CSIRO PUBLISHING

Aust. J. Chem. **2015**, *68*, 1261–1267
http://dx.doi.org/10.1071/CH14613

Full Paper

Synthesis, Structure, and Characterisation of Two New Open-Framework Zinc Phosphites of Varying Dimensionality

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Using homopiperazine (hpip) as a structure directing agent, two new zinc phosphites $[H_2hpip][Zn_2(HPO_3)_3]$ (**1**) and $[H_2hpip][Zn_3(HPO_3)_4]$ (**2**), have been synthesised and structurally characterised by IR spectroscopy, elemental analysis, thermogravimetric analysis, and powder and single-crystal X-ray diffractions. Although both compounds are constructed from the same ZnO_4 and HPO_3 building units, the final frameworks are distinctly different due to their different connectivity. Compound **1** displays a 2D layered structure with 8-membered ring apertures, while compound **2** possesses a (3,4)-connected 3D architecture with multidirectional intersecting 8- and 12-ring channels. In addition, the simultaneous occurrence of four types of 8-ring channels intersecting the large 12-ring apertures in **2** is unique and observed here for the first time.

Manuscript received: 13 October 2014.
Manuscript accepted: 22 December 2014.
Published online: 25 February 2015.

Introduction

Crystalline microporous and open-framework materials have been extensively studied owing to their interesting structural features and wide applications in catalysis, absorption, ion-exchange, and separation, etc.[1–4] Since the discovery of microporous aluminophosphate molecular sieves in 1982 by Wilson et al.[5] considerable progress has been achieved in the construction of different non-aluminosilicate-based frameworks. Of these, metal phosphates with a variety of rich compositional and structural features constitute an important family, and a large number of such solids with zero- (monomer), one- (chain, ladder), two- (layer), and three-dimensional architectures have been reported in the literature.[6–14] However, the structural diversity in this family arises mainly from the selection of metal cations in the architecture and the replacement of various extra-framework structure-directing agents. Recently, using pseudo-pyramidal phosphite groups to substitute tetrahedral phosphate anion parts of the inorganic network has resulted in a new class of metal phosphites with great success. Compared with 4-connected phosphate groups, the presence of a 3-connected $[HPO_3]^{2-}$ group can reduce the M–O–P connectivity and favour the generation of more open interrupted frameworks with larger pore sizes and lower framework densities. Typical examples of metal phosphites with large 18-, 20-, 24-, 26-, 28-, 40-, 56-, 64-, and 72-ring channels have been successively isolated and characterised.[15–23]

It has been demonstrated that the use of various organic moieties as templates or structure-directing agents (SDAs) under hydro/solvothermal conditions is an effective method to tune the resultant framework topologies. Although some understanding has been achieved of the influence and roles of SDAs, the rational design and synthesis of such microporous materials are far from reality due to the interplay of many factors such as coordination preferences of the metal ions, stereochemistry of organic molecules, solvent effects, and the nature of the counter ion, etc. For example, a variety of organic amines may play different roles in the formation of interesting structures depending on the synthetic conditions, including a single role as templates or ligands, as well as dual roles of both ligands and countercations;[24–28] some metal phosphates/phosphites with versatile structures can be synthesised with the same template by careful tuning the synthetic parameters such as the ratio of reactants, temperature, pH, or solvent.[29–31] In our previous studies on metal phosphates/phosphites, we focussed on the influence of various organic templates on the inorganic compositions and topologies.[32,33] To further seek novel metal phosphites with interesting structures and gain a simultaneous better understanding of the relationship between structure and synthetic variables, we investigated the construction of zinc phosphites with the same template. Herein, using homopiperazine (hpip) as a SDA, two new organically templated zinc phosphites $[H_2hpip][Zn_2(HPO_3)_3]$ (**1**) and $[H_2hpip][Zn_3(HPO_3)_4]$ (**2**) with different structural features have been successfully synthesised by adjusting the synthesis conditions. Compound **1** possesses a sheet structure with 8-membered rings sandwiched by diprotonated $[H_2hpip]^{2+}$ templates; **2** displays a (3,4)-connected interrupted architecture with intersecting 8- and 12-ring channels.

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

Compounds	1	2
Empirical formula	$[C_5N_2H_{14}][Zn_2(HPO_3)_3]$	$[C_5N_2H_{14}][Zn_3(HPO_3)_4]$
Formula weight	472.86	618.12
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a [Å]	8.3788(7)	8.7559(5)
b [Å]	14.0896(2)	10.1290(2)
c [Å]	13.2973(3)	10.3390(2)
α [deg.]	90	90.760(3)
β [deg.]	105.078(5)	97.970(4)
γ [deg.]	90	93.650(5)
V [Å^3]	1515.75(13)	906.03(6)
D [g cm^{-3}]	2.072	2.266
Z	4	2
F(000)	952	616
μ(Mo$_{K\alpha}$) [mm^{-1}]	3.523	4.353
Reflection collected	15653	8976
Independent reflections	3468 [R(int) = 0.0657]	3733 [R(int) = 0.0311]
Parameters refined	190	235
Limiting indices	$-10 \le h \le 10$, $-18 \le k \le 18$, $-17 \le l \le 17$	$-10 \le h \le 10$, $-12 \le k \le 12$, $-12 \le l \le 12$
Goodness-of-fit on F^2	1.135	1.164
Final R_1, $wR_2[I > 2\sigma(I)]$	0.0536, 0.1049	0.0472, 0.0983

Experimental

Materials and Methods

All starting materials were commercially available, and used as purchased without further purification. Elemental analyses of C, H, and N were performed on an Elemental Vario EL III elemental analyser. IR spectra were measured on an ABB Bomen MB 102 series FTIR spectrophotometer with KBr pellets in the range 4000–400 cm^{-1}. Powder X-ray diffraction (XRD) data were obtained using a Philips X'Pert-MPD diffractometer with Cu$_{K\alpha1}$ radiation (λ 1.54076 Å). Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyser in a N_2 atmosphere with a heating rate of 10°C min^{-1} from 40 to 800°C.

Synthesis of **1**

A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$, H_3PO_3, hpip, H_2O, and ethanol with a molar composition of 1 : 13 : 9 : 121 : 149 (pH 5) was sealed in a 25 mL Teflon-lined autoclave and heated at 160°C for 6 days. After cooling to room temperature, colourless crystals of **1** were recovered by filtration, washed with distilled water, and dried in air (66.8 % yield based on zinc). Anal. Calc. for $C_5H_{17}N_2O_9P_3Zn_2$: C 12.70, H 3.62, N 5.92. Found: C 12.57, H 3.55, N 5.78 %.

Synthesis of **2**

Compound **2** was prepared using the same procedure as described for **1**. The mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$, H_3PO_3, hpip, H_2O, and ethanol with a molar composition of 1 : 2 : 0.6 : 49 : 54 (pH 3) was heated at 160°C for 6 days. Colourless crystals of **2** were collected in 71.2 % yield on the basis of zinc. Anal. Calc. for $C_5H_{18}N_2O_{12}P_4Zn_3$: C 9.72, H 2.94, N 4.53. Found: C 9.60, H 2.78, N 4.28 %.

X-Ray Crystallography Analysis

Suitable colourless single crystals of **1** and **2** were carefully selected under an optical microscope and glued to a thin glass fibre with epoxy resin. Crystal structure determination by XRD was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ (λ 0.71073 Å) in the ω and φ scanning mode at room temperature. An empirical absorption correction was applied using the *SADABS* program.[34] The structures were both solved by direct methods and refined by full-matrix least-squares methods on F^2 with the *SHELXL-97* program package.[35] The zinc and phosphorous atoms were first located, whereas the carbon, nitrogen, and oxygen atoms were found in the successive Fourier difference maps. The hydrogen atoms residing on the phosphorous were located by Fourier maps and the remaining hydrogen atoms were placed geometrically and refined in a riding model. The crystallographic data and structure refinements for **1** and **2** are given in Table 1. Selected bond distances and angles are given in Tables 2 and 3. CCDC 1003663 (**1**) and CCDC 1003664 (**2**) contain the supplementary crystallographic data for this paper.

Results and Discussion

Synthesis and IR Characterisation

In general, solvent plays an important role in the formation of microporous materials. By choosing the same water–ethanol mix as solvent, we only changed the ratio of reactants to obtain the two title compounds. In the hydrothermal conditions, the pH values of the homogeneous starting mixture are obviously different, which may be critical to the crystallisation of distinctly final frameworks. The IR spectra of the title compounds were similar and showed typical peaks, with minor differences between the spectra (Fig. 1). The strong bands in the region 1336–1561 cm^{-1} are characteristic of the organic homopiperazine amine cations. The intense bands in the range 1010–1135 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of the PO_3 groups, while symmetric and asymmetric PO_3 deformation can be observed approximately in the range 463–619 cm^{-1}. The weak band at around 2369 cm^{-1} for **1** and 2368 cm^{-1} for **2** indicated the presence of the P–H bond of the phosphite anions.

Table 2. Selected bond lengths and angles for 1[A]

Bond	Bond length [Å]	Bond	Bond angle [deg.]
Zn(1)–O(3)	1.902(4)	O(3)–Zn(1)–O(4)	117.11(18)
Zn(1)–O(4)	1.906(4)	O(3)–Zn(1)–O(6)	113.46(19)
Zn(1)–O(6)	1.942(4)	O(4)–Zn(1)–O(6)	105.66(19)
Zn(1)–O(5)	1.954(3)	O(3)–Zn(1)–O(5)	100.85(17)
Zn(2)–O(9)	1.909(4)	O(4)–Zn(1)–O(5)	112.1(2)
Zn(2)–O(2)#1	1.917(4)	O(6)–Zn(1)–O(5)	107.37(16)
Zn(2)–O(8)	1.919(4)	O(9)–Zn(2)–O(2)#1	121.81(19)
Zn(2)–O(7)	1.979(3)	O(9)–Zn(2)–O(8)	112.7(2)
P(1)–O(3)	1.502(4)	O(2)#1–Zn(2)–O(8)	111.9(2)
P(1)–O(1)	1.509(4)	O(9)–Zn(2)–O(7)	98.91(17)
P(1)–O(2)	1.514(4)	O(2)#1–Zn(2)–O(7)	107.75(17)
P(2)–O(6)	1.502(4)	O(8)–Zn(2)–O(7)	100.27(18)
P(2)–O(7)	1.511(3)	O(3)–P(1)–O(1)	110.8(2)
P(2)–O(5)#2	1.513(4)	O(3)–P(1)–O(2)	112.6(3)
P(3)–O(4)#1	1.487(4)	O(1)–P(1)–O(2)	110.9(2)
P(3)–O(8)#3	1.489(5)	O(6)–P(2)–O(7)	110.8(2)
P(3)–O(9)	1.493(4)	O(6)–P(2)–O(5)#2	112.3(2)
		O(7)–P(2)–O(5)#2	109.7(2)
		O(4)#1–P(3)–O(9)	113.3(3)
		O(8)#3–P(3)–O(9)	113.1(3)

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

Table 3. Selected bond lengths and angles for 2[A]

Bond	Bond length [Å]	Bond	Bond angle [deg.]
Zn(1)–O(4)	1.927(4)	O(4)–Zn(1)–O(1)	126.4(2)
Zn(1)–O(1)	1.929(4)	O(4)–Zn(1)–O(12)	104.6(2)
Zn(1)–O(12)	1.944(5)	O(1)–Zn(1)–O(12)	103.0(2)
Zn(1)–O(7)	1.956(5)	O(4)–Zn(1)–O(7)	110.0(2)
Zn(2)–O(2)#1	1.910(5)	O(1)–Zn(1)–O(7)	99.8(2)
Zn(2)–O(5)#1	1.924(4)	O(12)–Zn(1)–O(7)	113.1(2)
Zn(2)–O(9)	1.925(5)	O(2)#1–Zn(2)–O(5)#1	113.3(2)
Zn(2)–O(10)	1.942(4)	O(2)#1–Zn(2)–O(9)	109.5(3)
Zn(3)–O(6)#2	1.919(4)	O(5)#1–Zn(2)–O(9)	106.9(2)
Zn(3)–O(3)#3	1.919(5)	O(2)#1–Zn(2)–O(10)	105.9(2)
Zn(3)–O(11)	1.926(5)	O(5)#1–Zn(2)–O(10)	110.5(2)
Zn(3)–O(8)#4	1.952(4)	O(9)–Zn(2)–O(10)	110.8(2)
P(1)–O(3)	1.487(5)	O(6)#2–Zn(3)–O(3)#3	101.1(2)
P(1)–O(2)	1.490(5)	O(6)#2–Zn(3)–O(11)	115.0(2)
P(1)–O(1)	1.513(5)	O(3)#3–Zn(3)–O(11)	113.4(3)
P(2)–O(6)	1.504(5)	O(6)#2–Zn(3)–O(8)#4	112.9(2)
P(2)–O(5)	1.507(5)	O(3)#3–Zn(3)–O(8)#4	114.3(2)
P(2)–O(4)	1.526(5)	O(11)–Zn(3)–O(8)#4	100.7(2)
P(3)–O(7)	1.491(5)	O(3)–P(1)–O(2)	113.4(3)
P(3)–O(9)	1.496(5)	O(3)–P(1)–O(1)	107.5(3)
P(3)–O(8)	1.519(4)	O(2)–P(1)–O(1)	114.8(3)
P(4)–O(11)	1.487(5)	O(6)–P(2)–O(5)	114.0(3)
P(4)–O(12)	1.498(5)	O(6)–P(2)–O(4)	108.3(3)
P(4)–O(10)	1.529(5)	O(5)–P(2)–O(4)	112.0(3)
		O(7)–P(3)–O(8)	114.6(3)
		O(9)–P(3)–O(8)	107.6(3)
		O(11)–P(4)–O(12)	113.7(3)
		O(11)–P(4)–O(10)	111.6(3)
		O(12)–P(4)–O(10)	111.2(3)

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

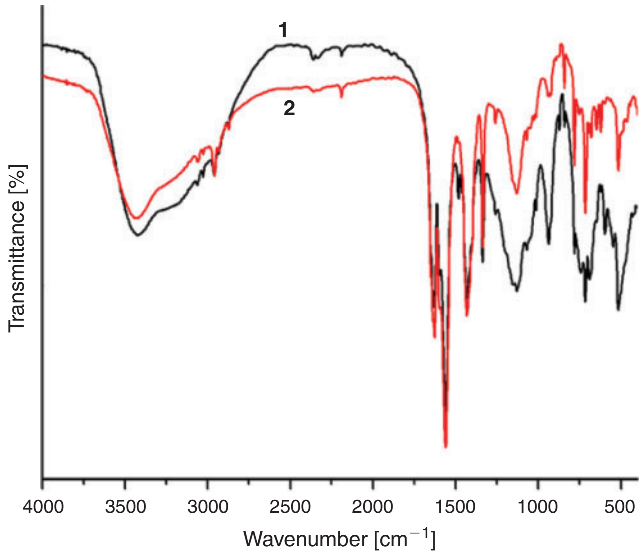

Fig. 1. IR spectra of **1** and **2**.

Crystal Structure

*[H_2hpip][$Zn_2(HPO_3)_3$] (**1**)*

Single-crystal XRD analysis reveals that compound **1** crystallises in the monoclinic $P2_1/n$ (no. 14) space group, and the asymmetric unit contains two distinct tetrahedrally coordinated Zn atoms, three pseudo-pyramidally coordinated P atoms, nine oxygen atoms, and one [H_2hpip]$^{2+}$ cation (Fig. 2a). Both zinc atoms are tetrahedrally coordinated by oxygen atoms with Zn–O bond lengths in the range of 1.902(4)–1.979(3) Å and O–Zn–O angles lying between 98.91(17)° and 117.11(18)°. Of the three P atoms, the P(2) and P(3) atoms each make three P–O–Zn linkages with adjacent Zn atoms, leaving the fourth vertex occupied by a terminal hydrogen atom, while the P(1) atom only makes two P–O–Zn linkages with the remaining two vertexes occupied by terminal hydrogen and oxygen atoms, respectively. Bond valence sum values[36] indicate that the terminal P(1)–O(1) linkage with a relatively shorter distance of 1.509(4) Å is a P=O double bond. Thus, considering the usual valence of Zn, P, O, and H to be +2, +3, −2, and +1 respectively, the composition of [$Zn_2(HPO_3)_3$] creates a net charge of −2, which should be compensated by one diprotonated [H_2hpip]$^{2+}$ cation. The P–O distances are in the range of 1.487(4)–1.514(4) Å (av. 1.503 Å), and the O–P–O bond angles are in the range of 109.7(2)°–113.3(3)° (av. 110.5°).

The inorganic framework of **1** is built up from strictly alternating ZnO_4 and HPO_3 units connected through their vertices, forming a 2D layered structure. Interestingly, such an inorganic layer can be understood to be constructed from ladder-like chains which consist of triple-fused 4-rings and HPO_3 units. As shown in Fig. 2b, the linkages between Zn(1)O3, Zn(2)O3, P(1)O_3H, and P(3)O_3H units form the triple corner-sharing 4-ring building units, which are alternatively bridged by P(2)O_3H nodes to give an infinite one-dimensional ladder-like chain. These ladders are then further linked with each other via Zn–O–P linkages to generate a 2D layer with 4- and 8-ring windows (Fig. 2c). The 8-ring window, delimited by four ZnO_4 tetrahedra and four HPO_3 pseudo pyramids, is severely puckered and has a pore size of ~4.2 × 6.8 Å (1.4 Å was used as the van der Waal radius of the oxygen atom). In the construction of the 2D structure, P(2) and P(3) atoms function as 3-connected

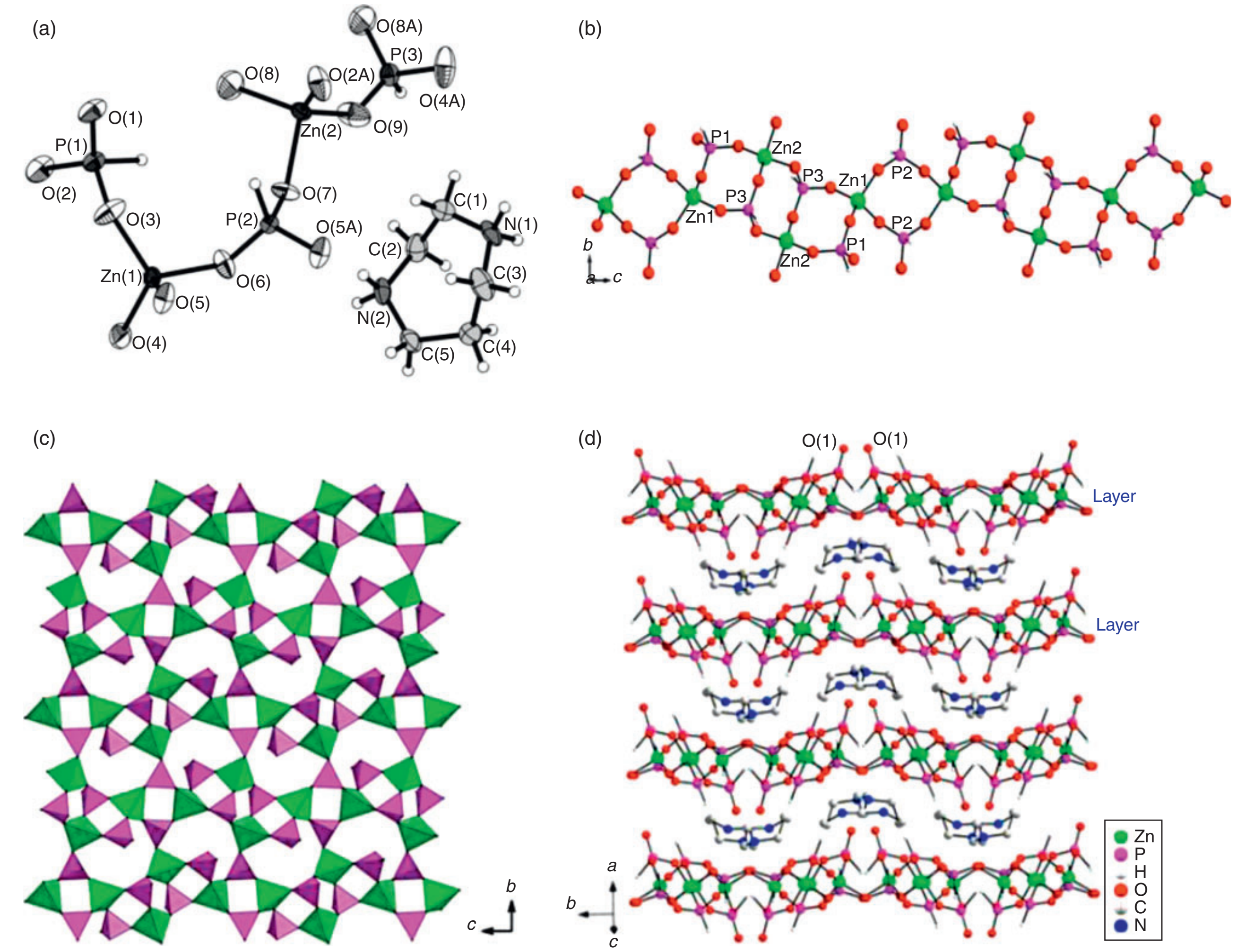

Fig. 2. (a) *ORTEP* plot of the molecular structure of **1**, drawn at the 50 % probability level. (b) View of the ladder-like chain constructed from triply-fused 4-rings and HPO_3 units. (c) Polyhedral view of the 2D layer along the [100] direction with 8-ring windows. (d) View of the packing of the sheets along the [100] direction and the location of homopiperazine cations. Colour code: ZnO_4 tetrahedra, green; HPO_3 pseudopyramids, purple.

nodes and P(1) only serves as a 2-connected node. Obviously, the presence of terminal P(1)=O(1) groups hinders the expansion of such layers into a higher-dimensional architecture. As shown in Fig. 2d, adjacent layers are stacked in an –AAAA– sequence along the *a*-axis and are further interconnected by extensive and strong H-bonding interactions (N(1)–H(1C)$\cdots$O(7) = 2.766(5) Å, N(1)–H(1D)$\cdots$O(1) = 2.683(6) Å, N(2)–H(2C)$\cdots$O(5) = 2.832(6) Å, N(2)–H(2D)$\cdots$O(1) = 2.706(6) Å) to generate a 3D supramolecular network. A void space analysis using the program *PLATON* indicates that the extra-framework organic cations in **1** occupy 39.0 % of the unit cell volume.

[H₂hpip][Zn₃(HPO₃)₄] (**2**)

Compound **2** crystallises in the triclinic, *P*-1 space group. The asymmetric unit consists of 26 independent non-hydrogen framework atoms, of which 19 atoms belong to the host framework and the remaining 7 atoms belong to the guest amine molecule (Fig. 3a). All the zinc atoms are tetrahedrally coordinated by oxygen atoms, and each makes four links with adjacent phosphorus atoms via Zn–O–P linkages. The four unique phosphorus atoms each share three oxygen atoms with adjacent zinc atoms, with the fourth vertex occupied by a terminal hydrogen atom. The Zn–O bond lengths are in the region of 1.910(5)–1.956(5) Å (av. 1.929 Å) and the P–O distances vary from 1.487(5) to 1.529(5) Å (av. 1.504 Å). These geometrical parameters of ZnO_4 and HPO_3 groups are typical of those observed in other open framework zinc phosphites. The composition of $[Zn_3(HPO_3)_4]$ creates a net charge of −2, which is also balanced by one diprotonated $[H_2hpip]^{2+}$ cation per formula unit.

The framework structure of **2** is also built up from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudopyramids via vertex-sharing. Different from the two-connected mode adopted by one HPO_3 unit in **1**, all phosphite groups in **2** are three-connected and thus vertex-linking the four-connected ZnO_4 groups to yield a unique (3,4)-connected three-dimensional architecture. Fig. 3b shows the single inorganic layer containing 12-membered apertures, viewed down the [001] direction. The 12-ring window was defined by six ZnO_4 tetrahedra and six HPO_3 pseudopyramids, with a free diameter size of ~5.9 × 11.0 Å. Such inorganic layers are stacked in an –ABAB– stacking sequence along the [001] direction to generate a complex 3D open-framework (Fig. 3c). Obviously, the elliptical 12-ring channels in **2** are not straight along the [001] direction and they propagate in a zig-zag way and are simultaneously intersected by 8-ring channels along the [100] direction and 12-ring channels along the [010] direction (Fig. 3d–f). Four

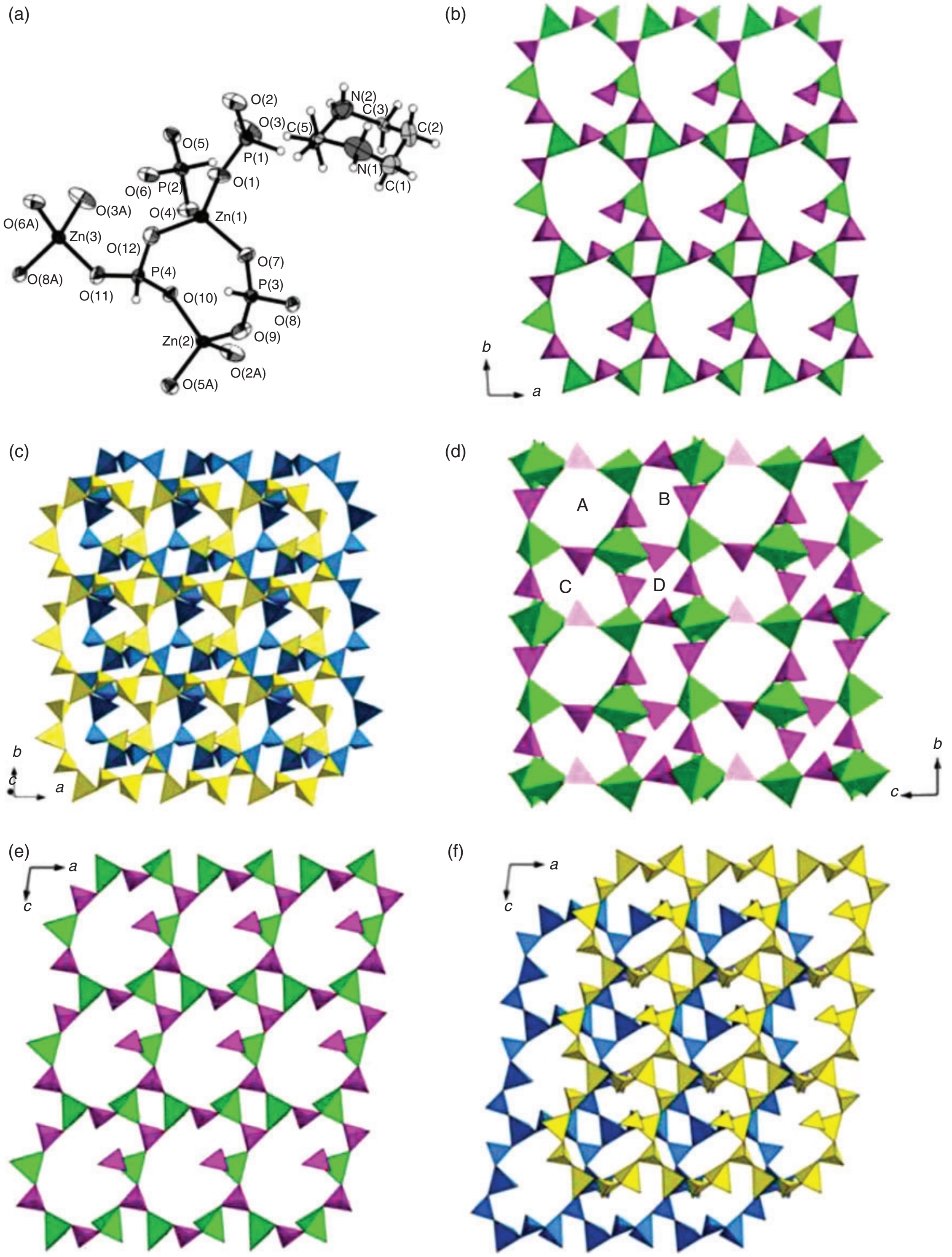

Fig. 3. (a) *ORTEP* plot of the molecular structure of **2**, drawn at the 50 % probability level. (b, c) Polyhedral view of the single layer along the [001] direction with 12-ring windows, and the stacking of the sheets. (d) Polyhedral view of the inorganic layer along the [100] direction containing four types of 8-ring channels. (e, f) View of the inorganic layer with 12-ring windows along the [010] direction, and the stacking of the sheets.

types of 8-ring windows (type A, B, C, and D) coexist in the [100] direction, and their shapes and pores are quite different. Due to various degrees of the phosphite P–H bonds protruding into the channels, the free pore size of the 8-ring aperture in type A is $\sim 9.0 \times 5.6$ Å, slightly larger than those in type B ($\sim 8.5 \times 4.9$ Å), C ($\sim 7.2 \times 5.8$ Å), and D ($\sim 8.0 \times 4.0$ Å). Compared with other reported metal phosphites with 12-ring channels, the simultaneous occurrence of four types of 8-ring channels intersecting the large 12-ring apertures in one direction is unique and, to the best of our knowledge, observed here for the first time. In addition, it is worthy to note that the 12-ring channels along the [010] direction are also not straight and run in a zig-zag way. The framework density (FD, defined as the number of polyhedra per 1000 Å^3) of **2** is 15.4. The guest

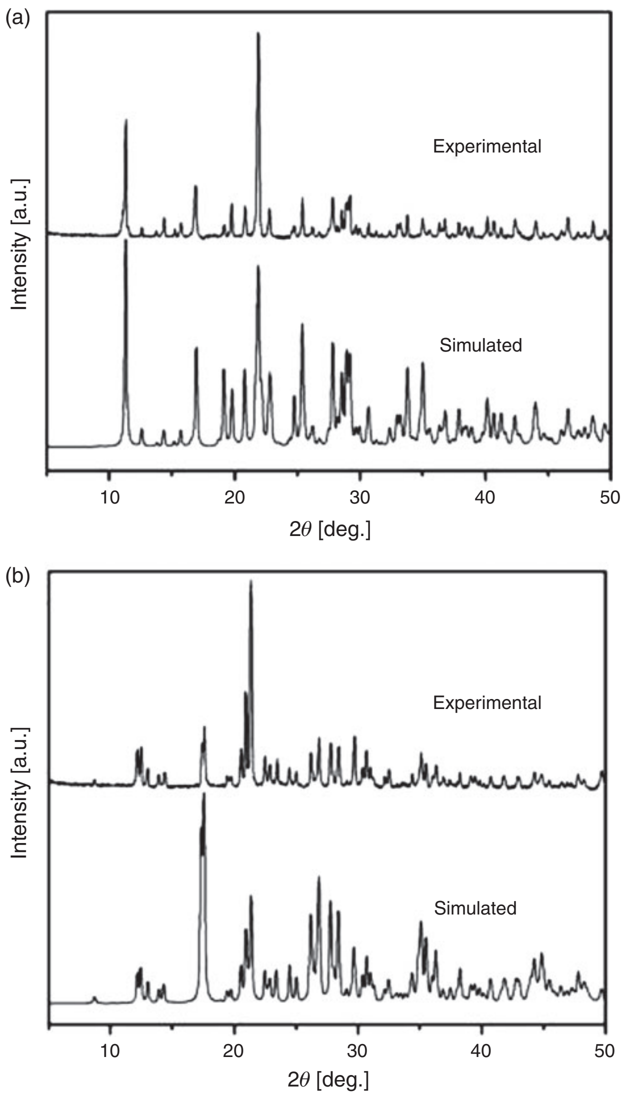

Fig. 4. Simulated and experimental X-ray powder diffraction patterns of compounds **1** (a) and **2** (b).

$[H_2hpip]^{2+}$ cations are found perfectly arranged in the middle region of the 12-ring channels and interact with the framework oxygen atoms through weak hydrogen bonds (N(2)–H(2C)$\cdots$O(10) = 2.802(7) Å, N(2)–H(2D)$\cdots$O(1) = 2.910(7) Å]. A void space analysis using the program *PLATON* indicates that the extra-framework organic cations in **2** occupy 33.1 % of the unit cell volume.

Power X-Ray Diffraction and TGA

In order to study the phase purity of **1** and **2**, their powder X-ray diffraction (PXRD) analysis were performed at room temperature. As shown in Fig. 4, the PXRD profiles of compounds **1** and **2** are in good agreement with the simulated patterns from single crystal X-ray structure data, indicating the purity of the as-synthesised samples.

TGA of the powder samples of **1** and **2** were performed under a flow of N_2 to investigate their thermal stabilities. As shown in Fig. 5, the structures of **1** and **2** remain stable up to 202 and 295°C, respectively. On further heating, both compounds show similar thermal behaviours and undergo continuous sharp weight losses. The total weight losses of 22.17 % in the temperature range 202–645°C for **1** and 17.36 % in the range 295–605°C for **2** correspond well with the loss of organic hpip molecules in the products (calculated 21.57 % for **1** and 16.65 % for **2**). The residues are amorphous after the calcination and their phases are unidentified.

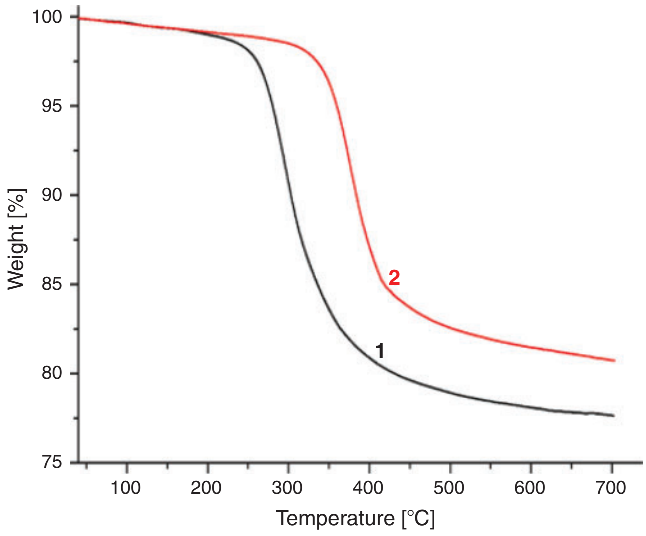

Fig. 5. Thermogravimetric curves of compounds **1** and **2**.

Conclusion

In summary, two new organically templated zinc phosphites, $[H_2hpip][Zn_2(HPO_3)_3]$ (**1**) and $[H_2hpip][Zn_3(HPO_3)_4]$ (**2**), have been made in the presence of the same homopiperazine template. Both compounds are constructed from the ZnO_4 tetrahedra and HPO_3 pseudopyramids. In the structure of **1**, the HPO_3 units make two or three linkages to adjacent zinc atoms to form a 2D layered structure with 8-membered ring windows. For **2**, however, each HPO_3 group shares three corners with adjacent ZnO_4 tetrahedra, producing a (3,4)-connected 3D architecture with intersecting 8- and 12-ring channels. The simultaneous occurrence of four types of 8-ring channels along one direction in the open structure of compound **2** is first observed in zinc phosphites here. The striking feature of our investigation is the construction of structurally complex open-framework metal phosphites with different dimensionality by subtly adjusting the synthetic conditions. In this case, the effect of the pH value may be critical to the formation of final frameworks. Further study of the correlation between the synthesis conditions and the final products is in progress.

Acknowledgements

This work was supported by the NNSF (20901043), A Project of Shandong Province Higher Educational Science and Technology Program (J13LD18), the Young Scientist Foundation of Shandong Province (BS2009CL041), the Development Project of Qingdao Science and Technology (13-1-4-187-jch), and Taishan Scholar Program.

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