GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL 14, NO. 4, 2008: 389 - 396
COPYRIGHT© BACHUDO SCIENCE CO. LTD PRINTED IN NIGERIA. ISSN 1118-0579

X-RAY STUDIES, SPECTRAL CHARACTERIZATION AND THERMAL BEHAVIOUR OF A TWO-DIMENSIONAL ZINC PHOSPHATE TEMPLATED BY TRIS (2-AMINOETHYL) AMINE $[C_6H_{21}N_4][Zn_6(P0_4)_3(HP0_4)_3]. H_20$.

A. A. AYI AND O. E. OFFIONG

(Received 5, April 2007; Revision Accepted 22, July 2008)

ABSTRACT

A two-dimensional (2D) layered zinc phosphate hydrate $[C_6H_{21}N_4]$ $[Zn_6(P0_4)_3(HP0_4)_3]$. H_20, I, was synthesized by reacting Zn^{2+} ions with tris-(2-aminoethyl) amine phosphate $[C_6H_{21}N_4][P0_4].5H_20$. The compound was characterized by powder x-ray diffraction analysis, energy dispersive analysis by x-ray and infrared spectroscopy. The thermal behaviour of compound **I** was studied under flowing nitrogen and the structure determined by single crystal x-ray crystallography. Compound **I** crystallizes in the orthorhombic space group Pna2(No. 33), a = 18.785(2), b = 8.2783(7), c = 18. 747(2)Å, volume = 2915.4(4) $Å^3$, z = 4. The structure consists of a network of $Zn0_4$, $P0_4$ and $HP0_4$ tetrahedra which are connected to form a layer with interlamelar region occupied by the protonated amine and water molecules.

KEYWORDS: Metal phosphates, open-framework solids, amine phosphates route, layered structure

INTRODUCTION

The synthesis and characterization of crystalline microporous materials is attractive, not only because of its fascinating structural diversities and many practical applications ranging from catalysis, separation and sensor technology to waste water treatment [Yaghi *et al.*, 1998; Kitagiwa and Kondo, 1998; Lercher and Jentys, 2004; Logar and Kaucic, 2006], but also because. they may be nanostructured with respect to pore diameters and overall size of the particles [Breck, 1974, van Grieken *et al.*, 2000, Reding *et al.*, 2003]. Zeolites, which are crystalline inorganic polymers based on a three-dimensional arrangement of SiO_4 and AlO_4 tetrahedra represent the well-known family of microporous materials. After the seminal work of Wilson *et al.*, 1982 on the synthesis of alumino phosphates, whose frameworks are formed from vertex-sharing of $Al0_4$ and $P0_4$ tetrahedra, extensive investigations in the last two decades have enabled the synthesis of a variety of novel inorganic materials with open framework structures (Cheethams *et al.*, 1999). By replacing Al^{3+} ions with Zn^{2+} ions, a large number of zinc phosphates encompassing a variety of architectures have been isolated and characterized. They include zero-, one-, two – and three-dimensional network structures. [Neeraj *et al.*, 1999, 2000; Ayi *et al.*, 2000, 2001, 2002, 2005, Harrison *et al.*, 1992, 1997, 1998] These materials are generally synthesized hydrothermally in the presence of organic amines as structure directing or templating agents. Neeraj *et al.*, (1999), discovered that phosphates of organic amines are intermediates in the formation of open-framework structures. The versatility of this synthetic route to hybrid open-framework materials has been proven through facile reactions between the amine phosphates and metal ions [Neeraj *et al.*, 2000; Rao, *et al.*, 2000, Ayi *et al.*, 2005]. In this paper, we report the synthesis of an organically templated layered zinc phosphate via amine phosphate route.

Experimental

A layered zinc phosphate of the formula $[C_6H_{21}N_4][Zn_6(PO_4)_3$ $(HPO_4)_3]$. H_2O was isolated via amine phosphate route. The amine phosphate tris(2-aminoethyl)aminephosphate (Trenphos) was prepared by following standard procedures of Neeraj *et al.*, (1999) and Ayi (2007). The amine phosphate was then interacted with an aqueous solution of Zn^{2+} ions. In a typical synthesis of compound I; 0.214g Zn (CH_3COO) was dispersed in 2.7ml H_2O followed by addition of 0.342g of Trenphos under effective stirring. The resulting thick gel having a pH of 5 was sealed in a steel autoclave and heated at 180°C for 48h. The colourless single crystals formed, were vacuum filtered, washed with distilled water and dried at 30°C.

Characterization

Powder X-ray Diffraction Analysis. Powder X-ray diffraction (PXRD) data were collected using Rich-Siefert. model XRD-3000TT, Cuk_{α}, Ni filter 40kV x 30mA

Thermogravimetric analysis (TGA)

This was carried out using a Mettler-Toledo TG850 instrument under flowing nitrogen with a heating rate of 5s per minute.

Infrared Spectroscopy

The Fourier Transform Infrared (FTIR) spectrum was recorded within 400 – 4000 cm^{-1} on IFS 66V/S beam spectrometer. Measurements were carried out by diffuse reflectance method (DRIFTS).

Determination of Crystal Structure

A single crystal with dimensions 0.05 x 0.05 x 0.20mm was selected under polarizing microscope and glued to a thin glass fibre with cryanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens Smart – CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube x-ray source (MoK_{α} radiation, λ = 0.71073A) operating at 50kV and 40mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with 20 scans (width of 0.30° and exposure time of 20s per frame) in the 2θ range 3 to 46.5°. Pertinent experimental details for the structure determinations are presented in Table 1.

A. A. Ayi, Materials Chemistry Unit, Department of Pure and Applied Chemistry, University of Calabar, P.M.B. 1115-Calabar, Nigeria
O. E. Offiong, Department of Pure and Applied Chemistry, University of Calabar, P. M.B. 1115- Calabar. Nigeria

Table 1: Crystal data and structure refinement parameters for compound I

Structural Parameter	**I**
Empirical formula	$C_6H_{29}H_5O_{25}P_6Zn_6$
Crystal system	**Orthorhombic**
Space group	**Pna2(1)**
a(Å)	**18.785(2)**
b(Å)	**8.278(7)**
c(Å)	**18.747(2)**
α	**90**
β(°)	**90**
γ	**90**
Volume (Å³)	**2915.4(4)**
Z	**27**
Formula mass	**170.28**
ρ_{calc} **(gcm⁻³)**	**2.619**
μ**(mm⁻¹)**	**5.298**
θ **range (°)**	**2.17 – 23.18**
Total data collected	**11429**
Index ranges	$-20 \leq h \leq 20$, $9 \leq k \leq 9$, $-20 \leq \ell \leq 13$
Unique data	**3157**
Data [1>2σ(1)]	**Full-matrix least-square on /F²/**
Refinement method	
R_{int}	**0.1251**
R[1>2σ(1)]	$R_1 = 0.0669$; $wr_2 = 0.1518$
R (all data)	$R_1 = 0.1022$; $wR_2 = 0.1727$
Goodness of fit	**1.010**
No. of variable	**194**
Largest diff.map peak and hole eÅ⁻³	**1.097 and – 1.372**

The structure was solved by direct methods using SHELXS – 86 (Sheldrick, 1986) and difference Fourier synthesis. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS program (Sheldrick, 1994). 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. Full-matrix-least-squares structures refinement against /F²/ was carried out using the SHELX TL – PLUS package of programs (Sheldrick, 1993).

RESULTS AND DISCUSSION

On the basis of the Weissenberg photographs, the powder pattern was index in the orthorhombic space group Pna2 (no 33). The least-squares refinement was carried out over the powder x-ray data. A least-square fit of the P X RD (Cu - K_α) lines, using the hkl indices generated from single crystal X-ray data gave the following unit cell dimensions: a = 18.785(2), b = 8.2783 (7), c = 18.747(2)Å which are in good agreement with that determined using single-crystal XRD.

The TGA reveals a two-step weight loss (Fig. 1). The weight loss of 2.82% during the first step from 90°C to 180°C corresponds to the removal of the guest water molecule (Calculated 2.62%). The weight loss of 22.78% during the second step from 180°C – 600°C is attributed to the complete removal of the amine molecules (Calculated 21.65%). The calcined product was weakly diffracting indicating collapse of the framework.

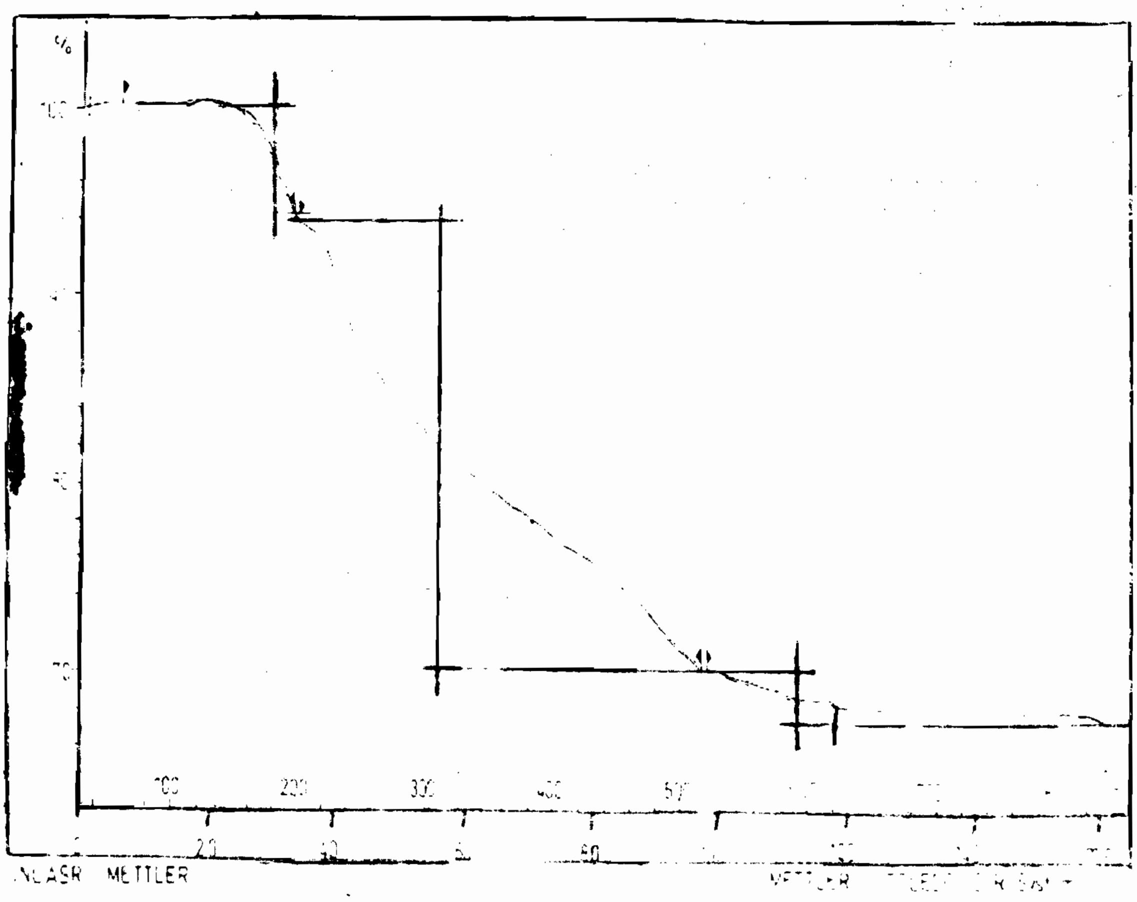

Fig.1: TGA Curve of compound I

The IR Spectrum of compound 1 (Fig. 2) reveals the presence of vibrational bands at 1112 – 1015cm^{-1} which are characteristic of the asymmetric stretching mode of the PO_4 units. The absorption at 955cm^{-1} is due to the symmetric vibrations of the PO_4 groups. The bands at 762 – 602cm^{-1} are attributed to the bending vibration of the PO_4 units [Nakamoto. 1997]. The bands due to the template cations are also observed. The asymmetric vibration of the N-H group (υ_{N-H}) is observed at 2919 cm^{-1} while the symmetric stretching is observed at 2851cm^{-1}. The *in-plane* vibration of the N-H group [$\delta_{(N-H)}$] appears at 1635 cm^{-1}. The absorption at 3622cm^{-1} is due to the lattice water molecules (Craver. 1982. Socrates. 1950)

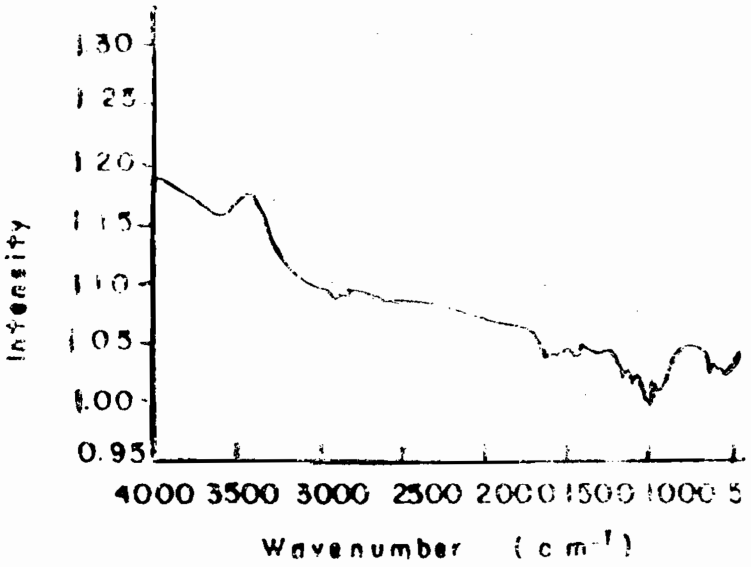

Fig. 2: Infrared Spectrum of Compound I

The atomic coordinates, selected bond lengths and bond angles for the single crystal data are presented in Tables 2 and 3, respectively. The single-crystal structure analysis revealed that compound I $[C_6H_{21}N_4)]$ $[Zn_6(PO_4)_3(HPO_4/_3.H_20$ is a 2D layered open-framework material The fundamental building units of I (Fig. 3) include six crystallographically independent Zn atoms and six P atoms belonging to the inorganic framework, four N atoms, six C atoms and one O atom belonging to the guest molecules.

Table 2 Atomic coordinates [x 10_4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for $[C_6N_{21}N_4]_2$ $[Zn_6 (PO_4)_3 (HPO_4)_3.H_2O$. I.

	x	Y	z	U(eq)
Zn(1)	5984(1)	-3520(3)	4822(1)	16(1)
Zn(2)	3182(1)	-410(3)	4818(1)	15(1)
Zn(3)	7089(1)	1417(3)	6383(1)	15(1)
Zn(4)	6786(1)	-3582(3)	6511(1)	16(1)
Zn(5)	6227(1)	1387(3)	4699(1)	16(1)
Zn(6)	4864(1)	-9536(3)	6281(1)	16(1)
P(1)	4832(3)	-746(7)	4687(3)	16(1)
P(2)	7224(3)	-1421(7)	5247(3)	16(1)
P(3)	5810 (3)	-6422(7)	5934(3)	14(1)
P(4)	8184(3)	-5715(7)	6426(3)	15(1)
P(5)	1925(3)	720(8)	3773(3)	15(1)
P(6)	6130(3)	-689(7)	7343(3)	13(1)
O(1)	5606(7)	-5362(17)	5284(8)	19(1)
O(2)	5276(7)	-2149(15)	4361(7)	8(3)
O(3)	6543(7)	-4191(17)	3982(7)	14(4)
O(4)	6646(7)	-2601(19)	5550(8)	18(4)
O(5)	2832(7)	-2590(16)	4910(8)	18(4)
O(6)	8245(7)	-6045(18)	5620(8)	18(4)
O(7)	2672(8)	849(17)	4083(8)	26(4)
O(8)	4108(7)	-659(18)	4295(8)	17(4)
O(9)	7809(7)	-7163(17)	6771(8)	21(4)
O(10)	6634(8)	735(20)	7286(9)	30(4)
O(11)	7514(7)	-435(17)	5867(7)	16(3)
O(12)	6383(7)	2326(17)	5674(7)	12(3)
O(13)	6152(7)	-5430(18)	6532(8)	21(4)
O(14)	6557(7)	-2289(18)	7345(8)	17(4)
O(15)	7801(8)	-4107(17)	6559(9)	23(4)
O(16)	6874(7)	-418(17)	4661(8)	18(4)
O(17)	5231(7)	2783(20)	4595(8)	16 (4)
O (18)	6472(8)	-7306(17)	3893(8)	25(4)
O(19)	5150(7)	-10822(18)	6211(8)	17(3)
O(20)	5568(8)	-9395(18)	6786(8)	23(4)
O(21)	3928(7)	-1054(18)	6755(8)	19(4)
O(22)	4686(8)	639 (18)	5488(9)	25(4)
O(23)	2011(7)	-584 (17)	2949(8)	20(4)
O(24)	5716(8)	9251(22)	8075(8)	22(4)
N(1)	872(10)	10706(27)	8425(11)	27(5)
C(1)	1352(11)	10237(29)	8287(13)	25(6)
C(2)	2134(12)	11740(24)	8296(14)	30(6)
N(2)	2561(11)	9678(29)	8286(12)	42(6)
C(3)	95(12)	9259(27)	8398(14)	29(6)
C(4)	-256(12)	7580(23)	766(13)	24(6)
N(2)	-546(9)	8558(28)	7697(10)	29(5)
C(5)	1009(11)	9743(25)	9168(12)	23(5)
C(6)	982(11)	9010(22)	9762(13)	22(5)
N(4)	1037(10)	-9253(20)	10491(11)	31(6)
N(5)	3969(8)	11809(17)	8179(9)	15(4)
O(100)	1060(7)		11300(9)	29(4)

Table 3: Selected bond distances and angles in $[C_6H_{21}N_4]$ $[Zn_6(PO_4)_3$ $(HPO_4)_3$ H_2O, 1.

Moiety	Distances (Å)	Moiety	Distances (Å)
Zn (1)-0(1)	1 89(2)	P(1)-0(17)	1.526(14)
Zn (1)-0(2)	1 950(13)	P(1)-0(8)	1 55(2)
Zn (1)-0(3)	1 972 (14)	P(1)-0(22)	1 556(2)
Zn (1)-0(4)	2 00 (2)	P(1)-0(2)	1 52(2)
Zn (2)-0(5)	1 928 (14)	P(1)-0(11)	1 53(2)
Zn (2)-0(6)#1	1.93 (2)	P(2)-0(16)	1 53(14)
Zn (2)-0(7)	1.98(2)	P(2)-0(5)#4	1 540(14)
Zn(2)-0(8)	2.009(14)	P(2)-0(5)#4	1 57(2)
Zn(3)-0(9)#2	1.934(14)	P(3)-0(19)	1.530(14)
Zn(3)-0(10)	1.98(2)	P(3)-0(13)	1.53(2)
Zn(3)-0(11)	1.981(14)	P(3)-0(1)	1.55(2)

Zn(3)-0(12)	2.022(14)	P(3)-0(1)	1.57(2)
Zn(4)-0(13)	1.94(2)	P(4)-0(15)	1.53(14)
Zn(4)-0(14)	1.943(14)	P(14)-0(15)	1.53(2)
Zn(4)-0(15)	1.96(2)	P(4)-0(9)	1.53(2)
Zn(4)-0(4)	2.00(2)	P(4)-0(6)	1.54(2)
Zn(5)-0(16)	1.927(14)	P(5)-0(3)#1	1.51(2)
Zn(5)-0(17)	1.934(13)	P(5)-0(18)#6	1.52(2)
Zn(5)-0(18)	1.96(2)	P(5)-0(7)	1.52(2)
Zn(6)-0(12)	2.009(14)	P(5)-0(23)	1.55(2)
Zn(6)-0(19)	1.928(14)	P(6)-0(20)#2	1.49(2)
Zn(6)-0(20)	1.94(2)	P(6)-0(10)	1.51(2)
Zn(6)-0(21)	1.973(14)	P(6)-0(14)	1.55(2)
Zn(6)-0(22)#3	1.97(2)	P(6)-0(24)	1.58(2)

Moiety	**Angles (^{0})**	**Moiety**	**Angles (^{0})**
0(1)- Zn (1)-0(2)	114.6(6)	0(19)-P(3)-0(1)	109.7(8)
0(1)- Zn (1)-0(3)	109.8(6)	0(13)-P(3)-0(1)	112.1(9)
0(2)- Zn (1)-0(3)	100.0(6)	0(19)-P(3)-0(12)#3	110.2(8)
0(1)- Zn (1)-0(4)	103.2(6)	0(13)-P(3)-0(12)#3	107.1(8)
0(2)- Zn (1)-0(4)	120.4(6)	0(1)-P(3)-0(12)#3	107.4(8)
0(3)- Zn (1)-0(4)	108.7(6)	0(21)#5-P(4)-0(15)	108.1(9)
0(5)- Zn (2)-0(6)#1	122.4(6)	0(21)#5-P(4)-0(9)	107.2(9)
0(5)- Zn (2)-0(7)	113.0(6)	0(15)-P(4)-0(9)	113.2(8)
0(6)#1- Zn (2)-0(7)	104.1(6)	0(21)#5-P(4)-0(6)	109.8(8)
0(5)- Zn (2)-0(8)	104.1(6)	0(15)-P(4)-0(6)	110.4(9)
0(6)#1-Zn(2)-0(8)	113.1(6)	0(9)-P(4)-0(6)	108.1(9)
0(7)-Zn(2)-0(8)	97.6(6)	0(3)#1-P(5)-0(18)#6	112.3(8)
0(9)#2-Zn(3)-0(10)	98.8(7)	0(3)#1-P(5)-0(7)	113.5(9)
0(9)#2-Zn(3)-0(11)	111.8(6)	0(3)#6-P(5)-0(7)	113.7(9)
0(10)-Zn(3)-0(11)	111.7(7)	0(3)#1-P(5)-0(23)	105.8(9)
0(9)#2-Zn(3)-0(12)	118.7(6)	0(18)#6-P(5)-0(23)	103.9(9)
0(10)-Zn(3)-0(12)	112.6(6)	0(7)-P(5)-0(23)	106.7(8)
0(11)-Zn(3)-0(12)	103.4(6)	0(20)#2-P(6)-0(10)	116.8(9)
0(13)-Zn(4)-0(14)	106.4(6)	0(20)#2-P(6)-0(14)	107.8(9)
0(13)-Zn(4)-0(15)	115.0(6)	0(10)-P(6)-0(14)	110.1(9)
0(14)-Zn(4)-0(15)	107.6(6)	0(20)#2-P(6)-0(24)	105.3(9)
0(13)-Zn(4)-0(4)	05.0(6)	0(10)-P(6)-0(24)	109.0(9)
0(14)-Zn(4)-0(4)	118.3(6)	0(14)-P(6)-0(24)	107.4(8)
0(15)-Zn(4)-0(4)	105.1(6)	P(3)-0(1)-Zn(1)	136.3(9)
0(16)-Zn(5)-0(17)	115.3(6)	P(1)-0(2)-Zn(1)	128.8(8)
0(16)-Zn(5)-0(18)	106.3(6)	P(5)#4-0(3)-Zn(1)	134.3(9)
0(17)-Zn(5)-0(18)	106.7(6)	P(2)-0(4)-Zn(4)	119.3(8)
0(16)-Zn(5)-0(12)	104.0(6)	Zn(2)-0(4)-Zn(1)	114.9(9)
0(17)-Zn(5)-0(12)	108.8(6)	P(4)-0(4)-Zn(1)	123.0(9)
0(18)-Zn(5)-0(12)	116.1(6)	P(2)#1-0(5)-Zn(2)	141.9(9)
0(19)-Zn(6)-0(20)	111.6(6)	P(4)-0(6)-Zn(2)#4	130.5(9)
0(19)-Zn(6)-0(21)	102.8(6)	P(5)-0(7)-Zn(2)	132.5(9)
0(20)-Zn(6)-0(21)	114.8(6)	P(1)-0(8)-Zn(3)	122.2(9)
0(19)-Zn(6)-0(22)#3	127.3(7)	P(4)-0)9)-Zn(3)#3	129.6(9)
0(20)-Zn(6)-0(22)#3	97.7(6)	P(6)-0(10)-Zn(3)	123.5(10)
0(21)-Zn(6)-0(22)#3	103.0(6)	P(2)-0(11)-Zn(3)	130.1(8)
0(17)P(1)-0(8)	109.8(8)	P(3)#2-0(12)-Zn(5)	116.0(8)
0(17)-P(1)-0(22)	109.8(9)	P(3)#2-0(12)-Zn(3)	119.4(8)
0(18)-P(1)-0(22)	108.3(8)	P(5)-0(12)-Zn(3)	123.3(7)
0(17)-P(1)-0(2)	109.7(8)	P(3)-0(13)-Zn(4)	131.7(10)
0(18)-P(1)-0(2)	108.6(8)	P(6)-0(14)-Zn(4)	125.7(9)
0(22)-P(1)-0(2)	110.7(8)	P(4)-0(15)-Zn(4)	130.0(9)
0(11)-P(2)-0(16)	114.4(8)	P(2)-0(16)-Zn(5)	131.9(10)
0(11)-p(2)-0(5)#4	109.5(8)	P(1)-0(17)-Zn(5)	131.6(8)
0(16)-P(2)-0(5)#4	108.3(8)	P(5)#7-0(18)-Zn(5)	136.7(10)
0(11)-P(2)-0(4)	107.8(8)	P(3)-0(19)-Zn(6)	135.0(9)
0(16)-P(2)-0(4)	107.5(8)	P(6)#3-0(20)-Zn(6)	141.6(10)
0(5)#4-P(2)-0(4)	109.3(8)	P(4)#8-0(21)-Zn(6)	129.5(9)
0(19)-P(3)-0(13)	110.3(8)	P(1)-0(22)-Zn(6)#2	126.5(9)

Organic Moiety

Moiety	Distances (Å)	Moiety	Distances $(^0)$
N(1)-C(3)	1.50(3)	C(3)-N(1)C(1)	112(2)
N(1)-C(1)	1.53(3)	C(3)-N(1)C(5)	106(2)
N(1)-C(5)	1.53(3)	C(1)-N(1)C(5)	110(2)
0(1)-C(2)	1.52(3)	C(2)-N(1)C(1)	112(2)
0(2)-N(2)	1.48(3)	N(1)-N(3)C(4)	113(2)
0(3)-C(4)	1.57(3)	N(2)-C(4)C(3)	109(2)
0(4)-N(2)	1.50(3)	C(6)-C(5)-N(1)	116(2)
0(5)-C(6)	1.48(3)	C(5)-C(6)-N(4)	114(2)
0(6)-N(4)	1.50(3)		

Summary Transformations used to generate equivalent atoms:
=1x-1/2,-y-12z #2x,y+1,y #3x,y-1,z #4x+1/2,-y ½,z
=5x+1/2,-y-3/2,z #6x-1/2,-y+1/2,z #7x+1/2,-y+1/2,z #8x-1/2,-y-3/2,z

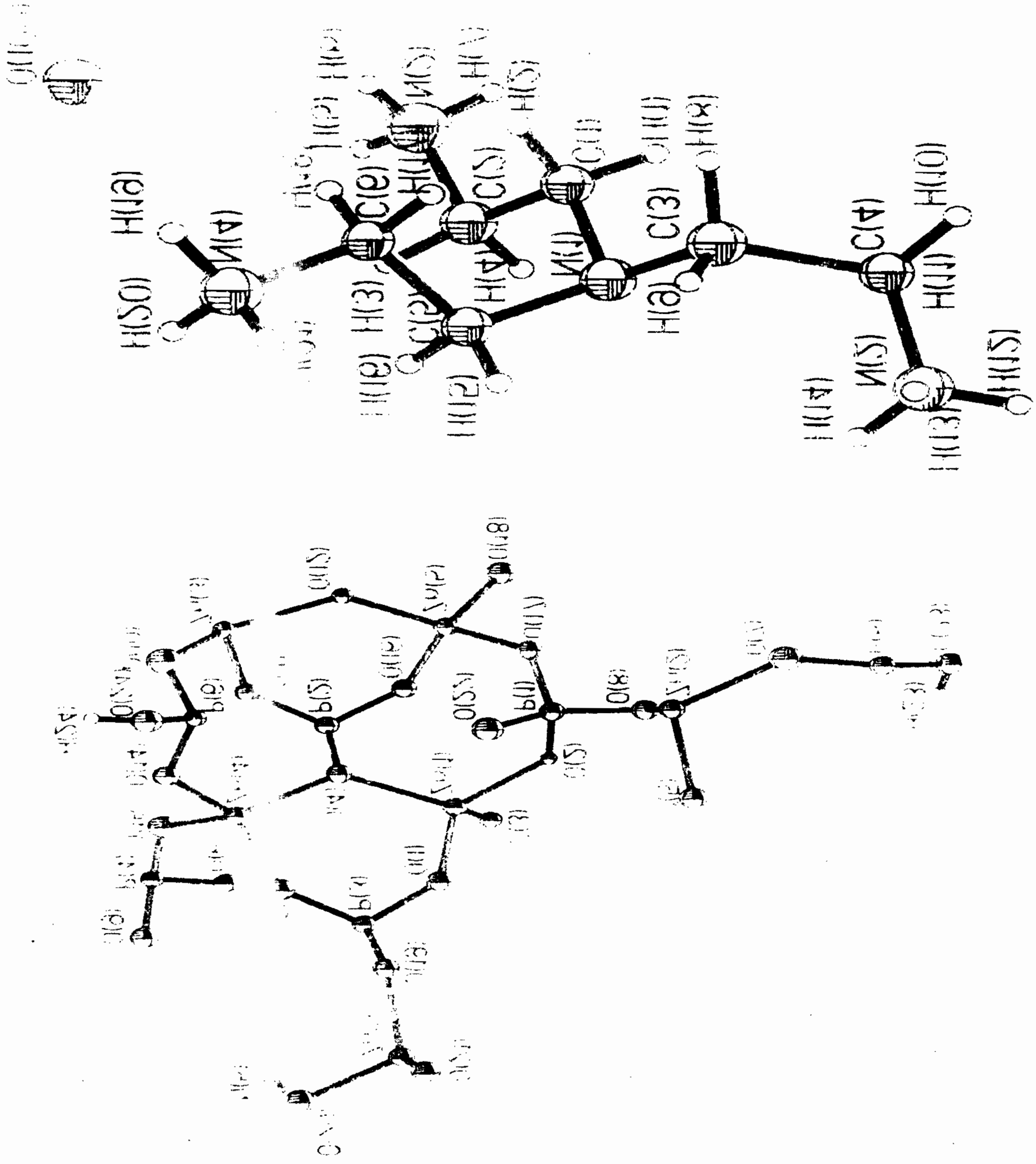

Fig. 3: ORTEP Plot of $[C_6H_{21}N_4][Zn_6(PO_4)_3(HPO_4)_3]\cdot H_2O$.

Each Zn atom is tetrahedrally coordinated with four oxygen atoms with Zn – O bond distances in the range 1.890(2) – 2.022 (14)Å (av. (Zn-O) = 1.961 Å). The O – Zn –O bond angles are in the range 97.6(6) – 127.37° [av. (O – Zn-O) = 109.5°]. Of the six independent P atoms, P(1), P(2), P(3), and P(4) are connected to Zn atoms via four Zn-O-P linkages, while P(5) and P(6) are connected via three Zn – O-P linkages with one terminal P-O bond. The average P – O distances of 1.545, 1.540, 1.545. 1.533, 1.525 and 1.533 Å result for P(1), P(2), P(3), and P(4), P(5) and P(6) respectively (Table 3). The O-P-O bond angles are in the range 103.9(9) – 113.5(9)° [av. (O – P- O)= 109.5]. The geometrical parameters observed in the present compound are in good agreement with similar open-framework zinc phosphates [Neeraj *et al.*, 2000; Ayi *et al.*, 2001].

The inorganic frame-work $[Zn_6(PO_4)_3(HPO_4)]$ is anionic with -3 charge. The charge neutrality is achieved by the incorporation of the triply protonated amine molecule. The structure of I thus, consists of a network of ZnO_4, PO_4 and HPO_4 moieties forming a layer with the interlamellar region occupied by the protonated amine and water molecules (Fig. 4).

In conclusion, by employing aminephosphate route, we have been able to isolate a 2D layered zinc phosphate similar to that obtained by Ayi *et al.*, (2001) as a transformation product of a zero-dimensional monomer $[C_6H_{21}H_{18}]$ [Zn $(HPO_4)(H_2PO_4)_2]$. Since compound I was obtained in high yield, we have been able to study the framework vibrations and its thermal properties in detail.

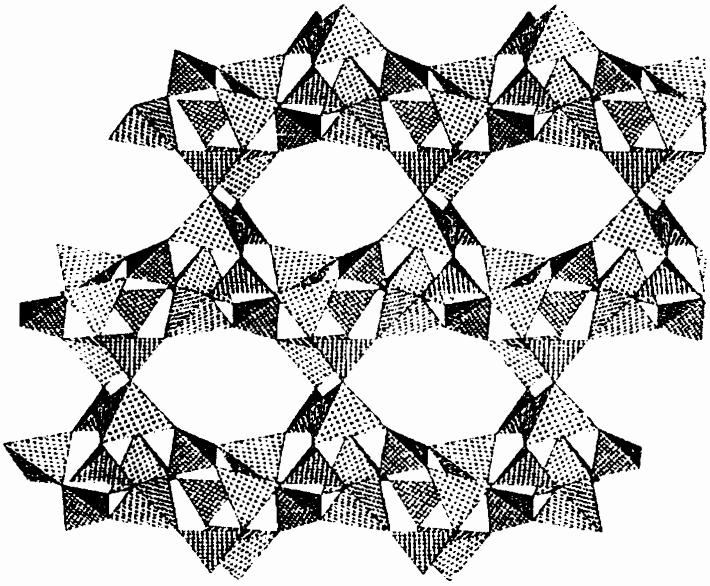

Fig. 4a : Polyhedral view of the single layer of I

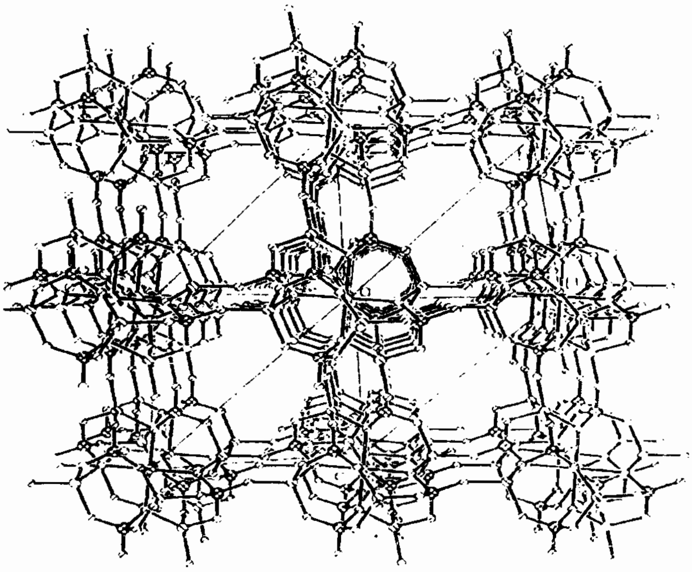

Fig. 4b: Structure of I along the *ac-plane* showing the layer arrangement.

ACKNOWLEDGEMENT

The authors are grateful to Prof. C. N. R. Rao for his kind support and encouragement and to the Academy of Sciences for the developing nations (TWAS) for the award of research fellowship.

REFERENCES

Ayi, A. A., Choudhury, A., Natarajan, S. and Rao, C. N. R., 2000. Solution-mediated synthesis of a three-dimensional zinc phosphate in the presence of a monoamine. J. Mater. Chem. 10: 2606 – 2608.

Ayi, A. A., Choudhury, A.; Natarajan. S.; Neeraj, S. and Rao, C. N. R., 2001. Transformation of low-dimensional zinc phosphates to complex open-dimensional to one-. two-and three-dimensional structures J Mater Chem 11 1181 – 1191

Ayi, A. A, Offiong, E. O and Akinchan, N T., 2002 Recent Trends in Open-framework solids J Chem. Soc. Nigeria 27: 52 – 60.

Ayi, A. A., Choudhury, A. and RaO. C N R. 2005 A versatile route to hybrid open-frame work materials Global J Pure & Applied Science 11. 523 – 534

Ayi. A A. 2007 X-ray Studies. vibrational spectra and thermal behaviour of linear chains aluminophosphate $[C_6H_{21}N_4]_2[Al_2(PO_4)_4].5H_2O$ and its transformation product $[C_6H_{21}N_4]_2[Al_3(PO_4)_4]$. J. Res Phy. Sciences 3: 86 - 93

Breck. D W., 1974. Zeolite Moecules Sieves. structure. chemistry and use John Widey & Sons

Cheetham, A. Ferey. G and Loiseau T 1999 Open-framework inorganic materials Angew Chem Int ed 38: 3268 – 3292.

Craver, C D, 1982. Desk Book of infrared spectra. The Coblentz society InC Kirkwood, MO

Harrison, W. T. A., Martin T E, Gier, T E and Stucky. G D. 1992. Tetrahedral atom zinco phosphates structures. synthesis and structural characterization of two novel anionic eight-ring frameworks contaming Cationic 1.4-diazobicyclo (2 2 2) octane quests J Mater Chem 2: 175 – 181

Harrison, W. T. A. and Hannooman L., 1997. $N(CH_3)_4.ZnH_3(PO_4)_2$: A large pore Zinco phosphate built up from a 12-ring architecture with a remarkably low tetrahedral-framework atom density Angew Chem Int ed 36 640 – 641

Harrison, W T A. Biresak Z Hannooman, L and Zhang, Z., 1998. Two new 1,3 –diammoniumpropane zinc hydrogen phosphates $H_3N(CH_2)_3NH_3.\ Zn_2(HPO_4)_2(H_2PO_4)$, with 12-rings layers and $H_3N(CH_2)_3N_2H_3\ Zn_2(HPO_4)_2$ with 4 ring ladders J Solid State Chem 136: 93 – 102

Kitagawa, S. and Kondo M. 1998 Functional micropore chemistry of crystalline metal complex-assembled compounds Bull Chem Soc Jpn. 71 1739 - 1753

Lercher, J. A and Jentys A.. 2004 Catalytic properties of micro-and mesoporous namomaterial. Dekker Encyclopedia of Nanoscience and Nanotechnology, 633 – 647.

Logar. N Z and Kaucic. V. 2006 Nanoporous materials: From catalysis and Hydrogen storage to waste water treatment. Acta Chim. Slov 53: 117 – 135

Nakamoto, K, 1997 Infrared and Raman spectra of inorganic and coordination compounds 5th edition John Wiley & Sons, Inc New York

Neeraj. S, Natarajan S and RaO C N R 1999 Amine phosphates as intermediates in the formation of open-framework structures Angew Chem Int ed 38 3480

Neeraj, S., Natarajan, S. and RaO. C N. R., 2000. isolation of a zinc phosphate primary building unit $[C_6N_2H_{18}][Zn(HPO_4)_2$ and its transformation to open-framework phosphate $[C_6N_2H_{18}]\ [Zn_3\ (H_2O)_4\ (HPO_4)_4]$ J Solid State Chem 150, 417

RaO, C. N R, Natarajan, S., and Neeraj. S., 2000. Building open-framework metal phosphates from amine phosphates and a monomeric four membered ring J Solid State Chem 152. 302

Reding, G., Maurer. T and Kraushaar C B, 2003. Comparing synthesis routes to nanocrystalline zeolite ZSM-5 Microporous Mesoporous Materials 57 83 – 92

Sheldrick G M 1986 SHELXS-86 program for crystal structure Determination. University of Gottingen, Gottingen. Germany (b) G M. Sheldrick (1990), Acta Crystalogr Sect A, 46, 467.

Sheldrick G M. 1993 SHELXTL – PLUS Program for Crystal Structure solation and Refinement University of Gottingen, Gottingen. Germany

Sheldrick, G M., 1994 SADABS Siemens Ara Detector Absorption Correction program. University of Gottingen. Gottingen. Germany

Socrates G. 1950 Infrared characteristic Group frequencies Wiley New York, Stone bridge. Press; Porsistol.

Van Grieken, R, Sotelo, J L. and Menendenz, J M, Melero, J A. 2000 Anomalous crystallization mechanism in the synthesis of nanocrystalline ZSM-5 Microporous Mesoporous Mater 39 135 – 147

Wilson, S T. Lok B M Messina C A Cannon, T R and Flanigen, E M. 1982 Aluminophosphate molecular sieves. A new class of microporous crystalline inorganic solids. J Am Chem Soc 104: 1146-1147

Yaghi O M Li H., Davis C, Richardson D. and Groy, T L. 1998 Synthetic strategies structure patterns and emerging properties in the chemistry of modular porous solids Acc Chem Res 31 477 – 484