Formation of One-, Two-, and Three-Dimensional Open-Framework Zinc Phosphates in the Presence of a Tetramine

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Received April 5, 2000

Five new open-framework zinc phosphates, encompassing the entire hierarchy of open-framework structures, have been synthesized hydrothermally in the presence of triethylenetetramine. The structures include one-dimensional ladders, two-dimensional layers, and three-dimensional structures as well as a zinc phosphate where the amine acts as a ligand. $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ (**I**): monoclinic, space group $P2_1/c$ (no. 14), $a = 5.2677(1)$ Å, $b = 13.3025(1)$ Å, $c = 14.7833(1)$ Å, $\beta = 96.049°$, $Z = 4$. $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$ (**II**): triclinic, space group $P\bar{1}$ (no. 2), $a = 7.515(1)$ Å, $b = 8.2553(1)$ Å, $c = 12.911(1)$ Å, $\alpha = 98.654(1)°$, $\beta = 101.274(1)°$, $\gamma = 115.791(1)°$, $Z = 2$. $[C_6N_4H_{22}]_{0.5}[Zn_2P_2O_8]$ (**III**): triclinic, space group $P\bar{1}$ (no. 2), $a = 8.064(1)$ Å, $b = 8.457(1)$ Å, $c = 9.023(1)$ Å, $\alpha = 111.9(1)°$, $\beta = 108.0(1)°$, $\gamma = 103.6(1)°$, $Z = 2$. $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (**IV**): triclinic, space group $P\bar{1}$ (no. 2), $a = 5.218(1)$ Å, $b = 8.780(1)$ Å, $c = 16.081(1)$ Å, $\alpha = 89.3(1)°$, $\beta = 83.5(1)°$, $\gamma = 74.3(1)°$, $Z = 2$. $[C_6N_4H_{20}]_{0.5}[Zn_4P_4O_{16}]$ (**V**): monoclinic, space group $P2_1/c$ (no. 14), $a = 9.219(1)$ Å, $b = 15.239(1)$ Å, $c = 10.227(1)$ Å, $\beta = 105.2(1)$, $Z = 4$. The structure of **I** is composed of ZnO_4 and HPO_4 tetrahedra, which are edge-shared to form four-membered rings, which, in turn, form a one-dimensional chain (ladder). In **II**, these ladders are fused into a layer. The structures of **III** and **IV** comprise networks of ZnO_4 and PO_4 tetrahedra forming three-dimensional architectures. In **V**, the amine molecule coordinates to the Zn and acts as a pillar supporting the zinc phosphate layers, which possess infinite Zn−O−Zn linkages. The 16-membered one-dimensional channel in **IV** and the ZnO_3N pillar, along with infinite Zn−O−Zn linkages in **V**, are novel features. The structure of the open-framework zinc phosphates is found to depend sensitively on the relative concentrations of the amine and phosphoric acid, with high concentrations of the latter favoring structures with lower dimensions.

Introduction

Open-framework metal phosphates are generally synthesized under hydrothermal conditions in the presence of an amine.[1] Among the several metal phosphates with open architecture that have been synthesized, the family of zinc phosphates is quite large.[2−8] Despite the success of the hydrothermal methods in generating these materials, the role of the amine is not entirely understood. It is, however, likely that the amine is involved in the formation of the open-framework phosphates in more ways than one. It has been recognized that the pH of the medium and the pK_a of the amine are important parameters.[9] The importance of these two factors is understandable, since the protonated amine generally contributes to the stability of the framework structure through H-bonding. The dual role of the amine as a structure-directing agent and also as a ligand to the metal has been reported recently in zinc phosphates.[3] An examination of the available literature suggests that the number of amino groups in the amine may play a role in the formation of these materials as well. Thus, in the case of the zinc phosphates, the use of a diamine or a triamine seems to be more effective than monoamines in yielding materials with open architecture.[4,5] To investigate the role of multiple amino groups in the organic amine, we have employed triethylenetetramine (TETA), $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, for the synthesis of open-framework zinc phosphates. The study has indeed

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10.1021/ic000366c CCC: $19.00

Table 1. Synthesis Conditions and Analysis for Compounds **I**−**V**

	synthetic conditions[a]				analysis				
					EDAX	TGA[c]			
	ZnO:HCl:H_3PO_4:TETA:H_2O	T (K)	time (h)	pH[b]	Zn:P	amine %	−OH %	formula	yield[e]
I	1:2:6:2:100	353	50	2(3)	1:2			$[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$	65
II	1:2:4:1:100	353	50	2(3)	1:1.5	16.20 (15.50)	5.2 (5.58)	$[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$[d]	40
III	1:2:6:4:100	353	50	6(6)	1:1	18.71 (18.94)		$[C_6N_4H_{22}]_{0.5}[Zn_2(PO_4)_2]$	65
IV	1:2:1:0.5:200	353	50	4(4)	3:2	14.42 (13.46)	1.3 (1.61)	$[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$	70
V	1:2:0.5:1:100	353	50	6(6)	4:3	13.84 (11.92)		$[C_6N_4H_{20}]_{0.5}[Zn_4(PO_4)_3]$	55

[a] In all the reaction mixtures, the amount of ZnO was 4 mmol. The HCl used was 35 wt %, and the H_3PO_4 was 85 wt %. [b] Numbers in the parentheses denote the final pH. [c] Numbers in the parentheses denote the calculated weight loss. [d] Compound **I** also appears as a contamination with compound **II**. [e] Yield has been calculated with respect to Zn.

Table 2. Crystal Data and Structural Parameters for Compounds **I**−**V**

parameter	**I**	**II**	**III**	**IV**	**V**
formula	$ZnP_2O_8N_2C_3H_{13}$	$Zn_2P_3O_{12}N_2C_3H_{14}$	$Zn_2P_2O_8N_2C_3H_{11}$	$Zn_3P_3O_{12}N_2C_3H_{12}$	$Zn_4P_3O_{12}N_2C_3H_{10}$
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
A (Å)	5.267(1)	7.515(1)	8.064(1)	5.218(1)	9.219(1)
B (Å)	13.302(1)	8.255(1)	8.457(1)	8.780(1)	15.239(1)
C (Å)	14.783(1)	12.911(1)	9.023(1)	16.081(1)	10.227(1)
α (deg)	90.0	98.6(1)	111.9(1)	89.3(1)	90.0
β (deg)	96.0(1)	101.2(1)	108.0(1)	83.5(1)	105.2(1)
γ (deg)	90.0	115.7(1)	103.6(1)	74.3(1)	90.0
volume (Å^3)	1030.2(1)	681.6(1)	498.1(1)	704.7(1)	1386.3(3)
Z	4	2	2	2	4
formula mass	332.46	483.81	395.8	557.2	620.5
ρ_{calc} (g cm^{-3})	2.144	2.406	2.639	2.626	2.973
μ (mm^{-1})	2.727	3.938	5.172	5.472	7.254
R(F_o^2) [$\sigma > 2\sigma(I)$]	R1 = 0.02[a] wR2 = 0.07[b]	R1 = 0.03[a] wR2 = 0.09[b]	R1 = 0.04[a] wR2 = 0.11[b]	R1 = 0.04[a] wR2 = 0.11[b]	R1 = 0.04[a] wR2 = 0.09[b]
R(F_o^2) (all data)	R1 = 0.03 wR2 = 0.09	R1 = 0.04 wR2 = 0.10	R1 = 0.05 wR2 = 0.11	R1 = 0.05 wR2 = 0.12	R1 = 0.04 wR2 = 0.10

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$. $P = [\max(F_o^2, 0) + 2(F_c)^2]/3$, where $a = 0.0531$ and $b = 0.7829$ for **I**, $a = 0.061$ and $b = 0.0$ for **II**, $a = 0.0653$ and $b = 1.181$ for **III**, $a = 0.0735$ and $b = 0.0$ for **IV**, and $a = 0.0319$ and $b = 6.9206$ for **V**.

revealed that TETA yields a variety of open-framework zinc phosphates encompassing a one-dimensional ladder at one end and a three-dimensional structure with a 16-membered channel at the other. Furthermore, the structure of the products seems to depend on the relative concentrations of the amine and phosphoric acid, with comparable concentrations of the amine and the acid yielding three-dimensional structures and high acid concentrations yielding structures with lower dimensions. In the extreme case, when the amine concentration is far in excess of the acid, the amine molecules bind covalently with the zinc.

Experimental Section

Synthesis and Initial Characterization. Five new zinc phosphates, **I**−**V**, were synthesized starting from a zinc phosphate gel containing triethylenetetramine (TETA). The compounds were obtained as a pure single-phase material by the adjustment of the synthetic conditions, except **II**, which always appeared in mixture with **I**. As a typical procedure, the synthesis of **I** is described. A 0.3255 g sample of zinc oxide was dispersed in 7.2 mL of water and 0.7 mL of hydrochloric acid (35%). A 2.6978 g sample of phosphoric acid (aq, 85 wt %) was added to the mixture under stirring. Finally, 1.19 mL of TETA was added, and the mixture was homogenized for ∼30 min. The final composition works out to be 1.0:2.0:6.0:2.0:100 ZnO:HCl:H_3PO_4:TETA:H_2O. The mixtures were transferred into a 23 mL PTFE bottle (fill factor ∼ 40%) and sealed in a stainless steel autoclave (Parr). The complete synthesis conditions, yields, and compositions of the products obtained by EDAX analysis are presented in Table 1. The resulting products, which predominantly contained good-quality single crystals suitable for single-crystal X-ray crystallography, were filtered and washed thoroughly with deionized water. The single crystals were used for all the subsequent characterization purposes. Powder X-ray diffraction (XRD) patterns on the powdered crystals indicated that the products were new; the pattern is entirely consistent with the structure determined by single-crystal X-ray diffraction.

Thermogravimetric analysis (TGA) of compounds **II**−**V** was carried out under nitrogen atmosphere in the range between 25 and 900 °C. TGA study of **I** was difficult, as the decomposition of the amine around 250 °C was highly exothermic and caused the sample to eject out of the crucible. All the other compounds showed one sharp mass loss in the region 350−450 °C. The mass losses correspond to the loss of the amine in all the cases and agree well with the calculated values (see Table 1). The loss of amine from the framework generally resulted in the collapse of the open architecture and formed condensed zinc phosphates, as determined by powder XRD. Thus, the calcined samples of **II** correspond to α-$Zn_2P_2O_7$ (JCPDS: 08-238), those of **III** and **IV** to $Zn_2P_2O_7$ (JCPDS: 39-0711), and those of **V** to α-$Zn_3(PO_4)_2$ (JCPDS: 29-1390).

Single-Crystal Structure Determination. A suitable single crystal of each compound was 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, a 2.4 kW sealed tube X-ray source (Mo Kα 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 of 3−46.5°. Pertinent experimental details for the structure determinations are presented in Table 2.

The structure was solved by direct methods using SHELXS-86[10] and difference Fourier syntheses. An empirical absorption correction

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Table 3. Select Bond Distances and Bond Angles for $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ (**I**)^{a}

moiety	distance (Å)	moiety	distance (Å)
Zn(1)−O(1)	1.913(3)	P(1)−O(6)	1.517(3)
Zn(1)−O(2)	1.924(3)	P(1)−O(7)	1.587(3)
Zn(1)−O(3)	1.964(3)	P(2)−O(1)	1.515(3)
Zn(1)−O(4)	1.969(3)	P(2)−O(2)^{1}	1.508(3)
P(1)−O(3)	1.527(3)	P(2)−O(4)^{2}	1.539(3)
P(1)−O(5)	1.509(3)	P(2)−O(8)	1.577(3)

organic moiety	distance (Å)	organic moiety	distance (Å)
N(1)−C(1)	1.482(7)	C(1)−C(2)	1.483(8)
N(2)−C(2)	1.501(7)	C(3)−C(3)^{3}	1.508(10)
N(2)−C(3)	1.480(6)		

moiety	angle (deg)	moiety	angle (deg)
O(1)−Zn(1)−O(2)	119.45(4)	O(3)−P(1)−O(7)	107.0(2)
O(1)−Zn(1)−O(3)	103.42(3)	O(2)^{1}−P(2)−O(1)	113.7(2)
O(1)−Zn(1)−O(4)	111.40(4)	O(2)^{1}−P(2)−O(4)^{2}	112.0(2)
O(2)−Zn(1)−O(3)	109.14(1)	O(1)−P(2)−O(4)^{2}	115.5(2)
O(2)−Zn(1)−O(4)	106.01(1)	O(2)^{1}−P(2)−O(8)	104.8(2)
O(3)−Zn(1)−O(4)	106.81(1)	O(1)−P(2)−O(8)	107.1(2)
O(5) −P(1)−O(3)	113.2(2)	O(4)^{2}−P(2)−O(8)	104.8(2)
O(5)−P(1)−O(6)	112.5(2)	P(2)−O(1)−Zn(1)	138.6(2)
O(5)−P(1)−O(7)	108.2(2)	P(1)−O(3)−Zn(1)	123.7(2)
O(6)−P(1)−O(3)	110.9(2)	P(2)^{2}−O(4)−Zn(1)	127.2(2)
O(6)−P(1)−O(7)	103.9(2)		

organic moiety	angle (deg)	organic moiety	angle (deg)
C(3)−N(2)−C(2)	115.8(4)	N(1)−C(1)−C(2)	113.9(5)
N(2)−C(3)−C(3)^{3}	110.3(5)		

^{a} Symmetry transformations in generating equivalent atoms: 1, $-x + 1, -y + 2, -z$; 2, $-x, -y + 2, -z$; 3, $-x + 2, -y + 2, -z + 1$.

Table 4. Select Bond Distances and Bond Angles for $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$ (**II**)^{a}

moiety	distance (Å)	moiety	distance (Å)
Zn(1)−O(1)	1.929(4)	P(1)−O(4)^{1}	1.528(4)
Zn(1)−O(2)	1.937(4)	P(1)−O(9)	1.586(4)
Zn(1)−O(3)	1.963(4)	P(2)−O(5)^{1}	1.514(4)
Zn(1)−O(4)	1.991(4)	P(2)−O(1)^{2}	1.519(4)
Zn(2)−O(5)	1.902(4)	P(2)−O(2)	1.525(4)
Zn(2)−O(6)	1.936(4)	P(2)−O(10)	1.588(4)
Zn(2)−O(7)	1.951(4)	P(3)−O(6)	1.505(4)
Zn(2)−O(8)	1.990(4)	P(3)−O(11)	1.520(4)
P(1)−O(7)	1.524(4)	P(3)−O(8)^{3}	1.530(4)
P(1)−O(3)	1.524(4)	P(3)−O(12)	1.591(4)

organic moiety	distance (Å)	organic moiety	distance (Å)
N(2)−C(3)	1.495(7)	C(1)−C(2)	1.511(8)
N(2)−C(2)	1.502(7)	C(3)−C(3)^{4}	1.509(11)
N(1)−C(1)	1.510(7)		

moiety	angle (deg)	moiety	angle (deg)
O(1)−Zn(1)−O(2)	112.1(2)	O(5)^{1}−P(2)−O(2)	112.9(2)
O(1)−Zn(1)−O(3)	105.1(2)	O(1)^{2}−P(2)−O(2)	112.7(2)
O(2)−Zn(1)−O(3)	114.2(2)	O(5)^{1}−P(2)−O(10)	110.5(2)
O(1)−Zn(1)−O(4)	106.7(2)	O(1)^{2}−P(2)−O(10)	106.6(2)
O(2)−Zn(1)−O(4)	113.5(2)	O(2)−P(2)−O(10)	102.6(2)
O(3)−Zn(1)−O(4)	104.5(2)	O(6)−P(3)−O(11)	111.9(2)
O(5)−Zn(2)−O(6)	106.4(2)	O(6)−P(3)−O(8)^{3}	112.7(2)
O(5)−Zn(2)−O(7)	116.7(2)	O(11)−P(3)−O(8)^{3}	110.5(2)
O(6)−Zn(2)−O(7)	108.5(2)	O(6)−P(3)−O(12)	108.8(2)
O(5)−Zn(2)−O(8)	115.7(2)	O(11)−P(3)−O(12)	109.2(3)
O(6)−Zn(2)−O(8)	118.2(2)	O(8)^{3}−P(3)−O(12)	103.3(2)
O(7)−Zn(2)−O(8)	91.1(2)	P(2)^{2}−O(1)−Zn(1)	129.1(2)
O(7)−P(1)−O(3)	110.7(2)	P(2)−O(2)−Zn(1)	132.9(2)
O(7)−P(1)−O(4)^{1}	112.2(2)	P(1)−O(3)−Zn(1)	129.5(2)
O(3)−P(1)−O(4)^{1}	111.3(2)	P(1)^{1}−O(4)−Zn(1)	120.0(2)
O(7)−P(1)−O(9)	106.1(2)	P(2)^{1}−O(5)−Zn(2)	134.9(3)
O(3)−P(1)−O(9)	107.7(2)	P(3)−O(6)−Zn(2)	128.4(2)
O(4)^{1}−P(1)−O(9)	108.7(2)	P(1)−O(7)−Zn(2)	131.5(2)
O(5)^{1}−P(2)−O(1)^{2}	111.0(2)	P(3)^{3}−O(8)−Zn(2)	128.6(2)

organic moiety	angle (deg)	organic moiety	angle (deg)
C(3)−N(2)−C(2)	111.8(4)	N(2)−C(2)−C(1)	113.5(5)
N(1)−C(1)−C(2)	112.2(5)	N(2)−C(3)−C(3)^{4}	109.3(6)

^{a} Symmetry transformations to generate equivalent atoms: 1, $-x + 1, -y + 1, -z$; 2, $-x + 1, -y, -z$; 3, $-x, -y + 1, -z - 1$; 4, $-x + 2, -y, -z - 1$.

based on symmetry equivalent reflections was applied for all the five compounds using SADABS[11] program. All the hydrogen positions for compounds **I**−**V** 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 hydrogen positions for **V**, though found in the difference Fourier map, have not been incorporated due to the bonding nature of the amine as well as to the disorder of the Zn atom to which it is attached. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[12] package of programs. Details of the final refinements are given in Table 2. The selected bond distances and angles for products **I**−**V** are presented in Tables 3−9.

Results

$[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ (I), with a Ladder Structure. The asymmetric unit contains 16 non-hydrogen atoms as shown in Figure 1a, with one Zn and two P atoms crystallographically distinct. The structure consists of a one-dimensional polymeric zinc−hydrogen−phosphate chain constructed from infinite edge-shared four-membered rings of ZnO_4 and HPO_4 tetrahedra. The Zn atom is tetrahedrally coordinated to four oxygen atoms with an average Zn−O bond length of ~1.942 Å. The Zn atoms are connected to the neighboring P via Zn−O−P linkages [$(Zn-O-P)_{av} = 130.9°$]. The O−Zn−O bond angles are in the range of 103.4−119.4° [$(O-Zn-O)_{av} = 109.3°$]. The two P atoms are connected such that P(1) is linked to Zn by one P−O−Zn linkage and P(2) is connected to Zn by three P−O−Zn linkages. The two phosphorus atoms have P−O bond lengths in the range of 1.508−1.587 Å [$(P(2)-O)_{av}$ = 1.527 Å and $(P(1)-O)_{av}$ = 1.535 Å]. A framework structure of $Zn(PO_4)_2$ would give a net framework charge of −4. The presence of $0.5[C_6N_4H_{22}]$ would account for the +2 charge arising from the tetraprotonation of the amine. The excess negative charge of −2 is then balanced by the protonation of the PO_4 moieties, as given in the formula. Bond-valence sum calculations[13] indicate that P(1)−O(7) and P(2)−O(8), with distances of 1.587 and 1.577 Å, respectively, are formally −OH groups. Similar P−OH bond lengths have been observed before.[2] Both the PO_4 groups in **I** are, in fact, HPO_4 groups. The structure of **I** is constructed from the linkages involving ZnO_4 and $HP(2)O_4$ groups. The units are so connected to form a four-membered ladder-like chain, and the $HP(1)O_4$ tetrahedra are grafted onto this chain. Thus, $HP(1)O_4$ acts as a pendant to the anionic one-dimensional chain (Figure 1b). A quadruply protonated TETA molecule in the middle of this chain provides the charge balance. Extensive intrachain H-bonding has been observed in **I**, involving the terminal −OH group, the pendant HPO_4 group, and the P═O oxygens. Additional hydrogen-bond interactions involving the chain and the amine

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(11) Sheldrick, G. M. *SADABS Siemens Area Detector Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1994.

(12) Sheldrick, G. M. *SHELXS-93 Program for Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, Germany, 1993.

(13) Brown, I. D.; Aldermatt, D. *Acta Crystallogr.* **1984**, *B41*, 244.

Table 5. Select Bond Distances for $[C_6N_4H_{22}]_{0.5}[Zn_2P_2O_8]$ (**III**)[a]

moiety	distance (Å)	moiety	distance (Å)
Zn(1)−O(1)^1	1.889(6)	P(1)−O(1)	1.490(7)
Zn(1)−O(2)	1.947(5)	P(1)−O(5)^2	1.495(5)
Zn(1)−O(3)	1.939(5)	P(1)−O(4)^3	1.505(6)
Zn(1)−O(4)	2.109(7)	P(1)−O(8)	1.536(5)
Zn(2)−O(5)	1.934(5)	P(2)−O(6)	1.515(6)
Zn(2)−O(6)	1.911(5)	P(2)−O(2)^4	1.522(5)
Zn(2)−O(7)	1.952(5)	P(2)−O(3)	1.542(5)
Zn(2)−O(8)	1.965(5)	P(2)−O(7)^5	1.540(5)

organic moiety	distance (Å)	organic moiety	distance (Å)
N(1)−C(1)	1.494(9)	C(1)−C(2)	1.507(10)
C(2)−N(2)	1.506(9)	N(2)−C(3)	1.484(9)
C(3)−C(3)^7	1.499(13)		

moiety	angle (deg)	moiety	angle (deg)
O(1)^1−Zn(1)−O(3)	95.9(4)	O(1)−P(1)−O(5)^2	108.9(5)
O(1)^1−Zn(1)−O(2)	111.6(3)	O(1)−P(1)−O(4)^3	106.2(6)
O(3)−Zn(1)−O(2)	110.7(2)	O(5)^2−P(1)−O(4)^3	110.8(3)
O(1)^1−Zn(1)−O(4)	131.0(4)	O(1)−P(1)−O(8)	112.0(4)
O(3)−Zn(1)−O(4)	104.1(2)	O(5)^2−P(1)−O(8)	111.5(3)
O(2)−Zn(1)−O(4)	102.3(2)	O(4)^3−P(1)−O(8)	107.3(3)
O(6)−Zn(2)−O(5)	111.9(3)	O(6)−P(2)−O(2)^4	110.5(3)
O(6)−Zn(2)−O(7)	108.4(3)	O(6)−P(2)−O(7)^5	110.5(3)
O(5)−Zn(2)−O(7)	104.6(3)	O(2)^4−P(2)−O(7)^5	110.8(3)
O(6)−Zn(2)−O(8)	101.6(2)	O(6)−P(2)−O(3)	106.8(3)
O(5)−Zn(2)−O(8)	107.4(2)	O(2)^4−P(2)−O(3)	109.6(3)
O(7)−Zn(2)−O(8)	123.0(2)	O(7)^5−P(2)−O(3)	108.6(3)
P(1)−O(1)−Zn(1)^6	153.1(5)	P(1)^2−O(5)−Zn(2)	135.3(4)
P(2)^4−O(2)−Zn(1)	120.1(3)	P(2)−O(6)−Zn(2)	149.3(3)
P(2)−O(3)−Zn(1)	140.4(3)	P(2)^5−O(7)−Zn(2)	123.2(3)
P(1)^3−O(4)−Zn(1)	110.1(4)	P(1)−O(8)−Zn(2)	135.9(3)

organic moeity	angle (deg)	organic moiety	angle (deg)
N(1)−C(1)−C(2)	111.4(6)	C(1)−C(2)−N(2)	112.4(6)
C(2)−N(2)−C(3)	112.1(5)	N(2)−C(3)−C(3)^7	110.7(7)

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

Table 6. Select Bond Distances for $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (**IV**)[a]

moiety	distance (Å)	moiety	distance (Å)
Zn(1)−O(1)	1.921(5)	P(1)−O(2)	1.506(5)
Zn(1)−O(2)	1.939(5)	P(1)−O(5)	1.513(5)
Zn(1)−O(3)	1.949(4)	P(1)−O(10)^2	1.542(5)
Zn(1)−O(4)	2.052(4)	P(1)−O(11)^3	1.585(5)
Zn(2)−O(5)	1.928(5)	P(2)−O(1)^4	1.505(5)
Zn(2)−O(6)	1.922(5)	P(2)−O(9)	1.519(5)
Zn(2)−O(7)	1.928(5)	P(2)−O(3)	1.544(5)
Zn(2)−O(8)	2.012(4)	P(2)−O(4)^e	1.569(5)
Zn(3)−O(4)^1	1.965(4)	P(3)−O(12)	1.520(5)
Zn(3)−O(9)	1.893(4)	P(3)−O(6)	1.520(5)
Zn(3)−O(10)	1.936(4)	P(3)−O(7)^6	1.533(5)
Zn(3)−O(11)	2.030(5)	P(3)−O(8)^7	1.577(5)

organic moiety	distance (Å)	organic moiety	distance (Å)
N(1)−C(1)	1.483(9)	C(1)−C(2)	1.510(11)
C(2)−N(2)	1.501(9)	N(2)−C(3)	1.490(9)
C(3)−C(3)^7	1.49(2)		

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

Table 7. Select Bond Angles for $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (**IV**)[a]

moiety	angle (deg)	moiety	angle (deg)
O(1)−Zn(1)−O(2)	113.1(2)	O(2)−P(1)−O(5)	110.1(3)
O(1)−Zn(1)−O(3)	117.3(2)	O(2)−P(1)−O(10)^2	112.9(3)
O(2)−Zn(1)−O(3)	100.4(2)	O(5)−P(1)−O(10)^2	112.4(3)
O(1)−Zn(1)−O(4)	114.0(2)	O(2)−P(1)−O(11)^3	108.2(3)
O(2)−Zn(1)−O(4)	98.3(2)	O(5)−P(1)−O(11)^3	106.6(3)
O(3)−Zn(1)−O(4)	111.4(2)	O(10)^2−P(1)−O(11)^3	106.2(3)
O(6)−Zn(2)−O(7)	115.6(2)	O(1)^4−P(2)−O(9)	111.7(3)
O(6)−Zn(2)−O(5)	108.1(2)	O(1)^4−P(2)−O(3)	112.8(3)
O(7)−Zn(2)−O(5)	108.5(2)	O(9)−P(2)−O(3)	106.6(3)
O(6)−Zn(2)−O(8)	108.6(2)	O(1)^4−P(2)−O(4)^e	111.2(3)
O(7)−Zn(2)−O(8)	110.2(2)	O(9)−P(2)−O(4)^e	110.3(3)
O(5)−Zn(2)−O(8)	105.4(2)	O(3)−P(2)−O(4)^e	104.0(2)
O(9)−Zn(3)−O(4)^1	116.6(2)	O(12)−P(3)−O(6)	109.6(3)
O(9)−Zn(3)−O(10)	115.0(2)	O(12)−P(3)−O(7)^6	108.0(3)
O(4)^1−Zn(3)−O(10)	110.1(3)	O(6)−P(3)−O(7)^6	113.5(3)
O(9)−Zn(3)−O(11)	102.5(2)	O(12)−P(3)−O(8)^7	110.4(3)
O(4)^1−Zn(3)−O(11)	112.5(2)	O(6)−P(3)−O(8)^7	113.5(3)
O(10)−Zn(3)−O(11)	98.4(2)	O(7)^6−P(3)−O(8)^7	108.9(3)
P(2)^4−O(1)−Zn(1)	139.8(3)	P(3)−O(6)−Zn(2)	132.2(3)
P(1)−O(2)−Zn(1)	137.0(3)	P(3)^6−O(7)−Zn(2)	136.0(3)
P(2)−O(3)−Zn(1)	132.4(3)	P(3)^7−O(8)−Zn(2)	120.4(2)
P(2)^e−O(4)−Zn(1)	109.6(2)	P(2)−O(9)−Zn(3)	143.1(3)
P(2)^e−O(4)−Zn(3)^2	127.6(3)	P(1)^1−O(10)−Zn(3)	123.4(3)
Zn(3)^2−O(4)−Zn(1)	116.5(2)	P(1)^8−O(11)−Zn(3)	127.4(3)
P(1)−O(5)−Zn(2)	127.9(3)		

organic moiety	angle (deg)	organic moiety	angle (deg)
N(1)−C(1)−C(2)	113.8(6)	C(1)−C(2)−N(2)	112.4(6)
C(2)−N(2)−C(3)	113.1(6)	N(2)−C(3)−C(3)^9	111.1(7)

[a] Symmetry transformations to generate equivalent atoms: 1, $x+1$, $y-1$, z; 2, $x-1$, $y+1$, z; 3, x, $y+1$, z; 4, $-x+1$, $-y$, $-z$; 5, $-x$, $-y$, $-z$; 6, $-x$, $-y+1$, $-z+1$; 7, $-x-1$, $-y+1$, $-z+1$; 8, x, $y-1$, z; 9, $-x+1$, $-y$, $-z+1$.

Table 8. Select Bond Distances for $[C_6N_4H_{20}]_{0.5}[Zn_4P_3O_{12}]$ (**V**)[a]

moiety	distance (Å)	moiety	distance (Å)
Zn(1)−O(1)	1.935(5)	Zn(4A)−O(11)^3	1.853(5)
Zn(1)−O(2)	1.967(5)	Zn(4A)−O(10)^2	1.909(5)
Zn(1)−O(3)	1.981(4)	Zn(4A)−O(12)	2.019(5)
Zn(1)−O(4)	2.015(4)	Zn(4A)−N(2)	2.060(7)
Zn(2)−O(5)	1.911(5)	P(1)−O(10)	1.508(5)
Zn(2)−O(6)	1.916(5)	P(1)−O(1)^e	1.517(5)
Zn(2)−O(4)	1.979(4)	P(1)−O(9)^6	1.541(5)
Zn(2)−O(7)	2.019(4)	P(1)−O(4)	1.577(5)
Zn (3)−O (8)	1.930(5)	P(2)−O(6)	1.520(5)
Zn (3)−O (9)	1.944(4)	P(2)−O(12)	1.527(5)
Zn(3)−O(7)	1.971(4)	P(2)−O(8)	1.537(5)
Zn(3)−O(3)^1	1.988(4)	P(2)−O(3)^6	1.573(5)
Zn(4)−O(10)^2	1.961(5)	P(3)−O(2)	1.520(5)
Zn(4)−O(12)	1.962(5)	P(3)−O(11)	1.521(5)
Zn(4)−O(11)^3	1.963(5)	P(3)−O(5)^7	1.531(5)
Zn(4)−N(1)^4	2.085(7)	P(3)−O(7)	1.577(5)

organic moiety	distance (Å)	organic moiety	distance (Å)
N(1)−C(1)	1.506(13)	C(1)−C(2)	1.534(14)
C(2)−N(2)	1.493(12)	N(2)−C(3)	1.512(13)
C(3)−C(3)^8	1.51(2)		

[a] Symmetry transformations used to generate equivalent atoms: 1, $-x+1$, $y-{}^1/_2$, $-z+{}^1/_2$; 2, $-x$, $y-{}^1/_2$, $-z-{}^1/_2$; 3, $-x+1$, $-y$, $-z$; 4, x, $-y-{}^1/_2$, $z-{}^1/_2$; 5, $-x+1$, $-y+1$, $-z$; 6,$=x$, $-y+{}^1/_2$, $z-{}^1/_2$; 7, x, $-y+{}^1/_2$, $z={}^1/_2$; 8, $-x$, $-y$, $-z$.

molecules have also been observed. The selected list of hydrogen-bond interactions is presented in Table 10.

$[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$ (II), with a Layer Structure. The asymmetric unit of **II** contains 22 non-hydrogen atoms (Figure 2), of which 17 atoms belong to the framework and five atoms to TETA. There are two crystallographically distinct Zn atoms and three P atoms. The structure is essentially constructed from the vertex linkage of ZnO_4 and HPO_4 tetrahedra forming macroanionic layers. The Zn atoms are all tetrahedrally coordinated to four oxygen atoms. The Zn−O distances are in the range of 1.902−1.991 Å [$(Zn(1)-O)_{av} = 1.955$ Å and $(Zn(2)-O)_{av} = 1.944$ Å], and the O−Zn−O angles are in the range of

Table 9. Selected Bond Angles for $[C_6N_4H_{20}]_{0.5}[Zn_4P_3O_{12}]$ (**V**)[a]

moiety	angle (deg)	moiety	angle (deg)
O(1)−Zn(1)−O(2)	95.6(2)	O(11)^{3}−Zn(4A)−O(10)^{2}	108.5(2)
O(1)−Zn(1)−O(3)	108.8(2)	O(11)^{3}−Zn(4A)−O(12)	109.6(2)
O(1)−Zn(1)−O(4)	121.0(2)	O(10)^{2}−Zn(4A)−O(12)	100.8(2)
O(2)−Zn(1)−O(3)	115.5(2)	O(11)^{3}−Zn(4A)−N(2)	99.9(3)
O(2)−Zn(1)−O(4)	101.0(2)	O(10)^{2}−Zn(4A)−N(2)	100.9(2)
O(3)−Zn(1)−O(4)	113.5(2)	O(12)−Zn(4A)−N(2)	135.1(3)
O(5)−Zn(2)−O(4)	101.1(2)	O(10)−P(1)−O(1)^{5}	112.2(3)
O(5)−Zn(2)−O(6)	118.7(2)	O(10)−P(1)−O(9)^{6}	109.3(3)
O(5)−Zn(2)−O(7)	112.4(2)	O(1)^{5}−P(1)−O(9)^{6}	112.2(3)
O(6)−Zn(2)−O(7)	104.3(2)	O(10)−P(1)−O(4)	109.4(3)
O(6)−Zn(2)−O(4)	115.6(2)	O(1)^{5}−P(1)−O(4)	105.0(3)
O(4)−Zn(2)−O(7)	104.1(2)	O(9)^{6}−P(1)−O(4)	108.6(3)
O(8)−Zn(3)−O(7)	106.7(2)	O(6)−P(2)−O(12)	109.5(3)
O(8)−Zn(3)−O(9)	109.1(2)	O(6)−P(2)−O(8)	112.5(3)
O(8)−Zn(3)−O(3)^{1}	108.2(2)	O(12)−P(2)−O(8)	110.0(3)
O(9)−Zn(3)−O(7)	106.292)	O(6)−P(2)−O(3)^{6}	108.9(3)
O(9)−Zn(3)−O(3)^{1}	105.0(2)	O(12)−P(2)−O(3)^{6}	109.1(3)
O(7)−Zn(3)−O(3)^{1}	121.2(2)	O(8)−P(2)−O(3)^{6}	106.7(3)
O(10)^{2}−Zn(4)−O(12)	101.0(2)	O(2)−P(3)−O(11)	109.8(3)
O(10)^{2}−Zn(4)−O(11)^{3}	102.2(2)	O(2)−P(3)−O(5)^{7}	113.2(3)
O(12)−Zn(4)−O(11)^{3}	107.5(2)	O(11)−P(3)−O(5)^{7}	108.4(3)
O(10)^{2}−Zn(4)−N(1)^{4}	95.9(2)	O(2)−P(3)−O(7)	107.3(3)
O(12)−Zn(4)−N(1)^{4}	138.5(3)	O(11)−P(3)−O(7)	108.6(3)
O(11)^{3}−Zn(4)−N(1)^{4}	105.5(3)	O(5)^{7}−P(3)−O(7)	109.4(3)
P(1)^{e}−O(1)−Zn(1)	133.0(3)	P(3)−O(7)−Zn(2)	121.3(3)
P(3)−O(2)−Zn(1)	134.3(3)	Zn(3)−O(7)−Zn(2)	118.8(2)
P(2)^{7}−O(3)−Zn(1)	125.0(3)	P(2)−O(8)−Zn(3)	130.1(3)
P(2)^{7}−O(3)−Zn(3)^{8}	116.7(2)	P(1)^{7}−O(9)−Zn(3)	136.7(3)
Zn(1)−O(3)−Zn(3)^{8}	118.0(2)	P(1)−O(10)−Zn(4A)^{9}	133.5(3)
P(1)−O(4)−Zn(2)	122.6(2)	P(1)−O(10)−Zn(4)^{9}	172.3(3)
P(1)−O(4)−Zn(1)	110.7(2)	P(3)−O(11)−Zn(4A)^{3}	154.6(4)
Zn(2)−O(4)−Zn(1)	108.9(2)	P(3)−O(11)−Zn(4)^{3}	127.6(3)
P(3)^{6}−O(5)−Zn(2)	135.4(3)	P(1)−O(10)−Zn(4A)^{9}	133.5(3)
P(2)−O(6)−Zn(2)	129.6(3)	P(1)−O(10)−Zn(4)^{9}	172.3(3)
P(3)−O(7)−Zn(3)	118.8(3)		

organic moiety	angle (deg)	organic moiety	angle (deg)
C(1)−N(1)−Zn(4)^{10}	117.1(5)	C(2)−N(2)−Zn(4A)	120.0(6)
N(1)−C(1)−C(2)	111.3(7)	C(3)−N(2)−Zn(4A)	107.4(5)
N(2)−C(2)−C(1)	109.4(7)	C(3)^{11}−C(3)−N(2)	108.1(9)
C(2)−N(2)−C(3)	111.0(6)		

[a] Symmetry transformations used to generate equivalent atoms: 1, $-x + 1, y - 1/2, -z + 1/2$; 2, $-x, y - 1/2, -z - 1/2$; 3, $-x + 1, -y, -z$; 4, $x, -y - 1/2, z - 1/2$; 5, $-x + 1, -y + 1, -z$; 6, $x, -y + 1/2, z - 1/2$; 7, $x, -y + 1/2, z + 1/2$; 8, $-x + 1, y + 1/2, -z + 1/2$; 9, $-x, y + 1/2, -z - 1/2$; 10, $x, -y - 1/2, z + 1/2$; 11, $-x, -y, -z$.

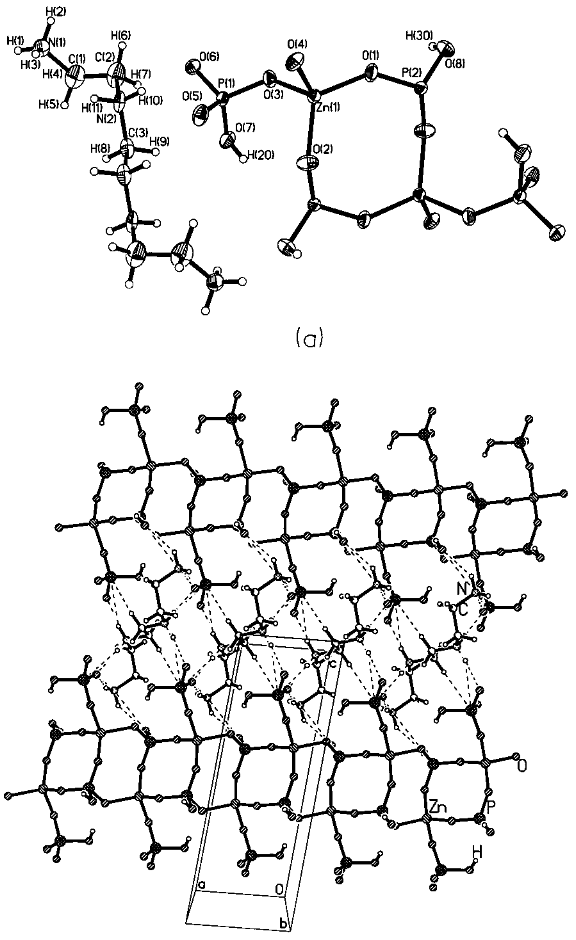

Figure 1. (a) ORTEP plot of $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ (**I**). Asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability. (b) Structure of **I** showing the four-membered ladder-like chain propagating along the *a* axis. The figure also shows the H-bonding interaction between the amine and the chain.

91.1−118.2° [$(O-Zn(1)-O)_{av} = 109.3°$ and $(O-Zn(2)-O)_{av} = 109.4°$]. Both the zinc atoms are connected to three neighboring P atoms via four Zn−O−P bonds with an average bond angle of 129.3°. Of the three P atoms, P(1) and P(2) make three P−O−Zn bonds and possess one P−O terminal linkage, while P(3) makes two P−O−Zn linkages and has two P−O terminal bonds. The three P atoms have P−O distances in the range of 1.505−1.591 Å [$(P(1)-O)_{av} = 1.540$ Å, $(P(2)-O)_{av} = 1.536$ Å, and $(P(3)-O)_{av} = 1.536$ Å], and the O−P−O angles are in the range of 102.6−112.9° [$(O-P-O)_{av} = 109.4°$ for all the P atoms]. These geometrical parameters are in good agreement with those observed earlier.[2−8] Assuming the usual valences of Zn, P, and O to be +2, +5, and −2, respectively, the framework stoichiometry of $Zn_2(PO_4)_3$ creates a net framework charge of −5. Taking into account the presence of $0.5[C_6N_4H_{22}]$, the excess negative charge of −3 can be balanced by the protonation of the PO_4 tetrahedra. One hydrogen position for each of the oxygens, O(9), O(10), and O(12), has been observed in the difference Fourier maps. Thus, P(1)−O(9), P(2)−O(10), and P(3)−O(12), with distances of 1.586, 1.588, and 1.591 Å, respectively, are all P−OH units. The second terminal P−O linkage, in the case of P(3) with a P−O distance of 1.520 Å, is a P═O unit. This assignment is consistent with bond-valence sum calculations.[13]

The connectivity between the ZnO_4 and HPO_4 tetrahedra gives rise to four-membered rings, which are connected edgewise, forming one-dimensional zigzag ladder-like chains. The chains are joined via a phosphate group, as shown in Figure 3. This results in the formation of a bifurcated 12-membered aperture within the layer. The amine molecule, forming the adjacent layer, sits in the middle of this aperture and interacts with the framework via hydrogen bonding (Figure 3). Thus, the layers in **II** are formed in such a manner that the cationic and anionic layers alternate. The inorganic layers are stacked exactly one over the other in an AAAAA fashion, forming a pseudo-one-dimensional channel with the amine molecule sitting in the middle of such channels. A similar layer arrangement has been observed recently in an open-framework cobalt phosphate.[14]

Three-Dimensional Structures of $[C_6N_4H_{22}]_{0.5}[Zn_2(PO_4)_2]$ (III) and $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (IV). $[C_6N_4H_{22}]_{0.5}$-$[Zn_2P_2O_8]$ (**III**) is a three-dimensional open-framework structure containing one-dimensional channels bound by eight tetrahedral (T) atoms (T = Zn and P). The structure is built from ZnO_4 and PO_4 tetrahedra and is connected via Zn−O−P bonds, the

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(14) Rao, C. N. R.; Natarajan, S.; Neeraj, S. *J. Am. Chem. Soc.* **2000**, *122*, 2810.

Table 10. Important Hydrogen Bond Interactions in Compounds **I**−**IV**

moiety	distance (Å)	moiety	angle (deg)
		I	
O(8)−H(1)	2.1086(5)	O(8)−H(1)−N(1)	146.2(5)
O(3)−H(2)	2.145(5)	O(3)−H(2)−N(1)	168.7(5)
O(5)−H(3)	1.789(5)	O(5)−H(3)−N(1)	160.5(5)
O(6)−H(10)	1.806(5)	O(6)−H(10)−N(2)	165.6(5)
O(5)−H(11)	1.803(5)	O(5)−H(11)−N(2)	164.4(5)
O(4)−H(20)	1.891(4)	O(4)−H(20)−O(7)	162.4(5)
O(6)−H(30)	1.885(4)	O(6)−H(30)−O(8)	141.9(4)
O(3)−H(4)	2.391(7)	O(3)−H(4)−C(1)	154.8(6)
O(1)−H(7)	2.351(7)	O(1)−H(7)−C(2)	145.9(6)
O(5)−H(8)	2.584(6)	O(5)−H(8)−C(3)	165.9(5)
		II	
O(3)−H(1)	2.216(6)	O(3)−H(1)−N(1)	143.3(6)
O(8)−H(2)	2.136(6)	O(8)−H(2)−N(1)	164.9(6)
O(2)−H(3)	2.210(7)	O(2)−H(3)−N(1)	141.4(6)
O(8)−H(8)	2.116(6)	O(8)−H(8)−N(2)	165.7(6)
O(11)−H(9)	1.883(7)	O(11)−H(9)−N(2)	162.5(6)
N(1)−H(30)	2.086(7)	N(1)−H(30)−O(10)	166.1(6)
O(1)−H(4)	2.525(7)	O(1)−H(4)−C(1)	144.0(6)
O(3)−H(6)	2.590(8)	O(3)−H(6)−C(2)	141.8(7)
		III	
O(8)−H(1)	2.115(2)	O(8)−H(1)−Nk(1)	147.8(2)
O(4)−H(2)	2.121(3)	O(4)−H(2)−N(1)	158.1(2)
O(3)−H(3)	2.147(2)	O(3)−H(3)−N(1)	131.7(2)
O(4)−H(8)	2.242(1)	O(4)−H(8)−N(2)	140.4(3)
O(8)−H(8)	2.295(1)	O(8)−H(8)−N(2)	150.1(3)
O(7)−H(9)	2.001(2)	O(7)−H(9)−N(2)	158.7(2)
O(5)−H(6)	2.275(2)	O(5)−H(6)−C(2)	161.2(1)
O(2)−H(7)	2.591(2)	O(2)−H(7)−C(2)	132.6(2)
O(8)−H(10)	2.599(4)	O(8)−H(10)−C(3)	139.5(2)
O(3)−H(11)	2.580(2)	O(3)−H(11)−C(3)	152.8(4)
O(6)−H(11)	2.382(4)	O(6)−H(11)−C(3)	135.7(2)
		IV	
O(7)−H(8)	2.046(2)	O(7)−H(8)−N(2)	157.7(1)
O(12)−H(8)	2.399(2)	O(12)−H(8)−N(2)	134.8(2)
O(12)−H(9)	1.813(2)	O(12)−H(9)−N(2)	164.6(2)
N(1)−H(20)	2.061(2)	N(1)−H(20)−O(12)	160.8(2)
O(12)−H(4)	2.547(2)	O(12)−H(4)−C(1)	138.0(2)
O(5)−H(6)	2.587(2)	O(5)−H(6)−C(2)	160.0(4)
O(6)−H(11)	2.353(3)	O(6)−H(11)−C(3)	138.8(2)

surrounding channels occupied by extraframework quadruply protonated TETA cations. The 17 non-hydrogen atoms of the asymmetric unit consist of 12 frameworks and five atoms of the guest species (Figure 4). The asymmetric unit contains two crystallographically independent zinc and phosphorus atoms. The two zinc atoms in **III** are both tetrahedrally coordinated by their O atom neighbors, with average zinc−oxygen bond distances of 1.971 Å for Zn(1) and 1.941 Å for Zn(2). The average O−Zn−O bond angles are in the range of 95.9−131.0° [$(O-Zn(1)-O)_{av}$ = 109.3° and $(O-Zn(2)-O)_{av}$ = 109.5°]. Both zinc and phosphorus atoms make four Zn−O−P bonds to two distinct P atom neighbors and have an average Zn−O−P bond angle of 133.4°, resulting from a fairly wide spread of angles (Table 5). The P−O bond distances are in the range of 1.490−1.542 Å [$(P(1)-O)_{av}$ = 1.507 Å and $(P(2)-O)_{av}$ = 1.530 Å], and the O−P−O angles are in the range of 106.2−112.0° [$(O-P-O)_{av}$ = 109.5° for both P(1) and P(2)]. These structural parameters are in good agreement with the results of previous structure determinations on similar compounds.[2−8] The framework stoichiometry of $Zn_2(PO_4)_2$ would give a net framework charge of −2, and the $0.5[C_6N_4H_{22}]$ per formula unit balances this negative charge. Bond-valence sum calculations[13] on the framework agree with the above results.

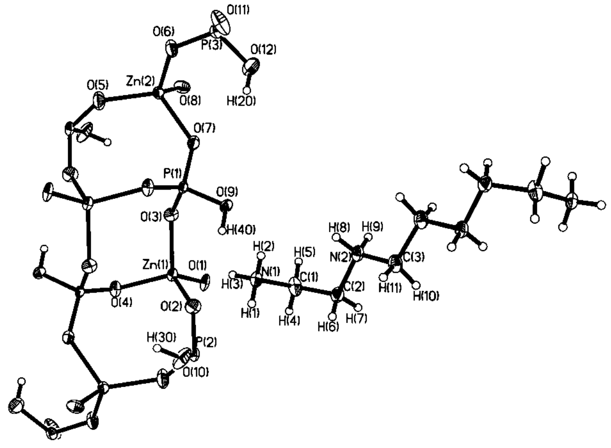

Figure 2. ORTEP plot of $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$ (**II**). Asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability.

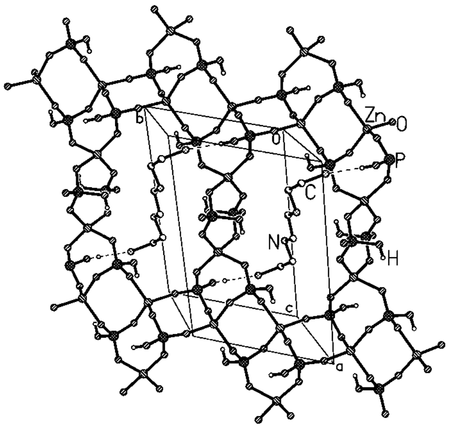

Figure 3. Layered structure of **II**, with the protonated amine molecule sitting in the 12-membered aperture. Dashed lines represent the hydrogen-bond interactions.

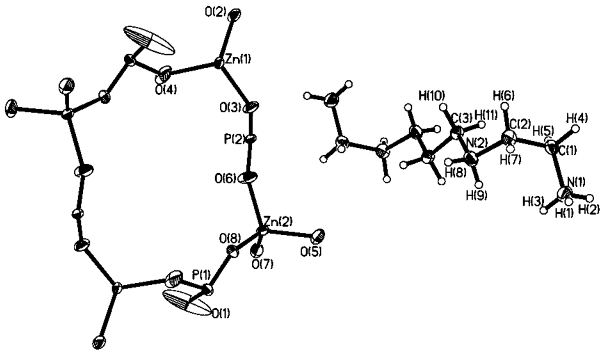

Figure 4. ORTEP plot of $[C_6N_4H_{22}]_{0.5}[Zn_2P_2O_8]$ (**III**). Asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability.

The framework structure of **III** is built from ZnO_4 and PO_4 tetrahedra sharing vertexes to form four-membered rings. The three-dimensional structure can be derived from two-dimensional sheets made by Zn(1), Zn(2), P(1), and P(2). The connectivity between these units is such that the oxygen neighbors of both P(1) and Zn(1) are all connected within the plane, and P(2) and Zn(2) have three of the four possible connections in the plane. The fourth connection needed for P(2) and Zn(2) is garnered from adjacent layers forming the three-dimensional connectivity. Alternatively, the eight-membered apertures are formed whenever the four-membered edge-shared ladders meet within the sheet. These apertures are linked via oxygen atoms, forming the eight-membered channels in **III**. The eight-membered channels along the [100] direction are shown in Figure 5. The width of the channels is ~3.6 × 4.8 Å. The quadruply protonated TETA molecule sits in the middle of this

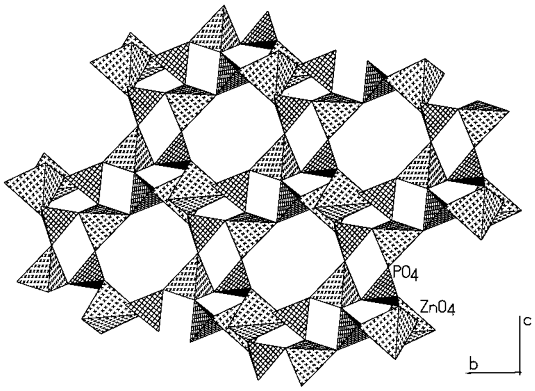

Figure 5. Polyhedral view of $[C_6N_4H_{22}]_{0.5}[Zn_2P_2O_8]$ (**III**) along the [100] direction. Note that the connectivity produces an eight-membered channel.

channel. Along the [010] and [001] directions, the connectivity between the ZnO_4 and PO_4 units also creates eight-membered channels.

$[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$, **IV**, is an anionic open-framework zinc phosphate built from tetrahedral ZnO_4 and PO_4 blocks connected via Zn−O−P bonds. The channels, thus formed, are occupied by quadruply protonated TETA molecules. The asymmetric unit contains 28 non-hydrogen atoms, of which 23 belong to the framework and five to the guest species (Figure 6a). There are three crystallographically independent zinc and phosphorus atoms. The Zn atoms are all tetrahedrally coordinated by their oxygen atom neighbors, with average Zn−O bond distances of 1.965 Å for Zn(1), 1.948 Å for Zn(2), and 1.956 Å for Zn(3). The O−Zn−O bond angles are in the range of 98.3−117.3° $[(O{-}Zn(1){-}O)_{av} = 109.1°$, $(O{-}Zn(2){-}O)_{av} = 109.4°$, and $(O{-}Zn(3){-}O)_{av} = 109.2°]$. Additionally, Zn(1) is also bonded to Zn(3) via a Zn−O−Zn linkage. The three Zn atoms are connected to three P atoms via Zn−O−P bonds with an average bond angle of 128.7° resulting from a fairly wide spread of angles (Table 7). Of the three P atoms, P(1) and P(2) make four P−O−Zn bonds, and P(3) makes three P−O−Zn bonds and possesses one terminal linkage. The P−O bond distances are in the range of 1.505−1.585 Å $[(P(1){-}O)_{av} = 1.537$ Å, $(P(2){-}O)_{av} = 1.534$ Å, and $(P(3){-}O)_{av} = 1.538$ Å], and the O−P−O angles are the range of 104.0−112.8° [(O−P−O)av = 109.5° for P(1), P(2), and P(3)]. These geometrical parameters are in agreement with those observed earlier.[2−8] Assuming the normal valences of Zn, P, and O to be +2, +5, and −2, respectively, the framework stoichiometry of $Zn_3(PO_4)_3$ creates a charge of −3. Taking into account the presence of the 0.5-$[C_6N_4H_{22}]$ molecule, the excess negative charge of −1 can be balanced by the protonation of one of the PO_4 groups. The attachment of a proton with the terminal oxygen is suggested by the bond-valence sum calculations as well.[13]

The framework structure of **IV** is built from ZnO_4 and PO_4 tetrahedra sharing vertexes to form four-membered rings. The three-dimensional structure can be derived from two-dimensional sheets made by the networking between the Zn and P atoms. The connectivity between the ZnO_4 and PO_4 units forms four-membered rings. Thus, there are three types of such four-membered rings in **IV**——those formed by Zn(1) and P(1), by Zn(3) and P(2), and by Zn(2) and P(3). The linkages between the four-membered rings made by Zn(1) and P(1) and by Zn(3) and P(2) form a one-dimensional edge-shared chain. These chains are linked by a three-membered ring, formed by Zn(1), Zn(3), and P(1), and a four-membered ring, made by Zn(2) and P(3), forming a 16-membered aperture within the plane. These planes are linked to each other via the oxygen atoms, forming a 16-membered one-dimensional channel along the *bc* plane. The width of this channel is 5.8 × 13.6 Å. The quadruply protonated TETA molecule is present in the middle of this channel (Figure 6b).

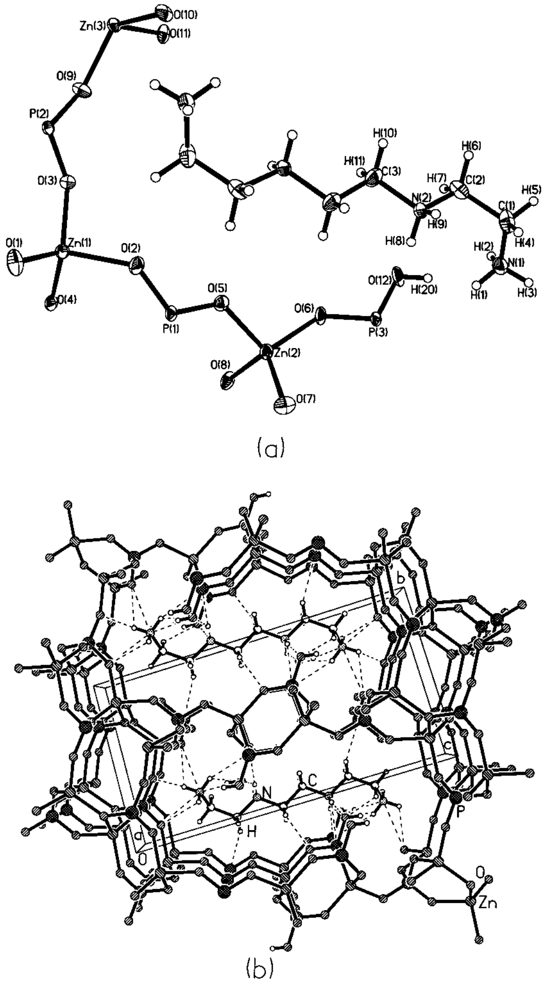

Figure 6. (a) ORTEP plot of $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (**IV**). Thermal ellipsoids are given at 50% probability. (b) Structure of **IV** showing the 16-membered channel with the amine molecule. Dashed lines represent the various possible hydrogen-bond interactions.

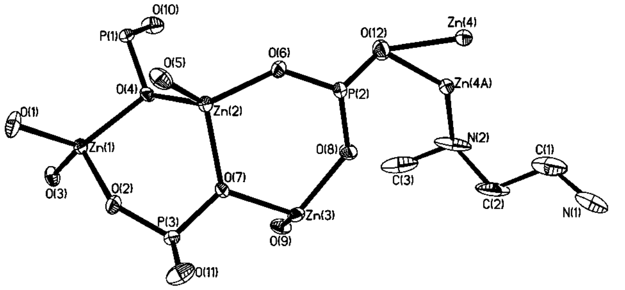

Figure 7. ORTEP plot of $[C_6N_4H_{20}]_{0.5}[Zn_4P_3O_{12}]$ (**V**). Thermal ellipsoids are given at 50% probability.

$[C_6N_4H_{20}]_{0.5}[Zn_4P_3O_{12}]$ (V), with the Ligating Amine. $[C_6N_4H_{20}]_{0.5}[Zn_4P_3O_{12}]$, **V**, is an unusual open-framework zinc phosphate built from ZnO_4, ZnO_3N, and PO_4 units and connected via Zn−O−P bonds. The channels, thus formed, are occupied by doubly protonated TETA molecules extending from Zn centers. The asymmetric unit contains 24 non-hydrogen atoms, as shown in Figure 7. The Zn atoms are all tetrahedrally coordinated with respect to oxygens, except Zn(4), which is

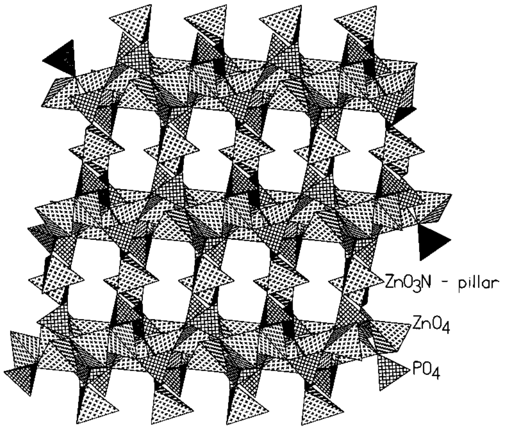

Figure 8. Polyhedral view of **V** along the [010] direction, showing pillaring of the zinc phosphate layer by ZnO_3N tetrahedra (both the disordered positions are presented). Such a connectivity forms an eight-membered channel.

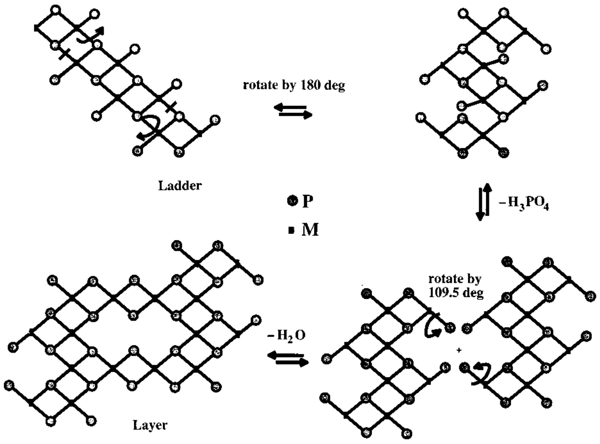

Figure 9. Schematic representation of the ladder-to-layer transformation.

three coordinated with oxygens, and the fourth connection needed for the tetrahedral arrangement comes from nitrogen of the amine. Zn(4) is disordered equally over two different positions with site occupancies of 0.49 and 0.51, and the disorder causes different nitrogen atoms of the amine molecule to bind with the two disordered sites, a terminal nitrogen in one case [Zn(4)] and a middle nitrogen atom in the other [Zn(4a)].

The framework structure of **V** is built from ZnO_4, ZnO_3N, and PO_4 tetrahedral moieties sharing vertexes. The connectivity between ZnO_4 and PO_4 units is such that it forms infinite two-dimensional sheets along the *bc* plane. Within each sheet, the linkages involve alternating three- and four-membered rings that are connected edgewise. This layer may also be considered as a continuous corrugated chain of three-membered rings connected by their edges and corners. This type of connectivity between the three-membered rings leads to the formation of a one-dimensional Zn−O−Zn sinusoidal chains within the *bc* plane. In **V**, the sheets are covalently linked by ZnO_3N tetrahedra acting as a pillar, forming one-dimensional eight-membered channels along the *b* and *c* axes. The eight-membered channel along the *b* axis is shown in Figure 8. This type of channel formed by the pillaring of ZnO_3N units, to our knowledge, is observed in open-framework zinc phosphates for the first time.

The Zn atoms make three Zn−O−P bonds with three P neighbors, with a spread of Zn−O−P angles (average, 127.9°), as given in Table 9. The fourth connection for a tetrahedral linkage in the case of Zn(1) to Zn(3) is obtained through Zn−O−Zn linkages (average, 115.2°) and through a terminal N atom in the case of Zn(4). Of the nine O atoms that are bound with Zn(1) to Zn(3), three have trigonal coordination (25%), resulting in infinite one-dimensional Zn−O−Zn chains. The Zn(4) atom with a terminal N linkage in **V** is disordered with a site occupancy factor of ~0.5. The Zn−O bond distances within the layer are in the range of 1.911−2.019 Å [$(\mathrm{Zn(1)-O})_{av} = 1.975$ Å, $(\mathrm{Zn(2)-O})_{av} = 1.956$ Å, and $(\mathrm{Zn(3)-O})_{av} = 1.958$ Å], and the O−Zn−O bond angles are in the range of 95.6−121.2° [$(\mathrm{O-Zn(1)-O})_{av} = 109.2°$, $(\mathrm{O-Zn(2)-O})_{av} = 109.4°$, and $(\mathrm{O-Zn(3)-O})_{av} = 106.5$]. The longest bond distances and the largest bond angles are associated with the oxygens having trigonal coordination. The three independent P atoms are all connected to Zn atoms within the layer via four P−O−Zn linkages. The average P−O distances of 1.536, 1.539, and 1.537 Å result for P(1), P(2), and P(3), respectively. The O−P−O bond angles are in the range of 105.0−113.2° [$(\mathrm{O-P-O})_{av} = 109.5°$]. The usual valences for the Zn, P, and O atoms produce a framework stoichiometry of $Zn_4(PO_4)_3$, giving a net framework charge of −1. Charge compensation is attained by the presence of $0.5[C_6N_4H_{20}]$. It would appear that the amine is diprotonated in this phosphate. This assignment is also consistent with bond-valence sum calculations.[13] The various geometrical parameters observed for **V** are in good agreement with other similar open-framework zinc phosphates.[2−8]

Discussion

Five new zinc open-framework phosphate materials, $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ (**I**), $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_3]$ (**II**), $[C_6N_4H_{22}]_{0.5}[Zn_2P_2O_8]$ (**III**), $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (**IV**), and $[C_6N_4H_{20}]_{0.5}[Zn_4P_3O_{12}]$ (**V**), have been obtained as good-quality single crystals by hydrothermal synthesis in the presence of the tetramine TETA. All the compounds except **II** have been made in pure form by changing the ratio between the amine and the phosphoric acid. This observation underscores the importance of controlling the various synthesis parameters that are responsible for the formation of open-framework structures. Although all the compounds involve linkages between ZnO_4, PO_4, and HPO_4 units, there are distinct differences between them.

While the amine in **I**−**IV** appears to be the fully protonated form, it is diprotonated in **V**. We also notice that the phosphoric acid is not fully deprotonated, especially in **I** and **II**, and there are −OH groups attached to phosphorus. Thus, the HPO_4 units in **I**, **II**, and **IV** indicate that the phosphoric acid has lost only two of its protons. Deprotonation of the acid and the protonation of the amine appear to be related, both depending on the ratio of the concentrations of the acid and the amine in the starting synthesis mixture. Thus, in the syntheses of **I** and **II**, the acid is far in excess of the amine, resulting in a fully protonated amine but not a completely deprotonated acid and giving rise to a solid with HPO_4 units. On the other hand, a comparable ratio of the acid and the amine, as in **III** and **IV**, results in a solid possessing predominantly PO_4 units. In **V**, the presence of excess amine compared to the acid leads to the complete deprotonation of the acid but not in the protonation of the amine. This is also apparent in the net framework charges in **I**−**V** discussed earlier.

From the previously described structures, it would seem that the structures of **I** and **II** are closely related. While **I** is formed as a ladder comprising edge-shared four-membered rings, **II** is formed by connecting such chains. In Figure 9, we show schematically how **II** can be generated from **I**. Compounds **III**and **V** consist of three-dimensional networks formed predominantly by Zn−O−P linkages. In addition, Zn−O−Zn linkages are present in **V**. The Zn−O−Zn linkages in **V** are due to ∼25% of all the oxygen atoms being trigonally coordinated. The presence of a large number of three-coordinated oxygen atoms in **V** leads to the formation of infinite chains of Zn−O−Zn linkages.

Both compounds **III** and **IV** have a Zn:P ratio of 1:1, while in **V** the ratio is 1.33:1. Despite the Zn:P ratio of 1:1, there are no terminal P−OH linkages in **III** and **IV** possessing a single P−OH bond. The formation of framework protons or P−OH-type linkages arise in these materials to obtain charge neutrality, as it is difficult to pack enough organic cations into the available extraframework voids. In the present material, the fact that the framework is built from a 1:1 tetrahedral arrangement of Zn and P atoms (at least in the cases of **III** and **IV**) suggests indirectly that the organic cations, which are linear, are arranged in such a way that their charges balance in the framework. Such zinc phosphate structures without terminal P−OH bonds have been known in the literature and are usually templated by alkali metals.[2d] Compound **V**, on the other hand, is unusual in that it possesses eight-memebred channels similar to those of **III**, but at the same time, the amine molecule is bonded directly to Zn. Thus, the structure possesses zinc phosphate layers pillared by the ligated ZnO_3N tetrahedra. Additionally, within each zinc phosphate layer, the presence of three-coordinated oxygens and the consequent Zn−O−Zn linkages appear to be unique in a three-dimensional structure, though such features have been observed in layered Zn phosphates.[5a] The pillaring of such sheets by ZnO_3N tetrahedra, to our knowledge, has been observed for the first time in open-framework zinc phosphates. Other than in Zn phosphates, ligation of amine molecules with the metal centers is known only in a gallium phosphate.[15]

The role of the amine molecule (TETA) in these compounds merits some attention. From the survey of the available literature,[2−8] it appears that the formation of open-framework zinc phosphates is facilitated by the use of diamines rather than monoamines. The formation of more than one type of zinc phosphate structure with varying Zn:P ratios has been shown recently by Harrison et al.[4a,b] with guanidine as the amine. The amine of the nitrogen-rich guanidine cation, $[C(NH_2)_3]^+$, was presumed to have a symmetrical, propeller shape. We have, on the other hand, found that linear triamines such as diethylenetriamine (DETA), $NH_2(CH_2)_2NH(CH_2)_2NH_2$, favor the formation of dissimilar structures. Thus, we have synthesized zinc phosphates with helical pores[7c] and ladder-like layers[7d] and with the DETA acting as a ligand in a 10-membred, one-dimensional channel structure.[8a] The formation of the spectrum of structures from DETA could be due to the linear nature of the amine and the presence of a middle nitrogen atom, which, in addition to the terminal ones, can also favorably interact with the framework. By using a tetramine in the present study, we have obtained three different three-dimensional structures, all of which possess channels. Though the exact mechanism of formation of these architectures is far from being understood, it can be safely presumed that the nitrogens of the amine molecule play a vital role.

The "openness" of a structure is defined in terms of the tetrahedral atom density[16] (framework density, FD), itself defined as the number of tetrahedral (T) atoms per 1000 Å^3. In the present materials, the number of T atoms per 1000 Å^3 (here, T = Zn and P) is 16.1 for **III**, 17.0 for **IV**, and 20.2 for **V**. These values are in the middle of the range of FD values observed in aluminosilicate zeolites,[16] where the presence of channels is common. In **V**, the FD values are higher than in the other three, thereby indicating that the bonding of the amine probably leads to a denser framework.

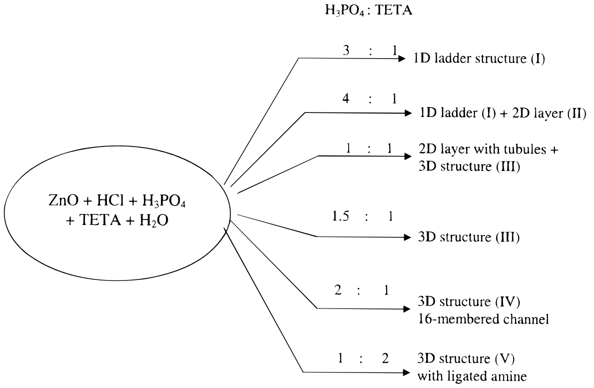

Figure 10. Relationship between the structures of the Zn phosphates and the phosphoric acid-to-amine ratio.

It is well known that multipoint hydrogen-bond interactions are necessary for the phase formation and stability of open architectures. We find this to be so in the present study as well, wherein strong interactions exist between the hydrogen atoms attached to nitrogen and the framework oxygen atoms. In addition, the hydrogens attached to some of the carbons also seem to form hydrogen bonds. The select hydrogen-bond interactions for compounds **I**−**IV** are presented in Table 10. As can be seen, the majority of the interactions are quite strong, as indicated by the short hydrogen-acceptor distances (∼2.2 Å) and a donor−hydrogen-acceptor angle of ∼150°. Hydrogen-bond interactions in **V** are not presented in Table 10 because of the disorder in the Zn atom [Zn(4)] to which the nitrogen is bonded.

We have described the structures of five different open-framework zinc phosphates obtained by using TETA. We also obtained another layer phosphate whose structure we have not described here for the purpose of brevity. In Figure 10, we show all the structures obtained with TETA, along with the relative concentrations of the amine and the phosphoric acid employed in the synthesis. We see that the one-dimensional (ladder) and the two-dimensional (layer) structures are obtained when the relative concentration of phosphoric acid is high, with the ratio of concentrations of the acid and the amine being in the range of 3:1−4:1. This is in contrast to the three-dimensional structures where the ratio is in the range of 2:1−1:1. The ligation of the amine to the metal occurs when this ratio is 1:2 or when the amine concentration is very high; a low concentration of the metal ions with respect to the amine would also favor ligation. An examination of the available literature also supports these findings. Thus, chain and layer zinc phosphates are obtained with ethylenediamine (en),[6] 1,3-diamino-2-hydroxypropane (DAHP),[6] 1,3-diaminopropane (DAP),[7] and diethylenetriamine (DETA),[5a] where the phosphoric acid-to-amine ratio is high (3:1−4:1); the ratio is close to 1:1 in the case of the three-dimensional structure. Metal ligation by the amine reported in zinc phosphates with diazabicyclo[2,2,2]octane (DABCO)[8] and DAP[3] occurs when the relative amine concentration is high (acid:amine ≈ 1:3−1:4).

Conclusions

A variety of open-framework zinc phosphates have been synthesized hydrothermally in the presence of a tetramine,

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TETA. The obtained compounds have a one-dimensional ladder structure, two two-dimensional layer structures, three three-dimensional structures with channels, and a three-dimensional structure where the amine also acts as a ligand to the metal. The structure of the open-framework phosphate appears to depend on the relative concentrations of the amine and the phosphoric acid, with high acid concentrations generally favoring structures with lower dimensions. A high amine concentration is necessary to obtain structures where the amine acts as a ligand. While these observations are supported by recent synthetic reports in the literature with en, DAP, DABCO, and other amines, it is important to carefully investigate this subject by determining the pK_a values of the various amino groups in the polyamine employed and monitoring the pH values before, during, and after the reaction. In the meantime, however, the operational guidelines indicated by the present study may serve a useful purpose in the synthesis of interesting open-framework structures.

Acknowledgment. A.C. thanks the Council of Scientific and Industrial Research (CSIR) of India for the award of a research fellowship.

Supporting Information Available: X-ray crystallographic files and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000366C