

Transformations of two-dimensional layered zinc phosphates to three-dimensional and one-dimensional structures

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Transformations of the layered zinc phosphates of the compositions $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$, **I**, $[C_3N_2H_{12}][Zn_2(HPO_4)_3]$, **II** and $[C_3N_2OH_{12}][Zn_2(HPO_4)_3]$, **III**, containing triethylenetetramine, 1,3-diaminopropane, and 1,3-diamino-2-hydroxypropane, respectively, have been investigated under different conditions. On heating in water, **I** transforms to a one-dimensional (1-D) ladder and a three-dimensional (3-D) structure, while **II** gives rise to only a two-dimensional (2-D) layered structure. In the transformation reaction of **I** with zinc acetate, the same ladder and 3-D structures are obtained along with a tubular layer. Under similar conditions **II** gives a layered structure formed by the joining of two ladder motifs. **III**, on the other hand, is essentially unreactive when heated with water and zinc acetate, probably because the presence of the hydroxy group in the amine which hydrogen bonds to the framework. In the presence of piperazine, **I**, **II** and **III** give rise to a four-membered, corner-shared linear chain which is likely to be formed *via* the ladder structure. In addition, 2-D and 3-D structures derived from the 1-D linear chain or ladder structures are also formed. The primary result from the study is that the layers produce 1-D ladders, which then undergo other transformations. It is noteworthy that in the various transformations carried out, most of the products are single-crystalline.

Introduction

A variety of metal phosphates with open architectures of different dimensionalities have been prepared and characterized in recent years.¹ These include one-dimensional chain and ladder structures, two-dimensional layer structures and a large number of three-dimensional structures with channels.^{2–7} In addition, four-membered ring metal phosphates which we can consider to be zero-dimensional monomers have been isolated.⁸ The relationship amongst the structures of different dimensionalities constitutes an aspect of great relevance in understanding the formation of these fascinating architectures.⁹ There is reason to believe that zero- or one-dimensional structures act as the basic units in the building up process. Thus, we have shown recently that zero-dimensional monomeric zinc phosphates can be transformed into one-dimensional ladder (1-D), two-dimensional layer (2-D) and three-dimensional (3-D) channel structures.¹⁰ A detailed study of zinc phosphates with the one-dimensional ladder structure has revealed that they transform to two-dimensional layers as well as three-dimensional structures with channels under appropriate conditions.¹¹ A gallium phosphate with a linear chain structure has also been shown to transform to a three-dimensional structure.¹² It was there of importance to study whether the two-dimensional layers transform under mild reaction conditions to three-dimensional structures.

We have carried out extensive investigations of the transformations of three layered zinc phosphates – $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$, **I**, $[C_3N_2H_{12}][Zn_2(HPO_4)_3]$, **II**, and $[C_3N_2OH_{12}][Zn_2(HPO_4)_3]$, **III** – under different conditions. The topologies of the three layered structures are identical with a bifurcated 12-membered aperture. The only difference between these structures is in the stacking of the inorganic layer (AAAA-type in **I** and ABAB-type in **II** and **III**). Three important types of reactions of the layered phosphates have

been carried out: (i) heating **I–III** at 150 °C in water under hydrothermal conditions; (ii) hydrothermal treatment of **I–III** in the presence of zinc acetate; and (iii) hydrothermal treatment of **I–III** in the presence of varying concentrations of an added amine, namely, piperazine (PIP) or imidazole (IMD). The results are somewhat unexpected in that the transformations not only yield 3-D phosphates with channels, but also one-dimensional structures. It appears that the transformations of the 2-D layers to 3-D structures is a complex process possibly involving a one-dimensional intermediate. Linear chain structures are also formed by the transformations of the layered compounds in the presence of amines such as PIP.

Experimental

Synthesis and initial characterization

The two-dimensional layered zinc phosphates $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$, **I**, $[C_3N_2H_{12}][Zn_2(HPO_4)_3]$, **II**, and $[C_3N_2OH_{12}][Zn_2(HPO_4)_3]$, **III**, were prepared hydrothermally from a zinc phosphate gel containing triethylenetetramine, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ (TETA), 1,3-diaminopropane, $NH_2-CH_2-CH_2-CH_2-NH_2$ (DAP) and 1,3-diamino-2-hydroxypropane, $NH_2-CH_2-CH(OH)-CH_2-NH_2$ (DAHP) respectively. The synthesis of these layered structures has been reported in the literature,^{2b,3d,4a,5a} but in order to get good yields of the pure phases, we had to modify the synthetic procedures. In a typical synthesis of **I**, 0.3255g of ZnO was dispersed in 7.2 ml of water followed by the addition of 0.68 ml of conc. HCl (36%) to get a clear solution. Then 0.76 ml of H_3PO_4 (88%) was added to this solution and finally TETA was added dropwise under continuous stirring. The stirring was continued for another 30 min to obtain a gel of the final composition $ZnO:2HCl:3H_3PO_4:0.75TETA:100H_2O$, which was then transferred into a 23 ml PTFE-lined acid

Table 1 Synthetic conditions for I–III^a

Material	Composition				T/ °C	Time/ h
	ZnO	conc. HCl	H ₃ PO ₄	Amine		
I	1	2	3	0.75 (TETA)	100	72
II	1	—	8.25	1.93 (DAP)	—	55
III	1	—	8.19	1.948 (DAHP)	6.5	48

^aAbsolute amount of ZnO taken: 0.3255 g for **I**, 1 g for **II**, 0.6950 g for **III**; HCl 36% (w/w), H₃PO₄ 88% (w/w); TETA 70% (w/w) aqueous solution.

digestion bomb and heated at 150 °C for 72 h. The resulting product contained thin, plate-like crystals which were filtered and washed thoroughly with double distilled deionized water, and dried under ambient conditions. We summarize the synthetic conditions for preparing **I**, **II** and **III** in Table 1. All the three materials were characterized using powder X-ray diffraction (PXRD). The powder diffraction patterns were in good agreement with the simulated patterns generated from known single crystal data.

All the transformations were carried out in a 7 ml PTFE-lined acid digestion bomb by taking 0.100 g of starting materials at a temperature of 150 °C for a period of 24 h. The experimental parameters along with the products obtained in the transformations of **I–III** are listed in Tables 2–4. The resulting products were generally single crystalline although the starting layered phosphates were taken in the form of fine powders. The products were characterized by single-crystal and powder X-ray diffraction.

Powder X-ray diffraction and single crystal study

X-Ray powder diffraction data of the bulk samples of each batch of solid products obtained in the transformation reactions of **I**, **II** and **III** were collected. Based on a comparison of the powder pattern of the product with the reported data on the known open-framework zinc phosphates enabled us to identify most of the phases (**IV–XV**) formed in the transformation reactions. Single crystal structure determination of the new phase **XVI** was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus 2.4 kV sealed tube

Table 2 Conditions for the transformation of the layered zinc phosphate **I**

Composition	Conditions				Product	Ref.
	T/°C	t/h	pH	End pH		
I: H₂O	150	24	3.5	2.0	IV + V	5a
I: zinc acetate: H₂O						
1:0.25:200	150	24	2.5	2.5	IV, V, hopeite	5a
1:0.5:200	150	24	2.5	2.5	IV	5a
1:1:200	150	24	3.5	2.5	IV	5a
1:1.5:200	150	24	3.5	3.5	IV, VI, hopeite	4d
1:2:200	150	24	3.5	3.5	IV, hopeite, N-1	5a
I: PIP: H₂O						
1:0.25:200	150	24	>10.5	3.5	IV, V	5a
1:0.5:200	150	24	>10.5	4.0	IV, VII	5a
1:1:200	150	24	>10.5	6.0	VII, VIII, IX	5a,7
1:1.5:200	150	24	>10.5	6.5	VIII, X	5a,11
1:2:200	150	24	>10.5	7.0	VIII, X	5a,11
I: IMD: H₂O						
1:0.25:200	150	24	6.0	3.5	IV, V	5a
1:0.5:200	150	24	6.5	4.0	IV, V	5a
1:1:200	150	24	6.5	4.5	VIII, V, XI	5a,10
1:1.5:200	150	24	6.5	5.0	VIII, XI	5a,10
1:2:200	150	24	7.0	6.5	VIII, XI	5a,10

Table 3 Conditions for the transformation of the layered zinc phosphate **II**

Composition	Conditions				Product	Ref.
	T/°C	t/h	pH	End pH		
II: H₂O	150	24			XII	3e
II: zinc acetate: H₂O						
1:0.25:200	150	24	3.5	3.5	XIII	4b
1:0.5:200	150	24	3.5	3.5	XIII	4b
1:1:200	150	24	3.5	4.0	XIII, hopeite	4b
1:1.5:200	150	24	4.0	4.0	XIII, hopeite	4b
1:2:200	150	24	4.0	4.0	XIII, hopeite	4b
II: PIP: H₂O						
1:0.25:200	150	24	>10.5	4.0	VII, N-2, XIV	6e,7
1:0.5:200	150	24	>10.5	5.0	VII, N-2, XIV	6e,7
1:1:200	150	24	>10.5	6.0	XIV	6e
1:1.5:200	150	24	>10.5	7.5	XIV, XV	6e,7
1:2:200	150	24	>10.5	9.0	XIV, XV	6e,7
II: IMD: H₂O						
1:0.25:200	150	24	6.5	4.0	XII, III, XIV	3e,4b, 6e
1:0.5:200	150	24	6.5	4.0	III, XIV	4b,6e
1:1:200	150	24	6.5	4.5	III, XIV	4b,6e
1:1.5:200	150	24	6.5	4.5	XIV	6e
1:2:200	150	24	7.0	4.5	XIV	6e

X-ray source (Mo K α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame) in the 2θ range 3–46.5°.

The structure of **XVI** was solved by direct methods using SHELXS-86¹³ and difference Fourier syntheses. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.¹⁴ In the cation, all the atoms except the end nitrogen atoms of the amine molecule 1,3-diamino-2-hydroxypropane are disordered with site occupancy of 0.5. All the hydrogen positions were initially observed in the difference Fourier maps, and for the final refinement the hydrogen atoms were not included. The last cycles of refinement included atomic positions for all the atoms and anisotropic thermal parameters for all the atoms except

Table 4 Conditions for the transformation of the layered zinc phosphate **III**

Composition	Conditions				Product	Ref.
	T/°C	t/h	pH	end pH		
III: H₂O	150	24			No change	
III: zinc acetate: H₂O						
1:0.25:200	150	24	4.0	3.0	Hopeite	
1:0.5:200	150	24	4.0	3.0	Hopeite	
1:1:200	150	24	4.0	3.5	Hopeite	
1:1.5:200	150	24	4.0	3.5	Hopeite	
1:2:200	150	24	4.0	3.5	Hopeite	
III: PIP: H₂O						
1:0.25:200	150	24	>10.5	5.0	VII	7
1:0.5:200	150	24	>10.5	5.5	VII	7
1:1:200	150	24	>10.5	5.5	XVI	^a
1:1.5:200	150	24	>10.5	6.5	XV, XVI	7, ^a
1:2:200	150	24	>10.5	9.0	XV, XVI	7, ^a
III: IMD: H₂O						
1:0.25:200	150	24	5.0	4.5	XVI	^a
1:0.5:200	150	24	6.0	4.5	XVI	^a
1:1:200	150	24	6.0	4.5	XI, XVI	10, ^a
1:1.5:200	150	24	7.0	6.0	XI, XVI	10, ^a
1:2:200	150	24	7.0	6.0	XI, XVI	10, ^a

^aPresent work.

Table 5 Lattice parameters for the compounds I–XVI

Compd.	Lattice parameter					$V/\text{\AA}^3$	Space group	Formula	Ref.
	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\alpha/^\circ$	$\beta/^\circ$				
I	7.515(6)	8.2553(7)	12.9115(11)	98.6540(10)	101.274(2)	681.69(10)	$P\bar{1}$	$[\text{C}_6\text{N}_4\text{H}_{22}\text{O}_5]_2[\text{Zn}_3(\text{HPO}_4)_3]$	5a
II	8.6145(9)	9.6187(10)	17.038(2)	90.0	93.571(2)	1409.0(3)	$P2_1/c$	$[\text{C}_3\text{N}_2\text{H}_{12}]_2[\text{Zn}_2(\text{HPO}_4)_3]$	2b, 3d
III	8.6154(6)	9.6480(7)	17.2086(12)	90.0	93.0160(10)	1428.42(17)	$P2_1/c$	$[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Zn}_2(\text{HPO}_4)_3]$	4a
IV	5.2176(2)	8.7802(4)	16.0811(17)	89.340(2)	83.5370(10)	704.70(5)	$P1$	$[\text{C}_6\text{N}_4\text{H}_{22}\text{O}_5]_2[\text{Zn}_3(\text{PO}_4)_3(\text{HPO}_4)]$	5a
V	5.2677(5)	13.3025(13)	14.7833(14)	90.0	96.0490(10)	1030.2(2)	$P2_1/c$	$[\text{C}_6\text{N}_4\text{H}_{22}\text{O}_5]_2[\text{Zn}(\text{HPO}_4)_2]$	5a
VI	9.8809(4)	16.8571(8)	8.2862(2)	90.0	96.702(2)	1370.75(9)	$P2_1/c$	$[\text{C}_6\text{N}_4\text{H}_{22}][\text{Zn}_6(\text{HPO}_4)_2]$	4d
VII	8.931(2)	14.025(6)	9.311(2)	90.0	95.41(2)	1161.0(6)	$P2_1/n$	$[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$	7
VIII	8.0636(9)	8.4566(10)	9.0234(11)	111.941(2)	107.957(2)	498.09(10)	$P1$	$[\text{C}_6\text{N}_4\text{H}_{22}\text{O}_5]_2[\text{Zn}_2(\text{PO}_4)_2]$	5a
IX	13.4143(13)	12.8712(13)	8.2251(8)	90.0	94.780(2)	1415.2(2)	$C2/c$	$[\text{C}_4\text{N}_2\text{H}_{12}\text{O}_5]_2[\text{Zn}_2(\text{HPO}_4)_2]$	7
X	5.1351(7)	10.760(2)	10.771(2)	66.541(2)	89.025(2)	539.70(13)	$P\bar{1}$	$[\text{Zn}(\text{HPO}_4)(\text{C}_2\text{N}_2\text{H}_5)]$	11
XI	5.1971(6)	7.6972(9)	17.336(2)	90.0	90.618(2)	693.37(14)	$P2_1/c$	$[\text{Zn}(\text{HPO}_4)(\text{C}_2\text{N}_2\text{H}_5)]$	10
XII	5.2220(12)	12.756(4)	15.674(6)	90.0	90.0	1044.1(6)	$P2_12_12_1$	$[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$	3e
XIII	17.2792(7)	5.1929(2)	20.1154(6)	90.0	92.569(2)	1803.12(11)	$C2/c$	$[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_4)_2]$	4b
XIV	9.2994(4)	9.7510(4)	14.3348(6)	90.0	90.9740(10)	1299.67(9)	$P2_1$	$[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_5(\text{H}_2\text{O})(\text{PO}_4)_3(\text{HPO}_4)]$	6e
XV	16.1048(3)	8.2564(10)	22.9979(3)	90.0	103.9950(10)	2967.21(8)	$C2/c$	$[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_{3.5}(\text{PO}_4)_3(\text{H}_2\text{O})]$	7
XVI	22.9824(5)	7.6791(9)	6.6178(3)	90.0	90.0	1167.94(7)	$Pbcn$	$[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Zn}_2(\text{PO}_4)_2]$	a

*Present work.

those associated with the cation. All the atoms associated with the cations were refined isotropically because of the disorder. Full-matrix, least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS package of programs.¹⁵ The unit cell parameters of the various products obtained from the transformation reactions of **I**, **II**, and **III** are listed in Table 5. Details of the final refinements, selected bond angles, and bond lengths of the new zinc phosphate **XVI** are presented in Table 6, and 7.

Table 6 Crystal data and structure refinement parameters for **XVI**, $[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Zn}_2(\text{PO}_4)_2]$

Empirical formula	$\text{Zn}_2\text{P}_2\text{O}_9\text{C}_3\text{N}_2\text{H}_{12}$
Formula mass	439.74
Crystal system	Orthorhombic
Space group	$Pbcn$
$a/\text{\AA}$	22.9824(5)
$b/\text{\AA}$	7.6791(3)
$c/\text{\AA}$	6.6178(3)
$\alpha/^\circ$	90.0
$\beta/^\circ$	90.0
$\gamma/^\circ$	90.0
$V/\text{\AA}^3$	1167.94(7)
Z	8
$D_c/\text{g cm}^{-3}$	2.279
μ/mm^{-1}	4.420
θ Range/ $^\circ$	1.77–23.25
Total data collected	4347
Index ranges	$-23 \leq h \leq 25$, $-5 \leq k \leq 8$, $-7 \leq l \leq 7$
Unique data	844
Observed data [$I > 2\sigma(I)$]	671
Refinement method	Full-matrix, least-squares on $ F^2 $
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0542$, $wR_2 = 0.1147$
R indices (all data)	$R_1 = 0.0750$, $wR_2 = 0.1243^a$
Goodness of fit (S)	1.236
No. of variables	77
Largest difference map peak and hole/ $e \text{\AA}^{-3}$	0.830 and -0.522

^a $w = 1/[\sigma^2(F_o)^2 + (0.0328P)^2 + 14.3426P]$, where $P = [F_o^2 + 2F_c^2]/3$.

Table 7 Selected bond distances (\AA) and bond angles ($^\circ$) in **XVI**, $[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Zn}_2(\text{PO}_4)_2]$

Zn(1)–O(1)	1.938(6)
Zn(1)–O(2)	1.941(6)
Zn(1)–O(3) ^{#1}	1.963(6)
Zn(1)–O(3)	1.980(6)
P(1)–O(4)	1.510(6)
P(1)–O(1) ^{#2}	1.529(7)
P(1)–O(2) ^{#3}	1.535(7)
P(1)–O(3)	1.588(6)
O(1)–Zn(1)–O(2)	102.8(3)
O(1)–Zn(1)–O(3) ^{#1}	107.7(3)
O(2)–Zn(1)–O(3) ^{#1}	108.5(3)
O(1)–Zn(1)–O(3)	105.5(3)
O(2)–Zn(1)–O(3)	112.6(3)
O(3) ^{#1} –Zn(1)–O(3)	118.5(3)
O(4)–P(1)–O(1) ^{#2}	110.8(4)
O(4)–P(1)–O(2) ^{#3}	111.8(4)
O(1) ^{#2} –P(1)–O(2) ^{#3}	112.3(4)
O(4)–P(1)–O(3)	109.6(4)
O(1) ^{#2} –P(1)–O(3)	105.8(4)
O(2) ^{#3} –P(1)–O(3)	106.3(4)
P(1) ^{#4} –O(1)–Zn(1)	134.4(4)
P(1) ^{#5} –O(2)–Zn(1)	130.7(4)
P(1)–O(3)–Zn(1) ^{#6}	120.9(4)
P(1)–O(2)–Zn(1)	115.7(3)
Zn(1) ^{#6} –O(3)–Zn(1)	114.1(3)

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

CCDC reference number 172864.

See <http://www.rsc.org/suppdata/jm/b1/b105899c/> for crystallographic data in CIF or other electronic format.

Results

Transformation of the layered phosphate, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{HPO}_4)_3]$, I

The layered zinc phosphate I [Fig. 1(a)] undergoes facile transformation to a three-dimensional structure, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_3(\text{HPO}_4)]$, IV, and a one-dimensional ladder structure, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}(\text{HPO}_4)_2]$, V, on heating with water at 150 °C under hydrothermal conditions (see Table 2). The structures of both IV and V have been reported in the literature.⁵ IV has a three-dimensional structure with a 16-membered, one-dimensional channel as shown in Fig. 2(a). The one-dimensional ladder in V is constructed from infinite edge-shared, four-membered rings of ZnO_4 and HPO_4 tetrahedra as shown in Fig. 2(b). An important feature of the ladder structure is the presence of pendant HPO_4 groups from the Zn center.

When I was heated in a relatively dilute aqueous solution of $\text{Zn}(\text{OAc})_2$ at 150 °C under hydrothermal conditions, a mixture of IV and V was obtained along with a small proportion of the condensed zinc phosphate hopeite (JCPDS card no. 37-0465) (Table 2). On increasing the concentration of the zinc salt, IV was obtained in pure form, followed by the formation of another layered zinc phosphate, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4)]$, VI. The structure of VI is a two-dimensional layer formed by one-dimensional tubes^{4b} as shown in Fig. 2(c). At the highest concentration of zinc acetate employed (Table 2), the hopeite phase was the predominant product along with IV and a new phase, N-I, with a low angle reflection at $d = 14.38 \text{ \AA}$.

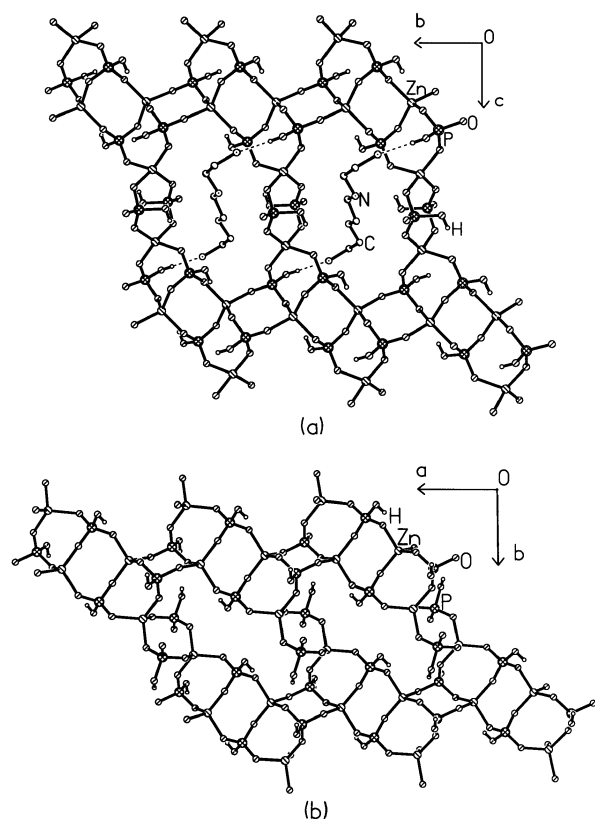


Fig. 1 (a) Layered structure of $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{HPO}_4)_3]$, I, with the amine molecules sitting in the 12-membered aperture. The hydrogens of the amines are not shown. (b) Layered structure of $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{HPO}_4)_3]$, II, showing the bifurcated 12-membered aperture. The amine molecules are not shown.

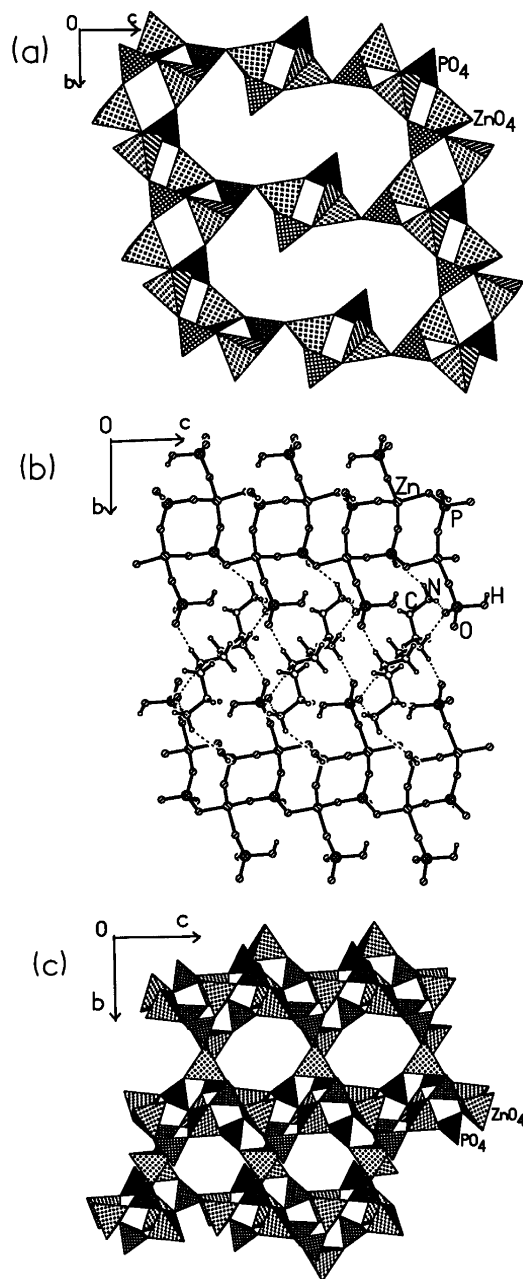


Fig. 2 (a) Polyhedral view of $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_3(\text{HPO}_4)]$, IV, along the *a*-axis showing the 16-membered channel. The amine (TETA) present in the 16-membered channel has been omitted for clarity. (b) Structure of $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}(\text{HPO}_4)_2]$, V, showing the ladder structure with edge-shared, four-membered rings propagating along the *a*-axis. Dashed lines represent H-bond interactions. (c) Polyhedral view of the structure of $[\text{C}_6\text{N}_4\text{H}_{22}][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2]$, VI, along the *a*-axis, showing the eight-membered aperture. Amine molecules are omitted for clarity.

The new phase could not be characterized since we could not isolate a single crystal. The evolution of the different phases with varying concentrations of $\text{Zn}(\text{OAc})_2$ can be seen from the powder diffraction patterns given in Fig. 3.

The transformation of the layered zinc phosphate I was studied under hydrothermal conditions in the presence of varying concentrations of piperazine (PIP) and imidazole (IMD). When I was heated with PIP, the 3-D zinc phosphate IV and the ladder zinc phosphate V formed initially (Table 2). With an increasing concentration of PIP, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2] \cdot \text{H}_2\text{O}$, VII, with a one-dimensional, corner-shared chain structure was obtained along with IV, followed by the formation of two known 3-D structures,^{5a,7}

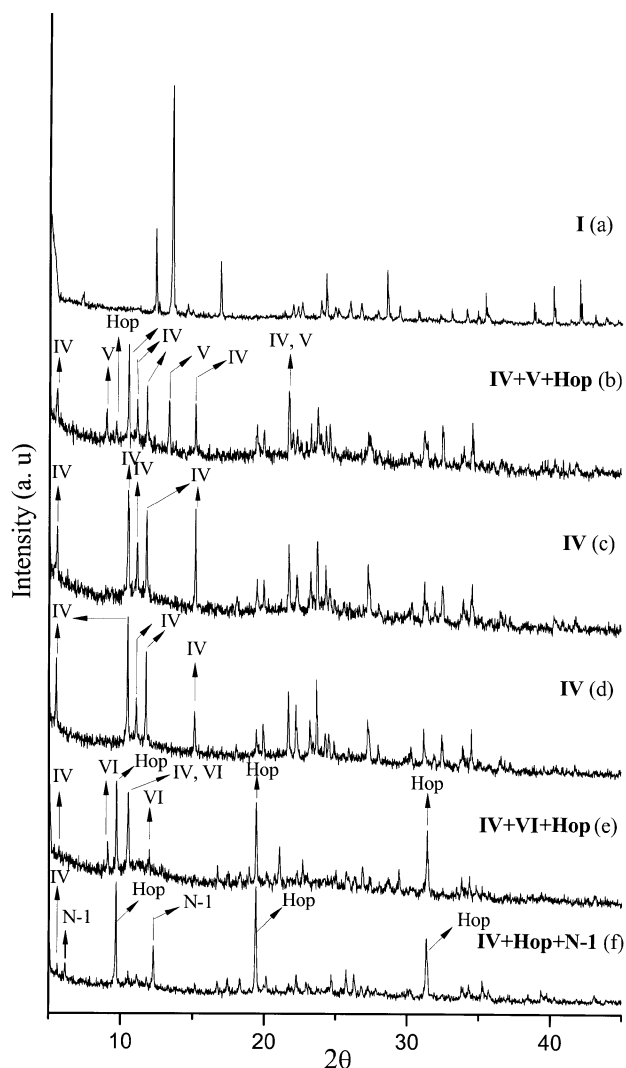


Fig. 3 Powder XRD patterns of the products obtained by the transformation of **I** with different molar ratios of $\text{Zn}(\text{OAc})_2$ with respect to **I** (150 °C for 24 h). (a) Pure **I**; (b) **I**: 0.25 $\text{Zn}(\text{OAc})_2$: 200 H_2O ; (c) **I**: 0.50 $\text{Zn}(\text{OAc})_2$: 200 H_2O ; (d) **I**: 1.00 $\text{Zn}(\text{OAc})_2$: 200 H_2O ; (e) **I**: 1.50 $\text{Zn}(\text{OAc})_2$: 200 H_2O ; (f) **I**: 2.00 $\text{Zn}(\text{OAc})_2$: 200 H_2O . (see Table 2).

$[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{PO}_4)_2]$, **VIII**, and $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2]$, **IX**. On further increase in the concentration of PIP, another layered zinc phosphate $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{PO}_4)_2]$, **X**, appeared along with **VIII**. At the highest concentration of the PIP employed (see Table 2), **X** was the predominant product. In **VII**, **IX** and **X** obtained by the transformation of **I** in the presence of PIP, PIP replaces the amine present originally (TETA). In the one-dimensional chain of **VII** there are no pendant HPO_4 groups [Fig. 4(a)]⁷ unlike in the ladder structure of **V**. The three-dimensional structures of **VIII** and **IX** have an eight-membered channel and a clover-like 16-membered channel respectively. While **VIII** has channels in all the three crystallographic directions^{5a} [Fig. 4(b)], **IX** has infinite chains of corner-shared, four-membered rings running in two different directions with a 16-membered clover-like aperture present in the junctions of four such chains as shown in Fig. 5(a). The structure of **X** is two-dimensional and is constructed from the fusion of 4- and 3-membered ring ladders¹¹ as shown in Fig. 5(b). The linear chain phosphate **VII** is clearly formed by the ladder as described earlier.⁹ More interestingly the structure **IX** formed in the presence of PIP is clearly derived from the linear chain **VII**.⁷ The transformations of **I** to various open framework structures in the presence of PIP are presented in the form of powder X-ray patterns given in Fig. 6.

When **I** was heated with IMD under hydrothermal

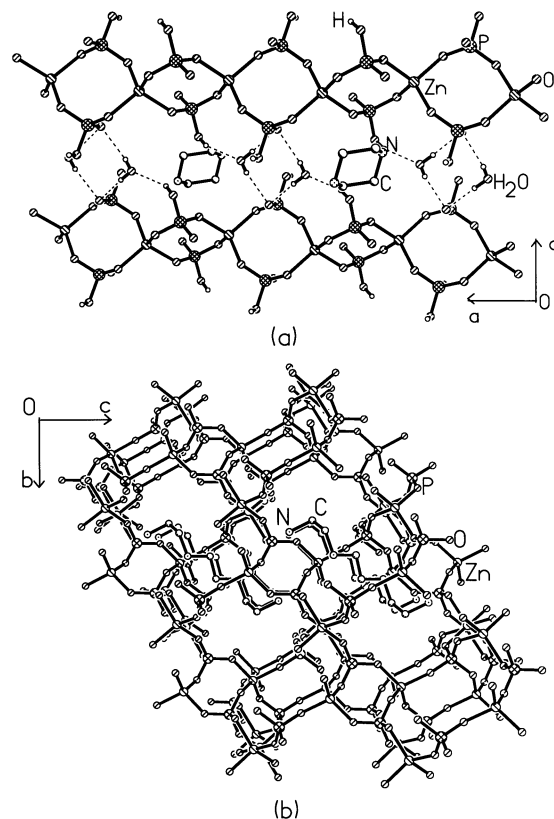


Fig. 4 (a) Structure of **VII**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]\cdot\text{H}_2\text{O}$, showing the linear chains of corner-shared rings and the amine (PIP), and H_2O molecules. Dotted lines represent possible H-bond interactions. (b) Structure of **VIII**, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{PO}_4)_2]$ along the [100] direction showing the eight-membered channel with the amine TETA. The hydrogens of the amine are omitted for clarity.

conditions, the 3-D zinc phosphate **IV** and the ladder zinc phosphate **V** were formed first. Just as in the case of PIP, with the increasing concentration of IMD **IV** forms predominantly, followed by **VIII** and a one-dimensional structure of the composition $[\text{Zn}(\text{HPO}_4)(\text{C}_2\text{N}_2\text{H}_5)]$, **XI**. At the highest concentration of IMD, **XI** was the predominant product (Table 2). The ladder structure of **XI** is similar to that of **V** except that the ladder is neutral in the former while it is anionic in **V**. Instead of the pendant HPO_4 groups, it has imidazole units bonded to the Zn centers.¹⁰ Thus **XI** is derived from **V** by the replacement of the pendant HPO_4 groups by the amine.

Transformation of the layered zinc phosphate, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{HPO}_4)_3]$, **II**

On heating the layered zinc phosphate **II** [Fig. 1(b)] in water, it undergoes facile transformation to a one-dimensional ladder structure, **XII**, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$, whose structure is reported in the literature.^{3c} The ladder in **XII** [Fig. 7(a)] is identical to that of **V**, the only difference being the charge balancing cation. In **XII**, the cation is protonated DAP, while it is protonated TETA in **V**. No 3-D structure was formed in reactions of **II** in water at 150 °C. When **II** was heated with $\text{Zn}(\text{OAc})_2$ under hydrothermal conditions, a layered compound, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_4)_2]$, **XIII**, of known structure^{4b} was formed along with a small amount of hopeite. With the increasing concentration of $\text{Zn}(\text{OAc})_2$ (Table 3), the proportion of hopeite increases. The structure of **XIII** can be described as formed by the fusion of two ladders through the insertion of Zn^{2+} ions as shown in Fig. 7(b).

When **II** was heated with PIP under hydrothermal conditions, the one-dimensional chain phosphate **VII** formed initially along with a known 3-D structure of the composition $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_5(\text{H}_2\text{O})(\text{PO}_4)_4(\text{HPO}_4)]$, **XIV** and a new phase,

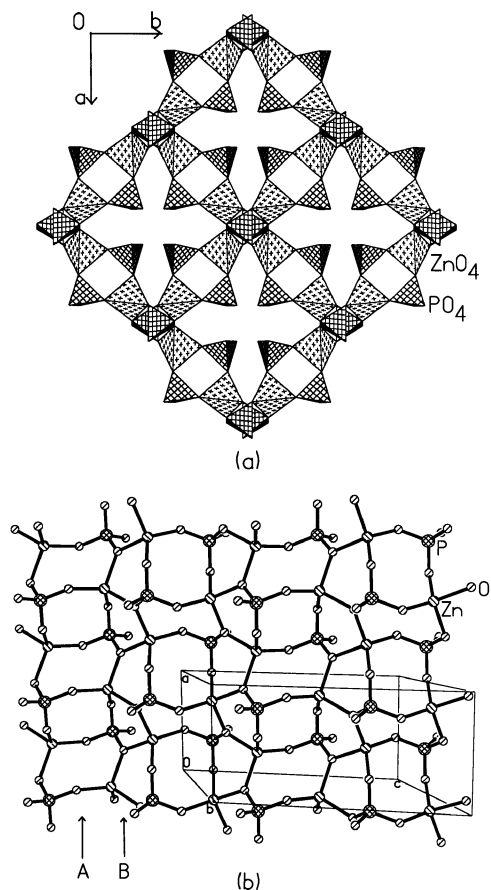


Fig. 5 (a) Polyhedral view of **IX**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{0.5}[\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$, along the c -axis showing clover-like 16-membered channels. Amine molecules (PIP) are omitted for clarity. (b) The layer structure of **X**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{PO}_4)_2]$, showing the fusion of four-membered ring ladders (A) with three-membered ring ladders (B).

N-2, exhibiting a low-angle reflection at $d = 10.2655 \text{ \AA}$. **N-2** could not be characterized since a suitable single crystal was not found for structure solution. With increasing concentration of PIP, another 3-D structure $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_{3.5}(\text{PO}_4)_3(\text{H}_2\text{O})]$, **XV**, formed along with **XIV**, the latter being the predominant product (Table 3). The structure of **XIV** is close to that of the aluminosilicate mineral thomsonite [Fig. 8(a)] and has been reported recently.^{6e} On the other hand, **XV** has a complex 3-D structure based on ZnO_4 and PO_4 tetrahedra.⁷ The connectivity between the ZnO_4 and PO_4 tetrahedra creates an eight-membered channel along the (001) and (011) directions [Fig. 8(b)]. While PIP replaced DAP in **XV**, DAP is still present in **XIV**. The formation of the different open framework structures by the transformation of **II** in the presence of varying concentrations of PIP is shown in Fig. 9 through the powder XRD patterns.

When **II** was heated with imidazole, the one-dimensional ladder **XII** was obtained along with the two-dimensional layer **XIII** and the three-dimensional **XIV**. On increasing the concentration of IMD, only the last two were formed, and at the highest concentration of IMD employed (Table 3), **XIV** was the only product (Table 3).

Transformation of the layered zinc phosphate $[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Zn}_2(\text{HPO}_4)_3]$, **III**

Encouraged by the results from the transformations of the layered zinc phosphates **I** and **II**, we carried out a similar series of experiments with another layered zinc phosphate with a comparable structure, but containing the amine DAHP. To our surprise we found that this layered phosphate is relatively unreactive. Thus, on heating **III** with water at 150°C , it did not

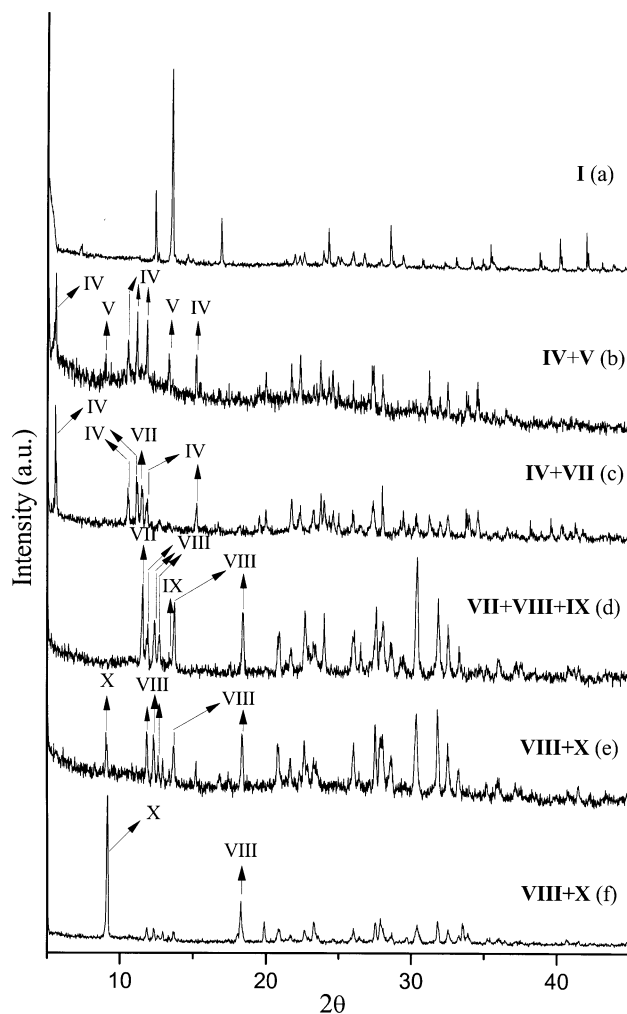


Fig. 6 Powder XRD patterns of the products obtained by the transformation of **I** with different molar ratios of PIP with respect to **I** (150°C for 24 h). (a) Pure **I**; (b) **I**:0.25 PIP:200 H_2O ; (c) **I**:0.50 PIP:200 H_2O ; (d) **I**:1.00 PIP:200 H_2O ; (e) **I**:1.50 PIP:200 H_2O ; (f) **I**:2.00 PIP:200 H_2O (see Table 2).

undergo any change. Even when **III** was treated with varying concentrations of $\text{Zn}(\text{OAc})_2$ it underwent no change, except for the formation of hopeite (Table 4). However, when treated with PIP and IMD, **III** underwent some transformations. Thus, on heating with PIP, **III** formed the one-dimensional, corner-shared chain **VII**, and a new two-dimensional zinc phosphate $[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Zn}_2(\text{PO}_4)_2]$, **XVI**. With the increasing concentration of PIP, the proportion of **XVI** increased. At the highest concentration of PIP employed (Table 4), **XVI** was the major product along with the 3-D structure **XV**. When **III** was heated with IMD, the new phase **XVI** was again obtained as a primary product. With increasing the concentration of IMD, the ladder structure **XI** containing IMD units was obtained along with **XVI**. The evolution of the different phases with varying IMD concentration can be seen from the powder diffraction patterns given in Fig. 10.

The new layered zinc phosphate **XVI**, $[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Zn}_2(\text{PO}_4)_2]$ consists of a network of ZnO_4 and PO_4 tetrahedra. The asymmetric unit of **XVI** contains ten non-hydrogen atoms [Fig. 11(a)] of which six belong to the framework and four to the guest. The Zn atom is tetrahedrally coordinated by oxygens with an average Zn–O distance of 1.955 \AA . Of the four oxygens that are connected with Zn, three oxygens connect with the distinct P atom via a Zn–O–P linkage and the fourth oxygen links up with the adjacent Zn atom forming infinite one-dimensional Zn–O–Zn linkages. The P atom makes three P–O–Zn bonds and the remaining is a terminal P–O bond. The P–O

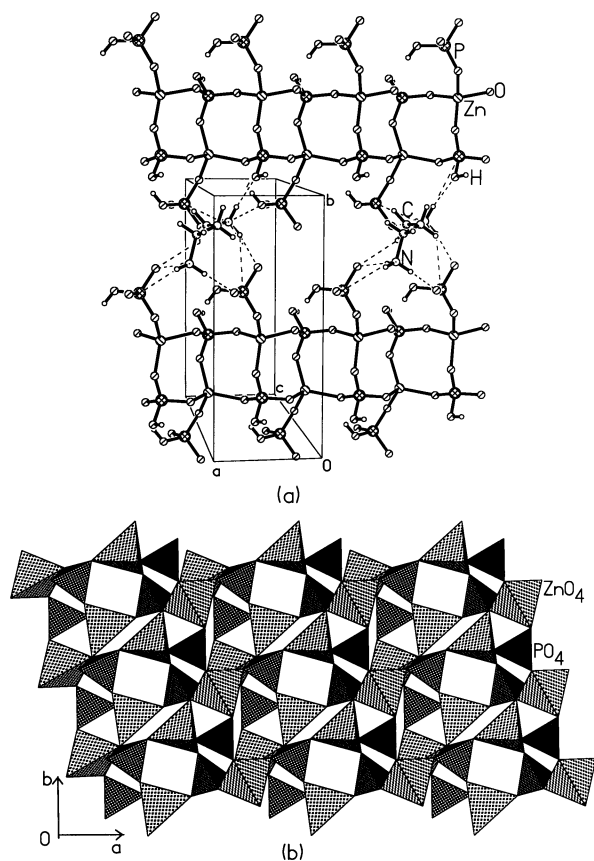


Fig. 7 (a) Structure of **XII**, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$, showing the four-membered ladder-like chain propagating along the a -axis. Dashed lines represent the H-bond interactions between the 1,3-diammonium ion and pendant HPO_4 group. (b) Polyhedral view of a single layer of **XIII**, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_4)_2]$.

distances are in the range 1.510(6)–1.588(6) Å, the longest distance being associated with the three-coordinated oxygen and the shortest being the P=O bond. Selected bond distances and angles for **XVI** are given in Table 7 and are in good agreement with the literature values for similar compounds.^{3–6}

The layered framework structure of **XVI** is built up from ZnO_4 and PO_4 tetrahedra sharing vertices, forming 3- and 4-membered rings as shown in Fig. 11(b). The terminal P=O group of the PO_4 unit projects into the interlamellar space in an alternating pattern above and below the plane [Fig. 11(c)]. The disordered di-protonated 1,3-diamino-2-hydroxypropane molecules occupy the interlamellar space and interact with the framework *via* hydrogen bond interactions. Thus, in **XVI**, the inorganic and organic layers alternate. The structure of **XVI** is the Zn analogue of a layered CoPO_4 obtained with DAHP and with other amines.¹⁶

Discussion

The results discussed above clearly demonstrate that the 2-D layered zinc phosphates undergo interesting transformations, under simple reaction conditions. The 2-D layered zinc phosphates **I** and **II** give rise to 3-D channel structures under the different conditions employed, but the 2-D to 3-D transformation is not as straightforward as one imagined.¹⁷ Thus, on heating the layered compound **I** in water we get 3-D structure **IV** along with the ladder structure **V**. This observation suggests that the formation of ladder structure may play an important role in the formation of the 3-D structure. Accordingly, we find that the layered structure **II** gives only a ladder structure **XII** on heating with water. We are therefore tempted to propose that the one-dimensional ladder is the

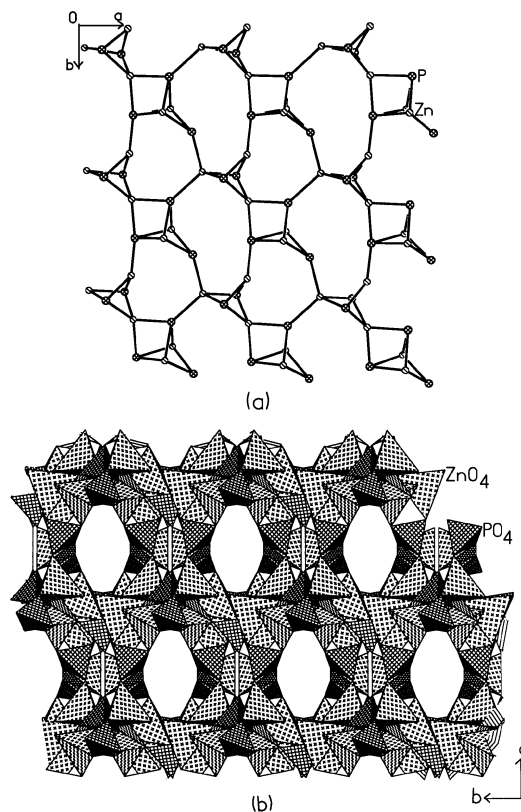
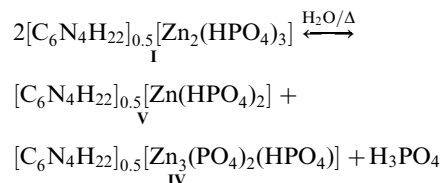


Fig. 8 (a) The T atom (T = Zn and P) connectivity in the structure of **XIV**, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_5(\text{H}_2\text{O})(\text{PO}_4)_4(\text{HPO}_4)]$, along the c -axis showing the channels. (b) Polyhedral view of **XV**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_{3.5}(\text{PO}_4)_3(\text{H}_2\text{O})]$, along the $[001]$ direction showing the eight-membered channels.

initial (primary) product of the transformation of the layer structures. The ladder then transforms to the 3-D structures as indeed described in an earlier study.¹¹ A possible mechanistic pathway can be given for the hydrothermal reaction of **I** in water:



The above reaction requires H_3PO_4 to be one of the products, and this is in fact manifested by the decrease in the pH of the medium after the reaction (see Table 2). Further, from the above reaction one would expect that **IV** (a 3-D structure), on treatment with H_3PO_4 , should yield the layer compound **I**. We have found this to be so in a reaction of **IV** with H_3PO_4 carried out independently.

In the reactions carried out in the presence of $\text{Zn}(\text{OAc})_2$ it is possible that the acetate ion plays a role in the deprotonation of the HPO_4 groups. Accordingly, in the presence of $\text{Zn}(\text{OAc})_2$, we get a ladder and a 3-D structure in the case of **I** while in the case of **II** a different layered structure **XIII** is obtained. The structure of **XIII** is likely to be formed by the condensation of ladders through the insertion of Zn^{2+} ions. The layered structure **III** is different from either **I** or **II** in that it is not very reactive. This may be due to the presence of the hydroxy group in the amine, which interacts with the framework through H-bonding to give extra stability.

The transformations of the layered structures in the presence of amines is, however, more complex because the amines can interact with the framework HPO_4 groups and deprotonate them. Accordingly, we found that the products formed in the

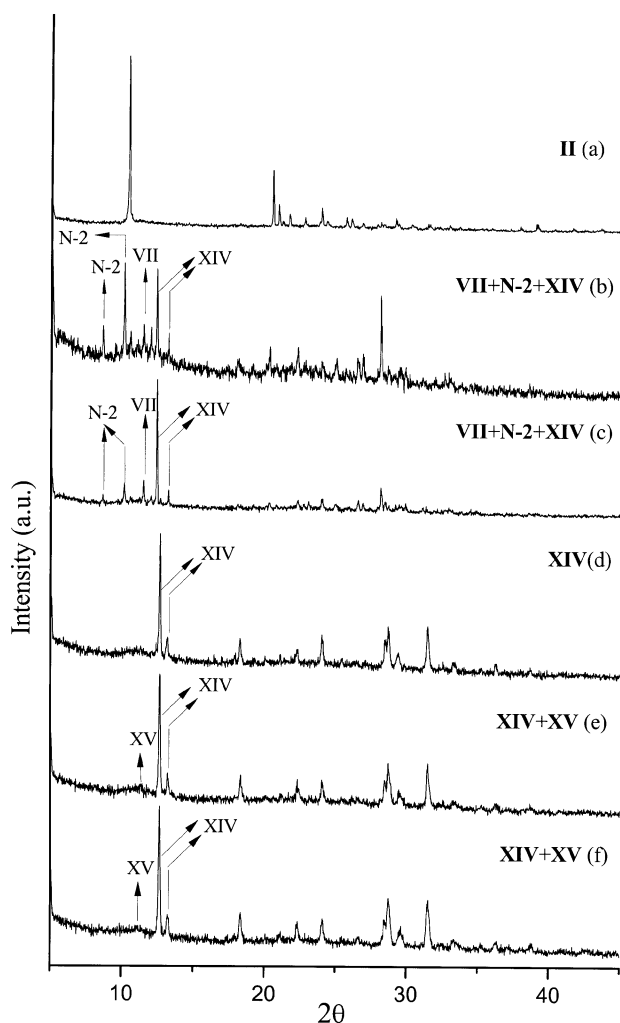
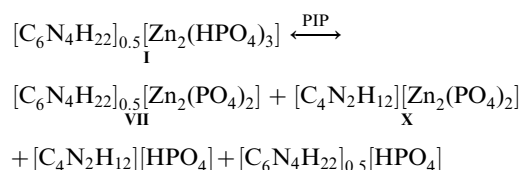


Fig. 9 Powder XRD patterns of the products obtained by the transformation of **II** with different molar ratios of PIP with respect to **II** (150 °C for 24 h). (a) Pure **II**; (b) **II**:0.25 PIP:200 H₂O; (c) **II**:0.50 PIP:200 H₂O; (d) **II**:1.00 PIP:200 H₂O; (e) **II**:1.50 PIP:200 H₂O; (f) **II**:2.00 PIP:200 H₂O; (see Table 3).

presence of high concentrations of amine are devoid of HPO₄ groups. At high amine concentrations, the added amine replaces the amines of the starting material (**I**, **II**, **III**). A typical reaction of the layered phosphates in the presence of high amine concentrations can be represented as follows:



We have isolated the amine phosphates, formed as by-products, in the above reaction. The added amine can also compete with the amine present originally in the starting layered compound. It is because of this reason that the amines are able to give rise to the linear chain structure (**VII**) on reaction with **I**, **II**, and **III**. The linear chain is likely to be formed *via* the ladder initially produced through the transformation of the layer phosphate. When the amine concentration is low we get the same structures as we get with pure water, as one would expect. Another significant aspect in the present study is that we always obtain single crystalline products even though we start with finely ground powders of the starting layered phosphates. Such crystallization is clearly related to the

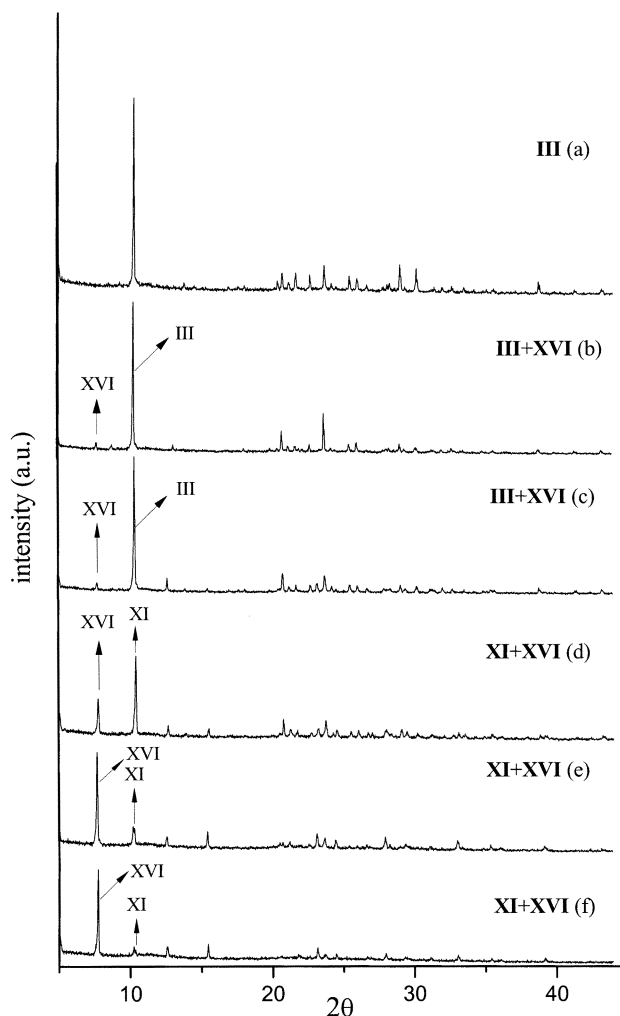


Fig. 10 Powder XRD patterns of the products obtained by the transformation of **III** with different molar ratios of IMD with respect to **III** (150 °C for 24 h). (a) Pure **III**; (b) **III**:0.25 IMD:200 H₂O; (c) **III**:0.50 IMD:200 H₂O; (d) **III**:1.00 IMD:200 H₂O; (e) **III**:1.50 IMD:200 H₂O; (f) **III**:2.00 IMD:200 H₂O; (see Table 4).

unusual nature of the self-assembly (and dis-assembly) in these systems.

Conclusions

Careful investigations of the transformations of the 2-D layered zinc phosphates have clearly demonstrated that they generally transform to a ladder and a 3-D structure or a ladder alone under relatively mild conditions. This observation suggests that the ladder is the initial (primary) product of the transformation, which then gives rise to a 3-D structure, or a new layered structure. In the presence of a high concentration of amines such as PIP and IMD, the layered phosphates give rise to 3-D structures as well as linear chain structures containing corner-shared chains of four-membered rings. The linear chains can be derived from the ladder structures initially formed in the reaction. Some of the 3-D structures formed in the reaction of the layered phosphate with amines appear to be derived from the linear chain structures. The results of this study not only throw light on the intricate relationship among the open framework phosphates of different dimensionalities, but also provide a mechanism of formation of the complex structures. It appears that the 2-D layer structures are incidental products of the transformation of 1-D ladder structures, the latter constituting the primary building units.

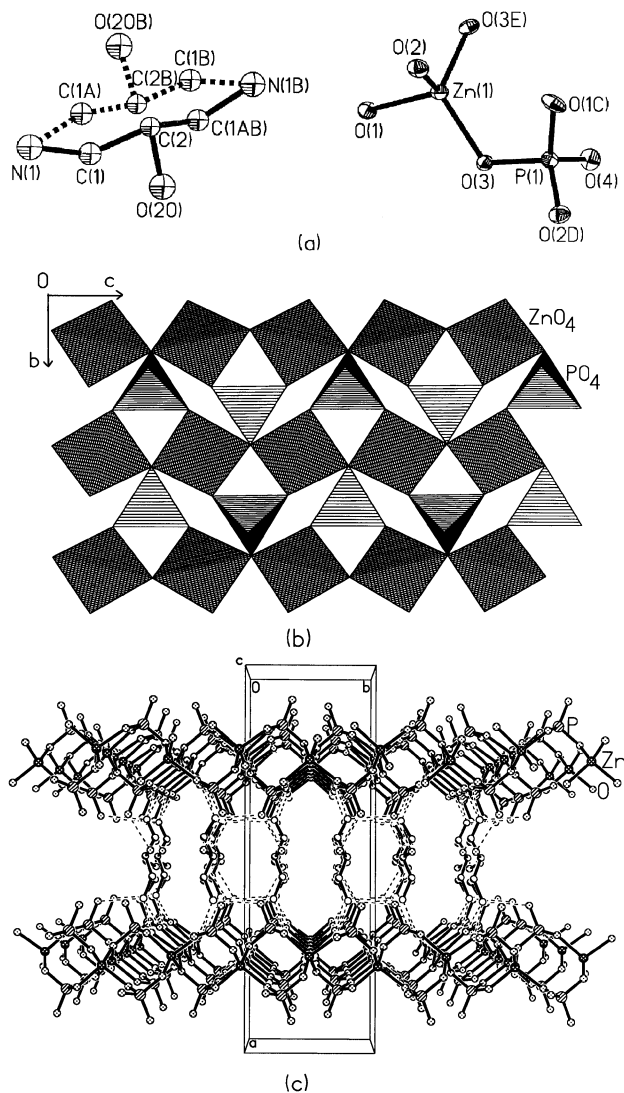


Fig. 11 (a) ORTEP plot of XVI, $[C_3N_2OH_{12}][Zn_2(PO_4)_2]$ showing the atom labelling scheme. Thermal ellipsoids are given at 50% probability. The atoms labelled with B, C, D and E are at the symmetry positions $(-x, +y, 1/2 - z)$, $(-1/2 - x, -1/2 + y, +z)$, $(1/2 - x, 1/2 + y, -1/2 - z)$ and $(+x, -y, -1/2 + z)$ respectively. Note the disorder in the amine molecule. (b) The polyhedral view of a single layer of XVI along the a -axis. Note that the connectivity gives rise to infinite Zn–O–Zn linkages. (c) Structure of XVI along the c -axis. Dotted lines represent hydrogen bond interactions between the amine molecules and framework oxygens. [The 3-D view of the structure is generated by packing the extended asymmetric unit [shown in Fig. 11(a)] along the c -axis with a plot box of size 20 by 10].

It is not therefore surprising that once the 1-D ladder structures are formed from the 2-D layers, transformation to 3-D and other structures occurs in a manner similar to that in the transformation of the ladder structures.¹¹

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