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Hydrothermal synthesis and structural characterization of novel organically templated zincophosphites: $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ and $[CH_3CH_2CH_2NH_3]_2\cdot[Zn_3(HPO_3)_4]$

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Abstract

Two novel organically templated zincophosphites, $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ and $[CH_3CH_2CH_2NH_3]_2\cdot[Zn_3(HPO_3)_4]$ have been synthesized under hydrothermal conditions with different template 1,3-Bis(aminomethyl)benzene and propylamine, and characterized by single-crystal X-ray diffraction. $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ crystallizes in the monoclinic space group $P2_1/c$, with cell parameters, $a = 9.5467(10)$ Å, $b = 26.405(2)$ Å, $c = 7.9946(8)$ Å, and $\beta = 99.472(2)°$. $[CH_3CH_2CH_2NH_3]_2\cdot[Zn_3(HPO_3)_4]$ crystallizes in the orthorhombic space group $Pccn$, with cell parameters, $a = 9.8162(15)$ Å, $b = 23.284(4)$ Å, and $c = 8.9306(12)$ Å. Two compounds consist of vertex linking of ZnO_4 tetrahedral and $[HPO_3^{2-}]$ pseudopyramidal units. They have similar inorganic frameworks with the same compositions. They are both built up from two-dimensional layers with four- and eight-membered rings and one-dimensional chains composed of four-memberd rings, but their layered structures are different due to the influence of corresponding organic template. To our knowledge, $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ is the first mention of a zinc phosphite material with an aromatic template. Two compounds were also characterized by IR spectroscopy, thermogravimetric and differential thermal analyses, and proton-decoupled ^{31}P MAS solid-state NMR spectroscopy.

Keywords: Hydrothermal synthesis; Zincophosphite; Structure template

1. Introduction

In the past few decades a number of organically templated metal phosphate compounds were prepared because of their important potential applications in the fields of exchange, absorption, catalysis, and chemical sensor [1–10]. Among these, the organically templated zincophosphates show rich structural chemistry, where the vertex-linked ZnO_4 and PO_4 tetrahedra are basic building blocks [11–16]. Since the first report on the organically templated zincophosphite by Harrison [17], a number of studies on the zincophosphites have been carried out [18–22], and compared to the zincophosphates, the organically templated zincophosphites based on incorporations of the pseudopyramidal hydrogen phosphite group $[HPO_3]^{2-}$, created their structural diversity. Based on our previous work on the syntheses of inorganic-organic hybrid phosphates [23,24] and organically templated phosphites [25,26], we extended our research into the investigation of template effect in a similar synthetic system. In this paper, we describe the syntheses and crystal structures of two three-dimensional zincophosphites, $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ **1**, and $[CH_3CH_2CH_2NH_3]_2\cdot[Zn_3(HPO_3)_4]$ **2**. They were hydrothermally synthesized with different organic templates, but have similar inorganic frameworks with the same compositions. To our knowledge, compound **1** is the first mention of a zinc phosphite material with an aromatic template.

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2. Experimental

2.1. Synthesis and characterization

Compounds **1** and **2** were synthesized under hydrothermal conditions. All reagents were of analytical grade. In a typical synthesis for **1**, 0.219 g (1 mmol) of zinc acetate dihydrate ($Zn(ac)_2 \cdot H_2O$) was dissolved in 5.0 mL (166 mmol) of water, to which 0.410 g (5 mmol) of H_3PO_3 and 0.45 mL (3.5 mmol) of 1,3-Bis(aminomethyl)benzene were added under constant stirring to form a solution and the whole solution was stirred for another 30 min. The final reaction mixture with pH = 5.1 was transferred in a PTFE-lined stainless steel autoclave and heated at 160°C for 120 h. The resulting product was washed with deionized water, and dried under ambient conditions. In the synthesis of **2**, 0.810 g (1 mmol) of zinc oxide (ZnO) was dissolved in 5.0 mL (166 mmol) of water, to which 0.410 g (5 mmol) of H_3PO_3 and 0.30 mL (3.6 mmol) of propylamine were added under constant stirring to form a solution, and the solution was stirred for another 30 min. The final reaction mixture with pH = 4.6 was transferred in a PTFE-lined stainless-steel autoclave and heated at 160°C for 72 h. The resulting product was washed with deionized water, and dried under ambient conditions.

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 product were also consistent with the theoretical values. Anal. Calcd. for **1**: Zn, 29.99%; P, 18.96%; C, 14.68%; H, 2.75%; N, 4.28%. Found: Zn, 30.06%; P, 19.01%; C, 14.61%; H, 2.71%; N, 4.26%. Calcd. for **2**: Zn, 30.84%; P, 19.49%; C, 11.32%; H, 3.77%; N, 4.40%. Found: Zn, 30.79%; P, 19.53%; C, 11.29%; H, 3.80%; N, 4.35%.

The infrared (IR) spectrum was recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410FTIR spectrometer using KBr pellets. The IR spectra of the compounds showed typical peaks, with very little differences in the spectra. Strong absorption bands for N–H bending and stretching vibrations are observed from 3409 to 3426 cm^{-1} for all of the compounds. The bands at 2385 and 1091 cm^{-1} were attribute to the terminal P–H stretch and deformation. The large band at 997 cm^{-1} arises from P–O stretching vibrations. In compound **1**, the intense bands at 1616 and 1623 cm^{-1} were associated with the stretching vibrations of phenyl.

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}. The ^{31}P MAS-NMR spectra of the compounds were collected on a Varian Unity-400 NMR spectrometer.

Table 1
Crystal data and structure refinement parameters for $[C_6H_4(CH_2NH_3)_2] \cdot [Zn_3(HPO_3)_4]$ **1**, $[CH_3CH_2CH_2NH_3]_2 \cdot [Zn_3(HPO_3)_4]$ **2**

	1	**2**
Empirical formula	$C_8H_{18}N_2O_{12}P_4Zn_3$	$C_6H_{24}N_2O_{12}P_4Zn_3$
Fw	654.23	318.13
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Space group	$P2_1/c$	$Pccn$
a (Å)	9.5467(10)	9.8162(15)
b (Å)	26.405(2)	23.284(4)
c (Å)	7.9946(8)	8.9306(12)
β (deg)	99.472(2)	
V (Å^3)	1987.8(3)	2041.2(5)
Z	4	4
D_{calc} (g cm^{-3})	2.186	2.070
μ (mm^{-1})	3.975	3.867
R_1[a] $[I>2\theta(I)]$	0.0443	0.0330
wR_2[b] $[I>2\theta(I)]$	0.1114	0.0863

[a] $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$.

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

2.2. Determination of crystal structure

A suitable colorless single crystal of each compound was carefully selected for X-ray diffraction analysis. The intensity data were collected on a Siemens SMART CCD diffractometer with graphite-monochromatic Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation at a temperature of 298 ± 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 [27]. The structure was solved by Direct Methods using the SHELXTL crystallographic software package [28]. The zinc and phosphorus atoms were first located, whereas the carbon, nitrogen, and oxygen atoms were found in the difference Fourier maps. The hydrogen atoms residing on the phosphorus were located by Fourier maps. For **1**, the hydrogen atoms residing on the amine molecules were placed geometrically. For **2**, because of the disordering of the carbon and nitrogen atoms of the amine molecule, hydrogen atoms attached to the nitrogen and carbon atoms were not located. All non-hydrogen atoms were refined anisotropically. Details of the final refinement are given in Table 1.

3. Results and discussion

3.1. Characterization

The TGA studies indicate that the weight loss occurred in one step for **1** and **2**. The release of the template amine from the structure was observed to be highly exothermic. In the case of **1** (Fig. 1a), a mass loss of 19.8% in the range 290–510°C corresponds to the loss of the amine (calcd. 21.1%). In the case of **2** (Fig. 1b), a mass loss of 18.1% in the range 260–400°C corresponds to the loss of the amine (calcd. 18.9%). Accordingly, the DTA curve exhibits the exothermic peaks for the decomposition of the organic template in air, respectively. Each of the structure collapsed and converted to an amorphous phase after the calcination at 600°C for 2 h. At 800°C, and both of the amorphous phases recrystallized to the $Zn_2P_2O_7$ (JCPDS: 72-1702), confirmed by powder X-ray diffraction.

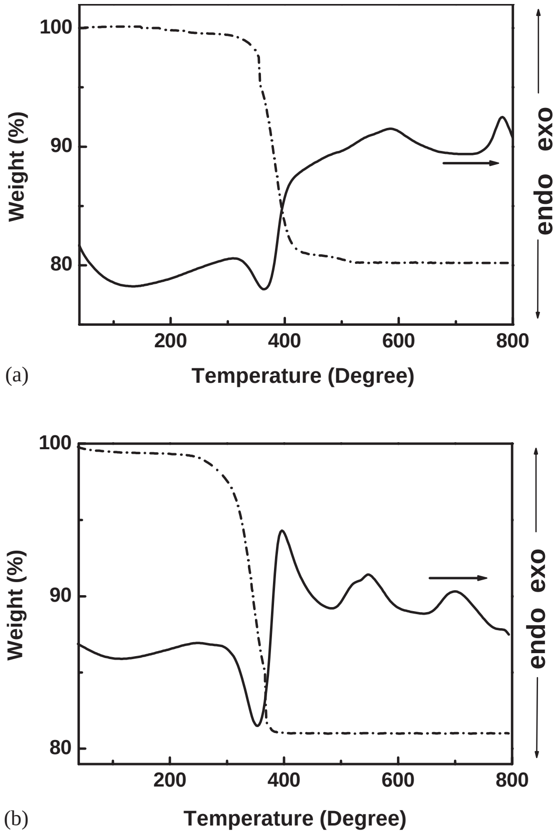

Fig. 1. (a) TG-DTA curves of compound **1**. (b) TG-DTA curves of compound **2**.

^{31}P MAS NMR spectra of the products show four resonances at 7.89, 4.42, 1.65, −3.22 ppm for **1** and two resonances at 6.01, 0.43 ppm for **2**, relative to a standard of 85% H_3PO_4. The chemical shifts of P atoms correspond to the crystallographically equivalent phosphorus sites in the structure as indicated by X-ray structural analysis.

3.2. *Crystal structural of* $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ **1**

The asymmetric unit of **1** contains 29 non-hydrogen atoms, of which 19 atoms belong to the framework and 10 atoms to the guest amine molecule (Fig. 2). There are three Zn and four P atoms that are independent in the asymmetric unit. The Zn atom is tetrahedrally coordinated by four oxygen atoms, with average Zn–O bond distances of 1.945 Å for Zn(1), 1.935 Å for Zn(2), 1.930 Å for Zn(3). The O–Zn–O bond angles are in the range of 96.87–116.7° (av. O–Zn(1)–O = 109.2°, O–Zn(2)–O = 109.4°, O–Zn(3)–O = 109.2°). The Zn atom is connected to two P atoms via Zn–O–P links. Four distinct P atoms form the centers of pseudopyramid with hydrogen phosphite groups, with average P–O bond distances of 1.503 Å for P(1), 1.514 Å for P(2), 1.511 Å for P(3), 1.503 Å for P(4). The O–P–O bond angles are in the range of 110.3–114.6° (av. O–P(1)–O = 112.5°, O–P(2)–O = 111.5°, O–P(3)–O = 111.7°, O–P(4)–O = 112.2°).

The three-dimensional structure can be derived from one-dimensional chains composed of Zn(2), P(2), P(3)

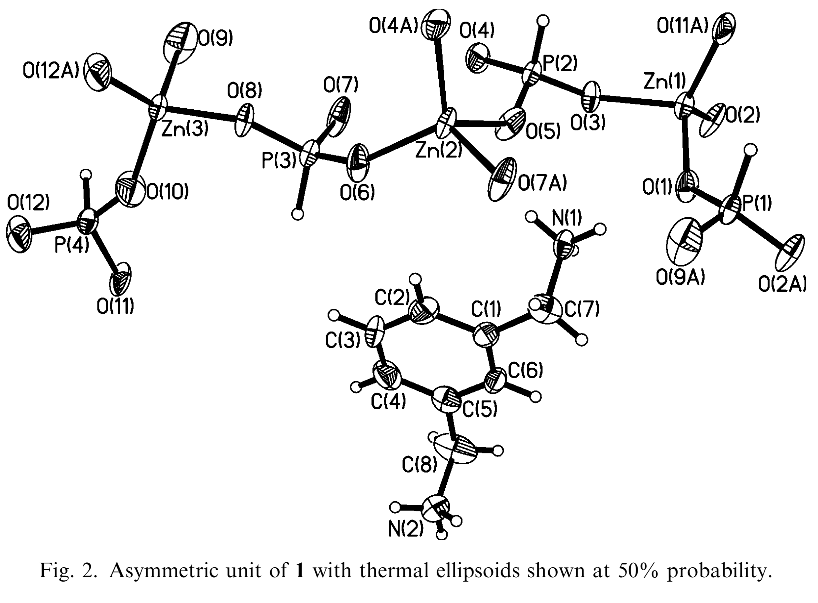

Fig. 2. Asymmetric unit of **1** with thermal ellipsoids shown at 50% probability.

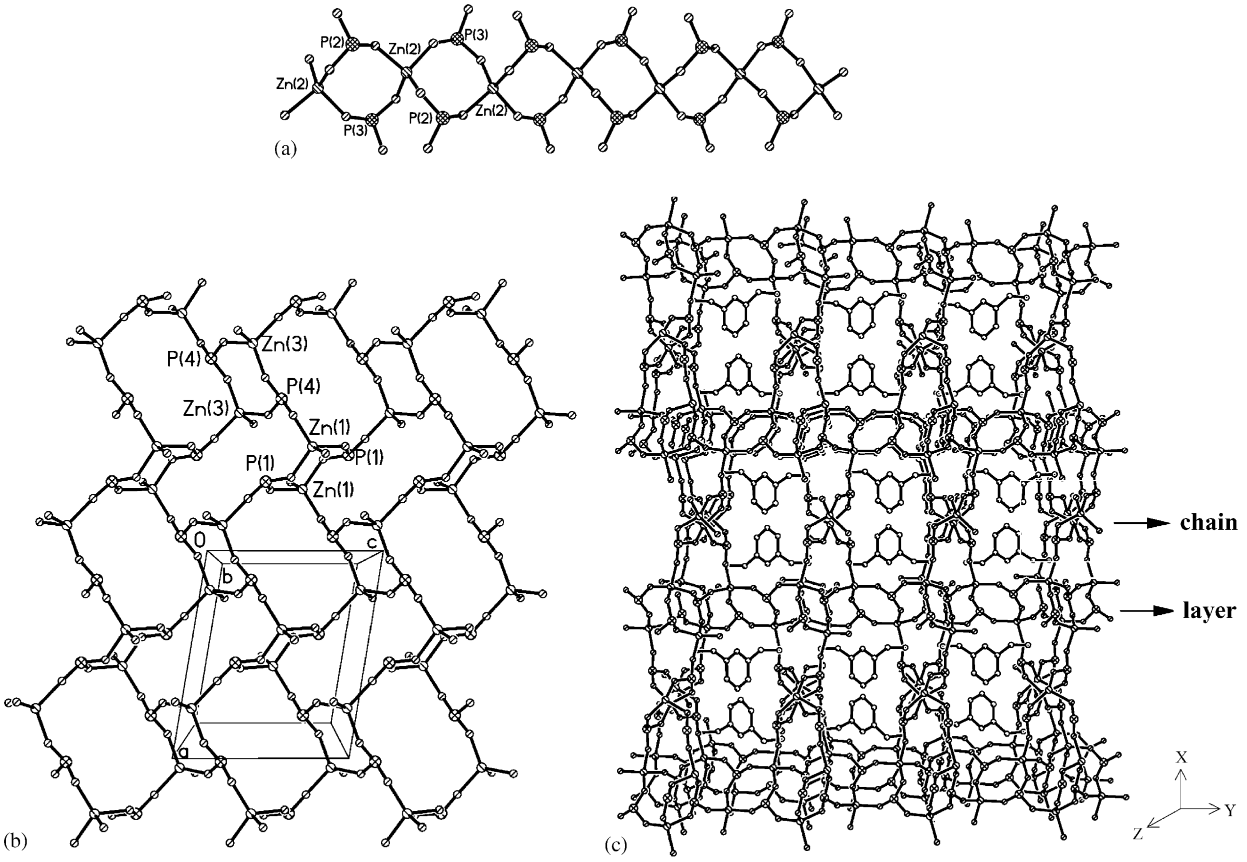

Fig. 3. (a) View of infinite four-membered ring chain of **1**. (b) View of the layer of **1**. (c) The framework structure of **1** along the *c*-axis.

and two-dimensional sheets composed of Zn(1), Zn(3), P(1), P(4). These chains have only one kind of four-membered ring which is built up from two Zn(2) atoms, one P(2) atom and one P(3) atom. They are linked through their corners, forming the one-dimensional chains (Fig. 3a). In the layer mentioned above, the vertex linked ZnO_4 tetrahedra and HPO_3 pseudopyramids form four- and eight-membered rings. There exists two types of four-membered rings built up from Zn(1), P(1), Zn(3) and P(4) centered polyhedra which propagate along [010] as shown in Fig. 3b. Every four-membered ring is polyhedrally connected with other four four-membered rings by bridge oxygen atoms. As the result, one eight-membered ring comes into being that is enclosed by the four four-membered rings.

The polyhedral connectivity in $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ results in a three-dimensional topology based on the two-dimensional network and one-dimensional chain reported above. The Zn(1), Zn(3) centered tetrahedra of the layer link P(2), P(3) centered pseudo-pyramids of the chain via bridge oxygen atoms to yield the three-dimensional structure and result in an anionic network with a Zn/P ratio of 3/4. This polyhedral connectivity results in a system of 12-membered ring channels propagating along [001], which appear to have formed around the $[C_8N_2H_{12}]^{2+}$ cations (Fig. 3c). Organic amines exit as charge-balanced cations in the diprotonated state and serve as H-bond donors to the nearest framework oxygen.

3.3. Crystal structural of $[CH_3CH_2CH_2NH_3]_2\cdot[Zn_3(HPO_3)_4]$ 2

The asymmetric unit of **2** contains 14 non-hydrogen atoms, of which 10 atoms belong to the framework and 4 atoms to the guest amine molecule (Fig. 4). There are two Zn and two P atoms that are independent in the asymmetric unit. The Zn atom is tetrahedrally coordinated by four oxygen atoms, with average Zn–O bond distances of 1.934 Å for Zn(1), 1.938 Å for Zn(2). The O–Zn–O bond angles are in the range of 102.9–117.5° (av. O–Zn(1)–O = 109.3°, O–Zn(2)–O = 109.5°). The Zn atom is connected to the P atoms via Zn–O–P links. Two distinct P atoms form the centers of pseudopyramid with hydrogen phosphite groups, with average P–O bond distances of 1.512 Å for P(1), 1.508 Å for P(2). The O–P–O bond angles are in the range of 109.8–115.3° (av. O–P(1)–O = 111.8°, O–P(2)–O = 112.4°).

The inorganic framework in **2** is similar with that in **1**. The three-dimensional structure can also be derived from one-dimensional chains composed of Zn(2), P(2) and two-dimensional sheets composed of Zn(1), P(1). These chains have only one kind of four-membered rings. Each four-membered ring is built up from two Zn(2) atoms and two P(2) atoms. They are linked through their corners forming the one-dimensional chains, which appeared in compound **1** (Fig. 5a). In the layer, there exists one type of four-membered ring built up from Zn(1), P(1) centered polyhedra which propagate along [010] as shown in Fig. 5b. Every four-membered ring polyhedrally connected with other four same four-membered rings by bridge oxygen atoms. As the result, one eight-membered ring came into being that enclosed by the four four-membered rings.

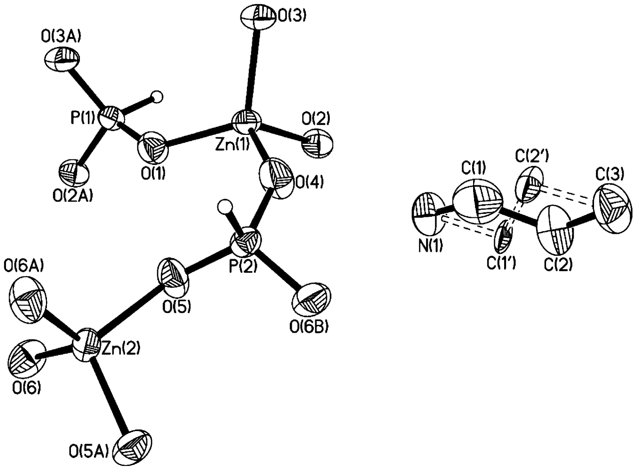

Fig. 4. Asymmetric unit of **2** with thermal ellipsoids shown at 50% probability.

In compound **2**, Zn(1) centered tetrahedra of the layer link P(2) centered pseudopyramids of the chain via bridge oxygen atoms to yield the three-dimensional structure and resulted in an anionic network with a Zn/P ratio of 3/4. This polyhedral connectivity results in a system of 12-membered ring channels propagating along [001], which appear to have formed around the $[C_3NH_9]^+$ cations (Fig. 5c). Organic amines exit as charge-balanced cations in the protonated state and serve as H-bond donors to the nearest framework oxygen.

Compound **1** and **2** have similar inorganic frameworks. The inorganic structures of **1** and **2** are closely related to that of $[C_4N_2H_{12}]_{0.5} \cdot [Zn_3(HPO_3)_4] \cdot H_3O$ [25], all of which contain an anionic $[Zn_3(HPO_3)_4]^{2-}$ layer with 4×8 nets. The difference among them is the configuration of unit in the inorganic layers. In compound **1**, the four-membered rings are not in the same plane as the eight-membered ring which they enclose, two above and the other two below the plane and the configuration is just like a 'chair' (Fig. 6a). In compound **2**, the four-membered rings are in the same plane as the eight-membered ring (Fig. 6b). The unit of inorganic layers in $[C_4N_2H_{12}]_{0.5} \cdot [Zn_3(HPO_3)_4] \cdot H_3O$, due to the torsion of the eight-, four- and eight-membered rings, makes a 'V' configuration (Fig. 6c).

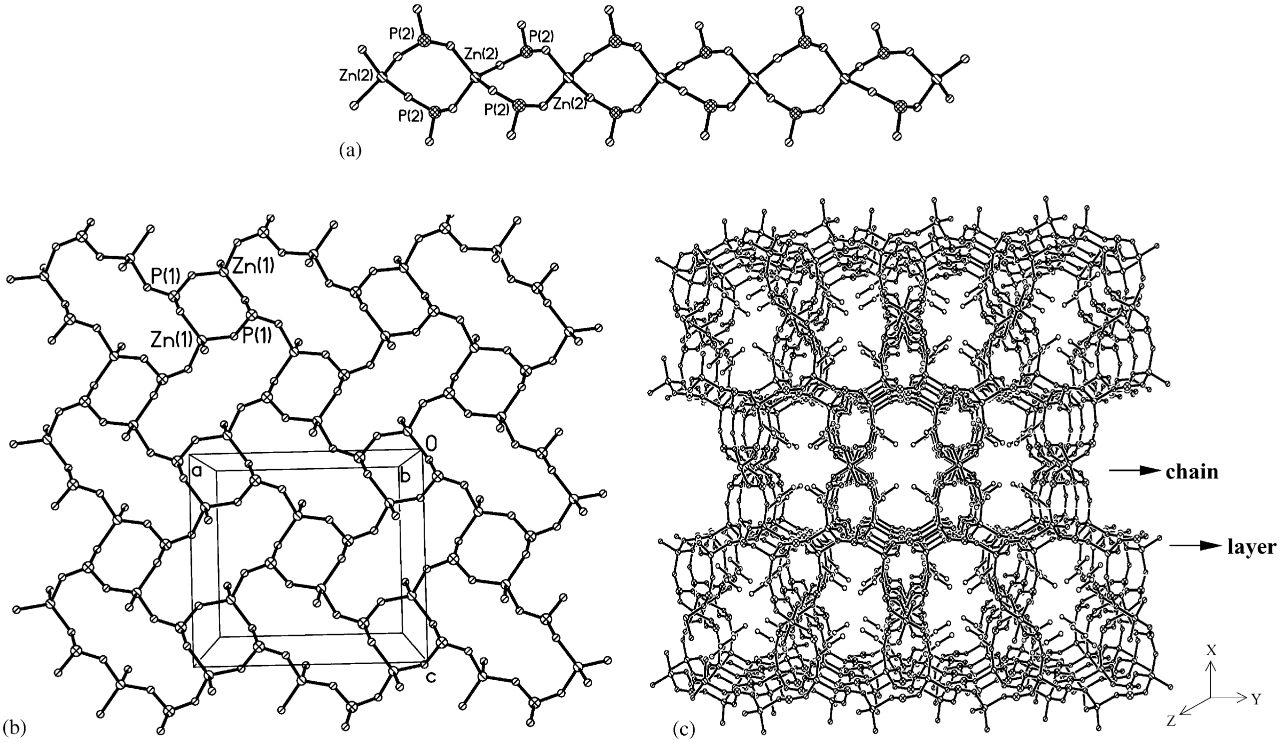

Fig. 5. (a) View of infinite four-membered ring chain of **2**. (b) View of the layer of **2**. (c) The framework structure of **2** along the *c*-axis.

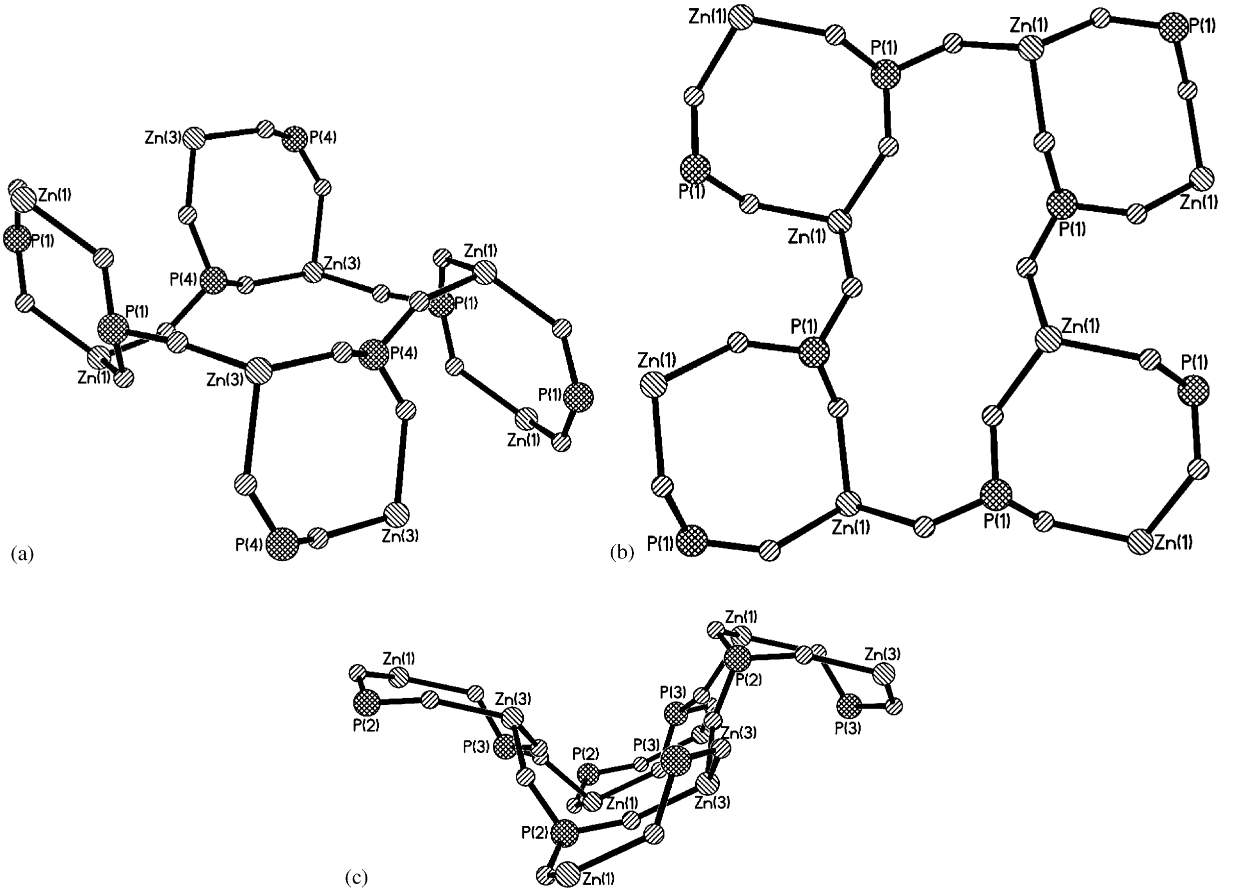

Fig. 6. (a) View of the unit of the inorganic layer in **1**. (b) View of the unit of the inorganic layer in **2**. (c) View of the unit of the inorganic layer in $[C_4N_2H_{12}]_{0.5}\cdot[Zn_3(HPO_3)_4]\cdot H_3O$.

Interestingly, three different organic amines including 1,3-Bis(aminomethyl)benzene, propylamine and piperazine hexahydrate can all direct the formation of a similar layered structure. It is well known that multipoint hydrogen bond interactions are necessary in the formation and stability of open architectures. In the present case also, we find strong hydrogen-bond interactions involving the hydrogens attached to the nitrogen of the amine and the framework oxygen atoms. Because the three compounds have different amines, the structure direct effects of the template are definitely distinct. The sizes and shapes of these three templated molecules are different, and the organic amines also occupy different position in the similar framework. Though the exact mechanism of formation of these architectures is far from being understood, it can be safely presumed that the nitrogen atoms of the amine molecule play a vital role. These diprotonated or protonated template cations not only balance the negative charge of the layers, but also interact with the host layers through H-bonding to oxygen atoms. This suggests that the sizes and shapes of the template molecules significantly affect the framework structure.

4. Conclusions

In summary, two three-dimensional zincophosphites with the formulas $[C_6H_4(CH_2NH_3)_2]\cdot[Zn_3(HPO_3)_4]$ **1** and $[CH_3CH_2CH_2NH_3]_2\cdot[Zn_3(HPO_3)_4]$ **2** have been hydrothermally synthesized. They have similar inorganic frameworks with the same compositions $[Zn_3(HPO_3)_4]^{2-}$. Two compounds consist of vertex linking of ZnO_4 tetrahedral and $[HPO_3^{2-}]$ pseudopyramidal units. They are both built up from two-dimensional layers with four- and eight-membered rings and one-dimensional chains composed of four-memberd rings, but their layered structures are different due to the influence of corresponding organic template. The network has a Zn/P ratio of 3/4.

Acknowledgments

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