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Tetranuclear Copper(II) Complex with N,N'-bis(2-N-Tosylaminobenzylidene)-1,3-Diaminopropan-2-ol: Crystal Structure and Magnetic Properties

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Abstract—Tetranuclear copper(II) complex, $[Cu_4L_2(OOCCH_2COO)]$, where L is triply deprotonated bis-N,N'-(2-N-tosylaminobenzylidene)-1,3-diaminopropan-2-ol, in which two binuclear fragments are linked by the malonate dianion, is synthesized. The exchange interaction in the binuclear clusters is shown to be antiferromagnetic ($2J = -59$ cm^{-1}), whereas the intercluster interaction is ferromagnetic ($zJ' = 7.5$ cm^{-1}). The structure of the DMSO solvate of the complex is determined by X-ray diffraction analysis.

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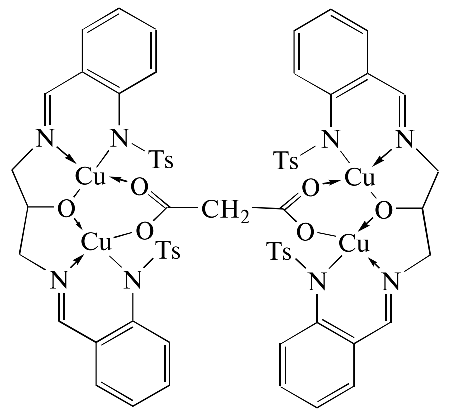
INTRODUCTION

Bis(azomethines) are the condensation products of salicylaldehyde and its derivatives with 1,3-diaminopropan-2-ol are classical binuclearing ligand systems [1–5]. These compounds coordinate with metals in the triply deprotonated form as pentadentate-bridging ligands to form “unsymmetrical” binuclear complexes in which the alkoxyl oxygen atom is one of the bridges connecting two metal ions, and an exogenic bridging ligand is the second bridge. Residues of carboxylic acids, phosphate ion derivatives, and the pyrazolate or azaindolate ion can serve as the latter [5]. A series of the tetranuclear copper(II) complexes with these ligands was also described [6–9]. In these ligands, two binuclear fragments are linked due to the bridging coordination of the dicarboxylic acid residue. The mono- and binuclear complexes with bis(azomethine) based on *o*-tosylaminobenzaldehyde and 1,3-diaminopropan-2-ol have earlier been synthesized [10–12].

The results of the synthesis and magnetochemical study of the new tetranuclear complex based on bis-N,N'-(2-N-tosylaminobenzylidene)-1,3-diaminopropan-2-ol (H_3L) with the composition $[Cu_4L_2(OOCCH_2COO)]$ (**I**) and the X-ray diffraction analysis data for its DMSO solvate (**Ia**) are presented in this report.



(I)

EXPERIMENTAL

Commercially available 1,3-diaminopropan-2-ol, copper(II) perchlorate, and sodium malonate were used as the starting compounds. 2-N-Tosylaminobenzaldehyde was synthesized using a described procedure [13]. Ligand H_3L was synthesized according to a described procedure [10]. Solvents were purified and dried using standard procedures [14].

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in the range from 400 to 4000 cm^{-1} (suspensions in Nujol). Elemental analysis was carried out on a PerkinElmer 240C instrument at the Laboratory of Microanalysis of the Southern Federal University. Thermogravimetric analysis was performed on a PerkinElmer Diamond TG/DTA instrument on heating the samples to 650°C with a rate of 10 deg/min. The specific magnetic susceptibility was determined by the relative Faraday method in the temperature range from 77.4 to 300 K.

Synthesis of I. Triethylamine (2 mmol) and then a solution of copper(II) perchlorate (2 mmol) in hot methanol (10 mL) with sodium malonate (1 mmol) were added to a hot solution of azomethine (1 mmol) in methanol (10 mL). The reaction mixture was refluxed for 1 h. A precipitate was filtered off, washed with hot methanol, and dried in vacuo. The yield of compound **I** was 0.37 g (48%).

For $C_{65}H_{60}N_8O_{14}Cu_4$				
anal. calcd. (%):	C, 50.06;	H, 3.88;	N, 7.18;	Cu, 16.30.
Found (%):	C, 50.61;	H, 3.99;	N, 7.29;	Cu, 16.42.

IR (ν, cm^{-1}): 1632 s ν(C=N), 1294 s ν(C–N), 1252 s $\nu_{as}(SO_2)$, 1141 s $\nu_s(SO_2)$.

Single crystals of DMSO solvate **Ia** suitable for X-ray diffraction analysis were obtained by the slow crystallization of complex **I** from a DMSO solution. They represented thin plates with the very low reflection ability.

X-ray diffraction analysis of complex **Ia** was carried out on a Bruker SMART APEX2 CCD diffractometer (MoK_α, λ = 0.71073 Å, graphite monochromator, ω scan mode) at 100(2) K. The initial array of the measured intensities was processed using the SAINT and SADABS programs included into the APEX2 program package [15]. 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}. The hydrogen atoms at carbon were placed in the geometrically calculated positions. All hydrogen atoms were included into refinement in terms of the riding model. All calculations were performed using the SHELXTL program package [16]. The crystallographic data and experimental characteristics for structure **I** are given 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 (no. 859839; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

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

Parameter	Value
Molecular formula	$C_{72.3}H_{85.6}Cu_4N_8O_{19.5}S_{7.3}$
Formula weight	1866.89
Crystal size, mm	0.16 × 0.11 × 0.02
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	15.2242(5)
b, Å	17.7089(6)
c, Å	19.0814(10)
α, deg	114.3740(10)
β, deg	102.3750(10)
γ, deg	104.5190(10)
V, Å^3	4231.4(3)
Z	2
ρ_{calcd}, g/cm^3	1.465
μ, mm^{-1}	1.242
F(000)	1928
$2\theta_{max}$, deg	54.00
Ranges of reflection indices	$-19 < h < 19$, $-22 < k < 22$, $-24 < l < 24$
Number of measured reflections	43541
Number of independent reflections	18338
Number of reflections with $I \geq 2\sigma(I)$	12913
Number of refined parameters	1050
Goodness-of-fit (all reflections)	1.054
R_1 ($I > 2\sigma(I)$)	0.0589
wR_2 (all reflections)	0.1632
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.574/–1.062

RESULTS AND DISCUSSION

The composition and structure of complex **I** were determined from the elemental analysis, IR spectroscopy, TG/DTA, and magnetochemical data. The structure of DMSO adduct **Ia** was established by X-ray diffraction analysis.

Complex **I** with the composition $[Cu_4L_2(OOCCH_2COO)]$ is formed from copper(II) perchlorate and bis-N,N'-(2-N-tosylaminobenzylidene)-1,3-diaminopropan-2-ol in the presence of malonate ions and triethylamine as a deprotonating agent. The derivatogram of the complex below 290°C contains no mass loss and endotherms, indicating the absence of solvent molecules in the composition of this compound [17]. The IR spectral data indicate the coordination of the azomethine ligand in the triply deprotonated form: the spectrum of complex **I** exhibits no absorption bands ν(OH) at 3200–3500 cm^{-1}. The ν(C=N) band in the spectrum of the complex shifts to a region of 1630 cm^{-1}, which confirms the

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the copper atoms in structure **Ia**

Bond	d, Å	Bond	d, Å
Cu(1)–O(1)	1.890(4)	Cu(2)–O(3SA)	2.382(19)
Cu(1)–N(1)	1.931(4)	Cu(3)–O(8)	1.925(3)
Cu(1)–O(2)	1.937(3)	Cu(3)–O(9)	1.928(3)
Cu(1)–N(5)	1.957(4)	Cu(3)–O(4)	2.728(3)
Cu(1)–O(5)	2.033(3)	Cu(3)–N(3)	1.948(4)
Cu(2)–O(3)	1.930(3)	Cu(3)–N(7)	1.973(3)
Cu(2)–O(1)	1.934(4)	Cu(4)–O(8)	1.902(3)
Cu(2)–N(2)	1.950(4)	Cu(4)–O(10)	1.914(3)
Cu(2)–N(6)	1.972(4)	Cu(4)–N(4)	1.944(4)
Cu(2)–O(3SB)	2.345(10)	Cu(4)–N(8)	1.967(3)
		Cu(4)–O(13)	2.853(3)
Angle	ω, deg	Angle	ω, deg
O(1)Cu(1)N(1)	83.27(17)	O(8)Cu(3)O(9)	93.29(12)
O(1)Cu(1)O(2)	92.60(15)	O(8)Cu(3)N(3)	84.20(13)
N(1)Cu(1)O(2)	161.71(19)	O(9)Cu(3)N(3)	169.43(14)
O(1)Cu(1)N(5)	169.90(19)	O(8)Cu(3)N(7)	166.69(14)
N(1)Cu(1)N(5)	90.17(18)	O(9)Cu(3)N(7)	95.13(13)
O(2)Cu(1)N(5)	95.97(15)	N(3)Cu(3)N(7)	89.30(14)
O(3)Cu(2)O(1)	93.42(15)	O(8)Cu(4)O(10)	94.82(12)
O(3)Cu(2)N(2)	176.4(2)	O(8)Cu(4)N(4)	84.58(13)
O(1)Cu(2)N(2)	83.73(19)	O(10)Cu(4)N(4)	160.51(14)
O(3)Cu(2)N(6)	94.59(15)	O(8)Cu(4)N(8)	168.97(14)
O(1)Cu(2)N(6)	169.93(16)	O(10)Cu(4)N(8)	94.18(14)
N(2)Cu(2)N(6)	88.01(18)	N(4)Cu(4)N(8)	89.06(14)

coordination of the azomethine nitrogen atoms to the copper(II) ions.

The effective magnetic moment of complex **I**, being 1.74 μ_B at 293 K, decreases substantially on cooling to the boiling point of liquid nitrogen (1.51 μ_B). This indicates an antiferromagnetic exchange interaction between the copper(II) ions.

The exchange interaction parameter in complex **I** was calculated in the framework of the Heisenberg–Dirac–van Vleck isotropic exchange model [18] using the Bleaney–Bowers equation [19]

$$\chi'_M = \frac{2N_A g^2 \beta^2}{3kT} \times \left[(1-f)\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + fS(S+1)\right] + N_\alpha, \qquad (1)$$

where χ'_M, N_A, g, β, k, J, f, and N_α are the molar magnetic susceptibility corrected to diamagnetism of atoms, Avogadro's number, Lande factor, Bohr magneton, Boltzmann constant, exchange parameter, molar fraction of a paramagnetic impurity, and temperature-independent paramagnetism, respectively. The fixed value N_α equal to 120×10^{-6} cm^3 mol^{-1} was used in the calculation.

Since a molecule of the complex contains two binuclear fragments bound by the malonic acid residue, the correct interpretation of the magnetic properties needs to take into account the intercluster exchange using the equation [18]

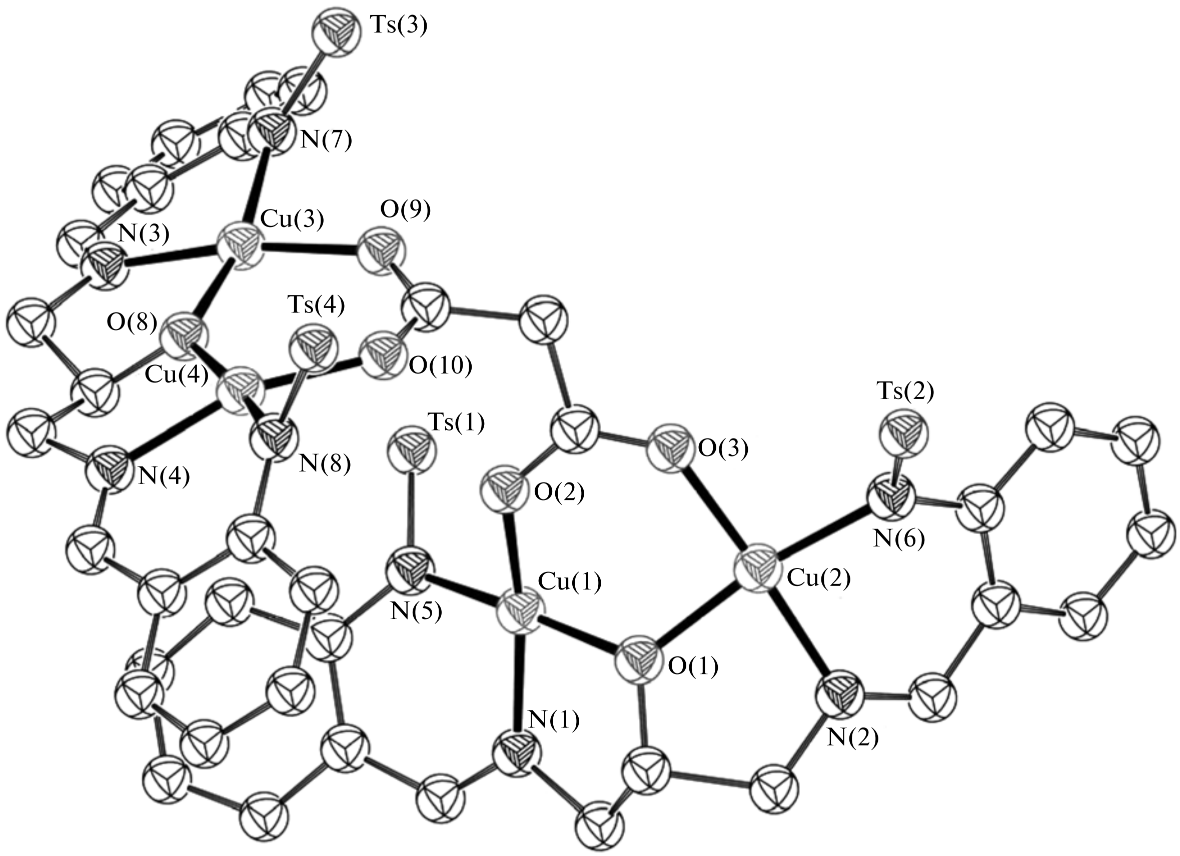
$$\chi_M = \frac{\chi'_M}{\left(1 - \frac{2zJ'}{Ng^2\beta^2}\chi'_M\right)}, \qquad (2)$$

where χ'_M is the molar magnetic susceptibility of the binuclear cluster calculated by Eq. (1), and zJ' is the intercluster exchange parameter.

The best agreement between the theory and experiment is observed at the following parameters of the model: $2J = -59$ cm^{-1}, $zJ' = 7.5$ cm^{-1}, $g = 2.03$, and $f = 0$.

The antiferromagnetic exchange interaction in complex **I** is somewhat weaker than that in the binuclear copper(II) complexes based on N,N'-bis(salicylidene)-1,3-diaminopropan-2-ol with the acetate bridge [5]. In this case, the weakening of the antiferromagnetic exchange interaction can be due to a distortion of the exchange fragment because of steric hindrances created by the closely arranged tosyl groups and an additional coordination of the copper ions by the oxygen atoms of the tosyl moieties. It should be mentioned that the magnetic exchange is ferromagnetic in the described copper(II) complexes with N,N'-bis(salicylidene)-1,3-diaminopropan-2-ol in which two binuclear fragments are linked due to the bridging coordination of the dicarboxylic acid residue [6–9]. The very weak intercluster exchange interaction of the antiferromagnetic type was also observed [6, 7].

Tetranuclear complex **Ia** can conveniently be described as consisting of two binuclear fragments bound by the malonate dianion (figure). The binuclear fragment containing the Cu(3) and Cu(4) atoms is nearly planar. On the average, the deviation of the atoms from the mean planar of the six-membered bimetallic chelate cycle Cu(3)–O(9)–C(34)–O(10)–Cu(4)–O(8) is 0.067 Å, and the dihedral angle between the coordination planes of the Cu(3) and Cu(4) atoms is 13.0(2)°. The second binuclear fragment is somewhat distorted because of the inflection along the line connecting the alkoxyl bridging oxygen atom and the carbon atom of the malonate dianion, and the dihedral angle between the coordination planes of the Cu(1) and Cu(2) atoms is 40.62(14)°. The difference in the geometry of these fragments is manifested as the distance between the copper atoms: the Cu(1)···Cu(2) distance (3.3115(8) Å is noticeably shorter than Cu(3)···Cu(4) (3.5047(7) Å).



Structure of complex **Ia** in the representation of atoms by thermal displacement ellipsoids with the 50% probability. Hydrogen atoms are omitted, and the tosyl groups ($SO_2C_7H_7$) are designated as Ts(1), Ts(2), etc. (the numeration coincides with that of the sulfur atoms).

The coordination polyhedron of the copper atoms in compound **Ia** is a square supplemented to the extended tetragonal pyramid (4 + 1) by weak interactions with the oxygen atoms of the tosyl groups and solvent. The coordination sphere of the Cu(1), Cu(3), and Cu(4) atoms is supplemented by the oxygen atoms O(5) (Ts(1)), O(4) (Ts(1)), and O(13) (Ts(2)) of the tosyl fragments remote at distances of 2.933(3), 2.728(3), and 2.853(3) Å, respectively. An additional coordination of the Cu(2) atom by the solvent molecule (DMSO) disordered over two positions is observed in 60% of the molecules (Table 2). The first position is occupied by 60% and represents a superposition of two DMSO molecules (by 15 and 25%, respectively) and methanol (20%). The second position (40%) occupied by the DMSO molecule additionally disordered over two positions (by 20%) is not involved in the coordination of the complex.

A similar additional coordination of the oxygen atoms of the tosyl fragments is observed in almost all earlier described transition metal complexes with azomethines based on 2-N-tosylaminobenzaldehyde [10–12, 20].

The crystal structure of compound **Ia** includes additional three DMSO molecules and one methanol molecule that occupy cavities between the molecules of the complex. No specific interactions were found between the molecules of the solvent and tetranuclear complex.

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