

Synthesis and structure of an open-framework chlorophosphate, $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]^\dagger$

S. Neeraj and Srinivasan Natarajan*

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India. E-mail: raj@jncasr.as.in; Fax: +(080)-846-2766

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A zinc chlorophosphate, of the composition $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$, with a layered architecture has been synthesized, for the first time, in the presence of cyclohexylamine as the structure-directing agent. The structure comprises a network of ZnO_3Cl and PO_4 tetrahedra forming macroanionic layers with four- and eight-membered apertures. Charge compensation is achieved by the protonated amine occupying inter-lamellar space and interacts with the framework *via* hydrogen bonding. The crystal structure of the new compound was determined.

Introduction

A large number of open-framework metal phosphates have been synthesized and characterized in the last decade.¹ The synthesis of some of these materials has been carried out in the presence of F^- ions but the role of F^- is not entirely understood.^{2,3} In many cases F^- ions acts as a mineralizer.⁴ However, there are some cases where F^- ion is also part of the structure and acts as a bridge between the metal centers. Chloride ions are also known to act as a mineralizer in the synthesis of open-framework metal phosphates.⁵ There is no chlorophosphate reported in the literature wherein the Cl^- ion is part of the network. In this report we describe the synthesis of an open-framework chlorophosphate of zinc. An examination of the material, $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$, shows that it has a layered structure with 4- and 8-membered rings and the Cl^- ions protrude in a direction perpendicular to the plane of the layer. This positioning of the Cl^- ions is reminiscent of lone pairs of $\text{Sn}(\text{II})$ in open-framework layered $\text{Sn}(\text{II})$ phosphates.^{6,7}

Experimental

The zinc chlorophosphate, $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$, was synthesized starting from a gel containing cyclohexylamine (CHA) as the structure-directing agent. In a typical synthesis, 0.081 g of zinc oxide was dispersed in 7.7 ml of a mixture of butan-2-ol and water (ratio: 80:20). 0.174 ml of hydrochloric acid (35%) and 0.127 ml of phosphoric acid (85 wt.%) was added to the above under constant stirring. Finally, 0.114 ml of cyclohexylamine was added and the mixture was homogenized for ~30 min. The final composition of the mixture was: 1.0 ZnO :2.0 HCl :2.0 H_3PO_4 :1.0 CHA :100 ($\text{H}_2\text{O} + \text{C}_4\text{H}_9\text{OH}$). All the chemicals were obtained from Aldrich and used without any further purification. The starting mixtures were transferred to and sealed into a 23 ml capacity PTFE-lined stainless steel autoclave (Parr, Moline, IL, USA). The initial pH of the mixture was close to 2.0. The sealed pressure bombs were heated at 170 °C for 115 h under autogeneous pressure. The resulting product, predominantly containing large quantities of crystals, were filtered and washed thoroughly with deionized

water. The final yield of the product was ~40%. The powder X-ray diffraction (XRD) pattern of the powdered single crystals indicated that the product was a new material; the pattern was entirely consistent with the structure determined by single-crystal X-ray diffraction. A least-squares fit of the powder XRD (Rich-Siefert, Model: XRD-3000-TT, Cu-K α , Ni filter, 40 kV \times 30 mA) lines, using the *hkl* indices garnered from single crystal X-ray data, gave the following cell: $a = 13.653(2)$, $b = 9.718(5)$, $c = 8.692(2)$ Å, $\beta = 94.97(3)^\circ$, which is in good agreement with that determined by single crystal XRD.

A suitable colorless plate of $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ 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-K α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame). Pertinent details of crystal structure determination are presented in Table 1. The structure was solved by direct methods using SHELXS-86,⁸ which readily revealed all the heavy atom positions (Zn, Cl, P) and enabled us to locate the

Table 1 Crystal data and structural refinement parameters for $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ (298 K)

Empirical formula	$\text{Zn}_1\text{P}_1\text{O}_4\text{Cl}_1\text{C}_6\text{N}_1\text{H}_{15}$
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> /Å	13.653(1)
<i>b</i> /Å	9.718(1)
<i>c</i> /Å	8.691(1)
α /°	90.0
β /°	94.9(1)
γ /°	90.0
Volume/Å ³	1148.9(1)
<i>Z</i>	4
Formula mass	297.9
μ/mm^{-1}	2.499
Total data collected	4678
Unique data	1646
Observed data ($\sigma > 2\sigma(I)$)	1334
<i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.04$, $wR_2 = 0.11$
<i>R</i> indices (all data)	$R_1 = 0.06$, $wR_2 = 0.13^a$
$^a w = 1/[\sigma^2(F_o)^2 + (0.0882P)^2]$ where $P = [F_o^2 + 2F_c^2]/3$.	

[†]Supplementary data available: X-ray powder data for $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ available from BLDSC (SUPP. NO. 57695, 2 pp.). See Information for Authors, Issue 1 (<http://www.rsc.org/materials>).

Table 2 Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Zn(1)	4027(1)	524(1)	1873(1)	36(1)
P(1)	5004(1)	2270(1)	-640(1)	32(1)
O(1)	4120(2)	1796(3)	163(3)	43(1)
O(2)	4708(3)	-1252(3)	1864(4)	44(1)
O(3)	4836(2)	1311(3)	3648(3)	40(1)
O(4)	5921(2)	2365(3)	595(4)	43(1)
Cl(1)	2480(1)	146(2)	2356(2)	66(1)
N(1)	6688(3)	-396(5)	4021(6)	56(1)
C(1)	7467(5)	-134(7)	2970(7)	60(2)
C(2)	8242(6)	-1176(8)	3129(14)	128(4)
C(3)	9059(8)	-865(12)	2071(16)	166(6)
C(4)	9473(7)	526(10)	2279(15)	122(4)
C(5)	8659(6)	1563(9)	2103(12)	111(3)
C(6)	7853(5)	1295(7)	3164(9)	74(2)

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

other non-hydrogen positions from the difference Fourier maps. All the hydrogen positions were found in the difference Fourier maps. One of the oxygen atoms bonded to phosphorus [O(4)] was found have a proton attached to it. For the final refinement the hydrogen positions 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 SHELXTL-PLUS⁹ package of programs. The final atomic coordinates and selected bond distances and bond angles for $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ are presented in Tables 2 and 3.

Results and discussion

An open-framework chlorophosphate of zinc, $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$, has been synthesized by hydrothermal methods. To our knowledge, this is the first example of an open-framework chlorophosphate wherein chlorine is part of the framework. The incorporation of chlorine has been achieved by the addition of HCl to the reaction mixture. This is noteworthy since the use of Cl^- ions in the conventional synthesis of framework solids did not result in the incorporation of chlorine into the framework.⁵ Clearly the more common

role of Cl^- ion is as a mineralizer,⁵ similar to F^- ions in the synthesis of open-framework phosphate materials.⁴

The asymmetric unit of $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ consists of 14 non-hydrogen atoms. There is only one crystallographically independent zinc and phosphorus atom in the asymmetric unit. Both the zinc and phosphorus atoms are tetrahedrally coordinated with respect to the nearest atom neighbors but there exist only three Zn–O–P bonds. The remaining connection needed for the tetrahedral linkage comes from terminal bonding with the zinc having a chlorine (Zn(1)–Cl(1) = 2.220 Å) and phosphorus with an oxygen atom (P(1)–O(4) = 1.579 Å), which is formally a –OH group. Bond valence sum calculations¹⁰ also agree with the above formalism. The Zn–O and P–O bond distances as well as the O–Zn–O and O–P–O angles are all as expected for this type of bonding (Table 3).

The framework structure of $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$ consists of alternating inorganic and organic layers. The macroanionic inorganic layers are built up from a network of ZnO_3Cl and $\text{PO}_3(\text{OH})$ tetrahedra sharing vertices. Each inorganic layer consists of strictly alternating Zn and P tetrahedra forming 4- and 8-membered apertures within the layer as shown in Fig. 1. The chlorine atoms are so arranged as to project in a direction perpendicular to the layer. This arrangement of the chlorine atoms facilitates closer interaction with the structure-directing amines *via* $\text{Cl}\cdots\text{H}-\text{N}/\text{C}$ type interactions. The compensating protonated amine molecule is situated between the inorganic layers that are separated by a distance of ~ 7 Å, as shown in Fig. 2 and 3. As can be seen, there are two amine molecules that are present in between the layers, which is similar to the amine positioning observed in a layered aluminium phosphate,¹¹ though such occurrences are rare. Since the Cl^- ions project into the layers, a shorter inter-layer distance would experience repulsive interactions from the Cl^- ions of the adjacent layers and hence the layers are, probably, forced apart. The two amine molecules present in between the layers may, therefore, be needed to impart stability to such a framework *via* hydrogen bonding.

It is instructive to compare the role of the chlorine atoms in these solids with that of the lone-pair of electrons of Sn(II)

Table 3 Selected bond distances and angles in $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$

Moiety	Distance/Å	Moiety	Distance/Å
Zn(1)–O(1)	1.945(3)	P(1)–O(1)	1.518(3)
Zn(1)–O(2)	1.961(3)	P(1)–O(3) ^a	1.521(3)
Zn(1)–O(3)	1.972(3)	P(1)–O(2) ^b	1.529(3)
Zn(1)–Cl(1)	2.220(2)	P(1)–O(4)	1.579(3)
Organic moiety			
N(1)–C(1)	1.482(7)	C(1)–C(2)	1.463(10)
C(2)–C(3)	1.536(11)	C(3)–C(4)	1.470(13)
C(4)–C(5)	1.499(12)	C(5)–C(6)	1.518(9)
C(6)–C(1)	1.490(9)		
Moiety	Angle/°	Moiety	Angle/°
O(1)–Zn(1)–O(2)	119.62(13)	O(1)–P(1)–O(3) ^a	111.3(2)
O(1)–Zn(1)–O(3)	106.40(13)	O(1)–P(1)–O(2) ^b	112.7(2)
O(2)–Zn(1)–O(3)	96.38(14)	O(3) ^a –P(1)–O(2) ^b	110.0(2)
O(1)–Zn(1)–Cl(1)	112.06(11)	O(1)–P(1)–O(4)	108.7(2)
O(2)–Zn(1)–Cl(1)	108.31(12)	O(3) ^a –P(1)–O(4)	107.8(2)
O(3)–Zn(1)–Cl(1)	113.17(10)	O(2) ^b –P(1)–O(4)	105.9(2)
Organic moiety			
N(1)–C(1)–C(2)	112.0(6)	C(1)–C(2)–C(3)	111.3(8)
C(2)–C(3)–C(4)	113.5(8)	C(3)–C(4)–C(5)	109.4(8)
C(4)–C(5)–C(6)	113.1(7)	C(5)–C(6)–C(1)	111.1(6)
C(6)–C(1)–C(2)	112.9(6)	N(1)–C(1)–C(6)	110.9(5)

^a $x, -y+1/2, z-1/2$. ^b $-x+1, -y, -z$.

Table 4 Important hydrogen bond interactions in $[\text{C}_6\text{NH}_{14}][\text{ZnCl}(\text{HPO}_4)]$

Moiety	Distance/Å	Moiety	Angle/°
O(1)–H(1)	2.279	O(1)–H(1)–N(1)	144.9
O(3)–H(3)	2.157	O(3)–H(3)–N(1)	162.7
O(2)–H(20) ^a	1.994	O(2)–H(20)–O(4)	161.7
Cl(1)–H(2)	2.377	Cl(1)–H(2)–N(1)	173.2
Cl(2)–H(6)	2.773	Cl(2)–H(6)–C(2)	166.2

^aIntra-layer.

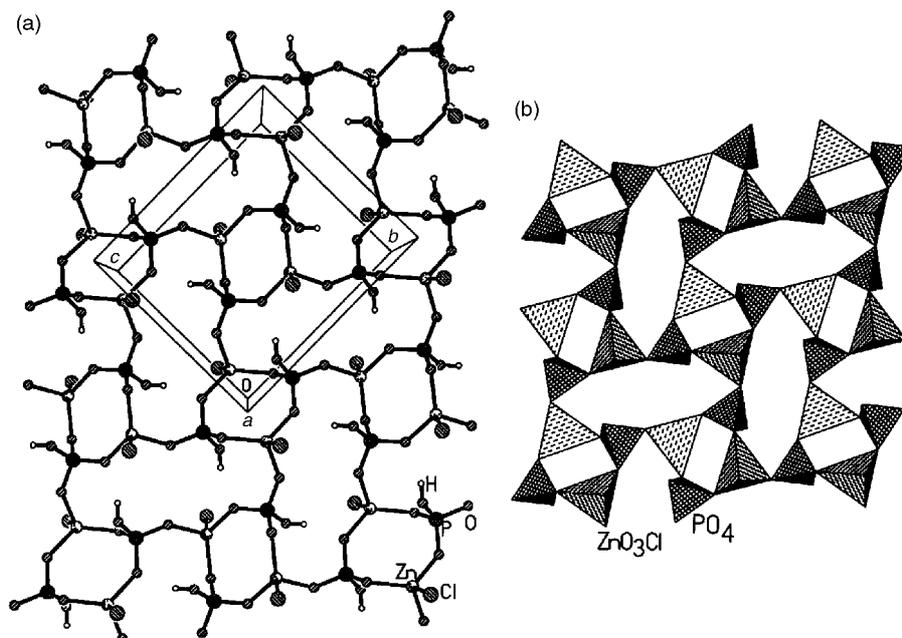


Fig. 1 Structure of $[C_6NH_{14}][ZnCl(HPO_4)]$ along the a axis showing a single layer. Note that the layers are made of 4- and 8-membered rings only. (a) Ball and stick view, (b) polyhedral view.

atoms in some of the tin(II) phosphates.^{6,7} It is clear from Fig. 1–3 that the chlorine atoms are directed perpendicular to the plane of the layer. Similar positioning has been observed for the lone-pair of electrons in the tin phosphate shown in Fig. 4 and 5. In the tin(II) phosphates, the Sn atoms are usually coordinated with three oxygen atoms and occupy the vertex of a trigonal pyramid. The oxygens are, in turn, connected to phosphorus completing the tin phosphate structure. The lone pair of electrons provides the fourth vertex needed for the tetrahedron, in the case of Sn(II). The stereo-active lone pairs manifest themselves in the lattice by creating open space between the two layers in these tin phosphates. In the present compounds, we have a similar situation with three oxygens bonded to the Zn linked to the phosphorus forming the layer arrangement. Since Zn is tetrahedrally coordinated, the fourth connection comes from the chlorine atoms, which occupy an identical position to that of the lone pair of electrons of Sn(II).

Multipoint hydrogen bond interactions are important in the structural stability and, possibly, in the formation of many low-dimensional open-framework solids. In $[C_6NH_{14}][ZnCl(HPO_4)]$, the hydrogens of the amine molecule interact strongly with the framework oxygens, especially with the chlorine. The important hydrogen bond interactions are: $O(3)-H(3)=2.157 \text{ \AA}$, $O(3)-H(3)-N(1)=162.7^\circ$; $Cl(1)-H(2)=2.377 \text{ \AA}$, $Cl(1)-H(2)-N(1)=173.2^\circ$. Furthermore, the terminal $-OH$ group of the $PO_3(OH)$ unit also participates in intra-layer hydrogen bonding ($O(2)-H(20)=1.994 \text{ \AA}$, $O(2)-H(20)-O(4)=161.7^\circ$). The complete hydrogen bond interactions are presented in Table 4. $[C_6NH_{14}][ZnCl(HPO_4)]$, thus, illustrates the importance of multipoint hydrogen bond interactions in the stability of two-dimensional solids.

The structure of $[C_6NH_{14}][ZnCl(HPO_4)]$ has common structural features with many of the previously known layered phosphate materials.^{12–18} The layered phosphates are, in

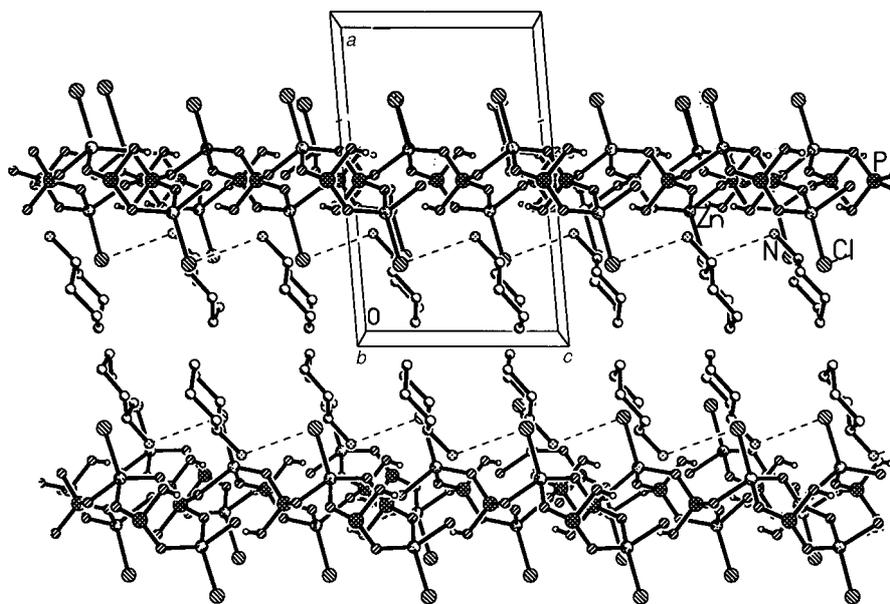


Fig. 2 Structure of $[C_6NH_{14}][ZnCl(HPO_4)]$ along the b axis showing the layer arrangement. Note that the chlorine atoms project into the inter-layer space and two cyclohexylamine molecules reside in the inter-lamellar space.

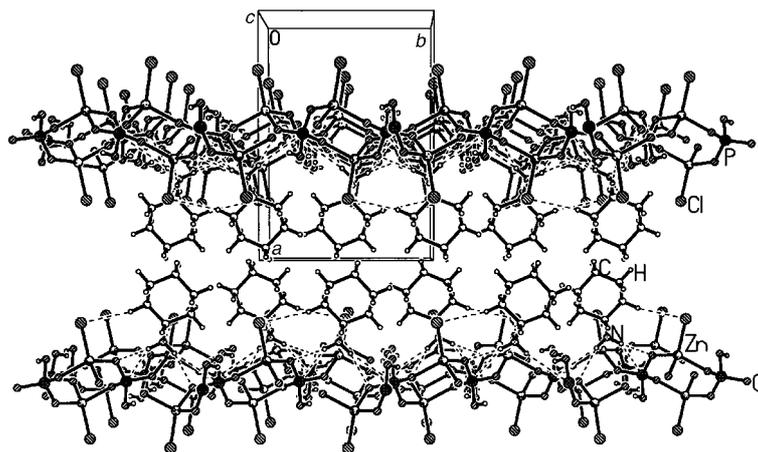


Fig. 3 Structure of $[C_6NH_{14}][ZnCl(HPO_4)]$ along the c axis showing the layer arrangement and the organic molecules. The dotted lines represent the various hydrogen bond interactions (Table 4).

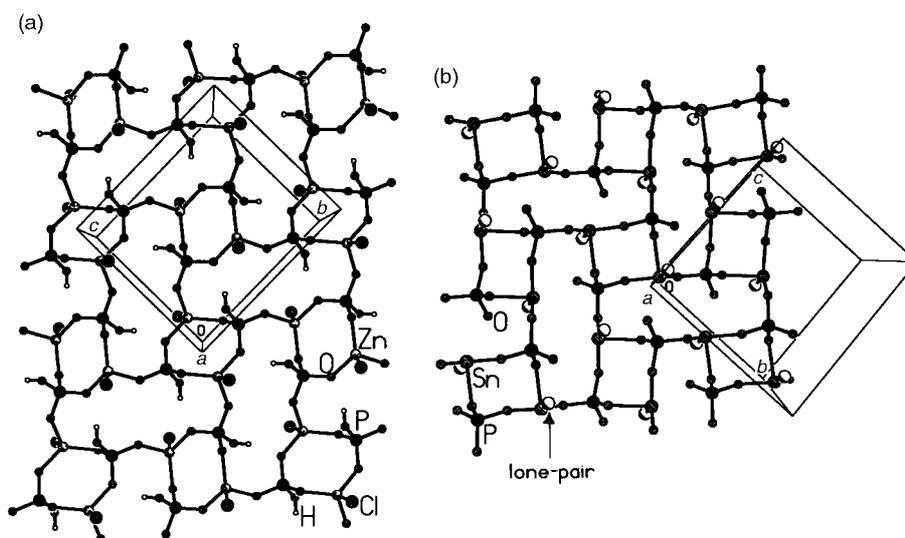


Fig. 4 (a) Structure showing a single layer of a tin(II) phosphate, $[C_3N_2H_{12}]_{0.5}[SnPO_4]$. (b) Structure showing the layer arrangement in $[C_6NH_{14}][ZnCl(HPO_4)]$. Note the identical positions for chlorine atoms and the lone pair of Sn^{II} .

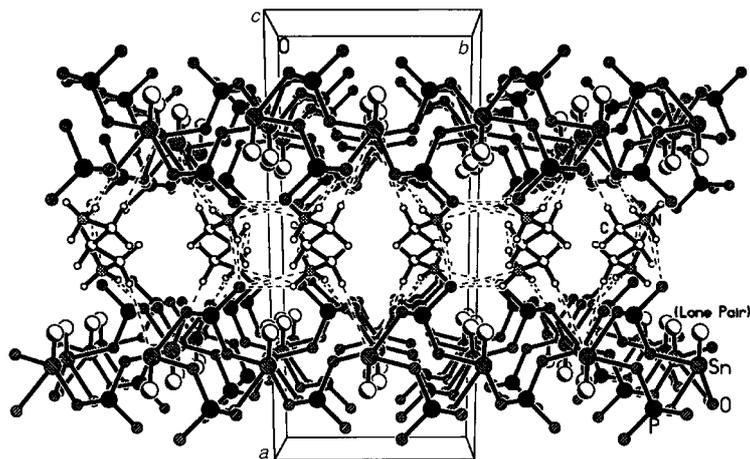


Fig. 5 Structure of the tin(II) phosphate, $[C_3N_2H_{12}]_{0.5}[SnPO_4]$. Note that the lone pair of electrons associated with Sn^{II} points into the layers similar to the chlorine atoms (Fig. 2 and 3).

general, made from the vertex linkage between the MO_x polyhedra and PO_4 tetrahedra and have either terminal double bonded oxygen atoms and/or hydroxyl groups originating from the phosphorus center. The organic amine molecules are usually situated in between these layers. The layers are held together by strong hydrogen bond interactions involving the

framework and the organic moieties. In $[C_6NH_{14}][ZnCl(HPO_4)]$, in addition to the above, there are terminal chlorine atoms which participate in hydrogen bonding.

The synthesis and structure of a layered zinc chlorophosphate, $[C_6NH_{14}][ZnCl(HPO_4)]$, consisting of alternating

inorganic–organic layers has been accomplished. The structure exhibits profound structural influences of the relatively little explored role of the chlorine atoms in the formation of low dimensional solids. The present solid represents yet another example illustrating the importance of multipoint hydrogen bonding in the synthesis and stability of open-framework materials. While the isolation of a two-dimensional solid with strictly alternating ZnO_3Cl and PO_4 moieties provides information about the stereo-chemical consequences of the chlorine atoms, further evaluation is required to exploit the structure-directing influence of this unit in the presence of other organic amines in the synthesis of open-framework materials.

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