pyroxenes in that the symmetries of both modifications of $Ca_2Nb_2O_7$ belong to the subgroup of the space group $Cmcm$ of this imaginary prototype.

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Phosphate Ion with Three 'Symmetric' Hydrogen Bonds: The Structure of Ca₂(NH₄)H₇(PO₄)₄.2H₂O

BY SHOZO TAKAGI, M. MATHEW AND W. E. BROWN

American Dental Association Health Foundation Research Unit, National Bureau of Standards, Washington, DC 20234, USA

Abstract

$Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 5\cdot693$ (2), $b = 12\cdot299$ (4), $c = 6\cdot297$ (2) Å, $\alpha = 103\cdot98$ (2), $\beta = 115\cdot10$ (2), $\gamma = 84\cdot22$ (2)° $[\lambda (Mo K\alpha_1) = 0\cdot70932$ Å$]$ at room temperature with $Z = 1$. The structure was refined by the method of least squares to $R(F) = 0\cdot048$; $R_w(F) = 0\cdot050$ for 904 reflections with $F_o > 2\sigma(F_o)$. The structure contains $[CaH_2PO_4]^+$ chains held together by Ca$\cdots$O bonds to form corrugated Ca–P(2)O$_4$ sheets analogous to those found in $Ca(H_2PO_4)_2.H_2O$ and several other calcium phosphates. Between these sheets are $[H_3(PO_4)_2]^{3-}$ ions, water molecules and $[NH_4]^+$ ions. Three of the O atoms of the P(1)O$_4$ group between the corrugated sheets are hydrogen bonded across three crystallographic centers of symmetry $[O(11)\cdots H\cdots O(11); O(13)\cdots H\cdots O(13); O(14)\cdots H\cdots O(14)]$ forming an infinite $[H_3(PO_4)_2]^{3-}_n$ sheet structure. The water molecule is bonded to a $[CaH_2PO_4]^+$ sheet and to a $[H_3(PO_4)_2]^{3-}_n$ sheet by multiple hydrogen bonds. The $[NH_4]^+$ ion is disordered across a center of symmetry. The Ca atom is coordinated to eight O atoms with Ca$\cdots$O distances in the range $2\cdot319$ to $2\cdot687$ Å.

Introduction

Gypsum, $CaSO_4.2H_2O$, contains a corrugated sheet-type structure (Wooster, 1936) which is common to a number of calcium phosphates, *e.g.* $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971), $CaHPO_4.2H_2O$ (Curry & Jones, 1971), and $CaHPO_4$ (Dickens, Bowen & Brown, 1971). Similar sheet-type structures have been proposed for a number of other calcium phosphates, namely $CaCl(H_2PO_4).H_2O$, $Ca(NO_3)(H_2PO_4).H_2O$, $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ and $Ca_2KH_7(PO_4)_4.2H_2O$ (Brown, Smith, Lehr & Frazier, 1958). The last two, which are apparently isomorphous, were erroneously assigned the formulae $Ca_9(NH_4)_4H_{32}(PO_4)_{18}.10H_2O$ and $Ca_9K_4H_{32}(PO_4)_{18}.10H_2O$ (Flatt, Brunisholz & Chapuis-Gottreux, 1951; Flatt, Brunisholz & Hotz, 1956); the formulae $Ca_2(NH_4)H_7(PO_4)_4$ 2H₂O and $Ca_2KH_7(PO_4)_4.2H_2O$ were proposed by Brown *et al.* (1958).

The fact that sheet-like structures are common to several calcium phosphates indicates that these sheet-type structures are very stable in spite of the differing composition of the material between the sheets. As part of a program to study the factors contributing to the stability of the corrugated sheet and the nature of the

hydrogen bonding, we have determined the crystal structure of $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$.

Experimental

Crystals of $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$ were prepared by Flatt's 'second method' (Flatt *et al.*, 1951). The Laue symmetry, refractive indices and the cell parameters agreed with the reported values (Brown *et al.*, 1958). New cell parameters were obtained by a least-squares fit of 2θ values of twelve reflections in the range 28–40° measured at both positive and negative settings by automatically centering reflections on a four-circle diffractometer with graphite-monochromatized Mo $K\alpha_1$ radiation ($\lambda = 0.70932$ Å). The diffractometer-controlling programs were those of Lenhert (1975). Crystal data are as follows: triclinic with $a = 5.693$ (2), $b = 12.299$ (4), $c = 6.297$ (2) Å, $\alpha = 103.98$ (2), $\beta = 115.10$ (2), $\gamma = 84.22$ (2)°, cell volume = 387.44 Å^3; space group $P\bar{1}$ with $Z = 1$; $D_c = 2.234$, $D_m = 2.19$ Mg m^{-3} (Brown *et al.*, 1958).

A crystal of dimensions $0.02 \times 0.08 \times 0.11$ mm mounted perpendicular to the plate was used for the data collection. All 1206 reflections in the hemisphere ($\pm h, -k, \pm l$) with $2\theta \le 45°$ were measured using the θ–2θ scan technique. The scan rate was $0.5°$ min^{-1} and backgrounds were counted for 10 s at each end of the scan range. Three standard reflections were measured every 30 reflections and their intensities varied randomly by $\simeq 10\%$. The data were scaled to allow for this fluctuation and were corrected for Lorentz and polarization factors but not for absorption ($\mu_{MoK\alpha} = 1.220$ mm^{-1}). These were merged into 1008 independent reflections of which 904 with $F_o > 2\sigma(F_o)$ were considered observed and used in the structure analysis.

There is only one $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$ formula unit per unit cell. The space group was assumed initially to be $P1$ since this would not require any symmetry restrictions on the $[NH_4]^+$ ion. The positions of two Ca and four P atoms were deduced from a three-dimensional Patterson map. The remaining atoms were located in subsequent Fourier syntheses. Initial refinements reduced $R = \sum\|F_o| - |F_c\|/\sum |F_o|$ to 0.15, but the correlation coefficients were very large. Closer examination of the structure then revealed a center of inversion. The space group was therefore assumed to be $P\bar{1}$ and was confirmed by the successful structure analysis. The N atom was statistically disordered across the center of inversion.

Refinement was by full-matrix least squares using the program *RFINE4* (Finger & Prince, 1975). The quantity minimized was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2$. The positions of the H atoms except for those of $[NH_4]^+$ were obtained from a difference Fourier synthesis. The non-hydrogen atoms

Table 1. *Fractional atomic coordinates in* $Ca_2(NH_4)$-$H_7(PO_4)_4 \cdot 2H_2O$

The parameters are multiplied by 10^4 and 10^3 for non-hydrogen and H atoms, respectively. E.s.d.'s given in parentheses refer to the least significant digit.

	x	y	z
Ca	−20 (2)	982 (1)	2976 (2)
P(1)	1524 (3)	6398 (1)	3811 (3)
P(2)	4970 (3)	−961 (1)	2110 (3)
O(11)	863 (10)	5995 (4)	1091 (8)
O(12)	1414 (7)	7653 (3)	4383 (7)
O(13)	4255 (8)	6000 (4)	5287 (8)
O(14)	−500 (9)	5901 (4)	4308 (9)
O(21)	2455 (7)	−328 (3)	1458 (7)
O(22)	7448 (7)	−316 (3)	3191 (7)
O(23)	5338 (8)	−1675 (4)	3971 (8)
O(24)	4621 (8)	−1795 (4)	−322 (8)
O(3)	1468 (10)	2429 (5)	1724 (8)
N	4944 (25)	5394 (10)	−119 (26)*
H(O11)	0	500	0
H(O13)	500	500	500
H(O14)	0	500	500
H(O23)	406 (16)	−176 (7)	383 (15)
H(O24)	567 (16)	−187 (7)	−82 (15)
H(O31)	68 (17)	277 (8)	106 (16)
H(O32)	191 (19)	268 (8)	270 (16)

* Atom is statistically disordered across a center of symmetry. An occupancy factor of 0.5 was used in all calculations.

were refined with anisotropic thermal parameters and the H atoms with fixed isotropic thermal parameters ($B = 3.5$ Å^2). Final R and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ for 904 observed reflections were 0.048 and 0.050, respectively, and $R = 0.055$ and $R_w = 0.050$ for all 1008 reflections. Final average and maximum shift-to-error ratios for the atomic parameters were 0.03 and 0.48 respectively. The maximum shift-to-error ratio, 0.48, was for the H(O32) atom, which is not involved in any significant hydrogen bonding. In the final difference synthesis, the maximum and minimum electron densities were 0.5 and −0.4 e Å^{-3} respectively and multiple peaks were observed in the vicinity of O(3), possibly indicating some disordering of H(O32). The standard error of an observation of unit weight was 1.63. The scattering factors used were those for neutral atoms taken from *International Tables for X-ray Crystallography* (1974). Final atomic parameters are listed in Table 1.*

Results and discussion

The structure of $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$ consists of corrugated sheets of $[CaH_2PO_4]^+$ with $[H_3(PO_4)_2]^{3-}$,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34963 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
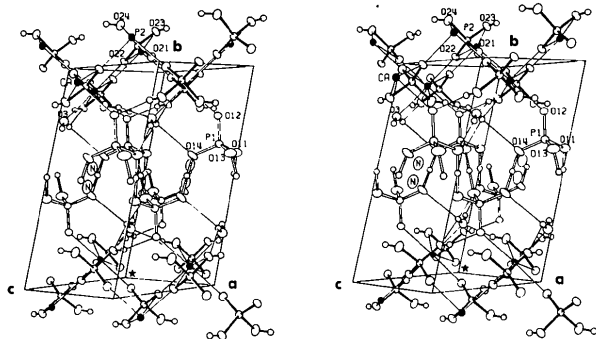
Fig. 1. The contents of the unit cell of $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$. The corrugated $Ca-P(2)O_4$ sheets are at the top and bottom of the unit cell with the $[H_3(PO_4)_2]_n^{3-}$ sheet in the middle. The Ca atoms are represented by black circles. The origin of the coordinate system is marked by a star.

$[NH_4]^+$ and H_2O in the interstitial space held together by a three-dimensional network of hydrogen bonds and $Ca \cdots O$ bonds (Fig. 1).

Opposite edges of the $P(2)O_4$ groups are co-ordinated to Ca atoms to give an infinite chain of Ca and PO_4
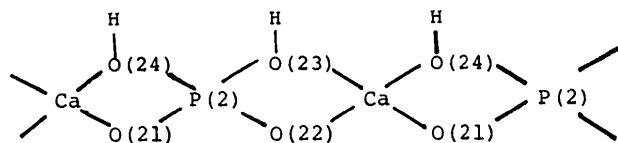
along [101]. Each chain is linked to two adjacent chains through Ca—O bonds forming a sheet. These chains are alternately displaced above and below the central plane of the sheet to form a 'corrugated' sheet (Figs. 1, 2). Alternate chains in this corrugated sheet are bridged by hydrogen bonds between O atoms directly bonded to Ca. Thus, the structure of the corrugated sheet of $[CaH_2PO_4]^+$ in $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$ is nearly identical to that in $Ca(H_2PO_4)_2 \cdot H_2O$ (Figs. 1, 3) as predicted by Brown et
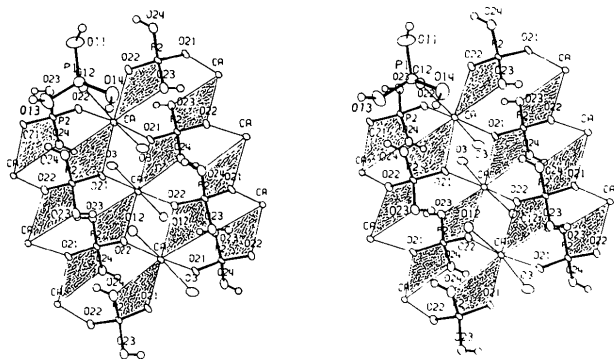
Fig. 2. The corrugated $Ca-P(2)O_4$ sheet parallel to the ac plane in $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$. Thermal ellipsoids are at 50% probability.
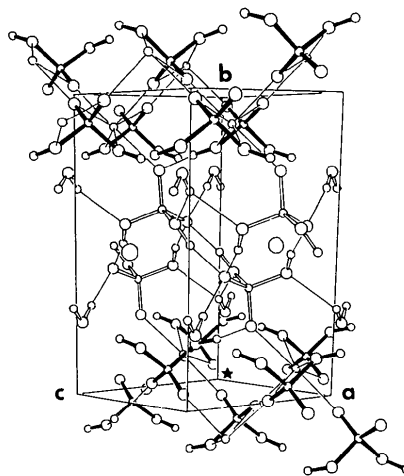

Fig. 3. The unit cell of $Ca(H_2PO_4)_2 \cdot H_2O$ in the same orientation as that of Fig. 1. The large open circles represent the relatively open area where the $[NH_4]^+$ ion is located in $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$.

Table 2. *Comparison of* Ca—O *distances* (Å) *in* $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$ (I) *and* $Ca(H_2PO_4)_2 \cdot H_2O$ (II)

E.s.d.'s given in parentheses refer to the least significant digit.

	(I)	(II)	Nature of Ca—O contacts
Ca—O(22)	2·319 (4)	2·309 (1)	Between chains
O(21)	2·332 (4)	2·326 (1)	
O(12)	2·391 (4)	2·393 (2)	Between chains and interlayer PO_4
O(3)	2·461 (6)	2·475 (2)	$Ca \cdots H_2O$
O(21)	2·494 (4)	2·521 (2)	Within a chain, with O having no covalently
O(22)	2·521 (4)	2·538 (2)	bonded H
O(23)	2·616 (5)	2·625 (2)	Within a chain, with O having covalently
O(24)	2·687 (5)	2·627 (2)	bonded H

al. (1958). The relationship between similar corrugated sheets in $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$ and $Ca(H_2PO_4)_2 \cdot H_2O$ has been described by Dickens & Bowen (1971) and Dickens, Bowen & Brown (1971).

The coordination of the Ca^{2+} ion (Fig. 2, Table 2) in this compound is quite similar to that in $Ca(H_2PO_4)_2 \cdot H_2O$. In each case, the Ca^{2+} ion is coordinated to eight O atoms, including two PO_4 edges and the water molecule. The corresponding Ca—O bond lengths in the two compounds are nearly identical (Table 2).

The linkages between the corrugated sheet and the interlayer contents in $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$ and $Ca(H_2PO_4)_2 \cdot H_2O$ are also quite similar in spite of the different interlayer contents. One O atom of $P(1)O_4$ and the water molecule are bonded to Ca. However, a unique feature of the structure is that the three remaining O atoms of this PO_4 group are hydrogen

Table 3. *Hydrogen-bonding geometry in* $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$

E.s.d.'s given in parentheses refer to the least significant digit.

	O–H (Å)	H···O (Å)	O···O (Å)	O–H···O (°)
O(11)–H···O(11)	1·28	1·28	2·561 (7)	180*
O(13)–H···O(13)	1·26	1·26	2·512 (7)	180*
O(14)–H···O(14)	1·25	1·25	2·501 (7)	180*
O(23)–H···O(12)[x, y − 1, z]	0·71 (10)	1·92 (10)	2·590 (7)	157 (10)
O(24)–H···O(3)[1 − x, ȳ, z̄]	0·77 (10)	1·96 (10)	2·707 (8)	164 (9)
O(3)–H(O31)···O(11)[x̄, 1 − y, z̄]	0·66 (10)	2·15 (10)	2·794 (8)	164 (11)
O(3)–H(O32)···O(23)[1 − x, ȳ, 1 − z]	0·57 (9)	2·54 (10)	2·865 (7)	119 (12)
···O(13)[1 − x, 1 − y, 1 − z]	0·57 (9)	2·53 (10)	2·917 (7)	128 (12)
···O(14)[x̄, 1 − y, 1 − z]	0·57 (9)	2·58 (10)	3·037 (7)	139 (12)

* Hydrogen atom is at a center of inversion.
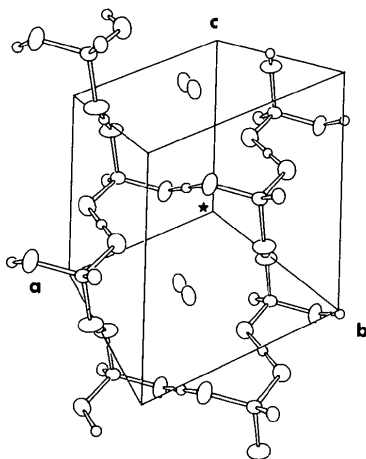
Fig. 4. A view of the $[H_3(PO_4)_2]_n^{3-}$ sheet in Ca_2-$(NH_4)H_7(PO_4)_4 \cdot 2H_2O$. Zig-zag chains are along a and c forming a cage for the $[NH_4]^+$ ion.

bonded across three crystallographic centers of inversion [O(11)···H···O(11); O(13)···H···O(13); O(14)···H···O(14)] forming an infinite $[H_3(PO_4)_2]_n^{3-}$ sheet structure (Figs. 1, 4, Table 3). Although the linking of PO_4 groups through symmetric hydrogen bonds* is known in other calcium phosphates, to our knowledge this is the first example of such an extensive network involving three symmetric hydrogen bonds. Two such symmetric bonds link the $H_2PO_4^-$ groups together to form an infinite chain in $Ca(H_2PO_4)_2$ (Dickens, Prince, Schroeder & Brown, 1973). A combination of X-ray and neutron diffraction and infrared spectral studies of $Ca(H_2PO_4)_2$ indicate that the protons are effectively centered in a broad symmetric potential well. A somewhat similar association of HPO_4^{2-} ions has been observed in $CaHPO_4$, although the two types of hydrogen bonds in its

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* A hydrogen bond is said to be 'symmetric' if the donor and acceptor atoms are crystallographically equivalent, regardless of the type of potential curve.

$(HPO_4)_n$ chain have been found to fit a disordered model (Dickens, Bowen & Brown, 1971; Catti, Ferraris & Filhol, 1977). Thus the tendency of HPO_4^{2-} and $H_2PO_4^-$ ions to form long chains through symmetric hydrogen bonds (ordered or disordered) is evident. The $[H_3(PO_4)_2]_n^{3-}$ sheet structure in the present study may be considered as a polymeric linkage of both HPO_4^{2-} and $H_2PO_4^-$ ions.

The $[H_3(PO_4)_2]_n^{3-}$ sheet is parallel to the $Ca–PO_4$ sheet (Fig. 1). Alternate PO_4 groups in the $[H_3(PO_4)_2]_n^{3-}$ sheet (either along a or along c) have one O atom directed above or below the sheet (Fig. 4) which serves as the only link between the two kinds of sheets. The $[NH_4]^+$ ions are imbedded in the $[H_3(PO_4)_2]_n^{3-}$ sheet with the $Ca–PO_4$ sheets covering the top and bottom.

The three hydrogen bonds in the $[H_3(PO_4)_2]_n^{3-}$ sheet, O(11)···O(11′) = 2·56 Å, O(13)···O(13′) = 2·51 Å and O(14)···O(14′) = 2·50 Å, are in the range of values 2·40–2·55 Å for symmetric bonds (Hamilton & Ibers, 1968). Later surveys have indicated lower values for symmetric bonds, for example 2·41–2·43 Å (Speakman, 1973). Although more recent studies have shown that there is no clearcut demarcation between symmetric and asymmetric bonds on the basis of O···O separation alone, the long symmetric bonds are more likely to be disordered (Ichikawa, 1978; Catti & Ferraris, 1976). The present study, using X-ray diffraction data, does not permit a detailed analysis of a disordered model (H atom statistically disordered across center of inversion) since the heavy atoms are essentially centrosymmetrically related as indicated by the refinement in space group $P\bar{1}$.

The $[NH_4]^+$ ion is located in a site which is relatively open in the structure of $Ca(H_2PO_4)_2 \cdot H_2O$ (Fig. 3) and is statistically disordered across a center of inversion at $\frac{1}{2}\frac{1}{2}0$. The disordered N atoms are separated by about 1·0 Å. In the potassium analogue, $Ca_2KH_7(PO_4)_4 \cdot 2H_2O$, the K^+ ion could occupy the center of inversion. The replacement of one proton in $Ca(H_2PO_4)_2 \cdot H_2O$ by an $[NH_4]^+$ ion has not affected

Table 4. *Selected bond distances* (Å) *and angles* (°) *in*
Ca$_2$(NH$_4$)H$_7$(PO$_4$)$_4$.2H$_2$O

E.s.d.'s are given in parentheses.

(a) Phosphate group

P(1)–O(11)	1·550 (5)	P(2)–O(21)	1·502 (5)
P(1)–O(12)	1·499 (4)	P(2)–O(22)	1·494 (5)
P(1)–O(13)	1·537 (5)	P(2)–O(23)	1·562 (5)
P(1)–O(14)	1·530 (6)	P(2)–O(24)	1·569 (5)
O(11)P(1)O(12)	108·1 (3)	O(21)P(2)O(22)	118·6 (2)
O(11)P(1)O(13)	109·8 (3)	O(21)P(2)O(23)	112·1 (3)
O(11)P(1)O(14)	107·7 (3)	O(21)P(2)O(24)	103·0 (3)
O(12)P(1)O(13)	110·1 (3)	O(22)P(2)O(23)	103·7 (3)
O(12)P(1)O(14)	110·8 (3)	O(22)P(2)O(24)	111·6 (3)
O(13)P(1)O(14)	110·4 (3)	O(23)P(2)O(24)	107·6 (3)
P(1)O(11)H(O11)	120	P(2)O(23)H(O23)	105 (7)
P(1)O(13)H(O13)	124	P(2)O(24)H(O24)	122 (7)
P(1)O(14)H(O14)	119		

(b) Nitrogen contacts

N···O(11)[x,y,z]	2·72 (2)	N···O(13)[x,y,z − 1]	3·02 (2)
O(11)[1 − x, 1 − y, z̄]	2·98 (2)	O(14)[1 + x,y,z]	2·87 (2)
O(11)[1 + x,y,z]	3·25 (2)	O(14)[x̄, 1 − y, z̄]	3·00 (2)

the corrugated sheet structure. However, the incorporation of more than one [NH$_4$]$^+$ ion would alter the corrugated sheet structure drastically. This may be the reason that in the series Ca$_2$(NH$_4$)$_x$H$_{8-x}$(PO$_4$)$_4$.2H$_2$O no compound has been isolated for $x = 2$ or 3. Although two modifications are known for $x = 4$ (Lehr, Brown, Frazier, Smith & Thrasher, 1967), it is not known whether they belong to the corrugated-sheet class of structures.

The dimensions of the two PO$_4$ groups are given in Table 4. The P–O distances support the assignment of covalently bonded H atoms on O(11), O(13) and O(14) of P(1)O$_4$ and O(23) and O(24) of P(2)O$_4$. In P(2)O$_4$, the average P–O distance is 1·565 Å where H is covalently bonded to the O atom and 1·498 Å where there is no H atom. In P(1)O$_4$, on the other hand, P–O(11), P–O(13) and P–O(14) are all intermediate in length as expected since only a 'half' hydrogen is associated with each of these O atoms. The long P(1)–O(11) = 1·550 Å may be due to the additional hydrogen bond from the water molecule (Table 3). The O–P–O angles in the P(1)O$_4$ group are nearly tetrahedral. However, the P(2)O$_4$ group is severely distorted. The O–P–O angles vary from 103·0 to 118·6°. The two smallest angles, O(21)–P(2)–O(24) = 103·0° and O(22)–P(2)–O(23) = 103·7°, involve the edges coordinated to Ca along the Ca–PO$_4$ chain.

Analysis of the distortion indices (Baur, 1974) and H–O–P–O–H torsion angles of the phosphate groups shows some interesting features. For the P(1)O$_4$ anion, [H$_3$(PO$_4$)$_2$]$^{3-}$, distortion indices of 0·010, 0·007 and 0·010 for the P–O and O···O distances and O–P–O angles, respectively, are in good agreement with the values for orthophosphates, 0·005, 0·009 and 0·006 (Baur, 1974), rather than acidic orthophosphates. Distortion indices of P(2)O$_4$ are 0·022, 0·025 and 0·043 compared to 0·018, 0·014 and 0·027 for P–O,

O···O and O–P–O respectively for acidic orthophosphates (Baur, 1974). The higher values are clearly indicative of the strain associated with the corrugated Ca–PO$_4$ sheet. However, the H–O–P–O–H torsion angles of −89 and −110° for P(2)O$_4$ fall in the range of favored conformations for H$_2$PO$_4^-$ ions, as predicted by Hayes, Kollman & Rothenberg (1977). In contrast, P(1)O$_4$ with less distortions shows a wider range (−54 to 94°) of the H–O–P–O–H torsion angles.

The water O(3) atom is bonded to Ca and is the acceptor in the hydrogen bond involving O(24). O(3) acts as a donor in a hydrogen bond to O(11), but the second H atom, H(O32), points towards the general direction of O(13), O(14) and O(24), thus indicating weak 'multiple' hydrogen bonds (Fig. 1, Table 3). Neutron diffraction studies have confirmed the presence of bifurcated hydrogen bonds for similar water molecules in Ca(H$_2$PO$_4$)$_2$.H$_2$O (Schroeder, Prince & Dickens, 1975) and H$_3$PO$_4$.$\frac{1}{2}$H$_2$O (Dickens, Prince, Schroeder & Jordan, 1974). In the present structure, no definite assignment is possible since the H positions are not known precisely. A neutron diffraction study should be of interest in defining the nature of this bond as well as in understanding the distribution of the H atoms in the three symmetric hydrogen bonds in the [H$_3$(PO$_4$)$_2$]$_n^{3-}$ sheet.

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Structure du Dichlorure d'Arsenic et de Dicadmium

PAR A. REBBAH, J. YAZBECK, A. LECLAIRE ET A. DESCHANVRES

Laboratoire de Cristallographie et Chimie du Solide, LA 251, ISMRA, Université de Caen, 14032 Caen CEDEX, France

Abstract

Cd_2AsCl_2, $M_r = 370\cdot63$, crystallizes in space group $P2_1/c$ with four formula units per cell of dimensions: $a = 7\cdot858$ (4), $b = 9\cdot193$ (9), $c = 8\cdot189$ (5) Å, $\beta = 119\cdot95$ (8)°, $V = 512\cdot6$ Å^3, $Z = 4$, $d_m = 4\cdot86$ (3), $d_c = 4\cdot80$ Mg m^{-3}. The structure was refined by the least-squares technique, based on 2835 independent reflexions measured on an automatic diffractometer. The final R_w is 0·099. The structure is built up of As_2Cd_6 groups characterized by As—As bonds. These As_2Cd_6 groups share a Cd—Cd edge forming layers along **b**. The cohesion of the structure is ensured by the Cl atoms.

Introduction

Le présent travail fait partie de l'étude systématique des diagrammes ternaires IIb(Cd,Hg)–V(As,P)–VIII(Cl,Br,I) entreprise dans le but de suivre l'évolution et de préciser la nature des liaisons dans les composés polyanioniques de l'arsenic et du phosphore.

Dans les systèmes Cd–(As,P)–Cl, nous avons synthétisé les composés isotypes Cd_2AsCl_2 (orange) et Cd_2PCl_2 (jaune foncé) dont l'existence avait été signalée par Puff & Berg (1966) dans le cas de l'arsenic.

Partie expérimentale

Nous avons préparé Cd_2AsCl_2 et Cd_2PCl_2 par transport en phase vapeur à partir des composés $CdCl_2$, $CdAs_2$ (CdP_2) et Cd_3As_2 (Cd_3P_2) pris en proportions stœchiométriques. Le mélange homogène, introduit dans une ampoule de verre scellée sous vide, est placé en zone chaude (693 K). Les cristaux se forment en zone froide (673 K). La durée moyenne du transport est de 36 h. Pour une température de zone froide inférieure à 673 K nous obtenons des cristaux de cette phase ainsi que des cristaux de composition $Cd_3(As,P)Cl_3$ dont la structure est en cours.

L'analyse chimique conduit aux résultats suivants:

	Cd (%)	As (%)	Cl (%)
théorique	60,65	20,21	19,13
expérimental	60,80	19,70	20,00.

Les paramètres de la maille ont été affinés par moindres carrés sur 25 réflexions indépendantes.

Les paramètres sont en désaccord avec les données cristallographiques publiées par Puff & Berg (1966), bien que les extinctions systématiques observées conduisent au même groupe spatial $P2_1/c$. |Cd_2AsCl_2: $a = 7,858$ (4), $b = 9,193$ (9), $c = 8,189$ (5) Å, $\beta = 119,95$ (8)°, $V = 512,6$ Å^3, $M_r = 370,63$, $d_m =$