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Binuclear Copper(II) Complex with Bis(azomethine) Based on 1,3-Diaminopropan-2-ol and 4-Hydroxy-3-Formylcoumarin: Crystal Structure and Magnetic Properties

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Abstract—The binuclear copper(II) complex $[Cu_2(L)(Mp)(H_2O)((CH_3)_2SO)]$ (Mp is 6-methoxypurinate anion) with the heterocyclic azomethine ligand, which is the condensation product of 1,3-diaminopropan-2-ol and 4-hydroxy-3-formylcoumarin (H_3L), is synthesized and structurally characterized (CIF file CCDC no. 982199). The temperature dependence of the magnetic susceptibility is measured and shows a significant exchange interaction of the antiferromagnetic type ($2J = -348$ cm^{-1}) in the compound. This sharply distinguishes the new complex from the earlier studied compounds with a similar exchange fragment characteristic of the ferromagnetic exchange. The antiferromagnetic exchange parameter is calculated by the quantum-chemical DFT method in the broken symmetry approximation.

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INTRODUCTION

Compartmental ligands are polydentate organic compounds with a specific structure: the spatial arrangement of their donor centers provides the formation of preorganized cavities for the coordination of one or several metal ions. Binuclear complexes with ligands of this type, in particular, bis(azomethines) based on 1,3-diaminopropan-2-ol, are convenient models for studying the main factors that determine the character and strength of exchange interactions between the paramagnetic centers linked by heterobridges, because they assume a wide variation of both the carbonyl component of the Schiff base and the nature of the exogenic bridging ligand providing an additional (to the alkoxide oxygen atom) exchange channel [1–5]. Among copper(II) complexes of this type, compounds, whose exchange fragment includes the carboxylate or pyrazolate exogenic bridges, are studied most completely, whereas compounds with heterocyclic exogenic bridges of the NCN' type are studied to a lesser extent.

In this work, we report the X-ray diffraction analysis data for the binuclear copper(II) complex $[Cu_2L(Mp)(H_2O)((CH_3)_2SO)]$ (**I**) containing the 6-methoxypurinate (Mp) exogenic bridge with bis(azomethine) (H_3L), which is the condensation product of 1,3-diaminopropan-2-ol with 4-hydroxy-3-formylcoumarin, and the results of the experimental study and quantum-chemical simulation of the magnetic exchange interaction in this complex.

EXPERIMENTAL

Elemental analysis was carried out on a Perkin-Elmer 240C instrument. ^{1}H NMR spectra were recorded in DMSO-d_6 on a Varian Unity 300 spectrometer (300 MHz) using the pulse Fourier mode. IR spectra were measured on a Varian Scimitar 1000 FT-IR instrument in the range 400–4000 cm^{-1} for samples prepared as suspensions in Nujol. The magnetic susceptibility was determined by Faraday's method in the temperature range from 77.4 to 294 K. The magnetic properties were interpreted in the framework of Heisenberg–Dirac–Van Vleck isotropic exchange model [6] using multidimensional fitting according to the Bleaney–Bowers equation [7].

Synthesis of bis(azomethine) H_3L. A solution of 1,3-diaminopropan-2-ol (6 mmol) in triethyl orthoformate (7.5 mL) was added to a hot solution of 4-hydroxycoumarin (12 mmol) in a dimethylformamide (DMF)–acetic acid (1 : 1) mixture (4 mL). The resulting mixture was heated for 10 min until a yellow precipitate was formed and left for 24 h. The precipitate was filtered off, washed with acetone, and recrystallized from a DMF–ethanol (3 : 2) mixture. The yield was 2.14 g (82%), mp = 140°C.

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

Parameter	Value
FW	803.73
Crystal size, mm	0.32 × 0.11 × 0.07
Temperature	150(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	9.2934(7)
b, Å	10.3382(7)
c, Å	18.2453(16)
α, deg	98.967(1)
β, deg	99.457(1)
γ, deg	113.600(1)
V, Å^3	1536.1(2)
Z	2
ρ(calcd.), g/cm^3	1.738
μ, mm^{-1}	1.52
F(000)	820
$2\theta_{max}$, deg	60.9
Ranges of reflection indices	$-13 \le h \le 13$, $-14 \le k \le 14$, $-25 \le l \le 25$
Number of measured reflections	18595
Number of independent reflections	9198
Number of reflections with $I > 2\sigma(I)$	7131
Number of refined parameters	477
GOOF (all reflections)	1.002
R_1 ($I > 2\sigma(I)$)	0.0497
wR_2 (all reflections)	0.1492
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	2.940/−0.869

For $C_{23}H_{18}N_2O_7$

anal. calcd., %:	C, 63.6;	H, 4.18;	N, 6.45.
Found, %:	C, 63.8;	H, 4.22;	N, 6.38.

IR, ν, cm^{-1}: 3300 ν(OH), 3176 ν(NH), 1701, 1688 ν(C=O), 1637 ν(C=N). ^{1}H NMR (DMSO-d_6), δ, ppm: 3.50–3.65 m (2H, CH_2); 3.67–3.83 m (2H, CH_2); 3.86–4.05 m (1 H, CH); 5.79 d (0.32 H, J = 5.6 Hz, OH, (*Z*)-isomer); 5.82 d (0.68 H, J = 5.5 Hz, OH, (*E*)-isomer); 7.21–7.36 m (4H, CH_{arom}); 7.53–7.64 m (2H, CH_{arom}); 7.79–7.95 m (2H, CH_{arom}); 8.42 d (1.36 H, J = 14.7 Hz, CHN, (*E*)); 8.54 d (0.64 H, J = 15.6 Hz, CHN, (*Z*)); 10.36 m (0.64 H, NH, (*Z*)); 11.65 m (1.36 H, NH, (*E*)).

Synthesis of complex I. A boiling solution of 6-methoxypurine (1 mmol) in methanol (3 mL) and then a hot solution of copper(II) perchlorate (2 mmol) in methanol (5 mL) were added to a boiling suspension of H_3L (1 mmol) in methanol (20 mL). A blue precipitate was formed immediately. The mixture was refluxed with a reflux condenser for 4 h, and the precipitate was filtered off, washed with boiling methanol and acetone, and dried in vacuo. The yield was 0.68 g (85%), mp > 250°C.

Single crystals of the complex suitable for X-ray diffraction analysis were obtained by recrystallization from aqueous dimethyl sulfoxide (DMSO).

For $C_{31}H_{28}N_6O_{10}SCu_2$

anal. calcd., %:	C, 46.3;	H, 3.51;	N, 10.5.
Found, %:	C, 46.2;	H, 3.54;	N, 10.5.

IR, ν, cm^{-1}: 1682 ν(C=O), 1617 ν(C=N). μ_{eff}: 1.28 μ_B (294 K), 0.44 μ_B (77.4 K).

The X-ray diffraction analysis of complex **I** was carried out on a Bruker APEX II diffractometer (MoK_α, radiation, λ = 0.71073 Å , graphite monochromator). The initial array of measured intensities was processed using the SAINT [8] and SADABS [9] programs. 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 the 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, n = 1.2 for other C atoms). All calculations were performed using the SHELXTL program package [10]. The experimental characteristics and crystallographic data for complex **I** are presented in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The geometric parameters of hydrogen bonds are given in Table 3. The atomic coordinates and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CCDC file no. 982199; 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 functional [11] with the Becke exchange part [12] and the Lee–Yang–Parr correlation part [13]. The 6-311G(*d*) extended split valence basis set was used for the calculation of the complex. The exchange parameters 2J were calculated using an earlier approved procedure [14, 15] based on the broken symmetry (*BS*) approach [16–19]. The Yamaguchi formula (1) [19] applicable in a wide range of values of the overlap integral of magnetic spin orbitals, which well recommended itself in combination with the hybrid functionals [18], was used for the calculation of the exchange parameter in the framework of the *BS* method

Table 2. Selected interatomic distances and bond angles in the structure of complex **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.974(2)	Cu(2)–O(1)	1.955(2)
Cu(1)–N(1)	1.943(3)	Cu(2)–N(2)	1.945(2)
Cu(1)–O(4)	1.951(2)	Cu(2)–O(4)	1.932(2)
Cu(1) –N(3)	2.011(3)	Cu(2)–N(6)	1.985(3)
Cu(1)–O(10)	2.363(3)	Cu(2)–O(9)	2.427(3)
Cu(1)–Cu(2)	3.6044(6)		
Angle	ω, deg	Angle	ω, deg
N(1)Cu(1)O(4)	84.18(9)	O(4)Cu(2)N(2)	85.20(9)
N(1)Cu(1)O(1)	89.64(10)	N(2)Cu(2)O(5)	90.18(10)
O(4)Cu(1)O(1)	165.23(10)	O(4)Cu(2)O(5)	167.33(10)
N(1)Cu(1)N(3)	178.21(11)	N(2)Cu(2)N(6)	175.07(12)
O(4)Cu(1)N(3)	94.79(9)	O(4)Cu(2)N(6)	94.54(10)
Cu(1)O(4)Cu(2)	136.30(11)		

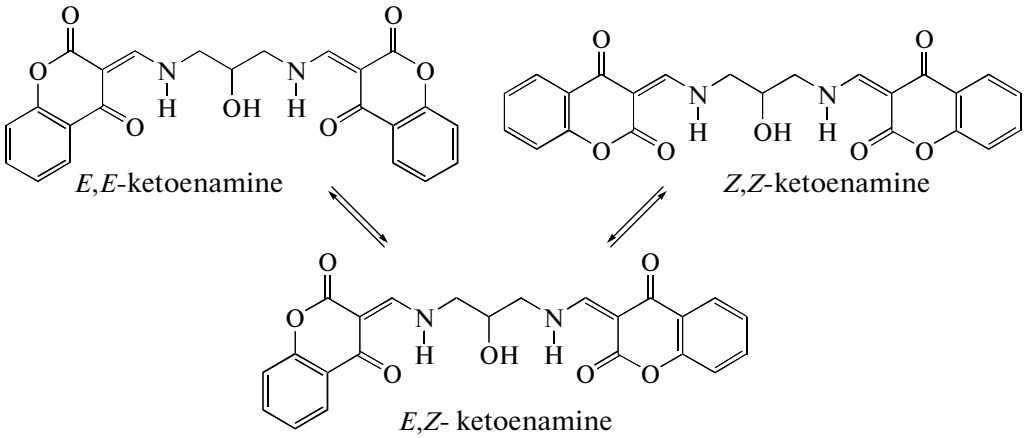
$$2J = \frac{2(E_{BS} - E_{HS})}{\left\langle S^2_{HS} \right\rangle - \left\langle S^2_{BS} \right\rangle}. \quad (1)$$

Here E and $\left\langle S^2 \right\rangle$ are the total energy and the expected value of the squared total spin of states, respectively; index *HS* is used to designate the high spin state ($S = 1$) with the parallel orientation of electron spins on the metal centers, and index *BS* designates the low spin state (broken symmetry state) with the opposite orientation.

The geometry of each spin state was optimized over all geometric parameters without symmetry restraints. The calculations were performed on the WSD cluster (Southern Federal University) using the Gaussian'03 program [20]. The energies of triplet states and broken symmetry states and the calculated and experimental exchange parameters 2*J* in complex **I** are presented in Table 4.

RESULTS AND DISCUSSION

Bis(azomethine) H_3L was synthesized by the Knott reaction of 4-hydroxycoumarin with 1,3-diaminopropan-2-ol in the presence of triethyl orthoformate in DMF without the isolation of 3-formyl-4-hydroxycoumarin formed in situ. The appearance of signals from the acidic protons, which disappear upon the addition of D_2O, as multiplets (superposition of a doublet and a triplet) in the ^1H NMR spectrum of H_3L in DMSO (see Experimental) indicates that a ketoenamine tautomer is formed in the solution, which is characteristic of some other 4-hydroxy-3-formylcoumarin mono- and bis(azomethienes) [21–23].



The ketoenamine tautomer exists in a solution as an equilibrium mixture of *Z*,*Z*-, *E*,*Z*-, and *E*,*E*-isomers. This is indicated by an increase in the number of signals from almost all protons of bis(azomethine). The effect is strongest for the NH protons, whose signals are detected in the spectrum as multiplets at 11.65

Table 3. Geometric characteristics of intermolecular hydrogen bonds in crystal of complex **I***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(10)–H(1*w*)···O(8)^{i}	0.84(3)	1.94(3)	2.781(4)	175(3)
O(10)–H(2*w*)···O(2)^{ii}	0.84(3)	2.16(4)	2.980(4)	164(3)

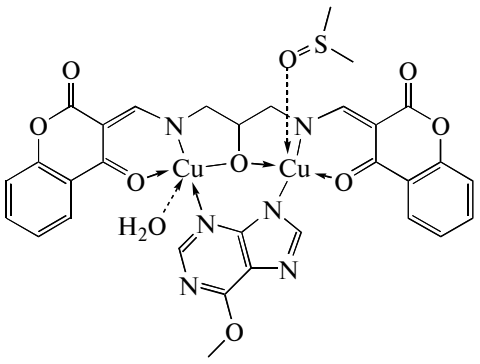
* Crystallographic positions: ^{i} $x + 1, y + 1, z$; ^{ii} $-x + 1, -y + 2, -z + 1$.

Table 4. Energies of the triplet state (HS), broken symmetry (BS) states, and calculated values of 2*J* for complex **I** at the fixed (according to the X-ray diffraction data) and optimized geometries (according to the B3LYP/6-311G(*d*) calculation)

Geometry	HS		BS		$2J$, cm^{-1}
	E, au	$\langle S^2 \rangle$	*E*, au	$\langle S^2 \rangle$	
Fixed (X-ray diffraction analysis)	−5958.349624	2.004	−5958.350297	0.987	−294
Optimized	−5329.060881	2.005	−5329.061482	0.985	−259

and 10.36 ppm with a ratio of integral intensities of 43 : 20, respectively. The downfield signal corresponds to the NH proton of the *E*-isomer, which is stabilized by a stronger hydrogen bond than that in the *Z*-isomer [21]. It follows from this that the *E,E*-isomer is the most stable conformer in the solution. If assuming that the relative stability of the *E*- and *Z*-isomers of each coumarin fragment is the same and, hence, the relative destabilization of the *Z,Z*-isomer with respect to the *E,E*-isomer is two times higher than that of the *E,Z*-isomer, the ratio of isomers of the *E,E*-, *E,Z*-, and *Z,Z*- type in a solution can be estimated as 53, 30, and 17%, respectively. According to the Boltzmann distribution, the relative stability of the *Z*- and *E*-isomers of each fragment can be estimated as 1.42 kJ/mol.

Complex **I** was synthesized by the reaction of bis(azomethine) H_3L with copper(II) perchlorate in the presence of 6-methoxypurine followed by recrystallization from aqueous DMSO. The IR spectroscopic data indicate the coordination of bis(azomethine) H_3L in complex **I** in the triply protonated form. Under the reaction conditions, 6-methoxypurine is deprotonated and enters into the complex as a monoanion similarly to amidines.



I

The molecular structure of complex **I** is shown in Fig. 1. In the binuclear complex, bis(azomethine) exists in the *E,E*-isomeric form coordinating two copper ions. The methoxypurinate ion acts as an exogenic bridge due to the coordination through the N(3) and N(6) atoms to the Cu(1) and Cu(2) ions, respectively. Both copper ions are in the coordination environment similar to the tetragonally extended square pyramid (4+1). The basal planes of both metal centers contain donor atoms of bis(azomethine) and methoxypurinate ion (O(1)N(1)O(4)N(3) for Cu(1) and O(4)N(2)O(5)N(6) for the Cu(2) ion). The axial positions are occupied by the coordinated water and DMSO molecules arranged at different sides of the

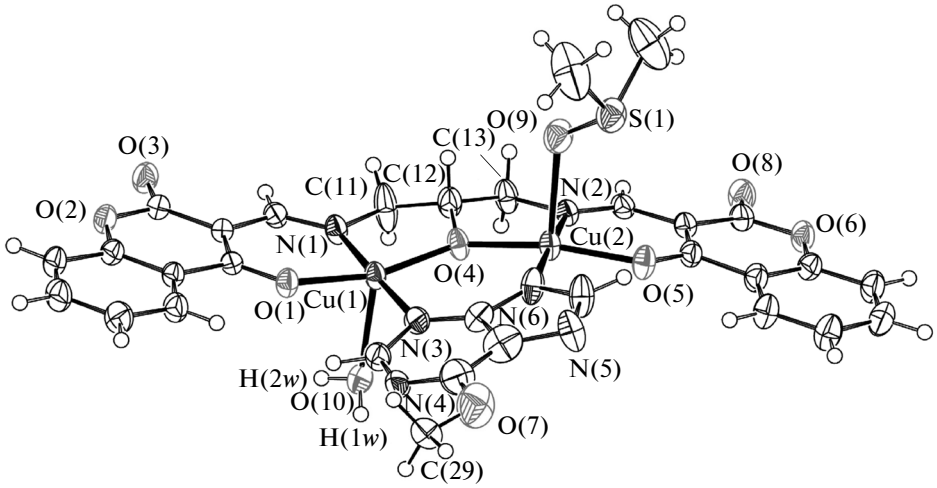


Fig. 1. Structure of complex **I** in the representation of atoms by atomic displacement ellipsoids with 50% probability.

plane of the molecule. The deviation of the O(1), N(1), O(4), and N(3) donor atoms coordinated to the Cu(1) ion from the root-mean-square plane determined by these atoms does not exceed 0.11 Å. The Cu(1) atom is shifted from this plane toward the O(10) atom of the coordinated water molecule by 0.1289(4) Å (Cu(1)–O(10) 2.363(3) Å). The maximum deviation of the O(4), N(2), O(5), and N(6) atoms from the corresponding root-mean-square plane is still lower: 0.06 Å. The Cu(2) atom is shifted from this plane by 0.1435(5) Å to the O(9) atom of the coordinated DMSO molecule (Cu(2)–O(9) 2.427(3) Å).

The formation of the shorter coordination bond between Cu(1) and the O(10) atom of the water molecule compared to the bond of Cu(2) with the O(9) atom of the DMSO molecule leads to the elongation of the interatomic distances between the Cu(1) ion and donor atoms in the equatorial plane compared to similar distances for Cu(2) (Table 2), except for the Cu(1)–N(1) and Cu(2)–N(2) distances that are approximately equal for both coordination sites.

The five-membered chelates involving the Cu(1) and Cu(2) ions are in the twist conformation relatively to the C(11)–C(12) bond and in the envelope conformation with the O(4) valve, respectively. The atoms of the six-membered chelates, including the copper ions, lie in the planes coinciding with the plane of the corresponding annelated coumarin fragment. The planes of two fragments are nearly parallel to each other, and the dihedral angle between them is 6.94(6)°. The plane of the 6-methoxypurinate ion is inclined to the plane of the molecule of the complex, probably, due to the steric repulsion of the H(27*A*) and H(24*A*) atoms of this fragment from the O(5) and O(1) atoms, respectively, in position 4 of the coumarin residues. The dihedral angles between the root-mean-square planes formed by the atoms of the endogenic bridge and the coumarin fragments are 22.70(8)° and 22.69(9)°.

The conformation of the nonsymmetric six-membered exchange fragment is also close to the planar one: the maximum deviation from the root-mean-square plane does not exceed 0.110(3) Å (for the N(6) atom). As a result, the alkoxide oxygen atom is not almost pyramidalized: the sum of bond angles at O(4) is 359.2(3)°, the Cu(1)O(4)Cu(2) bond angle at the alkoxide bridging atom is 136.29(14)°, and the copper–copper distance is 3.6044(6) Å.

The carbon atom of the oxymethyl group O(7)C(29) is disordered over two positions C(29) and C(29*A*)) with a population of 0.6 and 0.4, respectively. As it is usual in the complexes with the bis(azomethine) derivatives of 1,3-diaminopropan-2-ol, the carbon atom of the diaminopropanol linker bound to the O(4) atom is disordered and occupies two positions C(12) and C(12*A*) with approximately equal populations.

The supramolecular structure of crystal **I** is formed by a network of intermolecular hydrogen bonds involving the hydrogen atoms of the coordinated water molecule (Table 3). Each molecule of the complex in the crystalline lattice participates in the formation of four hydrogen bonds equivalent in pairs. The H(1*w*) atom forms a very strong hydrogen bond with the O(8)^{i} atom (^{i} $x + 1, y + 1, z$) of the coumarin fragment of the adjacent molecule. A similar hydrogen bond is formed between the O(8) and H(1*w*)^{iii} atoms (^{iii} $-1 + x, -1 + y, z$) of another molecule. The second pair of hydrogen bonds linking two molecules into centrosymmetric dimers is formed between the O(10)H(2*w*) group and O(2)^{ii} atom in the cycle of the coumarin fragment and between the O(2) atom and the H(2*w*)^{ii}O(10)^{ii} group of the molecule of the complex in the same crystallographic position: ^{ii} $-x + 1, -y + 2, -z + 1$. As a result, the hydrogen bonds of the first type join dimers formed by the hydrogen bonds of the second type into infinite extended layers of molecules parallel to the crystallographic plane [1 1 0] (Fig. 2).

The study of the temperature dependence of the magnetic susceptibility of complex **I** showed a fairly strong antiferromagnetic exchange interaction between the copper(II) ions. The effective magnetic moment (μ_{eff}) of the complex based on one copper(II) ion is 1.28 μ_B at room temperature and 0.44 μ_B at the boiling point of liquid nitrogen (Fig. 3). The exchange interaction parameter $2J$ calculated in the framework of the Heisenberg–Dirac–Van Vleck isotope exchange model [7] by the Bleaney–Bowers equation [8] is -348 cm^{-1} ($g = 2.09$, mole fraction of the paramagnetic impurity $f = 0.05$).

The strong antiferromagnetic exchange interaction in complex **I** sharply distinguishes this compound from four earlier studied analogs with the NCN' exogenic bridge (three complexes with the 7-azaindolate bridge and one complex with the 6-methoxypurinate bridge) in which the exchange interaction of the ferromagnetic type is observed [24–26].

The exchange parameters $2J$ for the fixed (from the X-ray diffraction data) and preoptimized geometry of the complex were calculated by the quantum-chemical broken symmetry method [27–31] for the theoretical study of the exchange interactions in complex **I**. The energies of the states and the calculated value of $2J$ are given in Table 4. The theoretical value of the exchange parameter obtained for the fixed geometry ($2J = -294$ cm^{-1}) is well consistent with the experimentally observed value (-348 cm^{-1}). The optimization of the geometry of the complex substantially decreases the energy of the states, and the calculated value of $2J$ agrees somewhat more poorly with the experiment (Table 4).

It should be mentioned that the roof-shaped conformation is observed in all earlier studied (by X-ray diffraction analysis) complexes based on the azomethine derivatives of 1,3-diaminopropan-2-ol with the NCN' exogenic bridge. This conformation is caused by the bend of the molecule over the C–O line of the isopropanol fragment due to different conformations

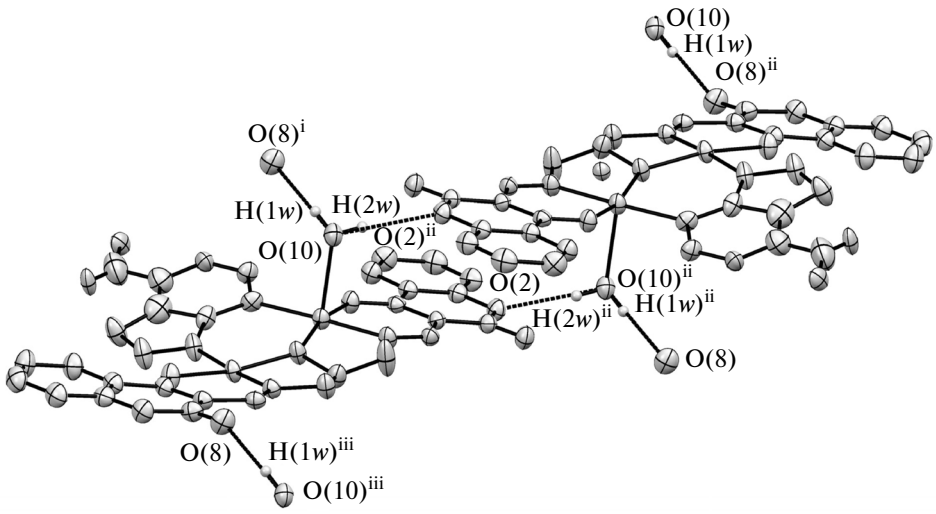


Fig. 2. Intermolecular hydrogen bonds in crystal of complex **I** (hydrogen atoms, except for those involved in hydrogen bonding, and coordinated DMSO molecules are omitted).

of the five-membered metallocycles conjugated over this bond, which differs sharply from the close to planar structure of complex **I**. The geometric and exchange characteristics of the complexes are compared in Table 5. The bend of the complex significantly affects the structure of the exchange fragment, decreases the CuOCu bond angle at the alkoxide bridging atom, and reduces its pyramidalization. These geometric characteristics decrease the overlapping of the singly occupied molecular orbitals of the paramagnetic centers, favoring the ferromagnetic exchange interaction. Thus, as shown previously [2, 14, 26], it is the conformation of the diaminopropanol ligand that exerts the determining effect on the character of the exchange interaction in the complexes based on 1,3-diaminopropan-2-ol.

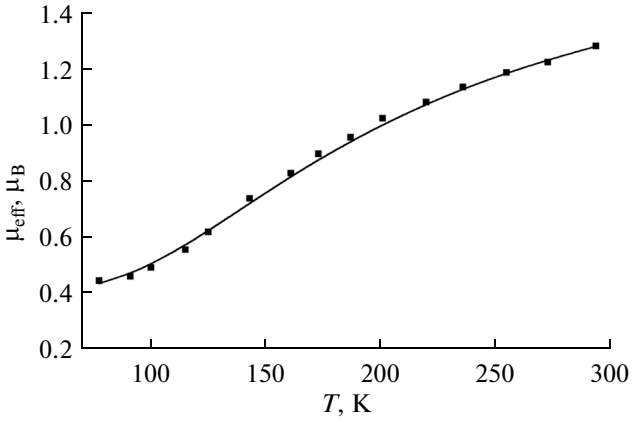


Fig. 3. Temperature dependence of μ_{eff} of complex **I** based on one Cu^{2+} ion (solid curve is the theoretical dependence).

The "distorted" conformation of complexes of this type is usually stabilized due to the axial μ^2-coordination of the oxygen atom of the solvent (DMSO or DMF) molecule to both copper ions. The cases of switching-over the character of exchange from the antiferromagnetic to ferromagnetic type after recrystallization from DMSO were experimentally confirmed for some complexes [14, 32]. Interestingly, in the case of complex **I**, the coordinated solvent molecule does not favor a distortion of this type. This can possibly be explained by a specific structure of the carbonyl fragment of the bis(azomethine) ligand: the short length of the coordinated exocyclic C=O bond equal to 1.270 Å compared to the salicylaldehyde and pyrazolone derivatives (1.300–1.310 Å) in similar complexes. This decrease favors the opening of the angle at the alkoxide bridge and flattening of the molecule of the complex. Indeed, among all 65 structurally characterized binuclear copper(II) complexes with the 1,3-diaminopropan-2-ol derivatives, complex **I** is inferior in the value of the CuOCu angle (136.29(14)°) to only two compounds in which the phosphate anion serves as an exogenic bridge (the largest angle is 137.7° [33]). In the case of the phosphate ion, the distance between the donor atoms (~2.6 Å) is considerably longer than that in 6-methoxypurine (2.448(3) Å).

Thus, complex **I** is the first structurally characterized compound based on 1,3-diaminopropan-2-ol in which the planar conformation of the binuclear exchange fragment is observed along with the NCN' exogenic bridge and the exchange interaction of the antiferromagnetic type occurs between the copper(II) ions.

Table 5. Comparison of the geometric and exchange parameters of the complexes with the NCN' exogenic bridge

Compound	Bridge*	Cu–Cu, Å	Angle CuOCu, deg	$\Sigma(O_{alk})$, deg	$2J$, cm^{-1}	Literature
I	Mp	3.6044(6)	136.29(14)	359.2	–348	This work
AYEYUY**	Az	3.266	114.4	334.4	34	[24]
AYEYOS**	Az	3.239	111.9	332.8	52	[24]
IGEJEK**	Mp	3.223	110.3	332.3	56.2	[25]
HAWBAK**	Az	3.117	105.3	332.2	106	[26]

* Az is 7-azaindolate and Mp is 6-methoxypurinate ions.

** Codes of compounds at the Cambridge Crystallographic Data Centre.

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