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New Types of 3D Organically Templated $Zn^{2+}/Cd^{2+}-Cu^{+}$ Mixed Metal Sulfites

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Two types of new organically templated mixed-metal sulfites, namely, $[H_2pip][NaZn_2Cu(SO_3)_4]$ (**1**) and $[H_2pip][CdCu_4(SO_3)_4]$ (**2**) (pip = piperazine), have been synthesized under hydrothermal conditions and structurally characterized. Both compounds exhibit a novel 3D mixed-metal inorganic framework with organic template molecules occupying the tunnels of the inorganic skeleton. Compound **1** features a 2D $Zn_2Cu(SO_3)_4^{3-}$ layer parallel to the *ac* plane in which the 1D chains of $Zn(SO_3)_2^{2-}$ anions along the *c* axis are interconnected with the Cu^+ ions via Cu−S bonds. Neighboring $Zn_2Cu(SO_3)_4^{3-}$ layers are further interconnected by bridging Na^+ ions via Na−O−S bonds into a 3D network, forming 1D tunnels along the *a* axis which are occupied by the doubly protonated piperazine cations. Compounds **2** features a novel 3D inorganic framework of $CdCu_4(SO_3)_4^{2-}$ with 2D layers based on $Cu_4(SO_3)_4^{4-}$ cubanelike clusters. The cluster layers are further interconnected by Cd(II) ions, forming 1D tunnels of eight-membered rings along the *c* axis in which the piperazine template cations are located. Luminescent property measurements as well as band structure calculations based on density functional theory methods were also made.

Introduction

Open-framework inorganic materials with microporous properties have widespread applications in many fields.[1] The use of organic templates as the structure-directing agents in the syntheses of porous materials has been widely studied owing to the diversities of novel architectures and topologies of the materials formed in addition to their applications in heterogeneous catalysis, gas sorption, and ion exchange.[1,2] A great number of such materials have been reported,[3−9] in particular, those based on phosphates.[3] Recently, this field has been extended to materials formed by the oxo anions of group 16 elements.[10] Cations with stereochemically active lone pair electrons such as Se^{IV} and Te^{IV} ions which are susceptible to second-order Jahn−Teller distortions have been reported to help in the formation of materials with noncentrosymmetric structures, which may subsequently possess interesting physical properties such as second harmonic generation (SHG).[11] Metal sulfites which also contain nonbonded lone pair electrons have been reported to possess redox and photophysical properties.[12] So far, a variety of organically templated metal selenites and tellurites have been reported.[13−18] Reports on organically templated metal

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sulfites are much fewer.[19] Two isostructural organically templated $Ln^{III}-Cu^{I}$ heteronuclear sulfite bromides with a layered inorganic skeleton were reported by our group.[19a] We also prepared two organically templated layered copper(I) sulfites with additional cyanide or bromide anions.[19b] Several vanadium or molybdenum−sulfite polyoxometalates have been reported.[20] A series of zinc sulfites ranging from 1D to 3D have been characterized; however, the organic amines act as organic ligands instead of the structure-directing template agents.[21] These metal sulfites are interesting materials from the standpoint of their applications to the thermal and photochemical oxidation of sulfite.[22] It should be mentioned that the sulfite anion contains both the "soft" S(IV) atom, which is able to directly bond with a d^{10} metal ion such as Cu^+ under suitable conditions,[19] and the "hard" O atom, which can bond with a variety of metal ions; hence it is possible to synthesize various copper(I) sulfites with additional transition metal ions. The Se^{4+} and Te^{4+} cations of the selenite and tellurite anions, on the other hand, are not involved in the metal coordination.

Inspired by our success in the preparation of organically templated 3d−4f mixed-metal sulfites, we deem that it is possible to introduce additional transition metal ions such as Zn^{2+} or Cd^{2+} ions into the copper(I) sulfites to yield organically templated mixed-metal sulfites; such a combination may lead to materials with good luminescence properties.[23] So far, no such compounds has been reported, though a few purely inorganic mixed-metal copper(I) sulfites have been reported.[24,25] For example, the 3D structure of $Cu_2Zn(SO_3)_2(H_2O)_2$ can be viewed as hydrated $[Zn(H_2O)_2]^{2+}$ cations occupying the 1D 8-MR tunnels of the 3D network of $\{Cu_2(SO_3)_2\}^{2-}$ anions;[24c] furthermore, isostructural 1D coordination polymers of composition $Na_3\{[Cu^{I}(SO_3)_4][M^{II}(H_2O)_2]_2\}\cdot H_2O$ (M = Zn, Co), isostructural 2D coordination polymers of composition $[Na_4(H_2O)_{17}][M^{II}(H_2O)_6]_2\{[Cu^{I}(SO_3)_4]_2[M(H_2O)_2]_3\}$ (M = Ni, Co), and a 3D coordination polymer of composition $Na(H_2O)_6\{[Cu^{I}(SO_3)_4][Mn^{II}(H_2O)_2]_3\}$ were prepared by Robson's group.[25]

Our related research efforts led to two novel organically templated mixed-metal sulfites, namely, $[H_2pip][NaZn_2Cu(SO_3)_4]$ and $[H_2pip][CdCu_4(SO_3)_4]$ (pip = piperazine). Both compounds exhibit novel 3D inorganic structures with 1D tunnels occupied by the template cations. Herein, we report their syntheses, band and crystal structures, and optical properties.

Experimental Section

Materials and Instrumentation. All of the chemicals were analytically pure from commercial sources and used without further purification. Elemental analyses for C, H, and N were performed on a German Elementary Vario EL III instrument. Microprobe elemental analyses for Zn, Cd, Na, Cu, and S were performed with a JEOL-6700F scan electronic microscope. Inductively coupled plasma elemental analyses for Zn, Cd, Na, and Cu were performed with an Ultima2 X-ray inductively coupled plasma optical emission spectrometer. X-ray powder diffraction (XRD) patterns (Cu Kα) were collected on an 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 with an Edinburgh FLS920 fluorescence spectrometer. The optical diffuse reflectance spectrum was measured at room temperature with a PE Lambda 900 UV−visible spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectrum using the Kubelka−Munk function: $\alpha/S = (1 - R)^2/2R$,[26] where α is the absorption coefficient, S is the scattering coefficient, which is practically wavelength-independent when the particle size is larger than 5 μm, and R is the reflectance.

Synthesis of $[H_2PiP][NaZn_2Cu(SO_3)_4]$ (1) and $[H_2PiP][CdCu_4(SO_3)_4]$ (2). The two compounds were hydrothermally synthesized through reactions of a mixture of CuBr, zinc(II) or cadmium acetate, $NaHSO_3$, and piperazine in 10 mL of distilled water, which was sealed in an autoclave equipped with a Teflon liner (25 mL) at 100 °C for 5 days, followed by cooling at a rate of 0.04 °C/min to room temperature. The loaded compositions are CuBr (0.0285 g, 0.199 mmol), $Zn(Ac)_2\cdot 2H_2O$ (0.1090 g, 0.5 mmol), $NaHSO_3$ (0.1126 g, 1.08 mmol), and $C_4H_{10}N_2\cdot 6H_2O$ (0.0588 g, 0.30 mmol) for $[H_2PiP][NaZn_2Cu(SO_3)_4]$ (**1**) and CuBr (0.1185 g, 0.83 mmol), $Cd(Ac)_2\cdot 2H_2O$ (0.1351 g, 0.51 mmol), $NaHSO_3$ (0.2114 g, 2.03 mmol), and $C_4H_{10}N_2\cdot 6H_2O$ (0.0991 g, 0.51 mmol) for $[H_2PiP][CdCu_4(SO_3)_4]$ (**2**). The initial and final pH values of the reaction media are close to 5.0 for $[H_2PiP][NaZn_2Cu(SO_3)_4]$ (**1**) and 3.0 for $[H_2PiP][CdCu_4(SO_3)_4]$ (**2**). Light yellow single crystals of **1** were collected in a yield of 38.5% (based on copper), but light yellow single crystals of **2** were collected in a very low yield (< 20.0 mg). Also, two other impurity phases, $Cd_5Cu_2(SO_3)_6(H_2O)_2$ and $Na(H_2O)_6\{[Cu^{I}(SO_3)_4][Cd^{II}(H_2O)_2]_3\}$, were also found in the reaction products for **2**. Attempts to improve the yield by changing reaction conditions such as the temperature, the molar ratio of the starting materials, and the use of different metal sources such as CuCl and $CdCl_2$ also were tried but were unsuccessful. Elem anal. calcd for $C_4H_{10}N_2NaZn_4CuS_4O_{12}$: C, 7.68; H, 1.93; N, 4.48; Na, 3.67; Cu, 10.1; Zn, 20.76%. Found: C, 7.72; H, 1.82; N, 4.41; Na, 3.45; Cu, 8.85; Zn, 18.52%. Elem anal. calcd for $C_4H_{24}N_2CdCu_4S_4O_{12}$: C, 6.19; H, 1.56; N, 3.61; Cu, 32.77; Cd, 14.5%. Found: C, 6.12; H, 1.38; N, 3.41; Cu, 30.46; Cd, 14.68%. IR data (KBr, cm^{-1}) for **1**: 3006 br, 1619 m, 1595 s, 1459 m, 1110 vs, 1041 vs, 962 s, 653 m, 586 m. IR data (KBr, cm^{-1}) for **2**: 3450 br, 1580 s, 1469 m, 1059 vs, 1031 s, 938 s, 659 m, 506 m. Microprobe analyses on several single crystals of **1** and **2** gave a Zn/Cu/Na/S molar ratio of 2.1:1.1:1:3.9 for **1** and

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a Cd/Cu/S molar ratio of 1:4.0:4.1 for **2**; both are in good agreement with those obtained from single-crystal X-ray diffraction studies.

Single-Crystal Structure Determination. Data collections for both compounds were performed on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Both data sets were corrected for Lorentz and polarization factors as well as for absorption using the multiscan method.[27a] Both structures were solved using direct methods and refined using full-matrix least-squares fitting on F^2 using SHELX-97.[27b] All non-hydrogen atoms were refined with anisotropic thermal parameters. N(1) of the template molecule in **2** is disordered over two symmetrically related orientations with an interatomic distance of 1.677(5) Å; hence, its occupancy factor is reduced to 50%. The hydrogen atoms of the template cation in **1** were located at geometrically calculated positions and refined with isotropic thermal parameters. The hydrogen atoms of the template cation in **2** were not included in the refinements due to the disorder problem. 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.

Computational Descriptions. Single-crystal structural data of the two compounds were used for the theoretical calculations and our calculations. For convenience, we excluded the template cations. The ab initio band structure calculations and density of states (DOS) were performed using the computer code CASTEP.[28] The code employs density functional theory (DFT) using a plane-wave basis set with Vanderbilt norm-conserving pseudopotentials to approximate the interactions between core and valence electrons.[29] The exchange-correlation energy was calculated using the Perdew−Burke−Ernzerhof modification to the generalized gradient approximation.[30] The number of plane waves included in the basis is determined by a kinetic-energy cutoff of 700 eV for $Zn_2NaCu(SO_3)_4^{2-}$ in **1** or 600 eV for $CdCu_4(SO_3)_4^{2-}$ in **2**. The numerical integration of the Brillouin zone is performed using a 4 × 3 × 2 Monkhorst−Pack k-point sampling for $Zn_2NaCu(SO_3)_4^{2-}$ and a 2 × 2 × 4 one for $CdCu_4(SO_3)_4^{2-}$. Pseudoatomic calculations were performed for O-$2s^22p^4$, S-$3s^23p^4$, Na-$2s^22p^63s^1$, Cu-$3d^{10}4s^1$, Zn-$3d^{10}4s^2$, and Cd-$4d^{10}5s^2$. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code.

Results and Discussion

The reactions of zinc(II) or cadmium(II) acetate and copper(I) bromide with $NaHSO_3$ in the presence of piperazine as the template agent afforded two novel organically templated mixed-metal sulfites with 3D framework structures, namely, $[H_2PiP]$ $[NaZn_2Cu(SO_3)_4]$ (**1**) and $[H_2PiP]$ $[CdCu_4(SO_3)_4]$ (**2**) (pip = piperazine). The two compounds represent the first examples of organically templated mixed-metal sulfites with 3D inorganic skeletons. It is interesting to note that both compounds contain no coordination or lattice water molecules, which is different from $Cu_2Zn(SO_3)_2(H_2O)_2$, $Na_3\{[Cu^I(SO_3)_4][M^{II}(H_2O)_2]_2\}\cdot H_2O$ (M = Zn, Co), $[Na_4(H_2O)_{17}][M^{II}(H_2O)_6]_2\{[Cu^I(SO_3)_4]_2[M(H_2O)_2]_3\}$ (M = Ni, Co), and $Na(H_2O)_6\{[Cu^I(SO_3)_4][Mn^{II}(H_2O)_2]_3\}$. The latter ones were synthesized at room temperature.[24c,25] Hence, the hydrothermal synthesis and the addition of the template amine help the sulfite anions to connect with as many metal centers as possible.

Table 1. Crystal Data and Structural Refinement Parameters for **1** and **2**

	1	**2**
formula	$C_4H_{12}N_2CuZn_2$-NaS_4O_{12}	$C_4H_{12}N_2Cu_4$-CdS_4O_{12}
fw	625.67	775
space group	$P\bar{1}$ (No. 2)	*Pban* (No. 50)
a, Å	7.648(5)	10.318(5)
b, Å	8.518(5)	10.981(5)
c, Å	13.820(7)	7.066(3)
α, deg	91.747(7)	90
β, deg	92.078(4)	90
γ, deg	113.059(7)	90
V, Å^3	826.8(8)	800.6(6)
Z	2	2
D_{calcd}, g cm^{-3}	2.513	3.331
μ, mm^{-1}	4.748	7.132
GOF on F^2	1.011	1.359
R1, wR2 [$I > 2\sigma(I)$][a]	0.0448, 0.1155	0.0371, 0.0816
R1, wR2 (all data)	0.0651, 0.1253	0.0387, 0.0821

[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**[a]

Compound **1**			
Zn(1)−O(6)	1.938(4)	Zn(1)−O(4)#3	1.943(4)
Zn(1)−O(7)#2	1.944(4)	Zn(1)−O(2)	1.963(4)
Zn(2)−O(12)#4	1.947(4)	Zn(2)−O(9)#2	1.955(4)
Zn(2)−O(3)	1.973(4)	Zn(2)−O(10)	1.978(4)
Cu(1)−S(3)	2.286(2)	Cu(1)−S(4)	2.306(2)
Cu(1)−S(1)	2.316(2)	Cu(1)−S(2)	2.319(2)
Na(1)−O(11)#1	2.236(5)	Na(1)−O(5)#1	2.274(5)
Na(1)−O(8)#2	2.305(5)	Na(1)−O(2)	2.454(5)
Na(1)−O(3)	2.553(5)		
Compound **2**			
Cd(1)−O(2)#1	2.343(4)	Cd(1)−O(2)#2	2.343(4)
Cd(1)−O(2)	2.343(4)	Cd(1)−O(2)#3	2.343(4)
Cd(1)−O(1)#1	2.566(5)	Cd(1)−O(1)	2.566(5)
Cd(1)−O(1)#2	2.566(5)	Cd(1)−O(1)#1	2.566(5)
Cu(1)−O(3)#4	2.078(4)	Cu(1)−O(2)#5	2.138(4)
Cu(1)−O(1)#6	2.150(4)	Cu(1)−S(1)	2.155(2)

[a] Symmetry transformations used to generate equivalent atoms. For **1**: #1 x, $y + 1$, z; #2 $x - 1$, y, z; #3 $-x + 1$, $-y$, $-z$; #4 $-x + 1$, $-y$, $-z + 1$. For **2**: #1 $-x + 1/2$, y, $-z$; #2 $-x + 1/2$, $-y + 1/2$, z; #3 x, $-y + 1/2$, $-z$; #4 $-x + 1$, $-y$, $-z + 1$; #5 $-x + 1/2$, y, $-z + 1$ #6 x, $-y + 1/2$, $-z + 1$.

The asymmetric unit of **1** contains two zinc ions, one copper(I) ion, one sodium ion(I), four sulfite anions, and a doubly protonated piperaine cation. As show in Figure 1a, both Zn^{2+} ions are tetrahedrally coordinated by four oxygens from four sulfite anions in a unidentate fashion. The Zn−O bond distances range from 1.938(5) to 1.976(5) Å, which is comparable to those reported for other zinc(II) sulfites.[21,24,25] The Cu^+ ion is also tetrahedrally coordinated but by four S atoms from four SO_3^{2-} anions. The Cu−S bond distances are in the range 2.286(2)−2.318(2) Å, which is comparable to those reported for other copper(I) sulfites.[19] The sodium(I) atom is five-coordinated by one sulfite anion

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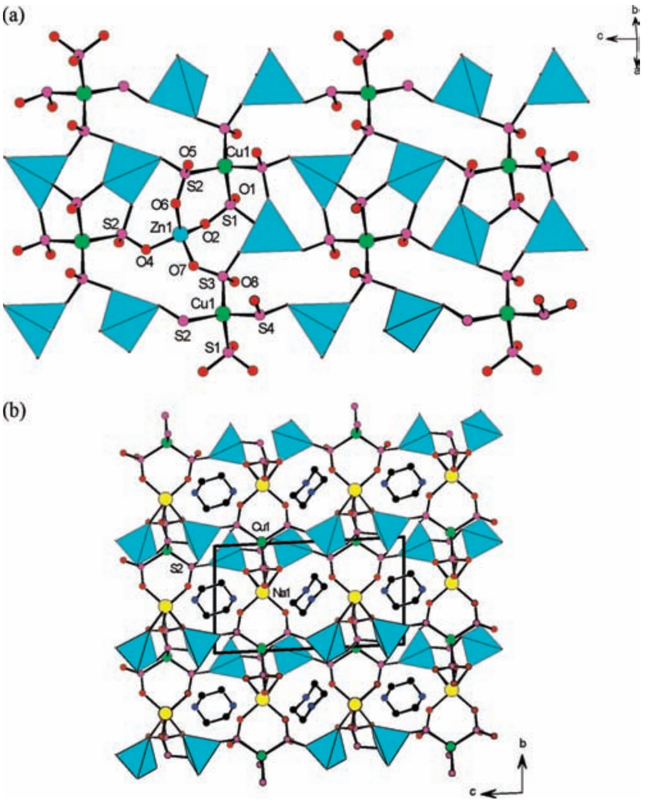
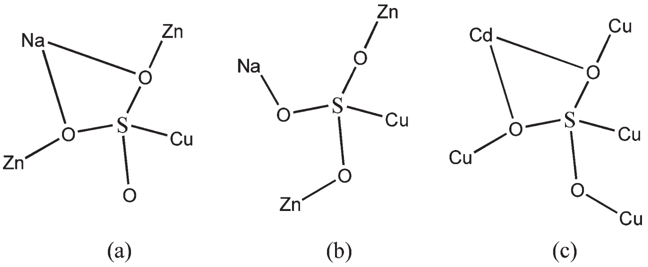


Figure 1. A 2D layer of $Zn_2Cu(SO_3)_4^{3-}$ anions (a) and a view of the structure of **1** along the *a* axis. ZnO4 tetrahedra are shaded in cyan. Cu, Na, S, O, N, and C atoms are represented by green, yellow, pink, red, and blue circles, respectively.

Scheme 1. Coordination Modes of the Sulfite Anions in Compounds **1** and **2**



in a bidentate chelating fashion and three sulfites in a unidentate fashion. The Na−O bond distances are in the range 2.236(5)−2.553(5) Å. There is also one very long Na−O bond of 3.250(5) Å (Na(1)−O(1)). According to the bond valence analyses,[31] both copper and the sodium atoms are +1 in charge; the calculated total bond valences are 1.1 for Cu(1) and 1.15 for Na(1).

The four SO_3^{2-} groups display two different coordinate modes (Scheme 1). The $S(1)O_3^{2-}$ anion is pentadentate; it forms a bidentate chelation with one Na^+ ion and also bridges with two Zn^{2+} ions by using two sulfite oxygen atoms and one Cu^+ ion with a S atom. The third oxygen atom remains noncoordinated (Scheme 1a). The other three sulfite anions adopt the same coordinate mode (Scheme 1b). Each sulfite anion is tetradentate, binding with two Zn^{2+} ions by using two oxygens, a Na^+ ion by using the third oxygen atom, and a Cu^+ ion by using the central sulfur atom (Scheme 1b).

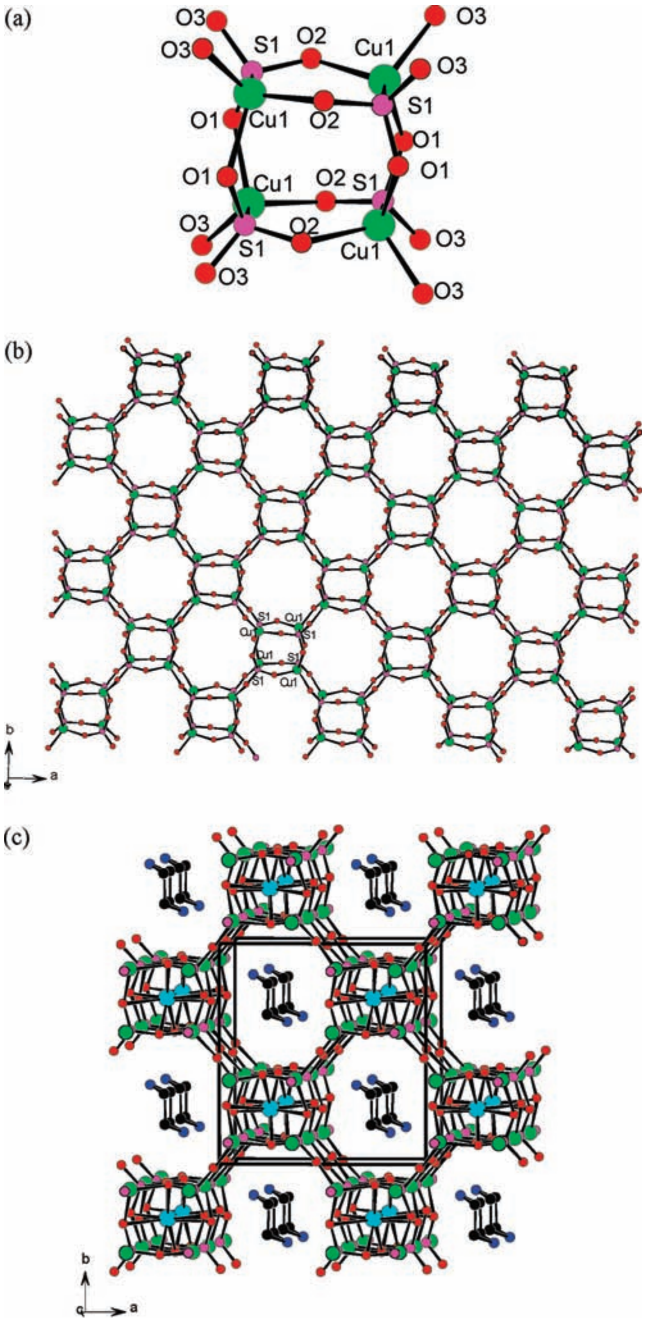


Figure 2. A $[Cu_4(SO_3)_4]^{4-}$ cubanelike cluster (a), a 2D layer based on $[Cu_4(SO_3)_4]^{4-}$ cubanelike clusters, and a view of the structure of **2** along the *c* axis. Cd, Cu, S, O, N, and C atoms are represented by cyan, green, yellow, pink, red, and blue circles, respectively.

The Zn^{2+} and Cu^+ ions are interconnected by bridging sulfite anions into a 2D layer parallel to the *ac* plane (Figure 1a). Neighboring layers are further interconnected by sodium(I) ions via Na−O−S bridges into a 3D network with 1D tunnels of $Na_2S_2Zn_2$ rings. The template cations are located at the above-mentioned 1D tunnels (Figure 1b).

It is should be pointed out that the inorganic anion framework of $\{Na[Zn_2Cu(SO_3)_4]\}$ is different from those of other zinc sulfites containing organic amines as coordination ligands reported previously.[21] In these compounds, low-dimensional 0D clusters and 1D and 2D inorganic subunits are assembled into higher 2D or 3D covalent frameworks by organic ligands, whereas the inorganic framework

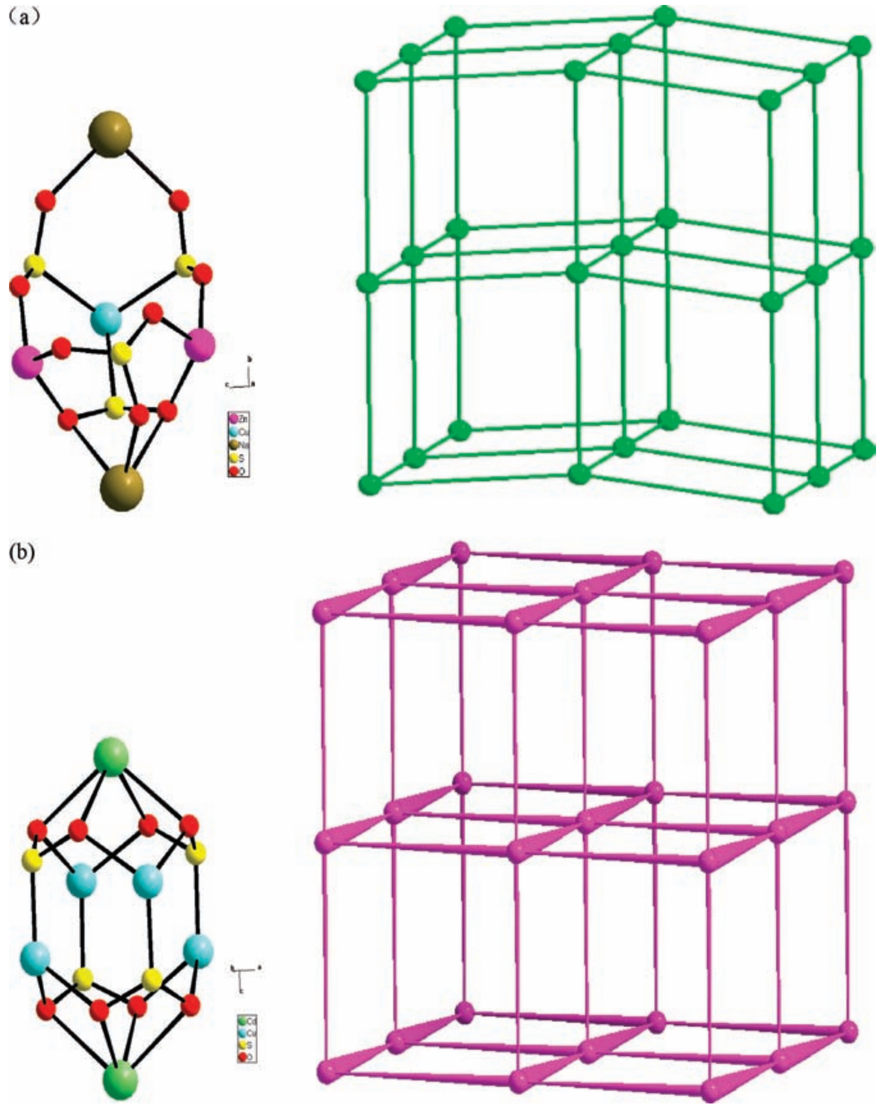


Figure 3. Topological diagrams showing the 3D structures and the nodes in compounds **1** (a) and **2** (b).

of $[(Zn_4(C_6H_{12}N_2)(SO_3)_2)(H_2O)]_4$ is 3D with the DABCO template molecule coordinated to the Zn^{2+} ion. The inorganic anion framework of $\{Na[Zn_2Cu(SO_3)_4]\}^{2-}$ is also different from the purely inorganic Cu−Zn−SO_3 phase reported, the structure of $Cu_2Zn(SO_3)_2(H_2O)_2$ can be considered as the hydrated $[Zn(H_2O)_2]^{2+}$ cations occupying the 1D 8-MR tunnels of the 3D network of $\{Cu_2(SO_3)_2\}^{2-}$ anions,[24c] whereas $Na_3\{[Cu^I(SO_3)_4][Zn^{II}(H_2O)_2]_2\}\cdot H_2O$ features a 1D chain composed of $Cu(SO_3)_4$ units that are bridged by octahedrally coordinated zinc(II) ions.[25]

When $Cd(Ac)_2\cdot 2H_2O$ is used instead of $Zn(Ac)_2\cdot 2H_2O$ in the preparation, compound **2** with a different 3D inorganic skeleton is isolated. The asymmetric unit of **2** consists of eight atoms, six of which belong to the anion framework (Cu, S, three O, and one Cd atom) and two of which are from the piperazine (one N atom and one C atom). The Cd^{2+} ion located at a site of −1 symmetry is eight-coordinated by four sulfites anions in a bidentate chelating fashion. The Cd−O bond distances range from 2.326(5) to 2.615(5) Å. The Cu(I) ion is tetrahedrally coordinated by one S and three O atoms from four separate SO_3^{2-} anions. The Cu−S and Cu−O bond distances are 2.155(2) and 2.072(4)−2.160(4) Å, respectively. These bond distances are comparable to those reported for other copper(I) sulfites.[19] According to the bond valence analyses,[31] the copper atoms are +1 in charge and the cadmium atoms are +2 in charge; the calculated total bond valences are 0.912 for Cu(1) and 1.89 for Cd(1).

The sulfite anion adopts a different coordination mode from those in **1**. It acts as a hexadentate metal linker, forming a bidentate chelation for a Cd^{2+} ion and also bridges with four different Cu^+ ions by using three O and one S atom (Scheme 1c).

The interconnection of Cd(II) and Cu(I) ions via bridging sulfite anions resulted in a novel three-dimensional architecture of $[CdCu_4(SO_3)_4]^{2-}$ anions (Figure 2). Such a 3D inorganic network can be viewed as being built from the $Cu_2(SO_3)_2^{2-}$ double layer based on $Cu_4(SO_3)_4^{4-}$ cubanes interconnected by the Cd^{2+} ions. Each $Cu_4(SO_3)_4^{4-}$ cubane is formed by four Cu^+ ions bridged by four sulfite anions in a tridentate fashion (Figure 2a). Each $Cu_4(SO_3)_4^{4-}$ cubane is connected to four neighboring ones via four pairs of Cu−O−S bridges into a 2D layer parallel to the *ab* plane (Figure 2b). In the view of topology, each cubane is a four-connector; hence, the layer can be considered as a (4,4)-connected layer. Within the 2D layer, there exists eight-membered rings with a size of

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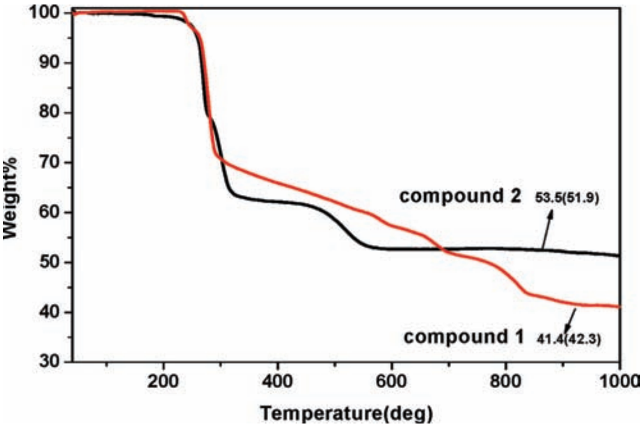

Figure 4. TGA diagrams for compounds **1** and **2**.

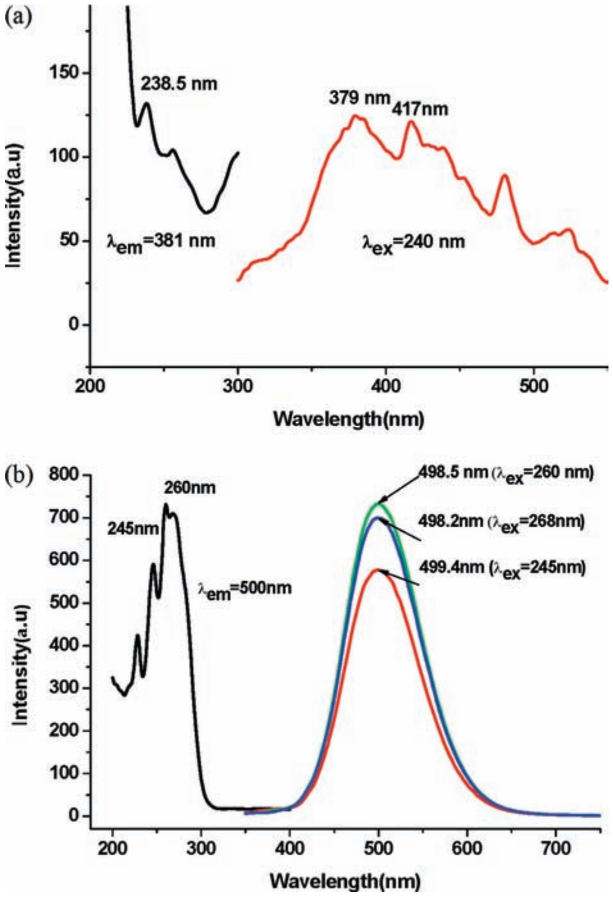

Figure 5. Excitation and emission spectra for compounds **1** (a) and **2** (b).

about 4.69 × 6.10 Å^2. Adjacent layers are interconnected by Cd^{2+} ions into a 3D network with 1D tunnels of 8-MR along the *c* axis (Figure 2c). The Cd^{2+} ion can be viewed as being sandwiched between two $Cu_4(SO_3)_4{}^{4-}$ cubanes. The doubly protonated piperazine cations are located at the above 8-MR tunnels.

To further understand the structures for both compounds, topological structures of both compounds were also investigated (Figure 3). In compound **1**, each $SO_3{}^{2-}$ anion connects with one copper(I) ion and two zinc(II) ions. The copper(I) or zinc(II) ion connects with four $SO_3{}^{2-}$ anions to form a $Zn_2Cu(SO_3)_4$ unit, which can be considered as a four-connected node. Hence, the 2D layer of Zn_2Cu

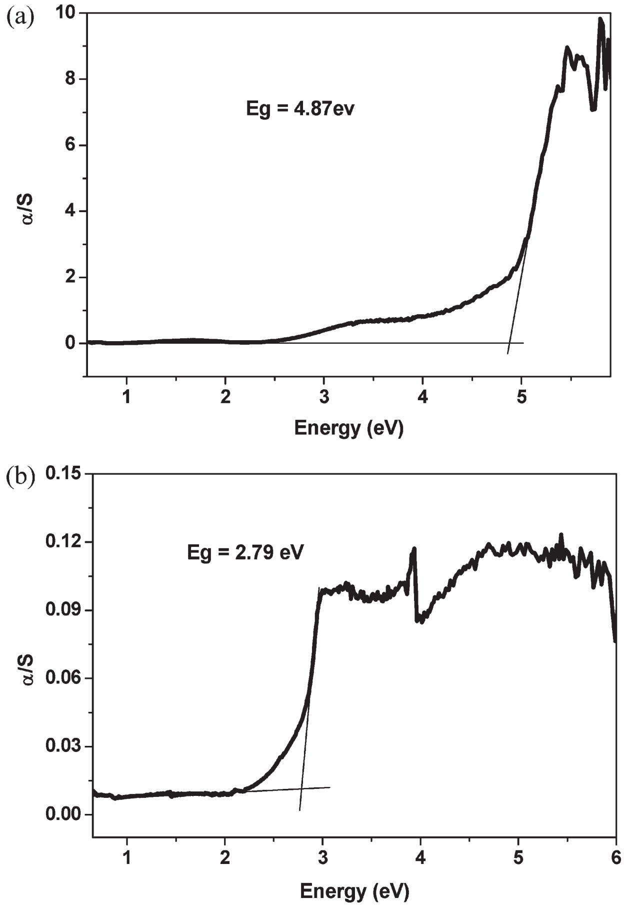

Figure 6. Optical diffuse reflectance spectra for compound **1** (a) and **2** (b).

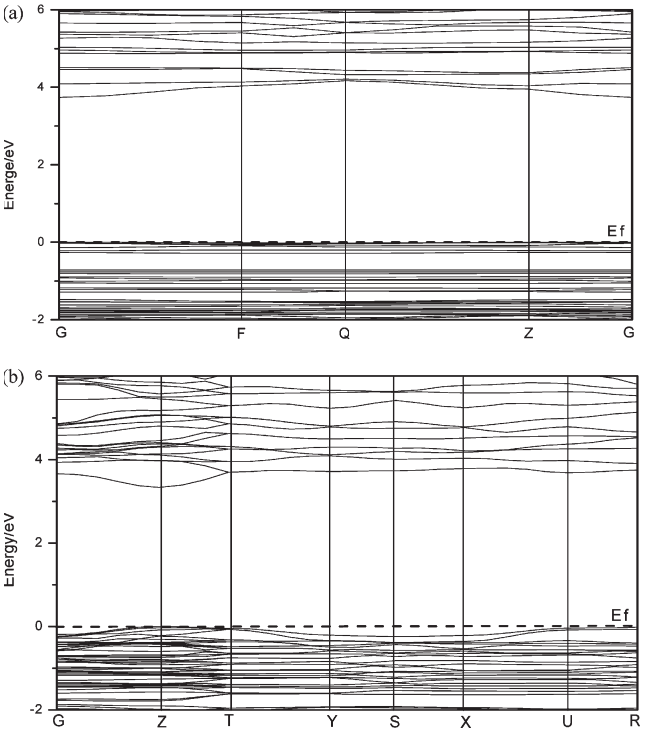

Figure 7. Band structures for $[Zn_2NaCu(SO_3)_4]^{2-}$ in **1** (a) and $[CdCu_4(SO_3)_4]^{2-}$ in **2** (b). The Fermi level is set at 0 eV.

Table 3. State Energies (eV) of the L-CB and the H-VB of the Compounds **1** and **2**

Compound **1**

k point	L-CB	H-VB
G (0.000, 0.000, 0.000)	3.73547	0
F (0.000, 0.500, 0.000)	4.03322	−0.01882
Q(0.000 0.500 0.500)	4.17128	−0.02111
Z(0.000 0.000 0.500)	3.94867	−0.0035
G (0.000, 0.000, 0.000)	3.73547	0

Compound **2**

k point	L-CB	H-VB
G (0.000, 0.000, 0.000)	3.65493	−0.19418
Z (0.000, 0.000, 0.500)	3.33359	0
T (−0.500, 0.000, 0.500)	3.69506	−0.04571
Y (−0.500, 0.000, 0.000)	3.71786	−0.21192
S (−0.500, 0.500, 0.000)	3.7313	−0.24343
X (0.000, 0.500, 0.000)	3.78271	−0.21764
U (0.000, 0.500, 0.500)	3.68295	−0.04019
R (−0.500, 0.500, 0.500)	3.74802	−0.0205

$(SO_3)_4{}^{3-}$ in **1** can be described as a 2D (4,4) topological net. Such 2D (4,4) nets are further interlinked by sodium(I) ions into an α-Po topology (Figure 3a). Similarly for compound **2**, each $SO_3{}^{2-}$ group connects with four copper(I) ions and one cadmium ion, and each cadmium(II) or copper(I) ion binds with four $SO_3{}^{2-}$ anions. Thus, the coop-like $CdCu_4(SO_3)_4$ unit can also be considered as a node. Such units are further interlinked into a 3D network, which can also be considered to be the pcu topology with a vertex symbol of $4^{12}.6^3$ (Figure 3b).[32]

The IR spectra of compounds **1** and **2** display absorption bands associated with the template cations at 1595 and 1459 cm^{-1} and 1580 and 1425 cm^{-1}, respectively.[18b] The characteristic bands of the sulfite ions in compounds **1** and **2** appear at around 938−1110(ν_1), 653−659(ν_2), 586−633(ν_3), and 505−506(ν_4) cm^{-1}.[19]

TGA analyses under a nitrogen atmosphere indicate that compounds **1** and **2** are stable up to 200 °C and 240 °C, respectively (Figure 4). Compound **1** exhibits one main step of continued decomposition in the temperature range of 200−940 °C; the weight loss corresponds to liberation of the SO_2 and pip molecules. The observed weight loss of 41.4% is close to the calculated one (42.3%). For compound **2**, the total weight loss at 1000 °C is 51.9%, which corresponds to the release of SO_2 and pip molecules with a calculated weight loss of 53.5%. The final residues were not characterized due to their melting with the TGA bucket made of Al_2O_3 under such a high temperature.

The excitation spectra of compounds **1** and **2** showed maximum peaks at 238.5 and 260 nm under the emission at 381 and 500 nm, respectively (Figure 5). Both compounds display a broad emission band in the ultraviolet or blue light region (379−417 and 498.5 nm, respectively, for **1** and **2**) under excitation at 240 and 260 nm, respectively. These emission bands probably originate from ligand-to-metal charge transfer or metal-to-ligand charge transfer.[23,33] Compound **2** may be potential materials for blue-light-emitting diode devices.

Optical reflectance spectrum measurements indicate that the band gaps of compounds **1** and **2** are approximately 4.87 and 2.79 eV, respectively (Figure 6). Hence, compound **1** is an insulator, whereas compound **2** is a semiconductor.

Theoretical Studies. To further understand the chemical bonding in both compounds, the band structure as well as DOS calculations for the 3D $Zn_2NaCu(SO_3)_4{}^{2-}$ and $CdCu_4(SO_3)_4{}^{2-}$ anions based on the DFT method were made by using the computer code CASTEP.[28]

The calculated band structures of $Zn_2NaCu(SO_3)_4{}^{2-}$ and $CdCu_4(SO_3)_4{}^{2-}$ along high symmetry points of the first Brillouin zone are plotted in Figure 7. As is shown in Figure 7a, the top of the valence bands (VBs) is almost flat, whereas the bottom of the conduction bands (CBs) displays a small dispersion for the $Zn_2NaCu(SO_3)_4{}^{2-}$ anion. Both the lowest energy (3.72 eV) and the highest energy (0.0 eV) of CBs are located at the G point. Hence, the $Zn_2NaCu(SO_3)_4{}^{2-}$ anion has a direct band gap of around 3.72 eV. Both the top of the VBs and the bottom of the CBs show a small dispersion for $CdCu_4(SO_3)_4{}^{2-}$. The lowest energy (3.33 eV) of CBs is located at the Z point, and the highest energy (0.0 eV) of VBs is located at the Z point. Accordingly, the $CdCu_4(SO_3)_4{}^{2-}$ anion displays a direct band gap of around 3.33 eV (Figure 7b). The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of both compounds are listed in Table 3. The calculated band gaps of both compounds are somehow different from the experimental values (4.87 and 2.79 eV, respectively, for compounds **1** and **2**). This is not surprising, as it is well-known that the generalized gradient approximation does not accurately describe the eigenvalues of the electronic states, which causes quantitative underestimation of the band gaps, especially for insulators.[34] Furthermore, our calculations excluded the effects of the template cations. The bands can be assigned according to the total and partial DOS, as plotted in Figure 8. For $Zn_2NaCu(SO_3)_4{}^{2-}$, the CBs above the Fermi level are mainly derived from O-2p, S-3p, Zn-4s, and Zn-4p states. The VBs from −4.67 eV to the Fermi level are mainly composed of O-2p and Cu-3d states, and those from −10.38 eV to −4.67 eV are mainly composed of Zn-3d and S-3P states. The lowest VBs ranging from −23.1 to −17.6 eV arise from mostly O-2s and Na-2p states. For $CdCu_4(SO_3)_4{}^{2-}$, the bands above the Fermi level are mainly derived from O-2P, S-3p, Cu-4s, and Cu-4p states. The VBs from −4.7 eV to the Fermi level are mainly composed of O-2p and Cu-3d states, whereas the O-2p, S-3p, and Cd-4d states dominate the VBs ranging from −10.3 to −5.2 eV. In addition, the VBs near −17.7 and −21.5 eV are mainly composed of O-2s, S-3s, and S-3p states.

Population analyses allow for a more quantitative bond analysis. The calculated bond orders of Zn−O, Cu−S, Na−O, and S−O bonds are 0.28−0.33, 0.36−0.41, 0.14−0.17, and 0.32−0.59 e, respectively, for $Zn_2NaCu(SO_3)_4{}^{2-}$. Hence, we can say that Zn−O and Cu−S bonds are more

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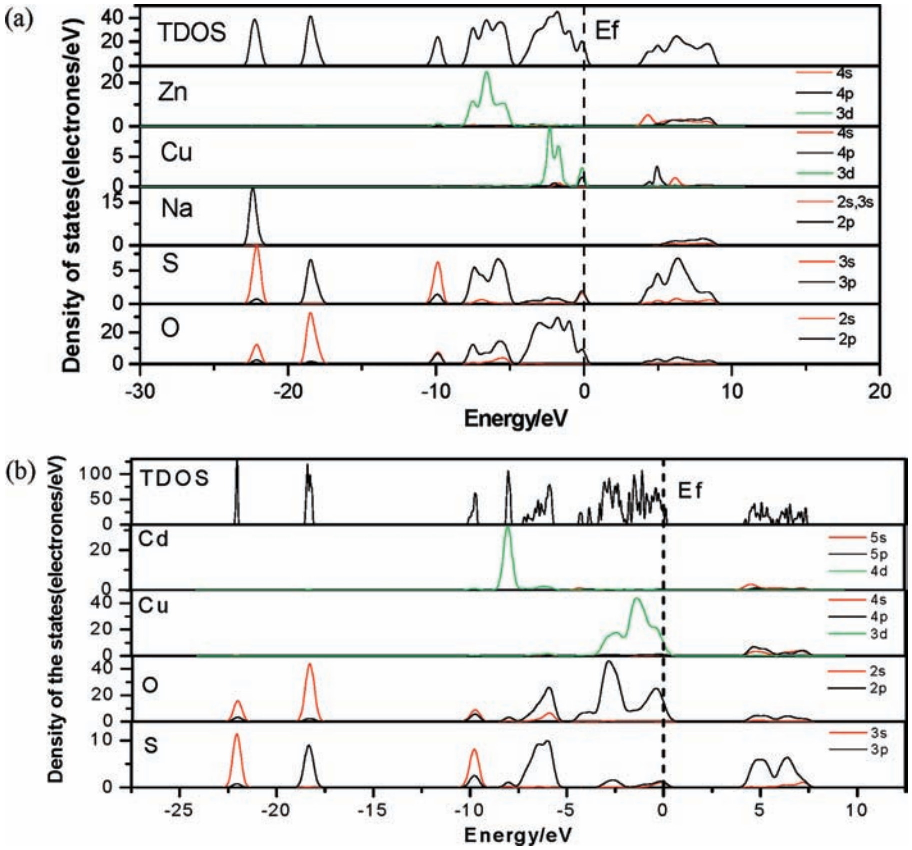

Figure 8. Total density of states and partial density of states of $[Zn_2NaCu(SO_3)_4]^{2-}$ (a) and $[CdCu_4(SO_3)_4]^{2-}$ (b). The Fermi level is set at 0 eV.

covalent, whereas Na−O bonds have more ionic character. For $CdCu_4(SO_3)_4^{2-}$, the calculated bond orders of Cd−O, Cu−S, Cu−O, and S−O bonds are 0.11, 0.44, 0.19−0.30, and 0.42−0.49 e, respectively. Accordingly, we can say that the covalent character of the Cu−S bond is larger than that of the Cu−O bond.

In summary, the first organically templated copper(I) sulfites with additional d^{10} transition metal ions and 3D open frameworks have been successfully prepared. In both compounds, the sulfite anions act as both a hard and soft ligand simultaneously. The sulfur(IV) atoms are bonded solely with copper(I) ions, whereas the oxygen atoms can bond with either Zn^{2+}/ Cd^{2+} or Cu^{+} ions. Both compounds are not SHG-active because of the centro-symmetrical structures. The lone pair electrons of the S(IV) atoms are not stereoactive due to their participation in the Cu−S bonding. However, we can choose other "hard" metal ions which do not like to form M−S bonds, and it may be still possible to design SHG materials in the future.

It is expected that other organic template mixed-metal sulfites with various types of open framework structures and novel physical properties can be synthesized using this synthetic route.

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Supporting Information Available: X-ray crystallographic files in CIF format, simulated and experimental XRD powder patterns, and IR spectra for compounds **1** and **2**. These materials are available free of charge via the Internet at http://pubs.acs.org.