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

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Physical measurements:

IR spectra (KBr pellets) were recorded on an Nicolet Impact 410 FTIR spectrometer. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N_2 with a heating rate of 10 ºC/min. The fluorescent spectra were measured on a Perkin-Elmer LS 55 luminescence spectrometer equipped with a 450 W xenon lamp.

Synthesis

Synthesis of $CN_3H_6{\cdot}Co(H_2PO_3)(C_2O_4)$ (1): A mixture of $Co(OAc)_2{\cdot}4H_2O$ (0.247 g), H_3PO_3 (0.173 g), $H_2C_2O_4{\cdot}2H_2O$ (0.251 g), and guanidinium carbonate (0.312 g) 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. Red crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (14.4 % yield based on cobalt).

Synthesis of $(CN_3H_6)_2{\cdot}Mn_{2.5}(HPO_3)(C_2O_4)_{2.5}(H_2O){\cdot}H_2O$ (2): A mixture of $Mn(OAc)_2{\cdot}4H_2O$ (0.569 g), H_3PO_3 (0.178 g), $H_2C_2O_4{\cdot}2H_2O$ (0.292 g), and guanidinium carbonate (0.360 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 10 d. The autoclave was subsequently allowed to cool to room temperature. Light-pink crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (18.9 % yield based on manganese).

Table 1. Summary of hydrogen bonding information for **1**

D-H···A[a]	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	<(DHA)/degree
O1-H2...O2_#1	0.82	1.91	2.716(3)	167.8
N1-H3...O4_#2	0.86	2.09	2.935(3)	165.4
N1-H4...O7_#3	0.86	2.27	2.903(3)	130.9
N2-H5...O5_#2	0.86	2.05	2.879(3)	162.3
N3-H8...O6_#3	0.86	2.23	3.086(3)	178.0

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+3/2, y+1/2, -z+1/2; #2 -x+1, -y+1, -z ; #3 x-1, y+1, z. The hydrogen atoms are located at calculated positions.

Table 2. Summary of hydrogen bonding information for **2**

D-H···A[a]	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	<(DHA)/degree
OW1-H2...O3_$1	0.85	1.91	2.746(3)	167.1
OW1-H3...O6_$2	0.85	2.01	2.824(3)	160.6
OW2-H4...O1	0.97	2.38	2.993(4)	120.5
N1-H6...O5_$3	0.86	2.18	2.926(4)	144.7
N1-H7...O2_$1	0.86	2.00	2.842(4)	166.3
N2-H8...O10_$4	0.86	2.12	2.963(5)	167.0
N3-H10...O4_$3	0.86	2.12	2.974(4)	169.4
N3-H11...O11_$4	0.86	2.04	2.862(4)	159.0
N6-H12...O1	0.86	2.29	3.139(6)	171.0
N6-H13...OW2_$5	0.86	2.33	3.110(7)	150.3

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z+1; #2 x, y, z-1; #3 -x+2, -y, -z+1; #4 -x+1, -y+1, -z+1; #5 -x, -y, -z+2. The hydrogen atoms are located at calculated positions.

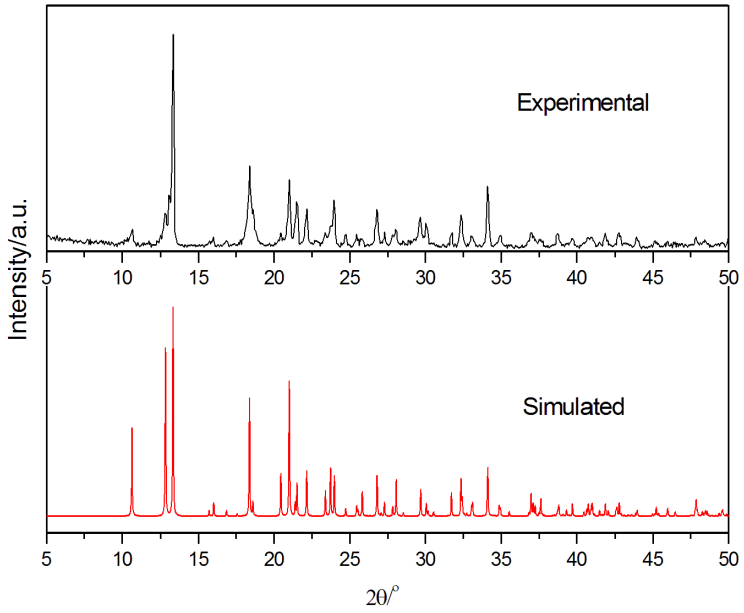

Fig. S1. Experimental and simulated powder XRD patterns of compound **1**.

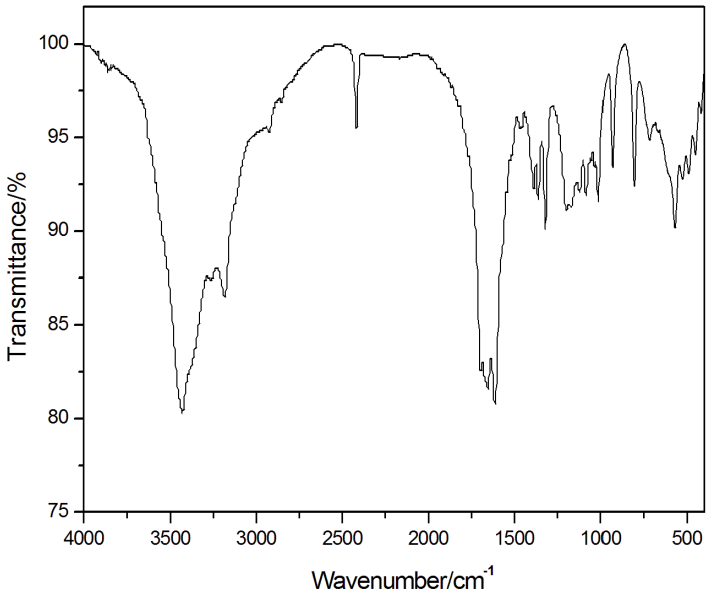

Fig. S2. IR spectrum of compound **1**.

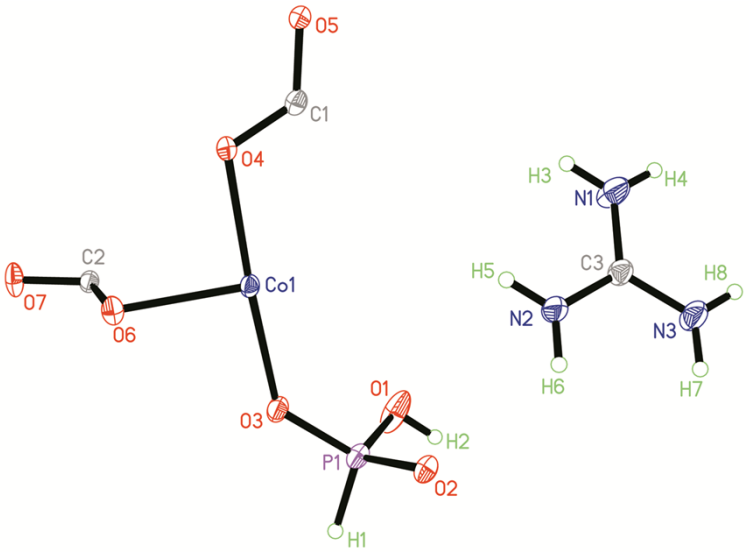

Fig. S3. ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 30% probability displacement ellipsoid.

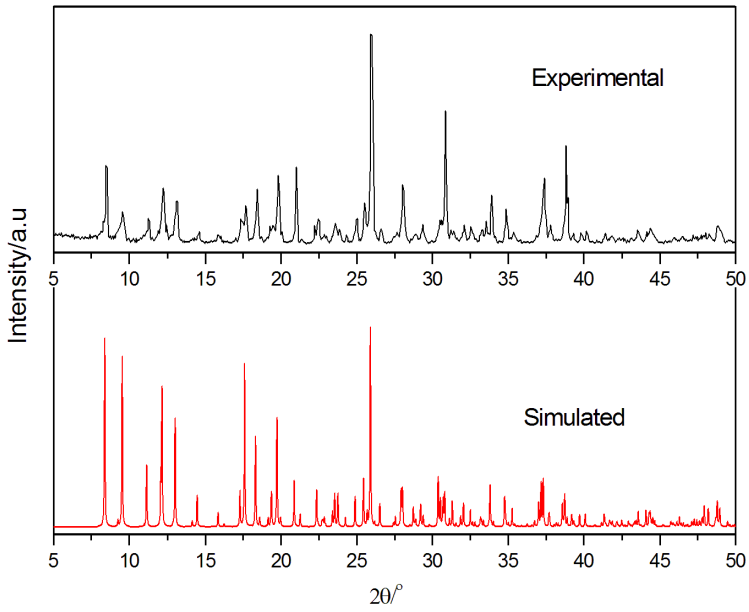

Fig. S4. Experimental and simulated powder XRD patterns of compound **2**.

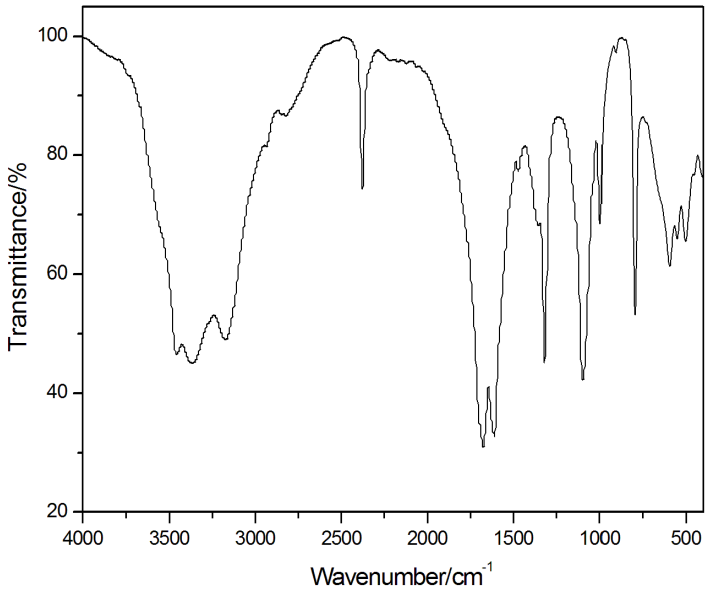

Fig. S5. IR spectrum of compound **2**.

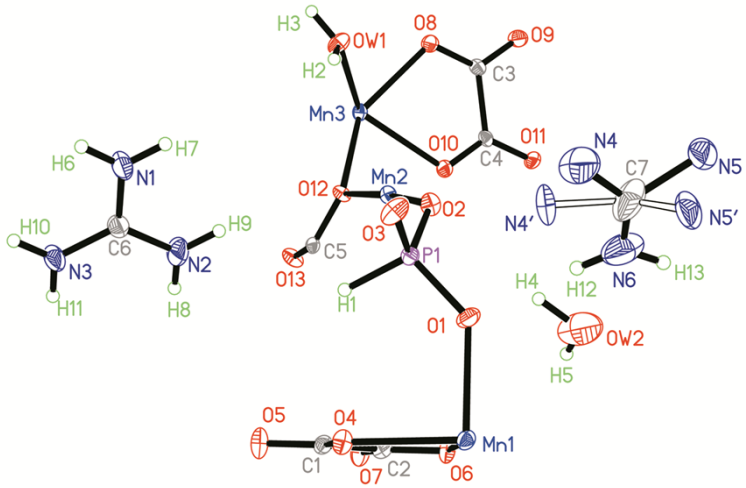

Fig. S6. ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 30% probability displacement ellipsoid.

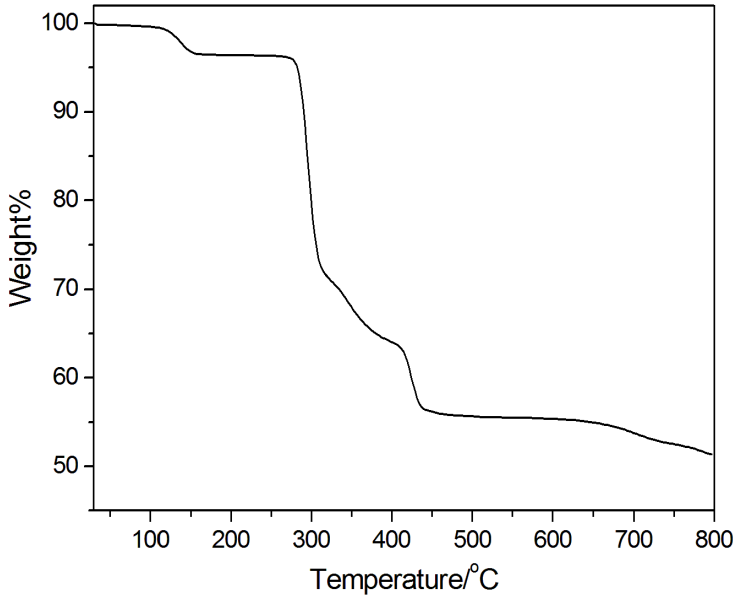

Fig. S7. TGA curve of compound **1**.

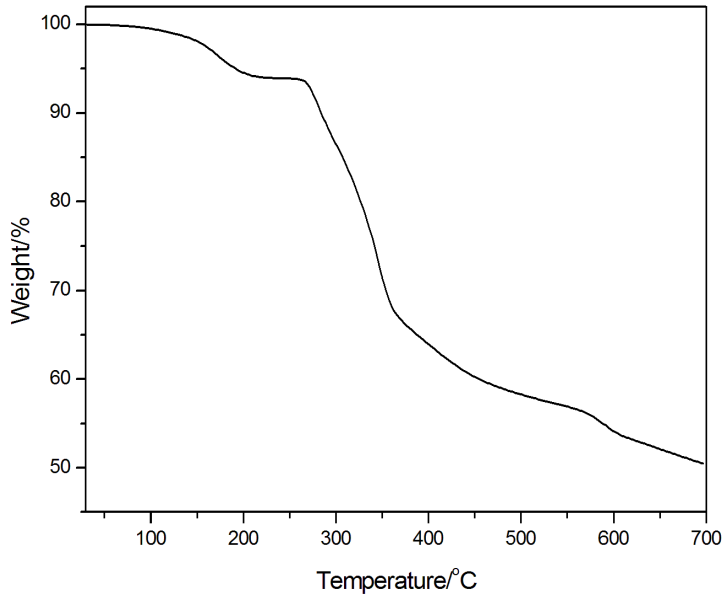

Fig. S8. TGA curve of compound **2**.

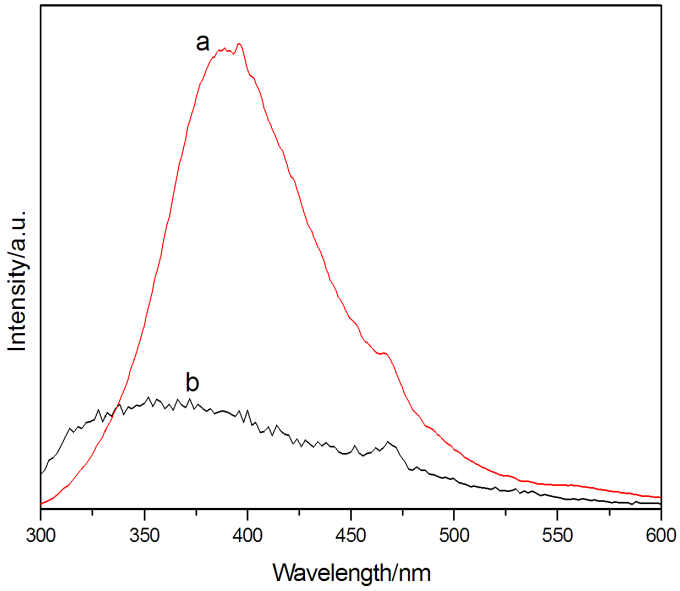

Fig. S9. Solid state fluorescent spectra of (a) compound **1** and (b) guanidinium carbonate at room temperature (λ_{ex} = 220 nm).

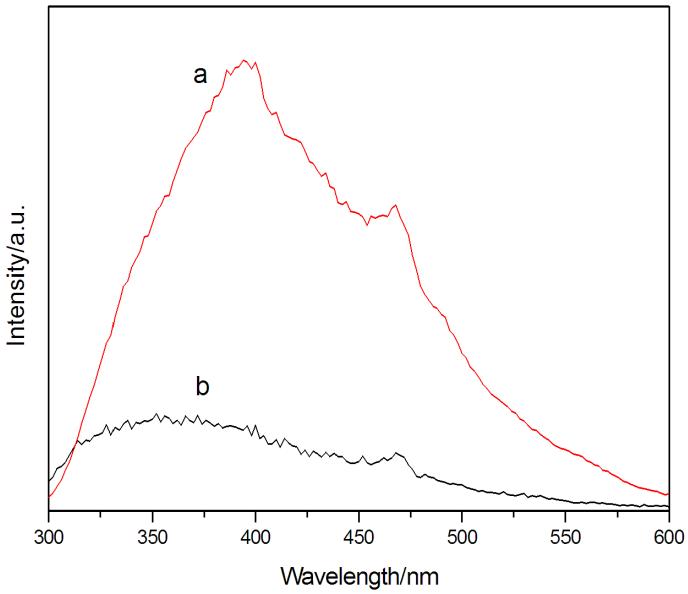

Fig. S10. Solid state fluorescent spectra of (a) compound **2** and (b) guanidinium carbonate at room temperature (λ_{ex} = 220 nm).