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Tetranuclear Copper(II) Complex with the Heterocyclic Azomethine Ligand: Crystal Structure and Magnetic Properties

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Abstract—A tetranuclear copper(II) complex based on azomethine, which is the condensation product of 1-phenyl-3-methyl-4-formylpyrazol-5-one with 1,3-diaminopropan-2-ol, is synthesized. The complex includes two different tetranuclear clusters: symmetrical and unsymmetrical. They have a pseudo-cubane structure and are in a ratio of 1 : 2. The quantum-chemical calculation shows that the "unsymmetrical" conformer does not correspond to the local minimum on the molecular potential energy surface. Its existence is thus determined by the crystalline packing effects. According to the results of measurements of the temperature dependence of the magnetic susceptibility, the ground spin state is a singlet caused by the overall antiferromagnetic interaction between the copper ions. Accepting the molar magnetic susceptibility of the complex to be equal to the sum of susceptibilities of the "symmetrical" and "unsymmetrical" clusters and assuming that the spin-Hamiltonian for both clusters includes three exchange parameters, the temperature dependence of the magnetic susceptibility of the complex is satisfactorily described with the following parameters of the model: $J_{1A} = -178$, $J_{2A} = 80$, $J_{3A} = 18$, $J_{1B} = -26$, $J_{2B} = -74$, $J_{3B} = 46$ cm^{-1}, $g_A = g_B = 2.05$.

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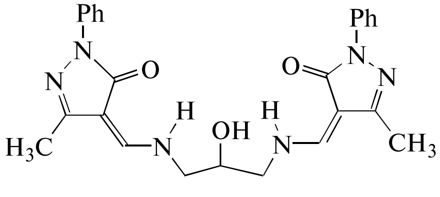
INTRODUCTION

Azomethines and hydrazones of polyfunctional carbonyl compounds are among the most studied types of ligand systems in the current coordination and supramolecular chemistry [1–6]. There are many data on the structure and magnetic properties of the binuclear copper(II) complexes with 1,3-diaminopropan-2-ol bisazomethines based on β-diketones or salicylaldehyde and its substituted derivatives, which are convenient models for studying the main factors determining the character and strength of exchange interactions between the paramagnetic centers due to a comparative easiness of variation of the nature of the donor centers, central ions, and exogenic bridging groups [7–10]. At the same time, the possibility of formation of tetra- and octanuclear complexes is mentioned in several works concerning these ligand systems [7].

The results of the X-ray diffraction analysis and magnetochemical study of the tetranuclear copper(II) complex with the azomethine ligand (the condensation product of 1-phenyl-3-methyl-4-formylpyrazol-5-one and 1,3-diaminopropan-2-ol, H_3L) are presented in this work.



H_3L

EXPERIMENTAL

Bisazomethine H_3L was synthesized according to a published procedure [11].

Synthesis of the copper(II) complex with azomethine (I). A hot solution of copper(II) perchlorate (0.002 mol) in methanol (10 mL) was poured to a hot solution of H_3L (0.001 mol) in methanol (30 mL), and sodium azide (0.02 mol) was added. The reaction mixture was refluxed with a reflux condenser for 4 h and left to stay overnight. The precipitate was filtered off, washed with methanol, dried in vacuo, and recrystallized from acetonitrile. The yield was 30%.

For $C_{168}H_{167}N_{63}O_{19}Cu_{12}$

anal. calcd., %:	C, 48.80;	H, 4.07;	N, 21.34;	Cu, 18.44.
Found, %:	C, 48.54;	H, 4.26;	N, 20.98;	Cu, 18.72.

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

Parameter	Value
Formula weight	4135.13
Crystal size, mm	0.14 × 0.09 × 0.02
Temperature, K	100(2)
Crystal system	Monoclinic
Space group	*C*2
a, Å	30.5916(17)
b, Å	12.2029(7)
c, Å	27.1373(15)
β, deg	117.0230(10)
V, Å^3	9024.5(9)
Z	2
ρ_{calcd}, g/cm^3	1.522
μ, mm^{-1}	1.464
F(000)	4232
θ scan range, deg	1.68–29.00
Number of measured reflections	53631
Number of independent reflections	23865
Number of reflections with $I > 2\sigma(I)$	16143
Ranges of reflection indices	$-41 < h < 41$, $-16 < k < 16$, $-37 < l < 37$
Number of refined parameters	1175
R_1 ($I > 2\sigma(I)$)	0.0542
wR_2 (all reflections)	0.1104
Goodness-of-fit (all reflections)	0.982
$\Delta\rho_{\max}/\Delta\rho_{\min}$, eÅ^{-3}	0.714/–0.506

IR (ν, cm^{-1}): 2062 $\nu_{as}(N_3)$, 1623, 1598 ν(C=N), 1312 $\nu_s(N_3)$.

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in a range of 400–4000 cm^{-1}, and the samples were prepared as suspensions in Nujol.

The magnetic susceptibility of complex **I** in the temperature range from 300 to 2 K was determined on a SQUID magnetometer (Quantum Design) in a magnetic field of 5 kOe.

X-ray diffraction analysis of I was carried out on a Bruker SMART APEX2 CCD diffractometer (MoK_α, λ = 0.71073 Å, graphite monochromator, ω scan mode). The initial array of measured intensities was processed using the SAINT and SADABS programs included into the APEX2 program package [12]. The structure was solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms for F^2_{hkl}. Hydrogen atoms were placed in the geometrically calculated positions, except for the hydrogen atoms of the water molecules found from the difference electron density synthesis and normalized to the O–H distance equal to 0.85 Å. All hydrogen atoms were included into the refinement in the framework of the riding model. The positions of the disordered acetonitrile molecules were refined in the isotropic approximation. The crystal structure is a racemic twin and, hence, the TWIN and BASF instructions were used for the refinement of the atomic coordinates; the BASF coefficient being 0.492(9). The structures were solved and refined using the SHELXTL program [13]. The experimental characteristics and crystallographic data are given in Table 1. Selected interatomic distances and bond angles are listed in Tables 2 and 3. The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (no. 854146; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Quantum-chemical simulation. Calculations were performed in the framework of the density functional theory (DFT) using the hybrid exchange-correlation B3LYP functional [14] in the extended 6-311G(d) basis set of Gaussian functions. The Gaussian'03 program [15] installed at the Supercomputer Center of the Southern Federal University was used for calculations. The molecular models in which the phenyl and methyl groups of the pyrazolone fragments were substituted by hydrogen atoms to decrease computational expenses. Geometry optimization was performed without any symmetry restraints.

RESULTS AND DISCUSSION

Complex **I**, $[Cu_{12}L_6(N_3)_6] \cdot 9C_2H_3N \cdot H_2O$, was obtained by the reaction of bisazomethine H_3L with copper(II) perchlorate in the presence of triethylamine and sodium azide followed by recrystallization from acetonitrile. The structure of complex **I** was determined by X-ray diffraction analysis.

The symmetrically independent part of the unit cell of compound **I** contains 1.5 molecules of the complex (**A** and **B**; **B** exists in the partial position in the 2-fold symmetry axis), 4.5 acetonitrile molecules, and 0.5 water molecule. The ratio of the **A** and **B** molecules in the unit cell is 2 : 1. The structures of both complexes **A** and **B** can formally be described as two binuclear fragments bound by the bridging azide groups (Fig. 1). This results in the formation of a distorted core cubic fragment $Cu_4N_2O_2$ in which the copper atoms lie in the vertices of the tetrahedron inscribed into this cube. The coordination modes of the copper atoms in the complex and the structures of these symmetrically independent molecules are different. In both molecules, the copper atoms are most strongly bound to four N and O atoms to form the square planar geometry. The Cu–O and Cu–N bond lengths lies in ranges of 1.91–1.99 and 1.93–2.07 Å, respectively (Tables 1, 2).

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

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.988(3)	Cu(3)–O(4)	1.953(3)
Cu(1)–O(2)	1.933(3)	Cu(3)–O(5)	1.919(3)
Cu(1)–N(1)	1.944(4)	Cu(3)–N(10)	2.071(4)
Cu(1)–N(7)	1.994(4)	Cu(3)–N(13)	1.933(4)
Cu(2)–O(1)	1.943(3)	Cu(4)–O(4)	1.934(3)
Cu(2)–O(3)	1.911(3)	Cu(4)–O(6)	1.926(3)
Cu(2)–N(4)	1.944(4)	Cu(4)–N(7)	1.990(4)
Cu(2)–N(10)	1.987(4)	Cu(4)–N(16)	1.955(4)
Angle	**α, deg**	**Angle**	**α, deg**
Cu(1)O(1)Cu(2)	121.48(16)	O(3)Cu(2)N(10)	93.95(15)
Cu(3)O(4)Cu(4)	101.91(15)	N(4)Cu(2)N(10)	168.30(16)
Cu(1)N(7)Cu(4)	113.67(19)	O(4)Cu(3)O(5)	178.65(14)
Cu(2)N(10)Cu(3)	94.23(15)	O(4)Cu(3)N(10)	93.06(15)
O(1)Cu(1)O(2)	174.49(14)	O(5)Cu(3)N(10)	85.96(15)
O(1)Cu(1)N(1)	83.85(14)	O(4)Cu(3)N(13)	84.19(16)
O(2)Cu(1)N(1)	95.64(14)	O(5)Cu(3)N(13)	96.96(15)
O(1)Cu(1)N(7)	92.77(15)	N(13)Cu(3)N(10)	167.72(16)
O(2)Cu(1)N(7)	87.96(15)	O(4)Cu(4)O(6)	177.79(15)
N(1)Cu(1)N(7)	175.81(17)	O(4)Cu(4)N(7)	86.81(15)
O(1)Cu(2)O(3)	178.13(15)	O(6)Cu(4)N(7)	93.24(15)
O(1)Cu(2)N(4)	84.05(15)	O(4)Cu(4)N(16)	83.26(15)
O(3)Cu(2)N(4)	97.10(15)	O(6)Cu(4)N(16)	96.91(15)
O(1)Cu(2)N(10)	84.81(14)	N(16)Cu(4)N(7)	168.40(16)

Significant differences are observed in structures of the ligands. The bicyclic pyrazole-containing fragments are planar, and the phenyl substituents are somewhat unfolded relatively to these planes (the corresponding torsion angles are the following: C(6)–N(3)–C(9)–C(10), 10.7(7)°; C(17)–N(6)–C(20)–C(25), 12.9(8)°; C(31)–N(15)–C(34)–C(35), 18.0(8)°; C(42)–N(18)–C(45)–C(46), 29.1(8)°; C(6)'–N(3)'–C(9)'–C(14)', 38.1(7)°; C(17)'–N(6)'–C(20)'–C(25)', 12.2(10)°). The main distinction in structures of the ligands is the angle between these bicycles (the inflection angle of the ligand relatively to the C(1)–O(1) and C(26)–O(4) in **A** and C(1)'–O(1)' bond in **B** or, which is the same, the angle between the coordination planes of the atoms Cu(1) and Cu(2), Cu(3) and Cu(4) in **A**; Cu(1)' and Cu(2)' in **B**). In molecule **A**, the angle between the coordination polyhedra of the Cu(1) and Cu(2) atoms is 67.18(12)° and that between the coordination polyhedra of the Cu(3) and Cu(4) atoms is 87.11(10)°. In molecule **B**, this angle is 81.84(11)°.

However, the most substantial difference in complexes **A** and **B** is observed for the structures of their core cubic fragment $Cu_4N_2O_2$ (Fig. 2). All copper atoms have an additional axial contact along with the square planar coordination mode. In complex **A**, the shortest additional coordination mode is observed for the Cu(3) atom (Cu(3)–O(1) 2.289(3) Å), which is doubtless for the interpretation of the coordination polyhedron of the Cu(3) atom as 4 + 1 (tetragonal pyramid). The distances to the O and N atoms, which supplement the coordination mode of other copper atoms, are substantially longer (Cu(1)–O(4) 2.688(3), Cu(2)–N(7) 3.331(4), and Cu(4)–N(10) 2.563(4) Å). According to these data, it seems most reasonable to describe the coordination mode of the Cu(2) atom as square planar and those of other copper atoms as 4 + 1. The **B** molecule has the *C*2 symmetry, and the cubic core is distorted to a considerably lower extent. Both symmetrically independent copper atoms have the coordination mode 4 + 1. The Cu(1)'–O(1)' and Cu(2)'–N(7)' distances are 2.437(3) and 2.829(4) Å, respectively; i.e., they are somewhat longer than the shortest similar distance in **A** and somewhat shorter than the longest one. Distortions of the cubic fragment appear in the Cu···Cu contacts. In complex **A**, the distances between the copper atoms Cu(2)···Cu(3) and Cu(3)···Cu(4) are fairly short (2.9743(8) and

Table 3. Selected interatomic distances and bond angles in the coordination polyhedra of the copper atoms in molecule **B** of compound **I***

Bond	d, Å	Bond	d, Å
Cu(1)'–O(1)'	1.977(3)	Cu(2)'–O(1)'	1.939(3)
Cu(1)'–O(2)'	1.915(3)	Cu(2)'–O(3)'	1.915(3)
Cu(1)'–N(1)'	1.950(4)	Cu(2)'–N(4)'	1.941(4)
Cu(1)'–N(7)'	2.035(4)	Cu(2)'–N(7)''	2.003(4)
Angle	**α, deg**	**Angle**	**α, deg**
Cu(1)'O(1)'Cu(2)'	109.16(15)	N(1)'Cu(1)'N(7)'	169.94(17)
Cu(1)'N(7)'Cu(2)''	103.52(18)	O(1)'Cu(2)'O(3)'	177.14(14)
O(1)'Cu(1)'O(2)'	174.20(14)	O(1)'Cu(2)'N(4)'	83.26(15)
O(1)'Cu(1)'N(1)'	83.56(15)	O(3)'Cu(2)'N(4)'	97.12(15)
O(2)'Cu(1)'N(1)'	95.72(16)	O(1)'Cu(2)'N(7)''	86.45(15)
O(1)'Cu(1)'N(7)'	92.03(15)	O(3)'Cu(2)'N(7)''	92.89(15)
O(2)'Cu(1)'N(7)'	87.75(16)	N(4)'Cu(2)'N(7)''	168.38(17)

* The atoms marked by two strokes were generated by the symmetry procedure $1 - x, y, -z$.

3.0187(9) Å, respectively), and the range of distances is 2.97–4.03 Å. In the cubic fragment of molecule **B**, the range of Cu···Cu distance is somewhat shorter: 3.17–3.92 Å.

The sole close analogue of complex **I** is the described [16] tetranuclear complex based on N,N'-(2-hydroxylpropane-1,3-diyl)bissalicylideneimine (**II**) (CCDC-239421, Refcode GAFQAG). In this structure, the molecule is in the general position, but the coordination mode of the copper atoms in pairs is approximately the same. The distances to the O and N atoms supplementing the coordination numbers of the copper atoms to five are 2.721(3) and 2.681(3) Å for Cu–N and 2.329(2) and 2.285(2) Å for Cu–O. Note that the authors consider the Cu–N distances to be rather long and describe the coordination mode of these atoms as square planar. A substantial distinction of compound **II** from **I** is the absence of bulky phenyl substituents, most likely, due to steric factors that prevent the strengthening of interactions of the copper atom with the N and O atoms supplementing its coordination polyhedron to a square pyramid (4 + 1).

It is most interesting that two conformations, which noticeably differ in structure of both ligands and cubic fragments, are observed in one crystalline lattice of compound **I**. A comparison of three described structures of the complexes assumes that, for the formation of the tetranuclear complex with the cubic geometry of the core $Cu_4N_2O_2$ fragment, the copper atoms tend to form the stable coordination mode 4 + 1 which is common for Cu(II) complexes. Evidently, the volume of the ligands affects the geometry of the cubic fragment. However, the manifestation of this influence shows that the symmetry of the cubic fragment can easily be distorted by the intermolecular interaction. In the crystal structure, the hydrogen bond between the water molecule and complex **A** is fairly weak (O(1*w*)–H(1*w*)···N(14): H···N 2.240, O···N 3.028(5) Å, OHN angle 154°).

A weak stacking interaction is observed between the planar fragments of the ligands of molecules **A** and **B** so that molecule **A** has two stacking neighbors and molecule **B** has four stacking neighbors (shortest distances: N(17)···C(3)' 3.353(7); C(42)···C(15)' 3.350(9); C(33)···N(9)' 3.405(8) Å), and other interactions between the complexes are van der Waals contacts. It is most likely that the total influence of these interactions (very weak if compared with the interactions inside the molecule) is responsible for the difference in structures of the symmetrically independent molecules, which suggests a fairly high lability of the core cubic fragment.

To check the stability of isomeric forms of the type of complexes **A** and **B**, it was attempted to optimize the geometry of the conformers in the framework of the B3LYP/6-311G(d) approximation. However, regardless of the choice of the initial approximation ("symmetrical" or "unsymmetrical" conformer according to the X-ray diffraction data), the geometry optimization procedure resulted in the same structure with the symmetry *C*2, which is very close to the structure of conformer **B**. No local minimum corresponding to conformer **A** was found on the molecular potential energy surface. The optimum geometric parameters of the cubic fragment according to the quantum-chemical calculation data are presented in Table 4. As can be seen from a comparison with the X-ray diffraction data (Table 5, molecule **B**), the bond lengths for the copper ions lying in the equatorial plane are consistent (except for the O(1)'–Cu(2)' bond, being 1.975 Å compared to an experimental value of 1.935 Å). The

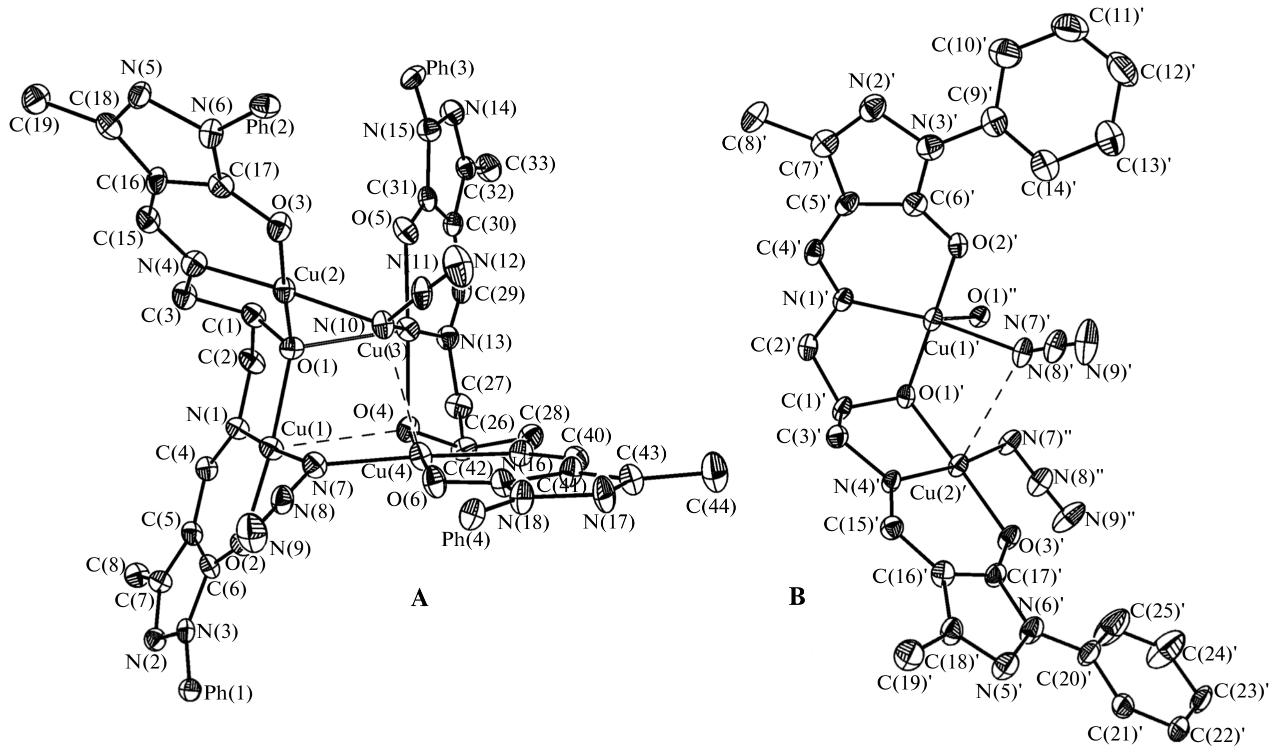


Fig. 1. General view of molecules **A** and **B** in complex **I** in the representation of atomic shift ellipsoids with 50% probability. Hydrogen atoms are omitted; phenyl groups of molecule **A** are replaced by the designation Ph. For molecule **B**, only the symmetrically independent part is shown, except for the coordination nodes of the Cu atoms shown entirely. The atoms marked by two strokes were generated by the symmetry procedures $1 - x, y, -z$. The Cu–N(O) bonds with lengths ranging from 2.1 to 2.5 Å are shown by solid lines, and the Cu–N(O) bonds with lengths ranging from 2.5 to 3.0 Å are dashed.

maximum deviation of the theoretical values from the experimental ones are observed for the lengths of the axial bonds N(7)'–Cu(2)' and N(7)''–Cu(2)'', which are considerably shorter: 2.646 Å compared to an experimental value of 2.829 Å, and bond angles at the pseudo-cubane side containing the Cu(2)' and Cu(2)'' atoms, being by ~10° smaller than the experimental value.

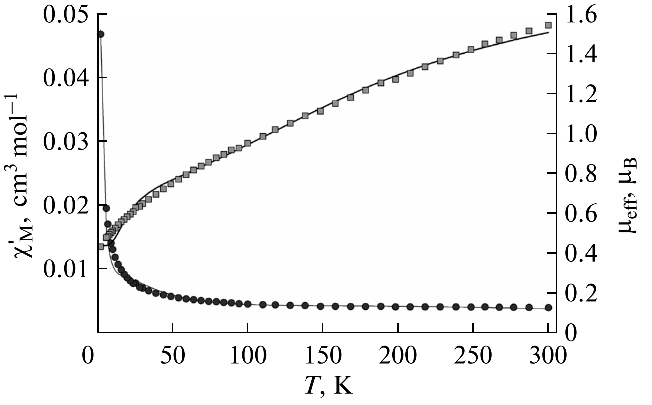


Fig. 2. (□) Temperature dependence of μ_{eff} per copper ion and (○) χ'_M for complex **I** (theoretical dependence is shown by solid line).

The quantum-chemical simulation performed suggests that the existence of two conformers of the complex in the crystalline lattice is exclusively determined by the intermolecular interaction in the solid body and packing effects rather than specific features of the structure of the molecules.

The study of the temperature dependence of the magnetic susceptibility of complex **I** (Fig. 2) showed that the magnetic moment of the complex per copper(II) ion decreased from 1.49 to 0.42 μ_B on cooling from 300 to 2 K. These data indicate that the resulting exchange interaction between the paramagnetic centers in the complex is antiferromagnetic.

The structure of the exchange fragments of molecules **A** and **B** shown in Fig. 3 predetermines a very complicated character of the exchange interaction, and the spin-Hamiltonian should include several parameters in both cases. The geometric parameters of the exchange fragment in molecules **A** and **B** are presented in Table 5. In the exchange fragment of molecule **A**, the magnetic exchange between the paramagnetic centers Cu(1) and Cu(2), Cu(1) and Cu(3), and Cu(3) and Cu(4) mainly occurs through the alkoxide

Table 4. Optimum geometric parameters of the exchange fragments according to the B3LYP/6-311G(d) calculation data. The designations of atoms were chosen similarly to those in isomer **B** (see Table 5). Symmetry channels bound by the symmetry procedure are omitted

Pair exchange channel	Bond angle, deg	Cu–D and D–Cu', Å	Cu···Cu', Å
Cu(1)'–O(1)'–Cu(2)'	109.0	1.978, 1.975	3.219
Cu(1)'–N(7)'–Cu(2)'	85.9	2.033, 2.646	
Cu(1)"–O(1)'–Cu(2)'	92.1	2.412, 1.975	3.173
Cu(1)"–N(7)"–Cu(2)'	103.6	2.033, 2.005	
Cu(1)'–O(1)'–Cu(1)"	100.5	1.978, 2.412	3.386
Cu(1)'–O(1)"–Cu(1)"	100.5	2.412, 1.978	
Cu(2)'–N(7)'–Cu(2)"	97.2	2.646, 2.005	3.514
Cu(2)'–N(7)"–Cu(2)"	97.2	2.005, 2.646	

bridging O(1) and O(4) atoms, and a fairly strong antiferromagnetic interaction should be expected in the first two cases [7]. The exchange between the Cu(2) and Cu(3), Cu(1) and Cu(4) ions can be translated mainly through the nitrogen atoms of the azide bridges N(10) and N(7), respectively. The exchange channel involving the O(1) alkoxide atom can noticeably contribute to the interaction between the Cu(2) and Cu(3) ions, and the exchange between the Cu(2) and Cu(3) ions should be ferromagnetic according to the known magnetic structural correlations [17–21]. A substantial exchange interaction between the Cu(2) and Cu(4) ions is hardly probable because of a long distance between the copper ions and a weak Cu(4)–N(10) bond (2.563 Å).

In order to decrease the number of varied parameters, when interpreting the temperature dependence of the magnetic susceptibility in complex **I**, we assumed that in unsymmetrical cluster **A** the pair exchange parameters between the Cu(1)–Cu(2) and Cu(1)–Cu(3) ions and also between Cu(1)–Cu(4) and Cu(3)–Cu(4) are similar. In this case, the spin-Hamiltonian for cluster **A** takes the following form [22, 23]:

$$\widehat{\mathrm{H}}_{\mathrm{A}} = -J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3) - J_2(\hat{S}_2\hat{S}_3) - J_3(\hat{S}_1\hat{S}_4 + \hat{S}_3\hat{S}_4).$$

In the “symmetrical” exchange fragment of molecule **B**, the magnetic exchange between the paramagnetic centers Cu(1)' and Cu(2)', Cu(1)" and Cu(2)" is possible through the alkoxide bridges, while the magnetic exchange between Cu(1)'–Cu(2)' and Cu(1)"–Cu(2)" occurs through the azide bridges with the exchange parameters J_1 and J_3, respectively. Taking into account the values of bond angles at the bridging atoms, one can expect that the exchange interaction character will differ, and the J_1 parameter will be negative and J_3 will be positive [17–21]. The antiferromagnetic exchange with the exchange parameter J_2 is possible between the Cu(1)' and Cu(1)" ions. A substantial exchange between the Cu(2)' and Cu(2)" ions in the symmetrical cluster is poorly probable and, hence, the spin-Hamiltonian for cluster **B** includes three exchange parameters [22, 23]

$$\widehat{\mathrm{H}}_{\mathrm{B}} = -J_1(\hat{S}_{1'}\hat{S}_{2'} + \hat{S}_{1''}\hat{S}_{2''}) - J_2(\hat{S}_{1'}\hat{S}_{1''}) - J_3(\hat{S}_{1'}\hat{S}_{2''} + \hat{S}_{1''}\hat{S}_{2'}).$$

Each tetranuclear exchange cluster includes six energy levels: one quintet level, three triplet levels, and two singlet levels [16, 24]

$$E_1 = -J_1 - J_2/2 - J_3, \quad S = 2$$

$$E_2 = J_1 - J_2/2 + J_3, \quad S = 1$$

$$E_3 = J_2/2 + [J_2^2 + (J_3 - J_1)^2]^{1/2}, \quad S = 1$$

$$E_4 = J_2/2 - [J_2^2 + (J_3 - J_1)^2]^{1/2}, \quad S = 1$$

$$E_5 = J_1 + J_3 + J_2/2 + \left[4\left(J_1^2 + J_3^2\right) + J_2^2 - 4J_1J_3 - 2J_2J_3 - 2J_1J_2\right]^{1/2}, \quad S = 0$$

$$E_6 = J_1 + J_3 + J_2/2 - \left[4\left(J_1^2 + J_3^2\right) + J_2^2 - 4J_1J_3 - 2J_2J_3 - 2J_1J_2\right]^{1/2}, \quad S = 0.$$

In this case, the equation for the magnetic susceptibility of the tetranuclear cluster takes the following form [24]:

$$\chi = \frac{2N\beta^2 g^2}{kT}\frac{A}{B}, \tag{1}$$

where

$$A = 5\exp(-E_1/kT) + \exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT),$$

$$B = 5\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT).$$

Taking into account the additive character of the magnetic susceptibility, the molar susceptibility of complex **I** can be presented as a sum of susceptibilities

Table 5. Comparison of the geometric parameters of the exchange fragments in molecules A and B of complex **I**

Pair exchange channel	Bond angle, deg	Cu–D and D–Cu', Å	Cu···Cu', Å
	Molecule **A**		
Cu(1)–O(1)–Cu(2)	121.48	1.988, 1.943	3.430
Cu(1)–O(1)–Cu(3)	110.83	1.988, 2.289	3.525
Cu(1)–O(4)–Cu(3)	97.63	2.688, 1.953	
Cu(2)–O(1)–Cu(3)	88.92	1.943, 2.289	2.974
Cu(2)–N(10)–Cu(3)	94.23	1.987, 2.071	
Cu(1)–O(4)–Cu(4)	90.85	2.688, 1.934	3.335
Cu(1)–N(7)–Cu(4)	113.67	1.994, 1.990	
Cu(3)–O(4)–Cu(4)	101.91	1.953, 1.934	3.019
Cu(3)–N(10)–Cu(4)	80.53	2.071, 2.563	
Cu(2)–N(10)–Cu(4)	124.09	1.987, 2.563	4.028
	Molecule **B**		
Cu(1)'–O(1)'–Cu(2)'	109.16	1.977, 1.939	3.192
Cu(1)'–N(7)'–Cu(2)'	80.21	2.035, 2.829	
Cu(1)''–O(1)''–Cu(2)''	109.16	1.977, 1.939	3.192
Cu(1)''–N(7)''–Cu(2)''	80.21	2.035, 2.829	
Cu(1)''–O(1)'–Cu(2)'	92.17	2.437, 1.939	3.172
Cu(1)''–N(7)''–Cu(2)'	103.51	2.035, 2.003	
Cu(1)'–O(1)''–Cu(2)''	92.17	2.437, 1.939	3.172
Cu(1)'–N(7)'–Cu(2)''	103.51	2.035, 2.003	
Cu(1)'–O(1)'–Cu(1)''	104.77	1.977, 2.437	3.508
Cu(1)'–O(1)''–Cu(1)''	104.77	2.437, 1.977	
Cu(2)'–N(7)'–Cu(2)''	107.13	2.829, 2.003	3.919
Cu(2)'–N(7)''–Cu(2)''	107.13	2.003, 2.829	

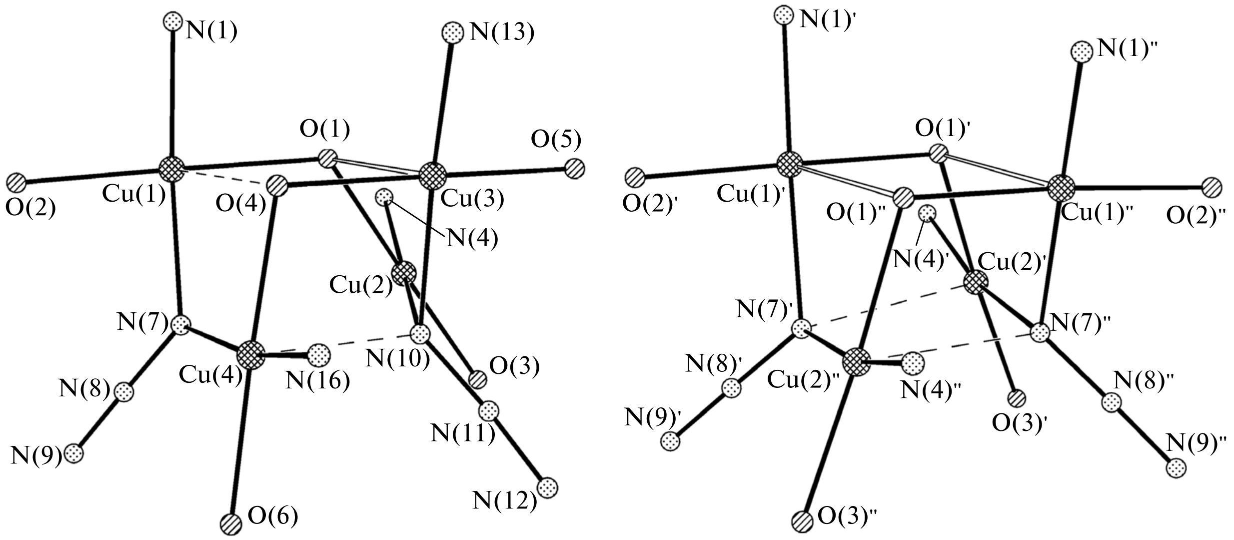


Fig. 3. Structures of the exchange fragments in molecules (left) **A** and (right) **B** of complex **I** (only donor atoms of the ligands and bridging N_3^- groups are shown).

of clusters **A** (χ_A) and **B** (χ_B) being in a ratio of 2 : 1 with allowance for a paramagnetic admixture [25]

$$\chi = (1 - f)\left(\frac{2}{3}\chi_A + \frac{1}{3}\chi_B\right) + f\frac{N\beta^2 g^2}{kT} + N_\alpha. \qquad (2)$$

The use of Eqs. (1) and (2) for the interpretation of the temperature dependence of the magnetic susceptibility of complex **I** results in a satisfactory agreement with the experiment (root-mean-square error R = 0.071) at the following parameters of the model: $J_{1A} = -178$, $J_{2A} = 80$, $J_{3A} = 18$, $J_{1B} = -26$, $J_{2B} = -74$, $J_{3B} = 46$ cm^{-1}, $g_A = g_B = 2.05$, $f = 0.04$. The values of all g factors were accepted to be equal in the calculation, and the fixed value $N_\alpha = 2.4 \times 10^{-4}$ cm^3 mol^{-1} was used [23]. The most deviations of the calculated values of the magnetic susceptibility from the experimental values are observed for temperatures lower than 50 K. It should be mentioned that the complication of the model using four or five pair exchange parameters for "unsymmetrical" cluster **A** results in a worse agreement between the theory and experiment.

The exchange parameters for "symmetrical" cluster **B** are substantially higher in absolute value that those in the case of the tetranuclear complex based on N,N'-(2-hydroxylpropane-1,3-diyl)bissalicylideneimine [16] for which the authors gave values of 7.5 (J_1), –3.6 (J_2), and –76.5 (J_3) cm^{-1}, respectively. However, the distribution of the ferromagnetic and antiferromagnetic exchange channels is similar in both cases.

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