

# A Layered Zinc Phosphate, $[\text{C}_6\text{N}_4\text{H}_{22}][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2]$ , Formed by One-Dimensional Tubes

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An open-framework zinc phosphate,  $[\text{C}_6\text{N}_4\text{H}_{22}][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2]$  (**I**), with alternating inorganic and organic layers has been synthesized hydrothermally from a starting mixture of ZnO, HCl,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , and triethylenetetramine. Single-crystal data for **I**: monoclinic, space group =  $P2_1/c$  (No. 14),  $a = 9.881(1)$ ,  $b = 16.857(1)$ ,  $c = 8.286(1)$  Å,  $\beta = 96.7(1)^\circ$ ,  $V = 1370.8(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_1 = 0.06$ , and  $wR_2 = 0.13$  [1408 observed reflections with  $I > 2\sigma(I)$ ]. The structure of **I** comprises a network of  $\text{ZnO}_4$ ,  $\text{PO}_4$ , and  $\text{PO}_3(\text{OH})$  tetrahedra forming one-dimensional tubes. The tubes, in turn, are linked via oxygen atoms forming macroanionic inorganic layers with eight-membered apertures. The one-dimensional tube-like architecture in **I** is a novel feature worthy of note. © 2001 Academic Press

## INTRODUCTION

A large number of open-framework zinc phosphates have been synthesized and characterized in the past decade (1–9). Although, a majority of them have three-dimensional structures, several zinc phosphates with lower dimensional structures have also been investigated. The lower dimensional structures include one-dimensional linear chains formed by corner-shared four-membered rings (9), one-dimensional ladders formed by edge-shared four-membered rings (6a, 7a), and two-dimensional layer structures (6, 7). Recently, the zero-dimensional monomer comprising the four-membered ring has also been isolated (8, 9). The structural variety in the open-framework zinc phosphates is truly remarkable. Thus, the three-dimensional structures possessing channels of various dimensions are known. A helical channel structure has also been reported (5a). Among the two-dimensional zinc phosphates, a noteworthy one is that possessing corrugated layers with steps (6b). During the course of our investigations of open-framework zinc phosphates, we have isolated an unusual layered material formed

by one-dimensional tubes. In this article, we describe the synthesis and structure of this novel zinc phosphate, obtained in the presence of triethylenetetramine (TETA). The compound has the composition  $[\text{C}_6\text{N}_4\text{H}_{22}][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2]$  (**I**).

## EXPERIMENTAL

The zinc phosphate, **I**, was synthesized starting from a mixture containing TETA. In a typical synthesis, 0.314 g of zinc oxide was dispersed in 7 ml of water and 0.66 ml of hydrochloric acid (aq. 35%). To the above 0.26 g of phosphoric acid (aq. 85 wt%) was added under stirring. Finally, 0.57 ml of TETA and 0.486 g of oxalic acid was added to the above and the mixture was homogenized for ~ 30 min. The final composition of the mixture was: 1.0 ZnO:1.0  $\text{H}_3\text{PO}_4$ :2.0 HCl:1.0 TETA:1.0  $\text{H}_2\text{C}_2\text{O}_4$ :100  $\text{H}_2\text{O}$ . All the chemicals were obtained from Aldrich and used without further purification. The starting mixture was transferred and sealed onto a 23-ml-capacity PTFE-lined stainless steel autoclave (Parr, Moline, IL). The sealed pressure bomb was heated at 180°C for 50 h under autogeneous pressure. The resulting product, containing large quantities of thin needle-like crystals suitable for single-crystal X-ray diffraction, was filtered and washed thoroughly with deionized water. We have not been able to determine the role of oxalic acid in the formation of **I** but its absence invariably leads to a mixture of new zinc phosphates,  $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2\text{P}_2\text{O}_8]$  and  $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4)]$ , along with **I**. The synthesis and structures of these new zinc phosphates have been reported recently by us (10). The powder X-ray diffraction (XRD) pattern (Siemen's D5000,  $\text{CuK}\alpha$ ,  $\lambda = 1.5418$  Å, graphite monochromator, Ni filter) of the powdered single crystals indicated that the product was a new material; the pattern was entirely consistent with the structure determined by single-crystal X-ray diffraction. A least squares fit of the powder XRD ( $\text{CuK}\alpha$ ) lines, using the  $hkl$  indices garnered from single-crystal X-ray data, has been carried out using PROSZKI program (11). The LSQ fit

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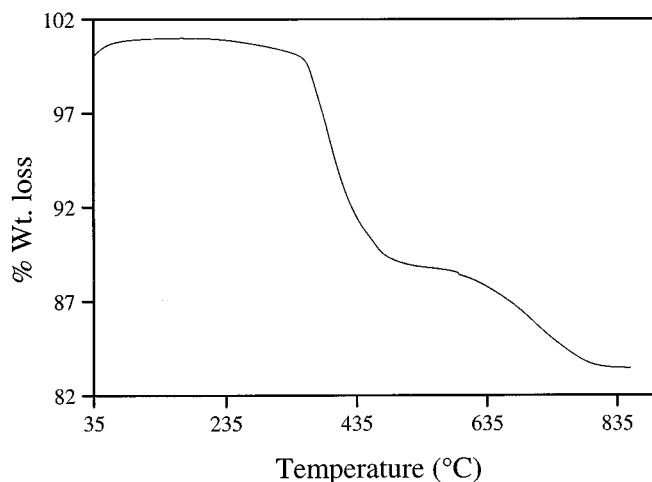
**TABLE 1**  
Powder X-Ray Data for [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>] (I)

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>obs</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>I</i> <sub>rel</sub>
1	0	0	9.787	9.779	32.2
1	1	0	8.481	8.479	100
0	1	1	7.404	7.398	52.4
0	2	1	5.896	5.889	4.8
1	1	1	5.628	5.624	7.9
1	2	-1	5.242	5.241	4.0
1	3	0	4.876	4.870	7.0
2	1	0	4.697	4.696	13.0
2	1	-1	4.296	4.291	13.9
2	2	0	4.229	4.229	38.3
0	0	2	4.116	4.117	13.2
2	2	-1	3.926	3.926	38.5
1	4	0	3.868	3.869	5.3
2	3	0	3.689	3.688	7.0
2	2	1	3.618	3.617	12.2
1	4	-1	3.567	3.565	34.2
1	4	1	3.442	3.441	17.4
0	3	2	3.321	3.321	73.9
2	3	1	3.261	3.261	26.3
1	5	0	3.187	3.186	12.5
3	2	0	3.041	3.040	21.0
2	1	2	2.937	2.937	18.9
3	3	0	2.820	2.819	5.9
3	1	-2	2.680	2.680	17.3
2	3	2	2.635	2.634	19.0
0	5	2	2.607	2.608	23.9
2	1	-3	2.496	2.494	3.5
3	3	-2	2.442	2.444	13.0
3	2	2	2.327	2.328	9.7
2	6	1	2.298	2.299	9.4
1	6	-3	1.955	1.956	2.0
5	1	2	1.684	1.683	5.5
6	1	0	1.622	1.622	4.6

Note. LSQ fitted lattice parameters:  $a = 9.857(1)$ ,  $b = 16.849(2)$ ,  $c = 9.291(1)$  Å,  $\beta = 96.69(1)^\circ$ .

gave the following cell:  $a = 9.857(1)$ ,  $b = 16.849(2)$ ,  $c = 9.291(1)$  Å,  $\beta = 96.69(1)^\circ$ , which is in good agreement with that determined by single-crystal XRD. Powder data for **I**, is listed in Table 1.

Thermogravimetric analysis (TGA) was carried out under a flow of nitrogen atmosphere (50 ml/min) in the range from 25 to 700°C using a heating rate of 10°C min<sup>-1</sup>. The results indicate only one sharp mass loss in the region 350–400°C and a broad tail in the range 550–650°C (Fig. 1). The mass loss of 12% corresponds to the loss of the amine from the structure (Calc. = 13.1%). The broad tail of 3% corresponds to the loss of water after condensation of the bonded -OH groups (Calc. = 2.3%). The framework collapses after the loss of the amine. The decomposed sample was found to be poorly crystalline (powder XRD) and corresponds to dense zinc phosphate ( $\beta$ -Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>; JCPDS:34-1275), indicating the loss of framework structure with the loss of the amine.



**FIG. 1.** TGA curve for [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>] (I).

A suitable single crystal (0.08 × 0.08 × 0.20 mm) of the title compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. Crystal structure determination by

**TABLE 2**  
Crystal Data and Structure Refinement Parameters for [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>] (I)

Empirical formula	Zn <sub>6</sub> P <sub>6</sub> O <sub>24</sub> C <sub>6</sub> N <sub>4</sub> H <sub>24</sub>
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size (mm)	0.08 × 0.08 × 0.20
<i>a</i> (Å)	9.881(1)
<i>b</i> (Å)	16.857(1)
<i>c</i> (Å)	8.286(1)
$\alpha$ (°)	90.0
$\beta$ (°)	96.7(1)
$\gamma$ (°)	90.0
Volume (Å <sup>3</sup> )	1370.8(1)
<i>Z</i>	2
Formula mass	1114.5
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2.7
$\lambda$ (MoK $\alpha$ )Å	0.71073
$\mu$ (mm <sup>-1</sup> )	5.626
$\theta$ range (°)	2.08–23.34
Total data collected	5738
Index ranges	$-10 \leq h \leq 11$ , $-18 \leq k \leq 11$ , $-8 \leq l \leq 9$
Unique data	1978
Observed data ( $\sigma > 2\sigma(I)$ )	1408
Refinement method	Full-matrix least-squares on $ F^2 $
<i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.06$ , $wR_2 = 0.13$
<i>R</i> indices (all data)	$R_1 = 0.10$ , $wR_2 = 0.17^a$
Goodness of fit ( <i>S</i> )	1.17
No. of variables	208
Largest difference map peak and hole (e Å <sup>-3</sup> )	1.268 and -1.088

<sup>a</sup> $W = 1/[\sigma^2(F_o)^2 + (0.0686P)^2 + 12.436P]$ , where  $P = [F_o^2 + 2F_c^2]/3$ .

**TABLE 3**  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{C}_6\text{N}_4\text{H}_{22}][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2]$  (I)

Atom	X	Y	z	$U_{\text{(eq.)}}^a$
Zn(1)	3702(2)	2649(1)	4291(2)	17(1)
Zn(2)	130(2)	2697(1)	3719(2)	15(1)
Zn(3)	1913(2)	488(1)	4975(2)	15(1)
P(1)	-946(4)	1250(2)	5737(4)	14(1)
P(2)	1993(4)	1624(2)	1882(4)	14(1)
P(3)	4641(4)	3728(2)	1613(4)	15(1)
O(1)	4976(9)	3186(6)	3088(10)	21(2)
O(2)	4789(9)	1724(6)	5046(11)	23(2)
O(3)	3327(9)	3301(5)	6117(10)	20(2)
O(4)	1935(9)	2308(5)	3159(11)	18(2)
O(5)	-993(10)	1845(6)	4347(11)	28(3)
O(6)	727(10)	3313(5)	5648(10)	21(2)
O(7)	-1158(10)	3339(6)	2333(10)	23(2)
O(8)	343(9)	767(6)	5952(11)	28(3)
O(9)	3294(9)	885(6)	6663(11)	28(3)
O(10)	1988(10)	823(5)	2748(10)	21(2)
O(11)	2171(10)	-679(5)	4759(10)	20(2)
O(12)	5710(9)	4415(5)	1772(11)	23(2)
N(1)	6275(14)	3446(10)	7369(15)	56(5)
N(2)	8200(13)	4605(8)	4534(14)	31(3)
C(1)	7187(18)	3569(12)	6116(19)	46(5)
C(2)	7007(18)	4420(11)	5457(20)	43(5)
C(3)	9417(15)	4926(10)	5534(18)	31(4)
H(1) <sup>b</sup>	6376(14)	2954(10)	7754(15)	84
H(2) <sup>b</sup>	5416(14)	3518(10)	6939(15)	84
H(3) <sup>b</sup>	6479(14)	3790(10)	8175(15)	84
H(4) <sup>b</sup>	6975(18)	3192(12)	5240(19)	55
H(5) <sup>b</sup>	8125(18)	3487(12)	6576(19)	55
H(6) <sup>b</sup>	6160(18)	4464(11)	4742(20)	52
H(7) <sup>b</sup>	6980(18)	4791(11)	6347(20)	52
H(8) <sup>b</sup>	8441(13)	4158(8)	4046(14)	37
H(9) <sup>b</sup>	7928(13)	4958(8)	3748(14)	37
H(10) <sup>b</sup>	9721(15)	4553(10)	6392(18)	37
H(11) <sup>b</sup>	9183(15)	5420(10)	6035(18)	37
H(20) <sup>b</sup>	6476(9)	4231(5)	1751(11)	34

<sup>a</sup> $U$  (eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>b</sup>The hydrogen atoms are refined isotropically.

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,  $\lambda = 0.71073$  \AA) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected at room temperature in 1321 frames with  $\omega$  scans (width of  $0.30^\circ$  and exposure time of 20 s per frame). The final unit cell constants were determined by a least squares fit of 1931 reflections in the range  $3^\circ < 2\theta < 46.5^\circ$ . Pertinent experimental details for the structure determinations are presented in Table 2.

The structure was solved by direct methods using SHELXS-86 (12) and difference Fourier syntheses. The hy-

drogen 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 nonhydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS (13) suit of programs. Details of the final refinements are given in Table 2. The final atomic coordinates, selected bond distances, and bond angles are given for I in Tables 3-5.

## RESULTS AND DISCUSSION

The asymmetric unit of I consists of 23 nonhydrogen atoms, 18 of which belong to the framework (consisting of 3 Zn, 3 P, and 12 O atoms) and 5 to the guest (2 N and 3 C atoms) (Fig. 2). Of the 12 oxygens in the asymmetric unit, one is three-coordinated, linking two zinc [Zn(1) and Zn(2)] and one P [P(2)] atom, and the remaining have normal Zn-O-P links. The structure consists of macroanionic layers of  $[\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2]$ , charge neutrality being achieved by incorporation of tetraprotonated TETA.

The structure consists of a network of  $\text{ZnO}_4$ ,  $\text{PO}_4$ , and  $\text{HPO}_4$  moieties forming a layer with the interlamellar region occupied by the protonated amine molecules. The Zn atoms are all tetrahedrally coordinated with respect to oxygens with the Zn-O bond distances in the range

**TABLE 4**  
Selected Bond Distances in  $[\text{C}_6\text{N}_4\text{H}_{22}][\text{Zn}_6(\text{PO}_4)_4(\text{HPO}_4)_2]$  (I)

Bond	Distance (\AA)	Bond	Distance (\AA)
Zn(1)-O(1)	1.921(8)	P(1)-O(8)	1.505(10)
Zn(1)-O(2)	1.955(9)	P(1)-O(5)	1.511(10)
Zn(1)-O(3)	1.940(9)	P(1)-O(7) <sup>a</sup>	1.544(8)
Zn(1)-O(4)	1.969(9)	P(1)-O(11) <sup>b</sup>	1.560(10)
Zn(2)-O(4)	2.005(9)	P(2)-O(6) <sup>c</sup>	1.524(10)
Zn(2)-O(5)	1.923(9)	P(2)-O(10)	1.529(9)
Zn(2)-O(6)	1.939(9)	P(2)-O(3) <sup>c</sup>	1.533(9)
Zn(2)-O(7)	1.941(9)	P(2)-O(4)	1.571(9)
Zn(3)-O(8)	1.891(9)	P(3)-O(9) <sup>c</sup>	1.487(10)
Zn(3)-O(9)	1.954(10)	P(3)-O(2) <sup>c</sup>	1.528(9)
Zn(3)-O(10)	1.940(8)	P(3)-O(1)	1.530(9)
Zn(3)-O(11)	1.994(9)	P(3)-O(12)	1.563(9)
		O(12)-H(20)	0.82
		Organic Moiety	
N(1)-C(1)	1.47(2)	C(1)-C(2)	1.54(2)
C(2)-N(2)	1.51(2)	N(2)-C(3)	1.48(2)
C(3)-C(3) <sup>d</sup>	1.55(3)		

<sup>a</sup> $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

<sup>b</sup> $-x, -y, -z + 1$ .

<sup>c</sup> $x, y + \frac{1}{2}, z - \frac{1}{2}$ .

<sup>d</sup> $-x + 2, -y + 1, -z + 1$ .

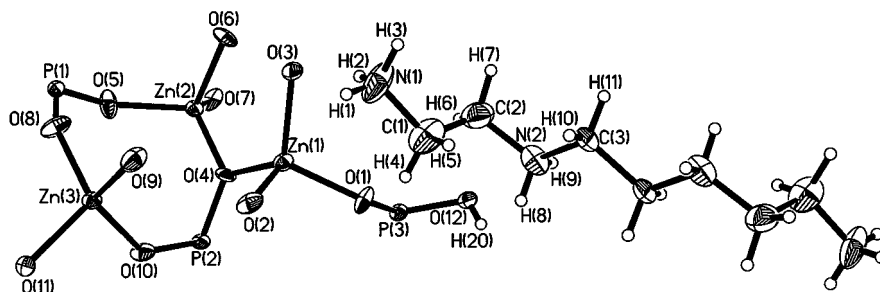


FIG. 2. ORTEP plot of [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>] (I). Asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability.

1.891–2.005 Å [(Zn(1)–O)<sub>av.</sub> = 1.946, (Zn(2)–O)<sub>av.</sub> = 1.950, (Zn(3)–O)<sub>av.</sub> = 1.945 Å]. The O–Zn–O bond angles are in the range 98.5–125.8° [(O–Zn(1)–O)<sub>av.</sub> = 109.5, (O–Zn(2)–O)<sub>av.</sub> = 109.3, (O–Zn(3)–O)<sub>av.</sub> = 109.5]. The longest bond distances and the largest bond angles are associated with the threefold coordinated oxygen atom. The zinc atoms are connected to three distinct P atoms via Zn–O–P

TABLE 5  
Selected Bond Angles in [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>] (I)

Moiety	Angle (°)	Moiety	Angle (°)
O(1)–Zn(1)–O(3)	109.5(4)	O(8)–P(1)–O(5)	114.0(5)
O(1)–Zn(1)–O(2)	100.0(4)	O(8)–P(1)–O(7) <sup>a</sup>	109.2(6)
O(3)–Zn(1)–O(2)	110.5(4)	O(5)–P(1)–O(7) <sup>a</sup>	111.0(5)
O(1)–Zn(1)–O(4)	119.3(4)	O(8)–P(1)–O(11) <sup>b</sup>	108.5(5)
O(3)–Zn(1)–O(4)	107.3(4)	O(5)–P(1)–O(11) <sup>b</sup>	105.4(5)
O(2)–Zn(1)–O(4)	110.1(4)	O(7) <sup>a</sup> –P(1)–O(11) <sup>b</sup>	108.5(5)
O(5)–Zn(2)–O(6)	107.9(4)	O(6) <sup>c</sup> –P(2)–O(10)	109.2(5)
O(5)–Zn(2)–O(7)	102.6(4)	O(6) <sup>c</sup> –P(2)–O(3) <sup>f</sup>	113.3(5)
O(6)–Zn(2)–O(7)	107.8(4)	O(10)–P(2)–O(3) <sup>f</sup>	108.5(5)
O(5)–Zn(2)–O(4)	112.0(4)	O(6) <sup>c</sup> –P(2)–O(4)	108.5(5)
O(6)–Zn(2)–O(4)	99.9(4)	O(10)–P(2)–O(4)	109.3(5)
O(7)–Zn(2)–O(4)	125.8(4)	O(3) <sup>f</sup> –P(2)–O(4)	108.5(5)
O(8)–Zn(3)–O(10)	117.3(4)	O(9) <sup>f</sup> –P(3)–O(2) <sup>f</sup>	114.6(6)
O(8)–Zn(3)–O(9)	98.5(4)	O(9) <sup>f</sup> –P(3)–O(1)	110.5(5)
O(10)–Zn(3)–O(9)	118.7(4)	O(2) <sup>f</sup> –P(3)–O(1)	110.4(5)
O(8)–Zn(3)–O(11)	113.8(4)	O(9) <sup>f</sup> –P(3)–O(12)	107.1(5)
O(9)–Zn(3)–O(11)	108.4(4)	O(2) <sup>f</sup> –P(3)–O(12)	108.1(5)
O(10)–Zn(3)–O(11)	100.5(4)	O(1)–P(3)–O(12)	107.1(5)
P(3)–O(1)–Zn(1)	127.0(5)	P(3) <sup>g</sup> –O(2)–Zn(1)	124.5(5)
P(2) <sup>b</sup> –O(3)–Zn(1)	128.4(6)	P(2)–O(4)–Zn(1)	115.8(5)
P(2)–O(4)–Zn(2)	119.9(5)	Zn(1)–O(4)–Zn(2)	123.9(4)
P(1)–O(5)–Zn(2)	137.0(6)	P(2) <sup>g</sup> –O(6)–Zn(2)	137.5(6)
P(1) <sup>c</sup> –O(7)–Zn(2)	128.2(6)	P(1)–O(8)–Zn(3)	143.4(6)
P(3) <sup>g</sup> –O(9)–Zn(3)	133.0(6)	P(2)–O(10)–Zn(3)	134.9(6)
P(1) <sup>b</sup> –O(11)–Zn(3)	121.9(5)	P(3)–O(12)–H(20)	109.5(4)
Organic Moiety			
N(1)–C(1)–C(2)	109.0(2)	C(1)–C(2)–N(2)	107.9(13)
C(2)–N(2)–C(3)	115.0(11)	N(2)–C(3)–C(3) <sup>d</sup>	110.4(14)

$$^a x, -y + \frac{1}{2}, z + \frac{1}{2}.$$

$$^b -x, -y, -z + 1.$$

$$^c x, y + \frac{1}{2}, z - \frac{1}{2}.$$

$$^d -x + 2, -y + 1, -z + 1.$$

links with the average bond angles of 128.9°, resulting from a wide spread of angles (Table 5). Of the three independent P atoms, P(1) and P(2) are connected to Zn atoms via four P–O–Zn linkage and P(3) is connected via three P–O–Zn linkages with one terminal P–O bond. The average P–O distances of 1.530, 1.539, and 1.527 Å result for P(1), P(2), and P(3), respectively. The O–P–O bond angles are in the range 105.4–114.6° [average (O–P–O) = 109.5]. The geometrical parameters observed for I are in good agreement with other similar open-framework zinc phosphates (1–10). Assuming the usual valences for Zn, P, and O, the framework stoichiometry of Zn<sub>3</sub>P<sub>3</sub>O<sub>12</sub> in I has a charge –3. The asymmetric unit contains only half the amine molecule.

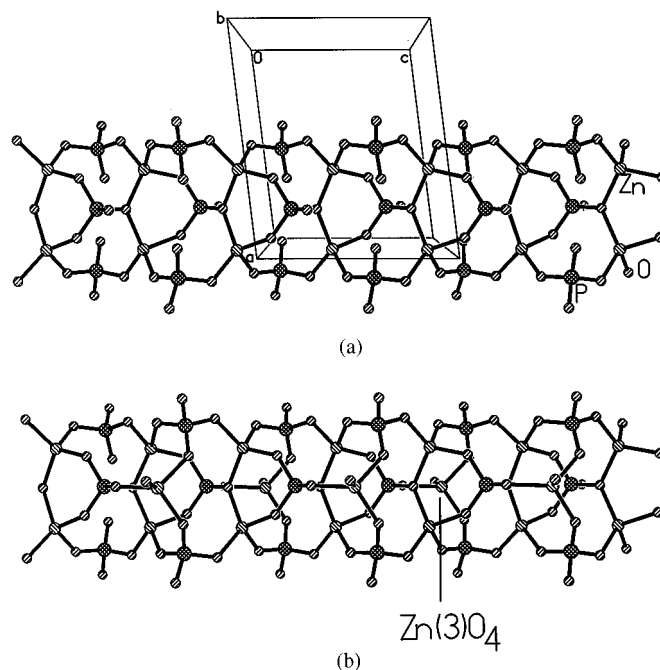
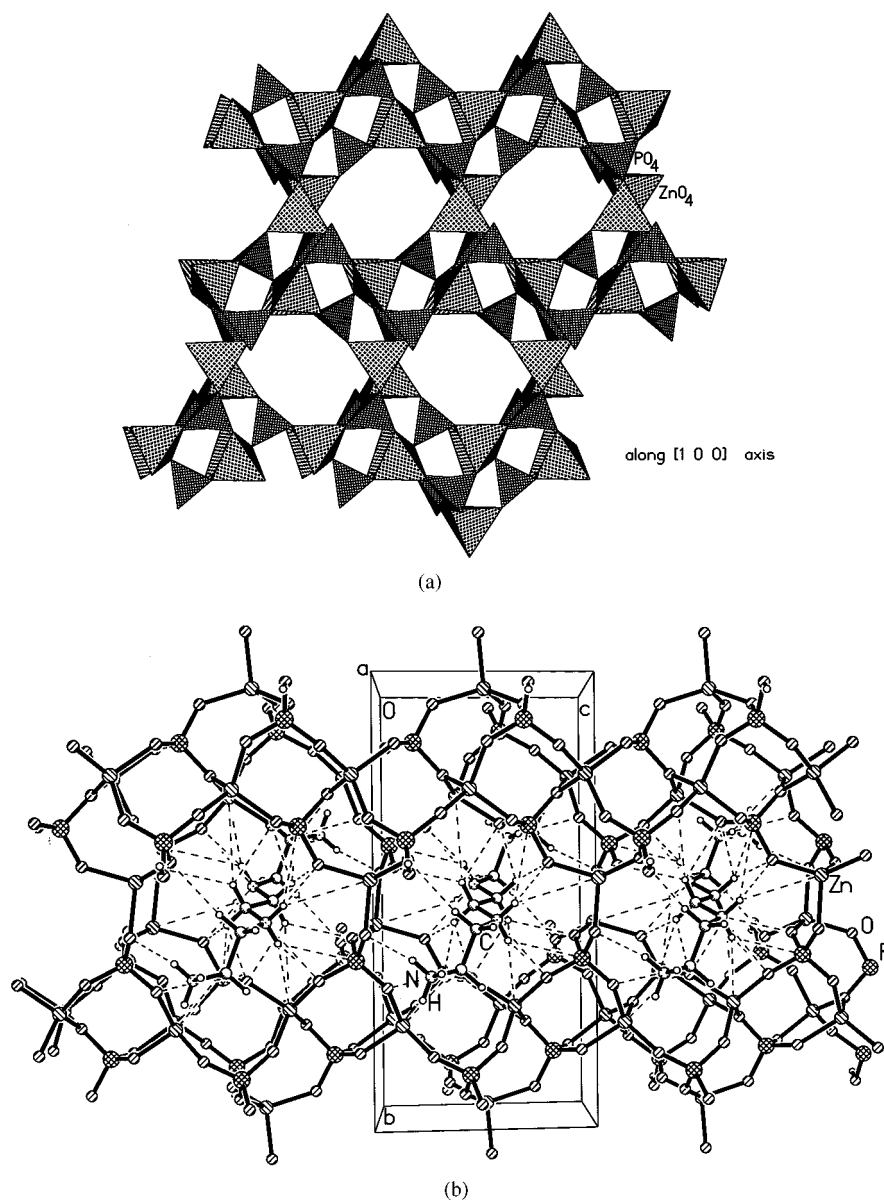


FIG. 3. (a) Strip-like arrangement along the *b* axis in I. The strip is formed by corner-shared four-membered rings connected via a three-coordinated oxygen (see text). (b) The strip with capped Zn(3)O<sub>4</sub> tetrahedra forming a one-dimensional tube. Note that the Zn tetrahedra cap either side of the strip.



**FIG. 4.** (a) Polyhedral arrangement of the structure of  $[C_6N_4H_{22}][Zn_6(PO_4)_4(HPO_4)_2]$  (I), along the  $a$  axis, showing the eight-membered aperture. Amine molecules are omitted for clarity. (b) Figure showing the eight-membered aperture with the amine molecule. Note that the amine molecule sits in the middle of the aperture. Dotted lines represent hydrogen bond interactions.

Assuming TETA to be fully protonated, charge compensation would still require one framework proton. The proton position observed in the difference Fourier map corresponds to a terminal P–O moiety. The P(3)–O(12) bond with a distance of 1.563 Å is thus a P–O(H) group. In order to evaluate the nature of bonding in I, extensive bond valence sum calculations (14) have been performed. The bond valence sum values for Zn(1) and Zn(2) are 2.0807 and 2.0535, and those of P(1), P(2), and P(3) are 5.0699, 4.0416, and 5.1151, respectively, indicating normal valences for Zn and P. The bond valence sum values for the oxygens,

O(1)–O(11), are in the range 1.621–1.9568 and that of O(12) is 1.1571. The value of 1.1571 indicates that O(12) is protonated, agreeing with the above formalism. The structure of I can therefore be considered to be made up of alternating anionic (inorganic) and cationic (organic) layers.

What is specially interesting about the framework structure of I is that it consists of one-dimensional tubes, linked together to form the layers. Each tube is made from an infinite strip-like arrangement along the  $c$ -axis (Fig. 3a). The strip is formed by linkages between three- and four-membered rings. The strip can be described as a one-dimensional

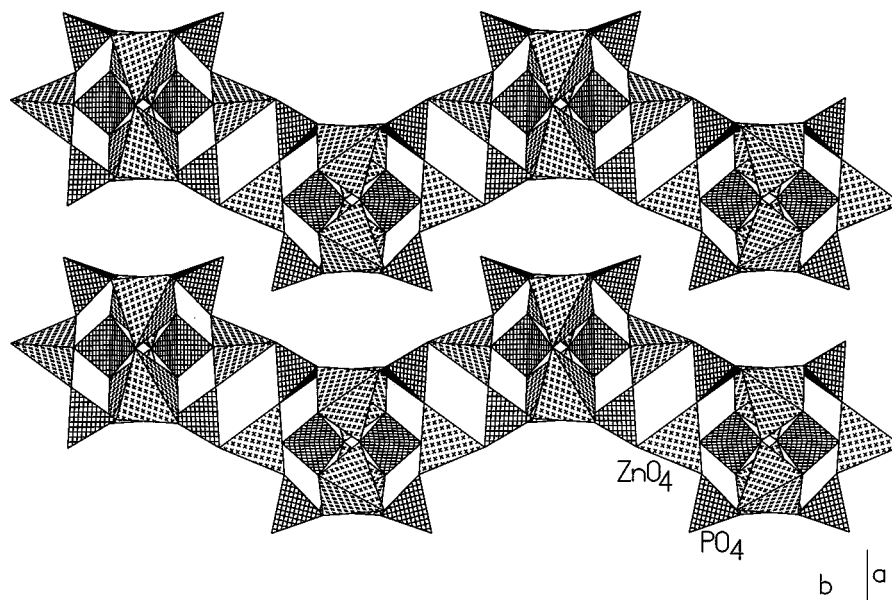


FIG. 5. The polyhedral structure of [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>] (I), along the *c* axis, showing the tube. Note that the tubes are connected by a four-membered ring and the tube positioning in adjacent layers resembling the lock and key type arrangement.

chain of three-membered rings edgewise connected by four-membered rings on either side. It can also be considered to consist of two corner-shared linear chains fused together by a three-coordinated oxygen completing the strip. The two different four-membered rings are made by Zn(1) (2X), P(2), P(3) and Zn(2) (2X), P(1), P(2), respectively. It may be recalled that chains formed by corner-shared four-membered rings are considered to constitute a basic building unit in open-framework structure (15). The strip (Fig. 3a) is capped by Zn(3)O<sub>4</sub> tetrahedra on either side, forming the tube as shown in Fig. 3b. The Zn(3)O<sub>4</sub> tetrahedra links all the P atoms of the strip and also connect to the adjacent tubes via oxygens. To our knowledge, this is the first instance when such a tube-like architecture has been observed in an open-framework phosphate. The connectivity between the tubes gives rise to an eight-membered aperture within the layer, along the *a* axis (Fig. 4). 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 (*c*-axis), we see that the tubes are connected to one another by four-membered rings and are arranged in a sinusoidal fashion as shown in Fig. 5. The connectivity of the tubes and their positions in adjacent layers is reminiscent of the lock and key arrangement, observed commonly in enzymes.

The presence of the oxygen atom [O(4)] with threefold coordination is essential for the formation of the tube-like architecture in I. Threefold coordination of the oxygen atoms has been observed in other Zn phosphates as well (6b). The presence of Zn(1)–O(4)–Zn(2) linkages in I, appears to be an electrostatic valence requirement of the bridging oxygen atoms, suggesting that such bridges occur with divalent atoms with tetrahedral coordination. The presence of such structural features in the zinc phosphates leads to novel framework topologies that have no structural counterparts in aluminosilicates or aluminophosphates. The layered architecture of the framework is stabilized by hydrogen bonding between the P(3)–O(12)H and that of the adjacent layer leading to the formation of pseudochannels along the *c* axis. The formation of such pseudochannels by hydrogen bonding between the terminal PO<sub>4</sub> and PO<sub>3</sub>(OH) of the adjacent layers is known to occur in layered zinc phosphates (16). The guest molecule, quadruply protonated TETA, also participates in hydrogen bonding with the framework lending additional structural stability to this material. Selected hydrogen bond parameters are listed in Table 6.

TABLE 6  
Important Hydrogen Bond Interactions  
in [C<sub>6</sub>N<sub>4</sub>H<sub>22</sub>][Zn<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>] (I)

Moiety	Distance (Å)	Moiety	Angle (°)
O(1)–H(1)	2.403(1)	O(1)–H(1)–N(1)	138.1(1)
O(3)–H(2)	2.128(1)	O(3)–H(2)–N(1)	141.6(1)
O(11)–H(3)	2.231(3)	O(11)–H(3)–N(1)	154.2(2)
O(7)–H(8)	2.052(1)	O(7)–H(8)–N(2)	163.1(2)
O(10)–H(9)	1.922(1)	O(10)–H(9)–N(2)	159.5(1)
O(9)–H(7)	2.509(3)	O(9)–H(7)–C(2)	171.3(1)

## CONCLUSIONS

A new layered zinc phosphate with alternate inorganic and organic layers has been synthesized in the presence of an organic amine. The distinctive feature of the layered architecture is the presence of one-dimensional tubes formed by the capping of a strip-like structure. The strip-like structure itself is rather unusual and has been observed only in one other instance, that of a cobalt(II) phosphate (9).

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