

$(C_6H_{17}N_3)[Zn_4(PO_4)_2(HPO_3)_2]$: a new layered zinc phosphate–phosphite templated by 1-(2-Aminoethyl) piperazine[☆]

Xiaoxin Chen, Yu Wang, Jihong Yu,* Yongchun Zou, and Ruren Xu*

College of Chemistry, State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, PR China

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Abstract

Employing 1-(2-Aminoethyl) piperazine as a template, a new organically templated layered zinc phosphate–phosphite $(C_6H_{17}N_3)[Zn_4(PO_4)_2(HPO_3)_2]$ has been prepared hydrothermally. Single-crystal X-ray diffraction analysis shows that it crystallizes in the monoclinic space group Cc with $a = 5.3272(11) \text{ \AA}$, $b = 17.146(3) \text{ \AA}$, $c = 22.071(4) \text{ \AA}$, $\beta = 94.58(3)^\circ$, $V = 2009.5(7) \text{ \AA}^3$, $Z = 4$, $R_1 = 0.0201$ ($I > 2\sigma(I)$) and $wR_2 = 0.0812$ (all data). The inorganic network is based on strictly alternating ZnO_4 tetrahedral units and P-centered units including PO_4 tetrahedra and HPO_3 pseudo-pyramids forming a double layered structure that contains columns of double six-membered rings. The diprotonated 1-(2-Aminoethyl) piperazine molecules reside in the interlayer region and interact with the inorganic network through H-bonds.

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Keywords: Layer; Zinc phosphate–phosphite; Hydrothermal synthesis; Structure; Host–guest system

1. Introduction

Over the past few decades, a large number of open-framework metal phosphates have been synthesized under hydrothermal/solvothermal conditions [1–3] following the discovery of microporous aluminophosphates in 1982 [4]. These materials have important applications in the fields of catalysis, biology, electrical conductivity, magnetism and photochemistry. So far, most of the metal elements in the periodic table including main group metals, transition metals, and rare-earth metals, etc. can be incorporated into the open-frameworks [1–3,5]. Open-framework metal phosphates show rich structure chemistry, in particularly the growing family of zinc phosphate family exhibits fascinating structural architectures, such as extra-large micropore structures [6,7], helical channel structures [8,9], and various low-dimensional structures with 0D clusters, 1D chains and 2D layers [2].

Recently, the synthesis of open-framework metal phosphites such as vanadium phosphites, iron phos-

phites, manganese phosphite and chromium phosphates, etc. has attracted considerable attention [10–13]. Harrison et al. [14] reported the first organically templated zincophosphite. To date, a number of organically templated zinc phosphites have been prepared with interesting structural architectures [15–25]. They are generally built up from Zn-centered tetrahedra (ZnO_4 or ZnO_3N) and P-centered $HP^{III}O_3^{2-}$ pseudo-pyramids. Examples for these compounds are known for 0D cluster $C_4N_3OH_7 \cdot Zn(H_2O)HPO_3$ [15], 1D chain $H_3N(CH_2)_3NH_3 \cdot Zn(HPO_3)_2$ [16], 2D layers $(C_5H_6N_2)Zn(HPO_3)$ [17] and $[H_2N(CH_2)NH_2]_{0.5} \cdot ZnHPO_3$ [18], and 3D open-framework $(NC_5H_{12})_2Zn_3(HPO_3)_4$ [19] and $[CN_3H_6]_2Zn(HPO_3)_2$ [20]. Recently, a new hybrid zinc phosphate–phosphite $(C_6H_{15}N_2)_2Zn_4(PO_4)_2(HPO_3)_2 \cdot (ZnPO-CJ12)$ has been hydrothermally prepared whose inorganic sheet contains both PO_4^{3-} and HPO_3^{2-} anions [25].

In this work, using H_3PO_3 as a phosphorus source, an interesting organically templated zinc phosphate–phosphite $(C_6H_{17}N_3)[Zn_4(PO_4)_2(HPO_3)_2]$ with double layered structure has been hydrothermally synthesized in the presence of 1-(2-Aminoethyl) piperazine as a structure-directing agent. As with $ZnPO-CJ12$, the zinc phosphate–phosphite layer contains the PO_4^{3-} and HPO_3^{2-} anions and exhibits a double layered structure.

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*Corresponding author. Fax: +86-431-567-1974.

E-mail address: jihong@mail.jlu.edu.cn (J. Yu).

The diprotonated 1-(2-Aminoethyl) piperazine molecules reside in the interlayer region and interact with the inorganic host through H-bonds.

2. Experimental section

The title compound was synthesized by a hydrothermal reaction of a mixture of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, H_3PO_3 , 1-(2-Aminoethyl) piperazine and H_2O in a molar ratio of 1:3:2.75:488. Typically, 0.25 g of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was first dissolved in 10 mL of H_2O , then 0.280 g H_3PO_3 was added with stirring. Finally, 0.42 mL of 1-(2-Aminoethyl) piperazine (97% Fluka) was added dropwise to the above reaction mixture. A gel was formed and further stirred for 1 h with until it was homogeneous. The reaction mixture with a pH value of 7 was sealed in a Teflon-lined stainless autoclave and then heated at 180°C for 5 d under static conditions. The product containing large plate-like single crystals in 70% yield in the product were separated by sonication and further washed by distilled water and then air-dried.

The X-ray power diffraction (XRD) data were collected on a Siemens D5005 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Infrared spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer using KBr pellets. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air with a heating rate of 10°C/min. The magic-angle-spinning (MAS) NMR spectra were recorded on a Varian Infinity Plus-400 spectrometer. The ^{31}P NMR spectrum was taken at 161.9 MHz with a spinning rate of 11 kHz. Chemical shifts were referenced to 85% H_3PO_4 . The recycle delay time was 60 s. ^1H decoupling was used to measure the ^{31}P NMR spectrum.

A suitable single crystal with dimensions $0.08 \times 0.08 \times 0.4 \text{ mm}$ was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Rigaku R-AXIS RAPID IP diffractometer by oscillation scans using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction were accomplished with the RAPID AUTO program. The structure was solved by the direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97 [26]. The Zn and P atoms were easily located, and O, C, N, and H atoms in HPO_3 were subsequently located in the difference Fourier maps. The C–H and N–H hydrogen atoms were located geometrically. Diprotonation of the 1-(2-Aminoethyl) piperazine molecules was suggested on the basis of charge balance. All non-hydrogen atoms were refined with anisotropic thermal parameters. Experimental

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

Empirical formula	$\text{C}_6\text{H}_{19}\text{N}_3\text{O}_{14}\text{P}_4\text{Zn}_4$
Formula weight	742.60
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Cc
Unit-cell dimensions	$a = 5.3272(11) \text{ \AA}$; $\alpha = 90^\circ$ $b = 17.146(3) \text{ \AA}$; $\beta = 94.58(3)^\circ$ $c = 22.071(4) \text{ \AA}$; $\gamma = 90^\circ$
Volume	$2009.5(7) \text{ \AA}^3$
Z, Calculated density	4, 2.455 Mg/m^3
Absorption coefficient	5.111 mm^{-1}
$F(000)$	1472
Crystal size	$0.08 \times 0.08 \times 0.4 \text{ mm}$
Theta range for data collection	$1.85\text{--}27.48^\circ$
Limiting indices	$0 \leq h \leq 6$, $0 \leq k \leq 22$, $-28 \leq l \leq 28$
Reflections collected/unique	2312/2312 ($R_{\text{int}} = 0.0000$) ^a
Completeness to $\theta = 27.48^\circ$	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2312/2/288
Goodness-of-fit on F^2	1.007
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0201$, $wR_2 = 0.0453$
R indices (all data)	$R_1 = 0.0283$, $wR_2 = 0.0812$
Absolute structure parameter	0.00
Largest diff. Peak and hole	0.717 and -0.701 e/\AA^3

^aThe intensity data were collected in a Rigaku R-AXIS RAPID IP diffractometer, the collected reflections have been merged for equivalents, the “reflections collected” here should be equal to “reflections unique”.

details for the structure determination are presented in Table 1. The deposition number CCDC 232208.

3. Results and discussion

The title compound, denoted as **1**, can be crystallized in an aqueous system with molar compositions 1.0 $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}:(3.0\text{--}5.0) \text{H}_3\text{PO}_3:(2.25\text{--}3.75) 1\text{-(2-Aminoethyl) piperazine}:488 \text{H}_2\text{O}$ at 180°C. The pH values of the initial gels are in the range of 5–8. A minor unidentified phase is frequently accompanied with **1**. Structural analysis indicates that both PO_4^{3-} and HPO_3^{2-} anions exist in the structure. This suggests that the initial H_3PO_3 source can be oxidized or disproportionated into PO_4^{3-} anions under hydrothermal conditions. Such phenomenon has been noted in the synthesis of hybrid zinc phosphate–phosphite ZnPO-CJ12 [25].

The X-ray powder diffraction pattern of **1** is shown in Fig. 1. Except for those marked peaks, the XRD pattern is in agreement with the simulated one generated on the basis of single-crystal structural data. ICP analysis indicates that **1** contains 32.1 and 15.2 wt% of Zn and P, respectively (calcd 35.2 and 16.7 wt% of Zn and P, respectively). The elemental analysis gives that **1** contains 9.96, 2.63, 5.75 wt% of C, H and N, respectively (calcd 9.70, 2.58 and 5.68 wt% of C, H,

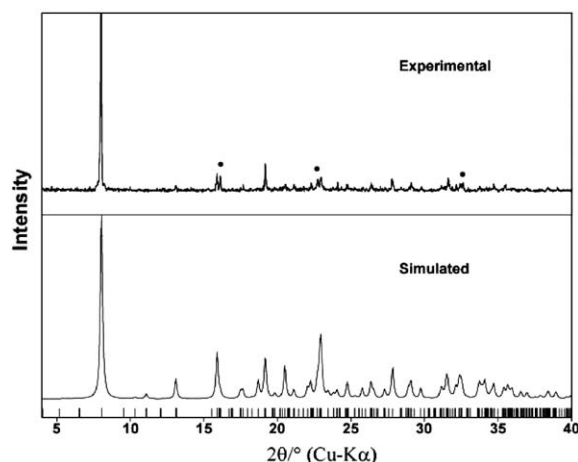


Fig. 1. Experimental and simulated XRD patterns for **1**.

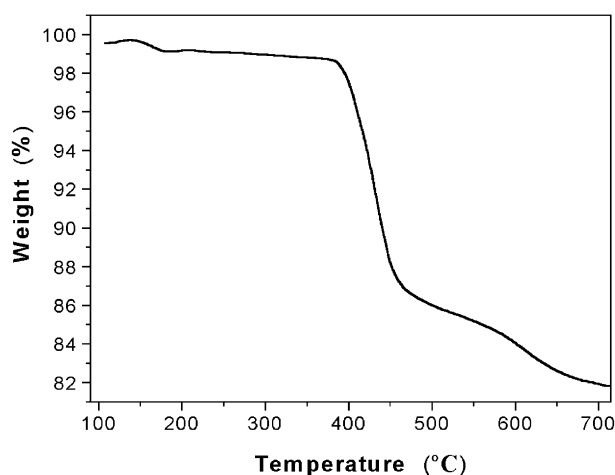


Fig. 2. Thermogravimetric curve of **1**.

and N, respectively). The deviation of experimental analysis data from the calculated data based on the empirical formula $(C_6H_{17}N_3)[Zn_4(PO_4)_2(HPO_3)_2]$ given by single-crystal structure analysis is due to the existence of minor impurity phase in the product.

TG analysis, as shown in Fig. 2, shows two stages of weight loss in a total of 18.34 wt% around 300–700°C, which are attributed to the decomposition of 1-(2-Aminoethyl) piperazine (calcd 17.37 wt%) accompanied by a water molecule (2.42%) XRD analysis indicates that **1** becomes amorphous after the decomposition of the occluded template molecules above 400°C and that it finally transforms to $Zn_2P_2O_7$ dense phase at 800°C.

Single-crystal structural analysis indicates that **1** has an empirical formula of $(C_6H_{17}N_3)[Zn_4(PO_4)_2(HPO_3)_2]$. Assuming the usual valence of Zn, O and H to be +2, –2 and +1, respectively, and of P to be +3 for phosphite and +5 for phosphate, respectively, the network stoichiometry of $[Zn_4(PO_4)_2(HPO_3)_2]$ creates a

net charge of –2. The presence of one diprotonated 1-(2-Aminoethyl) piperazine molecule would account for +2. Each asymmetric unit, as seen in Fig. 3, contains four crystallographically distinct Zn atoms, each of which is tetrahedrally coordinated and shares four oxygen atoms with adjacent P atoms. The Zn–O bond distances are in the range of 1.907(7)–2.057(7) Å. There are four crystallographically distinct P atoms. P(1) and P(4) each has a terminal P–H bond (1.39(9)–1.42(9) Å) and shares three oxygens with adjacent Zn atoms (P–O bond: 1.501(7)–1.526(7) Å) forming a HPO_3 pseudo-pyramid. The existence of P–H bond is also confirmed by the characteristic band of phosphite anions [$\nu(H-P)$, 2383 cm^{-1}] in the IR spectrum. P(2) and P(3) each shares four oxygen atoms with adjacent Zn atoms forming a ZnO_4 tetrahedron. The P–O bond lengths are in the range of 1.507(7)–1.569(7) Å, which are typical for zinc phosphate compounds [27–37].

The ^{31}P MAS NMR spectra with and without 1H decoupling are shown in Fig. 4. Without 1H decoupling the dipole–dipole interaction between 1H and ^{31}P causes a considerable broadening of the ^{31}P NMR spectrum (Fig. 4a). The 1H decoupling technique diminishes the interaction by saturating the magnetization of 1H nuclei and brings about four sharp resonance lines at 4.79, 3.93, 0.34 and –0.81 ppm, consisting with the four crystallographically distinct P atoms in **1** (Fig. 4b). The

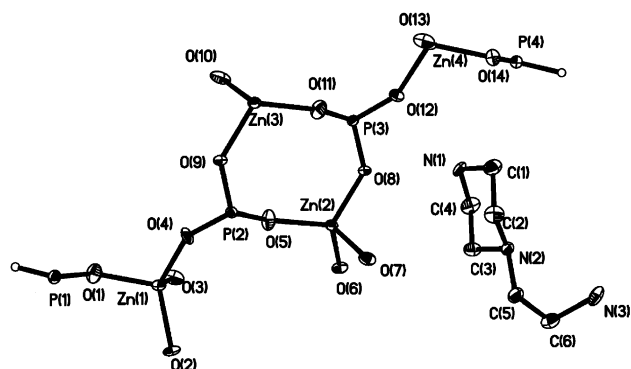


Fig. 3. Thermal ellipsoid plot (50%) for **1** showing the asymmetric unit.

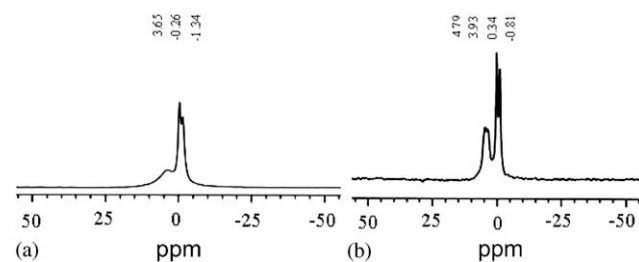


Fig. 4. ^{31}P MAS NMR spectra for **1**, (a) without 1H decoupling, (b) with 1H decoupling.

former two peaks associated with the dipole–dipole interaction between ^1H and ^{31}P without ^1H decoupling are assigned to the HPO_3 moieties and the latter two to the PO_4 moieties.

The inorganic layer of **1** is based on a network of strictly alternating Zn-centered units (ZnO_4) and P-centered units (PO_4 and HPO_3) in which all the vertices are shared excepted for the terminal H atoms in HPO_3 groups. There also exist $\mu_3\text{-O}$ atoms which link two Zn atoms. Fig. 5a shows the structure of the inorganic layer parallel to the ab plane. Interestingly, the layer contains columns of double six membered ring (D6MR) along the $[001]$ direction (Fig. 5b). The D6MR is composed of two 3-MRs, four 4-MRs, and two 6-MRs, denoted as a $3^24^46^2$ cage (Fig. 5c). Columns of D6MR interconnect with each other via oxygen atoms forming a puckered double layered structure. Alternatively, the double layer can be decomposed into two single sheets containing 3-MRs and 9-MRs (Fig. 6). Such a single sheet, denoted as a 3.9-net, has been never observed before.

Fig. 7 shows the packing of the inorganic sheets along the $[001]$ direction with ABAB stacking sequence. It is noticed that the P–H groups exclusively protrude into the interlayer region. The diprotonated 1-(2-Aminoethyl) piperazine molecules in a chair conformation reside in the interlayer region and interact with the host network through extensive H-bonds. Each diprotonated 1-(2-Aminoethyl) piperazine cation provides a total of 6 H-bonds to the bridging oxygens in the layers. The $\text{N}\cdots\text{O}$ separations are in the range of 2.814(11)–3.062(11) Å. The $\text{N}(2)\text{--}\text{N}(3)$ distance of 2.892(11) Å indicates an intricate H-bond inside the template molecule. The details of the H-bonds are summarized in the supporting information. The inorganic sheet structure cannot be kept upon removal of the occluded organic amine molecules by calcination. Therefore, the 1-(2-Aminoethyl) piperazine molecule plays an important role in stabilizing the inorganic network.

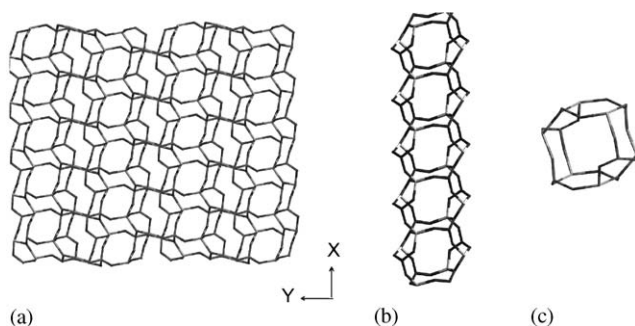


Fig. 5. (a) The puckered layer parallel to the ab plane; (b) column of D6MR by sharing common four-membered rings along the $[100]$ direction, (c) the $3^24^46^2$ cages composed of two 3-MRs, four 4-MRs and two 6-MRs.

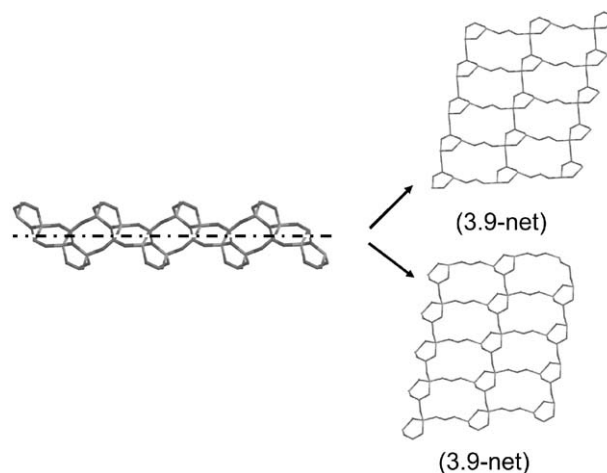


Fig. 6. The double layer viewed along the $[010]$ direction which can be viewed as made up of two 3.9-net single sheets.

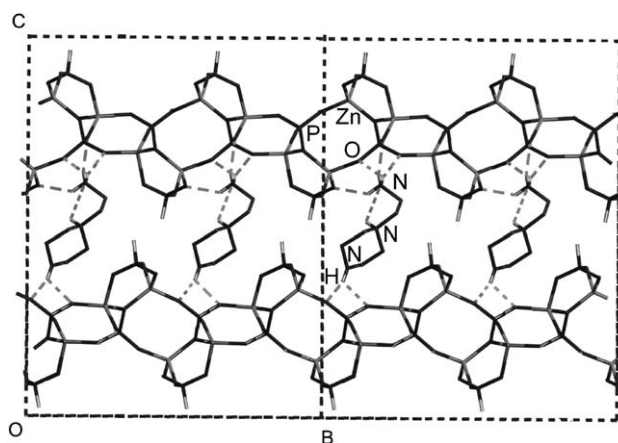


Fig. 7. The packing of the inorganic layers and the organic template along the $[001]$ direction with the ABAB stacking sequence. Dotted lines indicate H-bond.

4. Conclusions

Using H_3PO_3 as a phosphorus source, a new 2D layered zinc phosphate–phosphite $(\text{C}_6\text{H}_{17}\text{N}_3)[\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_3)_2]$ has been prepared hydrothermally in the presence of 1-(2-Aminoethyl) piperazine as the structure-directing agent. The strict alternation of Zn-centered units (ZnO_4) and P-centered units (PO_4 and HPO_3) via vertex oxygen atoms forms a double layered structure consisting of columns of D6MR. Interestingly, the double layer is composed of two single sheet with a 3.9-net. The 1-(2-Aminoethyl) piperazine molecules occluded in the interlayer region interact with the inorganic layer through H-bonds, which play an important role in stabilizing the inorganic network. The title compound is the first organically templated zinc phosphate–phosphite, and exhibits a new type of sheet structure. It is believed that more zinc phosphate–phosphites

with interesting structural architectures will be continuously synthesized under suitable synthesis conditions.

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