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Structure of the Planar Acetate-Bridged Binuclear Copper(II) Complex Based on 1,3-Bis(3-Formyl-5-*tert*-Butylsalicylidenimino)propanol-2

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Abstract—The X-ray diffraction and magnetochemical studies of the acetate-bridged binuclear copper(II) complex with 1,3-bis(3-formyl-5-*tert*-butylsalicylidenimino)propanol-2 with a nearly planar structure of the exchange fragment are carried out (CIF file CCDC 940849). The assumption that the magnetic exchange in the complexes with the anticomplementary carboxylate exogenic bridges 1,3-O,O' is determined only by the structural factors and the bridging coordination of the solvent molecule changes the type of the exchange interaction between the copper(II) ions is proved to be true.

Keywords: binuclear copper(II) complexes, magnetochemistry, exchange interaction, X-ray diffraction analysis

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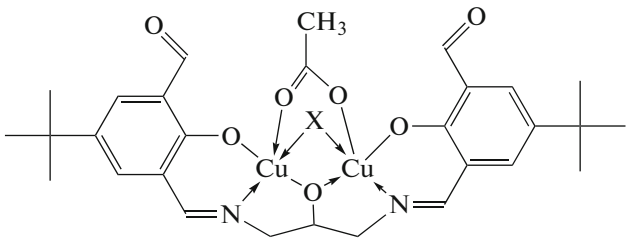
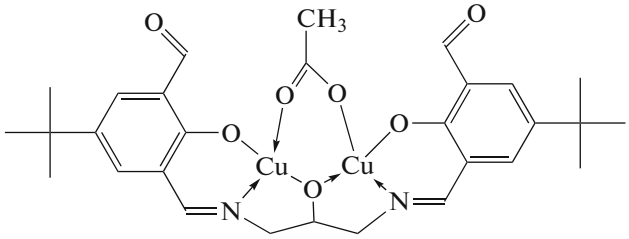
INTRODUCTION

We have previously described the structure of the binuclear copper(II) complex with 1,3-bis(3-formyl-5-*tert*-butylsalicylidenimino)propanol-2 (**I**) having a distorted (roof-shaped) structure due to the bridging coordination of the DMSO molecule [1]. A structure close to planar was proposed for complex **II** with the same ligand containing no DMSO molecule on the basis of the data of EXAFS spectroscopy [2]. The difference in structures of the exchange fragments results in the situation that the exchange interaction between the copper(II) ions in complex **I** is ferromagnetic and that in complex **II** is antiferromagnetic [1–3].



(I) X = DMSO



(II)

It was shown by the quantum-chemical simulation of the exchange interaction using the DFT method in the broken symmetry approach that the role of the DMSO molecule in the acetate-bridged binuclear copper(II) complexes was exclusively the stabilization of a distorted conformation of the exchange fragment rather than the formation of new exchange channels [2, 3]. A similar phenomenon was observed for

† Deceased.

Table 1. Crystallographic data and experimental and refinement characteristics for compound **I**

Parameter	Value
Empirical formula	$C_{29.5}H_{36}N_2O_{7.5}Cu_2$
FW	665.68
Crystal size, mm	0.28 × 0.20 × 0.12
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	12.2899(9)
b, Å	9.2124(7)
c, Å	26.3350(19)
β, deg	97.700(2)
V, Å^3	2954.7(4)
Z	4
ρ_{calcd}, g/cm^3	1.496
μ, mm^{-1}	1.490
F(000)	1380
Scan range over θ, deg	1.67–26.00
Number of measured reflections	21 630
Number of independent reflections	5766
Number of reflections with $I > 2\sigma(I)$	4202
Ranges of reflection indices	$-15 < h < 15$, $-11 < k < 11$, $-32 < l < 31$
Number of refined parameters	414
R_1 ($I > 2\sigma(I)$)	0.0419
wR_2 (all reflections)	0.0971
GOOF (all reflections)	1.017
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.517/–0.413

another pair of acetate-bridged binuclear copper(II) complexes with bis(azomethine), the condensation product of 1-phenyl-3-methyl-4-formylpyrazolone-5 and 1,3-diaminopropanol-2 [4].

The X-ray diffraction analysis results for the binuclear copper(II) complex with 1,3-bis(3-formyl-5-*tert*-butylsalicylidenimino)propanol-2 of the type of complex **II** with the nearly planar structure in which the exchange interaction is antiferromagnetic are presented in this report.

EXPERIMENTAL

The X-ray diffraction analysis for complex **II** was carried out on a Bruker APEX II CCD diffractometer (MoK_α, λ = 0.71073 Å, graphite monochromator, ω-scan mode) at 100 K. The initial array of measured intensities was processed using the SAINT and SADABS programs included into the APEX2 program package [5, 6]. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms for F^2_{hkl}. Hydrogen atoms were placed in geometrically calculated positions and refined by the riding model ($U_{iso}(H) = nU_{iso}(C)$, where $n = 1.5$ for the carbon atoms of the methyl groups and $n = 1.2$ for other C atoms). Decoding and refinement were performed using the SHELXTL program [7]. The PLATON program was used for the analysis of the molecular and crystal structures [8]. The experimental characteristics and crystallographic data for complex **II** are presented in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 940849; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

A single crystal of complex **II** was obtained by the slow crystallization of complex **I** from a methanol

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the copper atoms in a molecule of compound **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(4)	1.895(2)	Cu(2)–O(6)	1.891(2)
Cu(1)–O(3)	1.906(2)	Cu(2)–O(3)	1.920(2)
Cu(1)–O(2)	1.937(2)	Cu(2)–N(2)	1.929(3)
Cu(1)–N(1)	1.941(3)	Cu(2)–O(1)	1.954(2)
Angle	ω, deg	Angle	ω, deg
O(4)Cu(1)O(3)	170.00(11)	O(6)Cu(2)O(3)	175.23(10)
O(4)Cu(1)O(2)	89.27(10)	O(6)Cu(2)N(2)	93.75(11)
O(3)Cu(1)O(2)	95.40(10)	O(3)Cu(2)N(2)	84.49(11)
O(4)Cu(1)N(1)	92.21(11)	O(6)Cu(2)O(1)	87.29(10)
O(3)Cu(1)N(1)	85.18(11)	O(3)Cu(2)O(1)	95.18(10)
O(2)Cu(1)N(1)	167.28(11)	N(2)Cu(2)O(1)	170.49(12)

solution. The molecular structure of the complex is presented in Fig. 1. Both copper ions are in the coordination environment close to a square one. The O(1) and O(2) atoms of the carboxyl bridge shift from the mean plane of other donor atoms by 0.420 and 0.746 Å, respectively.

The six-membered metallocycle Cu(2)N(2)-C(18)C(19)C(29)O(6) is nearly planar. The Cu(1)N(1)C(14)C(13)C(3)O(4) cycle is nonplanar because of the shift of the Cu(1) atom from the mean plane of other atoms by 0.380 Å. The conformation of the five-membered metallocycle Cu(1)N(1)C(15)-C(16)O(3) can be described as a twist one relative to the C(15)–C(16) bond. The five-membered chelate cycle Cu(1)N(2)C(17)C(16)O(3) has an envelope conformation, whose valve, C(17) atom, shifts from the mean plane of other atoms by 0.545 Å.

The methylene carbon atoms C(15) and C(17) are located at one side common for both cycles of the C(16)–O(3) bonds, so that the λλ conformation of the complex takes place [9].

On the whole, the molecule of complex **II** is nearly planar as in the most part of the earlier described carboxylate-bridged copper(II) complexes with the bis(azomethine) derivatives of 1,3-diaminopropanol-2 [2, 10]. The alkoxide bridging O(3) atom is not pyramidalized, and the sum of bond angles at this atom is 359.86°. The value of the dihedral angle between the coordination planes, CuO_3N, usually used as a quantitative measure of the distortion of the binuclear fragment in similar complexes [11] is equal to 176.32°. The Cu(1)O(1)Cu(2) bond angle is 132.2(2)°.

The previously described binuclear complex **I** has a roof-shaped structure (δλ conformation [9]). The

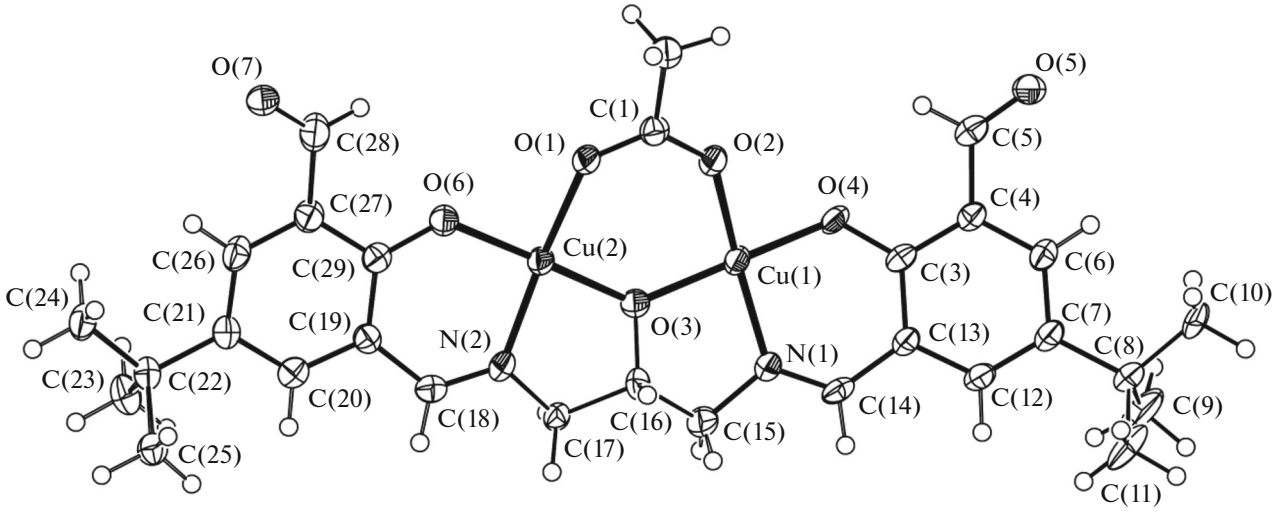


Fig. 1. Structure of the molecule of complex **II** in the representation of atoms by atomic shift ellipsoids of 50% probability.

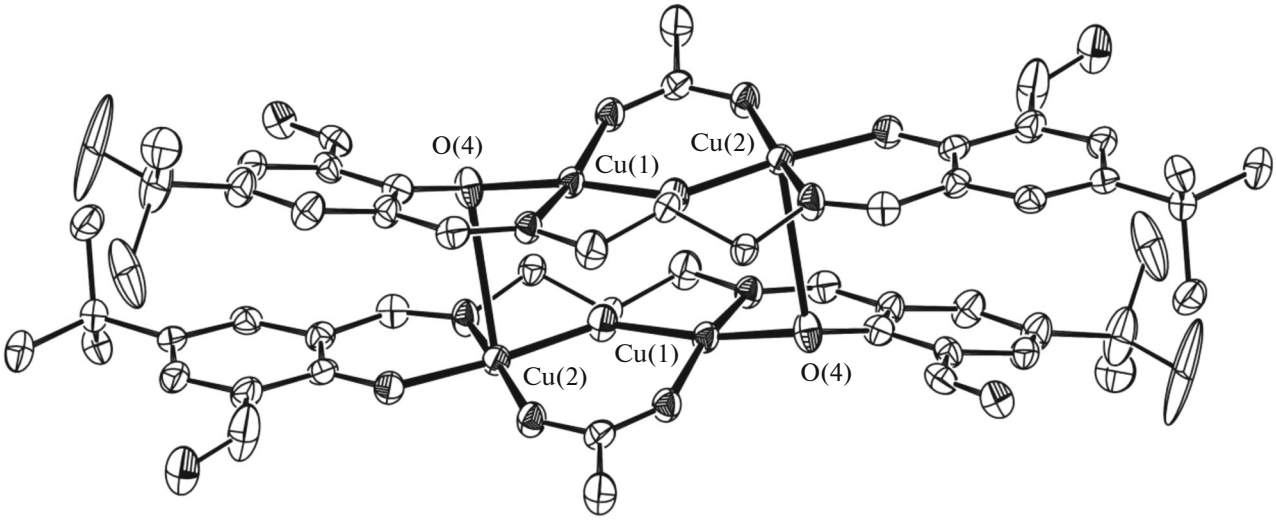


Fig. 2. Centrosymmetric dimers in a crystal of complex **II** (hydrogen atoms are omitted).

dihedral angle between the corresponding coordination planes is 128.59°, and the CuOCu bond angle at the alkoxide bridging atom is 109.29(11)° [1, 2].

The copper–copper distance in complex **II** is 3.4971(6) Å, which is consistent with the copper–copper distance obtained for the amorphous samples of the complex by EXAFS spectroscopy (3.51 Å) and with the results of the quantum-chemical calculation of the geometry using the DFT/B3LYP/6-311G(*d*, *p*) method (3.512 Å) [2]. This distance is substantially longer than Cu–Cu in complex **I** (3.168(3) Å) [1].

In the crystal of complex **II**, the phenoxide O(4) atom forms a weak coordination bond Cu(2)–O(4)^{i} 2.924(3) Å ($^{i}2 - x$, $1 - y$, $-z$) with the Cu(2)^{i} atom of the adjacent molecule, supplementing the coordination polyhedron of copper(II) to a strongly extended square pyramid (4 + 1). This leads to the formation of centrosymmetric dimers (Fig. 2) packed in infinite stacks extended along the crystallographic axis *y* (Fig. 3).

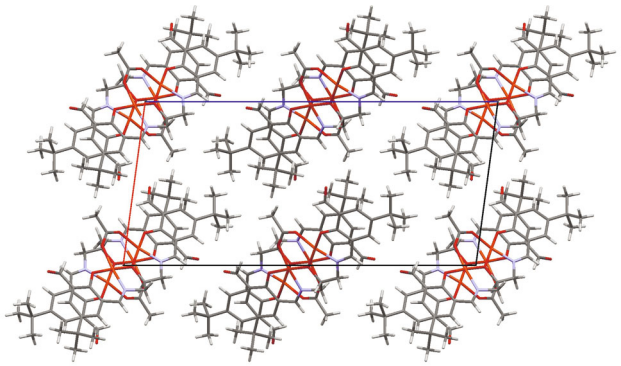


Fig. 3. Packing of the dimers in a single crystal of complex **II** (view along the crystallographic axis *y*).

The formation of similar dimers is fairly abundant among the carboxylate-bridged copper(II) complexes with bis(azomethines) based on the derivatives of salicyladehyde and 1,3-diaminopropanol-2 [9, 12, 13].

The structure of complex **II** also contains 0.5 methanol molecule, which is not coordinated to the copper atoms. The hydrogen bond O(1S)–H(1SO)···O(1) (D–H 0.96, H···O 2.27, O···O 2.920(6) Å, angle DHA 124°) is observed in the crystal.

The magnetic exchange parameter 2*J* between the copper(II) ions in complex **II** calculated in terms of the Heisenberg–Dirac–Van Vleck isotropic model [14] is –95 cm^{-1} (g = 2.20, temperature-independent paramagnetism $N_{\alpha} = 60 \times 10^{-6}$ cm^3/mol, molar fraction of the paramagnetic impurity f = 0.001). The magnetic properties of single-crystal complex **II** are completely identical to those for the amorphous sample ($2J = -94.8$ cm^{-1}) [1, 2].

Thus, the fact that both symmetric (λλ) and roof-shaped (δλ) conformations of the metallochelate cycles can take place in the acetate-bridged binuclear copper(II) complex with the same ligand 1,3-bis(3-formyl-*tert*-butylsalicylidenimino)propanol-2 [15] was directly confirmed by the X-ray diffraction method. The stabilization of the roof-shaped conformation is due to the bridging coordination of the solvent (DMSO) molecule. As a result, the magnetic exchange interaction can be both antiferromagnetic and ferromagnetic in the binuclear copper(II) complex with the same ligand. It can be considered proved that the character of the magnetic interaction in the complexes with the anticomplementary [16] carboxyl-

ate 1,3-O,O' exogenic bridges is determined by structural factors only.

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