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Effect of the Counterion and Guest Molecules on the Crystal Structures of the Coordination Compounds with the $Cu_2(HL)_2^{2+}$ Cation (H_2L = 4,4'-[2-(3-Hydroxyiminobutyl)imino]biphenyl): Syntheses, Structures, and Magnetic Properties

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Abstract—The molecular and crystal structures of complexes $[Cu_2(HL)_2(CH_3OH)_2](BF_4)_2 \cdot C_6H_3Cl_3$ (**I**), $[Cu_2(HL)_2(H_2O)_2](1,4\text{-}O_2CC_6H_4CO_2)$ (**II**), and $[Cu_2(HL)_2(H_2O)_2](4,4'\text{-}O_2CC_6H_4C_6H_4CO_2)$ (**III**) (H_2L is 4,4'-[2-(3-hydroxyiminobutyl)imino]biphenyl, $C_6H_3Cl_3$ is 1,2,4-trichlorobenzene) are determined by X-ray diffraction analyses. The crystalline lattices of complexes **I** and **II** contain discrete binuclear cations $Cu_2(HL)_2^{2+}$, whereas the crystalline lattice of compound **III** contains both discrete cations $Cu_2(HL)_2^{2+}$ and polymer chains $[Cu_2(HL)_2^{2+}]_n$. In compounds **I**–**III**, the crystalline lattice units are joined by hydrogen bonds. The analysis of the temperature dependence of the magnetic susceptibility shows that the magnetic properties of compound **III** are determined only by antiferromagnetic interactions of the Cu^{2+} ions within the cations $Cu_2(HL)_2^{2+}$.

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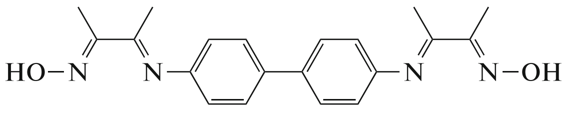
INTRODUCTION

Interest in coordination polymers of transition metals is due to wide prospects of using these systems as, for example, selective sorbents for the separation of various substances [1], catalysts [2], active cells of light-emitting devices and luminescent sensors [3], or photovoltaic cells [4]. Coordination polymers containing paramagnetic metal ions are considered as a basis for the preparation of new magnetic materials, whose properties can be controlled by the adsorption/desorption of guest molecules [5]. Among the approaches to the formation of coordination polymers, we can emphasize the assembling of these compounds using the binding of polynuclear units by neutral [6] and charged bridging ligands, including complex compounds [7–9]. This approach makes it possible to obtain systems with specified physical (magnetic, optical) or chemical (catalytic) properties, which are determined, as a rule, by the characteristics of the used units [10, 11]. However, the use of this approach is restricted by a possible decomposition and/or reorganization of the initial polynuclear fragment during the formation of coordination polymers; in situ transformation of the ligand [12]; a lack of correspondence of the number of formed coordination bonds and the number of vacant and donor positions in the building blocks, resulting in the formation of coordination polymers with a topology different from the expected one [13]; and the influence of the synthesis conditions or template on the packing of the crystalline lattice units (1D chains, 2D layers, or the presence/absence of mutual penetration) [14]. The study of the influence of the preparation conditions of the coordination polymers during the binding of the polynuclear complexes on the structures and properties of these systems is an important task of coordination chemistry.

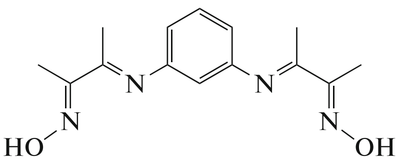
We have previously described a series of complexes and coordination polymers containing the binuclear cation $Cu_2(HL)_2^{2+}$ (H_2L is 4,4'-[2-(3-hydroxyiminobutyl)imino]biphenyl) that were obtained by the replacement of perchlorate anions ClO_4^- in the compound $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ by simple (N_3^-) or complex anions ($[Cr(SCN)_6]^{3-}$, $[Cr(NCS)_4(NH_3)_2]^-$) [15] or by the substitution of the water molecules coordinated to copper(II) in the compound $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ by the bridging 4,4'-bipyridine molecules [16]. A series of complexes containing 4,4'-bipyridine, 4,4'-*trans*-bis(4-pyridyl)ethylene, (4-pyridylethenyl)tetrathiofulvalene, and tetrafulvalene carboxylate anions was synthesized similarly on the basis of the binuclear cation $Cu_2(HL^1)_2^{2+}$, where H_2L^1 is 1,3-[2-(3-hydroxyiminobutyl)imino]benzene [9]. The magnetic properties of the compounds, which bear the cations $Cu_2(HL)_2^{2+}$ or $Cu_2(HL^1)_2^{2+}$, are determined by exchange interactions within this unit. Thus, the approach based on the use of chemically stable polynuclear magnetically active metal-containing fragments is promising for the formation of coordination polymers with specified magnetic characteristics.

The purpose of this work is to establish the effect of the nature of the anion or solvent on the crystal structures of the compounds based on the binuclear cation $Cu_2(HL)_2^{2+}$. Interest in studying the solvent effect on the crystal structure of the coordination polymers is due to several examples in which the solvent acted as a template in the assembling of porous coordination polymers [14] or substantially affected the crystal structure of the coordination polymers [17, 18].

It is shown that the replacement of the perchlorate ion in $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ by diphenyl dicarboxylate results in the formation of the coordination polymer and, hence, an additional aim was formulated as the determination of the contribution of exchange interactions within the binuclear cation and between the binuclear cations to the total magnetic susceptibility of the studied system.



H_2L



H_2L^1

A new complex $[Cu_2(HL)_2(CH_3OH)_2](BF_4)_2 \cdot 2C_6H_3Cl_3$ (**I**) ($C_6H_3Cl_3$ is 1,2,4-trichlorobenzene) was obtained from the earlier described compound $[Cu_2(HL)_2(H_2O)_2](BF_4)_2$, and new compounds $[Cu_2(HL)_2(H_2O)_2](1,4\text{-}O_2CC_6H_4CO_2)$ (**II**) and $[Cu_2(HL)_2(H_2O)_2](4,4'\text{-}O_2CC_6H_4C_6H_4CO_2)$ (**III**) were synthesized by the substitution of perchlorate in $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ by anions of linear dicarboxylic acids. The structures of all compounds were determined by X-ray diffraction analyses, and the magnetic properties of complex **III** were studied.

EXPERIMENTAL

All procedures associated with the synthesis of new complexes were carried out in air using commercially available solvents and reagents. The binuclear complex $[Cu_2(HL)_2(H_2O)_2](BF_4)_2$ was synthesized using a known procedure [16].

Single crystals of compound **I** were obtained by the diffusion of a solution of $[Cu_2(HL)_2(H_2O)_2](BF_4)_2$ in methanol into 1,2,4-trichlorobenzene.

Synthesis of compound II. A weighed sample of $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ (0.1 g, 0.0965 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF) (2 mL), and a solution of sodium terephthalate (0.021 g, 0.099 mmol) in water (2 mL) was added with stirring to the obtained solution. In 24 h a black precipitate was filtered off, washed with water, and dried. The yield was 0.084 g (84.5%).

For $C_{48}H_{50}N_8O_{10}Cu_2$

anal. calcd., %:	C, 56.2;	H, 4.88;	N, 10.93.
Found, %:	C, 55.5;	H, 5.05;	N, 10.65.

Single crystals of compound $\mathbf{II} \cdot 8H_2O$ suitable for X-ray diffraction analysis were grown by slow diffusion in a bilayer system, which was prepared by the deposition of a solution of $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ in DMF (5 mL) on a solution (5 mL) of sodium terephthalate in water for several days.

Synthesis of compound III. Compound $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ (0.11 g, 0.106 mmol) was dissolved in DMF (2 mL), and a solution of sodium 4,4'-diphenyl dicarboxylate (0.034 g, 0.140 mol) in water (2 mL) was added with stirring to the obtained solution. In 24 h a black precipitate was filtered off, washed with water, and dried. The yield was 0.097 g (82.9%).

For $C_{60}H_{74}N_{10}O_{15}Cu_2$ (based on the composition $[Cu_2(HL)_2(H_2O)_2](4,4'\text{-}O_2CPhPhCO_2) \cdot 3H_2O \cdot 2DMF$ ($\mathbf{III} \cdot 3H_2O \cdot 2DMF$))

anal. calcd., %:	C, 55.3;	H, 5.73;	N, 10.8.
Found, %:	C, 55.2;	H, 5.80;	N, 10.6.

Single crystals of compound $\mathbf{III} \cdot 3H_2O$ suitable for X-ray diffraction analysis were grown by slow diffusion for several days in a bilayer system, which was obtained by the deposition of a solution of $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ in DMF (5 mL) on a solution (5 mL) of sodium 4,4'-diphenyl dicarboxylate in water. Only solvate molecules were localized in

Table 1. Crystallographic parameters and refinement details for the structures of compounds **I**, **II** · $8H_2O$, and **III** · $3H_2O$

Parameter	Value		
	I	**II** · $8H_2O$	**III** · $3H_2O$
Empirical formula	$C_{27}H_{28}BCl_3CuF_4N_4O_3$	$C_{48}H_{56}Cu_2N_8O_{18}$	$C_{108}H_{102}Cu_4N_{16}O_{26}$
FW	713.23	1160.11	2294.26
Crystal size, mm	0.50 × 0.50 × 0.10	0.30 × 0.30 × 0.20	0.40 × 0.20 × 0.20
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P1$
a, Å	15.571(1)	10.5264(9)	10.6420(9)
b, Å	11.4342(5)	11.680(1)	14.7367(7)
c, Å	18.404(1)	12.033(2)	16.873(1)
α, deg	90	78.610(5)	89.822(4)
β, deg	110.410(2)	68.359(4)	98.486(3)
γ, deg	90	69.577(4)	93.544(4)
V, Å^3	3071.0(3)	1284.6(2)	2612.1(3)
Z	2	1	1
ρ_{calcd}, g/cm^3	1.543	1.500	1.458
μ, mm^{-1}	1.033	0.910	0.888
Data collection over θ range, deg	3.97–27.46	2.18–25.87	2.31–26.05
Number of measured reflections	12370	5447	15638
Number of independent reflections (R_{int})	6851 (0.0458)	3866 (0.0689)	15638 (0)
Number of reflections with $I > 2\sigma(I)$	4167	2375	7195
Number of refined parameters	432	367	1309
GOOF	1.029	1.033	0.982
R_1, wR_2 ($I > 2\sigma(I)$)	0.0788, 0.2049	0.0705, 0.1737	0.0750, 0.1850
R_1, wR_2 (all reflections)	0.1323, 0.2445	0.1236, 0.2202	0.1747, 0.2524
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.897/–0.524	0.435/–0.592	1.141/–0.565

the crystalline lattice of compound **III** · Solv using the X-ray diffraction method and, therefore, the composition of this complex will be indicated as **III** · $3H_2O$ in the discussion of the crystallographic data, whereas the data of magnetochemistry were processed using the composition **III** · $3H_2O$ · 2DMF determined by elemental analysis.

Elemental analysis was carried out on an automated Carlo Erba 1106 C,H,N analyzer. Magnetic measurements were conducted using a Quantum Design MPMS SQUID magnetometer in a temperature range of 2–300 K with the permanent magnetic field up to 5 T. A sample was measured in a Teflon capsule, and diamagnetic corrections were calculated using the Pascal constants.

The X-ray diffraction analyses of single crystals of complexes **I**, **II** · $8H_2O$, and **III** · $3H_2O$ were carried out on a Nonius four-axis diffractometer (CCD detector, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The structure was solved by direct methods and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were generated geometrically and refined in the riding model. The calculations were performed using the SHELX-97 program package [19]. The crystallographic data for compounds **I**, **II** · $8H_2O$, and **III** · $3H_2O$ are presented in Table 1. The coordinates of atoms and other parameters of the studied structures were deposited with the Cambridge Crystallographic Data Centre (CIF files 1441176, 1441180, and 1441181, respectively; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Compound **I** crystallizes upon the diffusion of 1,2,4-trichlorobenzene into a solution of compound $[Cu_2(HL)_2(H_2O)_2](BF_4)_2$ in methanol in a bilayer system. It is most likely that 1,2,4-trichlorobenzene acts as both a hydrophobic agent (the complex diffuses into 1,2,4-trichlorobenzene, whereas water molecules

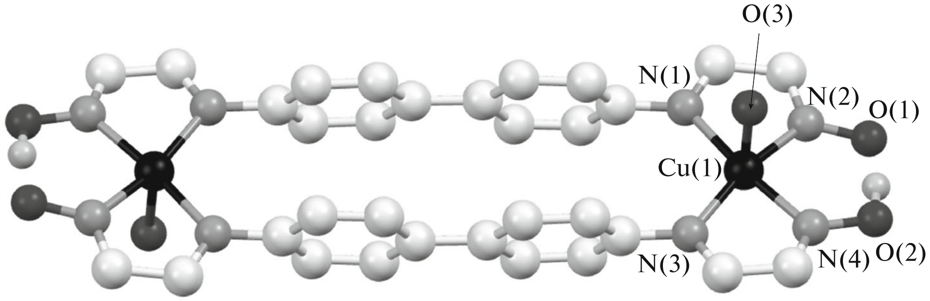


Fig. 1. Structure of the binuclear cation $[Cu_2(HL)_2(H_2O)_2]^{2+}$ for compound **II** as an example. The methyl groups HL^- and all hydrogen atoms, except oxime hydrogen atoms, are omitted. The atoms in the crystallographically nonequivalent part are numerated.

remain in the hydrophilic methanol layer) and a template for the formation of a certain crystalline lattice occupying its cavities. In compound **I**, the 1,2,4-trichlorobenzene molecules are not bound by coordination bonds and the methanol molecules are coordinated to the copper ions.

Compounds **II** and **III** were synthesized by the substitution of the perchlorate anions in $[Cu_2(HL)_2(H_2O)_2](ClO_4)_2$ by terephthalate or 4,4'-diphenyl dicarboxylate anions followed by the crystallization of the complexes. Of possible combinations of the cations present in the reaction ($[Cu_2(HL)_2(H_2O)_2]^{2+}$ and Na^+) and anions ($1,4\text{-}O_2CC_6H_4CO_2^-$ or $4,4'\text{-}O_2CC_6H_4C_6H_4CO_2^-$ and ClO_4^-), the compounds containing bulky two-charge ions ($[Cu_2(HL)_2(H_2O)_2]^{2+}$ and An^{2-}) crystallize, which is likely due to the efficient electrostatic interaction and the formation of a system of hydrogen bonds as will be shown below.

Compounds $\mathbf{II} \cdot 8H_2O$ and $\mathbf{III} \cdot 3H_2O$ contain the binuclear cation $[Cu_2(HL)_2(H_2O)_2]^{2+}$ (Fig. 1), whereas compound **I** contains the binuclear cation $[Cu_2(HL)_2(CH_3OH)_2]^{2+}$. All copper ions exist in a distorted square pyramidal environment N_4O, where the N atoms belong to the HL^- anion and occupy the equatorial positions and the O atom belongs to the coordinated methanol molecule in compound **I** or to the coordinated water molecule in compounds $\mathbf{II} \cdot 8H_2O$ and $\mathbf{III} \cdot 3H_2O$ and occupies the axial position. Selected bond lengths and interatomic distances in these binuclear cations are presented in Table 2.

In compound **I**, all binuclear cations $[Cu_2(HL)_2(CH_3OH)_2]^{2+}$ are crystallographically equivalent and centrosymmetric. The BF_4^- anions are connected to the binuclear cations by hydrogen bonds through the hydroxyl groups of methanol coordinated to the copper(II) ions (the O–F distances are 2.774(9) Å). The solvate trichlorobenzene molecules are disordered. In the crystalline lattice of compound **I** we can distinguish parallel layers formed by the $[Cu_2(HL)_2(CH_3OH)_2]^{2+}$ binuclear cations that are not bound to each other. The borofluoride anions and solvate trichlorobenzene molecules are located between these layers (Fig. 2a).

The distance from the nitrogen atoms of one HL^- fragment of the binuclear cation to the plane of the trichlorobenzene ring is 3.458(4)–3.505(4) Å, and the angle between the planes passing through the oxime–imine fragment of the HL^- ligand in $[Cu_2(HL)_2(CH_3OH)_2]^{2+}$ and the carbon atoms of trichlorobenzene is 1.5(4)°, possibly indicating the presence of π–π-stacking interactions between the trichlorobenzene molecule and alternated double bonds

Table 2. Selected bond lengths and interatomic distances within the binuclear cation in compounds **I**, $\mathbf{II} \cdot 8H_2O$, and $\mathbf{III} \cdot 3H_2O$

Bond	d, Å		
	I	$\mathbf{II} \cdot 8H_2O$	$\mathbf{III} \cdot 3H_2O$
Cu···Cu	12.3440(9)	12.304(2)	12.286(3), 12.300(3)
$Cu-N_{oxime}$	1.982(5)	1.989(7), 1.975(6)	1.94(1), 2.03(2), 1.97(1), 2.03(1)
	1.989(4)		1.94(2), 2.04(1), 1.92(2), 2.05(2)
$Cu-N_{Schiff\,base}$	2.031(4)	2.016(6), 2.026(7)	2.00(1), 2.07(1), 1.99(1), 2.08(1)
	2.040(4)		1.99(1), 2.11(1), 1.97(2), 2.07(2)
$Cu-O_{axial}$	2.255(6)	2.209(5)	2.36(2), 2.30(2), 2.16(2), 2.24(2)

in the oxime–imine fragment of the coordinated ligand HL^- (Fig. 2b). The distance from one of the chlorine atoms of trichlorobenzene to the copper(II) ion is 3.540(8) Å. Probably, this arrangement of the chlorine atoms relative to the copper ions favors the π–π-stacking interaction to occur between the molecules of the complex and solvate [20]. Examples of similar arrangement of the chlorine atoms above the copper(II) ion in the axial position have earlier been described for either the copper(II) complexes with the ligand containing the chlorobenzene residue (the distance from the Cu^{2+} ions to the Cl atoms of the adjacent molecules of the complex is 3.25 Å [21]), or the copper(II) complexes with solvate molecules of dichloromethane, chloroform, or dichloroethane (the distance from the Cu^{2+} ions to the Cl atoms of the solvate molecules ranges from 3.33 to 3.85 Å [22, 23]).

The binuclear cation $[Cu_2(HL)_2(H_2O)_2]^{2+}$ in compound **II** is centrosymmetric, whereas compound **III** contains two types of crystallographically independent binuclear cations. The cations of the first type in the crystalline lattice of compound **III** are connected by the Cu–O bonds, whose formation involves the oxygen atoms of the oxime groups of the N–O groups of the adjacent cations to form metallocycles $Cu_2(N{-}O)_2$ (Cu–O 2.81(1) Å). The distance between the copper(II) ions of the adjacent cations $[Cu_2(HL)_2(H_2O)_2]^{2+}$ (through the bridging oxime group) is 4.224(3) Å. The $[Cu_2(HL)_2(H_2O)_2]^{2+}$ cations of the second type are not directly bound between each other. The oxygen atoms of the oxime groups of the adjacent binuclear cations are also located under the bases of the CuN_4O pyramids in the cations of the second type, but the Cu···O distances exceed 3.1 Å. Thus, complex **III** contains 1D chains built by binding the binuclear cations $[Cu_2(HL)_2(H_2O)_2]^{2+}$ along with the discrete cations of the same composition. As in the case of tetrathiofulvalene carboxylate [9], the anions of terephthalic and diphenyldicarboxylic acids in compounds **II** and **III** are not coordinated to the copper ions.

The crystalline lattice of compound **II** has a branched system of hydrogen bonds between the terephthalate anions and solvate and coordinated water molecules. One carboxyl group of the terephthalate anion participates in the binding of these anions in pairs with two solvate water molecules (Fig. 3a), whereas the second carboxyl group binds two binuclear cations $[Cu_2(HL)_2(H_2O)_2]^{2+}$ through the solvate water molecules (Fig. 3b), which results in the formation of a chain structure. The distances between the oxygen atoms of these groups is 2.67(1)–2.96(1) Å, which is typical of the case of hydrogen bonding.

In compound **III** · $3H_2O$, the diphenyl dicarboxylate anions are joined with the $[Cu_2(HL)_2(H_2O)_2]^{2+}$ cations of the first type by hydrogen bonds between the carboxylate group of the anion and the water molecule coordinated to the copper(II) ion (the O···O distance is 2.80(2) Å). In the case of the second type cations, the solvate water molecule acts as a bridge between the carboxylate group and coordinated water molecule (the distance $O(carboxyl)\cdots O(H_2O)_{solvate}$ between the carboxyl group and solvate water molecule is 2.73(2) Å, $O(H_2O)_{solvate}\cdots O(H_2O)_{coord}$ 2.66(2) Å) (Fig. 3c). The branched system of hydrogen bonds between the binuclear cations and terephthalate/diphenyl dicarboxylate in compounds **II** · $8H_2O$ and **III** · $3H_2O$ can be a factor favoring the substitution of the borofluoride anions by the carboxylate residues due to an additional stabilization of the system (Figs. 3a–3c).

In the crystalline lattices of compounds **II** · $8H_2O$ and **III** · $3H_2O$, the binuclear cations and carboxylate anions are arranged in parallel alternating layers. These layers in compound **II** · $8H_2O$ are parallel to the crystallographic plane {1 0 0}, whereas in compound **III** · $3H_2O$ they are parallel to the plane {1 0 –1}.

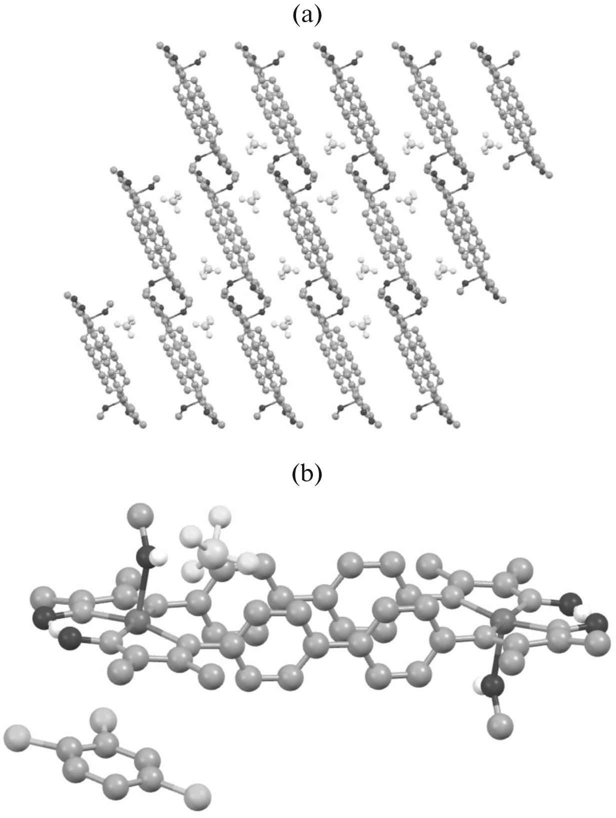


Fig. 2. (a) Fragment of the crystalline lattice of compound **I** and (b) the mutual arrangement of the binuclear cation and solvate trichlorobenzene molecule in the crystalline lattice of compound **I**. All hydrogen atoms bound to the (a and b) carbon atoms and (a) solvate trichlorobenzene molecules are omitted.

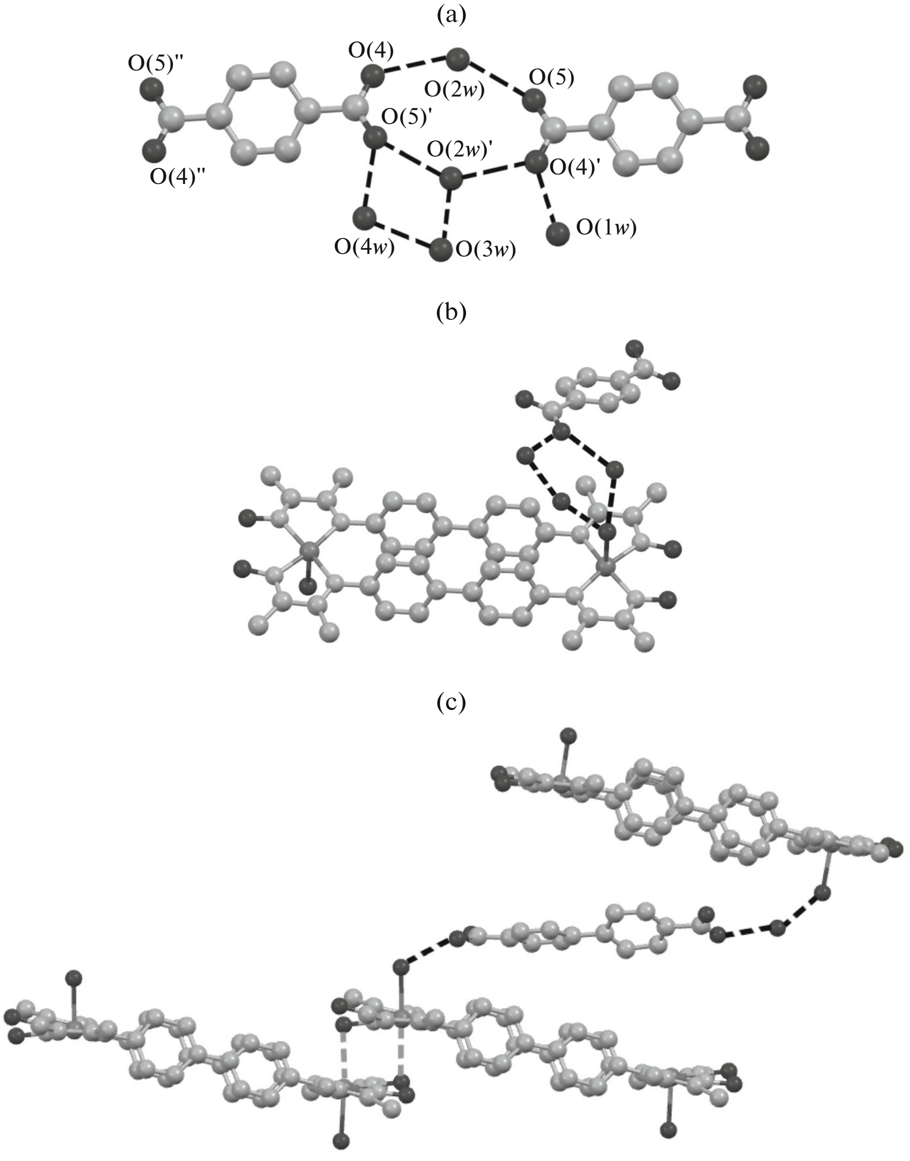


Fig. 3. System of hydrogen bonds in compound **II** · $8H_2O$ involving (a) the terephthalate anions and solvate water molecules and (b) the terephthalate anion, solvate water molecules, and cation $[Cu_2(HL)_2(H_2O)_2]^{2+}$; (c) in compound **III** · $3H_2O$ between the binuclear cations and anion. Hydrogen atoms are omitted. Hydrogen bonds in Figs. 3a and 3b are shown by black dash, and the bond between the oxygen atom of the oxime group and the copper(II) ion of the adjacent cation is shown by gray dash.

The magnetic properties of compound **III** · $3H_2O$ · 2DMF were characterized by the study of the molar magnetic susceptibility χ_M vs. temperature in the range from 2 to 300 K. As the temperature decreases, $\chi_M T$ monotonically decreases from 0.77 cm^3 K mol^{-1} at 300 K to 0.02 cm^3 K mol^{-1} at 2 K, indicating the predomination of antiferromagnetic interactions in the studied compound (Fig. 4).

The dependence of $\chi_M T$ on T can be interpreted in the framework of the model of isolated copper(II) dimers ($S = 1/2$) using the Hamiltonian (1) ignoring intermolecular interactions [24]

$$H = -2JS_1S_2, \tag{1}$$

where J is the exchange interaction parameter between two copper(II) ions in the binuclear fragment $[Cu_2(HL)_2(H_2O)_2]^{2+}$.

The best correspondence between the calculated and experimental dependences of $\chi_M T$ on T is achieved at the parameters $J = -9.89(6)$ cm^{-1}, $g = 2.058(1)$, and 2.8% of a paramagnetic impurity with $S = 1/2$ and $g = 2.0$ ($R^2 = 9.5 \times 10^{-5}$, $R^2 = \sum[(\chi_M T)_{\exp} - (\chi_M T)_{\text{theor}}]^2 / (\sum(\chi_M T)^2_{\exp})$). The obtained value of J is lower (by modulus) than the val-

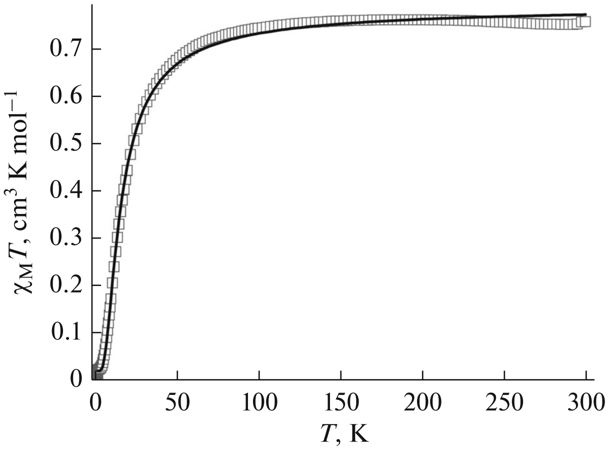


Fig. 4. Dependence of $\chi_M T$ on T for compound **III** · $3H_2O$ · 2DMF. Points are experiment, and solid line is calculation.

ues obtained earlier for similar binuclear systems with the $[Cu_2(HL)_2]^{2+}$ cation (J = −12.268(1) to −12.331(1) cm^{-1} [15]). Probably, J and g for compound **III** are averaged values for different crystallographically independent cations, and the introduction of an excessive number of parameters J and g is undesirable because of the possible reparametrization. The temperature dependence of $\chi_M T$ is satisfactorily described in the whole temperature range and, probably, the transfer of the exchange interactions between the binuclear cations in the 1D chain of compound **III** · $3H_2O$ · 2DMF is negligible.

Thus, the hydrogen bonds between the binuclear cations $[Cu_2(HL)_2(ROH)_2]^{2+}$ and anions or solvate water molecules are shown to play an important role in the formation of crystalline lattices of the obtained compounds. The antiferromagnetic interactions occur within the binuclear cations in compound **III** · $3H_2O$ · 2DMF, and the formation of bonds between the adjacent cations through the oxime groups or through the system of hydrogen bonds does not lead to the transfer of exchange interactions between the adjacent cations.

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