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Solvent-Free Synthesis of New Open-Framework Oxalate Structures

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Reagents were purchased commercially and used without further purification. The CHN analysis was carried out on a Euro EA3000 analyzer. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). IR spectra (KBr pellet) were recorded on an ABB Bomen MB 102 spectrometer. The thermogravimetric analyses were performed on a NETSCHZ STA-449C thermoanalyzer in a flow of N_2 with a heating rate of 10 ºC/min from 40 to 700 ºC.

Synthesis:

Synthesis of $(Hdpa)_4{\cdot}Zn_4(ox)_6{\cdot}1.5H_2O$ (**1**): A mixture of $Zn(OAc)_2{\cdot}2H_2O$ (0.439 g), $H_2C_2O_4{\cdot}2H_2O$ (0.126 g) and diisopropylamine (0.204 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 9 d. When the autoclave was cooled to room temperature, colorless block-like crystals were obtained (28.4% yield based on zinc). The product was washed with distilled water and dried in air. Elemental analysis confirmed its composition. Anal. Found: C, 34.92; H, 5.43; N, 4.52. Calcd: C, 35.28; H, 5.51; N, 4.57.

Synthesis of $(Hdpa)_2{\cdot}Co_2(ox)_3{\cdot}2H_2O$ (**2**): A mixture of $Co(OAc_2)_2{\cdot}2H_2O$ (0.498 g), $H_2C_2O_4{\cdot}2H_2O$ (0.630 g) and diisopropylamine (0.204 g) was sealed in a Teflon-lined

stainless steel autoclave and heated at 150 °C for 8 d. When the autoclave was cooled to room temperature, red prism-like crystals were obtained (27% yield based on cobalt). The product was washed with distilled water and dried in air. Elemental analysis confirmed its composition. Anal. Found: C, 33.18; H, 5.64; N, 4.53. Calcd: C, 34.74; H, 5.83; N, 4.50.

Synthesis of H_2dmpda·$Mn_2(H_2PO_4)_2(ox)_2·H_2O$ (**3**): A mixture of $Mn(H_2PO_4)_2·2H_2O$ (0.569 g), $H_2C_2O_4·2H_2O$ (0.378 g) and N, N-dimethyl-1,3-propanediamine (0.201 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 7 d. When the autoclave was cooled to room temperature, light-pink rod-like crystals were obtained (22% yield based on manganese). The product was washed with distilled water and dried in air. Elemental analysis confirmed its composition. Anal. Found: C, 17.61; H, 4.52; N, 4.57. Calcd: C, 17.95; H, 3.68; N, 4.65.

Synthesis of Zn(ox)(L1)·$0.4H_2O$ (**4**): A mixture of $Zn(OAc)_2·2H_2O$ (0.439 g), $H_2C_2O_4·2H_2O$ (0.756 g) and N, N-dimethyl-ethylenediamine (0.184 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 10 d. When the autoclave was cooled to room temperature, colorless block-like crystals were obtained (35% yield based on zinc). The product was washed with distilled water and dried in air. Elemental analysis confirmed its composition. Anal. Found: C, 29.12; H, 3.77; N, 8.74. Calcd: C,

29.95; H, 4.02; N, 8.73.

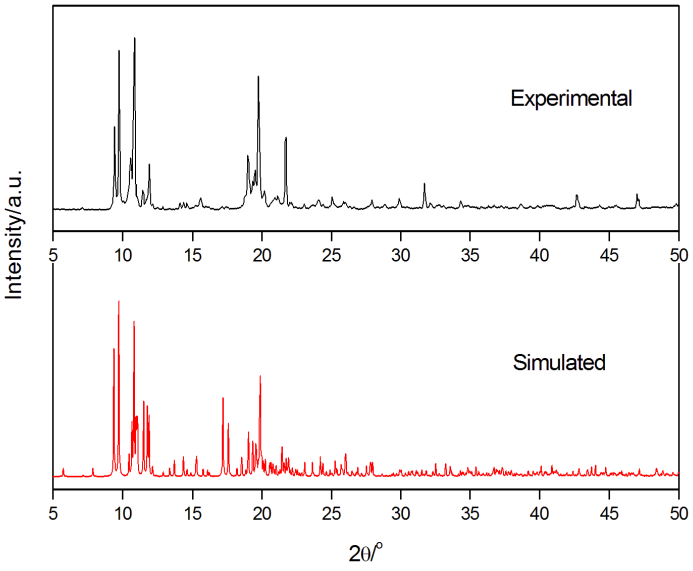

Figure S1. Experimental and simulated XRD patterns of compound **1**.

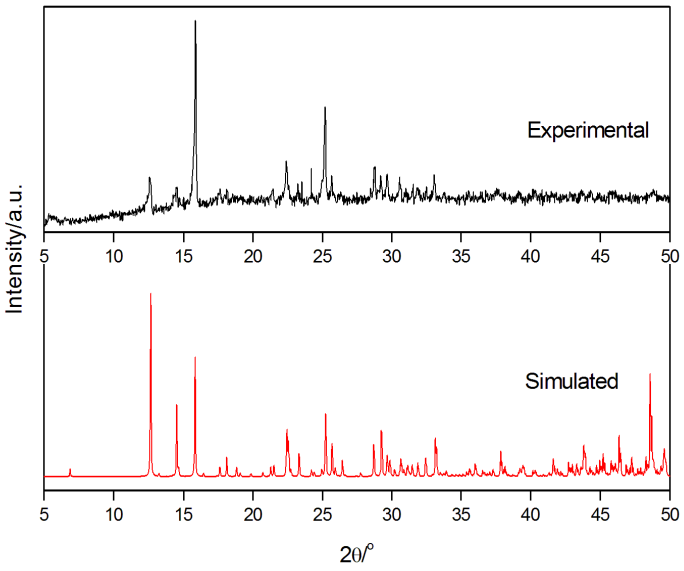

Figure S2. Experimental and simulated XRD patterns of compound **3**.

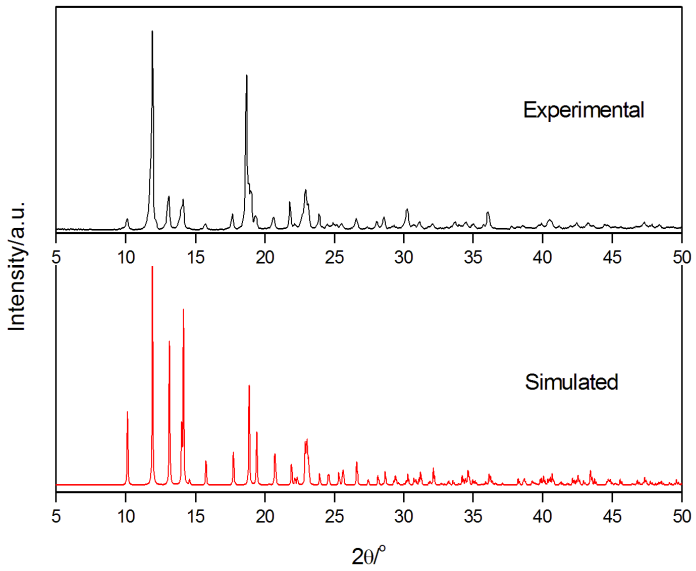

Figure S3. Experimental and simulated XRD patterns of compound **4**

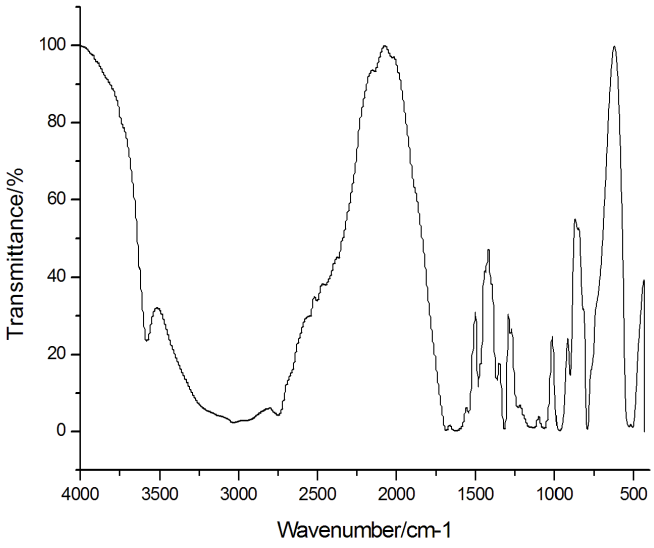

Figure S4. IR spectra of compound **1**

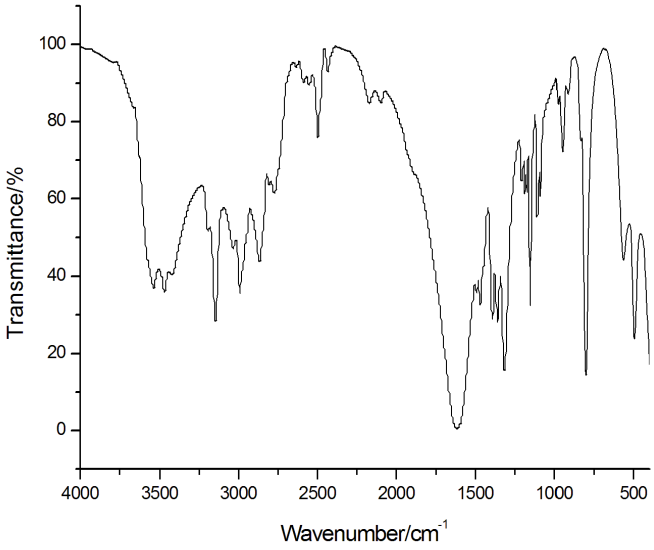

Figure S5. IR spectrum of compound **2**

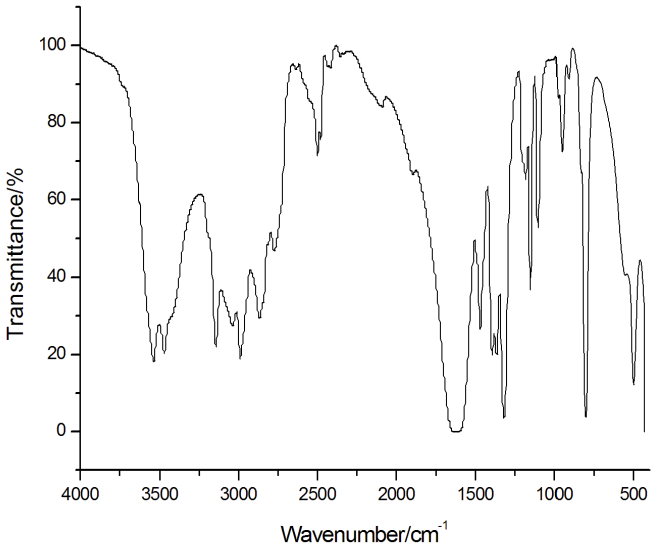

Figure S6. IR spectrum of compound **3**

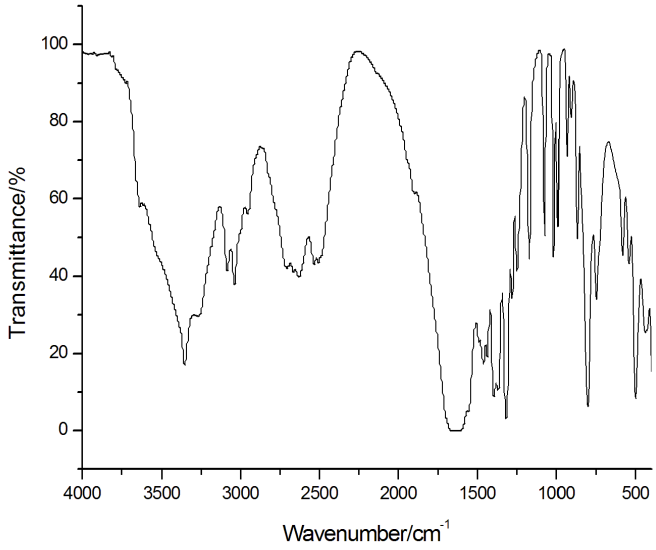

Figure S7. IR spectrum of compound **4**

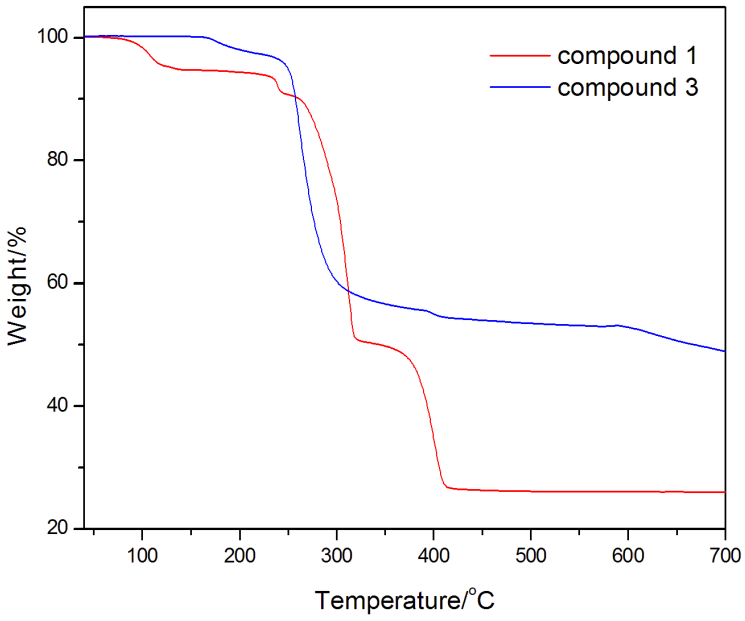

Figure S8. TGA curves of compounds **1** and **3**.

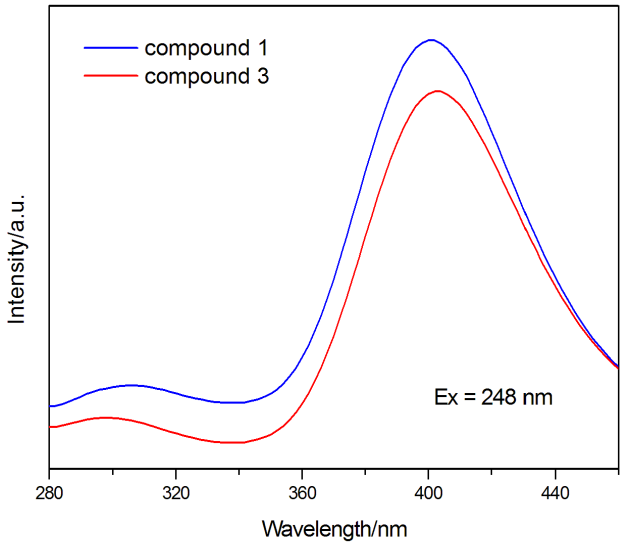

Figure S9. Solid state fluorescent spectra of compounds **1** and **3** at room temperature (λ_{ex} = 248 nm).

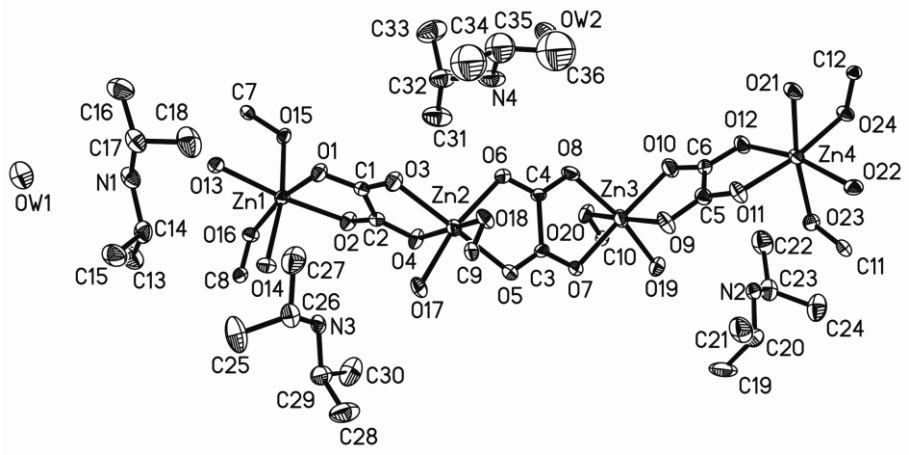

Figure S10. ORTEP plot of the asymmetric unit of compound **1** showing the labeling scheme and the 30% probability displacement ellipsoid.

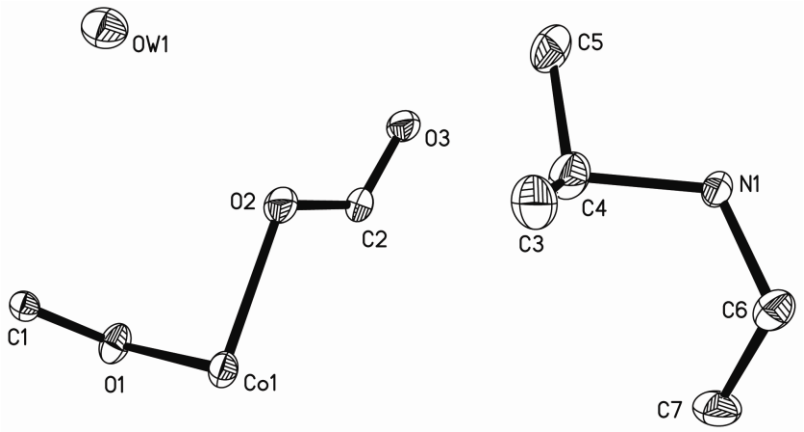

Figure S11. ORTEP plot of the asymmetric unit of compound **2** showing the labeling scheme and the 30% probability displacement ellipsoid.

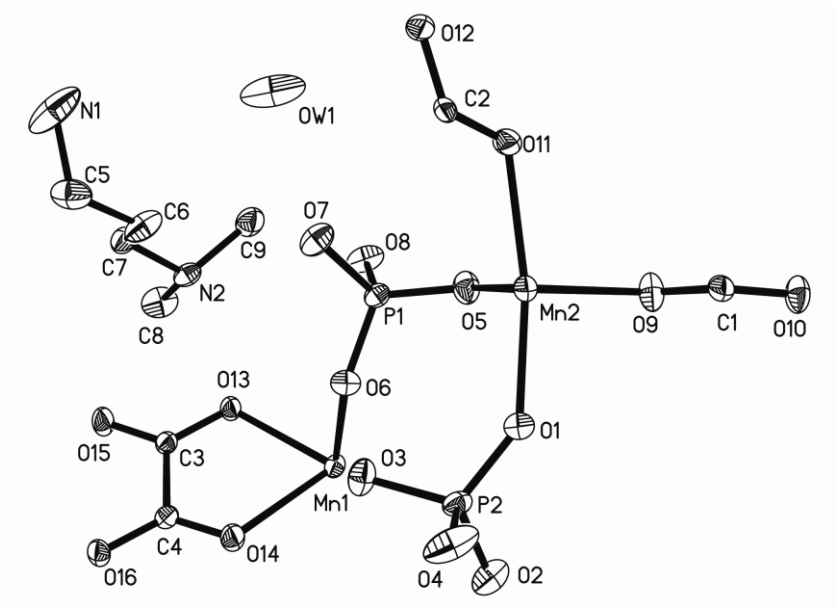

Figure S12. ORTEP plot of the asymmetric unit of compound **3** showing the labeling scheme and the 30% probability displacement ellipsoid.

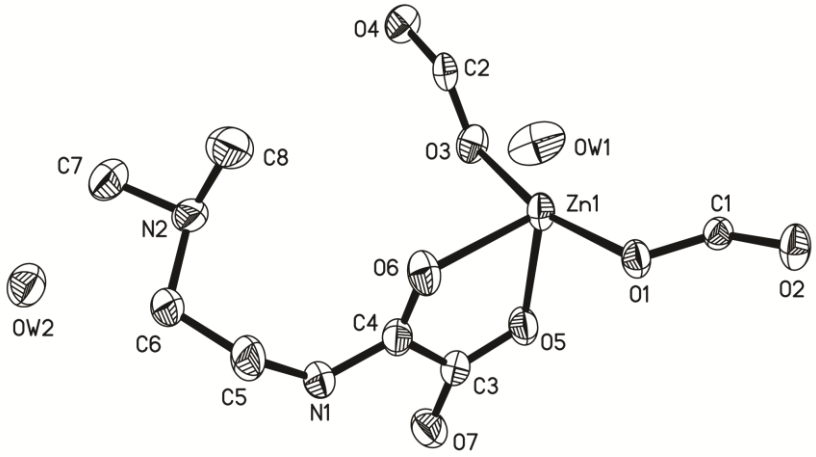

Figure S13. ORTEP plot of the asymmetric unit of compound **4** showing the labeling scheme and the 30% probability displacement ellipsoid.

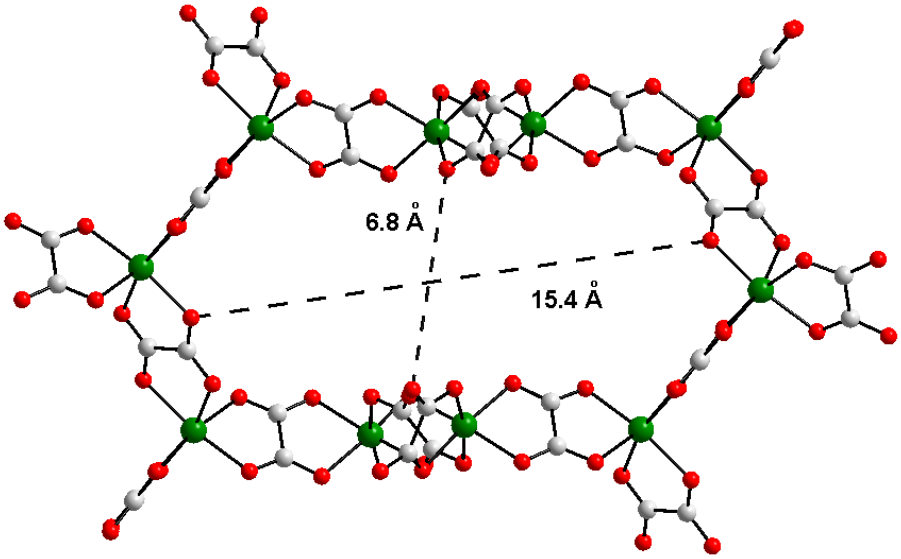

Figure S14. A view of the 20-ring window in compound **1**. Color code: Zn: green; C: gray; O, red.

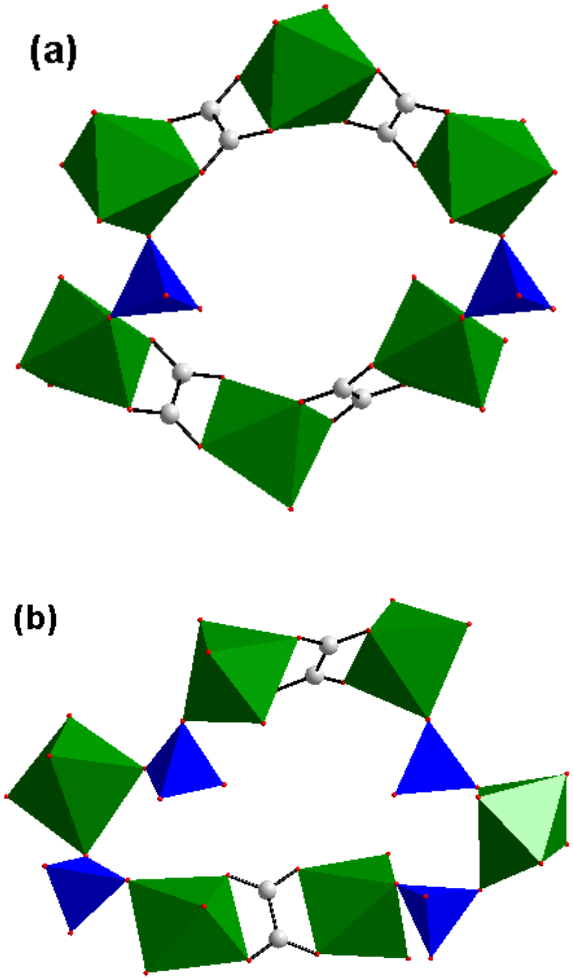

Figure S15. Two types of 12-ring windows in compound **3**. (a) Type I pore consists of six MnO_6, four oxalate groups, and two H_2PO_4 tetrahedra. (b) Type II consists of six MnO_6, two oxalate groups, and four H_2PO_4 tetrahedra. Color code: MnO_6 octahedra: green; H_2PO_4 tetrahedra: blue; C: gray; O, red.