# [Ni(C₆N₂H₁₄)₂][Zn₄(H₂O)(HPO₃)₅]: A new open-framework zinc phosphite with intersecting 8-, 12- and 16-ring channels

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## Abstract

A new three-dimensional (3-D) zinc phosphite with Zn/P ratio of 4/5, [Ni(C₆N₂H₁₄)₂][Zn₄(H₂O)(HPO₃)₅] (**1**), has been prepared by using self-assembled nickel complexes as the structure-directing agents. Its structure is built up from strict alternation of ZnO₄ tetrahedra and HPO₃ pseudo-pyramids, resulting in an open framework with multi-directional intersecting 8-, 12- and 16-ring channels. The unique nickel complexes Ni(DACH)₂ (DACH = 1,2-diaminocyclohexane) only involving the *cis*-DACH acting as ligands are self-assembled under hydrothermal conditions, and act as the structure-directing agents (SDAs) to direct the formation of compound **1**. Nickel complexes reside in the channels in a manner that the hydrophobic ends of the *cis*-DACH molecules exclusively protrude into the 16-ring pores and the amino groups closely interact with the charged inorganic framework through weak H-bonds. The interesting arrangements of nickel complexes imply a feasible approach to the design and synthesis of extra-large pore materials.
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*Keywords:* Open framework; Zinc phosphite; Nickel complex; Hydrothermal synthesis; Crystal structure

## 1. Introduction

Open-framework metal phosphates have been extensively studied due to their rich structural chemistry and potential applications in the catalysis, separation and ion-exchange processes [1–3]. In particular, the replacement of tetrahedral phosphate groups by pyramidal phosphite units has resulted in a new class of metal phosphite compounds with interesting structural architectures, such as clusters, chains or ladders, layers and three-dimensional (3-D) open-framework structures [4–23]. It is noted that zinc phosphites constitute an important class in the family of metal phosphites. Since the first discovery of zinc phosphites, ZnCa(HPO₃)₂(H₂O)₂ and ZnSr(HPO₃)₂(H₂O)₂, by Clearfield et al. [4] in 1990, more than 30 zinc phosphites with novel structures have been prepared hydrothermally in the presence of various organic amines or metal complexes as the structure-directing agents (SDAs) [9–23]. In general, their inorganic frameworks are built up from Zn-centered tetrahedra (ZnO₄, ZnO₃N) and P-centered HP^{III}O₃^{2−} pseudo-pyramids. Interestingly, the incorporating pyramidal units [HPO₃]^{2−} into the framework can partially reduce the connection of M–O–P, and thus may generate a more open framework structure. Up to now, four extra-large pore zinc phosphites have been prepared successfully, including [(CN₄H₇)₂][Zn₃(HPO₃)₄] [11], [(C₅NH₁₂)₂][Zn₃(HPO₃)₄] [12], [Ni(C₄N₃H₁₃)(H₂O)][Zn₂(HPO₃)₃] [19] and [Zn(H₂O)₆][Zn₃(HPO₃)₄] [22], all of which contain 16-ring channels.

The use of metal complexes as SDAs is promising for the design and synthesis of new open-framework compounds with unusual architectures. The metal complexes with large size favor the formation of large pore materials, for example [NiGe₁₄O₂₄(OH)₃]·2Ni(L)₃ (L = en or enMe) (FJ-1) with 24-ring channels [24]. Furthermore, the employment of chiral metal complexes as SDAs may lead to open frameworks with chiral features [25,26]. Up to date, however, open-framework metal phosphites templated by metal complexes are rare [19–21].

In this work, we present a new extra-large pore zinc phosphite, [Ni(C₆N₂H₁₄)₂][Zn₄(H₂O)(HPO₃)₅] (**1**), containing

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multi-directional intersecting 8-, 12- and 16-ring channels. The unique Ni(DACH)$_2$ (DACH = 1,2-diaminocyclohexane) complexes are self-assembled under hydrothermal conditions and act as SDAs to direct the formation of compound **1**.

## 2. Experimental section

### 2.1. Materials and methods

All reagents were purchased commercially and used without further purification. The X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). All the diffraction data were obtained by varying $2\theta$ from 4° to 40° with a step scan of 0.02°, at an X-ray tube voltage of 40 kV and a current of 30 mA. The time spent for collecting all the data was 3 h. 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 the air with a heating rate of 20 °C/min.

### 2.2. Synthesis of [Ni(C$_6$N$_2$H$_{14}$)$_2$][Zn$_4$(HPO$_3$)$_5$(H$_2$O)], (1).

In a typical synthesis of **1**, a reaction mixture of ZnO (0.36 g) and NiCl$_2 \cdot$6H$_2$O (0.79 g) were first dissolved in H$_2$O (10 mL), and then DACH (1.00 mL) was added with stirring under ambient conditions. Finally, H$_3$PO$_3$ (0.545 g) was added to the above reaction mixture. A homogeneous gel with a pH value about 6.5 was formed after stirring for 2 h. The mixture was sealed in a teflon-lined stainless-steel autoclave and heated at 160 °C for 5 days under static condition. The solid product consisting of large single crystals in the form of yellow prisms was obtained by filtration, washed by distilled water and then dried in the oven at 100 °C. The ICP and elemental analysis results of **1** were consistent with the theoretical values based on the crystal data. Calc: Zn, 27.05; Ni, 6.07; P, 16.02; C, 14.91; H, 3.65; N, 5.80 wt%. Found for **1**: Zn, 26.78; Ni, 5.85; P, 15.71; C, 14.80; H, 3.52; N, 5.90 wt%.

### 2.3. Determination of crystal structure

A suitable crystal with dimensions $0.20 \times 0.15 \times 0.10$ mm$^3$ for **1** was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Siemens SMART CCD diffractometer using graphite-monochromatic Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at a temperature of $20 \pm 2$ °C. Data processing was accomplished with the SAINT processing program [27] and the structure was solved by direct methods with the SHELXTL software package [28]. The zinc, nickel and phosphorus atoms were determined directly, and carbon, nitrogen and oxygen were subsequently found in the difference Fourier map. The P(3) atom was found to be disordered with half occupancy, similar to (H$_2$tmdp)[Zn$_3$Ga$_6$O(HPO$_4$)

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

| | |
|---|---|
| Empirical formula | C$_{12}$H$_{35}$N$_4$NiO$_{16}$P$_5$Zn$_4$ |
| Formula weight | 966.48 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, $C2/c$ |
| Unit cell dimensions | $a = 22.139(4)$ Å,  $\alpha = 90°$ |
| | $b = 13.661(3)$ Å,  $\beta = 90.06(3)°$ |
| | $c = 10.481(2)$ Å,  $\gamma = 90°$ |
| Volume | 3169.9(11) Å$^3$ |
| Z, calculated density | 4, 2.025 Mg/m$^3$ |
| Absorption coefficient | 3.889 mm$^{-1}$ |
| F(000) | 1944 |
| Crystal size | $0.20 \times 0.15 \times 0.10$ mm$^3$ |
| Theta range for data collection | 1.75–28.16° |
| Limiting indices | $-27 \leqslant h \leqslant 28, -17 \leqslant k \leqslant 16, -13 \leqslant l \leqslant 12$ |
| Reflections collected/unique | 9344/3504 [$R$(int) = 0.0718] |
| Completeness to theta = 27.89 | 90.1% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3504/0/216 |
| Goodness-of-fit on $F^2$ | 1.092 |
| Final $R$ indices [$I > 2\sigma(I)$]$^a$ | $R_1 = 0.0469$, w$R_2 = 0.1309$ |
| $R$ indices (all data) | $R_1 = 0.0554$, w$R_2 = 0.1352$ |
| Largest diff. peak and hole | 1.288 and $-0.591$ e Å$^{-3}$ |

$^a R_1 = \sum ||F_o| - |F_c||/ \sum |F_o|$, w$R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/ \sum[w(F_o^2)^2]\}^{1/2}$.

$(PO_4)] \cdot 5H_2O$ (NTHU-4) [29], so the H atom associated with P(3) atom was not located. Other H atoms of $HPO_3$ groups were found in the final difference Fourier map. The O(1) atom near P(3) and Zn(1) atoms was also disordered over two positions O(1) and O(1)′, which cannot exist together. The coordinated water molecule could be either O(1) or O(1)′. Water molecule is only linked to Zn(1) and cannot be linked to P(3) which moreover will be absent (half occupancy rate). The H atoms of water molecule were not located because of the disorder [30]. The H atoms residing on the DACH molecules were placed geometrically. All non-hydrogen atoms were refined with anisotropic thermal parameters. Experimental details for the structure determination are presented in Table 1.
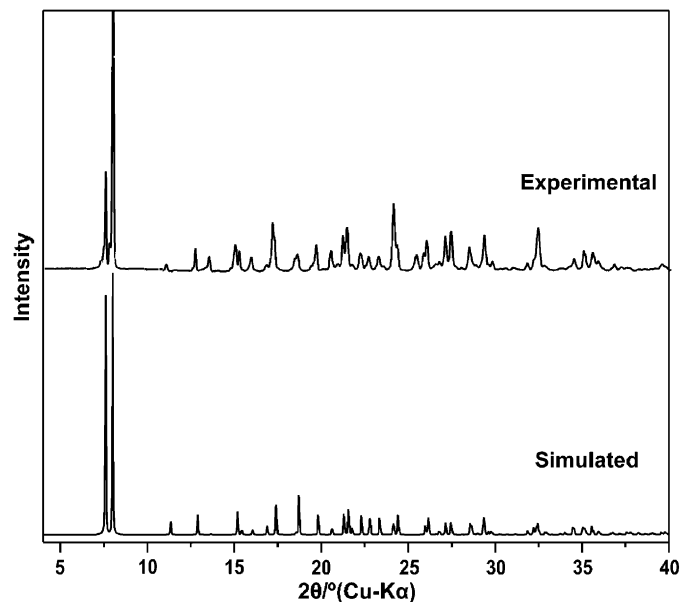


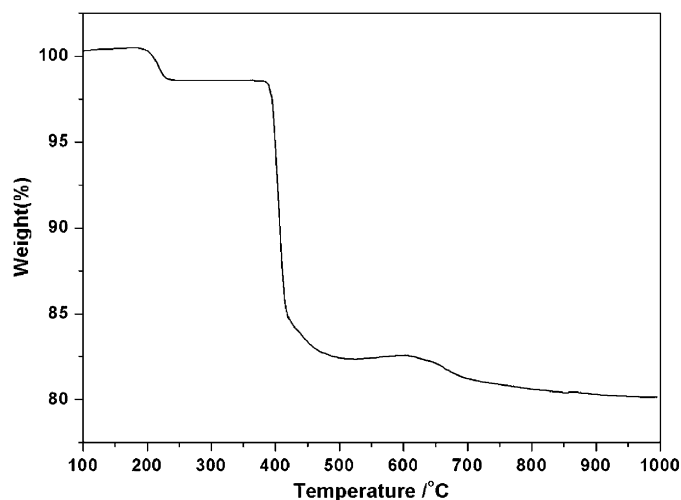Fig. 1. Simulated and experimental XRD patterns for **1**.



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

## 3. Results and discussion

### 3.1. Characterization

As seen in Fig. 1, the powder XRD pattern of **1** is consistent with the simulated one generated on the basis of single-crystal structural data, indicating the purity of the as-synthesized product. The differences in reflection intensity are probably due to preferred orientations in the powder sample.
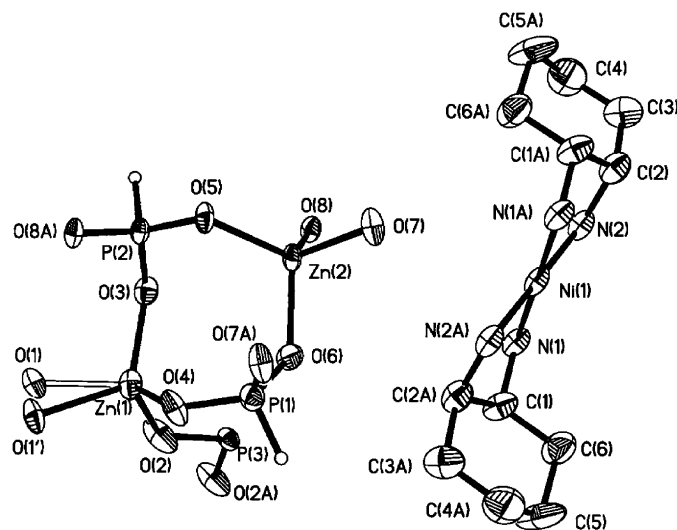


Fig. 3. Thermal ellipsoid plot (50%) for **1** showing the asymmetric unit and atomic labeling scheme.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**

|        | $x$      | $y$      | $z$       | $U$ (eq) |
|--------|----------|----------|-----------|----------|
| Zn(1)  | 3984(1)  | 406(1)   | 6886(1)   | 45(1)    |
| Zn(2)  | 2571(1)  | 1113(1)  | 4473(1)   | 34(1)    |
| Ni(1)  | 2500     | 2500     | 0         | 43(1)    |
| P(1)   | 3502(1)  | 2362(1)  | 5814(1)   | 43(1)    |
| P(2)   | 2643(1)  | −204(1)  | 6803(1)   | 32(1)    |
| P(3)   | 4724(1)  | 273(2)   | 4354(2)   | 37(1)    |
| O(1)   | 4134(5)  | −280(20) | 8442(17)  | 82(7)    |
| O(1′)  | 4249(7)  | 334(15)  | 8734(8)   | 53(5)    |
| O(2)   | 4658(2)  | 148(5)   | 5843(4)   | 85(2)    |
| O(3)   | 3284(2)  | −351(3)  | 6347(3)   | 45(1)    |
| O(4)   | 3762(2)  | 1768(3)  | 6902(4)   | 55(1)    |
| O(5)   | 2310(2)  | 590(3)   | 6088(3)   | 43(1)    |
| O(6)   | 3353(2)  | 1756(3)  | 4641(3)   | 49(1)    |
| O(7)   | 2031(2)  | 2050(3)  | 3712(4)   | 57(1)    |
| O(8)   | 2602(2)  | 54(2)    | 3238(3)   | 37(1)    |
| C(1)   | 3755(3)  | 2621(5)  | 220(6)    | 64(2)    |
| C(2)   | 1462(3)  | 2213(5)  | −1566(6)  | 62(2)    |
| C(3)   | 1077(4)  | 1488(7)  | −2306(8)  | 83(2)    |
| C(4)   | 921(5)   | 618(8)   | −1632(10) | 107(3)   |
| C(5)   | 4369(5)  | 4149(9)  | 319(11)   | 123(4)   |
| C(6)   | 3916(4)  | 3535(7)  | −457(8)   | 87(2)    |
| N(1)   | 3286(2)  | 2035(3)  | −456(4)   | 49(1)    |
| N(2)   | 2112(2)  | 1928(3)  | −1460(4)  | 49(1)    |

Thermogravimetric curve of **1** is shown in Fig. 2, which exhibits three stages of weight loss in a total of 20.02 wt% around 195–1000 °C. The first weight loss of 1.61 wt% at 195–250 °C corresponds to the loss of the coordinated water molecules (calc. 1.86 wt%). The weight loss of 18.41 wt% in the range of 250–1000 °C is attributed to the decomposition of DACH molecules (calc. 23.59 wt% for two DACH molecules per formula unit), the dehydration (calc. 4.66 wt% for two and half of water molecules per formula unit), and the weight increase due to aerial oxidation of phosphite to phosphate (calc. 8.28 wt%) [19,31]. XRD analysis indicates that the structure of **1** becomes amorphous after the decomposition of DACH molecules above 400 °C.

## 3.2. Structure determination of 1

Single-crystal X-ray diffraction analysis reveals that **1** has an empirical formula of $[Ni(C_6N_2H_{14})_2][Zn_4(H_2O)$ $(HPO_3)_5]$. The asymmetric unit of **1**, as seen in Fig. 3, contains two crystallographically distinct Zn atoms, one distinct Ni atom, and three distinct P atoms in which P(3) is disordered with half occupancy. The Zn(1) atom is tetrahedrally coordinated by four O atoms [Zn(1)–O: 1.883(4)–2.026(10) Å]. Because of disorders of O(1), O(1)′ and P(3) atoms, there are two surroundings for Zn(1) atom. One is that O(1) (or O(1)′) is coordinated water connected with Zn(1) atom to form $ZnO_3(H_2O)$ tetrahedron, and P(3) and O(1)′ (or O(1)) atoms are absent. The other is O(1) (or O(1)′) is bridging oxygen connected with Zn(1) and P(3) atoms to form $ZnO_4$ tetrahedron, and O(1)′(or O(1)) is absent. The Zn(2) atom connects four oxygen atoms with adjacent P atoms, the Zn(2)–O bond lengths are within the range of 1.925(4)–1.949(4) Å and O–Zn(2)–O angles are in the range of 103.98(16)– 115.11(17)°. All P atoms share three O atoms with nearby Zn atoms [P–O: 1.488(9)–1.617(12) Å], leaving terminal P–H bonds [P–H: 1.27(5)–1.36(4) Å]. The P–O bond

Table 3
Selected bond lengths (Å) and bond angles (deg.) for **1**

| | | | |
|---|---|---|---|
| Zn(1)–O(2) | 1.883(4) | P(2)–O(3) | 1.512(4) |
| Zn(1)–O(1) | 1.913(9) | P(2)–O(5) | 1.510(3) |
| Zn(1)–O(4) | 1.924(4) | P(2)–O(8)#3 | 1.521(3) |
| Zn(1)–O(3) | 1.947(4) | P(2)–H(2) | 1.36(4) |
| Zn(1)–O(1′) | 2.026(10) | P(3)–O(1′)#4 | 1.488(9) |
| Zn(2)–O(7) | 1.925(4) | P(3)–O(2)#5 | 1.500(5) |
| Zn(2)–O(5) | 1.927(3) | P(3)–O(2) | 1.577(5) |
| Zn(2)–O(8) | 1.942(3) | P(3)–O(1)#4 | 1.617(12) |
| Zn(2)–O(6) | 1.949(4) | Ni(1)–N(1)#1 | 1.914(5) |
| P(1)–O(7)#2 | 1.511(4) | Ni(1)–N(1) | 1.914(5) |
| P(1)–O(4) | 1.514(4) | Ni(1)–N(2) | 1.920(5) |
| P(1)–O(6) | 1.518(4) | Ni(1)–N(2)#1 | 1.920(5) |
| P(1)–H(1) | 1.27(5) | | |
| N(1)#1–Ni(1)–N(2) | 85.9(2) | O(4)–P(1)–H(1) | 107(2) |
| N(1)–Ni(1)–N(2) | 94.1(2) | O(6)–P(1)–H(1) | 105(2) |
| N(1)#1–Ni(1)–N(2)#1 | 94.1(2) | O(5)–P(2)–O(3) | 113.4(2) |
| N(1)–Ni(1)–N(2)#1 | 85.9(2) | O(3)–P(2)–O(8)#3 | 112.8(2) |
| N(1)#1–Ni(1)–N(1) | 180.0(3) | O(5)–P(2)–O(8)#3 | 111.35(19) |
| N(2)–Ni(1)–N(2)#1 | 180.0(2) | O(3)–P(2)–H(2) | 105.8(18) |
| O(2)–Zn(1)–O(1) | 105.4(6) | O(5)–P(2)–H(2) | 104.9(18) |
| O(2)–Zn(1)–O(4) | 112.9(3) | O(8)#3–P(2)–H(2) | 108.0(19) |
| O(1)–Zn(1)–O(4) | 120.9(10) | O(1′)#4–P(3)–O(2)#5 | 111.8(9) |
| O(2)–Zn(1)–O(3) | 111.27(19) | O(1′)#4–P(3)–O(2) | 107.8(4) |
| O(1)–Zn(1)–O(3) | 97.0(6) | O(2)#5–P(3)–O(2) | 100.4(2) |
| O(4)–Zn(1)–O(3) | 108.22(16) | O(2)#5–P(3)–O(1)#4 | 131.2(5) |
| O(2)–Zn(1)–O(1′) | 108.5(3) | O(2)–P(3)–O(1)#4 | 120.7(7) |
| O(4)–Zn(1)–O(1′) | 96.4(5) | O(1′)#4–P(3)–P(3)#5 | 121.8(9) |
| O(3)–Zn(1)–O(1′) | 118.7(7) | O(1)#4–P(3)–P(3)#5 | 155.5(11) |
| O(7)–Zn(2)–O(5) | 115.11(17) | P(3)#3–O(1)–Zn(1) | 129.6(9) |
| O(7)–Zn(2)–O(8) | 103.98(16) | P(3)#3–O(1′)–Zn(1) | 130.4(7) |
| O(5)–Zn(2)–O(8) | 108.66(15) | P(3)#5–O(2)–Zn(1) | 151.1(4) |
| O(7)–Zn(2)–O(6) | 106.77(18) | P(3)–O(2)–Zn(1) | 129.0(3) |
| O(5)–Zn(2)–O(6) | 110.82(16) | P(2)–O(3)–Zn(1) | 125.8(2) |
| O(8)–Zn(2)–O(6) | 111.34(15) | P(1)–O(4)–Zn(1) | 127.5(2) |
| O(7)#2–P(1)–O(4) | 109.4(2) | P(2)–O(5)–Zn(2) | 123.8(2) |
| O(7)#2–P(1)–O(6) | 112.8(2) | P(1)–O(6)–Zn(2) | 120.7(2) |
| O(4)–P(1)–O(6) | 113.6(2) | P(1)#2–O(7)–Zn(2) | 134.5(2) |
| O(7)#2–P(1)–H(1) | 109(2) | P(2)#4–O(8)–Zn(2) | 124.1(2) |

Symmetry transformations used to generate equivalent atoms: #1 $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z$, #2 $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z+1$, #3 $x$, $-y$, $z+\frac{1}{2}$, #4 $x$, $-y$, $z-\frac{1}{2}$, #5 $-x+1$, $-y$, $-z+1$.

lengths are typical except for P(3)–O bonds [P(3)–O(1)′: 1.488(9) Å and P(3)–O(1): 1.617(12) Å]. This might be produced by the disorder of P(3) atom, similar to $C_{26}H_{45}N_4O_{42}Ga_6Zn_3P_9$ (NTHU-4Y) [29]. The existence of P–H bonds is also confirmed by the characteristic band of phosphite groups [$v$(H–P), 2379 cm$^{-1}$] in the IR spectrum [5–9]. The Ni atom locates at an inversion center. It coordinates with four nitrogen atoms of two DACH ligands to form a plane square configuration [Ni–N: 1.914(5)–1.920(5) Å]. Two DACH molecules in one metal complex have opposite chirality, that is one with (1*S*, 2*R*) configuration and the other with (1*R*, 2*S*) configuration. Although a mixture of *trans*- and *cis*-DACH is used in the synthesis, only the *cis*-DACH molecule acted as a bidentate ligand bonds to the Ni center. This is different from other known metal phosphates and phosphites involving the *trans*-DACH molecules as SDAs or organic ligands, such as zinc phosphate ND-1 [32] and zinc phosphate–phosphite ZnPO-CJ12 [18]. To our best knowledge, such metal complex Ni(DACH)$_2$ self-assembled under hydrothermal system firstly appears in the metal phosphates and metal phosphites. The atomic coordinates, and the selected bond lengths and angles of compound **1** are shown in Tables 2 and 3, respectively.

The structure of compound **1** is constructed from strict alternation of ZnO$_4$ and HPO$_3$ units to form a 3-D open framework. It has a new Zn/P stoichiometry of 4/5, distinct from those reported 1/1, 1/2, 2/3, 3/4 and 5/6 [9–23]. Fig. 4a shows the framework of **1** viewed along the [001] direction. Its structure can also be described on the base of 2-D sheets parallel to the *bc* plane. These inorganic sheets consisting of 4- and 12-rings (Fig. 4b) are stacked along the [100] direction and further connected with each other through oxygen atoms to generate the open-framework structure of **1**.

Of particular interesting is that compound **1** possesses multi-directional intersecting channels with 8-ring, 12-ring and 16-ring windows. The 16-ring channel running along the [001] direction is elliptical with an aperture of approximately 7.9 × 13.3 Å (O–O distance). Furthermore, there are multi-directional 12-ring channels in compound **1** with a pore diameter of 5.3 × 6.9 Å running along the [110], [1$\bar{1}$0], [10$\bar{1}$], [$\bar{1}\bar{1}$1] and [$\bar{1}$11] directions, and 1-D 8-ring channels along the [010] direction. Fig. 5 shows the 12-ring channels of **1** along the [110] direction. To our best knowledge, such multi-directional intersecting large channels are rarely observed in the inorganic materials. These channels are intersecting with each other, and the Ni(DACH)$_2$ complexes reside in the "free" space of the intersecting channels (as seen in Fig. 6). Strikingly, four DACH ligands of four nickel complexes are occluded in one 16-ring pores. They arrange in a manner that the hydrophobic ends of four DACH ligands exclusively protrude into the center of 16-ring pore, thus reducing the free spaces. While the hydrophilic amino groups closely interact with the charged inorganic framework
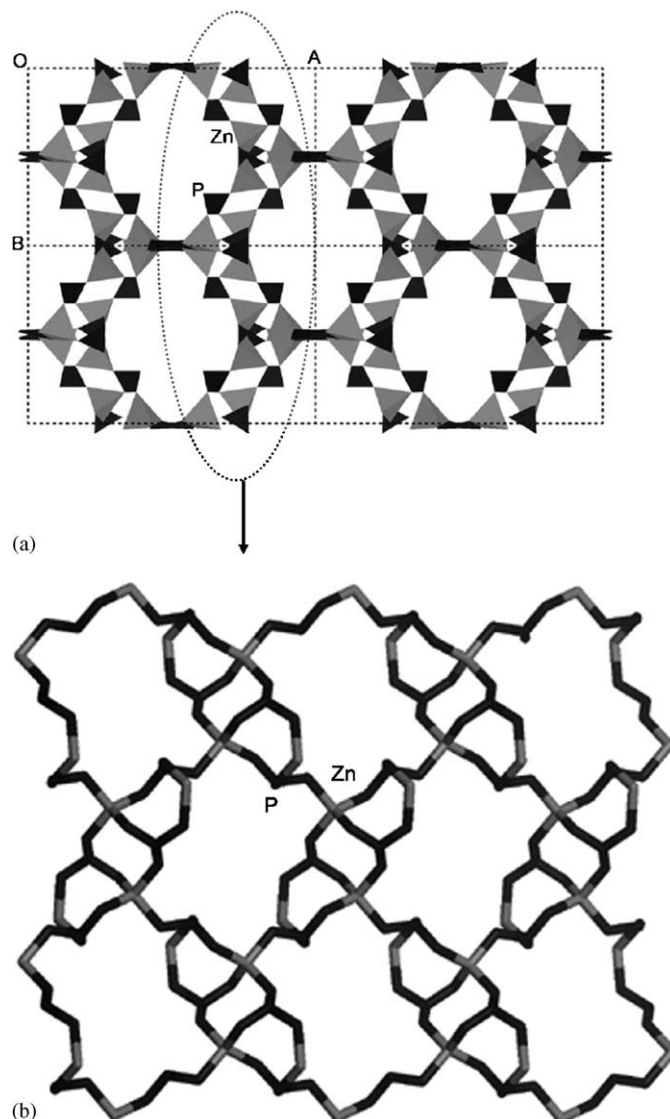


Fig. 4. (a) A polyhedral view of the framework of **1** along the [001] direction showing the 16-ring channels; (b) the zinc phosphite layer with 4.12-net along the [100] direction, all H atoms are omitted for clarity.

through weak H-bonds: N(1)–H(7A)···O(3): 2.977(6) Å, N(1)–H(7B)···O(4): 2.986(6) Å, and N(2)–H(8B)···O(8): 2.934(5) Å. The similar behavior has been found in other extra-large pore compounds, which include 24-ring zinc phosphate ND-1 templated by 1,2-DACH, 20-ring aluminophosphate JDF-20 templated by triethylamine, 16-ring gallophosphate ULM-16 templated by cyclopentylamine, etc. [32–34].

The openess of a structure is defined in terms of the number of polyhedral atom per 1000 Å$^3$, i.e. framework density (FD). The FD value of **1** is 11.25, similar to the values of 12.1 for Zn$_3$(PO$_4$)$_2$(PO$_3$OH)(C$_6$N$_2$H$_{16}$)·2H$_2$O (ND-1) with 24-ring channel [32] and 11.1 for [Ge$_9$O$_{17}$(OH)$_4$][N(CH$_2$CH$_2$NH$_3$)$_3$]$_{2/3}$[HCON(CH$_3$)$_2$]$_{1/6}$ (H$_2$O)$_{11/3}$ (FDU-4) with 24-ring channel [35].
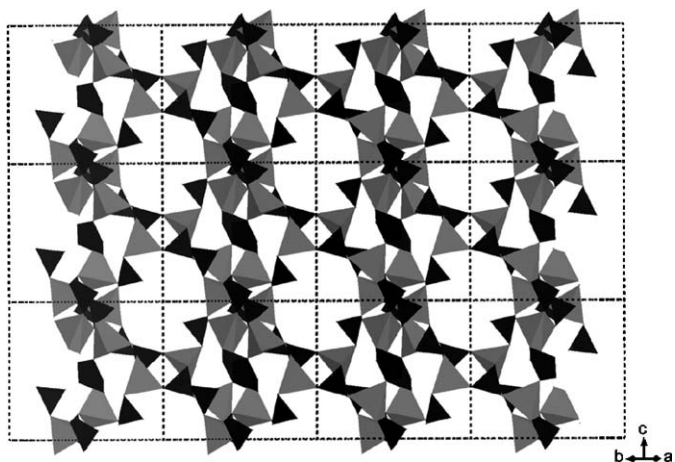
Fig. 5. A polyhedral view of the structure of **1** along the [110] direction showing the 12-ring channels.
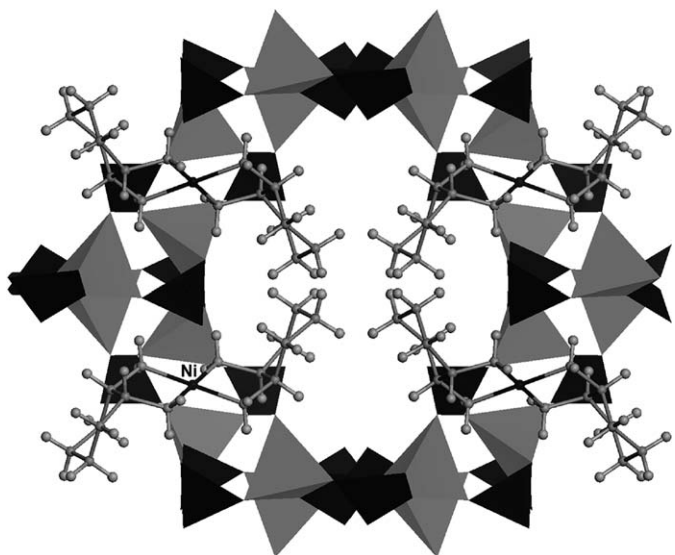
groups close interact with inorganic framework to form extensive H-bonds. The results imply a feasible method toward the synthesis of extra-large pore materials by using the bulky metal complexes acting as the SDAs.

### 4.1. Supporting information and structure details

Crystallographic data for the structure reported in this paper in the form of CIF file has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-292028 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

### Acknowledgment

### References

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Fig. 6. Four *cis*-1,2-diaminocyclohexane ligands of metal complexes reside in one 16-ring pore.

## 4. Conclusion

The hydrothermal synthesis and crystal structure of a novel open-framework zinc phosphite, [Ni(C$_6$N$_2$H$_{14}$)$_2$][Zn$_4$(H$_2$O)(HPO$_3$)$_5$] (**1**), has been described in this paper. The alternating connection of ZnO$_4$ tetrahedra and HPO$_3$ pseudo-pyramids results in the 3-D open framework of **1** processing multi-directional intersecting 8-, 12- and 16-ring channels. The Ni(DACH)$_2$ complexes with *cis*-DACH ligands and unique square configuration are self-assembled under hydrothermal system, and act as SDA molecules. They locate in the intersecting channels in an interesting manner that hydrophobic ends of four DACH ligands extend into the 16-ring pores and hydrophilic amino

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