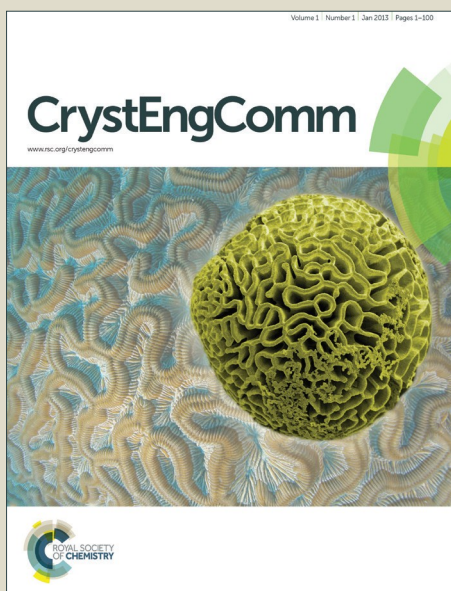


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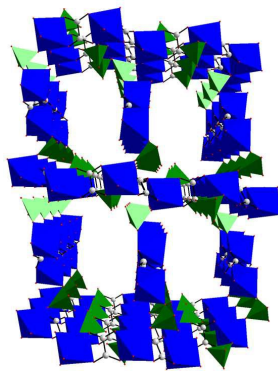
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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Solvent-free synthesis of new magnesium phosphate-oxalates displaying diverse framework topologies†

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Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

A series of open-framework magnesium phosphate-oxalates were prepared for the first time under solvent-free conditions. The pore apertures of these compounds range from small 8-membered ring (8 MR) to large 12 MR and extra-large 16 MR and 20 MR. Topological analyses reveal that they display ins, pcu, mmt, dia, fsh, fsc, and ths networks, respectively.

Solvent-free synthesis is of current interest in the preparation of open-framework inorganic solids, metal-organic frameworks, covalent-organic frameworks, and inorganic-organic hybrid solids.<sup>1</sup> This synthetic approach features simple process, low system pressure, and reduced pollution.<sup>2</sup> It avoids the influence of solvents on the framework structures, indicating that many new crystalline compounds that are unstable under hydrothermal and solvothermal conditions are potentially achieved.

Open-framework metal phosphate-oxalates are an important class of inorganic-organic hybrid solids due to their appealing physical properties such as photoluminescence.<sup>3</sup> Most crystalline metal phosphate-oxalates reported to date are based on transition metals and group 13 elements.<sup>4</sup> The use of rare earth ions as framework cations has also been investigated.<sup>5</sup> However, the synthesis of magnesium phosphate-oxalates is a particularly unexplored area. This is surprising given the similar ionic radius of Mg<sup>2+</sup> to many transition metal ions (Mg<sup>2+</sup>, 0.68 Å; Co<sup>2+</sup>, 0.69 Å; Ni<sup>2+</sup>, 0.70 Å; Zn<sup>2+</sup>, 0.71 Å) and the gravimetric advantage of magnesium in the synthesis of porous materials.<sup>6</sup> The experimental difficulty in the synthesis of magnesium phosphate-oxalates may be associated with the high solvation energy of Mg<sup>2+</sup>.

Here we use magnesium phosphate-oxalates as a model system to demonstrate the advantages of solvent-free synthesis in the creation of new open-framework structures. A series of new magnesium phosphate-oxalates were prepared in the presence of different amines as the structure-directing agents. A suitable single crystal of each compound was selected for single-crystal X-ray diffraction analysis (Table 1). Using Olex2, the structures were solved by direct methods and refined with the *ShelXL* refinement package.<sup>7</sup> These compounds display seven distinct topological features, including ins, pcu, mmt, dia, fsh, fsc, and ths networks.<sup>8</sup> As far as we know, the fsc and ths topologies have been observed for the first time in metal phosphate-oxalate structures.

In a typical synthesis, a mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub> (85 wt%), and ethylenediamine in a

stoichiometric ratio was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. Colorless crystals of compound **1** were obtained in a yield of 72.4%. Other magnesium phosphate-oxalates were prepared under similar synthetic conditions. It should be noted that when large quantities of water were added in the reactions, a hydrated magnesium phosphate MgHPO<sub>4</sub>·3H<sub>2</sub>O with a layered structure was always obtained as the resulting product.<sup>9</sup>

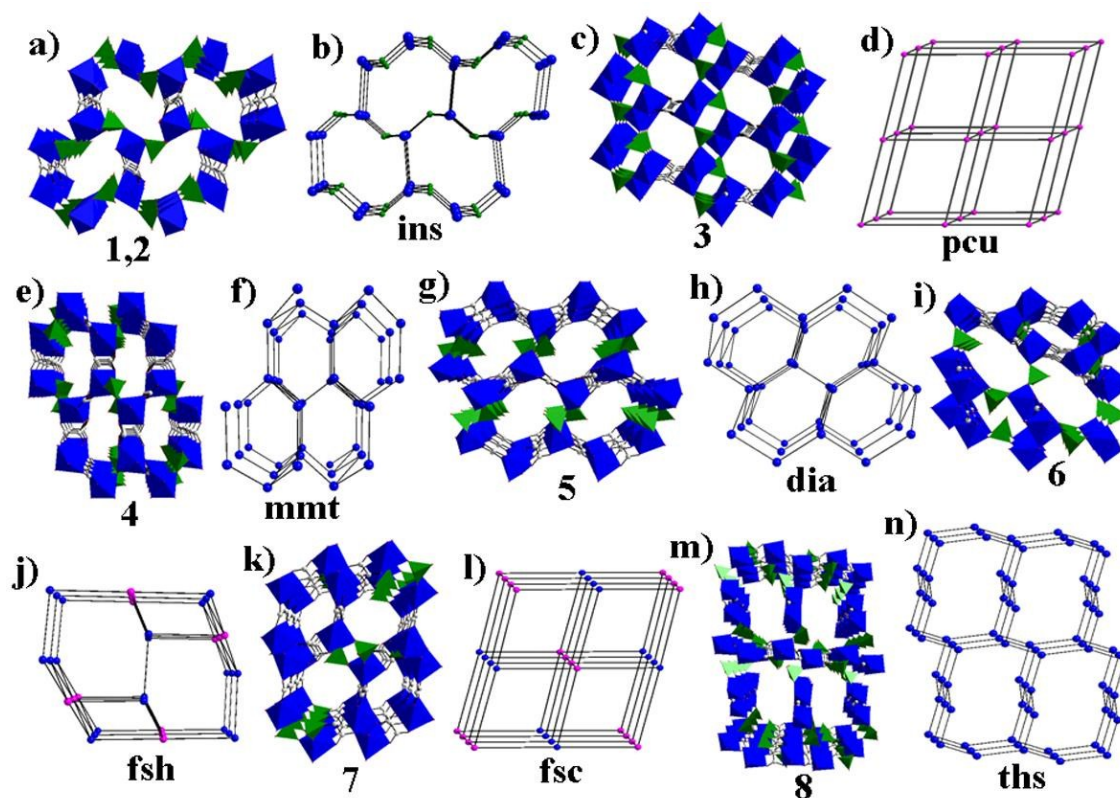
Compounds **1** and **2** are isostructural, therefore, only crystal structure of **1** is described as representative. Compound **1** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* (No. 14). The asymmetric unit contains one magnesium atom, one HPO<sub>4</sub> unit, one half of an oxalate ligand, one water molecule, and one half of an H<sub>2</sub>en cation. The H<sub>2</sub>en cation and oxalate ligand lie about independent inversion centers in the structure. The linkages between magnesium atoms and HPO<sub>4</sub> groups create hcb-type inorganic layers parallel to the *ac* plane, which are further pillared by oxalate ligands to give rise to a three-dimensional structure (Fig. 1a). Viewed along the [100] direction, the structure shows large 12-membered ring (12 MR) channels accommodating H<sub>2</sub>en cations. By regarding MgO<sub>6</sub> octahedra and HPO<sub>4</sub> groups as 4-, and 3-connected nodes, respectively, the hybrid framework has a (3,4)-connected ins topology (Fig. 1b).

Compound **3** crystallizes in the triclinic space group *P*-1 (No. 2). The asymmetric unit contains two magnesium atoms, one HPO<sub>4</sub> unit, one and a half of oxalate ligands, one water molecule, and one half of an H<sub>2</sub>dab cation. One of the oxalate ligands and the H<sub>2</sub>dab lie about independent inversion centers in this structure. This compound has an open-framework structure templated by H<sub>2</sub>dab cations. It contains magnesium phosphate ladders and magnesium oxalate ladders as the building blocks. Similar as compounds **1** and **2**, each phosphorus atom in the structure makes three P–O–Mg linkages to adjacent magnesium atoms. Two types of oxalate ligands are present in the structure. A type I oxalate ligand adopts a typical chelating bis-bidentate coordination mode, and a type II oxalate ligand adopts a chelating/bridging bis-bidentate coordination mode. The compound features 8 MR channels and a (3,6)-connected network with Mn<sub>2</sub>O<sub>10</sub> dimers and HPO<sub>4</sub> groups as 6-, and 3-connected nodes, respectively (Fig. 1c). The point symbol for the net is (4<sup>2</sup>.6)(4<sup>4</sup>.6<sup>10</sup>.8). The network can be further simplified as a pcu network if large Mg<sub>4</sub>P<sub>2</sub> clusters are regarded as the 6-connected nodes (Fig. 1d).

Table 1. Summary of crystal data and refinement results.

Compound <sup>a</sup>	Space group	<i>a</i> (Å)	<i>b</i> , (Å)	<i>c</i> (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	<i>R</i> (F)	Net <sup>b</sup>
H <sub>2</sub> en·Mg <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> (ox)(H <sub>2</sub> O) <sub>2</sub> (1)	<i>P2<sub>1</sub>/n</i>	5.4112(3)	14.2338(7)	8.9052(4)	90	95.922(5)	90	0.0340	ins
H <sub>2</sub> dap·Mg <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> (ox)(H <sub>2</sub> O) <sub>2</sub> (2)	<i>P2<sub>1</sub>/n</i>	5.4134(2)	15.2590(6)	9.0176(4)	90	94.704(4)	90	0.0464	ins
H <sub>2</sub> dab·Mg <sub>4</sub> (HPO <sub>4</sub> ) <sub>2</sub> (ox) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> (3)	<i>P-1</i>	7.6627(3)	7.8432(3)	9.7695(3)	72.092(3)	83.275(3)	84.998(3)	0.0416	pcu
H <sub>2</sub> dab·Mg <sub>2</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (ox) <sub>2</sub> (4)	<i>Pccn</i>	8.23203(11)	16.34232(15)	13.28134(15)	90	90	90	0.0539	mmt
Hmor·Mg(H <sub>2</sub> PO <sub>4</sub> )(ox) (5)	<i>P2<sub>1</sub>/n</i>	9.3755(2)	7.47460(10)	15.4310(2)	90	100.119(2)	90	0.0420	dia
H <sub>3</sub> ipa·Mg <sub>4</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>3</sub> (ox) <sub>4</sub> ·2H <sub>2</sub> O (6)	<i>C2/c</i>	15.1014(2)	10.96857(17)	22.3338(4)	90	103.0993(15)	90	0.0486	fsh
(H <sub>2</sub> pip) <sub>2</sub> ·Mg <sub>4</sub> (HPO <sub>4</sub> )(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (ox) <sub>4</sub> ·2H <sub>2</sub> O (7)	<i>P1</i>	7.7738(3)	9.4840(3)	11.9243(5)	78.102(3)	78.574(4)	86.183(3)	0.0473	fsc
H <sub>3</sub> dpta·Mg <sub>2</sub> (HPO <sub>4</sub> )(H <sub>2</sub> PO <sub>4</sub> )(ox) <sub>2</sub> (H <sub>2</sub> O)·2H <sub>2</sub> O (8)	<i>P-1</i>	9.3254(2)	9.4280(3)	14.3060(4)	96.449(2)	103.879(2)	104.350(2)	0.0462	ths

<sup>a</sup> en = ethylenediamine; ox = oxalate; dap = 1,3-diaminopropane; dab = 1,4-diaminobutane; mor = morpholine; ipa = 3,3'-iminobis(N,N-dimethylpropylamine); pip = piperazine; dpta = dipropyleneetriamine. <sup>b</sup> For definitions of three-letter abbreviations, see Reticular Chemistry Structure Resource (<http://rcsr.net/>).



**Fig.1.** A view of the framework structures of various magnesium phosphate-oxalates: (a) 1 and 2; (c) 3; (e) 4; (g) 5; (i) 6; (k) 7; (m) 8. These compounds display interesting networks: (b) ins; (d) pcu; (f) mmt; (h) dia; (j) fsh; (l) fsc; (n) ths. The amine molecules within the channels are omitted for clarity.

Compound 4 was prepared in the presence of the same amine as that used for compound 3. However, the two compounds have different framework structures as a result of different molar ratio of the starting materials used in the reactions. Compound 4 crystallizes in the orthorhombic space group *Pccn* (No. 56). The asymmetric unit contains one magnesium atom, one H<sub>2</sub>PO<sub>4</sub> unit, two halves of oxalate ligands, and one half of an H<sub>2</sub>dab cation. Of the two different oxalate ligands, one lies about an inversion center and the other lies about a twofold axis. The H<sub>2</sub>dab cation lies disordered about another twofold axis. This compound has an open-framework structure with 12 MR channels (Fig. 1e). It consists of magnesium phosphate chains and magnesium oxalate chains as the building blocks. Each phosphorus atom in the structure makes two P–O–Mg linkages to adjacent metal atoms.

15 The structure has a 4-connected mmt network by regarding MnO<sub>6</sub> octahedra as the structural nodes (Fig. 1f).

Compound 5 crystallizes in the monoclinic space group *P2<sub>1</sub>/n* (No. 14). The asymmetric unit contains one magnesium atom, one H<sub>2</sub>PO<sub>4</sub> unit, two halves of oxalate ligands, and one Hmor cation. Each oxalate ligand lies about an independent inversion center. This compound has a three-dimensional framework containing 12 MR channels along the [100] and [010] directions (Fig. 1g). It consists of similar magnesium phosphate chains and magnesium oxalate chains as found in compound 4. Topological analysis reveals that compound 5 has a 4-connected dia network with 6<sup>4</sup> cage unit (Fig. 1h), which is different from the mmt network (for compound 4) containing 6<sup>6</sup> cage unit. It is of interest to compare the openness of compounds 4 and 5 based on the

number of magnesium atoms per 1000 Å<sup>3</sup>. The value is 3.76 Mg/1000 Å<sup>3</sup> for compound **5**, which is smaller than that of 4.48 Mg/1000 Å<sup>3</sup> for compound **4**. This suggests that compound **5** has a lower framework density than compound **4**. A void space analysis employing PLATON indicates that “solvent accessible” space in compound **5** occupies 40.4% of the unit cell volume.<sup>10</sup> In comparison, only 26.7% of the unit cell volume is “solvent accessible” in compound **4**.

Compound **6** crystallizes in the monoclinic space group *C2/c* (No. 15). The asymmetric unit contains two magnesium atoms, one and a half of H<sub>2</sub>PO<sub>4</sub> units, two oxalate ligands, one water molecule, and one half of an H<sub>3</sub>ipa cation. The central N(2) atom of the H<sub>3</sub>ipa cation and the P(2) atom lie on a twofold axis. This compound contains single-chain magnesium phosphate and double-chain magnesium oxalate as the building blocks. The two types of building blocks share common MgO<sub>6</sub> octahedra and Mg<sub>2</sub>O<sub>10</sub> dimers, forming a three-dimensional structure with 12 MR channels running along the [110] direction (Fig. 1i). By regarding MgO<sub>6</sub> octahedra as 4-connected nodes and Mg<sub>2</sub>O<sub>10</sub> dimers as 6-connected nodes, the compound has a (4,6)-connected fsh topology (Fig. 1j).

It should be noted that the framework topologies of **1-6** are also realized in some transition metal phosphate-oxalates.<sup>11</sup> One benefit of the use of magnesium atom as the framework cation is its gravimetric advantage in the synthesis of low-density materials. For example, the density of compound **2** (1.918 g cm<sup>-3</sup>) is only ca. 90% that of its manganese analogue (2.141 g cm<sup>-3</sup>).<sup>12</sup>

Compound **7** crystallizes in the triclinic space group *P1* (No. 1). The asymmetric unit contains three magnesium atoms, one HPO<sub>4</sub> unit, two H<sub>2</sub>PO<sub>4</sub> units, four oxalate ligands, two water molecules, and two H<sub>2</sub>pip cations. This compound has a three-dimensional structure containing two different types of inorganic building blocks: a cyclic Mg<sub>2</sub>P<sub>2</sub> tetramer constructed from two MgO<sub>6</sub> octahedra and two HPO<sub>4</sub> groups, and an infinite magnesium phosphate chain constructed from alternating Mg<sub>2</sub>O<sub>10</sub> dimers and H<sub>2</sub>PO<sub>4</sub> groups. These inorganic building blocks are further bridged by oxalate ligands to create an open-framework structure with 16 MR channels (Fig. 1k). By regarding Mg<sub>2</sub>P<sub>2</sub> tetramers and Mg<sub>2</sub>O<sub>10</sub> dimers as 4-, and 6-connected nodes, the compound has an fsc topology (Fig. 1l).

The most interesting structural feature of **7** is its resemblance to that of (H<sub>2</sub>mpip)<sub>1.5</sub>Mn<sub>3</sub>(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)(ox)<sub>3</sub> with a (4,6)-connected sqc125 topology.<sup>13</sup> Both compounds have interrupted pcu topologies containing Mg<sub>2</sub>O<sub>10</sub> dimers and Mg<sub>2</sub>P<sub>2</sub> tetramers as the structural nodes (M = Mg, Mn). For a pcu topology, all the structural nodes are Mg<sub>2</sub>O<sub>10</sub> dimers. If half of Mg<sub>2</sub>O<sub>10</sub> dimers in the pcu topology are replaced by cyclic Mg<sub>2</sub>P<sub>2</sub> tetramers, the (4,6)-connected fsc topology may be created. If one third of Mg<sub>2</sub>O<sub>10</sub> dimers in the pcu topology are replaced by cyclic Mg<sub>2</sub>P<sub>2</sub> tetramers, the (4,6)-connected sqc125 topology may be created. It is believed that the cyclic Mg<sub>2</sub>P<sub>2</sub> tetramers serve as “structural scissors” for the formation of different (4,6)-connected networks.

Compound **8** crystallizes in the triclinic space group *P-1* (No. 2). The asymmetric unit contains two magnesium atoms, one HPO<sub>4</sub> unit, one H<sub>2</sub>PO<sub>4</sub> unit, four half of oxalate ligands, three water molecules, and one H<sub>3</sub>dpta cation. Each oxalate ligand lies about an independent inversion center. This compound has a three-dimensional structure containing chain-like magnesium

oxalate building blocks. The magnesium oxalate chains run along the [100] and [010] directions, respectively, and are further bridged by HPO<sub>4</sub> groups to form an open-framework structure. Viewed along the [100] direction, the structure displays large 20 MR channels (Fig. 1m). The pore size of the 20 MR window, delimited by ten MgO<sub>6</sub> octahedra, six oxalate ligands, and four HPO<sub>4</sub> groups, is about 7.0 × 9.4 Å<sup>2</sup> (calculated from the distance between two oxygen atoms across the window). Similar 20 MR channels are also observed along the [010] and [001] directions. However, the terminal H<sub>2</sub>PO<sub>4</sub> groups attach to the walls of these 20 MR channels and reduce the free space. By regarding MgO<sub>6</sub> octahedra as 3-connected nodes, the compound has a ths topology (Fig. 1n). Prior to this work, metal phosphate-oxalates with 3-connected nodes always possess an hcb topology.

In summary, the use of magnesium ions as framework cations in the synthesis of new hybrid open-framework solids have been explored under solvent-free conditions. Seven types of framework topologies were created during the course of such investigations. The fsc and ths topologies are unprecedented in metal phosphate-oxalate structures. The 20 MR pore found in this compositional domain represents one of the largest pores in metal phosphate-oxalates. The present work illustrates that solvent-free synthesis will offer a lab-scale preparative method to find novel hybrid open-framework solids. Further work is in progress to scale-up this type of synthesis.

This work was supported by the NSFC (no. 21171121), and the Program for New Century Excellent Talents in University (no. NCET-12-0375).

## Notes and references

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- † Electronic Supplementary Information (ESI) available: X-ray data in CIF format, experimental details, additional figures, IR spectra, powder XRD patterns, and TGA curves. CCDC 1431026-1431033. See DOI: 10.1039/b0000000x/
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