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Hydrothermal synthesis and characterization of a new layered zinc phosphate intercalated with fully-protonated triethylenetetramine $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$

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A new two-dimensional zinc phosphate $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ has been prepared hydrothermally by using triethylenetetramine (tetam) as the structure-directing agent. The structure of the compound was solved by single-crystal X-ray diffraction analysis. $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with $a = 7.4876(8)$ Å, $b = 8.2336(8)$ Å, $c = 12.8592(13)$ Å, $\alpha = 98.723(2)°$, $\beta = 101.258(2)°$, $\gamma = 115.785(2)°$, $Z = 2$, and $V = 674.51(12)$ Å^3. The structure consists of macroanionic sheets stacked in an AAAA sequence. As primary building units in the individual sheet, alternating PO_4 tetrahedra with terminal –OH groups and "unsaturated" =O atoms and ZnO_4 tetrahedra are linked together to form elliptical twelve-membered rings as well as four-membered rings. These macroanionic sheets are held together by strong hydrogen bonding.

1 Introduction

Considerable efforts have been made during the past decade to prepare open-framework metal phosphates that may find applications in catalysis, adsorption, ionic conduction, ion-exchange, electronics and optoelectronics. After the discovery of the microporous crystalline aluminophosphates,[1] a large number of new metal phosphates with open-framework structures have appeared in the literature, and the metals include gallium,[2] indium,[3] iron,[4] tin,[5] vanadium,[6] molybdenum,[7] cobalt,[8] zirconium[9] and titanium.[10]

Since the first microporous zinc phosphates with zeolite-like topologies were reported by Stucky and Gier,[11] a great deal of effort has been devoted to the pursuit of novel open-framework structures within this system. The number of such compounds and the diversity of their structural features have been growing rapidly in recent years, and today there are more than thirty different zinc phosphates with 1-D,[12] 2-D[13] and 3-D[14] structures. Nowadays, Tina *et al.* synthesized a novel zinc phosphate phase under the use of the chiral D-glucosamine molecule,[15] Neeraj *et al.* synthesized a novel open-framework zinc phosphate with intersecting helical channels by using diethylenetriamine as the directing agent.[16] Moreover, a zinc phosphate with gigantic pores of 24-membered rings has been reported.[17] This variety has been achieved by varying a number of factors that can influence the structure, such as template, pH value, solvent, reaction temperature and metal cations. The structures of these compounds are built mainly from tetrahedra of ZnO_4 and PO_4 but examples of ZnO_6 and ZnO_5 subunits are also known.[18] There are two kinds of linkages in zinc phosphate compounds obtained by the hydrothermal or solvothermal way: Zn–O–P linkage and Zn–O–Zn linkage, but there is no P–O–P linkage. Among these compounds, some were organically templated and some contain either water or alkali-metal cations in their cavities.

The goal of this work is to synthesize zinc phosphate with novel topology. Here, we report the synthesis, structure and characterization of a novel layered zinc phosphate $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$.

2 Experimental

2.1 Synthesis and initial characterization

The compound was hydrothermally synthesized from a mixture of zinc acetate dihydrate (99%, Shanghai chemical reagent factory), phosphoric acid (85 wt%, Beijing chemical plant), triethylenetetramine (AR, 95%, Tianjin chemical reagent company) and distilled water. The molar composition of the initial mixture was 1 $Zn(AC)_2$: 1.98 H_3PO_4 : 0.86 triethylenetetramine : 78.87 H_2O. In a typical synthesis, 2.44 g zinc acetate dihydrate was added into 15 g H_2O to form a homogeneous solution; then 1.5 ml H_3PO_4 was slowly added, followed by dropwise addition of 1.5 ml triethylenetetramine (tetam) with stirring. The mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 423 K for 10 days under autogenous pressure. The resulting stick-like crystal product as a single phase (in about 80% yield on the basis of the Zn source) was recovered by filtration, washed thoroughly with distilled water and dried at room temperature.

Powder X-ray diffraction (XRD) data were obtained using a Siemens D5005 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). The step size was 0.02° and the count time was 4 s. The element analysis was performed on a Perkin-Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV ICP spectrometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer and a Perkin-Elmer DTA 1700 differential thermal analyzer, with a heating rate of 20 °C min^{-1}.

2.2 Structure determination

A stick-like crystal of approximate dimensions $0.20 \times 0.05 \times 0.03$ mm was mounted on a glass fiber. The X-ray and intensity data were collected on a Siemens Smart 1000 CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å). Intensity data were collected in 1271 frames with increasing ω

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(width of 0.3° per frame). The numbers of collected reflections and independent reflections were 3323 and 1928, respectively. The structure was solved by direct methods: the zinc and phosphorus atoms were first located, and the carbon, nitrogen, oxygen and hydrogen atoms were found in the final difference Fourier map. Refinement was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located easily in Fourier maps and relocated in optimized positions d(O–H) = 0.82 Å, d(N–H) = 0.89 Å and d(C–H) = 0.97 Å, and they were then allowed to ride on the atoms to which they were attached, with free isotropic thermal parameters. Structure solution and refinement were performed by using SHELXTL version 5.1.[19] Crystal data, details of data collection and refinement are given in Table 1. CCDC reference number 1145/213. See http://www.rsc.org/suppdata/jm/b0/b000658k/ for crystallographic files in .cif format.

3 Results and discussion

3.1 Synthesis and characterization

The powder XRD pattern of the as-synthesized $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ and the pattern simulated on the basis of the single crystal structure are presented in Fig. 1. The diffraction peaks on both patterns correspond well in position, indicating the phase purity of the as-synthesized sample. The ICP analysis shows that the compound contains 26.30 wt% Zn and 18.75 wt% P, in good agreement with the value (26.48 wt% Zn, 18.81 wt% P) based on the single crystal structure analysis. The elemental analysis shows that the C, H, and N contents are 7.29, 2.76, and 5.52 wt%, respectively (calculated: C, 7.30 wt%; H, 2.86 wt%; N, 5.67 wt%), corresponding to an empirical molar ratio of C : H : N = 3.0 : 14.0 : 2.0. These results also demonstrate that the solid sample of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ is a pure phase.

The TGA study carried out from room temperature to 700 °C shows that the weight loss of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ is *ca.* 24.3% from 250 °C to 420 °C, in good agreement with the calculated amount of 24.0% (14.8% for decomposition of the template, 9.1% for the removal of the water coming from condensation of the hydrogenphosphate groups). The DTA curve shows one endothermic peak at *ca.* 330 °C. It is attributed to the decomposition of the template and the removal of the water. After calcination at 400 °C for 4 h, the structure of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ collapses and converts into an amorphous phase. Above 700 °C the compound recrystallizes into a mixture of known structures: $Zn_2P_2O_7$ (JCPDS: 39-0711) and $Zn(PO_3)_2$ (JCPDS:10-0306).

Table 1 Crystal data and structure refinement for $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$

Empirical formula	$[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$
Formula weight	493.81
Wavelength/Å	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions:	
a/Å	7.4876(8)
b/Å	8.2336(8)
c/Å	12.8592(13)
α/°	98.723(2)
β/°	101.258(2)
γ/	115.785(2)
Volume/Å^3	674.51(12)
Z, Calculated density/g cm^{-3}	2, 2.431
Absorption coefficient/mm^{-1}	3.980
F(000)	494
Crystal size/mm	0.20 × 0.05 × 0.03
θ range for data collection/°	1.68 to 23.26
Limiting indices	$8 \geqslant h \geqslant -8$, $8 \geqslant k \geqslant -9$, $14 \geqslant l \geqslant -14$
Reflections collected/unique	3323/1928 [R(int) = 0.1669]
Completeness to $\theta = 23.26$ (%)	99.4
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1928/0/199
Goodness-of-fit on F^2	1.084
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0596$, $wR2 = 0.1521$
R indices (all data)	$R1 = 0.0627$, $wR2 = 0.1548$
Largest diff. peak and hole/e Å^{-3}	1.894 and −1.182

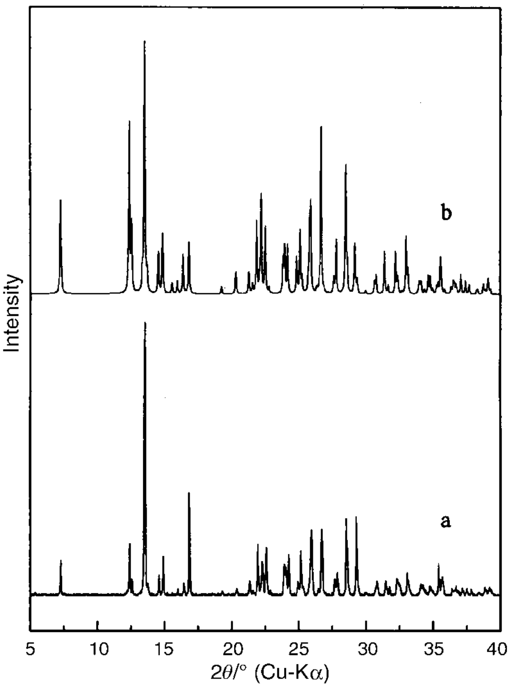

Fig. 1 Experimental (a) and simulated (b) powder X-ray diffraction patterns of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$.

3.2 Description of the structure

Selected bond distance/angle data are given in Table 2.

The asymmetric unit contains 22 independent nonhydrogen atoms, including 2 zinc atoms, 3 phosphorus atoms, 12 oxygen atoms, 3 carbon atoms and 2 nitrogen atoms, as shown in Fig. 2. Both zinc atoms make four Zn–O–P linkages to nearby phosphorus atoms, they have typical geometrical parameters, with d_{av}[Zn(1)–O] = 1.94 Å and d_{av}[Zn(2)–O] = 1.95 Å. Each Zn(1) atom is bound to one P(2), one P(3) and two P(1), whereas each Zn(2) atom is bound to two P(2) and two P(3). All three P atoms form the centers of tetrahedral phosphate groups, with d_{av}[P(1)–O] = 1.534 Å, d_{av}[P(2)–O] = 1.536 Å and d_{av}[P(3)–O] = 1.527 Å. The three independent P atoms repre-

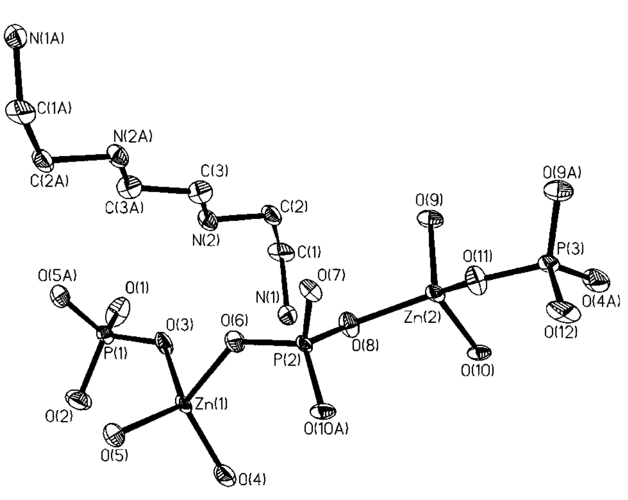

Fig. 2 Asymmetric unit of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ with thermal ellipsoids shown at 50% probability.

Table 2 Selected bond lengths [Å] and angles [°] for $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+a}$

Zn(1)–O(4)	1.898(4)	Zn(1)–O(6)	1.941(4)
Zn(1)–O(3)	1.986(4)	Zn(1)–O(5)	1.935(4)
Zn(2)–O(9)	1.932(4)	Zn(2)–O(8)	1.953(4)
Zn(2)–O(10)	1.979(4)	Zn(2)–O(11)	1.935(4)
P(1)–O(5)#1	1.502(4)	P(1)–O(1)	1.512(4)
P(1)–O(3)	1.527(4)	P(1)–O(2)	1.595(5)
P(2)–O(6)	1.519(4)	P(2)–O(10)#2	1.525(4)
P(2)–O(8)	1.522(4)	P(2)–O(7)	1.576(4)
P(3)–O(4)#2	1.503(5)	P(3)–O(11)	1.516(4)
P(3)–O(9)#3	1.507(4)	P(3)–O(12)	1.583(4)
O(4)–P(3)#2	1.503(5)	O(5)–P(1)#1	1.502(4)
O(9)–P(3)#3	1.507(4)	O(10)–P(2)#2	1.525(4)
C(1)–C(2)	1.516(9)	C(3)–C(3)#4	1.501(13)
N(1)–C(1)	1.496(8)	N(2)–C(3)	1.493(8)
N(2)–C(2)	1.500(8)		
O(4)–Zn(1)–O(5)	106.09(19)	O(4)–Zn(1)–O(6)	116.56(18)
O(5)–Zn(1)–O(6)	108.8(2)	O(4)–Zn(1)–O(3)	115.80(19)
O(5)–Zn(1)–O(3)	118.57(16)	O(6)–Zn(1)–O(3)	90.69(18)
O(9)–Zn(2)–O(11)	112.08(18)	O(9)–Zn(2)–O(8)	104.98(18)
O(11)–Zn(2)–O(8)	114.27(17)	O(9)–Zn(2)–O(10)	106.75(17)
O(11)–Zn(2)–O(10)	113.77(17)	O(8)–Zn(2)–(10)	104.19(18)
O(5)#1–P(1)–O(1)	111.5(2)	O(5)#1–P(1)–O(3)	112.5(2)
O(1)–P(1)–O(3)	110.5(2)	O(5)#1–P(1)–O(2)	109.2(3)
O(1)–P(1)–O(2)	108.9(3)	O(3)–P(1)–O(2)	103.9(2)
O(6)–P(2)–O(8)	110.5(2)	O(6)–P(2)–O(10)#2	112.6(2)
O(8)–P(2)–O(10)#2	111.1(2)	O(6)–P(2)–O(7)	106.6(2)
O(8)–P(2)–O(7)	107.5(2)	O(10)#2–P(2)–O(7)	108.3(2)
O(4)#2–P(3)–(9)#3	111.3(3)	O(4)#2–P(3)–O(11)	112.7(3)
O(9)#3–P(3)–O(11)	113.2(3)	O(4)#2–P(3)–O(12)	110.3(3)
O(9)#3–P(3)–O(12)	106.8(2)	O(11)–P(3)–O(12)	101.9(2)
P(1)–O(3)–Zn(1)	128.1(2)	P(3)#2–O(4)–Zn(1)	135.1(3)
P(1)#1–O(5)–Zn(1)	127.6(3)	P(2)–O(6)–Zn(1)	131.8(2)
P(2)–O(8)–Zn(2)	129.6(2)	P(3)#3–O(9)–Zn(2)	128.6(3)
P(2)#2–O(10)–Zn(2)	120.1(2)	P(3)–O(11)–Zn(2)	132.9(3)
C(3)–N(2)–C(2)	111.3(5)	N(1)–C(1)–C(2)	111.8(5)
N(2)–C(2)–C(1)	112.7(5)	N(2)–C(3)–C(3)#4	109.1(6)

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

sent two chemically distinct types of site. The first phosphorus atom, P(1), makes two bonds to neighboring Zn(1) atoms, and the other two oxygen-atom vertices are to a terminal –OH group and an "unsaturated" =O atom, respectively. These three different types of P–O bonds show their expected differences in bond lengths: d(P=O) = 1.512 Å; d_{av}(P–O_{Zn}) = 1.515 Å; d(P–OH) = 1.595 Å. Similarly differentiated P=O, P–O_{Zn}, and P−OH bond lengths have been observed in other Zn/P/O materials such as the organozinc phosphates $Zn_2(HPO_4)_2(H_2PO_4)_2{\cdot}NH_3(CH_2)_3NH_3$[20] and $Na_2Zn(HPO_4)_2{\cdot}4H_2O$.[21] For any P(2) or P(3) atom, three of the four oxygen coordinating atoms are bonded to zinc atoms and these P–O bond lengths range from 1.503 Å to 1.525 Å. The remaining P–O lengths are P(2)–O(7) = 1.576 Å and P(3)–O(12) = 1.583 Å. H(7) atom is attached to O(7) atom and H(12) atom is attached to O(12) atom.

The macroanionic inorganic sheet viewed down the [100] direction is shown in Fig. 3. The sheet structure consists of four-, twelve-membered rings that form a network of alternatively linked corner-sharing PO_4 and ZnO_4 tetrahedra. If the O atoms are omitted, a two-dimensional network with alternative Zn–P linkages is generated. The O-omitting network can be viewed as constructed from the following steps: I) three four-membered rings are edge-sharing linked together to form a triple edge-sharing 4-ring unit; II) these triple edge-sharing 4-ring units are edge-sharing linked together to form an infinite zigzag edge-sharing 4-ring chain; III) these infinite zigzag edge-sharing 4-ring chains are linked together by the P(1) groups to form a sheet structure. The formation of the

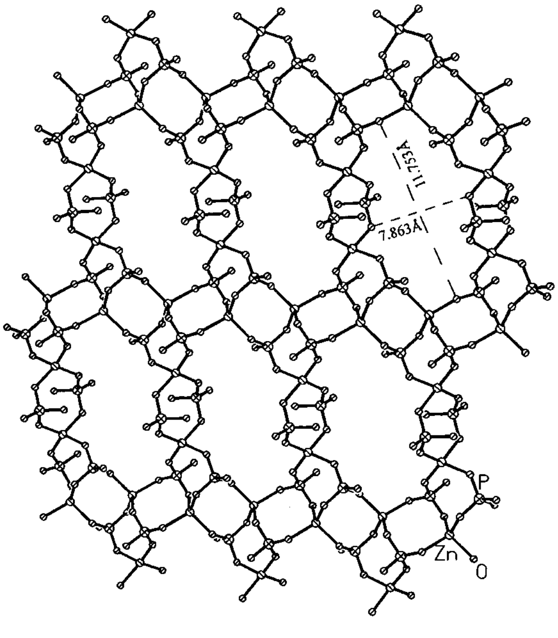

Fig. 3 The inorganic layer structure of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ viewed along the [100] direction.

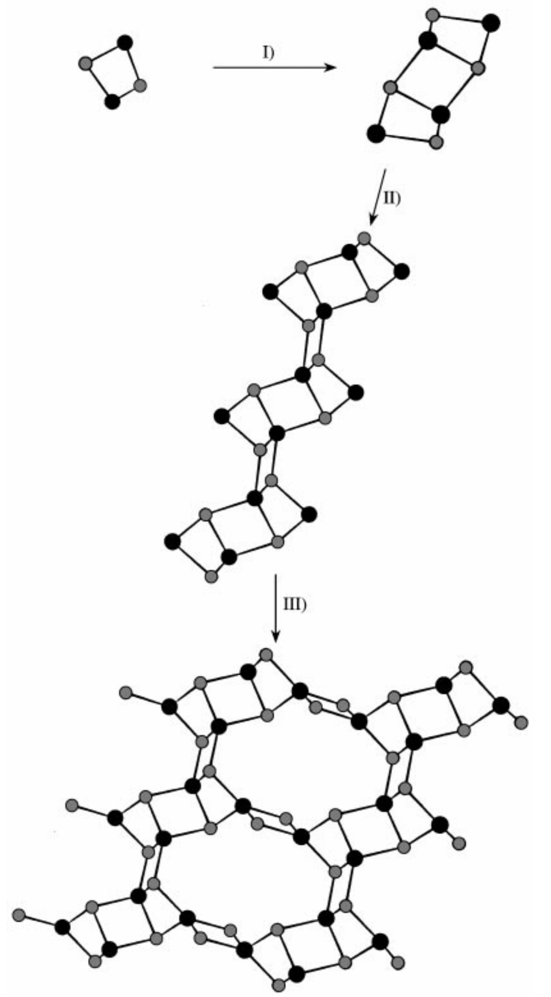

Fig. 4 Schematic representation of the formation of the layer structure of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$, the layer structure can be regarded as constructed from the three steps: I) the combination of three 4-member rings to form a triple edge-sharing 4-ring unit; II) the combination of triple edge-sharing 4-ring units to form an infinite 4-ring chain; III) the combination of the infinite 4-ring chains to form a layer structure. Black atoms, Zn; dotted atoms, P. The C, H, N, O atoms are omitted for clarity.

Table 3 Hydrogen bonds for $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+a}$

D–H···A	*d*(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	Angle D–H···A/°
O(2)–H(2)···O(1)#5	0.82	2.26	2.905(7)	135.8
O(2)–H(2)···O(2)#5	0.82	2.56	3.129(10)	127.2
O(2)–H(2)···O(6)#1	0.82	2.65	3.100(7)	116.3
O(7)–H(7)···N(1)#6	0.82	2.25	2.892(6)	135.9
O(7)–H(7)···O(11)	0.82	2.63	3.345(6)	146.6
O(12)–H(12)···N(1)#2	0.82	2.08	2.885(7)	165.4
N(1)–H(1A)···O(11)#7	0.89	2.20	2.947(6)	141.2
N(1)–H(1A)···O(7)#7	0.89	2.38	2.892(6)	117.1
N(1)–H(1B)···O(3)	0.89	2.13	3.000(6)	164.7
N(1)–H(1C)···O(8)	0.89	2.20	2.962(6)	142.8
N(2)–H(2A)···O(1)#8	0.90	1.89	2.754(6)	161.5
N(2)–H(2B)···O(3)	0.90	2.09	2.970(7)	164.9
N(2)–H(2B)···O(6)	0.90	2.63	3.220(7)	123.5

[a]Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z+1$ #2 $-x+1, -y+1, -z+2$ #3 $-x+1, -y, -z+2$ #4 $-x, -y, -z+1$ #5 $-x-1, -y+1, -z+1$ #6 $x+1, y, z$ #7 $x-1, y, z$ #8 $-x-1, -y, -z+1$.

sheet structure is illustrated in Fig. 4. These infinite edge-sharing 4-ring chains are parallel and these twelve-membered rings lies between every two zigzag 4-ring chains. The dimensions of the free aperture of the twelve-membered ring are 11.753 Å × 7.863 Å (corresponding to the interatomic O–O distances), as illustrated in Fig. 3.

These inorganic sheets are anionic and the empirical formula of the layer is $[Zn_2(HPO_4)_3]^{2-}$. The average charge attributed to every twelve-membered ring is −4. The negative charge is balanced by the fully-protonated tetam molecule and the positive charge of one fully-protonated tetam molecule is also 4. One tetam molecule obliquely gets through one twelve-membered ring. Based on the geometrical placement of the hydrogen atoms (see Table 3), all ten N–H of the tetam molecules make hydrogen bonds to acceptor oxygen species that are variously parts of Zn–O–P, P–OH and P=O. So, there is a strong interaction between the tetam molecule and the inorganic sheet, this kind of hydrogen not only attaches the tetam molecule to the twelve-membered ring, but also helps to hold the inorganic sheets together. Besides the hydrogen bonding between the N–H and the acceptor oxygen species, another type of layer bonding that helps to hold the inorganic sheets together is the hydrogen bonds between the terminal hydroxyl and an oxygen in the adjacent layer. The "puckered" layers are illustrated in Fig. 5.

4 Conclusions

A new organically templated zinc phosphate with a layered structure has been synthesized under hydrothermal conditions. Its structure is built up from alternatively linked PO_4 and ZnO_4. Its layer structure consists of parallel zigzag edge-sharing 4-ring chains. The fully-protonated tetam molecules obliquely get through the twelve-membered rings. H-bonds, which are believed to be responsible for stabilizing the layered structure, are prevalent in the compound. The successful preparation of $[Zn_2(HPO_4)_3]^{2-}[(C_6N_4H_{22})_{0.5}]^{2+}$ demonstrates that by varying the template and synthesis conditions, zinc phosphate with new structural features may crystallize.

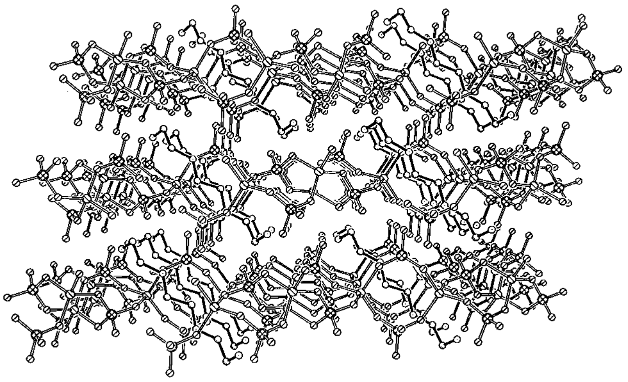

Fig. 5 The stacking of the layers with the intercalated organic cations viewed along the [010] direction, H atoms and H-bonds are not shown for clarity.

Acknowledgements

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