

Solvothermal synthesis of an open-framework zinc chlorophosphate, $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$, with a layer structure

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Abstract

A solvothermal reaction of ZnO, HCl, H_3PO_4 , and *N,N'*(3-bisaminopropyl)-1,2-ethylenediamine (BAPEN) in diethyleneglycol at 160°C yields a new zinc chlorophosphate, $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$, **I**. The structure comprises ZnO_4 , ZnO_3Cl , HPO_4 and PO_4 tetrahedral units connected through their vertices giving rise to a layered structure with 10-membered apertures. The position of the Zn and P atoms gives rise to double-four ring like building unit with one Zn missing. The fully protonated amine molecules occupy the inter-lamellar region and interacts with the framework through N–H...O hydrogen bonds. Crystal data: $M = 792.85$, orthorhombic, space group = $Pca2_1$ (no. 29), $a = 9.8410(2)$, $b = 15.0912(2)$, $c = 16.1220(4)$ Å, $V = 2394.32(8)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 2.199$ g cm⁻³, $\mu(\text{MoK}\alpha) = 3.443$ mm⁻¹, $R_1 = 0.0520$, $wR_2 = 0.1256$ and $S = 1.054$.
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1. Introduction

Synthesis of new compounds constitutes an important area of research. During the last two decades, synthesis and structures of a large number of new compounds possessing novel open structures have been reported [1]. Of these, the phosphate based ones appear to be prominent. In the family of open-framework phosphates, zinc phosphates occupy a prime position. Thus, zinc phosphates with zero- [2–4], one- [5–9], two- [10–13] and three-dimensionally [14–24] extended structures have been prepared and characterized. The zinc phosphates, in general, are synthesized employing hydrothermal methods in the presence of organic amine molecules. The synthesis of some of these materials has also been carried out in the presence of F^- ions [14], but the role of F^- ions is not entirely understood. The F^- ion appears to act both as a mineralizer and as a connector between the metal ions, especially in iron phosphates [25,26]. Chloride ions are also known as a mineralizer in some of the open-framework metal phosphates [10,21]. Unlike the F^- ions there have been

only two reports wherein the Cl^- ion is part of the phosphate framework [27,28]. In a continuing theme of research aimed at producing new materials, we have been investigating the formation of zinc phosphates in the presence of a variety of organic amine molecules. During the course of this study, we have now isolated a new zinc chlorophosphate, $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$, **I**, with a layered structure in the presence of *N,N'*(3-bisaminopropyl)-1,2-ethylenediamine (BAPEN). The present compound represents only the third example in which the chlorine is part of the framework. In this paper, we present the synthesis, single-crystal structure and characterization of this compound.

2. Synthesis of $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$, **I**

The title compound was synthesized under solvothermal conditions using diethyleneglycol (DEG) as the solvent. For the synthesis of **I**, 0.17 g zinc oxide (ZnO) was dispersed in 3 mL of diethyleneglycol $[(\text{OHCH}_2\text{CH}_2)_2\text{O}]$, DEG]. To this, 0.32 mL of H_3PO_4 (85 wt%) and 0.40 mL of HCl (35% v/v) were added under constant stirring. Finally, 0.41 mL of BAPEN was

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added to the mixture and the whole solution was homogenized for 30 min at room temperature. The final mixture with the composition, ZnO : 2.3H₃PO₄ : 2.0HCl : BAPEN : 14.2DEG, was transferred and sealed in a 7-ml acid-digestion bomb and heated at 160°C for 120 h. The initial pH of the reaction mixture was ~2 and no appreciable change in the pH was observed after the reaction. The resulting product contained large quantity of colorless plates only. The yield of the product was ~60% based on ZnO. The crystals were vacuum-filtered and washed with plenty of deionized water and dried at ambient conditions.

3. Single-crystal structure determination

A suitable colorless single crystal was carefully selected under a polarizing microscope and glued to the tip of a thin glass fiber. Crystal structure determination was performed by X-ray diffraction using a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$) 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 10 s per frame) in the 2θ range 3–46.5°. An empirical absorption correction was applied using the SADABS program [29]. The structure was solved and refined using SHELXTL-PLUS suite of programs [30]. The solution readily revealed a significant fragment of the structure (Zn, Cl, P, and O) to enable

the remainder of the non-hydrogen atoms to be located from difference Fourier maps and the refinements to proceed to $R < 10\%$. All the hydrogen positions were initially located in the difference Fourier map and for the final refinement the hydrogen atoms were placed in geometrically ideal positions and refined using the riding mode. 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 suite of programs [30]. Full details of the data collection and structure solution are given in Table 1. The final atomic coordinates, selected bond distances and angles for **I** are presented in Tables 2–4.

Table 1
Crystal data and structure refinement parameters for **I**, [C₈N₄H₂₆][Zn₃Cl(HPO₄)₃(PO₄)₄]

| | |
|--|--|
| Empirical formula | C ₈ H ₂₉ ClN ₄ O ₁₆ P ₄ Zn ₃ |
| Formula weight | 792.848 |
| Crystal system | Orthorhombic |
| Space group | <i>Pca</i> 2 ₁ (no. 29) |
| Crystal size (mm) | 0.08 × 0.08 × 0.20 |
| <i>a</i> (Å) | 9.8410(2) |
| <i>b</i> (Å) | 15.0912(2) |
| <i>c</i> (Å) | 16.1220(4) |
| Volume (Å ³) | 2394.32(8) |
| <i>Z</i> | 4 |
| ρ_{calc} (Mg m ⁻³) | 2.199 |
| μ (mm ⁻¹) | 3.443 |
| Total data collection | 9547 |
| Unique data | 3363 |
| R_{merge} | 0.0641 |
| R indexes [$I > 2\sigma(I)$] | $R_1 = 0.0520^a$, $wR_2 = 0.1256^b$ |
| R (all data) | $R_1 = 0.0696$, $wR_2 = 0.1346$ |
| Large difference map peak and hole e Å ⁻³ | 0.855 and $-0.679 \text{ e \AA}^{-3}$ |

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. $w = 1 / [\rho^2(F_o)^2 + (aP)^2 + bP]$. $P = [\max(F_o, 0) + 2(F_c)^2] / 3$, where $a = 0.0720$ and $b = 5.7512$.

Table 2
Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **I**, [C₈N₄H₂₆][Zn₃(HPO₄)₃(PO₄)₄Cl]

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^a |
|-------|----------|----------|-----------|-------------------|
| Zn(1) | 1655(1) | 3779(1) | 1499(1) | 25(1) |
| Zn(2) | 3276(1) | 7226(1) | 2387(1) | 28(1) |
| Zn(3) | 1004(1) | 933(1) | 1575(1) | 26(1) |
| P(1) | 899(3) | 2327(2) | 158(2) | 25(1) |
| P(2) | -2280(3) | 965(2) | 1466(2) | 25(1) |
| P(3) | 3637(3) | 5523(2) | 1378(2) | 29(1) |
| P(4) | 1525(3) | 2402(2) | 2727(2) | 26(1) |
| O(1) | 109(8) | 4526(5) | 1705(6) | 32(2) |
| O(2) | 1764(8) | 3120(5) | 473(6) | 29(2) |
| O(3) | 3156(8) | 4572(5) | 1246(6) | 38(2) |
| O(4) | 2514(7) | 3122(5) | 2419(6) | 31(2) |
| O(5) | -2733(9) | 1824(5) | 1871(6) | 37(2) |
| O(6) | 192(8) | 2559(6) | 2248(6) | 38(2) |
| O(7) | 2737(9) | 6060(5) | 1947(6) | 34(2) |
| Cl(1) | 2466(4) | 7292(3) | 3688(2) | 49(1) |
| O(8) | 1393(8) | 1444(6) | 500(6) | 31(2) |
| O(9) | 1591(7) | -291(5) | 1570(7) | 39(2) |
| O(10) | -893(8) | 624(6) | 1779(6) | 36(2) |
| O(11) | 2019(8) | 1462(5) | 2502(6) | 32(2) |
| O(12) | -606(8) | 2455(6) | 296(6) | 34(2) |
| O(13) | 1103(9) | 2277(6) | -820(6) | 33(2) |
| O(14) | -2176(9) | 1147(5) | 489(6) | 31(2) |
| O(15) | 3604(8) | 5941(5) | 491(5) | 33(2) |
| O(16) | 1378(8) | 2468(6) | 3677(6) | 29(2) |
| N(1) | 5117(11) | 6039(7) | -2091(7) | 38(3) |
| C(1) | 5731(11) | 5495(7) | -1412(8) | 36(3) |
| C(2) | 4712(11) | 4807(8) | -1066(7) | 34(3) |
| C(3) | 5434(12) | 4306(8) | -361(8) | 38(4) |
| N(2) | 4569(9) | 3542(6) | -91(6) | 32(3) |
| C(4) | 5322(12) | 2960(6) | 498(8) | 33(3) |
| C(5) | 4693(13) | 2019(7) | 533(7) | 35(3) |
| N(3) | 5126(11) | 1491(7) | -225(6) | 40(3) |
| C(6) | 4568(15) | 555(8) | -293(10) | 55(4) |
| C(7) | 5371(19) | 139(13) | -1051(11) | 96(7) |
| C(8) | 4393(16) | -510(13) | -1467(11) | 159(16) |
| N(4) | 5274(16) | -907(9) | -2133(9) | 67(5) |

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

Table 3
Selected bond distances and angles in I, $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$

| Bond | Distance (Å) | Bond | Distance (Å) |
|---------------------------|-------------------|-----------------------|-------------------|
| Zn(1)–O(1) | 1.921(7) [0.5562] | P(1)–O(13) | 1.595(9) [1.0727] |
| Zn(1)–O(2) | 1.934(8) [0.5385] | $\sum(\text{P(1)–O})$ | 5.0395 |
| Zn(1)–O(3) | 1.945(8) [0.5227] | P(2)–O(5) | 1.520(8) [1.3067] |
| Zn(1)–O(4) | 1.977(8) [0.4333] | P(2)–O(9)#2 | 1.519(7) [1.3138] |
| $\sum(\text{Zn(1)–O})$ | 2.0507 | P(2)–O(10) | 1.541(8) [1.2181] |
| Zn(2)–O(5)#1 | 1.926(8) [0.5399] | P(2)–O(14) | 1.605(9) 1.0413] |
| Zn(2)–O(6)#1 | 1.924(7) [0.5488] | $\sum(\text{P(2)–O})$ | 4.8799 |
| Zn(2)–O(7) | 1.975(8) [0.4859] | P(3)–O(1)#1 | 1.544(8) [1.2214] |
| Zn(2)–Cl(1) | 2.247(4) [0.5532] | P(3)–O(3) | 1.519(8) [1.2788] |
| $\sum(\text{Zn(2)–O/Cl})$ | 2.1278 | P(3)–O(7) | 1.509(8) [1.3317] |
| Zn(3)–O(8) | 1.941(8) [0.5356] | P(3)–O(15) | 1.557(9) [1.1571] |
| Zn(3)–O(9) | 1.936(7) [0.5356] | $\sum(\text{P(3)–O})$ | 4.9890 |
| Zn(3)–O(10) | 1.952(8) [0.5115] | P(4)–O(4) | 1.542(8) [1.2280] |
| Zn(3)–O(11) | 1.972(8) [0.4912] | P(4)–O(6) | 1.542(8) [1.2313] |
| $\sum(\text{Zn(3)–O})$ | 2.0739 | P(4)–O(11) | 1.538(8) [1.2214] |
| P(1)–O(2) | 1.555(8) [1.3353] | P(4)–O(16) | 1.541(9) [1.2313] |
| P(1)–O(8) | 1.515(8) [1.2962] | $\sum(\text{P(4)–O})$ | 4.9120 |
| P(1)–O(12) | 1.515(8) [1.3353] | | |

Values in brackets are the bond valences. Their sum SVB appears in bold type at the end of the list of the distances around every cations. Symmetry transformation used to generate equivalent atoms: #1, $x + 1/2, -y + 1, z$; #2, $x - 1/2, -y, z$.

Table 4
Selected bond angles (deg) in I, $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$

| Angle | Amplitude (deg) | Angle | Amplitude (deg) |
|---------------------|-----------------|-------------------|-----------------|
| O(1)–Zn(1)–O(2) | 119.4(3) | O(9)#2–P(2)–O(14) | 105.7(5) |
| O(1)–Zn(1)–O(3) | 105.8(3) | O(5)–P(2)–O(14) | 107.0(5) |
| O(2)–Zn(1)–O(3) | 95.6(3) | O(10)–P(2)–O(14) | 108.8(5) |
| O(1)–Zn(1)–O(4) | 120.3(4) | O(7)–P(3)–O(3) | 113.7(5) |
| O(2)–Zn(1)–O(4) | 111.3(3) | O(7)–P(3)–O(1)#1 | 111.9(5) |
| O(3)–Zn(1)–O(4) | 98.2(3) | O(3)–P(3)–O(1)#1 | 107.3(4) |
| O(6)#1–Zn(2)–O(5)#1 | 109.2(4) | O(7)–P(3)–O(15) | 109.2(5) |
| O(6)#1–Zn(2)–O(7) | 111.7(4) | O(3)–P(3)–O(15) | 104.1(5) |
| O(5)#1–Zn(2)–O(7) | 111.6(4) | O(1)#1–P(3)–O(15) | 110.4(5) |
| O(6)#1–Zn(2)–Cl(1) | 116.6(3) | O(6)–P(4)–O(16) | 113.9(5) |
| O(5)#1–Zn(2)–Cl(1) | 100.9(3) | O(6)–P(4)–O(4) | 105.5(5) |
| O(7)–Zn(2)–Cl(1) | 106.3(3) | O(16)–P(4)–O(4) | 109.3(5) |
| O(8)–Zn(3)–O(9) | 108.5(4) | O(6)–P(4)–O(11) | 107.3(5) |
| O(8)–Zn(3)–O(10) | 115.7(3) | O(16)–P(4)–O(11) | 109.1(5) |
| O(9)–Zn(3)–O(10) | 93.4(3) | O(4)–P(4)–O(11) | 111.7(5) |
| O(8)–Zn(3)–O(11) | 114.6(3) | P(3)#3–O(1)–Zn(1) | 131.1(5) |
| O(9)–Zn(3)–O(11) | 104.1(4) | P(1)–O(2)–Zn(1) | 130.2(5) |
| O(10)–Zn(3)–O(11) | 117.1(3) | P(3)–O(3)–Zn(1) | 142.2(5) |
| O(12)–P(1)–O(8) | 111.8(5) | P(4)–O(4)–Zn(1) | 108.9(4) |
| O(12)–P(1)–O(2) | 112.9(5) | P(2)–O(5)–Zn(2)#3 | 132.2(5) |
| O(8)–P(1)–O(2) | 112.6(5) | P(4)–O(6)–Zn(2)#3 | 143.3(6) |
| O(12)–P(1)–O(13) | 106.3(5) | P(3)–O(7)–Zn(2) | 122.5(5) |
| O(8)–P(1)–O(13) | 105.9(5) | P(1)–O(8)–Zn(3) | 127.6(5) |
| O(2)–P(1)–O(13) | 106.9(5) | P(2)#4–O(9)–Zn(3) | 149.2(5) |
| O(9)#2–P(2)–O(5) | 108.3(5) | P(2)–O(10)–Zn(3) | 135.4(5) |
| O(9)#2–P(2)–O(10) | 113.1(5) | P(4)–O(11)–Zn(3) | 113.1(4) |
| O(5)–P(2)–O(10) | 113.5(5) | | |

Symmetry transformation used to generate equivalent atoms: #1, $x + 1/2, -y + 1, z$; #2, $x - 1/2, -y, z$; #3, $x - 1/2, -y + 1, z$; #4, $x + 1/2, -y, z$.

4. Results and discussion

4.1. Initial characterization

The initial characterization was carried out using powder X-ray diffraction (XRD, Rich-Seifert, 3000TT,

CuK α radiation), thermogravimetric analysis (TGA, Mettler-Toledo, TG850), infrared (IR, Bruker, IFS 66 V/S), and solid state nuclear magnetic resonance (NMR, Bruker DSX 300 MHz) studies. An EDAX analysis on the single crystals indicated that Zn:P:Cl = 2.86:4.10:1, consistent with the single-crystal data (Zn:P:Cl = 3:4:1).

The XRD pattern indicated that the product was a new material; the pattern was consistent with the structure determined using the single-crystal X-ray diffraction. TGA of the powdered sample was carried out in N_2 atmosphere (flow rate = 50 mL min^{-1}) in the range between 25°C and 800°C (heating rate = 5°C min^{-1}). The results showed a sharp weight loss at 350°C followed by a long tail in the range of $550\text{--}800^\circ\text{C}$. The weight loss of 20.6% at 350°C is in good agreement with the loss of one equivalent of BAPEN (calcd. 22.8%). The weight loss of 14.3% occurring in the region between 550°C and 800°C corresponds to the condensation of the phosphoryl group (P–OH) along with the loss of the chloride ion (calc. 10.9%). It is likely that the water molecules formed during the condensation of the phosphoryl groups might have hydrolyzed the chloride ion from the framework, resulting in the formation of volatile hydrogen chloride. The calcined sample was found to be amorphous to powder XRD. The IR spectra, recorded in the range $400\text{--}4000 \text{ cm}^{-1}$ using the KBr pellet method, exhibited typical peaks corresponding to the organic amine, HPO_4 and PO_4 moieties. IR bands: $\nu(\text{CH}) = 3248 \text{ cm}^{-1}$, $\delta(\text{CH}) = 1470 \text{ cm}^{-1}$, $\nu(\text{NH}) = 3100 \text{ cm}^{-1}$, $\delta_a(\text{NH}) = 1524 \text{ cm}^{-1}$, $\delta_s(\text{NH}) = 1252 \text{ cm}^{-1}$, $\nu(\text{CN}) = 1123 \text{ cm}^{-1}$, $\nu(\text{P–OH}) = 1075 \text{ cm}^{-1}$.

4.2. Structure of $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$, **I**

The asymmetric unit consists of 36 non-hydrogen atoms, of which 24 atoms belong to the framework and 12 atoms belong to the amine (Fig. 1). Three Zn and four P atoms were found to be crystallographically independent. All the three Zn atoms are tetrahedrally coordinated with their nearest neighbors with Zn(1) and Zn(3) atoms being coordinated by four oxygen atoms

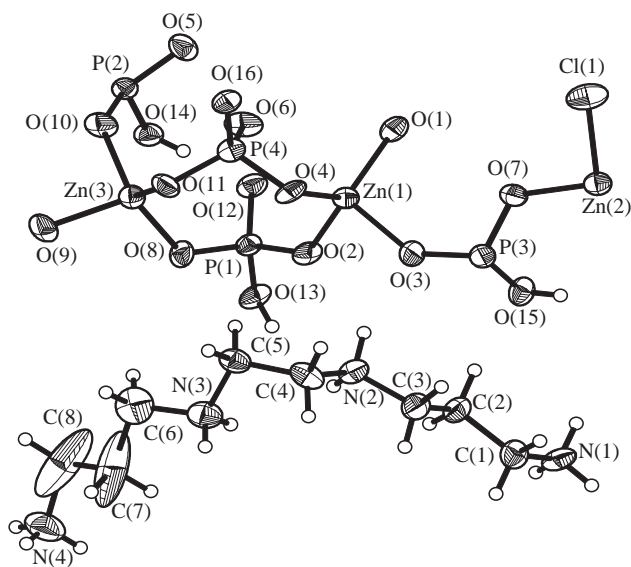


Fig. 1. ORTEP plot of $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$, **I**, showing the asymmetric unit. Thermal ellipsoids are given at 50% probability.

and Zn(2) by three oxygen atoms and one chlorine atom. The Zn–O distances are in the range $1.921(8)\text{--}2.067(9) \text{ \AA}$ [av. (Zn–O) = 1.945 \AA] and the O–Zn–O bond angles are in the range of $93.3(3)\text{--}120.3(4)^\circ$ [av. (O–Zn–O) = 109.5°]. The Zn(1) and Zn(3) appear to have some weak interactions with O(6) with distances of 2.632 and 2.799 \AA , which may be viewed as semi-chelation coordination mode [32]. Thus, one can describe the coordination environment of Zn(1) and Zn(3) atoms as distorted trigonal-bipyramidal geometry. Of the three Zn atoms, Zn(1) and Zn(3) are connected to P atoms through four Zn–O–P bonds and Zn(2) is connected only through three Zn–O–P bonds and possesses one terminal Zn–Cl linkage. An average Zn–O–P bond angle of 128.0° results from this connection. Of the four P atoms, P(1) is connected to the Zn atoms via two P–O–Zn linkages and possess two terminal P–O bonds, while P(2), P(3) and P(4) are connected through three P–O–Zn linkages and possess one terminal P–O bond. The P–O distances are in the range of $1.510(9)\text{--}1.602(10) \text{ \AA}$ [av. (P–O) = 1.541 \AA] and the O–P–O bond angles are in the range $104.3(5)\text{--}114.1(5)^\circ$ [av. (O–P–O) = 109.4°]. A framework formula of $[\text{Zn}_3\text{ClP}_4\text{O}_{16}]$ would result in a net framework charge of -7 . This net negative charge was compensated by the protonation of some of the framework oxygen atoms and the amine molecule. The proton positions observed in the difference Fourier map near the oxygen atoms, O(13), O(14) and O(15), indicates that these are protonated. The P(1)–O(13), P(2)–O(14) and P(3)–O(15) bonds with distance of $1.591(9)$, $1.602(10)$ and $1.563(9) \text{ \AA}$ are, thus, P–O(H) group. Bond valence sum calculations [31] also agree with the above formula. The selected bond distances and angles are listed in Tables 3 and 4.

The framework structure of **I** consists of alternating inorganic and organic layers. The inorganic layers are built up from a strictly alternating network of ZnO_4 , ZnO_3Cl , HPO_4 , PO_4 tetrahedra sharing vertices. If the semi-chelation of Zn(1) and Zn(3) with O(6) is considered, then O(6) appears to have a tetrahedral linkage with three Zn atoms and one P atom forming OZn_3P units, which is noteworthy. The connectivity between the tetrahedral units gives rise to a layered structure with 10-membered apertures within the layer (Fig. 2). The terminal chlorine atoms, hanging from the zinc center, project in a direction perpendicular to the layer. As with many two-dimensional structures, the amine molecules occupy the inter-lamellar space and participate in hydrogen bond interactions with the framework oxygen atoms through both $\text{N–H}\cdots\text{O}$ and $\text{C–H}\cdots\text{O}$ hydrogen bonds (Fig. 3). Both inter- and intra-layer hydrogen bond interactions are observed. In addition, the positioning of the chlorine atom in **I** gives rise to strong hydrogen bond interaction of the type $\text{N–H}\cdots\text{Cl}$. The important observed hydrogen bond interactions are listed in Table 5.

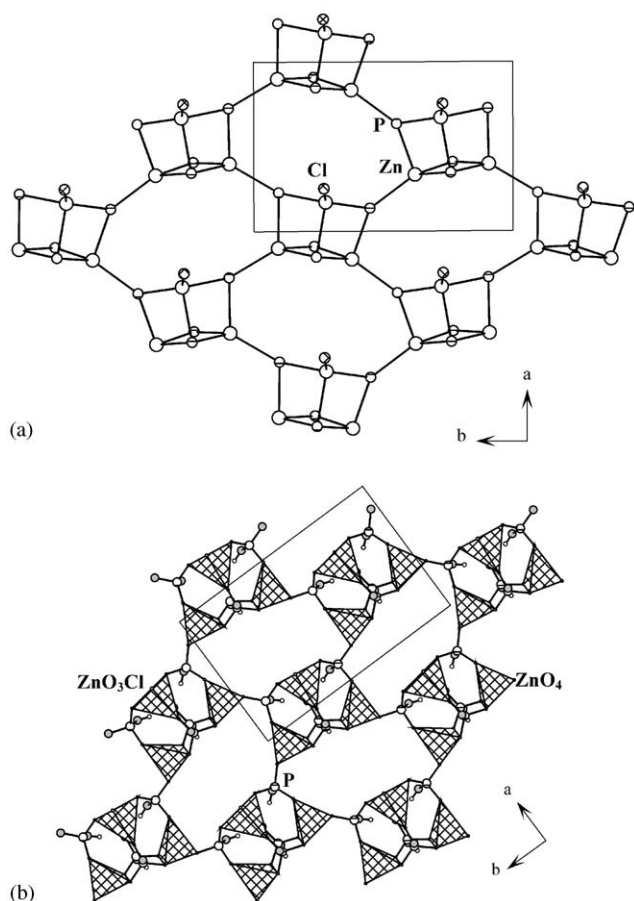


Fig. 2. (a) *T*-atom (*T*=Zn, P) connectivity showing a single layer. Note that the building unit resembles a double-four ring with one corner missing (see text). (b) View of a single layer of **I**. The Zn atoms are shown in polyhedral fashion.

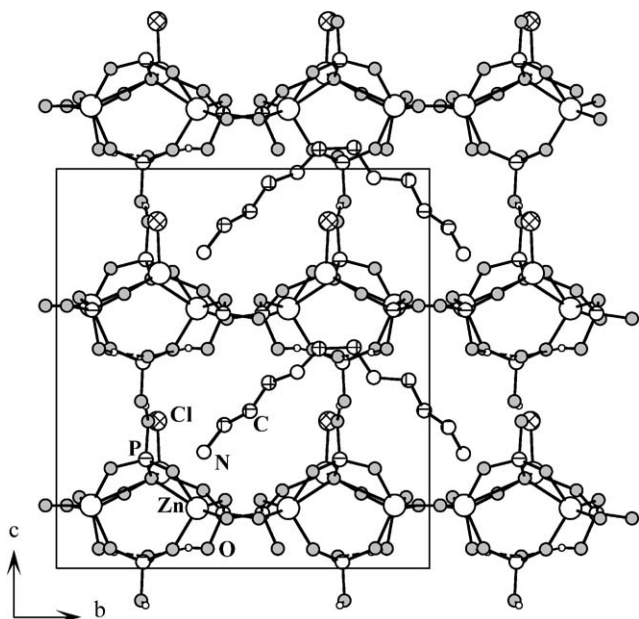


Fig. 3. Structure of **I** in the *bc* plane showing the arrangement of the layers. The hydrogen atoms on the amine molecule are not shown for clarity. The dotted lines represent possible hydrogen bond interactions.

NMR experiments were performed on a Bruker DSX 300 MHz with resonance frequencies of 121 MHz for ³¹P. Magic angle spinning (MAS) was performed at rotating frequencies of 7 kHz using a 4 mm rotor system. The spectra were chemical referenced relative to H₃PO₄ (85 wt%) for ³¹P. The proton decoupled ³¹P pulsed MAS NMR spectra were recorded with a pulse width of 4.75 μs and a total of 1000 scans were collected with a recycle time of 1 s. The spectrum indicates the presence of two phosphorous sites, with chemical shifts of δ_{iso} = 0.53 and 5.618 ppm (Fig. 4). The two peaks correspond to PO₄ and HPO₄ groups, consistent with the single-crystal data.

Table 5
Important hydrogen bond interactions in **I**, [C₈N₄H₂₆][Zn₃Cl(HPO₄)₃(PO₄)₃]

| <i>D</i> –H... <i>A</i> | <i>D</i> –H (Å) | H... <i>A</i> (Å) | <i>D</i> ... <i>A</i> (Å) | <i>D</i> –H... <i>A</i> (deg) |
|----------------------------------|-----------------|-------------------|---------------------------|-------------------------------|
| N(1)–H(1)...O(4) | 0.89 | 1.91 | 2.762(12) | 158 |
| N(1)–H(2)...Cl(1) | 0.88 | 2.53 | 3.423(11) | 174 |
| N(1)–H(3)...O(1) | 0.88 | 2.15 | 2.993(13) | 158 |
| N(2)–H(11)...O(16) | 0.89 | 1.84 | 2.737(12) | 170 |
| N(3)–H(16)...O(16) | 0.90 | 1.90 | 2.740(13) | 153 |
| N(3)–H(17)...O(14) | 0.90 | 2.15 | 2.936(13) | 146 |
| N(4)–H(24)...O(5) | 0.89 | 2.47 | 3.279(16) | 151 |
| N(4)–H(26)...O(10) | 0.89 | 2.10 | 2.983(15) | 171 |
| O(13)–H(27)...O(16) | 0.82 | 1.83 | 2.618(11) | 161 |
| O(14)–H(28)...O(12) ^a | 0.82 | 1.69 | 2.514(11) | 175 |
| O(15)–H(29)...O(12) ^a | 0.82 | 1.76 | 2.566(11) | 166 |
| C(5)–H(15)...O(2) | 0.97 | 2.70 | 3.319(13) | 144 |
| C(5)–H(15)...O(8) | 0.97 | 2.46 | 3.360(14) | 153 |

^a Intra-layer.

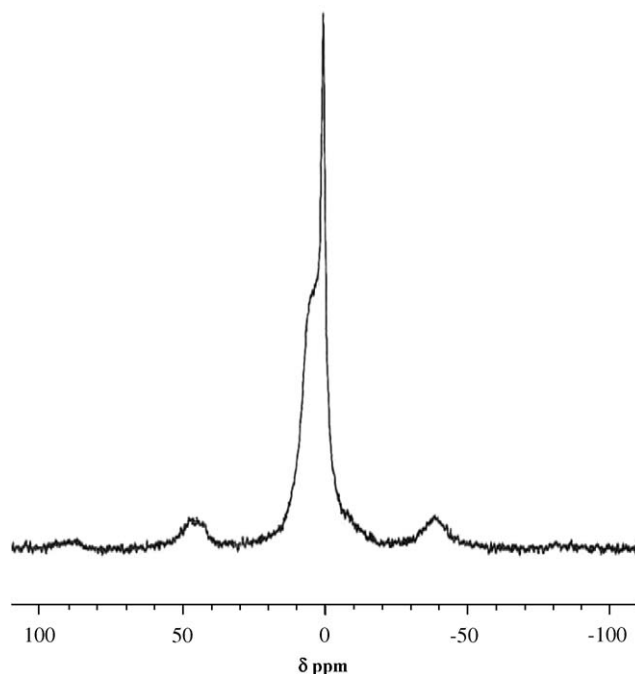


Fig. 4. ³¹P MAS-NMR spectra for **I**.

Hydro/solvothermal crystallization has given rise to many new materials with interesting structures and properties, and the present compound illustrates another example of the usefulness of this synthetic approach. A close examination of the structure reveals that the positioning of the three Zn and the four P atoms resembles a double-four ring, with one corner (Zn) missing. It is likely that the replacement of the Cl^- by oxygen and a Zn would result in forming the double-four ring. This is indeed a unique feature. Our attempts to replace the Cl^- ions by extending the reaction time or modifying the composition and temperature were not successful, as condensed zinc phosphates, generally, resulted in these preparations.

It is also illustrative to compare the present structure with other similar ones. Thus, **I** appears to have some structural similarities with the previously reported zinc chlorophosphate, $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ [27]. In Fig. 5, we have shown the arrangement of the layers in both the

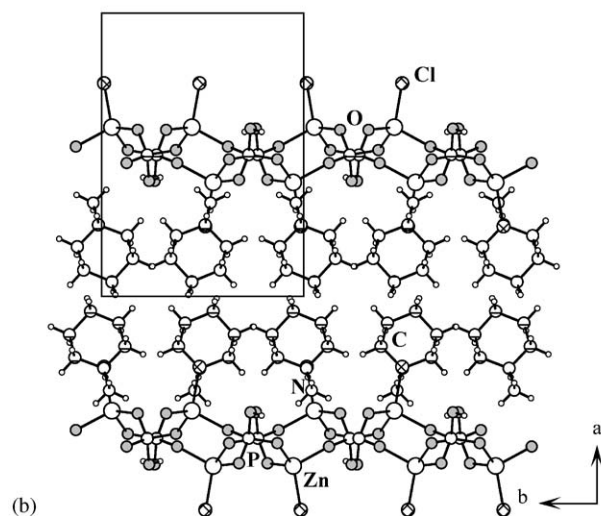
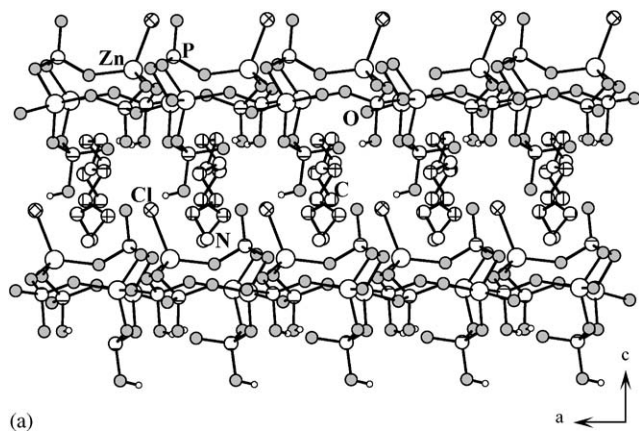
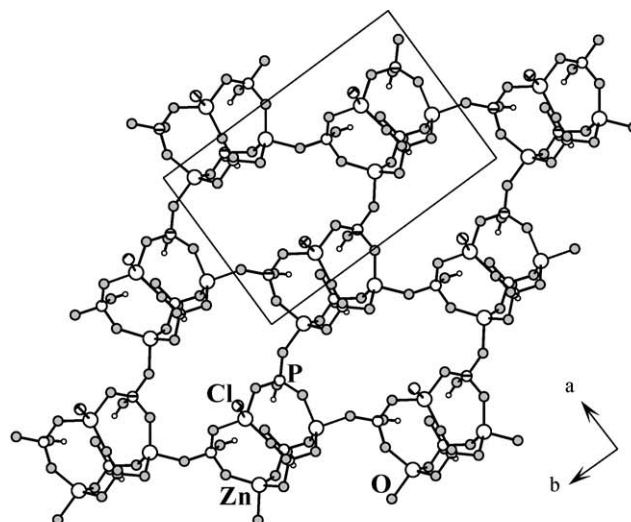


Fig. 5. (a) View of the structure of **I** in the ac plane showing two layers. Hydrogen atoms on the amine molecule are not shown for clarity. Note that the Cl^- ions point in the same direction. (b) View of the structure of $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ in the ab plane showing two layers. Note the separation between the two layers and the position of the amine molecules (see text).

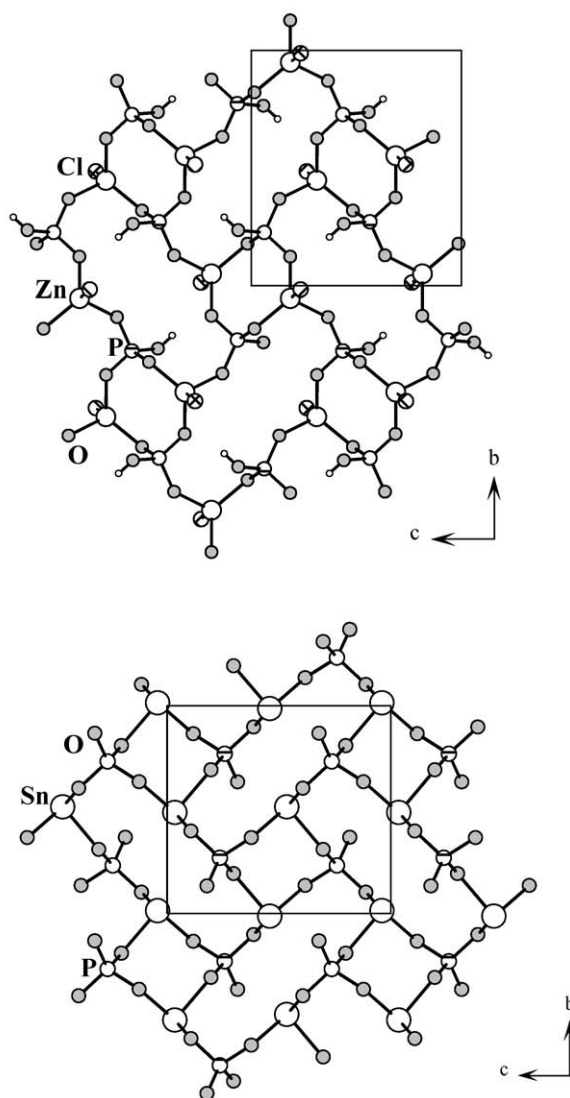


Fig. 6. Structure showing a single layer in (a) **I**, (b) $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ and (c) $[\text{C}_3\text{N}_2\text{H}_{12}][\text{SnPO}_4]$.

structures. As can be noted, in $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$, the Cl^- ions appear to be facing each other resulting in larger inter-layer separation (Fig. 5b). To compensate this large separation of layers, two amine molecules occupy the inter-lamellar region (Fig. 5b). In **I**, the Cl^- ions always face opposite directions and the inter-layer separation is comparable to many of the known layered phosphate structures. $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ has been compared to the tin(II) phosphate, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{SnPO}_4]$, especially with respect to the position of the lone-pairs of Sn^{II} [32]. The inter-layer separation in $[\text{C}_3\text{N}_2\text{H}_{12}][\text{SnPO}_4]$ appears to be similar to **I**. In Fig. 6 we have represented the individual layer arrangement of all the three compounds. It is clear that $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ and $[\text{C}_3\text{N}_2\text{H}_{12}][\text{SnPO}_4]$ have similar layer arrangement with apertures bound by 4- and 8-*T* atoms (*T* = Zn/Sn, P), while the unusual building unit in **I** gives rise to apertures bound by 10-*T* atoms (*T* = Zn, P).

5. Conclusions

The solvothermal synthesis and single-crystal structure of a new zinc chlorophosphate, $[\text{C}_8\text{N}_4\text{H}_{26}][\text{Zn}_3\text{Cl}(\text{HPO}_4)_3(\text{PO}_4)]$, **I**, with two-dimensional structure has been accomplished. The inorganic layers are built up from a strictly alternating network of ZnO_4 , ZnO_3Cl , HPO_4 , PO_4 tetrahedra sharing vertices. The terminal chlorine atoms, hanging from the zinc center, project in a direction perpendicular to the layer. It is likely that the replacement of the Cl^- by oxygen along with the incorporation of another Zn, might lead to a unique three-dimensional structure, formed by double-four rings, with 10-membered channels, of which there are no known examples of zinc phosphate. Further work is presently underway in this direction.

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