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Flux synthesis of three-dimensional open-framework zinc phosphite and manganese phosphite-oxalate with 12-ring channels

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ABSTRACT

New three-dimensional open-framework zinc phosphite and manganese phosphite-oxalate, $H_2dah \cdot Zn_3(HPO_3)_4$ (**1**) and $H_2dab \cdot Mn_2(HPO_3)_2(C_2O_4)(H_2O)_2$ (**2**), were prepared in a flux of phosphorous acid without the addition of water as a solvent (dah = 1,7-diaminoheptane, dab = 1,4-diaminobutane). Compound **1** is constructed from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudo pyramids, and has zigzag 12-ring channels running along the [0 0 1] direction. Compound **2** consists of neutral manganese phosphites layers, which are pillared by oxalate ligands to form a three-dimensional hybrid framework with 12-ring channels running along the [0 1 0] direction. Magnetic susceptibility measurements demonstrate the existence of antiferromagnetic interaction in **2**. Crystal data: **1**, orthorhombic, *Pbcn*, $a = 9.9096(8)$ Å, $b = 15.6780(6)$ Å, $c = 13.8022(6)$ Å, $V = 2144.3(2)$ Å^3, $Z = 4$; **2**, monoclinic, $P2_1/n$, $a = 5.616(3)$ Å, $b = 15.431(3)$ Å, $c = 9.445(3)$ Å, $\beta = 91.72(2)°$, $V = 818.2(5)$ Å^3, $Z = 2$.

1. Introduction

Microporous and open-framework inorganic solids have been extensively studied due to their industrial applications in catalysis, separation, and ion-exchange processes [1–5]. Zeolites (aluminosilicates) are the most well known family of such materials. The discovery of aluminophosphate molecular sieves in 1982 has spurred a widespread enthusiasm in making non-aluminosilicate based zeolitic materials, such as germanates, metal phosphates, arsenates, etc. [6–10]. Currently, metal phosphites are of particular interest for several reasons. First, the HPO_3 unit possesses a characteristic pseudo pyramidal geometry, which can lead to the formation of a new family of interrupted frameworks different from those found in 4-connected zeolitic networks [11–20]. Second, metal phosphite represents a suitable system for the exploration of open frameworks with extra-large channels. Some metal phosphites with 16-, 18-, 20-, 24-, and 26-ring channels have been prepared and characterized [21–31]. Furthermore, the high flexibility of phosphite framework can incorporate new structural building elements. A notable example is $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$, which is the first organically templated M–P–O compound containing Cr^{III} [32].

Open-framework metal phosphites are usually synthesized under hydrothermal or solvothermal conditions. The formation of these open structures is kinetically controlled and is highly sensitive to the reaction conditions. The variation of synthetic parameters, such as temperature, pressure, pH, solvent, and so on, will affect the final structures. To reduce one synthetic parameter and decrease the system pressure, the phosphorous acid flux method has been developed to prepare open-framework metal phosphites without the addition of any liquid solvents like water or alcohols. So far, two layered zinc phosphites with eight-membered rings have been prepared by this solvent-free approach [33,34]. In this work, we report the flux synthesis and characterization of a new three-dimensional open-framework zinc phosphite, $H_2dah \cdot Zn_3(HPO_3)_4$ (**1**). This compound has zigzag 12-ring channels running along the [0 0 1] direction. A hybrid framework manganese phosphite-oxalate, $H_2dab \cdot Mn_2(HPO_3)_2(C_2O_4)(H_2O)_2$ (**2**), is also prepared to demonstrate that this synthetic method can be extended to other metal species such as Mn^{2+}.

2. Experimental

2.1. Synthesis

To prepare crystals of compound **1**, a mixture of dah (0.325 g), $Zn(OAc)_2 \cdot 2H_2O$ (0.548 g), and H_3PO_3 (0.308 g) in a molar ratio of 2:2:3 was sealed in a Teflon-lined steel autoclave and heated at 423 K for 5 days. The resulting product was washed with distilled water and collected by filtration (65.6% yield based on Zn). Chemical analysis confirms the stoichiometry (Anal. Found: C, 12.75; H, 3.58; N, 4.28. Calc: C, 12.97; H, 3.73; N, 4.32). The powder XRD pattern of the resulting product is in good agreement with the one

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simulated on the basis of the single-crystal structure, indicating phase purity.

To prepare crystals of compound **2**, a mixture of dab (0.176 g), $Mn(OAc)_2 \cdot 4H_2O$ (0.491 g), $H_2C_2O_4 \cdot 2H_2O$ (0.252 g) and H_3PO_3 (0.164 g) in a molar ratio of 1:1:1:1 was sealed in a Teflon-lined steel autoclave and kept at 393 K for 4 days before cooling to room temperature. The resulting product was washed with distilled water, and the pink prism-like crystals of **2** were collected by filtration (59.9% yield based on Mn). Elemental analysis confirmed its stoichiometry (Anal. Found: C, 14.88; H, 4.04; N, 5.57%. Calc: C, 14.89; H, 4.16; N, 5.79%). The powder XRD pattern of the resulting product is in good agreement with the one simulated on the basis of the single-crystal structure, indicating phase purity.

2.2. Characterization

The elemental analyses were carried out on an Elementar Vario EL III analyzer. Powder X-ray diffraction (XRD) data were obtained using a Philip X'Pert diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). IR spectra were recorded on a Bruker Alpha-P spectrometer. The thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA 851 analyzer in a flow of N_2 with a heating rate of 10 K/min from 313 to 1073 K. A Bruker ESP 300 spectrometer was used to record the ESR polycrystalline spectrum at the temperature of 100, 200, 300 K. The temperature dependence of the magnetic susceptibility was measured at 1000 G in the temperature range 2–300 K with a SQUID MPMS-7 magnetometer manufactured by Quantum Design.

2.3. Crystal structure determination

Crystal structure determination by X-ray diffraction was performed on a STOE IPDS-I diffractometer with graphite-monochromated MoKα ($\lambda = 0.71073$ Å) radiation at 173 K. The crystal structure of **1** was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the *SHELX97* program package [35]. The zinc and phosphorus atoms were first located, and the carbon, nitrogen, and oxygen atoms were found in the final difference Fourier map. The hydrogen atoms attached to phosphorus atoms were placed geometrically. Only zinc, phosphorous, and oxygen atoms were refined anisotropically, because the organic cations are disordered.

The determination of the crystal structure of **2** followed the same procedure as outlined for **1** with location of the manganese and phosphorous atoms from direct methods. The carbon, nitrogen, and oxygen atoms were derived from the successive difference Fourier syntheses. The hydrogen atoms attached to carbon, nitrogen, and phosphorus atoms were placed geometrically, and the hydrogen atoms of water molecules were found in the final difference Fourier map. All non-hydrogen atoms were refined anisotropically. The crystallographic data for **1** and **2** are summarized in Table 1. Selected bond distances and angles are given in Table 2.

Table 1
Crystal data and structure refinement for compound **1** and **2**.

	1	**2**
Empirical formula	$C_7H_{24}N_2O_{12}P_4Zn_3$	$C_6H_{20}N_2O_{12}P_2Mn_2$
Formula weight	648.27	484.06
Crystal system	Orthorhombic	Monoclinic
Space group	*P*bcn	$P2_1/n$
a, (Å)	9.9096(8)	5.616(3)
b, (Å)	15.6780(6)	15.431(3)
c, (Å)	13.8022(6)	9.445(3)
β, °	90	91.72(2)
Volume, (Å^3)	2144.3(2)	818.2(5)
Z	4	2
D_c, g/cm^3	2.008	1.965
μ (Mo Kα), mm^{-1}	3.683	1.802
Reflections collected	9470	6240
Independent reflections	2082	1581
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0430, 0.1073	0.0231, 0.0597

Table 2
Select bond lengths (Å) and angles (°) for **1** and **2**.[a]

Compound **1**			
Zn(1)–O(2)#1	1.929(4)	Zn(2)–O(4)#1	1.957(3)
Zn(1)–O(6)	1.931(3)	P(1)–O(1)	1.479(5)
Zn(1)–O(3)	1.944(5)	P(1)–O(2)	1.508(4)
Zn(1)–O(5)#2	1.953(4)	P(1)–O(3)	1.512(4)
Zn(2)–O(1)#3	1.890(5)	P(2)–O(6)	1.500(4)
Zn(2)–O(1)#4	1.890(5)	P(2)–O(5)	1.517(4)
Zn(2)–O(4)	1.957(3)	P(2)–O(4)	1.529(4)
O(2)#1–Zn(1)–O(6)	110.87(17)	O(1)#3–Zn(2)–O(4)#1	102.3(2)
O(2)#1–Zn(1)–O(3)	113.61(18)	O(1)#4–Zn(2)–O(4)#1	115.5(2)
O(6)–Zn(1)–O(3)	111.63(18)	O(4)–Zn(2)–O(4)#1	104.9(2)
O(2)#1–Zn(1)–O(5)#2	99.79(16)	O(1)–P(1)–O(2)	113.1(3)
O(6)–Zn(1)–O(5)#2	113.24(18)	O(1)–P(1)–O(3)	107.4(3)
O(3)–Zn(1)–O(5)#2	107.16(18)	O(2)–P(1)–O(3)	114.4(3)
O(1)#3–Zn(2)–O(1)#4	116.4(5)	O(6)–P(2)–O(5)	113.1(2)
O(1)#3–Zn(2)–O(4)	115.5(2)	O(6)–P(2)–O(4)	110.2(2)
O(1)#4–Zn(2)–O(4)	102.3(2)	O(5)–P(2)–O(4)	111.5(2)
Compound **2**			
Mn(1)–O(1)#1	2.1265(15)	P(1)–O(2)	1.5192(15)
Mn(1)–O(2)#2	2.1369(15)	P(1)–O(1)	1.5238(15)
Mn(1)–O(3)	2.1942(15)	P(1)–O(3)	1.5280(15)
Mn(1)–O(4)	2.2210(15)	O(4)–C(1)	1.255(2)
Mn(1)–O(5)#3	2.2478(15)	O(5)–C(1)	1.263(3)
Mn(1)–O(6)	2.2771(17)	C(1)–C(1)#3	1.550(4)
O(1)#1–Mn(1)–O(2)#2	97.40(6)	O(4)–Mn(1)–O(5)#3	73.99(5)
O(1)#1–Mn(1)–O(3)	90.06(6)	O(1)#1–Mn(1)–O(6)	83.17(6)
O(2)#2–Mn(1)–O(3)	92.12(6)	O(2)#2–Mn(1)–O(6)	87.99(6)
O(1)#1–Mn(1)–O(4)	173.61(5)	O(3)–Mn(1)–O(6)	173.18(6)
O(2)#2–Mn(1)–O(4)	88.97(6)	O(4)–Mn(1)–O(6)	97.56(6)
O(3)–Mn(1)–O(4)	89.26(6)	O(5)#3–Mn(1)–O(6)	92.72(6)
O(1)#1–Mn(1)–O(5)#3	99.65(6)	O(2)–P(1)–O(1)	112.14(8)
O(2)#2–Mn(1)–O(5)#3	162.90(6)	O(2)–P(1)–O(3)	113.61(9)
O(3)–Mn(1)–O(5)#3	89.18(6)	O(1)–P(1)–O(3)	110.82(8)

Compound **1**: #1 $-x, y, -z+1/2$; #2 $-x, -y+1, -z$; #3 $x+1/2, y+1/2, -z+1/2$; #4 $-x-1/2, y+1/2, z$.
Compound **2**: #1 $x+1/2, -y+3/2, z+1/2$; #2 $x+1, y, z$; #3 $-x, -y+1, -z+1$.

[a] Symmetry transformations used to generate equivalent atoms.

3. Results and discussion

3.1. Structural description

A single-crystal structural analysis reveals that compound **1** possesses a three-dimensional framework. The asymmetric unit of **1** consists of ten crystallographically independent non-hydrogen framework atoms, including two zinc atoms, two phosphorus atoms and six oxygen atoms (Fig. 1a). Zn(1) atom locates in a general position and Zn(2) atom occupies a special position with site multiplicity of 0.5. Both the zinc atoms are tetrahedrally coordinated with four oxygen atoms. The Zn—O bond distances are in the range of 1.890(5)–1.957(3) Å, with an average value of 1.931 Å. The two unique phosphorus atoms each share three oxygen atoms with adjacent zinc atoms, with the fourth vertex occupied by a hydrogen atom. The P—O distances vary from 1.479(5) to 1.529(4) Å, in excellent agreement with those previously reported. The stoichiometry of $[Zn_3(HPO_3)_4]$ results in a net charge of −2, which is balanced by one diprotonated dah cation per formula unit.

The structure of **1** is built up from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudo pyramids, linked through their vertices forming a three-dimensional framework. The framework density