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Acta Cryst. (1984). C**40**, 1662–1665

Planar Ca–PO_4 Sheet-Type Structures: Calcium Bromide Dihydrogenphosphate Tetrahydrate, $CaBr(H_2PO_4).4H_2O$, and Calcium Iodide Dihydrogenphosphate Tetrahydrate, $CaI(H_2PO_4).4H_2O$

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(*Received* 26 *January* 1984; *accepted* 10 *May* 1984)

Abstract. $CaBr(H_2PO_4).4H_2O$ (1): $M_r = 289{\cdot}04$, $C2/c$, $a = 20{\cdot}314$ (5), $b = 6{\cdot}558$ (1), $c = 6{\cdot}973$ (1) Å, $\beta = 90{\cdot}02$ (2)°, $V = 928{\cdot}9$ (7) Å^3, $Z = 4$, $D_m = 2{\cdot}09$ (2), $D_x = 2{\cdot}066$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 5{\cdot}16$ mm^{-1}, $F(000) = 576$, $T = 298$ K, $R = 0{\cdot}034$, 592 unique observed reflections. $CaI(H_2PO_4).4H_2O$ (2): $M_r = 336{\cdot}03$, $B2/c$, $a = 21{\cdot}416$ (4), $b = 6{\cdot}550$ (1), $c = 7{\cdot}000$ (1) Å, $\beta = 91{\cdot}03$ (2)°, $V = 981{\cdot}7$ (6) Å^3, $Z = 4$, $D_m = 2{\cdot}28$ (2), $D_x = 2{\cdot}273$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 3{\cdot}92$ mm^{-1}, $F(000) = 648$, $T = 298$ K, $R = 0{\cdot}030$, 345 unique observed reflections. Both compounds have planar sheet-type structures consisting of Ca–H_2PO_4 chains. The halide ions, X, and the water molecules are linked *via* O–H···X hydrogen bonds to form $X(H_2O)_6$ octahedra. These octahedral units are linked together to form a polymeric layer $[X(H_2O)_4]_n$ between the Ca–H_2PO_4 sheets.

Introduction. A number of calcium phosphates are known to have Ca–H_2PO_4 chains consisting of corrugated sheet-type structures (Dickens & Brown, 1972). This sheet-type structure is persistent despite variations in the composition of the material between the sheets. As part of a program to study the structures of calcium phosphates, we have determined the crystal structures of $CaBr(H_2PO_4).4H_2O$ (1) and $CaI(H_2PO_4).4H_2O$ (2).

Experimental. Samples prepared by adding 1 ml of 85% H_3PO_4 to 100 ml 4 mol dm^{-3} $CaBr_2$ and 100 ml 4 mol dm^{-3} CaI_2 and allowing the resultant solutions to evaporate at room temperature (Lehr, Brown, Frazier, Smith & Thrasher, 1967). D_m by flotation. Crystals of both (1) and (2) are hygroscopic and decompose slowly in air, and were therefore mounted in sealed capillary tubes for all diffraction work; Picker diffractometer, Mo $K\alpha$ radiation, graphite monochromator; θ–2θ scan technique, 0·5° min^{-1}; backgrounds counted for 20 s at each end of scan; diffractometer-controlling programs of Lenhert (1975); structures solved from three-dimensional Patterson syntheses, remaining atoms located in subsequent Fourier syntheses, H atoms from difference Fourier syntheses; refinements by full-matrix least-squares program *RFINE*4 (Finger & Prince, 1975), function minimized $\sum w(F_o - F_c)^2$, $w^{-1} = \sigma^2(F_o) + (0{\cdot}02F_o)^2$; scattering factors and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Compound (1). Crystal 0·07 × 0·13 × 0·34 mm, systematic absences ($h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$) consistent with space group $C2/c$ or Cc and confirmed as $C2/c$ by successful solution and refinement; unit-cell dimensions from least-squares fit of 15 reflections with $37 < 2\theta < 42°$; absorption correction applied, correction factors to F_o 1·41 to 1·83, $2\theta_{max} = 50°$; four check reflections, monitored every 25 reflections showed steady decrease in intensity by 60% of initial values; h 0–24, k 0–7, l −8–8; 821 unique reflections, 592 observed with $F_o > 3\sigma(F_o)$; H also refined; $R = 0{\cdot}034$, $R_w = 0{\cdot}030$, $S = 0{\cdot}88$; av. and max. Δ/σ 0·01 and 0·07, respectively; max. and min. $\Delta\rho$ 0·6 and −0·5 e Å^{-3} respectively.

Compound (2). Crystal 0·03 × 0·15 × 0·27 mm, systematic absences ($h + l = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$) consistent with space group $B2/c$, equivalent positions: $(0,0,0;\ \frac{1}{2},0,\frac{1}{2}) + x,y,z;\ \bar{x},\bar{y},\bar{z};$

Table 1. *Final atomic parameters* ($\times 10^4$) *for* $CaBr(H_2PO_4).4H_2O$ (1) *and* $CaI(H_2PO_4).4H_2O$ (2)

	x	y	z	U_{eq}(Å^2 $\times 10^4$)*
Compound (1)				
Br	2500	2500	0	483
Ca	0	6425 (2)	2500	169
P	0	1701 (2)	2500	193
O(1)	575 (2)	115 (4)	2533 (5)	331
O(2)	−7 (1)	3009 (4)	746 (3)	231
O(*w*1)	1167 (2)	5943 (6)	2292 (8)	425
O(*w*2)	3337 (2)	6655 (7)	935 (7)	514
Compound (2)				
I	2500	7104 (2)	0	425
Ca	0	6427 (4)	2500	152
P	0	1701 (5)	2500	182
O(1)	551 (3)	126 (9)	2521 (8)	295
O(2)	10 (3)	3002 (8)	753 (8)	212
O(*w*1)	1109 (3)	5937 (11)	2755 (11)	441
O(*w*2)	1579 (3)	1496 (11)	911 (11)	520

* The equivalent values of the anisotropic temperature factors correspond to the definitions given by Hamilton (1959).

$\bar{x},y,\frac{1}{2}-z$; $x,\bar{y},\frac{1}{2}+z$. Conventional space group $P2/c$ with $a = 11{\cdot}206$, $b = 6{\cdot}550$, $c = 7{\cdot}000$ Å and $\beta = 107{\cdot}17°$; unit-cell dimensions from least-squares fit of 15 reflections with $37 < 2\theta < 45°$; no absorption correction applied; $2\theta_{max} = 40°$; four check reflections monitored every 25 reflections showed a decrease in intensity by 70% at end of data collection; h 0–20, k 0–6, l −6–6; 394 unique reflections, 345 observed with $F_o > 3\sigma(F_o)$; H not refined; $R = 0{\cdot}030$, $R_w = 0{\cdot}035$, $S = 1{\cdot}41$; av. and max. Δ/σ 0·005 and 0·01, respectively; max. and min. $\Delta\rho$ 0·6 and $-0{\cdot}7$ e Å^{-3}, respectively.

Discussion. Final atomic parameters are listed in Table 1.*

Both compounds have planar sheet-type structures consisting of $Ca{-}H_2PO_4$ chains. The water molecules and the halide ions are linked by hydrogen bonds and occupy the interstitial space between the $Ca{-}H_2PO_4$ sheets. The structure of (1) is illustrated in Fig. 1, and (2) in Fig. 2.

The Ca and P atoms in both (1) and (2) are located along the twofold axes. The opposite edges of the H_2PO_4 groups are coordinated to the Ca atoms to give an infinite chain of Ca and H_2PO_4 and each chain is linked to two adjacent chains through Ca···O bonds forming a sheet. Adjacent chains within the same layer are separated by $c/2$ translation, and thus the $Ca{-}H_2PO_4$ sheets in these compounds are planar. A planar sheet-type structure has been observed in $Ca_2Cl(PO_4)$ (Greenblatt, Banks & Post, 1967).

* Lists of structure factors, anisotropic thermal parameters, parameters for H atoms and dimensions of hydrogen bonds for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39463 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In corrugated sheet-type structures the $Ca{-}PO_4$ chains are alternately displaced above and below the central plane of the sheet. Examples are $CaHPO_4.2H_2O$ (Jones & Smith, 1962), $CaHPO_4$ (Dickens, Bowen & Brown, 1972), $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971) and $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ (Takagi, Mathew & Brown, 1980). The relationships between these compounds have been described by Dickens *et al.* (1972) and Takagi *et al.* (1980).

The Ca ions in (1) and (2) are coordinated to eight O atoms, including two PO_4 edges in the $Ca{-}H_2PO_4$ chains, two O atoms between the chains, and two water molecules between the layers. The coordination of the Ca ions and the Ca···O bond lengths in these two compounds are quite similar to those in corrugated sheet-type structures (Table 2).

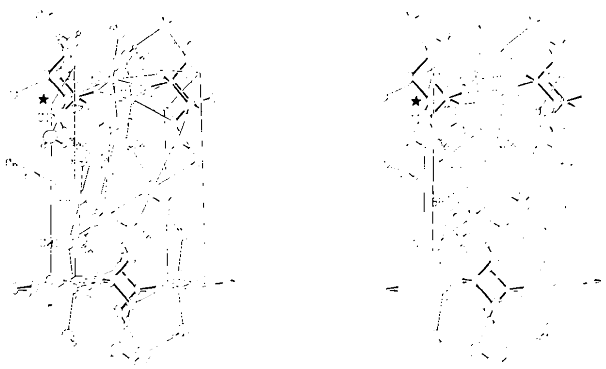

Fig. 1. A stereoscopic illustration of the crystal structure of $CaBr(H_2PO_4).4H_2O$. The origin of the crystallographic coordinate system is marked by an asterisk with **a** vertical, **b** horizontal and **c** into the plane of the paper. Only one-half of the unit cell (**a**/2) is shown.

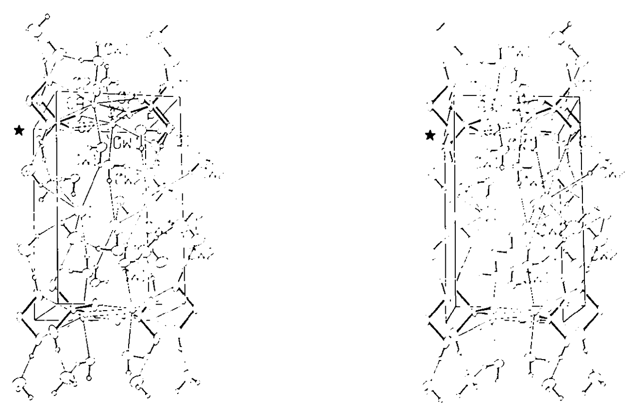

Fig. 2. A stereoscopic illustration of the crystal structure of $CaI(H_2PO_4).4H_2O$. The origin of the crystallographic coordinate system is marked by an asterisk with **a** vertical, **b** horizontal and **c** into the plane of the paper. Only one-half of the unit cell (**a**/2) is shown.

Table 2. *Comparison of* Ca–O *distances* (Å) *in* $CaBr(H_2PO_4).4H_2O$ (1), $CaI(H_2PO_4).4H_2O$ (2), $Ca(H_2PO_4)_2.H_2O$ (3) *and* $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ (4)

	(1)	(2)	(3)[a]	(4)[b]	Nature of Ca–O contacts
Ca–O(1)	2 × 2·689 (3)	2 × 2·695 (6)	2·626*	2·651*	Within a chain, with O having covalently bonded H
Ca–O(2)	2 × 2·552 (3)	2 × 2·555 (6)	2·530*	2·508*	Within a chain, with O having no covalently bonded H
Ca–O(2)	2 × 2·294 (2)	2 × 2·307 (6)	2·318*	2·325*	Between chains
Ca–O(*w*1)	2 × 2·396 (4)	2 × 2·400 (7)	2·475	2·461	$Ca-H_2O$ (interlayer)
			2·393	2·391	with interlayer PO_4
Mean	2·483	2·489	2·477	2·478	

References: (*a*) Dickens & Bowen (1971); (*b*) Takagi *et al.* (1980).

* Average values.

Table 3. *Dimensions of the phosphate groups* (Å, °) *in* $CaBr(H_2PO_4).4H_2O$ (1) *and* $CaI(H_2PO_4).4H_2O$ (2)

	(1)	(2)
P–O(1)	2 × 1·565 (4)	2 × 1·568 (7)
P–O(2)	2 × 1·494 (2)	2 × 1·491 (6)
O(1)–P–O(1′)	96·8 (2)	97·7 (3)
O(1)–P–O(2)	2 × 113·6 (2)	2 × 113·0 (3)
O(1)–P–O(2′)	2 × 111·2 (2)	2 × 111·2 (3)
O(2)–P–O(2′)	109·9 (1)	110·3 (3)

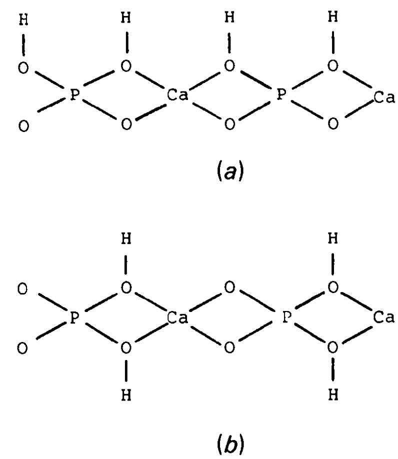

Fig. 3. Linkage of calcium and phosphate ions in a $Ca-H_2PO_4$ chain.

The dimensions of the $H_2PO_4^-$ groups are given in Table 3. The P–O distances support the assignment of covalently bonded H atoms on O(1) in both compounds. The smallest O–P–O angle [O(1)–P–O(1′) = 96·8° in (1) and 97·7° in (2)] involves the oxygen atoms covalently bonded to H atoms and the edge coordinated to the Ca along the $Ca-H_2PO_4$ chain.

The Br ion in (1) is located at a center of inversion, whereas the iodide ion in (2) is on a twofold axis. Each halide ion is hydrogen bonded to six water molecules, arranged at the corners of a distorted octahedron. These octahedral units are linked together to form polymeric $[X(H_2O)_4]_n$ sheets between the $Ca-H_2PO_4$ sheets. The linkages of the octahedral units $X(H_2O)_6$ are different in the two compounds. In the case of (1), the four corners involving the four O(*w*2) molecules are shared with adjacent octahedral units. In (2) a pair of edges [involving O(*w*2) molecules] are shared with two adjacent octahedral units. In each case, the O(*w*1) molecules occupying the two remaining corners are coordinated to the Ca ions. The only other link between the $Ca-H_2PO_4$ sheet and the $[X(H_2O)_4]_n$ sheet is the hydrogen bond O(1)–H···O(*w*2).

All available hydrogen atoms are involved in hydrogen bonds and the hydrogen-bonding schemes are identical in the two compounds.

Although the $Ca-H_2PO_4$ layers in (1) and (2) are almost identical, the stacking of these layers is not the same. Adjacent layers in (1) are related by a translation of $(\mathbf{a}+\mathbf{b})/2$ (*C* centering), whereas in (2) they are related by a translation of $(\mathbf{a}+\mathbf{c})/2$ (*i.e.* *B* centering), resulting in a slightly different arrangement of hydrated-iodide layers. Twinning is reported to occur, with (100) as the composition plane, in salt (2), but no mention is made of twinning in (1) (Lehr *et al.*, 1967). The presence of a pseudo diad axis parallel to the *c* axis in (2) but not in (1) would account for this twinning.

The general features of the $Ca-H_2PO_4$ chains and the linkage between chains in these compounds are similar to those in other calcium phosphates with corrugated sheet-type structures. However, the actual disposition of the Ca and $H_2PO_4^-$ ions within a chain is different. In $Ca(H_2PO_4)_2.H_2O$ and $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ the linkage of $H_2PO_4^-$ and Ca ions in a chain involves a pair of $P{<}^{OH}_{O}$ edges (Fig. 3*a*) and the corresponding O–P–O angles are in the range 102–104°. In the present studies (1 and 2) the coordination involves a $P{<}^{OH}_{OH}$ edge and a $P{<}^{O}_{O}$ edge (Fig. 3*b*). Although this is a consequence of restriction of the symmetry (twofold axis through P and Ca atoms in a chain) the small HO–P–OH angle may be indicative of the strain in the $Ca-H_2PO_4$ linkage. In addition, the Ca–O distances in the chains in (1) and (2) are longer than those in corrugated-sheet-type structures (Table 2). This is in agreement with the observation that crystals of both (1) and (2) have a perfect cleavage parallel to (010), perpendicular to the Ca–H_2PO_4 chain. The cleavage planes parallel to (100) are consistent with the layer-type structures in this planar direction and the paucity of bonding between the layers.

The investigation was supported in part by Research Grant DE 05030-05 to the American Dental Association Health Foundation by the National Institute of Dental Research and is part of the Dental Research Program conducted by the National Bureau of Standards in cooperation with the American Dental Association Health Foundation.

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Acta Cryst. (1984). C**40**, 1665–1668

The Structure of a New Magnetic Phase Related to the Sigma Phase: Iron Neodymium Boride $Nd_2Fe_{14}B$

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(*Received* 10 *April* 1984; *accepted* 13 *June* 1984)

Abstract. $M_r = 1081$, $P4_2/mnm$, $a = 8{\cdot}804$ (5), $c = 12{\cdot}205$ (5) Å, $V = 946{\cdot}0$ (9) Å^3, $Z = 4$, $F(000) = 1956$, $D_x = 7{\cdot}59$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 320$ cm^{-1}, $T = 293$ (2) K. Final $R = 0{\cdot}040$ (575 reflections $I > 2\sigma$). This is a new material of considerable current interest for making permanent magnets. The structure consists of layers of puckered sigma-phase-type nets (two main and one subsidiary layer) formed by Fe atoms, sandwiched between triangular nets in the mirror planes formed by Nd, Fe and B atoms. There are strings of alternating Nd and Fe (CN14) atoms parallel to the z axis corresponding to the rows of closely spaced CN14 atoms in the sigma phase. Our results agree with those of a recent neutron diffraction powder study [Herbst, Croat, Pinkerton & Yelon (1984). *Phys. Rev. B*, **29**, 4176–4178].

Introduction. The search for inexpensive materials for permanent magnets led Sagawa, Fujimura, Togawa, Yamamoto & Matsuura (1983) to the preparation of a material with the composition $Nd_{15}Fe_{77}B_8$, having high saturation magnetization and high magnetic anisotropy. The material was actually two-phase, with the main component a tetragonal phase of which they determined the cell dimensions. This tetragonal phase was subsequently prepared by one of us, RF (with Ph. l'Héritier), and a sample (of assumed composition $Nd_2Fe_{10}B$) was sent to CBS and DPS for structure determination since the powder pattern suggested a possible relationship to the σ phase (Bergman & Shoemaker, 1954). After completion of our crystal structure determination (which established that the composition actually was $Nd_2Fe_{14}B$) we learned that the crystal structure had been determined by powder neutron diffraction by Herbst, Croat, Pinkerton & Yelon (1984). The authors have kindly communicated to us their values of the atomic parameters, which are in essential agreement with ours, differing by 0·004 for Nd, at most 0·002 for Fe, and 0·009 for B (see Table 1).

Experimental. Crystal fragment, approximate dimensions $0{\cdot}12 \times 0{\cdot}06 \times 0{\cdot}04$ mm, Syntex $P\bar{1}$ diffractometer, graphite monochromator, Mo $K\alpha$ radiation, θ–2θ scan speed 1° min^{-1}, 2θ range 2·0° plus α_1,α_2

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