

*Dedicated to the memory of
Professor Maria Brezeanu (1924–2005)*

SUPRAMOLECULAR COPPER(II) DIMERS RESULTED FROM HYDROGEN BOND INTERACTIONS: SYNTHESIS, CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES

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Two copper(II) compounds of formula $[\text{Cu}_2(\text{Hmea})_2(\text{mea})_2\text{X}]\text{ClO}_4$ [$\text{Hmea} = 2\text{-aminoethanol}$ and $\text{X} = \text{ClO}_4^-$ (**1**) and SCN^- (**2**)] have been synthesized and characterized by X-ray diffraction studies. The copper atoms in **1** and **2** exhibit distorted square pyramidal surroundings with two nitrogen and two oxygen atoms from Hmea and mea ligands forming the basal plane (**1** and **2**) and a perchlorate oxygen (**1**) or a thiocyanate sulfur/nitrogen atom (**2**) in the apical position. Two crystallographically independent $[\text{Cu}(\text{Hmea})(\text{mea})]$ units occur in **1** and they form a centrosymmetric supramolecular dimer through symmetrical $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The two perchlorate groups in **1** play different structural functions: one acts as a bridge joining two copper(II) ions *via* apical coordination whereas the second one is just a counterion. Two $[\text{Cu}(\text{Hmea})(\text{mea})]$ units in compound **2** form a centrosymmetric dimer, the thiocyanate anions connecting neighboring dimers through end to end coordination mode. The cryomagnetic investigation of **1** shows the occurrence of an intermediate intramolecular antiferromagnetic interaction ($J = -22.3 \text{ cm}^{-1}$, $\mathbf{H} = -J\mathbf{S}_1 \cdot \mathbf{S}_2$) mediated by the hydrogen bonds.

INTRODUCTION

Hydrogen bonding is a useful tool in crystal engineering which has been used to generate high-dimensionality systems with interesting structural features.¹ Oligonuclear structures which are made up of mononuclear moieties connected through hydrogen bonds have been reported for a long time. The formation of binuclear complexes through intermolecular hydrogen bonds was first suggested by Yoneda and Kida.² The copper(II) complex $[\text{Cu}(\text{Eph})_2]_3$ (Eph = anion of *l*-ephedrine, a 2-aminoethanol derivative), which consists of trimeric units held together by nitrogen-oxygen hydrogen bonds, is the first documented example of cooperative hydrogen bonding in transition-metal complexes.³ The subject has been further expanded by Bertrand and Eller.⁴ X-ray diffraction studies on single crystals have shown the existence of cooperative hydrogen bonding in, for example, 2-aminoethanol (Hmea)-containing complexes of Co(III) ⁵, Ni(II) ⁵ and Cu(II) ⁶. Apart from the inherent interest in the role of the hydrogen bond in constructing supramolecular architectures, such complexes are useful models for the study of the exchange interactions between paramagnetic metal ions *via* hydrogen bonds.⁷

We are currently investigating the possibility to use homo- and hetero-binuclear complexes as building blocks in designing high-dimensionality systems. Amino-alcohols are known to generate a rich variety of copper(II) polynuclear complexes. The OH group can be easily deprotonated in the presence of copper(II)

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ions and the resulting alkoxo group usually acts as a bridge. We have reported new coordination polymers that have been obtained by connecting alkoxo-bridged binuclear Cu(II) complexes (the nodes) through bis(4-pyridyl) derivatives (the spacers).⁸⁻¹⁰

Aiming at obtaining extended structures by using binuclear copper(II)-mea complexes as nodes and CH₃COO⁻/SCN⁻ as spacers, we obtained two new compounds of formula [Cu₂(Hmea)₂(mea)₂X]ClO₄ [X = ClO₄⁻ (**1**) and SCN⁻ (**2**)] which are reported here in.

RESULTS AND DISCUSSION

The two compounds, [Cu₂(Hmea)₂(mea)₂OClO₃]ClO₄ (**1**), and [Cu(Hmea)(mea)(NCS)_{0.5}].0.5(ClO₄) (**2**), have as a common structural feature the fact that the alkoxo group does not bridge the copper(II) cations. The dimeric entities result through O-H⋯O hydrogen bonds established between the bis-chelated copper(II) monomers, where only one 2-aminoethanol ligand is deprotonated. The structure of a similar compound of formula [Cu(Hmea)(mea)]₂(NO₃)₂ having uncoordinated nitrate anions was reported by Bertrand *et al.*⁶

The molecular structure of [Cu₂(Hmea)₂(mea)₂OClO₃]ClO₄ (**1**) shows two independent [Cu(Hmea)(mea)]⁺ units (Fig. 1) where only one of the two ligands in each complex is deprotonated. Each of the two cationic complexes [Cu(1) and Cu(2)] forms a centrosymmetric dimer through symmetrical O-H⋯O type hydrogen bonds which are established between the alcohol hydroxo groups and the alkoxo oxygen atoms acting as hydrogen-bond acceptors. The oxygen ⋯ oxygen distances are 2.444(9) and 2.449(9) Å (Table 1). The intramolecular copper-copper distances concerning the units constructed from Cu(1) and Cu(2) atoms are 4.851(1) and 4.895(1) Å. The values of the O(1)-Cu(1)-O(2) and O(3)-Cu(2)-O(4) bond angles are 91.2(3), and 90.3(3)°, respectively.

Table 1

The hydrogen bonds within the centrosymmetric dimer in **1**

D-H⋯A	d(D-H), Å	d(H⋯A), Å	<DHA, °	d(D⋯A), Å
O1-H1⋯O2 [-x+1, -y, -z+1]	1.225	1.223	173.86	2.444(9)
O3-H2⋯O4 [-x+1, -y, -z+2]	1.227	1.225	174.29	2.449(9)

The ClO₄⁻ ions play different structural functions. One of the anions [that associated with Cl(2)] serves as a bridge and it joins two complexes *via* apical coordination [2.679(7) and 2.587(8) Å for Cu(1)-O(12) and Cu(2)-O(11), respectively]. Each copper atom shows a square-pyramidal coordination with a perchlorate anion in the axial position. O-H⋯O and N-H⋯O hydrogen bonds, as well as perchlorate ions join the copper(II) units resulting in infinite chains which run along the *c* axis (Fig. 2).

The dinuclear copper(II) units pack together in the solid with two amine nitrogens of one dimeric unit approaching an alkoxo oxygen and an alcohol hydroxo oxygen from another dimeric unit, with nitrogen⋯oxygen distances ranging from 3.036(11) to 3.127(10) Å. Hydrogen bonds also link N-H amino groups and perchlorate oxygen atoms, [2.447(17) and 2.471(9) Å for H(3C)-O(12) and H(4D)-O(9), respectively]. The chains are linked by N-H⋯O hydrogen bonds in a layer parallel to the (*bc*) plane and the perchlorate anions associated with Cl(1) are on the surfaces of such layers (Fig. 3).

The packing of the layers is illustrated in Fig. 4. The interlayer separation corresponds to the *a* parameter of the unit cell (9.550 Å).

The structure of copper complex **2** consists of supramolecular dinuclear copper(II) units which are similar to those found in compound **1** (Fig. 5).

The environment of the copper atom is a square pyramidal with a sulfur or nitrogen thiocyanate atom in the axial position. The axial copper-sulfur [Cu(1)-S(1) = 2.860(3) Å] and copper-nitrogen [Cu(1)-N(3) = 3.057(10) Å] distances are considerably longer than the copper-oxygen [Cu(1)-O(1) = 1.958(2) and Cu(1)-O(2) = 1.962(2) Å] and copper-nitrogen [Cu(1)-N(1) = 1.993(3), Cu(1)-N(2) = 2.006(3) Å] bond lengths in the basal plane. Two-fold related cationic complexes form the hydrogen bonded dinuclear unit due to relatively strong symmetrical O-H⋯O hydrogen bonds (Table 2). The hydrogen atoms from these hydrogen bonds are located on a two-fold axis.

Table 2

The hydrogen bonds within the centrosymmetric dimer in **2**

D-H...A	d(D-H), Å	d(H...A), Å	<DHA, °	d(D...A), Å
O1-H1...O1 [-x+1, -y, z]	1.224(5)	1.224(5)	171(5)	2.440(6)
O2-H2...O2 [-x+1, -y, z]	1.228(5)	1.228(5)	175(7)	2.453(6)

The disordered thiocyanate anions acts as end-to-end bridging groups linking the copper atoms of neighbouring dinuclear copper(II) units through apical positions. This results into copper(II) chains which run parallel to the crystallographic *b* axis. The value of the Cu-N (NCS⁻) distance is on the limit of a semi-coordinative bond [3.057(10) Å] (Fig. 6).

The perchlorate anions interact with two amino groups by weak hydrogen bonds [2.354(15) and 2.441(16) Å for N(1)-H(1B)...O(1Cl) and N(1)#-H(1B)#...O(1Cl), respectively]. In addition, the cationic dinuclear units are interlinked by N-H...O hydrogen bonds (Table 3) affording layers (Fig. 7).

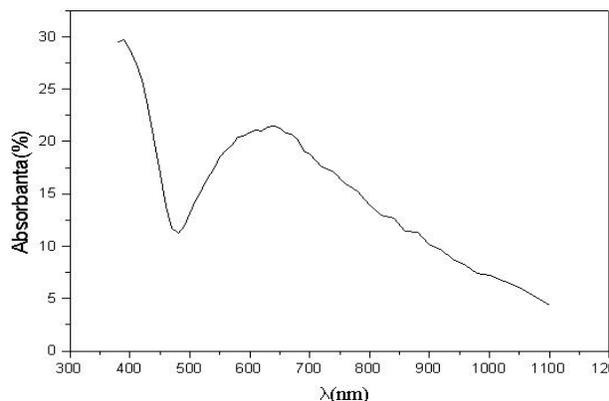
Table 3

N-H...O hydrogen bonds in **2**

	d(D-H), Å	d(H...A), Å	<DHA, °	d(D...A), Å
N2-H2B...O1 [-x+1/2, y+1/2, -z+1]	0.90	2.20	151(1)	3.022(4)
N1-H1A...O2 [-x+1/2, y+1/2, -z+1]	0.90	2.14	154(7)	2.982(4)

The cationic layers are stacked in such a way that they form infinite channels along the *c* axis filled by disordered ClO₄⁻ and SCN⁻ anions (Fig. 8).

The electronic spectra of the two compounds are typical of square planar copper(II) complexes.¹¹ So, the diffuse reflectance spectrum of compound **1** which is shown in Fig. 9 exhibits a broad band with a maximum at ~ 15 300 cm⁻¹ (ca. 650 nm).

Fig. 9 – Solid-state electronic spectrum of complex **1**.

The copper(II) supramolecular dimers, in which the mononuclear moieties are connected through hydrogen bonds, are very attractive from a magnetic point of view, since they allow us to investigate the exchange interactions at the supramolecular level (*i.e.*, mediated by hydrogen bonds). The magnetic properties of compound **1** were investigated from room temperature down to 2.0 K. The magnetic data of **1** under the form of $\chi_M T$ versus *T* plot [χ_M is the magnetic susceptibility per two copper(II) ions] are shown in Fig. 10. At room temperature, $\chi_M T$ is equal to 0.80 cm³ mol⁻¹ K, a value which is expected for two magnetically isolated spin doublets. This value remains constant upon cooling down to 70 K, and then decreases sharply at lower temperature to reach 0.006 cm³ mol⁻¹ K at 2 K. A maximum of the magnetic susceptibility occurs at 16 K.

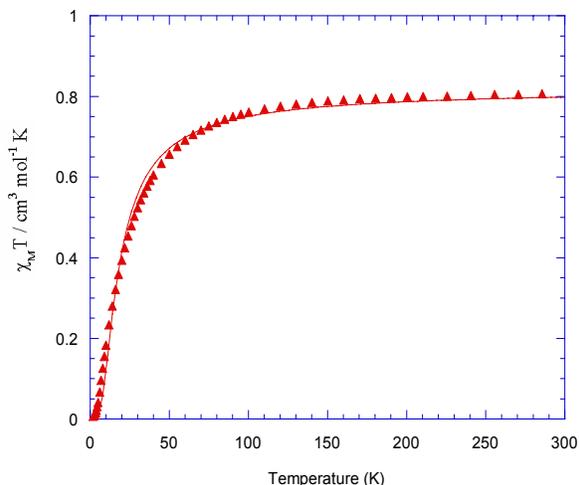


Fig. 10 – $\chi_M T$ vs. T plot for compound **1**: (\blacktriangle) experimental data; (—) best fit curve through eq (1).

In the light of the binuclear structure of complex **1**, we have analyzed its magnetic data by means of a simple Bleaney-Bowers expression [eq. (1)]

$$\chi_M T = [2Ng^2\beta^2/k][3 + \exp(-J/KT)]^{-1} \quad (1)$$

which was derived through the isotropic Hamiltonian $\mathbf{H} = -JS_1 \cdot S_2$. In that expression, J is the exchange coupling parameter and N , g , β and k have their usual meaning. The calculated curve matches very well the magnetic data in the whole temperature range. The magnetic orbital of the copper(II) ion in **1** is of the $d_{x^2-y^2}$ type. The shortest intermolecular copper-copper separations are 4.851(1) [Cu(1)⋯Cu(1a)] and 4.895(1) Å [Cu(2)⋯Cu(2b) atoms]. The exchange interaction then occurs along the Cu(1)-O(1)-H(1)⋯O(2a)-Cu(1a), [(a) = -x+1, -y, -z+1] and Cu(2)-O(3)-H(2)⋯O(4b)-Cu(2b), [(b) = -x+1, -y, -z+2] pathways, which correspond to the intermolecular hydrogen bonds established between one OH group and one alkoxo oxygen atom. Least-squares fit to the data led to the following values: $J = -22.3 \text{ cm}^{-1}$, $g = 2.09$. This J value characterizes the intradimer magnetic coupling mediated by hydrogen bonds. Theoretical calculations, supported by experimental data, for various hydrogen bonded copper(II) dimers, with different bridging geometries, have shown that the values of the J parameters vary between +0.33 and -94 cm^{-1} .¹² Accordingly, the exchange interaction in **1** can be considered as being moderately strong.

EXPERIMENTAL

Synthesis

[Cu₂(Hmea)₂(mea)₂OClO₃][ClO₄] (**1**). This compound was obtained by mixing methanolic solutions (10 mL) of 2-aminoethanol (1.85 mmol) and sodium perchlorate (1.84 mmol) with a methanolic solution (10 mL) of copper(II) acetate (0.62 mmol). The dark blue mixture was stirred on ice and after an hour was filtered. The resulting dark blue solution was allowed to stand for two weeks. Violet crystals separated and were collected and dried in a desiccator over calcium chloride.

[Cu₂(Hmea)₂(mea)₂SCN][ClO₄] (**2**). An ethanolic solution (15 mL) of Cu(ClO₄)₂·6H₂O (0.25 mmol) was reacted with Hmea (0.75 mmol) dissolved in 15 mL ethanol. An ethanolic solution (5 mL) of KSCN (0.25 mmol) was added to the resulting blue solution. X-ray quality blue crystals of **1** were grown from the mother liquor solution after a few days by slow evaporation at room temperature.

Caution! Perchlorate salts are potentially explosive and should be handled only in small quantities.

Physical measurements

The IR spectra (KBr pellets) were recorded in a BIO-RAD FTS 135 spectrophotometer. UV-VIS spectra (diffuse reflectance technique) were recorded with a VSU-2 (Carl Zeiss) spectrophotometer using MgO as a standard. Variable-temperature (2.0–290 K) magnetic susceptibility measurements were carried out with a Quantum Design SQUID magnetometer under an applied magnetic field of 0.1 T. The magnetic data were corrected by the diamagnetism of the constituents atoms and also for the TIP [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per copper(II) ion].

Crystallography

X-Ray diffraction measurements were performed at 100 K in a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo K α radiation. Crystal data, data collection parameters and structure refinement details are given in Table 4.

Table 4

Crystal data and structure refinement parameters for [Cu₂(Hmea)₂(mea)₂OClO₃]ClO₄ (**1**) and [Cu₂(Hmea)₂(mea)₂SCN]ClO₄ (**2**)

Empirical formula	C ₄ H ₁₃ ClCuN ₂ O ₆	C ₉ H ₂₆ ClCu ₂ N ₅ O ₈ S
Weight formula	284.15	526.94
Temperature (K)	293(2)	150(2)
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P2(1)/c</i>	<i>P2(1)2(1)2</i>
Unit cell dimensions		
<i>a</i> (Å)	9.5500(19)	10.9030(3)
<i>b</i> (Å)	14.531(3)	9.1850(4)
<i>c</i> (Å)	14.145(3)	9.4190(4)
β (°)	95.15(3)	
<i>V</i> (Å ³)	1955.0(7)	943.26(6)
<i>Z</i>	8	2
<i>D</i> _{calc} (g·cm ⁻³)	1.931	1.855
Absorption coefficient, μ (mm ⁻¹)	2.515	2.554
<i>F</i> (000)	1160	540
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0850 <i>wR</i> 2 = 0.1926	<i>R</i> 1 = 0.0345 <i>wR</i> 2 = 0.0802
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1346 <i>wR</i> 2 = 0.2095	<i>R</i> 1 = 0.0371 <i>wR</i> 2 = 0.0811
Goodness-of-fit on <i>F</i> ²	1.053	1.098
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	1.944 and -1.308	1.082 and -0.590

Lattice parameters were determined by least-squares from 4,169 reflections. The structure were solved by direct methods and refined by full-matrix least-squares techniques based on *F*². The non-H atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms connected with oxygen atoms have not been found. Calculations were performed using the SHELX-97 crystallographic software package. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. - crystal **1**: 601304; crystal **2**: 601305. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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