The structure of $TiCuD_{0 \cdot 9}$ can be thought of as formed by slices of TiD_2 and slices of Cu atoms (Fig. 3). In light of this structural property it becomes understandable why titanium hydride precipitates so easily when $TiCuD_{0 \cdot 9}$ is heated at relatively low temperatures (>200 °C). The introduction of the D atoms into the structure has the effect of increasing significantly the Ti—Cu distances, as compared with the corresponding distances in γ-TiCu, but does not alter the general configuration of the Ti and Cu atoms. As pointed out by Maeland (1978), this particular feature of the structure may well explain the failure of the rule of reversed stability in the series Ti*R* (*R* = Fe, Cu, Ni, Co). This rule is derived on the assumption that the Ti—D bonds are formed at the expense of the Ti—*R* bonds. This may be true for those structures in which the H is located between the atoms of the two metal species, but it is certainly not true for $TiCuD_{0 \cdot 9}$ in which the D atoms are entirely surrounded by Ti atoms and interfere little with the Ti—Cu bonds.

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Cadmium Hydroxyapatite

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Abstract. $Cd_5(PO_4)_3OH$, hexagonal, $P6_3/m$, $a = 9 \cdot 335$ (2), $c = 6 \cdot 664$ (3) Å, $Z = 2$, $D_x = 5 \cdot 694$ g cm^{-3}. Crystals were grown by a hydrothermal reaction; 0·5 g of $Cd_5H_2(PO_4)_4.4H_2O$ in 50 ml of distilled water with an initial pH of 3·3, controlled by adding 2·5 *M* H_3PO_4 solution, were heated at 200 °C for two weeks The final pH was 2·8. A comparison of interatomic distances and bond angles with those of Ca and Sr hydroxyapatites is presented.

Introduction. Cadmium hydroxyapatite is isostructural with calcium hydroxyapatite (Sudarsanan & Young, 1969), and Cd^{2+} has the possibility of substitution for Ca^{2+} in bone tissue. As part of a study of the apatite group compounds, single crystals of cadmium hydroxyapatite [$Cd_5(PO_4)_3OH$] were synthesized, and the crystal structure was investigated. The crystals were colourless, transparent, hexagonal prisms. Their sizes were 0·1–0·2 mm in length and 0·03–0·06 mm in diameter.

From Weissenberg and precession photographs, the crystal was found to have the hexagonal Laue symmetry $6/m$. Since the systematic absences were $00l$ for l odd, the space groups were determined to be $P6_3/m$ (centrosymmetric) or $P6_3$ (non-centrosymmetric).

Intensities were measured on an automated four-circle diffractometer (Philips PW 1100) with graphite-monochromated Mo $K\alpha$ radiation, by the ω–2θ scan technique with a scan speed of 4° min^{-1} in ω, using a crystal of length 0·1 mm and diameter 0·03 mm. A total of 524 independent reflexion data ($F_o > 3\sigma$) were obtained in the range $2\theta \leq 70°$.

Intensities were corrected for Lorentz and polarization factors. Absorption corrections ($\mu = 108 \cdot 8$ cm^{-1}, Mo $K\alpha$) were made with the program *ACACA* (Wuensch & Prewitt, 1965). The structure was solved by three-dimensional Patterson and difference Fourier syntheses. Two OH groups in the unit cell statistically occupy the four crystallographically equivalent positions (0,0,z). The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) to R = 0·0374 and weighted R_w = 0·0350, with anisotropic thermal parameters for all atoms. The weighting scheme employed was $w = 1/(A + B|F_o| + C|F_o|^2 + D|F_o|^3)$. The parameters A, B, C and D were varied so that $\langle w||F_o| - |F_c||^2\rangle$ became independent of the magnitude of F_o. The values of A, B, C and D for the last cycle were 1·437, −0·0653, −0·00046 and 0·000044, respectively. The atomic scattering factors for Cd, P and O were taken from *International Tables for X-ray Crystallography* (1974). The final isotropic thermal and positional parameters are given in Table 1.*

Discussion. Selected interatomic distances and bond angles are listed in Table 2. As a comparison, the values for Ca and Sr hydroxyapatites are also presented. There are two crystallographically independent Cd atoms in the unit cell. The Cd(2) atom is surrounded by six O atoms [O(1), O(2) and four O(3)] and an OH, whereas the Cd(1) atom is nearly octahedrally surrounded by six O atoms [three O(1) and three O(2)]. The mean value of Cd(1)—O is 2·382 Å and that of Cd(2)—O is 2·391 Å.

The side length of the Cd(2) triangle is 4·008 Å, whereas those of calcium hydroxyapatite (Sudarsanan & Young, 1969) and cadmium chlorapatite (Sudarsanan, Young & Donnay, 1973) are 4·08 and 4·14 Å, respectively. OH is not located at the centre of the Cd(2) triangle (0,0,$\frac{1}{4}$), but shifted by approximately 0·4 Å above or below the centre of the triangle, as is found in Ca and Sr hydroxyapatites (Sudarsanan & Young, 1969, 1972).

Table 1. *Final positional and isotropic thermal parameters for* $Cd_5(PO_4)_3OH$ (×10^4)

	x	y	z	B* (Å^2)
Cd(1)	3333	6667	33 (1)	10300
Cd(2)	2440 (1)	2516 (1)	2500	8900
P	3940 (2)	251 (2)	2500	5600
O(1)	3215 (7)	−1633 (6)	2500	11100
O(2)	5835 (8)	1178 (9)	2500	28700
O(3)	3373 (10)	807 (7)	671 (10)	39000
OH	0	0	1880 (21)	11000

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

Table 2. *Interatomic distances* (Å) *and bond angles* (°), *and a comparison of those values with* Ca *and* Sr *hydroxyapatites*

Symmetry code for Cd hydroxyapatite

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

	$Cd_5(PO_4)_3OH$	$Ca_5(PO_4)_3OH$*	$Sr_5(PO_4)_3OH$*
PO_4 tetrahedra			
P—O(1)^0	1·537 (6)	1·539 (1)	1·539 (4)
P—O(2)^0	1·532 (7)	1·539 (1)	1·546 (4)
P—O(3)$^{0,\text{iii}}$ (×2)	1·519 (8)	1·532 (1)	1·537 (5)
O(1)—O(3)$^{0,\text{iii}}$ (×2)	2·512 (9)	2·537 (1)	2·535 (5)
O(2)—O(3)$^{0,\text{iii}}$ (×2)	2·468 (11)	2·476 (1)	2·495 (5)
O(2)—O(1)^0	2·540 (7)	2·538 (2)	2·535 (5)
O(3)—O(3)$^{\text{iii}}$	2·437 (9)	2·475 (2)	2·489 (5)
O(1)^0—P—O(2)^0	111·7 (4)	111·13 (1)	110·5 (3)
O(1)^0—P—O(3)$^{0,\text{iii}}$ (×2)	111·1 (3)	111·41 (4)	110·9 (2)
O(3)$^{\text{iii}}$—P—O(3)^0	106·7 (5)	107·47 (5)	108·1 (2)
O(2)^0—P—O(3)$^{\text{iii},0}$ (×2)	107·9 (3)	107·76 (8)	108·2 (2)
Environment of metal atoms			
M(1)—O(1)$^{\text{i,iv,vii}}$ (×3)	2·326 (7)	2·405 (1)	2·561 (3)
M(1)—O(2)$^{\text{v,vi,viii}}$ (×3)	2·437 (8)	2·454 (1)	2·565 (3)
M(2)—O(1)$^{\text{i}}$	2·636 (9)	2·701 (1)	2·757 (5)
M(2)—O(2)$^{\text{iv}}$	2·354 (9)	2·357 (1)	2·467 (4)
M(2)—O(3)$^{0,\text{iii}}$ (×2)	2·487 (9)	2·511 (1)	2·661 (3)
M(2)—O(3)$^{\text{ii,v}}$ (×2)	2·241 (7)	2·345 (2)	2·512 (3)
M(2)—OH^0	2·351 (3)	2·389 (1)	2·498 (2)
M(2)—M(2)$^{\text{i,vi,viii}}$ (×3)	4·008 (1)	4·084 (1)	4·248 (2)

* The values for Ca and Sr hydroxyapatites were calculated by Sudarsanan & Young (1969, 1972).

The P—O bond lengths have a mean value of 1·527 Å. The mean distance is short, compared with that of calcium hydroxyapatite, 1·537 Å (Sudarsanan & Young, 1969). The bond lengths P—O(1) and P—O(2) are longer than P—O(3) and P—O(3)$^{\text{iii}}$. The bond angle O(1)—P—O(2) is larger than O(3)—P—O(3)$^{\text{iii}}$. Thus, in the structure of cadmium hydroxyapatite, the PO_4 tetrahedron is almost regular with only slight distortion, except for its rather unusual trends in the variation of the bond lengths and angles. Ordinarily the PO_4 tetrahedron is distorted as follows; if one of the P—O bonds becomes longer than the other P—O bonds, the O—P—O bond angle that contains the lengthened P—O bond becomes smaller than the ideal tetrahedral angle, and *vice versa*. The distortion of the PO_4 tetrahedron in cadmium hydroxyapatite is opposite to the normal case. This same tendency is also found in Ca and Sr hydroxyapatites (Table 2).

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

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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 33663 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Scandium Hydrogenselenate Dihydrate

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Abstract. $ScH(SeO_4)_2.2H_2O$, monoclinic, $C2/m$ (No. 12), $a = 8{\cdot}708$ (5), $b = 5{\cdot}632$ (4), $c = 9{\cdot}105$ (9) Å, $\beta = 101{\cdot}64$ (7)°, $V = 437{\cdot}3$ (6) Å^3, $Z = 2$, $D_x = 2{\cdot}79$ g cm^{-3}, μ(Mo $K\alpha$) = 91·0 cm^{-1}, $R = 0{\cdot}054$ for 1002 reflections. The structure consists of layers formed by ScO_6 octahedra and SeO_4 tetrahedra. The layers are connected together through water molecules by hydrogen bonds.

Introduction. Sc forms a very interesting series of compounds with selenium oxyacids. Some of these are normal salts [$Sc_2(SeO_4)_3.5H_2O$, Valkonen, Niinistö, Eriksson, Larsson & Skoglund, 1975; $Sc_2(SeO_4)_3$, Valkonen, 1978]. $(NH_4)_3Sc(SeO_4)_3$ is a complex compound (Valkonen & Niinistö, 1978) and $Sc(HSeO_3)_3$ (Valkonen & Leskelä, 1978) is an acid salt. In all these compounds Sc is six-coordinated to O atoms belonging to selenite or selenate groups or to the water of crystallization. For example, the structure of $(NH_4)_3$-$Sc(SeO_4)_3$ consists of $Sc(SeO_4)_3^{3-}$ columns connected by hydrogen bonds, and the structure of $Sc_2(SeO_4)_3$ consists of a three-dimensional network. In this study the structure of the title compound is solved.

Crystals of the title compound suitable for X-ray analysis were grown by dissolving scandium oxide in a very concentrated solution of selenic acid and letting it evaporate at 50°C for about one week. The colorless prisms were approximately 0·3 × 0·2 × 0·2 mm.

The formula of the title compound can also be written as $Sc_2(SeO_4)_3H_2SeO_4.4H_2O$ with $Z = 1$. Scandium hydrogensulfate has been assigned the formula $Sc_2(SO_4)_3.3H_2SO_4$ (Komissarova, Shatskii & Moiseichenko, 1965; Wirth, 1914), but there is also evidence of another phase with the formula $Sc_2(SO_4)_3$-$H_2SO_4.4H_2O$ (Trousil, 1938). The corresponding selenate has the formula $Sc_2(SeO_4)_3H_2SeO_4.4H_2O$ according to Trousil (1938). Bouissières, Gaume-Mahn, Henry la Blanchetais, Loriers & Trombe (1959), however, report only two molecules of water of crystallization.

Unit-cell parameters were determined and intensity data collected on a Syntex $P2_1$ (Fortran version) automatic four-circle single-crystal diffractometer with monochromatized Mo $K\alpha$ radiation. Unit-cell parameters were calculated by least-squares refinement of 20 reflections. Intensities of 1301 reflections were collected in the range $5 \leq 2\theta \leq 75°$ using the $\theta/2\theta$ technique and variable scan speed of 1–3° min^{-1}. The 1002 reflections with intensities greater than three times their standard deviations were used in the refinement. The unit cell was of the type C with no systematic absences (except those for type C). Therefore, space groups $C2$, Cm and $C2/m$ (Nos. 5, 8 and 12) were possible. An empirical absorption correction was made from the φ scan, after which Lorentz and polarization corrections were applied.

The structure was solved by direct methods with the computer program *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Refinement

Table 1. *Positional parameters* (× 10^4) *for* $ScH(SeO_4)_2.2H_2O$

The standard deviations of the last two figures are given in parentheses.

	x	*y*	*z*
Sc	0	0	0
Se	6023 (1)	0	8163 (1)
O(1)	4968 (5)	2375 (8)	8328 (5)
O(2)	6487 (9)	0	6505 (7)
O(3)	7598 (7)	0	9569 (7)
O(4)*	8726 (16)	902 (25)	4871 (16)

* With a population parameter of 0·5.