 were the first to be studied.



1

L is a pyridine or piperidine; $n = 0–2$, 4, 8.

The measurements of static magnetic susceptibility revealed that the effective magnetic moment (μ_{ef}) of compound **1** ($n = 0$) decreases from 1.62 at 300 K to 1.26 μ_B at 77 K. The experimental function $\mu_{ef}(T)$ may be adequately described by a

model of isotropic antiferromagnetic exchange between two centres with spins $S_1 = S_2 = 1/2$ and with the value of exchange parameter equal to $-2J = 80\ cm^{-1}$.

In the case of complexes **1** ($n \neq 0$), the μ_{ef} value is equal to $\sim 1.8\ \mu_B$ and does not depend on temperature. The lowest temperature was equal to 77 K, therefore in the presence of exchange interactions the exchange parameter value in these compounds should not exceed $10\ cm^{-1}$.

EPR spectra of polycrystalline samples of **1** contain lines narrowed due to exchange. The anisotropy of the *g*-factor is resolved only for compound **1** ($n = 0$). This may be explained by features of the crystal structure or by the weakening of intermolecular interactions due to strong intramolecular antiferromagnetism. The forbidden transition $\Delta M_S = \pm 2$ was observed in the EPR spectrum of dimer **1** ($n = 0$) at $H = 1700$ G. It is known,[3] that the intensity of this transition is proportional to $|D|$, where D is the parameter of anisotropic spin–spin interaction. Therefore, for the complex **1** ($n = 0$) the value of $|D|$ is maximum.

EPR spectra of frozen solutions of compounds **1** possess poorly resolved anisotropic HFS. This is not typical of mononuclear copper(II) complexes. As the fine structure caused by anisotropic spin–spin interactions is also unresolved, such spectra should be regarded as a superposition of fine and hyperfine structures with close values of the constants.

EPR spectra of liquid solutions of complexes **1** containing well resolved HFS from two equivalent copper atoms (Fig. 7) are the most interesting. As such spectra were not previously observed for binuclear copper(II) complexes with dihydrazones, let us discuss them in detail.

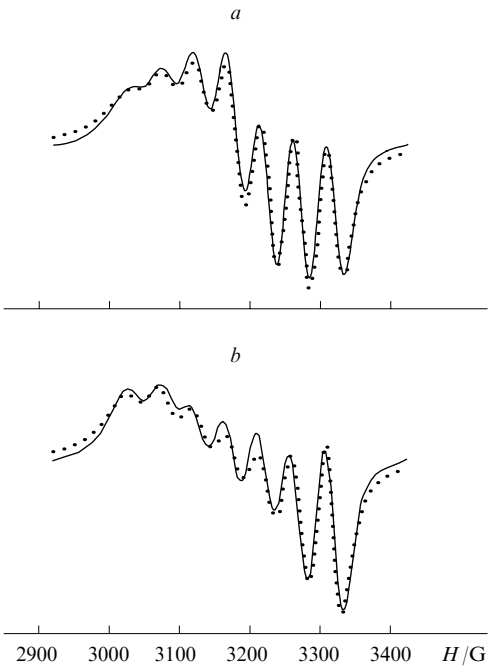


Figure 7. The ESR spectra of liquid solutions of complexes **1** with $n = 2$ (*a*) and 4 (*b*).
Solid line is the experimental spectrum, dotted line is the simulated spectrum.

EPR spectra of mononuclear complexes with $S = 1/2$ are described by the following spin Hamiltonian without taking into account the additional HFS from ligands [3]

$$\boldsymbol{H} = \beta S_i g_i H + S_i A_i I_i, \tag{8}$$

where g_i is the g-tensor, A_i is the tensor of HFS from the central ion. If two mononuclear fragments form a dimer in which the isotropic exchange between paramagnetic ions takes place, then, in the first approximation the spin Hamiltonian takes the form

$$\begin{aligned}\boldsymbol{H} &= H_1 + H_2 - 2JS_1S_2 = \beta(S_1 + S_2)gH + \\ &+ \frac{A}{2}(S_1 + S_2)(I_1 + I_2) + \frac{A}{2}(S_1 - S_2)(I_1 - I_2) - 2JS_1S_2 = \\ &= \beta SgH + \frac{A}{2}S(I_1 + I_2) + \frac{A}{2}(S_1 - S_2)(I_1 - I_2) - \\ &- g[S(S+1) - S_1(S_1+1) - S_2(S_2+1)],\end{aligned} \tag{9}$$

where at $S_1 = S_2 = 1/2$ the full spin $S = S_1 + S_2$ is equal to either 0 or ± 1. There are no transitions within the singlet state. However, at low values of $|-2J|$ the singlet–triplet transitions or the mixing of nuclear states of the singlet and the triplet by the operator $(A/2)(S_1 - S_2)(I_1 - I_2)$ is possible.[19] In both cases the resulting spectrum should be quite different from a simple set of seven equivalent lines. As only simple spectra were observed in the experiment, the exchange parameter should satisfy the following condition: $|J| \gg h\nu, |A|$.

When this condition is met, the spin Hamiltonian (9) is reduced to the effective spin Hamiltonian of the triplet state

$$\boldsymbol{H} = \beta SgH + \frac{A}{2}S(I_1 + I_2), \tag{10}$$

which (from the general considerations [3]) should contain the contribution of anisotropic spin–spin interaction. Therefore, the full spin Hamiltonian of the triplet state may be represented as

$$\boldsymbol{H} = \beta SgH + \frac{A}{2}S(I_1 + I_2) + DS^2, \tag{11}$$

where the tensor D is the sum of the so-called exchange (D_{ex}) and dipole–dipole (D_{dd}) contributions. The following approximation is valid for D_{ex} [19]

$$|D_{ex}| \approx -2J'\left(\frac{\Delta g}{g}\right)^2, \tag{12}$$

where $-2J'$ is an exchange parameter of the excited state of a dimer, Δg is the deviation of the *g*-factor value of the dimer from the value of the free electron *g*-factor.

For the single-point dipole approximation,

$$|D_{dd}| \approx \frac{\beta^2}{r^3}, \tag{13}$$

where r is a metal–metal distance.

The r value in complexes **1** exceeds 5 Å, therefore for these compounds $|D_{dd}| < 0.01\ cm^{-1}$. The $|D_{ex}|$ value depends on the degree of anisotropy of the *g*-factor and on the value of the exchange parameter. It is known [3] that $(\Delta g/g) \approx 0.1$ for the this type of complexes, therefore $|D_{ex}| \approx 0.01(-2J)$. Particularly this means that for the complex **1** ($n = 0$) the value of $|D_{ex}|$ may be as high as $\sim 1\ cm^{-1}$. Probably, the features of EPR specta of this compound are caused by such a high value of $|D|$. The values of $-2J$ for complexes **1** with $n > 0$ are unknown. However, they can be estimated on the basis of obtained results. Indeed, the effects of rotational averaging in the

experimental spectra of liquid solutions result in complete disappearance of anisotropy. According to the theory of rotational relaxation, this means that $|g\beta H|$, $|A|$, $|D|$ are much lower than the frequency of molecular rotation $1/j_R$. In mononuclear complexes $|g\beta H|$, $|A| < 1/j_R$. However, the spectra of frozen solutions of complexes **1** show that $|D| \approx |g\beta H|$, $|A|$, and therefore the averaging condition $|D| < 1/j_R$ is fulfilled. Moreover, from the relations

$$|D_{ex}| \approx |D| \approx |g\beta H|, |A| \approx 0.01 - 0.02\ cm^{-1}$$

and

$$|-2J| \approx 100\,|D_{ex}|$$

one may find that $|-2J| \approx 1 - 2\ cm^{-1}$.

It should be noted that this estimation does not contradict the magnetochemical data and corresponds well to the experimental value of $-2J \approx 3\ cm^{-1}$ obtained for the binuclear Cu(II) complex, where a channel of spin exchange through the dimethylene chain supposedly exists.[44]

As the following inequalities are valid for compounds **1**

$$|J| \gg h\nu,$$

$$|A| \text{ and } |D| < 1/j_R,$$

EPR spectra of their liquid solutions should be adequately described by the spin Hamiltonian (10). In order to verify this conclusion, we processed the experimental data by the method of best fitting of experimental and theoretical spectra. The HFS splitting was quite low ($\sim$40 G), therefore the solutions of spin Hamiltonian (10) of the first order of perturbation theory were used

$$h\nu = g_0\beta H M_S + \frac{A}{2} M(m_1 + m_2), \quad (14)$$

where $M = -1, 0, 1$ are the projections of the electronic spin; $m_1, m_2 = -I_i, \ldots I_i$ are the projections of the nuclear spin (for copper atoms $I = 3/2$). The expressions for resonance fields of allowed transitions now can be easily figured out

$$H_p = \frac{h\nu}{g_0\beta M} - \frac{A}{2g_0\beta}(m_1 + m_2). \quad (15)$$

Let us discuss the obtained results presented in Table 1. First of all, it should be noted that the values $g = 2.10$ are close to the known values for mononuclear Cu(II) complexes with similar coordination sphere [2O, 2N].[45] This means that the formation of a binuclear complex does not result in significant changes in geometrical and electronic structures of mononuclear fragments. Similar conclusion can be drawn from the analysis of broadening parameter values α, β and γ, the ratio between them ($\alpha \gg \beta > \gamma > 0$) is the same as that for most of mononuclear square-planar Cu(II) complexes.[46] Some increase in β and γ in the series of compounds **1** (n = 1, 2, 4) may be easily explained by the increase in the molecular size resulting in a longer rotational correlation time.

At the same time, the HFS constant from copper atoms is half that of mononuclear copper complexes with [2O, 2N] coordination sphere and exactly corresponds to the similar constant of copper dimers, which was observed in polycrystalline powders for a forbidden transition $\Delta M_S = \pm 2$ (Refs 7, 19 and 46).

The broadening parameter δ increases by almost an order of magnitude in compounds **1** on going from n = 1, 2 to n = 4. This result is rather expected, taking into account that this parameter reflects the dynamic spin exchange, which, in turn, is determined by conformational transitions. Indeed, the stereochemical flexibility of dimeric molecules should increase with lengthening of the $(CH_2)_n$ spacer.

Table 1 The parameters of ESR spectra of binuclear copper complexes with hydrazones based on aliphatic dicarbohydrazides.

n	$g \pm 0.003$	$A_{Cu} \times 10^4$ /cm^{-1}	α/G	β/G	γ/G	δ/G
Compounds **1**						
1	2.092	43.6	27.5	6.1	0.28	−0.1
2	2.094	44.5	27.8	7.0	0.46	−0.29
3	2.096	44.5	27.2	3.8	−0.60	3.81
4	2.097	45.7	26.1	7.2	0.56	6.7
5	2.096	76.2,[a] 81.6[b]	44.3	8.7	16.30	–
6	2.096	78.7,[a] 84.3[b]	50.8	9.8	5.60	–
7	2.092	82.9,[a] 88.8[b]	45.1	7.2	5.30	–
8	2.105	82.0	–	–	–	–
Compounds **2**						
1	2.110	38.5	26.6	3.50	−1.60	3.6
2	2.110	39.6	31.5	1.90	−3.5	3.9
3	2.110	40.0	29.7	4.60	−2.6	4.0
4	2.110	40.5	30.6	8.50	0.30	7.10
5	2.109	77.5	43.7	8.29	2.09	–
Compounds **3**						
1	2.144	57.0	50.0	4.60	2.00	–
2	2.141	51.1	60.0	6.20	1.1	–
3	2.118	62.1	26.7	9.4	6.5	–
4	2.117	60.1	23.3	8.10	6.4	–
5	2.117	66.9	51.1	11.6	2.6	–
Compounds **4**						
1	2.111	33.1	31.6	1.9	−1.3	−1.8
2	2.112	36.0	32.0	7.8	−3.3	−1.8
3	2.106	39.9	28.1	5.8	−0.3	3.6
4	2.105	39.3	32.1	6.9	−1.2	6.4
5	2.104	71.5,[a] 76.6[b]	51.8	10.9	2.8	–
6	2.110	71.4,[a] 76.5[b]	46.3	13.0	2.6	–
7	2.103	77.2,[a] 82.7[b]	42.4	9.1	2.2	–
8	2.105	76.8,[a] 82.3[b]	40.8	9.7	2.1	–
Compounds **5**						
1	2.110	38.2	29.5	3.0	−0.5	2.1
2	2.112	38.1	32.2	9.5	1.0	3.4
3	2.117	39.8	32.0	7.6	−1.1	5.3
4	2.112	40.3	32.6	8.9	−0.3	7.5
5	2.110	72.1	50.6	10.0	1.1	–
Compounds **6**						
2	2.112	38.0	27.6	6.6	−0.04	2.09
3	2.112	39.4	28.8	5.8	−1.82	4.05
4	2.112	39.1	34.1	10.1	−1.12	6.64
5	2.109	73.5	48.1	11.4	2.8	–

[a] For the ^{63}Cu isotope. [b] For the ^{65}Cu isotope.

And finally let us discuss the complex **1** with $(CH_2)_8$ spacer. Figure 8 shows the EPR spectrum of liquid solution of this compound, containing four HFS lines typical of mononuclear Cu(II) complexes. The values of EPR parameters listed in Table 1 are also typical of mononuclear complexes with a [2O, 2N] coordination sphere. According, for example, to Wilson and Kivelson [41] such a spectrum indicates that for the compound **1** ($n = 8$) the following expression is valid $|-2J| \ll |A|$. Thus, the energy of exchange interactions dramatically decreases upon transition from compound **1** with $n = 4$ to that with $n = 8$. This result is not surprising because the exchange interactions in the complex **1** ($n = 8$) take place through the relatively long $(CH_2)_8$ spacer and their energy, undoubtedly, is very small. The distinct broadening of HFS components may be explained by the influence of weak dipole–dipole and exchange interactions.

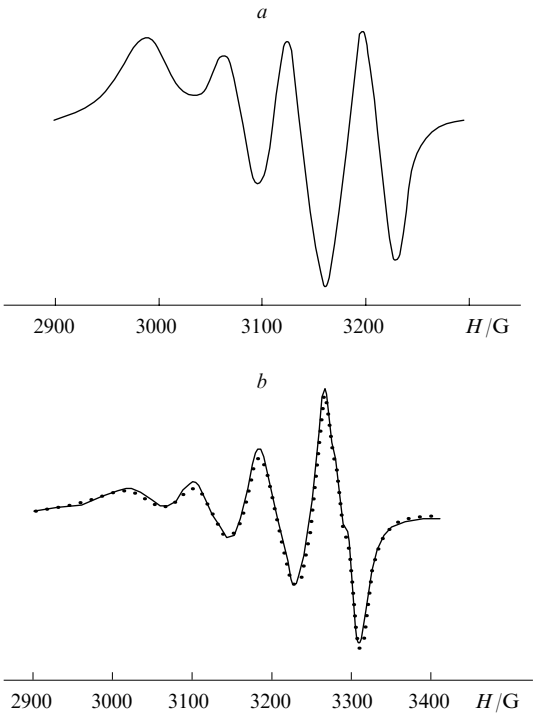


Figure 8. The spectra of compound **1** with $n = 8$ (*a*) and similar heterobinuclear complex of Cu and Ni with octamethylene spacer (*b*).
Solid line is the experimental spectrum, dotted line is the simulated spectrum.

However, it should be noted that the distance between the second and the third component of the spectrum is significantly smaller than those between other components. The distance between the first and the second components in the low magnetic field region is equal to 87 G, that between the second and the third ones is 75 G and that between the third and the fourth ones is 90 G. Typically, for monomeric metal complexes, according to the Breit–Rabi equation,[3,47] the minimum distance is observed between two first components at one side of the spectrum, which gradually increases and becomes maximum at the other side of the spectrum. It is these changes in the distances between adjacent components that were observed in the spectrum of heterobinuclear Cu and Ni complex with an octamethylene spacer (see Fig. 8). Besides, an additional HFS consisting of three lines from one nitrogen atom of the hydrazone ligand was resolved at the high-field HFS component of the copper atom.

Probably, the Breit–Rabi equation for compound **1** ($n = 8$) is not quite valid because even in the presence of a polymethylene spacer with 8 carbon atoms very weak exchange interactions between unpaired electrons of two copper atoms still exist. These interactions are responsible for decreasing the distance between the second and the third HFS components and for poor resolution of additional HFS from nitrogen atoms.

Thus, the exchange interactions through the polymethylene spacer are present in studied homobinuclear copper compounds **1** ($n = 1, 2, 4$). The exchange interactions are also present in the complex with the trimethylene spacer, but are virtually entirely suppressed with the increase of n up to 5–8,[24] although some residual effects, probably caused by very weak interactions, are still present in EPR spectra of complexes with n up to 8 (see Table 1). Obviously, the length of the polymethylene chain significantly affects the possibility of spin–spin exchange interactions between copper(II) cations in such complexes.

The possibility of exchange interactions through the polymethylene chain strongly depends on the character of the tridentate chelating group of the ligand. Thus, the substitution of one trifluoromethyl for the methyl group of the acetylacetonate ligand does not prevent the exchange interactions, and EPR spectra of complexes of dihydrazones derived from trifluoroacetylacetone ($n = 1–4$) contain seven HFS lines (Fig. 9).

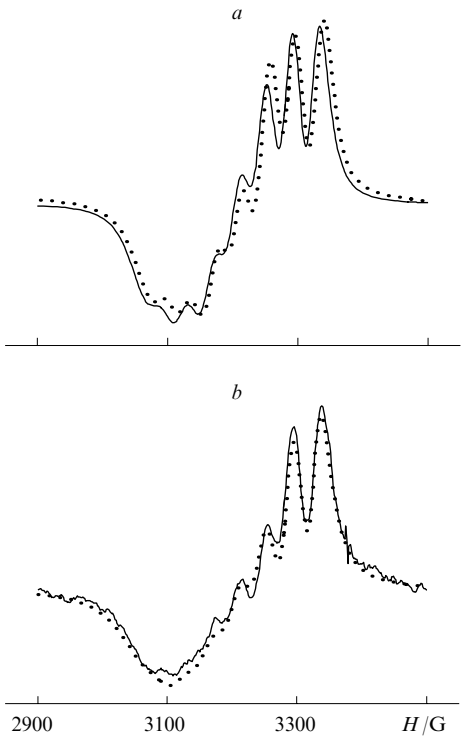
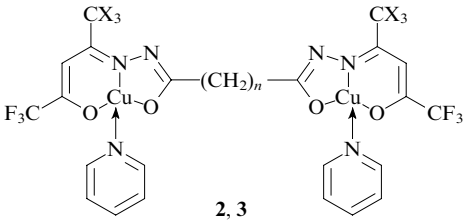


Figure 9. The ESR spectra of complexes **2** with $n = 1$ (*a*) and 4 (*b*).
Solid line is the experimental spectrum, dotted line is the simulated spectrum.



2, 3

n = 1–4; X = H (**2**), F (**3**).

The weak effect of electron-withdrawing acceptor CF_3 group on the EPR spectra of the binuclear complexes studied may be explained by its remoteness from the supposed channel of exchange interactions (see Fig. 4). The introduction of an additional trifluoromethyl group and passage to complexes of dihydrazones derived from hexafluoroacetylacetone (compounds **3**), suppresses the exchange interactions and their EPR spectra consist of four HFS lines typical of mononuclear copper(II) complexes (Fig. 10).[25] With some other β-diketones, such as benzoylacetone, 3-methylbenzoylacetone,[26] 3-methylacetylacetone and 6-propylundecane-5,7-dione [27] used in the synthesis of binuclear complexes analogous results were obtained. This, though somewhat unexpected may be explained by re-orientation of magnetic orbitals preventing the exchange interactions. Similar effect was observed in the study of exchange interactions in binuclear copper complexes with an oxalate bridge.[48]

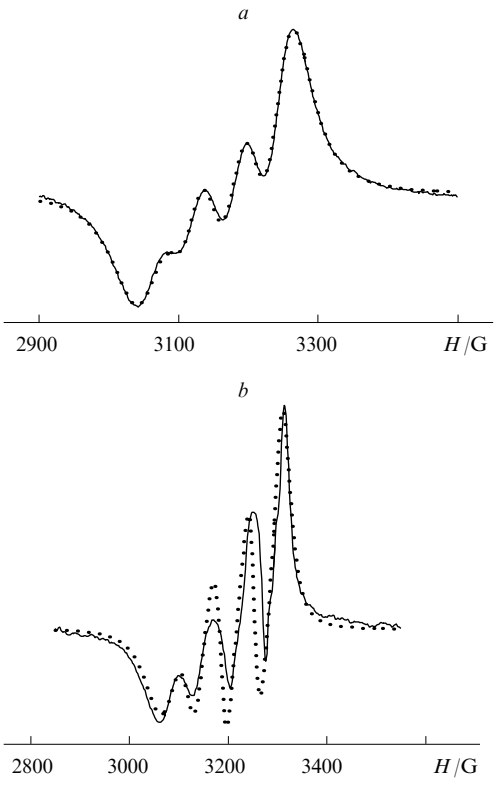
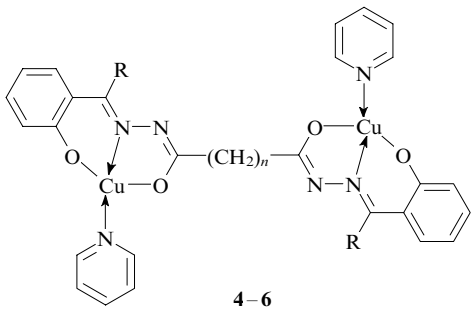


Figure 10. The ESR spectra of complexes **3** with n = 1 (*a*) and 4 (*b*). Solid line is the experimental spectrum, dotted line is the simulated spectrum.

The range of known dimers with aliphatic spacers significantly increased after the synthesis and study of binuclear copper(II) complexes of dihydrazones derived from salicylaldehyde (compounds **4**).



4–6

R = H, n = 1–8 (**4**); R = Me, n = 1–5 (**5**); R = Et, n = 2–5 (**6**).

A series of compounds **4**, from a copper complex based on a malonic acid derivatives (n = 1) to a complex of a hydrazone based on sebacohydrazide (n = 8), has been studied.[30–32] The structures of these compounds were determined by elemental and thermal analysis and IR spectroscopy. An X-ray diffraction study of the complex with salicylidene hydrazone derived from glutarohydrazide **4** (n = 3) has confirmed the structures of compounds **4**. It was found that the complex is binuclear and the two coordination polyhedra are linked through a trimethylene spacer. The distance Cu—Cu is equal to 9.182 Å (see Fig. 5). It may appear that the paramagnetic centres at such a long distance should be independent from each other. Nevertheless, EPR spectra of the solutions of complexes **4** based on salicylidene hydrazone with n = 1–4 contain well resolved seven lines of HFS with a constant of about 40 G, which indicates the interaction of unpaired electrons with two equivalent copper atoms. It is clear from Figure 11 and data listed in Table 1 that the spectra of complexes **4** with n = 1, 2 and with

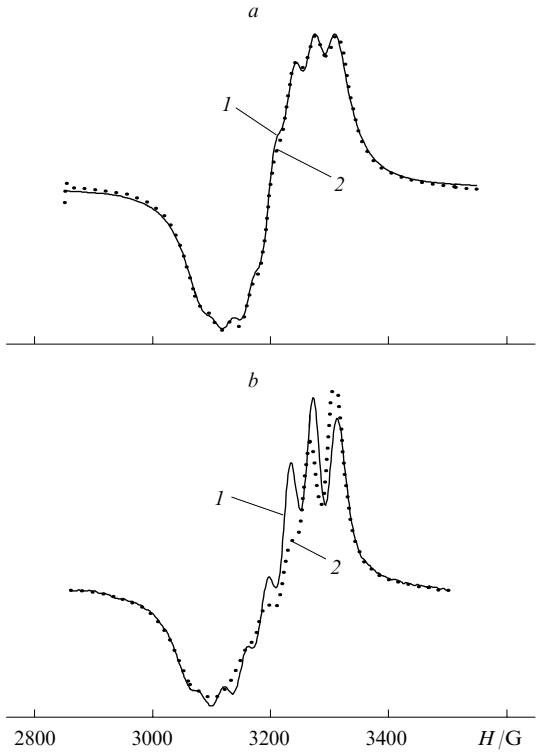


Figure 11. The ESR spectra of complexes **4**.
(*a*) g = 2.110; (*1*) n = 1, $A_{Cu} = 33 \times 10^{-4}$ cm^{-1}; (*2*) n = 2, $A_{Cu} = 36 \times 10^{-4}$ cm^{-1};
(*b*) g = 2.106; (*1*) n = 3, $A_{Cu} = 35 \times 10^{-4}$ cm^{-1}; (*2*) n = 4, $A_{Cu} = 40 \times 10^{-4}$ cm^{-1}.

$n = 3, 4$ possess similar values of *g*-factors and HFS constants, but differ slightly in the line width.

Lengthening of the polymethylene chain up to 5–8 units results in a drastic change in character of the absorption, and EPR spectra of compounds **4** contain signal of four HFS lines, usual for mononuclear copper(II) complexes, with constant $(72-83)\times10^{-4}$ cm^{-1} ($g = 2.10-2.11$), which suggests the suppression of exchange interactions between paramagnetic centres.

Monomeric binuclear copper(II) complexes with dihydrazones derived from 5-bromo- and 2,4-dihydroxybenzaldehyde as well as with 2-hydroxynaphthalene-1-carbaldehyde were studied in order to analyse the effect of the type of substitutent in the aromatic ring of the dihydrazone on the character of exchange interactions. It was found that the isotropic EPR spectra of the liquid solutions of complexes of substituted hydrazones based on malono-, succino- and glutarohydrazides ($n = 1-3$) contain signals of seven HFS lines. The increase in the number of σ-bonds between paramagnetic centres due to the intruduction of one additional methylene group results in a change in the character of absorption, and the spectra of solutions of the complexes of hydrazones based on adipohydrazide contain signals of four HFS lines.[31,32] Thus, the introduction of various substituents in the benzene ring of a dihydrazone decreases the 'conductivity' of spin density through the polymethylene spacer.

Acylhydrazones are convenient objects for modification and targeted molecular design of binuclear complexes. One of the ways of modification of the structure of acyldihydrazone is the use of various carbonyl compounds. Up to now, alongside with binuclear copper(II) complexes based on dihydrazones derived from β-diketones and salicylaldehyde, the coordination copper compounds with dihydrazones derived from aromatic ketones are relatively well studied. A series of copper complexes with coupling products of dicarbohydrazides ($n = 1-5$) with 2-hydroxyacetophenone (**5**) or its 5-substituted (Me, Cl, Br, NO_2) analogues was examined.[33–36]

The structure of the copper(II) complex based on dihydrazone derived from malonohydrazide and 5-nitroacetophenone [$Cu_2L\cdot4$ Mrf] was determined by X-ray crystallography (see Fig. 3).

The isotropic signal with seven well resolved HFS lines and the constant of approximately 40 G was observed in the EPR spectra of the solutions of complexes of dihydrazones based on 2-hydroxybenzophenone **5** ($n = 1-4$). Lengthening of the oligomethylene chain between coordination polyhedra up to five units results in the suppression of spin exchange, and the EPR spectrum consists of isotropic signal of four HFS lines from one nucleus with normal value of the constant, which is usual for monomeric copper(II) complexes (see Table 1). The introduction of various substituents in the benzene ring of dihydrazones based on 2-hydroxyacetophenone does not affect the propagation of weak spin–spin exchange interactions through the polymethylene spacer. The seven-line hyperfine structure can be resolved when the oligomethylene spacer contains from 1 to 4 methylene units in 5-methyl-, 5-chloro-, 5-bromo- and 5-nitro-derivatives. The four-line HFS is observed in EPR spectra of the corresponding complexes when the length of the oligomethylene chain is increased up to five units.[34–36]

The insensitivity of exchange interactions to the nature of substituents in the benzene ring of binuclear copper complexes with hydrazones of 2-hydroxyacetophenone may be explained by a strong positive inductive effect of the methyl group at the carbon atom of the azomethine fragment. Therefore, it seemed interesting to try to increase the conductivity of spin–spin exchange interactions through an oligomethylene spacer by further increase in the positive inductive effect of aliphatic part of the ketone. Coordination compounds **6** of dihydrazones derived from 2-hydroxypropiophenone were synthesised and studied in order to test this idea.[37,38]

The structure of the complex **6** ($n = 4$) based on dihydrazone derived from adipohydrazide, was confirmed by single-crystal X-ray crystallography.

The isotropic signal of seven well resolved HFS lines with the intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 and the constant of ~40 G was observed in the EPR spectra of the solutions of complexes **6** ($n = 2-4$). At the same time, the EPR spectrum of the complex with $n = 5$ consists of an isotropic signal of four HFS lines from one copper nucleus with a typical value of the constant characteristic of monomers (Fig. 12). This indicates that the increase in the electron-donating character of the aliphatic radical does not enhance the conductivity of spin–spin exchange interactions through the oligomethylene chain. One can suggest that the length of pentamethylene chain is critical, the chain of such length prevents the weak exchange interactions between copper(II) cations in this type of complexes.

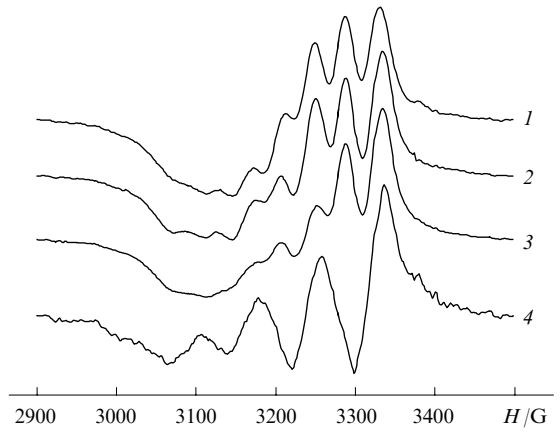


Figure 12. The ESR spectra of solutions of complexes **6** with $n = 2$ (*1*), 3 (*2*), 4 (*3*), 5 (*4*).

Interesting changes were observed in EPR spectra of frozen (77 K) solutions of these complexes (Fig. 13). These spectra

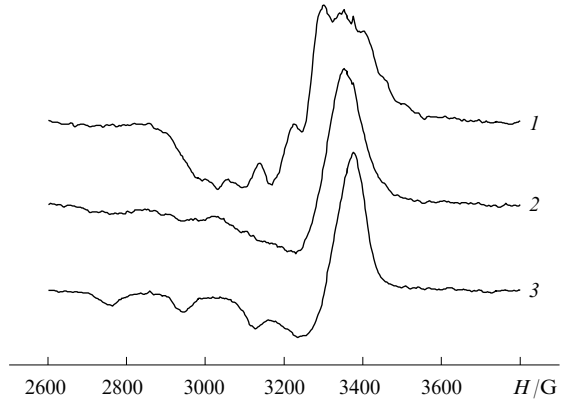
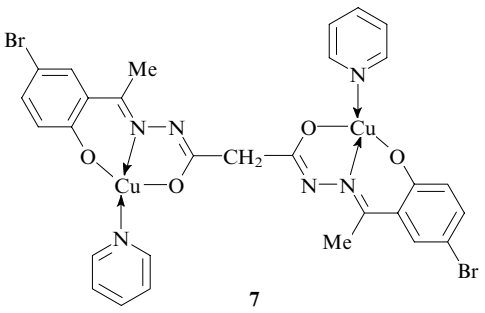


Figure 13. The ESR spectra of frozen (77 K) solutions of complexes **5** with $n = 1$ (*1*), 4 (*2*), 5 (*3*).

are typical of the systems possessing an axial symmetry and a $d_{x^2-y^2}$ ground state, but the character of hyperfine interaction, which can be seen at the parallel orientation of g-factor, is changing with lengthening of the oligomethylene chain. Thus the HFS of seven lines with halved constant ($\sim$70 G) was recorded in parallel orientation in the spectra of compounds based on malonic and succinic acids. If n is increased to 3 or 4, the parallel orientation signal consists of poorly resolved HFS of four lines with a constant ($\sim$150 G) usual for such monomeric complexes. Further lengthening of the oligomethylene spacer does not change the absorption character, and the HFS is more pronounced in perpendicular orientation (A_{Cu} = 185 G). This indicates that the weak exchange interactions between copper cations through the oligomethylene chain also take place in the frozen solutions but at significantly shorter distances.

A relatively well resolved signal containing fine as well as hyperfine structure was observed in the EPR spectrum of a solution of dimer **7** frozen at 77 K.[35]



7

The spectrum contains seven HFS lines from two equivalent copper atoms. The lines are not equally spaced and the distance between them notably increases with the increase in intensity of the external magnetic field and decreases again between two last components. The average distance between the lines is equal to 68.5 G. In addition to seven HFS lines superimposed on the signal with perpendicular orientation (g = 2.053) two weak lines are also present in a high field. The fine structure is particularly evident in the second derivative of the spectrum (Fig. 14).

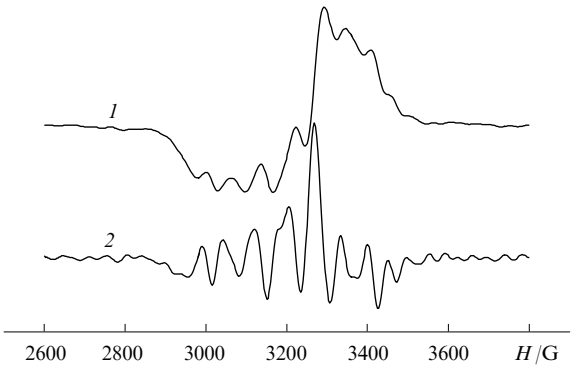


Figure 14. The ESR spectrum of complex **7** in the frozen solution (toluene – pyridine) at 77 K.
(*1*) First derivative, (*2*) second derivative.

The positions of the lines of the high-field components and the constant of fine structure, $D_{||}$, (74 G or 0.0074 cm^{-1}), can be calculated using the values of resonance fields of low-field components of the fine structure. As it was mentioned above, the tensor D may be represented as a sum of exchange and dipole – dipole contributions. According to the equation (13), the latter contribution is inversely proportional to the cubed distance between paramagnetic centres. According to the X-ray data, the distance between the copper cations in the binuclear copper complex with hydrazone derived from malonohydrazide and 5-nitro-2-hydroxyacetophenone is $\sim$7 Å, which makes the contribution of the dipole – dipole interaction in compound **7** vanishingly small. Substituting the data obtained from the spectrum to Eqn (12), one can calculate the value of $-2J' \approx 1-3$ cm^{-1}. This value may be regarded as an approximate estimation of $-2J$ in spite of the fact that the value of $-2J'$ may be significantly different from the exchange parameter in the ground state.[7] It should be noted that the obtained value of $-2J$ is almost identical to the estimated value of the exchange parameter in binuclear complex **1** (n = 1) with dihydrazone based on acetylacetone related to compound **7**.[21,22]

The EPR spectrum of a polycrystalline sample of complex **7** at room temperature contains an intensive exchange-narrowed line with the g-factor equal to 2.11. Cooling of the sample down to 77 K results in a significant increase in absorption intensity and a very weak signal of forbidden transition ($\Delta M_S = \pm 2$) with g = 4.18 typical of binuclear copper(II) complexes appears in the low field region. The forbidden transition was not observed in the EPR spectra of polycrystalline samples of other complexes with dihydrazones and only very intense signals of allowed transition ($\Delta M_S = \pm 1$) with the g-factor values of $\sim$2.1 were recorded.

VII. Conclusion

The analysis of literature and the authors' own results show that the exchange spin – spin interactions with $-2J \approx 1$ cm^{-1} take place between paramagnetic centres in binuclear copper(II) complexes with dihydrazones based on saturated dicarbohydrazides. The registration of seven HFS lines in EPR spectra of the solutions at room temperature is the most clear manifestation of such an interaction. Several possible mechanisms of the exchange interactions may be suggested.

1. The formation of phenoxy bridges between copper(II) cations resulting in the appearance of intra- or intermolecular dimeric fragments Cu_2O_2.

2. The stacking interaction between pseudo-aromatic systems formed upon double bond delocalisation in chelate rings of the coordination sphere.

3. The indirect exchange (hyperexchange) through the system of σ-bonds of dihydrazone oligomethylene spacer.

The first possible mechanism may be rejected taking into account the conditions of the EPR spectra recording, as low concentrations of the complex [$(1-5)\times10^{-3}$ mol litre^{-1}] prevent intermolecular interactions and the presence of a large excess of the base results in splitting of oxo-bridges between the copper cations.

The copper(II) chelates with salicylidene hydrazones based on carbohydrazides were synthesised and investigated in order to test the possibility of formation of intermolecular associates in the solutions of studied dimers. A series of Cu(II) compounds from pentanoic acid derivatives octanoic acid derivatives was studied.[31] It was found that irrespective of the length of the aliphatic radical the EPR spectra of liquid solutions of this type of complexes contain isotropic signals of four HFS

lines with the following parameters $g = 2.106 - 2.107$ and $A_{Cu} = (77.5 - 78.5) \times 10^{-4}$ cm^{-1} typical of monomeric copper(II) complexes. This proves that the dimeric structures with phenoxide bridges are not formed in the solutions of studied binuclear complexes during recording of the EPR spectra.

The intermolecular stacking interaction between pseudo-aromtic systems of chelate rings and benzene rings of hydrazone was found by X-ray crystallography in the structure of copper complex with hydrazone based on malonohydrazide and 5-nitro-2-hydroxyacetophenone.[36] Previously it has been shown that the HFS of seven lines can be caused by an interaction between copper(II) cations in dimer stacks both in a crystal[49] and in a frozen solution.[50] In the latter case, the form of the spectrum strongly depends on the concentration of the complex. The seven-line HFS is observed in concentrated solutions while the four-line HFS is present in dilute solutions (due to dissociation of the complexes). The EPR spectra of binuclear copper(II) complexes with dihydrazones are independent of concentration. It means that in this particular case the probability of exchange due to intermolecular stacking interactions is very low. The analysis of the molecular structure of the complex [$Cu_2L \cdot 4$ Mrf] (see Fig. 3) shows that at least for $n = 1$, the intramolecular stacking interaction is sterically impossible.

Thus, the oligomethylene chain is the only possible channel of spin – spin exchange interactions between unpaired electrons in binuclear copper(II) complexes with dihydrazones. The strong effect of the length of the aliphatic spacer on the intensity of spin – spin exchange interactions is an argument in favour of this suggestion. This effect may be caused by spin-polarisation[51] of the oligomethylene chain or by the formation of extended molecular orbitals which include carbon atoms of the spacer.

References

1. S J Weissman, J Townsend, D E Paul, G E Pake *J. Chem. Phys.* **21** 2227 (1953)
2. J H E Griffits, J Owen, I M Ward *Proc. R. Soc. London, Ser. A* **219** 526 (1953)
3. A Abragam, B Bleaney *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon Press, 1970)
4. S A Al'tshuler, B M Kozyrev *Elektronnyi Paramagnitnyi Rezonans Soedinenii Elementov Promezhutochnykh Grupp* (Electron Paramagnetic Resonance of Elements of Intermediate Groups) (Moscow: Nauka, 1972)
5. L A Blyumenfel'd, V V Voevodskii, L G Semenov *Primenenie Elektronnogo Paramagnitnogo Rezonansa v Khimii* (The use of Electron Paramagnetic Resonance in Chemistry) (Novosibirsk: Siberian Branch of Academy of Sciences of the USSR, 1962)
6. J Wertz, J Bolton *Electron Spin Resonance* (New York: McGraw-Hill, 1972)
7. Yu V Yablokov, V K Voronkova, L V Mosina *Paramagnitnyi Rezonans Obmennykh Klasterov* (Paramagnetic Resonance of Exchange Clusters) (Moscow: Khimiya, 1972)
8. P Atkins, M Symons *The Structure of Inorganic Radicals* (Amsterdam: Elsevier, 1967)
9. Yu V Rakitin, G M Larin, V V Minin *Interpretatsiya Spektrov EPR Koordinatsionnykh Soedinenii* (Interpretation of EPR Spectra of Coordination Compounds) (Moscow: Nauka, 1993)
10. B Bleaney *Philos. Mag.* **42** 441 (1951)
11. R Livington, H Zeldes *J. Chem. Phys.* **44** 1245 (1966)
12. B I Shapiro, V M Kazakova, Ya K Syrkin *Zh. Strukt. Khim.* **6** 540 (1965) [a]
13. V M Kazakova, B I Shapiro, I G Makarov, Ya K Syrkin *Dokl. Akad. Nauk SSSR* **165** 1340 (1965) [b]
14. B I Shapiro, V M Kazakova, Ya K Syrkin *Dokl. Akad. Nauk SSSR* **165** 619 (1965) [b]
15. J Bolton, A Carrington *Mol. Phys.* **4** 497 (1961)
16. T R Tuttle *J. Am. Chem. Soc.* **84** 2839 (1962)
17. Yu V Rakitin, V T Kalinnikov *Sovremennaya Magnetokhimiya* (Modern Magnetochemistry) (St Petersburg: Nauka, 1994)
18. F Neese, Dissertation Doctor of Natural Science University of Konstanz, Konstanz, 1996
19. T D Smith, J R Pilbrow *Coord. Chem. Rev.* **13** 173 (1974)
20. M E Barr, P H Smith, W E Antholine, B Spencer *J. Chem. Soc., Chem. Commun.* 1649 (1993)
21. G M Larin, B B Umarov, V V Minin, Yu V Rakitin, V G Yusupov, N A Parpiev, Yu A Buslaev *Dokl. Akad. Nauk SSSR* **303** 139 (1988) [b]
22. G M Larin, V V Minin, Yu V Rakitin *Neorg. Mater.* **30** 1424 (1994) [c]
23. G M Larin, V F Shul'gin, E A Sarnit, Yu V Rakitin *Koord. Khim.* **25** 356 (1999) [d]
24. V F Shul'gin, E A Sarnit, V Ya Zub, G M Larin *Uchen. Zap. Simferop. Univ.* **7** (46) 190 (1998)
25. G M Larin, V F Shul'gin, E D Mel'nikova, V Ya Zub, Yu V Rakitin *Izv. Akad. Nauk, Ser. Khim.* 585 (2002) [e]
26. V F Shul'gin, E D Mel'nikova, V Ya Zub, G M Larin *Ukr. Khim. Zh.* **69** (12) 67 (2003) [f]
27. V F Shul'gin, E D Mel'nikova, V Ya Zub, G M Larin *Ukr. Khim. Zh.* **73** (2) 74 (2007) [f]
28. V F Shul'gin, E A Sarnit, G M Larin *Koord. Khim.* **24** 222 (1998) [d]
29. G M Larin, V F Shul'gin, E A Sarnit *Mendeleev Commun.* 129 (1999)
30. G M Larin, V F Shul'gin, E A Sarnit *Zh. Neorg. Khim.* **45** 1010 (2000) [g]
31. G M Larin, V F Shul'gin, E A Sarnit, Yu V Rakitin *Izv. Akad. Nauk, Ser. Khim.* 777 (2001) [e]
32. V F Shul'gin, E A Sarnit, G M Larin, V Ya Zub *Ukr. Khim. Zh.* **66** (11) 10 (2000) [f]
33. V F Shul'gin, A N Gusev, V Ya Zub, G M Larin *Izv. Akad. Nauk, Ser. Khim.* 2107 (2002) [e]
34. V F Shul'gin, A N Gusev, V Ya Zub, G M Larin *Izv. Akad. Nauk, Ser. Khim.* 1230 (2003) [e]
35. V F Shul'gin, A N Gusev, V Ya Zub, G M Larin *Izv. Akad. Nauk, Ser. Khim.* 1752 (2005) [e]
36. V F Shul'gin, A N Gusev, A N Chernega, G M Larin *Izv. Akad. Nauk, Ser. Khim.* 229 (2007) [e]
37. G M Larin, V F Shul'gin, A N Gusev, A N Chernega *Dokl. Akad. Nauk* **390** 627 (2003) [b]
38. G M Larin, V F Shul'gin, A N Gusev, A N Chernega *Izv. Akad. Nauk, Ser. Khim.* 740 (2004) [e]
39. V F Shul'gin, E D Mel'nikova, G M Larin, A N Chernega *Uchen. Zap. Tavrichesk. Nats. Un-ta im. V I Vernadskogo, Ser. Biol. Khim.* **19** (58) 139 (2006)
40. Ya S Lebedev, V I Muromtsev *EPR i Relaksatsiya Stabilizirovannykh Radikalov* (EPR and Relaxation of Stabilised Radicals) (Moscow: Khimiya, 1972)
41. R Wilson, D Kivelson *J. Chem. Phys.* **44** 154 (1964)
42. V N Parmon, A I Kokorin, G M Zhidomirov *Stabil'nye Biradikaly* (Stable Biradicals) (Moscow: Nauka, 1980)
43. G M Larin, G A Zvereva, V V Minin, Yu V Rakitin *Zh. Neorg. Khim.* **33** 2011 (1988) [g]
44. B Chiari, W E Hatfild, O Piovesana, T Tarantelli, L W Ter Haar, P F Zanazzi *Inorg. Chem.* **22** 1468 (1983)
45. V A Kogan, V V Zelentsov, G M Larin, V V Lukov *Kompleksy Perekhodnykh Metallov s Gidrazonami* (Complexes of Transition Metals with Hydrazones) (Moscow: Nauka, 1990)
46. G F Konoszka, R W Duerst *Coord. Chem. Rev.* **5** 209 (1970)
47. B A Goodman, J B Raynor, in *Advances in Inorganic Chemistry and Radiochemistry* Vol. 13 (New York: Academic Press, 1970) p. 135
48. O Kahn *Angew. Chem.* **97** 837 (1985)
49. D Snaathorst, H M Doesburg, J A A J Perenboom, C P Keijzers *Inorg. Chem.* **20** 2526 (1981)

50. S Das, G P Muthukumaragopal, Sat Pal, Sam Pal *New. J. Chem.* 1102 (2003)
51. G M Larin *Koord. Khim.* **18** 699 (1992) [d]

[a] — *J. Struct. Chem. (Engl. Transl.)*
[b] — *Dokl. Phys. Chem. (Engl. Transl.)*
[c] — *Inorg. Mater. (Engl. Transl.)*
[d] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[e] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[f] — *Ukr. Chem. J. (Engl. Transl.)*
[g] — *Russ. J. Inorg. Chem. (Engl. Transl.)*