Hydrothermal Synthesis and Structure of Two 1-D Organic Hybrid Metal Sulfates

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Two new complex copper(II) sulfates [Cu(1,10-phen)(H_2O)$_2$]SO_4 (**1**, 1,10-phen = 1,10-phenanthroline) and [Cu(2,2′-bipy)(H_2O)$_2$]SO_4 (**2**, 2,2′-bipy = 2,2′-bipyridine) have been hydrothermally synthesized and characterized by IR spectroscopy, elemental analysis, thermogravimetric analysis, and X-ray crystallography. **1** and **2** consist of complex cations [Cu(1,10-phen/2,2′-bipy)(H_2O)$_2$]$^{2+}$ and $SO_4{}^{2-}$ anions, which are interconnected *via* weak Cu$\cdots$O interactions to form rare examples of 1-D metal sulfates.

Key words: Metal Sulfates, Crystal Structure, Hydrothermal Synthesis, Complex Cations

Introduction

Organically templated inorganic materials with microporous structures are of increasing interest, because of their potential applications in the areas of catalysis, ion exchange, intercalation chemistry, photochemistry, and material chemistry [1]. The inorganic skeleton of these materials is generally built up from the linkage of metal cations and oxoanions. The $SO_4{}^{2-}$ ion is a suitable oxoanion, because it displays tetrahedral geometry, as Al and Si do with oxygen in molecular sieve oxides [2], suggesting that a new family of materials with structures resembling those of the zeolites could exist. So far, a large number of metal sulfates have been prepared with organic amines as templating agents under hydrothermal conditions, as exemplified by [H_2en][$La_2(H_2O)_4(SO_4)_4$]·2H_2O (en = ethylenediamine) [3], [H_2en]$_2$[$Ln_2(H_2O)_2(SO_4)_5$] (*Ln* = La, Pr, Nd) [4], [H_2en]$_2${$La_2M(SO_4)_6(H_2O)_2$} (*M* = Co, Ni) [5], [$C_4N_2H_{12}$][$Ni_3F_2(SO_4)_3(H_2O)_2$] ($C_4N_2H_{12}$ = piperazine) [6], [$C_4N_2H_{12}$][$Ni_2F_4(SO_4)H_2O$] [6], and [$N_2C_4H_{14}$][$UO_2(H_2O)(SO_4)_2$] ($N_2C_4H_{14}$ = 1,4-diaminobutane) [7], whose cations are protonated organic amines, but sulfates combined with metal complex cations as counterions are still a less explored area [8]. In this work, we report two 1-D metal sulfates, [Cu(1,10-phen)(H_2O)$_2$]SO_4 (**1**) and [Cu(2,2′-bipy)(H_2O)$_2$]SO_4 (**2**), which are constructed from $SO_4{}^{2-}$ anions and [Cu(1,10-phen/2,2′-bipy)(H_2O)$_2$]$^{2+}$ complex cations.

Results and Discussion

Blue block-shaped crystals of **1** and **2** were obtained by hydrothermal reaction of Cu(CH_3COO)$_2$, H_3BO_3, and 1,10-phen (or 2,2′-bipy) in aqueous H_2SO_4 at 160 °C. The original aim of the syntheses was the linkage of [B_xO_y]$^{n-}$ polyhedra and [SO_4]$^{2-}$ tetrahedra, but all attempts failed. However, H_3BO_3 was found to enhance the crystal growth of **1** and **2**. A separate set of experiments was conducted in the absence of H_3BO_3, but only grey amorphous products were obtained. Both **1** and **2** crystallize in the monoclinic space group $C2/c$ and display similar structures. Therefore, only **1** is discussed here in detail. Complex **1** consists of complex cations [Cu(1,10-phen)(H_2O)$_2$]$^{2+}$ and $SO_4{}^{2-}$ anions (Fig. 1). The Cu^{2+} ion

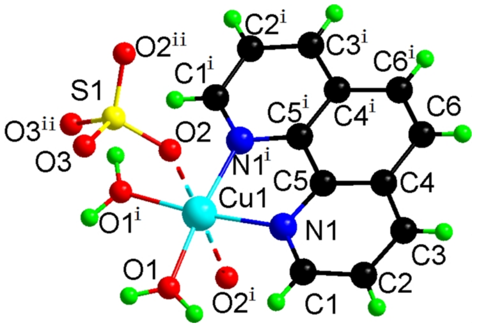


Fig. 1 (color online). The structure of **1** with crystallographic atom labeling adopted (symmetry operations: ^{i} $-x$, y, $1/2-z$; ^{ii} $-x$, y, $3/2-z$).

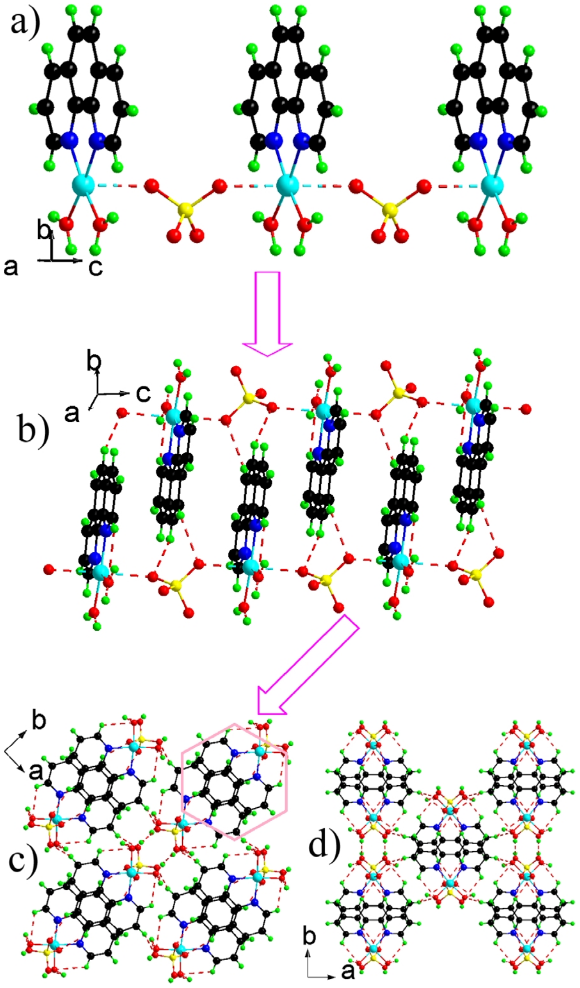
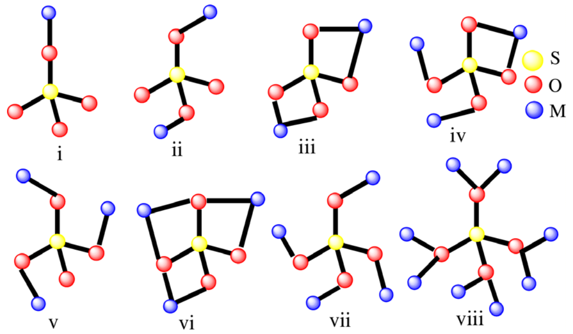


Fig. 2 (color online). a) $\{[Cu(1,10\text{-}phen)(H_2O)_2]SO_4\}_n$ chain in **1**; b) part of the crystal structure of **1**, showing the formation of a double chain constructed from C–H···O hydrogen bonds; 3-D hydrogen-bonded networks in the crystal structures of **1** (c) and **2** (d).



Scheme 1 (color online). Coordination modes of the $SO_4{}^{2-}$ anions.

is chelated by one 1,10-phen ligand and coordinated by two water molecules to form a distorted square-planar geometry with a *cis*-configuration. The Cu–N and Cu–O bond lengths are 2.008(3) and 1.967(3) Å, respectively. Interestingly, there are also weak Cu···O interactions (2.462 Å for **1** and 2.458 Å for **2**) between the $[Cu(1,10\text{-}phen/2,2'\text{-}bipy)(H_2O)_2]^{2+}$ and $SO_4{}^{2-}$ ions, whose distances are much shorter than the sum of the van der Waals radii (3.26 Å) [9]. As a result, the Cu atom completes its coordination sphere *via* weak bonds to O atoms forming a slightly distorted octahedron (CuN_2O_4). Adjacent $[Cu(1,10\text{-}phen)(H_2O)_2]^{2+}$ cations are linked by bridging $SO_4{}^{2-}$ ions to form chains along the [101] direction (Fig. 2a). Two chains inversely are connected *via* C–H···O hydrogen bonds forming pseudo double chains (Fig. 2b), which further interact *via* other C–H···O hydrogen bonds resulting in a three-dimensional network (Fig. 2c). The C···O distances vary from 3.058(5) to 3.354(6) Å, and the C–H···O angles vary from 114 to 148°. Similar intermolecular hydrogen bonding is observed in **2** (Fig. 2d).

The $SO_4{}^{2-}$ anion possesses four O atoms which may coordinate to metal atoms. They display a variety of coodination modes, as is shown in Scheme 1. The modes iii – viii are very common [3 – 7, 10], while i and ii are relatively rare, the known examples include $[Fe(tpp)(HOSO_3)]\cdot 0.5C_6H_6$ (mode i, tpp = tetraphenylporphinato) [11], $[Fe(bpp)_2(SO_4)]$ [mode ii, bpp = bis(4-pyridyl)propane] [8a], $(enH_2)_2[Ln_2(H_2O)_2(SO_4)_5]$ (mode ii, *Ln* = La, Pr, Nd) [4]. $SO_4{}^{2-}$ anions adopting mode ii with weak Cu···O interactions have been found in **1** and **2** for the first time.

As shown in Fig. 3, the IR spectra of **1** and **2** show bands centered around 1110 cm^{-1} and a band in

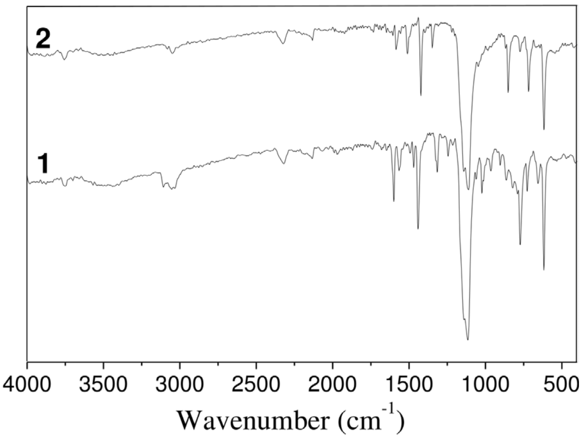


Fig. 3. IR spectra of **1** and **2**.

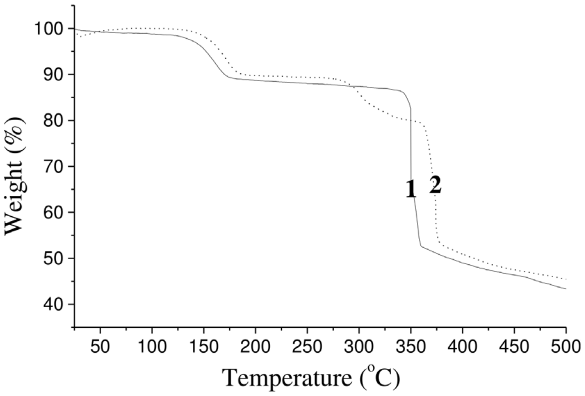


Fig. 4. TG curves of **1** and **2**.

the 610 cm^{-1} region due to the $SO_4{}^{2-}$ ion. Considering the splittings of these bands, it appears that the point group symmetry of the $SO_4{}^{2-}$ ion is much lower than T_d, probably C_{2v}. The bands at 3107 – 3052 cm^{-1} can be assigned to the stretching bands of the -CH groups, the broad band at 3470 cm^{-1} can be attributed to O-H stretching of H_2O molecules.

The thermal behavior of **1** and **2** was measured with TG methods under an N_2 stream (Fig. 4). A weight loss of 10.46 % for **1** from 25 to 187 °C is in agreement with the calculated amount of water (calcd. 9.58 %). A further 47.21 % weight loss occurs between 330 and 475 °C, corresponding to the loss of the 1,10-phen ligand (calcd. 47.95 %). For **2**, the first weight loss of 9.89 % in the range of 25 – 190 °C also corresponds to the loss of water (calcd. 10.23 %). Two further steps of weight loss of a total of 43.93 % are attributed to the removal of the 2,2′-bipy ligand (calcd. 44.39 %).

Experimental Section

General: All starting materials were purchased in analytically pure grade and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer from dry KBr pellets. Elemental analyses were carried out on an EA-1110 elemental analyzer. Thermogravimetric analyses (TGA) were performed using a Mettler TGA/SDTA851 thermal analyzer under N_2 atmosphere with a heating rate of 10 °C min^{-1} in the temperature region of 25 – 500 °C.

Synthesis of [Cu(1,10-phen)(H₂O)₂]SO₄ (1)

A mixture of $Cu(CH_3COO)_2$ (0.1080 g), H_3BO_3 (0.1852 g), 1,10-phen (0.0592 g), and aqueous H_2SO_4 (1 mL) was stirred for 1 h, sealed in a Teflon-lined steel autoclave (pH = 5 – 6), kept at 160 °C for 10 d, and then slowly cooled to r. t. Blue crystals were obtained (yield: 76 % based on Cu). – Anal. for **1**: calcd. C 38.35, H 3.22, N 7.45; found C 38.27, H 3.30, N 7.38. – IR (KBr disk, cm^{-1}): ν = 3473(w), 3107(w), 3040(w), 1608(m), 1565(m), 1476(w), 1437(m), 1321(m), 1243(w), 1115(s), 1009(m), 959(w), 854(w), 771(s), 715(m), 654(m), 615(s).

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

	1	**2**
Formula	$C_{12}H_{12}CuN_2O_6S$	$C_{10}H_{12}CuN_2O_6S$
M_r	375.86	351.84
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a, Å	14.886(4)	15.129(3)
b, Å	13.839(3)	12.462(3)
c, Å	7.0144(14)	7.0062(14)
β, deg	108.50(3)	106.00(3)
V, Å^3	1370.3(6)	1269.8(5)
Z	4	4
T, K	296(2)	296(2)
Calcd. density, g cm^{-3}	1.82	1.84
Abs. coeff., mm^{-1}	1.8	1.9
$F(000)$, e	764	716
2θ (max), deg	55.24	50.20
Reflns. collected / unique	4236 / 1556	3359 / 1133
No. of ref. param.	109	100
$R1$ [$I \geq 2\sigma(I)$]	0.0444	0.0232
$wR2$ (all data)	0.0961	0.0662
GOF (F^2)	1.007	1.102
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.441 / −0.516	0.401 / −0.317

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2**[a].

		1	
Cu1–O1	1.967(3)	Cu1–N1	2.008(3)
O1$^{\#1}$–Cu1–O1	94.41(16)	O1$^{\#1}$–Cu1–N1	173.65(11)
O1–Cu1–N1	91.80(11)	N1–Cu1–N1$^{\#1}$	82.03(15)
		2	
Cu1–O1	1.9736(14)	Cu1–N1	1.9938(16)
O1$^{\#2}$–Cu1–O1	93.14 (8)	O1–Cu1–N1	93.21(8)
O1–Cu1–N1$^{\#2}$	172.15(6)	N1–Cu1–N1$^{\#2}$	80.84(9)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, y, 1/2-z$; $^{\#2}$ $-x, y, -z-3/2$.

Synthesis of [Cu(2,2′-bipy)(H₂O)₂]SO₄ (2)

Blue block-shaped crystals of $[Cu(1,2'\text{-bipy})(H_2O)_2]SO_4$ were prepared by a similar method as used in the synthesis of the crystals of **1** except that, instead of 1,10-phen, 2,2′-bipy was used (yield: 72 % based on Cu). – Anal. for **2**: calcd. C 34.14, H 3.44, N 7.96; found C 34.07, H 3.51, N 7.89. – IR (KBr disk, cm^{-1}): ν = 3475(w), 3052(w), 1576(w), 1503(m), 1420(s), 1348(m), 1109(vs), 849(m), 771(w), 721(s), 610(s).

X-Ray structure determinations

Data collections were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromatized MoK_α

radiation (λ = 0.71073 Å) at 296(2) K with a maximum 2θ value of 55.24°. The intensities were corrected for Lorentz and polarization effects. The structures were solved with Direct Methods using SHELXS-97 [12], and the refinement was performed against F^2 using SHELXL-97 [13]. All non-hydrogen atoms were refined anisotropically. H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal data collection and refinement results can be found in Table 1. Selected bond lengths and angles for compounds **1** and **2** are listed in Table 2.

CCDC 846009 (**1**) and 846010 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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