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One-dimensional zinc phosphates with linear chain structure

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Dedicated to Professor Gérard Férey on his 60th birthday

Abstract

Three one-dimensional zinc phosphates, $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I**, $[C_{10}N_4H_{26}][Zn(HPO_4)_2].2H_2O$ **II**, and $[C_4N_2H_6]_2[Zn(HPO_4)]$, **III**, have been prepared employing hydro/solvothermal methods in the presence of organic amines. While **I** and **II** consist of linear chains of corner-shared four-membered rings, **III** is a polymeric wire where the amine molecule is directly bonded to the metal center. The wire, as well as the chain in these structures, are held together by hydrogen bond interactions involving the amine and the framework oxygens. The polymeric zinc phosphate with wire-like architecture, **III**, is only the second example of such architecture. Crystal data: **I**, monoclinic, $P2_1/c$ (no. 14), $a = 8.603(2)$, $b = 13.529(2)$, $c = 10.880(1)$ Å, $\beta = 94.9(1)°$, $V = 1261.6(1)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.893$ gcm − 3, $\mu(MoK\alpha) = 2.234$ mm^{-1}, $R_1 = 0.032$, $wR_2 = 0.086$, [1532 observed reflections with $I > 2\sigma(I)$], **II**, orthorhombic, Pbca (no. 61), $a = 8.393(1)$, $b = 15.286(1)$, $c = 22.659(1)$ Å, $V = 2906.9(2)$ Å^3, $Z = 8$, $\rho_{calc.} = 1.794$ gcm^{-3}, $\mu(MoK\alpha) = 1.957$ mm^{-1}, $R_1 = 0.055$, $wR_2 = 0.11$, [1565 observed reflections with $I > 2\sigma(I)$ and **III**, monoclinic, $P2_1/c$ (no. 14), $a = 8.241(1)$, $b = 13.750(2)$, $c = 10.572(1)$ Å, $\beta = 90.9(1)°$, $V = 1197.7(2)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.805$ gcm^{-3}, $(MoK\alpha) = 2.197$ mm^{-1}, $R_1 = 0.036$, $wR_2 = 0.10$, [1423 observed reflections with $I > 2\sigma(I)$].

1. Introduction

Open-framework metal phosphates of different dimensionalities have been isolated and characterized [1]. Among these materials the three-dimensional architectures occur most commonly, while the low-dimensional ones, in particular, the one-dimensional chains and ladders are rare. Thus, in the large family of zinc phosphates with open architectures [2–18], very few one-dimensional structures are known, although a large variety of three-dimensional structures have been reported. In this paper we report the synthesis and structures of two types of chain structure of zinc phosphates, prepared hydrothermally. These include, two linear chain structures formed by corner-shared four-membered rings, $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I**, $[C_{10}N_4H_{26}][Zn(HPO_4)_2].2H_2O$ **II**, and a polymeric wire $[C_4N_2H_6]_2[Zn(HPO_4)]$, **III**, wherein the amine coordinates to the metal center. The linear polymeric wire structure described here is indeed unusual amongst the phosphates.

2. Experimental

The zinc phosphates, **I**–**III**, were synthesized employing hydro/solvothermal methods in the presence of organic amines. Thus, for the synthesis of **I**, 0.439 g of Zn acetate was dispersed in 3.6 ml of water followed by the addition of 0.68 ml of $C_4O_2H_8$ (1,4-dioxane). To this mixture was added 0.26 ml of H_3PO_4 (88 wt%) and 0.2 g of 2-methylpiperazine (MPIP) under continuous stirring. The resulting gel with the composition, $Zn(OAc)_2.2H_2O:2H_3PO_4$:MPIP:4-dioxan:$100H_2O$, was homogenized, sealed in a PTFE-lined stainless steel autoclave (Parr, Moline, USA) and heated at 180°C for 48 h under autogeneous pressure. For the synthesis of **II**, 0.439 g of $Zn(OAc)_2$ was dispersed in 6.6 ml of deionized water and 0.22 ml of hydrochloric acid (35% v/v). To this mixture, 0.49 ml of phosphoric acid (88 wt%) and 0.25 ml of 1,4-*bis*(3-aminopropyl)piperazine (APPIP) were added slowly under continuous stirring. The resulting gel with the composition $3ZnO:2HCl:6.3H_3PO_4$:APPIP:$280H_2O$, was sealed in a 23 ml PTFE-lined stainless steel autoclave and heated at 110°C for 48 h under autogeneous pressure. For the synthesis of **III**, 0.081 g of ZnO was dispersed in a mixture of butan-2-ol and water

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Table 1
Crystal data and structure refinement parameters for $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I**, $[C_{10}N_4H_{22}][Zn(HPO_4)_2].2H_2O$, **II** and $[C_8N_4H_{12}][Zn(HPO_4)]$, **III**

Structural parameter	**I**	**II**	**III**
Empirical formula	$ZnP_2O_8C_5N_2H_{14}$	$ZnP_2O_{10}C_{10}N_4H_{34}$	$ZnPO_4C_8N_4H_{12}$
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (no. 14)	Pbca (no. 61)	$P2_1/c$ (no. 14)
a (Å)	8.603(2)	8.393(1)	8.241(1)
b (Å)	13.529(2)	15.286(1)	13.750(2)
c (Å)	10.880(1)	22.659(1)	10.572(1)
α	90.0	90.0	90.0
β (°)	94.9(1)	90.0	90.9(1)
γ	90.0	90.0	90.0
Volume (Å^3)	1261.6(1)	2906.9(2)	1197.7(2)
Z	4	8	4
Formula mass	359.51	392.52	325.56
ρ_{calc} (gcm^{-3})	1.893	1.794	1.805
μ (mm^{-1})	2.234	1.957	2.197
θ range (°)	2.41–23.24	1.80–23.26	2.43–23.25
Total data collected	5192	11200	4959
Index ranges	$-9 \le h \le 9$, $-14 \le k \le 14$, $-9 \le l \le 12$	$-8 \le h \le 9$, $-16 \le k \le 16$, $-20 \le l \le 25$	$-9 \le h \le 9$, $-15 \le k \le 15$, $-7 \le l \le 11$
Unique data	1793	2085	1797
Data [$I > 2\sigma(I)$]	1532	1565	1423
Refinement method	Full-matrix least-squares on $\|F^2\|$	Full-matrix least-squares on $\|F^2\|$	Full-matrix least-squares on $\|F^2\|$
R_{int}	0.044	0.15	0.048
R [$I > 2\sigma(I)$]	$R_1 = 0.032$; $wR_2 = 0.086$[1]	$R_1 = 0.055$; $wR_2 = 0.11$[a]	$R_1 = 0.036$; $wR_2 = 0.10$[a]
R (all data)	$R_1 = 0.041$; $wR_2 = 0.091$	$R_1 = 0.09$; $wR_2 = 0.14$	$R_1 = 0.05$; $wR_2 = 0.10$
Goodness of fit (S)	1.05	1.16	1.04
No. of variables	163	189	163
Largest difference map peak and hole eÅ^{-3}	0.433 and −0.450	0.952 and −0.637	0.543 and −0.692

[a] $W = 1/[\sigma^2(F_O)^2 + (aP)^2 + bP]$ where $P = [F_O^2 + 2F_C^2]/3$; $a = 0.0483$ and $b = 0.24322$ for **I**, $a = 0.0241$ and $b = 17.5501$ for **II**, and $a = 0.0561$ and $b = 0.0$ for **III**.

(4.6 + 0.4 ml). To this mixture, 0.18 ml of hydrochloric acid (35% v/v), 0.13 ml of phosphoric acid (88 wt%) were added along with 1.05 g of 4-methylimidazole (MI) under continuous stirring. The resulting gel with the composition of ZnO:2HCl:$2H_3PO_4$:13MI:50 Butan-2-ol:50H_2O, was sealed in a 23 ml PTFE-lined stainless steel autoclave at 165°C for 10 h under autogeneous pressure. The products contained colorless crystals in all of the three preparations (rod-like for **I** and **II**, needle-like for **III**). The crystals were filtered under vacuum, washed with deionized water and dried at ambient conditions. Initial characterizations were carried out using powder X-ray diffraction and EDAX.

Suitable single crystals of **I**–**III** 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 (MoKα 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 2 θ range 3–46.5°. Pertinent experimental details for the structure determinations are presented in Table 1. The structure was solved by direct methods using SHELXS-86 [19] and difference Fourier syntheses. An empirical absorption correction based on symmetry equivalent reflections was applied for all the compounds using SADABS [20] program. 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. 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 $|F|$ was carried out using the SHELXTL-PLUS [21] package of programs. Details of the final refinements are given in Table 1. The final atomic co-ordinates, bond distances and angles are given in Tables 2 and 3 for **I**, in Tables 4 and 5 for **II**, and in Tables 6 and 7 for **III**.

Table 2
Atomic co-ordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I**

Atoms	*X*	*Y*	*z*	*U*(eq)[a]
Zn(1)	2363(1)	5288(1)	9669(1)	22(1)
P(1)	421(1)	5801(1)	11885(1)	23(1)
P(2)	5471(1)	5883(1)	8570(1)	22(1)
O(1)	3871(3)	6133(2)	8982(3)	30(1)
O(2)	3227(3)	4059(2)	10369(3)	29(1)
O(3)	1197(3)	6118(2)	10737(2)	28(1)
O(4)	683(3)	5081(2)	8348(3)	31(1)
O(5)	− 434(3)	6660(2)	12422(3)	37(1)
O(6)	1752(3)	5465(2)	12887(3)	37(1)
O(7)	5541(3)	4883(2)	7932(3)	31(1)
O(8)	5890(3)	6691(2)	7611(3)	36(1)
C(1)	11824(8)	9184(5)	9582(5)	73(2)
C(2)	11351(5)	8226(4)	8942(4)	39(1)
C(3)	11007(6)	7429(4)	6881(5)	47(1)
C(4)	9341(6)	7164(4)	7116(6)	64(2)
C(5)	9699(6)	7929(4)	9175(5)	51(1)
N(1)	11477(4)	8331(2)	7596(3)	32(1)
N(2)	9227(5)	7034(3)	8446(5)	68(2)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond distances and angles for $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I**

Moiety	Distance (Å)	Moiety	Angle (°)
Zn(1)-O(1)	1.928(3)	O(3)-Zn(1)-O(4)	97.67(12)
Zn(1)-O(2)	1.948(3)	O(5)-P(1)-O(3)	111.1(2)
Zn(1)-O(3)	1.955(3)	O(5)-P(1)-O(4)$^{\#1}$	110.2(2)
Zn(1)-O(4)	1.968(3)	O(3)-P(1)-O(4)$^{\#1}$	113.1(2)
P(1)-O(5)	1.519(3)	O(5)-P(1)-O(6)	107.5(2)
P(1)-O(3)	1.528(3)	O(3)-P(1)-O(6)	107.6(2)
P(1)-O(4)$^{\#1}$	1.532(3)	O(4)$^{\#1}$-P(1)-O(6)	107.0(2)
P(1)-O(6)	1.578(3)	O(1)-P(2)-O(7)	113.8(2)
P(2)-O(1)	1.522(3)	O(1)-P(2)-O(2)$^{\#2}$	112.7(2)
P(2)-O(7)	1.525(3)	O(7)-P(2)-O(2)$^{\#2}$	109.4(2)
P(2)-O(2)$^{\#2}$	1.540(3)	O(1)-P(2)-O(8)	107.9(2)
P(2)-O(8)	1.574(3)	O(7)-P(2)-O(8)	107.1(2)
		O(2)$^{\#2}$-P(2)-O(8)	105.5(2)
Moiety	Angle (°)		
O(1)-Zn(1)-O(2)	114.24(12)	P(2)-O(1)-Zn(1)	129.7(2)
O(1)-Zn(1)-O(3)	106.65(12)	P(2)$^{\#2}$-O(2)-Zn(1)	118.6(2)
O(2)-Zn(1)-O(3)	117.13(12)	P(1)-O(3)-Zn(1)	127.4(2)
O(1)-Zn(1)-O(4)	106.12(12)	P(1)$^{\#1}$-O(4)-Zn(1)	129.5(2)
O(2)-Zn(1)-O(4)	113.30(11)		

Organic moiety

Moiety	Distance (Å)	Moiety	Angle (°)
C(1)-C(2)	1.510(7)	N(1)-C(2)-C(1)	109.4(4)
C(2)-N(1)	1.485(6)	N(1)-C(2)-C(5)	109.9(4)
C(2)-C(5)	1.519(6)	C(1)-C(2)-C(5)	111.6(5)
C(3)-N(1)	1.485(6)	N(1)-C(3)-C(4)	108.9(4)
C(3)-C(4)	1.520(7)	N(2)-C(4)-C(3)	109.8(4)
C(4)-N(2)	1.469(8)	N(2)-C(5)-C(2)	110.1(4)
C(5)-N(2)	1.485(7)	C(3)-N(1)-C(2)	113.5(4)
		C(4)-N(2)-C(5)	112.9(4)

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

3. Results and discussion

The asymmetric units of the one-dimensional phosphates, **I**, **II** and **III** contain 18, 20 and 18 non-hydrogen atoms as shown in Fig. 1(a)–(c), respectively. Of these three phosphates, **I** and **II** have identical structures consisting of one-dimensional zinc hydrogen phosphate anions of the formula, $[Zn(HPO_4)_2]^{2-}$ while **III** possesses a neutral $Zn(HPO_4)$ unit. The charge compensation, in the case of **I** and **II**, is achieved by the presence of protonated methyl piperazine and *bis*-(aminopropyl)piperazine, respectively.

The zinc atoms in both **I** and **II** are tetrahedrally co-ordinated by four oxygen atoms. The Zn-O bond lengths (av. 1.949 Å for **I** and 1.941 Å for **II**) are similar to those observed in other zinc phosphates, such as in the one-dimensional ladder compound, $[NH_3(CH_2)_3NH_3][Zn(HPO_4)_2]$, $(Zn\text{-}O)_{av} = 1.944$ Å [2]. The Zn atoms are connected to two distinct P atoms via four Zn-O-P linkages with average angles of 126.3 and 135.7° for **I** and **II**, respectively. The phosphorus atoms, on the other hand, make only two P-O-Zn linkages and possess two terminal P-O linkages. The P-O distances are in the range 1.506–1.578 Å [av. P(1)-O = 1.539, P(2)-O = 1.540 Å for **I**, and P(1)-O = 1.530, P(2)-O = 1.531 Å for **II**) and the O-P-O bond angles are in the range 105.5–114.1° [av. O-P-O = 109.4° for both **I** and **II**). The P-O distances of P(1)-O(6) = 1.578, P(2)-O(8) = 1.574 Å for **I** and P(1)-O(6) = 1.576, P(2)-O(8) = 1.574 Å for **II** suggests that the oxygen atoms are protonated (Tables 3 and 5). The presence of hydroxyl groups was confirmed by the observation of peaks corresponding to hydrogen positions close to these oxygens, in the difference Fourier maps. The various P-O distances and O-P-O angles in **I** and **II** agree well with those reported for similar compounds in the literature [2–18].

The strictly alternating ZnO_4 and HPO_4 tetrahedral units in **I** and **II** form four-membered rings, which are linked through their corners forming the one-dimensional chains (Fig. 2(a) and (b)). The individual chain units are held together by hydrogen bond interactions involving the amine. The arrangement of the amine molecules between the chains in **I**, is such that different orientations of the amine molecule alternate (Fig. 3). Hydrogen bond interactions involving the terminal P-OH linkages form a sheet-like architecture with apertures, wherein the amine molecules reside (Figs. 2(a) and 3). The one-dimensional chains in **I** interact with each other via hydrogen bonds and form cavities. The cavities formed by such interactions (Fig. 4)

closely resemble those in the organic channel structures formed through non-covalent interactions [22]. Interactions between the chains in **II**, on the other hand, form a column-like arrangement. Since the amine molecule in **II** is rather unusual, it is possible to have interactions between the columns, which provide stability to the arrangement (Fig. 5(a) and (b)). The additional water molecule present in **II** also participates in inter-chain interactions. The various hydrogen bond interactions observed in **I** and **II** are listed in Table 8.

Unlike **I** and **II**, compound **III** consists of linkages between the uncommon ZnO_2N_2 tetrahedra and the PO_3OH units. There is one each of crystallographically independent Zn and P. The Zn and P atoms make two connections and have two terminal linkages. For Zn, the terminal linkages are the nitrogen atoms of the amine molecule and for P it is the oxygens. The Zn-O and Zn-N bond distances and O-Zn-O, O-Zn-N and N-Zn-N angles are in the expected range for this type of bonding (Table 7). Of the two terminal P-O linkages, the P-O distance of

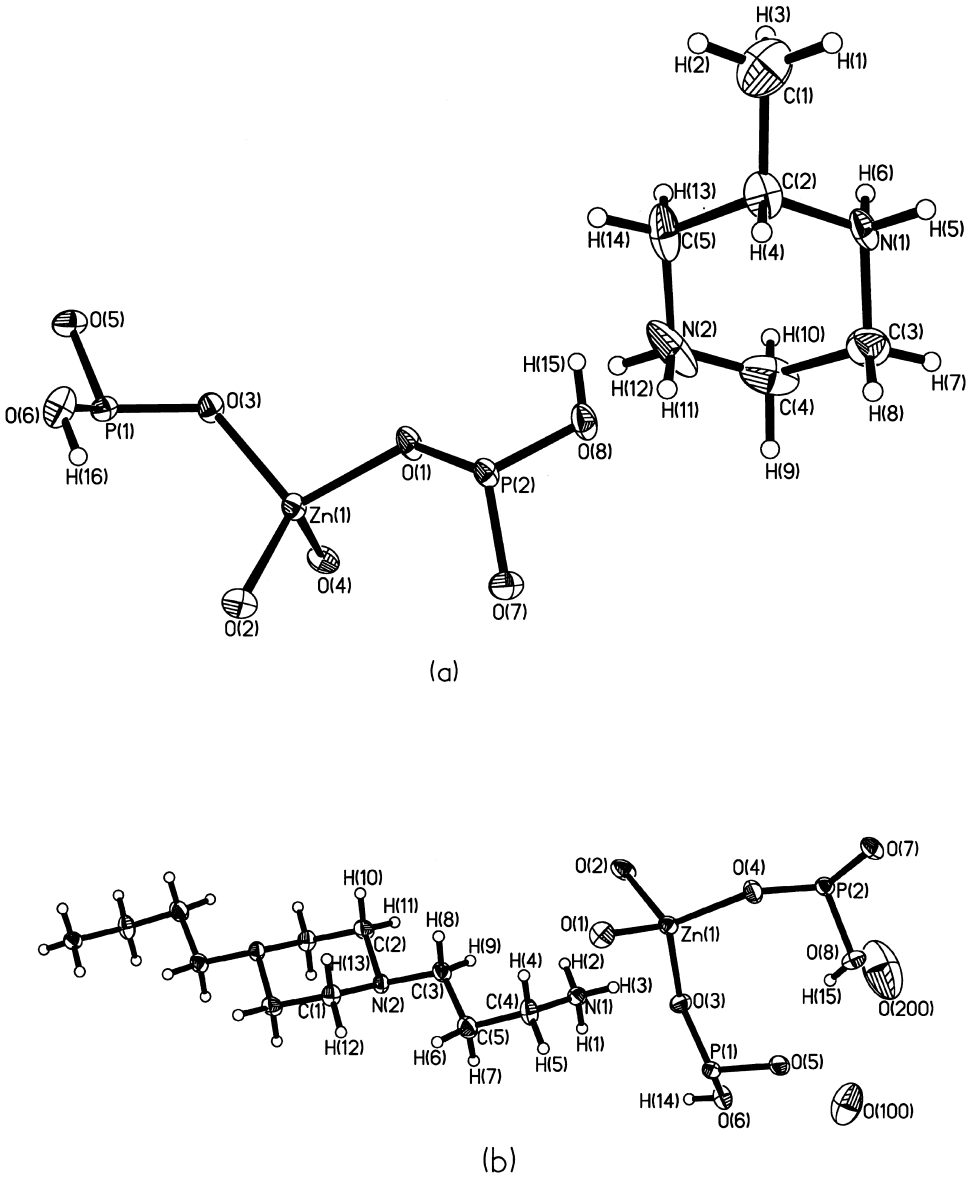
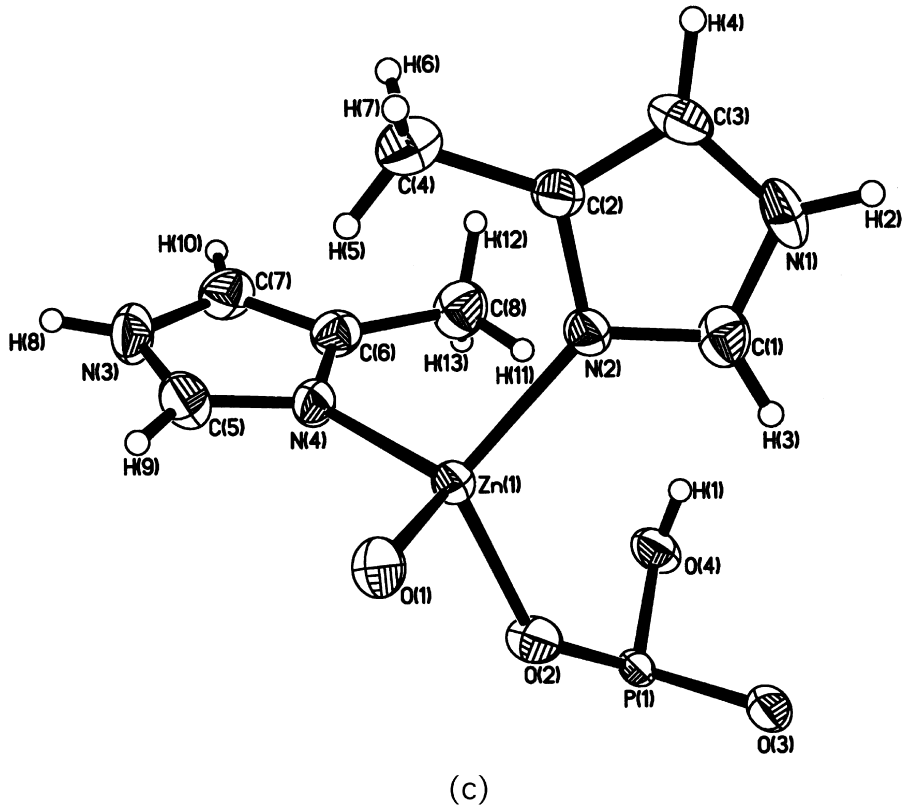


Fig. 1. (a) ORTEP plot of (a) $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I**., (b) $[C_{10}N_4H_{26}][Zn(HPO_4)_2].2H_2O$ **II** and (c) $[C_4N_2H_6]_2[Zn(HPO_4)]$, **III**. Thermal ellipsoids are given at 50% probability.



(c)

Fig. 1. (*continued*)

Table 4
Atomic co-ordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$A \times 10^3$] for $[C_{10}N_4H_{22}][Zn(HPO_4)_2].2H_2O$, **II**

	X	*Y*	*z*	U_{eq}^a
Zn(1)	2247(1)	836(1)	2304(1)	24(1)
P(1)	4241(2)	1608(1)	3388(1)	23(1)
P(2)	163(2)	− 248(1)	3247(1)	24(1)
O(1)	3773(6)	382(3)	1743(2)	36(1)
O(2)	945(6)	1591(3)	1819(2)	41(1)
O(3)	3096(6)	1685(3)	2869(2)	31(1)
O(4)	1201(6)	− 132(3)	2700(2)	33(1)
O(5)	3796(6)	855(3)	3790(2)	34(1)
O(6)	4035(6)	2465(3)	3768(2)	31(1)
O(7)	− 366(6)	− 1192(3)	3291(2)	33(1)
O(8)	1198(6)	− 56(4)	3811(2)	41(1)
N(1)	3201(7)	3197(4)	2193(2)	29(2)
N(2)	4715(7)	4651(4)	591(2)	26(1)
C(1)	5967(9)	4272(5)	193(3)	31(2)
C(2)	3397(9)	5020(5)	213(3)	34(2)
C(3)	4029(9)	3969(5)	1002(3)	31(2)
C(4)	4508(9)	2880(5)	1805(3)	36(2)
C(5)	5224(9)	3609(5)	1434(3)	39(2)
O(100)	2547(12)	2240(6)	4860(3)	98(3)
O(200)	− 551(17)	1539(7)	4470(5)	174(6)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

P(1)-O(4) = 1.553 Å indicates that the oxygen atom is protonated, in agreement with the proton position found in the difference Fourier map. Compound **III** does not possess a four-membered ring and the amine molecules are directly bonded to the Zn center. The structure is that of a polymeric wire formed by the direct linkage of ZnO_2N_2 and PO_3OH units, such that the bonded amine molecules protrude into the interwire region, interacting with one another through hydrogen bonds (Fig. 6(a) and Table 8). Along the *a* axis, the structure is sinusoidal with the amine molecules of the neighboring wire interacting strongly with the oxygens of the wire (Fig. 6(b)). This type of structure is rather unusual and this is only the second time such architecture has been isolated and characterized.

The linear chains formed by corner-shared four-membered rings in **I** and **II** are rare in the family of one-dimensional open-framework zinc phosphates. **I** and **II** possess the same framework formula as that reported by Chidambaram et al. [2], but the connectivity resulting from the four-membered rings is different. In the structure of Chidambaram et al. [2], edge-wise connectivity between the four-membered rings gives rise to a ladder-like structure with one HPO_4 units hanging from the Zn center, while in **I** and **II** the connectivity is through the corners with no hanging phosphates.

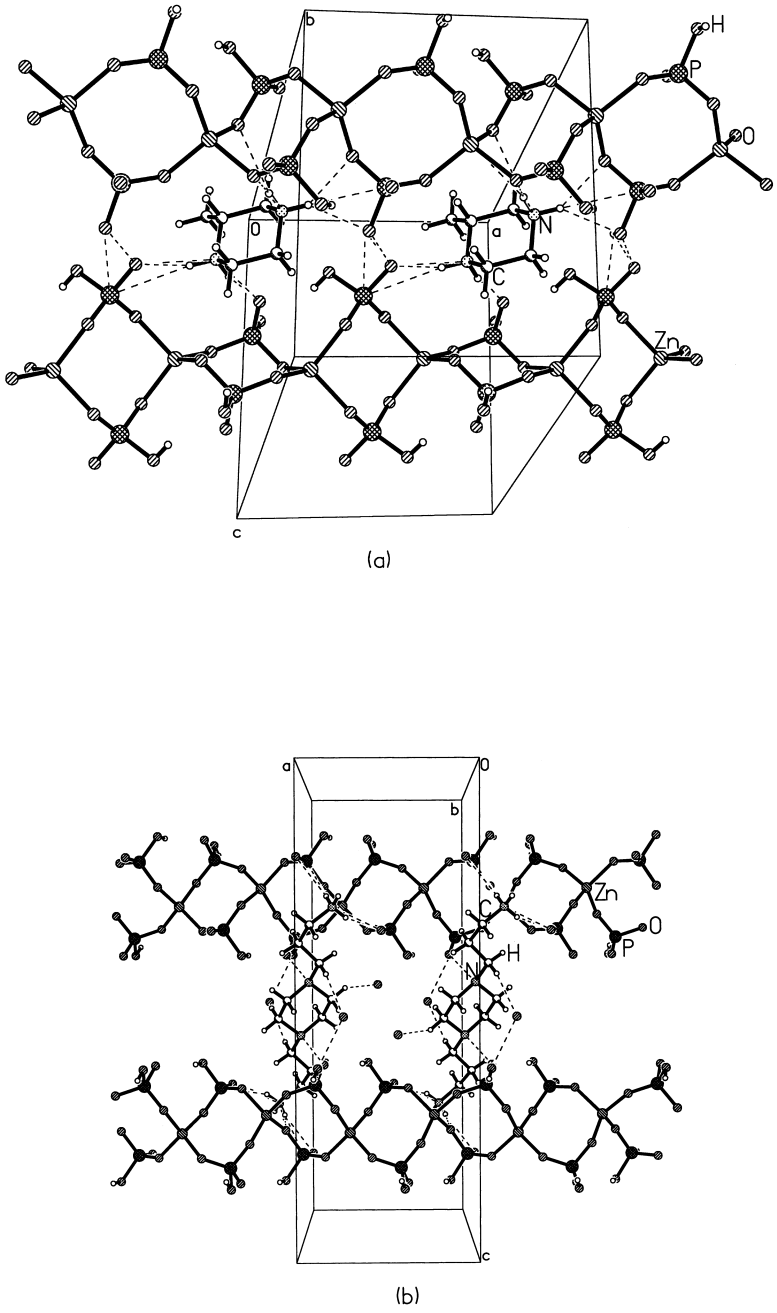


Fig. 2. (a) Structure of the zinc phosphate, **I**, $[C_5N_2H_{14}][Zn(HPO_4)_2]$ showing the four-membered corner-shared chains and the amine. Note that the interaction between the two chains form layer-like arrangement with apertures and (b) Structure of the zinc phosphate, **II**, $[C_{10}N_4H_{26}][Zn(HPO_4)_2].2H_2O$, in the *ac* plane. Note that both the water and amine molecules occupy the inter-chain voids. Dotted lines represent the possible hydrogen bond interactions.

Compound **III**, on the other hand, is formed as a molecular infinite wire with terminal amine molecules with comparable examples in the literature.

In Table 9, we list the various one-dimensional Zn phosphates synthesized and characterized to date. As can be seen, the corner-shared chains are indeed rare. The chain compounds **I** and **II** have architectures comparable to similar structures reported in the literature. In the

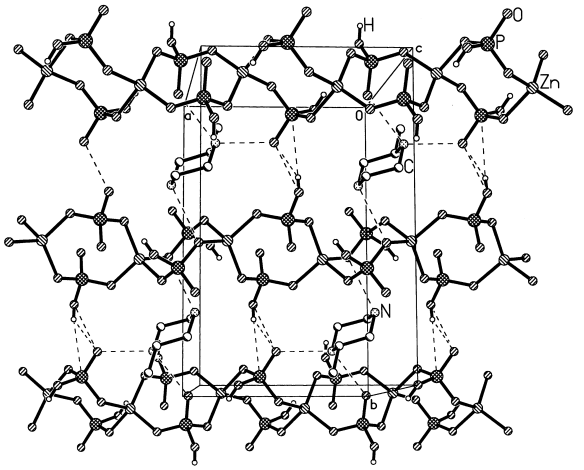


Fig. 3. Structure of the zinc phosphate, $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I** in the *ab* plane. Note that different orientations of the amine molecules occupy positions in between the chains.

Table 5
Selected bond distances and angles for $[C_{10}N_4H_{22}][Zn(HPO_4)_2].2H_2O$, **II**

Moiety	Distance (Å)	Moiety	Angle (°)
Zn(1)-O(2)	1.932(5)	O(1)-Zn(1)-O(3)	115.2(2)
Zn(1)-O(1)	1.934(5)	O(4)-Zn(1)-O(3)	111.6(2)
Zn(1)-O(4)	1.940(5)	$O(2)^{\#1}$-P(1)-O(5)	114.1(3)
Zn(1)-O(3)	1.957(5)	$O(2)^{\#1}$-P(1)-O(3)	111.1(3)
$P(1)-O(2)^{\#1}$	1.506(5)	O(5)-P(1)-O(3)	111.5(3)
P(1)-O(5)	1.515(5)	$O(2)^{\#1}$-P(1)-O(6)	106.8(3)
P(1)-O(3)	1.523(5)	O(5)-P(1)-O(6)	106.0(3)
P(1)-O(6)	1.576(5)	O(3)-P(1)-O(6)	106.8(3)
P(2)-O(7)	1.512(5)	$O(7)-P(2)-O(1)^{\#2}$	112.3(3)
$P(2)-O(1)^{\#2}$	1.513(5)	O(7)-P(2)-O(4)	109.5(3)
P(2)-O(4)	1.525(5)	$O(1)^{\#2}$-P(2)-O(4)	112.2(3)
P(2)-O(8)	1.574(5)	O(7)-P(2)-O(8)	106.6(3)
		$O(1)^{\#2}$-P(2)-O(8)	107.1(3)
		O(4)-P(2)-O(8)	108.8(3)

Moiety	Angle (°)		
O(2)-Zn(1)-O(1)	102.4(2)	$P(2)^{\#1}$-O(1)-Zn(1)	136.8(3)
O(2)-Zn(1)-O(4)	117.6(2)	$P(1)^{\#2}$-O(2)-Zn(1)	136.5(3)
O(1)-Zn(1)-O(4)	109.3(2)	P(1)-O(3)-Zn(1)	133.2(3)
O(2)-Zn(1)-O(3)	100.5(2)	P(2)-O(4)-Zn(1)	136.3(3)

Organic moiety

Moiety	Distance (Å)	Moiety	Angle (°)
N(1)-C(4)	1.488(9)	C(1)-N(2)-C(2)	108.4(5)
N(2)-C(1)	1.501(8)	C(1)-N(2)-C(3)	111.8(5)
N(2)-C(2)	1.509(9)	C(2)-N(2)-C(3)	109.2(5)
N(2)-C(3)	1.512(9)	$N(2)-C(1)-C(2)^{\#3}$	109.6(6)
$C(1)-C(2)^{\#3}$	1.517(10)	$N(2)-C(2)-C(1)^{\#3}$	110.7(6)
$C(2)-C(1)^{\#3}$	1.517(10)	C(5)-C(3)-N(2)	113.5(6)
C(3)-C(5)	1.505(10)	N(1)-C(4)-C(5)	112.4(6)
C(4)-C(5)	1.520(10)	C(3)-C(5)-C(4)	111.3(6)

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

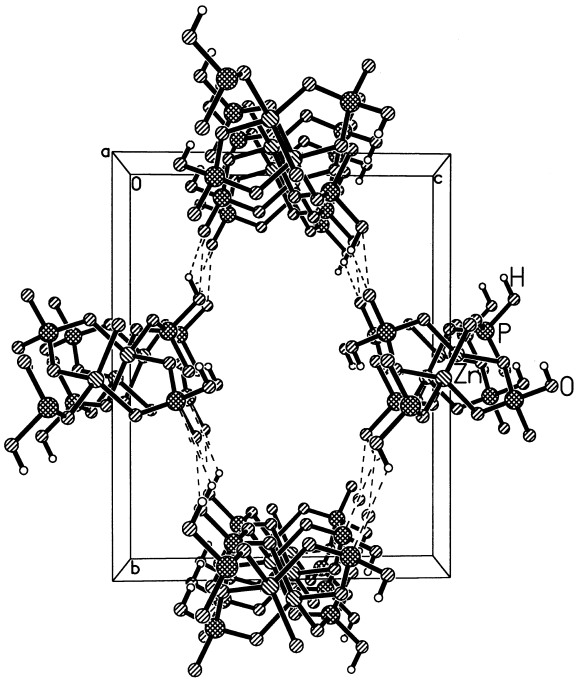


Fig. 4. The structure of the zinc phosphate, $[C_5N_2H_{14}][Zn(HPO_4)_2]$, **I**, along the chain axis. Note four different chains form a channel like structure through hydrogen bonds. Dotted lines represent the various hydrogen bond interactions.

Table 6
Atomic co-ordinates $[\times 10^4]$ and equivalent isotropic displacement parameters $[A^2 \times 10^3]$ for $[C_8N_4H_{12}][Zn(HPO_4)]$, **III**

Atom	*X*	*y*	*Z*	U_{eq}^a
Zn(1)	8323(1)	6889(1)	2184(1)	20(1)
P(1)	9662(1)	6548(1)	5066(1)	17(1)
O(1)	9619(4)	7741(2)	1152(3)	28(1)
O(2)	9403(4)	7084(2)	3813(3)	29(1)
N(2)	8492(4)	5534(3)	1531(3)	23(1)
N(4)	5965(4)	7252(3)	2168(4)	25(1)
O(3)	11318(3)	6031(2)	5092(3)	26(1)
O(4)	8304(3)	5780(2)	5251(3)	30(1)
N(1)	9166(5)	4003(3)	1329(4)	35(1)
C(1)	9341(6)	4794(3)	2021(5)	30(1)
C(2)	7751(6)	5166(3)	435(4)	27(1)
C(3)	8171(6)	4225(4)	325(5)	36(1)
C(4)	6722(7)	5796(4)	− 406(5)	45(2)
N(3)	3687(5)	7981(3)	1648(4)	35(1)
C(5)	5289(6)	8000(3)	1557(5)	33(1)
C(6)	4690(6)	6722(3)	2677(5)	28(1)
C(7)	3274(6)	7180(4)	2363(5)	34(1)
C(8)	4937(6)	5793(4)	3376(5)	38(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

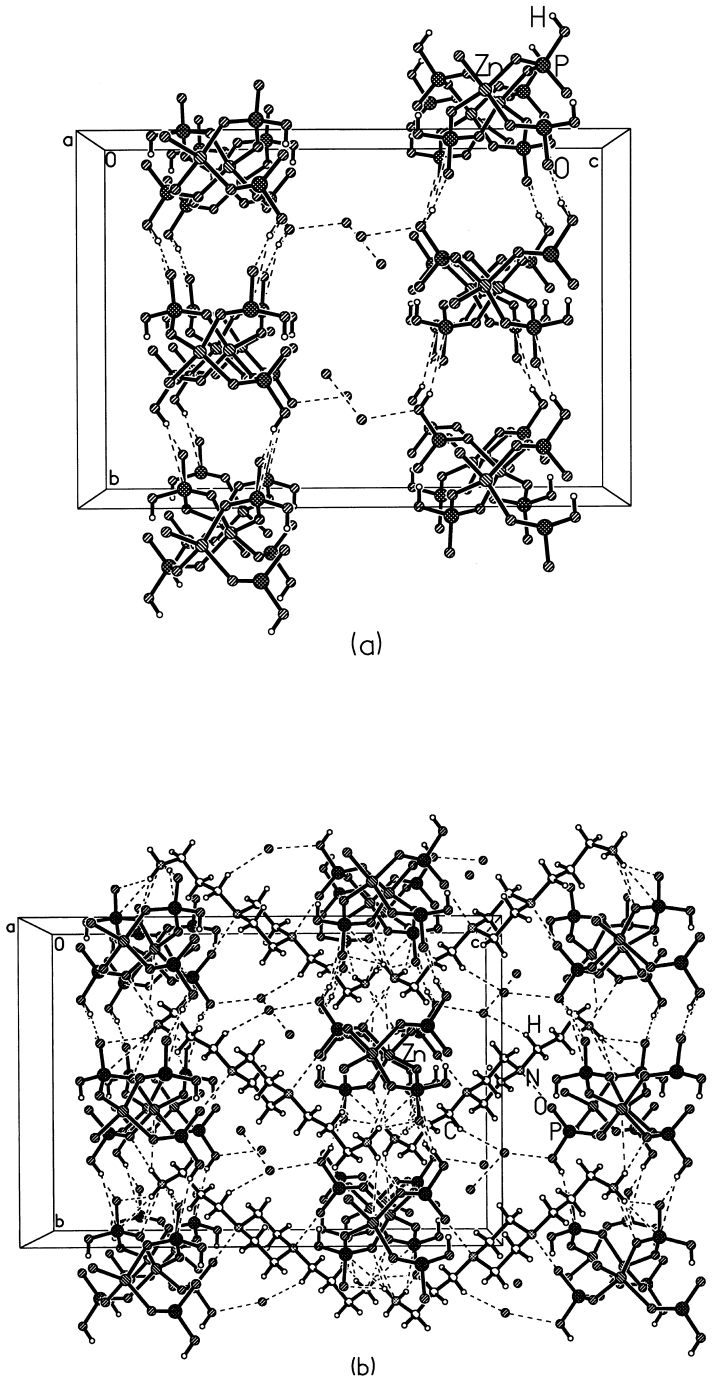


Fig. 5. (a) The structure of **II**, $[C_{10}N_4H_{26}][Zn(HPO_4)_2].2H_2O$ along the chain axis. The inter-chain interactions form a column-like arrangement and (b) Two columns joined interactions involving the amine and water molecules.

Table 7
Selected bond distances and angles for $[C_8N_4H_{12}][Zn(HPO_4)]$, **III**

Moiety	Distance (Å)	Moiety	Angle (°)
Zn(1)-O(1)	1.934(3)	O(2)-Zn(1)-N(4)	113.7(2)
Zn(1)-O(2)	1.944(3)	N(2)-Zn(1)-N(4)	107.6(2)
Zn(1)-N(2)	1.993(4)	$O(1)^{\#1}$-P(1)-O(2)	110.0(2)
Zn(1)-N(4)	2.006(4)	$O(1)^{\#1}$-P(1)-O(3)	108.6(2)
$P(1)-O(1)^{\#1}$	1.509(3)	O(2)-P(1)-O(3)	110.5(2)
P(1)-O(2)	1.528(3)	$O(1)^{\#1}$-P(1)-O(4)	108.6(2)
P(1)-O(3)	1.539(3)	O(2)-P(1)-O(4)	110.3(2)
P(1)-O(4)	1.553(3)	O(3)-P(1)-O(4)	108.9(2)
		$P(1)^{\#2}$-O(1)-Zn(1)	147.3(2)
		P(1)-O(2)-Zn(1)	139.2(2)
Moiety	Angle (°)		
O(1)-Zn(1)-O(2)	99.60(13)	C(1)-N(2)-Zn(1)	128.1(3)
O(1)-Zn(1)-N(2)	109.18(14)	C(2)-N(2)-Zn(1)	126.5(3)
O(2)-Zn(1)-N(2)	113.74(14)	C(5)-N(4)-Zn(1)	126.4(3)
O(1)-Zn(1)-N(4)	112.85(14)	C(6)-N(4)-Zn(1)	127.1(3)

Organic Moiety

Moiety	Distance (Å)	Moiety	Angle (°)
N(2)-C(1)	1.335(6)	C(1)-N(2)-C(2)	105.4(4)
N(2)-C(2)	1.395(5)	C(5)-N(4)-C(6)	106.2(4)
N(4)-C(5)	1.332(6)	C(1)-N(1)-C(3)	107.8(4)
N(4)-C(6)	1.394(6)	N(1)-C(1)-N(2)	111.2(4)
N(1)-C(1)	1.318(6)	C(3)-C(2)-N(2)	108.1(4)
N(1)-C(3)	1.366(6)	C(3)-C(2)-C(4)	130.6(5)
C(2)-C(3)	1.345(6)	N(2)-C(2)-C(4)	121.3(4)
C(2)-C(4)	1.495(6)	C(2)-C(3)-N(1)	107.5(4)
N(3)-C(5)	1.326(6)	C(5)-N(3)-C(7)	108.1(4)
N(3)-C(7)	1.380(6)	N(3)-C(5)-N(4)	111.0(4)
C(6)-C(7)	1.363(6)	C(7)-C(6)-N(4)	108.2(4)
C(6)-C(8)	1.488(6)	C(7)-C(6)-C(8)	128.9(5)
		N(4)-C(6)-C(8)	122.9(4)
		C(6)-C(7)-N(3)	106.5(4)

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

one-dimensional, $[C_2NH_8]_8[Zn_8(HPO_4)_8(H_2PO_4)_8].4H_2O$ [27] and $RbZn(HPO_4)(H_2PO_4).H_2O$ [28], the four-membered rings, forming the corner-shared chains, are made from the linkages involving ZnO_4, HPO_4 and H_2PO_4 units. The presence of H_2PO_4 units indicates that the chains can undergo further condensation giving rise to products with higher dimensional architectures, by deprotonation of terminal -OH groups. This suggestion is validated by the synthesis of a two-dimensional layer Zn phosphate from the same reaction mixture employed for the preparation of the one-dimensional chain [28]. The structures of compounds **I** and **II**, on the other hand, are akin to that of $[C_6N_2H_{14}]$ $[Zn(HPO_4)_2]$ [25], where the corner-sharing four-membered rings are made only from ZnO_4 and $PO_3(OH)$ tetrahedra. Isolation of zinc phosphates with

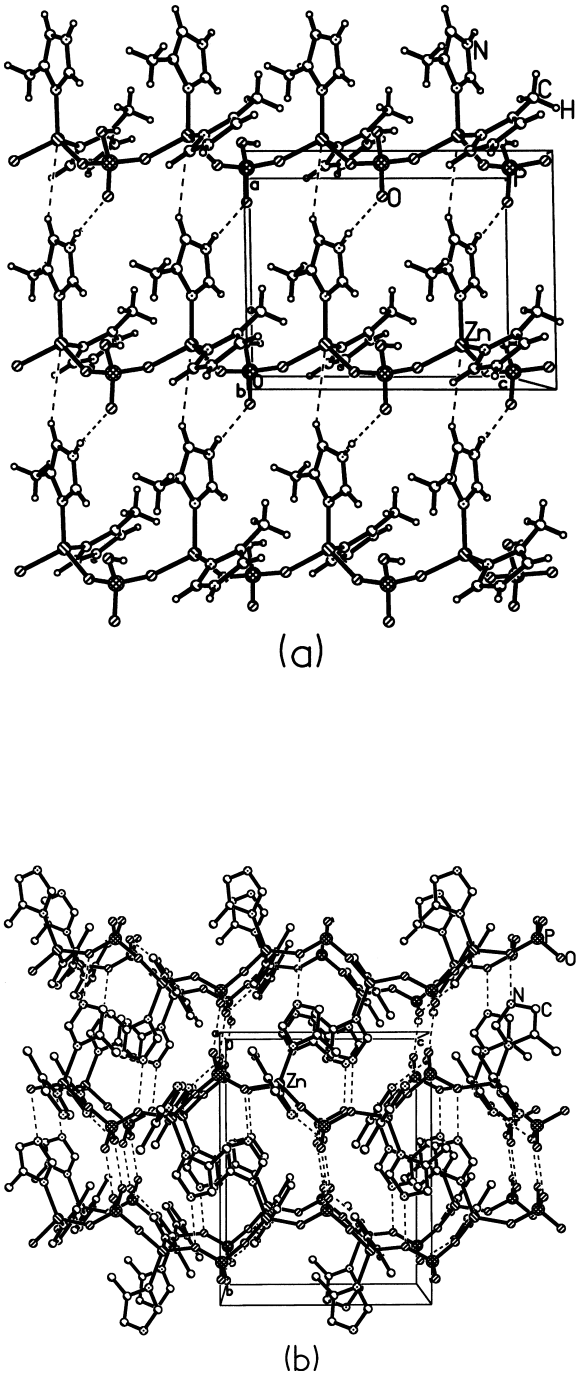


Fig. 6. (a) Structure of $[C_4N_2H_6]_2[Zn(HPO_4)]$, **III**, along the *ac* plane showing the polymeric wire-like arrangement. Note that the bonded amine molecule interacts with the neighboring wire through hydrogen bonds (dotted lines) and (b) Structure of **III** along the *bc* plane. Note that the architecture forms sinusoidal wave.

Table 8
Selected hydrogen bond interactions in compounds **I–III**

Moiety	Distance (Å)	Moiety	Angle (°)
I			
O(5)…H(5)	1.818(4)	O(5)…H(5)-N(1)	159.7(3)
O(7)…H(6)	1.868(4)	O(7)…H(6)-N(1)	167.2(4)
O(4)…H(11)	2.133(5)	O(4)…H(11)-N(2)	147.0(6)
O(8)…H(12)	2.207(5)	O(8)…H(12)-N(2)	142.4(6)
O(2)…H(12)	2.184(5)	O(2)…H(12)-N(2)	144.5(5)
O(6)…H(13)	2.593(6)	O(6)…H(13)-C(5)	163.7(5)
II			
O(4)…H(1)	2.031(8)	O(4)… H(1)-N(1)	151.7(6)
O(7)…H(1)	2.470(7)	O(7)…H(1)-N(1)	142.2(6)
O(7)…H(2)	1.921(8)	O(7)…H(2)-N(1)	161.8(6)
O(3)…H(3)	1.957(7)	O(3)…H(3)-N(1)	151.8(7)
O(7)…H(14)	1.799(7)	O(7)…H(14)-O(6)	157.1(6)
O(100)…H(8)	2.505(11)	O(100)…H(8)-C(3)	156.1(7)
O(200)…H(11)	2.589(15)	O(200)…H(11)-C(2)	142.2(7)
III			
O(2)…H(2)	2.069(5)	O(2)…H(2)-N(1)	160.5(5)
O(3)…H(8)	2.054(5)	O(3)…H(8)-N(3)	159.3(5)
O(4)…H(9)	2.452(6)	O(4)…H(9)-C(5)	155.0(5)

corner-shared chain architectures is important, because in one of the mechanisms proposed for the formation of open-framework phosphates considers the corner-shared chain structure to be the primary building unit [29,30]. A possible reason that such lower dimensional structures are seldom found under the conventional hydrothermal conditions may be because they undergo facile transformations to layer and three-dimensional structures.

The structure of **III** is closely related to that of $[C_6N_2H_{14}][Zn(HPO_4)(H_2PO_4)_2]$ [26], consisting of polymeric one-dimensional wires of $Zn(HPO_4)$ with two hanging terminal H_2PO_4 units from the Zn center. In **III**, the amine molecules are attached to the Zn center in the same way as the H_2PO_4 units. **III** is only the second example of such an architecture in open-framework phosphates. The three new one-dimensional compounds reported in this paper add to the interesting family of zinc phosphates with Zn/P ratio of non-unity.

Acknowledgements

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Table 9
List of the known ZnPOs with one-dimensional structure

Compound	Lattice parameters						Structure type	Ref.
	a Å)	*b* Å)	*c* Å)	α (°)	β, (°)	γ (°)	Sp. grp	
$[CN_3H_6)_6][Zn_2(OH)(PO_4)_3].\ H_2O$	20.016(7)	20.016(7)	13.955(6)	90.0	90.0	120.0	R^3	Oxo-bridged one-dimensional chain	[23]
$[C_3N_2H_{12}][Zn(HPO_4)_2]$	5.2206(7)	12.717(2)	15.570(2)	90.0	90.0	90.0	P212121	Edge sharing 4-ring chain	[24]
$[C_2N_2H_{10}][Zn(HPO_4)_2]$	5.161(1)	15.842(2)	12.027(2)	90.0	92.3(6)	90.0	P21/c	Edge sharing four-ring chain	[2]
$[C_6N_2H_{14}][Zn(HPO_4)_2].H_2O$	9.864(4)	8.679(4)	15.780(3)	90.0	106.8(6)	90.0	P21/n	Corner Shared four-ring chain	[25]
$[C_6N_2H_{14}][Zn(H_2PO_4)_2(HPO_4)_2]$	9.777(2)	10.640(2)	15.384(3)	90.0	90.0	90.0	$P2_12_12_1$	One-dimensional polymeric wire	[26]
$[C_2NH_8]_8[Zn_8(HPO_4)_8(H_2PO_4)_8].\ 4H_2O$	12.645(1)	10.847(7)	14.631(1)	90.0	98.8(1)	90.0	Cc	Corner Shared four-ring chain	[27]
Rb[Zn(HPO4)(H2PO4)].H2O	7.712(2)	7.982(7)	8.042(9)	64.3(1)	84.9(1)	72.3(6)	P(−1)	Corner Shared 4-ring chain	[28]
$[C_4N_2H_{12}][Zn(HPO_4)_2]$	8.931(2)	14.025(6)	9.311(2)	90.0	95.4(1)	90.0	$P2_1/n$	Corner Shared four-ring chain	[18]
$[C_5N_2H_{14}][Zn(HPO_4)_2]$	8.6031(2)	13.529(2)	10.880(1)	90.0	94.99	90.0	P21/n	Corner Shared 4-ring chain	This work
$[C_{10}N_4H_{26}]\ 2[Zn(HPO_4)_2].4H_2O$	8.3928(3)	15.285(9)	22.658(1)	90.0	90.0	90.0	Pbca	Corner Shared 4-ring chain	This work
$[Zn(HPO_4)(C_4N_2H_5]$	13.750(1)	10.571(5)	10.571(6)	90.0	90.9(3)	90.0	$P2_1/c$	One-dimensional polymeric wire	This work

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