Weak long-range spin–spin exchange interactions in a copper(II) complex

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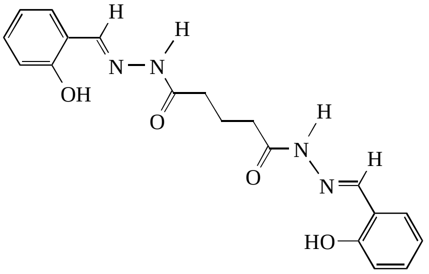
The molecular structure of the binuclear copper complex [$Cu_2L\cdot 2py\cdot 2MeOH$]$\cdot 2H_2O$ of glutaric acid bis(salicylidene)hydrazone (H_4L) was found by single-crystal X-ray diffraction analysis, and the EPR spectrum of this complex in solution was interpreted.

The synthesis and EPR spectra of binuclear copper complexes of dicarbonic acid bis(salicylidene)hydrazones in which two copper atoms are connected by a polymethylene chain have been described recently.[1] It was suggested that an exchange interaction between the paramagnetic ions through a chain of σ-bonds in these complexes takes place. Here we report the results of single-crystal X-ray diffraction analysis of the copper complex of glutaric acid bis(salicylidene)hydrazone (H_4L):



The compound was prepared according to the procedure described earlier.[1] Single crystals were prepared by recrystallization from a mixture of methanol with pyridine (20–30 vol%). The composition of the complex corresponds to the formula [$Cu_2L\cdot 2py\cdot 2MeOH$]$\cdot 2H_2O$ (**1**). The crystal structure and EPR spectra of compound **1** were examined.†

We found that molecular crystals of **1** are formed of discrete binuclear complexes [$Cu_2L\cdot 2py\cdot 2MeOH$] (Figure 1) without short intermolecular contacts. Two outer-sphere water molecules are located in the cavities of the crystal structure.

The coordination polyhedra of the copper atoms are equivalent and connected by the second-order axis; the Cu–Cu distance is 9.182 Å. The coordination polyhedra of the copper atoms exhibit the geometry of a distorted tetragonal pyramid the base of which is formed by a nitrogen atom and two oxygen atoms of the twice-deprotonated imidol form of salicylidenehydrazone and the nitrogen atom of pyridine. The apex of the pyramid is occupied by a weekly bonded methanol molecule. The angles at the copper atom are deflected from the ideal values 90.0 and 180.0° by 9.5°. The distances Cu–O(2) (1.969 Å) and Cu–N(1) (1.926 Å) are typical of copper complexes with the deprotonated imidol form of salicylidenehydrazone (1.96–1.98 and 1.92–1.94 Å, respectively).[7,8] At the same time, the copper–phenoxyl oxygen distance (1.901 Å) is shorter that that in dimeric complexes (1.92–2.04 Å) with bridging oxygen.[7,8] This can result from the disappearance of steric hindrances upon terminal coordination of the phenoxyl unit of the ligand. The distance between the copper atom and the oxygen atom of a methanol molecule suggests the formation of a weak coordination bond, which is typical of square-pyramidal copper complexes of salicylidenehydrazone. However, the Cu–O distance (2.422 Å) is longer than an analogous bond length of a coordinated ethanol molecule (2.22–2.31 Å) in dimeric complexes.[7,8] The carbon atom of a methyl group is disordered and occupies two approximately equivalent positions. The bonds C(1)–O(1) (1.309 Å), C(8)–O(2) (1.274 Å) and N(1)–N(2) (1.392 Å) are noticeably shorter that ordinary bonds; moreover, the bonds C(8)–N(2) (1.312 Å) and C(7)–N(1) (1.285 Å) are longer than double bonds.[9] This fact

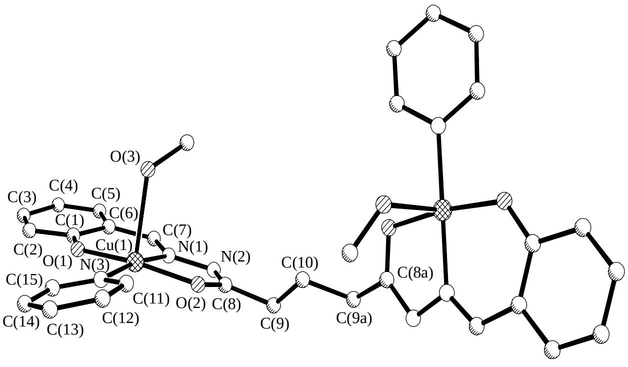


Figure 1 Molecular structure of complex **1** (the symbol 'a' was utilised for the atoms connected with initial by the axis 2). Selected bond lengths (Å): Cu(1)–O(1) 1.901(3), Cu(1)–O(2) 1.969(3), Cu(1)–O(3) 2.422(12), Cu(1)–N(1) 1.926(4), Cu(1)–N(3) 2.008(4), O(1)–C(1) 1.309(5), O(2)–C(8) 1.274(5), N(1)–N(2) 1.392(4), N(1)–C(7) 1.285(5), N(2)–C(8) 1.312(5), N(3)–C(11) 1.343(6), N(3)–C(15) 1.335(6), C(6)–C(7) 1.435(5), C(8)–C(9) 1.511(5), C(9)–C(10) 1.525(4); selected bond angles (°): O(1)–Cu(1)–O(2) 170.49(13), O(1)–Cu(1)–O(3) 94.7(3), O(2)–Cu(1)–O(3) 92.9(3), O(1)–Cu(1)–N(1) 92.99(16), O(2)–Cu(1)–N(1) 80.78(15), O(3)–Cu(1)–N(1) 94.0(3), O(1)–Cu(1)–N(3) 90.88(16), O(2)–Cu(1)–N(3) 94.57(16), O(3)–Cu(1)–N(3) 91.8(3), N(1)–Cu(1)–N(3) 172.69(14), Cu(1)–O(1)–C(1) 126.6(3), Cu(1)–O(2)–C(8) 109.8(2), Cu(1)–N(1)–N(2) 114.7(2), Cu(1)–N(1)–C(7) 127.2(3), N(2)–N(1)–C(7) 118.0(3), N(1)–N(2)–C(8) 109.5(3), Cu(1)–N(3)–C(11) 120.5(3), Cu(1)–N(3)–C(15) 121.2(3), C(11)–N(3)–C(15) 118.3(4).

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† The X-ray diffraction analysis of a single crystal of complex **1** with the linear dimensions 0.25×0.26×0.50 mm was carried out at ambient temperature on an Enraf-Nonius CAD-4 four-circle diffractometer (MoKα radiation, $\lambda = 0.71069$ Å, the ratio of scanning speeds $\omega/2\theta$ was 1.2, θ_{max} 27°, segment of sphere $-27 \le h \le 24$, $0 \le k \le 21$, $0 \le l \le 13$). For the determination of the parameters of an elementary cell and the orientation matrix, 22 reflections with $12.4 < \theta < 12.9°$ were used. 4122 reflections were collected (3787 unique reflections). Crystals of **1** are monoclinic, $a = 21.383(16)$ Å, $b = 16.866(8)$ Å, $c = 10.712(11)$ Å, $\beta = 114.75(7)°$, $V = 3508.4$ Å^3, $M = 749.76$, $Z = 4$, $d_{calc} = 1.42$ g cm^{-3}, $\mu = 12.68$ cm^{-1}. Space group $C2/c$. The structure was solved by a direct method and refined by a full-matrix least-squares technique using the CRYSTALS structure solution package.[2] In the specification, 2672 reflections with $I > 4\sigma(I)$ (207 refined parameters, the number of reflections per parameter 8.7) were used. All hydrogen atoms (except for H atoms of the disordered methyl group) were revealed objectively from the difference synthesis of electron densities and were included in the specification with fixed thermal and item parameters. The consideration of the absorption in a crystal was performed by the method of azimuth scanning.[3] In the refinement, the Tchebycheff weight function[4] with the parameters 1.20, –0.86, 0.45 and –0.84 was used. The final values were $R = 0.059$ and $R_w = 0.065$. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 1999. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/52.

The EPR spectra were recorded on a PS 100X spectrometer[5] [concentration ~5×10^{-3} M, solution in $CHCl_3$ + pyridine (20 vol%)]. The simulation of the EPR spectrum was carried out using the program package described elsewhere.[6]

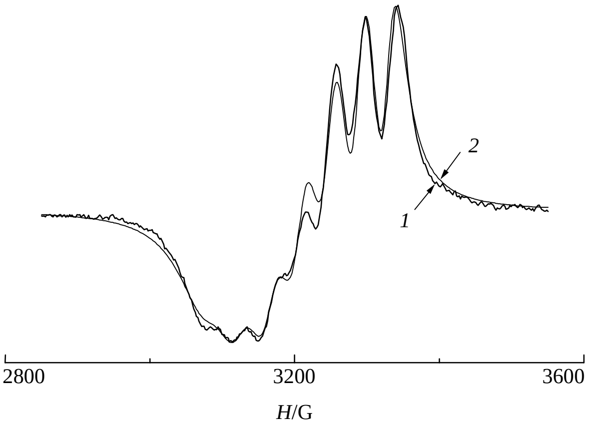

Figure 2 (*1*) Experimental and (*2*) theoretical EPR spectra of complex **1**.

may be indicative of delocalization of the double bonds in the chelates and formation of a pseudo-aromatic system. The bond lengths and valence angles of hydrazone hydrocarbon radicals and pyridine take standard values.

The group Cu(1)–O(1)–O(2)–N(1–3)–C(1–8,11–15) is approximately planar; the deviations of atoms from a plane are no higher than 0.38 Å. The atoms C(9) and C(10) are deflected from the plane by 0.51 and 0.52 Å, respectively. The Cu(1)–O(1)–N(1)–C(1)–C(6)–C(7) heterocycle is planar to within 0.078 Å, but the Cu(1)–O(2)–N(1)–N(2)–C(8), C(1–6) and N(3)–C(11–15) rings form dihedral angles of 7.2, 6.8 and 17.0°, respectively. The symmetrically connected groups Cu(1)–O(1)–O(2)–N(1)–N(2)–C(1–8) and Cu(1a)–O(1a)–O(2a)–N(1a)–N(2a)–C(1a–8a) are virtually perpendicular to one another; the corresponding dihedral angle is 81.88°.

Thus, the X-ray diffraction analysis demonstrated that binuclear complex **1** is monomeric and contains two copper cations connected by a chain of eight σ-bonds at a distance of 9.182 Å. Because of this, an independent behaviour of the paramagnetic centres would be expected. However, the EPR spectrum of a solution of complex **1** in MeCl–pyridine exhibits a seven-line isotropic signal of hyperfine structure with the intensity ratio 1:2:3:4:3:2:1 and the parameters $g = 2.106$; $a_{\mathrm{Cu}} = 39.9\times10^{-4}$ cm^{-1} (Figure 2) was observed. This spectrum was interpreted as a result of single-electron interactions with two equivalent nuclei of copper atoms. The solution of the spin-Hamiltonian for this system[10] shows that the hyperfine structure constant is equal to a half of the constant for the monomeric complexes, *i.e.*, about 40×10^{-4} cm^{-1}. A theoretical simulation of the EPR spectrum confirms this conclusion (Figure 2).

Seven lines with the above intensity ratio and hyperfine structure constants were usually observed in EPR spectra at forbidden transitions of dimeric copper complexes[10,11] which exhibit strong antiferromagnetic interactions (of several tens or hundreds of cm^{-1}). At allowed transitions, the isotropic EPR spectra of the binuclear copper complexes exhibit seven lines of the hyperfine structure at a lower energy (0.1–1 cm^{-1}).[6,12,13] It is believed that the bond lengths and valence angles in molecules of **1** in solution and in the solid state are similar, because the Cu–Cu distance in solutions and single crystals are similar. Consequently, the weak spin–spin exchange interaction in compound **1** can be realised by delocalization of single electrons *via* a σ-bond chain of the polymethylene bridge.

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