



Short communication

## Solvent-free synthesis of new metal sulfate–oxalates containing chain-like building blocks

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## ABSTRACT

Four new metal sulfate–oxalates were synthesized under solvent-free conditions. These compounds have single-layered, double-layered, and three-dimensional structures containing metal oxalate chains as building blocks. Topological analyses reveal that they have hcb, mog, and kgd topologies, respectively. Possible build-up processes for the formation of the hybrid frameworks were proposed.

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Hybrid open-framework materials have been extensively studied because of their appealing physical properties and potential applications in gas storage, ion-exchange, and sensing [1–3]. They display diverse structures combining the stability of zeolitic inorganic solids with the flexibility of metal–organic frameworks. Most hybrid open-framework structures reported to date are metal phosphate–oxalates [4–7]. An illustrative example is a layered vanadium phosphate–oxalate exhibiting facile extraction and insertion of alkali metal ions [8]. In comparison, little research has been done on the synthesis of new metal sulfate–oxalates, especially those containing transition metals [9–13]. This is in part due to the experimental difficulties associated with the low reactivity of sulfate groups and high solubility of metal sulfate under hydrothermal or solvothermal conditions [14,15].

To prepare new open-framework metal sulfate–oxalates, the elimination of the influence of solvent molecules on the framework structures is highly desirable. It is believed that solvent-free synthesis would create an ideal crystallization environment for the formation of open-framework metal sulfate–oxalates [16,17]. Recently, two new cobalt sulfate–oxalates with 20-membered-ring (20 MR) windows and 12 MR channels were prepared without the addition of water as a solvent [18]. Along this line of research, here we report the solvent-free synthesis of four new metal sulfate–oxalates, namely,  $\text{H}_2\text{dmpda} \cdot \text{Mn}(\text{SO}_4)(\text{ox})$  (**1**),  $\text{H}_2\text{mpip} \cdot \text{Zn}_2(\text{SO}_4)(\text{ox})_2(\text{H}_2\text{O})_2$  (**2**),  $\text{Zn}_3(\text{Haep})_2(\text{SO}_4)_2(\text{ox})_2$  (**3**), and  $\text{H}_2\text{dab} \cdot \text{Mn}_2(\text{SO}_4)(\text{ox})_2(\text{H}_2\text{O})$  (**4**), where dmpda = N,N'-dimethyl-1,3-propyldiamine, ox = oxalate, mpip = 1-methylpiperazine, aep = 1-

(2-aminoethyl)piperazine, and dab = 1,4-diaminobutane. These compounds have single-layered, double-layered, and three-dimensional framework structures containing chain-like metal oxalates as building blocks [19].

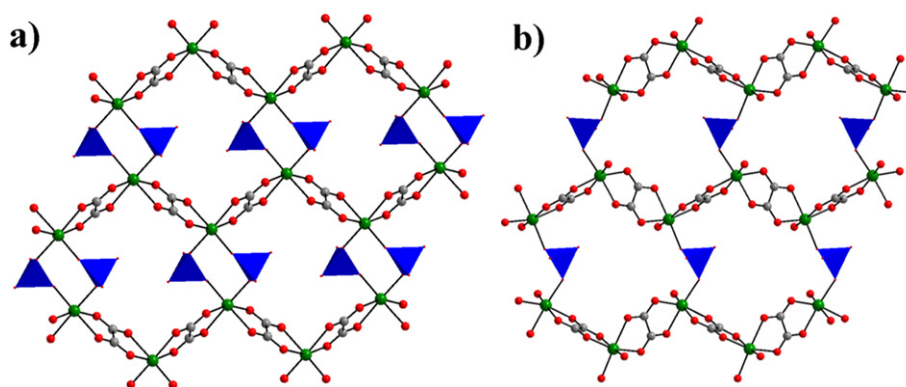
In a typical synthesis, a mixture of MnO (0.071 g),  $\text{H}_2\text{SO}_4$  (53  $\mu\text{L}$ , 98 wt%),  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (0.378 g), and N,N'-dimethyl-1,3-propyldiamine (125  $\mu\text{L}$ ) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 7 d. The autoclave was subsequently allowed to cool to room temperature. Yellow block-like crystals of **1** were recovered by filtration, washed with methanol, and finally dried at ambient temperature (51.2% yield based on manganese). Compounds **2–4** were prepared under similar solvent-free conditions in the presence of different structure-directing agents. The phase purity of all compounds was confirmed by powder X-ray diffraction.

Compound **1** crystallizes in the triclinic space group *P*-1 (no. 2). As shown in Fig. 1a, the linkages between manganese atoms and sulfate groups create cyclic  $\text{Mn}_2(\text{SO}_4)_2$  tetramers, which are further bridged by oxalate ligands to form a layered structure with an hcb topology [20]. These hybrid layers are stacked in an eclipsed fashion. Viewed along the [010] direction, the structure displays straight 12 MR channel encapsulating  $\text{H}_2\text{dmpda}$  cations. A void space analysis employing PLATON indicates that these extraframework cations occupy 50.0% of the unit cell volume [21].

Compound **2** crystallizes in the orthorhombic space group *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub> (no. 19). It has a layered structure with zinc oxalate chains cross-linked by sulfate groups (Fig. 1b). By regarding zinc atoms as 3-connected nodes, the layered structure has an hcb topology. One main difference between the structures of **1** and **2** is that, in **1**, two adjacent

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**Fig. 1.** A view of the layered structures of (a) **1** and (b) **2**. Color code: zinc/manganese, green;  $\text{SO}_4$  tetrahedra, blue; oxygen, red; carbon, gray.

metal centers of different metal oxalate chains are joined together through two sulfate groups, whereas in **2**, they are joined together through only one sulfate group. The hybrid layers of **2** are stacked in a staggered fashion. The  $\text{H}_2\text{mpip}$  cations are ordered within the interlayer region, which occupy 33.7% of the unit cell volume.

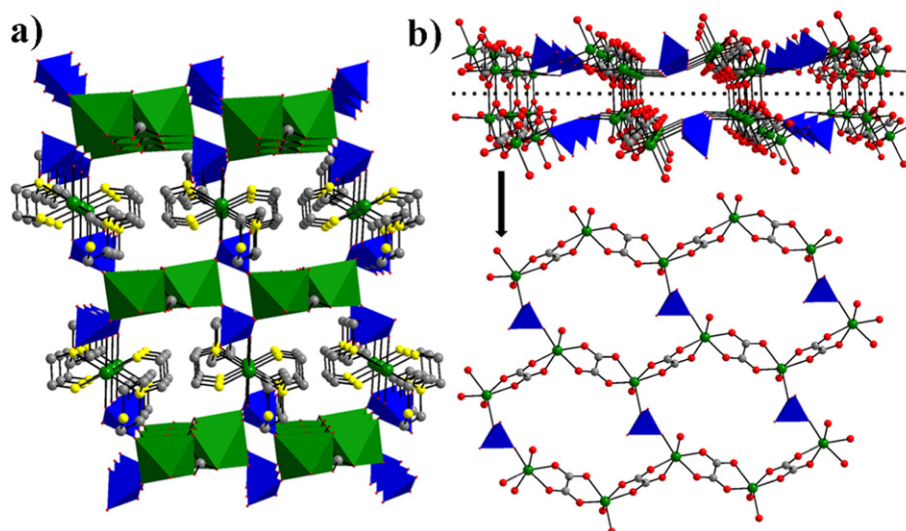
Compound **3** crystallizes in the triclinic space group  $P-1$  (no. 2). This compound is isostructural to the known cobalt sulfate–oxalate with an *mog* topology [18]. It has a three-dimensional structure containing two kinds of building blocks: a zinc sulfate–oxalate layer and a zinc-amine complex (Fig. 2a). The zinc sulfate–oxalate layers are stacked along the [010] direction in an eclipsed fashion, forming straight 12 MR channels. The zinc-amine complex attach to the walls of 12 MR channels through Zn–O bonds. They act as cross-linkers to connect adjacent metal sulfate–oxalate layers into a three-dimensional structure.

Compound **4** crystallizes in the triclinic space group  $P-1$  (No. 2). It has a double-layered structure with a thickness of ca. 10.7 Å. The structure comprises of two interconnected single layers, as shown in Fig. 2b. Each single layer has an *hcb* topology with metal oxalate chains linked by sulfate groups. An interesting structural feature of **4** is the coexistence of  $\text{MnO}_6$  octahedra and  $\text{Mn}_2\text{O}_{10}$  dimers in its layered structure. Each  $\text{Mn}_2\text{O}_{10}$  dimer connects six  $\text{MnO}_6$  octahedra through four oxalate ligands and two  $\text{SO}_4$  tetrahedra, and each  $\text{MnO}_6$  octahedron connects three  $\text{Mn}_2\text{O}_{10}$  dimers through two oxalate ligands and one  $\text{SO}_4$  tetrahedron. By regarding  $\text{Mn}_2\text{O}_{10}$  dimers and  $\text{MnO}_6$  octahedra as the 6-, and 3-

connected nodes, respectively, compound **4** has a (3,6)-connected framework with a *kgd* topology.

Despite the fact that compounds **1–4** display different structures, their hybrid frameworks are conceptually constructed from the same metal oxalate chains,  $\text{M}(\text{H}_2\text{O})_2(\text{ox})$  ( $\text{M}=\text{Zn}$  and  $\text{Mn}$ ). It is worth noting that metal oxalate chains are coexistent with the layered structure of compound **2**. When half of water molecules in the chains are replaced by sulfate groups and each metal center is coordinated by one sulfate group, the layered structure of **2** is created (Fig. 3). When all the coordinated water molecules in the metal oxalate chains are replaced by sulfate groups, the layered structure of compound **1** is produced. If the hybrid layers of compound **1** are further connected by metal-amine complexes through M–O–S linkages, the three-dimensional structure of compound **3** will be created. If half of water molecules in the single layered structure of **2** are replaced by oxalate oxygen atoms from the adjacent hybrid layer, the double-layered structure of **4** is formed.

Based on the proposed formation processes for structures **1–4**, other hybrid framework networks are potentially achieved. For example, when all the water molecules in the metal oxalate chains are replaced by sulfate oxygen atoms and the linkages between metal atoms and sulfate groups form one-dimensional chains, metal sulfate–oxalates with 4-connected topologies (e.g., *sql* and *dia*) will be created. Theoretically, the formation of a (4,6)-connected network with an *fsh* topology is also possible if the terminal water molecules in the *kgd*-type structure of **4**



**Fig. 2.** (a) A view of the framework structure of **3** constructed from metal sulfate–oxalate layers and metal-amine complexes. (b) A view of the double-layered structure of **4** comprising of two interconnected single layers.

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