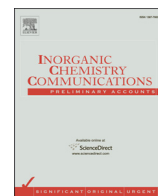




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Short communication

Solvent-free synthesis of open-framework metal sulfate oxalates with dia and ths topologies

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ABSTRACT

Two open-framework metal sulfate oxalates, namely, $\text{H}_2\text{dmen} \cdot \text{Mn}(\text{SO}_4)(\text{ox})$ (**1**) and $\text{H}_4\text{bapp} \cdot [\text{In}_2(\text{SO}_4)_3(\text{ox})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**2**), were prepared under solvent-free conditions, where dmen = *N,N*-dimethylethylenediamine, ox = oxalate, and bapp = *N,N'*-bis(3-aminopropyl)piperazine. Structural analyses reveal that compound **1** has a dia-type net with 12-ring channels, while compound **2** has a ths-type net with 20-ring channels. The proton-conducting properties of compound **2** were also investigated.

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Inorganic-organic hybrid solids are an important class of solid state materials that are usually constructed from metal ions, inorganic oxoanions, and organic ligands [1–3]. The synergetic effect of both inorganic oxoanions and organic components may endow the hybrid materials with appealing properties [4–6]. For example, the hybrid zeolitic imidazolate frameworks $\text{Zn}_4(\text{im})_6\text{TO}_4$ (im = imidazolate, T = Mo or W) display high thermal stability, permanent porosity, and promising catalytic properties by integrating the structural features and functions of zeolites and metal-organic frameworks [7]. Yaghi and co-workers illustrated that Fe-CAT-5 has a higher proton conductivity than that of Ti-CAT-5 because Fe-CAT-5 has a larger amount of both sulfate anions and organic cations per formula unit [8].

The incorporation of sulfate into metal oxalate structures is highly desirable for the synthesis of new inorganic-organic hybrid solids [9–11]. An illustrative example is the open-framework zinc oxalate $\{[(\text{Me}_2\text{NH}_2)_3(\text{SO}_4)]_2[\text{Zn}_2(\text{ox})_3]\}_n$ displaying a high proton conductivity of $4.2 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at ambient temperature under 98% relative humidity (RH) [12]. It is believed that the hydrogen-bonding networks formed between sulfate anions and organic cations in the structure provide pathways for proton transfer. However, the synthesis of metal sulfate oxalates is technically challenging because they are usually unstable under hydrothermal and solvothermal conditions. Recent developments showed that the elimination of solvent in material synthesis might create an ideal crystallization environment for open-framework metal sulfate oxalates [13–15]. Several metal sulfate

oxalates with hcb, kgd, and mog nets were prepared under solvent-free conditions [16,17]. Along this line of research, here we report the solvent-free synthesis of two new metal sulfate oxalates, namely, $\text{H}_2\text{dmen} \cdot \text{Mn}(\text{SO}_4)(\text{ox})$ (**1**) and $\text{H}_4\text{bapp} \cdot [\text{In}_2(\text{SO}_4)_3(\text{ox})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**2**), where dmen = *N,N*-dimethylethylenediamine, ox = oxalate, and bapp = *N,N'*-bis(3-aminopropyl)piperazine. Structural analyses reveal that the two compounds have three-dimensional open-framework structures with dia and ths topologies, respectively [18]. As far as we know, such networks have been observed for the first time in metal sulfate oxalates.

Compound **1** was prepared by heating a mixture of MnO (0.071 g), H_2SO_4 (54 μL , 98%), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.189 g), and dmen (110 μL) in a Teflon-lined stainless steel autoclave at 150 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. Light-pink crystals of **1** were separated from the resulting product by sonification, washed with methanol (the crystals are highly unstable in water), and dried in air (50.4% yield based on manganese). The phase purity of as-synthesized compound was confirmed by powder X-ray diffraction (XRD) analysis.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ (no. 14). There are one manganese atom, one SO_4 tetrahedra, two halves of oxalate ligands, and one H_2dmen cation in the asymmetric unit. The manganese atom is octahedrally coordinated by six oxygen atoms from two SO_4 tetrahedra and two oxalate ligands. The Mn—O bond lengths are in the region of 2.135(1)–2.242(2) Å, and the S—O bond lengths are between 1.469(2) and 1.485(2) Å. The strict alternation of MnO_6 octahedra and SO_4 tetrahedra creates zigzag chains running along the [101] direction, which are further bridged by oxalate ligands

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to form a three-dimensional structure (Fig. 1a). The open framework can be represented as a dia net with a point symbol of 6^6 by regarding the manganese atoms as 4-connected nodes (Fig. 1b) [19–21]. Viewed along the [100], [011], and [101] directions, compound **1** displays multidirectional 12-ring channels accommodating H_2dmen cations. The organic cations interact with the framework oxygen atoms through hydrogen bonds with the closest $\text{N}\cdots\text{O}$ distances in the region of 2.744(2)–2.852(2) Å. A void space analysis employing PLATON indicates that these extraframework species occupy 46.0% of the unit cell volume [22].

Compound **2** was prepared by heating a mixture of $\text{In}(\text{OH})_3$ (0.166 g), H_2SO_4 (81 μL , 98%), $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (0.126 g), and bapp (103 μL) in a Teflon-lined stainless steel autoclave at 150 °C for 6 days. The autoclave was subsequently allowed to cool to room temperature. Colorless crystals of **2** were recovered by filtration, washed with water and ethanol, and dried in air (46.3% yield based on indium). The phase purity of as-synthesized compound was confirmed by powder XRD analysis.

Compound **2** crystallizes in the monoclinic space group $I2/a$ (No. 15). The asymmetric unit contains one indium atom, one and a half sulfate anions, two halves of oxalate ligands, one and a half water molecules, and one half of an H_4bapp cation. The linkages between indium atoms and oxalate ligands result in the formation of linear indium oxalate chains, which are further bridged by $\text{S}(1)\text{O}_4$ tetrahedra to give rise to a 3D hybrid framework (Fig. 2a). By regarding indium atoms as 3-connected nodes, the hybrid framework can be represented as a ths net with a point symbol of 10^3 (Fig. 2b) [23–25].

Viewed along the [111] direction, the hybrid framework of **2** displays extra-large 20-ring channels delimited by ten InO_7 polyhedra, six oxalate ligands, and four SO_4 tetrahedra. As far as we know, 20-ring window represents one of the largest pore sizes in metal sulfate-oxalates. The pore size of the 20-ring window is about $7.8 \times 11.4 \text{ \AA}^2$, calculated from the distance between two oxygen atoms across the window. Furthermore, there are other 20-ring channels along the [100], [001], and [1–11] directions.

A striking structural feature of **2** is the presence of pendant $\text{S}(2)\text{O}_4$ anions on the hybrid framework. As seen in Fig. 2c, the sulfate anions interact with the protonated H_4bapp cations through strong hydrogen bonds to form a supramolecular layer with a sql topology. Each H_4bapp cation in the supramolecular layer connects four sulfate anions, while each sulfate anion acts as a bridge between two H_4bapp cations. The closest $\text{N}\cdots\text{O}$ distances are between 2.758(6) and 2.772(6) Å. The supramolecular layers can be understood as supramolecular templates (SMTs) for the formation of the ths-type net. They attach to the hybrid framework through $\text{In}\cdots\text{O}$ bonds, forming a complicated structure with two types of interpenetrating nets (Fig. 2d).

The entire structure of compound **2** is reminiscent of the open-framework aluminoborate $[\text{Zn}(\text{dap})_2][\text{AlB}_5\text{O}_{10}]$, which contains two

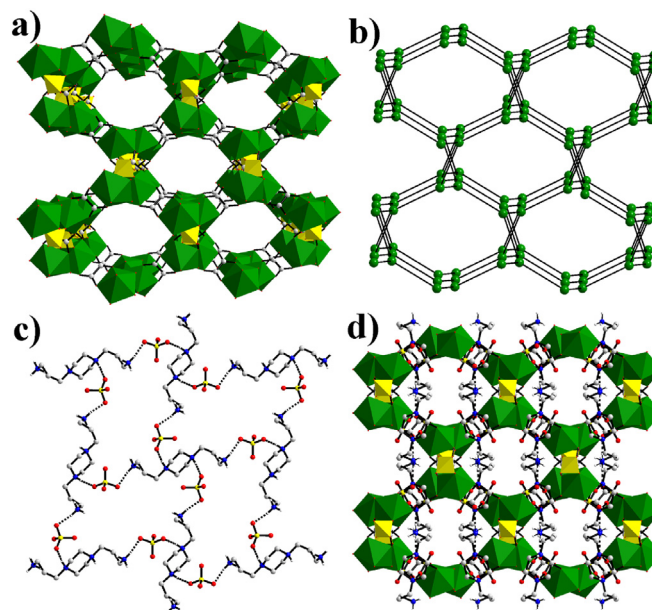


Fig. 2. (a) View of the hybrid framework of compound **2** with 20-ring channels. (b) The ths topology of the hybrid framework of compound **2**. (c) A supramolecular layer constructed from protonated amines and sulfate anions through strong hydrogen bonding. (d) View of the entire structure of **2** showing the 3D hybrid framework interpenetrated by the layered SMTs.

interpenetrating nets: a 3D dia net and a 2D sql net [26]. It is notable that the templating agent in the aluminoborate is a zinc-amine coordination polymer, whereas in compound **2**, the SMT is formed through extensive hydrogen-bonding interactions between amines and sulfate anions. Compared with metal-amine coordination frameworks, SMTs possess several advantages such as variable charges and unique hydrogen-bonding networks for proton transfer.

The temperature dependence of the magnetic susceptibility of compound **1** was measured in the temperature range 2–300 K (Fig. 3). The magnetic moment (μ_{eff}) at 300 K per mole of manganese atom is 5.94 μ_{B} , in agreement with the expected spin-only value of Mn(II) in the high spin state (5.92 μ_{B}) [27,28]. At 300 K, the $\chi_{\text{M}}T$ value is 4.41 $\text{cm}^3\text{-K mol}^{-1}$. Upon cooling, it decreases continuously and reaches a value of 0.17 $\text{cm}^3\text{ K mol}^{-1}$ at 2 K. The thermal evolution of χ_{M} obeys the Curie-Weiss rule at temperature above 60 K, with a Curie constant C_{M} of 4.71 $\text{cm}^3\text{ K mol}^{-1}$ and negative Weiss constant θ of -20.9 K. The curve trend of $\chi_{\text{M}}T$ versus T and the negative θ value imply the presence of antiferromagnetic interactions between the manganese ions [29,30].

The temperature dependence of proton conductivities of compound **2** was determined by alternating current impedance measurement

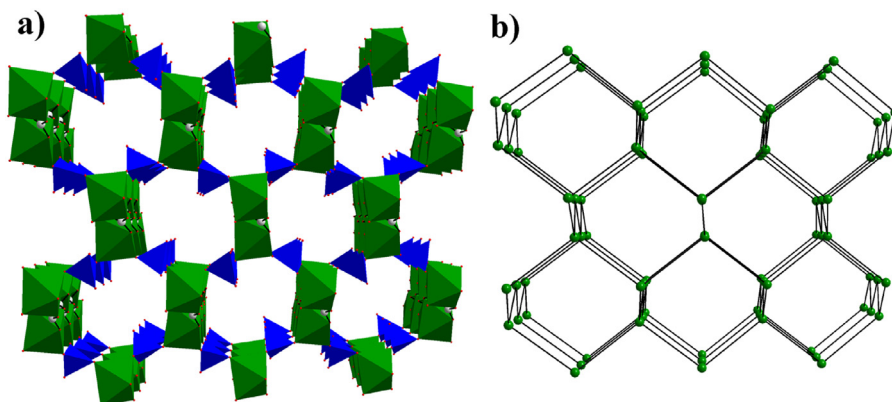


Fig. 1. (a) View of the open-framework structure of compound **1** with 12-ring channels. (b) The dia topology of compound **1**. Extraframework cations are omitted for clarity.

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