

Metal–Organic Frameworks from Zinc Sulfite Clusters, Chains, and Sheets: 4-Connected, (3,4)-Connected 3-D Frameworks and 2-D Arrays of Catenane-Like Interlocking Rings

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Even though open-framework solids have been made in a variety of compositions such as silicates, phosphates, germanates, borates, and phosphites, few are known that are based on trigonal-pyramidal sulfite anions. We report here the first synthetic and structural studies of metal–organic framework materials in the zinc sulfite composition. It is demonstrated here that Zn^{2+} and SO_3^{2-} can form various neutral inorganic subunits that can be 0-D clusters, 1-D chains, or 2-D sheets. These inorganic subunits of different dimensionality can subsequently be connected into extended frameworks of higher dimensionality through bifunctional ligands. In $(\text{ZnSO}_3)_2\text{en}$, infinite corrugated ZnSO_3 layers are pillared by ethylenediamine (en) molecules into a 3-D network that can be classified as a (3,4)-connected net based on tetrahedral Zn nodes and trigonal-pyramidal S nodes. In $(\text{ZnSO}_3)\text{pip}$, infinite ZnSO_3 chains are cross-linked with piperazine molecules into a 3-D framework that can be classified as 4-connected net based on tetrahedral Zn nodes only. In $(\text{ZnSO}_3)_2(\text{TMDPy})_2$, $(\text{ZnSO}_3)_2$ dimers are doubly bridged by trimethylenedipyridine molecules into an infinite chain with a string of circles. Each circle along the chain is interlocked with another circle from a chain in the perpendicular direction, creating a 2-D pattern with an infinite-square array of catenane-like units.

Introduction

Open-framework and crystalline microporous materials have attracted lots of interest because of their applications in many areas such as catalysis and gas sorption.^{1,2} In the synthetic design of new three-dimensional (3-D) open-framework and crystalline porous materials, one of most important considerations is the coordination chemistry of cationic species (e.g., Si^{4+} , P^{5+} , Ge^{4+} , Ti^{4+}) used for the construction of the framework. The local geometric feature surrounding individual cationic (polyhedral) centers plays a vital role in the overall topological features of the resulting open-framework architecture.³ In general, a low coordination number with more directional covalent bonds is desirable

for creating open architecture. For example, in known microporous oxides such as zeolites, one key structural feature is the tetrahedral coordination of its constituent Al^{3+} and Si^{4+} cations.^{4,5} Compared to octahedral units, tetrahedral blocks are far more likely to lead to open architectures.

We are particularly interested in the use of 3-connected centers as basic structural units for the construction of open-framework materials. The presence of 3-connected centers has been recognized to contribute to large pore sizes and low framework density (e.g., CLO, JDF-20), both of which are desirable for applications.^{6,7} There exist a number of different 3-connected building blocks, both organic and

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inorganic. Among inorganic units, oxoanions are the most common. Such oxoanions include planar BO_3^{3-} and CO_3^{2-} and pyramidal SnO_3^{4-} , SO_3^{2-} , SeO_3^{2-} , TeO_3^{2-} , and HPO_3^{2-} . Among these 3-connected units, HPO_3^{2-} and SnO_3^{4-} have been systematically studied.^{8–13} The formation of BO_3^{3-} units faces competing processes to form other configurations such as BO_4^{5-} and associated cluster units. There are also some limited successes with CO_3^{2-} and SeO_3^{2-} .^{14,15} In comparison, there have been very few studies on the use SO_3^{2-} as structural building units even though related tetrahedral SO_4^{2-} has been extensively studied.¹⁶

Here we report the first synthetic and structural studies of open-framework structures in the zinc sulfite compositions. It is demonstrated here that Zn^{2+} and SO_3^{2-} can form various inorganic subunits that can be zero-dimensional (0-D) clusters, one-dimensional (1-D) chains, or two-dimensional (2-D) sheets. Such inorganic subunits of different dimensionality (0–2) can subsequently be connected into extended frameworks with higher dimensionality (2 or 3) by using bifunctional organic ligands.

Experimental Section

Synthesis. (a) $(\text{ZnSO}_3)_2\text{en}$. Zinc carbonate (0.1154 g), sodium sulfite (0.2479 g), ethylenediamine (en; 0.1560 g), methanesulfonic acid (0.2778 g), ethylene glycol (1.236 g), and distilled water (5.982 g) were mixed in a 23-mL Teflon cup, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 120 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. The plate-shaped transparent colorless crystals were obtained in 42% yield.

(b) $(\text{ZnSO}_3)_3\text{pip}$. Zinc nitrate hexahydrate (98%, 0.2980 g), ammonium sulfite monohydrate (92%, 0.3980 g), piperazine (99%, 0.4992 g), and distilled water (4.018 g) were mixed in a 15-mL glass vial, and the mixture was stirred for 20 min. The vial was then sealed and heated at 110 °C for 4 days. The vial was subsequently allowed to cool to room temperature. The colorless crystals were obtained in 72% yield.

(c) $(\text{ZnSO}_3)_2(\text{TMDPy})_2$. Zinc carbonate (0.1260 g), potassium sulfite (0.2223 g), 4,4'-trimethylenedipiperidine (0.2369 g), acetic acid (0.1192 g), ethylene glycol (2.0326 g), and distilled water

Table 1. Summary of Crystal Data and Refinement Results^a

formula	$(\text{ZnSO}_3)_2\text{en}$	$(\text{ZnSO}_3)_3\text{pip}$	$(\text{ZnSO}_3)_2\text{-}(\text{TMDPy})_2$
temp (K)	293	150	293
size (μm)	$180 \times 140 \times 80$	$400 \times 360 \times 160$	$100 \times 80 \times 60$
<i>a</i> (Å)	4.8234(2)	7.3269(1)	16.032(1)
<i>b</i> (Å)	15.3064(7)	8.2922(1)	17.446(1)
<i>c</i> (Å)	6.2353(3)	12.1221(2)	21.621(2)
α (deg)	90	90	90
β (deg)	91.223(3)	90	100.87(6)
γ (deg)	90	90	90
<i>V</i> (Å ³)	460.24(4)	736.49(2)	5938.8(7)
<i>Z</i>	2	4	8
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>
2 θ_{max} (deg)	89	56	45
no. of total data	15 689	6462	15 400
no. of unique data	3646	1843	3844
no. of data, <i>I</i> > 2 σ (<i>I</i>)	2801	1836	1845
no. of param	64	101	361
<i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)]	2.87	2.53	7.72
<i>R</i> _w (<i>F</i> ²) [<i>I</i> > 2 σ (<i>I</i>)]	6.58	6.67	20.2
GOF	1.04	1.04	0.95

^a en = ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; pip = piperazine, $\text{C}_4\text{H}_{10}\text{N}_2$; TMDPy = trimethylenedipiperidine or 1,3-bis(4-pyridyl)propane, $\text{C}_{13}\text{H}_{14}\text{N}_2$.

(6.0658 g) were mixed in a 23-mL Teflon cup, and the mixture was stirred for 30 min. The resulting solution had a pH of 7.60. The vessel was then sealed and heated at 100 °C for 7 days. The vessel was subsequently allowed to cool to room temperature. The pale-yellow crystals of $(\text{ZnSO}_3)_2(\text{TMDPy})_2$ were obtained as a minor phase, and the major phase was identified to be potassium sulfate.

Thermal Analysis. The simultaneous differential scanning calorimetry—thermogravimetric thermal analysis was performed on a TA Instruments SDT Q600 under a flowing nitrogen atmosphere. The flow rate of the nitrogen gas was controlled at about 100 L/min. A total of 2.944 mg of $(\text{ZnSO}_3)_2\text{en}$ and 16.6210 mg of $(\text{ZnSO}_3)_3\text{pip}$ were heated in two separate runs between room temperature and 1000 °C at a heating rate of 5 °C/min.

Single-Crystal Structural Analysis. Each crystal was glued to a thin glass fiber with epoxy resin and mounted on a Bruker APEX II diffractometer equipped with a fine-focus, 2.0-kW sealed tube X-ray source (Mo K α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. The empirical absorption correction was based on equivalent reflections, and other possible effects, such as absorption by the glass fiber, were simultaneously corrected. Each structure was solved by direct methods followed by successive difference Fourier methods. All non-H atoms were refined anisotropically. Computations were performed using *SHELXTL*, and final full-matrix refinements were against *F*². The crystallographic results are summarized in Table 1. ORTEP diagrams for all three structures are shown in Figure 1.

Results and Discussion

As is observed in new zinc sulfite phases reported here, one of characteristic features of the zinc sulfite compositions is that the metal sites (Zn) and anionic sites (SO_3^{2-}) tend to alternate in a structural subunit that can be discrete clusters, infinite chains, or 2-D sheets. The strict alternation results in a neutral structural unit that can be cross-linked in various ways into higher dimensional inorganic—organic frameworks with interesting topological features detailed below.

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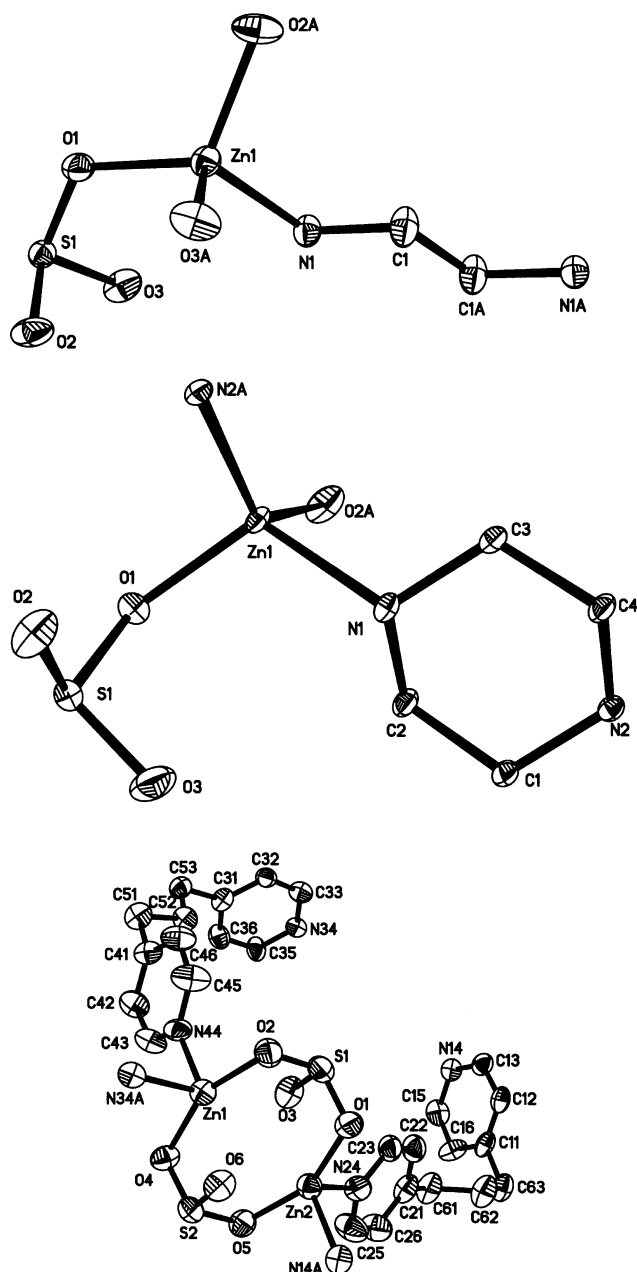


Figure 1. ORTEP diagrams of $(\text{ZnSO}_3)_2\text{en}$ (top), $(\text{ZnSO}_3)\text{pip}$ (middle), and $(\text{ZnSO}_3)(\text{TMDPy})_2$ (bottom) showing the local coordination environment and connectivity for atoms in the asymmetric unit. Atom labels containing “A” and “B” indicate symmetry-generated sites. Thermal ellipsoids are shown at the 50% level for $(\text{ZnSO}_3)_2\text{en}$ and $(\text{ZnSO}_3)\text{pip}$ and the 30% level for $(\text{ZnSO}_3)(\text{TMDPy})_2$.

3-D (3,4)-Connected Framework by Pillaring 2-D ZnSO_3 Sheets. In $(\text{ZnSO}_3)_2\text{en}$, tetrahedral Zn^{2+} sites alternate with trigonal-pyramidal SO_3^{2-} anions to form a 2-D corrugated sheet perpendicular to the crystallographic b axis. All three O sites are bicoordinated between one Zn^{2+} site and one S^{4+} site. Within each sheet, both Zn^{2+} and SO_3^{2-} sites are 3-connected, and they therefore form a neutral sheet, with the fourth bond on each Zn^{2+} site available for pillaring by organic ligands (Figure 2).

Two adjacent neutral ZnSO_3 sheets are related by the center of inversion rather than the unit cell translational symmetry. Thus, adjacent layers are stacked in a somewhat staggered configuration. They are joined together into a 3-D

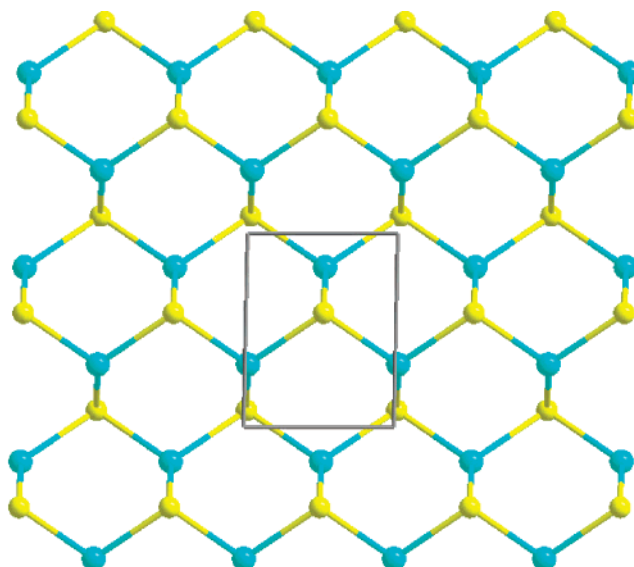


Figure 2. Infinite ZnSO_3 sheet in $(\text{ZnSO}_3)_2\text{en}$ viewed down the b axis. The bridging O atoms between Zn and S are omitted for clarity. Color code: cyan, Zn; yellow, S.

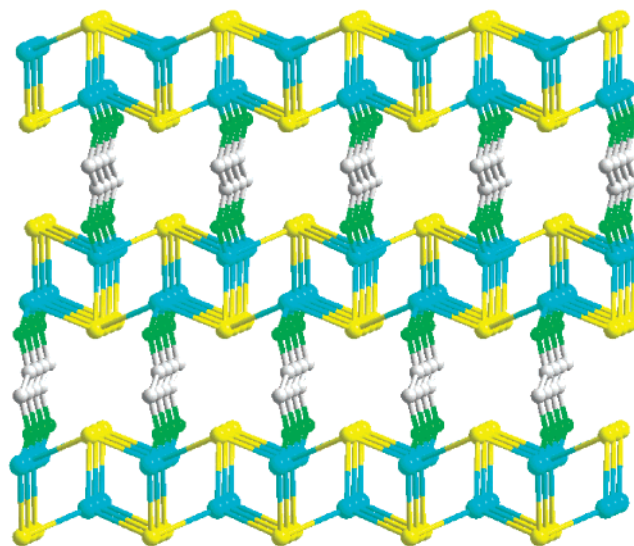


Figure 3. Viewed down the c axis, the infinite ZnSO_3 sheets pillared by neutral en molecules into a 3-D open framework in $(\text{ZnSO}_3)_2\text{en}$. The bridging O atoms between Zn and S are omitted for clarity. Color code: cyan, Zn; yellow, S; gray, C; green, N.

framework through the coordinative bond between en and Zn^{2+} sites in the form of $\text{Zn}-\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2-\text{Zn}$ linkages ($d_{\text{Zn}-\text{N}} = 2.010(1) \text{ \AA}$; Figure 3). The coordination environment of each Zn^{2+} site is therefore tetrahedral, ZnO_3N . Because each en molecule is coordinated to two Zn sites, the number of en molecules is half of the number of Zn sites.

Like bicoordinated O sites between Zn and S centers, each en molecule behaves like a bicoordinated pseudoatom between two Zn sites. All of these bicoordinated sites (oxygen and en) can be omitted when deriving the network topology based on cationic polyhedral centers, in this case, 4-connected Zn centers and 3-connected S sites. It is worth noting that here 4- and 3-connected centers are only alternating within each layer and that the interlayer connection is only through the $\text{Zn}\cdots\text{Zn}$ linkage (Figure 4). There-

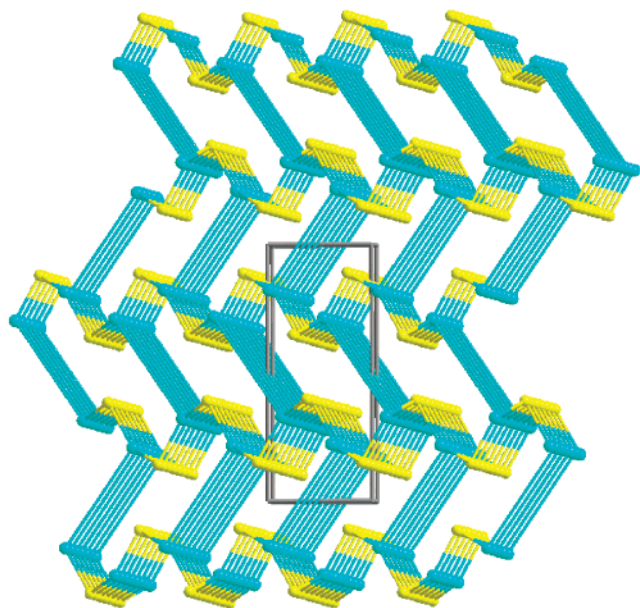


Figure 4. Viewed down the a axis, the (3,4)-connected net in $(\text{ZnSO}_3)_2\text{en}$. Color code: cyan, Zn; yellow, S.

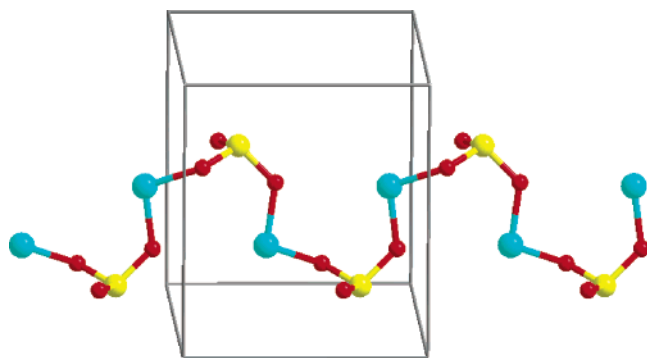


Figure 5. Infinite ZnSO_3 chain in $(\text{ZnSO}_3)\text{pip}$ propagating along the a axis. Color code: cyan, Zn; yellow, S; red, O.

fore, the ratio between 4- and 3-connected centers is 1, instead of $3/4$, which is commonly observed for (3,4)-connected 3-D frameworks.

The thermal analysis shows that $(\text{ZnSO}_3)_2\text{en}$ is stable until approximately $275\text{ }^\circ\text{C}$, which is the onset temperature for a sharp weight loss of 27.4% between 275 and $340\text{ }^\circ\text{C}$. Because the weight percentage of the organic component is only 17.1%, the loss of en is apparently accompanied by the loss of SO_2 . Between 340 and $1000\text{ }^\circ\text{C}$, there is a gradual weight loss of 29.3%. The total weight loss during the whole temperature range is 56.7%, which is slightly higher than the calculated value of 53.6% for the decomposition of $(\text{ZnSO}_3)_2\text{en}$ into ZnO.

4-Connected 3-D Framework from 1-D ZnSO_3 Chains. $(\text{ZnSO}_3)\text{pip}$ crystallizes in a chiral space group, $P2_12_12_1$. However, the refined Flack parameter is 0.524, suggesting that the crystal used for the data collection is a racemic twin. In $(\text{ZnSO}_3)\text{pip}$, Zn^{2+} and SO_3^{2-} alternate to form an infinite chain along the a direction (Figure 5). Different from $(\text{ZnSO}_3)_2\text{en}$ reported above, each tetrahedral Zn^{2+} site and each SO_3^{2-} group only use two bonds to connect with each other. As a result, one O on the sulfite anion is a terminal group with a much shorter S–O bond length [the terminal

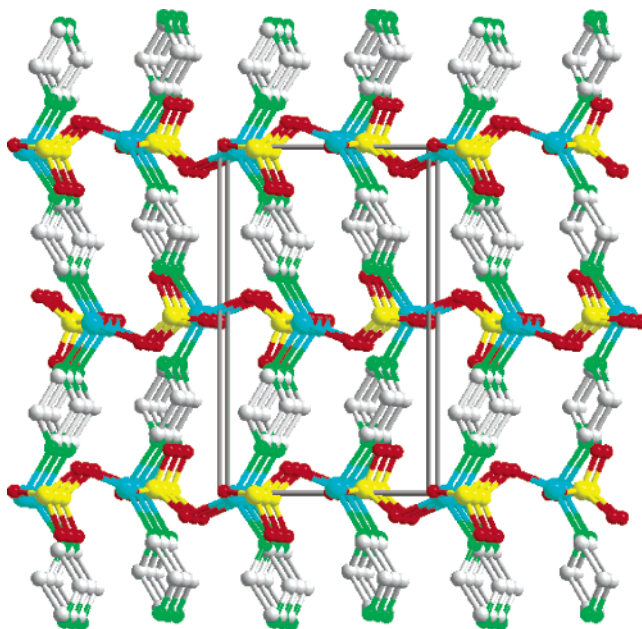


Figure 6. 3-D framework of $(\text{ZnSO}_3)\text{pip}$ projected down the crystallographic b axis. Color code: cyan, Zn; yellow, S; red, O; green, N; gray, C.

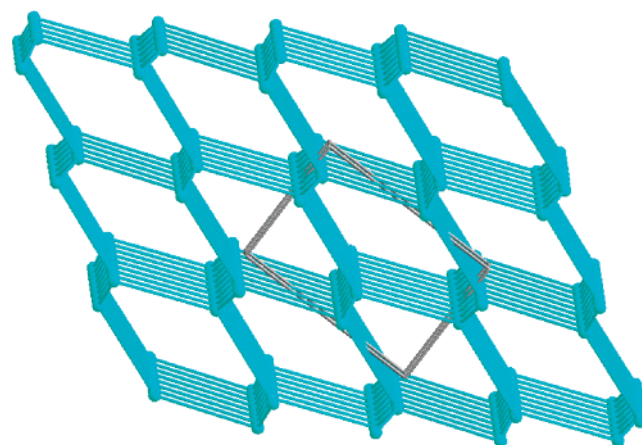


Figure 7. 4-connected net based on tetrahedral Zn nodes in $(\text{ZnSO}_3)\text{pip}$ projected down the crystallographic a axis.

$d_{\text{S-O}} = 1.489(2)\text{ \AA}$] while two other O sites are bicoordinated between one Zn site and one S site [$d_{\text{S-O}} = 1.540(2)$ and $1.565(2)\text{ \AA}$]. In addition, each Zn^{2+} site makes only two Zn–O bonds and has two available bonds for connecting with organic ligands.

It is worth noting that the ratio between ZnSO_3 and pip in $(\text{ZnSO}_3)\text{pip}$ is 1, different from 2 observed in $(\text{ZnSO}_3)_2\text{en}$. The reason is that, in $(\text{ZnSO}_3)\text{pip}$, each Zn site uses two bonds (out of four) to connect with two organic ligands, whereas in $(\text{ZnSO}_3)_2\text{en}$, each Zn site only uses one bond to connect with the organic ligand. Each pip molecule joins together two Zn sites through the Zn–N bond (Figure 6).

While $(\text{ZnSO}_3)_2\text{en}$ can be considered a (3,4)-connected net from 4-connected Zn sites and 3-connected S centers, $(\text{ZnSO}_3)\text{pip}$ exhibits a totally different topology. In $(\text{ZnSO}_3)\text{pip}$, the S sites are not 3-connected because of one terminal S–O group. In fact, the whole SO_3^{2-} group and piperazine molecule can be considered as pseudo-bicoordinated atoms

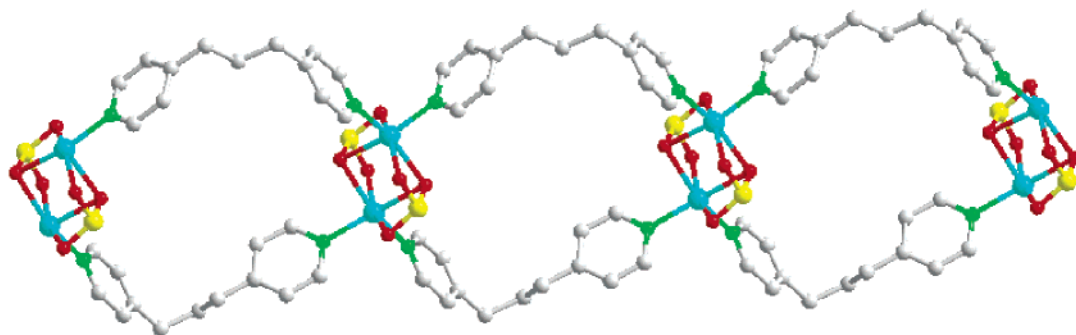


Figure 8. Infinite $(\text{ZnSO}_3)(\text{TMDPy})_2$ chain propagating along the (110) axis. Color code: cyan, Zn; yellow, S; red, O; green, N; gray, C.

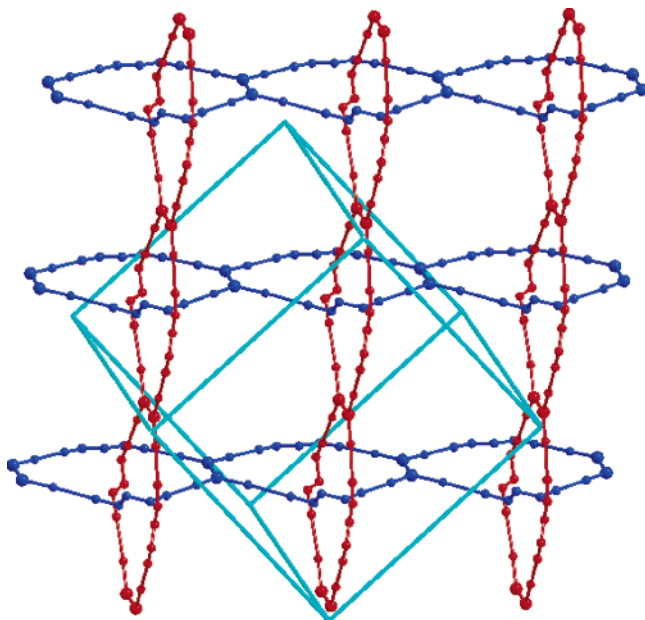


Figure 9. Layer of interlocked chains. The red chain runs along the (110) direction, while the blue chain runs along the (-110) direction. To simplify the figure, $(\text{ZnSO}_3)_2$ dimers are represented by the Zn–Zn line at the boundary of two circles. The pyridyl group is represented as the C–N line using C and N atoms at the 1 and 4 positions. The trimethylene group is shown at the center of each circle.

between two Zn^{2+} sites. This results in a 4-connected net based on the somewhat distorted tetrahedral Zn sites only (Figure 7).

The thermal analysis shows that $(\text{ZnSO}_3)\text{pip}$ is stable until approximately $250\text{ }^\circ\text{C}$, which is the onset temperature for a sharp weight loss of 50.8% between 250 and $375\text{ }^\circ\text{C}$. Because the weight percentage of the organic component is only 37.2%, the loss of piperazine is also accompanied by the loss of SO_2 . Between 375 and $1000\text{ }^\circ\text{C}$, there is a gradual weight loss of 16.6%. The total experimental weight loss during the whole temperature range is 67.4%, in good agreement with the calculated value of 64.9% for the decomposition of $(\text{ZnSO}_3)\text{pip}$ into ZnO.

2-D Arrays of Interlocking Chains with Catenane-Like Subunits in $(\text{ZnSO}_3)_2(\text{TMDPy})_2$. In $(\text{ZnSO}_3)_2(\text{TMDPy})_2$, there exists a dimeric unit, $(\text{ZnSO}_3)_2$, in which two Zn sites adopt the octahedral geometry. Two O sites on each SO_3^{2-} unit are bicoordinated between one Zn site and one S site, which leads to the formation of a cyclic four-ring (O sites not counted) made of $(-\text{Zn}-\text{O}-\text{S}-\text{O}-)_2$. The third O site

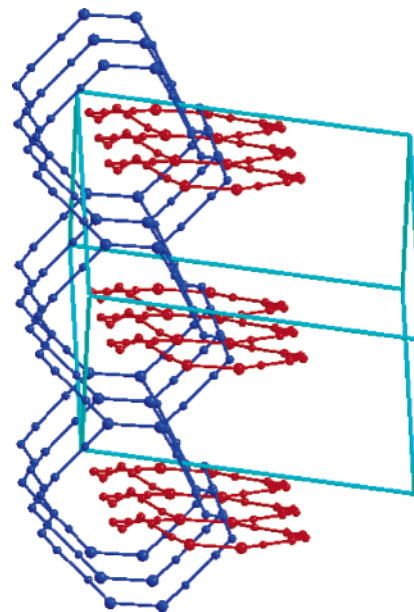


Figure 10. Two interlocked chains. The same simplification scheme as that used in Figure 8 is used here.

on each SO_3^{2-} coordinates to both Zn sites in the dimeric unit from two opposite sides of the four-ring.

Each Zn site has two available bonds (cis to each other) for connection with the organic ligand, and each dimer as a whole has four available bonds arranged approximately in the rectangular planar configuration. The dimers are doubly linked into an infinite chain by TMDPy molecules (Figure 8). From a geometric point of view, such a chain can be approximated as an infinite chain of circles, with the dimer as the boundary between adjacent circles (Figure 9). These chains propagate in two mutually perpendicular directions, (110) and (-110) . It is of particular interest that all circles along one chain direction are interlocked with circles from chains from the perpendicular direction (Figure 10). These interlocked chains form a 2-D sheet perpendicular to the c axis.

Comparison with Phosphites. Because there have been few studies on open-framework metal sulfites, it is of interest to evaluate the practical potential of the metal sulfite system for the development of open-framework architectures. The analysis can be based on the empirical knowledge obtained from other compositional domains such as silicates, germanates, phosphates, and phosphites, in which the effects of the local bonding geometry such as the T–O bond length

and O–T–O and T–O–T angles (T refers to a polyhedral site, often tetrahedral) on the framework topologies have been studied. The general observation is that the longer T–O distance leads to a smaller T–O–T angle and that a flexible T–O–T angle with an average close to 140–150° is more likely to give rise to a diversity of topologies.

The system that is closest to sulfites is open-framework phosphites, of which many structural examples are already known. Sulfites and phosphites share a number of similarities. Both carry a charge of -2 and have trigonal-pyramidal geometry. In terms of acid–base properties, H_3PO_3 and H_2SO_3 are also strikingly similar ($\text{p}K_{\text{a}1} = 1.6 \times 10^{-2}$, $\text{p}K_{\text{a}2} = 7.0 \times 10^{-7}$ for H_3PO_3 ; $\text{p}K_{\text{a}1} = 1.3 \times 10^{-2}$, $\text{p}K_{\text{a}2} = 6.3 \times 10^{-8}$ for H_2SO_3). The S–O distance is also very close to the P–O distance. For example, in $(\text{ZnSO}_3)_2\text{en}$, the S–O bond distance in SO_3^{2-} ranges from 1.519(1) to 1.536(1) Å with an average of 1.528 Å. This average distance is only slightly longer than the average P–O distance in a zinc phosphite, $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_3(\text{HPO}_3)_4$, in which the P–O distance ranges from 1.495(3) to 1.503(4) Å.¹⁷

The above similarities do not guarantee that many open-framework topologies discovered in phosphites can be duplicated in the sulfite system. This is, in part, because there is a fundamental difference: instead of the terminal P–H bond, a lone pair of electrons occupies the corresponding position in sulfites, which has a noticeable effect on O–T–O and T–O–T bond angles. In $[\text{N}(\text{CH}_3)_4]_2\text{Zn}_3(\text{HPO}_3)_4$, the O–P–O angle ranges from 111.9(2) to 114.4(2)° and the P–O–Zn angle ranges from 136.7(3) to 139.5(2)°, similar to those observed in aluminosilicate zeolites. In comparison, the O–S–O angle in $(\text{ZnSO}_3)_2\text{en}$ is much smaller and ranges

from 102.76(6) to 106.07(6)° and the S–O–Zn angle ranges from 122.94(6) to 124.97(6)°. Those geometrical data suggest that, compared with phosphites, a greater difficulty exists in the metal sulfite composition in terms of the construction of zeolite-like open-framework architecture. On the other hand, as demonstrated in this work, the sulfite system has some unique bonding features that can lead to the generation of novel structural patterns.

Conclusion

This work represents a beginning step in the exploration of the metal sulfite composition for the development of open-framework materials. It is demonstrated here that Zn^{2+} and SO_3^{2-} can form various inorganic subunits that can be clusters, 1-D chains, or 2-D sheets. Such inorganic subunits of different dimensionality can be connected into extended frameworks with higher dimensionality by using bifunctional organic ligands. The results reported here demonstrate the rich synthetic and structural chemistry of metal sulfites and their potential for the construction of crystalline open-framework materials.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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