



Synthesis and characterization of a novel inorganic–organic hybrid open-framework zinc phosphate with 16-ring channels



Guo-Ming Wang^{a,*}, Jin-Hua Li^a, Cui-Li Gao^a, Jun-Cheng Zhang^a, Xiao Zhang^a, Zhen-Zhen Bao^a, Ying-Xia Wang^b, Jian-Hua Lin^b

^a Teachers College, College of Chemical Science and Engineering, College of Physics Science, Qingdao University, Shandong 266071, China

^b Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT

A novel inorganic–organic hybrid open-framework zinc phosphate, $(\text{NH}_4)[\text{Zn}_5(\text{PO}_4)_3(\text{HPO}_4)_2(\text{HAPIM})_2] \cdot (\text{H}_2\text{O})$ (**1**), was solvothermally synthesized in the presence of 1-(3-aminopropyl)imidazole (APIM) as structure-directing agent. Its structure is built up by the alternate linkages between ZnO_4 , ZnO_3N , PO_4 and HPO_4 tetrahedral moieties, forming an unusual three-dimensional framework with intersecting 8-, 10-, and 16-ring channels. The arrangement of the monoprotonated APIM molecules in **1** is unique and they play dual roles as both ligands and counteranions. It is the first example with APIM as template in extra-large-channel structures in zincophosphates. The framework contains a Zn/P ratio of 1:1 and exhibits remarkable low framework density. Photoluminescence studies show that there is a ligand-to-metal charge transfer.

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1. Introduction

Microporous materials have attracted considerable research interest owing to their rich structural chemistry and potential applications in gas storage, catalysis, adsorption and separation [1–3]. Since the discovery of crystalline aluminophosphate molecular sieves in 1982 [4], considerable progress has been achieved in the synthesis of microporous metal phosphates/phosphites due to their compositional diversity and rich structural chemistry [5,6]. Therein, open-framework zinc phosphates/phosphites occupy an apical position and a large number of such solids with zero-, one-, two-, and three-dimensional structures have been prepared and characterized [7–12]. These structures are typically realized by versatile connections of tetrahedral (octahedral) metal oxide clusters with phosphate (phosphite) tetrahedra under hydrothermal conditions. One common structural feature in this system is that the inorganic frameworks are often anionic and a remarkable variety of protonated organoamine templates are introduced as charge compensating and space-filling constituents.

By contrast, the analogous organic-inorganic hybrid materials assembled from covalently bonded organic and inorganic moieties, have not been studied as extensively. Undoubtedly, the combination of different organic and inorganic moieties may offer opportunities for making new structural types and novel properties. A typical example in this system is $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2]_{0.5} \cdot \text{ZnHPO}_3$, in which the template is neutral, bonding directly to Zn atoms to produce an unprecedented architecture of two interpenetrated, independent mixed inorganic–organic network [13]. A review of the literature shows that anionic oxalate and neutral 4,4'-bipyridine (4,4'-bpy) are the most common organic ligands used in the preparation of inorganic–organic hybrid metal phosphates and phosphites [14–18]. Further, it is also observed that multifunctional organic ligands with N-donor or anionic O-donor groups, such as terephthalic acid, isonicotinate, pyrazine, imidazole, piperazine and natural amino acid etc., are good coordinates for the construction of hybrid frameworks. Notable examples include $[\text{Co}_3(4,4'\text{-bpy})(\text{HPO}_4)_2\text{F}_2] \cdot x\text{H}_2\text{O}$ and $[\text{BAEOE}][\text{Zn}(\text{HPO}_3)]_2$ containing neutral inorganic layers pillared through distinct rigid 4,4'-bipyridine and flexible 1,2-bis(2-aminoethoxy)ethane (= BAEOE) ligands respectively [19,20], $\text{Zn}(\text{HINT})(\text{HPO}_4)$ possessing neutral $\text{Zn}(\text{HPO}_4)$ sheets with pendent dipolar isonicotinate ligand [21], $(\text{H}_2\text{tmdp})[(\text{ZnHPO}_4)_2(1,4\text{-bdc})]$ (tmdp = 4,4'-trimethylenedipyridine; 1,4-bdc = 1,4-benzenedicarboxylate) with zeolite-like topology and

* Corresponding author.

E-mail address: gmwang_pub@163.com (G.-M. Wang).

bimodal porosity [22], [(Co(4-pya))₃PO₄] consisting of paddlewheel Co₃ clusters connected by PO₄³⁻ and 4-pyridinecarboxylate (= 4-pya) [23], ZnHPO-CJ56 and ZnHPO-CJ57 exhibiting homochiral inorganic–organic hybrid frameworks with chiral *L*-tryptophan and *L*-histidine molecules acting as both templates and the ligands [24], as well as several hybrid zinc phosphates/phosphites with different imidazole-types ligands [25–28]. Herein, we attempt to assemble tetrahedral Zn²⁺ with phosphate group and 1-(3-aminopropyl)imidazole (APIM) ligand for the construction of novel hybrid open frameworks. Excitingly, a new inorganic–organic zinc phosphate (NH₄)[Zn₅(PO₄)₃(HPO₄)₂(HAPIM)₂]·(H₂O) (**1**), has been solvothermally synthesized. In this paper, we describe the synthesis, structure and luminescent properties of this compound.

2. Experimental section

2.1. Materials and methods

All reagents were purchased commercially and used without further purification. The CHN analyses were carried out on an Elemental Vario EL III CHNOS elemental analyzer. Infrared spectra were obtained from sample powder pelletized with KBr on an ABB Bomen MB 102 series FTIR spectrophotometer over a range 400–4000 cm⁻¹. The thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer in N₂ atmosphere with a heating rate of 10 °C/min from 40 to 800 °C. Fluorescent spectra were measured on a Jasco FP-6500 fluorescence spectrophotometer.

2.2. Synthesis

The title compound was synthesized solvothermally under autogenous pressure. In a typical synthesis, a mixture of ZnO (0.162 g, 2.0 mmol), H₃PO₄ (85%, 0.20 mL, 3.1 mmol), 1-(3-aminopropyl)imidazole (0.24 mL, 2.0 mmol), methanol (3.50 mL, 86.5 mmol) and H₂O (2.50 mL, 139.0 mmol) was sealed in a Teflon-lined steel autoclave and heated at 160 °C for 6 days. After cooling to room temperature, the resulting product, containing colorless chunk-shaped crystals was recovered by filtration, washed with distilled water and dried in air (46.2% yield based on zinc). CHN elemental analysis confirmed its stoichiometry (Anal. Calcd: C 13.19, H 2.93, N 8.97%; Found: C 13.02, H 2.66, N 8.86%). The X-ray powder diffraction profile of the resulting product is in agreement with the simulated pattern from single-crystal X-ray structure data,

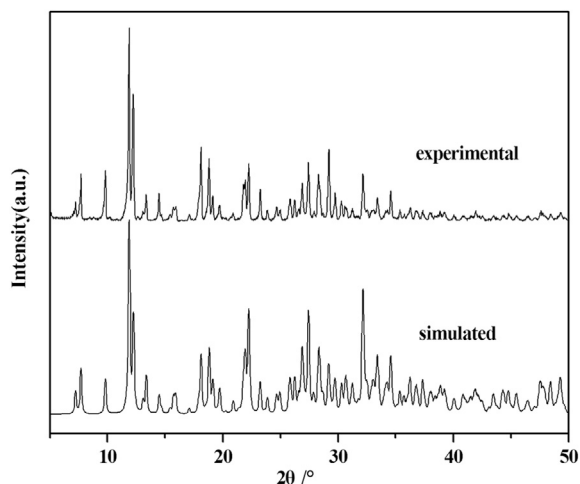


Fig. 1. Experimental and simulated XRD patterns of **1**.

indicating the purity of the as-synthesized sample of the title compound (Fig. 1).

2.3. Determination of crystal structure

A suitable colorless single crystal of as-synthesized compound was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) in the ω and φ scanning mode at room temperature. An empirical absorption correction was applied using the SADABS program [29]. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELXL-97 program package [30]. The zinc and phosphorus atoms were first located, whereas the carbon, nitrogen, and oxygen atoms were found in the successive difference Fourier maps. The C(2), C(3), C(4), C(5), C(8), C(9) and N(5) atoms are found to be disordered over two positions with an equal occupancy. The hydrogen atoms associated with the hydroxyl groups (O(7) and O(17)) were placed geometrically and refined in a riding model. All of the non-hydrogen atoms were refined anisotropically. Crystallographic data and structure refinements for this compound are listed in Table 1. CCDC 1009196 contains the supplementary crystallographic data for this paper.

3. Results and discussion

3.1. Infrared (IR) spectra

The IR spectrum of the title compound is shown in Fig. 2. The broad bands at 3422–2870 cm⁻¹ correspond to the stretching bands of the OH, NH₂ and CH₂. The bending bands of NH₂ and CH₂ are present at 1635–1433 cm⁻¹. The bands at the region of 1118–897 cm⁻¹ can be assigned to the asymmetric stretching vibrations of PO₄ group, and the symmetric vibration of PO₄ group is observed at around 780 cm⁻¹. The bending vibrations of PO₄ groups can be observed in the range 483–705 cm⁻¹.

3.2. Structural description

Single crystal X-ray analysis reveals that **1** crystallizes in the orthorhombic space group *Pna*2₁ (No. 33). The asymmetric unit

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

Empirical formula	C ₁₂ H ₃₂ N ₇ O ₂₁ P ₅ Zn ₅
Formula weight	1092.15
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 ₁
<i>a</i> /Å	9.7925(2)
<i>b</i> /Å	22.9726(6)
<i>c</i> /Å	14.4497(3)
α /°	90
β /°	90
γ /°	90
<i>V</i> /Å ³	3250.59(13)
<i>Z</i>	4
<i>D_c</i> /g cm ⁻³	2.232
μ (Mo-K α)/mm ⁻¹	3.978
<i>F</i> (000)	2184
Reflection collected	76525
Independent reflections	5696 [R(int) = 0.0544]
Parameters refined	108
Limiting indices	−11 ≤ <i>h</i> ≤ 11, −27 ≤ <i>k</i> ≤ 27, −17 ≤ <i>l</i> ≤ 17
Goodness-of-fit on F^2	1.081
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0437, 0.0903

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