Two manganese sulfates, \([\text{C}_2\text{H}_4\text{O}_6][\text{MnSO}_4]\) (1) and \([\text{C}_4\text{N}_2\text{H}_12][\text{Mn(SO}_4)_2(\text{H}_2\text{O})]\) (2), were solvothermally synthesized in the presence of ethylene glycol and piperazine. Both compounds are constructed from 4-membered ring ladder chains made of MnO₆ and SO₄ units, with 1 displaying a 3D zeolite gismondine (GIS) framework and 2 possessing a 1D chain structure, respectively.

Open-framework materials, especially zeolites based on TO₄ (T = Si, Al, P, etc.) tetrahedra have been extensively studied because of their intriguing structural topologies and potential applications in the fields of catalysis, ion-exchange, and gas adsorption. Nowadays, the constituent elements of the inorganic skeleton of these materials have been expanded largely from the main group to transition metal. Among the numerous open-framework materials, metal sulfates have not attracted much attention due to the poor hydro- and thermo-stability till Rao et al. reported the first organo-templated metal sulfate in the last decade. Since then, a number of transition metal sulfates, lanthanum sulfates, and uranium sulfates, with diverse structures and interesting properties, have been synthesized and reported. Different to those tetrahedron-based zeolites, the metals in the metal sulfates usually exhibit 6- or higher coordination numbers. There has been no report, to the best of our knowledge, on the synthesis of metal sulfates with 4-connecting zeolite topology.

Our studies aimed at exploring new porous materials with interesting structure and properties, which have led to a series of metal phosphates, fluoro-transition metal sulfates with 2-D and 3-D frameworks, and rare earth sulfates with fluorescent properties. Herein, we reported the synthesis of two manganese sulfates from a mixed solvent of ethylene glycol (EG) and water by using piperazine sulfate (PzH₂SO₄) as structure directing agents (SDAs), one of which possesses a 4-connecting zeolite gismondine (GIS)-type structure and the other is a 1D chain polymer.

The title compounds were synthesized in the mixed solvent of EG and water with PzH₂SO₄ (synthesized by following the reported method) as SDAs. Both compounds were obtained under the same conditions except the different metal salts used as raw materials. Chloride salt was used in the synthesis of 1 while manganese acetate was used in 2. Although the anions were not included into the final products, they were thought to be one of the key factors in the formation of title compounds. In the meanwhile, the solvent and SDAs also played important roles during the synthesis, which were not included in the structure of 1 either. Many attempts to obtain 1 without the use of PzH₂SO₄ have not been successful. The anions and SDAs may affect the composition and acidity of the starting gel, which play important roles in the formation of the title compounds. The purities of both compounds were verified by powder X-ray diffraction studies (Fig. S1 in ESI).

Compound 1 crystallizes in the orthorhombic space group of Fddd. The asymmetric unit of 1 contains only six crystallographically unique non-hydrogen atoms, including three O atoms, and one each Mn, S, C atom, respectively (Fig. S3 in ESI). The Mn atom, sitting on the 2-folded axis along the [010] direction, adopts a six-coordinated octahedral geometry with four basal O atoms shared with adjacent SO₄ units and two axial O atoms from the EG molecules. The S atom is located on the 2-folded axis along the [001] direction and is in a tetrahedron environment. The averaged bond lengths of Mn-O and S-O are 2.174(5) and 1.478(1) Å, respectively, which are consistent with those of other reported manganese sulfates. The valence bond calculations of Mn1 (2.13) suggest it is divalent.

The 3D framework of 1 is constructed from the strict alternate linkage between MnO₆ octahedra and SO₄ tetrahedra, with no Mn-O-Mn connection. Each MnO₆ octahedron connects with four SO₄ tetrahedra, and vice versa. As shown in Fig. 1, the linkages of MnO₆ octahedra and SO₄ tetrahedra result in two sets of zigzag chains consisting of 4-membered rings (4-MRs) along the [011] and [0-11] direction, respectively. These chains connect to each other through vertexes to form a 3D framework of 1. The
Connections give rise to interconnecting 8-MR channels along the [011] and [0-11] direction, respectively. These channels are occupied by the EG molecules to fulfill the octahedral coordination requirement of the metal sites (Fig. S4 in ESI).

The framework of 1 can be simplified into a topological net by considering the MnO$_6$ octahedra and SO$_4$ tetrahedra as a 6- and 4-connected node, respectively, by using the TOPOS software. The structure can thus be reduced to a sqc3751 network, and the point (Schlafli) symbol is (4$^3$.5$^7$). On the other hand, when the coordinated EG molecules in the structure were omitted, both MnO$_6$ and SO$_4$ units can be simplified as 4-connected nodes. The framework of 1 can thus be considered as a zeolite-type structure of gismondine (GIS) topology, as shown in Fig. 2. The point (Schlafli) symbol is (4.3$^6$.8). The GIS-type materials, including silicates, arsenates, phosphates and phosphonates etc. are one of the most important members in the family of zeolite materials. Although several metal sulfates reported so far possess open frameworks, they are not considered as members of the zeolite family. To the best of our knowledge, 1 is the first example of transition metal sulfates with a zeolite structure. Compared to other reported GIS-type compounds, the structure in 1 is unique as the solvent EG molecules were introduced into the framework through coordination to the metal sites to form a hybrid structure.

Compound 2 crystallizes in the monoclinic $P2_1/c$ space group. The two crystallographically independent Mn atoms in 2 are six-coordinated with five O atoms from four adjacent sulfate units and one hydroxyl O atom to form a MnO$_6$ octahedron geometry (Fig. S5 in ESI). All the S atoms are in a SO$_4$ tetrahedral configuration. The lengths of Mn–O and S–O bonds are in the range of 2.103(2)–2.349(2), and 1.463(2)–1.486(2) Å, respectively. The valence bond calculations of Mn1 (2.07) and Mn2 (2.12) suggest both are divalent, while those of O9 (0.37) and O18 (0.39) indicate the existence of coordinated water molecules.

Compound 2 is a 1D polymer consisting of an anionic infinite chain [Mn(SO$_4$)$_2$(H$_2$O)$_2$]$^{2-}$. The chain was formed by alternating connections of MnO$_6$ octahedra and SO$_4$ tetrahedra, as shown in Fig. 3. It consists of a 4-MR ladder similar to that in compound 1 but decorated with SIO$_4$ antennas. It is noted that the 4-MR ladder appears in high dimensional structures of metal sulfates, but seldom in 1D structures. Moreover, the 4-MR ladder with antennas can often be found in zeolitic metal phosphates with the constituents of MO$_4$ tetrahedra and PO$_4$ tetrahedra, rarely with the compositions of MO$_6$ octahedra and TO$_4$ tetrahedra. In 2, the 4-MR ladder chains are arranged parallel to the a axis to form a three dimensional array (Fig. 3). The protonated Pz molecules lie between the anionic chains as charge balance, which form strong hydrogen bonding interactions with adjacent chains to stabilize the 3D network of 2.

The thermogravimetric (TG) curves of 1 and 2 are shown in Fig. S6 (ESI). Compound 1 lost coordinated EG molecules (observed 28.7%, 29.1% calculated) in the range of 280–330 °C, transforming...
to MnSO₄ (PDF No. 35-0751). The weight loss beginning at ca. 600 °C could be attributed to the evaporation of SO₃ owing to the further decomposition of MnSO₄. Compound 2 started to lose weight from 240 °C to 280 °C, with a loss of 5.9%, which could be contributed to the loss of coordinating water molecules (5.1% calculated). It lost 69.3% of its total weight continuously starting from 330 °C to 600 °C, which belongs to the evaporation of Pz and SO₃ (70.2% calculated) as a result of structure decomposition. The final product turned out to be a mixture of manganosite (MnO, PDF No. 07-0230) and hausmannite (MnO₂, PDF No. 24-0734) after calcination at 800 °C in air. It is noted that both compounds are stable below 240 °C and began to decompose by loss of their guest molecules at a relatively high temperature of ca. 240 °C owing to the interactions between the guest molecules and the framework. Both TGA profiles resemble those of other reported organo-templated metal sulfates.²⁵,²⁶,¹９²

The temperature dependence of the magnetic susceptibility for both compounds were measured on the powdered samples in the range of 1.8–300 K at a 2000 Oe external field. The plots of $\chi M/T$ vs. $T$ and $1/\chi M$ vs. $T$ for 1 and 2 are shown in Fig. 4. The $\chi M/T$ value at room temperature is 4.28 (for 1) and 4.55 (for 2) cm³ K mol⁻¹, respectively, which is comparable with the expected value of 4.38 cm³ K mol⁻¹ for single uncoupled Mn²⁺ ions (for $S = 5/2$ and $g = 2$). Along with the decrease in temperature, the value of $\chi M/T$ for both compounds decreased slowly till about 60 K, after which it decreased rapidly. The shapes of the $\chi M/T$ vs. $T$ curve are characteristic of the occurrence of antiferromagnetic coupling between the Mn²⁺ centers.²² The susceptibility data of 1 and 2, in the range of 50–300 K, can be well fitted by using the Curie–Weiss law $\chi M = C/(T - \theta)$. The best fitted Weiss constants ($\theta$) are −9.33 K (for 1) and −12.04 K (for 2) with the Curie constants of 6.396 and 3.072 cm³ K mol⁻¹, respectively. The negative Curie–Weiss temperature again indicates an antiferromagnetic coupling between the neighboring Mn²⁺ ions, which is consistent with the observed structure units of the –OSO– sulfate-bridged Mn²⁺ in both compounds. The magnetic interactions in 1 and 2 are different with those reported –O– bridged manganese sulfates,¹¹ but resemble those isolated Mn²⁺ compounds.²²

In summary, two manganese sulfates $[\text{C}_{2}\text{H}_{6}\text{O}_{2}][\text{MnSO}_{4}]$ (1) and $[\text{C}_{6}\text{H}_{12}\text{N}_{8}\text{H}_{12}][\text{Mn(SO}_{4})_{2}][\text{H}_{2}\text{O}]$ (2) were synthesized and characterized. Compound 1 possesses a 3D GIS-type zeolite structure, and is the first metal sulfate with zeolite structure. 2 is an anionic chain polymer with unusual antenna-decorated 4-MR ladders. The synthesis of two title compounds indicates that sulfate is a promising building unit for constructing inorganic materials with interesting structures such as zeolites and properties.

**Acknowledgements**

We are grateful for financial support from the National Basic Research Program (2011CB808704), and the National Natural Science Foundation of China (21071075 and 21021062).

**References**


