Solution-mediated synthesis of a three-dimensional zinc phosphate in the presence of a monoamine

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A new open-framework zinc phosphate of the formula $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$, **I**, has been synthesized at 60 °C in a THF–water medium in the presence of ethylamine. The structure consists of a network of strictly alternating ZnO_4 and PO_4 tetrahedra forming 4- and 8-membered rings, which connect to form intersecting elliptical channels bound by 12- and 8-T atoms (T = Zn, P) along the *c* and *b* axes, respectively. The amine molecule sits in the channel bound by 12-T atoms and the –OH group of the HPO_4 unit protrudes into the 8-membered channel. An interesting feature of **I** is that it has a very low framework density. Crystal data: $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$, monoclinic, C2/c (no. 15), *a* = 17.351(4), *b* = 9.507(5), *c* = 9.806(5) Å, *β* = 102.68(2)°, *V* = 1578.3(1) Å^3, *Z* = 4.

Introduction

A variety of open-framework zinc phosphates possessing linear chain,[1] ladder,[2] layered[3] and three-dimensional[4,5] structures have been reported in the recent literature. These structures also exhibit several novel structural motifs such as Zn_2O_2 dimers, OZn_4 tetrahedra and infinite Zn–O–Zn chains.[5–7] Open-framework metal phosphates are generally synthesized under hydrothermal conditions in the presence of di-, tri- and tetramines. While several open-framework aluminium phosphates have been synthesized with monoamines,[8] there are very few zinc phosphates obtained with monoamines.[1b,9] We have been attempting to synthesize open-framework Zn phosphates employing monoamines, and during the course of these investigations we have isolated a material of the composition $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$, **I**. This open-framework zinc phosphate is formed in the presence of a simple monoamine, under non-hydrothermal conditions at 60 °C. Furthermore, **I** has channels bound by 12-T atoms (T = Zn, P) and has a very low framework density. We describe the synthesis and structure of this material here.

Experimental

The title compound, **I**, was prepared under mild conditions by solvent-mediated synthesis. In a typical synthesis, 0.439 g of Zn acetate was dispersed in a THF–water mixture (75 : 25) and 0.46 g of phosphoric acid (85 wt%) was added under constant stirring. 0.27 g of ethylamine (EA) was added and the resulting thick gel was homogenized for 30 min at room temperature. The mixture with the composition $Zn(OAc)_2 \cdot 2H_2O : 4H_3PO_4 : 3EA : 7THF : 3H_2O$ was left to crystallize at about 60 °C for 2 weeks. The resulting product, a crop of large colorless rod-like single crystals, was filtered, washed with deionized water and dried under ambient conditions. The final yield of the product was ~50%. EDAX analysis indicated that the Zn : P ratio is 1 : 1.5, consistent with the formula derived from single crystal data. Initial characterizations were carried out by powder X-ray diffraction and thermogravimetric analysis (TGA).

A suitable colorless rod-like single crystal was selected and mounted at the tip of a glass fiber using cyanoacrylate (superglue) adhesive. 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 (Mo-Kα radiation, λ = 0.71073 Å) operating at 40 kV and 40 mA. A hemisphere of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 10 s per frame). Pertinent details of the crystal structure determination are presented in Table 1. The structure was solved by direct methods using SHELX-86,[10] which readily revealed all the heavy atom positions (Zn, P) and enabled us to locate the other non-hydrogen positions from the difference Fourier maps. All the hydrogen positions were found in the difference Fourier maps. For the final refinement, hydrogen atoms for both the framework as well as the amine were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[11] package of programs. The final atomic coordinates for $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$ are presented in Table 2.

Table 1 Crystal data and structure refinement parameters for $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$

Chemical formula	$Zn_2P_3O_{12}N_2C_4H_{19}$
Space group	C2/c
T/K	293
a/Å	17.351(4)
b/Å	9.507(5)
c/Å	9.806(5)
α/°	90.0
β/°	102.68(2)
γ/°	90.0
Volume/Å^3	1578.3(1)
Z	4
Formula mass	510.86
ρ_{calc}/g cm^{-3}	2.154
λ(Mo-Kα)/Å	0.71073
μ/mm^{-1}	3.406
$R(F_o^2)$ [$I > 2\sigma(I)$]	$R_1 = 0.0266$; $wR_2 = 0.0706^a$

$^a W = 1/[\sigma^2(F_O)^2 + (0.0882P)^2]$ where $P = [F_O^2 + 2F_C^2]/3$.

Table 2 Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$

Atom	x	y	z	$U_{(eq)}{}^a$
Zn(1)	1789(1)	795(1)	3752(1)	16(1)
P(1)	1896(1)	1779(1)	6812(1)	17(1)
P(2)	0	446(2)	2500	18(1)
O(1)	2506(2)	2087(3)	3193(3)	32(1)
O(2)	1869(2)	619(3)	5735(3)	25(1)
O(3)	2030(2)	−1142(3)	3282(3)	24(1)
O(4)	741(2)	1351(3)	2653(3)	22(1)
O(5)	1064(2)	2549(3)	6501(3)	31(1)
O(6)	−89(2)	−543(3)	1204(3)	22(1)
N(1)	1363(2)	2669(4)	10383(4)	33(1)
C(1)	887(3)	3953(5)	10089(7)	59(2)
C(2)	1097(3)	4885(5)	9059(5)	48(1)

$^a U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

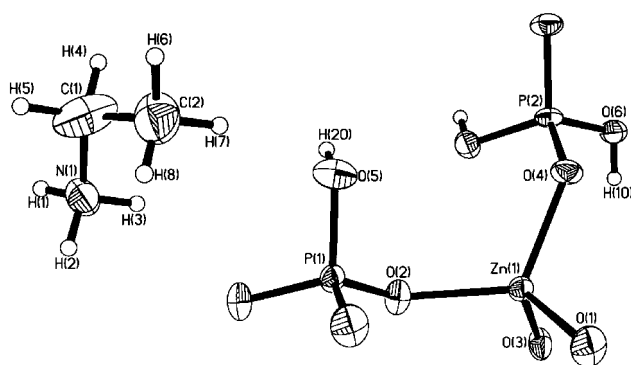**Fig. 1** ORTEP plot of $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$. Thermal ellipsoids are given at 50% probability.

CCDC reference number 1145/241. See http://www.rsc.org/suppdata/jm/b0/b004972g/ for crystallographic files in .cif format.

Results and discussion

The framework structure of $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$, **I**, consists of strictly alternating ZnO_4 and PO_4 tetrahedra linked through their vertices to form the three-dimensional architecture. The asymmetric unit contains 12 non-hydrogen atoms, of which 9 belong to the framework and 3 to the amine (Fig. 1). There is one Zn and two crystallographically independent P atoms present in the asymmetric unit. One of the P atoms, [P(2)], occupies a special position with a site occupancy of 0.5. Thus, the framework has the formula $[Zn_2(HPO_4)_3]^{2-}$ and charge neutrality is achieved by the

incorporation of two protonated amine molecules, $2[C_2H_5NH_3]^+$.

Selected bond lengths and angles of **I** are listed in Table 3. The crystallographically independent Zn atom is tetrahedrally coordinated with oxygen atoms [$(Zn-O)_{av.} = 1.944$ Å]. The Zn atom is connected via oxygens to the two distinct P atoms with an average Zn–O–P bond angle of 135.6°. Both the P atoms are coordinated with oxygens with average P–O distances of 1.538 Å. The O–Zn–O and O–P–O bond angles are close to the expected tetrahedral angle of 109.5°. Assuming the 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 two protonated ethylamine molecules, 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(5) and O(6) has been observed in the difference Fourier maps. Thus, P(1)–O(5) and P(2)–O(6) have distances of 1.586 and 1.561 Å corresponding to P–OH units. These assignments are consistent with bond valence sum calculations.[12] Infrared spectra also support the presence of P–OH groups.

The structure of $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$ is built up by the vertex linking ZnO_4 and PO_4 tetrahedra forming 4- and 8-membered rings. Projecting on the ac plane, each 4-membered ring appears to be surrounded by eight 8-membered rings as shown in Fig. 2. Similarly, each 8-membered ring is surrounded by six 8-membered and two 4-membered rings (Fig. 2). This unusual connectivity, to our knowledge, has not been observed before in open-framework zinc phosphate structures. The complex connectivity between the 4- and the 8-membered rings forms 12-membered elliptical channels of width 5.9×10.4 Å (shortest O–O contact distance not including the van der Waals radii) along the c axis as shown in Fig. 3. The protonated amine

Table 3 Selected bond distances and bond angle in $[C_2H_5NH_3]_2[Zn_2(HPO_4)_3]$

Moiety	Distance/Å	Moiety	Angle/°	Moiety	Angle/°
Zn(1)–O(1)	1.912(3)	O(1)–Zn(1)–O(2)	115.99(12)	O(3)^c–P(1)–O(5)	107.9(2)
Zn(1)–O(2)	1.926(3)	O(1)–Zn(1)–O(3)	110.43(12)	O(4)^d–P(2)–O(4)	111.4(2)
Zn(1)–O(3)	1.966(3)	O(2)–Zn(1)–O(3)	100.60(11)	O(4)^d–P(2)–O(6)	109.17(14)
Zn(1)–O(4)	1.972(3)	O(1)–Zn(1)–O(4)	104.53(12)	O(4)–P(2)–O(6)	110.54(13)
P(1)–O(1)^b	1.498(3)	O(2)–Zn(1)–O(4)	115.36(12)	O(4)^d–P(2)–O(6)^d	110.54(13)
P(1)–O(2)	1.521(3)	O(3)–Zn(1)–O(4)	109.95(12)	O(4)–P(2)–O(6)^d	109.17(14)
P(1)–O(3)^c	1.533(3)	O(1)^b–P(1)–O(2)	115.8(2)	O(6)–P(2)–O(6)^d	105.9(2)
P(1)–O(5)	1.586(3)	O(1)^b–P(1)–O(3)^c	109.0(2)	P(1)^b–O(1)–Zn(1)	163.5(2)
P(2)–O(4)^d	1.527(3)	O(2)–P(1)–O(3)^c	110.0(2)	P(1)–O(2)–Zn(1)	128.6(2)
P(2)–O(4)	1.528(3)	O(1)^b–P(1)–O(5)	105.6(2)	P(1)^e–O(3)–Zn(1)	126.5(2)
P(2)–O(6)	1.561(3)	O(2)–P(1)–O(5)	108.2(2)	P(2)–O(4)–Zn(1)	123.9(2)
P(2)–O(6)^d	1.561(3)				
Organic moiety:					
N(1)–C(1)	1.467(6)	C(2)–C(1)–N(1)	115.4(4)		
C(1)–C(2)	1.450(7)				

^{a}Symmetry transformations used to generate equivalent atoms: $^b -x+1/2, -y+1/2, -z+1$; $^c x, -y, z+1/2$; $^d -x, y, -z+1/2$; $^e x, -y, z-1/2$.
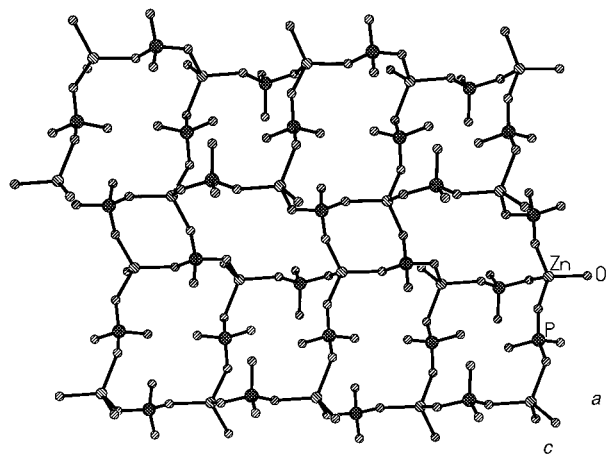
Fig. 2 Diagram showing the positions of the 4- and 8-membered rings projected on the *ac* plane. Note that eight 8-membered rings surround the 4-membered rings, and six 8-membered rings and two 4-membered rings surround the 8-membered rings.

molecules sit in the channel and interact with the framework *via* hydrogen bonds (Fig. 4). Similar connectivity forms an 8-membered channel (6.4×5.5 Å) along the *b* axis. The terminal –OH group of HPO$_4$ units protrudes into this channel.

As in many inorganic framework solids, [C$_2$H$_5$NH$_3$]$_2$-[Zn$_2$(HPO$_4$)$_3$] exhibits significant hydrogen bond interactions involving the ethylamine and the framework oxygens. In addition to these, owing to the presence of terminal –OH groups, intra-framework hydrogen bonds are also observed. The various hydrogen bond interactions observed are listed in Table 4.

The openness of a structure is defined in terms of the tetrahedral atom density[8] (framework density, FD) defined as the number of tetrahedral (T) atoms per 1000 Å^3. In [C$_2$H$_5$NH$_3$]$_2$[Zn$_2$(HPO$_4$)$_3$], the number of T atoms per 1000 Å^3 is 12.7. This is one of the lowest values found in phosphates based on tetrahedral connectivity and is comparable to that found in CoAPO-50[8] (FD = 12.5). Lower framework densities have been observed for interrupted tetrahedral gallofluorophosphate framework of cloverite[13] (FD = 11.1), the vanadium phosphate, Cs$_3$[V$_5$O$_9$(PO$_4$)$_2$]·xH$_2$O[14] (FD = 9.3), zinc phosphate, [N(CH$_3$)$_4$] [ZnH$_3$(PO$_4$)$_2$][15] (FD = 10.1), gallium phosphate, [NH$_3$(CH$_2$)$_4$NH$_3$]$_2$[Ga$_4$(HPO$_4$)$_2$(PO$_4$)$_3$(OH)$_3$]·yH$_2$O ($y \approx 5.4$)[16] (FD = 10.7) and iron phosphate, [NH$_3$(CH$_2$)$_3$-NH$_3$]$_2$[Fe$_4$(OH)$_3$ (HPO$_4$)$_2$(PO$_4$)$_3$]·xH$_2$O[17] (FD = 10.5).

Thermogravimetric analysis (TGA) was carried out in a flowing N$_2$ atmosphere (flow rate = 50 ml min^{-1}) in the temperature range from room temperature to 700 °C (heating
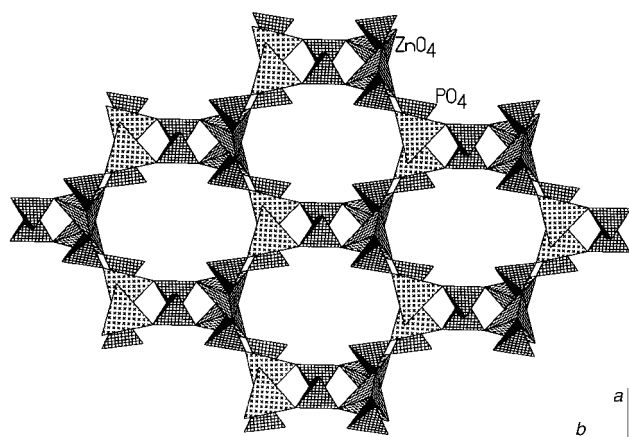

Fig. 3 Polyhedral view of [C$_2$H$_5$NH$_3$]$_2$[Zn$_2$(HPO$_4$)$_3$] along the *c* axis showing the 12-membered elliptical channel.
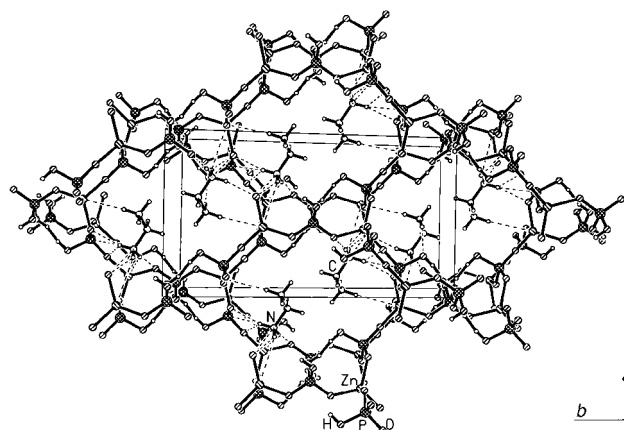
Fig. 4 The 12-membered channels with the amine molecules along the *c* axis. Dotted lines represent the various hydrogen bond interactions.

Table 4 Selected hydrogen bond interactions in [C$_2$H$_5$NH$_3$]$_2$-[Zn$_2$(HPO$_4$)$_3$]

Moiety	Distance/Å	Moiety	Angle/°
O(4)···H(1)	2.080(5)	O(4)···H(1)–N(1)	168.7(4)
O(3)···H(2)	2.155(5)	O(3)···H(2)–N(1)	166.1(4)
O(3)···H(3)	2.207(5)	O(3)···H(3)–N(1)	141.5(4)
O(5)···H(10)[a]	1.931(4)	O(5)···H(10)–O(6)	161.1(4)
O(5)···H(20)[a]	1.919(5)	O(6)···H(20)–O(5)	171.7(7)
O(5)···H(7)	2.418(6)	O(5)···H(7)–C(2)	161.2(5)

[a]Intra-framework.

rate = 10 °C min^{-1}). The results indicate a single broad mass loss in the region 220 °C to 500 °C. The total mass loss of 24.8% corresponds well with the loss of the amine and the –OH group (calcd. 23.3%). The powder X-ray diffraction pattern of the decomposed sample shows weak XRD lines that correspond to the condensed phase Zn$_2$P$_2$O$_7$ (JCPDS: 11-0026), indicating the collapse of the framework with the removal of the amine molecule. The decomposed product contains amorphous P$_2$O$_5$ as well.

In conclusion, an open-framework Zn phosphate, **I**, prepared under mild conditions in the presence of a monoamine, has been characterized. **I** represents only the fourth zinc phosphate that has been synthesized in the presence of the monoamine. Earlier use of monoamines has resulted in a one-dimensional linear-chain phosphate,[1b] [C$_2$H$_8$N][Zn(HPO$_4$)(H$_2$PO$_4$)]·0.5H$_2$O, and three-dimensional phosphates, [C$_2$H$_5$NH$_3$][Zn$_4$(H$_2$O)(PO$_4$)$_3$][9a] and [CH$_3$NH$_3$][Zn$_4$O(PO$_4$)$_3$].[9b] In the three-dimensional materials novel structural features such as OZn$_4$ tetrahedral clusters[9b] and Zn–O–Zn linkages[9a] are observed, in addition to the presence of channels bound by 8-T atoms (T = Zn, P). It is likely that the presence of higher Zn compared to P in these materials contributes to such features. The present compound adds to this family of interesting Zn phosphates in that it has large elliptical channels bound by 12-T atoms, besides a very low framework density.

Acknowledgements

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