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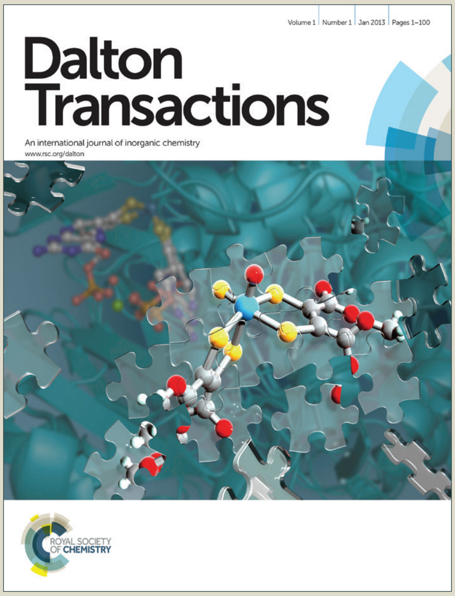

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ARTICLE TYPE

Solvent-free synthesis of new inorganic-organic hybrid solids with finely tuned manganese oxalate structures†

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Three manganese phosphate-oxalates have been synthesized under solvent-free conditions. These inorganic-organic hybrid solids are based on a pcu-type topology with nanobelt-like, sql-, and cds-type manganese oxalate skeletons, respectively. The amine molecules play a novel structure-directing role for the formation of different metal-organic skeletons within a specific framework topology.

Crystalline microporous materials such as zeolites and metal-organic frameworks (MOFs) have been extensively studied due to their appealing properties and potential applications in catalysis, gas storage, separation, and sensing.[1] These open-framework compounds are usually synthesized under hydrothermal or solvothermal conditions.[2] Recent developments indicate that solvent-free synthesis offers an alternative crystallization condition for open-framework structures.[3] Some new secondary building blocks may form under solvent-free conditions, which provide exciting opportunities to achieve novel framework structures. An illustrative example is the solvent-free synthesis of a new pcu-type manganese phosphate-oxalate containing Mn_4P_2 and Mn_6P_4 clusters as the building blocks.[4] In comparison, its hydrothermal analogues only contain M_4P_2 clusters (M = Mn, Fe, Co) in their pcu-type structures.[5]

One effective way to create new open-framework structures is the use of different amines as the structure-directing agents. According to the host-guest symmetry and charge matching concept, the variation of the size, shape, and charge of amine molecules should affect the formation of different framework structures.[6] During the past years, a large number of new open-framework inorganic solids have been prepared based on this synthetic strategy. Meanwhile, the synthesis of isostructural host frameworks from different amines is also not uncommon, which is in part due to the relatively weaker templating effect of these amine molecules.[7]

Here we report a novel structure-directing role of amines for the formation of new open-framework structures under solvent-free conditions. Three manganese phosphate-oxalates, namely, $(H_2mpip)_{1.5}\cdot Mn_3(HPO_4)(H_2PO_4)(ox)_3$ (**1**), $H_2dap\cdot Mn_2(HPO_4)(ox)_2$ (**2**), and $Hpa\cdot Mn_2(H_2PO_4)(ox)_2$ (**3**), were obtained in the presence of different amines, where mpip = 1-methylpiperazine, ox = oxalate, dap = 1,2-diaminopropane, and pa = propylamine. All the compounds are based on a pcu-type topology with Mn_2O_{10} dimers as the 6-connected nodes.[8] However, these compounds display different manganese oxalate skeletons and pore apertures, demonstrating that amine molecules could finely tune metal-organic skeletons within a specific network. Such structure-directing behavior of amine molecules has been rarely observed in the chemistry of zeotype materials.

In a typical synthesis, a mixture of mpip, MnO, H_3PO_4(85 wt%), and $H_2C_2O_4\cdot 2H_2O$ in a molar ratio of 1.5:3:2:3 was heated in a Teflon-lined stainless steel autoclave at 150 °C for 8 days. The autoclave was allowed to cool to room temperature. Block-like single crystals of compound **1** were obtained in 81 % yield. Compounds **2** and **3** are prepared under similar solvent-free conditions in the presence of different structure-directing agents. The phase purity of compounds **1-3** is confirmed by powder X-ray diffraction and CHN elemental analysis. Their framework structures are determined by single-crystal X-ray diffraction.‡

Compound **1** crystallizes in the triclinic space group *P*-1 (no. 2). It has a three-dimensional structure templated by doubly protonated mpip cations. Viewed along the [100] direction, the structure display 8-membered-ring (8 MR), and 12 MR channels (Fig. 1a). Different 8 MR, and 16 MR channels are also observed along the [010] direction. The 16 MR window is highly puckered, which is delimited by eight MnO_6 octahedra, four PO_4 tetrahedra, and four oxalate ligands. Despite the presence of 24 MR and 20

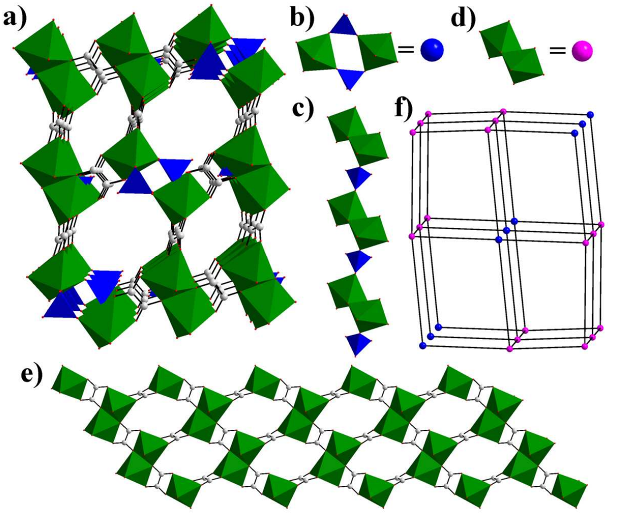

Fig.1. Perspective view of (a) the framework structure of **1** constructed from two different inorganic building blocks: (b) the cyclic Mn_2P_2 tetramer and (c) the linear manganese phosphate chain with (d) Mn_2O_{10} dimers bridged by phosphate groups. (e) The nanobelt-like manganese oxalate skeleton in **1**. (f) The structure has an interrupted pcu topology.

MR windows in metal phosphates and metal oxalates, metal phosphate-oxalates often contain much smaller pores.[9] With the exception of NTHU-6, we are not aware of any examples of open-framework metal phosphate-oxalates with 16 MR channels.[10] The doubly protonated mpip cations locate within the channels, which occupy 36.2% of the unit cell volume.

Compound **1** features two different types of inorganic building blocks: a cyclic Mn_2P_2 tetramer constructed from two MnO_6 octahedra and two $H_2P(1)O_4$ groups (Fig. 1b), and an infinite inorganic chain constructed from Mn_2O_{10} dimers and $HP(2)O_4$ tetrahedra (Fig. 1c, 1d). For a specific hybrid framework, it usually only contains one kind of inorganic building blocks, such as 4 MR cluster in NTHU-10, corner-sharing 4-ring chain in NTHU-8 and fes-type sheet in NTHU-2.[11] The coexistence of two different types of inorganic building blocks creates new possibilities for the formation of new hybrid open-framework structures.

Also interesting is the presence of nanobelt-like manganese oxalate with a formula of $Mn_6(ox)_6$, as seen in Fig. 1e. The width of the nanobelt is ca. 11.8 Å, calculated from the shortest distance between two manganese atoms on both sides of the nanobelt. Notably, the nanobelt-like structure can be understood as a fragment of the sql-type layer with Mn_2O_{10} dimers as the nodes. It is believed that the cyclic Mn_2P_2 tetramers act as “structural scissors” to create the nanobelt-like fragment. On the other hand, the manganese phosphate chains serve as the backbones for the formation of the pcu-type network.

By regarding the cyclic Mn_2P_2 tetramers as 4-connected nodes and Mn_2O_{10} dimers as 6-connected nodes, the structure of **1** can be simplified as a (4,6)-connected sqc125 network with a point symbol of $(4^4.6^2)(4^8.6^7)_2$ (Fig. 1f). Such a (4,6)-connected network can be understood as an interrupted pcu topology. The Mn_2O_{10} to Mn_2P_2 ratio in the network is 2:1.

Based on the structural model of compound **1**, different manganese oxalate nanobelts with variable widths are potentially achieved. For example, when the Mn_2O_{10} to Mn_2P_2 ratio in the structure is changed to 3:1, manganese oxalate nanobelt $Mn_8(ox)_8$ with the width of ca. 17.5 Å will be created. Theoretically, the formation of even wider manganese oxalate naobelt such as $Mn_{10}(ox)_{10}$ is also possible.

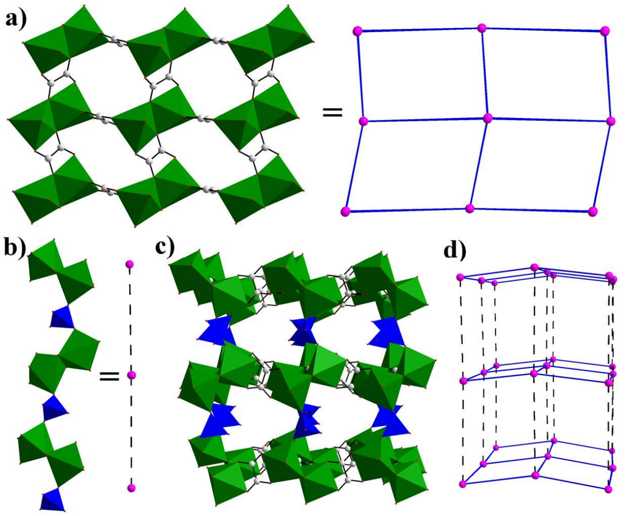

Fig.2. (a) The sql-type manganese oxalate layer in **2**. (b) The manganese phosphate chain in the structure of **2**. (c) Perspective view of the framework structure of **2** along the [001] direction. (d) The pcu topology of **2** with Mn_2O_{10} dimers acting as the nodes.

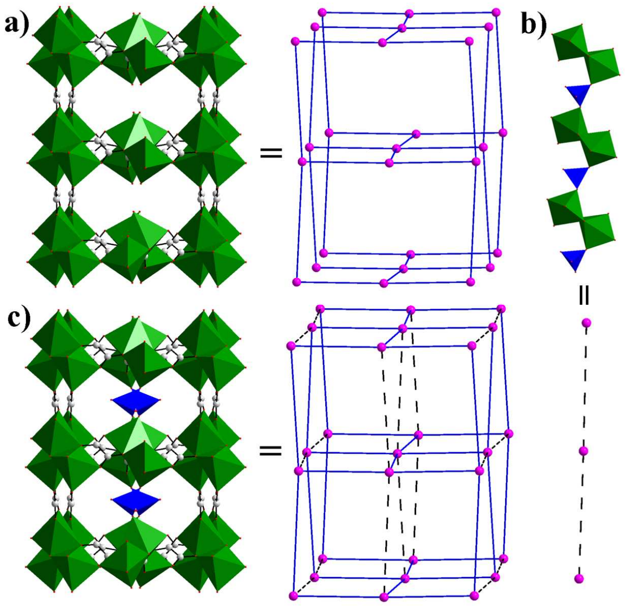

Fig.3. (a) The cds-type manganese oxalate layer in **3**. (b) The manganese phosphate chain in the structure of **3**. (c) The structure of **3** has a pcu topology with Mn_2O_{10} dimers acting as the nodes.

If only Mn_2O_{10} dimers act as the nodes, compounds **2** and **3** will be obtained. Structural analysis reveals that compound **2** crystallizes in the monoclinic space group $P2_1/c$ (No. 14). This compound contains a layered manganese oxalate substructure parallel to the *ac* plane (Fig. 2a). By regarding Mn_2O_{10} dimers as the nodes, the manganese oxalate layer has a sql topology. On the other hand, the linkages between Mn_2O_{10} dimers and HPO_4 tetrahedra give rise to linear manganese phosphate chain as found in **1**. The manganese oxalate skeletons are pillared by HPO_4 groups to form a three-dimensional structure with a pcu topology (Fig. 2c, 2d). Viewed along the [100], [010], and [001] directions, the compound displayed 8 MR, 8 MR, and 10 MR channels. The doubly protonated dap cations locate within the channels, which occupy 29.5% of the unit cell volume.

The structure of **2** is reminiscent of other pcu-type metal phosphate-oxalates, such as $H_2pip{\cdot}Mn_4(HPO_4)_2(C_2O_4)_3(H_2O)_2$ containing Mn_4P_2 cluster as the 6-connected nodes.[4] We noted that this compound contains a ladder-like metal oxalate with a formula of $Mn_4(ox)_3$, which can be also understood as the fragment of the sql-type layer found in **2**. The replacement of large Mn_4P_2 clusters by small Mn_2O_{10} dimers removes some inorganic partitions between the metal oxalate ladders. As a result, the ladder-like metal oxalate skeleton is extended into a sql layer within the pcu-type network.

Compound **3** crystallizes in the orthorhombic space group $Pna2_1$ (No. 33). This compound has a three-dimensional open-framework structure. Viewed along the [100], and [001] directions, it displays 10 MR, and 8 MR channels. The protonated pa cations locate within the channels, which occupy 34.1% of the unit cell volume. Compound **3** features a three-dimensional metal oxalate framework with a cds topology by regarding Mn_2O_{10}

clusters as the 4-connected nodes (Fig. 2a). The H_2PO_4 groups are encapsulated within its 12-ring channels and each of them connects two Mn_2O_{10} dimers through P–O–Mn linkages. As a result, the 4-connected cds-type metal-organic framework is transformed into a 6-connected pcu-type inorganic-organic hybrid network.

Compound **3** shares several common structural features with compound **2**. Both compounds have the same Mn:P:ox ratio, the same pcu-topology, and the same Mn_2O_{10} dimers as the 6-connected nodes. In addition, all the phosphate groups and oxalate ligands in the two structures act as μ_2-linkers between two Mn_2O_{10} dimers. In zeolite chemistry, different open-framework structures sharing these common structural features are always regarded to be isostructural. However, careful analysis of the two structures reveals some significant differences. For example, the two compounds have different metal-organic skeletons and pore apertures. Another difference is given by the packing modes of manganese phosphate chains. In compound **2**, all manganese phosphate chains run along the same direction, while in compound **3**, the inorganic chains run along the [011] and [01-1] directions, respectively.

Thermogravimetric analyses, performed under a flow of N_2 with a heating rate of 10 °C min^{-1}, showed that the three compounds remained stable up to ca. 270 °C. On further heating, their frameworks started to decompose. The total weight losses of 52.8% (for **1**), 50.8% (for **2**), and 49.2% (for **3**) in the temperature region of 270-600 °C are attributed to the decomposition of organic cations and oxalate ligands (expected: 51.9% for **1**, 51.7% for **2**, and 49.9% for **3**). The remaining residues are assumed to be a mixture of MnO and $MnHPO_4$.

The temperature dependence of the magnetic susceptibility of compounds **1**-**3** was measured in the temperature range 2-300 K. The magnetic moment (μ_{eff}) at 300 K per mole of manganese atom, determined from the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$, is 5.83 μ_B (for **1**), 5.84 μ_B (for **2**), and 5.75 μ_B (for **3**), in agreement with the expected spin-only value of Mn(II) in the high spin state (5.92 μ_B).[12] The thermal evolution of χ_m follows the Curie-Weiss law at temperature above 30 K with C_m = 4.51 cm^3 K mol^{-1} and θ = -17.8 K (for **1**), C_m = 4.56 cm^3 K mol^{-1} and θ = -20.7 K (for **2**), and C_m = 4.48 cm^3 K mol^{-1} and θ = -23.4 K (for **3**). The negative and small θ values indicate the existence of weak antiferromagnetic interactions between the manganese centers.

In summary, three new inorganic-organic hybrid solids have been synthesized in the presence of different amines as the structure-directing agents under solvent-free conditions. The synergetic effect of two different inorganic building blocks for the formation of a hybrid open-framework structure is noteworthy. These compounds are intriguing since they provide an ideal structural model to illustrate how to tune metal-organic skeletons within a specific network. Given the large number of amine molecules, we believe that this synthetic approach will offer exciting opportunities for the design and synthesis of new hybrid open-framework structures.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray data in CIF format, experimental details, additional figures, CHN elemental analysis results, IR spectra, powder XRD patterns, TGA curves, and magnetic data. CCDC 1046114-1046116. See DOI: 10.1039/b000000x/

‡ Crystal data for compound **1**, $C_{13.5}H_{24}Mn_3N_3O_{20}P_2$, M = 775.12, triclinic, space group P-1 (no. 2), a = 8.0352(2) Å, b = 10.1895(2) Å, c = 16.0266(5) Å, α = 93.349(2)º, β = 94.504(3)º, γ = 92.452(2)º, V = 1304.40(7) $Å^3$, Z = 2, Dc = 1.973 g cm^{-3}, μ = 13.706 mm^{-1}, 14041 reflections measured, 4655 unique (R_{int} = 0.0384). Final wR_2 (all data) = 0.1262, final R_1 = 0.0442. Crystal data for compound **2**, $C_7H_{13}Mn_2N_2O_{12}P$, M = 458.04, monoclinic, space group $P2_1$/c (no. 14), a = 15.8041(3) Å, b = 16.2451(3) Å, c = 11.5352(2) Å, β = 93.837(2)º, V = 2954.92(9) $Å^3$, Z = 8, Dc = 2.059 g cm^{-3}, μ = 15.625 mm^{-1}, 18797 reflections measured, 5270 unique (R_{int} = 0.0398). Final wR_2 (all data) = 0.1202, final R_1 = 0.0437. Crystal data for compound **3**, $C_7H_{12}Mn_2NO_{12}P$, M = 443.03, orthorhombic, space group $Pna2_1$ (no. 33), a = 11.6599(3) Å, b = 10.9336(3) Å, c = 11.7669(3) Å, V = 1500.10(7) $Å^3$, Z = 4, Dc = 1.962 g cm^{-3}, μ = 15.342 mm^{-1}, 4374 reflections measured, 2214 unique (R_{int} = 0.0660). Final wR_2 (all data) = 0.1438, final R_1 = 0.0572.

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