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Structure of Ammonium Calcium Phosphate Heptahydrate, $Ca(NH_4)PO_4.7H_2O$

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Abstract. $M_r = 279 \cdot 19$, monoclinic, $P2_1$, $a = 6 \cdot 300\ (1)$, $b = 11 \cdot 929\ (2)$, $c = 7 \cdot 176\ (2)$ Å, $\beta = 91 \cdot 62\ (2)°$, $V = 539 \cdot 08$ Å^3, $Z = 2$, $D_m = 1 \cdot 71$, $D_x = 1 \cdot 720$ Mg m^{-3}, $T = 298$ K, Mo $K\alpha$, $\lambda = 0 \cdot 7107$ Å, $\mu = 0 \cdot 76$ mm^{-1}, $F(000) = 296$, $R = 0 \cdot 021$ for the 453 reflections used in the refinement. The structure consists of $Ca(H_2O)_7$ polyhedra and PO_4 groups linked together by hydrogen bonds forming an interpenetrating layer-type structure, similar to struvite, $Mg(NH_4)PO_4.6H_2O$. All seven water molecules are coordinated to the Ca^{2+} ion, forming a distorted pentagonal bipyramid.

Introduction. The occurrence of a large number of struvite-type compounds named after the biomineral struvite, $Mg(NH_4)PO_4.6H_2O$ (Whitaker & Jeffrey, 1970) has been reported by Dickens & Brown (1972). Most of these compounds contain Mg^{2+} as the divalent cation and are very stable. In contrast, the calcium phosphate analogue of struvite, $Ca(NH_4)PO_4.7H_2O$, is very unstable and decomposes at room temperature to hydroxyapatite (Lehr, Brown, Frazier, Smith & Thrasher, 1967), the major component of bone and tooth mineral. Although $Ca(NH_4)PO_4.7H_2O$ contains a highly hydrated nucleus, it is not a known biomineral. However, it may either exist transiently in the early stages of crystallization of biominerals or possess some of the important structural features of the precursors to biominerals. As part of a study of the structural characteristics of highly hydrated phosphatic compounds, we have determined the crystal structure of $Ca(NH_4)PO_4.7H_2O$.

Experimental. Crystals prepared by the method reported by Lehr *et al.* (1967). All diffraction work carried out with a crystal mounted in a sealed capillary tube. Syntex automatic four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Tabular crystal of dimensions $0 \cdot 15 \times 0 \cdot 21 \times 0 \cdot 23$ mm. Cell parameters by least-squares fit of 15 2θ values ($24° < 2\theta < 30°$). All hkl and $hk\bar{l}$ reflections with $2\theta \leq 40°$ measured, θ–2θ scan technique, variable scan rate $2 \cdot 0$ to $29 \cdot 3°$ min^{-1}, background counts made for half the scan time at each end of the scan range. Four standard reflections measured at intervals of 25 reflections showed considerable loss of intensity (about 75%) during data collection; measured intensities corrected for this variation in scale factors as well as for the Lorentz and polarization effects and for absorption, max. and min. absorption corrections to intensities $1 \cdot 133$ and $1 \cdot 109$ respectively. Equivalent reflections merged into a set of 534 independent reflections; 453 with $F_o > 3\sigma(F_o)$ considered observed and used in the structure analysis. Positions of Ca and P atoms deduced from a Patterson synthesis; the remaining atoms located in a subsequent Fourier synthesis. Difference Fourier syntheses clearly indicated the positions of all H atoms. Refinement by full-matrix least squares; $\sum w(F_o - F_c)^2$ minimized, $w^{-1} = \sigma^2(F_o) + (0 \cdot 01 F_o)^2$. Scattering factors of Cromer & Mann (1968) for neutral Ca, P, O, N and of Stewart, Davidson & Simpson (1965) for H; dispersion corrections for Ca, P, O and N from *International Tables for X-ray Crystallography* (1974). All calculations performed with the program *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Non-hydrogen atoms refined with anisotropic thermal parameters and the H atoms included in the calculations with fixed $U = 0 \cdot 03$ Å^2, but not refined. Isotropic extinction correction (Zachariasen, 1967); extinction parameter refined to $0 \cdot 6\ (3) \times 10^{-3}$ cm^{-1}. Final R and R_w $0 \cdot 021$ and $0 \cdot 025$, respectively, for the 453 reflections used in the refinement and $0 \cdot 028$ and $0 \cdot 031$ for all reflections; goodness of fit $0 \cdot 75$. Final average and max. Δ/σ for the atomic parameters $0 \cdot 001$ and $0 \cdot 007$, respectively. Peaks on final $\Delta\rho$ map $< |1 \cdot 01|$ e Å^{-3}.

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

The structure consists of $Ca(H_2O)_7$ polyhedra and PO_4 groups linked together by hydrogen bonds forming an interpenetrating layer-type structure. The interstitial space is occupied by the NH_4^+ ions (Figs. 1 and 2). The structure of $Ca(NH_4)PO_4.7H_2O$ is quite similar to that of struvite, $Mg(NH_4)PO_4.6H_2O$.

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* Lists of structure factors, anisotropic temperature factors, positional parameters of hydrogen atoms and the lengths and angles of the hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39227 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic parameters*

Positional parameters are multiplied by 10^4. E.s.d.'s are given in parentheses.

	x	y	z	U_{eq}*(Å^2)
Ca	1334 (2)	0	2410 (2)	1·68 (1)
P	5200 (3)	1379 (2)	7590 (3)	1·37 (1)
O(1)	5336 (7)	93 (4)	7536 (6)	2·40 (3)
O(2)	6399 (7)	1871 (4)	5937 (6)	1·73 (3)
O(3)	6195 (7)	1810 (4)	9437 (6)	1·98 (3)
O(4)	2875 (7)	1754 (4)	7441 (6)	2·10 (3)
O(w1)	392 (7)	1461 (5)	310 (6)	3·04 (3)
O(w2)	3994 (7)	1543 (4)	2676 (6)	2·50 (3)
O(w3)	96 (8)	678 (5)	5210 (7)	2·96 (3)
O(w4)	5559 (8)	4185 (4)	5863 (7)	2·51 (3)
O(w5)	7300 (8)	4000 (5)	165 (7)	2·53 (3)
O(w6)	9797 (7)	3234 (4)	6411 (7)	2·52 (3)
O(w7)	7642 (7)	−269 (5)	1527 (8)	3·33 (3)
N	1188 (9)	3617 (5)	2573 (8)	2·21 (4)

* The equivalent values of the anisotropic temperature factors ($\times 10^2$) correspond to the definitions given by Hamilton (1959).

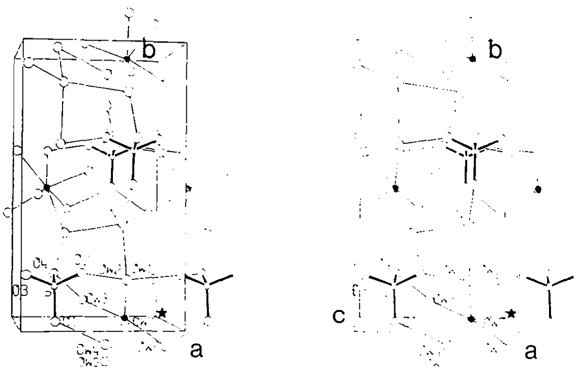

Fig. 1. A stereoscopic illustration of the unit cell of $Ca(NH_4)PO_4.7H_2O$. Ca is represented by a black circle. The origin is labeled with a star.

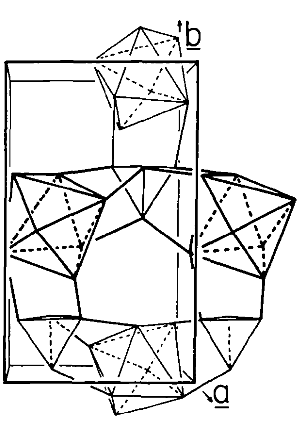

Fig. 2. The packing of $Ca(H_2O)_7$ polyhedra and PO_4 tetrahedra in $Ca(NH_4)PO_4.7H_2O$. The open channel along **a** is occupied by the NH_4^+ ions.

The environment of the Ca^{2+} ion consists of seven water molecules forming a distorted pentagonal bipyramid. The water molecules O(w1), O(w2), O(w4), O(w6) and O(w7) are in the equatorial plane and the O(w)—Ca—O(w) angles between the adjacent water molecules in the plane are in the range 70·2–74·5° (mean 72·5°). The O—Ca—O angles between these water molecules and the apical water molecules O(w3) and O(w5) show considerable distortion (range 83·7–102·1°).

The Ca—O(w) distances vary from 2·321 to 2·493 Å (mean 2·407 Å). A survey of the geometry of calcium–water interactions in crystalline hydrates has indicated that water molecules with two or three interactions (class 1, as defined by Einspahr & Bugg, 1980) occur generally at shorter Ca···O distances while water molecules with four or more interactions (class 2) occur more commonly at longer Ca···O distances although the separation between the classes is not abrupt (Einspahr & Bugg, 1980). The longest Ca—O(w) contacts, O(w2) and O(w4), involve class 2 water molecules, while the two shortest Ca···O(w) contacts involve class 1 water molecules. Thus the variations in Ca—O distances appear to be related to the class of interaction of the water molecules.

Ca^{2+} ions in hydrated compounds generally exhibit seven or eight-fold coordination, although a few examples of six and nine coordination exist (Einspahr & Bugg, 1980). However, in most of these compounds the coordination polyhedra involve ligands other than water molecules. Complete hydration of Ca^{2+} ions in the crystalline state is rare. In $CaKAsO_4.8H_2O$ (Dickens & Brown, 1972) the Ca^{2+} ion is coordinated to eight water molecules arranged in an approximately square antiprism. The heptahydrated Ca^{2+} ion has been observed in a calcium dichromate complex (Dahan, 1975). Since both these hydrates are stable, it is unlikely that the instability of $Ca(NH_4)PO_4.7H_2O$ is related to the heptahydrated Ca^{2+} ion.

All P—O distances agree within an e.s.d. from the mean value of 1·537 Å, in excellent agreement with the value 1·536 Å calculated for orthophosphate groups (Baur, 1974). The O—P—O angles show only slight variations from ideal tetrahedral angles (Table 2).

The environment of the PO_4^{3-} ion consists of 13 water molecules and an NH_4^+ ion; all are hydrogen bonded to the phosphate O atoms (Table 2). The PO_4 oxygen atoms O(2) and O(3) accept four hydrogen bonds; O(1) and O(4) accept three. If tetrahedral geometry of the phosphate O atoms is assumed, only 12 hydrogen bonds are to be expected. Such configurations have been observed in several stable crystalline hydrates, *e.g.* $Mg_3(PO_4)_2.22H_2O$ (Schroeder, Mathew & Brown, 1978), $MgNaPO_4.7H_2O$ (Mathew, Kingsbury, Takagi & Brown, 1982), and $Mg(NH_4)PO_4.6H_2O$ (Whitaker & Jeffery, 1970). Although the PO_4^{3-} ion in $SrNaPO_4.9H_2O$ is apparently hydrogen bonded to 15

Table 2. *Selected bond lengths* (Å) *and angles* (°)

(*a*) Ca^{2+} and PO_4^{3-} ions; mean e.s.d.'s for bond lengths and bond angles are 0·005 Å and 0·3°, respectively

Ca···O(*w*1)	2·369	Ca···O(*w*5)	2·381
Ca···O(*w*2)	2·493	Ca···O(*w*6)	2·386
Ca···O(*w*3)	2·321	Ca···O(*w*7)	2·415
Ca···O(*w*4)	2·485		
P—O(1)	1·537	O(1)—P—O(2)	109·4
P—O(2)	1·540	O(1)—P—O(3)	109·5
P—O(3)	1·538	O(1)—P—O(4)	110·1
P—O(4)	1·532	O(2)—P—O(3)	109·8
		O(2)—P—O(4)	108·9
		O(3)—P—O(4)	109·2

(*b*) Probable hydrogen-bond contacts; mean e.s.d. 0·007 Å

O(*w*1)···O(3)	2·732	O(*w*5)···O(3)	2·751
O(*w*1)···O(4)	2·644	O(*w*6)···O(2)	2·702
O(*w*2)···O(3)	2·759	O(*w*6)···O(4)	2·710
O(*w*2)···O(2)	2·779	O(*w*7)···O(3)	3·025
O(*w*3)···O(2)	2·791	O(*w*7)···O(*w*4)	2·866
O(*w*3)···O(4)	2·688	N···O(1)	2·812
O(*w*4)···O(2)	2·811	N···O(*w*2)	3·041
O(*w*4)···O(1)	2·713	N···O(*w*5)	2·993
O(*w*5)···O(1)	2·709	N···O(*w*6)	2·950

water molecules, the positions of these water molecules are primarily controlled by cation hydrate polyhedra, and the PO_4^{3-} ions are disordered (Takagi, Mathew & Brown, 1982). The instability of $Ca(NH_4)PO_4.7H_2O$ may be related to the overcrowding of 14 hydrogen bonds around the PO_4^{3-} ion, since most of these hydrogen bonds are weaker (mean O···O distances 2·755 Å, for 13 water) than those in other hydrates with only 12 hydrogen bonds.

All available H atoms are involved in hydrogen bonding. Of the 14 H atoms on the water molecules, 13 are hydrogen bonded to PO_4 oxygen atoms, and one to another water molecule. The NH_4^+ ions are hydrogen bonded to one PO_4 oxygen and to three water molecules. Bond lengths and angles involving the H atoms are within the range of values expected for normal hydrogen bonds.

The linkages of the PO_4 tetrahedra and $Ca(H_2O)_7$ polyhedra constitute a cross-linked layer-type structure (along **b** and **c**) leaving relatively open channels along **a**, which are occupied by NH_4^+ ions. The structure also has a pseudotrigonal symmetry through the NH_4^+ ion along **a**. Two of the triangular faces [O(*w*1)—O(*w*2)—O(*w*5); O(*w*2)—O(*w*3)—O(*w*4)] of the $Ca(H_2O)_7$ polyhedra are linked to two faces of two different PO_4 tetrahedra *via* hydrogen bonding (Fig. 2). These features are quite similar to those in struvite, $Mg(NH_4)PO_4.6H_2O$. Thus $Ca(NH_4)PO_4.7H_2O$ is a true Ca analogue of struvite, although $Ca(NH_4)PO_4.7H_2O$ possesses a lower-symmetry space group than struvite and most other related struvite-type compounds (listed by Takagi *et al.*, 1982). The monoclinic cell of $Ca(NH_4)PO_4.7H_2O$ is nearly orthogonal ($\beta = 91{\cdot}62°$); that of struvite is orthorhombic. The slightly larger cell dimensions are associated with the larger size of the divalent cations and the presence of the extra water molecule. There is a pseudo mirror plane through NH_4, PO_4 and $Ca(H_2O)_7$ perpendicular to the *c* axis [at $z = \frac{1}{4}$ and $\frac{3}{4}$ (Fig. 1)]. A true screw axis (2_1) along **b** is common to both compounds, which in $Ca(NH_4)PO_4.7H_2O$ generates a pseudo *n*-glide perpendicular to **a**. Thus the space group of $Ca(NH_4)PO_4.7H_2O$ corresponds to a subset of $Pn2_1m$, the space group of struvite.

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