



Flux synthesis of (3,4)-connected zinc phosphites with different framework topologies

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ABSTRACT

Two three-dimensional open-framework zinc phosphites, $\text{H}_2\text{aem} \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot 0.5\text{H}_2\text{O}$ (**1**) and $\text{H}_2\text{apm} \cdot \text{Zn}_3(\text{HPO}_3)_4$ (**2**), have been synthesized by a phosphorous acid flux method, where $\text{aem} = 4$ -(2-aminoethyl)morpholine and $\text{apm} = 4$ -(3-aminopropyl)morpholine. Compound **1** crystallizes in the monoclinic system, $P2_1/c$, $a = 9.5852(7) \text{ \AA}$, $b = 20.3941(8) \text{ \AA}$, $c = 10.5339(8) \text{ \AA}$, $\beta = 94.125(9)^\circ$, $V = 2053.8(2) \text{ \AA}^3$, $Z = 4$, $R_1 = 0.0319$, $wR_2 = 0.0628$. Compound **2** crystallizes in the monoclinic system, $P2_1/n$, $a = 8.589(2) \text{ \AA}$, $b = 14.020(3) \text{ \AA}$, $c = 16.606(3) \text{ \AA}$, $\beta = 97.190(8)^\circ$, $V = 1983.9(7) \text{ \AA}^3$, $Z = 4$, $R_1 = 0.0692$, $wR_2 = 0.1479$. Both compounds are based on (3,4)-connected networks with 8- and 12-ring channels, which are constructed from $\text{Zn}_3(\text{HPO}_3)_4$ clusters as the same secondary building units. These inorganic clusters are spatially organized by different structure-directing agents into different three-dimensional frameworks.

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1. Introduction

Crystalline microporous materials have found widespread applications in catalysis, separation, gas storage and ion-exchange processes [1–5]. Of fundamental importance is to synthesize new zeolitic materials with novel topologies and pore structures. During the past decades, a great deal of attention has been paid to the use of tetrahedral anions, such as SiO_4^{4-} , GeO_4^{4-} and PO_4^{3-} units, to construct open-framework structures [6–8]. The presence of dangling units in these building blocks such as the hydroxyl group in HPO_4^{2-} anion, enable the formation of open structures with large pores and low framework density. Notable examples include an open-framework gallium phosphate cloverite and an aluminophosphate JDF-20 with extra-large 20-ring channels [9,10]. As a structural analog of HPO_4^{2-} , the HPO_3^{2-} unit is of current interest in the construction of open-framework structures. A number of main group and transition metal elements, including Be, Al, Ga, In, V, Cr, Mn, Fe, Co, Ni, and Zn, have been successfully incorporated into phosphite frameworks [11–32].

Open-framework metal phosphites are generally synthesized with water as the main solvent under hydrothermal conditions. The formation of these open structures is kinetically controlled and is sensitive to the reaction conditions, such as pH, temperature, and solvent. Recently, the H_3PO_3 flux method has been

developed to prepare open-framework metal phosphites in an attempt to eliminate the influence of the solvent and to decrease the system pressure [33]. Two layered zinc phosphites were prepared under H_3PO_3 flux conditions in the presence of bulky diamines as the structure-directing agents [33,34]. The use of small amines as the structure-directing agents may favor the formation of three-dimensional structures [35]. We report here the H_3PO_3 flux synthesis of two new three-dimensional open-framework zinc phosphites, $\text{H}_2\text{aem} \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot 0.5\text{H}_2\text{O}$ (**1**) and $\text{H}_2\text{apm} \cdot \text{Zn}_3(\text{HPO}_3)_4$ (**2**), where $\text{aem} = 4$ -(2-aminoethyl)morpholine and $\text{apm} = 4$ -(3-aminopropyl)morpholine. The two compounds have (3,4)-connected frameworks with 8- and 12-ring channels. Although they are constructed from the same $\text{Zn}_3(\text{HPO}_3)_4$ clusters, they adopt different framework topologies due to the spatial organization of these building units by different templating agents.

2. Experimental

2.1. Synthesis

To prepare compound **1**, a mixture of aem (0.325 g), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (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 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 (68.8% yield based on zinc).

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Colorless crystals of compound **2** were obtained in a yield of 72.8% (based on zinc) under the same reaction conditions as used for **1**, except that aem was replaced by apm (0.361 g).

2.2. Characterization

The CHN analyses were carried out on an Elementar Vario EL III analyzer. Powder X-ray diffraction (XRD) data were obtained using a Philips X'Pert diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). IR spectra were recorded on a Bruker Alpha-P spectrometer. The thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA 851e analyzer in a flow of N_2 with a heating rate of $10^\circ\text{C}/\text{min}$ from 40 to 800°C .

2.3. Crystal structure determination

Suitable single crystals of each compound with the dimensions of $0.14 \times 0.10 \times 0.08 \text{ mm}^3$ for **1** and $0.10 \times 0.06 \times 0.06 \text{ mm}^3$ for **2** were carefully selected under an optical microscope. Crystal structure determination by X-ray diffraction was performed on a Stoe IPDS-I diffractometer with graphite-monochromated $\text{MoK}\alpha$ ($\lambda=0.71073 \text{ \AA}$) radiation at 193 K. The crystal structures were solved by direct methods. The P(4) atom in **2** is disordered over two positions with according site occupancy factors of 0.7:0.3. All the hydrogen atoms were located by calculation and refined using a riding model, except the hydrogen atoms of the water molecules in **1** and the hydrogen atom attached to the disordered P(4) atom in **2**. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL program package [36]. All non-hydrogen atoms were refined anisotropically except the oxygen atom of the water molecule in **1**. The crystallographic data for **1** and **2** are summarized in Table 1.

2.4. Ion-exchange experiment

The ion-exchange experiments of compounds **1** and **2** were carried out by immersing 120 mg samples of the as-synthesized compounds **1** and **2**, respectively, in 10 ml of 1 M NaNO_3 aqueous solution at room temperature for 2 days. The exchanged solids were then recovered, washed thoroughly with water and dried in air.

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

	1	2
Empirical formula	$\text{C}_6\text{H}_{21}\text{N}_2\text{O}_{13.5}\text{P}_4\text{Zn}_3$	$\text{C}_7\text{H}_{22}\text{N}_2\text{O}_{13}\text{P}_4\text{Zn}_3$
Formula weight	657.24	662.26
Temperature (K)	193 (2)	193 (2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
<i>a</i> (\AA)	9.5852 (7)	8.589 (2)
<i>b</i> (\AA)	20.3941 (8)	14.020 (3)
<i>c</i> (\AA)	10.5339 (8)	16.606 (3)
β (deg)	94.125 (9)	97.190 (8)
Volume (\AA^3)	2053.8 (2)	1983.9 (7)
<i>Z</i>	4	4
ρ_{calc} (g cm^{-3})	2.126	2.217
μ (mm^{-1})	3.852	3.987
Reflections collected	16,012	8231
Independent reflections	3998 [$R(\text{int})=0.0716$]	3464 [$R(\text{int})=0.1604$]
GOF on F^2	0.856	0.903
Final <i>R</i> indices [$I>2\sigma(I)$]	$R_1=0.0319$, $wR_2=0.0628$	$R_1=0.0692$, $wR_2=0.1479$
<i>R</i> indices (all data)	$R_1=0.0607$, $wR_2=0.0712$	$R_1=0.0937$, $wR_2=0.1585$

3. Results and discussion

3.1. Characterization

The powder XRD patterns of as-synthesized compounds **1** and **2** and the simulated patterns based on the single crystal structures were compared (Fig. 1). The diffraction peaks on simulated and experimental patterns corresponded well in position, indicating the phase purity of the as-synthesized compounds **1** and **2**. CHN analysis results confirmed their stoichiometry (Anal. Found for **1**: C, 10.66; H, 2.80; N, 4.15%. Calculated: C, 10.96; H, 3.22; N, 4.26%; Anal. Found for **2**: C, 12.21; H, 2.87; N, 4.14%. Calculated: C, 12.69; H, 3.35; N, 4.23%).

The IR spectra contain the characteristic bands at 2379 cm^{-1} for **1** and at 2373 cm^{-1} for **2**, which are caused by the stretching vibration of the P–H bonds [30]. The intense bands in the region $993\text{--}1163 \text{ cm}^{-1}$ for **1** and $963\text{--}1165 \text{ cm}^{-1}$ for **2** are associated with the symmetric and asymmetric stretching vibrations of PO_3 groups. The bending vibrations of PO_3 groups can be observed in the range $460\text{--}607 \text{ cm}^{-1}$ for **1** and $476\text{--}600 \text{ cm}^{-1}$ for **2**. The existences of organic templating agents in the two structures are clearly shown by the bands in the region $1424\text{--}1646 \text{ cm}^{-1}$ for **1** and $1400\text{--}1643 \text{ cm}^{-1}$ for **2**.

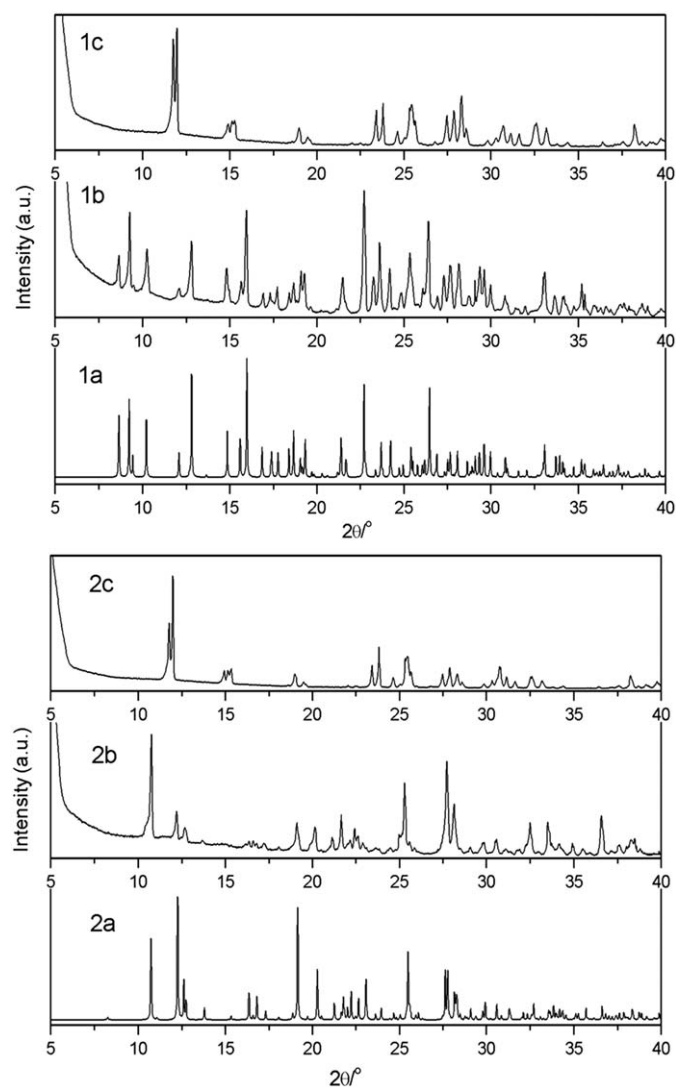


Fig. 1. Powder XRD patterns ($\text{CuK}\alpha$ radiation): (a) simulated from crystal structure data; (b) as-synthesized compound; and (c) ion-exchanged product.

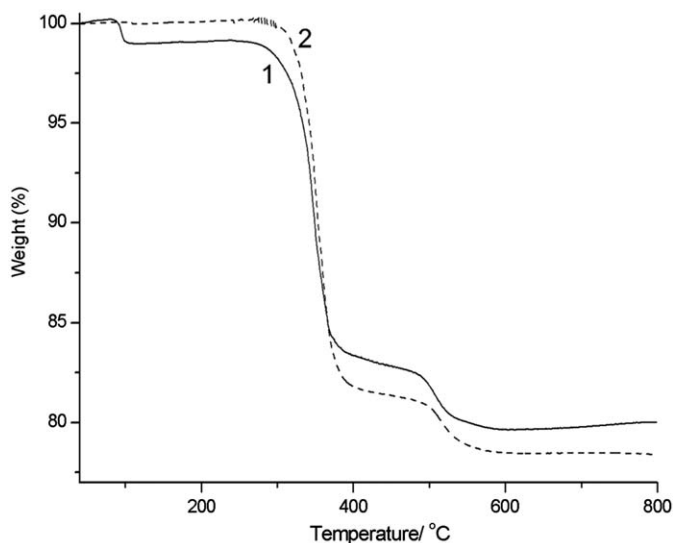


Fig. 2. TGA curves of **1** and **2** with a heating rate of 10 °C/min.

Thermogravimetric analyses of the powder samples of **1** and **2** were carried out under N₂ atmosphere with a heating rate of 10 °C/min (Fig. 2). For compound **1**, three stages of weight loss are observed over the temperature range 40–800 °C. The initial weight loss below 110 °C can be attributed to the departure of water molecules (observed: 1.21%; calculated: 1.37%). The second stage occurring between 260 and 430 °C corresponds to the partial decomposition of the organic molecules (observed: 16.08%; calculated: 19.81%). The remaining organic species was removed from the sample at the last stage starting at 470 °C with a weight loss of 2.99%. Compound **2** remains stable up to 270 °C. On further heating, a weight loss of 21.49% appears, which is continuous up to 590 °C and is assigned to the decomposition of the organic species (calculated weight loss: 21.77%).

3.2. Description of the structure

The asymmetric unit of **1** consists of three crystallographically independent zinc atoms and four crystallographically independent phosphorus atoms, as seen in Fig. 3a. All the zinc atoms are tetrahedrally coordinated by oxygen atoms with the Zn–O bond lengths of 1.921(3)–1.997(3) Å. The phosphorus atoms each share three oxygen atoms with adjacent zinc atoms, with the fourth vertex occupied by a terminal hydrogen atom. The P–O bond lengths vary from 1.506(4) to 1.524(3) Å, in agreement with those of other open-framework zinc phosphites.

The inorganic framework of **1** is built up from strictly alternating ZnO₄ tetrahedra and HPO₃ pseudopyramids, forming a three-dimensional framework with 8- and 12-ring channels. Fig. 4a and b shows the framework of **1** viewed along the [001] and [011] directions, respectively. It possesses large 12-membered rings defined by six ZnO₄ tetrahedra and six HPO₃ pseudopyramids. The calculated free diameters of the 12-ring pores are 4.4 Å × 6.5 Å and 3.6 Å × 6.8 Å, respectively (1.4 Å was used as the van der Waal radius of oxygen atom). The 12-ring channels are intersected by channels with 8-member-ring windows, which run along the [100] direction and have the free pore size of 3.3 Å × 3.7 Å (Fig. 4c).

The doubly protonated organic cations are encapsulated in the free voids of the intersecting channels and balance the overall negative charge of the zinc phosphite framework. These extra framework cations interact with the framework oxygen atoms via extensive N–H⋯O hydrogen bonds. The N⋯O distances are in the

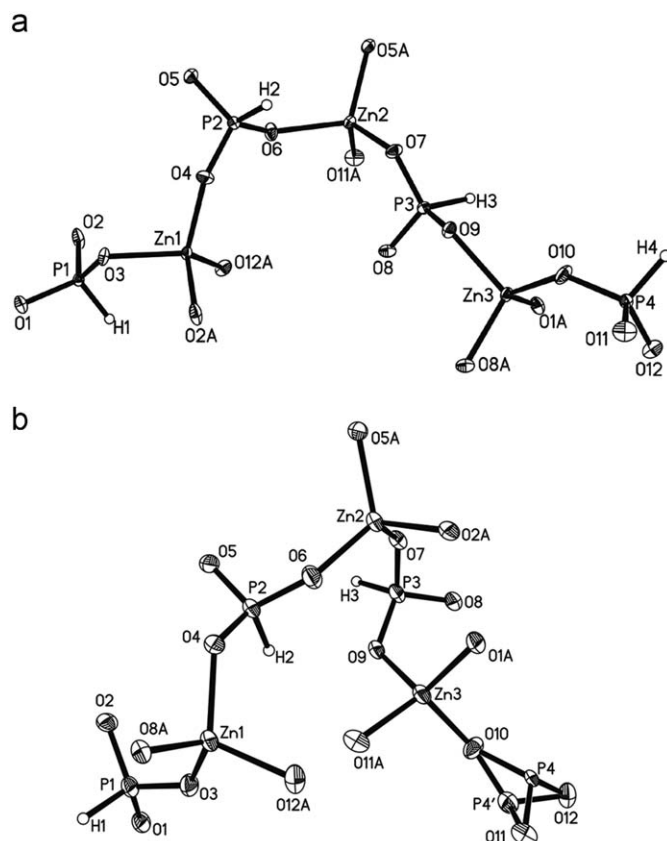


Fig. 3. View of the coordination environments of the zinc and phosphorus atoms in (a) **1** and (b) **2**, showing the atom labeling scheme, and with 30% thermal ellipsoids. Atom labels having "A" refer to symmetry-generated atoms.

region of 2.755(5)–2.994(5) Å. A void space analysis performed by use of the program PLATON indicates that the extra-framework organic cations in **1** occupy 40.8% of the unit cell volume [37].

The single-crystal X-ray diffraction analysis indicates that the structure of compound **2** consists of a three-dimensional zinc phosphite framework and H₂apm cations. The asymmetric unit of **2** contains 29 non-hydrogen atoms, of which 19 atoms belong to the host network and 10 atoms to the guest amine molecule. There are three crystallographically independent zinc atoms and four crystallographically independent phosphorus atoms, as seen in Fig. 3b. All the zinc atoms are tetrahedrally coordinated by their oxygen neighbors. The phosphorus atoms each form three P–O–Zn linkages, leaving one terminal P–H bond. The Zn–O bond lengths are in the region 1.912(6)–1.959(6) Å, and the P–O bond lengths vary from 1.489(7) to 1.556(7) Å. The stoichiometry of [Zn₃(HPO₃)₄] would result in a net charge of –2, which is balanced by one doubly protonated apm cation per formula unit.

The connectivity of the strictly alternating ZnO₄ tetrahedra and HPO₃ pseudopyramids results in a three-dimensional framework. There are two types of channels with different pore apertures. The type I channel has 8-membered-ring windows with different apertures and runs along the [100], [110] and [101] directions, respectively (Fig. 5a–c). The type II channel contains 12-membered-ring windows and runs along the [010] direction (Fig. 5d). The 12-membered-ring window is somewhat puckered and the free diameter of the window is nearly 4.9 Å × 7.0 Å (1.4 Å was used as the van der Waal radius of oxygen atom).

The doubly protonated dpm cation orderly resides in the center of a cage delimited by two 12-ring, four 8-ring, two 6-ring, and four 4-ring windows. The N atoms of the organic cation interact with the framework oxygen atoms via hydrogen bonds. The N⋯O

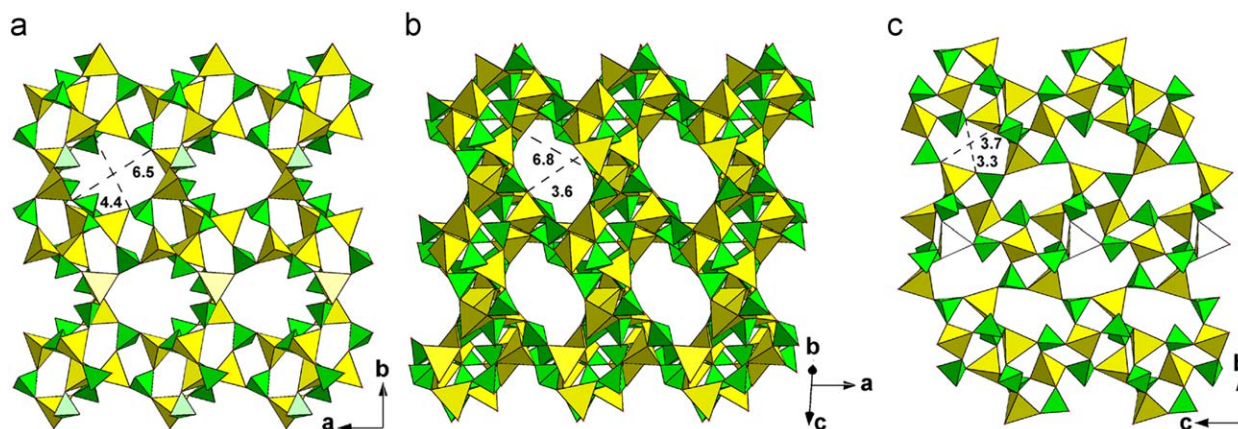


Fig. 4. The three-dimensional inorganic framework of **1**, exhibiting 12-ring channels running along (a) the [001] and (b) the [011] directions, and (c) 8-ring channels running along the [100] direction. Color code: ZnO_4 tetrahedra, yellow; HPO_3 pseudopyramids, green (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

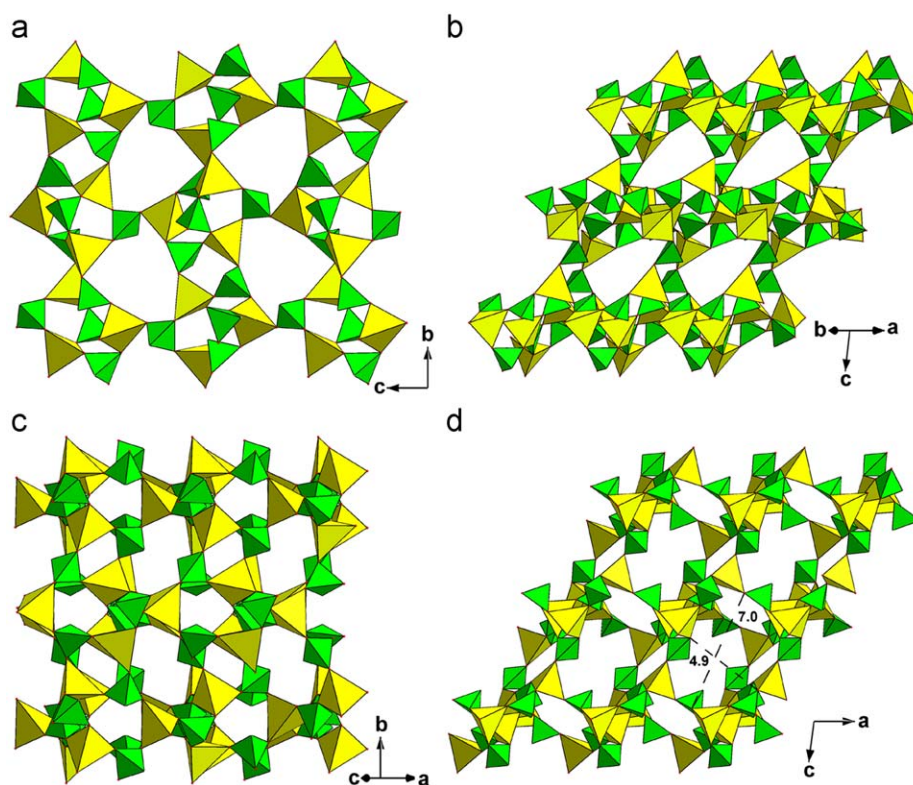


Fig. 5. The three-dimensional inorganic framework of **2**, exhibiting 8-ring channels running along the (a) [100], (b) [110] and (c) [101] directions, and (d) 12-ring channels running along the [010] direction. Color code: ZnO_4 tetrahedra, yellow; HPO_3 pseudopyramids, green (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

distances range from 2.782(9) to 3.422(9) Å. A void space analysis using the program *PLATON* indicates that these extra-framework species in **2** occupy 40.6% of the unit cell volume.

The “openness” of the two structures can be evaluated in terms of their framework densities (FD, defined as the number of polyhedra per 1000 \AA^3). The FD value is 13.6 for compound **1** and 14.1 for compound **2**, which are comparable to aluminophosphate molecular sieves such as VPI-5 and DAF-1.

3.3. Topological analysis

The three-dimensional structures of **1** and **2** can be alternatively described based on a heptameric building unit containing

three ZnO_4 tetrahedra and four HPO_3 pseudopyramids, as shown in Fig. 6a. In this $\text{Zn}_3(\text{HPO}_3)_4$ cluster, three ZnO_4 tetrahedra and three HPO_3 pseudopyramids alternate by sharing vertices to form a 6-membered ring. The fourth HPO_3 pseudopyramid bridges two zinc atoms in the 6-membered ring to give rise to the heptameric cluster with 4- and 6-membered rings.

It has been demonstrated that different framework structures can be generated from the same inorganic cluster through various ways of connections of these building units. For example, in the presence of different structure-directing agents, Ge_7X_{19} ($X = \text{O}, \text{OH}, \text{F}$) clusters have been assembled into crystalline germanate frameworks with chainlike, tubular, layered, and three-dimensional structures [38–41]. In this work, the $\text{Zn}_3(\text{HPO}_3)_4$ heptameric unit possess eight oxygen sites that protrude outside of the

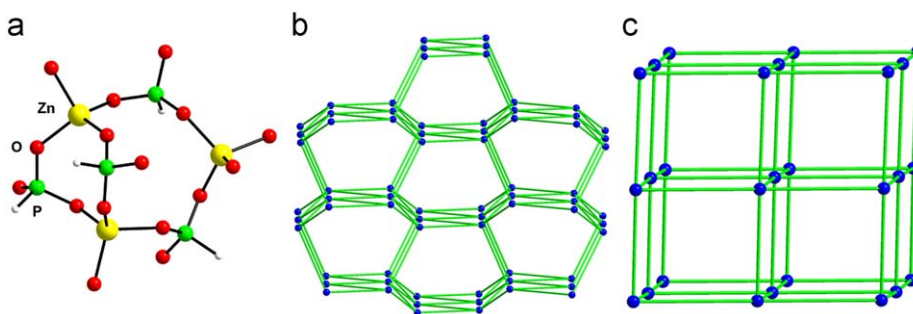


Fig. 6. The inorganic frameworks of compounds **1** and **2** are constructed from (a) $\text{Zn}_3(\text{HPO}_3)_4$ secondary building units and have (b) noz topology for **1** and (c) pcu topology for **2** with blue spheres representing $\text{Zn}_3(\text{HPO}_3)_4$ clusters.

building unit, indicating that the $\text{Zn}_3(\text{HPO}_3)_4$ cluster may exhibit diverse ways of connections to adjacent clusters via oxygen bridges. In the structure of **1**, every $\text{Zn}_3(\text{HPO}_3)_4$ cluster is connected to five adjacent clusters and the framework structure has noz topology, as shown in Fig. 6b [42]. Such framework topology has been rarely reported in open-framework inorganic solids. In the case of **2**, every $\text{Zn}_3(\text{HPO}_3)_4$ cluster is linked to six adjacent clusters and the framework structure has pcu topology, as shown in Fig. 6c. Theoretically, various framework topologies may be generated by using $\text{Zn}_3(\text{HPO}_3)_4$ clusters as secondary building units in the presence of different structure-directing agents, which is subject matter of ongoing studies.

3.4. Ion-exchange study

Ion-exchange experiments of the two compounds were carried out by immersing each crystalline samples in a solution of sodium nitrate (1.0 M) at room temperature for 2 days. Powder XRD patterns of the exchanged samples are obviously different from those of as-synthesized samples, indicating the phase change (Fig. 1). IR spectra of the exchanged samples show the disappearance of the characteristic peaks associated with organic cations in the region $1400\text{--}1650\text{ cm}^{-1}$. Both the powder XRD patterns and IR spectra of the ion-exchange samples are similar with those of $\text{Zn}_2(\text{H}_2\text{O})_4(\text{HPO}_3)_2 \cdot \text{H}_2\text{O}$, which has an open-framework structure with 12- and 16-ring channels [43]. These results indicate that during ion-exchange process the structures of as-synthesized compounds collapse and convert into the open-framework zinc phosphite, $\text{Zn}_2(\text{H}_2\text{O})_4(\text{HPO}_3)_2 \cdot \text{H}_2\text{O}$.

4. Conclusions

Two three-dimensional open-framework zinc phosphites, $\text{H}_2\text{aem} \cdot \text{Zn}_3(\text{HPO}_3)_4 \cdot 0.5\text{H}_2\text{O}$ (**1**) and $\text{H}_2\text{apm} \cdot \text{Zn}_3(\text{HPO}_3)_4$ (**2**), were obtained as good quality single crystals under flux synthetic conditions. Structural analyses indicate that both compounds are constructed from the same $\text{Zn}_3(\text{HPO}_3)_4$ clusters. For compound **1**, each $\text{Zn}_3(\text{HPO}_3)_4$ cluster is connected to five adjacent clusters, producing an unusual framework with noz topology. For compound **2**, each $\text{Zn}_3(\text{HPO}_3)_4$ cluster is linked to six adjacent clusters, generating a three-dimensional framework with pcu topology. The organic cations, accommodated in the free voids of the intersecting channels, interact with the inorganic frameworks via extensive hydrogen bonds. Thus, attempts to remove them by ion-exchange cause the collapse of the structures.

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Appendix A. Supplementary Materials

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.jssc.2009.08.031](https://doi.org/10.1016/j.jssc.2009.08.031).

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