

Hydrothermal synthesis and structural characterization of organically templated zincophosphites: $[\text{Zn}(\text{C}_4\text{N}_3\text{H}_{13})][\text{Zn}_4(\text{HPO}_3)_6]\cdot(\text{C}_4\text{N}_3\text{H}_{15})$ and $[\text{Zn}_5(\text{H}_2\text{O})_4(\text{HPO}_3)_6]\cdot(\text{C}_7\text{NH}_{10})_2(\text{H}_2\text{O})$

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Abstract

Two organically templated zincophosphites, $[\text{Zn}(\text{C}_4\text{N}_3\text{H}_{13})][\text{Zn}_4(\text{HPO}_3)_6]\cdot(\text{C}_4\text{N}_3\text{H}_{15})$ and $[\text{Zn}_5(\text{H}_2\text{O})_4(\text{HPO}_3)_6]\cdot(\text{C}_7\text{NH}_{10})_2(\text{H}_2\text{O})$ were synthesized using diethylenetriamine and benzylamine as templates and characterized by single-crystal X-ray diffraction. $[\text{Zn}(\text{C}_4\text{N}_3\text{H}_{13})][\text{Zn}_4(\text{HPO}_3)_6]\cdot(\text{C}_4\text{N}_3\text{H}_{15})$ crystallizes in orthorhombic *Cmca* with cell parameters $a = 18.9617(7)$ Å, $b = 10.0192(3)$ Å, $c = 16.1415(4)$ Å. $[\text{Zn}_5(\text{H}_2\text{O})_4(\text{HPO}_3)_6]\cdot(\text{C}_7\text{NH}_{10})_2(\text{H}_2\text{O})$ crystallizes in triclinic *P-1* with cell parameters $a = 10.0039(9)$ Å, $b = 10.2172(9)$ Å, $c = 11.6488(9)$ Å, and $\alpha = 69.646(5)^\circ$, $\beta = 88.003(5)^\circ$, $\gamma = 62.994(5)^\circ$. $[\text{Zn}(\text{C}_4\text{N}_3\text{H}_{13})][\text{Zn}_4(\text{HPO}_3)_6]\cdot(\text{C}_4\text{N}_3\text{H}_{15})$ consist of alternatively linked ZnO_4 , ZnO_2N_3 and $[\text{HPO}_3]^{2-}$ units. In this structure, the structure-directing amines as ligands to zinc are present in two distinct forms, the free state and bonded state, and the two species occurring in channels. $[\text{Zn}_5(\text{H}_2\text{O})_4(\text{HPO}_3)_6]\cdot(\text{C}_7\text{NH}_{10})_2(\text{H}_2\text{O})$ is made up of ZnO_4 , ZnO_6 and $[\text{HPO}_3]^{2-}$ moieties forming distinct channels, the protonated aromatic amine molecules are located in the intersection of the channels. In the compounds, the connections ZnO_2N_3 and ZnO_6 of Zn atoms are the first reported in the synthesis of zincophosphite materials. Two zincophosphites, having two-dimensional structures with 4, 6, 8-membered rings channels, were also characterized by IR spectroscopy, thermogravimetric and differential thermal analyses.

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Keywords: Hydrothermal synthesis; Organic–inorganic hybrid composites; X-ray diffraction; N ligands; Layered compounds

1. Introduction

In the past decades, the preparation and structural chemistry of a number of organically templated metal phosphates were extensively studied for their potential applications in ion exchange, absorption, catalysis, and chemical sensor [1–10]. Structurally, the tetrahedral PO_4 are basic building block in the phosphates [11–16]. Since 2001, when Harrison proposed the substitution of P(III) for P(V) and prepared the organically templated zincophosphite [17], some zincophosphites have been reported for replacing zincophosphates [18–22]. Compared to tetrahedral phosphate, the phosphite has a pseudo pyramidal geometry. The hydrogen phosphite group $[\text{HPO}_3]^{2-}$ as a new basic building block led to diversity of novel structures

in organically templated zincophosphites. Moreover, open-framework metal phosphites have been synthesized, including $[\text{C}_2\text{H}_{10}\text{N}_2]\cdot[\text{V}(\text{HPO}_3)_2]$, $[\text{C}_2\text{H}_{10}\text{N}_2]\cdot[\text{Fe}(\text{HPO}_3)_2]$ [23], $[\text{C}_2\text{H}_{10}\text{N}_2]\cdot[\text{Co}_3(\text{HPO}_3)_4]$ [24], $[\text{C}_2\text{H}_{10}\text{N}_2]\cdot[\text{Cr}(\text{HPO}_3)_3\text{F}_3]$ [25] and $[\text{C}_2\text{H}_{10}\text{N}_2]\cdot[\text{Mn}_3(\text{HPO}_3)_4]$ [26], $[\text{C}_2\text{H}_{10}\text{N}_2]\cdot[\text{Al}(\text{OH})\{\text{H}(\text{HPO}_3)\}_2]$ [27], $[\text{C}_4\text{H}_{12}\text{N}_2]\cdot[(\text{UO}_2)_2(\text{PO}_3\text{H})_2\{\text{PO}_2(\text{OH})\text{H}_2\}]$ [28]. As an extension of our previous study on the inorganic–organic hybrid phosphates [29,30] and organically templated phosphites [31–35], we continue our research on the investigation of the templating effect by finding a similar synthetic system. In this paper, we describe the syntheses and crystal structures of two two-dimensional zincophosphites, $[\text{Zn}(\text{C}_4\text{N}_3\text{H}_{13})][\text{Zn}_4(\text{HPO}_3)_6]\cdot(\text{C}_4\text{N}_3\text{H}_{15})$ **1** and $[\text{Zn}_5(\text{H}_2\text{O})_4(\text{HPO}_3)_6]\cdot(\text{C}_7\text{NH}_{10})_2(\text{H}_2\text{O})$ **2**, with four, six, eight-membered rings, containing two types of amine molecules. Compound **1** is composed of alternating ZnO_4 tetrahedra, ZnO_2N_3 trigonal bipyramid and HPO_3 pseudo pyramids. Compound **2** involves

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a network of ZnO_4 tetrahedra, ZnO_6 octahedral and HPO_3 pseudo pyramids with shared vertices. The connections of Zn in the two compounds, ZnO_2N_3 and ZnO_6 , are the first mentioned in zincophosphite materials. And we have discovered in compound **1** of open-framework structure where the organic amine plays the dual space-filling agent. The structure-directing amine is present in two distinct forms, in the free state and the bonded state as a ligand to zinc, the two species occurring in distinct channels. In compound **2**, using aromatic molecules as template is also seldom reported in the synthesis of the zinc phosphate or zincophosphite. Two compounds were characterized by IR spectroscopy, thermogravimetric and differential thermal analyses.

2. Experimental

2.1. Synthesis and characterization

In a typical synthesis for compound **1**, a mixture of $\text{Zn}(\text{ac})_2 \cdot 2\text{H}_2\text{O}$ (0.219 g), H_3PO_3 (0.410 g), diethylenetriamine (0.35 mL), and water (5.0 mL) in a molar ratio of 1 : 5 : 3 : 166 was stirred under ambient conditions until it was homogeneous. The final reaction mixture with pH = 5.0 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 96 h. Compound **2** was prepared from a mixture of $\text{Zn}(\text{ac})_2 \cdot 2\text{H}_2\text{O}$ (0.219 g), H_3PO_3 (0.410 g), benzylamine (0.5 mL), and water (5.0 mL) in a molar ratio of 1 : 5 : 5 : 166 and it was stirred under ambient conditions until it was homogeneous. The final reaction mixture with pH = 6.0 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 120 h. The resulting products, consisting of colorless block single crystals, were filtered, washed with distilled water and dried under ambient conditions (75% yield based on Zn for **1** and 85% yield based on Zn for **2**).

The elemental analyses were performed on a Perkin–Elmer 2400 element analyzer. The inductively couple plasma (ICP) analysis was carried out on a Perkin–Elmer Optima 3300DV ICP instrument. The ICP and elemental analysis results of the bulk products were also consistent with the theoretical values. Anal. calcd. for **1**: C, 9.46; H, 3.35; N, 8.28%. Found: C, 9.7; H, 3.30; N, 8.37%. Calcd. for **2**: C, 15.09; H, 3.23; N, 2.52%. Found: C, 15.39; H, 3.26; N, 2.58%.

The IR spectra of the compounds showed typical peaks, with very little differences in the spectra. Strong absorption bands at 3413 cm^{-1} for N–H and 2500–3300 cm^{-1} for C–H bending stretching vibrations are observed. The bands at 2412 cm^{-1} for **1** and 2399 cm^{-1} for **2** were attributed to the terminal P–H stretch and deformation. The intense bands in the range 1087 cm^{-1} for **1** and 1150 cm^{-1} for **2** were attributed to the asymmetric and symmetric stretching vibrations of O–P–O. The bands at 1382.7, 1457.9, 1542.7, 1616.1 cm^{-1} were assigned to the benzene ring stretching vibrations for **2**.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out on a Perkin–Elmer DTA 1700 differential thermal analyzer and a Perkin–Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of 10 °C min^{-1} .

Table 1

Crystal data and structure refinement parameters for $[\text{Zn}_4\text{Zn}(\text{C}_4\text{N}_3\text{H}_{13})_6](\text{HPO}_3)_6 \cdot (\text{C}_4\text{N}_3\text{H}_{15})$ **1** and $[\text{Zn}_5(\text{H}_2\text{O})_4(\text{HPO}_3)_6] \cdot (\text{C}_7\text{NH}_{10})_2(\text{H}_2\text{O})$ **2**

	1	2
Empirical formula	$\text{C}_8\text{H}_{34}\text{N}_6\text{O}_{18}\text{P}_6\text{Zn}_5$	$\text{C}_{14}\text{H}_{36}\text{N}_2\text{O}_{23}\text{P}_6\text{Zn}_5$
Fw	1015.08	1113.12
<i>T</i> (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Space group	<i>Cmca</i>	<i>P</i> -1
<i>a</i> (Å)	18.9617(7)	10.0039(9)
<i>b</i> (Å)	10.0192(3)	10.2172(9)
<i>c</i> (Å)	16.1415(4)	11.6488(9)
		$\alpha = 69.646(5)$
		$\beta = 88.003(5)$
		$\gamma = 62.994(5)$
<i>V</i> (Å ³)	3066.58(16)	983.72(15)
<i>Z</i>	4	1
<i>D</i> _{calc.} (g cm ⁻³)	2.199	1.879
μ (mm ⁻¹)	4.249	3.327
<i>R</i> ₁ ^a [<i>I</i> > 2 θ (<i>I</i>)]	0.0463	0.0595
<i>wR</i> ₂ ^b [<i>I</i> > 2 θ (<i>I</i>)]	0.1499	0.1671

$$^a R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right\}^{1/2}$$

2.2. Structural determination

Crystals were carefully selected for X-ray diffraction analysis. The intensity data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation at a temperature of 293 ± 2 K. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. Data processing was accomplished with the SAINT processing program [36]. The structure was solved by Direct Methods, which use the SHELXTL crystallographic software package [37]. The zinc and phosphorus atoms were first located, whereas the carbon, nitrogen, and oxygen atoms were found in the difference Fourier maps. In compound **1**, O(5) splits to O(5'), N(1) splits to N(1'). The hydrogen atoms residing on the phosphorus were located by Fourier maps. And the hydrogen atoms residing on the amine molecules were placed geometrically except compound **1**. Hydrogen atoms associated with the hydrogen phosphite moieties (P–H) and template molecules (N–H and C–H) were refined by riding on their parent atoms. All non-hydrogen atoms were refined anisotropically. Details of the final refinement are given in Table 1.

3. Results and discussion

3.1. Crystal structure of

$[\text{Zn}(\text{C}_4\text{N}_3\text{H}_{13})][\text{Zn}_4(\text{HPO}_3)_6] \cdot (\text{C}_4\text{N}_3\text{H}_{15})$ **1**

Compound **1** contains ZnO_4 tetrahedra, ZnO_2N_3 trigonal bipyramid and HPO_3 pseudo pyramids as the polyhedral-building units (Fig. 1(a)). In this structure, two independent zinc atoms present two different coordination geometries. The Zn(1) is tetrahedrally coordinated by four oxygen atoms, with Zn–O bond distances from 1.914 to 1.963 Å. The O–Zn–O bond

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