

The Crystal Structure of Calcium Ammonium Hydrogenpyrophosphate $\text{CaNH}_4\text{HP}_2\text{O}_7$

BY M. MATHEW* AND L. W. SCHROEDER*

Institute for Materials Research, National Bureau of Standards, Washington, DC 20234, USA

(Received 26 February 1977; accepted 26 March 1977)

$\text{CaNH}_4\text{HP}_2\text{O}_7$ is monoclinic, space group $P2_1/n$, with $a = 10.523$ (2), $b = 17.672$ (6), $c = 7.266$ (3) Å, $\beta = 90.47$ (2)°, $Z = 8$ (25°C). The structure was refined to $R_w(F) = 0.044$, $R(F) = 0.039$ for 2895 observed reflections. The structure consists of layers of Ca^{2+} and $\text{HP}_2\text{O}_7^{3-}$ ions alternating with layers of NH_4^+ and $\text{HP}_2\text{O}_7^{3-}$ ions. The two independent Ca^{2+} ions are each coordinated to seven O atoms whose arrangement forms a distorted pentagonal bipyramid. A short, probably symmetric [O...O = 2.473 (4) Å], hydrogen bond links $\text{HP}_2\text{O}_7^{3-}$ ions as dimers. Two additional $\text{HP}_2\text{O}_7^{3-}$ ions act as donors to form two hydrogen bonds with the $\text{HP}_2\text{O}_7^{3-}$ dimers. The NH_4^+ ions participate in strong hydrogen bonds.

Introduction

The effects of inorganic pyrophosphates on teeth and bone have been reviewed (Fleisch & Russell, 1972). Some of the roles of Ca pyrophosphates in disease and metabolism have been identified, e.g. when pseudogout occurs Ca pyrophosphate dihydrate, and possibly other Ca pyrophosphate crystals, are found in joint cavities. Inorganic pyrophosphates are known to inhibit the formation and dissolution of apatite crystals *in vitro*. Steps toward a better understanding of the solubilities of Ca pyrophosphates have been taken by Brown & Gregory (1976).

Although several Ca pyrophosphates are known (Brown, Lehr, Smith & Frazier, 1963), their crystal chemistry lacks a firm foundation. A better understanding of the phase transformations in pyrophosphates, especially those occurring near 35°C, depends on knowing what atomic rearrangements are involved. Structural information can also be used to evaluate the likelihood of epitaxial overgrowths of Ca pyrophosphates on hydroxyapatite which would interfere with crystal growth and dissolution.

As an initial step in our program to elucidate the crystal chemistry of Ca pyrophosphates we report the structure of $\text{CaNH}_4\text{HP}_2\text{O}_7$.

Experimental

Crystals were prepared by the procedure given by Brown *et al.* (1963). 1 g of $\text{CaH}_2\text{P}_2\text{O}_7$ was added to a solution of 2.4 g of NH_4Cl in 75 ml of H_2O heated to 65°C. The solution was allowed to cool to 52°C over a period of a few hours without stirring. The solution was

then held at that temperature overnight to encourage the growth of $\text{CaNH}_4\text{HP}_2\text{O}_7$.

Examination of the crystals under the polarizing microscope showed no evidence of twinning and the refractive indices agreed with those of Brown *et al.* (1963). The crystal used for data collection was a rectangular plate, 0.21 × 0.07 × 0.03 mm, mounted in a general orientation with the longest dimension roughly parallel to the goniometer axis.

As reported (Brown *et al.*, 1963), $\text{CaNH}_4\text{HP}_2\text{O}_7$ crystallizes in space group $P2_1/n$ with $Z = 8$. The cell parameters were obtained by a least-squares fit of thirty $\pm 2\theta$ values measured on a four-circle diffractometer with $\text{Mo } K\alpha_1$ radiation ($\lambda = 0.70930$ Å) and a graphite monochromator (Lenhert, 1975).

A quadrant ($\pm hkl$) with $2\theta \leq 60^\circ$ was collected with θ - 2θ scans. The 2θ scan rate was $0.5^\circ \text{ min}^{-1}$ and backgrounds were counted for 40 s at each end of the range. Reflections with $40^\circ < 2\theta \leq 60^\circ$ were scanned if a test at the calculated position produced more than six counts in 10 s. These were merged into a set of 3090 independent reflections of which 2895 had $I > 3\sigma(I)$ and were considered observed. Three standards were measured every 30 reflections; their intensities varied by 3%. The data were scaled to allow for this small fluctuation but were not corrected for absorption ($\mu R_{\text{max}} = 0.14$).

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The 300 largest E values were used. The resulting E map from the best combination contained eight large peaks, of which two pairs were too close to be either Ca or P. A Fourier synthesis phased on the four readily identified atoms clearly indicated the positions of all the remaining atoms. As it turned out, one of the pairs was a P–O position and the other a Ca position and a spurious peak. Full-matrix least-squares refinement with individual isotropic temperature factors reduced R ($= \sum \|F_o| - |F_c| \| / \sum |F_o|$) to 0.055, and two additional

* Research Associates of the American Dental Association Health Foundation Research Unit at the National Bureau of Standards, Washington, DC 20234, USA.

cycles with anisotropic thermal parameters further reduced it to 0.043. The positions of all the H atoms were located in a difference synthesis. Block-diagonal refinement, in which all heavy atoms were assigned anisotropic, and the H atoms isotropic, thermal parameters, converged to $R = 0.039$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.044$ for 2895 reflections.

The quantity minimized was $\sum w[(F_o) - (F_c)]^2$, where $w = [\sigma(F_o)^2 + 0.0004(F_o)^2]^{-2}$. Scattering factors were taken from *International Tables for X-ray*

Table 1. The final positional parameters ($\times 10^4$) of non-hydrogen atoms in $\text{CaNH}_4\text{HP}_2\text{O}_7$

The values in parentheses are estimated standard deviations in the last significant digit.

	x	y	z
Ca(1)	3442 (1)	2205 (1)	4811 (1)
Ca(2)	2644 (1)	2517 (1)	9819 (1)
P(1)	604 (1)	2889 (1)	7037 (2)
P(2)	675 (1)	3376 (1)	3272 (2)
P(11)	6986 (1)	4197 (1)	7160 (2)
P(12)	4168 (1)	3916 (1)	7134 (2)
O(1)	1712 (2)	2340 (1)	6798 (4)
O(2)	678 (2)	3276 (2)	8883 (4)
O(3)	-682 (2)	2517 (1)	6818 (4)
O(4)	736 (2)	3529 (1)	5474 (4)
O(5)	1779 (2)	2878 (2)	2795 (4)
O(6)	853 (3)	4206 (2)	2525 (4)
O(7)	-640 (2)	3114 (2)	2758 (4)
O(11)	7798 (3)	4015 (2)	8814 (4)
O(12)	7126 (3)	5046 (1)	6665 (4)
O(13)	7120 (3)	3701 (2)	5522 (4)
O(14)	5557 (3)	4140 (2)	7900 (4)
O(15)	3489 (3)	3652 (2)	8815 (4)
O(16)	3605 (3)	4693 (2)	6517 (4)
O(17)	4243 (3)	3386 (2)	5532 (4)
N(1)	5139 (3)	4005 (2)	2095 (5)
N(2)	1329 (3)	4869 (2)	8608 (6)

Table 2. The final parameters of hydrogen atoms in $\text{CaNH}_4\text{HP}_2\text{O}_7$

Positional parameters are multiplied by 10^3 . Estimated standard deviations are given in parentheses.

	x	y	z	B (\AA^2)
H(1)	155 (3)	447 (2)	298 (7)	4.4 (1.1)
H(2)	324 (4)	482 (3)	489 (7)	6.2 (1.3)
H(3)	463 (4)	401 (3)	117 (8)	5.1 (1.3)
H(4)	477 (4)	385 (3)	311 (8)	5.8 (1.5)
H(5)	539 (4)	447 (3)	233 (7)	4.6 (1.4)
H(6)	586 (4)	370 (2)	168 (7)	4.3 (1.2)
H(7)	208 (4)	489 (2)	773 (6)	4.5 (1.1)
H(8)	79 (4)	510 (2)	802 (7)	3.6 (1.2)
H(9)	97 (4)	436 (3)	880 (8)	4.2 (1.4)
H(10)	165 (4)	520 (2)	974 (6)	3.3 (1.1)

Crystallography (1974), except for H (Stewart, Davidson & Simpson, 1965).

The final positional parameters and isotropic thermal parameters (for H) are listed in Tables 1 and 2.*

Results and discussion

The structure consists of a compact assembly of Ca^{2+} , $\text{HP}_2\text{O}_7^{3-}$ and NH_4^+ ions held together by a three-dimensional network of strong hydrogen bonds and $\text{Ca}\cdots\text{O}$ ionic bonds (Fig. 1). The structure can also be described in terms of layers of Ca^{2+} and $\text{HP}(1)\text{-P}(2)\text{O}_7^{3-}$ ions alternating with layers of NH_4^+ and $\text{HP}(11)\text{P}(12)\text{O}_7^{3-}$ ions roughly parallel to the *ac* plane.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32622 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

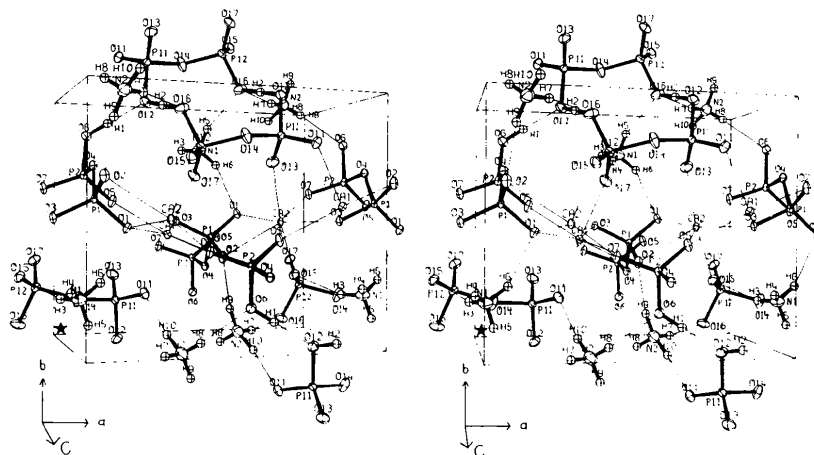


Fig. 1. A stereoscopic view of one-half the unit cell of $\text{CaNH}_4\text{HP}_2\text{O}_7$. The origin of the coordinate system is marked by a star.

The Ca^{2+} and NH_4^+ ions are well separated as the $\text{Ca}\cdots\text{Ca}$ distances are over 3.70 and the $\text{N}\cdots\text{N}$ over 3.40 Å.

The coordination around the two independent Ca(1) and Ca(2) atoms is quite similar. Each Ca is strongly coordinated to seven O atoms, in the range 2.274–2.606 Å. The geometry of the coordination can be best represented by a distorted pentagonal bipyramid with a chelate P_2O_3 , a shared PO_3 edge and a PO_3 corner in the equatorial plane and two PO_3 corners at the axial positions (Fig. 1).

The two $\text{HP}_2\text{O}_7^{3-}$ ions have quite different environments. In $\text{HP}(1)\text{P}(2)\text{O}_7^{3-}$ [hereafter referred to as (A)] each O atom (except the bridging O and OH) is coordinated to two Ca^{2+} ions. Coordination of Ca^{2+} ions by two chelate rings, two shared PO_3 edges and two PO_3 corners results in ten $\text{O}\cdots\text{Ca}$ contacts (Fig. 2). All chelating rings and shared PO_3 edges from (A) are in the equatorial plane of the Ca coordination. Pairs

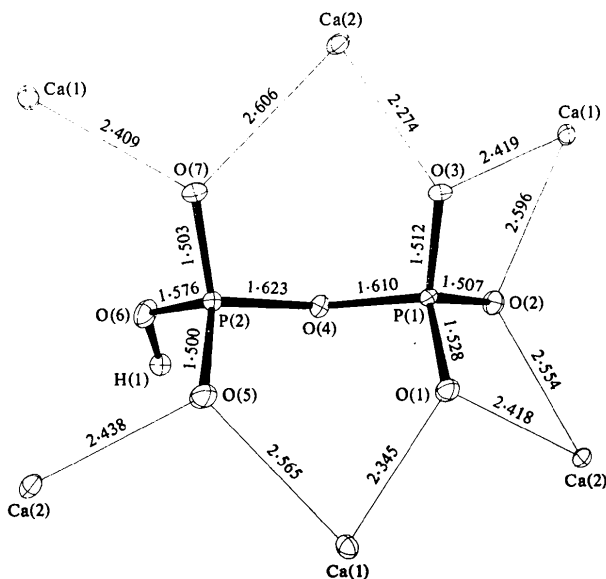


Fig. 2. Bond distances (Å) for hydrogenpyrophosphate ion A. Estimated standard deviations for all distances are 0.003 Å.

of $\text{Ca}\cdots\text{O}$ contacts on either side of the bridging O atoms are nearly equal in length with the result that the $\text{HP}_2\text{O}_7^{3-}$ ion is quite symmetrical with a nearly eclipsed conformation. (A) acts as an acceptor in three of the four hydrogen bonds it forms.

$\text{HP}(11)\text{P}(12)\text{O}_7^{3-}$ (B), on the other hand, is coordinated to only four Ca^{2+} ions, one to each O atom except the bridging O and OH (Fig. 3). However, (B) serves as an acceptor for seven hydrogen bonds.

The dimensions of (A) and (B) are given in Figs. 2 and 3. Bond angles are given in Table 3. The $\text{P}-\text{O}_i$ (terminal) distances range from 1.486 to 1.527 Å. The variations in $\text{P}-\text{O}_i$ distances appear to be related to the number and strength of $\text{Ca}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ interactions. For example, the longest $\text{P}-\text{O}_i$ distance [$\text{P}(1)-\text{O}(1) = 1.527$ Å] involves an O atom which has strong bonds to two Ca^{2+} ions and forms a strong hydrogen bond. On the other hand, the shortest $\text{P}-\text{O}_i$ [$\text{P}(11)-\text{O}(13) = 1.486$ Å] involves an O atom with only a single $\text{Ca}\cdots\text{O}$ contact and no participation in any hydrogen bond.

As Mandel (1975) pointed out for $\text{P}_2\text{O}_4^{4-}$ ions, $\text{P}-\text{O}_b$ (bridging) distances observed here appear to be related to $\text{P}-\text{O}_b-\text{P}$ angles (the larger the angle the shorter the bond). This has been interpreted on the basis of $d\pi-p\pi$ bonding (*i.e.* increasing the angle $\text{P}-\text{O}-\text{P}$ enhances

Table 3. Bond angles ($^\circ$) for the $\text{HP}_2\text{O}_7^{3-}$ ions

Estimated standard deviations are 0.2 $^\circ$.

O(1)–P(1)–O(2)	110.9	O(11)–P(11)–O(12)	109.8
O(1)–P(1)–O(3)	113.3	O(11)–P(11)–O(13)	117.2
O(1)–P(1)–O(4)	107.2	O(11)–P(11)–O(14)	104.3
O(2)–P(1)–O(3)	109.3	O(12)–P(11)–O(13)	112.0
O(2)–P(1)–O(4)	107.7	O(12)–P(11)–O(14)	103.3
O(3)–P(1)–O(4)	108.3	O(13)–P(11)–O(14)	109.0
O(4)–P(2)–O(5)	107.5	O(14)–P(12)–O(15)	103.5
O(4)–P(2)–O(6)	100.5	O(14)–P(12)–O(16)	103.1
O(4)–P(2)–O(7)	109.0	O(14)–P(12)–O(17)	111.7
O(5)–P(2)–O(6)	111.8	O(15)–P(12)–O(16)	109.1
O(5)–P(2)–O(7)	118.3	O(15)–P(12)–O(17)	117.9
O(6)–P(2)–O(7)	108.3	O(16)–P(12)–O(17)	110.5
P(1)–O(4)–P(2)	125.2	P(11)–O(14)–P(12)	138.7

Table 4. Details of the hydrogen bonds

The numbers in parentheses are standard deviations.

X–H \cdots Y	X–H (Å)	H \cdots Y (Å)	X \cdots Y (Å)	$\angle\text{X–H}\cdots\text{Y}$ ($^\circ$)
O(6)–H(1) \cdots O(12)	0.93 (4)	1.65 (4)	2.568 (4)	168 (4)
O(12)–H(2) \cdots O(16)	1.21 (5)	1.26 (5)	2.473 (4)	179 (4)
N(1)–H(3) \cdots O(15)	0.86 (5)	2.18 (5)	3.003 (5)	161 (5)
N(1)–H(4) \cdots O(17)	0.89 (5)	2.02 (6)	2.892 (5)	169 (5)
N(1)–H(5) \cdots O(16)	0.89 (5)	1.99 (5)	2.835 (5)	158 (5)
N(1)–H(6) \cdots O(16)	0.98 (5)	2.05 (4)	2.906 (5)	145 (4)
N(2)–H(7) \cdots O(16)	1.02 (4)	1.87 (4)	2.863 (5)	164 (4)
N(2)–H(8) \cdots O(6)	0.82 (4)	2.15 (4)	2.932 (5)	159 (4)
N(2)–H(9) \cdots O(2)	0.98 (5)	1.94 (5)	2.904 (5)	165 (4)
N(2)–H(10) \cdots O(11)	1.06 (4)	1.84 (4)	2.866 (5)	163 (4)

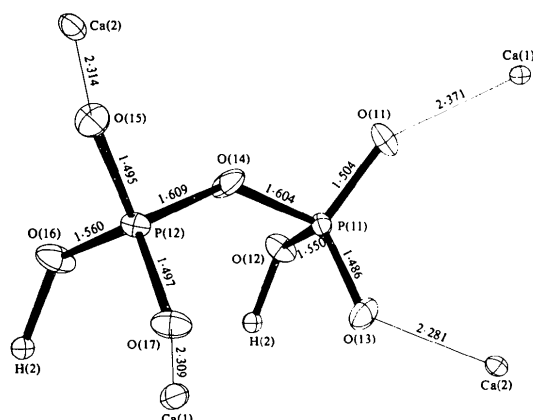


Fig. 3. Geometry of hydrogenpyrophosphate ion *B*. Estimated standard deviations for all distances are 0.003 Å.

overlap of $d\pi$ and $p\pi$ orbitals) and has been the subject of several studies (e.g. Lager & Gibbs, 1973).

The following considerations suggest that the P—O—P angle in the $\text{HP}_2\text{O}_7^{3-}$ ion is also sensitive to the cation coordination. On the basis of P—O_b distances the $\text{HP}_2\text{O}_7^{3-}$ ion in $\text{K}_3\text{HP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ resembles (*A*) but the P—O—P angle of 132.8° is more like that for (*B*). Now, (*A*) coordinates Ca by means of two chelating rings in contrast to (*B*) which does not. Chelation of K also occurs in $\text{K}_3\text{HP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, but the K...O distances are much longer as K is larger than Ca. This suggests that the smaller P—O—P angle in (*A*) is partially the result of the chelation to Ca ions.

Table 4 gives distances and angles associated with the hydrogen bonds. There is no disorder of NH_4 groups; the N—H...O hydrogen-bond lengths are fairly typical of those observed in ammonium salts (Hamilton & Ibers, 1968; Choi, Mapes & Prince, 1972). O(16) participates in three strong hydrogen bonds (two N—H...O and one O—H...O) and this may be the reason why O(16) does not coordinate to any Ca ion.

Hydrogen bonds [O(16)—H(2)...O(12)] link pyrophosphate ions *B* together in a dimeric configuration across a center of symmetry (Fig. 1, top). The O(16)...O(12) distance [2.473 (4) Å] is quite short and corresponds to a symmetric single- or double-minimum type of hydrogen bond (Novak, 1973). This conclusion is supported by the observation that H(2) refined to almost the midpoint of the O(16)...O(12) vector, even though not required to do so by any symmetry element. The O—H...O angle (179°) is also characteristic of symmetric hydrogen bonds. This situation is somewhat unusual in that O(12) is also involved in the hydrogen bond O(6)—H(1)...O(12). Although the O(6)...O(12) distance of 2.568 (4) Å falls within the range 2.48–2.58 Å (Novak, 1973) for the double-minimum type hydrogen bond, H(1) refined to a location much closer to O(6) (Table 3). Both H(1) and H(2) were treated the same way in the refinement

and thus the two hydrogen bonds must be quite different. The P(2)—O(6) distance (1.575 Å) is one of the longest terminal P—O distances and also supports the assignment of H(1) to O(6).

In principle, spectroscopic methods should be able to distinguish between a single- or double-minimum potential for the proton in the O(16)...H(2)...O(12) hydrogen bonds. Wood (1973) has given the spectroscopic features expected for the various potentials, although the spectra are likely to be complicated because of the dimeric configuration that leads to correlated motion of two protons (Coulson, 1959).

Hydrogen bonding of $\text{HP}_2\text{O}_7^{3-}$ ions has also been observed in $\text{K}_3\text{HP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (Dumas, Galigné & Falgueirettes, 1973). In that structure, $\text{HP}_2\text{O}_7^{3-}$ ions are linked by short hydrogen bonds (O...O = 2.489 Å, $\angle\text{O—H...O} = 179^\circ$) forming a spiral array about a 2₁ axis. Thus, the tendency of $\text{HP}_2\text{O}_7^{3-}$ ions to form short hydrogen bonds seems established.

The strong hydrogen bonds observed in hydrogenpyrophosphate salts suggest that $\text{HP}_2\text{O}_7^{3-}$ ions may be strongly absorbed on the surface of hydroxyapatite. Thus, under appropriate conditions the $\text{HP}_2\text{O}_7^{3-}$ ion may play a role in the inhibition of the formation and dissolution of hydroxyapatite.

We thank P. B. Kingsbury for technical help. The figures were drawn with a local version of the ORTEP program of C. K. Johnson. This investigation was supported in part by Research Grant DE00572 to the American Dental Association Health Foundation made available by the National Institute of Dental Research.

References

- BROWN, E. H., LEHR, I. R., SMITH, J. P. & FRAZIER, A. W. (1963). *J. Agric. Food Chem.* **11**, 214–222.
- BROWN, W. E. & GREGORY, T. M. (1976). *Arthritis Rheumat.* **19**, 446–462.
- CHOI, C. S., MAPES, J. E. & PRINCE, E. (1972). *Acta Cryst.* **B28**, 1357–1361.
- COULSON, C. A. (1959). *Hydrogen Bonding*, edited by D. HADZI, pp. 350–354. New York: Pergamon Press.
- DUMAS, Y., GALIGNÉ, J. L. & FALGUEIRETTES, J. (1973). *Acta Cryst.* **B29**, 1623–1630.
- FLEISCH, H. & RUSSELL, R. G. G. (1972). *J. Dent. Res.* **51**, 324–332.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- International Tables for X-ray Crystallography* (1974). Vol. IV, p. 71. Birmingham: Kynoch Press.
- LAGER, G. A. & GIBBS, G. V. (1973). *Amer. Min.* **58**, 756–764.
- LENHART, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.
- MANDEL, N. (1975). *Acta Cryst.* **B31**, 1730–1734.
- NOVAK, A. (1973). *Struct. Bond.* pp. 1777–1797.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WOOD, J. L. (1973). *J. Mol. Struct.* **17**, 307–328.