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ARTICLE TYPE

# Solvent-free synthesis of new metal phosphite-oxalates with open-framework structures†

Lin Liu,<sup>a</sup> Daibing Luo,<sup>b</sup> Defu Li<sup>a</sup> and Zhien Lin<sup>\*a</sup>

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Two new metal phosphite-oxalates,  $\text{CN}_3\text{H}_6 \cdot \text{Co}(\text{H}_2\text{PO}_3)(\text{C}_2\text{O}_4)$  (1) and  $(\text{CN}_3\text{H}_6)_2 \cdot \text{Mn}_{2.5}(\text{HPO}_3)(\text{C}_2\text{O}_4)_{2.5}(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$  (2), have been prepared under solvent-free conditions. The two open-framework compounds have diamondoid and pillared-layered structures, respectively. Their photoluminescence and magnetic properties are also investigated.

Microporous and open-framework materials, such as zeolites and coordination polymers, have been extensively studied for their potential applications in catalysis, ion-exchange, gas storage, separation, and sensor technology.<sup>1</sup> Recent developments show that new open-framework structures can be created by integrating both structural and compositional features of zeolitic inorganic solids and coordination polymers.<sup>2</sup> During the past years, great efforts have been focused on the synthesis of metal phosphate-oxalate hybrid solids.<sup>3</sup> In comparison, the inorganic-organic hybrid frameworks containing phosphite units have been rarely reported.<sup>4</sup> It has been demonstrated that the replacement of phosphate groups by phosphite units can reduce the M–O–P connectivity and generate interrupted framework structures.<sup>5</sup> A notable example is NTHU-13 with tunable pore sizes ranging from 24-membered ring (24 MR) to 72 MR.<sup>6</sup>

Crystalline open-framework compounds are usually prepared under hydrothermal or solvothermal conditions. A challenging goal in this research is to eliminate the safety concerns associated with high reaction pressure. One feasible strategy is the replacement of molecular solvents by ionic liquids.<sup>7</sup> For example, Morris and co-workers have succeeded in the ionothermal syntheses of a number of new zeotype inorganic solids and metal-organic frameworks by using ionic liquids as both solvents and templates.<sup>8</sup> The ionothermal reactions may take place at ambient pressure due to the negligible vapor pressure of ionic liquids. Another approach is to remove liquid solvents from porous material synthesis. It has been demonstrated that solvent-free mechanochemical synthesis is particularly effective for the preparation of porous coordination polymers.<sup>9</sup> However, the products obtained by mechanochemical approach are usually microcrystalline powders, indicating that single-crystal X-ray diffraction cannot be used to determine their structures.<sup>10</sup>

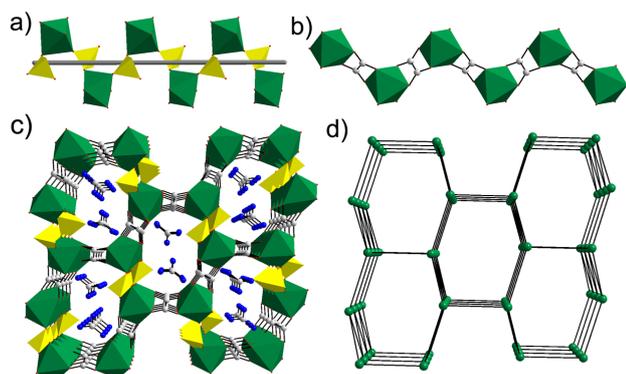
Inspired by the successful isolation of an open-framework inorganic solid  $\text{NH}_4[\text{BPO}_4\text{F}]$  in a solvent-free flux of  $\text{H}_3\text{BO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ ,<sup>11</sup> we expect that the combination of phosphorous acid (melting point: 73 °C) and oxalic acid (melting point: 102 °C) under solvent-free conditions may produce new inorganic-organic

hybrid solids. During the course of such investigation, two open-framework metal phosphite-oxalates,  $\text{CN}_3\text{H}_6 \cdot \text{Co}(\text{H}_2\text{PO}_3)(\text{C}_2\text{O}_4)$  (1) and  $(\text{CN}_3\text{H}_6)_2 \cdot \text{Mn}_{2.5}(\text{HPO}_3)(\text{C}_2\text{O}_4)_{2.5}(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$  (2), have been prepared in the presence of guanidinium cations as the structure-directing agents. Their structures were solved from single crystal X-ray diffraction data collected at room temperature on an Oxford Xcalibur diffractometer.‡

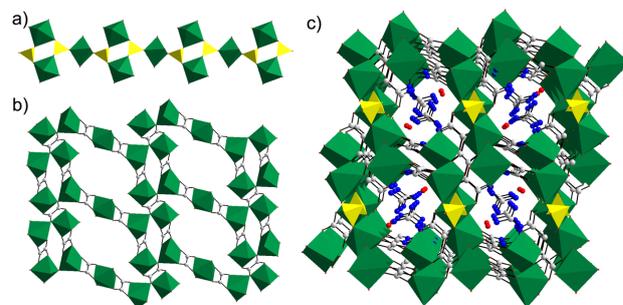
Red crystals of compound 1 were obtained by heating a mixture of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , guanidinium carbonate,  $\text{H}_3\text{PO}_3$ , and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in a molar ratio of 1 : 1 : 2 : 2 at 150 °C for 7 days. The powder X-ray diffraction pattern of as-synthesized compound is in good agreement with the simulated one on the basis of single crystal data, indicating the phase purity of as-synthesized compound (Fig. S1, ESI†). The variation of the molar ratio of reactants often resulted in the formation of a layered cobalt phosphite  $(\text{H}_3\text{O})_2 \cdot \text{Co}_3(\text{HPO}_3)_4$  or a mixture of this inorganic solid and compound 1.<sup>12</sup> CHN elemental analysis of compound 1 gave C 12.16 wt%, H 2.72 wt% and N 14.36 wt%, consistent with the calculated values of C 12.51 wt%, H 2.80 wt% and N 14.59 wt%. IR spectrum indicates the presence of phosphite units and oxalate ligands in the structure (Fig. S2, ESI†). The band at 2420  $\text{cm}^{-1}$  is due to the stretching vibration of P–H bonds, and the strong bands at 1610 and 1320  $\text{cm}^{-1}$ , correspond to the C=O and C–O stretching vibrations of the oxalate groups.

Compound 1 crystallizes in the monoclinic space group  $P2_1/n$  (no. 14). There are one Co atom, one  $\text{H}_2\text{PO}_3$  unit, two halves of oxalate ligands, and one guanidinium cation in the asymmetric unit (Fig. S3, ESI†). The Co atom is octahedrally coordinated by six oxygen atoms from two oxalate ligands and two  $\text{H}_2\text{PO}_3$  units. The  $\text{H}_2\text{PO}_3$  unit makes two P–O–Co connections to adjacent metal centers. The linkages between  $\text{H}_2\text{PO}_3$  units and  $\text{CoO}_6$  octahedra generate inorganic helical chains running along the [010] direction, as shown in Fig. 1a. The pitch of the helix is 7.4104(2) Å, which is equal to the periodicity along the crystallographic *b* axis. Each oxalate ligand in the structure connects two Co atoms in a bisbidentate chelating coordination mode. As a result, zigzag cobalt oxalate chains are generated, which run along the [100] direction (Fig. 1b). The Co–O bond lengths are in the range of 2.041(2)–2.119(2) Å, and the P–O bond lengths vary from 1.493(2) Å to 1.557(2) Å.

The helical inorganic chains are linked by zigzag oxalate chains through common  $\text{CoO}_6$  octahedra to result in a three-dimensional open-framework structure, as shown in Fig. 1c.



**Fig.1.** (a) Polyhedral view of the cobalt phosphite helical chain. (b) A view of the zigzag cobalt oxalate chain. (c) A view of the framework structure of **1** with 12-ring channels delimited by six  $\text{CoO}_6$  octahedra, two  $\text{H}_2\text{PO}_3$  pseudo pyramids, and four oxalate ligands. (d) Compound **1** has a diamondoid framework topology. Color code:  $\text{CoO}_6$  octahedra, green;  $\text{H}_2\text{PO}_3$  pseudo pyramids, yellow; carbon, gray; nitrogen, blue.



**Fig.2.** (a) Polyhedral view of the manganese phosphite chain. (b) A view of the manganese oxalate layer with 16-ring windows. (c) A view of the framework structure of **2** with 12-ring channels running along the [001] direction. Color code:  $\text{MnO}_6$  octahedra, green;  $\text{HPO}_3$  pseudo pyramids, yellow; carbon, gray; nitrogen, blue; oxygen, red.

Viewed along the [100] direction, the structure exhibits 12-ring channels delimited by six  $\text{CoO}_6$  octahedra, four  $\text{H}_2\text{PO}_3$  pseudo pyramids, and two oxalate ligands. There are another type of 12-ring channels running along the [010] direction, which is delimited by six  $\text{CoO}_6$  octahedra, two  $\text{H}_2\text{PO}_3$  pseudo pyramids, and four oxalate ligands. The guanidinium cations are orderly within the intersecting channels and interact with the host framework through extensive hydrogen bonds. The closest  $\text{N}\cdots\text{O}$  distances are between 2.716(3)–3.086(3) Å. These organic cations occupy 40.4% of the unit cell volume (calculated using the program *PLATON*).<sup>13</sup>

By regarding Co atoms as the 4-connected nodes, the framework structure of **1** can be understood as a diamondoid network (Fig. 1d). Such framework topology is observed for the first time in phosphite-oxalate hybrid solids. Prior to this work, only one example of open-framework cobalt phosphite-oxalate is known:  $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Co}_4(\text{HPO}_3)_2(\text{C}_2\text{O}_4)_3]$ .<sup>14</sup> This hybrid solid contains one-dimensional 8-ring channels with infinite Co–O–Co chains, which is different from the framework structure of compound **1**.

Light-pink crystals of compound **2** were obtained by heating a mixture of  $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ , guanidinium carbonate,  $\text{H}_3\text{PO}_3$ , and  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  in a molar ratio of 1 : 1 : 1 : 1.2 at 150 °C for 10 days. The variation of the molar ratio of reactants often resulted in the formation of a mixture of a new manganese phosphite ( $\text{H}_3\text{O})_2\cdot\text{Mn}_2(\text{HPO}_3)_3$  and compound **2**. The phase purity of as-synthesized compound **2** was confirmed by powder X-ray diffraction pattern (Fig. S4, ESI†) and elemental analysis (anal. C 13.94 wt%, H 2.83 wt% and N 14.07 wt%; calc. C 14.16 wt%, H 2.89 wt% and N 14.16 wt%). IR spectrum contains a strong band at about 2380  $\text{cm}^{-1}$ , in good agreement with the existence of  $\text{HPO}_3$  pseudo pyramids in the crystal structure (Fig. S5, ESI†). The stretching vibration of C=O and C–O bonds are observed at 1610 and 1320  $\text{cm}^{-1}$ .

Compound **2** crystallizes in the triclinic space group *P*-1 (no. 2). The asymmetric unit contains 32 independent non-hydrogen atoms, of which Mn1 lies on an inversion center (Fig. S6, ESI†). Each Mn atom is octahedrally coordinated by oxygen atoms with

the Mn–O bond lengths in the range of 2.095(2)–2.304(2) Å. The P atom makes three P–O–Mn connections to adjacent Mn atoms, with the fourth vertex occupied by a terminal hydrogen atom. The linkages between  $\text{MnO}_6$  octahedra and  $\text{HPO}_3$  pseudo pyramids create a chain-like substructure, as shown in Fig. 2a. The P–O bond lengths are between 1.516(2)–1.523(2) Å, and the P–H bond length is 1.369 Å.

There are two types of oxalate ligands in the structure. Type I oxalate ligands adopt a typical bisbidentate chelating coordination mode, as that found in compound **1**. Type II oxalate ligands adopt a bisbidentate chelating/bridging coordination mode. The connectivity between  $\text{MnO}_6$  octahedra and oxalate ligands results in the formation of a layered substructure, which featured large 16-ring windows and  $\text{Mn}_2\text{O}_{11}$  dimers (Fig. 2b).

The manganese phosphite chains share common  $\text{MnO}_6$  octahedra with manganese oxalate layers to produce a three-dimensional open-framework structure (Fig. 2c). Viewed along the [100] direction, the structure has 10-ring channels delimited by six  $\text{MnO}_6$  octahedra, two  $\text{HPO}_3$  pseudo pyramids, and two oxalate ligands. Intersecting these 10-ring channels are those large 12-ring channels running along the [010] and [001] directions, respectively. The guanidinium cations locate in the free voids and balance the overall negative electrostatic charge of the hybrid framework. A void space analysis using the program *PLATON* indicates that all extraframework cations occupy 39.6% of the unit cell volume.

It is of interest to compare the structure of compound **2** with other related inorganic-organic hybrid frameworks. So far, three open-framework manganese phosphite-oxalates were prepared in the presence of different diamines as the structure-directing agents.<sup>15</sup> All of them have three-dimensional structures with manganese phosphites layers cross-linked by oxalate ligands. In comparison, the framework structure of compound **2** can be understood as manganese oxalate layers linked through  $\text{HPO}_3$  units.

We have also investigated the use of other transition metal ions (i.e.,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$ ) as the framework cations to prepare new open-framework structures. Preliminary results showed that the replacement of  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  by  $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ , but otherwise similar synthetic conditions as used for **1** gave rise to a new Zn-based compound isostructural to compound **1**. In the case of other metal ions, only powder or microcrystalline products

with unidentified structures were obtained.

Thermogravimetric analysis, carried out in a flow of air with a heating rate of 10 °C/min, showed that compound **1** remained stable up to 100 °C (Fig. S7, ESI†). The weight loss of 3.3% between 100–150 °C may be attributed to the dehydrated process involving H<sub>2</sub>PO<sub>3</sub> units (observed: 3.3%; expected 3.2%). The organic cations and oxalate ligands started to decompose over 265 °C. For compound **2**, the weight loss of 6.0% between 100–220 °C is due to the departure of crystalline water molecules (expected 6.1%). A plateau region in the temperature region 220–260 °C indicates that the framework structure is stable up to 260 °C. On further heating, the organic cations in the structure start to decompose (Fig. S8, ESI†).

The fluorescent spectra of compounds **1** and **2** were measured in solid state at room temperature. Upon excitation at 220 nm, the two compounds displayed a luminescence with a peak maximum at 392 nm and 396 nm, respectively (Fig. S9, S10, ESI†). These emissions are probably originated from the extraframework organic cations since similar weak emissions were also observed for guanidinium carbonate. The extensive hydrogen bond interactions between guanidinium cations and framework oxygen atoms may increase the rigidity of organic species, which effectively reduces the loss of energy. The similar enhanced fluorescence efficiency was also observed in an open-framework metal phosphite.<sup>16</sup>

The temperature dependence of the magnetic susceptibility of the two compounds was measured in the temperature range 2–300 K (Fig. 3). The magnetic moment ( $\mu_{\text{eff}}$ ) at 300 K per mole of metal atom is 5.09  $\mu_{\text{B}}$  for **1**, which, while significantly larger than the spin-only value of 3.87  $\mu_{\text{B}}$  due to strong orbital contributions, is comparable to those reported for other Co(II) compounds.<sup>17</sup> For compound **2**, the magnetic moment at 300 K per mole of metal atom is 5.73  $\mu_{\text{B}}$ , in agreement with the expected spin-only value of Mn(II) in the high spin state (5.92  $\mu_{\text{B}}$ ).<sup>18</sup> The thermal evolution of  $\chi_{\text{M}}$  follows the Curie-Weiss law at temperature above 20 K (for **1**) and 13 K (for **2**), with  $C_{\text{M}} = 4.46 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -95.0 \text{ K}$  (for **1**), and  $C_{\text{M}} = 4.61 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -26.3 \text{ K}$  (for **2**). The negative  $\theta$  values indicate the existence of antiferromagnetic interactions between the metal centers.

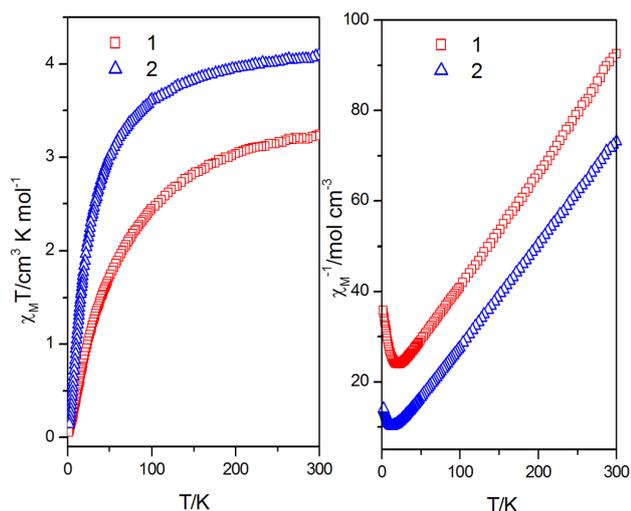


Fig. 3. Temperature dependence of  $\chi_{\text{M}}T$  (left) and  $\chi_{\text{M}}^{-1}$  (right) for compounds **1** and **2**.

In summary, two new metal phosphite-oxalates have been synthesized in a solvent-free flux of phosphorous acid and oxalic acid. The two compounds display different open frameworks with diamondoid and pillared-layered structures, demonstrating that solvent-free approach is effective in the growth of good quality single crystals of open-framework structures. Given the large variety of structure-directing agents, various metal ions and oxo anions, and rich coordination modes of oxalate ligand, we believe that this synthetic approach will offer exciting opportunities to prepare new crystalline inorganic-organic hybrid solids with open frameworks and appealing properties.

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## Notes and references

- <sup>a</sup> College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. E-mail: zhienlin@scu.edu.cn
- <sup>b</sup> Analytical & Testing Center, Sichuan University, Chengdu 610064, P. R. China.
- † Electronic Supplementary Information (ESI) available: X-ray data, experimental details, additional crystallographic figures, IR spectra, powder XRD patterns, TGA curves, fluorescent spectra. CCDC 982206-982207. See DOI: 10.1039/b000000x/
- ‡ Crystal data for compound **1**, C<sub>3</sub>H<sub>8</sub>CoN<sub>3</sub>O<sub>7</sub>P,  $M = 288.02$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 8.8749(3)$ ,  $b = 7.4104(2)$ ,  $c = 15.2333(5)$  Å,  $\beta = 102.172(3)^\circ$ ,  $V = 979.32(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.954 \text{ g cm}^{-3}$ ,  $\mu = 1.938 \text{ mm}^{-1}$ , 3900 reflections measured, 1721 unique ( $R_{\text{int}} = 0.0199$ ). Final  $wR_2$  (all data) = 0.0689, final  $R_1 = 0.0272$ . Crystal data for compound **2**, C<sub>7</sub>H<sub>17</sub>Mn<sub>2</sub>N<sub>6</sub>O<sub>15</sub>P,  $M = 593.59$ , triclinic, space group  $P-1$  (no. 2),  $a = 9.7205(6)$ ,  $b = 9.7468(6)$ ,  $c = 10.8926(5)$  Å,  $\alpha = 83.989(4)^\circ$ ,  $\beta = 75.467(5)^\circ$ ,  $\gamma = 78.545(5)^\circ$ ,  $V = 977.45(10) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 2.017 \text{ g cm}^{-3}$ ,  $\mu = 1.177 \text{ mm}^{-1}$ , 7356 reflections measured, 3448 unique ( $R_{\text{int}} = 0.0254$ ). Final  $wR_2$  (all data) = 0.0930, final  $R_1 = 0.0360$ .
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