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The Structure of Diammonium Tricalcium Bis(pyrophosphate) Hexahydrate

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(*Received* 12 *February* 1980; *accepted* 13 *May* 1980)

Abstract

$Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ crystallizes in the monoclinic space group $P2_1/n$ with a = 7·674 (1), b = 11·455 (2), c = 11·014 (2) Å, β = 92·44 (5)° and Z = 2 at room temperature. The structure was refined to R = 0·059, R_w = 0·057 for 2179 reflections with $F_o > 3\sigma(F_o)$. The structure consists of layers of Ca^{2+} and $[P_2O_7]^{4-}$ ions alternating with layers of Ca^{2+} and $[NH_4]^+$ ions and water molecules. The coordinations of the Ca^{2+} ions in the two layers are different. $[NH_4]^+$ ions and water molecules are hydrogen bonded to $[P_2O_7]^{4-}$ ions.

Introduction

Inorganic pyrophosphates are known to play an important role in the mineralization of teeth and bones (Fleisch & Russel, 1972). Detailed structural analyses of a number of pyrophosphates, particularly those formed at or about the physiological conditions, are necessary for any generalizations on their structural features and related properties. A survey of the known pyrophosphates has shown that the $[P_2O_7]^{4-}$ ion is capable of adopting a wide variety of conformations with different cations (Mandel, 1975). As part of our program to elucidate the crystal chemistry of calcium pyrophosphates, we report the structure of $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$.

Experimental

Suitable crystals of $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ were prepared by a slight modification of the procedure given by Brown, Lehr, Smith & Frazier (1963). Freshly precipitated $Ca_2P_2O_7$ (prepared by mixing $K_4P_2O_7$ and

$CaCl_2$) was added to a 5 *M* solution of NH_4Cl with continuous stirring. The mixture was then kept at 308 to 313 K for about 3 days; at that point small crystals started to appear. The solution was then cooled slowly to room temperature. Large plate-like crystals were obtained. The refractive indices and X-ray powder diffraction pattern agreed with those reported (Brown *et al.*, 1963).

Preliminary photographs confirmed the space group $P2_1/n$ with $Z = 2$ as reported (Brown *et al.*, 1963). A rectangular plate 0·24 × 0·16 × 0·04 mm mounted along the longest dimension was used for the data collection. The cell parameters (Table 1) were obtained by a least-squares fit of the setting angles of 15 reflections with $45° < 2\theta < 60°$, by automatically centering at both positive and negative 2θ values. Monochromatized Mo $K\alpha_1$ radiation ($\lambda = 0{\cdot}70932$ Å) was used. Intensity data were collected on a four-circle automated diffractometer. The diffractometer-controlling programs were those of Lenhert (1975). A summary of the experimental conditions used in the data collection is given in Table 1. An absorption correction was applied using the program XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

The positions of the Ca and P atoms were deduced from a three-dimensional Patterson synthesis. The remaining atoms were located in subsequent Fourier syntheses. Refinement was by full-matrix least squares using the program *RFINE*4 (Finger & Prince, 1975). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + (0{\cdot}02F_o)^2$ and $\sigma^2(F_o)$ is obtained from counting statistics. The scattering factors used were those for the neutral atoms taken from *International Tables for X-ray Crystallography* (1974). The positions of all H atoms were located from a difference Fourier synthesis. Their positions were also refined with fixed isotropic thermal parameters ($B = 3{\cdot}0$ Å^2) in subsequent calculations. Results of the refinements are summarized in Table 1. Final atomic parameters are listed in Table 2.*

Table 1. *Crystal data and experimental and refinement parameters for* $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$

Crystal data

$Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$, $M_r = 612{\cdot}30$, monoclinic, space group $P2_1/n$, $Z = 2$, $a = 7{\cdot}674$ (1)*, $b = 11{\cdot}455$ (2), $c = 11{\cdot}014$ (2) Å, $\beta = 92{\cdot}44$ (5)°, $V = 967{\cdot}32$ Å^3, $D_c = 2{\cdot}102$, $D_m = 2{\cdot}08$ Mg m^{-3} (Brown *et al.*, 1963), μ(Mo $K\alpha$) = 1·255 mm^{-1}.

Experimental and refinement parameters

Number of reflections	
Total measured	3581 ($h, -k, \pm l$ quadrant, $2\theta \le 60°$)
Unique	2835 [656 with $F_o < 3\sigma(F_o)$]
Data collection mode	θ–2θ scan mode at a rate of 0·5° min^{-1}
Background	Counted for 20 s at each end of the scan
Absorption correction (XRAY 76, Stewart *et al.*, 1976)	
Maximum correction to F_o^2	1·200
Minimum correction to F_o^2	1·055
Number of reflections in refinement, *m*	2179 [$F_o > 3\sigma(F_o)$]
Number of variables, *n*	164
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0·059 (0·081 for all reflections)
$R_w = (\sum w \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2 / \sum w \lvert F_o\rvert^2)^{1/2}$	0·057 (0·058 for all reflections)
$S = [\sum w \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2/(m-n)]^{1/2}$	1·56
Average shift/error	0·04

* Throughout this paper, numbers in parentheses are standard deviations in the least significant digits.

Results and discussion

The structure consists of a compact assembly of Ca^{2+}, $[P_2O_7]^{4-}$ and $[NH_4]^+$ ions and water molecules held together by a three-dimensional network of hydrogen bonds and Ca···O ionic bonds (Fig. 1). However, the structure can be best described as a layer-type structure containing two types of layers. The $Ca(2)^{2+}$ and $[P_2O_7]^{4-}$ ions form one layer (*A*). The $Ca(1)^{2+}$ and $[NH_4]^+$ ions and water molecules, arranged

Table 2. *Final atomic parameters for* $Ca_3(NH_4)_2$-$(P_2O_7)_2.6H_2O$

	x	*y*	*z*	B_{eq} (Å^2)*
Ca(1)	0·0	0·0	0·0	0·98
Ca(2)	0·6069 (1)	0·2721 (1)	0·9293 (1)	0·97
P(1)	0·3802 (1)	0·2537 (1)	0·6413 (1)	0·77
P(2)	0·7601 (1)	0·2794 (1)	0·6351 (1)	0·87
O(1)	0·3928 (4)	0·3015 (3)	0·7686 (3)	1·37
O(2)	0·3214 (4)	0·3443 (3)	0·5467 (3)	1·24
O(3)	0·2715 (4)	0·1444 (3)	0·6213 (3)	1·46
O(4)	0·5748 (4)	0·2131 (3)	0·6076 (3)	1·23
O(5)	0·7335 (4)	0·4059 (3)	0·5985 (3)	1·80
O(6)	0·8043 (4)	0·2666 (3)	0·7701 (2)	1·33
O(7)	0·8811 (4)	0·2133 (3)	0·5568 (3)	1·35
O(8)	0·5541 (5)	0·3964 (4)	0·3205 (3)	2·22
O(9)	0·0143 (5)	0·4262 (4)	0·3771 (4)	2·49
O(10)	0·1448 (10)	0·0249 (4)	0·3853 (4)	4·44
N	0·6100 (6)	0·0862 (4)	0·3697 (4)	1·95

	x	*y*	*z*
H(O81)	0·475 (8)	0·349 (6)	0·308 (5)
H(O82)	0·626 (8)	0·396 (6)	0·277 (6)
H(O91)	0·102 (8)	0·487 (6)	0·389 (5)
H(O92)	−0·074 (8)	0·449 (6)	0·391 (6)
H(O101)	0·118 (8)	0·017 (6)	0·320 (6)
H(O102)	0·122 (8)	−0·051 (6)	0·418 (5)
H(N1)	0·511 (8)	0·100 (6)	0·330 (5)
H(N2)	0·597 (8)	0·009 (6)	0·382 (5)
H(N3)	0·688 (8)	0·115 (6)	0·336 (5)
H(N4)	0·622 (7)	0·100 (5)	0·471 (5)

* The equivalent values of anisotropic temperature factors correspond to the definitions given by Hamilton (1959). Fixed isotropic thermal parameters ($B = 3{\cdot}0$ Å^2) were used for all hydrogen atoms.

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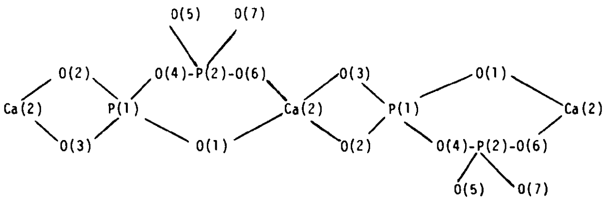
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35435 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

interstitially between these *A* layers, constitute the second layer (*B*). The layers are perpendicular to the *b* axis (Fig. 1).

Layer *A* contains Ca–P_2O_7 chains of along [101]. In this respect, these chains resemble those found in several calcium orthophosphates where opposite edges of PO_4 groups are linked to Ca atoms; for example: $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971); $CaHPO_4.2H_2O$ (Curry & Jones, 1971); $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ (Takagi, Mathew & Brown, 1980). These chains are linked together by a strong Ca···O bond [Ca(2)–O(7) = 2·282 Å] and by bridging hydrogen bonds involving O(8) and the $[NH_4]^+$ ion.



The structure is related to that of $Ca(NH_4)HP_2O_7$ (Mathew & Schroeder, 1977) which also contains layers perpendicular to the *b* axis, made up of Ca–P_2O_7 chains with alternating edge- and chelate-type coordination. In $Ca(NH_4)HP_2O_7$ the edge- and chelate-type linkages are approximately coplanar, whereas in $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ they are approximately perpendicular as in calcium orthophosphates. The *c* and *a* axes of $Ca(NH_4)HP_2O_7$ are approximately the same as the *a* and *c* axes respectively of $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$. The formula $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ can be represented by replacement of two H^+ ions in $2[Ca(NH_4)HP_2O_7]$ by $Ca.6H_2O$, which forms the major portion of the *B* layer; this results in a corresponding increase in length of the *b* axis.

The structure of $Ca_2P_2O_7.2H_2O$ (Mandel, 1975) can also be described in terms of a layer-type structure. Layers containing $[P_2O_7]^{4-}$ and H_2O are interleaved with layers of Ca^{2+} and H_2O. The layered-type structure thus appears to be a common feature of several calcium pyrophosphates, in spite of variations in the composition. The layered structural type is an important class of compounds among calcium orthophosphates (Dickens & Brown, 1972).

The geometry of the calcium coordination in the two layers of $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$ is quite different. Ca(1) is at a crystallographic center of inversion and its environment in layer *B* is close to a perfect octahedron, with a mean Ca···O distance of 2·333 Å (Table 3). The coordination involves two chelating P_2O_7 groups from its adjacent *A* layers and two water molecules. Ca(2), in layer *A*, is coordinated to seven O atoms

Table 3. *Bond lengths* (Å) *in the coordination sphere of* Ca *in* $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$

Ca(1)–O(2)	2·320 (3)	Ca(1)–O(8)	2·358 (4)
Ca(1)–O(5)	2·320 (3)		
Ca(2)–O(1)	2·387 (3)	Ca(2)–O(7)	2·282 (3)
Ca(2)–O(2)	2·445 (3)	Ca(2)–O(9)	2·441 (5)
Ca(2)–O(3)	2·599 (3)	Ca(2)–O(10)	2·396 (5)
Ca(2)–O(6)	2·366 (3)		

Table 4. *Bond lengths* (Å) *and bond angles* (°) *for the* $[P_2O_7]^{4-}$ *ion in* $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$

E.s.d.'s for the angles are 0·2°.

P(1)–O(1)	1·504 (4)*	O(1)–P(1)–O(2)	113·2
P(1)–O(2)	1·525 (4)‡	O(1)–P(1)–O(3)	116·7
P(1)–O(3)	1·515 (4)†	O(1)–P(1)–O(4)	107·1
P(1)–O(4)	1·622 (3)	O(2)–P(1)–O(3)	108·5
P(2)–O(4)	1·629 (3)	O(2)–P(1)–O(4)	106·7
P(2)–O(5)	1·516 (4)*	O(3)–P(1)–O(4)	103·7
P(2)–O(6)	1·518 (4)†	O(5)–P(2)–O(4)	106·8
P(2)–O(7)	1·499 (3)*	O(5)–P(2)–O(6)	112·0
		O(5)–P(2)–O(7)	114·2
		O(6)–P(2)–O(4)	107·1
		O(6)–P(2)–O(7)	113·4
		O(7)–P(2)–O(4)	102·4
		P(1)–O(4)–P(2)	128·9

* Involved with one Ca atom and one H bond.
† Involved with one Ca atom and two H bonds.
‡ Involved with two Ca atoms.

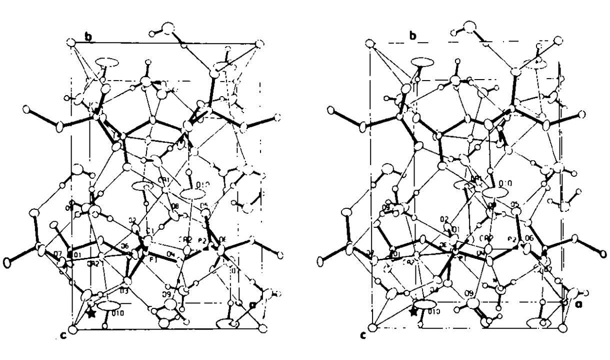


Fig. 1. The unit-cell contents of $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$. The origin of the coordinate system is marked by a star.

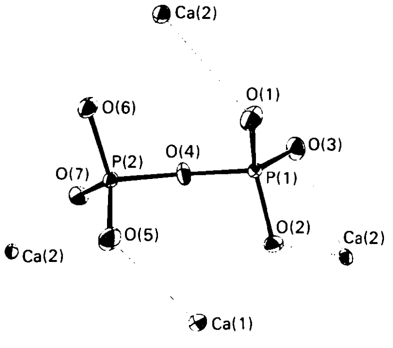


Fig. 2. The environment around the $[P_2O_7]^{4-}$ ion.

Table 5. *Details of the hydrogen bonds in* $Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$

D—H···*A**	Position of *A*	*D*—H (Å)	H···*A* (Å)	D···*A* (Å)	∠*D*—H···*A* (°)
O(8)—H(O81)···O(6)	$x-\frac{1}{2},\frac{1}{2}-y,z-\frac{1}{2}$	0·82 (6)	1·90 (6)	2·716 (5)	175 (6)
O(8)—H(O82)···O(3)	$\frac{1}{2}+x,\frac{1}{2}-y,z-\frac{1}{2}$	0·75 (6)	2·14 (6)	2·851 (5)	161 (7)
O(9)—H(O91)···O(5)	$1-x,1-y,1-z$	0·97 (7)	1·76 (7)	2·734 (5)	176 (6)
O(10)—H(O101)···O(8)	$\frac{1}{2}-x,y-\frac{1}{2},\frac{1}{2}-z$	0·75 (7)	2·42 (7)	3·056 (7)	144 (6)
O(10)—H(O102)···O(7)	$1-x,\bar{y},1-z$	0·96 (7)	1·88 (7)	2·811 (6)	163 (6)
N—H(N1)···O(6)	$\frac{1}{2}+x,\frac{1}{2}-y,z-\frac{1}{2}$	0·87 (6)	2·28 (6)	3·055 (6)	148 (5)
N—H(N2)···O(3)	$1-x,\bar{y},1-z$	0·90 (7)	2·03 (7)	2·794 (6)	142 (5)
N—H(N3)···O(1)	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	0·79 (6)	2·01 (6)	2·795 (6)	173 (6)
N—H(N4)···O(4)	x,y,z	1·13 (6)	2·03 (6)	3·019 (6)	144 (4)

* *D*—H at *x*,*y*,*z*.

consisting of a chelate-type P_2O_7 group, a shared PO_3 edge, a PO_3 corner and two water molecules. The arrangement of the O atoms around Ca(2) is rather irregular, but may be described as pentagonal bipyramidal, as in $Ca(NH_4)HP_2O_7$, or as a capped octahedron, as in $CaP_2O_7.2H_2O$, with severe distortions.

The molecular dimensions of the $[P_2O_7]^{4-}$ ion and its environment are given in Fig. 2 and Table 4. Each O atom, except the bridging O(4), has at least one O···Ca contact. All O atoms except O(2) are involved in hydrogen bonds (Table 5); O(2) is linked to two Ca^{2+} ions.

The P—O_t (terminal) distances range from 1·499 to 1·525 Å. The variation in P—O_t bond lengths appears to be correlated to the number and strength of O···Ca and O···H—O or O···H—N interactions. The O_b (bridge)—P—O_t angles vary from 102·4 to 107·1° and the O_t—P—O_t angles from 108·5 to 116·7°. The relatively large variation in angles is characteristic of the pyrophosphate ions. All dimensions of the pyrophosphate ion are well within the range of values observed in other pyrophosphates (Mandel, 1975). The conformation about P···P is approximately midway between eclipsed and staggered, with a mean O_t—P···P—O_t angle of 29·8° (Fig. 3).

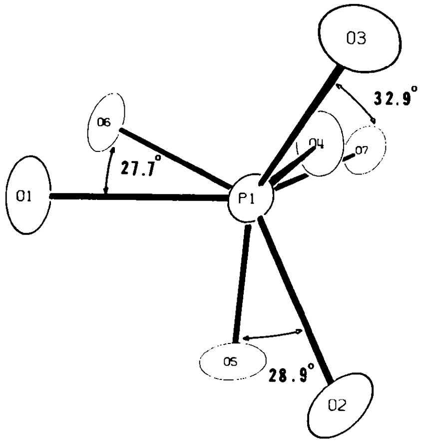


Fig. 3. The conformation of the $[P_2O_7]^{4-}$ ion as viewed along the P(1),P(2) direction.

The dimensions of the hydrogen bonds are given in Table 5. All available H atoms of $[NH_4]^+$ ions and water molecules except H(O92) are involved in hydrogen bonds.

We thank P. B. Kingsbury for technical help. The figures were drawn with a local version of the *ORTEP* program (Johnson, 1965). This investigation was supported in part by Research Grant DE005030-2 to the American Dental Association Health Foundation Research Unit 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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