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Tetranuclear Copper(II) Complex with the μ_4-1,6-Hexadicarboxylate Linker: Crystal Structure and Magnetic Properties

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Abstract—Tetranuclear copper(II) complex $[Cu_4L_2(OOC(CH_2)_6COO)]$ (**I**) based on bis(azomethine), condensation product of 1-phenyl-3-methyl-4-formylpyrazolone-5 with 1,3-diaminopropanol-2, is synthesized. The structure of its DMSO-adduct (**Ia**) is determined by X-ray diffraction analysis (CIF file CCDC 1447891). The complexes contain two binuclear fragments bonded by the μ_4-1,6-hexadicarboxylate linker. The magnetic exchange interaction in complex **I** is antiferromagnetic ($2J = -155$ cm^{-1}), whereas that in complex **Ia** is ferromagnetic ($2J = 129$ cm^{-1}), which is due to different conformations of the metallochelate cycles.

Keywords: azomethines, copper(II) complexes, magnetochemistry, exchange interaction, X-ray diffraction analysis

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INTRODUCTION

Bis(azomethines), being condensation products of polyfunctional aldehydes with 1,3-diaminopropanol-2, are classical binucleating ligand systems [1–5]. They are characterized by the formation of binuclear complexes in which the alkoxyl oxygen atom is one bridge linking two metal ions and the second bridge is the exogenic bridging ligand, such as residues of carboxylic acids and pyrazolate, azaindolate, or purinate ions [5–13]. In several cases, the formation of the tetranuclear complexes was described in which two binuclear fragments are bonded by the dicarboxylate or dipyrazolate linkers [14–17]. Similar complexes with the nonsymmetric exchange fragment are convenient models for studying the main factors determining the character and strength of exchange interactions between paramagnetic centers [5, 18].

We have earlier shown that in the binuclear copper(II) complexes with similar ligands the character of the magnetic exchange is determined by the geometry of the exchange fragment rather than the nature of the exogenic bridging ligand. In the complexes with anticomplementary [7, 8] 1,3-O,O' or 1,3-N,N' exogenic bridges, the exchange interaction can be both antiferromagnetic (for the planar, or λλ, conformation of metallocycles) and ferromagnetic (in the case of the roof-shaped, or δλ, conformation) [13, 18–20]. As a rule, the latter is stabilized due to the bridging coordination of the solvent molecule (DMSO or DMF).

The results on the synthesis and physicochemical study of the tetranuclear copper(II) complex $[Cu_4L_2(OOC(CH_2)_6COO)]$ (**I**) and its DMSO-solvate (**Ia**), which demonstrate basically different magnetic properties, are reported.

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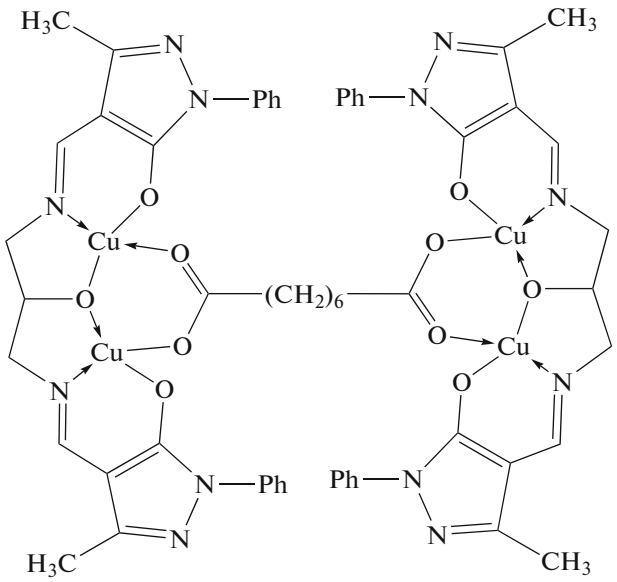
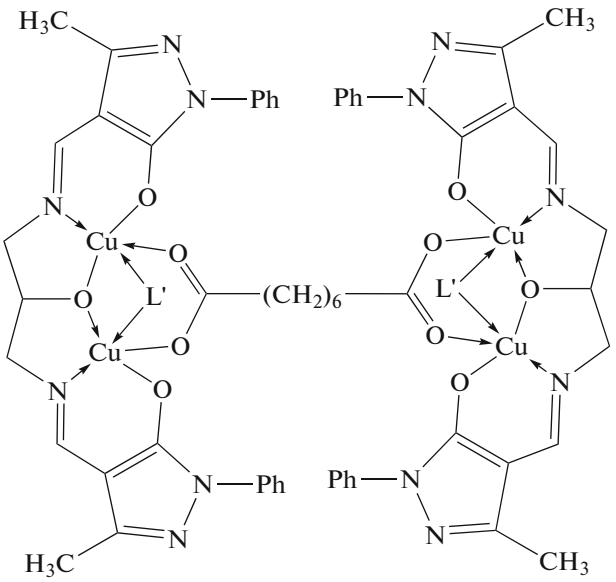


(**I**)



(**Ia**), L' = DMSO

EXPERIMENTAL

Bis(azomethine) H_3L was synthesized according to a described procedure [20].

Synthesis of complex I. Triethylamine (0.5 mmol), octanedionic acid (0.1 mmol), and a hot solution of copper(II) perchlorate (0.5 mmol) in methanol (10 mL) were added to a hot solution of bis(azomethine) H_3L (0.2 mmol) in methanol (10 mL). The solution was refluxed with a reflux condenser for 1 h. The precipitate was filtered off, washed with hot methanol, and dried in vacuo. The yield was 0.47 g (35%); mp > 250°C.

For $C_{29}H_{29}Cu_2N_6O_5$

Anal. calcd., %	C, 52.1;	H, 4.37;	N, 12.6;	Cu, 19.0.
Found, %:	C, 52.4;	H, 4.51;	N, 12.3;	Cu, 18.8.

IR (ν, cm^{-1}): 1630, 1599 ν(C=N); 1555, 1440 ν(μ_2-COO).

Complex Ia was synthesized by the recrystallization of compound **I** from DMSO (mp > 250°C). IR (ν, cm^{-1}): 1630, 1600 ν(C=N); 1560, 1445 ν(μ_2-COO).

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 a suspension in Nujol.

The specific magnetic susceptibility of the complexes was determined by the relative Faraday method in the temperature range 77.4–300 K using $Hg[Co(CNS)_4]$ as a standard for calibration.

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). The initial array of measured intensities was processed using the SAINT and SADABS programs included into the APEX2 program package [21, 22]. 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 geometrically calculated positions. The structures were solved and refined using the SHELXTL program [23]. The experimental characteristics and crystallographic data are presented in Table 1. Selected interatomic distances and bond angles are given in Table 2.

The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1447891; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The composition and structure of compound **I** were determined on the basis of the data of elemental analysis, IR spectroscopy, TG–DTA, and magnetochemistry. The structure of DMSO-adduct **Ia** was established by X-ray diffraction analysis.

In the presence of octanedionic acid and triethylamine as a deprotonating agent, bis(azomethine) H_3L and copper(II) perchlorate form complex **I** of the composition $[Cu_4L_2(OOC(CH_2)_6COO)]$. No mass loss and endothermic effects are observed on the derivatogram of the complex in the region lower than 290°C, indicating that the composition contains no solvent molecules [24]. The data of IR spectroscopy indicate the coordination of the azomethine ligand in the triply deprotonated form: the spectrum of complex **I** contains no absorption bands in a range of 3200–

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

Parameter	Value
Empirical formula	$C_{66}H_{82}N_{12}O_{14}S_4Cu_4$
FW	1649.88
Crystal size, mm	0.19 × 0.12 × 0.07
Temperature, K	173(2)
Crystal system	Monoclinic
Space group	*P*2(1)/c
a, Å	18.1675(11)
b, Å	13.6456(9)
c, Å	15.7064(10)
β, deg	112.6680(10)
V, Å^3	3592.9(4)
Z	4
ρ_{calcd}, g/cm^3	1.525
μ, mm^{-1}	1.355
F(000)	1708
Scan range over θ, deg	1.21–27.51
Number of measured reflections	35193
Number of independent reflections	8267
Number of reflections with $I > 2\sigma(I)$	5917
Ranges of reflection indices	$-23 \le h \le 23$, $-17 \le k \le 17$, $-20 \le l \le 20$
Refined parameters	461
R_1 ($I > 2\sigma(I)$)	0.0384
wR_2 (all reflections)	0.1217
GOOF (all reflections)	1.000
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.593/–0.552

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

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–N(3)	1.937(2)	Cu(2)–N(4)	1.942(2)
Cu(1)–O(1)	1.9401(19)	Cu(2)–O(5)	1.953(2)
Cu(1)–O(3)	1.9415(19)	Cu(2)–O(2)	1.954(2)
Cu(1)–O(4)	1.952(2)	Cu(2)–O(3)	1.9553(19)
Cu(1)–O(6)	2.379(2)	Cu(2)–O(6)	2.572(2)
		Cu(2)–O(7)	2.560(4)
Angle	ω, deg	Angle	ω, deg
Cu(1)O(3)Cu(2)	103.97(9)	Cu(1)O(6)Cu(2)	76.54(6)
N(3)Cu(1)O(1)	160.96(9)	N(4)Cu(2)O(5)	95.07(9)
N(3)Cu(1)O(3)	84.79(9)	N(4)Cu(2)O(2)	178.10(9)
O(1)Cu(1)O(3)	92.91(8)	O(5)Cu(2)O(2)	85.78(8)
N(3)Cu(1)O(4)	96.15(9)	N(4)Cu(2)O(3)	85.28(9)
O(1)Cu(1)O(4)	86.86(8)	O(5)Cu(2)O(3)	179.55(9)
O(3)Cu(1)O(4)	177.75(8)	O(2)Cu(2)O(3)	93.86(8)

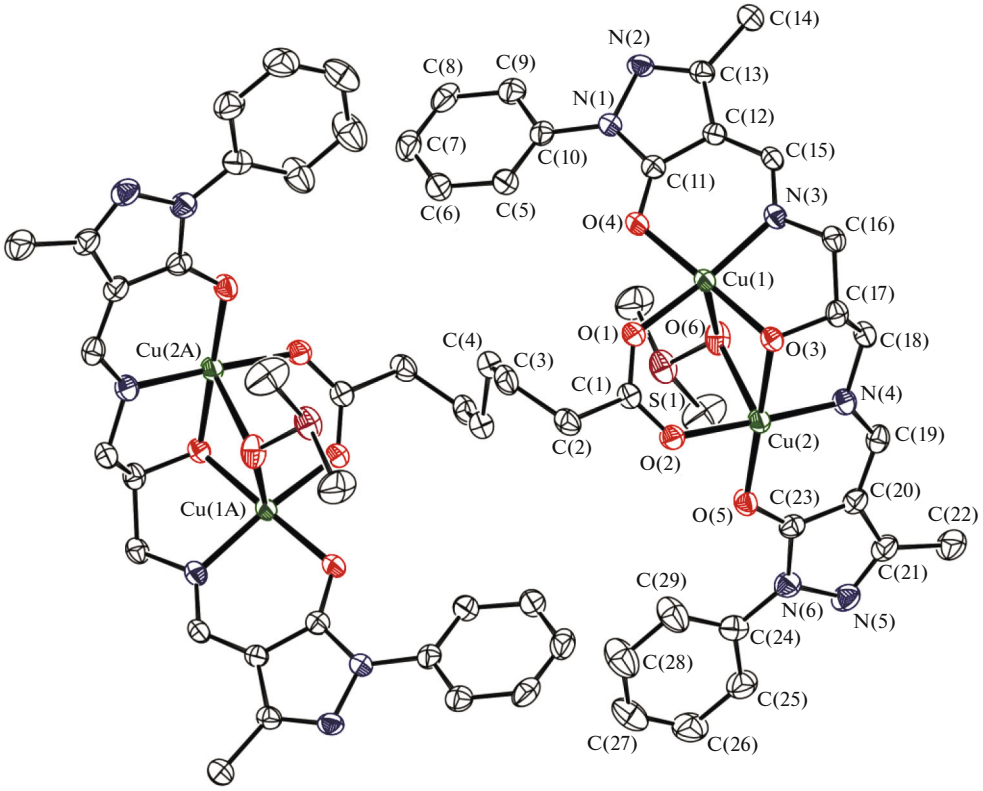


Fig. 1. General view of complex **Ia** in the representation of atoms by atomic shift ellipsoids with 50% probability (hydrogen atoms are omitted).

3500 cm^{-1}, indicating the deprotonation of the alkoxyl group. The ν(C=N) band in the spectrum of the complex shifts to 1630 cm^{-1}, which confirms the coordination of the azomethine nitrogen atoms to the copper(II) ions. The absorption bands at 1599 and 1440 cm^{-1} were assigned to ν_{as} and ν_s of the bridging carboxyl groups of the 1,6-hexanedicarboxylate ion.

Complex **Ia** was obtained by the recrystallization of complex **I** from DMSO. The general view of complex **Ia** is shown in Fig. 1.

Tetranuclear centrosymmetric complex **Ia** of the composition $\{[Cu_2L(DMSO)_2]_2(OOC(CH_2)_6COO)\}$ can be described as consisting of two binuclear fragments with the μ_4-1,6-hexanedicarboxylate linker. The structure of the binuclear fragment of complex **Ia** is shown in Fig. 2.

The doubly deprotonated residue of bis(azomethine) acts as a hexadentate-bridging ligand, and the alkoxide O(3) atom performs the bridging function. The pyrazole fragments are near planar. The phenyl substituents at the N(1) and N(6) atoms are unfolded relative to the planes of the pyrazole cycles (the corresponding torsion angles are 16.80° and 6.18°).

The binuclear fragment in complex **Ia** is substantially distorted. The dicarboxylate exogenic bridge fixes the roof-shaped (δλ) conformation of the metallochelate cycles, which is additionally favored by the bidentate-bridging coordination mode of the DMSO molecule (Fig. 2). The crystal structure of complex **Ia** contains two DMSO molecules, whose O(7) atoms are disordered and occupy two positions with a population of ~1/2. In one of them, the O(7) atom is linked by a comparatively weak (Cu–O 2.560(4) Å) coordination bond with the Cu(2) atom. The coordination polyhedron of the Cu(1) atom is an extended square pyramid (4 + 1) with the apical O(6) atom. The Cu(2) atom is located in the distorted octahedral environment, and the axial positions are occupied by the O(6) and O(7) atoms of two DMSO molecules.

Both six-membered metallochelate cycles in complex **Ia** are nearly planar: all atoms lie in the plane of the pyrazole cycle. The deviations of the copper atoms from the plane passing through the atoms of the chelate and pyrazole cycles are 0.110 and 0.139 Å for Cu(1) and Cu(2), respectively. The Cu(1)O(3)Cu(2) bond angle is 103.97(9)°, and the alkoxide bridging O(3) atom is strongly pyramidalized (the sum of the bond angles at this atom is 328.5°).

As a whole, the binuclear fragments in complex **Ia** are generally roof-shaped, and the dihedral angle between the Cu(1)O(3)C(17) and Cu(2)O(3)C(17) planes, which is usually used as a quantitative measure of this distortion, is 63.30°.

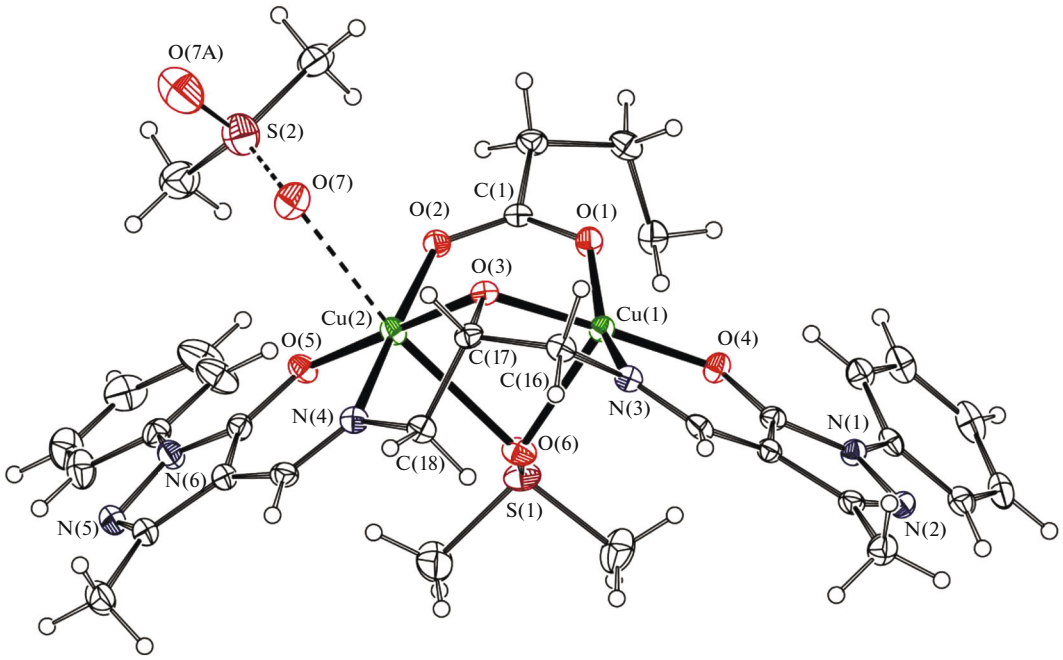


Fig. 2. Structure of the binuclear fragment of complex **Ia** in the representation of atoms by atomic shift ellipsoids with 30% probability.

The distortion of the bimetallic fragment is caused by different conformations of the five-membered chelate cycles separated by the alkoxo group. The cycle including the Cu(1) atom has a twist conformation relative to the C(16)–C(17) bond, and the cycle including the Cu(2) atom has an envelope conformation, whose valve is formed by the methylene C(18) atom shifted from the plane of other four atoms by 0.456 Å. As a result, the methylene C(16) and C(18) atoms are located at different sides from the C(17)–O(3) bond common for both cycles, and the roof-shaped (δλ) [25] conformation of the binuclear complex takes place.

The Cu···Cu distance in complex **Ia** is 3.0702(4) Å, which is substantially shorter than that in the carboxylate-bridged binuclear copper(II) complexes with bis(azomethines) based on 1,3-diaminopropanol-2, whose structures are close to planar (λλ conformation) [18, 25].

On the whole, the structure of the binuclear fragments in complex **Ia** is close to that for the earlier described acetate-bridged complex with the same ligand also containing the bidentate-bridging coordinated DMSO molecule [19]. Insignificant differences in bond lengths and bond angles are caused, most likely, by packing effects.

The study of the temperature dependence of the magnetic susceptibility of the complexes shows that the magnetic properties of complex **I** and DMSO-adduct **Ia** differ substantially. The exchange interaction of the antiferromagnetic type takes place between the copper(II) ions in complex **I**. The exchange parameter $2J$ calculated in terms of the Heisenberg–Dirac–Van Vleck isotropic model [26] using the Bleaney–Bowers equation [27] is -155 cm^{-1} ($g = 2.11$, molar fraction of paramagnetic impurity $f = 0.005$). The ferromagnetic exchange takes place between the copper(II) ions in DMSO-adduct **Ia**. The best accord between the theory and experiment is achieved at the following parameters of the model: $2J = 129$ cm^{-1}, $g = 2.16$, $f = 0.015$. In both cases, a correction to the interdimer exchange interaction was not required for the theoretical interpretation of the temperature dependence of the magnetic susceptibility, which indicates the magnetic isolation of the dimers because of the presence of the extended linker. It should be mentioned that the magnetic properties of complexes **I** and **Ia** are similar to those for the earlier described acetate-bridged binuclear copper(II) complex with the same bis(azomethine) ($2J = -169$ cm^{-1} for the planar complex and $2J = 154$ cm^{-1} for the DMSO-adduct) [19]. Some increase in the ferromagnetic contribution to the resulting exchange interaction in DMSO-adduct **Ia** compared to the acetate-bridged analog can be due to the axial coordination of the DMSO molecule to one of the copper(II) ions [28].

Thus, we found one more example for "switching-off" the magnetic exchange sign from antiferromagnetic and ferromagnetic in the carboxylate-bridged copper(II) complexes with bis(azomethines) based on 1,3-diaminopropanol-2 due to the recrystallization of the complexes from the coordinating solvent. We have previously shown [18, 19, 29] that the antiferromag-

netic character of the exchange in complexes of this type is due to the "symmetric" conformation of the binuclear fragment, whereas the ferromagnetic character is observed due to the roof-shaped conformation. The role of the solvent molecule as a "switcher" of the exchange interaction character is only the stabilization of the roof-shaped conformation of the metallocycles as a result of the axial coordination to both paramagnetic centers.

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