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

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## **Physical measurements:**

The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N<sub>2</sub> with a heating rate of 10 °C/min. IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. Powder X-ray diffraction (XRD) data were obtained using a Shimazu XRD-6100 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Single crystal X-ray diffraction data were collected on a New Gemini, Dual, Cu at zero, EosS2 diffractometer (for compounds **3-8**) or on an Oxford Xcalibur diffractometer (for compounds **1** and **2**) at room temperature.

## Synthesis

Synthesis of 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): A mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.429 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 135  $\mu$ l), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.126 g), and ethylenediamine (67  $\mu$ l) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (72.4 % yield based on magnesium). The solvent-free synthesis was also carried out in a gram scale. In a typical synthesis, a mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (1.712 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 545  $\mu$ l), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.504 g), and ethylenediamine (270  $\mu$ l) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient (270  $\mu$ l) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (83.3 % yield based on magnesium).

Synthesis of  $H_2$ dap·Mg<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>(ox)( $H_2$ O)<sub>2</sub> (2): A mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.429 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 135 µl), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.126 g), and 1,3-diaminopropane

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(83 µl) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (29.1 % yield based on magnesium). The solvent-free synthesis was also carried out in a gram scale. In a typical synthesis, a mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (1.712 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 545 µl), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.504 g), and 1,3-diaminopropane (335 µl) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (35.7 % yield based on magnesium).

Synthesis of 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): A mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.428 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 200  $\mu$ l), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.126 g), and 1,4-diaminobutane (200  $\mu$ l) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (38.0 % yield based on magnesium).

Synthesis of 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): A mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.214 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 68  $\mu$ l), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.126 g), and 1,4-diaminobutane (50  $\mu$ l) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (32.7 % yield based on magnesium). The yield of 4 could be improved to 46.7% by using Mn(OH)<sub>2</sub> as the magnesium source.

Synthesis of Hmor·Mg(H<sub>2</sub>PO<sub>4</sub>)(ox) (5): A mixture of Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.428 g),

 $H_3PO_4$  (85 wt%, 200 µl),  $H_2C_2O_4 \cdot 2H_2O$  (0.126 g), and morpholine (250 µl) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (24.1 % yield based on magnesium).

Synthesis of 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): A mixture of Mn(OH)<sub>2</sub> (0.122 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 135  $\mu$ l), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.252 g), and 3,3'-iminobis(N,Ndimethylpropylamine) (114  $\mu$ l) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (35.0 % yield based on magnesium).

Synthesis of  $(H_2pip)_2 \cdot Mg_4(HPO_4)(H_2PO_4)_2(ox)_4 \cdot 2H_2O$  (7): A mixture of Mn(OH)<sub>2</sub> (0.122 g), H<sub>3</sub>PO<sub>4</sub> (85 wt%, 102 µl), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O (0.252 g), and piperazine (0.086 g) 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 7, together with a large amount of unidentified impurity, were recovered by filtration, washed with distilled water, and finally dried at ambient temperature.

Synthesis of  $H_3$ dpta·Mg<sub>2</sub>(HPO<sub>4</sub>)( $H_2$ PO<sub>4</sub>)(ox)<sub>2</sub>( $H_2$ O)·2H<sub>2</sub>O (8): A mixture of Mn(OH)<sub>2</sub> (0.122 g),  $H_3$ PO<sub>4</sub> (85 wt%, 170 µl),  $H_2C_2O_4$ ·2H<sub>2</sub>O (0.252 g), and dipropylenetriamine (154 µl) 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 were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (45.1 % yield based on magnesium).

	1	2
Empirical formula	$C_4 H_{16} M g_2 N_2 O_{14} P_2$	$C_{5}H_{18}Mg_{2}N_{2}O_{14}P_{2}$
Formula weight	426.75	440.77
Temperature	293	293
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/n$	$P2_{1}/n$
<i>a</i> , Å	5.4112(3)	5.4134(2)
<i>b</i> , Å	14.2338(7)	15.2590(6)
<i>c</i> , Å	8.9052(4)	9.0176(4)
α,°	90	90
eta , °	95.922(5)	94.704(4)
γ, °	90	90
Volume, Å <sup>3</sup>	682.24(6)	742.37(5)
Ζ	2	2
$D_{\rm c}$ , g/cm <sup>3</sup>	2.077	1.972
$\mu$ (Mo-K $\alpha$ ), mm <sup>-1</sup>	0.498	0.461
Reflections collected	2938	3165
Independent reflections	1394 [ $R_{\rm int} = 0.0221$ ]	1517 [ $R_{\rm int} = 0.0226$ ]
Final <i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0340, wR_2 = 0.0860$	$R_1 = 0.0464, wR_2 = 0.1188$
Final <i>R</i> indexes (all data)	$R_1 = 0.0426, wR_2 = 0.0924$	$R_1 = 0.0539, wR_2 = 0.1248$

Table S1. Crystal data and structure refinement for  ${\bf 1}$  and  ${\bf 2}$ 

	3	4
Empirical formula	$C_{10}H_{20}Mg_4N_2O_{22}P_2$	$C_8H_{18}Mg_2N_2O_{16}P_2$
Formula weight	679.46	508.80
Temperature	293	293
Crystal system	triclinic	orthorhombic
Space group	<i>P</i> -1	Pccn
<i>a</i> , Å	7.6627(3)	8.23203(11)
<i>b</i> , Å	7.8432(3)	16.34232(15)
<i>c</i> , Å	9.7695(3)	13.28134(15)
α,°	72.092(3)	90
eta , °	83.275(3)	90
γ,°	84.998(3)	90
Volume, Å <sup>3</sup>	554.04(4)	1786.74(4)
Ζ	1	4
$D_{\rm c}$ , g/cm <sup>3</sup>	2.036	1.891
$\mu$ (Cu-K $\alpha$ ), mm <sup>-1</sup>	3.997	3.788
Reflections collected	9707	8378
Independent reflections	1979 [ $R_{\rm int} = 0.0296$ ]	1594 [ $R_{\rm int} = 0.0362$ ]
Final <i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0416, wR_2 = 0.1107$	$R_1 = 0.0539, wR_2 = 0.1483$
Final <i>R</i> indexes (all data)	$R_1 = 0.0419, wR_2 = 0.1112$	$R_1 = 0.0561, wR_2 = 0.1513$

Table S2. Crystal data and structure refinement for  ${\bf 3}$  and  ${\bf 4}$ 

	5	6
Empirical formula	C <sub>6</sub> H <sub>12</sub> NO <sub>9</sub> MgP	$C_{18}H_{38}Mg_4N_3O_{30}P_3\\$
Formula weight	297.45	966.66
Temperature	292.1(3)	293.15
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/n$	C2/c
<i>a</i> , Å	9.3755(2)	15.1014(2)
<i>b</i> , Å	7.47460(10)	10.96857(17)
<i>c</i> , Å	15.4310(2)	22.3338(4)
α,°	90	90
eta , °	100.119(2)	103.0993(15)
γ, °	90	90
Volume, Å <sup>3</sup>	1064.55(3)	3603.13(10)
Ζ	4	4
$D_{\rm c}$ , g/cm <sup>3</sup>	1.856	1.782
$\mu$ (Cu-K $\alpha$ ), mm <sup>-1</sup>	3.362	3.260
Reflections collected	9914	9857
Independent reflections	1896 [ $R_{int} = 0.0366$ ]	$3214 [R_{int} = 0.0326]$
Final <i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0420, wR_2 = 0.1123$	$R_1 = 0.0486, wR_2 = 0.1333$
Final <i>R</i> indexes (all data)	$R_1 = 0.0452, wR_2 = 0.1159$	$R_1 = 0.0514, wR_2 = 0.1366$

Table S3. Crystal data and structure refinement for  ${\bf 5}$  and  ${\bf 6}$ 

	7	8
Empirical formula	$C_{16}H_{33}Mg_4N_4O_{30}P_3\\$	$C_{10}H_{29}N_3O_{19}Mg_2P_2$
Formula weight	951.61	605.92
Temperature	293.15	292.8(4)
Crystal system	triclinic	triclinic
Space group	<i>P</i> 1	<i>P</i> -1
<i>a</i> , Å	7.7738(3)	9.3254(2)
<i>b</i> , Å	9.4840(3)	9.4280(3)
<i>c</i> , Å	11.9243(5)	14.3060(4)
α,°	78.102(3)	96.449(2)
eta , °	78.574(4)	103.879(2)
γ,°	86.183(3)	104.350(2)
Volume, Å <sup>3</sup>	842.90(6)	1163.07(6)
Ζ	1	2
$D_{\rm c}$ , g/cm <sup>3</sup>	1.875	1.730
$\mu$ (Cu-K $\alpha$ ), mm <sup>-1</sup>	3.482	3.128
Reflections collected	9059	20658
Independent reflections	4630 [ $R_{\rm int} = 0.0315$ ]	4163 [ $R_{\rm int} = 0.0381$ ]
Final <i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0473, wR_2 = 0.1243$	$R_1 = 0.0462, wR_2 = 0.1285$
Final <i>R</i> indexes (all data)	$R_1 = 0.0480, wR_2 = 0.1257$	$R_1 = 0.0487, wR_2 = 0.1327$
Flack parameter	0.163(16)	N/A

Table S4. Crystal data and structure refinement for  ${\bf 7}$  and  ${\bf 8}$ 



Fig. S1. Simulated and experimental powder XRD patterns of compound 1.



Fig. S2. Simulated and experimental powder XRD patterns of compound 2.



Fig. S3. Simulated and experimental powder XRD patterns of compound 3.



Fig. S4. Simulated and experimental powder XRD patterns of compound 4.



Fig. S5. Simulated and experimental powder XRD patterns of compound 5.



Fig. S6. Simulated and experimental powder XRD patterns of compound 6.



Fig. S7. Simulated and experimental powder XRD patterns of compound 8.



**Fig. S8.** IR spectrum of compound **1**. The strong bands at 1680 and 1340 cm<sup>-1</sup> correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The bands at 1540, and 1380 cm<sup>-1</sup> are the characteristic peaks of H<sub>2</sub>en molecules. The bands at 1100 and 1010 cm<sup>-1</sup> are due to the asymmetric stretch of PO<sub>4</sub> tetrahedra.



**Fig. S9.** IR spectrum of compound **2**. The strong bands at 1660 and 1320 cm<sup>-1</sup> correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The bands at 1550 and 1380 cm<sup>-1</sup> are the characteristic peaks of H<sub>2</sub>dap cations. The bands at 1080 and 1010 cm<sup>-1</sup> are due to the asymmetric stretch of PO<sub>4</sub> tetrahedra.



**Fig. S10.** IR spectrum of compound **3**. The strong bands at 1650 and 1330 cm<sup>-1</sup> correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The bands at 1520, and 1380 cm<sup>-1</sup> are the characteristic peaks of H<sub>2</sub>dab cations. The bands at 1150, 1110, and 1020 cm<sup>-1</sup> are due to the asymmetric stretch of PO<sub>4</sub> tetrahedra.



**Fig. S11.** IR spectrum of compound **4**. The strong bands at 1660 and 1330 cm<sup>-1</sup> correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The bands at 1520, and 1380 cm<sup>-1</sup> are the characteristic peaks of H<sub>2</sub>dab cations. The bands at 1150, 1110, and 1020 cm<sup>-1</sup> are due to the asymmetric stretch of PO<sub>4</sub> tetrahedra.



**Fig. S12.** IR spectrum of compound **5**. The strong bands at 1640 and 1320 cm<sup>-1</sup> correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The bands at 1460, 1420, and 1380 cm<sup>-1</sup> are the characteristic peaks of Hmor cations. The bands at 1150, 1110, and 1020 cm<sup>-1</sup> are due to the asymmetric stretch of  $PO_4$  tetrahedra.



**Fig. S13.** IR spectrum of compound **6**. The strong bands at 1639 and 1321 cm<sup>-1</sup> correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The bands at 1473, and 1373 cm<sup>-1</sup> are the characteristic peaks of  $H_3$ ipa cations. The bands at 1200, and 1122 cm<sup>-1</sup> are due to the asymmetric stretch of PO<sub>4</sub> tetrahedra.



**Fig. S14.** IR spectrum of compound **8**. The strong bands at 1630 and 1320 cm<sup>-1</sup> correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The bands at 1510, 1470, and 1380 cm<sup>-1</sup> are the characteristic peaks of  $H_3$ dpta cations. The bands at 1110, and 1080 cm<sup>-1</sup> are due to the asymmetric stretch of PO<sub>4</sub> tetrahedra.



Fig. S15. TGA curve of compound 1.



Fig. S16. TGA curve of compound 2.



Fig. S17. TGA curve of compound 3.



Fig. S18. TGA curve of compound 4.



Fig. S19. TGA curve of compound 5.



Fig. S20. TGA curve of compound 6.



Fig. S21. TGA curve of compound 8.



**Fig. S22.** ORTEP plot of the asymmetric unit of compound 1, showing the labeling scheme and the 30% probability displacement ellipsoid.



**Fig. S23.** ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 30% probability displacement ellipsoid.



**Fig. S24.** ORTEP plot of the asymmetric unit of compound **3**, showing the labeling scheme and the 30% probability displacement ellipsoid.



**Fig. S25.** ORTEP plot of the asymmetric unit of compound **4**, showing the labeling scheme and the 30% probability displacement ellipsoid.



**Fig. S26.** ORTEP plot of the asymmetric unit of compound **5**, showing the labeling scheme and the 30% probability displacement ellipsoid.



**Fig. S27.** ORTEP plot of the asymmetric unit of compound **6**, showing the labeling scheme and the 30% probability displacement ellipsoid.



**Fig. S28.** ORTEP plot of the asymmetric unit of compound 7, showing the labeling scheme and the 30% probability displacement ellipsoid.



**Fig. S29.** ORTEP plot of the asymmetric unit of compound **8**, showing the labeling scheme and the 30% probability displacement ellipsoid.



Fig. S30. Polyhedral representation of the magnesium phosphate layer in the structure of 1. Color code:  $MgO_6$  octahedra, blue;  $PO_4$  tetrahedra, green.



**Fig. S31.** (a) Ball-and stick and polyhedral representation of the  $Mg_4P_2$  cluster in compound **3**. (b) Magnesium phosphate ladder. (c) Magnesium oxalate ladder. Color code:  $MgO_6$  octahedra, blue; PO<sub>4</sub> tetrahedra, green; oxygen, red; carbon, gray.



**Fig. S32.** The framework structure of **4** consists of two different building blocks: (a) magnesium phosphate chain; (b) magnesium oxalate chain.



**Fig. S33.** A view of the different cage units in two different 4-connected networks: (a) a  $6^4$  cage for dia net; (b) a  $6^6$  cage unit for mmt net.



**Fig. S32.** The framework structure of **6** consists of two different building blocks: (a) single-chain magnesium phosphate; (b) double-chain magnesium oxalate.



**Fig. S33.** (a) A view of framework structure of 7. (b) Compound 7 has a (4,6)connected fsc topology. (c) Cyclic Mg<sub>2</sub>P<sub>2</sub> cluster as the 4-connected node. (d) Mg<sub>2</sub>O<sub>10</sub>
dimer as the six-connected node.



**Fig. S34.** (a) A view of framework structure of  $(H_2mpip)_{1.5}$ ·Mn<sub>3</sub>(HPO<sub>4</sub>) $(H_2PO_4)(ox)_3$ . (b) This compound has a (4,6)-connected sqc125 topology. (c) Cyclic Mg<sub>2</sub>P<sub>2</sub> cluster as the 4-connected node. (d) Mg<sub>2</sub>O<sub>10</sub> dimer as the six-connected node.



**Fig. S35.** A view of the different types of 20-ring channels along (a) [100]; (b) [010]; (c) [001] directions. It should be noted that the 20-ring channels along the [010] and [001] directions are blocked by the dangling  $H_2PO_4$  groups.