

The Crystal Structure of Hydrothermally Grown Manganese Chlorapatite, $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$

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Hydrothermally grown manganese chlorapatite with the approximate composition $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ crystallizes in space group $P6_3/m$ with $Z=2$, $a=9.532$ (1) and $c=6.199$ (1) Å. It is isostructural with calcium fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. The structure was refined to an R_w of 0.054 for 2107 F_{obs} [automatic four-circle diffractometer, graphite monochromator, $\lambda(\text{Mo } K\alpha)=0.7107$ Å]. The phosphate group is more distorted than in any other apatite refined so far [P–O: 1.530 (2), 1.544 (1) (twice) and 1.573 (1) Å, distortion index 0.008]. The c cell edge (6.2 Å) is considerably shorter than the sum of the diameters of two Cl ions (taken as 7.2 Å) even though two such ions are arranged along the c direction. The shape of the electron density at the chlorine site is anisotropic: it is elongated in the c direction. This may be an indication of disorder in the positions of the individual chlorine ions and is possibly related to the OH ion content. The length of the c axis seems to be determined by the size of the distorted trigonal prismatic coordination polyhedra around Mn(1) which share faces and thus form chains parallel to the c direction. Divalent Mn is the smallest of the M^{2+} cations observed so far to form a phosphate apatite structure and the small Mn polyhedra compress the Cl atoms down to the short distance of 3.10 Å. A computer simulation of manganese chlorapatite confirms this interpretation.

Introduction

Apatites, $\text{M}_2^+(\text{XO}_4)_3\text{Y}$, crystallize with $\text{X}=\text{P, As, V}$, $\text{Y}=\text{F, OH, O, Cl, Br, I}$, and $\text{M}^{2+}=\text{Ca, Sr, Ba, Pb, Cd, Mn}$ and a variety of other ions. Of these cations Cd is the smallest ($r=0.95$ Å) which is able to form a wide variety of apatite compounds (Engel, 1968, 1970). Most divalent elements of the first transition series can only substitute partly for Ca *etc.* in the M positions (Klement & Haselbeck, 1965; Kreidler & Hummel, 1970). An exception is Mn^{2+} which is the largest of these transition ions ($r=0.82$ Å according to Shannon & Prewitt, 1969). But even Mn^{2+} forms only one apatite compound, namely $\text{Mn}_5(\text{PO}_4)_3\text{Cl}$. Klement & Haselbeck (1965) were the first to prepare $\text{Mn}_5(\text{PO}_4)_3\text{Cl}$. They obtained it in microcrystalline form by sintering of $\text{Mn}_3(\text{PO}_4)_2$ and MnCl_2 mixed in stoichiometric ratio. Our synthesis of chlorapatite in relatively large single crystals was the result of an investigation into the hydrothermal growth of halogen apatites (Engel, 1970, unpublished results).

The general designation 'apatite' for these compounds does not mean that their crystal structures are all exactly alike. A complete crystal structure determination of the mineral apatite itself, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, was performed by Nařay-Szabó (1930) and confirmed by Sudarsanan, Mackie & Young (1972). The space group

was found to be $P6_3/m$. The fluorine ions are located at the intersections of the 6_3 axes and the mirror planes in $0, 0, \frac{1}{4}$ and $0, 0, \frac{3}{4}$. It was assumed that in chlorapatites the chlorine ion should be located in $0, 0, 0$ and $0, 0, \frac{1}{2}$ (Hendricks, Jefferson & Mosley, 1932). This was based on approximate calculations of the distances between the metal ions and the chlorine ions assuming for the individual atoms positional parameters as determined in $\text{Ca}_5(\text{PO}_4)_3\text{F}$. A detailed investigation of several apatite structures in recent years has modified this picture somewhat:

1. In hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, it was found that the oxygen atoms of the OH groups are displaced from the mirror planes by approximately 0.3 Å (Sudarsanan & Young, 1969).

2. A crystal structure determination of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ showed that this compound has the space group $P2_1/b$ where the monoclinic b axis is doubled compared with the corresponding hexagonal b axis. This lowering of symmetry is interpreted to be due to an ordered, non-statistical displacement of the chlorine ions along the c axis by 0.38 Å from the $0, 0, 0$ position, connected with a shifting of some other atoms (Mackie, Elliott & Young, 1972). The individual monoclinic crystals very often form pseudo-hexagonal twins (Prener, 1967).

3. A study of $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ showed that in this particular compound the chlorine ions are located in $0, 0, \frac{1}{4}$ and $0, 0, \frac{3}{4}$, and that this apatite forms microscopic twins by merohedry (Sudarsanan, Young & Donnay, 1973).

The cadmium chlorapatite (and bromapatite) both have small values for their c cell edges (6.46 Å, Engel, 1968). Since the widely accepted value of the radius of the chlorine ion is 1.8 Å one would expect the c cell

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edge to be 7.2 Å long. Surprisingly, however, *c* measures only 6.2 Å in manganese chlorapatite corresponding to a chlorine ion radius of 1.55 Å. This observation was the starting point for the crystal structure determination (Pretzsch, 1972).

Experimental

1 g $Mn_3(PO_4)_2$, 2 g $MnCl_2 \cdot 4H_2O$ and 11 ml H_2O were sealed into a silver capsule with a volume of 18 ml and heated in a steel pressure vessel to 425°C. This corresponds to an H_2O pressure of 1000 atm. After 3 to 5 days the vessels were slowly cooled. A chemical analysis of the batch from which the crystal for the X-ray study was taken yielded for Mn 46.12% (46.16%), for PO_4 48.31% (47.88%) and Cl 5.47% (5.96%), where the values in parentheses correspond to the theoretical composition $Mn_5(PO_4)_3Cl$. Therefore the crystals from this batch had a deficit of approximately 8% compared with the theoretical Cl content. Samples from runs prepared at temperatures ranging from 425 to 375°C displayed consistently a Cl deficit of 6–12% compared with the theoretical composition, while the possible error in the Cl determination is 2%. The hydrothermal syntheses of apatites of different chemical compositions gave the following results: the barium, strontium and calcium chlorapatites were formed without any indication of substitution by OH ions. The $Cd_5(PO_4)_3Cl$ compound had a 5% chlorine deficit (crystals grown from an anhydrous melt with excess $CdCl_2$ had no Cl deficit, and did not show OH bands in the infrared; see below). The $Cd_5(PO_4)_3Br$ apatite was found to have a 32% bromine deficit. In both cases the infrared spectra indicated the presence of OH ions. Manganese bromapatite could not be synthesized. The subsequent discussion can be summarized in the following way.

1. The infrared spectra indicate the presence of OH ions.

2. The occupancy factors do not indicate extended occurrences of vacancies.

3. We therefore assume that the missing 10% Cl ions are substituted by OH ions.

4. The approximate chemical composition of the hydrothermally grown manganese chlorapatite is $Mn_5(PO_4)_3Cl_{0.9}(OH)_{0.1}$. We shall use this formulation

as an abbreviation of hydrothermally grown manganese chlorapatite in the remainder of this paper.

The crystals of manganese chlorapatite are pale orange. A microscopic investigation showed the presence of hexagonal prism faces of the form {100}. The prisms are capped mostly by the pyramids {101}, and more rarely by {201} and {102}. The length of the prisms is about 0.5 mm, the diameter 0.3 mm. When viewed in an electron scanning microscope many crystals clearly showed skeletal growth. The crystals are optically uniaxial and have negative birefringence.

The infrared spectrum (Perkin-Elmer 225, RbI discs) of $Mn_5(PO_4)_3Cl_{0.9}(OH)_{0.1}$ was recorded in the range of 4000 to 200 cm^{-1} . The assignment of the stretch and bending vibrations of the phosphate group in the range from 1200 to 400 cm^{-1} is based on previous studies (Klee, 1970; Klee & Engel, 1970): $\nu_{3a} = 1085$, $\nu_{3,b,c} = 1009$, $\nu_1 = 944$, $\nu_{4a} = 605$, $\nu_{4b,c} = 545$, $\nu_{2a,b} = 491$ cm^{-1} . The splitting of the components of ν_3 (76 cm^{-1}) and of ν_4 (60 cm^{-1}) is remarkably large. Splitting of this magnitude has been observed for ν_3 in Pb, Cd and Mn apatites, but not in alkaline-earth apatites. It may be due to the more pronounced distortion of the phosphate tetrahedra in the first-named apatites. The extent of splitting of the ν_4 component seems to be determined by the length of the *c* cell edge: the shorter *c*, the more pronounced the splitting (Klee & Engel, 1970). Below frequencies of 400 cm^{-1} the bands are broad and overlap. They are lattice vibrations and have not yet been assigned. The OH stretch frequency in $Mn_5(PO_4)_3Cl_{0.9}(OH)_{0.1}$ and other hydroxyapatites as well as halogen apatites has been discussed in a previous communication (Engel & Klee, 1972). In all samples of $Mn_5(PO_4)_3Cl_{0.9}(OH)_{0.1}$ a band at 3380 cm^{-1} was observed. In the case of the above-mentioned cadmium chlorapatite and bromapatite the corresponding bands are at 3404 and 3405 cm^{-1} . These frequencies have to be compared with the 3532 cm^{-1} band measured for $Cd_5(PO_4)_3OH$. In the case of the manganese compound a comparison with the pure OH apatite is not possible because $Mn_5(PO_4)_3OH$ has not been synthesized yet. Based on the assignments given in Engel & Klee (1972) the band at 3380 cm^{-1} in manganese chlorapatite is assigned to the stretch vibration of OH groups hydrogen-bonded to chlorine ions. It is impossible to prove from the infrared spectrum alone that

Table 1. $Mn_5(PO_4)_3Cl_{0.9}(OH)_{0.1}$, positional and thermal parameters (Å²)

Positional parameters, except fractions, are multiplied by 10⁵, thermal parameters by 10⁴. Standard deviations of independently varied parameters are given in parentheses. The definition of the Debye-Waller temperature factor is $\exp(-2\pi^2 \sum_{i,j=1,2,3} h_i h_j a_i^* a_j^* u_{ij})$

where a_i^* are the reciprocal axes lengths.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i> ₁₁	<i>u</i> ₂₂	<i>u</i> ₃₃	<i>u</i> ₁₂	<i>u</i> ₁₃	<i>u</i> ₂₃
Mn(1)	$\frac{1}{4}$	$\frac{2}{3}$	672 (6)	$2u_{12}$	$2u_{12}$	76 (1)	59 (1)		
Mn(2)	27763 (4)	3415 (4)	$\frac{1}{4}$	128 (1)	102 (1)	96 (1)	51 (1)		
P	40676 (6)	38085 (6)	$\frac{1}{4}$	75 (2)	72 (2)	79 (2)	42 (1)		
Cl	0	0	$\frac{1}{4}$	$2u_{12}$	$2u_{12}$	255 (5)	58 (1)		
O(1)	36003 (20)	51276 (19)	$\frac{1}{4}$	131 (6)	105 (5)	109 (5)	84 (5)		
O(2)	59621 (19)	45779 (19)	$\frac{1}{4}$	80 (5)	100 (5)	137 (6)	44 (4)		
O(3)	34343 (15)	26841 (13)	5128 (19)	151 (4)	104 (4)	96 (4)	69 (3)	-28 (3)	-22 (3)

the missing chlorine atoms are completely replaced by OH ions. However, the spectrum shows that at least part of the deficit can be explained by the presence of OH ions.

The cell constants were obtained by a least-squares refinement of 14 lines measured on a Guinier powder photograph [$\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$]. A ground sphere with a radius $R = 0.13 \text{ mm}$ was used for the collection of intensity data on a computer-controlled four-circle diffractometer. Graphite monochromatized $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) was employed for the θ - 2θ scans in a 2θ range of 4 to 114° . The 10380 measured intensities were averaged and reduced to 2355 unique structure factors of which 248 were considered to be of zero intensity. Reflexions were considered to be unobserved if their intensity was smaller than three times their estimated standard deviation. The internal R value of the intensities, $R_I = \sum |I - I_{\text{mean}}| / \sum I_{\text{mean}}$, is 0.022, where I is an individual intensity value and I_{mean} is averaged over symmetrically equivalent reflexions (Schwarzenbach, 1972, X-ray data analysis program *INTENS*). This good agreement indicates that the data set is hexagonal within the limits of accuracy. X-ray photographs taken at temperatures down to -120°C did not indicate the existence of superstructure reflexions as previously observed for lead arsenate apatites

(Brenner, Engel & Wondratschek, 1970; Weitz, 1971) and for the low-temperature modification of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (Young & Elliott, 1966; Prener, 1967).

All calculations were performed using the X-RAY System (Stewart, Kundell & Baldwin, 1970).

Crystal data

The hydrothermal $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ is hexagonal with $a = 9.532 (1)$ and $c = 6.199 (1) \text{ \AA}$, $V = 487.8 \text{ \AA}^3$, $Z = 2$, pycnometric $D_m = 4.09$, $D_x = 4.03 \text{ g cm}^{-3}$, F.W. 593.64, $\mu(\text{Mo } K\alpha) = 74.4 \text{ cm}^{-1}$, $\mu R = 0.95$ for the spherical crystal. The space group $P6_3/m$ was established from the systematic absences (000 l only present when $l = 2n$) and from the successful refinement of the structure.

Structure refinement

The atomic scattering factors were taken from Cromer & Waber (1965). The scattering factors of Mn, Cl and P were corrected for dispersion using an approximation (James, 1950):

$$f = f_0 + \Delta f' + \frac{1}{2}(\Delta f'')^2 / (f_0 + \Delta f').$$

The values of $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1962).

Table 3. Comparison of bond distances (\AA) and angles ($^\circ$) in $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ (this work), $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ (Sudarsanan *et al.*, 1973), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (Sudarsanan & Young, 1969), $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (Sudarsanan *et al.*, 1972), $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ (Sudarsanan & Young, 1974) and $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ (Sudarsanan & Young, 1972)

The multiplicities of symmetrically equivalent distances and angles are indicated by $2 \times$ and $3 \times$. The symbol Y indicates the anion Cl, OH or F. The distortion indices DI express the average relative deviations of P-O, O-O, and O-P-O from their means (Baur, 1974).

	Mn, Cl	Cd, Cl	Ca, OH	Ca, F	Sr, Cl	Sr, OH
P—O(1)	1.530 (2)	1.527 (1)	1.537 (1)	1.534 (1)	1.540 (2)	1.541 (3)
P—O(3) ($2 \times$)	1.544 (1)	1.540 (1)	1.545 (1)	1.534 (1)	1.537 (2)	1.537 (3)
P—O(2)	1.573 (1)	1.557 (1)	1.529 (1)	1.541 (1)	1.544 (2)	1.546 (3)
P—O(mean)	1.548	1.541	1.539	1.536	1.540	1.540
DI(PO)	0.008	0.005	0.004	0.002	0.002	0.002
O(1)—O(3) ($2 \times$)	2.569 (2)	2.552 (2)	2.533 (1)	2.529 (1)	2.545 (3)	2.536 (5)
O(1)—O(2)	2.554 (3)	2.537 (2)	2.541 (2)	2.538 (1)	2.542 (3)	2.536 (4)
O(3)—O(3)	2.464 (2)	2.467 (2)	2.471 (1)	2.473 (1)	2.496 (4)	2.490 (4)
O(3)—O(2) ($2 \times$)	2.496 (2)	2.492 (2)	2.479 (1)	2.487 (1)	2.476 (3)	2.496 (4)
DI(OO)	0.016	0.013	0.012	0.010	0.012	0.008
O(1)—P—O(3) ($2 \times$)	113.4 (1)	112.6 (1)	111.4 (1)	111.1 (1)	111.6 (1)	111.0 (1)
O(1)—P—O(2)	110.8 (1)	110.8 (1)	111.1 (1)	111.3 (1)	111.0 (1)	110.4 (2)
O(3)—P—O(3)	105.9 (1)	106.3 (1)	107.8 (1)	107.4 (1)	108.6 (1)	108.2 (2)
O(3)—P—O(2) ($2 \times$)	106.4 (1)	107.1 (1)	107.5 (1)	108.0 (1)	107.0 (1)	108.1 (1)
DI(OPO)	0.029	0.024	0.017	0.015	0.018	0.012
M(1)—O(1) ($3 \times$)	2.206 (2)	2.309 (1)	2.406 (1)	2.397 (1)	2.567 (2)	2.560 (3)
M(1)—O(2) ($3 \times$)	2.278 (2)	2.377 (1)	2.452 (1)	2.453 (1)	2.580 (2)	2.564 (3)
M(1)—O(3) ($3 \times$)	2.846 (1)	2.872 (2)	2.805 (1)	2.801 (1)	2.859 (2)	2.900 (3)
CN[M(1)]	6(+3)	6(+3)	9	9	9	9
M(2)—O(3) ($2 \times$)	2.118 (1)	2.202 (1)	2.344 (1)	2.398 (1)	2.510 (2)	2.511 (3)
M(2)—O(2)	2.200 (2)	2.246 (2)	2.357 (1)	2.384 (1)	2.437 (2)	2.475 (3)
M(2)—O(3) ($2 \times$)	2.344 (1)	2.459 (1)	2.512 (1)	2.344 (1)	2.696 (2)	2.661 (3)
M(2)—O(1)	3.275 (2)	3.147 (2)	2.705 (1)	2.814 (1)	2.847 (2)	2.758 (4)
M(2)—Y	2.500 (1)	2.536 (1)	2.383 (1)	2.231 (1)	3.086 (1)	2.497 (2)
CN[M(2)]	6	6	7	6(+1)	7	7
Y—Y*	3.100 (1)	3.242 (2)	3.440 (2)	3.442 (1)	3.603 (1)	3.633 (1)

* The Y—Y distances given here are simply $c/2$. In the OH apatites the closest possible approaches of two oxygen atoms of the OH groups could be 2.721 (7) \AA for $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and 2.697 (14) \AA for $\text{Sr}_5(\text{PO}_4)_3\text{OH}$, because the OH groups are statistically disordered about the mirror planes. Such approaches should be rare.

The positional parameters of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (Sudarsanan & Young, 1969) were used as a starting point for a least-squares refinement of $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$. The chlorine atom was first placed in $0, 0, \frac{1}{2}$ but this model did not refine. A full-matrix, unit-weight refinement with Cl in $0, 0, \frac{1}{4}$ yielded with anisotropic temperature factors an R of 0.098. At this point an absorption correction for a spherical crystal (*International Tables for X-ray Crystallography*, 1959) was applied to the data. The subsequent weighted refinement [with extinction correction according to Larson (1965)] ended after a few cycles with parameters as listed in Table 1 and a weighted R of 0.054 ($R_w = \sum w|F_o - F_c| / \sum w|F_o|$). The weighting was proportional to the inverse square of the estimated standard deviations as obtained from the counting statistics. The value of the extinction parameter is 0.00354 (13). The conventional unweighted R for the structure factors as listed in Table 2* is 0.067. Three-dimensional Fourier and difference syntheses show that the position of the chlorine atom is centred on $0, 0, \frac{1}{4}$.† The syntheses indicate that the electron density along the line $0, 0, z$ is zero (within the limits of accuracy) at all values of z except in the area of the chlorine atom located at $0, 0, \frac{1}{4}$. The shape of the chlorine atom

maximum is, however, clearly anisotropic. The root-mean-square thermal displacements in the c direction are twice as large as normal to the c direction. The highest peaks in the difference synthesis are, as to be expected, close to the Mn atom positions. The positive and negative areas of the difference densities around Mn(1) alternate in spherical shells. An electron diffraction pattern of the ab plane of a crystal platelet of $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ showed hexagonal symmetry. Thus, it did not give any indication of a lowering of the symmetry or for twinning which could explain the pattern around Mn(1). No such pattern was observed around Mn(2).

Discussion

The refinement shows that $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ is, as far as the chlorine position is concerned, isostructural with $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and not with $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$. The pertinent bond lengths and angles for manganese chlorapatite and the other five hexagonal apatite structures which have been refined carefully up to now are listed in Table 3.

The coordination polyhedron around Mn(1) has the point-group symmetry 3 and is a trigonal prism in which the two triangles of oxygen atoms are slightly rotated relative to each other (Fig. 1). Both triangular faces are shared with neighbouring trigonal prisms. If the distance Mn(1)–O(3) of 2.846 Å is taken into consideration the coordination figure is a tricapped trigonal prism. However, the sum of the ionic radii of Mn^{2+} and O^{2-} is 2.19 Å (Shannon & Prewitt, 1969) and the ratio between the length Mn(1)–O(3) and the mean of Mn(1)–O(1) and Mn(1)–O(2) is 1.27 Å. Therefore it seems preferable to call Mn(1) six-coordinated.

The coordination polyhedron around Mn(2) is a severely distorted octahedron. The seventh distance Mn(2)–O(1) is too long to be counted as a coordinating contact, because it is 50% longer than the sum of the radii of manganese and oxygen. In $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ these seventh distances complete pentagonal dipyramidal coordinations, because the Ca(2)–O(1) and the Sr(2)–O(1) distances are respectively only 11 and 7% longer than the sums of their ionic radii. In $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ the chlorine atoms are in different positions and therefore Ca(2) is eight-coordinated and the coordination polyhedron approximates a dicapped trigonal prism.

The phosphate group in $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ is more distorted than in any of the other apatites. The distortion indices for the distances P–O and O–O and the angle O–P–O which are defined as mean relative deviations from the mean (Baur, 1974) appear to be inversely linearly correlated with the radii of the cations. The smaller the cation M the larger the three distortion indices. Specifically the distortion is connected

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30889 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† A photograph of this map has been included in Supplementary Publication No. SUP 30889 (see footnote above).

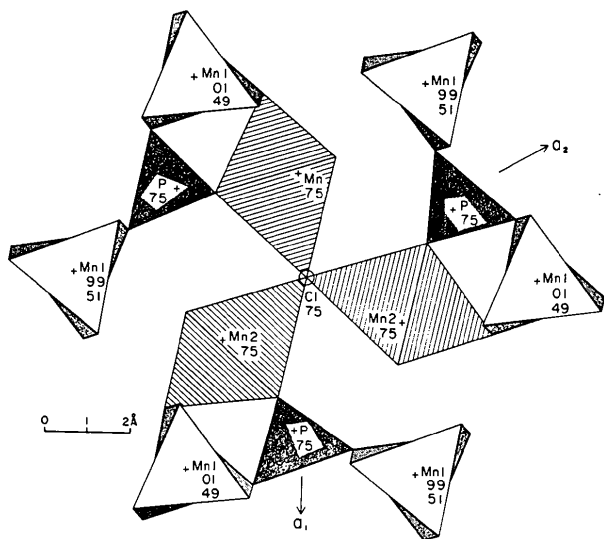


Fig. 1. Polyhedral representation of a layer of $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ normal to c at a height of $\frac{1}{4}$. The position of the cations at the centres of the coordination polyhedra and their heights in $100z$ are marked by crosses, the chlorine position is indicated by a circle. The distorted trigonal prisms around Mn(1) share the triangular faces and form chains parallel to c . The phosphate groups share an edge with the octahedra around Mn(2). The layer at $\frac{1}{4}$ is identical, but rotated by 60° relative to the layer at $\frac{3}{4}$.

with the more uneven electrostatic bond strength distribution in the Mn and Cd apatites [$p_{O(2)}=2.25$ valence units, $p_{O(1)}=p_{O(3)}=1.92$ v.u.] as compared with the Ca and Sr apatites, and with the shortening of the edge O(3)-O(3) shared by the tetrahedron and the M(2) coordination polyhedron. This pronounced distortion is reflected in the splitting of the ν_3 and ν_4 components in the infrared spectrum. The mean P-O distance for the phosphate tetrahedra (Table 3) is positively correlated with the distortion indices. This is analogous to the observation made on a sample of 211 phosphate groups (Baur, 1974).

The chlorine atom is located in the centre of an equilateral triangle formed by three Mn(2) atoms. The Cl-Cl distance along c measures only 3.10 \AA . The shape of the thermal ellipsoid precludes the possibility of increasing this Cl-Cl distance by a displacement of Cl normal to the c axis as proposed originally by Engel (1968, 1970). A relatively large thermal parameter u_{33} as compared with u_{11} was observed also in $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (Mackie, Elliott & Young, 1972) and in $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ (Sudarsanan, Young & Donnay, 1973). In this context Prener's (1971) results have to be discussed. He started with stoichiometric $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ and succeeded in removing some of the CaCl_2 from it by annealing in vacuum at temperatures between 900 and 1200°C . He obtained a CaCl_2 deficient apatite of the general formula $\text{Ca}_{5-x/2}(\text{PO}_4)_3\text{Cl}_{1-x}$, where x can be as high as 0.23 if the compound is annealed at 1200°C . According to Sudarsanan, Young & Donnay (1973) the cadmium chlorapatite investigated by them is CdCl_2 -deficient in analogy to Prener's compound. These authors assume that a 15 to 18% deficiency in Cl is indicated. However, the occupancy factors of the Cd positions show only a very slight deficiency for Cd(1) which does not balance at all the assumed Cl deficiency. The crystals used by Sudarsanan *et al.* were synthesized and made available by Engel (1968). They were crystallized out of a melt with a considerable excess of CdCl_2 . Repeated chemical analyses confirmed the composition $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$. Within the limits of the analytical accuracy ($\pm 2\%$ if the stoichiometric Cl content is taken as 100%) the chlorine content was found to agree with the theoretical composition. A deficiency of 15 to 18% in the chlorine content, therefore, can be excluded in the case of the cadmium chlorapatite investigated by Sudarsanan *et al.* (1973). In the case of our hydrothermally grown manganese chlorapatite the refinement of the occupancy factor of Cl resulted in a 97% occupancy with an estimated standard deviation of 1%. Both manganese positions were found to be 100% occupied with an estimated standard deviation of 0.5%. These values do not give any indication of an extended occurrence of vacancies. The slightly low chlorine occupancy can be explained by a 10% substitution of chlorine by OH ions. It has to be taken into account that Prener's (1971) CaCl_2 -deficient apatite was obtained by evaporation of CaCl_2 in the vacuum. In contrast manganese chlorapatite was syn-

thesized in the presence of excess chloride and water, while cadmium chlorapatite was formed with excess chloride. Therefore, in these two cases the thermodynamic equilibrium is shifted toward a filling of the vacancies.

For comparative purposes a sample of manganese chlorapatite was prepared by reaction of $\text{Mn}_3(\text{PO}_4)_2$ with a stoichiometric quantity of MnCl_2 . The mixture was heated to 850°C in an evacuated quartz vial. An excess of MnCl_2 could not be employed because $\text{Mn}_2\text{PO}_4\text{Cl}$ is then formed (Klement & Haselbeck, 1965; Kreidler & Hummel, 1970). The resulting microcrystalline product did not show OH bands in the infrared, had no Cl deficiency and had the following cell constants: $a=9.533$ (1), $c=6.192$ (1) \AA , $V=487.3 \text{ \AA}^3$. The non-existent hypothetical compound $\text{Mn}_5(\text{PO}_4)_3\text{OH}$

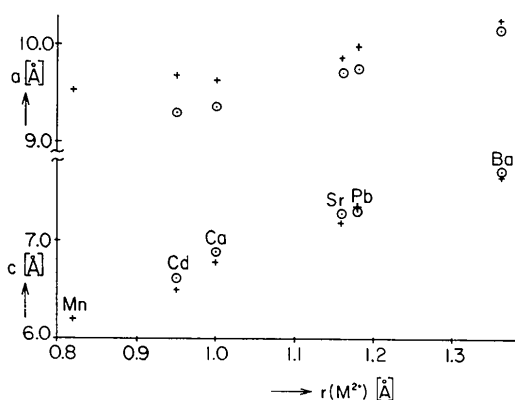


Fig. 2. $\text{M}_3^{2+}(\text{PO}_4)_3\text{F}$ (circles) and $\text{M}_3^{2+}(\text{PO}_4)_3\text{Cl}$ (crosses): cell constants a and c (from Klee, 1972) versus ionic radii (Shannon & Prewitt, 1969) of M^{2+} . The cell constants of $\text{M}_3^{2+}(\text{PO}_4)_3\text{Br}$ are not entered in the plot, since the c constants are practically identical with the values for the chlorapatites.

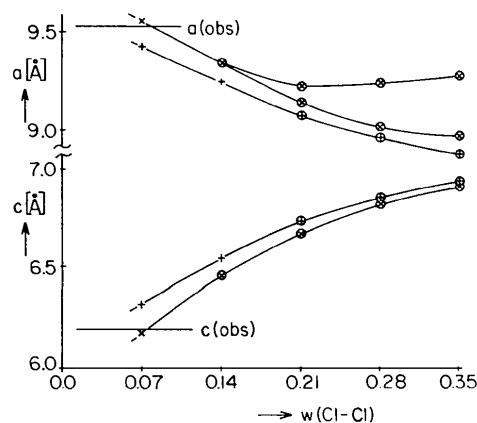


Fig. 3. $\text{Mn}_5(\text{PO}_4)_3\text{Cl}$, calculated cell constants versus weight given to the Cl-Cl distance in the computer simulations. Observed cell constants indicated by horizontal lines, simulation based on observed interatomic distances: +; simulation based on predicted distances: × (see text). Simulations which did not converge are circled: the values oscillated in the refinement either slightly or very pronouncedly (see a' ×).

would be expected to have a smaller a cell constant, a larger c cell constant and a smaller cell volume. Therefore, the differences of the crystal data of pure $\text{Mn}_5(\text{PO}_4)_3\text{Cl}$ and of $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ are in the expected direction.

Because of the above-mentioned reasons we assume that the hydrothermally grown manganese chlorapatite has a partial substitution of OH ions for chlorine and an approximate formula of $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$. This substitution does not allow sufficient space for the chlorine atoms to have an effective radius of 1.8 Å in the c direction. Even if this compound did not have any OH substitution so that 10% vacancies would occur there would not be sufficient room to allow an effective radius of 1.8 Å along the c axis. We still would have to assume that the chlorine atoms are compressed in the c direction. Therefore, the following discussion is not affected by deviations from the assumed chemical formula.

The anisotropic shape of the chlorine atom can be taken as an indication of preferred thermal vibrations parallel to c . On the other hand it is possible that this shape is caused by disorder of the atoms occupying the chlorine site. This would mean that $0,0,\frac{1}{4}$ is only a mean value around which the chlorine atoms and OH groups are distributed in the c direction. The deviations from $0,0,\frac{1}{4}$ must be on the average small because the difference between u_{33} and u_{11} amounts to a difference in the mean thermal vibrations of 0.2 Å in the two directions. The disorder is possibly related to the presence of the OH ions: the chlorine atoms may be displaced in the direction of neighbouring OH groups which have a slightly smaller diameter. As a consequence of this the effective space available to the chlorine atoms becomes greater. This interpretation is analogous to the scheme given by Prener (1967) for the assumed disorder of the chlorine atoms in calcium chlorapatite, except that in this case the chlorine atoms are assumed to be displaced in the direction of vacancies.

Anion-anion distances which are appreciably shorter than the sum of the ionic radii have been observed for oxygen ions in the case of small trigonal groups such as NO_3^- and CO_3^{2-} . The oxygen-oxygen edges are there about 2.2 Å long, while the sum of the ionic radii is about 2.7 Å. Very short oxygen-oxygen contacts can also occur when both oxygen atoms are in an edge shared by two coordination polyhedra as in rutile type SiO_2 ($\text{O}-\text{O}=2.29$ Å, Baur & Khan, 1971). Similarly a Cl-Cl distance of 3.12 Å has been observed in an edge shared between two tetragonal pyramidal coordinations in Cl_3VNCl (Strähle & Bärnighausen, 1968). However, the close Cl-Cl approach in manganese chlorapatite is not in the edge of a coordination polyhedron. A clue to the reason for the short Cl-Cl distance is provided by the dependence of the c cell edge on the radius of the M cations (Fig. 2). Obviously the radius of the metal ions influences c much more than the radius of the halogen ions. This must mean that

the chlorine atoms do not resist very strongly the compression imposed upon them by the framework of the apatite structure. Most likely the c cell constant is primarily determined by the size of the trigonal prismatic M(1) coordination polyhedra which share faces and thus form chains parallel to c in the crystal structure (Fig. 1). However, the a cell constants are sensitive to the Cl for F substitution because a depends on the cation-halogen distances (Fig. 2).

Computer simulation of manganese chlorapatite

This idea can be explored quantitatively by computer simulation of the structure of manganese chlorapatite (Meier & Villiger, 1969; Baur, 1972; Tillmanns, Gebert & Baur, 1973). The structure was simulated by using as input 23 Mn-O, P-O, O-O, O-Cl and Cl-Cl distances. The weight assigned to the Cl-Cl distance was varied from 0.07 to 0.35 in steps of 0.07. The weights assigned to the O-O distances were taken uniformly as 0.07, while the electrostatic bond strengths were used as weights for the cation-anion distances. Two series of calculations were performed: in one all interatomic distances except Cl-Cl were put in as observed experimentally, in the second the distances were predicted from the extended electrostatic valence rule (Baur, 1970) and by taking account of the lengths of shared edges (Baur, 1972, 1974). The distance Cl-Cl was put in at 3.60 Å, twice the radius of Cl, in all simulations. The simulated structure with input distances as observed in the actual structure (except for Cl-Cl equal 3.60 Å) and a weight for the Cl-Cl distance of 0.07, reproduced the observed structure satisfactorily. From the plot of the simulated cell constants *versus* the weights assigned to the Cl-Cl distance (Fig. 3) it is obvious that with weights between 0.035 and 0.07 the simulation reproduces the observed cell constants satisfactorily. In a number of simulations of silicates (Baur, 1972) it was found that a weight of 0.07 for the O-O distances gave models which closely reproduced cell constants and interatomic distances of the structures. Since the chloride ion has a formal charge of -1, compared with -2 for the oxygen, a weight between 0.035 and 0.07 appears just right for the Cl-Cl interaction. The simulation indicates that in manganese chlorapatite the short contact can be caused by a compression forced upon the Cl ions by the whole apatite structure.

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The Crystal and Molecular Structure of Bis-[(3,6-diethyl-4-octyne-3,6-diol)]platinum(0), Pt[(C₂H₅)₂C(OH)C≡CC(OH)(C₂H₅)₂]₂

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Crystals of bis-[(3,6-diethyl-4-octyne-3,6-diol)]platinum(0), Pt[(C₂H₅)₂C(OH)C≡CC(OH)(C₂H₅)₂]₂, are monoclinic, space group *C*2/*c* (*C*_{2h}²) with four molecules in a unit cell of dimensions *a* = 21.751 (5), *b* = 9.275 (6), *c* = 17.079 (9) Å and β = 129.54 (4)°. X-ray diffracted intensities were measured on a four-circle diffractometer using θ–2θ scans and graphite-monochromatized Mo Kα radiation. The structure was solved by the heavy-atom method. Full-matrix least-squares refinement gave a final *R* of 0.074, and *R_w* of 0.075 based on the 2695 reflexions with *I* > 3σ(*I*). The crystal structure is composed of molecules lying on the twofold (crystallographic) axis through the Pt atom. The prominent feature of the molecular geometry is that the two acetylenic groups bonded to the central Pt atom are 180° apart and perpendicular to each other. The bond distances are 2.066 (11), 2.043 (11) Å for Pt–C, 1.35 (3), 1.36 (2) Å for C≡C, and 1.95, 1.93 Å for Pt ⊥ C≡C. Each molecule is stabilized by four OH···O hydrogen bonds.

Introduction

The title compound was prepared by Rochon & Theophanides (1972) during a study of platinum–acetylenic

ligands (ac). The structural assignment for the Pt(ac)₂ complex, where (ac) = R₁R₂C(OH)–C≡C–C(OH)R₁R₂ and R₁ = R₂ = ethylenic groups, was accomplished by means of infrared, e.s.r. and n.m.r. experiments. The structure determination was undertaken to confirm this assignment by the X-ray diffraction method.

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