



Two novel organic–inorganic hybrid compounds with straight and zigzag chain alignments of Cu(II) centers: Synthesis, crystal structure, spectroscopy, thermal analysis and magnetism



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ABSTRACT

Two hybrid salts, viz. bis(guanidinium) bis(oxalato)cuprate(II) (**1**) and bis(2-aminopyridinium) bis(oxalato)cuprate(II) trihydrate (**2**) have been synthesized and characterized by elemental and thermal analyses, IR spectroscopy, single-crystal X-ray diffraction and SQUID magnetometry. Compounds **1** and **2** crystallize in the monoclinic $P2_1/c$ and triclinic $P\bar{1}$ space groups, respectively. In both structures, the four-coordinated Cu(II) ion in $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ unit weakly interacts with two axial O-atoms of neighboring units to build a prolate CuO_6 octahedron, with regular axial Cu–O bonds of 2.825 Å in **1**, whereas in **2** two different Cu–O bonds (2.814 Å and 2.701 Å) are found. In **1**, stacking of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ units across internal symmetry-related O-atoms results in equidistantly spaced monomers, thus forming straight Cu(II) chains with regular spacing of $\text{Cu}\cdots\text{Cu} = 3.582$ Å. By contrast, in **2**, stacking of the $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ entities occurs via external symmetry-related O-atoms, yielding zigzag Cu(II) chains with shorter *intra*-dimer spacing of $[\text{Cu}\cdots\text{Cu}]_{\text{intra}} = 3.430$ Å and longer *inter*-dimer spacing of $[\text{Cu}\cdots\text{Cu}]_{\text{inter}} = 4.961$ Å. The anhydrous compound **1** is stable up to 250 °C, whereas the hydrated compound **2** shows a significant weight loss of solvent water molecules at about 70 °C, followed by the decomposition of the network. The magnetic measurements in the 2–300 K temperature range revealed weak antiferromagnetic coupling in the two hybrid salts.

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1. Introduction

Recently, organic–inorganic hybrid salts have been introduced as an attractive area of study within the field of crystal engineering [1–3]. The flourishing diversity of structures and dimensionalities observed in these multifunctional materials has aroused a remarkable research interest [4,5]. As a result of structural integration of organic cations and inorganic counterparts, molecular electronic and spintronic [6], peculiar magnetic [7,8], optical [9,10], metallic conductivity [11] and catalytic [12] properties have arisen in this class of chemical hybrid systems. Moreover, these materials may be used as model compounds for ferroelectric and ferroelastic applications [13,14]. Self assembly processes of such materials in

solid state are due to the variety of interactions which include hydrogen bonding network between organic and inorganic components, ionic interactions, π – π and/or van der Waals interactions [15–17].

Over the past years, many salts of organic cations combined to the well-known bis(oxalato)cuprate(II) anion have been intensely studied among other reasons for their fascinating network topologies as well as for gaining a better understanding of the correlations between structural and physical properties [18–20]. In these salts, the steric parameters of the organic cations, the nature of the additional ligand or solvent molecule, and the medium of the synthesis are thought to be the notable factors to affect the obtained frameworks which, indeed, are still difficult to be predicted and controlled. For example, pyridinium cations combined to bis(oxalato)cuprate(II) anions lead to the formation of hydrogen-bonded copper(II) chain structures [19]. Benzylammonium copper(II) oxalate salt results in layers of $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$ ions connected by long axial Cu–O bonds [20].

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With propylenediammonium cations, stacks of bis(oxalato)cuprate(II) anions are obtained [20]. This flexibility of the structural topology in (organic cation)-oxalato)cuprate(II) compounds bears testimony to the renewed interest in their coordination chemistry.

In the present paper, we report on the structural characterization of two novel copper(II) hybrid salts bis(guanidinium) bis(oxalato)cuprate(II), $(\text{CN}_3\text{H}_6)_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$ (**1**), and bis(2-aminopyridinium) bis(oxalato)cuprate(II) trihydrate, $(\text{C}_5\text{H}_7\text{N}_2)_2[\text{Cu}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ (**2**), the structures of which the common anionic bis(oxalato)cuprate(II) entities exhibit different stacking patterns. Low temperature magnetic studies reveal weak antiferromagnetic behavior in both compounds.

2. Experimental

2.1. Materials and physical measurements

Oxalic acid dihydrate, chromium(III) chloride hexahydrate, 2-aminopyridine and copper(II) oxalate hemihydrate were purchased from Riedel de Haën. The guanidinium carbonate salt was obtained from Aldrich and the starting compound, $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, was prepared following the literature procedure [21]. All the chemicals were used without further purification and the chemical reactions were carried out in distilled water as the solvent. Elemental analysis (C, H, N) was performed on a Vario EL (Heraeus) CHNS analyzer. The infrared spectra were recorded on a Perkin–Elmer (System 2000) FT-IR spectrometer with a pressed KBr pellet in the scan range $4000\text{--}400\text{ cm}^{-1}$ and the UV–Vis spectra on a Perkin–Elmer Lambda 900 spectrophotometer, in water solution, in the range $200\text{--}800\text{ nm}$ ($c = 5.571 \times 10^{-5}\text{ mol/L}$). Thermal analyses (TGA and TDA) were performed with a Mettler Toledo TGA/SDTA 851 thermal analyzer. The powdered sample (*ca.* 15 mg) was heated from 25 to $600\text{ }^\circ\text{C}$ with a rate of $10\text{ }^\circ\text{C}/\text{min}$ in dry nitrogen gas flowing at 60 mL/min. Magnetic susceptibility data for the polycrystalline complexes **1** and **2** were recorded using a Quantum Design MPMS-5XL SQUID magnetometer in the temperature range $2\text{--}300\text{ K}$ at an applied magnetic field of 0.1 T. The diamagnetic corrections of the constituent atoms were estimated from Pascal's constants [22]. The effective magnetic moment was calculated as $\mu_{\text{eff}}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$.

2.2. Syntheses

2.2.1. Synthesis of $(\text{CN}_3\text{H}_6)_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$ (**1**)

An aqueous solution (20 mL) of guanidinium carbonate (180 mg, 1 mmol) was added dropwise to a blue solution of $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ (350 mg, 1 mmol) in 30 mL of warm water. The mixture was stirred at $50\text{ }^\circ\text{C}$ for 1 h. After cooling to room temperature, the resulting solution was filtered, and the filtrate was allowed to stand undisturbed at room temperature for about one week. Blue-greenish single crystals were isolated by filtration and dried in air. Yield: 80%. *Anal. Calc.* for $\text{C}_6\text{H}_{12}\text{CuN}_6\text{O}_8$ (359.76): C, 20.03; H, 3.36, N, 23.36. Found: C, 20.02; H, 3.33, N, 23.56%. IR (cm^{-1}): 3470m, 1710m, 1660s, 1610m, 1410m, 1280m, 800w, 553w.

2.2.2. Synthesis of $(\text{C}_5\text{H}_7\text{N}_2)_2[\text{Cu}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ (**2**)

$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (126 mg, 1 mmol) and 2-aminopyridine (188 mg, 2 mmol) were dissolved in warm water (30 mL), giving a yellowish solution. $\text{CuC}_2\text{O}_4 \cdot 1/2\text{H}_2\text{O}$ (72 mg, 0.5 mmol) was added in successive small portions to the above solution and the mixture stirred at $60\text{ }^\circ\text{C}$ for 1 h and then cooled to room temperature under ambient conditions. The resulting green solution was

filtered and left to stand in the hood at room temperature. After two days, elongated crystals were isolated by filtration and dried in air. Yield: 72%. *Anal. Calc.* for $\text{C}_{14}\text{H}_{14}\text{CuN}_4\text{O}_8$ (429.88) which is the non-hydrated form of $\text{C}_{14}\text{H}_{20}\text{CuN}_4\text{O}_{11}$ (483.88): C, 39.08; H, 3.26, N, 13.03. Found: C, 39.16; H, 3.24, N, 13.05%. IR (cm^{-1}): 3310m, 3150m, 1710s, 1670s, 1630s, 1480w, 1400m, 1270m, 1000w, 802w, 763w, 552w.

2.3. X-ray crystallography

Appropriate single crystals of **1** and **2** were mounted in random orientation on a glass fiber. Intensity data were collected at 293 K on a Bruker APEX CCD area-detector diffractometer with graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The X-ray intensities were corrected for absorption using a semi-empirical procedure [23]. The structures were solved by direct methods with SHELXS-97 [24] and refined by full-matrix least squares method based on F^2 with SHELXL-97 [24]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were added in idealized geometrical positions for the organic cations. The positions of hydrogen atoms from the water molecules were assigned from the electronic density map generated by Fourier difference and they were refined freely. The ORTEP-3 program [25] was used within the winGX software package [26] to deal with the processed crystallographic data and artwork representations. Crystal data and structure refinement parameters for **1** and **2** are given in Table 1, selected bond lengths and bond angles in Table 2.

Table 1
Crystal data and structure refinement for **1** and **2**.

Compound	1	2
Empirical formula	$\text{C}_6\text{H}_{12}\text{CuN}_6\text{O}_8$	$\text{C}_{14}\text{H}_{20}\text{CuN}_4\text{O}_{11}$
Formula weight	359.76	483.88
<i>T</i> (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
<i>Unit cell parameters</i>		
<i>a</i> (Å)	3.5821(4)	7.7104(17)
<i>b</i> (Å)	15.7044(17)	9.159(2)
<i>c</i> (Å)	11.2936(12)	14.853(3)
α (°)	90	72.902(3)
β (°)	96.968(2)	88.896(3)
γ (°)	90	77.962(3)
<i>V</i> (Å ³)	630.63(12)	979.5(4)
<i>Z</i>	2	2
<i>D</i> _{calc} (g/cm ³)	1.895	1.641
μ (mm ⁻¹)	1.787	1.182
<i>F</i> (000)	366	498
Crystal size (mm)	0.18 x 0.03 x 0.01	0.18 x 0.03 x 0.01
θ range for data collection (°)	5.19 – 36.15	4.68 – 33.02
Index ranges	$-5 < h < 5$, $-25 < k < 23$, $-18 < l < 12$	$-11 < h < 9$, $-12 < k < 14$, $-22 < l < 22$
Total reflections	6805	9477
Unique reflections (<i>R</i> _{int})	2765 (0.0257)	6919 (0.0419)
Max. and min. transmission	0.988 and 0.813	0.988 and 0.813
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	1987/0/121	3456/9/348
Goodness-of-fit (GOF) on F^2	1.057	0.990
<i>R</i> factor [$I > 2\sigma(I)$]	$R_1 = 0.0397$, $wR_2 = 0.0944$	$R_1 = 0.0686$, $wR_2 = 0.1201$
<i>R</i> factor (all data)	$R_1 = 0.0634$, $wR_2 = 0.1122$	$R_1 = 0.1515$, $wR_2 = 0.1569$
Max and min residual electron density (e/Å ³)	0.521 and -0.365	2.679 and -1.947

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