

A layered chlorophosphate, $\text{Na}_3[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]$, containing Na^+ ions in the interlamellar space

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Received (in Montpellier, France) 11th April 2001, Accepted 6th June 2001

First published as an Advance Article on the web 17th August 2001

Reaction between $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ under hydrothermal conditions gives rise to a new cadmium chlorophosphate of the formula $\text{Na}_3[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]$, **I**. This material crystallizes in the orthorhombic system with space group *Fmm2* (no. 42). **I** has macroanionic layers of $[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]^{3-}$ with Na^+ ions in the interlamellar space. The discovery of such compounds suggests that metathetic reactions carried out under hydrothermal conditions may provide a novel route for the synthesis of new open-framework structures.

Amongst the large variety of open-framework inorganic structures, the metal phosphates form one of the largest families.¹ Several open-framework metal carboxylates,^{2,3} especially oxalates,⁴ have also been synthesized and characterized in recent years. All these open-framework compounds are generally prepared under hydrothermal conditions, which generally afford the formation of unusual compounds with novel structures. Accordingly, by carrying out hydrothermal reactions of alkali metal oxalates with cadmium chloride an entirely new variety of organic-inorganic hybrid materials with cadmium oxalate layers incorporating extended alkali halide structures has been obtained.⁵ In the light of this interesting finding, we considered it entirely possible to prepare metal phosphates incorporating alkali halide structures. With this objective in mind, we carried out reactions of cadmium chloride with alkali metal phosphates under hydrothermal conditions. By this means, we have synthesized a new sodium cadmium chlorophosphate having the formula $\text{Na}_3[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]$, **I**, which contains macroanionic layers of $[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]^{3-}$ with Na^+ ions in the interlamellar space. Both Cd and Na in **I** have both oxygen and chlorine atoms as near neighbors.

Experimental

Compound **I** was synthesized under mild solvo/hydrothermal conditions. In a typical synthesis 0.2005 g of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ was dissolved in 3 ml of *n*-butanol (without drying) with constant stirring. To this solution 0.2743 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was added and the stirring continued for several hours to get a homogeneous mixture. Finally, 0.06 ml of HCOOH (99%) was added to the homogeneous mixture and stirring continued for another 30 min. The final mixture, with a molar ratio of 1 : 2 : 1.6 : 33 $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ – $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ – HCOOH –*n*-butanol was transferred into a 7 ml PTFE-lined acid digestion bomb and heated at 423 K for 48 h. The resulting product contained only colorless chunky crystals (yield ca. 70% with respect to Cd), suitable for single crystal X-ray diffraction, which were filtered off and washed thoroughly with doubly distilled deionized water. The product was characterized by single crystal X-ray diffraction, powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA).

A suitable single crystal of **I** was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed with a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected using SMART software⁶ at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame) in the 2θ range 3 to 46.5° . The total collected data were reduced using the SAINT⁶ program and the orientation matrix along with the detector and the cell parameters were refined every 40 frames on all the measured reflections. Pertinent experimental details for the structure determination are presented in Table 1.

The structure of **I** was solved by direct methods using

Table 1 Crystal data and structural refinement parameters for $\text{Na}_3[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]$

| | |
|--|--|
| Empirical formula | $\text{H}_{10}\text{Cd}_4\text{Cl}_3\text{Na}_3\text{O}_{24}\text{P}_6$ |
| Formula mass | 1204.80 |
| Crystal system | Orthorhombic |
| Space group | <i>Fmm2</i> |
| <i>a</i> /Å | 14.5678(4) |
| <i>b</i> /Å | 21.26020(10) |
| <i>c</i> /Å | 7.8893(2) |
| α /° | 90.0 |
| β /° | 90.0 |
| γ /° | 90.0 |
| <i>U</i> /Å ³ | 2443.43(9) |
| <i>Z</i> | 16 |
| μ /mm ⁻¹ | 4.313 |
| <i>T</i> /K | 293(2) |
| Total data collected | 2566 |
| Unique data | 919 |
| Observed data [<i>I</i> > 2 σ (<i>I</i>)] | 882 |
| <i>R</i> _{int} | 0.0342 |
| <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0199, <i>wR</i> ₂ = 0.0444 ^a |
| <i>R</i> (all data) | <i>R</i> ₁ = 0.0216, <i>wR</i> ₂ = 0.0450 |

^a $R_1 = \|F_0\| - \|F_c\| / \|F_0\|$; $wR_2 = \{[w(F_0^2 - F_c^2)^2] / [w(F_0^2)^2]\}^{1/2}$, $w = 1 / [\sigma^2(F_0)^2 + (aP)^2 + bP]$, $P = [\max(F_0^2, 0) + 2(F_c)^2] / 3$, where $a = 0.0180$ and $b = 0.0000$ for **I**.

SHELXS-86,⁷ which readily established the heavy atom positions (Cd, P and Na) and facilitated the identification of the light atoms (O and H) from difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS⁸ program. Other effects, such as absorption by the glass fiber, *etc.*, were simultaneously corrected. All the hydrogen positions for the phosphate groups 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. 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-PLUS⁹ package of programs. Details of the final refinements are given in Table 1. The bond distances and angles for **I** are presented in Table 2.

CCDC reference number 166478. See <http://www.rsc.org/suppdata/nj/b1/b103278j/> for crystallographic data in CIF or other electronic format.

The experimental powder pattern of the bulk sample is in good agreement with the simulated pattern generated from the single crystal data.

Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere in the 25–850 °C range.

Results and discussion

The asymmetric unit of **I** contains fourteen non-hydrogen atoms of which twelve belong to the framework (consisting of one Cd, two P, two Cl and seven O), and two Na⁺ ions of the guest (Fig. 1). The asymmetric unit contains one crystallographically distinct Cd atom and two P atoms. Both of the Na⁺ ions sit in special positions with site occupancy factors (SOF) of 0.5 for Na(1) and 0.25 for Na(2). The Cd atom is octahedrally coordinated by four oxygen atoms and two chlorine neighbors.

The structure of **I** is constructed from macroanionic framework layers of $[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]^{3-}$, held together *via* strong ionic bonding interactions with the Na⁺ ions

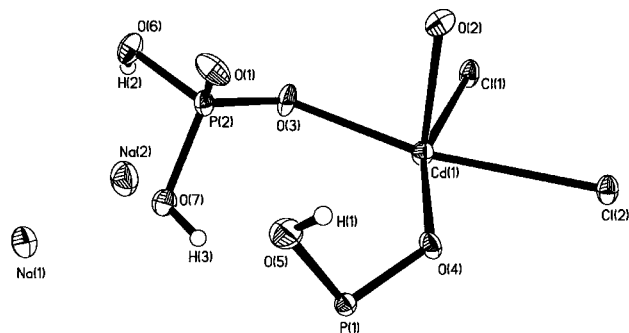


Fig. 1 An ORTEP plot of the asymmetric unit of **I**, $\text{Na}_3[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]$. The thermal ellipsoids are given at 50% probability.

located in the interlamellar space. The inorganic layer consists of a complicated network of CdCl_2O_4 octahedra and $\text{PO}_3(\text{OH})$ as well as $(\text{PO}_2)(\text{OH})_2$ tetrahedra.

The Cd–O distances in **I** are in the range 2.232(5)–2.277(3) Å (av. Cd–O = 2.259 Å) and the two Cd–Cl bonds have an average distance of 2.712 Å. The *trans* O–Cd–O/Cl bond angles are in the range 159.99(11)–179.0(2)° (av. *trans* O–Cd–O/Cl = 168.52°) and the *cis* Cl/O–Cd–O/Cl bond angles are in the range 80.16(11)–112.79(14)° (av. *cis* Cl/O–Cd–O/Cl = 90.03°). The great deviation in bond distances and bond angles from the ideal values for CdO_2Cl_4 octahedra suggests that it is highly distorted. The two phosphorous atoms are tetrahedrally coordinated by their oxygen neighbors with P–O distances in the range 1.496(4)–1.580(6) Å [av. P(1)–O = 1.534, P(2)–O = 1.539 Å]. The O–P–O bond angles are in the range 102.8(2)–116.1(2)° [ave. O–P(1)–O = 109.4, O–P(2)–O = 109.3°]. The Cd atom makes four Cd–O–P bonds to two distinct P atoms along with two Cd– μ -Cl–Cd bonds and one Cd–O–Cd bond. The two P atoms form four P–O–Cd bonds with the remaining P–O vertex being terminal. Out of seven O atoms, four [O(1), O(2), O(3), O(4)] form four Cd–O–P linkages between two P and one Cd atoms and one Cd– μ -O(4)–Cd linkage and the remaining three form terminal P–O bonds. So, one oxygen [O(4)] out of the seven is tri-coordinated, which constitutes 15% of the total O. Of the two Cl atoms, one forms a Cd– μ -Cl(1)–Cd bond and the other

Table 2 Selected bond distances (Å) and bond angles (°) for $\text{Na}_3[\text{Cd}_4\text{Cl}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_4]^a$

| | | | |
|--|------------|--|------------|
| Cd(1)–O(1) ⁱ | 2.232(5) | P(1)–O(2) ^{iv} | 1.516(5) |
| Cd(1)–O(2) | 2.255(4) | P(1)–O(4) | 1.527(5) |
| Cd(1)–O(3) | 2.275(3) | P(1)–O(5) | 1.580(6) |
| Cd(1)–O(4) | 2.277(3) | P(2)–O(1) | 1.496(4) |
| Cd(1)–Cl(1) | 2.6064(12) | P(2)–O(3) | 1.521(4) |
| Cd(1)–Cl(2) | 2.8178(6) | P(2)–O(6) | 1.567(4) |
| P(1)–O(2) ⁱ | 1.516(5) | P(2)–O(7) | 1.575(4) |
| O(1) ⁱ –Cd(1)–O(2) | 179.0(2) | Cd(1)–Cl(2)–Cd(1) ^v | 81.66(2) |
| O(1) ⁱ –Cd(1)–O(3) | 94.4(2) | O(2) ⁱ –P(1)–O(2) ^{iv} | 113.9(3) |
| O(2)–Cd(1)–O(3) | 84.6(2) | O(2) ⁱ –P(1)–O(4) | 111.6(2) |
| O(1) ⁱ –Cd(1)–O(4) | 91.0(2) | O(2) ^{iv} –P(1)–O(4) | 111.6(2) |
| O(2)–Cd(1)–O(4) | 89.3(2) | O(2) ⁱ –P(1)–O(5) | 106.0(2) |
| O(3)–Cd(1)–O(4) | 112.79(14) | O(2) ^{iv} –P(1)–O(5) | 106.0(2) |
| O(1) ⁱ –Cd(1)–Cl(1) | 88.39(12) | O(4)–P(1)–O(5) | 107.3(3) |
| O(2)–Cd(1)–Cl(1) | 91.66(11) | O(1)–P(2)–O(3) | 116.1(2) |
| O(3)–Cd(1)–Cl(1) | 87.20(10) | O(1)–P(2)–O(6) | 109.3(3) |
| O(4)–Cd(1)–Cl(1) | 159.99(11) | O(3)–P(2)–O(6) | 109.4(2) |
| O(1) ⁱ –Cd(1)–Cl(2) | 88.61(12) | O(1)–P(2)–O(7) | 108.1(2) |
| O(2)–Cd(1)–Cl(2) | 92.43(11) | O(3)–P(2)–O(7) | 110.3(2) |
| O(3)–Cd(1)–Cl(2) | 166.59(10) | O(6)–P(2)–O(7) | 102.8(2) |
| O(4)–Cd(1)–Cl(2) | 80.16(11) | P(2)–O(1)–Cd(1) ^{vi} | 139.7(3) |
| Cl(1)–Cd(1)–Cl(2) | 79.82(4) | P(1) ^{vii} –O(2)–Cd(1) | 134.9(3) |
| Cd(1) ⁱⁱ –Cl(1)–Cd(1) | 105.51(7) | P(2)–O(3)–Cd(1) | 124.7(2) |
| Cd(1)–Cl(2)–Cd(1) ⁱⁱⁱ | 159.95(12) | P(1)–O(4)–Cd(1) | 125.87(10) |
| Cd(1)–Cl(2)–Cd(1) ⁱⁱⁱ | 94.84(3) | P(1)–O(4)–Cd(1) ^v | 125.87(10) |
| Cd(1) ⁱⁱⁱ –Cl(2)–Cd(1) ⁱⁱⁱ | 81.67(2) | Cd(1)–O(4)–Cd(1) ^v | 108.0(2) |

^a Symmetry transformations used to generate equivalent atoms: (i) $-x - \frac{1}{2}, y, z + \frac{1}{2}$; (ii) $-x - 1, y, z$; (iii) $-x - 1, -y - 2, z$; (iv) $-x - \frac{1}{2}, -y - 2, z + \frac{1}{2}$; (v) $x, -y - 2, z$; (vi) $-x - \frac{1}{2}, y, z - \frac{1}{2}$; (vii) $-x - \frac{1}{2}, -y - 2, z - \frac{1}{2}$.

interacts with 4 Cd atoms through a Cd- μ_4 Cl-Cd linkage. Three terminal oxygens of the PO₄ moiety are formally terminal -OH groups [P(1)-O(5) = 1.580(6), P(2)-O(6) = 1.567(4), P(2)-O(7) = 1.575(4) Å]. The proton positions were observed in the difference Fourier map and they correspond to terminal P-O moieties. The P-OH bond lengths are also in agreement with the standard literature values for terminal hydroxyl groups; for example, H₃PO₄·0.5H₂O and α -zirconium phosphate have distances of 1.551 and 1.558 Å, respectively.¹⁰ This assignment of proton positions is consistent with the bond valence sum calculation.¹¹ A detailed bond valence calculation also indicated that the valence states of Cd, P and O are +2, +5 and -2, respectively. So, the framework stoichiometry of [CdCl_{0.75}(H₂PO₄)(HPO₄)_{0.5}] produces a net negative charge of 0.75, which is balanced by the two extra framework Na⁺ cations with site occupancy factors of 0.5 and 0.25. Thus, the final formula of the compound has been assigned as Na₃[Cd₄Cl₃(H₂PO₄)₄(HPO₄)₂].

The guest Na(1)⁺ cation is coordinated to four nearest neighbor oxygens and 2 nearest neighbor Cl atoms with distances in the range 2.376–2.420 Å for Na(1)-O and 2.804–2.824 Å for Na(1)-Cl. Na(2) is coordinated to six nearest neighbor oxygens with Na-O distances in the 2.248–2.961 Å range. A Cl atom is present at a distance of 2.862 Å from Na(2). The average Na-O distances are 2.398 and 2.529 Å for Na(1)-O and Na(2)-O, respectively.

The topology of the layer in **I** can be described in terms of a tetrameric cluster of Cd₄Cl₃O₁₂ formed by the edge-sharing of CdCl₂O₄ octahedra through the weakly coordinating Cd- μ_4 -Cl-Cd bonds as shown in Fig. 2(a). H₂PO₄ and HPO₄ groups connect the tetrameric clusters in the *ac* plane to form the layer shown in Fig. 2(b). Such a connectivity leads to the formation of 4- and 10-membered rings within the layer. The layer in **I** can also be described in terms of the strip-like building unit found recently in a Co phosphate.¹² This strip structure is shown in Fig. 3(a). The isolated one-dimensional strip structure here is formed by linkages between three- and four-membered rings wherein the chain of three-membered rings are connected edge-wise by four-membered rings on either side. It can also be considered to consist of two corner-shared linear chains fused together by a three-coordinated oxygen completing the strip. The presence of such a strip-like building unit has also been found in a layered zinc phosphate¹³ where ZnO₄ tetrahedra cap either side of the strip to form a tube as shown in Fig. 3(b). The capping ZnO₄ units join the adjacent tubes to form the layer. The strip-like unit present in **I** is shown in Fig. 3(c). This strip varies slightly from that in the

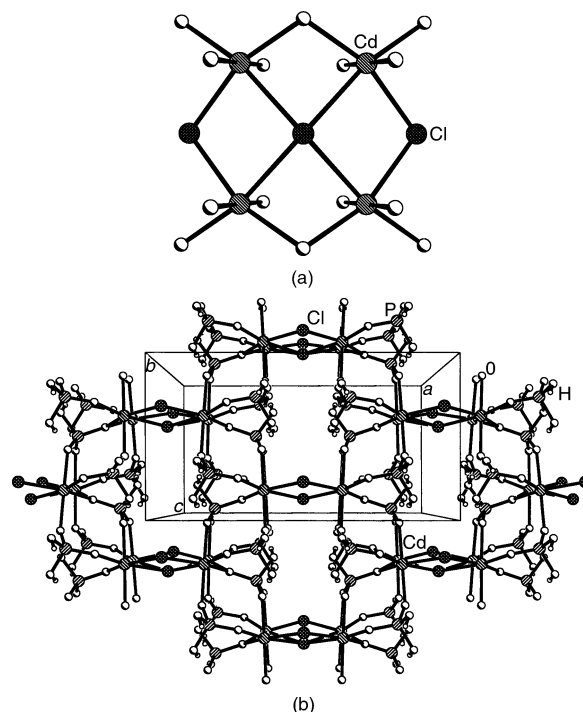


Fig. 2 (a) Tetrameric cluster of Cd₄Cl₃O₁₂. Note the nearly planar tetra-coordinated Cl atom. (b) The layer structure of **I**, projected on to the *ac* plane.

Co and Zn phosphates. The metal atom in **I** has an octahedral coordination, while in the latter two phosphates, the metal atoms are in tetrahedral coordination states. In addition, **I** also contains Cl atoms in the strip, which satisfy the fifth and sixth coordinations of Cd and connect the adjacent strips along the *a* axis to form the layer. This connectivity creates the 12-membered aperture of width 3.208 × 7.730 Å, (nearest O-O and Cl-Cl contacts, not including the van der Waals radii) and also the tetrameric Cd₄ cluster.

The layers in **I** are stacked one above the other along the *b* axis in an AAAA fashion and the interlayer space is occupied by Na⁺ ions as shown in Fig. 4(a). Other than the Na(1)⁺ ions in the interlamellar space, there is also another type of Na⁺ ion [Na(2)] residing in the aperture formed by the 10-membered rings as shown in Fig. 4(b). It is interesting that though the P-OH groups protrude into the interlamellar region there is no evidence of hydrogen bonding. The nearest O...O contact across the layers is 3.476 Å (not including the

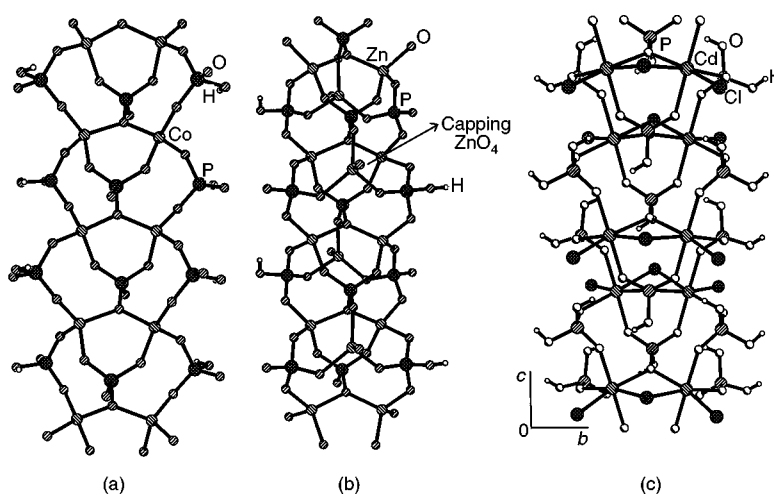


Fig. 3 (a) The strip structure of [C₄N₂H₁₂]_{1.5}[Co(HPO₄)(PO₄)]·H₂O. Note the fusion of two 4-membered corner-shared chains by a three-coordinated oxygen. (b) The strip with capped ZnO₄ tetrahedra forming a one-dimensional tube in [C₆N₄H₂₂][Zn₆(PO₄)₄(HPO₄)₂]. (c) The strip-like structure in **I**.

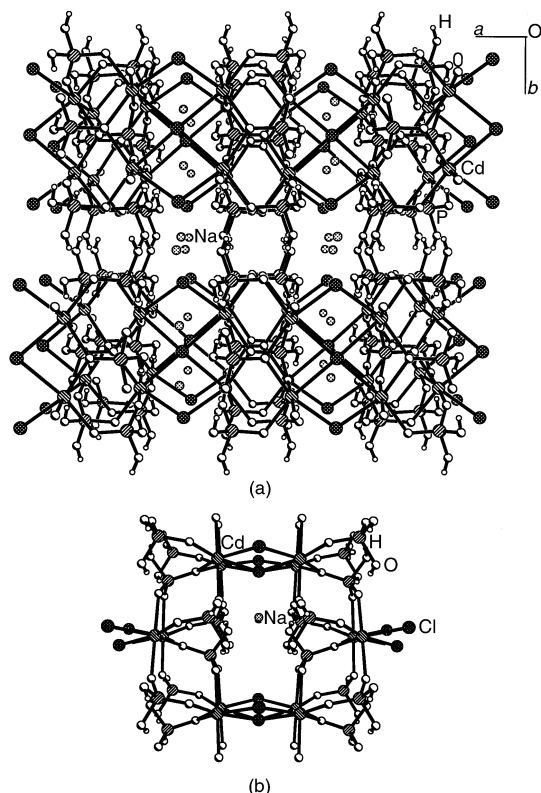


Fig. 4 (a) Stacking of layers along the *b* axis with Na(1)⁺ ions located in the interlayer spacing. Note the absence of hydrogen bonding in the interlayer region. (b) Na(2)⁺ ions residing in the 10-membered aperture.

van der Waals radii). This is in contrast to the structure in potassium intercalated layered cadmium phosphate reported recently,¹⁴ in which both hydrogen bonding and ionic interactions in the interlamellar region stabilize the structure.

There are many noteworthy features in the structure **I**. The presence of the Cd₄Cl₃O₁₂ cluster has been observed for the first time in a cadmium phosphate though various metal-oxygen clusters have been observed in the family of zinc phosphates.¹⁵ The only known cadmium chlorophosphate is a dense phosphate¹⁶ and does not contain any cluster. In the entire literature of open-framework phosphates there are only two examples of chlorophosphates with an open structure where the chlorine occupies a terminal position in the metal coordination.¹⁷ This is the first open-framework cadmium phosphate with Na⁺ ion intercalation and only the second in the family of open-framework cadmium phosphates. The presence of Na⁺ ions in two positions indicates that the location of guest species in the host lattices is governed by very subtle interactions with the host, leading to minimization of the potential energy. Though both chlorine and Na⁺ ions are present in the structure they do not form any recognizable alkali halide lattice in the host structure.⁵ The presence of the strip-like building unit in an octahedral metal coordination framework supports our hypothesis that the strip is also a fundamental building unit in the progressive building-up process of open-framework metal phosphates.¹⁸

The thermogravimetric analysis of **I**, indicates that there are two distinct weight loss steps in the range 25 to 850 °C. The first one, centered around 250 °C, and relatively sharp, corresponds to the loss of -OH groups from the HPO₄ groups,

while a broad tail in the range 300–600 °C corresponds to the loss of Cl atoms. The total weight loss of 16.31% is in good agreement with the theoretical value of 16.44% for the loss of -OH and Cl. The well-ground sample shows a weight loss of 2% at 55 °C due to adsorbed water.

Attempts were made to carry out ion-exchange reactions by reacting **I** with aqueous solutions of KCl and NH₄Cl. Preliminary experiments show that Na⁺ could be exchanged with K⁺ to some extent without loss of the structure. However, after extensive exchange, the structure collapses. The behavior was similar when NH₄⁺ was exchanged with Na⁺.

In conclusion, a layered chlorophosphate of cadmium has been obtained by carrying out the metathetic reaction between NaH₂PO₄ · H₂O and CdCl₂ · H₂O under hydrothermal conditions. This finding suggests that it may indeed be possible to synthesize several new and novel open-framework inorganic structures by such a procedure.

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