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Structure of Barium Chlorapatite

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Abstract. $Ba_5Cl(PO_4)_3$, hexagonal, $P6_3/m$, a = 10·284 (2), c = 7·651 (3) Å, Z = 2. The crystals were grown by hydrothermal reaction of $BaCl_2.2H_2O$ and K_2HPO_4 at 473 K. Refinements were carried out by the full-matrix least-squares method to R = 0·034 and R_w = 0·039 with 810 independent reflexion data. Comparisons with the structures of other chlorapatites are presented.

Introduction. Chlorapatites, $M_5Cl(PO_4)_3$ (M = Ca, Ba, Sr, Mn, Cd, *etc.*), belong to the apatite group of compounds. The crystal structures have been investigated for $Ca_5Cl(PO_4)_3$ (Mackie, Elliott & Young, 1972), $Cd_5Cl(PO_4)_3$ (Sudarsanan, Young & Donnay, 1973), $Sr_5Cl(PO_4)_3$ (Sudarsanan & Young, 1974) and $Mn_5Cl_{0.9}OH_{0.1}(PO_4)_3$ (Engel, Pretzsch, Gramlich & Baur, 1975) by X-ray diffraction. All these apatites have the space group $P6_3/m$, except $Ca_5Cl(PO_4)_3$ which crystallizes in $P2_1/b$. The locations of the Cl^- ions are not the same among these crystals. The anion occupies the special position 2(b) (0,0,0) in $Sr_5Cl(PO_4)_3$, and 2(a) (0,0,$\frac{1}{4}$) in $Cd_5Cl(PO_4)_3$ and $Mn_5Cl_{0.9}OH_{0.1}(PO_4)_3$. In $Ca_5Cl(PO_4)_3$, it lies at 4(e) (0,0,z) with z = 0·06, giving a similar atomic configuration to that of $Sr_5Cl(PO_4)_3$.

As part of a study of the apatite group compounds, single crystals of $Ba_5Cl(PO_4)_3$ were synthesized by a hydrothermal reaction and the crystal structure was refined. The structure is in principle the same as that of $Sr_5Cl(PO_4)_3$.

Single crystals of barium chlorapatite were prepared by hydrothermal reaction of $BaCl_2.2H_2O$ and K_2HPO_4. 0·05 mol of $BaCl_2.2H_2O$ and 0·03 mol of K_2HPO_4 in 50 ml of distilled water were heated at 473 K for 2 weeks. Single crystals of barium chlorapatites grew at pH 5–6 with $BaHPO_4$. The crystals obtained were colourless, transparent hexagonal prisms 0·1–0·3 mm in length and 0·03–0·1 mm in diameter.

The infrared spectrum of $Ba_5Cl(PO_4)_3$ was recorded in the range 4000 to 400 cm^{-1}, but the OH stretching band was not observed. This indicates that Cl is not replaced by OH in the crystal.

Weissenberg photographs showed Laue symmetry $6/m$ and the systematic absences $00l$ for l odd. The possible space groups are, therefore, $P6_3/m$ (centrosymmetric) and $P6_3$ (noncentrosymmetric). $P6_3/m$ was employed in the structure refinement, since all the apatite group compounds known to date belong to this space group.

Intensities were measured on an automated four-circle diffractometer (Philips PW 1100/20), with graphite-monochromated Mo $K\alpha$ radiation, by the 2θ–ω scan technique with a scan speed of 4° min^{-1} in ω, using a crystal 0·15 mm in length and 0·06 mm in diameter. 810 independent reflexion data $[F_o > 3\sigma(F_o)]$ were obtained within the range $2\theta \leq 80°$. Intensities were corrected for Lorentz and polarization factors. Absorption corrections (μ = 14·868 mm^{-1} for Mo $K\alpha$) were made with the program *ACACA* (Wuensch & Prewitt, 1965).

The refinement was started from the parameters of cadmium hydroxyapatite, $Cd_5OH(PO_4)_3$ (Hata, Okada, Iwai, Akao & Aoki, 1978), and the position of Cl was determined in the difference Fourier syntheses. The calculation with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) converged to the residual $R = \sum ||F_o| - |F_c||/\sum |F_o|$ = 0·034 and the weighted residual $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ = 0·039 with anisotropic temperature factors. The weighting scheme employed was that of Hughes, with $w = 1$ if $F_o < F_{o\,\max}$, and $w = F_{o\,\max}/F_o$ if

Table 1. *Final positional parameters* (×10⁴) *and isotropic thermal parameters* (×10⁴) *for* $Ba_5Cl(PO_4)_3$

	x	y	z	B (Å^2)*
Ba(1)	3333	6667	7 (1)	7300
Ba(2)	2449 (1)	2606 (1)	2500	6900
P	4064 (3)	346 (3)	2500	5000
O(1)	3432 (10)	−1374 (8)	2500	12500
O(2)	5790 (9)	1157 (10)	2500	12200
O(3)	3568 (6)	858 (6)	874 (8)	12300
Cl	0	0	0	9700

* Calculated from the anisotropic thermal parameters according to the expression: $B = 4(a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma)/3$.

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$F_o \geq F_{o\,\mathrm{max}}$ with $F_{o\,\mathrm{max}} = 181$. The atomic scattering factors for Cl^-, Ba^{2+} and P^{5+} and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974) and the scattering factors given by Tokonami (1965) were used for O^{2-}.

The final positional and isotropic thermal parameters are given in Table 1.*

Discussion. Selected interatomic distances and bond angles are given in Table 2. There are two crystallographically independent Ba atoms in the unit cell. Ba(1) is surrounded by nine O atoms [three O(1), three O(2) and three O(3)] at a mean distance of 2·824 Å, whereas Ba(2) is surrounded by six O atoms [O(1), O(2) and four O(3)] and two Cl atoms at mean distances of 2·791 and 3·230 Å for Ba(2)–O and Ba(2)–Cl respectively. The PO_4 tetrahedron is almost regular. The mean P–O distance of 1·540 Å is almost the same as those in $Sr_5Cl(PO_4)_3$ (1·539 Å, Sudarsanan & Young, 1974) and $Cd_5Cl(PO_4)_3$ (1·541 Å, Sudarsanan *et al.*, 1973), but a little shorter than those in $Ca_5Cl(PO_4)_3$ (1·544 Å, Mackie *et al.*, 1972) and $Mn_5Cl_{0.9}OH_{0.1}(PO_4)_3$ (1·548 Å, Engel *et al.*, 1975). The O(1)–P–O(2) and O(1)–P–O(3) bond angles are larger than O(2)–P–O(3) and O(3)–P–O(3)^{iii}, as is observed in other chlorapatites. The difference between the largest and the smallest bond angles increases with the decrease in ionic radii of the metal ions.

The Cl^- ions are located at 2(*b*) (0,0,0) in $Ba_5Cl(PO_4)_3$ and $Sr_5Cl(PO_4)_3$, whereas in $Cd_5Cl(PO_4)_3$ and $Mn_5Cl_{0.9}OH_{0.1}(PO_4)_3$ they are at the centre of the metal triangle, 2(*a*) (0,0,$\frac{1}{4}$). In $Ca_5Cl(PO_4)_3$ the Cl^- ions occupy 4(*e*) (0,0,0·06), slightly deviating from the (0,0,0) position along the *c* axis. Fig. 1 shows the local atomic environment around the 6_3 axis in $Ba_5Cl(PO_4)_3$ and $Cd_5Cl(PO_4)_3$ and the corresponding part in $Ca_5Cl(PO_4)_3$. In the structure of $M_5Cl(PO_4)_3$, the location of the Cl^- ion depends upon the size of M^{2+}; it occupies the (0,0,0) position when M^{2+} is larger than Ca^{2+} and (0,0,$\frac{1}{4}$), when M^{2+} is smaller than Ca^{2+}. The location of the Cl^- ion in $Ca_5Cl(PO_4)_3$ is intermediate between (0,0,0) and (0,0,$\frac{1}{4}$). In contrast to chlorapatites, hydroxyapatites, $Ca_5OH(PO_4)_3$ (Sudarsanan & Young, 1969) and $Cd_5OH(PO_4)_3$ (Hata *et al.*, 1978), have the OH^- ions at the same sites. The radius ratio of anion to M^{2+} seems to be responsible for the location of the anion. The *M*(2) atom in Ca, Sr or Ba chlorapatites is coordinated by two Cl atoms and six O atoms and its coordination number is 8, whereas *M*(2) in Cd or Mn chlorapatites is coordinated by one Cl atom and five O atoms, since the distance *M*(2)–O(1) in Cd or Mn chlorapatites is too long to be counted as a coordinating contact.

The distortion of the PO_4 tetrahedron in $Ba_5Cl(PO_4)_3$ was quantified by the use of the distortion indices DI(PO), DI(OO) and DI(OPO), after Baur (1974), which express the average relative deviations of P–O, O–O and O–P–O from their mean values.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Symmetry code

(0)	x,y,z	(v)	$x-y, x, -z$
(i)	$-y, x-y, z$	(vi)	$y, y-x+1, -z$
(ii)	$x-y, x, \frac{1}{2}+z$	(vii)	$x, y+1, -z$
(iii)	$x, y, \frac{1}{2}-z$	(viii)	$1-x, 1-y, -z$
(iv)	$y-x+1, 1-x, z$		

PO_4 tetrahedra	
P–O(1)^{0}	1·548 (8)
P–O(2)^{0}	1·539 (9)
P–O(3)^{0,iii} (×2)	1·536 (7)
O(1)–O(2)^{0}	2·519 (10)
O(1)–O(3)^{0,iii} (×2)	2·554 (11)
O(2)–O(3)^{0,iii} (×2)	2·484 (11)
O(3)–O(3)^{iii}	2·489 (9)
O(1)–P–O(2)^{0}	109·4 (6)
O(1)–P–O(3)^{0,iii} (×2)	111·8 (3)
O(2)–P–O(3)^{0,iii} (×2)	107·8 (3)
O(3)–P–O(3)^{iii}	108·2 (4)

Environment of the metal atoms	
Ba(1)–O(1)^{i,iv,vii} (×3)	2·740 (5)
Ba(1)–O(2)^{v,vi,viii} (×3)	2·736 (10)
Ba(1)–O(3)^{v,vi,viii} (×3)	2·995 (7)
Ba(2)–O(1)^{i}	2·972 (14)
Ba(2)–O(2)^{iv}	2·601 (12)
Ba(2)–O(3)^{0,iii} (×2)	2·857 (8)
Ba(2)–O(3)^{ii,v} (×2)	2·730 (6)
Ba(2)–Cl^{0,iii} (×2)	3·230 (1)

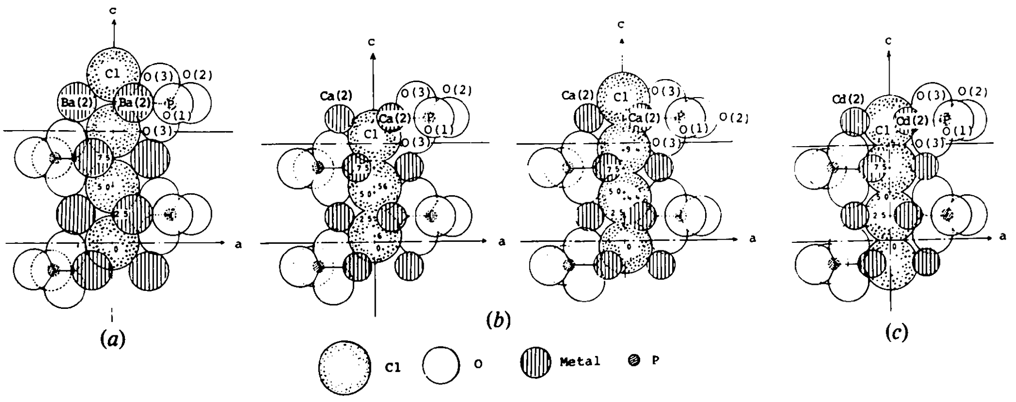

Fig. 1. The location of the Cl atom in (*a*) $Ba_5Cl(PO_4)_3$, (*b*) $Ca_5Cl(PO_4)_3$ and (*c*) $Cd_5Cl(PO_4)_3$, where each ionic radius is drawn to scale.

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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 34567 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of the distortion indices* (*Baur*, 1974) *in four chlorapatites*

	$Ba_5Cl(PO_4)_3$	$Sr_5Cl(PO_4)_3$(1)	$Ca_5Cl(PO_4)_3$(2)	$Cd_5Cl(PO_4)_3$(3)
DI(PO)	0·002	0·002	0·003	0·005
DI(OO)	0·014	0·018	0·020	0·024
DI(OPO)	0·011	0·012	0·013	0·013

References: (1) Sudarsanan & Young (1974); (2) Mackie *et al.* (1972); (3) Sudarsanan *et al.* (1973).

These values are given in Table 3 along with those of other chlorapatites for comparison. Among the metal ions which form the apatite structure, the ionic radius of Ba^{2+} is the largest and gives the smallest distortion of the PO_4 tetrahedron.

We are very grateful to Professor M. Kato of Tokyo Institute of Technology for his kindness in allowing us to use an automated four-circle diffractometer. Computations were carried out on an M-180 (Hitachi) computer at the Computation Center of Tokyo Institute of Technology.

References

BAUR, W. H. (1974). *Acta Cryst.* **B30**, 1195–1215.

COPPENS, S. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.

ENGEL, G., PRETZSCH, J., GRAMLICH, V. & BAUR, W. H. (1975). *Acta Cryst.* **B31**, 1854–1860.

HATA, M., OKADA, K., IWAI, S., AKAO, M. & AOKI, H. (1978). *Acta Cryst.* **B34**, 3062–3064.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MACKIE, P. E., ELLIOTT, J. C. & YOUNG, R. A. (1972). *Acta Cryst.* **B28**, 1840–1848.

SUDARSANAN, K. & YOUNG, R. A. (1969). *Acta Cryst.* **B25**, 1534–1543.

SUDARSANAN, K. & YOUNG, R. A. (1974). *Acta Cryst.* **B30**, 1381–1386.

SUDARSANAN, K., YOUNG, R. A. & DONNAY, J. D. H. (1973). *Acta Cryst.* **B29**, 808–814.

TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.

WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.

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Orthorhombic Oxonium Hydrogenselenate*

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Abstract. $[H_3O]^+[HSeO_4]^-$, orthorhombic, *Pbca*, $Z = 8$, $a = 8{\cdot}4958\ (2)$, $b = 10{\cdot}4528\ (2)$, $c = 9{\cdot}1307\ (1)$ Å, m.p. 296·8 K. X-ray intensities were recorded at 223 K. Refinement with 780 observed data gave $R_w(F^2) = 0{\cdot}056$. The structure contains $HSeO_4^-$ ions hydrogen bonded to each other to form chains with $O-H\cdots O$ lengths of 2·751 (3) Å, and H_3O^+ ions hydrogen bonded to $HSeO_4^-$ ions. The $OH_3^+\cdots O$ bonds are 2·571 (3), 2·577 (3) and 2·632 (3) Å.

Introduction. The present investigation forms part of a series of systematic studies of crystalline hydrates of strong acids in progress at this Institute. One of our objectives is to study the geometry of the oxonium ion in different environments. Neutron diffraction studies of oxonium *p*-toluenesulphonate, where the H_3O^+ environment has virtually threefold symmetry, and oxonium trifluoromethanesulphonate, with an asymmetric environment around H_3O^+, have been reported by Lundgren & Williams (1973) and Lundgren, Tellgren & Olovsson (1978). A neutron diffraction study of the present compound is in progress.

Anhydrous selenic acid was prepared by the oxidation of selenous acid with hydrogen peroxide (Gilbertson & King, 1936). Crystals of the monohydrate grown from a selenic acid–water solution (molar ratio 1:1) were purified by recrystallization. The final product contained only 0·10% selenous acid. Crystals used for the X-ray work were grown in capillaries filled with an acid–water (1:1) solution. Crystallization could be induced in the capillaries only in the presence of seed crystals of the monohydrate. These were taken from a larger batch where crystallization was more readily attainable. At least two modifications of the monohydrate were found to exist: an orthorhombic form with a melting point of 296·8 K in agreement with literature values (297 K, Meyer &

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* Hydrogen Bond Studies. CXXXVII. Part CXXXVI: Lundgren (1979*a*).