



Flux synthesis of two new organically templated zinc phosphites with different 3,4-connected frameworks

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ABSTRACT

Two new organically templated zinc phosphites, $\text{H}_2\text{depda} \cdot \text{Zn}_3(\text{HPO}_3)_4$ (**1**) and $\text{H}_2\text{dmpda} \cdot \text{Zn}_3(\text{HPO}_3)_4$ (**2**), have been synthesized under flux conditions, where depda = *N,N*-diethyl-1,3-propanediamine and dmpda = *N,N*-dimethyl-1,3-propanediamine. The two compounds have different (3,4)-connected inorganic frameworks constructed by strictly alternating ZnO_4 tetrahedra and HPO_3 pseudo pyramids. The presence of large 12-ring channels in the two open-framework structures is noteworthy.

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1. Introduction

The research in the synthesis of new microporous and open-framework materials is very intense for their diverse structures and potential applications in catalysis, separation, and ion-exchange processes [1–5]. One class of these materials is metal phosphites, which have interrupted framework structures containing pseudo pyramidal HPO_3^{2-} unit as the building unit [6–8]. Different from 4-connected zeolitic frameworks, (3,4)-connected framework topologies are often found in metal phosphite structures [9–12]. It has been recognized that the presence of 3-connected HPO_4^{2-} building unit enabled the formation of open-framework structures with large pore sizes and low framework density (e.g. cloverite and JDF-20) [13,14]. As a structural analogue of HPO_4^{2-} , the HPO_3^{2-} unit is of current interest in the synthesis of new open-framework structures [15–20]. Some metal phosphites with large 16-, 18-, 20-, 24- and 26-ring channels have been prepared and characterized [21–31]. Metal phosphites with homochiral network and helical channels are also known [32–35].

Open-framework metal phosphites are generally synthesized under hydrothermal or solvothermal conditions. Recently, the H_3PO_3 flux method has been developed to prepare new metal phosphites in

an attempt to eliminate the influence of solvent on the formation of open-framework structures [36]. It has been demonstrated that the use of amine molecules with different size and shape as the structure-directing agents is an effective way to tune the framework topologies of metal phosphites [37–40]. Several amine molecules, such as 1,4-diaminobutane, 1,7-diaminoheptane, 1,3-bis(4-pyridyl)propane, 4,4'-trimethylenedipiperidine, 4-(2-aminoethyl)morpholine, 4-(3-aminopropyl)morpholine, 1-(2-aminoethyl)piperazine, and tris(2-aminoethyl)amine, have been investigated during the past years. In an attempt to study the structure-directing roles of 1,3-propanediamine-derivative molecules, we report here the flux synthesis and structural characterization of two open-framework zinc phosphites, $\text{H}_2\text{depda} \cdot \text{Zn}_3(\text{HPO}_3)_4$ (**1**) and $\text{H}_2\text{dmpda} \cdot \text{Zn}_3(\text{HPO}_3)_4$ (**2**), where depda = *N,N*-diethyl-1,3-propanediamine and dmpda = *N,N*-dimethyl-1,3-propanediamine. The two compounds have different (3,4)-connected frameworks containing large 12-ring channels.

2. Experimental

2.1. Materials and methods

Reagents were purchased commercially and used without further purification. The CHN analyses were carried out on an Elemental Vario EL III analyzer. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-K α

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

	1	2
Empirical formula	C ₇ H ₂₄ N ₂ O ₂ P ₄ Zn ₃	C ₅ H ₂₀ N ₂ O ₁₂ P ₄ Zn ₃
Formula weight	648.27	620.22
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	9.6380(3)	7.7782(3)
<i>b</i> (Å)	20.5979(6)	9.9174(4)
<i>c</i> (Å)	10.4207(3)	12.7946(4)
α (°)	90	99.559(3)
β (°)	95.034(3)	94.030(3)
γ (°)	90	94.803(3)
Volume (Å ³)	2060.76(11)	966.28(6)
<i>Z</i>	4	2
ρ_{calc} (g cm ⁻³)	2.089	2.132
μ (mm ⁻¹)	3.832	4.081
Reflections collected	7969	7111
Independent reflections	3634 [<i>R</i> (int) = 0.0194]	3403 [<i>R</i> (int) = 0.0190]
GOF on <i>F</i> ²	0.970	1.013
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0240, <i>wR</i> ₂ = 0.0574	<i>R</i> ₁ = 0.0252, <i>wR</i> ₂ = 0.0648
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0331, <i>wR</i> ₂ = 0.0586	<i>R</i> ₁ = 0.0313, <i>wR</i> ₂ = 0.0658

radiation ($\lambda = 1.5418$ Å). IR spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer. The thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA 851e analyzer in a flow of N₂ with a heating rate of 10 °C/min from 30 to 700 °C.

2.2. Synthesis and initial characterization

Compounds **1** and **2** were prepared by a phosphorous acid flux method without the addition of water as a solvent. To synthesize compound **1**, a mixture of depda (0.265 g), Zn(OAc)₂·2H₂O (0.439 g), and H₃PO₃ (0.328 g) in a molar ratio of 1:1:2 was sealed in a Teflon-lined steel autoclave and heated at 130 °C for 3 days. After cooling to room temperature, the resulting colorless product was recovered by filtration, washed with distilled water and dried in air (73.4% yield based on zinc). The powder XRD pattern of the crystals is in well accord with the one simulated on the basis of the single-crystal structure, indicating phase purity. Chemical analysis confirms the stoichiometry (Found: C, 12.58; H, 3.57; N, 4.25%. Calcd: C, 12.97; H, 3.73; N, 4.32%). Selected IR bands (cm⁻¹): 3440s, 3010w, 2920w, 2360m, 1630m, 1520m, 1470m, 1110vs, 602s.

To synthesize compound **2**, a mixture of dmpda (0.199 g), Zn(OAc)₂·2H₂O (0.439 g), and H₃PO₃ (0.246 g) in a molar ratio of 2:2:3 was sealed in a Teflon-lined steel autoclave and heated at 130 °C for 3 days. After cooling to room temperature, the resulting colorless

product was recovered by filtration, washed with distilled water and dried in air (84.5% yield based on zinc). The powder XRD pattern of the crystals is in well accord with the one simulated on the basis of the single-crystal structure, indicating phase purity. Chemical analysis confirms the stoichiometry (Found: C, 9.34; H, 3.11; N, 4.39%. Calcd: C, 9.68; H, 3.25; N, 4.52%). Selected IR bands (cm⁻¹): 3430w, 3080w, 2920w, 2370s, 1630m, 1470m, 1090vs, 1000s, 609s, 513m.

2.3. Crystal structure determination

Suitable single crystals of each compound with the dimensions of 0.12 × 0.10 × 0.08 mm for **1** and 0.10 × 0.08 × 0.06 mm for **2** were carefully selected under an optical microscope. Crystal structure determination by X-ray diffraction was performed on an Oxford Xcalibur diffractometer with graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation at 293 K. The crystal structures were solved by direct methods. The zinc and phosphorus atoms were first located. The oxygen, nitrogen, carbon, and the hydrogen atoms attached to phosphorus atoms were found in the difference Fourier map. The hydrogen atoms attached to carbon and nitrogen atoms are added by calculation and refined using a riding model. The structures were refined on *F*² by full-matrix least-squares methods using the *SHELXTL* program package [41]. All non-hydrogen atoms were refined anisotropically. The crystallographic data for **1** and **2** are summarized in Table 1.

3. Results and discussion

Single-crystal structural analysis reveals that the asymmetric unit of **1** consists of three crystallographically independent zinc atoms and four crystallographically independent phosphorus atoms. All the zinc atoms are tetrahedrally coordinated by oxygen atoms. The phosphorus atoms each make three P–O–Zn linkages with adjacent zinc atoms, with the fourth vertex occupied by a terminal hydrogen atom [(P–H)_{av} = 1.33 Å]. The presence of P–H bonds is also confirmed by the band in the IR spectrum, which is characteristic of phosphite group [$\nu(\text{P–H}) = 2360$ cm⁻¹]. The Zn–O bond lengths are in the region of 1.891(2)–1.9575(19) Å, and the P–O bond lengths vary from 1.493(2) to 1.5267(19) Å, in agreement with those of other open-framework zinc phosphites. The stoichiometry of [Zn₃(HPO₃)₄] would result in a net charge of –2, which is balanced by one doubly protonated depda cation per formula unit.

The inorganic framework of **1** is made up of strictly alternating ZnO₄ tetrahedra and HPO₃ pseudo pyramids, giving rise to a three-dimensional structure with 12-ring channels. An instructive way to view the network of compound **1** involves in two distinct structural

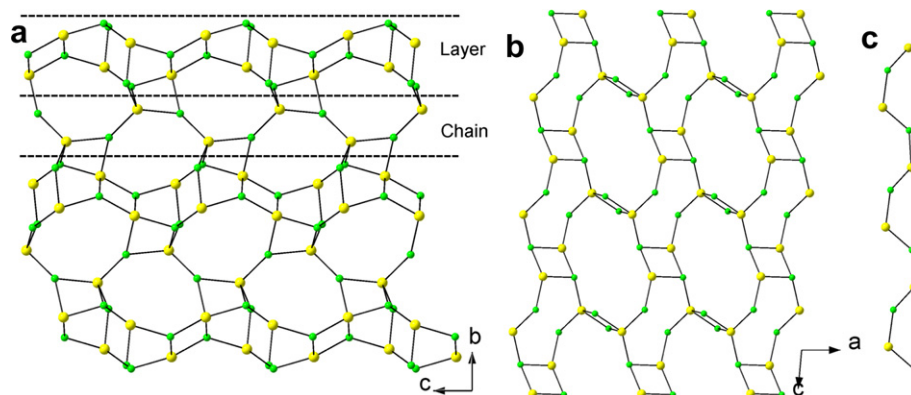


Fig. 1. (a) The three-dimensional inorganic framework of **1** can be constructed from (b) a (4,6,12) layered structure and (c) a linear chain. The framework oxygen and hydrogen atoms are omitted for clarity. Color code: zinc, yellow; and phosphorus, green.

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