

The First Open-Framework Cadmium Phosphate, $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$, with a Layered Structure

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

A layered cadmium phosphate of the formula $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$, **I**, containing six-membered apertures, constituting the first example of an open-framework cadmium phosphate, has been synthesized under hydrothermal conditions. Crystal data: monoclinic, $P2_1/n$ (No. 14), $a = 9.0698(3)$, $b = 6.7341(3)$, and $c = 18.2663(7)$ Å, $\beta = 93.092(1)^\circ$, $V = 1114.03$ Å³, $Z = 4$. The structure consists of a network of CdO_6 octahedra and $PO_3(OH)$ and $PO_2(OH)_2$ tetrahedra forming a spiro unit, which are connected through Cd_2O_2 two-membered rings forming one-dimensional chains. The chains are further connected forming two-dimensional macroanionic layers with six-membered apertures possessing hanging phosphate units on either side of the layer. The layers are stabilized by strong hydrogen bond interactions between the terminal P–OH groups forming pseudo channels in which the charge-compensating extraframework K^+ ions are located. The presence of the spiro unit and the infinite one-dimensional Cd–O–Cd chains, along with the hanging phosphates are noteworthy structural features. © 2001 Elsevier Science

Key Words: spiro units; one-dimensional chains; framework; cadmium phosphate.

INTRODUCTION

A large variety of metal phosphates with open-framework structures have been synthesized and characterized in the past few years (1). These materials are generally prepared under hydrothermal conditions in the presence of organic amines. Of the many varieties of structures that have been synthesized and characterized, those of the zinc phosphates constitute a large family (1–6). Interestingly, there appears to be no report of open-framework cadmium phosphate, although many cadmium phosphates with condensed structures are known (7–9). We have now isolated the first example of an open-framework cadmium phosphate of the formula $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$, **I**, with a layered struc-

ture. A noteworthy feature of this compound is the presence of a spiro unit formed by three-membered rings. The spiro units are connected by Cd_2O_2 two-membered rings forming one-dimensional chains, which are further connected through Cd–O–P linkage to form layers with six-membered apertures. The phosphate tetrahedra, grafted onto the layers, interact with those from the neighboring layers via hydrogen bonds, giving rise to pseudo channels in which the K^+ ions reside.

EXPERIMENTAL

The title compound, $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$, **I**, was synthesized under hydrothermal conditions. In a typical synthesis, 0.4 g of $CdCl_2 \cdot H_2O$ was dissolved in a mixture of 6 ml of $n\text{-C}_4\text{H}_9\text{OH}$ and 0.6 ml of H_2O . To this were added 0.541 g of KH_2PO_4 and 0.24 ml of $HCOOH$ under constant stirring. The reaction mixture was homogenized for 30 min at room temperature. The final mixture, with a composition, $CdCl_2 \cdot H_2O : 2KH_2PO_4 : 3.2HCOOH : 33n\text{-C}_4\text{H}_9\text{OH} : 17H_2O$, was sealed in a 23-ml PTFE-lined stainless steel autoclave (Parr, Moline, IL) and heated at 150°C for 112 h. The resulting product, a crop of platelike crystals, was filtered, washed thoroughly with distilled water, and dried under ambient conditions. The yield of the product was about 30%. **I** can also be synthesized using CdO , in place of $CdCl_2 \cdot H_2O$, employing a composition of $CdO : 2HCl : 2KH_2PO_4 : 3.2HCOOH : 33n\text{-C}_4\text{H}_9\text{OH} : 17H_2O$. The yield in this preparation was about 60%, but the formation of **I** appears to be dependent on the sequence of addition, with the largest yields obtained when KH_2PO_4 was added at the end. The product appears to be completely stable when stored in a sealed vessel in dry air. Initial characterization was carried out using powder X-ray diffraction (XRD, Siefert diffractometer, $CuK\alpha$ radiation, $\lambda = 1.5418$ Å) and thermogravimetric analysis (TGA). The powder XRD pattern indicated that the product was a new material; the pattern was entirely consistent with the structure

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determined using single-crystal X-ray diffraction. A least-squares fit of the powder XRD lines, using the hkl indices generated from single-crystal X-ray data, gave the following cell, $a = 9.0662(4)$, $b = 6.7293(3)$, and $c = 18.2651(8)$ Å, $\beta = 93.07(4)^\circ$, which is in good agreement with that determined using single-crystal XRD. Powder data for **I** are listed in Table 1.

Thermogravimetric analysis (TGA) of **I** was carried out in a nitrogen atmosphere (50 ml/min) from room temperature to 700°C using a heating rate of 10°C min⁻¹. The results indicate a gradual mass loss of ~6.7% in the temperature range 250–450°C, indicating the nominal elimination of the hydroxyl groups from the PO₃OH and PO₂(OH)₂ units (calcd 6.72%). The calcined product was poorly crystalline with weak diffraction lines that appear to correspond to the condensed cadmium phosphate, Cd₃P₆O₁₈ (JCPDS: 39-0165); it is likely that the amorphous component might contain some potassium oxide.

TABLE 1
X-Ray Powder Data for **I**, K₄[Cd₃(HPO₄)₄(H₂PO₄)₂]

h	k	l	$2\theta_{\text{obs}}$	$\Delta(2\theta)^a$	d_{calc}	$\Delta(d)^b$	I_{rel}^c
0	0	2	9.612	-0.086	9.119	0.082	100.0
0	1	1	14.086	0.058	6.313	-0.026	61.6
1	1	-1	17.058	0.087	5.224	-0.026	34.4
0	0	4	19.49	0.023	4.560	-0.006	28.4
2	1	2	26.065	0.009	3.420	-0.001	30.2
2	1	-3	27.326	-0.023	3.261	0.003	38.7
1	2	0	28.287	-0.009	3.154	0.001	45.13
2	1	3	28.467	-0.016	3.134	0.001	47.38
0	0	6	29.368	-0.013	3.040	0.001	39.15
3	0	-1	29.728	-0.019	3.003	0.002	23.19
1	2	-3	31.717	0.002	2.821	0.000	16.95
3	0	-3	32.4	-0.005	2.763	0.000	26.43
2	2	0	33.151	-0.024	2.700	0.002	27.93
3	0	3	33.84	-0.022	2.647	0.002	16.20
3	1	2	34.472	-0.009	2.601	0.001	16.21
	1	-6	37.204	-0.009	2.416	0.001	8.48
2	1	6	38.945	0.009	2.313	0.000	7.20
0	0	8	39.516	-0.011	2.280	0.000	19.45
0	3	1	40.477	-0.040	2.226	0.002	6.73
1	3	0	41.437	-0.035	2.177	0.002	10.22
2	2	5	42.278	0.006	2.138	0.000	13.97
1	3	2	42.79	-0.035	2.112	0.001	7.98
3	1	-6	43.21	-0.028	2.092	0.002	8.48
1	2	-7	44.68	-0.017	2.027	0.001	7.48
2	2	6	45.641	-0.003	1.988	0.000	17.46
1	3	4	46.572	0.125	1.955	-0.005	15.21
3	0	7	47.323	0.026	1.922	-0.001	11.47
2	3	3	47.983	-0.028	1.895	0.001	10.47
4	2	0	48.464	-0.008	1.878	0.000	15.21
5	1	0	52.368	0.046	1.748	-0.001	9.98
3	0	-9	53.055	-0.009	1.726	0.000	8.98
1	2	-9	53.388	0.119	1.720	-0.004	12.97
1	2	9	54.169	-0.088	1.691	0.002	9.22

$$^a 2\theta_{\text{obs}} - 2\theta_{\text{calc}} \quad ^b d_{\text{obs}} - d_{\text{calc}} \quad ^c 100 \times I/I_{\text{max}}$$

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 on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoK 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) in the 2θ range 4.46 to 46.5°. Pertinent experimental details for the structure determinations are presented in Table 2.

An absorption correction based on symmetry equivalent reflections was applied using the SADABS program (10). Other effects, such as absorption by the glass fiber, were simultaneously corrected. The structure was solved by direct methods using SHELXS-86 (11), which readily revealed all the heavy atom positions (K, Zn, and P) and enabled us to locate the other nonhydrogen positions from the Fourier difference maps. All the hydrogen positions for both compounds were initially located in the difference Fourier maps and were refined isotropically. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all nonhydrogen 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 (12) package of programs. Details of the final refinements are given in Table 2. The final atomic coordinates, and selected bond distances for **I**, are presented in Tables 3 and 4.

RESULTS AND DISCUSSION

The asymmetric unit of **I** contains 17 nonhydrogen atoms, of which 15 atoms belong to the framework and 2 to the guest K⁺ ions. The asymmetric unit contains two crystallographically distinct cadmium atoms and three independent phosphorus atoms. Of the two distinct Cd atoms, one [Cd(1)] sits in the special position with a site occupancy factor (SOF) of 0.5. Of the 12 oxygen atoms, three [O(2), O(3) and O(5)] have three-fold coordination linking two Cd and one P atoms (25%). The three-coordinated oxygen atom gives rise to two- (Cd₂O₂) and three-membered (Cd₂PO₃) rings through Cd–O–Cd and Cd–O–Cd/P linkages.

The cadmium atoms are octahedrally coordinated by the oxygen neighbors with Cd–O distances in the range 2.226(5)–2.615(5) Å (av. Cd(1)–O = 2.276; Cd(2)–O = 2.340 Å). The O–Cd–O bond angles are in the range 77.4(2)–180.0° (av. O–Cd(1)–O = 108.0, O–Cd(2)–O = 102.09°). The two Cd atoms make nine Cd–O–P bonds to three distinct P atom neighbors with a fairly wide spread of angles (av. Cd–O–P bond angle, 120.5°). The phosphorus atoms make six P–O–Cd linkages. The P–O bond distances are in the range of 1.509(5)–1.603(7) Å (av. P(1)–O = 1.538;

TABLE 2
Crystal Data and Structure Refinement Parameters for I,
 $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$

Empirical formula	$H_4Cd_{1.5}K_2O_{12}P_3$
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal size (mm)	$0.06 \times 0.06 \times 0.1$
a (Å)	9.0698(3)
b (Å)	6.7341(3)
c (Å)	18.2663(7)
α (°)	90.0
β (°)	93.0920(10)
γ (°)	90.0
Volume (Å ³)	1114.03(8)
Z	4
Formula mass	535.74
ρ (g cm ⁻³)	3.194
λ (MoK α) Å	0.71073
μ (mm ⁻¹)	4.126
Temperature of measurement (K)	293(2)
θ range (°)	2.23 to 23.25
Total data collected	4449
Index ranges	$-7 \leq h \leq 10, -6 \leq k \leq 7,$ $-19 \leq l \leq 20$
Unique data	1600
Observed data [$I > 2\sigma(I)$]	1452
R_{int}	0.0354
Refinement method	Full-matrix least-squares on $ F^2 $
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0328,^a wR_2 = 0.0752^b$
R (All data)	$R_1 = 0.0399, wR_2 = 0.0777$
Goodness of fit (S)	1.165
No. of variables	185
Largest difference map peak and hole (e Å ⁻³)	0.611 and -0.738

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2(F_c^2)^2] / 3$, where $a = 0.0182$ and $b = 7.5537$.

P(2)–O = 1.541; P(3)–O = 1.546 Å) and the O–P–O bond angles are in the range 105.9(3)–113.1(3)° (av. O–P–O = 109.4°). Assuming the valences of Cd, P, and O to be +2, +5, and –2, respectively, the framework stoichiometry of $Cd_{1.5}(PO_4)_3$ creates a net negative charge of –6. Taking into account the presence of two K^+ ions, the excess negative charge of –4 can be balanced by protonation of the PO_4 tetrahedra. One hydrogen position for each of the oxygens, O(7), O(8), O(11), and O(12), has been observed in the difference Fourier maps. Thus, P(1)–O(7), P(1)–O(8), P(2)–O(11), and P(3)–O(12), with distances of 1.544(6), 1.562(6), 1.577(6), and 1.603(7) Å, respectively, are all P–OH units. The second terminal P–O linkages, in the case of P(1) and P(2) with distances of P–O(9) = 1.509(6) and P–O(10) = 1.527(6) Å, are P = O units. The extraframework cation, $K(1)^+$, is coordinated to eight nearest-neighbor oxygen atoms, while K(2) is coordinated to seven nearest-neighbor oxygens with distances of less than 3.1 Å, which is the upper limit for significant

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for I, $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$

Atom	x	y	z	$U(eq)^a$
Cd(1)	0	0	0	11(1)
Cd(2)	3624(1)	1856(1)	–36(1)	13(1)
K(1)	5227(2)	4870(3)	–1832(1)	24(1)
K(2)	282(2)	–4904(3)	1169(1)	24(1)
P(1)	2433(2)	808(3)	1549(1)	13(1)
P(2)	2252(2)	1016(3)	–1554(1)	12(1)
P(3)	2877(2)	6680(3)	–114(1)	10(1)
O(1)	1270(5)	7158(7)	–3(3)	16(1)
O(2)	1765(5)	1269(8)	793(2)	14(1)
O(3)	1536(5)	1415(8)	–837(3)	15(1)
O(4)	3429(6)	4928(8)	346(3)	18(1)
O(5)	6069(5)	1529(7)	–3(3)	15(1)
O(6)	3912(6)	1480(8)	–1446(3)	19(1)
O(7)	4119(7)	1133(9)	1547(3)	26(2)
O(8)	2096(7)	–1407(8)	1730(3)	30(2)
O(9)	1846(6)	2207(9)	2109(3)	28(1)
O(10)	1968(6)	–1084(8)	–1845(3)	18(1)
O(11)	1517(6)	2518(9)	–2127(3)	21(1)
O(12)	2967(7)	6004(11)	–951(4)	23(2)

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

K···O interaction (13). The K–O distances are in the range of 2.687(5)–3.114(5) Å (av. K(1)–O = 2.879 and K(2)–O = 2.923 Å). The various geometrical parameters observed in I are in the ranges expected for this type of bonding and agree well with the values of similar compounds reported in the literature (13). Bond length/bond strength calculations (14) also agree with the above formalism and show valence sums of 2.2 and 1.96 for Cd(1) and

TABLE 4
Selected Bond Distances for I, $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$

Moiety	Distance (Å)	Moiety	Distance (Å)
Cd(1)–O(1) # 5	2.234(5)	P(1)–O(2)	1.509(5)
Cd(1)–O(1) # 3	2.234(5)	P(1)–O(9)	1.509(6)
Cd(1)–O(2)	2.268(5)	P(1)–O(7)	1.544(6)
Cd(1)–O(2) # 4	2.268(5)	P(1)–O(8)	1.562(6)
Cd(1)–O(3) # 4	2.327(5)	P(2)–O(3)	1.518(5)
Cd(1)–O(3)	2.327(5)	P(2)–O(10)	1.527(6)
Cd(2)–O(4)	2.193(5)	P(2)–O(6)	1.540(5)
Cd(2)–O(5)	2.226(5)	P(2)–O(11)	1.577(6)
Cd(2)–O(5) # 2	2.296(5)	P(3)–O(1)	1.517(5)
Cd(2)–O(3)	2.349(5)	P(3)–O(4)	1.517(6)
Cd(2)–O(2)	2.360(5)	P(3)–O(5) # 1	1.547(5)
Cd(2)–O(6)	2.615(5)	P(3)–O(12)	1.603(7)

Note. Symmetry transformations used to generate equivalent atoms: # 1, $-x + 1, -y + 1, -z$; # 2, $-x + 1, -y, -z$; # 3, $x, y - 1, z$; # 4, $-x, -y, -z$; # 5, $-x, -y + 1, -z$.

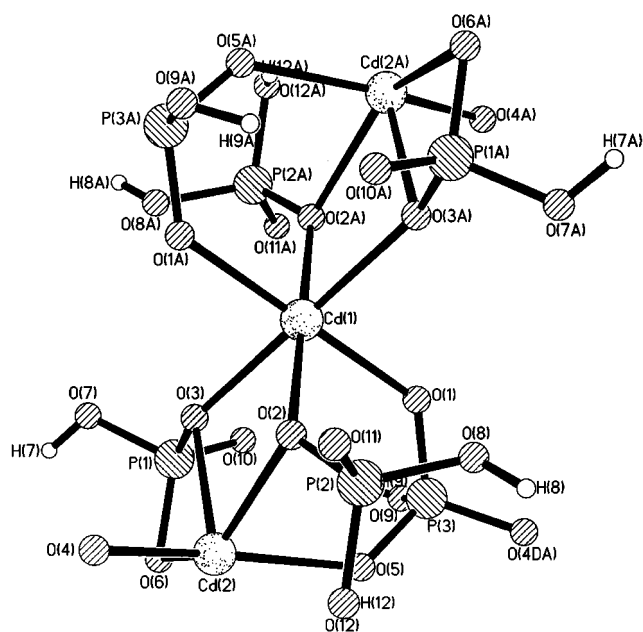


FIG. 1. Basic building unit in I.

Cd(2); 5.05, 4.92, and 4.86 for P(1), P(2), and P(3); and 0.988 and 0.938 for K(1) and K(2), respectively. The bond valance sums for the oxygens O(1)–O(6) are in the range 1.88–2.03 and for O(7)–O(12) in the range 1.24–1.59. These typically indicate the valence states of the various species. The selected bond distances are presented in Table 4.

The framework structure of I consists of a network of CdO_6 octahedra and $\text{PO}_3(\text{OH})$ and $\text{PO}_2(\text{OH})_2$ tetrahedra connected through their vertices forming a layered architecture, with the K^+ ions being located in the interlamellar region. The connectivity between the CdO_6 octahedra and the $\text{P(3)O}_3(\text{OH})$ tetrahedra form a basic building unit. The $\text{P(1)O}_3(\text{OH})$ and $\text{P(2)O}_2(\text{OH})_2$ tetrahedra are grafted onto this, through their three-coordinated oxygen atoms, giving rise to a spiro unit which forms the basic building link, as shown in Fig. 1. The three-coordinated oxygen atoms also give rise to two-membered Cd_2O_2 rings within the spiro unit. The spiro units are linked to each other via another two-membered Cd_2O_2 ring, forming one-dimensional chains as shown in Figs. 2a and 2b. It may be noted that the chain units present in I resemble those in tancoite (15), connected through Cd_2O_2 units. Variants of such chain units consisting of one or two octahedra and one, two, or four tetrahedra or triangles are observed commonly in many of the naturally occurring minerals (16). The connectivity between the spiro unit in I is such that it forms infinite Cd-O-Cd chains (CdO_6 octahedra connected through the edges). To our knowledge, this is the first time such Cd-O polymeric chains have been observed in cadmium phosphates. The chain units are connected with each other through a four-membered ring of the composition

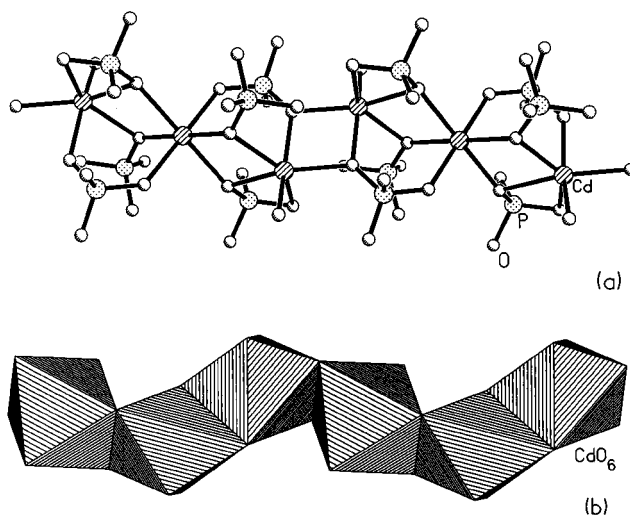


FIG. 2. (a) Connectivity between the basic building units in I. Note that the connectivity is via the Cd_2O_2 two-membered rings. (b) The polyhedral connectivity between CdO_6 octahedra in I forming the infinite Cd-O-Cd chains.

$[\text{Cd}_2\text{P}_2\text{O}_4]$ (via Cd-O-P bonds), giving rise to a macro-anionic two-dimensional layer structure with six-membered apertures in the ab plane (Fig. 3). The $\text{P(1)O}_3(\text{OH})$ and $\text{P(2)O}_2(\text{OH})_2$ tetrahedra, connected to the Cd center through the three-coordinated oxygen atoms, hang from the layer into the interlamellar region and interact with the phosphate tetrahedra of the neighboring layer through hydrogen bonds forming pseudo channels ($7.3 \times 3.9 \text{ \AA}$, shortest O–O distances not including van der Waals radii) (Fig. 4). The charge-compensating K^+ ions, located in the inter-

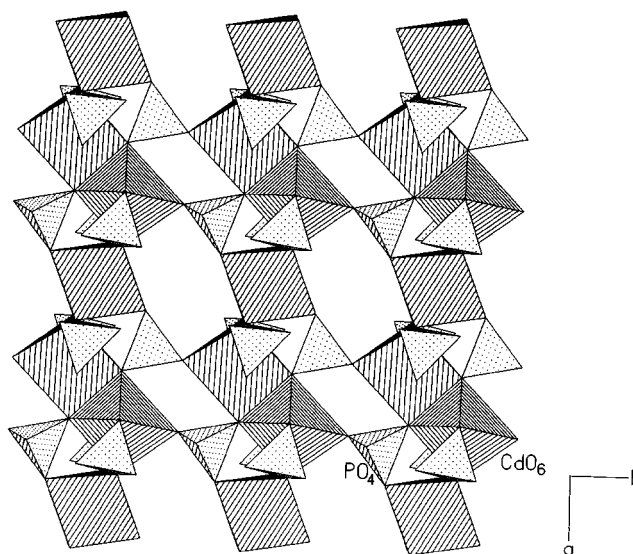


FIG. 3. Polyhedral view of a single layer in I. Note the connectivity forms a six-membered aperture within the layer.

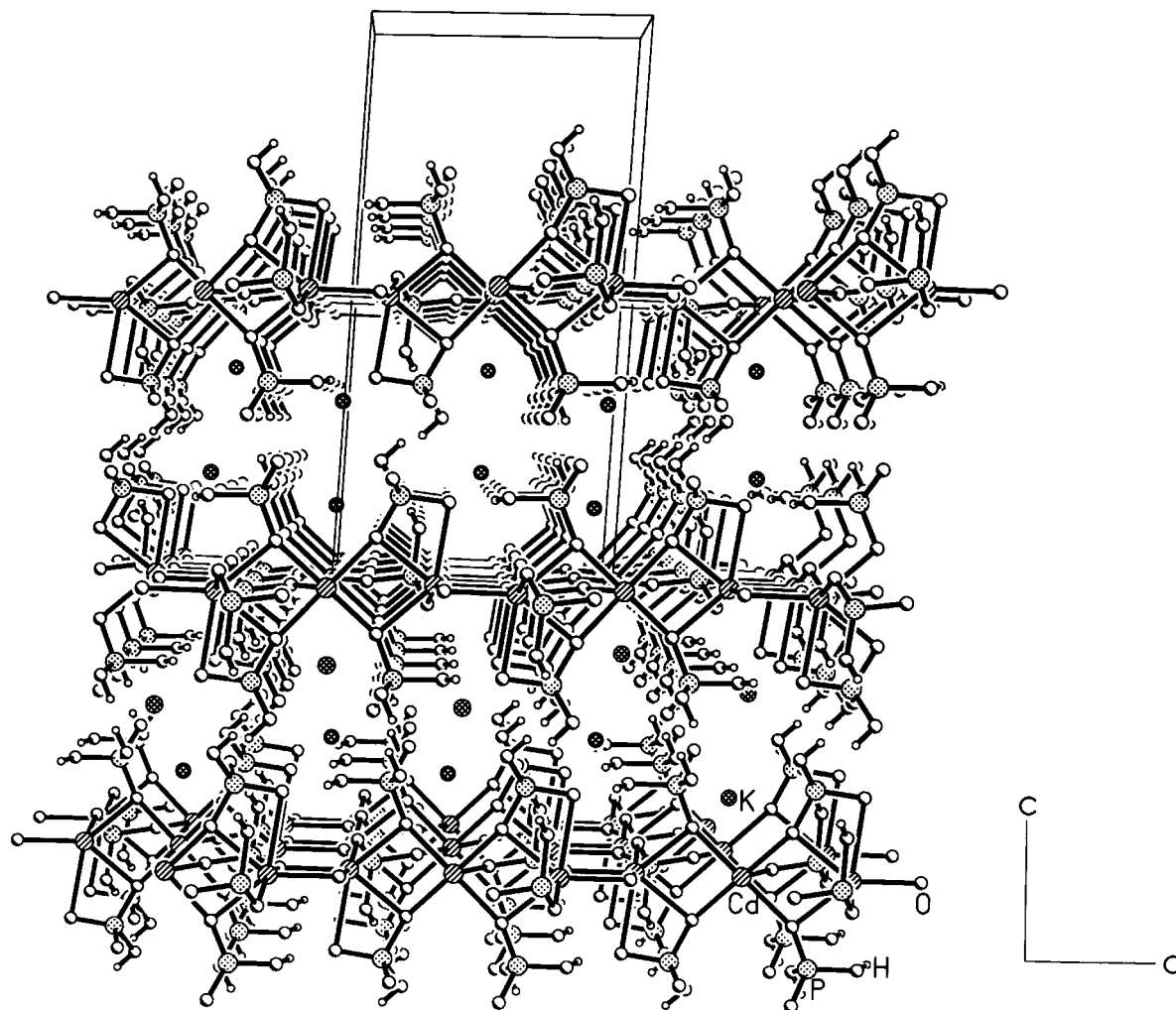


FIG. 4. Position of K^+ ions in the interlamellar region.

lamellar region, are positioned in the pseudo channels as shown in Fig. 4.

It may be noted that **I** possesses a relatively large number of three-membered rings in its structure, in addition to the unusual two-membered Cd_2O_2 rings. This is due to the presence of three three-coordinated oxygen atoms (25%), and leads to the formation of infinite one-dimensional $Cd-O-Cd$ chains. Such three-fold coordination of the oxygen atoms in the $Cd-O-Cd$ bridge is an electrostatic valence requirement of the bridging oxygen atoms, leading to the formation of odd-numbered rings. As is typical of such solids, the present structure is stabilized by $O-H \cdots O$ hydrogen bond interactions between the terminal $PO_2(OH)_2$ units. Typically, the $H \cdots O$ distances are less than 2.0 Å and the $O-H \cdots O$ bond angles are nearly planar ($\sim 170^\circ$). A list of hydrogen bond interactions is presented in Table 5.

It is instructive to compare the structure of **I** with those of similar compounds. Thus, the hourglass-type spiro unit in

I is somewhat comparable to the spiro unit present in the zincophosphates of the formula $M_3Zn_4O(PO_4)_3 \cdot nH_2O$ (17). In the zincophosphates, the network contains a pair of three-membered rings forming the spiro units. Eight-membered apertures result from the connectivity between the spiro units, which propagate into a three-dimensional structure providing a eight-membered channel. Extraframework

TABLE 5
Important Hydrogen Bond Interactions in **I**,
 $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$

Moiety	(H \cdots A), Å	(D \cdots A), Å	(D-H \cdots A), °
O(7)-H(10) \cdots O(6)	1.7870(2)	2.5214(1)	173.82(2)
O(8)-H(20) \cdots O(9)	1.2001(2)	2.4627(3)	173.41(3)
O(11)-H(30) \cdots O(10)	1.7403(3)	2.5654(2)	167.86(1)
O(12)-H(40) \cdots O(10)	2.0587(1)	2.6778(4)	174.72(2)

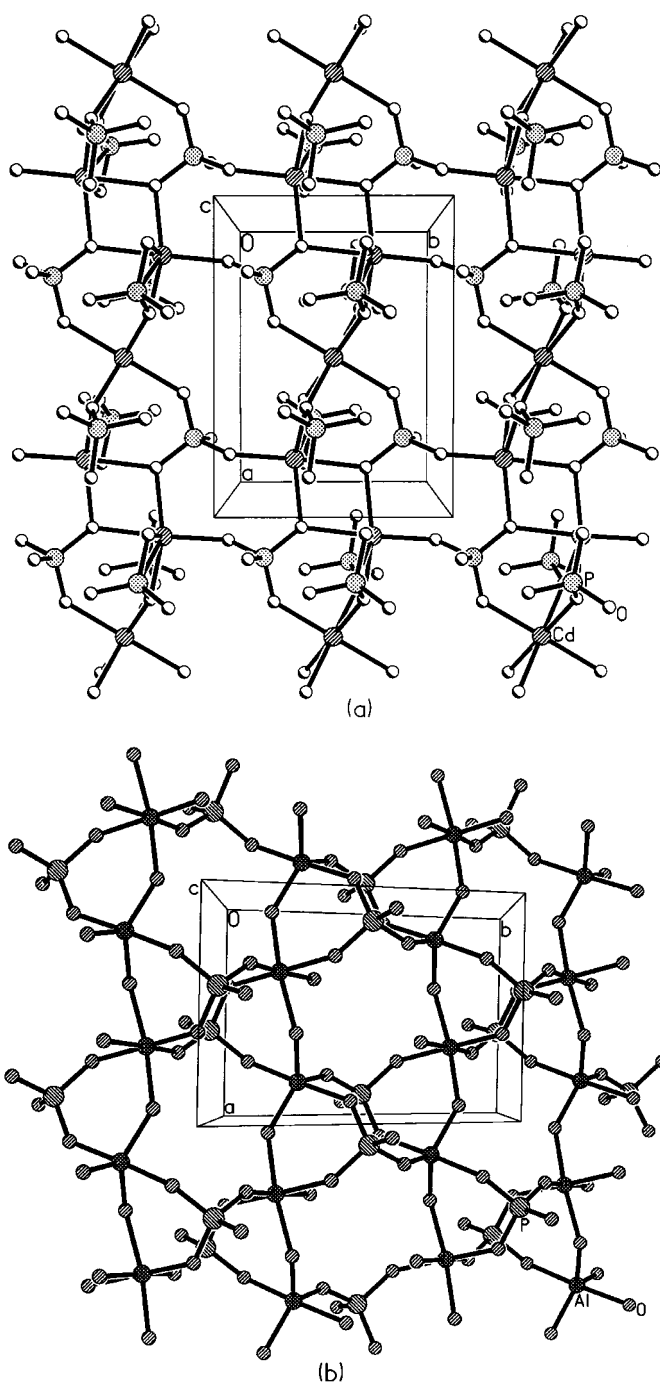


FIG. 5. (a) Single layer in **I**. (b) Layer architecture observed in the aluminum phosphate, $[\text{C}_2\text{N}_2\text{H}_{10}][\text{Al}_2(\text{OH})_2\text{H}_2\text{O}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$. Note the differences in the connectivity between the spiro-like units.

cations and water molecules fill these channels. In **I**, however, there are no extraframework water molecules and the charge-compensating cations reside in the pseudo channels formed by hydrogen bond interactions between the layers. The structure of **I** is closely related to the layered aluminum

phosphate described recently (18). In the layered aluminum phosphate, $[\text{C}_2\text{N}_2\text{H}_{10}][\text{Al}_2(\text{OH})_2\text{H}_2\text{O}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$, the one-dimensional tancoite chains are connected through four-membered rings, forming a layer possessing six-membered apertures, with the charge-compensating protonated organic amine situated between the layers. In **I**, the spiro units form an interrupted tancoite chain, and are connected to each other via four-membered rings, forming the layer possessing six-membered apertures, with the K^+ ions situated between the layers. The layer arrangements of the aluminum phosphate and **I** are presented in Fig. 5. **I** is also related to the aluminum diphosphonate, $\text{Al}_2[\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3](\text{H}_2\text{O})\text{F}_2 \cdot \text{H}_2\text{O}$ (19). In the aluminum diphosphonate, the connectivity between the AlO_4F_2 octahedra gives rise to spiro-like units, which form interrupted tancoite chains connected through the ethylenediphosphonate groups to give rise to eight-membered apertures. The spiro unit appears to be good linkers, just as the oxalates and higher dicarboxylates (20, 21).

CONCLUSIONS

A new open-framework cadmium phosphate, $\text{K}_4[\text{Cd}_3(\text{HPO}_4)_4(\text{H}_2\text{PO}_4)_2]$, **I**, has been synthesized, for the first time, under hydrothermal conditions. The presence of a large number of three-coordinated oxygen atoms in **I** gives rise to infinite Cd-O-Cd chains. Connectivity amongst the CdO_6 , $\text{PO}_3(\text{OH})$, and $\text{PO}_2(\text{OH})_2$ polyhedral units results in a layered architecture with hanging $\text{PO}_2(\text{OH})_2$ units pointing into the interlamellar region and forming pseudo one-dimensional channels in which the K^+ ions reside.

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