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Hydrothermal synthesis and characterization of organically templated zincophosphites with two- and three-dimensional structures, $[CH_3CH(NH_3)CH_2NH_3]\cdot[Zn_2(HPO_3)_3]\cdot H_2O$ and $[H_3N(CH_2)_6NH_3]\cdot[Zn_3(HPO_3)_4]$

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Abstract

Two organically templated zincophosphites, $[CH_3CH(NH_3)CH_2NH_3]\cdot[Zn_2(HPO_3)_3]\cdot H_2O$ (1) and $[H_3N(CH_2)_6NH_3]\cdot[Zn_3(HPO_3)_4]$ (2) were hydrothermally synthesized and characterized by single-crystal X-ray diffraction. Compound 1 crystallizes in the monoclinic system, space group $P2_1/c$ with cell parameters: $a = 9.9875(13)$ Å, $b = 10.3402(11)$ Å, $c = 14.4373(16)$ Å, $\beta = 102.093°$, and $Z = 4$. It possesses a layered architecture and organic template molecules located between the inorganic layers forming hydrogen bonds. The inorganic layers, which consist of four-, eight-membered rings, are constructed of alternating ZnO_4 tetrahedra and $[HPO_3^{2-}]$ pseudo-pyramid by sharing vertices. Each four-membered ring is capped by a $[HPO_3^{2-}]$ pseudo-pyramid. The 1,2-diammonium-propane template molecules are located above the eight-membered rings. Compound 2 crystallizes in the orthorhombic system, space group $Pbcn$ with cell parameters: $a = 8.8754(14)$ Å, $b = 16.667(3)$ Å, $c = 13.864(2)$ Å, and $Z = 4$. It is built up from three-dimensional Zn/P/O frameworks. Corner-linked ZnO_4 tetrahedra and $[HPO_3^{2-}]$ pseudo-pyramids form four-, six-, eight-membered rings and 12-membered ring channels. 1,6-diaminohexane cations are located in the 12-membered ring channel systems. Two compounds were characterized by IR spectroscopy, and differential thermal and thermogravimetric analyses.
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1. Introduction

In the past two decades, a large number of open-framework metal phosphates have been synthesized in the presence of organic amines as the templates [1–3], for their potential applications in the fields of catalysis, biology, electrical conductivity, magnetism and photochemistry [4–9]. As part of the renaissance in the study of open-framework metal phosphates, [10] a series of novel compositions of inorganic frameworks with one-, two- or three-dimensions (1D, 2D or 3D) have been recently prepared by using polar organic molecules as structural directors. Open framework zincophosphates, in the presence of organic templates, formed a growing

family of compounds. Among these, the zinc phosphates as inorganic parts, building up from vertex-linked ZnO_4 and PO_4 tetrahedra showed considerable structural diversity [11–12], such as the successful synthesis of ND-1 [13] with 24-membered ring channels. Since the synthesis of vanadium phosphites in the presence of piperazinium cation as structure director by Zubieta et al. [14] the interest in the synthesis of new transition metal phosphites has been aroused. To date, transition metal phosphites have been extensively studied, and compounds with V(III) [15], Fe(III) [15] Co(II) [16], Mn(II) [17–18] and Zn(II) [19–21] have been published. Open framework zincophosphites with 1D [22], 2D [23] and 3D [24] structures showed novel and some similarity compared to their zincophosphate.

In this paper, two novel open-framework zincophosphites have been synthesized under mild hydrothermal

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conditions, $[CH_3CH(NH_3)CH_2NH_3] \cdot [Zn_2(HPO_3)_3] \cdot H_2O$
1 has a 2D structure and $[H_3N(CH_2)_6 NH_3] \cdot [Zn_3(HPO_3)_4]$
2 a 3D structure. They are built from strictly alternative
ZnO_4 tetrahedra and $[HPO_3^{2-}]$ pseudo-pyramids. The
structure of compound **1** contains inorganic layers with
four- and eight-membered rings, whereas compound **2**
contains 12-membered ring channels.

2. Experimental

2.1. Synthesis and characterization

All syntheses were carried out in 23 mL Teflon-lined
stainless-steel vessels under autogenous pressure with a
filling capacity of ∼15%. The element analysis was
performed on a Perkin-Elmer 2400 element analyzer,
and inductively coupled plasma (ICP) analysis was
performed on a Perkin-Elmer optima 3300 DV ICP
spectrometer. Infrared spectra were obtained on a
Nicolet 5DX FT-IR instrument. A Perkin-Elmer DTA
1700 differential thermal analyzer and a Perkin-Elmer
TGA 7 thermogravimetric analyzer were used to obtain
DTA and TGA curves in air with a temperature
increasing rate of $10\,^{\circ}C\,min^{-1}$.

2.1.1. Synthesis of $[CH_3CH(NH_3)CH_2NH_3] \cdot$ $[Zn_2(HPO_3)_3] \cdot H_2O$ **1**

The reactants $Zn(AC)_2$ (0.219 g, 1 mmol), H_3PO_3
(0.410 g, 5 mmol) and 1,2-diammonium-propane
(0.3 mL, 3.53 mmol) were added to 2 mL (166 mmol)
distilled water. The initial pH was 4.2. The reaction was
carried out in a 23 mL capacity Teflon-lined stainless-
steel hydrothermal bomb, under autogenous pressure,
heated at 180°C for 120 h, followed by slow cooling to
room temperature. The pH of the mixtures was 5.6. The
product was washed with deionized water and dried at
room temperature. The elemental analysis found (wt%):
Zn, 28.42; P, 21.02; C, 7.68; N, 6.21; H, 3.51. These
values are consistent with the calculated values from the
formula values of $[CH_3CH(NH_3)CH_2NH_3] \cdot [Zn_2(HPO_3)_3] \cdot$
H_2O: Zn, 28.12; P, 19.98; C, 7.75; N, 6.02; H, 3.23. IR (KBr
pellet, cm^{-1}): 2362 (w), 1637 (s), 1544 (m), 1080 (s), 578 (s),
448 (w).

2.1.2. Synthesis of $[H_3N(CH_2)_6NH_3] \cdot [Zn_3(HPO_3)_4]$ **2**

The reactants $Zn(AC)_2$ (0.219 g, 1 mmol), H_3PO_3
(0.4100 g, 5 mmol) and 1,6-diaminohexane (3 mmol,
0.349 g) were added to 2 mL (166 mmol) distilled water.
The initial pH was 3.1. The reaction was carried out in a
23 mL capacity Teflon-lined stainless-steel hydrothermal
bomb, under autogenous pressure, heated at 180°C for
120 h, followed by slow cooling to room temperature.
The pH of the mixture was 4.5. The product was washed
with deionized water and dried at room temperature.

The elemental analysis found (wt%): Zn, 29.48; P, 20.64;
C, 10.89; N, 4.33; H, 3.57. These values are consistent
with the calculated values from the formula of
$[H_3N(CH_2)_6NH_3] \cdot [Zn_3(HPO_3)_4]$: Zn, 30.93; P, 19.53;
C, 11.35; N, 4.42; H, 3.50. IR (KBr pellet, cm^{-1}): 2920
(m), 2390 (s), 1630 (s), 1530 (m), 1090 (s), 625 (s),
577 (m).

2.2. Determination of the crystal structures

Two crystals of dimensions $0.40 \times 0.40 \times 0.20$ mm for
1 and $0.10 \times 0.10 \times 0.04$ mm for **2** were 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 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 [25]. The structure was
solved by Direct Methods using the SHELXTL crystal-
lographic software package [26]. The zinc and phos-
phorus atoms were first located, whereas the carbon,
nitrogen, and oxygen atoms were found in the different
Fourier maps. The hydrogen atoms residing on the
amine molecules were placed geometrically. The hydro-
gen atoms residing on the phosphorus were located by
Fourier maps. The total number of measured reflections
and observed unique reflections were 3270 and 2067 for
1 and were 9027 and 1471 for **2**. For compound **1**,
intensity data of 3270 independent reflections
($-11 \leqslant h \leqslant 4$, $-11 \leqslant k \leqslant 11$, $-15 \leqslant l \leqslant 15$) were collected
in the ω scan mode. For compound **2**, intensity data of
9027 independent reflections ($-9 \leqslant h \leqslant 9$, $-12 \leqslant k \leqslant 18$,
$-15 \leqslant l \leqslant 15$) were collected in the ω scan mode.
Crystallographic data for two compounds are listed in
Table 1.

3. Results and discussion

3.1. Description of structure

3.1.1. Crystal structure of $[CH_3CH(NH_3)CH_2NH_3] \cdot$ $[Zn_2(HPO_3)_3] \cdot H_2O$ **1**

Final atomic positional and thermal parameters for
$[CH_3CH(NH_3)CH_2NH_3] \cdot [Zn_2(HPO_3)_3] \cdot H_2O$ are given
in Table 2, and selected bond distance and bond angle
data are summarized in Table 3. The asymmetric unit of
1 is presented in Fig. 1. The asymmetric unit of the
zincophosphite **1** contains 20 non-hydrogen atoms, 14 of
which belong to the "framework" (two Zn, three P and
nine O atoms) and six to the guest (three C, two N and
O). The two zinc atoms adopt tetrahedral coordination
with typical geometrical parameters of $d_{av}(Zn1–O) =$
1.928 (3) Å, $d_{av}(Zn2–O) = 1.937$ (3) Å. The O–Zn–O

Table 1
Crystal data for $[CH_3CH(NH_3)CH_2NH_3]\cdot[Zn_2(HPO_3)_3]\cdot H_2O$ **1** and $[H_3N(CH2)_6NH_3]\cdot[Zn_3(HPO_3)_4]$ **2**

Empirical formula	$C_3H_{17}N_2Zn_2P_3O_{10}$	$C_6H_{22}N_2Zn_3P_4O_{12}$
Formula weight	464.84	634.25
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbcn$
Unit-cell dimensions	$a = 9.9875(13)$ Å	$a = 8.8754(14)$ Å
	$b = 10.3402(11)$ Å	$b = 16.667(3)$ Å
	$c = 14.4373(16)$ Å	$c = 13.864(2)$ Å
	$\beta = 102.093(2)°$	
Volume	1457.9(3) Å^3	2050.7(6)
Z	4	4
Calculated density (mg m^{-3})	2.118	2.054
Absorption coefficient (mm^{-1})	3.665	3.849
$F(000)$	936	1272
Crystal size (mm^3)	$0.400 \times 0.400 \times 0.200$	$0.100 \times 0.100 \times 0.040$
Reflections collected/unique	3270/2067 [R(int) = 0.0256]	9027/1471 [R(int) = 0.0499]
Data/restraints/parameter	2067/3/202	1471/0/131
Goodness-of-fit on F^2	1.052	1.078
Final R indices $[I > 2\sigma(I)]^*$	$R_1 = 0.0279$, w$R_2 = 0.0733$	$R_1 = 0.0221$, w$R_2 = 0.0615$
R indices (all data)	$R_1 = 0.0352$, w$R_2 = 0.0760$	$R_1 = 0.0237$, w$R_2 = 0.0626$
Largest diff. peak and hole (Å^{-3})	0.779 and $-0.404e$	0.407 and $-0.302e$

Note: $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$; w$R_2 = \left\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\right\}^{1/2}$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[CH_3CH(NH_3)CH_2NH_3]\cdot[Zn_2(HPO_3)_3]\cdot H_2O$

	x	y	z	U(eq)
Zn(1)	11,084(1)	−1519(1)	7929(1)	28(1)
Zn(2)	5921(1)	1485(1)	6954(1)	24(1)
P(1)	12,630(1)	−3009(1)	9766(1)	25(1)
P(2)	13,957(1)	−548(1)	7556(1)	23(1)
P(3)	8959(1)	792(1)	8101(1)	25(1)
O(1)	11,773(3)	−4193(3)	9831(2)	38(1)
O(2)	11,794(3)	−1909(3)	9244(2)	42(1)
O(3)	10,367(3)	−3095(3)	7285(3)	50(1)
O(4)	12,414(3)	−673(3)	7351(2)	36(1)
O(5)	9444(3)	−494(3)	7813(3)	45(1)
O(6)	7419(3)	825(3)	7875(2)	37(1)
O(7)	4394(3)	293(3)	6814(2)	30(1)
O(8)	5316(3)	3154(3)	7347(2)	31(1)
O(9)	6116(3)	1653(3)	5644(2)	36(1)
O(1W)	2771(4)	2815(4)	7820(3)	50(1)
C(1)	11,300(5)	−7259(5)	10,342(4)	51(1)
C(2)	12,729(5)	−7491(5)	10,319(4)	51(1)
C(3)	12,947(6)	−8817(5)	9942(4)	56(2)
N(1)	11,043(4)	−6150(4)	10,966(3)	36(1)
N(2)	13,281(4)	−6491(4)	9747(3)	38(1)

Note: U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (deg) for $[CH_3CH(NH_3)CH_2NH_3]\cdot[Zn_2(HPO_3)_3]\cdot H_2O$

Zn(1)–O(4)	1.921(3)	Zn(2)–O(6)	1.908(3)
Zn(1)–O(2)	1.925(3)	Zn(2)–O(7)	1.938(3)
Zn(1)–O(5)	1.927(3)	Zn(2)–O(9)	1.949(3)
Zn(1)–O(3)	1.938(3)	Zn(2)–O(8)	1.951(3)
P(1)–O(1)	1.508(3)	P(2)–O(7)#2	1.513(3)
P(1)–O(2)	1.515(3)	P(2)–O(4)	1.513(3)
P(1)–O(9)#1	1.534(3)	P(2)–O(8)#1	1.519(3)
P(1)–H(1)	1.29(4)	P(2)–H(2)	1.36(4)
P(3)–O(3)#3	1.498(3)	P(3)–O(6)	1.504(3)
P(3)–O(5)	1.504(3)	P(3)–H(3)	1.34(3)
O(4)–Zn(1)–O(2)	112.23(14)	O(6)–Zn(2)–O(7)	109.30(12)
O(4)–Zn(1)–O(5)	111.37(13)	O(6)–Zn(2)–O(9)	118.99(13)
O(2)–Zn(1)–O(5)	109.36(15)	O(7)–Zn(2)–O(9)	101.06(12)
O(4)–Zn(1)–O(3)	113.19(14)	O(6)–Zn(2)–O(8)	111.07(13)
O(2)–Zn(1)–O(3)	108.66(15)	O(7)–Zn(2)–O(8)	107.95(12)
O(5)–Zn(1)–O(3)	101.47(14)	O(9)–Zn(2)–O(8)	107.63(13)
O(1)–P(1)–O(2)	112.29(19)	O(7)#2–P(2)–O(4)	110.16(16)
O(1)–P(1)–O(9)#1	111.06(17)	O(7)#2–P(2)–O(8)#1	111.75(17)
O(2)–P(1)–O(9)#1	112.89(18)	O(4)–P(2)–O(8)#1	112.96(17)
O(1)–P(1)–H(1)	108.7(16)	O(7)#2–P(2)–H(2)	105.1(17)
O(2)–P(1)–H(1)	105.9(16)	O(4)–P(2)–H(2)	109.4(16)
O(9)#1–P(1)–H(1)	105.6(15)	O(8)#1–P(2)–H(2)	107.1(17)
O(3)#3–P(3)–O(5)	112.4(2)	P(1)–O(2)–Zn(1)	134.3(2)
O(3)#3–P(3)–O(6)	114.88(18)	P(3)#1–O(3)–Zn(1)	132.44(19)
O(5)–P(3)–O(6)	109.52(18)	P(2)–O(4)–Zn(1)	136.35(19)
O(3)#3–P(3)–H(3)	109.1(16)	P(3)–O(5)–Zn(1)	141.2(2)
O(5)–P(3)–H(3)	105.2(16)	P(3)–O(6)–Zn(2)	140.9(2)
O(6)–P(3)–H(3)	105.1(15)	P(2)#4–O(7)–Zn(2)	128.96(17)
P(2)#3–O(8)–Zn(2)	129.62(17)	P(1)#3–O(9)–Zn(2)	130.61(19)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x+2, y-1/2, -z+3/2$; #2 $x+1, y, z$; #3 $-x+2, y+1/2, -z+3/2$; #4 $x-1, y, z$.

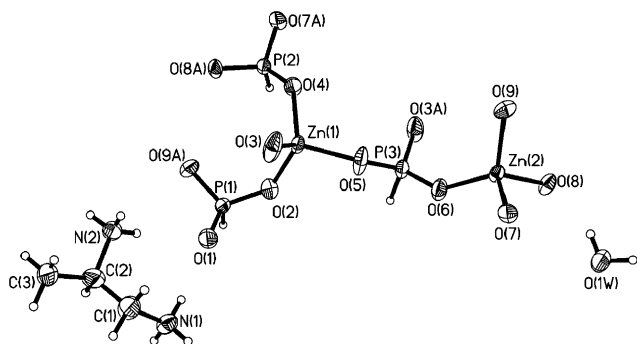angles are in the range of 101.47–113.19° (av. O–Zn(1)–O = 109.38°, O–Zn(2)–O = 109.33°). All these zinc species bond to P atoms via Zn–O–P links. As expected, the three distinct P atoms form the centers of pseudo-pyramid hydrogen phosphite groups with

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

$d_{av}(P1–O) = 1.543$ Å, $d_{av}(P2–O) = 1.515$ Å, $d_{av}(P3–O) = 1.502$ Å P(1) has two connections to zinc atoms via oxygen and one terminal P=O bond. The terminal P=O distance is 1.534 Å P(2) and P(3) make three links to zinc neighbors and are presumed to possess the characteristic $[HPO_3^{2-}]$ terminal P–H bond. The O–P–O bond angles are in the range 109.52–114.88°, while the H–P–O angles range from 105.1° to 109.4°. The H(1)–P(1), H(2)–P(2) and H(3)–P(3) bond distances are close to those in common phosphite anions.

The framework structure of $[CH_3CH(NH_3)CH_2NH_3] \cdot [Zn_2(HPO_3)_3] \cdot H_2O$ consists of alternating inorganic and organic layers stacked along *c*-axis. Fig. 2 shows the inorganic layer viewed down the *c*-axis direction. The basic structure units of the inorganic layer are ZnO_4 tetrahedra and $[HPO_3^{2-}]$ pseudo-pyramid. The building block of the inorganic layer contains two ZnO_4 tetrahedra and three $[HPO_3^{2-}]$ pseudo-pyramid units. The two ZnO_4 tetrahedra (Zn(1), Zn(2)) and two of the $[HPO_3^{2-}]$ pseudo-pyramid (P(2) and P(3)) units are linked alternatively by sharing vertices and formed the four-membered ring. The third $[HPO_3^{2-}]$ (P(1)) pseudo-pyramid unit is capped above the four-membered ring by sharing vertices with the two ZnO_4 tetrahedra units. The four-membered rings are linked via Zn–O–P bridge within the inorganic layer. Surrounded by four building blocks, an eight-membered distorted pore is formed. The capping $[HPO_3^{2-}]$ units situate alternatively up and down the inorganic layer.

Fig. 3 shows the stacking of the inorganic layer with the intercalated organic cations viewed along the *b*-axis direction. The inorganic layers are stacked exactly one over the other in an *AAAA* fashion. The 1,2-diammonium-propane cation occupies the region between two zincophosphite layers and interacts with the layers through N–H···O hydrogen bonds as shown in Fig. 4. The important hydrogen bonds of compound **1** are listed in Table 4. The water molecule connects with the inorganic layer via hydrogen bonds as the evidence by the short O(1w)···O(5) and O(1w)···O(8) distances of 2.818 and 2.788 Å, respectively. Both 1,2-diammonium-
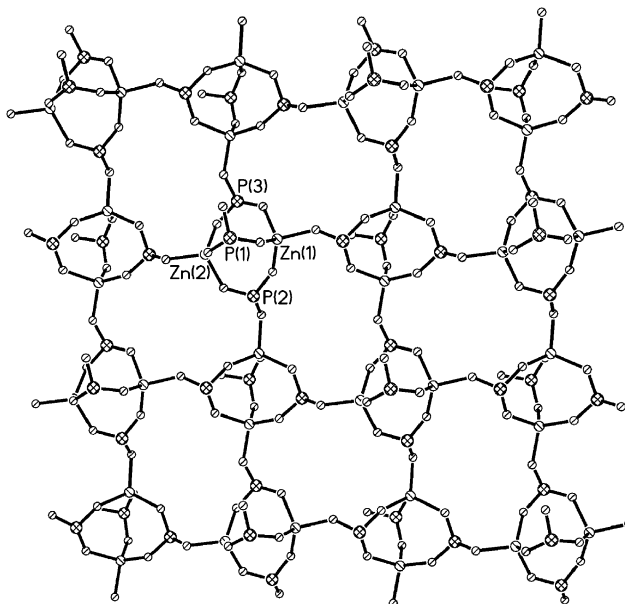

Fig. 2. The inorganic layer structure of $[Zn_2(HPO_3)_3]^{2-}$ of compound **1** viewed along the [001] direction.
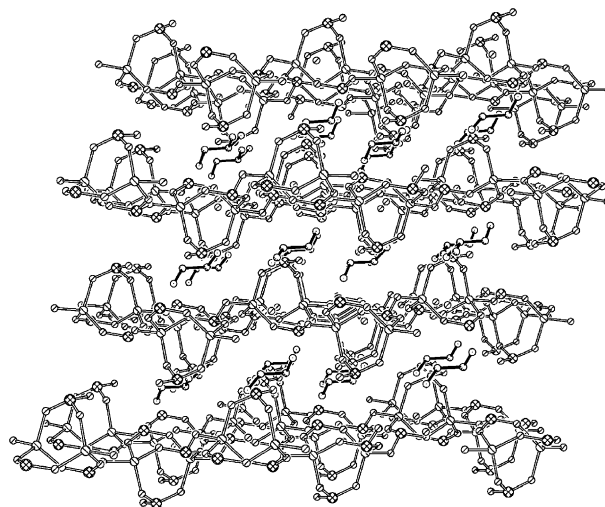

Fig. 3. The stacking of the layers of compound **1** with the intercalated organic cations viewed along the [010] direction.

propane and water are encapsulated in the eight-membered ring channel along the *c*-axis.

3.1.2. Crystal structure of $[H_3N(CH_2)_6NH_3] \cdot [Zn_3(HPO_3)_4]$ **2**

Compound **2** is a new organo-zincophosphite consisting of a 3D network of vertex-linked ZnO_4 and $[HPO_3^{2-}]$ tetrahedra incorporating 1,6-diaminohexane cations into its pores. Final atomic positional and thermal parameters for $[H_3N(CH_2)_6NH_3] \cdot [Zn_3(HPO_3)_4]$ are given in Table 5, and selected bond distance and bond angle data are summarized in Table 6.

The asymmetric unit of **2** is presented in Fig. 5. There are 23 distinct non-hydrogen atoms in compound **2**, 15 of which belong to the "framework" (two Zn, two P and 11 O atoms) and eight to the guest (six C, two N). The two zinc atoms adopt tetrahedral coordination with typical geometrical parameters of $d_{av}(Zn1-O) = 1.931$ (2) Å, $d_{av}(Zn2-O) = 1.945$ (2) Å. The O–Zn–O angles are in the range 99.11–115.52° (av. O–Zn(1)–O = 109.42°, O–Zn(2)–O = 109.52°). All zinc species bond to P atoms via Zn–O–P links. As expected, two distinct P atoms form the centers of a pseudo-pyramid with hydrogen phosphite groups $d_{av}(P1-O) = 1.519$ Å, $d_{av}(P2-O) = 1.502$ Å. The O–P–O bond angles are in the range 104.4–115.95°.

Compound **2** has a complex 3D network containing four-, six-, eight- and 12-membered ring windows. The structure of **2** along the [010] direction is shown in Fig. 6a from which the 1D channel of the compound propagating along the b-axis can be seen. The 3D structure of **2** can be understood in that inorganic layers (shown in Fig. 6b) are connected to each other via

oxygens. Meanwhile, the connection between ZnO$_4$ and HPO$_3$ units leads to an infinite 2D sheet parallel to the (001) plane (Fig. 6b). The basic unit of the framework formed by a capped four-membered ring. The four-membered ring is built up from 2 Zn(1) and 2 P(2) tetrahedra, whereas the capping moiety is built up from 2 P(1) and 1 Zn(2) tetrahedra. Meanwhile, there is a six-membered ring formed by Zn(2), 2 P(1), 2 Zn(1) and P(2) atoms which connects the capping moiety and the four-membered ring through common atoms.

Zn(1) connected with next layered P(1) via bridge O(3) and formed 3D structure. The 1,6-diaminohexane cations are diprotonated, occupying space above the 12-membered ring, and forms hydrogen bonds to framework atoms. Fig. 7a shows the connectivity between ZnO$_4$ and [HPO$_3^{2-}$] moieties that creates the 12-membered channel system along the c-axis. The structure directing amine molecule, diprotonated 1,6-diaminohexane molecule, sits in these channels and interacts with the framework through hydrogen bonds. The wall of the 12-ring channels of **2** is composed of alternated 4-, 6-, 8-rings (Fig. 7b). 1,6-diaminohexane molecule occupied the 8-ring windows. The hydrogen bonds of compound **2** are listed in Table 7.
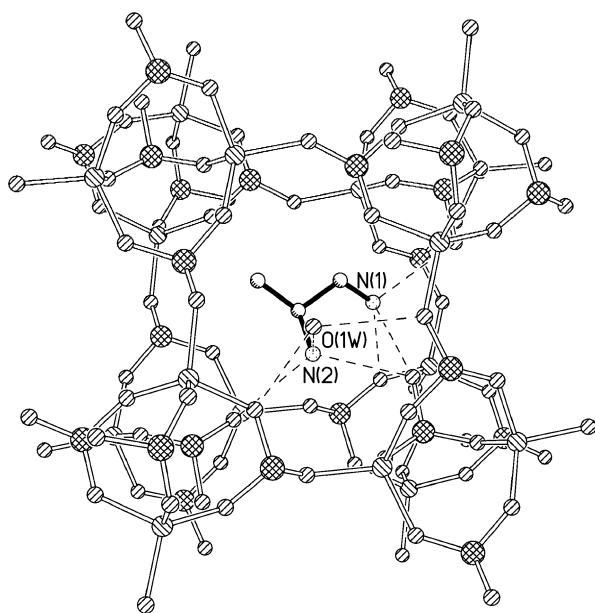

Fig. 4. Structure of **1** showing a single eight-membered channel along with the amine. Dotted lines represent the various hydrogen bond interactions.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[H_3N(CH_2)_6NH_3] \cdot [Zn_3(HPO_3)_4]$

	x	y	z	U(eq)
Zn(1)	4469(1)	9231(1)	1062(1)	29(1)
Zn(2)	5000	12,507(1)	2500	28(1)
P(1)	5054(1)	11,083(1)	1114(1)	27(1)
P(2)	2417(1)	8816(1)	2799(1)	33(1)
O(1)	4032(2)	10,364(1)	1022(2)	36(1)
O(2)	3116(3)	8598(1)	1845(2)	46(1)
O(3)	4119(3)	8716(1)	−185(2)	44(1)
O(4)	6521(3)	9090(2)	1438(2)	72(1)
O(5)	4177(2)	11,808(1)	1490(2)	33(1)
O(6)	6459(3)	13,141(1)	1807(2)	45(1)
C(1)	4913(4)	6810(2)	731(3)	53(1)
C(2)	4919(5)	5907(2)	881(3)	51(1)
C(3)	4887(5)	5445(2)	−66(3)	53(1)
N(1)	3469(3)	7098(2)	295(2)	37(1)

Note: U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Hydrogen bonds information for $[CH_3CH(NH_3)CH_2NH_3] \cdot [Zn_2(HPO_3)_3] \cdot H_2O$

D–H⋯A	d(D–H) (Å)	d(H⋯A) (Å)	d(D⋯A) (Å)	<(DHA) (deg)
N(1)–H(1C)⋯O(1)#1	0.89	2.02	2.829(5)	151.2
N(1)–H(1D)⋯O(1)	0.89	1.96	2.796(5)	155.1
N(1)–H(1E)⋯O(4)#2	0.89	2.44	2.878(5)	110.5
N(2)–H(2A)⋯O(9)#3	0.89	2.10	2.862(5)	142.7
N(2)–H(2B)⋯O(1)	0.89	2.10	2.830(5)	138.0

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y - 1, -z + 2$; #2 $x, -y - 1/2, z + 1/2$; #3 $x + 1, -y - 1/2, z + 1/2$.

Table 6
Selected bond lengths (Å) and angles (deg) for $[H_3N(CH_2)_6NH_3]\cdot$ $[Zn_3(HPO_3)_4]$

Zn(1)–O(4)	1.909(3)	Zn(2)–O(6)#1	1.927(2)
Zn(1)–O(2)	1.933(2)	Zn(2)–O(5)	1.962(2)
Zn(1)–O(1)	1.928(2)	Zn(2)–O(6)	1.927(2)
Zn(1)–O(3)	1.955(2)	Zn(2)–O(5)#1	1.962(2)
P(1)–O(1)	1.509(2)	P(2)–O(4)#1	1.489(3)
P(1)–O(5)	1.530(2)	P(2)–O(6)#3	1.512(2)
P(1)–O(3)#2	1.519(2)	P(2)–O(2)	1.505(2)
P(1)–H(1)	1.33(3)	P(2)–H(2)	1.41(4)
C(1)–N(1)	1.496(5)	C(2)–C(3)	1.523(5)
C(1)–C(2)	1.520(5)	C(3)–C(3)#5	1.507(7)
O(4)–Zn(1)–O(1)	108.67(12)	O(6)#1–Zn(2)–O(6)	113.50(15)
O(1)–Zn(1)–O(2)	115.20(10)	O(6)–Zn(2)–O(5)	102.70(9)
O(4)–Zn(1)–O(3)	109.82(13)	O(6)–Zn(2)–O(5)#1	115.52(9)
O(4)–Zn(1)–O(2)	111.86(11)	O(6)#1–Zn(2)–O(5)	115.52(9)
O(1)–Zn(1)–O(3)	111.88(10)	O(6)#1–Zn(2)–O(5)#1	102.70(9)
O(2)–Zn(1)–O(3)	99.11(9)	O(5)–Zn(2)–O(5)#1	107.20(12)
O(1)–P(1)–O(3)#2	113.23(12)	O(4)#1–P(2)–O(2)	115.95(15)
O(3)#2–P(1)–O(5)	111.11(13)	O(2)–P(2)–O(6)#3	111.67(12)
O(3)#2–P(1)–H(1)	104.4(13)	O(2)–P(2)–H(2)	105.6(14)
O(1)–P(1)–O(5)	110.51(13)	O(4)#1–P(2)–O(6)#3	109.16(16)
O(1)–P(1)–H(1)	108.1(11)	O(4)#1–P(2)–H(2)	105.8(15)
O(5)–P(1)–H(1)	109.2(12)	O(6)#3–P(2)–H(2)	108.2(15)
P(1)–O(1)–Zn(1)	130.88(14)	P(2)#1–O(4)–Zn(1)	146.70(18)
P(2)–O(2)–Zn(1)	128.16(13)	P(1)–O(5)–Zn(2)	121.51(12)
P(1)#2–O(3)–Zn(1)	125.14(14)	P(2)#4–O(6)–Zn(2)	127.29(13)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+1/2$; #2 $-x+1, -y+2, -z$; #3 $x-1/2, y-1/2, -z+1/2$; #4 $x+1/2, y+1/2, -z+1/2$; #5 $-x+1, -y+1, -z$.
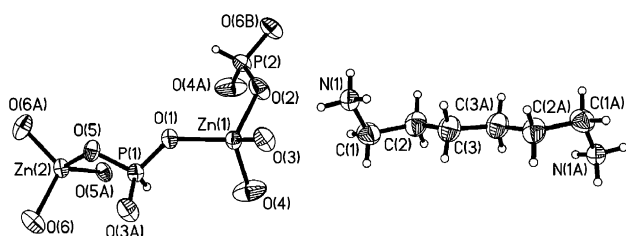

Fig. 5. Asymmetric unit of **2** with thermal ellipsoids shown at 50% probability.

Fig. 6. (a) View of the crystal structure of compound **2** along [010]. (b) Each layer of the structure **2** along [001].

3.2. Thermogravimetic analysis

Thermogravimetic analysis (TGA) study was carried out from room temperature to 1000°C. TGA for **1** showed that a weight loss of 3.50% from 100°C to 230°C, which was in agreement with the calculated amount of the removal of water. In addition, there was a weight loss of 15.46% from 260°C to 400°C, which was due to the removal of organic template (calculated value of 16.05%). The DTA curve had two endothermic effects in the ranges from 174.1°C to 277.2°C. The TGA for **2** showed that a weight loss of 18.3% occurred from 380°C to 640°C, due to the removal of organic template (ca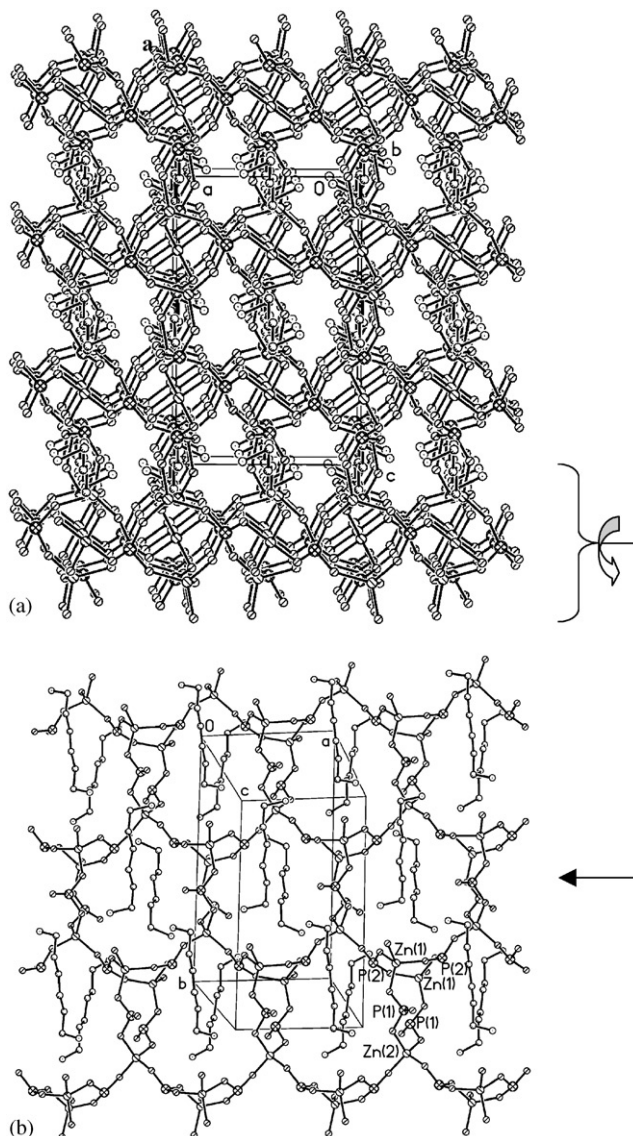lculated value of 18.6%). The DTA curve had a strong endothermic peak which can be assigned to the loss of organoamine. The structure of the title compounds collapsed and converted to an amorphous phase after the calcination at 600°C for 2 h. At 800°C, compound **1** recrystallized to the $Zn_3(PO_4)_2$ (JCPDS: 30-1490) and compound **2** recrystallized to the ZnP_2O_7 (JCPDS: 34-0623), confirmed by powder X-ray diffraction.

4. Conclusions

In summary, two novel open-framework zinco-phosphites, $[CH_3CH(NH_3)CH_2NH_3]\cdot[Zn_2(HPO_3)_3]\cdot$ H_2O **1** and $[H_3N(CH_2)_6NH_3]\cdot[Zn_3(HPO_3)_4]$ **2**, were obtained as good quality single crystals by hydrothermal
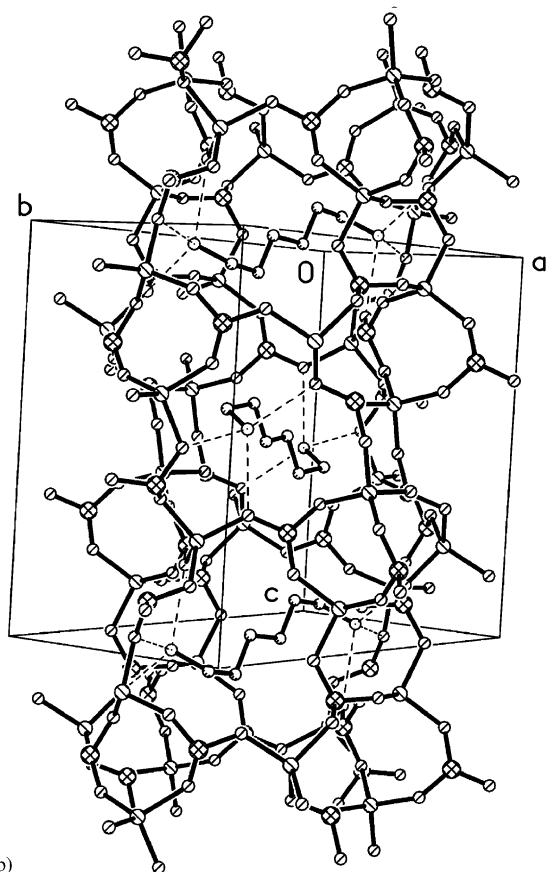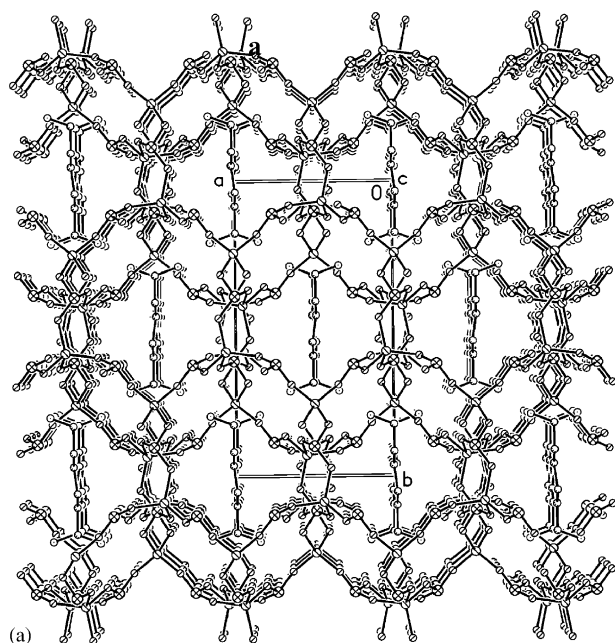
(a)

(b)

Fig. 7. (a) View along the *c*-axis, showing the virtue channels of compound **2**. (b) View of compound **2** showing the 12-membered ring channel occupied by the organic amine. The N–H···O interactions between the template and framework are indicated by dotted lines.

Table 7
Hydrogen bonds information for $[H_3N(CH_2)_6NH_3]\cdot[Zn_3(HPO_3)_4]$

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (deg)
N(1)–H(1C)···O(3)	0.89	1.97	2.837(3)	164.6
N(1)–H(1D)···O(5)#1	0.89	2.03	2.915(3)	173.3
N(1)–H(1E)···O(6)#2	0.89	2.14	2.941(3)	149.3

Note. Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, y-1/2, z$; #2 $-x+1, -y+2, -z$.

structure and **2** a 3D structure. These results and others reported before show that it is possible to prepare structural complex open-framework zincophosphites possessing cavity size, limiting apertures, and framework densities rivaling those of the most open zeolites and aluminophosphates. At present, we synthesize a wide variety of novel new structure types using other organic species.

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methods. Thus, under similar synthetic conditions, the use of different amines results in products with differing structures and no obvious relationship. **1** has a 2D

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