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Crystal structure and magnetic properties of a tetranuclear carbonate-bridged Cu^{II} complex with a Schiff base compartmental ligand with the N_2OS_2 donor set

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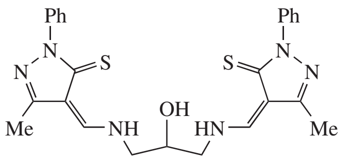
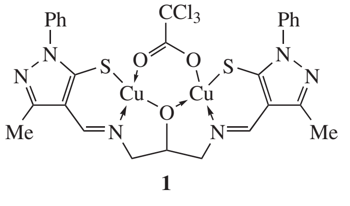
A carbonate-bridged tetranuclear Cu^{II} complex of the general formula $[(Cu_2L)_2CO_3]\cdot 2MeCN$ (L is triply deprotonated Schiff base condensation product of 1,3-diaminopropan-2-ol and 1-phenyl-3-methyl-4-formyl-5-mercaptopyrazole) has been obtained by the slow crystallization of dinuclear complex $[(Cu_2L)CCl_3COO]$ from acetonitrile and studied by X-ray diffraction and low-temperature magnetic measurements.

Bis-azomethines derived from 1,3-diaminopropan-2-ol and polyfunctional aldehydes such as salicylic aldehyde and its analogues are classical compartmental ligands, which commonly have N_2O_3 or N_4O donor set.[1–3] These compounds react with copper(II) ions as pentadentate ligands forming so-called heterobridged complexes – binuclear complexes with nonequivalent exchange pathways between metal paramagnetic centers: the endogenous alkoxyl oxygen atom as first, and exogenous bridging ligand (carboxylate, pyrazolate or azaindolate ion) as the second one.[4–6] These ligands can also favor the formation of tetranuclear complexes of two types. The first type is represented by the complexes in which two binuclear moieties are linked by the dicarboxylic acid or dipyrazolate entities.[7–9] The second-type complexes are tetranuclear ones possessing pseudocubane structure with hydroxy, alkoxy or azido ions as exogenous bridging ligands.[10–12] All these complexes are convenient models for developing magneto-structural correlations, which attract interest for the design of novel molecular magnetic materials[3,13] and the synthetic models of metal sites in non-heme metalloproteins.[14,15]

Here, we describe the synthesis and magnetic properties of the μ_2-trichloroacetate-bridged binuclear Cu^{II} complex $[Cu_2L(CCl_3COO)]$ **1** and μ_4-η^2:η^1:η^1 carbonate-bridged tetranuclear Cu^{II} complex $[Cu_4L_2(CO_3)]\cdot 2MeCN$ **2** and the XRD study of complex **2** (L is triply deprotonated condensation product of 1,3-diaminopropan-2-ol and 1-phenyl-3-methyl-4-formyl-5-mercaptopyrazole[†]).


H_3L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In accordance with the ^{1}H NMR spectroscopic data, compound **H_3L** exists in a DMSO solution in the thiopyrazolonic form.[16,17] Complex **1**[‡] was obtained by the reaction of **H_3L** with copper(II) trichloroacetate in the presence of triethylamine as a deprotonating agent. For the complex, a medium-strength magnetic exchange coupling between two copper(II) ions is observed. The magnetic susceptibility data of complex **1** were successfully fitted using the Bleaney–Bowers equation with the isotropic spin Hamiltonian $\hat{H} = 2J\hat{S}_1\hat{S}_2$.[18] The best-fit parameters are $2J = -151$ cm^{-1}, $g = 2.12$ and paramagnetic impurity $f = 0.008$. The value of the exchange parameter in **1** is typical of binuclear copper complexes with a carboxylate exogenous bridge.[3,9]

By the slow crystallization of complex **1** from an acetonitrile solution (for a month), the single crystals of tetranuclear complex **2** were obtained and studied by X-ray diffraction (Figure 1).[§] Unexpectedly, the composition of the crystals differed from the composition of **1**; instead of trichloroacetate, it contains a

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[†] *Synthesis of* **H_3L**. A solution of 1,3-diaminopropan-2-ol (0.09 g, 1 mmol) in benzene (5 ml) was added to a hot solution of 1-phenyl-3-methyl-4-formyl-5-mercaptopyrazole (0.44 g, 2 mmol) in benzene (10 ml). The mixture was refluxed for 1 h. The precipitate was filtered off, washed with benzene and dried *in vacuo* at room temperature. Yield, 0.32 g (65%). Yellow powder, mp 238 °C. IR (Nujol, ν/cm^{-1}): 3309 (ν_{OH}), 3190 (ν_{NH}), 1651, 1585 ($\nu_{C=N}$), 1231 ($\nu_{C=S}$). ^{1}H NMR (DMSO-d_6) δ: 2.25 (s, 6H, Me), 3.58–3.65 (m, 2H, CH_2), 3.78–3.82 (m, 2H, CH_2), 4.02 (br. s, 1H, CH), 5.90 (d, 1H, OH, J 5.4 Hz), 7.28–7.33 (m, 2H, H_{Ar}), 7.44 (t, 4H, H_{Ar}, J 7.8 Hz), 7.90 (d, 4H, H_{Ar}, J 7.8 Hz), 8.44 (d, 2H, CHN, J 14.1 Hz), 12.60 (m, 2H, NH). Found (%): C, 61.35; H, 5.18; N, 17.47. Calc. for $C_{25}H_{26}N_6OS_2$ (%): C, 61.20; H, 5.34; N, 17.13.

[‡] *Synthesis of complex* **1**. A small excess of triethylamine and a solution of copper(II) trichloroacetate monohydrate (0.41 g, 1 mmol) in methanol (10 ml) were added to a hot solution of **H_3L** (0.25 g, 0.5 mmol) in methanol (10 ml) The mixture was refluxed for 1 h. The precipitate was filtered off, washed with hot methanol and dried *in vacuo* at room temperature. Yield, 0.14 g (55%). Green powder, mp > 250 °C. IR (Nujol, ν/cm^{-1}): 1618, 1596 ($\nu_{C=N}$). Found (%): C, 41.49; H, 3.09; N, 11.00; Cu, 16.51. Calc. for $C_{27}H_{23}Cl_3Cu_2N_6O_3S_2$ (%): C, 41.73; H, 2.98; N, 10.81; Cu, 16.35. μ_{eff} per mole (μ_B): 2.331 (300 K), 0.242 (5 K).

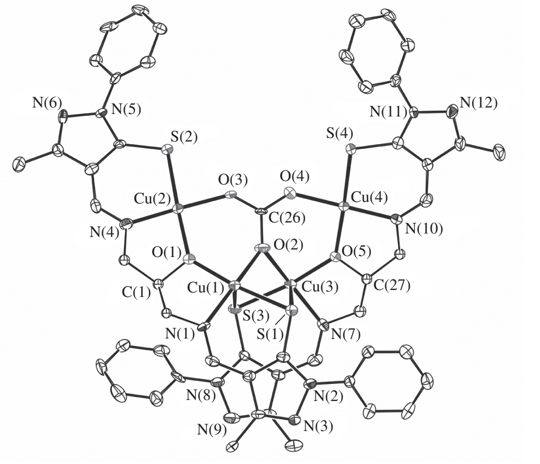

Figure 1 ORTEP view of complex **2** with a 50% ellipsoid probability (hydrogen atoms are omitted for clarity; the solvent molecule are not shown). Selected bond distances (Å) and angles (°): Cu(1)–O(1) 1.905(5), Cu(1)–N(1) 1.932(7), Cu(1)–O(2) 1.992(5), Cu(1)–S(1) 2.280(2), Cu(2)–O(1) 1.918(5), Cu(2)–N(4) 1.940(7), Cu(2)–O(3) 1.965(6), Cu(2)–S(2) 2.275(2), Cu(3)–O(5) 1.899(5), Cu(3)–N(7) 1.953(6), Cu(3)–O(2) 1.996(5), Cu(3)–S(3) 2.259(2), Cu(4)–O(5) 1.911(5), Cu(4)–N(10) 1.953(7), Cu(4)–O(4) 1.989(6), Cu(4)–S(4) 2.244(2), Cu(1)–Cu(3) 2.9892(15); Cu(1)–O(1)–Cu(2) 133.4(3), Cu(1)–O(2)–Cu(3) 97.1(2), Cu(3)–O(5)–Cu(4) 131.2(3), Cu(1)–S(1)–Cu(3) 70.68(6), Cu(1)–S(3)–Cu(3) 69.82(6).

carbonate bridging ligand, which probably originates from atmospheric carbon dioxide.[19,20] The possible mechanism of similar reaction was proposed[21] for the assemblage of a tetranuclear Ni^{II} complex from a binuclear one synthesized in an inert atmosphere.

The structure of complex **2** can be described as two cationic binuclear moieties $[Cu_2L]^+$, which are linked in a tetranuclear complex by means of carbonate dianion in a μ_4-η^2:η^1:η^1 fashion. Both $[Cu_2L]^+$ fragments adopt a 'symmetric' conformation of chelate cycles.[9] The copper(II) ions in these fragments are connected by alkoxide oxygen atoms and a carbonate group.

The coordination polyhedron of Cu(2) and Cu(4) atoms in compound **2** is a distorted square planar one. For the atoms Cu(1) and Cu(3), the same surroundings are completed towards a distorted tetragonal pyramid (4+1) by weak interaction with the S(3) and S(1) sulfur atoms separated by distances of 2.887(2) and 2.830(2) Å, respectively. In the crystals of complex **2** the tetranuclear molecules are combined in the dimers by means of several intermolecular contacts. Each of copper(II) atoms has a short contact with a donor atom of another tetranuclear molecule: Cu(1)···S(4)^i [d = 3.236(2) Å], Cu(2)···O(4)^i [d = 3.007(6) Å], Cu(3)···S(2)^i [d = 3.355(2) Å] and Cu(4)···O(3)^i [d = 3.086(6) Å] (symmetry code i = 1/2 + x, y, 1/2 – z).

Thus, the exchange interaction within $[Cu_2L]^+$ binuclear units in compound **2** between unpaired electrons on Cu(1) and Cu(3), as well as Cu(2) and Cu(4), ions can be passed through two bridges: O(1) and O(5) alkoxide atoms and O(2)C(26)O(3) and O(2)C(26)O(4) carbonate bridging groups, respectively.

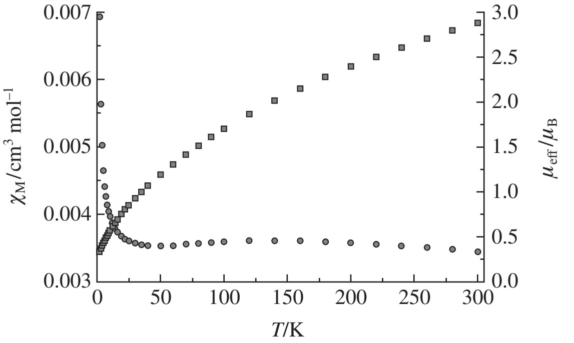

Figure 2 Temperature dependence of (▪) μ_{eff} per mole and (●) χ_M of complex **2**.

In accordance with common magneto-structural correlations[3,9] for these pathways one can expect antiferromagnetic exchange interaction of a medium strength. The exchange interaction between Cu(1) and Cu(4), Cu(2) and Cu(3), Cu(2) and Cu(4) atoms can be transmitted through a carbonate anion. The Cu(1) and Cu(3) atoms appear to be triply connected by the O(2) atom of the carbonate group and two sulfur atoms S(1) and S(3).

The value of μ_{eff} for **2** at room temperature is 2.875μ_B [calculated per one copper(II) atom]. Upon cooling, a smooth decrease of μ_{eff} is observed to reach a value of 0.333μ_B at 2 K (Figure 2). This behavior supports the idea that the overall spin coupling in complex **2** is antiferromagnetic with a singlet ground state.

Assuming the pseudo C_2-symmetry of the tetranuclear molecule, the isotropic spin Hamiltonian describing spin-states can be simplified to the form with four independent J-values: $\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) - 2J_2(\hat{S}_2\hat{S}_4) - 2J_3(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3) - 2J_4(\hat{S}_1\hat{S}_3)$.[22] Unfortunately, we fail to find the satisfactory fit of complex **2** experimental magnetic susceptibility temperature dependence data by utilizing this spin Hamiltonian. The possible explanation of the fact can be a considerable contribution of intermolecular exchange interaction.[18]

To further support our findings, the quantum-chemical calculations of exchange parameters were executed within a broken symmetry approach (DFT-BS)[23] at B3LYP/6-311G(d) level of theory. The energies of six spin states (Table 1) were calculated at the same XRD geometry: (αααα), (βααα), (αβαα), (ααββ), (αβαβ), (αββα) (α and β denote the spin-up and spin-down local states of the corresponding copper center). In accordance with experimental data, the ground state of the complex was found to be (αββα) with the total spin S = 0. The highest energy was calculated for the high-spin state with S = 2 (αααα), which is 312 cm^{-1} above the ground state.

The calculated exchange parameters for the above spin-Hamiltonian are J_1 = –103 cm^{-1}, J_2 = –44 cm^{-1}, J_3 = +7 cm^{-1} and J_4 = –64 cm^{-1}. As expected, the highest antiferromagnetic coupling is observed within $[Cu_2L]^+$ binuclear units. Note that a high antiferromagnetic exchange parameter between triply connected Cu(1) and Cu(3) centers can be explained by the small Cu–S–Cu angles favoring the effective overlap of magnetically active spin MOs.

In conclusion, it is worth mentioning that in case of the Cu^{II} complex with the 1,3-diaminopropanol bis-azomethine based on

Table 1 Spin states and their energies relative to the most stable one (E), calculated at the B3LYP/6-311G(d) level of theory.

State	S	E/cm^{-1}	State	S	E/cm^{-1}
αααα	2	312	ααββ	0	219
βααα	1	151	αβαβ	0	121
αβαα	1	171	αββα	0	0

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§ *Crystal data for complex* **2**: dark-green needle crystals, crystal size 0.24×0.18×0.03 mm, $C_{51}H_{46}Cu_4N_{12}O_5S_4\cdot 2(C_2H_3N)$ (M = 1371.51), orthorhombic, space group *Pbca*, at 100(2) K: a = 11.5779(18), b = 27.076(4) and c = 36.183(5) Å, V = 11343(3) Å^3, Z = 8, d_{calc} = 1.606 g cm^{-3}, F(000) = 5600, μ = 1.689 mm^{-1}, θ_{max} = 26.0°. Bruker Smart Apex II CCD diffractometer, 70074 reflections collected, R_{int} = 0.0676, R_1 = 0.0686 and wR_2 = 0.1159 for 5371 observed reflections with $I > 2\sigma(I)$, R_1 = 0.1765 and wR_2 = 0.1559 for all 11151 independent reflections, 740 parameters, GOOF = 0.994.

CCDC 966639 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

1-phenyl-3-methyl-4-formyl-5-pyrazole (N_2O_3 donor set) the similar reaction was not observed giving rise to proposition of peculiar sulfur atom role in it.

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