

# Hydrothermal synthesis and characterization of a new inorganic–organic hybrid layered zinc phosphate–phosphite $(C_6H_{15}N_2)_2Zn_4(PO_4)_2(HPO_3)_2$

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Using  $H_3PO_3$  or  $H_3PO_2$  as a phosphorus source, the first inorganic–organic hybrid layered zinc phosphate–phosphite  $(C_6H_{15}N_2)_2Zn_4(PO_4)_2(HPO_3)_2$  (denoted ZnPO-CJ12) has been hydrothermally synthesized in the presence of 1,2-diaminocyclohexane (DACH) as a structure-directing agent. Single-crystal X-ray diffraction analysis shows that its structure is made up of inorganic–organic hybrid sheets containing both  $PO_4^{3-}$  and  $HPO_3^{2-}$  anions. Only the *trans*-isomers are involved in the structure even though a mix of *trans*- and *cis*-isomers of DACH molecules are added in the reaction mixture. The hydrophobic ends of the DACH molecules exclusively protrude into the interlayer region.

## Introduction

Following the discovery of microporous aluminophosphates in 1982,<sup>1</sup> the synthesis of new open-framework metal phosphates has attracted considerable attention because of their potential applications in catalysis, adsorption and separation. Among metal phosphates, zinc phosphates constitute an important family which exhibits a rich structural and compositional diversity. By using a hydrothermal synthesis technique, they have been prepared with three-dimensional (3D) open-frameworks, 2D layers, 1D chains and 0D clusters in the presence of organic amines, alkali metal cations or metal complexes as a structure-directing agent.<sup>2–16</sup> Notable examples are zinc phosphate ND-1 with 24-membered ring channels,<sup>8</sup> and chiral zinc phosphates  $[NH_3(CH_2)NH_2(CH_2)_2NH_3][Zn_4(PO_4)_3(HPO_4)] \cdot H_2O$ <sup>9</sup> and  $[Na_{12}(H_2O)_{12}][Zn_{12}P_{12}O_{48}]$ .<sup>13</sup>

In contrast to the large numbers of zinc phosphates, the reports on organically templated zinc phosphites are rare. So far, only three organically templated zinc phosphites have been reported. The zinc phosphites, typically built up by Zn-centered tetrahedra ( $ZnO_4$  and  $ZnO_3N$ ) and P-centered  $HPO_3$  pseudo pyramids, show interesting structural architectures. There are  $(NC_5H_{12})_2Zn_3(HPO_3)_4$  with 16-membered ring windows,<sup>17</sup> and  $(N_4C_2H_4)ZnHPO_3$ <sup>18</sup> and  $[H_2N(CH_2)_2NH_2]_{0.5}[ZnHPO_3]$ ,<sup>19</sup> both of which contain a similar 4.8-net.

In this work, using  $H_3PO_3$  or  $H_3PO_2$  as a phosphorus source, an interesting inorganic–organic hybrid layered zinc phosphate–phosphite  $(C_6H_{15}N_2)_2Zn_4(PO_4)_2(HPO_3)_2$  (denoted ZnPO-CJ12) has been hydrothermally synthesized in the presence of 1,2-diaminocyclohexane (DACH) as a structure-directing agent. To our knowledge, this compound is the first inorganic–organic hybrid metal phosphate–phosphite containing both  $PO_4^{3-}$  and  $HPO_3^{2-}$  anions. Interestingly, the title compound has certain molecule recognition ability for the *trans*- and *cis*-isomers of 1,2-DACH molecules. This phenomenon has also been noticed in the extra-large-pore zinc phosphate ND-1.<sup>8</sup>

## Results and discussion

ZnPO-CJ12 was crystallized in an aqueous system containing  $Zn(OAc)_2 \cdot 2H_2O$ ,  $H_3PO_3$  or  $H_3PO_2$ , and 1,2-diaminocyclohexane (DACH, a mixture of *cis*- and *trans*-isomers) at 200 °C. Both  $H_3PO_3$  and  $H_3PO_2$  could be used as the phosphorus source. Table 1 lists the synthesis conditions and results. ZnPO-CJ12 was crystallized in a pH value range of 6.5–8.0. Extra-large-pore zinc phosphate ND-1, which was reported to be prepared using  $H_3PO_4$  as a phosphorus source,<sup>8</sup> frequently coexisted with ZnPO-CJ12 in the products. The amount of  $H_3PO_3$ ,  $H_3PO_2$  and DACH determines the as-made products.

Table 1 Synthesis conditions and results

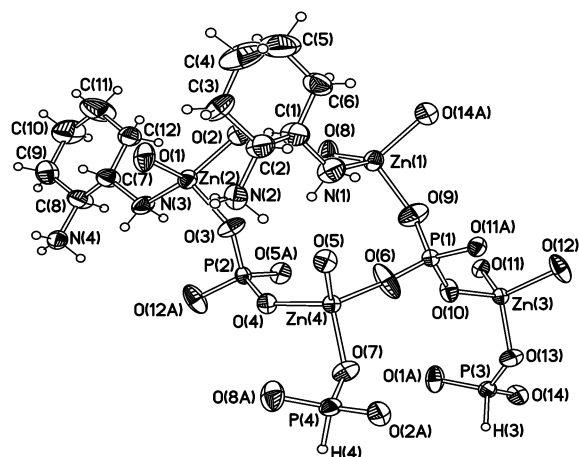
Run	Gel molar composition					Product
	Zn(OAc) <sub>2</sub>	H <sub>3</sub> PO <sub>2</sub> or H <sub>3</sub> PO <sub>3</sub>	DACH	H <sub>2</sub> O	pH	
1	1.0	1.0 <sup>a</sup>	1.0	488	7.0	ZnPO-CJ12, ND-1
2	1.0	1.0 <sup>a</sup>	2.0	488	7.5	ZnPO-CJ12, ND-1
3	1.0	1.0 <sup>a</sup>	3.0	488	8.0	ZnPO-CJ12
4	1.0	2.0 <sup>a</sup>	2.5	488	7.0	ZnPO-CJ12
5	1.0	3.0 <sup>a</sup>	2.0	488	6.5	ZnPO-CJ12, unidentified phase
6	1.0	3.0 <sup>a</sup>	3.0	488	7.5	ZnPO-CJ12, ND-1
7	1.0	1.0 <sup>b</sup>	1.0	488	7.0	ZnPO-CJ12, ND-1
8	1.0	1.0 <sup>b</sup>	2.0	488	7.0	ZnPO-CJ12, ND-1
9	1.0	3.0 <sup>b</sup>	2.0	488	6.5	ZnPO-CJ12, ND-1
10	1.0	3.0 <sup>b</sup>	3.0	488	7.0	ZnPO-CJ12
11	1.0	4.0 <sup>b</sup>	4.0	488	7.5	ZnPO-CJ12
12	1.0	4.0 <sup>b</sup>	5.0	488	7.5	ZnPO-CJ12, unidentified phase

<sup>a</sup>  $H_3PO_3$ . <sup>b</sup>  $H_3PO_2$ ; crystallization temperature: 200 °C; crystallization time: 8 days.

As seen in runs 1 and 2, using  $\text{H}_3\text{PO}_3$  as a phosphorus source, ZnPO-CJ12, coexisted with ND-1, was prepared in the gels with molar compositions 1.0  $\text{Zn}(\text{OAc})_2$ :1.0  $\text{H}_3\text{PO}_3$ :(1.0–2.0) DACH:488  $\text{H}_2\text{O}$  (pH: 7.0–7.5), while increasing the molar amount of DACH to 3.0 and keeping other conditions unchanged, pure ZnPO-CJ12 could be prepared in the gel with a pH value of 8.0. This indicates that a weak basic condition might be favorable for isolating ZnPO-CJ12 in the above gel system. Pure ZnPO-CJ12 could also be prepared using  $\text{H}_3\text{PO}_2$  as a phosphorus source in runs 10–11. ND-1 also frequently coexisted with ZnPO-CJ12 (runs 6–9). It is noticed that ZnPO-CJ12 contains both  $\text{PO}_4^{3-}$  and  $\text{HPO}_3^{2-}$  anions and that ND-1 contains only  $\text{PO}_4^{3-}$  anions. This indicates that part of  $\text{H}_2\text{PO}_3^-$  or  $\text{H}_2\text{PO}_2^-$  anions in the reaction mixture might be oxidized or disproportionated into  $\text{PO}_4^{3-}$  anions under hydrothermal condition.

Inductively coupled plasma (ICP) analysis of ZnPO-CJ12 shows that the as-made compound contains 31.2 and 14.8 wt% of Zn and P, respectively (calc. 31.08 and 14.73 wt%, respectively). Elemental analysis indicates that ZnPO-CJ12 contains 16.80, 3.76, 6.06 wt% of C, H and N, respectively (calc. 17.11, 3.80 and 6.65 wt%, respectively). The compositional analysis results are in agreement with those calculated values based on the empirical formula  $(\text{C}_6\text{H}_{15}\text{N}_2)_2\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_3)_2$  given by single-crystal structural analysis.

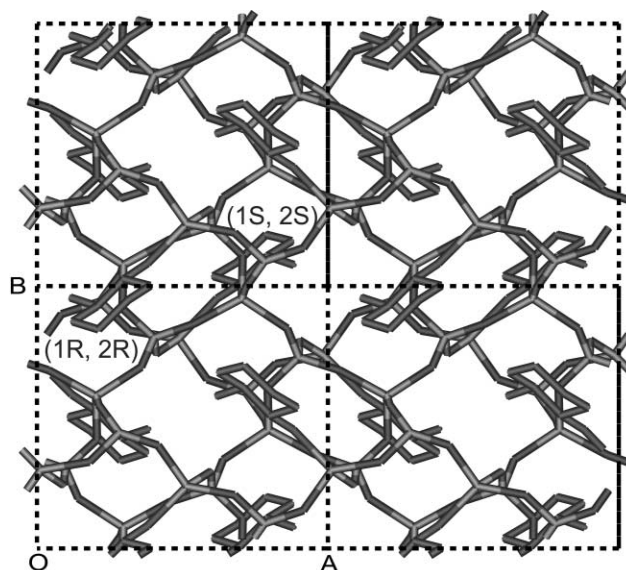
ZnPO-CJ12 crystallizes in the monoclinic space group  $P2_1/n$  (no. 14) with  $a = 9.7060(17)$  Å,  $b = 9.9929(16)$  Å,  $c = 27.557(5)$  Å and  $\beta = 96.795(3)^\circ$ . Selected bond lengths and angles are listed in Table 2. As seen in Fig. 1, each asymmetric unit



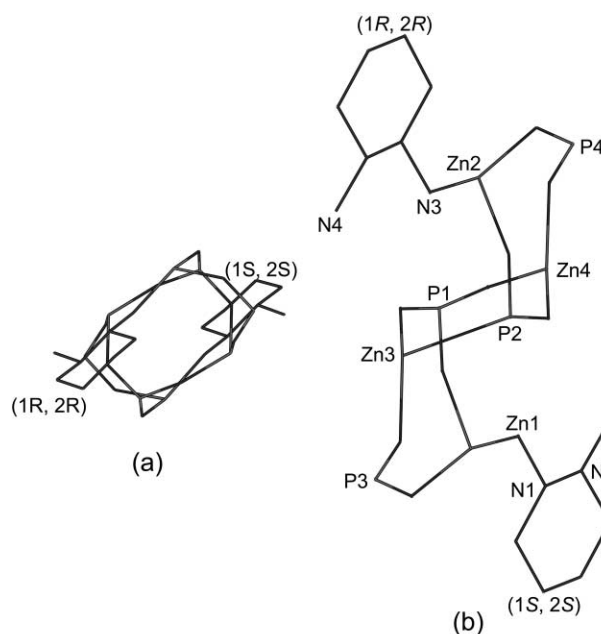
**Fig. 1** Thermal ellipsoid plot (50%) for ZnPO-CJ12 showing the atom labeling scheme.

contains four crystallographically distinct Zn atoms. Zn(1) and Zn(2) each is tetrahedrally coordinated and share three oxygen atoms with adjacent P atoms (Zn–O bond distances: 1.926–1.964 Å), with the fourth ligand being a Zn–N bond (2.001 and 2.005 Å, respectively). Zn–N bonds have been observed in reported zinc phosphites.<sup>18,19</sup> Zn(3) and Zn(4) each shares four oxygen atoms with adjacent P atoms (Zn–O bond distances: 1.907–1.957 Å). Of the four crystallographically distinct P atoms, P(1) and P(2) each share four oxygens with adjacent Zn atoms (P–O: 1.486–1.539 Å), whereas P(3) and P(4) each share three oxygens with adjacent Zn atoms (P–O: 1.499–1.523 Å), with the fourth ligand being a terminal P–H bond (1.31 and 1.33 Å, respectively). The existence of P–H bonds is also confirmed by the characteristic bands of phosphite anions [ $\nu(\text{H}-\text{P})$  2395  $\text{cm}^{-1}$ ] in the IR spectrum.<sup>20</sup> There are two crystallographically distinct monoprotonated DACH molecules in each asymmetric unit. One N atom in each DACH molecule coordinates to a Zn atom forming a Zn–N bond. It is noted that only the *trans*-isomers of the DACH molecules are involved in the structure of ZnPO-CJ12.

The alternation of Zn-centered tetrahedra and P-centered pseudo pyramids leads to a two-dimensional sheet structure. Fig. 2 shows the sheet structure viewed along the [001] direction. It contains a series of structural motifs, each of which is composed of three edge-sharing four-membered rings with two crystallographically distinct DACH molecules dangling at both ends (Fig. 3). The two DACH molecules in one structural motif



**Fig. 2** The puckered inorganic-organic hybrid sheet viewed along the [001] direction.



**Fig. 3** The characteristic structural motif composed of three edge-sharing four-membered rings with two pendant crystallographically distinct DACH molecules at both ends, (a) viewed along the [001] direction and (b) viewed along the [010] direction.

have opposite chirality, that is, one with (1*S*, 2*S*) configuration and the other with (1*R*, 2*R*) configuration. It is noted that those motifs with different orientations in the sheet are related by a  $2_1$  screw axis operation. Such structural motifs interconnect with each other via vertex oxygens forming a puckered sheet containing four-, six-, eight- and ten-membered rings.

Fig. 4 shows the packing of the sheets along the [001] direction. Two adjacent layers are related by the inversion centers. The configurations of the DACH molecules are indicated in the figure. Interestingly, the hydrophobic ends of the DACH molecules exclusively protrude into the interlayer

**Table 2** Selected bond lengths [Å] and angles [°] for ZnPO-CJ12

Bond lengths [Å]			
Zn(1)–O(8)	1.926(6)	Zn(1)–O(14) <sup>a</sup>	1.937(6)
Zn(1)–O(9)	1.964(6)	Zn(1)–N(1)	2.001(7)
Zn(2)–O(1)	1.930(6)	Zn(2)–O(2)	1.942(6)
Zn(2)–O(3)	1.962(6)	Zn(2)–N(3)	2.005(7)
Zn(3)–O(12)	1.907(6)	Zn(3)–O(10)	1.914(5)
Zn(3)–O(13)	1.930(5)	Zn(3)–O(11)	1.951(5)
Zn(4)–O(6)	1.912(6)	Zn(4)–O(7)	1.940(6)
Zn(4)–O(4)	1.942(5)	Zn(4)–O(5)	1.957(5)
P(1)–O(6)	1.486(6)	P(1)–O(9)	1.515(6)
P(1)–O(11) <sup>a</sup>	1.532(5)	P(1)–O(10)	1.539(6)
P(2)–O(12) <sup>b</sup>	1.502(6)	P(2)–O(4)	1.520(5)
P(2)–O(3)	1.526(6)	P(2)–O(5) <sup>c</sup>	1.530(5)
P(3)–O(1) <sup>c</sup>	1.510(6)	P(3)–O(13)	1.519(6)
P(3)–O(14)	1.523(6)	P(3)–H(3)	1.33(5)
P(4)–O(8) <sup>d</sup>	1.499(6)	P(4)–O(7)	1.502(6)
P(4)–O(2) <sup>d</sup>	1.510(6)	P(4)–H(4)	1.31(10)
Bond angles [°]			
O(8)–Zn(1)–O(9) <sup>a</sup>	110.7(3)	O(8)–Zn(1)–O(9)	104.9(3)
O(14) <sup>a</sup> –Zn(1)–O(9)	101.4(3)	O(8)–Zn(1)–N(1)	109.3(3)
O(14) <sup>a</sup> –Zn(1)–N(1)	118.9(3)	O(9)–Zn(1)–N(1)	110.5(3)
O(1)–Zn(2)–O(2)	111.3(3)	O(1)–Zn(2)–O(3)	104.2(3)
O(2)–Zn(2)–O(3)	101.7(3)	O(1)–Zn(2)–N(3)	108.8(3)
O(2)–Zn(2)–N(3)	119.5(3)	O(3)–Zn(2)–N(3)	110.2(3)
O(12)–Zn(3)–O(10)	106.6(3)	O(12)–Zn(3)–O(13)	110.6(3)
O(10)–Zn(3)–O(13)	106.2(2)	O(12)–Zn(3)–O(11)	109.6(2)
O(10)–Zn(3)–O(11)	111.4(2)	O(13)–Zn(3)–O(11)	112.3(2)
O(6)–Zn(4)–O(7)	110.0(3)	O(6)–Zn(4)–O(4)	107.1(3)
O(7)–Zn(4)–O(4)	106.4(2)	O(6)–Zn(4)–O(5)	109.3(3)
O(7)–Zn(4)–O(5)	112.6(2)	O(4)–Zn(4)–O(5)	111.3(2)
O(6)–P(1)–O(9)	112.3(5)	O(6)–P(1)–O(11) <sup>a</sup>	110.7(3)
O(9)–P(1)–O(11) <sup>a</sup>	109.2(3)	O(6)–P(1)–O(10)	107.5(4)
O(9)–P(1)–O(10)	107.8(3)	O(11) <sup>a</sup> –P(1)–O(10)	109.3(3)
O(12) <sup>b</sup> –P(2)–O(4)	107.0(3)	O(12) <sup>b</sup> –P(2)–O(3)	111.0(4)
O(4)–P(2)–O(3)	107.6(3)	O(12) <sup>b</sup> –P(2)–O(5) <sup>c</sup>	110.6(3)
O(4)–P(2)–O(5) <sup>c</sup>	109.6(3)	O(3)–P(2)–O(5) <sup>c</sup>	110.8(3)
O(1) <sup>c</sup> –P(3)–O(13)	112.6(4)	O(1) <sup>c</sup> –P(3)–O(14)	114.8(4)
O(13)–P(3)–O(14)	111.6(3)	O(1) <sup>c</sup> –P(3)–H(3)	103(5)
O(13)–P(3)–H(3)	104(4)	O(14)–P(3)–H(3)	110(4)
O(8) <sup>d</sup> –P(4)–O(7)	112.7(4)	O(8) <sup>d</sup> –P(4)–O(2) <sup>d</sup>	115.0(3)
O(7)–P(4)–O(2) <sup>d</sup>	111.3(4)	O(8) <sup>d</sup> –P(4)–H(4)	103(5)
O(7)–P(4)–H(4)	104(4)	O(2) <sup>d</sup> –P(4)–H(4)	109(4)
P(3) <sup>d</sup> –O(1)–Zn(2)	144.3(4)	P(4) <sup>c</sup> –O(2)–Zn(2)	120.6(3)
P(2)–O(3)–Zn(2)	132.2(4)	P(2)–O(4)–Zn(4)	139.0(3)
P(2) <sup>d</sup> –O(5)–Zn(4)	125.8(3)	P(1)–O(6)–Zn(4)	168.3(4)
P(4)–O(7)–Zn(4)	135.4(4)	P(4) <sup>c</sup> –O(8)–Zn(1)	145.5(4)
P(1)–O(9)–Zn(1)	134.5(4)	P(1)–O(10)–Zn(3)	140.9(4)
P(1) <sup>e</sup> –O(11)–Zn(3)	127.1(3)	P(2) <sup>f</sup> –O(12)–Zn(3)	168.0(4)
P(3)–O(13)–Zn(3)	132.3(4)	P(3)–O(14)–Zn(1) <sup>e</sup>	120.8(3)
Zn(1)–N(1)–H(1A)	106.9	Zn(1)–N(1)–H(1B)	106.9
Hydrogen bonding: H ⋯ O/Å N–H ⋯ O/P			
N(2)–H(2A) ⋯ O(10) <sup>d</sup>	2.816(9)	141.9	
N(2)–H(2A) ⋯ O(6) <sup>d</sup>	3.083(9)	144.7	
N(2)–H(2B) ⋯ O(5)	2.792(9)	156.3	
N(2)–H(2C) ⋯ O(3)	2.923(9)	131.0	
N(4)–H(4A) ⋯ O(4) <sup>g</sup>	2.792(9)	143.2	
N(4)–H(4A) ⋯ O(12) <sup>c</sup>	3.094(9)	144.4	
N(4)–H(4B) ⋯ O(9) <sup>b</sup>	2.910(9)	132.2	
N(4)–H(4C) ⋯ O(11) <sup>b</sup>	2.802(9)	154.3	

Symmetry transformations used to generate equivalent atoms:<sup>a</sup>  $-x + 3/2, y - 1/2, -z + 1/2$  <sup>b</sup>  $x - 1, y, z^c -x + 1/2, y + 1/2, -z + 1/2$  <sup>d</sup>  $-x + 1/2, y - 1/2, -z + 1/2$  <sup>e</sup>  $-x + 3/2, y + 1/2, -z + 1/2$  <sup>f</sup>  $x + 1, y, z^g -x - 1/2, y + 1/2, -z + 1/2$

region. A similar behavior has been found in zinc phosphate ND-1 templated by 1,2-diaminocyclohexane<sup>8</sup> and gallium phosphate MIL-46 templated by cyclopentylamine.<sup>21</sup> There exist extensive H-bonds between the amino groups and the bridging oxygen atoms within the layer. Table 2 summarizes the H-bonding information. The N ⋯ O distances are in the range of 2.792–3.094 Å. It is noted that there are no H-bonds between adjacent layers. Since each individual layer has a net charge of zero, the layers are in van der Waals contact.

The TG curve of ZnPO-CJ12 shows a major weight loss of 27.0 wt% at 370–520 °C, which corresponds to the decomposition of the organic molecules in the product (calc. 27.1 wt% based on the empirical formula given by single-crystal structural analysis). XRD analysis indicates that the structure of ZnPO-CJ12 collapses after the removal of the organic templates.

ZnPO-CJ12 exhibits the first inorganic–organic hybrid sheet structure which contains both PO<sub>4</sub><sup>3-</sup> and HPO<sub>3</sub><sup>2-</sup> anions. More

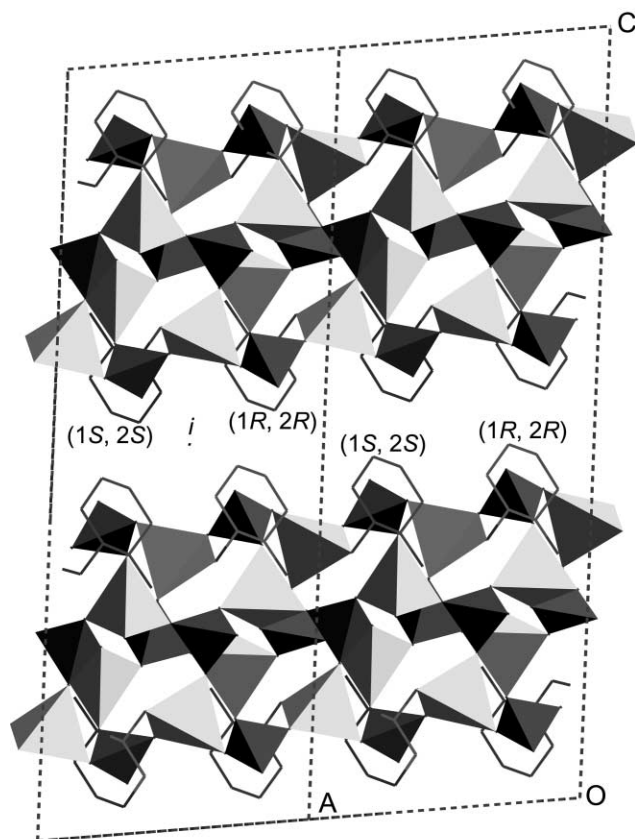


Fig. 4 Polyhedral view of the packing of the sheets along the [001] direction (*i* is an inversion center).

interestingly, even though a mix of the *trans*- and *cis*-isomers of 1,2-DACH molecules is added in the reaction mixture, only the *trans*-isomers are involved in the structure. This indicates that the compound has molecule recognition ability for the *trans*- and *cis*-isomers of the DACH molecules, as has been discussed in zinc phosphate ND-1.<sup>8</sup> ZnPO-CJ12 might be potentially used in the separation of the *trans*- and *cis*-isomers of 1,2-DACH molecules.

## Experimental

### Synthesis and characterization

ZnPO-CJ12 was synthesized by a hydrothermal reaction of a mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_3$  or  $\text{H}_3\text{PO}_2$ , 1,2-diaminocyclohexane (DACH, a mixture of *cis*- and *trans*-isomers, 85wt%, Fluka), and  $\text{H}_2\text{O}$ . Typically, 0.25 g of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was first dissolved in 10 mL of  $\text{H}_2\text{O}$ , then 0.19 g  $\text{H}_3\text{PO}_3$  was added with stirring. Finally, 0.33 mL of DACH was added dropwise to the above reaction mixture. A gel was formed and further stirred for 1 h until it was homogeneous. The reaction mixture was sealed in a Teflon-lined stainless steel autoclave and then heated at 200 °C for 8 d under static condition. The product containing large plate-like single crystals was separated by sonication and further washed by distilled water and then air-dried.

The X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). 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. Thermogravimetric analysis was performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of 10 °C  $\text{min}^{-1}$ . Infrared spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer using KBr pellets.

## Crystallography

A suitable single crystal with dimensions  $0.1 \times 0.08 \times 0.08 \text{ mm}$  was glued to a fine glass fiber and mounted on a Siemens diffractometer fitted with a Bruker SMART CCD detector using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data processing was accomplished with the SAINT processing program.<sup>22</sup> The structure was solved in the space group  $P2_1/n$  by direct methods and refined on  $F^2$  by full-matrix least squares with the SHELXTL97.<sup>23</sup> The zinc and phosphorus atoms were first located, and the carbon, nitrogen, oxygen atoms and the hydrogen atoms in the P-H groups were found in Fourier difference maps. The hydrogen atoms residing in the amine molecules were located geometrically. The monoprotection of the DACH molecules is suggested on the basis of charge balance. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Crystal data for ZnPO-CJ12:  $\text{C}_{12}\text{H}_{32}\text{N}_4\text{O}_{14}\text{P}_4\text{Zn}_4$ ,  $M = 841.78$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 9.7060(17)$ ,  $b = 9.9929(16)$ ,  $c = 27.557(5) \text{ \AA}$ ,  $\beta = 96.795(3)^\circ$ ,  $U = 2654.0(8) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ ,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 3.884 \text{ mm}^{-1}$ , 6017 reflections measured, 3705 unique ( $R_{\text{int}} = 0.0345$ ) which were used in all calculations. The final  $wR(F^2)$  was 0.1263 (all data).

CCDC reference number 171183.

See <http://www.rsc.org/suppdata/dt/b2/b204876k/> for crystallographic data in CIF or other electronic format.

## Acknowledgements

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