Crystal structure, phase transition and thermal decomposition of a copper (II) sulfate dihydrate containing a chiral organic ammonium cation

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ABSTRACT

The directed synthesis of a new organically templated copper sulfate has been achieved through the use of chiral organic amine. Reaction containing S-2-methylpiperazine, $CuSO_4 \cdot 5H_2O$, H_2SO_4 and H_2O were subjected to the slow evaporation conditions, resulting in the growth of single crystals of $[(S)-C_5H_{14}N_2][Cu(SO_4)_2(H_2O)_4] \cdot (H_2O)_2$. At room temperature, it crystallises in the non-centrosymmetric space group $P2_1$, $Z = 2$, $a = 7.5583(5)$, $b = 10.1721(6)$, $c = 10.7974(7)$ Å, $\beta = 94.425(4)°$ and $V = 827.67(9)$ Å³. The structure consists of trimeric units $[Cu(SO_4)_2(H_2O)_4]^{2-}$, $[(S)-C_5H_{14}N_2]^{2+}$ cations and free water molecules, donating hydrogen bonds that stabilize the three-dimensional structure and filling space. The title compound undergoes a reversible phase transition of first-order, which is detected by differential-scanning calorimetry at 347.2 K in the heating cycle and at 318.9 K in the cooling cycle. The evolution of the dielectric constant as a function of frequency and temperature revealed this transition to be ferro-paraelectric. Thermogravimetric analyses indicate that its decomposition proceeds through three stages giving rise to the copper oxide.

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1. Introduction

The open-framework compounds constitute an important class of materials that has attracted much attention as evidenced by the vast number of research papers published in the last few years [1–4]. Considerable effort has been expended during the study of these materials owing to the great structural diversity [5–9] and desirable physical properties such as catalysis, sensing technology, optoelectronics, and nonlinear optical activity, etc. [10–12]. The presence of these technologically advanced is solely dependent upon symmetry [13]. A large number of these materials are synthesized in the presence of organic amine, which is considered to be a structure-directing agent [14], especially some double sulfates combining transition metal and chiral organic amines are also prepared [15]. Using this literature; we challenge to synthesis new non-centrosymmetric complex architectures, defining a new direction in the chemistry of hybrid materials. In this paper, we report the effects from inclusion of chiral organic amines into systems containing a Jahn–Teller cations and comment upon this technique as an approach toward the synthesis of non-centrosymmetric materials. The structure, the differential-scanning calorimetry (DSC), dielectric measurements and the thermal decomposition of $[(S)-C_5H_{14}N_2][Cu(SO_4)_2(H_2O)_4] \cdot (H_2O)_2$ are discussed.

2. Experimental

2.1. Synthesis

The title compound was synthesized by slow evaporation at room temperature of an aqueous solution containing $CuSO_4 \cdot 5H_2O/[(S)-C_5H_{12}N_2]/H_2SO_4$ in the 1/3/1 molar ratio. The transparent blue single crystals were crystallized and the product was filtered off and washed with a small amount of distilled water.

2.2. Data collection, structure solution and refinement

Suitable single crystals of the title compound were glued to a glass fibre mounted on a four-circle Nonius Kappa CCD area-detector diffractometer. Intensity data sets were collected using Mo Kα radiation through the program COLLECT [16]. Corrections for Lorentz-polarisation effect, peak integration and background determination were carried out with the program DENZO [17]. Frame scaling and unit cell parameters refinement were performed with the program SCALEPACK [17]. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS [18] program. Pertinent details of the crystal structure of $[(S)-C_5H_{14}N_2][Cu(SO_4)_2(H_2O)_4] \cdot (H_2O)_2$ are listed in Table 1. The crystal structure has been solved in the monoclinic symmetry, space group $P2_1$, according to the automated search for space group available in WINGX [19]. Copper and sulfur atoms were located using

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Table 1
Crystallographic data for [(S)-C5H14N2][Cu(SO4)2(H2O)4]·(H2O)2.

Empirical formula	$CuS_2O_{14} N_2C_5H_{26}$
Formula weight	465.94
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	7.5583(5)
b (Å)	10.1721(6)
c (Å)	10.7974(7)
β(°)	94.425(4)
V (Å^3)	827.67(9)
Z	2
ρ_{calc}	1.870
Crystal size (mm^3)	0.09 × 0.03 × 0.02
Habit-colour	blue
λ (Mo Kα) (Å)	0.71073
Extinction coefficient	0.031(2)
μ (mm^{-1})	1.646
Θ range (°)	1.89–43.07
Index ranges	$-10 \leqslant h \leqslant 14$
	$-19 \leqslant k \leqslant 19$
	$-13 \leqslant l \leqslant 20$
Unique data	10 872
Observed data [$I > 2\sigma(I)$]	6454
$F(0\,0\,0)$	486
Refinement method	full matrix least-squares on $|F^2|$
R_1	0.0489
WR_2	0.1326
Goodness-of-fit (GOF)	0.970
No. parameters	230
Transmission factors	0.5816 and 0.7743
Largest difference map peak and hole (eÅ^{-3})	−0.701 and 0.527

direct methods with the program SHELXS-97 [20]. The oxygen atoms and the organic moieties were found from successive difference Fourier calculations using SHELXL-97 [21]. All the hydrogen atoms of water molecules were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. H–O and H–H distances, within water molecules, were restrained to 0.85(1) and 1.39(1) Å, respectively, so that the H–O–H angles fitted the theoretical value, 105.4°. All the hydrogen positions of the diprotonated amine were placed geometrically and held in the riding mode (the C–H and N–H bonds were fixed at 0.97 and 0.89 Å, respectively). Bond distances and angles calcu-

Table 2
Selected bond distances (Å) and angles (°).

Octahedron around Cu		Tetrahedron around S1	
Cu–O1	2.356(2)	S1–O1	1.475(3)
Cu–O5	2.380(2)	S1–O2	1.483(3)
Cu–OW3	1.980(3)	S1–O3	1.456(3)
Cu–OW4	1.977(3)	S1–O4	1.477(3)
Cu–OW5	2.013(3)	O3–S1–O1	110.9(2)
Cu–OW6	1.949(3)	O3–S1–O4	110.76(17)
OW6–Cu–OW4	179.11(18)	O1–S1–O4	107.64(17)
OW6–Cu–OW3	91.24(15)	O3–S1–O2	110.06(19)
OW4–Cu–OW3	89.65(12)	O1–S1–O2	109.51(15)
OW6–Cu–OW5	89.25(11)	O4–S1–O2	107.9(2)
OW4–Cu–OW5	89.86(15)	Tetrahedron around S2	
OW3–Cu–OW5	179.34(17)	S2–O5	1.482(3)
OW6–Cu–O1	89.72(10)	S2–O6	1.477(3)
OW4–Cu–O1	90.31(10)	S2–O7	1.462(3)
OW3–Cu–O1	89.99(11)	S2–O8	1.476(3)
OW5–Cu–O1	90.45(11)	O7–S2–O8	110.25(18)
OW6–Cu–O5	90.24(10)	O7–S2–O6	109.83(17)
OW4–Cu–O5	89.73(10)	O8–S2–O6	109.0(2)
OW3–Cu–O5	90.80(11)	O7–S2–O5	109.9(2)
OW5–Cu–O5	88.75(11)	O8–S2–O5	109.54(14)
O1–Cu–O5	179.20(14)	O6–S2–O5	108.31(16)

Table 3
Hydrogen bonding geometry (Å, °).

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠D–H···A (°)
N1–H1A···O1	0.90	1.95	2.834(4)	167.1
N1–H1B···O2^I	0.90	1.86	2.742(6)	166.1
N2–H2A···O5^{II}	0.90	1.96	2.855(4)	170.2
N2–H2B···O8^{III}	0.90	1.93	2.808(5)	164.1
OW1–HW1···O3^{IV}	0.94	2.11	2.886(5)	138.7
OW2–HW3···O6	0.93	1.91	2.823(5)	165.0
OW2–HW4···O7^V	0.94	1.92	2.854(5)	171.9
OW6–HW12···O4^{VI}	0.97	1.77	2.643(4)	147.0
OW5–HW10···OW1	0.91	1.86	2.756(4)	169.2
OW4–HW7···O6^{VII}	0.91	1.77	2.649(4)	160.1
OW3–HW5···OW2	0.94	1.86	2.703(5)	147.3
OW6–HW11···O8	0.96	1.87	2.651(4)	136.8
OW3–HW6···O7^{VIII}	0.97	1.96	2.758(4)	137.7
OW4–HW8···O2	0.91	1.79	2.688(4)	166.3
OW5–HW9···O3^{IX}	0.90	1.83	2.725(4)	173.6

Symmetry codes: ^{I} $-x, y + 1/2, -z$; ^{II} $x, y, z - 1$; ^{III} $-x + 1, y - 1/2, -z$; ^{IV} $-x, y-1/2, -z$; ^{V} $-x + 1, y + 1/2, -z + 1$; ^{VI} $-x, y + 1/2, -z$; ^{VII} $-x + 1, y - 1/2, -z + 1$; ^{VIII} $x - 1, y, z$; ^{IX} $x + 1, y, z$.

lated from the final atomic coordinates, as well as probable hydrogen bonds, are given in Tables 2 and 3, respectively.

2.3. Infrared spectroscopy

Infrared measurements were obtained using a Perkin–Elmer FT-IR spectrum. Samples were diluted with spectroscopic grade KBr and pressed into a pellet. A scan was run over the range of 400–4000 cm^{-1}.

2.4. Thermal behaviour

The differential-scanning calorimetry at high temperature was performed with a SETARAM DSC131 instrument for temperatures ranging from 20 to 200 °C at a rate of 5 °C min^{-1}, in air atmosphere. A polycrystalline sample of 7 mg was placed in a hermetic aluminium cell. The measurements of the complex dielectric permittivity, ε^*, were performed with an impedance analyzer Hewlett–Packard 4192 A LF in the frequency range from 1 KHz to 100 KHz. Crystals of the title compound were crushed and pressed to dense and translucent pellets (12 mm in diameter; 0.8 mm in thickness) at a pressure of 200 MPa. Both planar faces of these pellets were coated with silver paint and the pellets were then sandwiched between metal electrodes, which were also coated with silver paint. The measurements were carried out in a vacuum between 240 and 400 K. A thermogravimetric (TG) measurement was performed with a Rigaku Thermoflex instrument under flowing air, with a heating rate of 5 °C min^{-1} from ambient temperature to 900 °C.

3. Results and discussion

3.1. Crystal structure of [(S)-C5H14N2][Cu(SO4)2(H2O)4]·(H2O)2

The crystal structure of [(S)-C5H14N2][Cu(SO4)2(H2O)4]·(H2O)2 belongs to the non-centrosymmetric space group $P2_1$. It consists of isolated tetraaquabis(sulfato-O) copper anions [Cu(SO4)2-(H2O)4]$^{2-}$, S-2-methylpiperazinediium cations [(S)-C5H14N2]$^{2+}$ and free water molecules linked together by two types of hydrogen bonds, O–H···O and N–H···O. This type of structure has already been observed in other organically templated metal sulfate [22]. The Cu(II) central atoms, lying in a general position, are coordinated by two oxygen atom of sulfate groups at a distances (Cu–O1 = 2.356(2) and Cu–O5 = 2.380(2) Å) and four corners of water molecules (Cu–OW vary from 1.949(3) to 2.013(3) Å) forming a distorted octahedra geometry. The Cu ions in this compound display the so-called (4 + 2) type of coordination that has often been