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*}

^a College of Chemistry, Sichuan University, Chengdu 610064, P. R. China.

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

* To whom correspondence should be addressed. Tel: +86-28-85412284. E-mail: ouyame@sina.com (M. Yang); zhienlin@scu.edu.cn (Z. Lin)

Physical measurements:

Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å). IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N₂ with a heating rate of 10 °C/min. Magnetic measurements were performed in the temperature range 2-300 K with a SQUID MPMS-7 magnetometer manufactured by Quantum Design. Background corrections for the sample holder assembly and diamagnetic components of the compound were applied. Single crystal X-ray diffraction data were collected on a New Gemini, Dual, Cu at zero, EosS2 diffractometer at room temperature. The crystal structures were solved by direct methods. The structures were refined on *F*² by full-matrix least-squares methods using the *SHELXTL* program package.¹

Reference

1. G. M. Sheldrick, Acta Cryst., Sect. A, 2008, 64, 112.

Synthesis

Synthesis of $(H_2dab)_{0.5}$ ·Co $(H_2PO_4)(ox)$ (1): A mixture of CoO (0.150 g), H_3PO_4 (85 wt%, 136 µL), $H_2C_2O_4$ ·2H₂O (0.252 g), and 1,4-diaminobutane (100 µL) in a molar ratio of 2:2:2:1 was sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. Reddish violet block-like crystals were recovered by filtration, washed with distilled water and ethanol, and finally dried at ambient temperature (70.2% yield based on cobalt).

Synthesis of $(H_2dab)_{0.5}$ ·Zn $(H_2PO_4)(ox)$ (2): A mixture of ZnO (0.162 g), H_3PO_4 (85 wt%, 136 µL), $H_2C_2O_4$ ·2H₂O (0.252 g), and 1,4-diaminobutane (100 µL) in a molar ratio of 2:2:2:1 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 block-like crystals were recovered by filtration, washed with distilled water and ethanol, and finally dried at ambient temperature (32.6% yield based on zinc).

Synthesis of $(H_2dab)_{0.5}$ ·Mn $(HPO_4)(ox)_{0.5}(H_2O)$ (3): A mixture of MnO (0.142 g), H₃PO₄ (85 wt%, 136 µL), H₂C₂O₄·2H₂O (0.126 g), and 1,4-diaminobutane (100 µL) in a molar ratio of 2:2:1:1 was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 8 d. The autoclave was subsequently allowed to cool to room temperature. Light-pink block crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (61.4 % yield based on manganese).

Synthesis of $(H_2dab)_{0.5}$ ·Cd $(HPO_4)(ox)_{0.5}(H_2O)$ (4): A mixture of CdO (0.256 g), H₃PO₄ (85 wt%, 136 µL), H₂C₂O₄·2H₂O (0.126 g), and 1,4-diaminobutane (100 µL) in a molar ratio of 2:2:1:1 was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 7 d. The autoclave was subsequently allowed to cool to room temperature. Colorless block crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (46.8 % yield based on cadmium).

Synthesis of $(H_2dab)_2 \cdot Ga_4(HPO_4)_5(H_2PO_4)_2(ox)_2(H_2O)_2$ (5): A mixture of Ga_2O_3 (0.187 g), H_3PO_4 (85 wt%, 240 µL), $H_2C_2O_4 \cdot 2H_2O$ (0.252 g), and 1,4-diaminobutane (100 µL) in a molar ratio of 1:3.5:1:1 was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 7 d. The autoclave was subsequently allowed to cool to room temperature. Colorless prism-like crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (23.6 % yield based on gallium).

Synthesis of $(H_2dab)_{0.5}$ ·In $(HPO_4)(H_2PO_4)(ox)_{0.5}$ (6): A mixture of In₂O₃ (0.138 g), H₃PO₄ (85 wt%, 136 µL), H₂C₂O₄·2H₂O (0.126 g), and 1,4-diaminobutane (50 µL) in a molar ratio of 1:4:2:1 was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 7 d. The autoclave was subsequently allowed to cool to room temperature. Colorless block crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (95.0 % yield based on indium).



Fig. S1. Simulate and experimental powder XRD patterns of compound 1 and the assynthesized samples upon treatment at 325 °C for 2 h.



Fig. S2. Simulate and experimental powder XRD patterns of compound 2 and the assynthesized samples upon treatment at 295 °C for 2 h.



Fig. S3. Simulate and experimental powder XRD patterns of compound **3** and the assynthesized samples upon treatment at 325 °C for 2 h.



Fig. S4. Simulate and experimental powder XRD patterns of compound **4** and the assynthesized samples upon treatment at 330 °C for 2 h.



Fig. S5. Simulate and experimental powder XRD patterns of compound 5 and the assynthesized samples upon treatment at 350 °C for 2 h.



Fig. S6. Simulate and experimental powder XRD patterns of compound **6** and the assynthesized samples upon treatment at 385 °C for 2 h.



Fig. S7. IR spectrum of compound 1.



Fig. S8. IR spectrum of compound 2.



Fig. S9. IR spectrum of compound 3.



Fig. S10. IR spectrum of compound 4.



Fig. S11. IR spectrum of compound 5.



Fig. S12. IR spectrum of compound 6.



Fig. S13. TGA curve of compound 1.



Fig. S14. TGA curve of compound 2.



Fig. S15. TGA curve of compound 3.



Fig. S16. TGA curve of compound 4.



Fig. S17. TGA curve of compound 5.



Fig. S18. TGA curve of compound 6.



Fig. S19. ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 30% probability displacement ellipsoid.



Fig. S20. ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 30% probability displacement ellipsoid.



Fig. S21. ORTEP plot of the asymmetric unit of compound **3**, showing the labeling scheme and the 30% probability displacement ellipsoid.



Fig. S22. ORTEP plot of the asymmetric unit of compound **4**, showing the labeling scheme and the 30% probability displacement ellipsoid.



Fig. S23. ORTEP plot of the asymmetric unit of compound **5**, showing the labeling scheme and the 30% probability displacement ellipsoid.



Fig. S24. ORTEP plot of the asymmetric unit of compound **6**, showing the labeling scheme and the 30% probability displacement ellipsoid.



Fig. S25. A view of the different cage units: (a) a 6^4 cage for dia net and (b) a 6^6 cage unit for mmt net.



Fig. S26. A view of the 20 MR channel in compound 5. Disordered HP(4)O₄ tetrahedra attach to the wall of 20 MR channel as pendants and reduce the free space. Color code: GaO_6 octahedra, green; P/PO₄, blue; O, red; C; gray.



Fig. S27. Compound **6** has a supramolecular framework with a (3,4)-connected moc topology. The hydrogen bonds between adjacent layers are shown as dotted lines. Color code: In, green; P, blue.