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Article

Coordination Polymers and Hybrid Networks of Different Dimensionalities Formed by Metal Sulfites

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In our effort to explore the use of the sulfite ion to design hybrid and open-framework materials, we have been able to prepare, under hydrothermal conditions, zero-dimensional $[Zn(C_{12}H_8N_2)(SO_3)]\cdot 2H_2O$, **I** ($a = 7.5737(5)$ Å, $b = 10.3969(6)$ Å, $c = 10.3986(6)$ Å, $\alpha = 64.172(1)°$, $\beta = 69.395(1)°$, $\gamma = 79.333(1)°$, $Z = 2$, and space group $P\bar{1}$), one-dimensional $[Zn_2(C_{12}H_8N_2)(SO_3)_2(H_2O)]$, **II** ($a = 8.0247(3)$ Å, $b = 9.4962(3)$ Å, $c = 10.2740(2)$ Å, $\alpha = 81.070(1)°$, $\beta = 80.438(1)°$, $\gamma = 75.66(5)°$, $Z = 2$, and space group $P\bar{1}$), two-dimensional $[Zn_2(C_{10}H_8N_2)(SO_3)_2]\cdot H_2O$, **III** ($a = 16.6062(1)$ Å, $b = 4.7935(1)$ Å, $c = 19.2721(5)$ Å, $\beta = 100.674(2)°$, $Z = 4$, and space group $C2/c$), and three-dimensional $[Zn_4(C_6H_{12}N_2)(SO_3)_4(H_2O)_4]$, **IV** ($a = 11.0793(3)$ Å, $c = 8.8246(3)$ Å, $Z = 2$, and space group $P42nm$), of which the last three are coordination polymers. A hybrid open-framework sulfite–sulfate of the composition $[C_2H_{10}N_2][Nd(SO_3)(SO_4)(H_2O)]_2$, **V** ($a = 9.0880(3)$ Å, $b = 6.9429(2)$ Å, $c = 13.0805(5)$ Å, $\beta = 91.551(2)°$, $Z = 2$, and space group $P2_1/c$), with a layered structure containing metal–oxygen–metal bonds has also been described.

Introduction

Coordination polymers, open-framework materials, and hybrid compounds built up with various anions have been described in the literature. The most common anions employed in open-framework structures are silicates and phosphates.[1−3] Metal carboxylates with a variety of structures and dimensionalities have also been described in the recent literature.[4,5] In recent years, other oxyanions such as sulfate, selenate, selenite, and tellurite have also been employed to design these structures.[6,7] Surprisingly, coordination polymers and open-framework structures employing the sulfite ion do not appear to have been synthesized and characterized hitherto. This is not entirely surprising since the sulfur atom in the sulfite ion is in the 4+ oxidation state, which is relatively unstable under hydrothermal and acidic conditions. The sulfite ion gets readily oxidized to the sulfate ion. It is possible that in the sulfite-based materials, the lone pair of electrons may act as an invisible structure-directing agent. Due to the lone pair, many of the compounds analogous to the sulfites such as selenites and tellurites crystallize in noncentrosymmetric structures, with interesting nonlinear physical properties, such as second harmonic generation.[8]

In this article, we describe the synthesis and structures of the first examples of metal sulfite-based coordination polymers and hybrid structures with different dimensionalities between one and three as well as a zero-dimensional coordination compound. These compounds have the compositions $[Zn(C_{12}H_8N_2)(SO_3)]\cdot 2H_2O$, **I**, $[Zn_2(C_{12}H_8N_2)(SO_3)_2(H_2O)]$, **II**, $[Zn_2(C_{10}H_8N_2)(SO_3)_2]\cdot H_2O$, **III**, and $[Zn_4(C_6H_{12}N_2)(SO_3)_4(H_2O)_4]$, **IV**. In addition, we have obtained a layered sulfite−sulfate, $[C_2H_{10}N_2][Nd(SO_3)(SO_4)(H_2O)]_2$, **V**, containing metal−oxygen−metal bonds. The present results suggest

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Table 1. Crystal Data and Structure Refinement Parameters for **I**−V

structure params	**I**	**II**	**III**	**IV**	**V**
empirical formula	$ZnSO_5N_2C_{12}H_{12}$	$Zn_2S_2O_7N_2C_{12}H_{10}$	$Zn_2S_2O_7N_2C_{10}H_{10}$	$Zn_4S_4O_{16}N_2C_6H_{20}$	$Nd_2S_4O_{16}N_2C_2H_{14}$
fw	361.67	489.08	465.06	765.96	738.87
crystal syst	triclinic	triclinic	monoclinic	tetragonal	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No.15)	$P42nm$ (No. 102)	$P2_1/c$ (No. 14)
a /Å	7.5737(5)	8.0247(3)	16.6062(1)	11.0793(3)	9.0880(3)
b /Å	10.3969(6)	9.4962(3)	4.7935(1)	11.0793(3)	6.9429(2)
c /Å	10.3986(6)	10.2740(2)	19.2721(5)	8.8246(3)	13.0805(5)
α /deg	64.172(1)	81.070(1)	90	90	90
β /deg	69.395(1)	80.438(1)	100.674(2)	90	91.551(2)
γ /deg	79.333(1)	75.66(5)	90	90	90
V /Å^3	689.38(7)	742.63(4)	1507.55(5)	1083.23(6)	825.04(5)
Z	2	2	4	2	2
D (calc)/g cm^{-3}	1.742	2.187	2.049	2.348	2.974
μ /mm^{-1}	1.955	3.554	3.495	4.839	6.816
total data collected	2822	3095	2897	4268	13359
unique data	1931	2115	1084	763	1514
R indices R_1,[a] R_2[b] [$I > 2\sigma(I)$]	0.0387, 0.0978	0.0369, 0.0946	0.0248, 0.0642	0.0272, 0.0706	0.0175, 0.0472
R indices R_1,[a] R_2[b] (all data)	0.0417, 0.0993	0.0399, 0.0957	0.0267, 0.0650	0.0293, 0.0726	0.0176, 0.0473

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0402$ and $b = 0.0$ for **I**, $a = 0.0567$ and $b = 0.0$ for **II**, $a = 0.0369$ and $b = 0.7579$ for **III**, $a = 0.0396$ and $b = 0.1992$ for **IV**, and $a = 0.0225$ and $b = 1.710$ for **V**.

that it should be possible to utilize the sulfite ion to build up hybrid network materials.

Experimental Section

Synthesis. Ammonium sulfite monohydrate, 4,4′-bipyridyl, 1,4-diazabicyclo[2.2.2]octane (DABCO), neodymium(III) nitrate hexahydrate (Aldrich), 1,10-phenanthroline, ethylenediamine (SD Fine, India), and zinc acetate dihydrate (Qualigens, India) of high purity were used for the synthesis.

Compounds **I**−**V** were synthesized by the hydrothermal method by heating the homogenized reaction mixture in a 23 mL (for **IV**, 7 mL) PTFE-lined bomb at 125 °C (for **V**, 150 °C) over a period of 72 h (for **IV**, 120 h) under autogenous pressure. The pH of the starting reaction mixture was 7, and the pH after the reaction showed little change. The products of the hydrothermal reactions were vacuum-filtered and dried under ambient conditions. The products, containing light yellow block-shaped crystals in the case of **I** and **II**, colorless flakes in **III** and **IV**, and needle-shaped pink crystals of **V**, were isolated in 50−60% yield. The compositions of the starting mixtures for **I**−**V** were as follows: **I**, $Zn(OAc)_2{\cdot}2H_2O$ (0.2194 g, 1 mmol), $(NH_4)_2SO_3{\cdot}H_2O$ (0.2683 g, 2 mmol), ethylenediamine (0.07 mL, 1 mmol), 1,10-phenanthroline (0.1982 g, 1 mmol), and H_2O (5 mL, 278 mmol); **II**, $Zn(OAc)_2{\cdot}2H_2O$ (0.2194 g, 1 mmol), $(NH_4)_2SO_3{\cdot}H_2O$ (0.2683 g, 2 mmol), ethylenediamine (0.07 mL, 1 mmol), 1,10-phenanthroline (0.0660 g, 0.333 mmol), and H_2O (5 mL, 278 mmol); **III**, $Zn(OAc)_2{\cdot}2H_2O$ (0.1097 g, 0.5 mmol), $(NH_4)_2SO_3{\cdot}H_2O$ (0.1342 g, 1 mmol), ethylenediamine (0.034 mL, 0.5 mmol), 4,4′-bipyridyl (0.0195 g, 0.125 mmol), and H_2O (5 mL, 278 mmol); **IV**, $Zn(OAc)_2{\cdot}2H_2O$ (0.0768 g, 0.35 mmol), $(NH_4)_2SO_3{\cdot}H_2O$ (0.0536 g, 0.4 mmol), DABCO (0.0112 g, 0.1 mmol), and H_2O (2 mL, 111 mmol); and **V**, $Nd(NO_3)_3{\cdot}6H_2O$ (0.2192 g, 0.5 mmol), $(NH_4)_2SO_3{\cdot}H_2O$ (0.1342 g, 1 mmol), ethylenediamine (0.02 mL, 0.25 mmol), and H_2O (5 mL, 278 mmol).

Characterization. CHNS analysis was carried using the Thermo Finnigan FLASH EA 1112 CHNS analyzer. Energy dispersive analysis of X-rays (EDAX) was carried using the OXFORD EDAX system. Infrared spectroscopic studies of KBr pellets were recorded in the mid-IR region (Bruker IFS-66v). Thermogravimetric analysis was carried out (Metler-Toledo) in nitrogen atmosphere (flow rate = 50 mL/min) in the temperature range of 25−900 °C (heating rate = 10 °C/min).

The structural compositions of **I**−**V** are consistent with the elemental analysis. For **I**, $ZnSO_5N_2C_{12}H_{12}$, Anal. Calcd: C, 39.85; H, 3.34; N, 7.74; S, 8.87. Found: C, 39.72; H, 3.28; N, 7.72; S, 8.81. For **II**, $Zn_2S_2O_7N_2C_{12}H_{10}$, Anal. Calcd: C, 29.47; H, 2.06; N, 5.73; S, 13.11. Found: C, 29.55; H, 2.11; N, 5.69; S, 13.15. For **III**, $Zn_2S_2O_7N_2C_{10}H_{10}$, Anal. Calcd: C, 25.83; H, 2.17; N, 6.02; S, 13.79. Found: C, 25.75; H, 2.08; N, 6.15; S, 13.84. For **IV**, $Zn_4S_4O_{16}N_2C_6H_{20}$, Anal. Calcd: C, 9.40; H, 2.63; N, 3.66; S, 16.75. Found: C, 9.27; H, 2.78; N, 3.65; S, 13.78. For **V**, $Nd_2S_4O_{16}N_2C_2H_{14}$, Anal. Calcd: C, 3.25; H, 1.91; N, 3.79; S, 17.36. Found: C, 3.19; H, 1.87; N, 3.66; S, 17.28. EDAX gave the expected metal/sulfur ratios of 1:1 for **I**−**IV** and of 1:2 for **V**.

Infrared spectra of **I**−**IV** showed the characteristic bands of the SO_3^{2-} ion[9] around 970(ν_1), 620(ν_2), 930(ν_3), and 470(ν_4) cm^{-1}. The spectra of **I**−**III** showed the C−H stretching bands of the aromatic ring[10,11] in the region of 3090−3000 cm^{-1}. In **IV**, the C−H stretching vibrations of the methylene group of DABCO molecule were observed[10] around 2870 and 2850 cm^{-1}, in addition to the bands, due to the bending modes. In **V**, in addition to the SO_3^{2-} bands, bands in the regions of 1015−850 and 640−580 cm^{-1} due to the SO_4^{2-} ion were observed.[11]

X-ray Diffraction and Crystal Structures. Powder XRD patterns of the products were recorded using Cu Kα radiation (Rich-Seifert, 3000TT). The patterns agreed with those calculated by single-crystal structure determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 40

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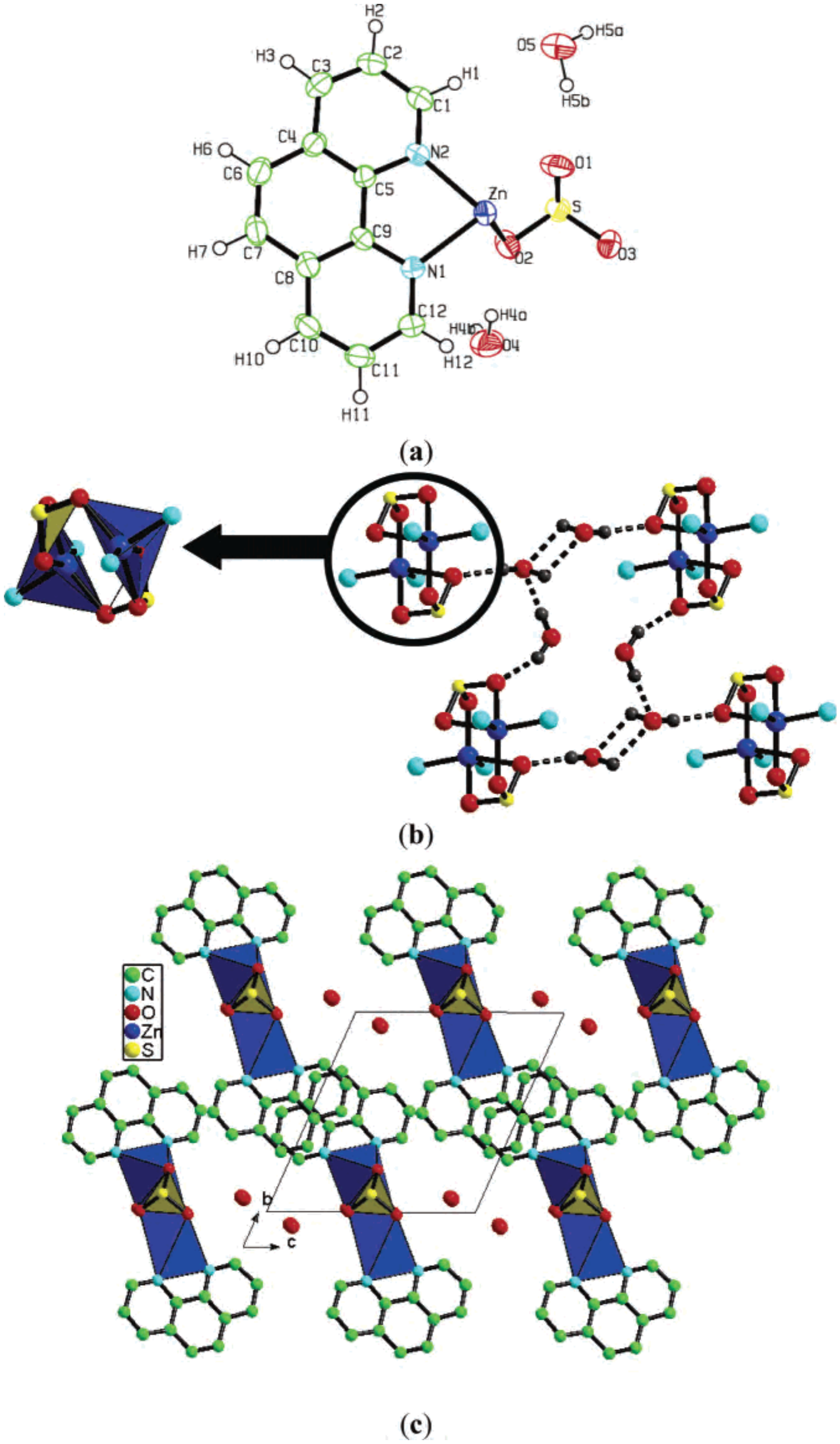

Figure 1. (a) ORTEP diagram (at 50% probability) of **I** showing the atom-labeling scheme. (b) $Zn_2S_2O_6N_4$ polyhedra and the hydrogen-bonded network. (c) Packing diagram, viewed along the *a*-axis of **I**.

kV and 40 mA. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.[12] The structure was solved and refined using the WinGX suite of programs.[13] The graphic programs[14,15] DIAMOND and ORTEP were used to draw the structures. The final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. The aromatic hydrogen atoms for **I**−**III**, methylene hydrogen atoms of the DABCO unit (for **IV**), and ethylenediammonium ion (for **V)** were introduced in the

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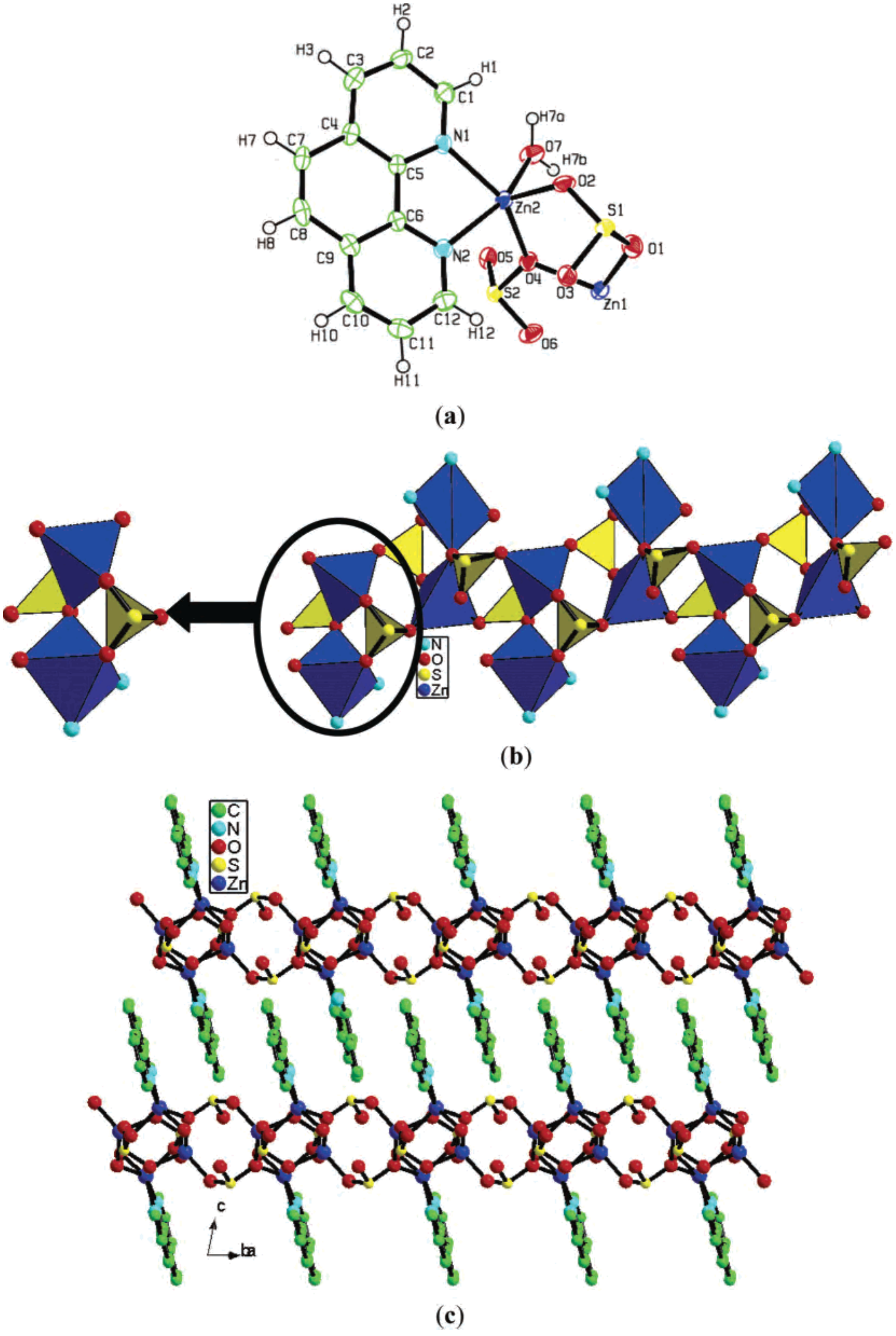


Figure 2. (a) ORTEP diagram (at 50% probability) of **II** showing the atom-labeling scheme. (b) Polyhedral representation of $Zn_2S_2O_9N_2$ unit and the one-dimensional chain. (c) Packing diagram, viewed along ∼*b*-axis of **II**.

calculated positions and refined isotropically. Hydrogens of the water molecules were located by difference-Fourier maps and included in the final refinement. The O−H bond lengths of all the water molecules were constrained to 0.950 Å. Details of the structure solution and final refinements for compounds **I**−**V** are given in Table 1.

Results and Discussion

We have obtained three zinc sulfite-based coordination polymers involving different amines. The structure is one-dimensional with phenanthroline, two-dimensional with 4,4′-bipyridine, and three-dimensional with DABCO. With

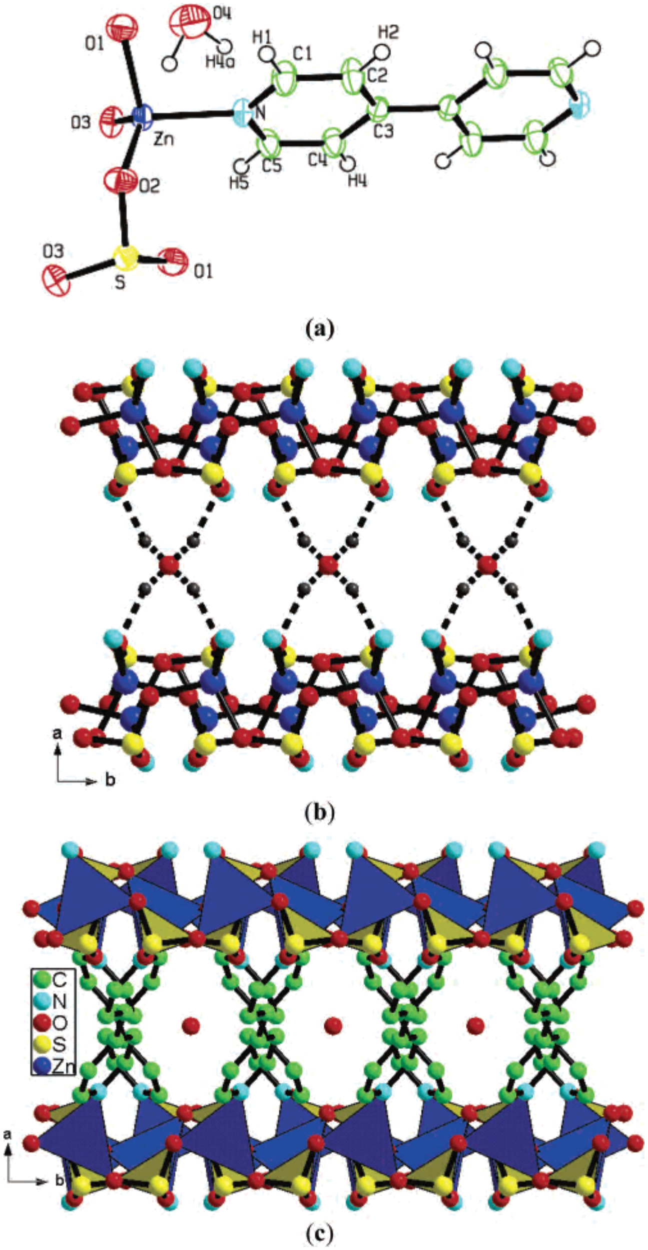


Figure 3. (a) ORTEP diagram (at 50% probability) of **III** showing the atom-labeling scheme. (b) Ball-and-stick representation of the two-dimensional hydrogen-bonded network. (c) Packing diagram of **III**, viewed along the *c*-axis.

phenanthroline, we have also obtained a zero-dimensional coordination compound. The zero-dimensional compound has the formula $[Zn(C_{12}H_8N_2)(SO_3)]{\cdot}2H_2O$ (**I**), with an asymmetric unit containing 21 non-hydrogen atoms wherein one crystallographically distinct Zn^{2+} ion, one SO_3^{2-} ion, one phenanthroline group (C1−C12, N1 and N2), and two water molecules are present (Figure 1a). The zinc ion is five-coordinated to three oxygens of the sulfite ion and two nitrogens of phenanthroline. The Zn−O and Zn−N bond distances are in the range of 2.028(3)−2.265(3) Å. The ZnO_3N_2 polyhedron shares an edge and a corner of two different sulfite ions forming $Zn_2S_2O_6N_4$ units (Figure 1b), which are hydrogen bonded to two water molecules along the *b*- and *c*-axes with O−O distances in the range of 2.765(6)−2.867(7) Å. The molecular units are packed along the *a*-axis with π−π interactions between the phenanthroline rings (Figure 1c), the shortest C−C distance being 3.433(3) Å.

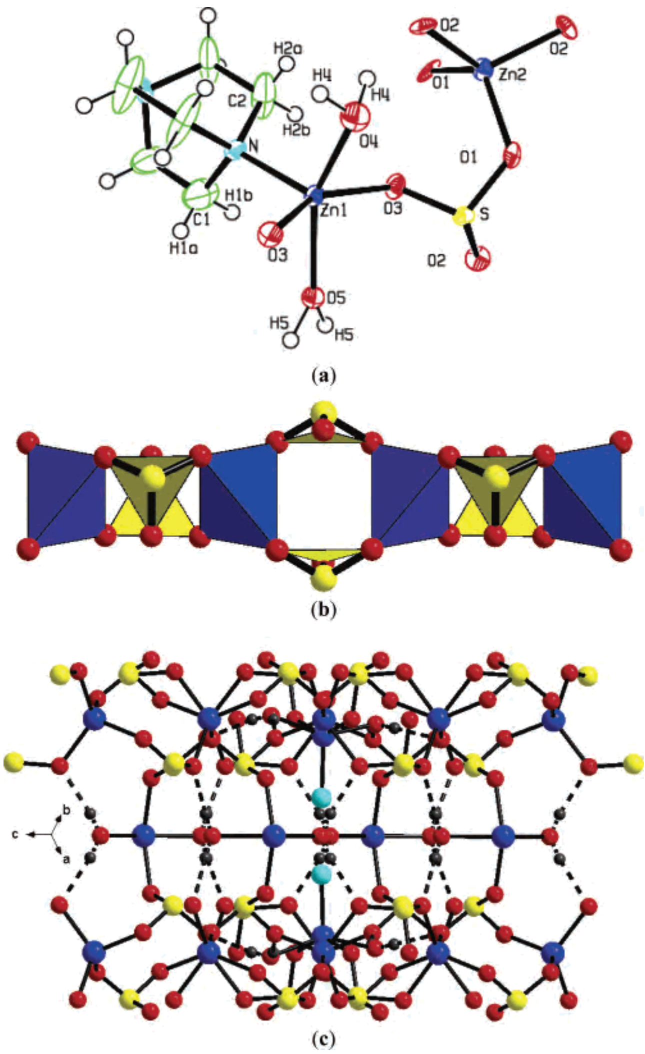
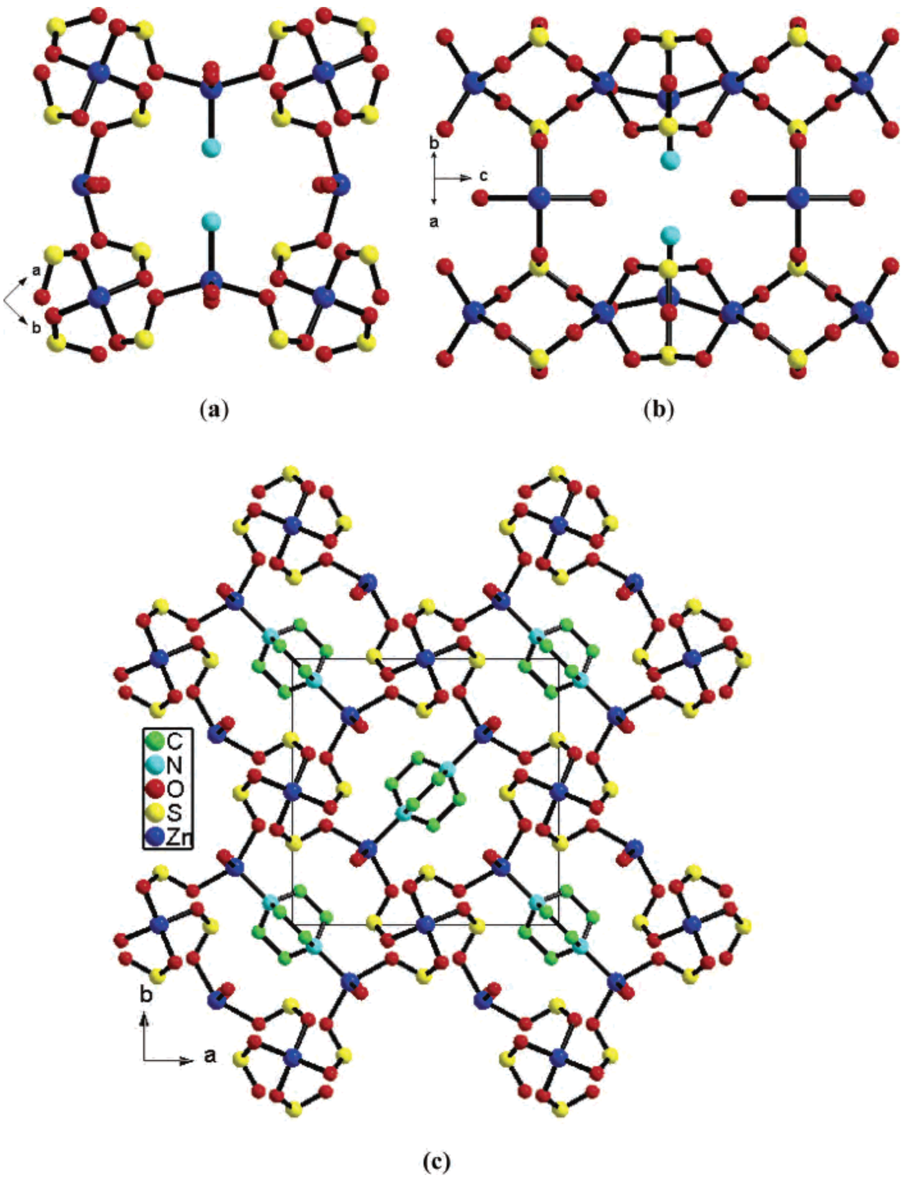


Figure 4. (a) ORTEP diagram (at 50% probability) of **IV** showing the atom-labeling scheme. (b) Polyhedral representation of the twisted chain. (c) Three-dimensional hydrogen-bonded network of **IV**.

$[Zn_2(C_{12}H_8N_2)(SO_3)_2(H_2O)]$, **II**, is a one-dimensional compound with an asymmetric unit of 25 non-hydrogen atoms containing two crystallographically distinct Zn^{2+} ions, two SO_3^{2-} ions, one phenanthroline unit, and one water molecule (Figure 2a). The Zn1 ion is tetrahedrally coordinated to the oxygens of the sulfite ions, whereas the Zn2 ion is five-coordinated to two oxygens of the sulfite, two nitrogens of the phenanthroline, and a water molecule. The Zn−O and Zn−N bond distances are in the range of 1.953(3)−2.156(3) Å. The $Zn1O_4$ tetrahedron and the $Zn2O_3N_2$ polyhedron share an oxygen of one sulfite ion and are connected to two of the sulfite ions forming $Zn_2S_2O_9N_2$ units (Figure 2b), which share corners along the *a*-axis to form a one-dimensional chain (Figure 2b). The chains are hydrogen bonded to water molecules along the *b*-axis forming a two-dimensional layer along the *a*-axis allowing π−π interaction (with the shortest C−C distance of 3.468(3) Å) between the phenanthroline units (Figure 2c). There is O···H···O hydrogen bonding between water and sulfite oxygens within the



(a) (b)

(c)

Figure 5. (a) Two-dimensional micropore, viewed along the *c*-axis. (b) Two-dimensional micropore, viewed along the *ab*-plane. (c) Three-dimensional packing diagram, viewed along the *c*-axis of **IV**.

same chain or in the adjacent chain. The O−O distances are in the range of 2.750(4)−2.881(4) Å. The chain compound **II** has a lower water content (or lower H_2O/Zn ratio) component compared with the molecular compound **I**.

$[Zn_2(C_{10}H_8N_2)(SO_3)_2]\cdot H_2O$, **III**, is a two-dimensional compound with an asymmetric unit of 11.5 non-hydrogen atoms containing one crystallographically distinct Zn^{2+} ion, one SO_3^{2-} ion, half of the 4,4′-bipyridine unit, and half of a water molecule (Figure 3a). The Zn atom at the 8*f* crystallographic position is tetrahedrally coordinated to three oxygens of the sulfite ion and a nitrogen atom. The Zn−O and Zn−N bond distances are in the 1.940(2)−2.037(2) Å range. Each ZnO_3N tetrahedron is connected to three different sulfite ions, and each sulfite ion is coordinated to three different Zn ions, forming a one-dimensional ladder along the *b*-axis. The ladders are hydrogen bonded to the water molecules with a O−O distance of 2.956(4) Å along the *a*-axis forming a two-dimensional hydrogen-bonded network (Figure 3b). The hydrogen-bonded layers are diagonally connected by the 4,4′-bipyridine units to the *ac*-plane forming the two-dimensional layered structure (Figure 3c).

$[Zn_4(C_6H_{12}N_2)(SO_3)_4(H_2O)_4]$, **IV**, is a three-dimensional compound, crystallizing in the noncentrosymmetric space group *P*4$_2$*nm* (No. 103). The asymmetric unit of **IV** contains eight non-hydrogen atoms with two crystallographically distinct Zn^{2+} ions with half occupancy, one SO_3^{2-} ion, one-quarter of the DABCO molecule, and one water molecule (Figure 4a). The Zn1 atom at the 4*c* crystallographic position is five-coordinated to an oxygen of the sulfite ion, two oxygens of the water molecules, and a nitrogen atom. The Zn2 atom at the 4*b* crystallographic position is tetrahedrally coordinated to two oxygens of the sulfite ion. The Zn−O and Zn−N bond distances are in the range of 1.969(7)−2.11(1) Å. Each $Zn2O_4$ tetrahedron shares its corners with four different sulfites, forming a twisted one-dimensional ladder along the *c*-axis (Figure 4b). The ladders are connected through $Zn1O_4N$ polyhedra by the sharing of two corners along the *ab*-plane as well as along the diagonal to the *ab*-

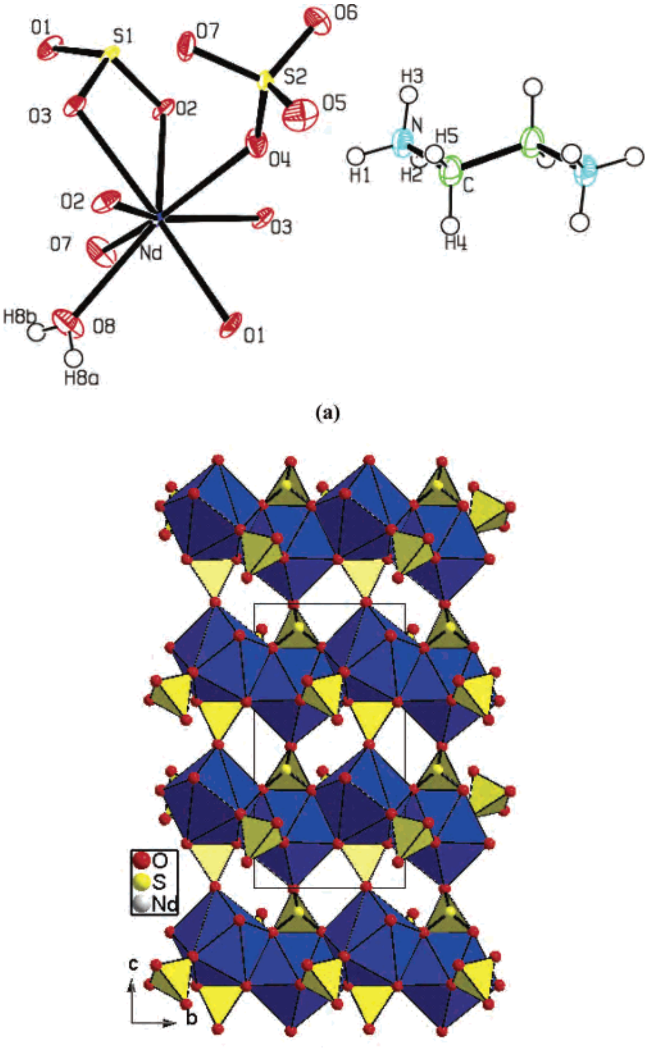


Figure 6. (a) ORTEP diagram (at 50% probability) of **V** showing the atom-labeling scheme. (b) Polyhedral representation of the anionic layer, $[Nd(SO_3)(SO_4)(H_2O)]^-$, viewed along the *c*-axis of **V**.

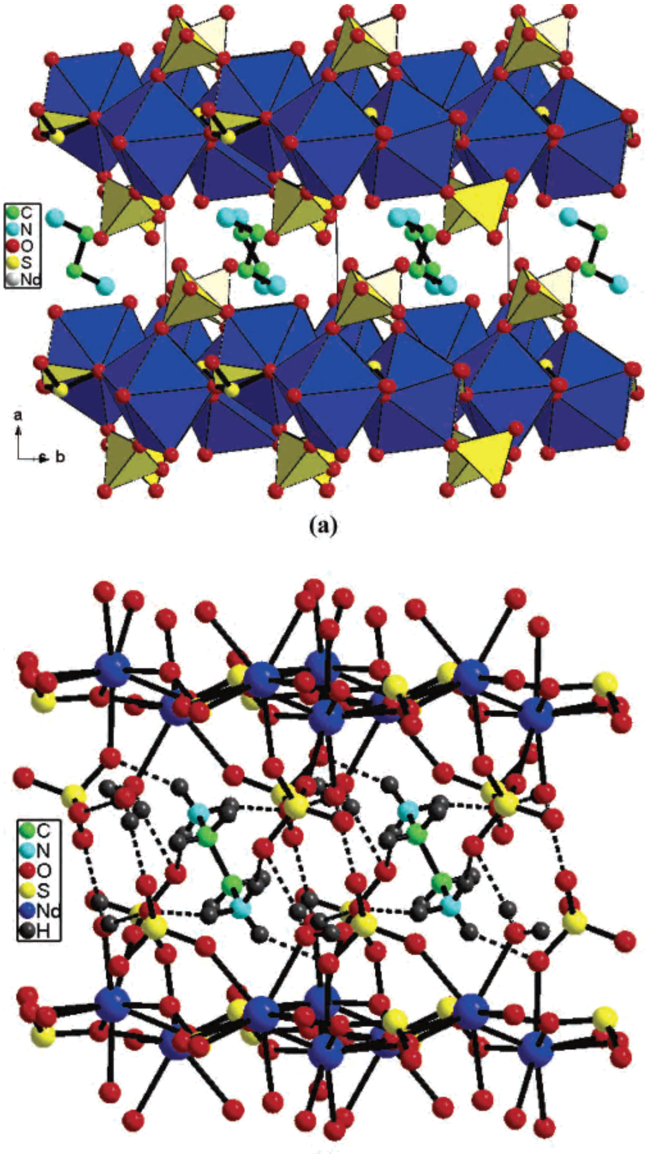


Figure 7. (a) Packing diagram of **V** viewed along the *c*-axis. (b) Three-dimensional hydrogen-bonded network of **V**.

plane, forming a three- dimensional framework. The three-dimensional framework is stabilized by hydrogen bonding between the coordinated water molecules and the oxygens of the sulfite ion with O−O distances in the range of 2.679(9)−2.715(8) Å in all three crystallographic directions (Figure 4c). This arrangement leads to two-dimensional micropores along the *c*-axis and along the *ab*-plane as shown in parts a and b of Figure 5, respectively. The DABCO molecule plays a dual role by satisfying the coordination of Zn1 and also directing the structure of the three-dimensional framework as shown in Figure 5c.

$[C_2H_{10}N_2][Nd(SO_3)(SO_4)(H_2O)]_2$, **V**, is an open-framework two-dimensional compound, crystallizing in the space group $P2_1/c$ (No. 14). The asymmetric unit contains 13 non-hydrogen atoms with one crystallographically distinct Nd^{3+} ion, one SO_3^{2-} ion, one SO_4^{2-} ion, half of the ethylenediammonium ion, and a water molecule (Figure 6a). The Nd^{3+} ion at the 4*e* crystallographic position is eight-coordinated to three oxygens of the sulfite ion, two oxygens of the sulfate ion, and a water molecule. The Nd−O bond distances are in the range of 2.367(3)−2.544(2) Å. Each NdO_8 polyhedron shares an edge with an adjacent NdO_8 polyhedron through two different sulfites (one corner of each), forming helical one-dimensional Nd−O−Nd chains along the *b*-axis (Figure 6b). The $\{NdO_8\}_\infty$ helical chains are connected through corners of the sulfite ions forming two-dimensional layers along the *c*-axis. The sulfate ion bridges two adjacent NdO_8 polyhedra through an O4−O7 edge on either side of the $\{NdO_8\}_\infty$ helical chain. The O5 and O6 oxygens of the sulfate ions are pointed perpendicular to the layer. This arrangement leads to two-dimensional $[Nd(SO_3)(SO_4)(H_2O)]^-$ anionic layers (Figure 6b), which are stacked one over the other along the *a*-axis, separated by the charge-compensating protonated ethylenediamine units as shown in Figure 7a. The ethylenediammonium ion forms hydrogen bonds (N−H⋯O) with O4−O6 of the sulfate ion, (*d*(N⋯O4) 2.940(4), (*d*(H1⋯O4) 2.13(5) Å, *θ*(N−H1⋯O4) 149(4)°; (*d*(N⋯O5) 2.871(4), (*d*(H2⋯O5) 1.84(5) Å, *θ*(N−H2⋯O5) 165(4)°; (*d*(N⋯O6) 2.853(4), (*d*(H3⋯O6) 2.05(6) Å, *θ*(N−H3⋯O6) 152(5)°. The coordinated water molecule forms hydrogen

Table 2. S−O Bond Distances in Compounds **I**−V

compound	S−O	distance (Å)	compound	S−O	distance (Å)
I	S−O1	1.537(3)	**IV**	S−O1	1.550(8)
	S−O2	1.531(3)		S−O2	1.515(7)
	S−O3	1.534(3)		S−O3	1.518(3)
II	S1−O1	1.521(3)	**V**	S1−O1	1.496(3)
	S1−O2	1.547(3)		S1−O2	1.531(3)
	S1−O3	1.536(3)		S1−O3	1.561(3)
	S2−O4	1.588(3)		S2−O4	1.480(3)
	S2−O5	1.519(3)		S2−O5	1.454(3)
	S2−O6	1.489(3)		S2−O6	1.462(3)
III	S−O1	1.529(2)		S2−O7	1.475(3)
	S−O2	1.519(2)			
	S−O3	1.523(2)			

bonds (O8−H···O) with O5 and O6 of the sulfate ion within the chain, (*d*(O8···O5) 2.732(4), (*d*(H8A···O5) 1.98(5) Å, θ(O8−H8A···O5) 155(5)°; (*d*(O8···O6) 2.811(4), (*d*(H2···O5) 2.11(6) Å, and θ(O8−H8A···O6) 168(6)°) as can be seen from Figure 7b.

In **I**−V, the sulfite ion has pyramidal geometry with the lone pair of electrons directed toward the fourth tetrahedral vertex. The S1−O bond distances are in the range of 1.489(3)−1.588(3) Å. In **V**, the sulfate ion has the tetrahedral geometry, with S2−O bond distances in the 1.454(3)−1.480(3) Å range (Table 2).

Thermal Analysis. Thermogravimetric analysis of **I**−V reveals that they are stable up to temperatures of 50, 150, 150, 280, and 350 °C, respectively, after which time they undergo weight losses of 77, 66, 64, 57, and 22%, respectively, in the temperature range of 30−700 °C. Compounds **I**−**III** and **V** undergo weight loss in two steps, the second step being that of major weight loss. Compound **IV** undergoes weight loss in a single step. In compound **V**, the first step is that of major weight loss. Powder X-ray diffraction patterns of the decomposed products of **I**−**IV** at 700 °C correspond to ZnO (JCPDS file card 1-1136). The powder X-ray diffraction pattern of the decomposed product of **V** at 700 °C corresponds to $Nd_2(SO_4)_3$ (JCPDS file card 23-1265).

Conclusions

In conclusion, zinc sulfite-based coordination polymers and hybrid networks of different dimensionalities have been synthesized and characterized. An open-framework hybrid sulfite−sulfate, where both SO_3^{2-} and SO_4^{2-} are part of a two-dimensional layer, has also been synthesized and characterized. On the basis of the present studies, it appears that many more metal sulfite-based open-framework and hybrid materials can be synthesized.

Supporting Information Available: A crystallographic information file (CIF) for the compounds **I**−**V** is available free of charge via the Internet at http://pubs.acs.org.

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