

# Transformations of low-dimensional zinc phosphates to complex open-framework structures. Part 1: zero-dimensional to one-, two- and three-dimensional structures

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Zero-dimensional 4-membered zinc phosphate monomers,  $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$ , **I**, and  $[C_6N_4H_{21}][Zn(HPO_4)_2(H_2PO_4)]$ , **II**, transform under simple reaction conditions to one-, two- and three-dimensional structures. Monomer **II**, on heating with zinc acetate dihydrate ( $Zn(OAc)_2$ ) in aqueous solution, gives a layered phosphate  $[C_6N_4H_{21}][NH_4][Zn_6(PO_4)_4(HPO_4)_2]H_2O$ , **III**. A novel three-dimensional structure  $[C_6N_4H_{21}]_4[Zn_7(PO_4)_6]_3$ , **IV**, with channels comprising  $Zn_7O_6$  clusters is obtained on heating **II** in water under hydrothermal conditions. The monomer **I** transforms to a one-dimensional ladder,  $[C_3N_2H_5][Zn(HPO_4)]$ , **V**, on heating with imidazole and to a three-dimensional structure,  $[C_4N_2H_{12}][Zn_2(H_2O)(PO_4)(HPO_4)]_2$ , **VI**, on heating with piperazine under ordinary conditions. **I** also transforms to a layered zinc phosphate,  $[C_6N_2H_{18}][Zn_3(H_2O)_4(HPO_4)_4]$ , **VII**, on heating in water. In addition to the monomer, **II**, compounds **III–VI** have been obtained for the first time. The structures formed by the transformations of the monomers also exhibit unique structural features. Thus, in the ladder structure, **V**, the imidazole molecule is linked to the Zn center similar to the phosphate unit in a typical ladder structure, while in the layered phosphate, **III**, one-dimensional tubules are linked *via*  $ZnO_4$  tetrahedra and the three-dimensional structure, **IV**, possesses  $Zn_7O_6$  clusters. Isolation of several related solids encompassing a variety of architectures through the transformations of zero-dimensional monomeric phosphates demonstrates not only that the 4-membered ring is a basic structural building unit in these open-framework materials, but also sheds light on the building-up process involved in their formation.

## Introduction

Open-framework metal phosphates have received much attention in recent years, the primary motivation being the discovery of new types of porous solids. These materials have generally been synthesized hydrothermally in the presence of an organic amine. A real outcome of such studies has been the isolation and characterization of a large number of metal phosphates with fascinating structures. These include one-dimensional chains or ladders, two-dimensional layers and three-dimensional structures with channels.<sup>1</sup> The primary structural unit in these materials appears to be a 4-membered ring of the composition  $M_2P_2O_4$ .<sup>2,3</sup> Such monomeric metal phosphates comprising 4-membered rings have only been isolated recently.<sup>4,5</sup> Furthermore, it has been shown that heating the monomeric zinc phosphate,  $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$ , **I**, in water gives a layered zinc phosphate.<sup>5</sup> This observation encouraged us to investigate the role of zero-dimensional monomeric phosphates in the construction of complex metal phosphate architectures. Our experiments showed that the monomeric Zn phosphate, **I**, also transforms into a one-dimensional ladder structure or to a three-dimensional structure under appropriate reaction conditions. With this in view, we have synthesized another monomeric zinc phosphate,  $[C_6N_4H_{21}][Zn(HPO_4)_2(H_2PO_4)]$ , **II**, and studied its transformations under relatively simple reaction conditions. Our experiments show that this monomeric phosphate, **II**, also transforms to two- and three-dimensional structures. In this paper, we discuss the transformations of the two zero-dimensional zinc phosphates, **I** and **II**, into higher dimensional structures. The results obtained in the present study, along with those obtained

in the transformations of the one-dimensional phosphates,<sup>6</sup> make a significant contribution to our understanding of the formation of the fascinating architectures of metal phosphates. The finding that a primary building unit transforms to yield complex architectures is of direct relevance to the mechanism of the building-up process in other types of complex inorganic structures, many of which would also involve supramolecular assembly.

## Experimental

### Synthesis and initial characterization

The zinc phosphate monomer, **I**, was prepared by the procedure described earlier.<sup>5</sup> The new monomeric phosphate,  $[C_6N_4H_{21}][Zn(HPO_4)_2(H_2PO_4)]$ , **II**, was prepared under hydro/solvothermal conditions in the presence of tris(2-aminoethyl)amine (TREN). In a typical synthesis, 0.221 g of ZnO was dispersed in 2.7 ml of  $H_2O$  followed by the addition of 0.2 ml of 1,4-dioxane and 0.25 ml of HCl under constant stirring. To this solution, 0.13 ml of  $H_3PO_4$  (85 wt%) and 0.23 ml of TREN were added to produce a clear solution. The mixture, which had the composition  $ZnO : 3H_3PO_4 : TREN : 2dioxane : 2HCl : 100H_2O$ , was transferred and sealed into a PTFE-lined stainless steel autoclave (Parr, USA) and heated at 180 °C for 2 days. The resulting crop of colorless rod-like crystals was vacuum filtered and dried under ambient conditions. We obtained  $[C_6N_4H_{21}][NH_4][Zn_6(PO_4)_4(HPO_4)_2]H_2O$ , **III**, by heating **II** with zinc acetate dihydrate under hydrothermal conditions. Typically, 0.5 g of **II** and 0.214 g of  $Zn(OAc)_2$  were dispersed in 1.8 ml of  $H_2O$  and heated in an autoclave at 180 °C for 24 h.

**Table 1** Crystal data and structure refinement parameters for  $[\text{C}_6\text{N}_4\text{H}_{21}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$ , **II**,  $[\text{C}_6\text{N}_4\text{H}_{21}][\text{NH}_4][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$ , **III** and  $[\text{C}_6\text{N}_4\text{H}_{21}]_4[\text{Zn}_7(\text{PO}_4)_6]_3$ , **IV**

Structural parameter	<b>II</b>	<b>III</b>	<b>IV</b>
Empirical formula	$\text{ZnP}_3\text{O}_{12}\text{C}_6\text{N}_4\text{H}_{25}$	$\text{Zn}_6\text{P}_6\text{O}_{25}\text{C}_6\text{N}_5\text{H}_{29}$	$\text{Zn}_{21}\text{P}_{18}\text{O}_{72}\text{C}_{24}\text{N}_{16}\text{H}_{84}$
Crystal system	Orthorhombic	Orthorhombic	Trigonal
Space group	$Pbca$ (no. 61)	$Pna2_1$ (no. 33)	$R\bar{3}$ (no. 148)
$T/K$	293	293	293
$a/\text{\AA}$	12.325(8)	18.785(2)	13.608(4)
$b/\text{\AA}$	14.837(9)	8.278(7)	13.608(4)
$c/\text{\AA}$	19.327(12)	18.747(2)	15.277(8)
$\alpha/^\circ$	90.0	90.0	90.0
$\beta/^\circ$	90.0	90.0	90.0
$\gamma/^\circ$	90.0	90.0	120.0
Volume/ $\text{\AA}^3$	3534.5(4)	2915.4(4)	2450.3(2)
$Z$	8	4	18
Formula mass	503.58	1149.38	3612.98
$\mu/\text{mm}^{-1}$	1.730	5.298	5.448
Total data collected	13962	11429	3418
Unique data	2574	3157	790
Data [ $I > 2\sigma(I)$ ]	1696	2376	734
$R_{\text{int}}$	0.111	0.125	0.057
$R$ [ $I > 2\sigma(I)$ ]	$R_1 = 0.041$ ; $wR_2 = 0.081^a$	$R_1 = 0.067$ ; $wR_2 = 0.152^a$	$R_1 = 0.043$ ; $wR_2 = 0.155^a$
$R$ (all data)	$R_1 = 0.079$ ; $wR_2 = 0.091$	$R_1 = 0.102$ ; $wR_2 = 0.173$	$R_1 = 0.051$ ; $wR_2 = 0.162$

$^a W = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$  where  $P = [F_o^2 + 2F_c^2]/3$ ;  $a = 0.0382$  and  $b = 0.0$  for **II**,  $a = 0.1000$  and  $b = 0.0$  for **III**, and  $a = 0.1000$  and  $b = 0.0$  for **IV**.

The resulting product contained colorless very thin needle-like single crystals of **III**. When the crystals of **II** were placed in water and heated for 24 h in an autoclave at 180 °C, we obtained  $[\text{C}_6\text{N}_4\text{H}_{21}]_4[\text{Zn}_7(\text{PO}_4)_6]_3$ , **IV**. **IV** could also be obtained independently by heating a mixture with the composition  $\text{ZnO}:\text{H}_3\text{PO}_4:\text{TREN}:\text{2HCl}:\text{100H}_2\text{O}$  at 180 °C for 48 h. In both cases, colorless truncated octahedral type crystals were obtained. The crystals were filtered under vacuum and dried under ambient conditions.

On reacting 0.0104 g (0.0219 mM) of the monomer **I** with 0.0022 g (0.0323 mM) of imidazole in 0.2 ml (11 mM) of  $\text{H}_2\text{O}$  in a polypropylene bottle at 60 °C for 4 days, we obtained  $[\text{C}_3\text{N}_2\text{H}_5][\text{Zn}(\text{HPO}_4)]$ , **V**, with a one-dimensional ladder structure, in the form of rod-shaped crystals. By reacting a mixture of 0.0095 g (0.02 mM) of the monomer **I** with 0.0017 g (0.02 mM) of piperazine in 0.2 ml (11 mM) of  $\text{H}_2\text{O}$  at 60 °C for 4 days in a polypropylene bottle a three-dimensional zinc phosphate,  $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{H}_2\text{O})(\text{PO}_4)(\text{HPO}_4)]_2$ , **VI**, was obtained in the form of colorless irregular shaped crystals.

Both these products were vacuum filtered and washed with de-ionized water and dried under ambient conditions. In all the transformation reactions, the products obtained were pure single crystals, except **III**, single crystals of which were found mixed with a condensed zinc phosphate, hoepite (JCPDS: 37-0465). The phosphates thus obtained were characterized by powder X-ray diffraction (XRD), EDAX (elemental analysis) and thermogravimetric analysis (TGA).

#### Single crystal X-ray diffraction

Suitable single crystals of **II–VI** were carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoK $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321

**Table 2** Crystal data and structure refinement parameters for  $[\text{C}_6\text{N}_2\text{H}_{18}][\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$ , **I**,  $[\text{C}_3\text{N}_2\text{H}_5][\text{Zn}(\text{HPO}_4)]$  **V** and  $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{H}_2\text{O})(\text{PO}_4)_2(\text{HPO}_4)]_2$ , **VI**

Structural parameter	<b>I</b>	<b>V</b>	<b>VI</b>
Empirical formula	$\text{ZnP}_3\text{O}_{12}\text{C}_6\text{N}_2\text{H}_{23}$	$\text{ZnPO}_4\text{C}_3\text{N}_2\text{H}_5$	$\text{Zn}_4\text{P}_4\text{O}_{19}\text{C}_4\text{N}_2\text{H}_{20}$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
$T/K$	293	293	293
$a/\text{\AA}$	8.627(2)	5.197(1)	12.075(5)
$b/\text{\AA}$	8.894(9)	7.697(3)	14.888(7)
$c/\text{\AA}$	12.674(2)	17.336(2)	11.835(8)
$\alpha/^\circ$	88.9(4)	90.0	90.0
$\beta/^\circ$	75.1(7)	90.61(8)	97.7(2)
$\gamma/^\circ$	63.0(6)	90.0	90.0
Volume/ $\text{\AA}^3$	832.82(3)	693.45(14)	2108.66(7)
$Z$	2	4	4
Formula mass	473.565	229.45	785.66
$\mu/\text{mm}^{-1}$	6.085	3.74	6.008
Total data collected	3555	2830	4339
Unique data	2369	1007	1525
Data [ $I > 2\sigma(I)$ ]	2346	909	1434
$R_{\text{int}}$	0.086	0.0658	0.053
$R$ [ $I > 2\sigma(I)$ ]	$R_1 = 0.048$ ; $wR_2 = 0.131^a$	$R_1 = 0.043$ ; $wR_2 = 0.118^a$	$R_1 = 0.03$ ; $wR_2 = 0.077^a$
$R$ (all data)	$R_1 = 0.049$ ; $wR_2 = 0.131$	$R_1 = 0.052$ ; $wR_2 = 0.133$	$R_1 = 0.034$ ; $wR_2 = 0.08$

$^a W = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$  where  $P = [F_o^2 + 2F_c^2]/3$ ;  $a = 0.0802$  and  $b = 1.9306$  for **I**,  $a = 0.0352$  and  $b = 6.0376$  for **V**, and  $a = 0.0454$  and  $b = 6.2079$  for **VI**.

**Table 3** Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for **II**,  $[\text{C}_6\text{N}_4\text{H}_{21}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Zn(1)	566(1)	352(1)	1150(1)	21(1)
P(1)	1976(1)	-284(1)	2458(1)	19(1)
P(2)	-552(1)	2064(1)	1789(1)	22(1)
P(3)	1665(1)	13(1)	-370(1)	23(1)
O(1)	410(2)	1573(2)	1471(2)	26(1)
O(2)	1517(3)	314(2)	360(2)	34(1)
O(3)	1133(3)	-401(2)	1891(2)	26(1)
O(4)	-762(2)	-259(2)	863(2)	27(1)
O(5)	2975(2)	-853(2)	2339(2)	27(1)
O(6)	1486(2)	-468(2)	3166(2)	23(1)
O(7)	2307(3)	755(2)	2427(2)	26(1)
O(8)	-527(3)	2105(2)	2567(2)	31(1)
O(9)	-1640(3)	1667(2)	1562(2)	34(1)
O(10)	-402(3)	3041(2)	1478(2)	41(1)
O(11)	1851(3)	-1013(2)	-382(2)	40(1)
O(12)	2723(3)	501(3)	-612(2)	38(1)
N(2)	-2500(3)	2569(3)	3360(2)	27(1)
C(1)	-1742(4)	2122(3)	4494(3)	26(1)
C(2)	-2279(4)	2853(4)	4080(3)	28(1)
N(1)	-653(3)	1898(3)	4227(2)	23(1)
C(3)	157(4)	2554(4)	4479(3)	31(2)
C(4)	1111(4)	2629(4)	3988(3)	42(2)
N(3)	805(4)	3109(3)	3354(2)	44(1)
C(5)	-348(4)	978(4)	4422(3)	31(2)
C(6)	-891(4)	270(4)	3978(3)	32(2)
N(4)	-516(3)	338(3)	3251(2)	26(1)
N(2)	-2500(3)	2569(3)	3360(2)	27(1)
C(1)	-1742(4)	2122(3)	4494(3)	26(1)
C(2)	-2279(4)	2853(4)	4080(3)	28(1)
N(1)	-653(3)	1898(3)	4227(2)	23(1)
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C(4)	1111(4)	2629(4)	3988(3)	42(2)
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N(4)	-516(3)	338(3)	3251(2)	26(1)

<sup>a</sup>*U*(eq) is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

frames with  $\omega$  scans (width of 0.30° and exposure time of 20 s per frame) in the  $2\theta$  range 3 to 46.5°. Pertinent experimental details for the structure determinations are presented in Table 1.

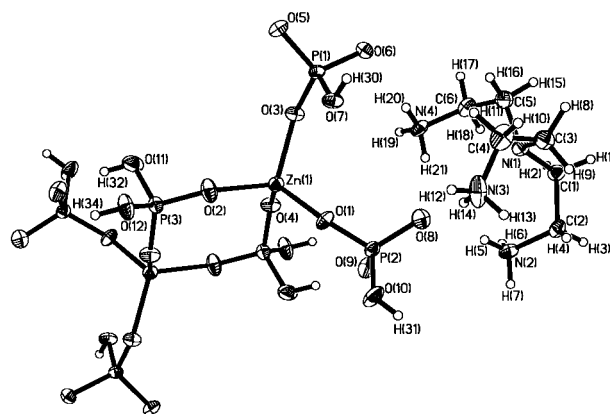
The structure was solved by direct methods using SHELXS-86<sup>7</sup> and difference Fourier syntheses. An empirical absorption correction based on symmetry equivalent reflections was applied for all the compounds using the SADABS program.<sup>8</sup> All the hydrogen positions were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. In the case of **III**, the crystals were found to be weakly diffracting and only isotropic refinement was carried out. For compounds **II**, **IV**, **V** and **VI**, the last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS package of programs.<sup>9</sup> Details of the final refinements for compounds **II–IV** are presented in Table 1 and for compounds **I**, **V** and **VI** in Table 2.

CCDC reference number 1145/271. See <http://www.rsc.org/suppdata/jm/b0/b008286o/> for crystallographic files in .cif format.

## Results

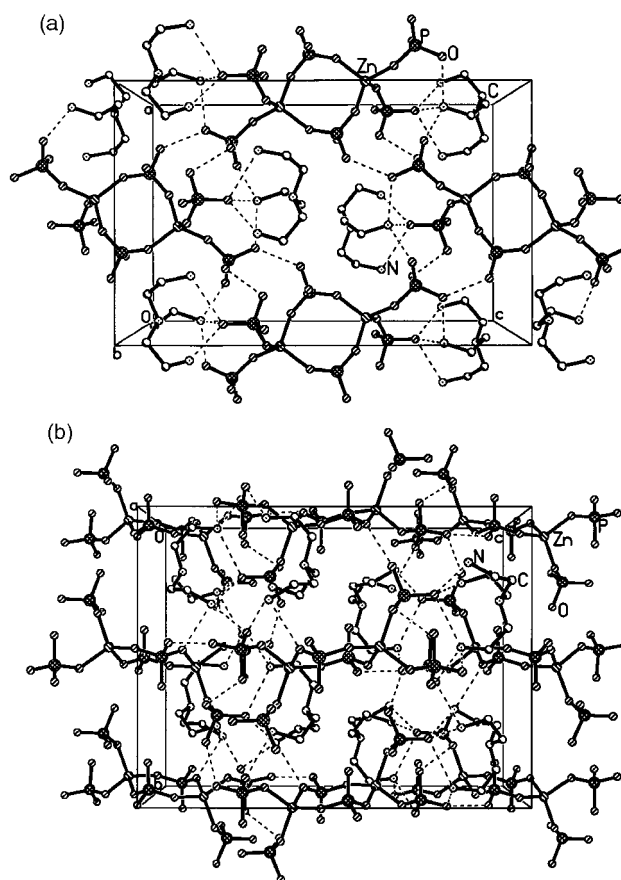
### Structure of the monomer, $[\text{C}_6\text{N}_4\text{H}_{21}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$ , **II**

The atomic coordinates of **II** are listed in Table 3. The 26 non-hydrogen atoms present in the asymmetric unit (Fig. 1)



**Fig. 1** ORTEP plot of the zinc phosphate monomer **II**,  $[\text{C}_6\text{N}_4\text{H}_{21}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)]$ . The asymmetric unit is labeled.

comprise three crystallographically independent phosphorus and a single zinc atom. The structure of **II** consists of 4-membered rings formed by  $\text{ZnO}_4$  and  $\text{PO}_2(\text{OH})_2$  tetrahedra. The  $\text{PO}_3(\text{OH})$  unit hangs from the Zn center as shown in Fig. 2. The framework is stabilized by extensive intra-molecular multi-point hydrogen bonding involving the phosphate units as well as the triply protonated amine molecules forming a sheet-like structure. Note that all the terminal nitrogens of the amine, TREN, are protonated. The TREN cations interact through hydrogen bonding with the double bonded oxygens as well as with the hydroxyl oxygens (Fig. 2a and 2b). The amine



**Fig. 2** (a) Packing diagram showing the arrangement of the monomer and the amine in **II**, in the *ac* plane. Note that the claw-like amine holds and interacts with two different monomers. Hydrogen atoms on the amine and monomer are omitted for clarity. Dotted lines represent possible interactions between the amine and the monomer. (b) The amine and monomer in the *bc* plane. Note the monomer forms a one-dimensional chain-like arrangement, along the *a* axis, separated by the amine molecule.

**Table 4** Selected bond distances and angles in **II**, [C<sub>6</sub>N<sub>4</sub>H<sub>21</sub>][Zn(HPO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>]

Moiety	Distance/Å	Moiety	Angle/°	Moiety	Angle/°
Zn(1)–O(1)	1.925(3)	O(2)–Zn(1)–O(1)	110.2(2)	O(1)–P(2)–O(10)	101.2(2)
Zn(1)–O(2)	1.925(3)	O(2)–Zn(1)–O(3)	110.4(2)	O(9)–P(2)–O(10)	110.3(2)
Zn(1)–O(3)	1.946(3)	O(1)–Zn(1)–O(3)	109.80(14)	O(8)–P(2)–O(1)	114.0(2)
Zn(1)–O(4)	1.953(3)	O(2)–Zn(1)–O(4)	105.76(14)	O(8)–P(2)–O(9)	108.7(2)
P(1)–O(5)	1.510(3)	O(1)–Zn(1)–O(4)	116.43(14)	O(2)–P(3)–O(4) <sup>#1</sup>	115.7(2)
P(1)–O(3)	1.520(3)	O(3)–Zn(1)–O(4)	104.07(14)	O(2)–P(3)–O(11)	109.1(2)
P(1)–O(6)	1.522(3)	O(5)–P(1)–O(3)	112.6(2)	O(4) <sup>#1</sup> –P(3)–O(11)	109.9(2)
P(1)–O(7)	1.596(3)	O(5)–P(1)–O(6)	111.1(2)	O(2)–P(3)–O(12)	104.2(2)
P(2)–O(8)	1.504(4)	O(3)–P(1)–O(6)	110.9(2)	O(4) <sup>#1</sup> –P(3)–O(12)	108.3(2)
P(2)–O(1)	1.521(3)	O(5)–P(1)–O(7)	109.0(2)	O(11)–P(3)–O(12)	109.3(2)
P(2)–O(9)	1.530(3)	O(3)–P(1)–O(7)	105.0(2)	P(2)–O(1)–Zn(1)	131.2(2)
P(2)–O(10)	1.580(4)	O(6)–P(1)–O(7)	107.9(2)	P(3)–O(2)–Zn(1)	146.4(2)
P(3)–O(2)	1.493(4)	O(1)–P(2)–O(9)	112.5(2)	P(1)–O(3)–Zn(1)	135.3(2)
P(3)–O(4) <sup>#1</sup>	1.509(3)	O(8)–P(2)–O(10)	110.0(2)	P(3) <sup>#1</sup> –O(4)–Zn(1)	133.2(2)
P(3)–O(11)	1.539(4)				
P(3)–O(12)	1.563(3)				

## Organic moiety

Moiety	Distance/Å	Moiety	Angle/°
N(2)–C(2)	1.479(6)	C(1)–N(1)–C(3)	110.6(4)
C(1)–N(1)	1.475(6)	N(1)–C(3)–C(4)	111.5(4)
C(1)–C(2)	1.502(6)	N(3)–C(4)–C(3)	111.0(5)
N(1)–C(5)	1.466(6)	N(1)–C(5)–C(6)	112.8(4)
N(1)–C(3)	1.477(6)	N(4)–C(6)–C(5)	110.6(4)
C(3)–C(4)	1.516(7)		
C(5)–C(6)	1.513(7)		
C(6)–N(4)	1.483(6)		

Symmetry transformations used to generate equivalent atoms: #1  $-x, -y, -z$ .

molecules are so arranged that they form three talons of a claw. **II** is only the third known zero-dimensional zinc phosphate and its structure is similar to that of **I**, [C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>][Zn(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>],<sup>5</sup> and to [N(CH<sub>3</sub>)<sub>4</sub>][Zn(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub>], reported earlier.<sup>10</sup>

The Zn atoms in **II** are tetrahedrally coordinated with respect to the oxygen atoms with average Zn–O bond distances of 1.937 Å and O–Zn–O angles of 107.8°. The zinc atom is connected to three distinct P atoms *via* Zn–O–P links and an average bond angle of 136.5° results from such a linkage. Of the three independent P atoms, P(1) and P(2) make only one P–O–Zn linkage and have three terminal P–O bonds, and P(3) is connected to Zn *via* two P–O–Zn linkages with two terminal P–O bonds. The P–O bond distances are in the range 1.493(4)–1.596(3) Å (av. P(1)–O = 1.537, P(2)–O = 1.534 and P(3)–O = 1.529 Å) and an average O–P–O angle of 109.4° results for all the P atoms (Table 4). A framework with the formula Zn(PO<sub>4</sub>)<sub>3</sub> would result in a net negative charge of –7, which is balanced by the protonation of the amine and some of the oxygen atoms. Bond valence sum values<sup>11</sup> clearly indicate that P(1)–O(7), P(2)–O(10), P(3)–O(11) and P(3)–O(12) with distances of 1.596(3), 1.580(4), 1.539(4) and 1.563(3) Å are P–OH linkages in agreement with the proton positions found in the difference Fourier maps.

**Transformation of the zero-dimensional monomer II to two- and three-dimensional structures**

The two transformation products of the monomer **II**, obtained in the present study, possess two-dimensional layered and three-dimensional structures, respectively. We first discuss the two-dimensional layer structure [C<sub>6</sub>N<sub>4</sub>H<sub>21</sub>][NH<sub>4</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>](H<sub>2</sub>O), **III**, obtained by heating **II** with zinc acetate dihydrate in water at 180 °C under hydrothermal conditions. The atomic coordinates of **III** are listed in Table 5. The asymmetric unit of **III** consists of 48 non-hydrogen atoms, 36 of which belong to the framework (comprising of six Zn, six P and twenty-four O atoms) and twelve to the guest (five N, six C atoms and one O) (Fig. 3). Of the twenty-four oxygens in the

asymmetric unit, two are three-coordinated linking two Zn and one P atom and the remaining have normal Zn–O–P links. The structure of **III** consists of a network of ZnO<sub>4</sub>, PO<sub>4</sub> and HPO<sub>4</sub> moieties forming a layer with the interlamellar region occupied by the protonated amine, ammonium and water molecules.

The Zn atoms in **III** are all tetrahedrally coordinated with respect to oxygens with the Zn–O bond distances in the range 1.890(2)–2.022(14) Å [av. (Zn–O) = 1.961 Å] (Table 6). The O–Zn–O bond angles are in the range 97.6(6)–127.3(7)° [av. (O–Zn–O) = 109.5°]. The longest bond distances and the largest bond angles are associated with the oxygen with trigonal coordination. The zinc atoms are connected to three distinct P atoms *via* Zn–O–P links with average bond angles of 129.1°, resulting from a wide spread of angles. Of the six independent P atoms, P(1), P(2), P(3) and P(4) are connected to Zn atoms *via* four P–O–Zn linkages and P(5) and P(6) are connected *via* three P–O–Zn linkages with one terminal P–O bond. The average P–O distances of 1.545, 1.540, 1.545, 1.533, 1.525 and 1.533 Å result for P(1), P(2), P(3), P(4), P(5) and P(6), respectively (Table 6). The O–P–O bond angles are in the range 103.9(9)–113.5(9)° [av. (O–P–O) = 109.5°]. The geometrical parameters observed for **III** are in good agreement with other similar open-framework zinc phosphates.<sup>2,3,5</sup> The complete listing of bond distances is given in Tables 6. Assuming the usual valences for Zn, P and O, the framework stoichiometry of Zn<sub>6</sub>P<sub>6</sub>O<sub>24</sub> in **III** has a charge of –6. The charge compensation is achieved by the presence of the triply protonated TREN along with the terminal P–OH linkages for the P(5)–O(23) and P(6)–O(24) moieties. The proton position observed in the difference Fourier maps corresponds with the above formalism. This assignment is also consistent with the bond valence sum calculations.<sup>11</sup> The structure of **III** can therefore be considered to be made up of alternating anionic (inorganic) and cationic (organic) layers.

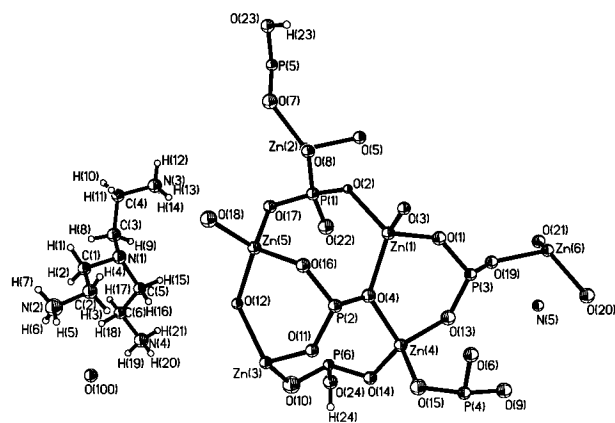
The framework structure of **III** consists of one-dimensional tubes, linked together forming the layers. Each tube is made from an infinite strip-like arrangement along the *bc* plane. As can be seen from Fig. 4, the strip is formed by the linkages



**Table 5** Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for **III**,  $[\text{C}_6\text{N}_4\text{H}_{21}][\text{NH}_4][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Zn(1)	5984(1)	-3520(3)	4822(1)	16(1)
Zn(2)	3182(1)	-410(3)	4818(1)	15(1)
Zn(3)	7089(1)	1417(3)	6383(1)	15(1)
Zn(4)	6786(1)	-3582(3)	6511(1)	16(1)
Zn(5)	6227(1)	1387(3)	4699(1)	16(1)
Zn(6)	4864(1)	-9536(3)	6281(1)	16(1)
P(1)	4832(3)	-746(7)	4687(3)	16(1)
P(2)	7224(3)	-1421(7)	5247(3)	16(1)
P(3)	5810(3)	-6422(7)	5934(3)	14(1)
P(4)	8184(3)	-5715(7)	6426(3)	15(1)
P(5)	1925(3)	720(8)	3773(3)	15(1)
P(6)	6130(3)	-689(7)	7343(3)	13(1)
O(1)	5606(7)	-5362(17)	5284(8)	19(4)
O(2)	5276(7)	-2149(15)	4361(7)	8(3)
O(3)	6543(7)	-4191(17)	3982(7)	14(4)
O(4)	6646(7)	-2601(19)	5550(8)	18(4)
O(5)	2832(7)	-2590(16)	4910(8)	18(4)
O(6)	8245(7)	-6045(18)	5620(8)	18(4)
O(7)	2672(8)	849(17)	4083(8)	26(4)
O(8)	4108(7)	-659(18)	4295(8)	17(4)
O(9)	7809(7)	-7163(17)	6771(8)	21(4)
O(10)	6634(8)	735(20)	7286(9)	30(4)
O(11)	7514(7)	-435(17)	5867(7)	16(3)
O(12)	6383(7)	2326(17)	5674(7)	12(3)
O(13)	6152(7)	-5430(18)	6532(8)	21(4)
O(14)	6557(7)	-2289(18)	7345(8)	17(4)
O(15)	7801(8)	-4107(17)	6559(9)	23(4)
O(16)	6874(7)	-418(17)	4661(8)	18(4)
O(17)	5231(7)	846(16)	4595(8)	16(4)
O(18)	6472(8)	2783(20)	3893(8)	25(4)
O(19)	5150(7)	-7306(17)	6211(8)	17(3)
O(20)	5568(8)	-10822(18)	6786(8)	23(4)
O(21)	3928(7)	-9395(18)	6755(8)	19(4)
O(22)	4686(8)	-1054(18)	5488(9)	25(4)
O(23)	2011(7)	639(18)	2949(8)	20(4)
O(24)	5716(8)	-584(17)	8075(8)	22(4)
N(1)	872(10)	9251(22)	8425(11)	27(5)
C(1)	1352(11)	10706(27)	8287(13)	25(6)
C(2)	2134(12)	10237(29)	8296(14)	30(6)
N(2)	2561(11)	11740(24)	8286(12)	42(6)
C(3)	95(12)	9678(29)	8398(14)	29(6)
C(4)	-256(12)	9259(27)	7664(13)	24(6)
N(2)	-549(9)	7580(23)	7697(10)	29(5)
C(5)	1009(11)	8558(28)	9168(12)	23(6)
C(6)	982(11)	9743(25)	9762(13)	22(5)
N(4)	1037(10)	9010(22)	10491(11)	31(6)
N(5)	3960(8)	-9253(20)	8179(9)	15(4)
O(100)	1060(7)	11809(17)	11300(9)	29(4)

<sup>a</sup>*U*(eq) is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

**Fig. 3** ORTEP plot of the layered zinc phosphate, **III**,  $[\text{C}_6\text{N}_4\text{H}_{21}][\text{NH}_4][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$ .**Table 6** Selected bond distances in **III**,  $[\text{C}_6\text{N}_4\text{H}_{21}][\text{NH}_4][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$ 

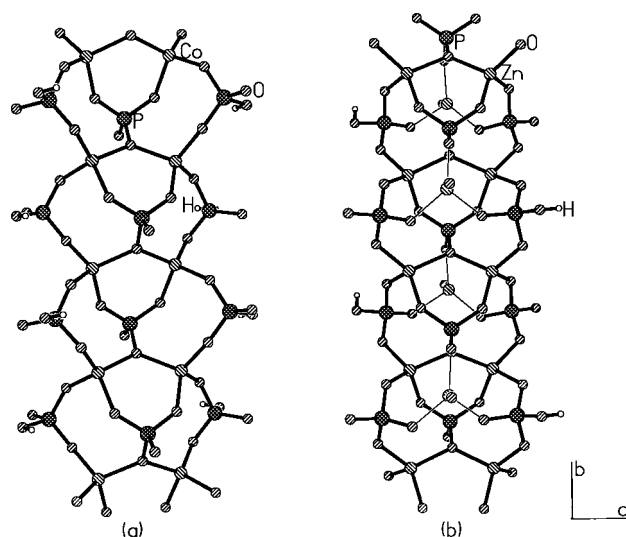
Moiety	Distance/ $\text{\AA}$	Moiety	Distance/ $\text{\AA}$
Zn(1)–O(1)	1.89(2)	P(1)–O(17)	1.526(14)
Zn(1)–O(2)	1.950(13)	P(1)–O(8)	1.55(2)
Zn(1)–O(3)	1.972(14)	P(1)–O(22)	1.55(2)
Zn(1)–O(4)	2.00(2)	P(1)–O(2)	1.556(14)
Zn(2)–O(5)	1.928(14)	P(2)–O(11)	1.52(2)
Zn(2)–O(6) <sup>#1</sup>	1.93(2)	P(2)–O(16)	1.53(2)
Zn(2)–O(7)	1.98(2)	P(2)–O(5) <sup>#4</sup>	1.540(14)
Zn(2)–O(8)	2.009(14)	P(2)–O(4)	1.57(2)
Zn(3)–O(9) <sup>#2</sup>	1.934(14)	P(3)–O(19)	1.530(14)
Zn(3)–O(10)	1.98(2)	P(3)–O(13)	1.53(2)
Zn(3)–O(11)	1.981(14)	P(3)–O(1)	1.55(2)
Zn(3)–O(12)	2.022(14)	P(3)–O(12) <sup>#3</sup>	1.57(2)
Zn(4)–O(13)	1.94(2)	P(4)–O(21) <sup>#5</sup>	1.531(14)
Zn(4)–O(14)	1.943(14)	P(4)–O(15)	1.53(2)
Zn(4)–O(15)	1.96(2)	P(4)–O(9)	1.53(2)
Zn(4)–O(4)	2.00(2)	P(4)–O(6)	1.54(2)
Zn(5)–O(16)	1.927(14)	P(5)–O(3) <sup>#1</sup>	1.51(2)
Zn(5)–O(17)	1.934(13)	P(5)–O(18) <sup>#6</sup>	1.52(2)
Zn(5)–O(18)	1.96(2)	P(5)–O(7)	1.52(2)
Zn(5)–O(12)	2.009(14)	P(5)–O(23)	1.55(2)
Zn(6)–O(19)	1.928(14)	P(6)–O(20) <sup>#2</sup>	1.49(2)
Zn(6)–O(20)	1.94(2)	P(6)–O(10)	1.51(2)
Zn(6)–O(21)	1.973(14)	P(6)–O(14)	1.55(2)
Zn(6)–O(22) <sup>#3</sup>	1.97(2)	P(6)–O(24)	1.58(2)

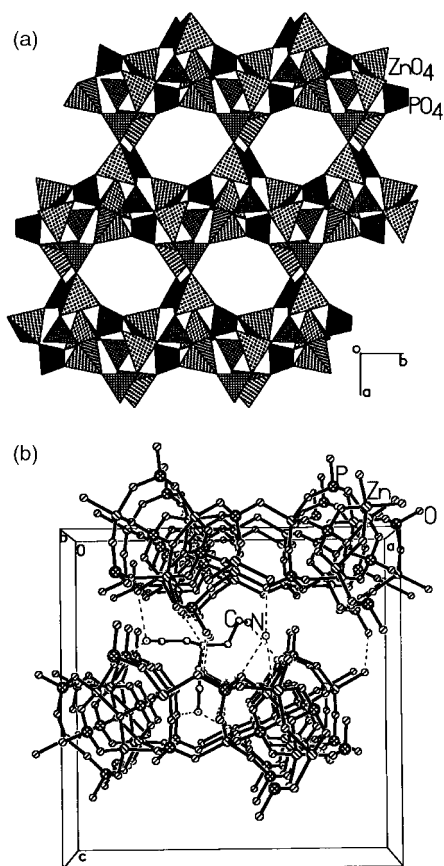
## Organic moiety

Moiety	Distance/ $\text{\AA}$	Moiety	Distance/ $\text{\AA}$
N(1)–C(3)	1.50(3)	C(3)–C(4)	1.57(3)
N(1)–C(1)	1.53(3)	C(4)–N(2)	1.50(3)
N(1)–C(5)	1.53(3)	C(5)–C(6)	1.48(3)
C(1)–C(2)	1.52(3)	C(6)–N(4)	1.50(3)
C(2)–N(2)	1.48(3)		

Symmetry transformations used to generate equivalent atoms: #1  $x-1/2, -y-1/2, z$ ; #2  $x, y+1, z$ ; #3  $x, y-1, z$ ; #4  $x+1/2, -y-1/2, z$ ; #5  $x+1/2, -y-3/2, z$ ; #6  $x-1/2, -y+1/2, z$ .

between 3- and 4-membered rings. The strip can be described as a one-dimensional chain of 3-membered rings edgewise connected by 4-membered rings on either side. On the other hand, the strip can be viewed as consisting of two corner-shared linear chains used together through a 3-coordinated oxygen atom. A similar strip-like arrangement, shown in Fig. 4a, has been observed recently in a cobalt phosphate.<sup>2</sup> It may be

**Fig. 4** (a) Strip-like arrangement found in  $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{HPO}_4)(\text{PO}_4)\text{H}_2\text{O}]$ , formed by fusing two corner-shared chains. (b) The strip with the capped  $\text{ZnO}_4$  tetrahedra (marked by thin lines). Note the tetrahedra caps on either side of the tube.



**Fig. 5** (a) Polyhedral view of a single layer of **III** showing the 8-membered apertures. (b) Structure of **III** in the *ac* plane showing the layer arrangement. Hydrogens are not shown for clarity.

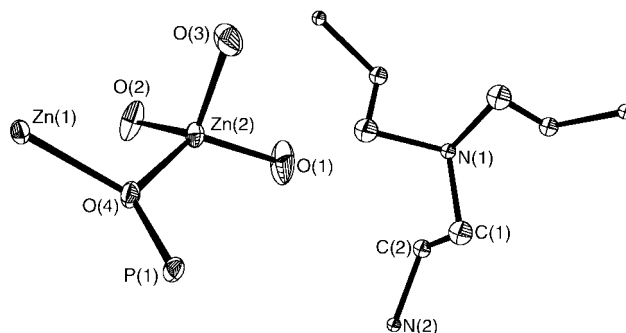
recalled that chains formed by corner-shared 4-membered rings have been suggested to be the basic building unit in open-framework aluminophosphate structures.<sup>12</sup> The strip in **III** (Fig. 4a) is capped by Zn(4)O<sub>4</sub> and Zn(5)O<sub>4</sub> tetrahedra on either side forming the tube as shown in Fig. 4b. The Zn(4)O<sub>4</sub> and Zn(5)O<sub>4</sub> tetrahedra link all the P atoms of the strip and also connect to the adjacent tubes *via* oxygens. The connectivity between the tubes gives rise to an 8-membered aperture within the layer, along the *c*-axis (Fig. 5a). The arrangement of the layers is AAAA type, such that it results in a one-dimensional channel-like arrangement, of the type commonly observed in aluminosilicate zeolites. Looking down the tube axis (*a*-axis), the tubes are connected to one another by 4-membered rings as shown in Fig. 5b.

The three-dimensional [C<sub>6</sub>N<sub>4</sub>H<sub>21</sub>]<sub>4</sub>[Zn<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>]<sub>3</sub>, **IV**, obtained by the transformation of the monomer **II**, has several

**Table 7** Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for **IV**, [C<sub>6</sub>N<sub>4</sub>H<sub>21</sub>]<sub>4</sub>[Zn<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>]<sub>3</sub>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Zn(1)	0	0	0	18(1)
Zn(2)	-280(1)	2155(1)	899(1)	22(1)
P(1)	-2268(1)	-201(1)	1065(1)	20(1)
O(1)	-897(6)	2947(6)	1490(4)	60(2)
O(2)	1178(4)	2567(5)	1364(4)	46(2)
O(3)	-243(5)	2733(5)	-281(3)	46(2)
O(4)	-998(3)	472(3)	790(3)	24(1)
N(1)	-3333	3333	-359(18)	149(9)
C(1)	-2075(45)	4601(45)	66(41)	346(21)
C(2)	-1415(28)	4312(24)	-373(19)	212(11)
N(2)	0	5000	0	124(6)

<sup>a</sup>*U*(eq) is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.



**Fig. 6** ORTEP plot of the three-dimensional zinc phosphate, [C<sub>6</sub>N<sub>4</sub>H<sub>21</sub>]<sub>4</sub>[Zn<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>]<sub>3</sub>, **IV**.

interesting structural features. In Table 7, we list the atomic coordinates of **IV**. The asymmetric unit of **IV**, presented in Fig. 6, contains 11 non-hydrogen atoms, of which 7 belong to the framework and 4 to the guest amine molecule. The structure of **IV** consists of a network of ZnO<sub>6</sub>, ZnO<sub>4</sub> and PO<sub>4</sub> polyhedra that are vertex linked forming the three-dimensional structure, in the channels of which the protonated molecules reside. Of the two distinct Zn atoms, Zn(1) is located in a special position and is octahedrally coordinated with oxygens and Zn(2) has the normal tetrahedral environment. The average Zn–O distances are 2.141 Å and 1.940 Å for Zn(1) and Zn(2), respectively. The O–Zn–O bond angles are in the expected range (Table 8) for this type of bonding. While Zn(1) is bonded only with Zn(2), Zn(2) is connected to the distinct P atom *via* Zn–O–P linkages. The P–O bond distances and angles have average values of 1.521 Å and 109.5°, respectively. Selected bond distances and angles are listed in Table 8. A framework with the formula Zn<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub> would result in a net negative charge of -4, which is balanced by the complete protonation of the terminal nitrogens of the amine molecule. Bond valence sum calculations<sup>11</sup> agree with this formalism.

The framework structure of **IV** is unusual in more ways than one. In addition to the presence of the octahedrally coordinated Zn atoms, rarely observed in open-framework zinc phosphates, **IV** possesses a unique tooth-wheel type cluster of the composition Zn<sub>7</sub>O<sub>6</sub>, formed by the Zn–O–Zn linkages (Fig. 7). The P atom links and caps the Zn–O cluster. Two such capped-clusters are connected *via* a 4-membered ring as shown in Fig. 8a, forming a sheet-like structure (Fig. 8b). One of the oxygen atoms of the capping PO<sub>4</sub> links the sheets into the third dimension forming one-dimensional channels along the [111] direction as shown in Fig. 9a. A similar connectivity results in channels along the *a* and *b* axes as well (Fig. 9b).

#### Transformation of the Zn phosphate monomer **I** to one-, two- and three-dimensional structures

The Zn phosphate monomer, [C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>][Zn(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>], **I**, was recently shown to transform to a layered phosphate of the composition [C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>][Zn<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>(HPO<sub>4</sub>)<sub>4</sub>], **VII**, under mild conditions.<sup>5</sup> We now find that this monomer also undergoes facile transformation to a new one-dimensional ladder, [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>][Zn(HPO<sub>4</sub>)], **V**, as well as to a three-dimensional, [C<sub>4</sub>N<sub>2</sub>H<sub>12</sub>][Zn<sub>2</sub>(H<sub>2</sub>O)(PO<sub>4</sub>)(HPO<sub>4</sub>)<sub>2</sub>], **VI**, structure in the presence of imidazole and piperazine respectively under hydrothermal conditions. The structure of the three-dimensional phosphate, **VI**, has been reported in the literature,<sup>13</sup> and will not be discussed here. What is significant is that the monomer **I** transform to one-, two- and three-dimensional structures.

The asymmetric unit of **V** contains 11 non-hydrogen atoms as shown in Fig. 10a. The structure is built up of ZnO<sub>3</sub>N and PO<sub>4</sub> tetrahedra sharing vertices. There is one each of crystallographically independent zinc and phosphorus atoms in the

**Table 8** Selected bond distances and angles in IV,  $[C_6N_4H_{21}]_4[Zn_7(PO_4)_6]_3$ 

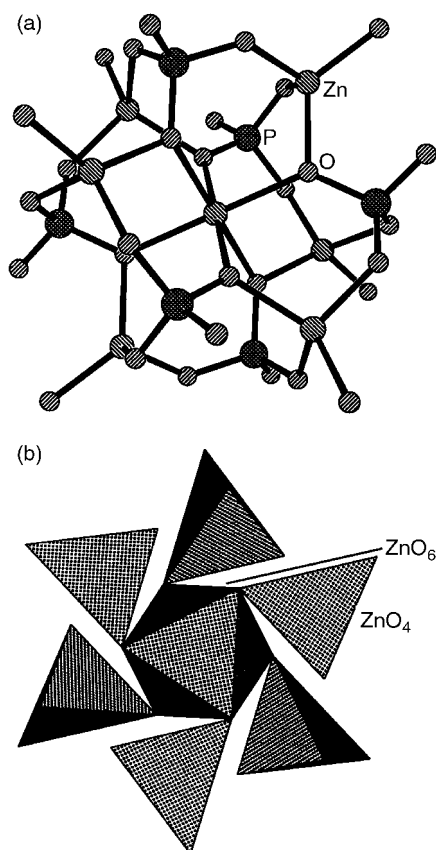
Moiety	Distance/Å	Moiety	Angle/°	Moiety	Angle/°
Zn(1)–O(4)	2.141(4)	O(4) <sup>#1</sup> –Zn(1)–O(4) <sup>#2</sup>	88.7(2)	O(1) <sup>#6</sup> –P(1)–O(3) <sup>#3</sup>	112.1(3)
Zn(2)–O(1)	1.894(5)	O(4) <sup>#1</sup> –Zn(1)–O(4) <sup>#3</sup>	91.4(2)	O(1) <sup>#6</sup> –P(1)–O(2) <sup>#2</sup>	107.1(3)
Zn(2)–O(2)	1.909(5)	O(4) <sup>#1</sup> –Zn(1)–O(4)	180	O(3) <sup>#3</sup> –P(1)–O(2) <sup>#2</sup>	111.6(4)
Zn(2)–O(3)	1.958(5)	O(4) <sup>#2</sup> –Zn(1)–O(4)	91.3(2)	O(1) <sup>#6</sup> –P(1)–O(4)	108.6(3)
Zn(2)–O(4)	1.997(4)	O(4) <sup>#3</sup> –Zn(1)–O(4)	88.6(2)	O(3) <sup>#3</sup> –P(1)–O(4)	107.9(3)
P(1)–O(1) <sup>#6</sup>	1.513(5)	O(4) <sup>#3</sup> –Zn(1)–O(4) <sup>#5</sup>	91.4(2)	O(2) <sup>#2</sup> –P(1)–O(4)	109.6(3)
P(1)–O(3) <sup>#3</sup>	1.521(5)	O(1)–Zn(2)–O(2)	110.3(2)	P(1) <sup>#6</sup> –O(1)–Zn(2)	154.6(4)
P(1)–O(2) <sup>#2</sup>	1.526(5)	O(1)–Zn(2)–O(3)	98.0(2)	P(1) <sup>#4</sup> –O(2)–Zn(2)	131.0(3)
P(1)–O(4)	1.555(4)	O(2)–Zn(2)–O(3)	114.2(3)	P(1) <sup>#5</sup> –O(3)–Zn(2)	119.1(3)
		O(1)–Zn(2)–O(4)	126.2(3)	P(1)–O(4)–Zn(2)	114.5(2)
		O(2)–Zn(2)–O(4)	102.0(2)	P(1)–O(4)–Zn(1)	131.3(2)
		O(3)–Zn(2)–O(4)	106.5(2)	Zn(2)–O(4)–Zn(1)	111.8(2)
Organic moiety					
Moiety	Distance/Å	Moiety	Angle/°		
N(1)–C(1)	1.84(5)	C(1) <sup>#6</sup> –N(1)–C(1)	108(2)		
C(1)–C(2)	1.33(5)	C(2)–C(1)–N(1)	90(3)		
C(2)–N(2)	1.76(3)	C(1)–C(2)–N(2)	114(3)		

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

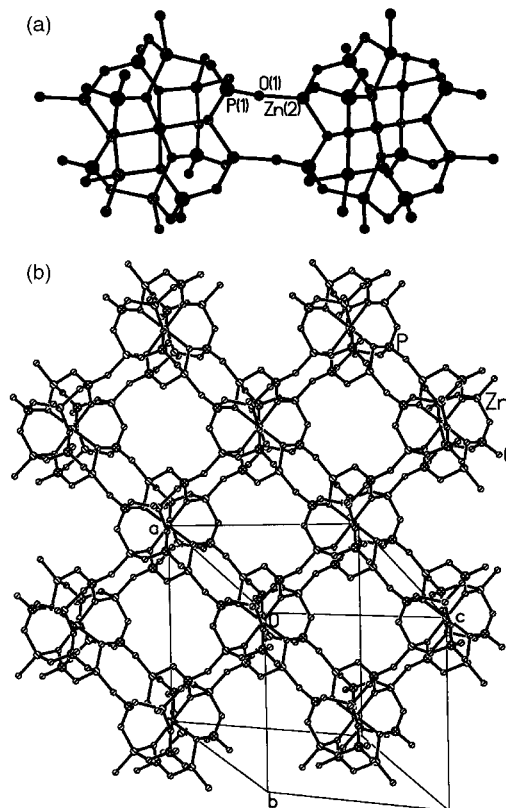
asymmetric unit. Both the zinc and phosphorus atoms are tetrahedrally coordinated with respect to the nearest atom neighbors but there exist only three Zn–O–P bonds. The remaining connection needed for the tetrahedral linkage comes from a terminal bonding with the zinc having a nitrogen (Zn(1)–N(1)=1.987(7) Å) and phosphorus with an oxygen atom (P(1)–O(4)=1.576(6) Å), which is formally an –OH group. The Zn–O and Zn–N bond distances and O–Zn–O and O–Zn–N angles are all as expected for this type of bonding

(Table 9). Bond valence sum calculations<sup>11</sup> agree with the above formalism.

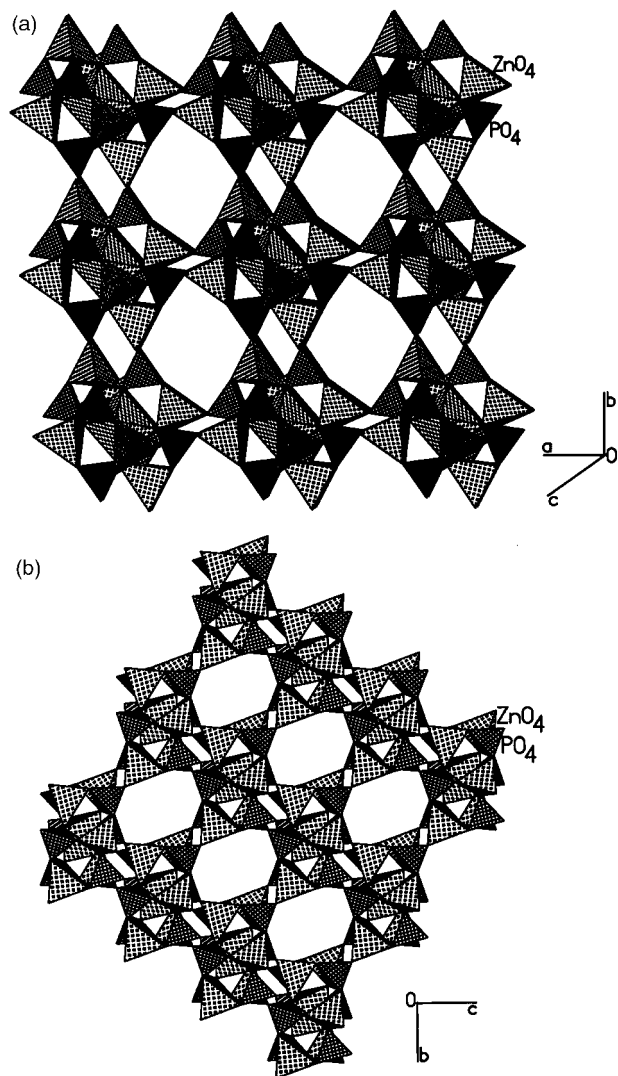
The framework structure of  $[C_3N_2H_5][Zn(HPO_4)]$  consists of ladders made up of 4-membered rings, onto which the imidazole molecules are grafted. The one-dimensional ladder consists of a network of strictly alternating  $ZnO_3N$  and  $PO_3(OH)$  tetrahedra sharing vertices. The connectivity between the tetrahedra is such that they form 4-membered rings that are shared edge-wise forming the ladder (Fig. 10b). The amine molecule is connected to the Zn center *via* the Zn–N bond and



**Fig. 7** (a) Ball and stick diagram showing the basic building unit in IV. (b) The unique  $Zn_7O_6$  cluster in a tooth-wheel arrangement.



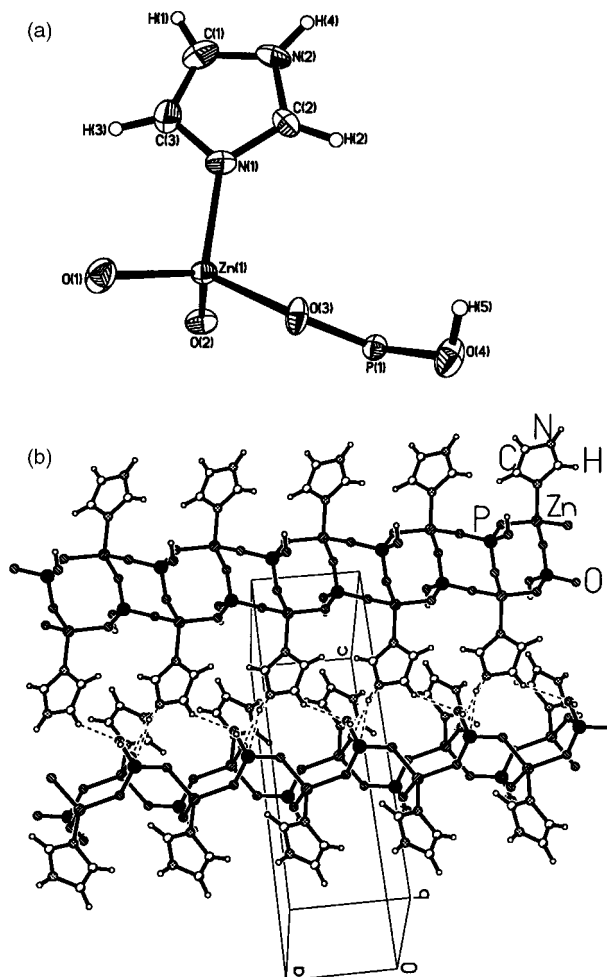
**Fig. 8** (a) Connectivity between two basic building units in IV. Note that the connectivity is through a 4-membered ring. (b) Layer-like arrangement in the  $ac$  plane formed by connecting the basic building units.



**Fig. 9** (a) Polyhedral representation of the structure of **IV** along the [111] direction showing an 8-membered channel. (b) Structure of **IV** along the *a* axis showing channels.

is situated in between the ladders as shown in Fig. 10b. The ladders are stabilized by extensive hydrogen bond interactions through N–H⋯O and C–H⋯O bonds.

It is well known that multipoint hydrogen bond interactions are necessary in the formation and stability of open architectures, especially so for solids possessing low dimensional structures. In the present case also, we find strong hydrogen bond interactions involving the hydrogens attached



**Fig. 10** (a) ORTEP plot of the one-dimensional ladder zinc phosphate, [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>][Zn(HPO<sub>4</sub>)], **V**. (b) The ladder structure with bonded imidazole molecules protruding in between two ladders.

to the nitrogen of the amine and framework oxygen atoms. The majority of the interactions are quite strong as indicated by the short hydrogen–acceptor distances ( $\sim 2.2$  Å) and a donor–hydrogen–acceptor angle of  $\sim 150^\circ$ . The important hydrogen bond interactions for the solids derived from monomer **I** and **V**, **II** and **III** are presented in Tables 10 and 11, respectively.

## Discussion

Three new zinc phosphates, [C<sub>6</sub>N<sub>4</sub>H<sub>21</sub>][NH<sub>4</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O], **III**, [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>7</sub>(PO<sub>4</sub>)<sub>6</sub>]<sub>3</sub>, **IV** and [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>][Zn(HPO<sub>4</sub>)], **V**, have been obtained in addition to

**Table 9** Selected bond distances and angles for **V**, [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>][Zn(HPO<sub>4</sub>)]

Moiety	Distance/Å	Moiety	Angle/°	Moiety	Angle/°
Zn(1)–O(1)	1.927(6)	O(1)–Zn(1)–O(2)	117.3(3)	O(3)–P(1)–O(4)	106.6(3)
Zn(1)–O(2)	1.941(6)	O(1)–Zn(1)–O(3)	109.3(2)	P(1) <sup>#3</sup> –O(1)–Zn(1)	134.2(4)
Zn(1)–O(3)	1.947(5)	O(2)–Zn(1)–O(3)	109.7(2)	P(1) <sup>#2</sup> –O(2)–Zn(1)	134.4(4)
Zn(1)–N(1)	1.987(7)	O(1)–Zn(1)–N(1)	106.5(3)	P(1)–O(3)–Zn(1)	126.0(3)
P(1)–O(1) <sup>#1</sup>	1.497(6)	O(2)–Zn(1)–N(1)	102.2(3)	C(2)–N(1)–C(3)	104.7(8)
P(1)–O(2) <sup>#2</sup>	1.521(6)	O(3)–Zn(1)–N(1)	111.6(3)	C(2)–N(1)–Zn(1)	128.1(6)
P(1)–O(3)	1.524(6)	O(1) <sup>#1</sup> –P(1)–O(2) <sup>#2</sup>	112.8(4)	C(3)–N(1)–Zn(1)	127.0(6)
P(1)–O(4)	1.576(6)	O(1) <sup>#1</sup> –P(1)–O(3)	110.3(3)	C(1)–N(2)–C(2)	107.3(8)
N(1)–C(2)	1.323(12)	O(2) <sup>#2</sup> –P(1)–O(3)	112.5(3)	C(3)–C(1)–N(2)	107.6(8)
N(1)–C(3)	1.396(12)	O(1) <sup>#1</sup> –P(1)–O(4)	111.5(4)	N(1)–C(2)–N(2)	110.5(8)
N(2)–C(1)	1.350(13)	O(2) <sup>#2</sup> –P(1)–O(4)	102.8(3)	C(1)–C(3)–N(1)	109.9(9)
N(2)–C(2)	1.359(12)				
C(1)–C(3)	1.319(14)				

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



**Table 10** Selected hydrogen bond interactions in **I** and **V**

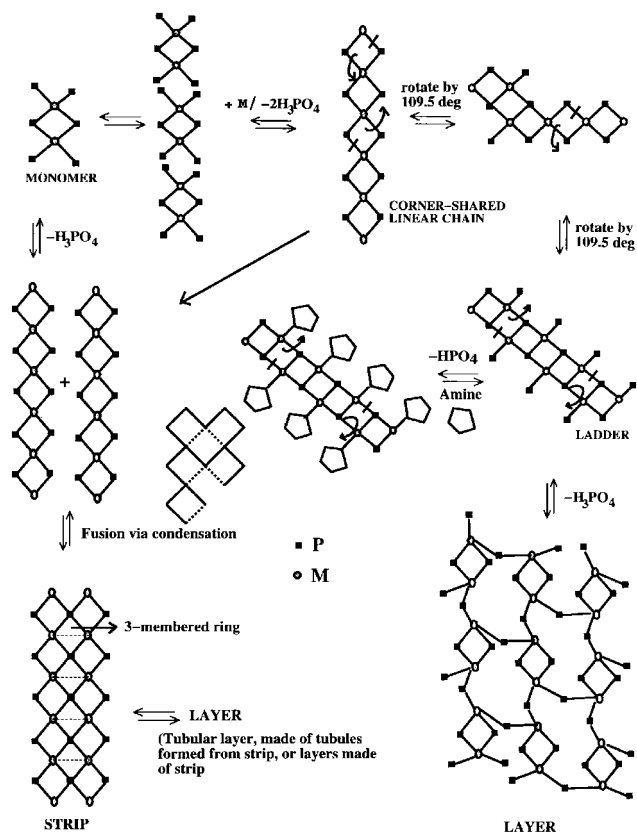
Moiety	Distance/Å	Moiety	Angle/°
<b>I</b>			
O(5)⋯H(3)	1.933(5)	N(1)–H(3)⋯O(5)	155.2(5)
O(4)⋯H(12)	1.928(6)	N(2)–H(12)⋯O(4)	165.5(5)
O(11)⋯H(20)	1.716(5)	O(8)–H(21)⋯O(6)	169.6(5)
O(11)⋯H(22)	1.849(5)	O(9)–H(22)⋯O(11)	149.9(4)
O(5)⋯H(23)	1.809(5)	O(10)–H(23)⋯O(5)	153.3(4)
O(6)⋯H(24)	1.872(5)	O(12)–H(24)⋯O(6)	140.9(5)
O(6)⋯H(1)	2.560(8)	C(1)–H(1)⋯O(6)	169.5(7)
<b>V</b>			
O(2)⋯H(4)	1.960(9)	N(2)–H(4)⋯O(2)	161.5(9)
O(3)⋯H(5)	2.049(8)	O(4)–H(5)⋯O(3)	134.5(7)
O(4)⋯H(1)	2.394(12)	C(1)–H(1)⋯O(4)	149.0(11)

the known  $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{H}_2\text{O})(\text{PO}_4)(\text{HPO}_4)_2]$ , **VI** and  $[\text{C}_6\text{N}_2\text{H}_{18}][\text{Zn}_3(\text{H}_2\text{O})_4(\text{HPO}_4)_4]$ , **VII**, by the transformations of zero-dimensional monomeric zinc phosphates **I** and **II**. The zero-dimensional zinc phosphates themselves are identical monomers formed with two different amines. Both the monomers, **I** and **II**, along with  $[\text{N}(\text{CH}_3)_4][\text{Zn}(\text{H}_2\text{PO}_4)_3]^{10}$  have the same configuration for the 4-membered ring, made with Zn and  $\text{PO}_2(\text{OH})_2$  units, but the terminal moieties create the subtle differences between the two. While in the zinc phosphate,  $[\text{N}(\text{CH}_3)_4][\text{Zn}(\text{H}_2\text{PO}_4)_3]^{10}$  the terminal hanging units from the Zn center are made up of  $\text{PO}_2(\text{OH})_2$  units, in **I** they are  $\text{PO}_3(\text{OH})$  and  $\text{PO}_2(\text{OH})_2$  units, and in **II** it is  $\text{PO}_3(\text{OH})$  units only. It has been postulated that the facile formation of higher dimensional structures from a lower dimensional one occurs *via* the deprotonation of the terminal  $-\text{OH}$  groups. The difference in the number of terminal  $-\text{OH}$  groups between the two monomers, **I** and **II**, could be one of the reasons why there

**Table 11** Selected hydrogen bond interactions in compounds **II** and **III**

Moiety	Distance/Å	Moiety	Angle/°
<b>II</b>			
O(8)–H(5)	2.069(5)	O(8)–H(5)–N(2)	173.7(4)
O(1)–H(6)	2.201(5)	O(1)–H(6)–N(2)	147.1(4)
O(5)–H(7)	1.915(5)	O(5)–H(7)–N(2)	159.3(4)
O(4)–H(13)	2.079(5)	O(4)–H(13)–N(3)	145.2(5)
O(8)–H(14)	1.819(6)	O(8)–H(14)–N(3)	165.5(5)
O(5)–H(19)	1.964(5)	O(5)–H(19)–N(3)	157.9(4)
O(6)–H(20)	1.922(5)	O(6)–H(20)–N(4)	153.5(5)
O(8)–H(21)	2.082(5)	O(8)–H(21)–N(4)	160.4(4)
O(9)–H(30)	1.964(5)	O(9)–H(30)–O(7)	150.4(4)
O(6)–H(31)	1.923(4)	O(6)–H(31)–O(10)	151.9(4)
O(9)–H(32)	1.709(5)	O(9)–H(32)–O(11)	159.4(5)
O(6)–H(34)	1.788(5)	O(6)–H(34)–O(12)	155.5(5)
O(2)–H(2)	2.487(6)	O(2)–H(2)–C(1)	170.2(6)
O(2)–H(18)	2.556(6)	O(2)–H(18)–C(6)	151.8(6)
<b>III</b>			
N(5)–H(5)	1.88(3) <sup>a</sup>	N(5)–H(5)–N(2)	171.0(2) <sup>a</sup>
O(5)–H(6)	2.39(3)	O(5)–H(6)–N(2)	148.0(2)
O(10)–H(7)	2.52(3)	O(10)–H(7)–N(2)	147.0(2)
O(100)–H(12)	2.06(2) <sup>b</sup>	O(100)–H(12)–N(3)	145.3(19) <sup>b</sup>
O(18)–H(13)	1.96(2)	O(18)–H(13)–N(3)	167.0(2)
O(24)–H(14)	2.10(2)	O(24)–H(14)–N(3)	170.6(19)
O(100)–H(19)	1.90(5) <sup>b</sup>	O(100)–H(19)–N(4)	164.0(2) <sup>b</sup>
O(19)–H(21)	2.05(5)	O(19)–H(21)–N(4)	145.0(2)
O(13)–H(1)	2.51(3)	O(13)–H(1)–C(1)	141.0(2)
O(2)–H(8)	2.41(3)	O(2)–H(8)–C(3)	145.0(3)
O(17)–H(15)	2.37(3)	O(17)–H(15)–C(5)	174.0(2)
O(5)–H(18)	2.21(3)	O(5)–H(18)–C(6)	162.0(3)

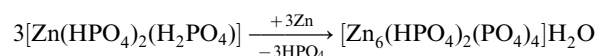
<sup>a</sup>Interactions between the amine and ammonium ion. <sup>b</sup>Interactions between the water molecule and ammonium ion.

**Fig. 11** A schematic showing the possible pathways in the formation of one- and two-dimensional structures from the monomer.

are more isolable higher dimensional structures for **I** compared to **II**. It is likely that the zero-dimensional zinc phosphate,  $[\text{N}(\text{CH}_3)_4][\text{Zn}(\text{H}_2\text{PO}_4)_3]^{10}$  with two  $\text{PO}_2(\text{OH})_2$  groups would be more reactive than **I** and **II**, and would possibly result in many interesting structures.

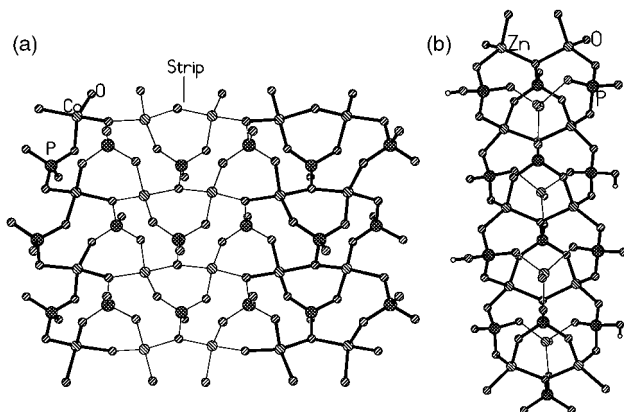
Among the higher dimensional phosphates obtained, **IV** and **VI** have three-dimensional structures, while **III** and **VII** have layered structures. The only one-dimensional structure produced by the transformations of the monomeric phosphate is **V** with a ladder structure. Compound **IV** can also be synthesized from the constituents, but **III** can be obtained only by the reaction of  $\text{Zn}(\text{OAc})$  with the monomer **II**. The ladder structure **V**, on the other hand, has been obtained by the reaction of imidazole with the monomer, **I**, resulting in the amine molecule directly bonding with the Zn center. The formation of structures of varying dimensionality from simple monomers points to the seminal role of the 4-membered ring.

The synthesis of the layered structure of **III** can be visualized as a simple addition of Zn and elimination of phosphate from **II** according to the following equation:



It is to be noted that **III** is formed by the reaction of **I** with  $\text{Zn}(\text{OAc})$  with the acetate anions favoring the deprotonation of the  $\text{H}_2\text{PO}_4$  units. It is known that poly-condensation of phosphoric acid generally occurs *via* the deprotonation of the terminal  $-\text{OH}$  groups, and that the deprotonation of the  $\text{PO}_3(\text{OH})$  and  $\text{PO}_2(\text{OH})_2$  occurs in the presence of either excess amine or acetate anions in the reaction mixture.<sup>14,15</sup>

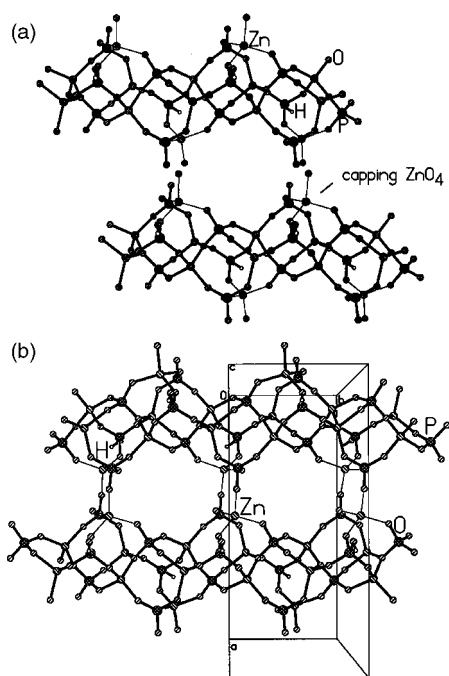
Compounds **V** and **VI** have been prepared by the addition of imidazole and piperazine to the monomer, **I**. The excess amine, imidazole, replaces the terminal hanging phosphate of the typical ladder structure of the zinc phosphate.<sup>16</sup> To our knowledge, the one-dimensional ladder structure of **V** has not



**Fig. 12** (a) Connectivity between two strips forming a layered structure. The strip is shown in thin lines for the purpose of clarity. (b) A strip with capped  $\text{ZnO}_4$  tetrahedra forming a tube-like architecture as found in **III**. The capping  $\text{ZnO}_4$  tetrahedra are outlined in thin lines.

been encountered hitherto. The formation of a typical ladder and **V** from the monomer is shown schematically in Fig. 11.

Although the layer structure of **III** does not appear to be related to the monomer **II**, it can be derived from a one-dimensional chain structure. From Fig. 11, one can visualize the formation of the chain from the monomer phosphate by the elimination of a phosphate group. From the structure of **III**, it is clear that the basic unit is a strip-like arrangement of two corner-shared chains joined *via* a 3-coordinated oxygen atom. Such an intermediate structure has been isolated recently in a cobalt phosphate.<sup>2</sup> The connectivity between the strips, along with the deprotonation of the phosphoryl group, can influence the final framework structure. Thus, when two strips are connected 'side-on', a layer structure of the type shown in Fig. 12a would be formed. Such layer structures have been isolated and characterized in cobalt phosphates.<sup>17</sup> On the other hand, when two strips are joined 'one over the other' by a capping  $\text{ZnO}_4$  unit, this results in the formation of a tube-like architecture (Fig. 12b). The tubes are joined to form a layer, as



**Fig. 13** (a) One-dimensional tubes with the  $\text{ZnO}_4$  tetrahedra that connected to the next tube (thin lines). (b) The layer zinc phosphate with the tubular unit. Note that the tubes are joined *via* a 4-membered ring.

observed in **II**. The formation of a layer structure from the tubes is shown in Fig. 13. Layered zinc phosphates with similar tube-like features have been described recently.<sup>18</sup> Understanding the formation of three-dimensional structures from the monomer, however, appears to be somewhat more difficult. It is possible that the 4-membered ring monomer first polymerizes into one- or two-dimensional structures, which then condense or assemble to form the three-dimensional ones.

## Conclusions

The present study establishes that zero-dimensional monomeric zinc phosphates can on transformation yield one-, two- and three-dimensional structures. An examination of the literature shows that the 3-dimensional open-framework structures are the most common among the phosphates and that the lower dimensional solids are few in number. There are only three monomeric phosphate structures known to date. The 4-membered ring unit monomeric phosphates are isolated only when a complex amine is employed, indicating that the isolation of the lower dimensional structures may in some way be also related to the steric inhibition of the assemblage of larger structures. The synthesis of zinc phosphate monomers comprising only the 4-membered rings and their condensation into layered and three-dimensional open-framework structures are therefore of considerable significance. In this context, it is to be noted that recent studies from this laboratory have shown that one-dimensional ladder zinc phosphates transform to two-dimensional layers as well as three-dimensional structures on heating in appropriate media. Walton *et al.*<sup>19</sup> have found that a linear gallium phosphate transforms to a three-dimensional structure on heating. It is possible that the difficulty in isolating low dimensional structures as well as the 4-membered ring monomers may be because they are both precursors to the complex 3-dimensional structures, which are formed by further assemblage of these units. Such an assemblage may occur spontaneously. Clearly the 4-membered ring monomers and one-dimensional structures are the basic building blocks of the open-framework structures.

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