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New Organically Templated Copper(I) Sulfites: the Role of Sulfite Anion as Both Soft and Hard Ligand

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Two new organically templated layered copper(I) sulfites, namely, $\{H_2pip\}\{Cu_3(CN)_3(SO_3)\}$ (**1**) and $\{H_2pip\}\{NaCu_2(SO_3)_2Br(H_2O)\}\cdot 2H_2O$ (**2**) (pip = piperazine), have been synthesized by hydrothermal reactions of copper(I) cyanide or copper(I) bromide with $NaHSO_3$ and piperazine. Both compounds exhibit a layered structure. The 2D layer of $\{Cu_3(CN)_3(SO_3)\}^{2-}$ in **1** is composed of 1D chains of copper(I) cyanide interconnected by sulfite anions via both Cu–S and Cu–O bonds, whereas the 2D layer of $\{NaCu_2(SO_3)_2Br\}^{2-}$ in **2** is formed by 1D chains of copper(I) bromide and 1D sodium(I) aqua chains that are interconnected by sulfite anions via Na–O, Cu–S, and Cu–O bonds. Chemical bonding in **1** and **2** has been also investigated by theoretical calculations based on DFT methods.

Introduction

The widespread applications of open-framework inorganic materials in heterogeneous catalysis, separations, and ion-exchange processes have stimulated considerable research interest of using organic templates as the structurally directing agent in the syntheses of porous materials.[1] The organic amines usually occupy the structural voids and are well-isolated from the inorganic skeleton.[1] A remarkable variety of such materials have been reported,[2−9] in particular those based on phosphates.[2,3] Recently, this research field has been extended to the oxo anions of Group 16 elements. The stereochemically active lone pair electrons of Se(IV) and Te(IV) ions have a dramatic effect on their coordination geometry, as well as on the structures of their metal complexes. It has been reported that the asymmetric coordination geometry adopted by Se(IV) or Te(IV) atoms may aid in the crystallization of metal selenites or tellurites in non-centrosymmetric space groups which may possess interesting physical properties such as nonlinear optical second harmonic generation (SHG).[10] A variety of organically templated metal selenites and tellurites have been reported.[11−16] The corresponding metal sulfites are much less understood due to the unstable nature of S(IV) under hydrothermal conditions.[17−19] Several vanadium or molybdenum sulfite polyoxometalates have been reported.[17] Very recently, a few coordination polymers based on zinc sulfites

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ranging from 1D to 3D have been characterized; however, the organic amines are involved in metal coordination instead of acting as the structural directing agents.[18] So far, to the best of our knowledge, only one organically templated neodymium(III) sulfite-sulfate with a layered structure, $[H_2\text{-en}]\{Nd(SO_3)(SO_4)(H_2O)\}_2$ has been reported;[18a] therefore, open frameworks of the organic-templated metal sulfites remain almost a virgin land waiting for our exploration. It should be mentioned that the S(IV) atoms in the above metal complexes are not involved in metal coordination, hence their lone pairs are stereochemically active. However, it is possible for the S(IV) atom to directly bond with a metal ion under suitable conditions;[19] therefore, sulfite anion can behave as both a soft and hard ligand to transition metal ions, which is different from the selenite and tellurite anions. We deem that the exploration of organically templated metal sulfites would lead to a variety of new compounds with novel structures and chemical bonding, as well as physical properties. These metal sulfites are also interesting materials from the standpoint of their applications to the thermal and photochemical oxidation of sulfite.[20] Our research efforts resulted in the isolation of two new organically templated copper(I) sulfites, namely, $\{H_2pip\}\{Cu_3(CN)_3(SO_3)\}$ (**1**) and $\{H_2pip\}\{NaCu_2(SO_3)_2\,Br\,(H_2O)\}\cdot 2H_2O$ (**2**) (pip = piperazine). Both of them display a layered inorganic framework. Herein we report their syntheses, crystal structures, and chemical bonding.

Experimental Section

Materials and Instrumentation. All of the chemicals were analytically pure from commercial sources and used without further purification. XRD patterns were collected on a XPERT-MPD $\theta-2\theta$ diffractometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000−400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out with a NETZSCH STA 449C unit, at a heating rate of 10 °C/min under a nitrogen atmosphere. Photoluminescence analyses were performed on a Perkin Elemer LS55 fluorescence spectrometer.

$\{H_2pip\}\{Cu_3(CN)_3(SO_3)\}$ (1). A mixture of CuCN (0.1186 g, 1.3 mmol), $NaHSO_3$ (0.3190 g, 3.1 mmol), and pip·$6H_2O$ (0.1899 g, 1mmol) in 10 mL of distilled water was sealed in an autoclave equipped with a Teflon liner (25 mL) and then heated at 95 °C for 5 days, followed by cooling at 0.04 °C/min to room temperature. The initial and final pH values of the reaction media are both close to 6.0. Light yellow crystals of **1** were collected in a yield of 52.9% (based on copper). Anal. Calcd for $C_7H_{12}N_5Cu_3SO_3$: C, 18.98; H, 2.73; N, 15.8%. Found: C, 19.3; H, 2.94; N, 17.1%. IR(KBr, cm^{-1}): 3433 br, 2133 m, 2120 s, 1627 s, 1470 m, 1446 m, 1089 m, 1012 m, 991 s, 980 m, 952 vs, 904 s, 884 m, 872 m, 643 m, 592 s.

Table 1. Crystal Data and Structural Refinements for Compounds **1** and **2**

	1	**2**
formula	$C_7H_{12}N_5Cu_3SO_3$	$C_4H_{18}BrCu_2N_2NaO_9S_2$
fw	436.90	532.30
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	7.452(6)	11.267(4)
b, Å	8.103(6)	19.993(9)
c, Å	11.452(8)	6.752(3)
α, deg	82.32(2)	90
β, deg	88.47(3)	90.592(7)
γ, deg	67.02(1)	90
V, $Å^3$	630.7(8)	1521(1)
Z	1	4
D_{calcd}, g/cm^3	2.301	2.325
μ, mm^{-1}	5.187	5.767
GOF on F^2	1.082	1.093
R1, wR2 $[I > 2\sigma(I)]^a$	0.060, 0.097	0.061, 0.160
R1, wR2 (all data)	0.099, 0.114	0.070, 0.165

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) for Compounds **1** and **2**.

	1		
Cu(1)−C(3)#1	1.890(7)	Cu(1)−N(2)	1.936(6)
Cu(1)−O(2)	2.098(4)	Cu(1)−Cu(2)	2.876(2)
Cu(2)−C(2)#2	1.886(7)	Cu(2)−N(1)	1.926(6)
Cu(2)−O(1)	2.266(5)	Cu(3)−C(1)#3	1.902(7)
Cu(3)−N(3)	1.909(6)	Cu(3)−S(1)	2.413(2)
S(1)−O(3)	1.509(5)	S(1)−O(1)	1.513(5)
S(1)−O(2)	1.532(5)	N(1)−C(1)	1.153(8)
N(2)−C(2)	1.165(9)	N(3)−C(3)	1.167(8)
	2		
Cu(1)−O(4)#1	2.007(5)	Cu(1)−S(2)	2.197(2)
Cu(1)−Br(1)	2.597(1)	Cu(1)−Br(1)#2	2.617(1)
Cu(2)−O(1)#1	2.007(6)	Cu(2)−S(1)	2.193(2)
Cu(2)−Br(1)	2.609(2)	Cu(2)−Br(1)#2	2.626(1)
Na(1)-O(1W)	2.351(6)	Na(1)-O(1W)#2	2.372(7)
Na(1)−O(5)	2.420(7)	Na(1)−O(3)#3	2.516(6)
Na(1)−O(3)#4	2.557(7)	Na(1)−O(5)#2	2.597(7)
S(1)−O(3)	1.490(6)	S(1)−O(2)	1.511(6)
S(1)−O(1)	1.524(5)	S(2)−O(5)	1.480(6)
S(2)−O(6)	1.515(5)	S(2)−O(4)	1.542(5)

[a] Symmetry transformations used to generate equivalent atoms. For compound **1**: #1 $x - 1, y + 1, z$; #2 $-x + 1, -y + 1, -z$; #3 $-x + 1, -y, -z + 1$. For compound **2**: #1 $x, -y + 3/2, z + 1/2$; #2 $x, -y + 3/2, z - 1/2$; #3 $x - 1, -y + 3/2, z - 1/2$; #4 $x - 1, y, z$.

$\{H_2pip\}\{NaCu_2(SO_3)_2Br(H_2O)\}\cdot 2H_2O$ (2). A mixture of CuBr (0.1059 g, 0.74 mmol), $NaHSO_3$ (0.1898 g, 1.82 mmol), and pip·$6H_2O$ (0.1369 g, 0.705 mmol) in 5 mL of distilled water was sealed into an autoclave equipped with a Teflon liner (25 mL) and heated at 120 °C for 4 days, followed by cooling at 0.04 °C/min to room temperature. The initial and final pH values of the reaction are both close to 6.0. Yellow single crystals of **2** were isolated in a small quantity (<20.0 mg). Attempts to improve the yield by changing reaction conditions such as temperature and molar ratio of the starting materials were tried but unsuccessful. Anal. Calcd for $C_4H_{18}BrCu_2N_2NaO_9S_2$: C, 9.03; H, 3.41; N, 5.26%. Found: C, 9.13; H, 3.55; N, 5.12%. IR (KBr, cm^{-1}): 3368 br, 1629 m, 1452 m, 1084 s, 973 s, 926 vs, 868 m, 646 s, 603 m, 477 m.

Single-Crystal Structure Determination. Data collections for the two compounds were performed on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Both data sets were corrected for Lorentz and polarization factors, as well as for absorption by the Multi-scan method.[21a] Both structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[21b] All non-hydrogen atoms were refined with aniso-

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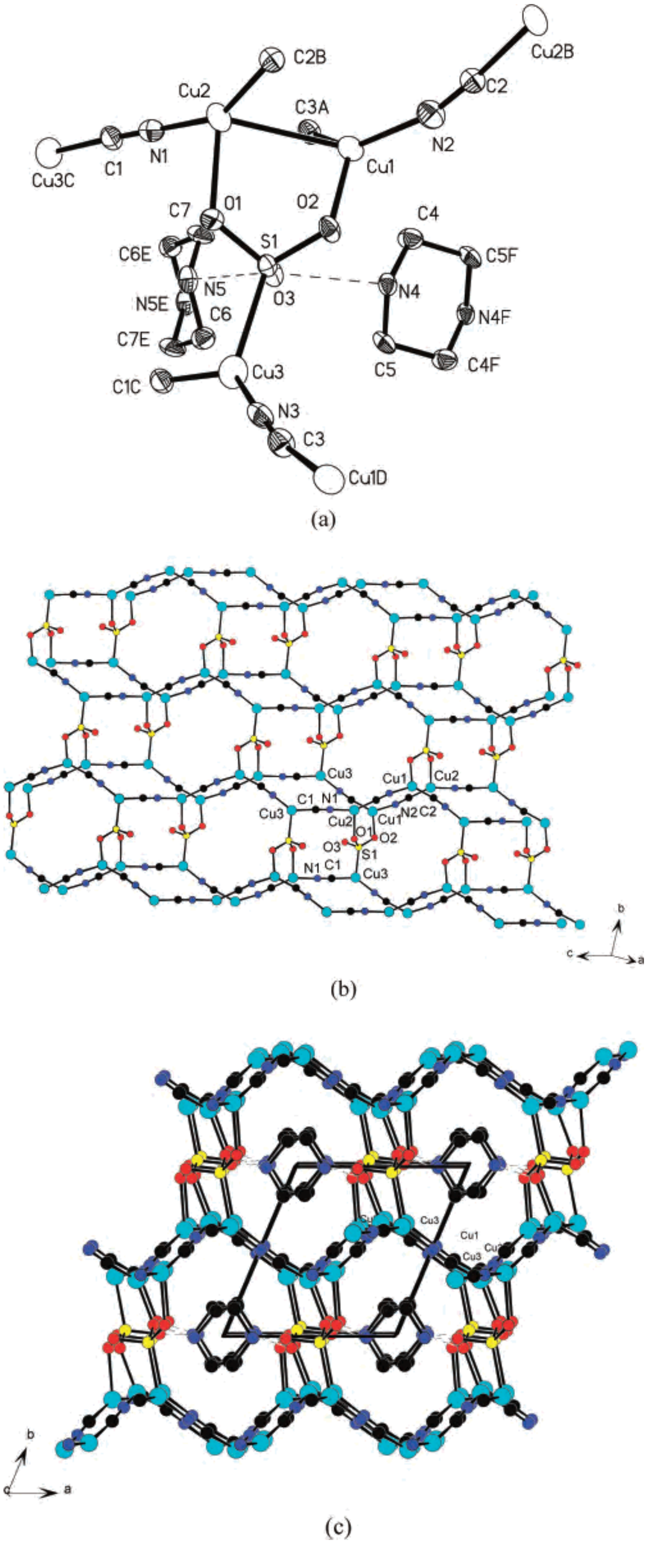

Figure 1. (a) ORTEP representation of the selected unit of **1**. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are drawn as dashed lines. Symmetry codes for the generated atoms: (a) $-1 + x$, $1 + y$, z; (b) $1 - x$, $1 - y$, $-z$; (c) $1 - x$, $-y$, $1 - z$; (d) $1 + x$, $y - 1$, z; (e) $-x$, $-y$, $1 - z$; (f) $-x$, $-y$, $-z$. (b) A 2D layer of the $\{Cu_3(CN)_3(SO_3)\}^{2-}$ anion. (c) View of the structure of **1** down the *c* axis.

tropic thermal parameters. All the hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic data and structural refinements for the two compounds are summarized in Table 1. Important bond distances are listed in Table 2. More details on the crystallographic studies, as well as atomic displacement parameters, are given as Supporting Information.

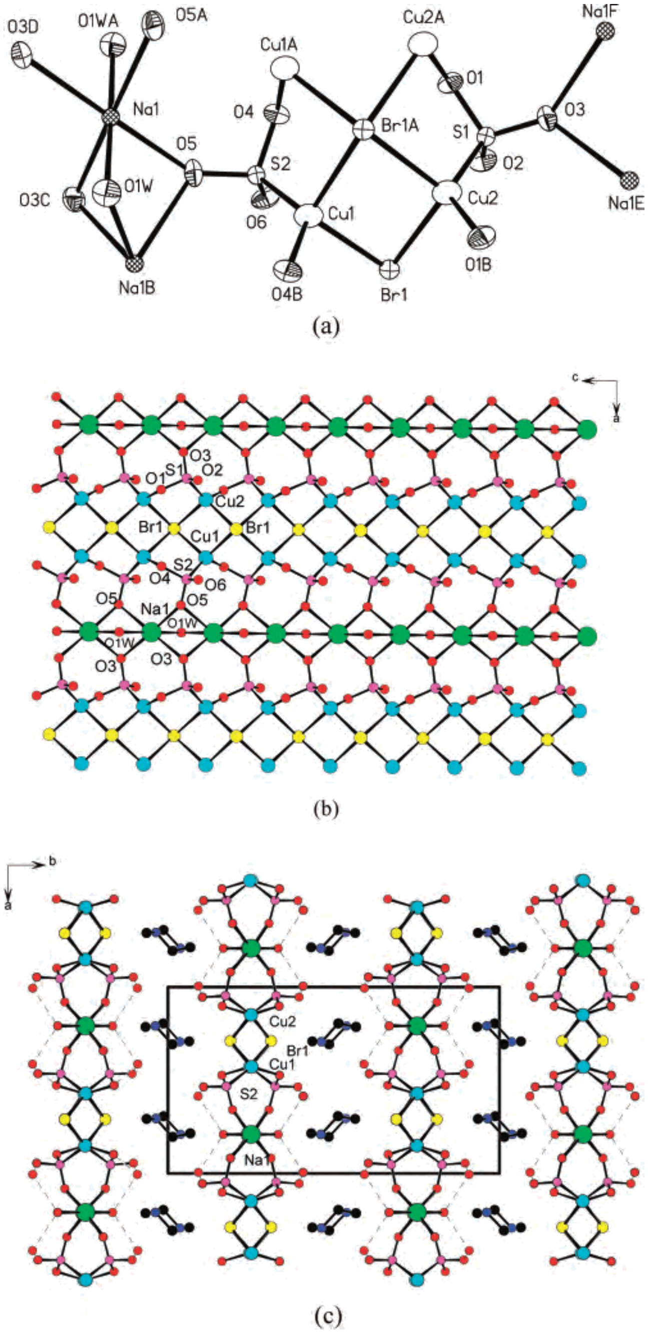

Figure 2. (a) ORTEP representation of the selected unit of **2**. The thermal ellipsoids are drawn at the 50% probability level. The lattice waters and the template cations were omitted for clarity. Hydrogen bonds are drawn as dashed lines. Symmetry codes for the generated atoms: (a) x, $3/2 - y$, $-1/2 + z$; (b) x, $3/2 - y$, $1/2 + z$; (c) $x - 1$, y, z; (d) $1 - x$, $3/2 - y$, $-1/2 + z$; (e) $1 + x$, $3/2 - y$, $1/2 + z$; (f) $x + 1$, y, z. (b) A 2D layer of the $\{NaCu_2(SO_3)_2Br(H_2O)\}^{2-}$ anion. (c) View of the structure of **2** down the *c* axis. Hydrogen bonds are represented by dashed lines.

Computational Descriptions. The crystallographic data of compounds **1** and **2** were used for the band structure calculations. The ab initio band structure calculations were performed by using

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(21) (a) *CrystalClear ver. 1.3.5*; Rigaku Corp.: The Woodlands, TX, 1999. (b) Sheldrick, G. M. *SHELXTL*, *Crystallographic Software Package*, Version 5.1; Bruker-AXS: Madison, WI, 1998.

Table 3. Hydrogen Bonds for Compounds **1** and **2**

D−H···A	d(D−H)/Å	d(H···A)/Å	(D−H···A)/deg	d(D−H···A)/Å	symmetry code
1					
N4−H4C−O3	0.90	1.903	163.6	2.778(7)	
N5−H5D−O3	0.90	1.807	160.6	2.673(7)	
2					
O1W−H1WA−O2w	0.85	1.980	154.1	2.745(8)	
O1W−H1WB−O3W	0.85	1.908	168.2	2.770(8)	
O2W−H2WA−O2	0.85	2.228	127.1	2.824(8)	$x - 1, 3/2 - y, -1/2 + z$
O3W−H3WA−O6	0.85	2.289	118.1	2.792(8)	$x, 3/2 - y, -1/2 + z$

the computer code CASTEP.[22] This code employs density functional theory using a plane-wave basis set with Vanderbilt ultrasoft pseudopotentials to approximate the interactions between core and valence electrons.[23] The exchange-correlation energy was calculated using the Perdew−Burke−Ernzerhof modification to the generalized gradient approximation.[24] A kinetic-energy cutoff of 340 (for **1**) or 370 eV (for **2**) was used throughout our work. Pseudoatomic calculations were performed for H $1s^1$, C $2s^22p^2$, N $2s^22p^3$, O $2s^22p^4$, S $3s^23p^4$, Na $2s^22p^23s^1$, Br $4s^22p^5$, and Cu $3d^{10}4s^1$. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code.[22]

Results and Discussion

Hydrothermal reactions of copper(I) cyanide or copper(I) bromide with $NaHSO_3$ in the presence of piperazine as the template agent led to two new organically templated layered copper(I) sulfites, namely, **1** and **2**. It is found that the counteranion of the copper(I) salt plays an important role in the chemical composition of the resulting compounds. These two compounds added two new important examples of open frameworks of metal sulfites templated by organic amines. Both of them exhibit a layered structure.

There are three unique copper(I) ions, three cyanide anions, a sulfite group, and a doubly protonated piperazine cation in the asymmetric unit of **1**. Both Cu(1) and Cu(2) are three-coordinated by a carbon atom and a nitrogen atom from two cyanide anions and an oxygen atom from a sulfite anion, whereas Cu(3) is three-coordinated by a carbon atom and a nitrogen atom from two cyanide anions and a sulfur atom from a sulfite anion (Figure 1a). The Cu−O, Cu−N, and Cu−C bond distances are in the range of 2.098(4)−2.266(5), 1.909(6)−1.936(6), and 1.886(7)−1.902(7) Å, respectively. The Cu−S distance of 2.413(2) Å is significantly longer than those of the Cu−O, Cu−N, and Cu−C bonds. These bond distances are comparable to those reported in the inorganic copper(I) sulfites.[25] The sulfite anion is tridentate and bridges with three copper(I) ions by using the sulfur(IV) atom and two oxygen atoms into a $\{Cu_3(SO_3)\}^-$ trinuclear unit. The bridging of copper(I) ions via cyanide anions resulted in 1D zigzag chains of copper(I) cyanide along the *c* axis. These 1D chains are further interconnected by tridentate bridging sulfite anions into a novel layered structure (Figure 1b). Such a 2D layer can also be considered as built from $\{Cu_3(SO_3)\}^-$ trinuclear clusters bridged by cyanide anions. Packing of $\{Cu_3(CN)_3(SO_3)\}^{2-}$ layers led to large apertures along the *c* axis which are occupied by doubly protonated piperazine cations (Figure 1c). These apertures are formed by 18-member rings composed of six copper(I) cations, four cyanide anions, and two sulfite anions. Hydrogen bonds are formed between the piperazine nitrogen atoms and non-coordination sulfite oxygen atoms (O(3)) with N···O separations ranging from 2.673(7) to 2.778(7) Å (Table 3).

The use of copper(I) bromide instead of copper(I) cyanide afforded a different layered compound, **2**. Both copper(I) ions in the asymmetric unit of **2** are tetrahedrally coordinated by one oxygen and one sulfur atom from two sulfite groups and two bromide anions (Figure 2a). The Cu−Br distances (2.597(1)−2.626(1) Å) are significantly longer than those of the Cu−S bonds (2.193(2)−2.197(2) Å) and Cu−O bonds (2.007(5)−2.007(6) Å). The sodium(I) ion is octahedrally coordinated by six oxygen atoms from two aqua ligands and four sulfite anions with Na−O distances ranging from 2.351(6) to 2.597(7) Å. Unlike those in compound **1**, the sulfite anions in **2** act as tetradentate metal linker, bridging with two Cu(I) ions by using an oxygen atom and the sulfur atom and two sodium(I) ions by using another oxygen atom. The third oxygen atom (O(2) or O(6)) remains non-coordinated. The bromide anion is tetradentate and bridges with four Cu(I) ions. The interconnection of copper(I) ions via bromide anions resulted in a 1D chain of $\{Cu_2Br\}^+$ along the *c* axis. Neighboring sodium(I) ions are bridged by the aqua ligands into a 1D chain along the *c* axis (Figure 2b). The above two types of 1D chains are further cross-linked by bridging sulfite anions into a layered architecture (Figure 2b). Such a type of layered structure has not been observed yet. The doubly protonated piperazine cations and lattice water molecules are located at the interlayer region (Figure 2c). The lattice water molecules form a number of hydrogen bonds with aqua ligands and non-coordination sulfite oxygen atoms, which further increases the stability of the structure (Table 3).

To further understand the structures for both compounds, topological structures of both compounds were also investigated (Figure 3). In compound **1**, the cyanide groups are two-connectors; hence, they are not important in the view

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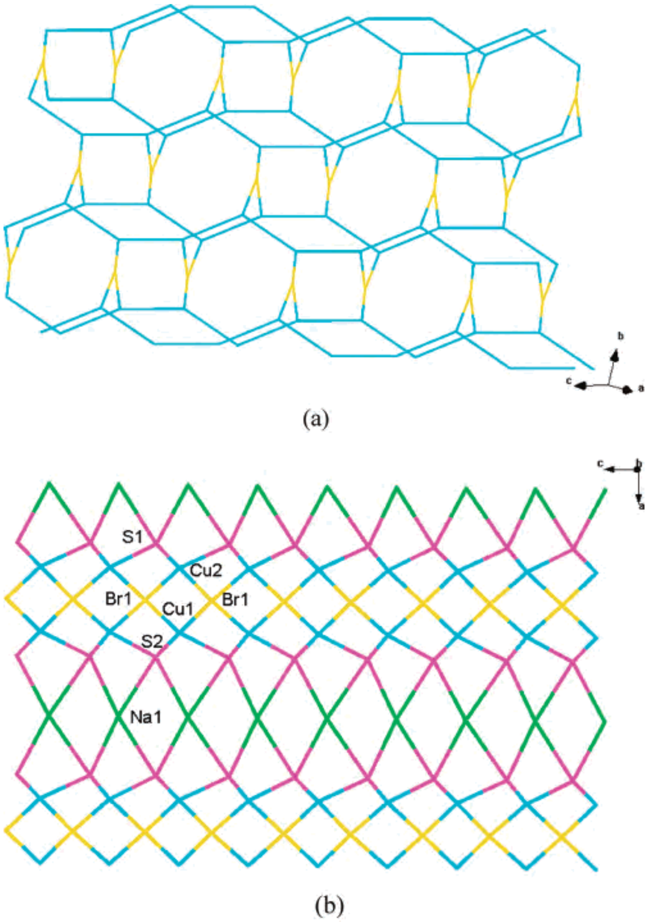


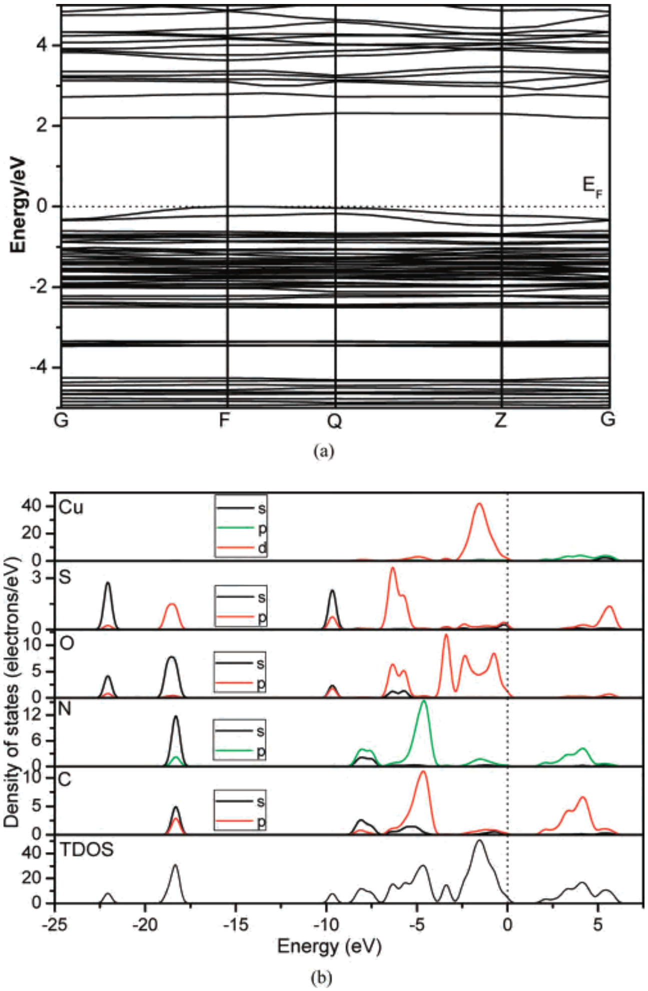
(a)

(b)

Figure 3. Topological diagrams showing the layered structures in compounds **1** (a) and **2** (b).

of topology. Each SO_3^{2-} group connects with three copper(I) ions, and each copper(I) ion is connected to one SO_3^{2-} and two cyanide anions. Thus, both the sulfite group and copper(I) ion can be considered as three-connected nodes and the resultant framework can be described as a (3,3)-connected 2D net (Figure 3a) in which the vertex symbols are 6.8.10 for Cu(I) ions and 6.6.10 for SO_3^{2-}. Similarly for compound **2**, SO_3^{2-}, Cu(I), Br^-, and Na(I) can be considered as four-connected nodes. These four types of nodes have the same vertex symbol 4.4.4.4, and the whole structure can be simplified as a four-connected 2D net (Figure 3b).

A search of CSD/ICSD indicates that there are five inorganic copper sulfites reported in the literature, namely, $NH_4Cu^I(SO_3)$, $Tl^ICu^{II}(SO_3)_2$, $Cu^I_2Cu^{II}(SO_3)_2(H_2O)_2$, $Cu^I_2Zn^{II}(SO_3)_2(H_2O)_2$, and $(NH_4)_2\{Cu^{II}(H_2O)_6\}\{Cu^ISO_3\}_4$.[25] Their structures differ significantly from the above two organically templated copper(I) sulfites. The structure of $NH_4Cu^I(SO_3)$ features a three-connected hexagonal layer, and $Tl^ICu^{II}(SO_3)_2$ also displays a layered structure in which Tl(I) ion is six-coordinated in a severely distorted octahedral geometry due to the lone pair of Tl(I) ion; the copper(II) ion is six-coordinated with a slightly distorted octahedral geometry; in both compounds, the sulfur atoms of the sulfite anions are non-coordinated. $Cu^I_2Cu^{II}(SO_3)_2(H_2O)_2$ and $Cu^I_2Zn^{II}(SO_3)_2(H_2O)_2$ are isostructural, and their structures can be described as the copper(I) sulfite forms a 3D four-connected network (4.8^2-net) with the tunnels of eight-membered rings being occupied by the hydrated copper(II) or zinc(II) ions. The structure of $(NH_4)_2\{Cu^{II}(H_2O)_6\}\{Cu^ISO_3\}_4$ features a four-connected double layer ($4^2.8^2$-net) of copper(I) sulfite. Packing of such double layers resulted in tunnels of four- and eight-membered rings; the isolated hexahydrated copper(II) ions are located at the large tunnels, and the ammonia cations occupy both types of tunnels (see Supporting Information).[25]



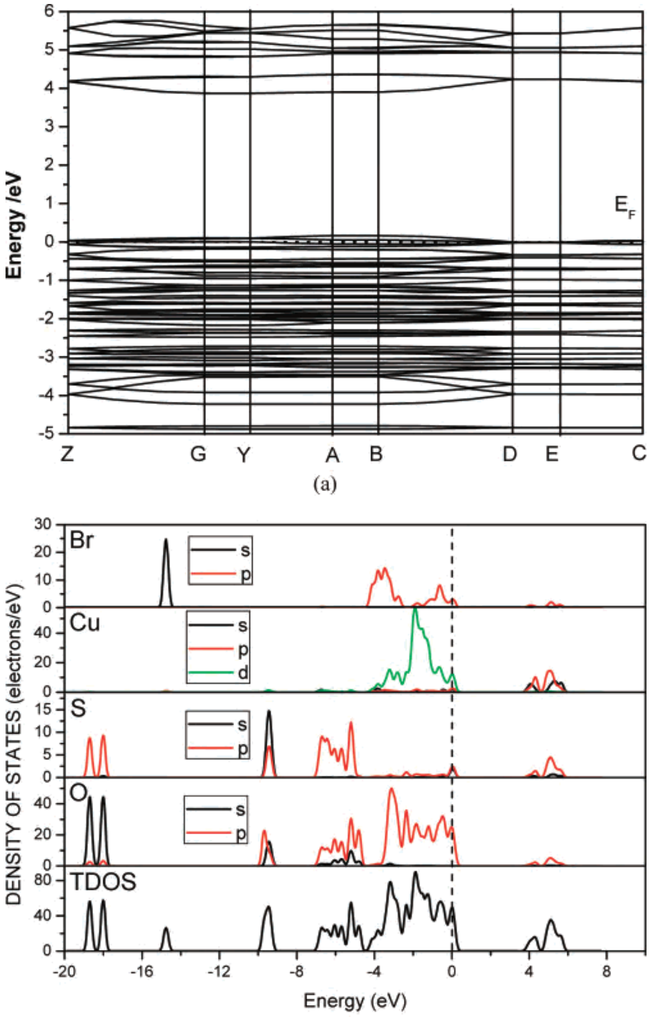
(a)

(b)

Figure 4. Band structure (a) and total and partial density of states (DOS) for $\{Cu_3(CN)_3(SO_3)\}^{2-}$ in compound **1** (b). The Fermi level is set at 0 eV.

To further understand the chemical bonding in both compounds, band structure as well as density-of-states (DOS) calculations for the 2D $\{Cu_3(CN)_3(SO_3)\}^{2-}$ and $\{NaCu_2(SO_3)_2\ Br\ (H_2O)\}^{2-}$ anions based on the DFT method have been made by using the computer code CASTEP.[22] Resulted are shown in Figures 4 and 5, respectively.

As is shown in Figure 4a, the top of the valence bands (VBs) for the $\{Cu_3(CN)_3(SO_3)\}^{2-}$ anion shows a small dispersion whereas the bottom of the conduction bands (CBs) is nearly flat. The lowest energy (2.19 eV) of CBs is located at the G point, whereas the highest energy (0.0 eV) of VBs is located at the F point. Hence, the $\{Cu_3(CN)_3(SO_3)\}^{2-}$ anion has an indirect band gap of around 2.19 eV. As shown in Figure 4b, the VBs from −25.0 to −20.0 eV are mainly



(a)

(b)

Figure 5. Band structure (a) and total and partial density of states (DOS) for $\{NaCu_2(SO_3)_2\ Br\ (H_2O)\}^{2-}$ in compound **2** (b). The Fermi level is set at 0.0 eV.

contributions of s and p orbitals of S, O, N, and C atoms. The bands from −10 eV to the Fermi level are dominated by Cu 3d, S 3p, O 2p, N 2p, and C 2p mixing with small amounts of S 3s, O 2s, N 2s, and C 2s. The CBs are dominated by unoccupied Cu 4p, S 3p, N 2p, and O 2p states. On the basis of atomic populations, S (+1.6) and Cu (+0.33 to +0.50) atoms are positively charged, whereas C (−0.14 to −0.21), N (−0.50 to −0.52), and O (−0.94 to −0.99) atoms are negatively charged. The absolute values are not so meaningful, but the relative values do provide some useful information. The bond population analyses are more informative. The bond orders of C−N bonds are in the range of 1.75−1.79 e (a single bond is assumed to be 1.0 e), indicating its nature of multiple bonding. The bond orders for Cu−C, Cu−N, and Cu−O bonds are in the range of 0.47−0.51, 0.34−0.36, and 0.22−0.28 e, respectively. Hence, Cu−C bonds are more covalent whereas Cu−O bonds have more ionic characters.

Similar to that for the $\{Cu_3(CN)_3(SO_3)\}^{2-}$ anion, the top of the VBs for $\{NaCu_2(SO_3)_2\ Br(H_2O)\}^{2-}$ anions shows a small dispersion whereas the bottom of the CBs is nearly flat (Figure 5a). The lowest energy of CBs is located at the G point, whereas the highest energy of VBs is located at the B point. Hence, the $\{NaCu_2(SO_3)_2\ Br\ (H_2O)\}^{2-}$ anion has an indirect band gap of around 3.70 eV, which is much larger than that for the $\{Cu_3(CN)_3(SO_3)\}^{2-}$ anion. As shown in Figure 5b, the bands from −8 eV to the Fermi level are dominated by Cu 3d, S 3p, O 2p, and Br 4p mixing with small amount of O 2s. The CBs are dominated by unoccupied Cu 4p, Cu 4s, S 3p, Br 4p, and O 2p states. The contributions from hydrogen and sodium atoms to the bands around the Fermi level are very small. On the basis of atomic populations, S (+1.71 to +1.73), H (+0.53 to +0.55), Na (+0.96), and Cu (+0.30 to +0.33) atoms are positively charged whereas Br (−0.10) and O (−0.78 to −1.09) atoms are negatively charged. The absolute values are not so meaningful, but the relative values do provide some useful information. The bond population analyses are more informative. The bond orders for Cu−Br, Na−O, Cu−S, and Cu−O bonds are in the range of 0.07−0.15, −0.02−0.11, 0.39−0.40, and 0.40 e, respectively. Hence Cu−O and Cu−S bonds are more covalent whereas Cu−Br and Na−O bonds have more ionic characters.

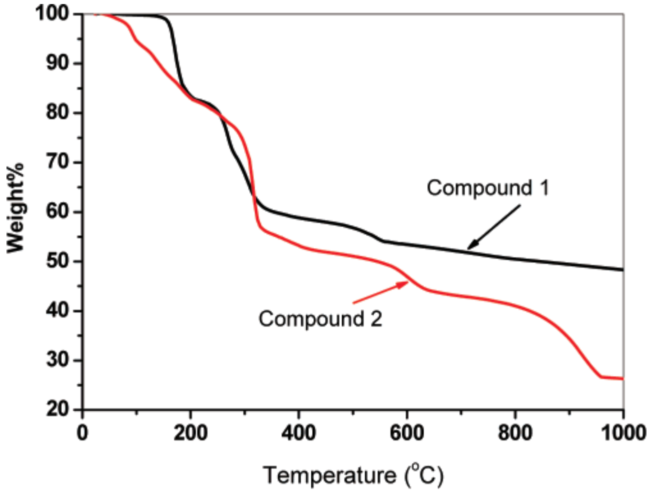


Figure 6. TGA diagrams for compounds **1** and **2**.

The IR spectra of compounds **1** and **2** display absorption bands associated with the template cations at 1627, 1446 and 1630, 1453 cm^{-1}, respectively.[26] The characteristic bands of the sulfite ions in compounds **1** and **2** appear at around 974−980(ν_1), 643−647(ν_2), 951−927(ν_3), and 470−477(ν_4) cm^{-1}.[19] Compound **1** also showed the characteristic bands of the cyanide anions at 2120 and 2094 cm^{-1}.[27]

Compound **1** is stable up to 140 °C; above that temperature, it exhibits three main steps of weight losses (140−211, 211−344, and 344−1000 °C), which correspond to the release of the template, cyanide group, and SO_2, respectively (Figure 6). The total weight losses at 1000 °C is 51.6%, and the final residuals are expected to be copper(I) oxide (calculated total weight losses: 50.9%). TGA curves of the compound **2** display two main steps of weight losses (42−330 and 330−950 °C). The first one corresponds the release

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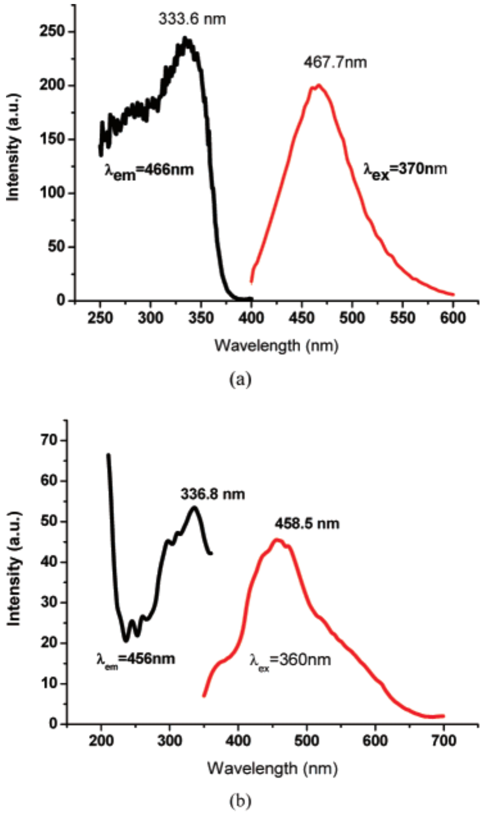

Figure 7. Excitation and emission spectra for compounds **1** (a) and **2** (b).

of water molecules and the template, whereas the second one corresponds to the further decomposing of the compound. The total weight loss at 1000 °C is 73.6%, and the final residuals are not characterized.

The excitation spectra of compounds **1** and **2** showed maximum peaks at 333.6 and 336.8 nm under the emission at 466 and 456 nm, respectively (Figure 7). Both compounds display a weak broad ligand-based (sulfite) emission band in the blue light region (467.7 and 458.5 nm, respectively, for **1** and **2**) under excitation at 370 and 360 nm, respectively.[28] The much weaker luminescence of compound **2** can be attributed to the quenching effect of the water molecules in the structure. The high-frequency vibrating O−H groups of the water molecules cause energy loss of the luminescent states through nonradiative process and effectively quench the luminescence of the compound.[29]

In summary, we have isolated the first layered copper(I) sulfites templated by organic amines. Also, both the center S(IV) atom and the oxygen atoms of the sulfite anions are involved in metal coordination, which is unique in the metal complexes with oxy anions of Group 16 elements. The coordination of $+4$-charged S(IV) to the copper(I) ion can be considered as the lone pairs of the S(IV) atom are donated to an empty p orbital of the Cu(I) ion; therefore, its lone pair is no longer photochemically active due to its involvement in the metal coordination. We can also expect that sulfite anion can bind with both soft and hard metal ions simultaneously to form many mixed-metal sulfites with various open-framework architectures and novel physical properties; currently we are exploring such possibilities.

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Supporting Information Available: X-ray crystallographic files in CIF format, simulated and experimental XRD powder patterns, IR spectra for compounds **1** and **2,** some figures showing the structures of the inorganic copper sulfites reported in the literature. This material is available free of charge via the Internet at http://pubs.acs.org.

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