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Solvent-Free Synthesis of Crystalline Metal Phosphate Oxalates with a (4,6)-Connected fsh Topology

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Supporting Information

ABSTRACT: Two new organically templated manganese phosphate oxalates were synthesized under solvent-free conditions. They have different three-dimensional structures with a (4,6)-connected fsh topology. It is interesting that the amine molecules can reverse the structure-building roles of the metal phosphate skeleton and metal oxalate substructure for formation of their fsh-type frameworks.

Open-framework materials such as zeolites and metal−organic frameworks have been extensively studied because of their potential applications in catalysis, gas storage, separation, and sensing.[1] These crystalline materials are usually prepared under hydrothermal or solvothermal conditions. The utilization of ionic liquids, urea derivatives, and surfactants as solvents has also been investigated.[2] Recently, the synthesis of zeotype materials under solvent-free conditions is of great interest.[3] Compared with conventional solution-mediated syntheses, this synthetic strategy possesses several advantages, such as pollution reduction, simple process, and low system pressure.[4]

One successful way to control open-frameworks structures is to use different amines as the structure-directing agents.[5] Variation of the sizes, shapes, and charges of amine molecules often leads to the formation of new framework topologies. Meanwhile, there are also a large number of examples in which the same host structure could be created by a variety of different amines. It is well-known that more than 20 organic molecules can lead to the formation of a ZSM-5 molecular sieve.

The structure-directing role of amines is more subtle in an inorganic−organic hybrid system. Conceptually, a hybrid framework such as metal phosphate oxalate consists of two parts: a metal phosphate skeleton and a metal oxalate substructure. When a new amine is involved in the synthesis of new metal phosphate oxalates, it may affect the whole framework structure, metal phosphate skeleton, and metal oxalate substructure all at the same time. A great deal of attention has been paid to the structure-directing role of amines on the whole framework structure. Much less work has been carried out to investigate the influence of amines on metal phosphate skeletons and metal oxalate substructures. To enable the rational design and synthesis of new open-framework materials, a deep understanding of the structure-directing role of amines is essential but highly challenging.

Here we report a novel structure-directing role of amines in the solvent-free synthesis of two new open-framework manganese phosphate oxalates, formulated as $C_5N_2H_{14}\cdot Mn_2(HPO_4)(H_2PO_4)(C_2O_4)_{1.5}(H_2O)\cdot 2H_2O$ (**1**) and $(C_{10}N_3H_{28})_{0.5}\cdot Mn_2(H_2PO_4)_{1.5}(C_2O_4)_2\cdot H_2O$ (**2**). Both compounds have a (4,6)-connected fsh topology with MnO_6 octahedra as 4-connected nodes and Mn_2O_{10} dimers as 6-connected nodes. Compound **1** consists of a double-chain manganese phosphate skeleton and a single-chain manganese oxalate substructure, while compound **2** consists of a single-chain manganese phosphate skeleton and a double-chain manganese oxalate substructure. Despite the large differences between the sizes, shapes, and coordination behaviors of the phosphate groups and oxalate ligands, the amine molecules can apparently reverse the structure-building roles of the metal phosphate and metal oxalate substructures for the formation of two hybrid framework structures. As far as we know, such a structure-directing role of amines has been observed for the first time in zeotype material chemistry.

Light-yellow crystals of compound **1** were prepared by heating a mixture of MnO, $H_2C_2O_4\cdot 2H_2O$, H_3PO_4 (85 wt %), and homopiperazine (hpip) in a stoichiometric ratio at 150 °C for 7 days (yield: 53.1%). Compound **2** was prepared under similar synthetic conditions in the presence of 3,3′-iminobis(*N*,*N*-dimethylpropylamine) (ipa) as the templating agent. The phase purity of the two compounds was confirmed by powder X-ray diffraction (XRD; Figures S1 and S2 in the Supporting Information, SI). Thermogravimetric analysis (TGA) showed that compounds **1** and **2** lost their water molecules below 180 °C (for **1**: observed, 8.9%; expected, 9.1%) and 135 °C (for **2**: observed, 3.5%; expected, 3.3%). Their frameworks started to decompose at 180 and 260 °C, respectively (Figures S6 and S7 in the SI).

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (No. 2). The asymmetric unit contains two manganese atoms, one HPO_4 unit, one H_2PO_4 unit, one and a half oxalate ligands, three water molecules, and one H_2hpip cation. The linkages between the manganese atoms and phosphorus-centered tetrahedra generate a double-chain substructure (Figure 1a). On the other hand, the linkages between the manganese atoms and oxalate ligand produce a single-chain substructure (Figure 1b). The two different substructures are coupled with each other by sharing common MnO_6 octahedra and Mn_2O_{10} dimers, forming a three-dimensional structure. Viewed along the [100] direction, the structure of **1** displays two types of different channels (Figure 1c). The large channel has a 12-ring window, while the small channel has an 8-ring window. H_2dab cations and water

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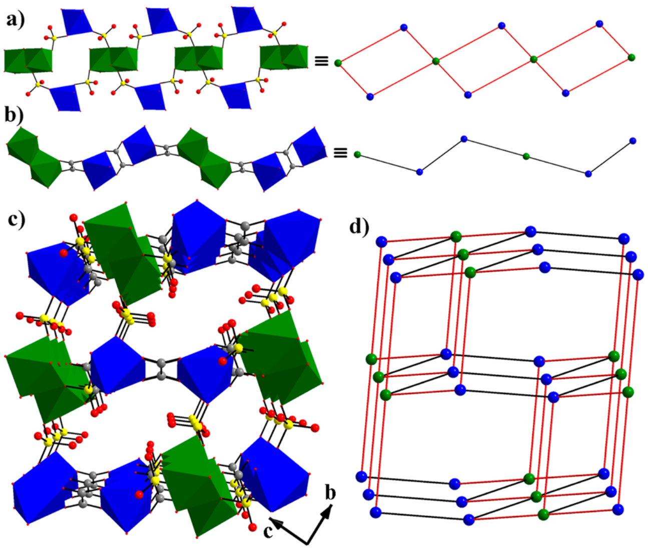

Figure 1. (a) Double-chain manganese phosphate skeleton. (b) Single-chain manganese oxalate substructure. (c) View of the structure of **1** along the [100] direction. (d) Compound **1** with a (4,6)-connected fsh topology. Color code: Mn_2O_{10} dimers, green; $Mn(2)O_6$ octahedra, blue; phosphorus, yellow; oxygen, red; carbon, gray.

molecules are ordered within the 12- and 8-ring channels, respectively. These extraframework species occupy 35.4% of the unit cell volume.

By regarding MnO_6 octahedra as the 4-connected nodes and Mn_2O_{10} dimers as the 6-connected nodes, the framework structure of **1** can be understood as a (4,6)-connected fsh topology (Figure 1d).[6] Prior to this work, 4-connected dia topology (MnO_6 octahedra as the nodes) and 6-connected pcu topology (Mn_2O_{10} dimers as the nodes) have been observed in open-framework manganese phosphate oxalates.[7] The coexistence of the two different structural nodes in the same manganese phosphate oxalate framework is unprecedented.

Compound **2** crystallizes in the monoclinic space group *C*2/*c* (No. 15). This compound has a three-dimensional structure constructed from two types of different building blocks: a single-chain manganese phosphate skeleton (Figure 2a) and a double-chain manganese oxalate substructure (Figure 2b). It is worth noting that the manganese phosphate skeleton has a meso-helical structure, which is rarely found in open-framework metal phosphate oxalates. The inorganic skeletons and metal−organic substructures share common MnO_6 octahedra and Mn_2O_{10} dimers, forming an fsh-type structure with 8- and 12-ring channels (Figure 2c,d). The extraframework species (i.e., H_3ipa cations and water molecules) are located within the channels and occupy 39.6% of the unit cell volume.

Strikingly, the structural motif of metal phosphate in **1** is similar to that of metal oxalate in **2** and the structural motif of metal oxalate in **1** is similar to that of metal phosphate in **2**. Also noteworthy is that the PO_4/oxalate ratio in **1** is equal to the oxalate/PO_4 ratio in **2**. Given that the two compounds have the same fsh topology and the same structural nodes (MnO_6 octahedra as 4-connected nodes and Mn_2O_{10} dimers as 6-connected nodes), we believe that the structure-building roles of the metal phosphate and metal oxalate substructures in **1** and **2** are reversed within the fsh network by amine molecules.

It is of interest to examine the various influences of amines on the metal phosphate and metal oxalate substructures. When different amines are used in a specific network synthesis, four kinds of hybrid frameworks are possibly achieved, which can be represented with the notations P(u)O(u), P(u)O(c), P(c)O(u), and P(c)O(c), where P refers to metal phosphate, O refers to metal oxalate, and u and c refer to substructures that remain unchanged (u) or that have changed (c). For example, isostructural compounds can be represented as P(u)O(u) because they have the same framework topology and metal phosphate and metal oxalate substructures.[8] Recently, the P(u)O(c) frameworks were found in pcu-type manganese phosphate oxalates that contain the same metal phosphate skeleton but different metal oxalate substructures.[7b] The P(c)O(u) situation, which is opposite to that of P(u)O(c), remains to be discovered. The P(c)O(c) frameworks found in compounds **1** and **2** reported here are quite uncommon because changes of both the metal phosphate and metal oxalate substructures always result in the formation of a new framework topology.

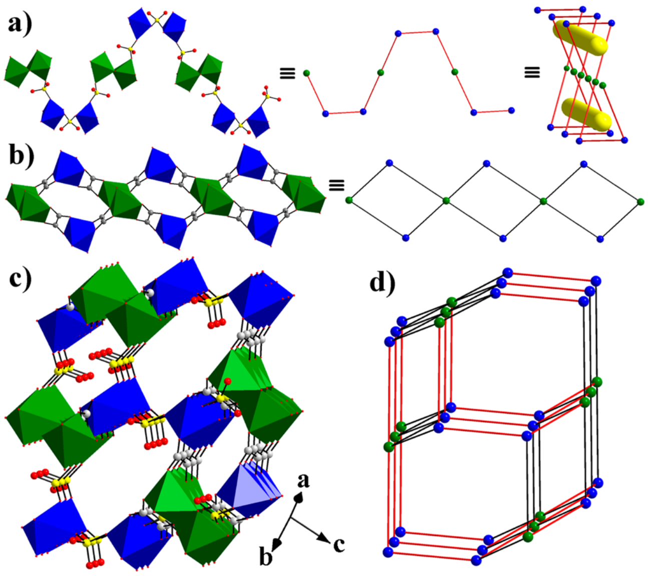

Figure 2. (a) Single-chain manganese phosphate skeleton. (b) Double-chain manganese oxalate substructure. (c) View of the structure of **2** along the [110] direction. (d) Compound **2** with a (4,6)-connected fsh topology. Color code: Mn_2O_{10} dimers, green; $Mn(2)O_6$ octahedra, blue; phosphorus, yellow; oxygen, red; carbon, gray.

Compound **1** remains stable in water for several days. However, compound **2** is quite unstable in water. The light-yellow crystals of **2** turned dark when they were immersed in water for 30 min. The IR spectrum of the dark product showed the disappearance of the characteristic peaks of PO_4 groups (1050−1200 cm^{-1} in **2**) and amine molecules (1460 cm^{-1} in **2**). The peaks at 1630 and 1320 cm^{-1} are attributed to the stretching vibrations of C=O and C−O in oxalate ligands (Figure S5 in the SI). The powder XRD pattern of the dark product (Figure S3 in the SI) indicates that it is a mixture of $Mn(C_2O_4)(H_2O)_2$ and $Mn(C_2O_4)(H_2O)_2 \cdot H_2O$.[9]

The temperature dependence of the magnetic susceptibility of compounds **1** and **2** was measured in the temperature range 2−300 K (Figure 3). The values of $\chi_M T$ at 300 K are 4.40 and 4.34 cm^3 K mol^{-1} for **1** and **2**, respectively, in agreement with the spin-only value of 4.38 cm^3 K mol^{-1} for one manganese(II) ion in the high-spin state.[10] Upon cooling, the $\chi_M T$ values decrease continuously and reach the values of 0.17 cm^3 K mol^{-1} (for **1**) and 0.19 cm^3 K mol^{-1} (for **2**) at 2 K. Thermal evolution of χ_M follows the Curie−Weiss law at temperature above 20 K, with C_m

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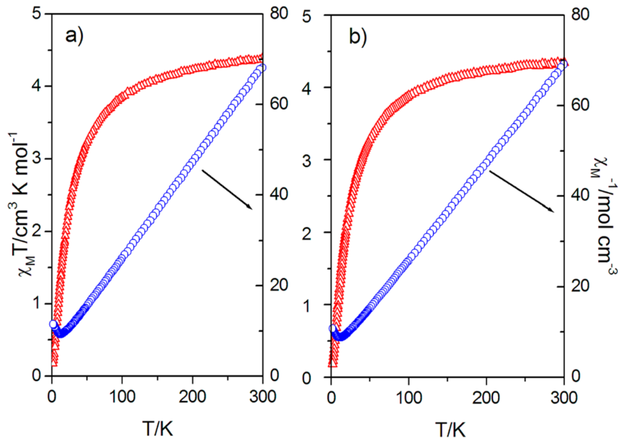

Figure 3. Temperature dependence of $\chi_M T$ (Δ) and χ_M^{-1} (O) for compounds **1** (a) and **2** (b).

= 4.74 cm^3 K mol^{-1} and $\theta = -24.1$ K for **1** and $C_m = 4.67$ cm^3 K mol^{-1} and $\theta = -21.6$ K for **2**. The negative θ values indicate the existence of antiferromagnetic interactions between the manganese ions.

In summary, two different open-framework manganese phosphate oxalates were synthesized under solvent-free conditions. The influence of amines on the metal phosphate and metal oxalate substructures is described. The present work provides an ideal structural model to illustrate that amine molecules could reverse the structure-building roles of metal phosphate and metal oxalate within a fsh-type network. We believe that solvent-free synthesis will offer exciting opportunities for the construction of novel inorganic−organic hybrid solids such as P(c)O(u) frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01569.

Experimental details, additional figures, including IR spectra, TGA curves, and powder XRD patterns (PDF)
X-ray data in CIF format (CIF)
X-ray data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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