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Synthesis, crystal structure, and thermal property of piperazine-templated copper(II) sulfate, $\{H_2\overline{NCH_2CH_2NH_2CH_2CH_2}\}\{Cu(H_2O)_6\}(SO_4)_2$

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Abstract : The title compound, $\{H_2\overline{NCH_2CH_2NH_2CH_2CH_2}\}\{Cu(H_2O)_6\}(SO_4)_2$, **I**, has been synthesized under solvo/hydrothermal conditions and their crystal structure analyzed by X-ray single crystallography. Compound **I** crystallizes in the monoclinic system, $P2_1/n$ space group with a = 6.852(1), b = 10.160(2), c = 11.893(1) Å, β = 92.928(8)°, V = 826.9(2)Å^3, Z = 2, D_x = 1.815 g/cm^3, R_1 = 0.031 and ωR_2 = 0.084. The crystal structure of the piperazine templated Cu(II)-sulfate demonstrate zero-dimensional compound constituted by doubly protonated piperazine cations, hexahydrated copper cations and sulfate anions. The central Cu atom has a elongated octahedral coordination geometry. The crystal structure is stabilized by three-dimensional networks of the intermolecular O_{water}-H···$O_{sulfate}$ and N_{pip}-H···$O_{sulfate}$ hydrogen bonds between the water molecules and sulfate anions and protonated piperazine cations. Based on the results of thermal analysis, the thermal decomposition reaction of compound **I** was analyzed to have three distinctive stages.

Key words : Copper sulfate, piperazine, solvo/hydrothermal synthesis, crystal structure, thermal property

1. Introduction

Inorganic open-framework materials[1] such as metal silicates,[2] phosphates,[3] carboxylates,[4] fluorides,[5] germanates,[6] arsenates,[7] and selenites[8] have been widely investigated during the past two decades. Among these materials, aluminosilicate zeolites and metal phosphates templated by organic ions have been of the great interest in both academic research and industrial applications owing to great structural diversity and desirable physical properties as catalysis, adsorption and ion exchange.[1-3]

There has been employed sulfate tetrahedron as a strategy for the design of new inorganic open-framework architectures.[9-12] The preparation of organically templated metal sulfates is of interest for several reasons.[13] First, the $[SO_4]^{2-}$ tetrahedron is approximately the same size (S-O 1.49Å, P-O 1.53Å) and shape as $[PO_4]^{3-}$ tetrahedron. However, the difference in charge can result in the formation of new structural assemblies. Second, majority of reports detailing the preparation of templated metal sulfates have appeared in the past five years and this area is under-explored in comparison with extensively studied phosphate chemistry. Third, great structural diversity is exhibited in the small set of reported metal sulfates, because of sulfate ion can act as a monodentate, bidentate (chelating) or bridging ligand.

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Recently, we undertook a comparative study of piperazine templated Co(II)-, Ni(II)- and Cu(II)-sulfates with the original goal of producing structural analogue of the reported metal phosphates. In this paper, we report the synthesis, crystal structure and thermal property of the copper(II) sulfate compound, $\{H_2\overline{NCH_2CH_2NH_2CH_2CH_2}\}\{Cu(H_2O)_6\}(SO_4)_2$, **I**, which was templated by piperazine.

2. Experimental

2.1. Synthesis and analysis

The title compound was synthesized by employing solvo/hydrothermal methods. In a typical synthesis, 0.20 g of $Cu(OOCCH_3)_2 \cdot H_2O$ was dissolved in a 4 mL of H_2O under constant stirring. To this solution 0.1 mL of H_2SO_4 and 3 mL of ethylene glycol (EG) were added. Finally, 0.78 g of piperazine (PIP) was added to the mixture, and the mixture was stirred for 30 min to obtain a homogeneous gel. The final mixture with the molar composition of $Cu(OOCCH_3)_2 \cdot H_2O/H_2SO_4/PIP/EG/H_2O$ (1 : 2 : 4 : 50 : 200) was transferred into a 23-mL Teflon-lined stainless-steel autoclave and heated at 180°C for 4 days. The resulting product was a pale green block-shaped crystals mixed with some amorphous materials. The single crystal was picked out and submitted to composition analysis and structure determination.

IR spectrum of the crystal was recorded with a BioRad Digilab FTS-165 infrared spectrophotometer using a KBr wafer. Piperazine, sulfate ion and water molecule were assigned by the relevant IR absorption bands, respectively.[14] The EDS spectrum obtained on a Philips XL-30S FEG scanning electron microscope/EDAX Phoenix energy-dispersive X-ray spectrometer showed the presence of C, N, O, S and Cu. The contents of the carbon, hydrogen, nitrogen, sulfur and oxygen were analyzed by a CE EA-1110 elemental analyzer. The content of the copper was analyzed by a Jobin-Yvon Ultima-C inductively coupled plasma-atomic emission spectrometer. The composition of the crystal was deduced from the elemental analyses; the formula of $\{H_2\overline{NCH_2CH_2NH_2CH_2CH_2}\}\{Cu(H_2O)_6\}(SO_4)_2$, **I**, is consistent with the results of X-ray single crystallography. *Anal. Found*: C 10.39, H 5.43, N 6.46, S 14.41, Cu 14.0%. *Calc. for* $C_4H_{24}N_2O_{14}S_2Cu$: C 10.63, H 5.35, N 6.20, O 49.57, S 14.19, Cu 14.06%. The thermal decomposition of the compound **I** was investigated on a TA Instruments 2960 SDT thermogravimetric analyzer/differential thermal analyzer. Sample was loaded into an alumina crucible and heated from ambient temperature to 800°C at 10°C/min under flowing nitrogen.

2.2. X-ray crystallography

A pale green crystal of dimensions 0.17×0.31×0.38 mm for the title compound was coated with epoxy glue in order to prevent spontaneous liberation of water molecules from the specimen under ambient conditions. The epoxy-coated crystal was mounted on a Siemens P4 four-circle X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The intensity data were collected in the θ-2θ scan mode with operating 50 kV, 30 mA at a temperature 295± 2 K. The cell parameters and orientation matrix were determined from the least-squares fit of 39 reflections in the 2θ range of 4.86~12.49°. Three standard reflections were measured every 97 reflections: no remarkable decays were observed throughout data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-

Table 1. Crystallographic and experimental data for compound **I**

Formula	$C_4H_{24}N_2O_{14}S_2Cu$
Formula weight	451.91
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	6.852(1)
b (Å)	10.160(2)
c (Å)	11.893(1)
β (°)	92.928(8)
V (Å^3)	826.9(2)
Z	2
Dc (g/cm^3)	1.815
μ(Mo-Ka) (mm^{-1})	1.645
F(000)	470
θ range for data collection (°)	2.6~26.5
Index range	$0 \le h \le 8$, $0 \le k \le 12$, $-14 \le l \le 14$
Reflections collected	2253
Independent reflections	1603 [R_{int} = 0.0354]
Data/restraints/parameters	1603/0/131
Goodness-of-fit on F^2	1.091
Final R indices [I>2σ(I)]	R_1=0.031, wR_2=0.084

empirical absorption correction based on the psi-scans was applied.[15]

All calculations were carried out using the Siemens SHELXTL crystallographic software programs.[16] The space group was assigned based on the systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by the direct method[17] and refined by successive full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms fixed at the calculated positions with the isotropic thermal parameters were included in the final structure factor calculations. Final difference of electron density maps contained no significant features. The crystallographic and experimental data are summarized in *Table* 1.

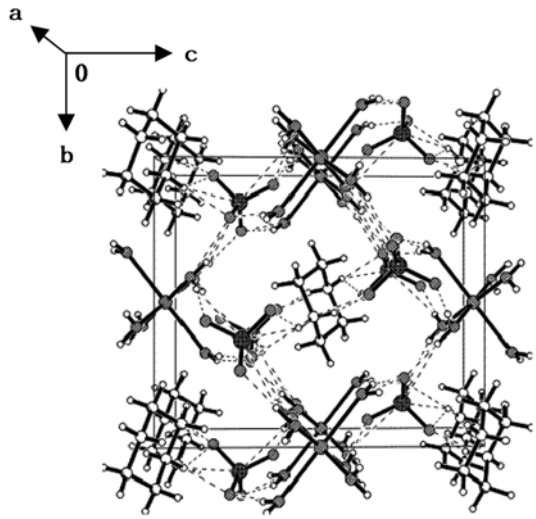

Fig. 2. Perspective view of the unit cell of compound **I** along the *a* axis; hydrogen bonds are shown by broken lines.

3. Results and Discussion

Fig. 1 and 2 show molecular structures with atomic numbering and a perspective view of the $\{H_2NCH_2CH_2NH_2CH_2CH_2\}\{Cu(H_2O)_6\}(SO_4)_2$, **I**, respectively. The selected bond lengths and bond angles are listed in *Table* 2.

As shown in *Fig.* 1, the compound **I** constituted by doubly protonated piperazine cation, hexa-hydrated copper cation and two sulfate anions. Doubly protonated piperazine cation take a chair conformation. Bond lengths and angles of this piperazine cation are not unusual as listed in *Table* 2. The copper metal ion lies on an inversion center and is six-coordinated by water molecules with no direct bonding to the sulfate groups. Its structural coordination feature can be described as an elongated octahedral arrangement by the Jahn-Teller effect. The axial Cu-O_{water} bond length of 2.397(2)Å is longer than the equatorial Cu-O_{water} bond lengths of 1.962(2) and 1.960(2)Å. The O_{water}-Co-O_{water} bond angles from 86.34(9) to 92.87(8)° and 180°. The S-$O_{sulfate}$ bond lengths in the sulfate anion range from 1.455(2) to 1.479(2)° and the $O_{sulfate}$-S-$O_{sulfate}$ bond angles from 107.7(1) to 111.9(2)°. The bond lengths, and angles of the sulfate anion are similar to those of the previously reported results.[12,18]

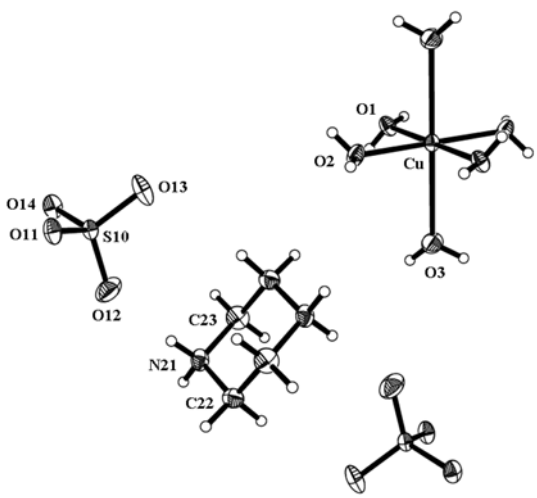

Fig. 1. The molecular structure of compound **I** with the atomic numbering scheme and displacement ellipsoids at the 30% probability level.

As shown in *Fig.* 2, the piperazine templated Cu(II)-sulfate compound **I** demonstrate zero-dimensional structure constituted by protonated piperazine cations, hexaaqua copper cations and sulfate anions. The crystal structure is stabilized by three-dimensional networks of the intermolecular O_{water}-H···$O_{sulfate}$, and N_{pip}-H···$O_{sulfate}$ hydrogen bonds between the water molecules and sulfate anions and protonated piperazine cations. The protonated

Table 2. Selected bond lengths (Å) and angles (°) for compound **I**

Cu-O(1)	1.962(2)	Cu-O(2)	1.960(2)
Cu-O(3)	2.397(2)	S(10)-O(11)	1.471(2)
S(10)-O(12)	1.455(2)	S(10)-O(13)	1.462(2)
S(10)-O(14)	1.479(2)	N(21)-C(22)	1.478(4)
C(22)-C(23)^{i}	1.503(4)	N(21)-C(23)	1.490(4)
O(1)-Cu-O(2)	86.34(9)	O(1)-Cu-O(3)	92.87(8)
O(2)-Cu-O(3)	87.56(9)	O(11)-S(10)-O(12)	110.2(1)
O(11)-S(10)-O(13)	108.7(1)	O(11)-S(10)-O(14)	108.6(1)
O(12)-S(10)-O(13)	111.9(2)	O(12)-S(10)-O(14)	107.7(1)
O(13)-S(10)-O(14)	109.7(1)	N(21)-C(22)-C(23)^{i}	110.3(2)
N(21)-C(23)-C(22)^{i}	110.5(2)	C(22)-N(21)-C(23)	111.7(2)

Symmetry transformations used to generate equivalent atoms: $^{i)}$ $-x+1$, $-y+1$, $-z+1$.

piperazine cations, sulfate anions and hexahydrated copper cations are linked together in -PIP-SO_4-$Cu(H_2O)_6$-SO_4-PIP- hydrogen bonding chains along the *c* direction by the N_{pip}-H···$O_{sulfate}$ and O_{water}-H···$O_{sulfate}$ bonds. The sulfate anions and hexahydrated copper cations are linked together in -SO_4-$Cu(H_2O)_6$- hydrogen bonding chains along the *b* direction by the O_{water}-H-$O_{sulfate}$ bonds. These hydrogen bonding planes are inter-linked along the *a* direction *via* another hydrogen bonds. The detailed hydrogen bonding interactions between the sulfate anions and coordinated water molecules and piperazine nitrogen atoms are described in follows: O(1)-H(1a)···O(13), 2.671(3)Å, 172(4)°; O(1)-H(1a)···S(10), 3.648(2)Å, 159(3)°; O(1)-H(1b)···O(11), 2.690(3)Å, 170(4)°; O(2)-H(2a)···O(11), 2.652(3)Å, 173(4)°; O(2)-H(2a)···S(10), 3.661(2)Å, 161(3)°; O(2)-H(2b)···O(14), 2.687(3)Å, 162(3)°; O(3)-H(3a)···O(13), 2.867(3)Å, 161(4)°; O(3)-H(3b)···O(14), 2.906(3)Å, 172(4)°; N(21)-H(21a)···O(12), 2.732(3)Å, 162.1°; N(21)-H(21b)···O(14), 2.885(3)Å, 155.4°; N(21)-H(21b)···S(10), 3.587(2)Å, 161.4°.

As shown in *Fig.* 3, IR spectrum of compound **I** has dominant characteristic bands of the water molecules and sulfate groups whereas the modes arising from the piperazinium cations are systematically weak. A broad strong absorption bands observed in the 2900~3600 cm^{-1} region are due to the OH and NH stretching, together with CH stretching. The strong absorption bands in the 1090 and 610 cm^{-1} regions can be attributed to sulfate groups. The typical sharp peaks in the 900~1600 cm^{-1} region are used to confirm the presence of the piperazine template.

As shown in *Fig.* 4, the thermal decomposition reaction of the compound **I** would proceed through three

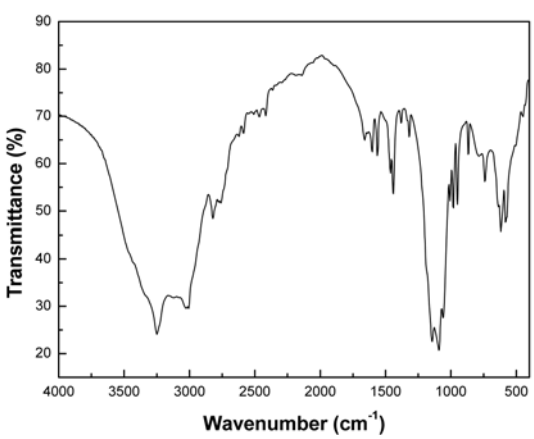

Fig. 3. Infrared spectrum of compound **I**.

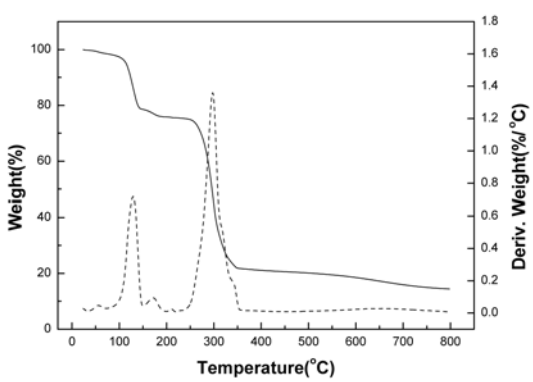

Fig. 4. Thermogravimetric and differential thermal analysis curves for compound **I**.

stages under our experimental condition: the dehydration of coordinated water molecules, the decomposition of piperazine and sulfate group, and the formation of metal oxide. The first step of dehydration is the loss of coordinated six water molecules in the temperature of 30~210°C. The weight loss of 24.5% exactly matches with the theoretical calculation for the loss of six water molecules from compound **I**. The second step occurs from 210 to 380°C and the sharp weight loss of 53.9% due to the loss of piperazine molecules and sulfate ions. The high decomposition temperature of piperazine molecule is not surprising compare with boiling point 145~146°C, due to the fact that the molecule is strongly hydrogen bonded to sulfate ions.[19] The final stage of the decomposition starts at 380°C and the weight loss is 7.2%. This step leads to formation of CuO and the weight percentage of metal oxide is 14.4%. The total weight loss of three decomposition stages is 85.6%.

4. Supporting Information Available

Tables of crystallographic details, atomic coordinates, interatomic distances and angles, torsional angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for title compound are available from C. H. Kim.

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