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# Crystal Structure and Magnetic Properties of Binuclear Copper(II) Complex with 2-*N*-(Phenylhydrazono)-3-((Ethyl-2-Olato)imino)-1-Phenyl-1,2,3-Butanetrione

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**Abstract**—The binuclear copper(II) complex based on azomethine, being a condensation product of 2-aminoethanol with 1-phenyl-1,2,3-butanetrione phenylhydrazone, is structurally characterized (CIF file CCDC 1059996). The structure is compared with the structure of an analog containing the axially coordinated pyridine molecule. The influence of the axial coordination of pyridine on the magnetic exchange interaction is studied by the DFT method in the broken symmetry approach.

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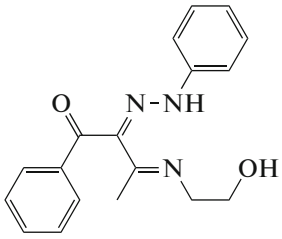
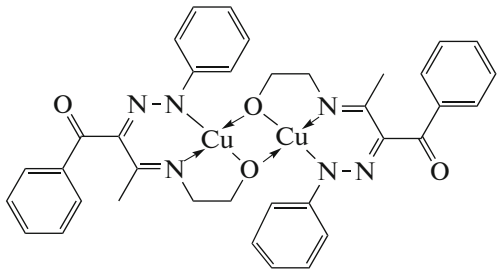
## INTRODUCTION

Hydrazones and azomethines of polyfunctional carbonyl compounds are among the most studied ligand systems of the modern coordination and supramolecular chemistry, since they readily form coordination compounds with the most part of transition metals [1–3]. The corresponding bi- and polynuclear complexes are good models for the construction of magnetostructural relationships that are demanded due to developments of novel molecular magnetic materials [4–7]. The problem of the influence of an additional coordination of solvent molecules to metal ions on the character of the magnetic exchange interaction is rather poorly studied [8]. We have previously shown [9–11] that the coordination of a DMSO molecule can exert such a substantial influence on the structure of the exchange fragment in the binuclear copper(II) complexes that this results in a change in the sign of the exchange interaction from antiferromagnetic and ferromagnetic.

The results of X-ray diffraction analyses of binuclear complex (**I**), the copper(II) complex with 2-*N*-(phenylhydrazono)-3-((ethyl-2-olato)imino)-1-phenyl-1,2,3-butanetrione ($H_2L$), and its analog containing the axially coordinated pyridine molecule (**II**) described by us earlier [12] and the data on the quantum-chemical simulation of the influence of the axial coordination of pyridine on the magnetic exchange interaction in the complex are reported.




($H_2L$)




(**I**)

## EXPERIMENTAL

Complex **I** was synthesized according to a described procedure [13].

**The X-ray diffraction analysis** of complex **I** was carried out on a KUMA-P4 diffractometer (Mo$K_\alpha$ radiation, $\alpha = 0.71073$ Å, graphite monochromator, $\omega/2\theta$ scan mode). The structure was solved by a direct method and refined by the full-matrix least-squares

† Deceased.

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

| Parameter | Value |
|---|---|
| Empirical formula | $C_{36}H_{34}Cu_2N_6O_4$ |
| *FW* | 741.77 |
| Crystal size, mm | 0.20 × 0.18 × 0.18 |
| Temperature, K | 295(2) |
| Crystal system | Orthorhombic |
| Space group | *Pbca* |
| *a*, Å | 13.133(2) |
| *b*, Å | 14.233(3) |
| *c*, Å | 17.701(2) |
| *V*, Å$^3$ | 3308.7(9) |
| *Z* | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.489 |
| μ, mm$^{-1}$ | 1.335 |
| *F*(000) | 1528 |
| Scan θ range, deg | 2.30–26.09 |
| Number of measured reflections | 3218 |
| Number of independent reflections | 3218 |
| Number of reflections with $I > 2\sigma(I)$ | 1742 |
| Ranges of reflection indices | $0 < h < 16$<br>$0 < k < 17$<br>$0 < l < 21$ |
| Number of refined parameters | 217 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0351 |
| $wR_2$ (all reflections) | 0.1263 |
| GOOF (all reflections) | 1.030 |
| $\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å$^{-3}$ | 0.355/–0.575 |

method in the anisotropic approximation for non-hydrogen atoms for $F^2_{hkl}$ (SHELXTL) [14]. The experimental characteristics and crystallographic data 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 1059996; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Quantum-chemical calculations were performed in the framework of the density functional theory (DFT) using the B3LYP hybrid exchange-correlation potential [15, 16]. The earlier approved [17] procedure based on the broken symmetry approach was used for the calculation of the exchange parameters 2*J* [18–21]. The extended (by added polarization functions) split-valence 6-311G(*d*) basis set was used. The calculations were performed using the Gaussian 03 program [22]. The Chemcraft program [23] was used for the preparation of data and presentation graphics and for the visualization of results. The energies of triplet and broken symmetry states, the calculated exchange parameters 2*J*, and some structural parameters for complexes **I** and **II** are presented in Table 3.

## RESULTS AND DISCUSSION

A single crystal of complex **I** was obtained by slow crystallization from DMSO. The molecular structure of the complex is shown in Fig. 1.

Complex **I** is a centrosymmetric dimer. The coordination polyhedron of the copper(II) ion is a weakly distorted square. The bond angle at the bridging oxygen atom in Cu(1)O(l)Cu(1a) is equal to 102.3(1)°, and the Cu–Cu distance is 2.983(1) Å.

The conformation of the five-membered chelate Cu(1)N(1)C(11)C(12)O(1) in complex **I** can be described as twist over the C(11)–C(12) bond. The six-membered metallocycle Cu(1)N(1)C(9)C(8)N(3)N(2) has a half-chair conformation, and the Cu(1) atom is shifted from the mean plane of other five atoms by 0.405 Å.

In the earlier described complex **II** with the same ligand containing the pyridine molecule axially coordinated to one of the copper(II) atoms [12], the central bimetallic fragment is distorted due to the inflection along the O–O line by 7.3° and the bond angles at the bridging oxygen atoms are 101.8(1)° and 103.5(1)°. In spite of the inflection of the four-membered ring, the

**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)–N(1) | 1.919(3) | Cu(1)–O(1) | 1.919(2) |
| Cu(1)–N(2) | 1.909(2) | Cu(1)–O(1a) | 1.911(2) |
| Angle | ω, deg | Angle | ω, deg |
| N(2)Cu(1)O(1) | 172.35(11) | N(1)Cu(1)O(1) | 84.72(10) |
| N(2)Cu(1)N(1) | 92.98(10) | N(1)Cu(1)O(1a) | 160.22(10) |
| N(2)Cu(1)O(1a) | 105.58(10) | O(1)Cu(1)O(1a) | 77.71(10) |

**Table 3.** Energies of triplet (*HS*) and broken symmetry (*BS*) states, the calculated exchange parameters $2J$, bond angles α at the alkoxide bridging atom, and the Cu–Cu distances in complexes **I** and **II**

| Complex | ω, deg | Cu···Cu, Å | Full energy of state, aeu | | $2J_{calcd}$, $cm^{-1}$ |
|---|---|---|---|---|---|
| | | | *HS* | *BS* | |
| **I** | 102.3(1) | 2.983(1) | −5302.521373 | −5302.523243 | −411 |
| **II** | 103.5(1)<br>101.8(1) | 3.029(1) | −5550.934969 | −5550.936772 | −396 |

Cu–Cu distance in complex **II** (3.029(1) Å) is somewhat longer than that in complex **I**.

Nevertheless, when the molecules of complexes **I** and **II** are superimposed by the positions of the Cu atom (coordination number 4) and its nearest environment, the distance between the Cu(1a) atom in complex **I** and Cu(2) in complex **II** is 0.155 Å and the corresponding fragments of the superimposed molecules diverge insubstantially. For example, the distance between the C(6) and C(13) atoms and that between their analogs are 0.73 and 0.38 Å, respectively. Thus, the axial coordination of the pyridine molecule to one of the copper ions in dimeric complex **II** changes the structural parameters only in the moiety of the dimer containing the copper ion with the coordination number 5.

Since the main structural parameters of compounds **I** and **II** affecting the magnetic exchange interaction in the binuclear complexes [3] are fairly close, their experimental magnetic properties differ insignificantly. The exchange parameter $2J$ in complexes **I** and **II** is −396 and −380 $cm^{-1}$, respectively.

For the theoretical study of exchange interactions in complexes **I** and **II**, we performed the quantum-chemical calculation of parameter $2J$ in the framework of the broken symmetry (*BS*) approach [18–21] for the fixed (according to the X-ray diffraction analysis data) geometry of the complexes. The Ruiz equation [24] based on the assumption of strong overlapping of molecular spin orbitals of the paramagnetic centers was used for the calculation of the exchange parameter in terms of the *BS* approach.

The quantum-chemical calculation of the exchange interaction parameter in the complexes using fixed geometry gives an excellent agreement with experiment. The pyridine molecule in complex **II** exerts almost no effect on the difference in energies between the triplet and *BS* states. Since the *p*-orbital factor along with the geometric factors exerts a substantial effect on the exchange interaction between the paramagnetic centers, the shape of the molecular spin orbitals and the spin density distribution in the complexes were examined (the spin density distribution in the *BS* state of complexes **I** and **II** are presented in Fig. 2). In both cases, the highest occupied molecular spin orbitals are substantially delocalized over the molecule of the complexes. In addition to the contribution of the copper(II) ions, the contribution from the atomic orbitals of the bridging oxygen atoms and the donor atoms of the nearest coordination environment is significant. Although each molecular spin

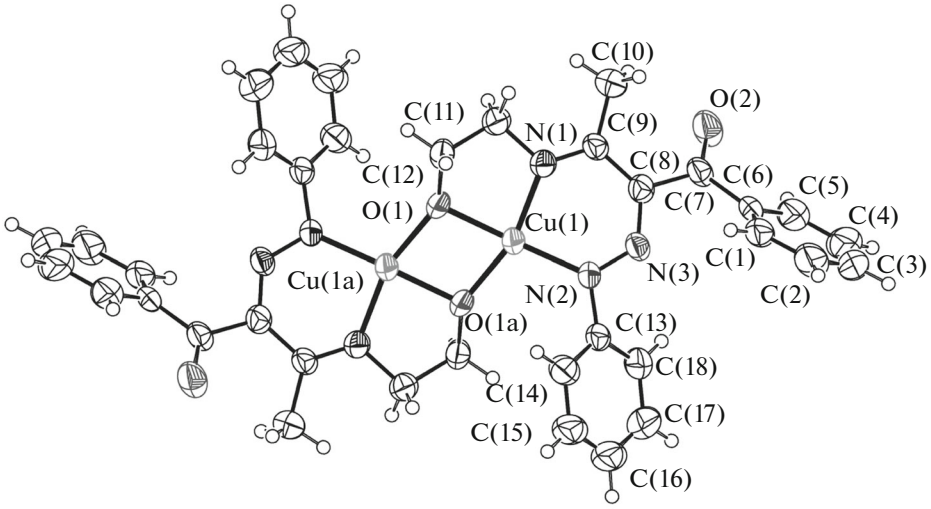



**Fig. 1.** General view of a molecule of complex **I** in the representation of atoms by atomic shift ellipsoids with 50% probability.

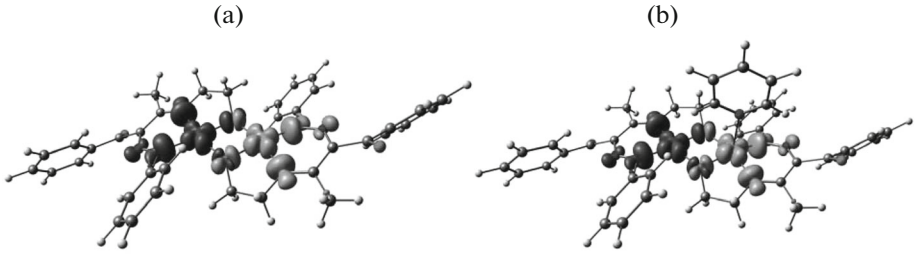



**Fig. 2.** Spin density distribution in the *BS* state for complexes (a) **I** and (b) **II**.

orbital is predominantly localized on the atoms of one of the paramagnetic centers, there is a contribution of the *d* atomic orbital of the second copper(II) ion. The coordination of the pyridine molecule in complex **II** does not substantially change the shape of the molecular spin orbital and the spin density distribution. The spin density on the pyridine nitrogen atom is equal to zero in both the triplet and *BS* states. This indicates that the pyridine molecule is not involved in the redistribution of the density of the lone electron on the copper atom, which is completely explained by the formally orthogonal character of the molecular spin orbital of the paramagnetic center and the σ orbital of the pyridine nitrogen atom [25].

Thus, the axial coordination of the pyridine molecule to one of the copper ions in the dimeric copper(II) complex with 2-*N*-(phenylhydrazono)-3-((ethyl-2-olato)imino)-1-phenyl-1,2,3-butanetrione results in some change in the structural parameters but exerts almost no effect on the magnetic exchange interaction between the copper(II) ions.

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