

Three-dimensional open-framework zinc phosphates with the structure-directing organic amines acting as ligands†

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Received (in Montpellier, France) 18th November 1998, Accepted 8th January 1999

Two new three-dimensional zinc phosphates **I**, $[\text{NH}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{Zn}_5(\text{PO}_4)_4]^{2-}$, and **II**, $[\text{CN}_5\text{H}_6]^+[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$, where the structure-directing organic amine acts as a ligand, have been synthesized hydrothermally. Crystal data for **I**: $a = 27.071(2)$, $b = 5.215(1)$, $c = 17.920(1)$ Å, $\beta = 130.3(1)^\circ$; $U = 1930.9(3)$ Å³; space group = Cc (no. 9); $Z = 4$; $M = 811.01$; $D_{\text{calc}} = 2.789$ g cm⁻³; MoK α and for **II**: $a = 8.089(1)$, $b = 12.771(1)$, $c = 10.067(1)$ Å, $\beta = 105.3(1)^\circ$; $U = 1000.3(2)$ Å³; space group = $P2_1/n$ (no. 14); $Z = 4$; $M = 409.8$; $D_{\text{calc}} = 2.713$ g cm⁻³; MoK α . Compound **I** is novel in the sense that it is dominated by the presence of a large number of three-coordinated oxygen atoms (25%), leading to the formation of infinite Zn—O—Zn chains. The presence of a distorted bipyramidal ZnO₃N₂ unit as well as a 2-membered ring in **II** is noteworthy. These structures are formed by the networking of ZnO₄, ZnO₃N, PO₄ and ZnO₃N₂ moieties, leading to the formation of three-dimensional structures possessing channels with **I** forming a 10-membered one-dimensional channel system and **II** forming two 8-membered channels.

A variety of open-framework metal phosphates of different structures have been synthesized in the last few years by employing hydrothermal or solvothermal conditions in the presence of structure-directing organic amines. Amongst these, the zinc phosphates possessing 3-, 4-, 6-, 8-, 12-membered and other size rings and infinite —Zn—O—Zn— chains constitute a relative large family.^{1–5} Surprisingly, 10-membered rings have not so far been reported in the zinc phosphates, although they are commonly found in other open-framework systems. Our continued research for metal phosphate open-framework structures with novel features has enabled us to isolate two new zinc phosphates having three-dimensional connectivity and possessing channels. The zinc phosphate **I** forms with a 10-membered one-dimensional channel, akin to that in aluminosilicates.⁶ More importantly, the structure-directing amine, in the middle of the channel, also satisfies the Zn coordination by acting as a ligand. Such a bifunctional role of the amine is also seen by us in the second zinc phosphate, **II**, where the amine directs the formation of two 8-membered channels (8- or 10-member refers to the number of tetrahedral atoms [Zn, P] forming the rings). In this paper, we describe the synthesis, structural and other characterizations of the two open-framework zinc phosphates where the structure-directing amines act as ligands. In the context of such organic-inorganic hybrid open-framework structures, the recent report of Halasyamani *et al.*⁷ of a zinc fluorophosphate where the nitrogen atoms of the 4,4'-bipyridyl bound to Zn form a pillared-layer network is noteworthy.

Experimental

Synthesis and initial characterization

Compound **I** was synthesized by the following procedure: 0.407 g of ZnO was dispersed in 9 ml of water, and 0.365 g of

HCl and 0.98 g of 85 wt% of H₃PO₄ added to the mixture, which was then stirred for 10 min. To this mixture 0.516 g of diethylenetriamine (DETA) was added and the mixture was homogenized, transferred into a Parr pressure bomb and heated initially at 150 °C for 5 days. At the end of the initial heating, half the mixture was removed from the container and 2 ml of H₂O were added to the remaining mixture, which was heated for a further period of 4 days at 150 °C. This resulted in the formation of needle- and plate-shaped crystals. The final composition of the mixture was ZnO : 2 H₃PO₄ : 2 HCl : DETA : 100 H₂O. The plate-shaped crystals were separated easily from the mixture as they are the predominant product of the synthesis and all further characterizations and studies were carried out on them.

Compound **II** was synthesized as follows: 0.407 g of ZnO was dispersed in 5 ml of water, and 1.145 g of 85 wt% of H₃PO₄ added to the mixture under continuous stirring. 1,3-Diaminoguanidine monohydrochloride (DAG, 2.98 g) was added to the above and stirring continued until the mixture became homogeneous. The composition of the mixture was ZnO : 2.3 H₃PO₄ : 4.8 DAG : 55 H₂O. The mixture was transferred into a teflon-lined stainless steel autoclave (Parr, USA) and heated at 110 °C for 4 days. The product contained large quantities of rod-like single crystals.

The initial characterizations of the samples were carried out by powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The XRD pattern of the crushed single crystals of **I** (plates) and **II** indicate the products to be new materials; the individual patterns are entirely consistent with the structures determined by single crystal X-ray diffraction (simulated pattern from the atomic coordinates derived from the single crystal study).

Single crystal structure determination

A suitable single crystal of each compound (plate for **I** and rod for **II**) was carefully selected under a polarizing microscope and glued to a thin glass fiber with 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

† Supplementary material available: Atomic coordinates and isotropic displacement parameters for **I** and **II**. For direct electronic access see <http://www.rsc.org/suppdata/nj/1999/303/>, otherwise available from BLDSC (No. SUP 57483, 3 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/njc>).

Table 1 Crystal data and structure refinement parameters for **I**, $[\text{NH}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{Zn}_5(\text{PO}_4)_4]^{2-}$ and **II**, $[\text{CN}_5\text{H}_6]^{+}[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^{-}$

| | I | II |
|--|---|---|
| Empirical formula | $\text{Zn}_5\text{P}_4\text{O}_{16}\text{C}_4\text{N}_3\text{H}_{14}$ | $\text{Zn}_2\text{P}_2\text{O}_8\text{C}_1\text{N}_5\text{H}_7$ |
| Crystal system | Monoclinic | Monoclinic |
| Space group | <i>Cc</i> (no. 9) | $P2_1/n$ (no. 14) |
| Crystal size/mm | $0.04 \times 0.1 \times 0.16$ | $0.06 \times 0.08 \times 0.14$ |
| <i>a</i> /Å | 27.071(2) | 8.089(1) |
| <i>b</i> /Å | 5.215(1) | 12.771(1) |
| <i>c</i> /Å | 17.920(1) | 10.067(1) |
| α /° | 90.0 | 90.0 |
| β /° | 130.3(1) | 105.3(1) |
| γ /° | 90.0 | 90.0 |
| Volume/Å ³ | 1930.8(3) | 1003.2(2) |
| <i>Z</i> | 4 | 4 |
| Formula mass | 811.01 | 409.80 |
| $\rho_{\text{calc}}/\text{g cm}^{-3}$ | 2.789 | 2.713 |
| λ (MoK α)/Å | 0.71073 | 0.71073 |
| μ/mm^{-1} | 6.543 | 5.151 |
| θ range/° | 1.97–23.28 | 2.63–23.28 |
| Total data collected | 3775 | 4109 |
| Index ranges | $-29 \leq h \leq 29, -5 \leq k \leq 5, -19 \leq l \leq 17$ | $-8 \leq h \leq 5, -14 \leq k \leq 13, -11 \leq l \leq 10$ |
| Unique data | 2089 | 1436 |
| Observed data [$\sigma > 2\sigma(I)$] | 1994 | 1193 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| <i>R</i> indices [$I > 2\sigma(I)$] | $R_1 = 0.0389; wR_2 = 0.0901$ | $R_1 = 0.0422; wR_2 = 0.993$ |
| <i>R</i> indices (all data) | $R_1 = 0.0433; wR_2 = 0.1168$ | $R_1 = 0.0554; wR_2 = 0.1095$ |
| Goodness of fit (<i>S</i>) | 1.14 | 1.08 |
| No. of variables | 291 | 163 |
| Largest difference map peak and hole/e Å ⁻³ | 1.159 and -1.002 | 0.769 and -0.813 |

X-ray source (MoK α radiation, $\lambda = 0.71073$ Å) operating at 40 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). The final unit-cell constants were determined by a least squares fit of 3568 reflections for **I** and 2148 reflections for **II** in the range $3^\circ < 2\theta < 46.5^\circ$. Pertinent experimental details for the structure determination are presented in Table 1.

The structure was solved by direct methods using SHELXS-86⁸ and difference Fourier syntheses. All the hydrogen positions, in **I** and **II**, were initially located in the difference Fourier maps for both the compounds. For the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. No absorption correction was applied for either **I** or **II**. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXLTL-PLUS⁹ suite of programs. Details of the final refinements are given in Table 1. The selected bond distances and bond angles are given in Table 2 for **I** and Table 3 for **II**.

CCDC reference number 440/093. See <http://www.rsc.org/suppdata/nj/1999/303/> for crystallographic files in .cif format.

Results

Structure of **I**, $[\text{NH}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{Zn}_5(\text{PO}_4)_4]^{2-}$

The asymmetric unit is represented on Fig. 1(a). The structure of **I** consists of a network of ZnO_4 , PO_4 and ZnO_3N moieties, connected by Zn—O—P bonds. The framework has the formula $[\text{Zn}_5(\text{PO}_4)_4]^{2-}$ and charge neutrality is achieved by the incorporation of the doubly protonated amine molecule. The Zn atoms are all tetrahedrally coordinated and connected to P atoms *via* oxygen links and to each other *via* three-coordinated oxygen atoms (bonding two Zn atoms and one P

atom). Four of the 16 oxygen atoms in the asymmetric unit are three-coordinated. This is an unusually large percentage (25%) of such units in an open-framework material.

The Zn atoms in **I** make three Zn—O—P bonds with four P neighbours, with a spread of Zn—O—P angles (ave. 127.3°) as given in Table 2. The fourth connections needed for a tetrahedral linkage in the case of Zn(1) to Zn(4) are obtained through Zn—O—Zn linkages (ave. 115.7°), and *via* the terminal N atom of the amine in the case of Zn(5). Thus, there are infinite one-dimensional Zn—O—Zn chains in this structure. The average values of Zn—O bond lengths $\{d_{\text{av}}[\text{Zn}(1)\text{—O}] = 1.947$ Å; $d_{\text{av}}[\text{Zn}(2)\text{—O}] = 1.956$ Å; $d_{\text{av}}[\text{Zn}(3)\text{—O}] = 1.957$ Å; $d_{\text{av}}[\text{Zn}(4)\text{—O}] = 1.958$ Å; $d_{\text{av}}[\text{Zn}(5)\text{—O}] = 1.968$ Å} and O—Zn—O bond angles [O—Zn(1)—O = 109.1° ; O—Zn(2)—O = 109.1° ; O—Zn(3)—O = 109.4° ; O—Zn(4)—O = 108.1° ; O—Zn(5)—O = 109.4°] indicate that the environment around the Zn atoms is tetrahedral and the values are in good agreement with those reported earlier.^{1–5,7} The four distinct phosphorus atoms are linked to Zn atoms *via* the oxygens. The P—O bond lengths are in the range 1.517–1.582 Å and the O—P—O bond angles are in the range 104.8–113.9°. The longest P—O distances, however, involve the three-coordinated oxygen atom. These values agree well with those reported in the literature.

The polyhedral connectivity between the ZnO_4 and PO_4 units leads to the formation of infinite Zn—O—Zn chains and 3-membered rings *via* the three-coordinated oxygen atoms. The structure also possesses 4-membered $\text{Zn}_2\text{P}_2\text{O}_4$ units. It should be noted that 4-membered rings appear to be the basic building blocks of many of the open-framework structures such as aluminophosphates and tin phosphates.¹⁰ The 3- and 4-membered rings in **I** share their edges, forming a one-dimensional chain (Fig. 2). The individual ribbons (columns of one-dimensional chains) are joined together by ZnO_3N tetrahedra, giving rise to a 10-membered channel system along the *a* axis. Such a linkage between one-dimensional chains by the ZnO_3N moiety requires the amine molecule to be in the middle of the 10-membered channel (10.36×4.62 Å; oxygen-to-oxygen contact distance excluding the van der Waals radii).

Table 2 Selected bond lengths (Å) and angles (°) for **I**, $[\text{NH}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{Zn}_5(\text{PO}_4)_4]^{2-}$

| | | | |
|--------------------------------|-----------|--|-----------|
| Zn(1)—O(1) | 1.950(8) | Zn(5)—O(15) | 1.922(9) |
| Zn(1)—O(2) | 1.919(9) | Zn(5)—N(3) | 2.022(10) |
| Zn(1)—O(3) | 1.997(8) | P(1)—O(6) | 1.518(9) |
| Zn(1)—O(4) | 1.922(9) | P(1)—O(12) | 1.522(9) |
| Zn(2)—O(1) ¹ | 2.021(8) | P(1)—O(14) ⁴ | 1.536(9) |
| Zn(2)—O(5) | 1.938(9) | P(1)—O(9) | 1.561(9) |
| Zn(2)—O(6) | 1.931(9) | P(2)—O(11) | 1.510(10) |
| Zn(2)—O(7) | 1.934(10) | P(2)—O(5) | 1.518(9) |
| Zn(3)—O(3) | 1.953(8) | P(2)—O(16) | 1.535(10) |
| Zn(3)—O(8) | 1.956(8) | P(2)—O(1) ⁵ | 1.580(9) |
| Zn(3)—O(9) | 1.986(8) | P(3)—O(15) ⁶ | 1.525(10) |
| Zn(3)—O(10) ² | 1.933(8) | P(3)—O(7) ⁷ | 1.526(10) |
| Zn(4)—O(8) | 2.020(9) | P(3)—O(2) | 1.527(8) |
| Zn(4)—O(9) ³ | 1.987(8) | P(3)—O(3) ³ | 1.582(9) |
| Zn(4)—O(11) | 1.913(9) | P(4)—O(13) | 1.517(10) |
| Zn(4)—O(12) | 1.911(9) | P(4)—O(4) | 1.521(10) |
| Zn(5)—O(13) | 1.977(9) | P(4)—O(10) | 1.554(8) |
| Zn(5)—O(14) | 1.952(9) | P(4)—O(8) | 1.580(9) |
| O(2)—Zn(1)—O(4) | 111.3(4) | O(15)—Zn(5)—N(3) | 105.5(4) |
| O(2)—Zn(1)—O(1) | 119.7(3) | O(14)—Zn(5)—N(3) | 119.8(4) |
| O(4)—Zn(1)—O(1) | 111.5(4) | O(13)—Zn(5)—N(3) | 112.1(4) |
| O(2)—Zn(1)—O(3) | 106.6(4) | O(6)—P(1)—O(12) | 113.9(5) |
| O(4)—Zn(1)—O(3) | 100.1(4) | O(6)—P(1)—O(14) ⁴ | 108.1(5) |
| O(1)—Zn(1)—O(3) | 105.4(3) | O(12)—P(1)—O(14) ⁴ | 110.2(5) |
| O(6)—Zn(2)—O(7) | 101.4(6) | O(1)—P(1)—O(9) | 108.5(5) |
| O(6)—Zn(2)—O(5) | 120.5(4) | O(12)—P(1)—O(9) | 108.6(5) |
| O(7)—Zn(2)—O(5) | 118.0(4) | O(14)—P(1)—O(9) | 107.5(5) |
| O(6)—Zn(2)—O(1) ¹ | 114.9(4) | O(11)—P(2)—O(5) | 112.2(5) |
| O(7)—Zn(2)—O(1) ¹ | 95.9(3) | O(11)—P(2)—O(16) | 108.1(6) |
| O(5)—Zn(2)—O(1) ¹ | 104.3(4) | O(5)—P(2)—O(16) | 109.9(5) |
| O(10) ² —Zn(3)—O(3) | 121.0(4) | O(11)—P(2)—O(1) ⁵ | 104.8(5) |
| O(10) ² —Zn(3)—O(8) | 106.1(3) | O(5)—P(2)—O(1) ⁵ | 109.6(5) |
| O(3)—Zn(3)—O(8) | 102.5(4) | O(16)—P(2)—O(1) ⁵ | 112.2(5) |
| O(10) ² —Zn(3)—O(9) | 97.2(3) | O(15) ⁶ —P(3)—O(7) ⁷ | 109.3(6) |
| O(3)—Zn(3)—O(9) | 118.2(4) | O(15) ⁶ —P(3)—O(2) | 111.1(5) |
| O(8)—Zn(3)—O(9) | 111.5(4) | O(7) ⁷ —P(3)—O(2) | 112.9(5) |
| O(12)—Zn(4)—O(11) | 124.1(4) | O(15) ⁶ —P(3)—O(3) ³ | 108.4(5) |
| O(12)—Zn(4)—O(9) ³ | 111.4(4) | O(7) ⁷ —P(3)—O(3) ³ | 106.9(5) |
| O(11)—Zn(4)—O(9) ³ | 107.2(4) | O(2)—P(3)—O(3) ³ | 108.0(5) |
| O(12)—Zn(4)—O(8) | 102.6(4) | O(13)—P(4)—O(4) | 112.2(6) |
| O(11)—Zn(4)—O(8) | 104.9(4) | O(13)—P(4)—O(10) | 107.3(5) |
| O(9) ³ —Zn(4)—O(8) | 104.8(3) | O(4)—P(4)—O(10) | 111.4(5) |
| O(15)—Zn(5)—O(14) | 114.0(4) | O(13)—P(4)—O(8) | 109.7(5) |
| O(15)—Zn(5)—O(13) | 113.0(4) | O(4)—P(4)—O(8) | 108.9(5) |
| O(14)—Zn(5)—O(13) | 92.2(4) | O(10)—P(4)—O(8) | 107.1(5) |

Organic Moiety

| | | | |
|-----------|---------|-----------------|-----------|
| N(2)—C(3) | 1.46(2) | C(3)—N(2)—C(2) | 110.3(12) |
| N(2)—C(2) | 1.47(2) | C(4)—N(3)—Zn(5) | 119.8(8) |
| N(1)—C(1) | 1.47(2) | N(2)—C(2)—C(1) | 111.2(12) |
| N(3)—C(4) | 1.52(2) | N(1)—C(1)—C(2) | 112.2(11) |
| C(2)—C(1) | 1.51(2) | N(2)—C(3)—C(4) | 111.2(13) |
| C(3)—C(4) | 1.48(2) | C(3)—C(4)—N(3) | 111.5(12) |

Symmetry transformations used to generate equivalent atoms:

¹ $x - 1/2, -y - 7/2, z - 1/2$. ² $x, y - 1, z$. ³ $x, y + 1, z$. ⁴ $x, -y - 3, z - 1/2$. ⁵ $x - 1/2, -y - 5/2, z - 1/2$. ⁶ $x, -y - 2, z - 1/2$. ⁷ $x + 1/2, -y - 5/2, z + 1/2$. ⁸ $x + 1/2, -y - 7/2, z + 1/2$. ⁹ $x, -y - 3, z + 1/2$. ¹⁰ $x, -y - 2, z + 1/2$.

Structure of II, $[\text{CN}_5\text{H}_6]^+[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$

Fig. 1(b) represents the asymmetric unit. The structure is built up from the vertex-linkage of PO_4 , ZnO_4 and ZnO_3N_2 moieties. The framework is anionic and has the formula $[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$. Charge neutrality is achieved by the incorporation of the protonated amine molecule, with one protonated 1,3-diaminoguanidine, $[\text{CN}_5\text{H}_6]^+$, per framework formula unit. Of the eight oxygens in the asymmetric unit, one is three-coordinated.

There are two crystallographically distinct Zn as well as P atoms. Of the two Zn atoms in the asymmetric unit, Zn(1) is bound with two nitrogens and three oxygens, forming a dis-

Table 3 Selected bond lengths (Å) and angles (°) for **II**, $[\text{CN}_5\text{H}_6]^+[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$

| | | | |
|------------------------------|----------|------------------------------|----------|
| Zn(1)—O(1) | 1.954(5) | P(1)—O(1) | 1.514(5) |
| Zn(1)—O(2) | 2.004(4) | P(1)—O(5) ² | 1.521(5) |
| Zn(1)—N(3) | 2.110(6) | P(1)—O(4) | 1.543(5) |
| Zn(1)—N(5) | 2.115(6) | P(1)—O(7) | 1.573(5) |
| Zn(1)—O(2) ¹ | 2.126(4) | P(2)—O(3) ³ | 1.526(5) |
| Zn(2)—O(3) | 1.929(5) | P(2)—O(8) | 1.526(5) |
| Zn(2)—O(4) | 1.955(5) | P(2)—O(2) | 1.539(5) |
| Zn(2)—O(5) | 1.957(5) | P(2)—O(6) ⁴ | 1.553(5) |
| Zn(2)—O(6) | 1.968(5) | | |
| O(1)—Zn(1)—O(2) | 111.2(2) | O(4)—Zn(2)—O(6) | 101.6(2) |
| O(1)—Zn(1)—N(3) | 101.0(2) | O(5)—Zn(2)—O(6) | 94.6(2) |
| O(2)—Zn(1)—N(3) | 100.5(2) | O(1)—P(1)—O(5) ² | 112.1(3) |
| O(1)—Zn(1)—N(5) | 127.4(2) | O(1)—P(1)—O(4) | 109.3(3) |
| O(2)—Zn(1)—N(5) | 121.1(2) | O(5) ² —P(1)—O(4) | 110.9(3) |
| N(3)—Zn(1)—N(5) | 75.9(2) | O(1)—P(1)—O(7) | 107.1(3) |
| O(1)—Zn(1)—O(2) ¹ | 89.7(2) | O(5) ² —P(1)—O(7) | 111.6(3) |
| O(2)—Zn(1)—O(2) ¹ | 81.2(2) | O(4)—P(1)—O(7) | 105.7(3) |
| N(3)—Zn(1)—O(2) ¹ | 167.6(2) | O(3) ³ —P(2)—O(8) | 110.9(3) |
| N(5)—Zn(1)—O(2) ¹ | 92.7(2) | O(3) ³ —P(2)—O(2) | 108.0(3) |
| O(3)—Zn(2)—O(4) | 111.7(2) | O(8)—P(2)—O(2) | 109.9(3) |
| O(3)—Zn(2)—O(5) | 113.2(2) | O(8)—P(2)—O(6) | 109.5(3) |
| O(4)—Zn(2)—O(5) | 107.5(2) | O(8)—P(2)—O(6) ⁴ | 109.7(3) |
| O(3)—Zn(2)—O(6) | 125.9(2) | O(2)—P(2)—O(6) ⁴ | 108.7(3) |

Organic Moiety

| | | | |
|-----------|----------|-----------------|----------|
| N(1)—C(1) | 1.330(9) | C(1)—N(2)—N(5) | 118.6(6) |
| N(2)—C(1) | 1.359(9) | C(1)—N(3)—N(4) | 115.1(6) |
| N(2)—N(5) | 1.401(8) | C(1)—N(3)—Zn(1) | 117.4(5) |
| N(3)—C(1) | 1.318(9) | N(4)—N(3)—Zn(1) | 127.3(4) |
| N(3)—N(4) | 1.432(8) | N(2)—N(5)—Zn(1) | 112.4(4) |
| | | N(3)—C(1)—N(1) | 126.7(7) |
| | | N(3)—C(1)—N(2) | 105.5(6) |
| | | N(1)—C(1)—N(2) | 117.7(6) |

Symmetry transformations used to generate equivalent atoms:

¹ $-x, -y + 1, -z$. ² $-x, -y + 2, -z$. ³ $-x - 1/2, y - 1/2, -z - 1/2$. ⁴ $x + 1/2, -y + 3/2, z - 1/2$. ⁵ $-x - 1/2, y + 1/2, -z - 1/2$. ⁶ $x - 1/2, -y + 3/2, z + 1/2$.

torted trigonal bipyramidal ZnO_3N_2 unit, while Zn(2) is tetrahedrally coordinated to four oxygens. The observation of the distorted trigonal bipyramidal environment for the Zn atom is unusual and only a few examples are known for such coordination of the Zn atom, for example in $\text{Zn}(\text{acac})_2$.¹¹ The average Zn—O bond distances $\{d_{\text{av}}[\text{Zn}(1)\text{—O/N} = 2.062 \text{ Å}]; d_{\text{av}}[\text{Zn}(2)\text{—O} = 1.952 \text{ Å}]\}$ and O—Zn—O bond angles $[\text{O—Zn}(1)\text{—O/N} = 106.8^\circ; \text{O—Zn}(2)\text{—O} = 109.0^\circ]$ are consistent with the coordination environment of the Zn atoms. Both P(1) and P(2) are connected by three oxygens to Zn atoms and the last neighbour is a terminal oxygen [P(1)—O(7) and P(2)—O(8)]. The average bond distances involving P atoms [P(1)—O = 1.538 Å; P(2)—O = 1.536 Å] and bond angles $[\text{O—P—O} = 109.5^\circ]$ suggest a regular P tetrahedron, unlike Zn. Bond valence sum calculations¹² indicate that the oxygen O(7) is protonated and O(8) has a double-bond character. As usual, the longest P—O [P(1)—O(7) = 1.573 Å] distance is the P—O···H one.

The polyhedral connectivity between the ZnO_4 , ZnO_3N_2 and PO_4 units leads to the formation of the observed three-dimensional structure. Linking of two ZnO_3N_2 units results in the formation of a 2-membered Zn_2O_2 ring [Fig. 1(b)], the N atoms being part of the amine molecule. The 2-membered ring is connected to P atoms *via* the Zn—O—P links. The formation of a 2-membered ring in an open-framework solid is not common and to our knowledge, there is only one such report in the literature.¹³ The ZnO_4 and PO_4 units form two interconnected 4-membered rings [Fig. 3(b)], which are three-dimensionally connected through the ZnO_3N_2 units involving the 2-membered Zn—O—Zn linkage. The linkages between these building blocks lead to the formation of two 8-

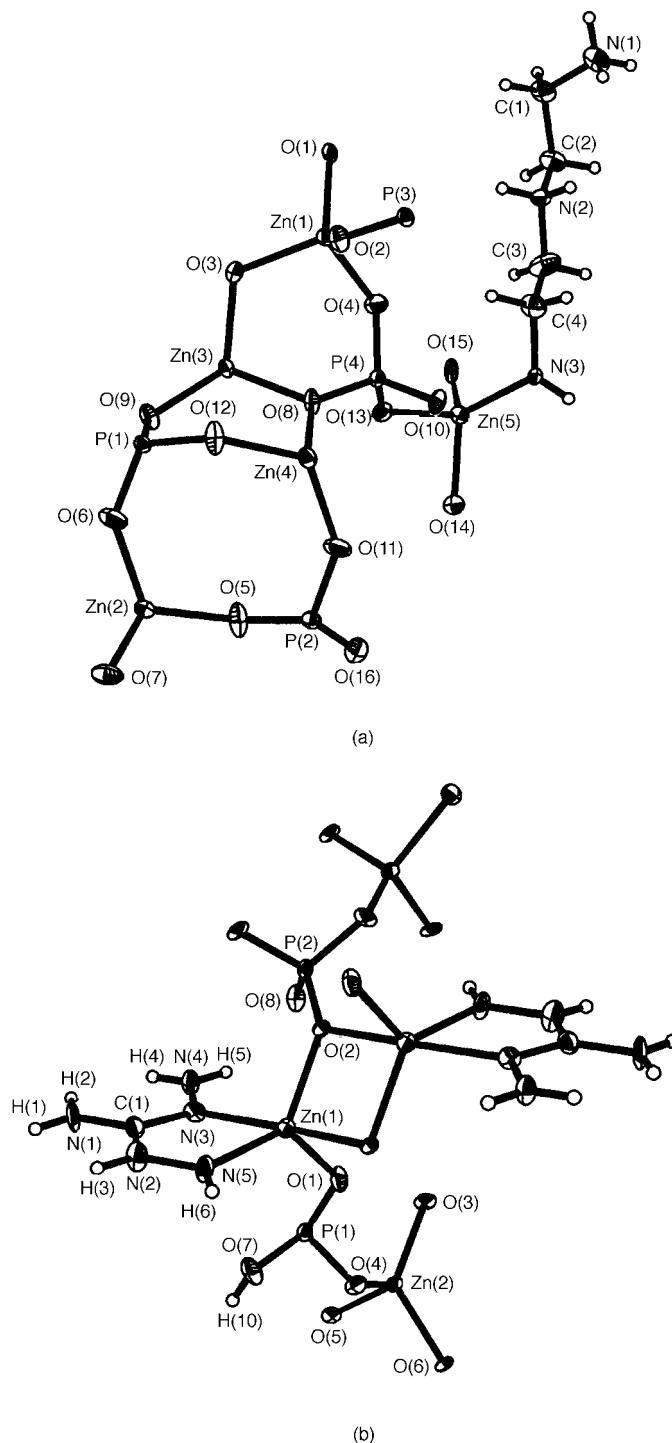


Fig. 1 (a) Asymmetric unit of **I**, $[\text{NH}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{Zn}_5(\text{PO}_4)_4]^{2-}$. (b) Asymmetric unit of **II**, $[\text{CN}_5\text{H}_6]^+[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$. (Thermal ellipsoids are shown at 50% probability).

membered channels running along the $[100]$ ($7.67 \times 5.64 \text{ \AA}$) and $[101]$ ($7.30 \times 5.81 \text{ \AA}$) directions (Fig. 3). The amine molecule protrudes from the Zn centres into the channels along the $[101]$ direction.

Discussion

Two zinc phosphates, $[\text{NH}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{Zn}_5(\text{PO}_4)_4]^{2-}$ **I**, and $[\text{CN}_5\text{H}_6]^+[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$ **II**, have been synthesized by hydrothermal methods in the presence of structure-directing agents. As with kinetically controlled processes, there is no relation between the starting stoichiometry and the final composition of the product. Compound **I** has been prepared in the presence of HCl and it appears that the role of Cl^- is similar to that of F^- ions in

some of the phosphate-based open-framework materials reported in the literature.^{14,15} We are presently evaluating the role of Cl^- , $(\text{SO}_4)^{2-}$ and other similar ions in determining the structure of the products. The structures of **I** and **II** are both built up from the regular ZnO_4 , PO_4 , the unusual ZnO_3N tetrahedra and the distorted trigonal bipyramidal ZnO_3N_2 , leading to the three-dimensional connectivity. We may recall that most of the known zinc phosphates contain ZnO_4 and PO_4 tetrahedra only, although distinct differences exist between the structures.

The two structures described here are unusual in that they form $\text{Zn}-\text{O}-\text{Zn}$ linkages although the $\text{Zn}:\text{P}$ ratio is 1 in **II** and 1.25 in **I**. The presence of more Zn than P in **I** may be responsible for the infinite one-dimensional $-\text{Zn}-\text{O}-\text{Zn}-$ linkages. In **II**, these linkages may be attri-

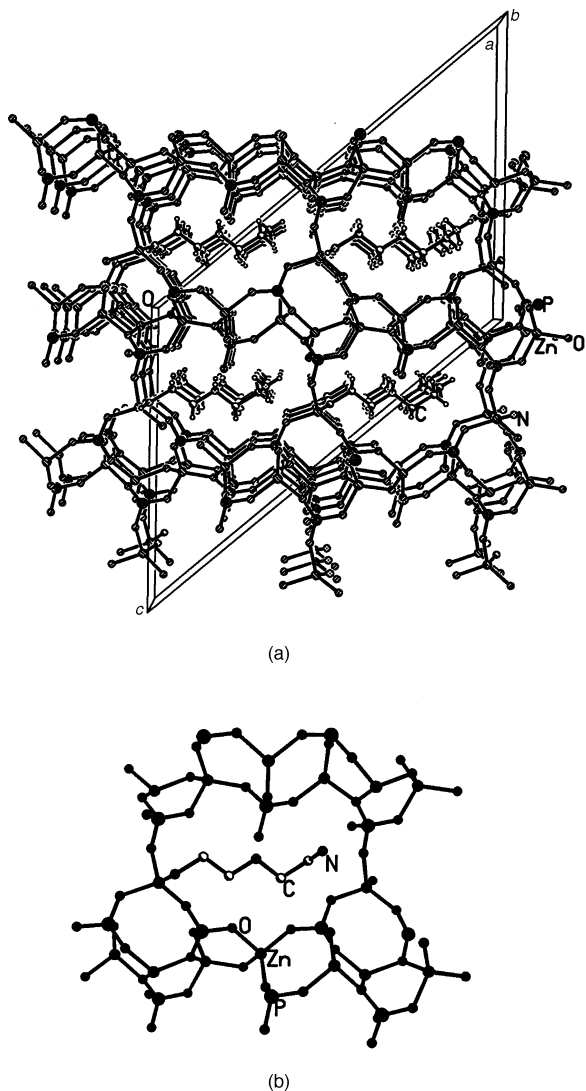


Fig. 2 (a) Structure of **I**, $[\text{NH}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^{2+} \cdot [\text{Zn}_5(\text{PO}_4)_4]^{2-}$, showing the one-dimensional 10-membered channel system along the *a* axis. (b) Figure showing the connectivity between the chain units and ZnO_3N unit leading to the formation of the 10-membered ring.

butted to the presence of the rare trigonal bipyramidal coordination of the Zn atom. No P—O—P type linkages are seen in either of the materials. The —Zn—O—Zn— linkages are always accompanied by three-coordinated bridging oxygen atoms and the third coordination is to a phosphorus. The trigonal coordination of the oxygen in the —Zn—O—Zn— bridge is apparently an electrostatic valence requirement of bridging oxygen atoms. There are other examples where such trigonal coordination has been observed.^{3,16,17} The trigonal and tetrahedral coordinations of oxygen bridges are generally common when divalent tetrahedral atoms are involved and we would therefore expect such a feature in the zinc phosphates to yield novel open-framework topologies that have no analogues in aluminosilicates and aluminophosphates.

Another interesting aspect of the Zn phosphates examined here relates to the protonation of the framework oxygen atoms. In **II**, only one oxygen atom is protonated in spite of the fact that the Zn:P ratio is 1, and no oxygens are protonated in **I**. This may be due to the presence of Zn—N linkages present in these materials. In the zinc phosphates reported in the literature, some of the oxygen atoms are invariably protonated to compensate the charge imbalance. It is also hypothesized that the oxygens are protonated due to the difficulty in

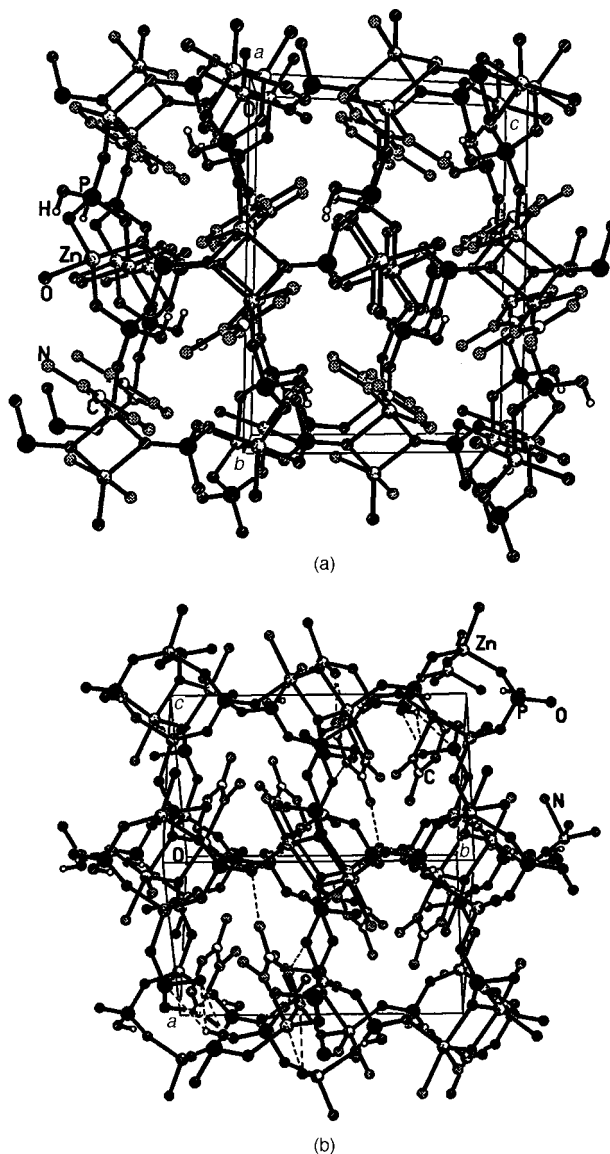


Fig. 3 Structure of **II**, $[\text{CN}_5\text{H}_6]^+ [\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$, showing the 8-membered channels (a) along [100] and (b) [101] directions. Note that the amine molecules protrude into the channels along the [101] direction. Hydrogens of the amine molecule are not shown for clarity.

packing enough bulky organic cations into the extra framework pores to achieve charge balance.¹⁸ In the case of the aluminosilicate materials, the Si:Al ratio is variable (for the same framework topology) and affects the charge-balance requirement; the zinc phosphates appear to have a precisely defined Zn:P ratio for a particular topology. In the present study, the nitrogen atoms of the amine molecule covalently binding with Zn centres possibly create a situation where the bulky organic cation can be accommodated within the pores/channels and achieve charge balance. This type of observation is unique as in many of the channel structures the structure-directing organic amine molecules sit in channels and cavities and interact with the framework through hydrogen bonds only.

The 'openness' of a structure is defined in terms of the tetrahedral atom density⁶ (framework density, FD) defined as the number of tetrahedral (T) atoms per 1000 Å³. In the present materials, the number of T atoms per 1000 Å³ (here Zn and P) is 18.6 for **I** and 16.0 for **II**. These values are in the middle of the range of FD values observed in aluminosilicate zeolites,⁶ where the presence of channels is common. Furthermore, the position of the amine is such that the linear chain DETA (compound **I**) forms a well-defined 10-membered

Table 4 Important hydrogen bond interactions in **I** and **II**

| I | | | |
|--------------|----------|-------------------|----------|
| O(11)···H(1) | 2.235(1) | O(11)···H(1)—N(1) | 136.5(1) |
| O(16)···H(1) | 2.185(1) | O(16)···H(1)—N(1) | 154.9(1) |
| O(14)···H(2) | 1.925(1) | O(14)···H(2)—N(1) | 156.0(1) |
| O(10)···H(3) | 1.968(1) | O(10)···H(3)—N(1) | 175.8(1) |
| O(5)···H(8) | 2.362(1) | O(5)···H(8)—N(2) | 140.7(1) |
| O(16)···H(9) | 1.930(1) | O(16)···H(9)—N(2) | 172.9(1) |
| O(4)···H(12) | 2.467(1) | O(4)···H(12)—C(4) | 161.9(1) |
| II | | | |
| O(1)···H(1) | 2.176(1) | O(1)···H(1)—N(1) | 137.7(1) |
| O(7)···H(2) | 2.447(1) | O(7)···H(2)—N(1) | 133.5(1) |
| O(6)···H(3) | 1.991(1) | O(6)···H(3)—N(2) | 170.6(1) |

channel system. In **II**, however, the distorted trigonal pyramidal ZnO_3N_2 unit links with another ZnO_3N_2 unit to form two $-\text{Zn}-\text{O}-\text{Zn}-$ linkages (2-membered rings) that connect the double 4-membered rings, creating distortion of the 8-membered channels.

Thermogravimetric analysis (TGA) of **I** and **II** was carried out in air from room temperature to 600 °C. The results show only one mass loss for **I** in the region 350–440 °C. The mass loss of 16.5% corresponds to the loss of the amine molecule from the structure (calcd 13%) and some adsorbed water. In the case of **II**, the mass loss of 22.6% occurring in the temperature range 350–450 °C corresponds to the loss of the amine molecule (calcd 21.5%). In both the cases the loss of the amine molecule resulted in the collapse of the framework structure, leading to the formation of largely amorphous weakly diffracting materials (XRD) that corresponds to dense zinc phosphate phases consistent with their structures.

In addition to the coordination of the amine with the metal atoms in the framework, both the structures show dominant hydrogen bond interactions between the amine and the framework (Table 4). In **I**, since the amine has a linear chain, hydrogen bonding is prominent. The strongest hydrogen bonding in **I** is between the hydrogens attached to the nitrogens N(1) and N(2) and the framework oxygens. The following hydrogen bond parameters reveal this: $\text{O}(10)\cdots\text{H}(3) = 1.986 \text{ \AA}$ and $\text{O}(10)\cdots\text{H}(3)-\text{N}(1) = 175.8^\circ$; $\text{O}(16)\cdots\text{H}(9) = 1.930 \text{ \AA}$ and $\text{O}(16)\cdots\text{H}(9)-\text{N}(2) = 172.9^\circ$. Here, O(16) is one of the terminal double-bonded oxygen atoms attached to P. There is only one strong hydrogen bond in **II** as given by $\text{O}(6)\cdots\text{H}(3) = 1.991 \text{ \AA}$ and $\text{O}(6)\cdots\text{H}(3)-\text{N}(2) = 170.6^\circ$.

Compared to other open-framework zinc phosphates, **I** and **II** are also novel because of the three-dimensional connectivity arising from the linkage between the ZnO_4 , ZnO_3N , PO_4 tetrahedra and distorted trigonal bipyramidal ZnO_3N_2 . In the work of Halasyamani *et al.*,⁷ where similar bonding of the amine with the Zn centres is reported, the linkages between the ZnO_3N and PO_3F tetrahedra lead to the formation of layers. Covalent bonding between the nitrogen of the amine

and the Zn atoms and the position of the amine molecule in the organic-inorganic hybrid structure described by these workers are reminiscent of pillared materials.

Conclusions

The synthesis and structure of a new family of three-dimensional open-framework zinc phosphates, where the amine molecule acts not only as a structure-directing agent but also fulfils the coordination sphere of Zn centres, are described. The noteworthy structural features of these materials are a 10-membered channel system in **I** as well as a distorted bipyramidal ZnO_3N_2 unit and a 2-membered ring along with two 8-membered channels in **II**. It would be of interest to explore other structures where the structure-directing amine plays a dual role as in **I** and **II**.

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Paper 8/09030K