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Amine-Controlled Assembly of Metal Sulfite Architecture from 1-D Chains to 3-D Framework

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Abstract

While open-framework materials have been made in a variety of chemical compositions, few are known in which three-connected SO_3^{2-} anions serve as basic building units. Here we report four new metal sulfite polymeric structures, $(\text{ZnSO}_3)\text{Py}$ (**1**, py = pyridine), $(\text{ZnSO}_3)_2(2,2'\text{-bipy})\text{H}_2\text{O}$ (**2**, 2,2'-bipy = 2,2'-bipyridine), $(\text{ZnSO}_3)_2(\text{TMDPy})$ (**3**, TMDPy = 4,4'-trimethylenedipyridine), and $(\text{MnSO}_3)_2\text{en}$ (**4**, en = ethylenediamine) that have been synthesized by hydrothermal method and structurally characterized. In these compounds, low-dimensional 1-D and 2-D inorganic subunits are assembled into higher 2- or 3-D covalent frameworks by organic ligands. In addition to the structure-directing effect of organic ligands, the flexible coordination chemistry of Zn^{2+} and SO_3^{2-} also contributes to the observed structural diversity. In compounds **1–3**, Zn^{2+} sites alternate with trigonal pyramidal SO_3^{2-} anions to form three types of $[\text{ZnSO}_3]_n$ chains, whereas in compound **4**, a 2-D corrugated $[\text{MnSO}_3]_n$ layer is present. Compound **1** features a rail-like chain with pendant pyridine rings. The π - π interaction between 2,2'-bipy ligands is found between adjacent chains in compound **2**, resulting in 2-D sheets that are further stacked through interlayer hydrogen bonds. Compound **3** exhibits a very interesting inorganic $[(\text{ZnSO}_3)_2]_n$ chain constructed from two chair-like subunits, and such chains are bridged by TMDPy ligands into a 2-D sheet. In compound **4**, side-by-side helical chains permeate through 2-D corrugated $[\text{MnSO}_3]_n$ layers, which are pillared by neutral ethylenediamine molecules into a 3-D framework that can be topologically represented as a (3, 6)-connected net. The results presented here illustrate the rich structural chemistry of metal sulfites and the potential of sulfite anions as a unique structural building block for the construction of novel open-framework materials, in particular, those containing polymeric inorganic subunits that may have interesting physical properties such as low-dimensional magnetism or electronic properties.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF), ORTEP diagrams, experimental and simulated X-ray powder patterns, and TGA plots for compounds 1–4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Table of Contents Synopsis

Reported here are four new polymeric materials developed in the rarely explored metal sulfite composition. In these compounds, 1-D and 2-D inorganic subunits are assembled into 2- or 3-D covalent frameworks. The rich crystal chemistry is a combination of the unique structural directing effect of organic ligands and variable coordination chemistry of M^{2+} and SO_3^{2-} building units.

Introduction

Open-framework and porous solids have found widespread applications as catalysts, adsorbents, ion-exchangers, and so forth.¹ These important materials have been made in a variety of compositions such as silicates, phosphates, germanates, borates, phosphites, and sulfides.^{2–4} Recently, there has been an increasing interest in the use of three-connected centers as basic structural units for the construction of open-framework materials.^{5–8} The presence of three-connected centers has been recognized to lead to large pore sizes and low framework density (e.g., -CLO, JDF-20), both of which are desirable features in porous materials.⁹

There exist a number of different three-connected building blocks, both organic and inorganic. Among inorganic units, oxoanions are most common. Such oxoanions include planar BO_3^{3-} and CO_3^{2-} and pyramidal SnO_3^{4-} , SO_3^{2-} , SeO_3^{2-} , and HPO_3^{2-} .^{10–12} Among these three-connected units, phosphites are particularly useful for creating open-framework solids. In comparison, little is known about open-framework sulfites.¹³ The work reported here is part of our systematic exploration of open-framework materials containing three-connected building units such as phosphites and sulfites.^{14–15} It deals with a compositional domain (i.e., inorganic-organic hybrid metal sulfites) about which very little crystal chemistry is known.

Here we report four new metal sulfite polymeric structures, $(ZnSO_3)Py$ (**1**, py = pyridine), $(ZnSO_3)_2(2,2'-bipy)H_2O$ (**2**, 2,2'-bipy = 2,2'-bipyridine), $(ZnSO_3)_2(TMDPy)$ (**3**, TMDPy = 4,4'-trimethylenedipyridine), and $(MnSO_3)_2en$ (**4**, en = ethylenediamine) that have been synthesized by hydrothermal method and structurally characterized. This work represents an early step towards the exploration of the inorganic-organic hybrid system based on metal sulfites. Unlike many metal organic framework structures in which isolated organic and inorganic units (0-D) are joined into higher-dimensional frameworks (1-D to 3-D), these metal sulfite materials have a strong tendency to form polymeric inorganic subunits that are subsequently joined into higher dimensional structures through bifunctional organic ligands. The existence of polymeric inorganic subunits opens the door for the integration of useful physical properties (e.g., low-dimensional magnetism, electronic conductivity) into these

materials. In the materials reported here, 1-D and 2-D inorganic subunits are assembled into 2-D and 3-D covalent frameworks. The rich crystal chemistry is a result of unique structural directing effect of organic ligands, coupled with variable coordination chemistry of Zn^{2+} (or Mn^{2+}) and SO_3^{2-} building units.

Experimental Section

Synthesis

(ZnSO_3)Py (1)—Zinc nitrate hexahydrate (98%, 0.3050 g), ammonium sulfite monohydrate (92%, 0.4028 g), pyridine (0.2058 g), and distilled water (3.990 g) were mixed in a 15-ml glass vial, and the mixture was stirred for 20 min. The pH of the mixture was 7.10. The vial was then sealed and heated at 110°C for 5 d. The vial was subsequently allowed to cool to room temperature. The colorless crystals were obtained in 65% yield. Results of elemental analysis (in wt %) for **1**, $\text{C}_5\text{H}_5\text{NO}_3\text{SZn}$, are 26.29 (calcd 26.75) for C, 2.52 (calcd 2.24) for H, and 6.40 (calcd 6.24) for N.

(ZnSO_3)₂(2,2'-bipy)H₂O (2)—Zinc carbonate (0.1582 g), ammonium sulfite monohydrate (0.1725 g), 2,2'-bipyridine (0.1543 g), methanesulfonic acid (99.5%, 0.1915 g, used for the adjustment of pH), ethylene glycol (1.7002 g) and distilled water (6.2176 g) were mixed in a 23ml Teflon cup and the mixture was stirred for 20 min. The pH value was 5.43. The vessel was then sealed and heated at 120°C for 7 d. The autoclave was subsequently allowed to cool to room temperature. The plate-shaped transparent colorless crystals were obtained with 56% yield. Results of elemental analysis (in wt %) for **2**, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_7\text{S}_2\text{Zn}_2$, are 25.98 (calcd 25.83) for C, 2.39 (calcd 2.17) for H, and 5.80 (calcd 6.02) for N.

(ZnSO_3)₂(TMDPy) (3)—Zinc carbonate (0.1267 g), potassium sulfite (0.2058 g), 4,4'-trimethylenedipyridine (0.3000 g), acetic acid (0.1401 g, used for the adjustment of pH), ethylene glycol (2.0223 g) and distilled water (6.2188 g) were mixed in a 23ml Teflon cup and the mixture was stirred for 20 min. The pH value was 6.13. The vessel was then sealed and heated at 120°C for 7 d. The autoclave was subsequently allowed to cool to room temperature. The plate-shaped transparent colorless crystals were obtained with 67% yield. Results of elemental analysis (in wt %) for **3**, $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_6\text{S}_2\text{Zn}_2$, are 32.15 (calcd 31.99) for C, 2.60 (calcd 2.68) for H, and 5.49 (calcd 5.74) for N.

(MnSO_3)₂en (4)—Manganese nitrate hydrate (98%, 0.277 g), ammonium sulfite monohydrate (0.408 g) and 6g water was mixed in a vial for 10 min. Then ethylenediamine (0.100 g) was added to the above mixture and stirred for another 10 min. The pH of the resulting mixture was 9.40. The vessel was sealed and heated at 110 °C for 4 days. After cooling to room temperature, clear orange-brown needle-shaped crystals were obtained with 45% yield. Results of elemental analysis (in wt %) for **4**, $\text{CH}_4\text{NO}_3\text{SMn}$, are 6.85 (calcd 7.28) for C, 2.12 (calcd 2.44) for H, and 8.61 (calcd 8.49) for N.

Thermal Analysis—The thermogravimetric analysis was performed on a TA Instruments SDT Q600 under the flowing nitrogen atmosphere. The flow rate of the nitrogen gas was

controlled at about 100 liters per minute. A total of 5.6090 mg of **1**, 9.3120 mg of **2**, 7.3890 mg of **3** and 29.5120 mg of **4** were heated between room temperature and 1000°C at a heating rate of 5°C/min.

X-ray Powder Diffraction—X-ray powder diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40kV and 40mA (CuK α radiation, $\lambda = 1.5418\text{\AA}$). The data collection was carried out with a step size of 0.03 degree and counting time of 1s per step. The 2-theta angular range is from 5 to 40 degrees.

Single-Crystal Structure 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 (MoK α radiation, $\lambda = 0.71073\text{\AA}$) operating at 50kV and 30mA. 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-hydrogen 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.

Results and Discussion

(ZnSO₃)Py (**1**): a rail-like inorganic ZnSO₃ double chain with pendant organic ligands

In compound **1**, Zn²⁺ and SO₃²⁻ form an infinite neutral rail-like double-chain along the *a* axis. As shown in Figure 1, all Zn²⁺ ions in the ZnSO₃ double-chain are tri-coordinated to three O atoms of three different SO₃²⁻ units, and each SO₃²⁻ unit connects to three Zn²⁺ ions. Thus both Zn²⁺ and SO₃²⁻ serve as 3-connected centers. The distances between adjacent Zn—Zn centers are 3.832(1), 4.001(1) and 4.940(1) Å, respectively. Each neutral pyridine ligand binds to one Zn²⁺ ion via its N site, which completes the fourth coordination of Zn²⁺ ions (Zn—N 2.055(6) Å). Within the ZnSO₃ double-chain, two Zn atoms and two S atoms (from two sulfite anion) form a 4-membered ring (Zn₂S₂, not counting four bridging oxygen sites). Such 4-membered rings extend in two directions to form the ZnSO₃ double-chain through the edge-sharing of 4-ring units.

The thermal analysis shows that compound **1** is stable until approximately 180°C which is the onset temperature for a gradual weight loss of 65.6% between 180 and 800°C. Because the weight percentage of the organic component is only 35.23%, the loss of pyridine is also accompanied by the loss of SO₂ (calc. 28.51%). The total experimental weight loss is about 1% lower than the calculated value of 36.3% for the decomposition of (ZnSO₃)Py into ZnO.

(ZnSO₃)₂(2,2'-bipy)H₂O (**2**): an inorganic double chain from alternating 3- and 4-membered rings

In compound **2**, Zn²⁺ ions are also bridged by SO₃²⁻ anions to form an infinite neutral double-chain along the *c* axis. However, the bonding pattern in compound **2** is dramatically different from that in compound **1**, illustrating the structural diversity that can be achieved in the Zn-SO₃²⁻ system. As shown in Figure 2, there are two independent Zn²⁺ ions with

different coordination geometry. Zn1 is tetrahedrally coordinated by four O atoms coming from four different SO_3^{2-} anions. In contrast, Zn2 has distorted octahedral coordination geometry and is bonded by three O atoms coming from only two different SO_3^{2-} anions. The three remaining coordination bonds of Zn2 are made to one aqua O atom and two N atoms of the same 2,2'-bipy ligand. It is worth noting that Zn1 and Zn2 share one common oxygen site from a SO_3^{2-} group.

The structural complexity of compound **2** is further increased by the occurrence of two independent and coordinatively different SO_3^{2-} anions. While both of them use all three O atoms to connect to three Zn^{2+} ions, their bonding modes are not the same. One SO_3^{2-} group (S2) is connected to three Zn^{2+} sites with all oxygen sites bi-coordinated between Zn^{2+} and S^{4+} site, similar to the bonding pattern in compound **1**. On the other hand, in the other SO_3^{2-} group (S1), one oxygen site is tri-coordinated between two Zn^{2+} and one S^{4+} sites. The Zn-O-Zn linkage allows the formation of the 3-membered ring (Zn1, Zn2, and S2, three bridging oxygen sites not counted). The 4-membered ring is formed between two crystallographically identical Zn1 sites, one S1 site, and one S2 site. These 3- and 4-membered rings alternate to form a wavy double-chain.

The 2,2'-bipy ligands chelate the Zn2 sites and are located at two sides of the double-chain with molecular planes parallel to one another. Along the same side, the distance between two adjacent 2,2'-bipy ligands is 8.513 Å. The gap is so wide that the 2,2'-bipy ligand from the adjacent chain partially fills the gap, as shown in Figure 3. Weak π - π interactions are found between two pyridine rings of two 2,2'-bipy ligands with the center-to-center distance of 3.638 Å. Such π - π interactions result in the formation of a layer parallel to the *bc* plane.

It is interesting to note that the aqua ligand forms two types of hydrogen bonds. One is the intra-chain hydrogen bond ($\text{O1W}\dots\text{O6} = 2.7919(19)$ Å), and another is the inter-chain hydrogen bond ($\text{O1W}\dots\text{O2}^i = 2.7892(17)$ Å; symmetry code: $i = -x+1, -y+1, -z+1$). Two adjacent layers are linked face-to-face by inter-chain hydrogen bonds, forming a double layer structure (Figure 4). The further stacking of such double layers leads to the observed crystal structure. The interactions between double layers are assumed to be van der Waals forces.

The thermal analysis of compound **2** shows two steps of weight losses. The first weight loss occurs between 50–200 °C with an observed weight loss of 3.46% corresponding to the loss of the water molecules (calcd 3.87 %). The second weight loss of 63.04 % occurs in the range of 225–945 °C, which can be attributed to the elimination of 2,2'-bipy (calcd 33.55 %) and SO_2 (calcd 27.53%). The remaining weight of 33.5 % is likely that of ZnO (calcd 35.06%).

(ZnSO₃)₂(TMDPy) (3): from 1-D inorganic chain to 2-D inorganic-organic hybrid layers

Compound **3** also contains inorganic ZnSO_3 chains, but it is very different from chains in compounds **1** and **2**. As shown in Figure 5, two independent Zn^{2+} ions (Zn1 and Zn2) and two independent SO_3^{2-} anions alternate to form an infinite chain along the *b* direction. Two independent SO_3^{2-} anions have the same coordination mode as that in the complex **2**, and both of them use all three O atoms to connect to three Zn^{2+} ions. On the other hand, the

bonding modes of two Zn^{2+} sites differ from those observed in compounds **1** and **2**. Two Zn^{2+} ions have tetrahedral (Zn2) and distorted square pyramidal geometries (Zn1), respectively.

Two symmetry-related SO_3^{2-} anions (S1) coordinate to two Zn1 centers with the Zn-Zn distance of 3.610 Å, which leads to the formation of a chair-like dimeric unit. In comparison, two symmetry-related SO_3^{2-} anions (S2) bridge two Zn2 centers, which also lead to the formation of a chair-like dimeric unit, distinctly different from the dimeric unit formed by Zn1 and S1 sites. The Zn-Zn distance within the second type of dimer is slightly shorter (3.489 Å). These two types of chair-like dimeric units are linked through a 3-ring unit ($-\text{S2-O-Zn1-O-Zn2-O}-$) into an infinite inorganic chain (Figure 5).

Each Zn site has an available bond for connection with the organic ligand, and each TMDPy ligand joins together two independent Zn sites (Zn1 and Zn2) of two adjacent chains through the Zn-N bond ($\text{Zn1-N2} = 2.052(2)$ Å and $\text{Zn2-N1} = 2.024(2)$ Å). The distance between two TMDPy connected Zn sites is 13.953 Å. A 2-D sheet parallel to the *ab* plane is formed (Figure 6).

The thermal analysis shows that compound **3** is stable until approximately 220°C which is the onset temperature for a gradual weight loss of 66.9% between 250 and 975°C. Because the weight percentage of the organic component is only 40.57%, the loss of TMDPy is also accompanied by the loss of SO_2 (calc. 26.23%). The total experimental weight loss is about 0.3% lower than the calculated value of 33.4 % for the decomposition of $(\text{ZnSO}_3)_2(\text{TMDPy})$ into ZnO .

$(\text{MnSO}_3)_2\text{en}$ (4): a 3-D framework by pillaring helix-containing layers

In compound **4**, Mn^{2+} and SO_3^{2-} form infinite neutral 2-D layers that are crosslinked into a 3-D framework by ethylenediamine molecules through Mn-N bonds. Within the MnSO_3 layer, Mn^{2+} and O^{2-} (from the sulfite anion) form an approximately square grid-type structure (Mn_4O_4) (Figure 7). Each Mn^{2+} is bonded to five oxygen atoms of four separate SO_3^{2-} groups (two oxygen sites from a single SO_3^{2-} group and three other oxygen sites from three separate SO_3^{2-} groups). Each SO_3^{2-} group is in turn connected to four Mn^{2+} sites with one oxygen site bi-coordinated between one Mn^{2+} and S^{4+} site and two oxygen sites tri-coordinated between two Mn^{2+} and one S^{4+} site. In other words, two oxygen atoms of the SO_3^{2-} anion form a bridging mode across two Mn^{2+} sites with Mn-Mn distance being 3.896 Å. Such tri-coordinated O atoms link Mn^{2+} sites to form left- and right-handed helices along the *b* axis. The left- and right-handed helices are not intertwined together. Instead, they are arranged side by side along the *c*- direction.

Within the MnSO_3 layer, the S^{4+} site and two tri-coordinated O atoms of SO_3^{2-} anion behave as 3-connected nodes and the Mn^{2+} sites act as 5-connected nodes. The layer can be topologically represented as a 2D (3,5)-connected plane. The coordination environment of each Mn^{2+} site is completed by the N atoms of the ethylenediamine ligand and exhibits distorted octahedral geometry. Ethylenediamine molecules on two adjacent Mn^{2+} sites are distributed at two opposite sides of the layer (Figure 8), which serves to crosslink adjacent neutral MnSO_3 layers into a 3-D framework (Figure 9). When the bridging ethylenediamine

molecules are taken into consideration, each Mn^{2+} site becomes 6-connected and the whole framework is thus a 3-D (3,6)-connected net.

The thermal analysis shows that compound **4** is stable until approximately 200°C which is the onset temperature for a gradual weight loss of 52.9% between 200 and 690°C. Because the weight percentage of the organic component is only 18.45%, the loss of ethylenediamine is also accompanied by the loss of SO_2 (calc. 38.81%). The total experimental weight loss is about 4% lower than the calculated value of 57.3% for the decomposition of $(\text{MnSO}_3)_2\text{en}$ into MnO .

The magnetic susceptibility of **4** was measured in the range 2–300 K at 5000 Oe (Figure 10). The $\chi_m T$ value of each Mn unit ($4.45 \text{ cm}^3 \text{ K mol}^{-1}$) at 300 K is almost equal to that ($4.37 \text{ cm}^3 \text{ K mol}^{-1}$) expected for one magnetically isolated high-spin Mn(II) ion. Upon cooling, $\chi_m T$ decreases smoothly to a minimum ($1.99 \text{ cm}^3 \text{ K mol}^{-1}$) at 22 K, indicating the presence of a dominant antiferromagnetic interaction. Then it increases rapidly as the temperature decreases to 13 K ($\chi_m T$ value = $2.71 \text{ cm}^3 \text{ K mol}^{-1}$). These features are indicative of ferrimagnetic behavior. The decrease of $\chi_m T$ below 13 K results from a saturation of the χ_m value and/or the zero-field splitting effect. Since the $\text{Mn}(\text{SO}_3)$ layers in **4** are well separated by the en bridges, the ferrimagnetic behavior can be suggested to arise from intralayer magnetic interactions. The magnetic susceptibility above 22 K obeys the Curie-Weiss law ($1/\chi_m = (T - \Theta)/C$) with the Curie constant, C , of $4.93 \text{ cm}^3 \text{ K mol}^{-1}$ and a negative Weiss constant, Θ , of -34.86 K , which also indicates an intralayer antiferromagnetic coupling between the adjacent Mn(II) ions through the SO_3 bridges.

Structural variations, comparisons, and trends

From the above structural descriptions, it is clear that metal ions and SO_3^{2-} anions can form unique inorganic subunits that can be chains or layers. The large structural variations are closely associated with the flexible coordination chemistry of SO_3^{2-} and metal cations. Within these structures, the oxygen atoms in the SO_3^{2-} anion exhibits two types of bonding modes: (I) the bi-coordination mode between one metal site and one sulfur site as in **1**, **2**, **3**, and **4**; and (II) the tri-coordination mode between two metal sites and one sulfur site as in **2**, **3**, and **4**. Such bonding modes have been observed before in other sulfites such as $[\text{Zn}_2(\text{SO}_3)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})]_n$ and $[\text{Zn}_2(\text{SO}_3)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$.¹³ The bonding mode (II) is much less common in phosphites, which accounts for the observed structural differences between these sulfites and similarly prepared phosphites.

The four polymeric materials possess combinations of bonding types (I) and (II) in different ratios. In compound **1**, only the type (I) is observed (I to II ratio = 100:0) whereas in compounds **2** and **3**, only one oxygen site on the S1 site is type (II) and five other oxygen sites (two on the S1, three on S2) are type (I) (I to II ratio = 83.3:16.7). In contrast, compound **4** has a much higher percentage of the type (II) mode with two oxygen sites being type (II) and only one oxygen site being type (I) (I to II ratio = 33.3:66.7). Thus there is a progressive increase in the type (II) bonding mode from **1** to **4**.

Another structural feature in these sulfites is the chelating bonding mode, which is rarely found in phosphites. In compounds **2** and **3**, two oxygen sites (type I and II) of the same

sulfite group bind to the same metal site. In comparison, in compound **4**, two oxygen sites (both type II) of the same sulfite group bind to the same metal site.

Parallel to the coordination variations of the SO_3^{2-} , the metal site in these polymeric structures also displays different coordination geometry. In compound **1**, all metal sites (Zn^{2+}) are tetrahedrally coordinated whereas in compound **2**, octahedrally coordinated Zn^{2+} sites coexist with tetrahedrally coordinated Zn^{2+} sites. Compound **3** has a unique combination between penta-coordinated Zn^{2+} sites and tetrahedrally coordinated Zn^{2+} sites. All metal sites (Mn^{2+}) in compound **4** are octahedrally bonded because of the stronger preference for the octahedral coordination by Mn^{2+} .

The interplay of these coordination features of metal sites and SO_3^{2-} results in neutral inorganic units with alternating metal sites and SO_3^{2-} anions. Such inorganic subunits of different dimensionality (1-D and 2-D) are subsequently connected into extended frameworks of higher-dimensionality (2-D and 3-D) by using bifunctional organic ligands as in compounds **3** and **4**. In comparison, metal phosphites are more likely to form negatively charged polymeric units from 1-D to 3-D with protonated amine molecules as extra-framework charge-balancing species. So far, no 2-D or 3-D metal sulfite frameworks encapsulating protonated organic amines have been prepared, which highlights the different crystal chemistry between sulfites and phosphites.

Conclusion

This work reports four new inorganic-organic hybrid structures based on metal sulfite chains and layers. The tendency of the metal sulfite system to form polymeric inorganic units is different from commonly observed metal-organic frameworks that are dominated by structures with isolated inorganic and organic units. Because of the occurrence of the polymeric inorganic unit, the metal sulfite system illustrated here has the potential for the development of framework materials with unique physical properties such as low-dimensional magnetism and electronic properties that are characteristic of inorganic materials. It is clear from the results reported here that the inorganic-organic hybrid metal sulfite system is very unique and its crystal chemistry can not be extrapolated from earlier studies of other related systems such as metal phosphites. Its potential for the construction of crystalline open-framework materials awaits further synthetic and structural exploration.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
The rail-like chain in complex **1**. Purple: Zn; Yellow: S; Red: O; Blue: N; Grey: C.

Figure 2.
The double chain in complex **2**. Hydrogen bonds were shown as dashed lines. Purple: Zn;
Yellow: S; Red: O; Blue: N; Grey: C.

Figure 3.
The space filling view of two 2,2'-bipy ligands and the π - π interactions in complex 2.
Purple: Zn; Yellow: S; Red: O; Blue: N; Grey: C.

Figure 4.
The 3D stacking structure of complex **2**. Hydrogen bonds were shown as dashed lines.
Purple: Zn; Yellow: S; Red: O; Blue: N; Grey: C.

Figure 5. View of a chain containing of two types of chair-like dimeric units in complex **3**. Purple: Zn; Yellow: S; Red: O.

Figure 6.
The 2-D layer in complex **3** viewed down the c axis. Purple: Zn; Yellow: S; Red: O; Blue: N;
Grey: C.

Figure 7.

Top: the infinite MnSO₃ layer in complex **4** viewed down the *a* axis; bottom: the layer viewed down the *b* axis, showing left- and right- helices. Purple: Mn; Yellow: S; Red: O.

Figure 8.

(a) The ethylenediamine ligands are located at two sides of the layer. (b) The schematic representation of the (3,5)-connected plane in complex **4**; solid circles and open circles represent two different bonding directions of the ethylenediamine ligands.

Figure 9.

Viewed down the b axis, the infinite MnSO_3 sheets are pillared by neutral ethylenediamine molecules into a 3-D open framework in $(\text{MnSO}_3)_2\text{en}$. Purple: Mn; Yellow: S; O: Red; Blue: N; Grey: C.

Figure 10.

$1/\chi_m$ and $\chi_m T$ vs T plot with the theoretical fit (—) for compound 4.

Table 1

A Summary of Crystal Data and Refinement Results.

Complexes	1	2	3	4
empirical formula	C ₅ H ₅ NO ₃ SZn	C ₁₀ H ₁₀ N ₂ O ₇ S ₂ Zn ₂	C ₁₃ H ₁₃ N ₂ O ₆ S ₂ Zn ₂	CH ₄ NO ₃ SMn
structural formula	(ZnSO ₃)py	(ZnSO ₃) ₂ (2,2'-bpy)H ₂ O	(ZnSO ₃) ₂ (TMDPy)	(MnSO ₃) ₂ en
Fw.	224.53	465.06	488.11	165.06
temp (K)	293	293	293	293
A (Å)	4.9404(3)	14.1016(10)	10.56520(10)	15.7400(6)
B (Å)	8.7820(5)	12.4216(8)	9.64940(10)	4.8958(2)
C (Å)	17.1114(9)	8.5128(6)	17.0340(2)	5.9311(2)
β(deg)	96.395(4)	105.538(3)	102.6820(10)	90.00
V (Å ³)	737.79(7)	1436.64(17)	1694.21(3)	457.05(3)
Z	4	4	4	4
space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /n	Pnnm
2θ _{max} (deg)	42	71	48	72
total data	6395	39891	25145	11022
unique data	745 [R(int) = 0.0563]	6006 [R(int) = 0.0245]	2749 [R(int) = 0.0842]	1072[R(int) = 0.0210]
data, I>2σ(I)	556	4713	2145	998
parameters	100	208	226	41
R(F) (I>2σ(I))	0.0331	0.0261	0.0302	0.0178
R _w (F ²)(I>2σ(I))	0.0760	0.0713	0.0747	0.0507
GOF	1.095	1.125	0.954	1.193