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ARTICLE TYPE

Solvent-free synthesis of new metal phosphate-oxalates: influence of different metal ions on the framework structures†

Lindong Luan,^{a,b} Meng Yang,^{*a} Yixuan Bian,^a Zhien Lin,^{*a} and Hui Huang^b

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A series of new metal phosphate-oxalates were synthesized under solvent-free conditions. These compounds display interesting open-framework structures with mmt, ins, fsd, and hcb topologies, respectively. The extra-large 20-ring channel, nanobelt-like inorganic skeleton, and the use of cadmium ions as framework cations are unprecedented in metal phosphate-oxalate structures.

Crystalline metal phosphate-oxalates are an important class of inorganic-organic hybrid solids due to their appealing physical properties and potential applications in gas storage, ion-exchange, cathode materials, and sensing.¹ These open-framework materials exhibit diverse networks combining both structural features of zeolitic metal phosphates and metal-organic frameworks.² They are usually synthesized under hydrothermal conditions.³ The “dry” hydrothermal synthesis of a neutral manganese phosphate-oxalate was also known by the use of reduced amounts of water in the reaction.⁴ Recent progresses indicate that solvent-free approach may provide a new access to prepare open-framework structures without the addition of solvent in the reaction.⁵ For example, some porous coordination polymers or metal-organic frameworks have been synthesized by grinding metal salts (e.g., Cu(NO₃)₂·2.5H₂O) with organic ligands.⁶ It is noteworthy that the water molecules in hydrated metal salts may play an important role in the formation of the framework structures by serving as material transporters. However, the grinding processes often create microcrystalline powders as the main products. As a result, single-crystal X-ray diffraction cannot be applied to determine their structures.

From the view point of structural chemistry, two components of metal phosphate-oxalates could influence the overall framework structures: structure-directing agent and metallic cation. Previously, we reported the solvent-free synthesis of several manganese phosphate-oxalates by using different amines as the structure-directing agents.⁷ Yet the influence of different metal ions on the framework structures has not been investigated under solvent-free conditions. It is expected that the use of different metal ions as the framework cations will not only realize the structural diversity, but also endow the hybrid structures with interesting properties, such as magnetism and photoluminescence.⁸

Here we report the solvent-free synthesis of six new metal phosphate-oxalates containing different metal ions as the framework cations, formulated as (H₂dab)_{0.5}·M(H₂PO₄)(ox) (M =

Co (1), Zn (2)), (H₂dab)_{0.5}·M(HPO₄)(ox)_{0.5}(H₂O) (M = Mn (3), and Cd (4)), (H₂dab)₂·Ga₄(HPO₄)₅(H₂PO₄)₂(ox)₂(H₂O)₂ (5), and (H₂dab)_{0.5}·In(HPO₄)(H₂PO₄)(ox)_{0.5} (6), where dab = 1,4-diaminobutane, and ox = oxalate. These inorganic-organic hybrid solids were prepared in the presence of the same structure-directing agent. They display interesting framework structures with mmt (for 1 and 2), ins (for 3 and 4), fsd (for 5), and hcb (for 6) topologies.⁹ It is noteworthy that compound 4 represents the first example of open-framework cadmium phosphate-oxalate. Moreover, the 20-membered-ring (20 MR) channel in the structure of 5 is the largest pore opening in metal phosphate-oxalate chemistry.

In a typical synthesis, a mixture of CoO (0.150 g), H₂C₂O₄·2H₂O (0.252 g), H₃PO₄ (85 wt%, 136 μL), and 1,4-diaminobutane (100 μL) in a stoichiometric ratio was sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 75 days. The autoclave was subsequently allowed to cool to room temperature. Reddish violet crystals of compound 1 were obtained in a yield of 70.2%. Compounds 2-6 were prepared under similar synthetic conditions. All the reactions were carried out by using different metal oxides as the metal sources to eliminate the effect of the anions (e.g., Cl⁻, NO₃⁻, and CH₃COO⁻) of metal salts on the framework structures. The phase purity of as-synthesized compounds was confirmed by powder X-ray diffraction. Their framework structures are determined by single-crystal X-ray diffraction.‡

Compounds 1 and 2 are isostructural, therefore, only crystal

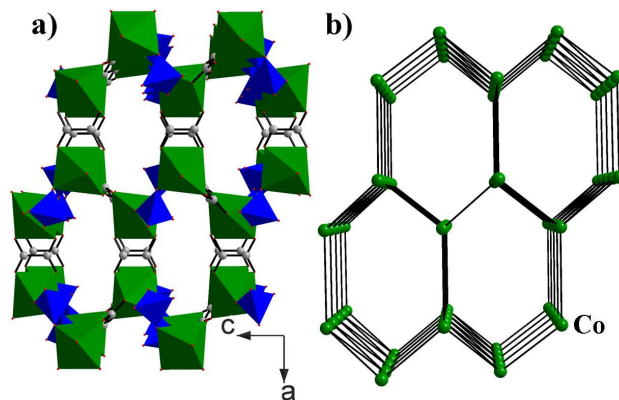


Fig. 1. (a) A view of the structure of 1 along the [010] direction showing the 12 MR channels. (b) Compound 1 has a rare 4-connected mmt topology. The amine molecules within the channels are omitted for clarity. Color code: CoO₆ octahedra, green; PO₄ tetrahedra, blue; carbon, gray; oxygen, red.

structure of compound **1** is described in detail. Compound **1** crystallizes in the orthorhombic space group *Pccn* (No. 56). There are one cobalt atom, one H_2PO_4 unit, two halves of oxalate ligands, and half of H_2dab cation in the asymmetric unit. The cobalt atom has an octahedrally coordinated geometry, bonded to six oxygen atoms from two H_2PO_4 units and two oxalate ligands. The H_2PO_4 unit and oxalate ligand each connects two cobalt atoms. The linkages between cobalt atoms, H_2PO_4 units, and oxalate ligands generate a three-dimensional structure (Fig. 1a). It contains cobalt phosphate chain and cobalt oxalate chain as its building blocks.

Viewed along the [010] and [001] directions, the structure of **1** exhibits different 12 MR channels. The H_2dab cations are ordered within the 12 MR channels and occupy 26.7% of unit cell volume. By regarding Co atoms as the 4-connected nodes, the framework structure can be understood as an mmt topology, as shown in Fig. 1b.

The structure of **1** is reminiscent of a manganese phosphate-oxalate, $\text{H}_2\text{dmpda}\cdot\text{Mn}_2(\text{HPO}_4)_2(\text{ox})_2\cdot\text{H}_2\text{O}$, with a dia topology.¹⁰ Both compounds have similar 12-ring channels and chain-like building block. It is well known that dia network is very common in crystal chemistry.¹¹ In comparison, mmm network has been rarely reported. As far as we know, it has been observed for the first time in metal phosphate-oxalate chemistry. One main difference between dia and mmt nets lies in their different cage units: a 6^4 cage unit for dia net and a 6^6 cage unit for mmt net.

Compound **3** crystallize in the monoclinic space group $P2_1/n$ (No. 14). The asymmetric unit consists of one manganese atom, one HPO_4 unit, half of oxalate ligand, one water molecule, and half of H_2dab cation. The manganese atom is octahedrally coordinated by six oxygen atoms from three HPO_4 units, one oxalate ligand and one water molecule. The HPO_4 unit makes three P–O–Mn connections to adjacent metal centers, and each oxalate ligand connects two metal centers in a bisbidentate chelating coordination mode. The linkages between MnO_6 octahedra and HPO_4 units create inorganic layers parallel to the *ac* plane. These inorganic layers are further pillared by oxalate ligands to give rise to a three-dimensional structure with 12-ring channels running along the [100] direction (Fig. 2a). The H_2dab cations are accommodated within the 12 MR channels, which occupy 32.3% of unit cell volume. Different from the 4-

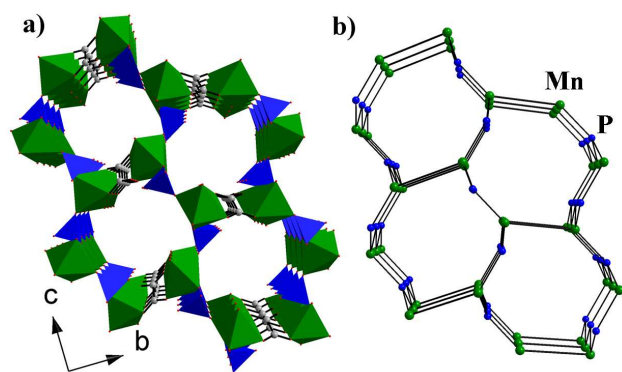


Fig.2. (a) A view of the structure of **3** along the [100] direction showing the 12 MR channels. (b) Compound **3** has a (3,4)-connected ins topology. The amine molecules within the channels are omitted for clarity. Color code: MnO_6 octahedra, green; PO_4 tetrahedra, blue; carbon, gray; oxygen, red.

connected topology found in compounds **1** and **2**, compound **3** has a (3,4)-connected ins topology by regarding manganese atoms as the 4-connected nodes and phosphorus atoms as 3-connected nodes (Fig. 2b).

Compound **4** has the same framework topology as compound **3**. As far as we know, this compound is the first example of open-framework cadmium phosphate-oxalate. The difficulty in the synthesis of cadmium phosphate-oxalate hybrid frameworks may be related to the large ionic radius of Cd^{2+} . It is well known that the ionic radius of Cd^{2+} (0.91 Å) is much larger than those of Mn^{2+} (0.77 Å), Co^{2+} (0.69 Å), Fe^{2+} (0.74 Å), and Zn^{2+} (0.71 Å).¹² As a result, it may be difficult for Cd^{2+} ions to fit into those hybrid frameworks as found in $\text{M-PO}_4\text{-ox}$ ($\text{M} = \text{Mn, Co, Fe, Zn}$) systems.

Compound **5** crystallizes in the monoclinic space group $P2_1/n$ (No. 14). It consists of a gallium phosphate nanobelt as its building block (Fig. 3a). The nanobelt can be conceptually built up by two different substructures: a ladder-like substructure constructed from $\text{Ga}(1)\text{O}_6$ octahedra and $\text{P}(1)\text{O}_4$ tetrahedra, and a chain-like substructure of alternating $\text{Ga}(2)\text{O}_6$ octahedra and $\text{P}(3)\text{O}_4$ tetrahedra. Two chain-like substructures and one ladder-like substructure are joined by $\text{P}(2)\text{O}_4$ tetrahedra to form the nanobelt-like building block with 8 MR windows. The width of the nanobelt is ca. 14.2 Å, calculated from the shortest distance between two gallium atoms on both sides of the building block. These inorganic nanobelts are further bridged by oxalate ligands to give rise to a three-dimensional structure (Fig. 3b). By regarding the $\text{Ga}(2)$ atoms as the 4-connected nodes and $\text{Ga}(1)_2\text{P}(1)_2$ tetramers as the 6-connected nodes, the structure of **5** can be simplified as a (4, 6)-connected fsd topology (Fig. 3c).

The most interesting structural feature of compound **5** is the presence of extra-large 20 MR channels. Prior to this work, the largest pore opening in metal phosphate-oxalates is found in

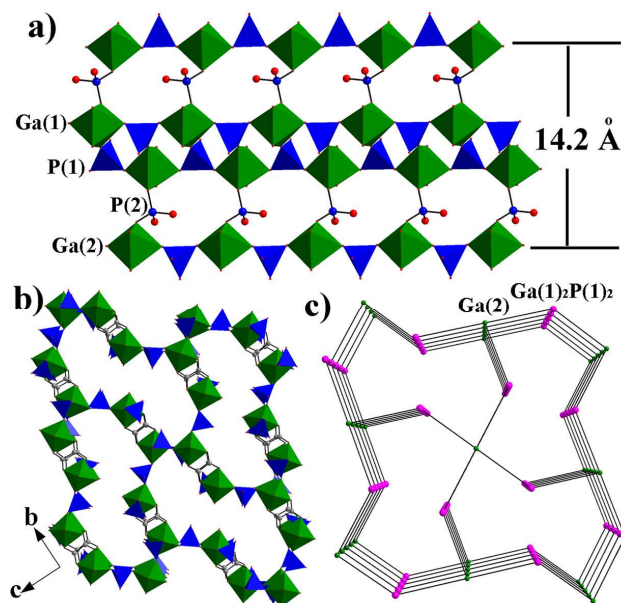


Fig.3. (a) The nanobelt-like gallium phosphate substructure in **5**. (b) A view of the structure of **5** along the [100] direction showing the 20 MR channels. (c) Compound **5** has a (4,6)-connected fsd topology. The amine molecules and dangling $\text{HP}(4)\text{O}_4$ tetrahedra are omitted for clarity. Color code: GaO_6 octahedra, green; phosphorus/ PO_4 tetrahedra, blue; carbon, gray; oxygen, red.

some open-framework hybrid structures with 16 MR channels.¹³ The 20 MR window in **5** is highly puckered, which is delimited by ten GaO₆ octahedra, six PO₄ tetrahedra, and four oxalate ligands. Disordered HP(4)O₄ tetrahedra attach to the wall of 20 MR channels as pendants and reduce the free space.

Compound **6** crystallizes in the triclinic space group *P*-1 (No. 2). The asymmetric unit consists of one indium atom, one HPO₄ unit, one H₂PO₄ unit, half of oxalate ligand, and half of H₂dab cation. The linkages between indium atoms and P-centered tetrahedra create corner-sharing 4-ring chains, which are further bridged by oxalate ligands to form a layered structure (Fig. 4a). It has 12 MR windows delimited by six InO₆ octahedra, four P-centered tetrahedra, and two oxalate ligands. By regarding the indium atoms as 6-connected nodes, the layered structure has a hcb topology (Fig. 4b). These hybrid layers are stacked along the [010] direction in the eclipsed configuration. There are strong O(4)–H(1)⋯O(2) hydrogen bonds (*d* = 1.83 Å) between adjacent layers. As a result, the hcb-type layer is extended into a supramolecular framework with a (3,4)-connected moc topology.

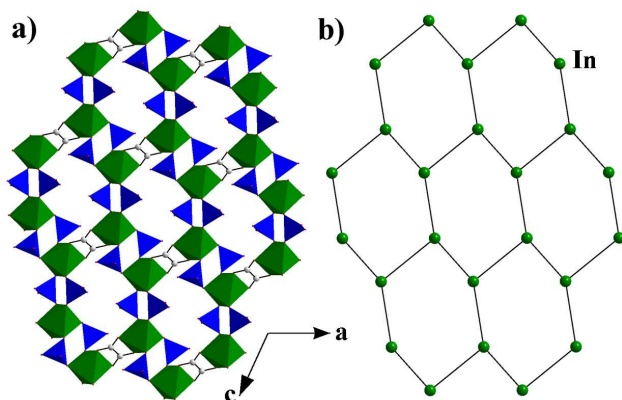


Fig. 4. (a) A view of the layered structure of **6** along the [010] direction showing the 12 MR windows. (b) Compound **6** has a 3-connected hcb topology. Color code: InO₆ octahedra, green; PO₄ tetrahedra, blue; carbon, gray; oxygen, red.

Thermogravimetric analyses for compounds **1–6** were carried out in a flow of N₂ with a heating rate of 10 °C/min. For compounds **1** and **2**, the weight loss in the temperature region 290–420 °C (for **1**; observed: 46.7%, expected: 46.4%) and 260–520 °C (for **2**; observed: 44.5%, expected: 45.4%) was attributed to the decomposition of amine molecules and oxalate ligands. For compound **3** and **4**, the weight loss in the temperature region 170–600 °C (for **3**; observed: 38.3%, expected: 41.5%) and 170–800 °C (for **4**; observed: 33.2%, expected: 33.9%) was caused by the departure of water molecules and the decomposition of amine molecules and oxalate ligands. Compound **5** lost its crystalline water molecules below 230 °C (observed: 2.3%; expected: 2.7%). On further heating, its framework started to decompose. The weight loss in the temperature region 230–600 °C was caused by the decomposition of amine molecules and oxalate ligands (observed: 25.8%, expected: 26.5%). Compound **6** remained stable up to 320 °C. The weight loss below 500 °C was caused by the decomposition of amine molecules and oxalate ligands (observed: 22.0%, expected: 22.4%). Powder XRD analysis reveals that all the structures collapse after the removal of amine molecules.

The temperature dependence of the magnetic susceptibility of compounds **1** and **3** was measured in the temperature range 2–300 K (Fig. 5). The values of $\chi_M T$ at 300 K are 2.74 and 4.38 cm³ K mol⁻¹ for **1** and **3**, respectively. The magnetic moment (μ_{eff}) at 300 K per mole of metal atom, determined from the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$, is 4.68 μ_B (for **1**) and 5.92 μ_B (for **3**), in agreement with those reported for other Co(II) and Mn(II) compounds.¹⁴ Upon cooling, the $\chi_M T$ values decrease continuously and reach the values of 0.05 cm³ K mol⁻¹ (for **1**) and 0.32 cm³ K mol⁻¹ (for **3**) at 2 K. The thermal evolution of χ_M follows the Curie-Weiss law at temperature above 35 K (for **1**) and 10 K (for **3**), with $C_m = 3.28$ cm³ K mol⁻¹ and $\theta = -58.9$ K for **1** and $C_m = 4.59$ cm³ K mol⁻¹ and $\theta = -13.9$ K for **3**. The negative θ values indicate the existence of antiferromagnetic interactions between the metal ions.

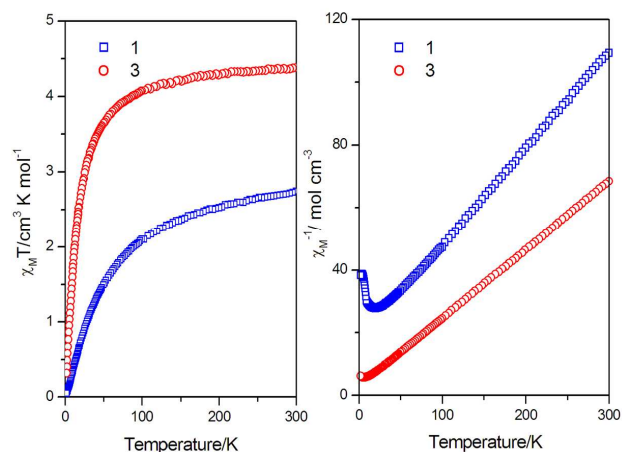


Fig. 5. Temperature dependence of $\chi_M T$ (left) and χ_M^{-1} (right) for compounds **1** and **3**.

In summary, six different metal ions (i.e., Co²⁺, Zn²⁺, Mn²⁺, Cd²⁺, Ga³⁺, and In³⁺) have been used as the framework cations for the solvent-free synthesis of new open-framework metal phosphate-oxalates. Four types of framework topologies were created during the course of such investigations. By increasing the largest pore sizes from 16 MR to 20 MR in metal phosphate-oxalates, the present work makes a step forward toward creating new extra-large porous materials. We believe that the solvent-free approach offers exciting opportunities to find novel open-framework materials with new chemical compositions, framework topologies, and large pore apertures.

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Notes and references

^a College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. E-mail: ouyame@sina.com (M. Yang); zhienlin@scu.edu.cn (Z. Lin)

^b School of Chemistry, Beijing Institute of Technology, Beijing 100081, P. R. China.

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- ‡ Crystal data for compound **1**, $C_4H_9CoNO_8P$, $M = 289.02$, orthorhombic, space group *Pccn* (no. 56), $a = 16.3686(9)$ Å, $b = 8.2405(5)$ Å, $c = 13.1615(8)$ Å, $V = 1775.29(18)$ Å³, $Z = 8$, $D_c = 2.163$ g cm⁻³, $\mu = 2.141$ mm⁻¹, 5460 reflections measured, 1821 unique ($R_{int} = 0.0243$). Final wR_2 (all data) = 0.0803, final $R_1 = 0.0320$. Crystal data for compound **2**, $C_4H_9NO_8PZn$, $M = 295.46$, orthorhombic, space group *Pccn* (no. 56), $a = 8.2185(2)$ Å, $b = 16.3878(3)$ Å, $c = 13.2772(2)$ Å, $V = 1788.22(6)$ Å³, $Z = 8$, $D_c = 2.195$ g cm⁻³, $\mu = 5.879$ mm⁻¹, 5107 reflections measured, 1597 unique ($R_{int} = 0.0296$). Final wR_2 (all data) = 0.1218, final $R_1 = 0.0458$.
- Crystal data for compound **3**, $C_3H_{10}MnNO_7P$, $M = 258.03$, monoclinic, space group *P2₁/n* (no. 14), $a = 5.5667(1)$ Å, $b = 15.6297(3)$ Å, $c = 9.5408(2)$ Å, $\beta = 91.804(2)^\circ$, $V = 829.69(3)$ Å³, $Z = 4$, $D_c = 2.066$ g cm⁻³, $\mu = 14.973$ mm⁻¹, 4944 reflections measured, 1481 unique ($R_{int} = 0.0460$). Final wR_2 (all data) = 0.1150, final $R_1 = 0.0436$. Crystal data for compound **4**, $C_3H_{10}CdNO_7P$, $M = 315.49$, monoclinic, space group *P2₁/n* (no. 14), $a = 5.6339(1)$ Å, $b = 15.9428(2)$ Å, $c = 9.6183(2)$ Å, $\beta = 91.116(2)^\circ$, $V = 863.75(2)$ Å³, $Z = 4$, $D_c = 2.426$ g cm⁻³, $\mu = 22.209$ mm⁻¹, 6211 reflections measured, 1540 unique ($R_{int} = 0.0430$). Final wR_2 (all data) = 0.1046, final $R_1 = 0.0395$. Crystal data for compound **5**, $C_{12}H_{41}Ga_4N_4O_{38}P_7$, $M = 1345.16$, monoclinic, space group *P2₁/n* (no. 14), $a = 6.2152(1)$ Å, $b = 18.8391(2)$ Å, $c = 16.6568(1)$ Å, $\beta = 92.229(1)^\circ$, $V = 1948.84(3)$ Å³, $Z = 2$, $D_c = 2.292$ g cm⁻³, $\mu = 7.109$ mm⁻¹, 20197 reflections measured, 3486 unique ($R_{int} = 0.0927$). Final wR_2 (all data) = 0.1377, final $R_1 = 0.0500$. Crystal data for compound **6**, $C_3H_{10}InNO_{10}P_2$, $M = 396.88$, triclinic, space group *P-1* (no. 2), $a = 7.6595(6)$ Å, $b = 8.4550(4)$ Å, $c = 9.6469(6)$ Å, $\alpha = 91.768(5)^\circ$, $\beta = 111.205(6)^\circ$, $\gamma = 115.495(6)^\circ$, $V = 512.64(6)$ Å³, $Z = 2$, $D_c = 2.571$ g cm⁻³, $\mu = 2.667$ mm⁻¹, 6283 reflections measured, 2090 unique ($R_{int} = 0.0340$). Final wR_2 (all data) = 0.0593, final $R_1 = 0.0232$.
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The influence of different metal ions on the framework structures were investigated under solvent-free conditions, which gave rise to six new metal phosphate-oxalates with mmt, ins, fsd, and hcb topologies, respectively.

