

& Brun (1973) by employing the lattice constants used in this study, the bond distances listed in Table 2 are obtained. It can be seen that the bond distances that were in disagreement earlier have all been corrected, but now the equatorial $M-O$ and the third $O-O$ distances deviate by 4σ and 3.4σ respectively. This is somewhat better agreement, but obviously a shift of approximately 2σ in the y parameter of the O atom would bring these distances into line. These studies graphically illustrate the need to pay closer attention to determination of accurate lattice constants if accurate bond distances are to result.

Two of us (GWB and WOM) acknowledge support from National Science Foundation Grant No. DMR-72-03131-A-03, and two (JK and IB) acknowledge support from National Science Foundation Grant No. MPS-74-13718 and The Robert A. Welch Foundation

Grant No. E-594. Also, we thank BNL Chemistry Department for the use of the neutron diffraction facilities at BNL and R. McMullan for help during data collection.

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The Structures of Some Cadmium 'Apatites' $Cd_5(MO_4)_3X$.

I. Determination of the Structures of $Cd_5(VO_4)_3I$, $Cd_5(PO_4)_3Br$, $Cd_5(AsO_4)_3Br$ and $Cd_5(VO_4)_3Br$

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(Received 17 September 1976; accepted 22 December 1976)

The compounds are approximately isostructural with fluorapatite, $Ca_5(PO_4)_3F$, ($P6_3/m$, $Z = 2$) and the positional parameters of the nonhalogen atoms are very similar for all. The halogen atoms, however, do not occupy the ideal positions $\pm(0,0,\frac{1}{4})$ or any unique positions $\pm(0,0,z)$ on the hexad axis. Relative to the O atoms they are present in less than stoichiometric amounts, the deficiency decreasing from about 27% for the iodide to ~8% for the arsenate bromide. This deficiency appears to result from steric hindrance, the usual ionic diameters of the halogens exceeding $\frac{1}{2}c$ by 10–20%. Refinements of the crystal structures of the title compounds and of $Cd_5(PO_4)_3Cl$ (final R 's about 0.05) indicate that the formulae should be written $Cd_{5-x}(MO_4)_3X_{1-2x}$, where x can be as large as 0.13 in one (the iodide) case.

Introduction

Cadmium has been linked to hardening of the arteries and high blood pressure (Carroll, 1966; Schroeder, 1965). As a pollutant in the Jintsu river in Japan, cadmium caused many cases of *itai itai* (Tsuchiya, 1969), a very painful bone disease with some osteoporotic-like effects. In several areas of the USA, cadmium and arsenic levels in the water supply have

been found to be in excess of those permitted by US Public Health Service standards—50 parts per billion (10^9) for As, and 10 ppb for Cd (Carper, 1971). Both of these metals are readily incorporated in the apatite structure, the model system for the inorganic portion of bones and teeth. Hence, crystal structure studies of apatites in which Cd has replaced Ca and those in which As has replaced P take on relevance in dental research.

In calcium apatites the X ions (*e.g.* F, OH or Cl) occur in linear arrays on the hexad axis with an interatomic distance $X-X$ of $c/2$. Cadmium apatites in which $X = \text{Cl, Br or I}$ are found to have short c dimensions compared with calcium apatites (Engel, 1968). This short c dimension implies interatomic distances considerably less than the sum of ionic radii if the linear array is retained. Hence it was thought that the halogen packing problem posed by the short c dimension may introduce some modifications in the apatite structure. The structure of cadmium chlorapatite is described elsewhere (Sudarsanan, Young & Donnay, 1973). Results of the refinements of the structures of the compounds $\text{Cd}_5(\text{PO}_4)_3\text{Br}$, $\text{Cd}_5(\text{AsO}_4)_3\text{Br}$, $\text{Cd}_5(\text{VO}_4)_3\text{Br}$ and $\text{Cd}_5(\text{VO}_4)_3\text{I}$ are presented here. Detailed discussion of the actual distributions of the halogen ions along the hexad axis, and of the several ways the diffraction data can be analyzed to determine them, are given in part II (Wilson, Sudarsanan & Young, 1977).

Experimental

The specimen crystals were grown from the melt by Engel (1968) in platinum crucibles charged with $\text{Cd}_3(\text{MO}_4)_2$ and an excess of CdX_2 , where $M = \text{As, V, or P}$ and $X = \text{Br or I}$. The crucibles were not perfectly closed against air (Engel, 1971). Infrared spectroscopic analysis (Perkin-Elmer 621, OH stretch mode) for OH substituting at its normal structural position, in apatite, for halogen showed no such OH present in the bromides or the chloride. The estimated detectability limit is less than 5 at.% OH for halogen. In the iodide, a barely detectable amount was present. [In large crystals of $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ grown hydrothermally at 500°C and 800–1400 atm from Na- and NH_4 -containing solutions, Ivanov, Simonov & Belov (1976) did find, by chemical analysis, 0.80 wt% 'water' and 0.5% Na_2O .]

Single hexagonal-prismatic crystals, very approximately 0.5 mm (length) \times 0.05 mm (lateral dimension), were used for collection of X-ray data with a computer-controlled four-circle diffractometer and $\text{Mo K}\alpha$ radiation. The space group $P6_3/m$ reported by Engel (1968) was confirmed for each compound.

Table 1. Lattice parameters (standard deviations in parentheses)

	a	c
$\text{Cd}_5(\text{VO}_4)_3\text{I}$	10.307 (1) Å	6.496 (1) Å
$\text{Cd}_5(\text{PO}_4)_3\text{Br}$	9.733 (1)	6.468 (1)
$\text{Cd}_5(\text{AsO}_4)_3\text{Br}$	10.100 (1)	6.519 (1)
$\text{Cd}_5(\text{VO}_4)_3\text{Br}$	10.173 (2)	6.532 (1)
$\text{Cd}_5(\text{PO}_4)_3\text{Cl}^*$	9.633 (4)	6.484 (4)

* From Sudarsanan, Young & Donnay (1973).

The intensities of those reflections for which all Bragg peaks from the $K\beta$ radiation are outside the range of the peak and background scan were measured with unfiltered radiation by the 2θ -scan method, whereas the other reflections were collected by either the balanced-filter ω -scan method or by the single-filter 2θ -scan method, as described by Mackie (1972). Lattice parameters (Table 1) were determined from least-squares fitting of the positions of 12 reflections in each case on a single-crystal diffractometer ($\lambda = 0.7092$ Å). Simultaneous-diffraction effects were assessed by remeasurement of each reflection intensity after the specimen had been rotated about the diffraction vector by one degree. Those reflections which differed by more than three times the estimated standard deviation (from counting statistics) were not used in the refinements. Each reflection was repeatedly scanned to a maximum of 16 times or to yield 2% statistical precision in the net intensities, whichever came first. Absorption corrections were applied by the method of Busing & Levy (1957) (*ORABS-2* by H. A. Levy and R. D. Ellison was used); maximum and minimum absorption corrections differed by 30 to 40%, depending on the crystal.

Refinement of the structure

A full-matrix least-squares refinement of all variable positional and temperature parameters was attempted with the halogen held at $(0,0,\frac{1}{2})$, starting with the parameters of cadmium chlorapatite (Sudarsanan, Young & Donnay, 1973). A version of the Busing, Martin & Levy (1962) least-squares refinement program, as modified by Busing, Johnson, Ellison, Thiessen & Levy (1973) to include anomalous-dispersion and isotropic and anisotropic extinction corrections (*ORXFLS3*), was used. The atomic scattering factors for Cd^{2+} , As^{5+} and V^{5+} given by Cromer & Waber (1965) and the values calculated for O^{2-} by Tokonami (1965) were used. Values for P^{5+} were taken from Fukamachi (1971). Relevant corrections for anomalous dispersion were made with values of $\Delta f'$ and $\Delta f''$ calculated by Cromer (1965). The observed structure factors were corrected for isotropic secondary extinction. Only four reflections, three from one crystal and one from another, required extinction correction greater than 10%.

In the least-squares refinements, the weights used were reciprocal estimated variances, σ^{-2} , for the individual reflections. The estimated variance for each observation was revised according to $\sigma^2 = \sigma_c^2 + \sigma_x^2$, where $\sigma_x = k|F|^2$ and σ_c is the standard deviation estimated from counting statistics. Normal probability plots (δR type, Abrahams & Keve, 1971) (Fig. 1) and correlation plots of the type $\Delta|F|^2/\sigma$ vs $\log |F_o|^2$ (Fig. 2) and $\Delta|F|^2/\sigma$ vs $\sin \theta/\lambda$ (Sudarsanan & Young, 1974) were used to check the distribution of random errors

corresponding to different values assigned for k . That value of k , found to be about 0.05 to 0.06, which straightened the normal probability plot, bringing its best straight-line slope to about 1.0, was used in calculating σ^2 for use in the final refinements in each case. The $\Delta|F|^2/\sigma$ plots then showed no obvious correlation with $\sin \theta/\lambda$. The horn-shaped character of $\Delta|F|^2/\sigma$ vs $\log |F|^2$ was largely, but not entirely, removed (Fig. 2b).

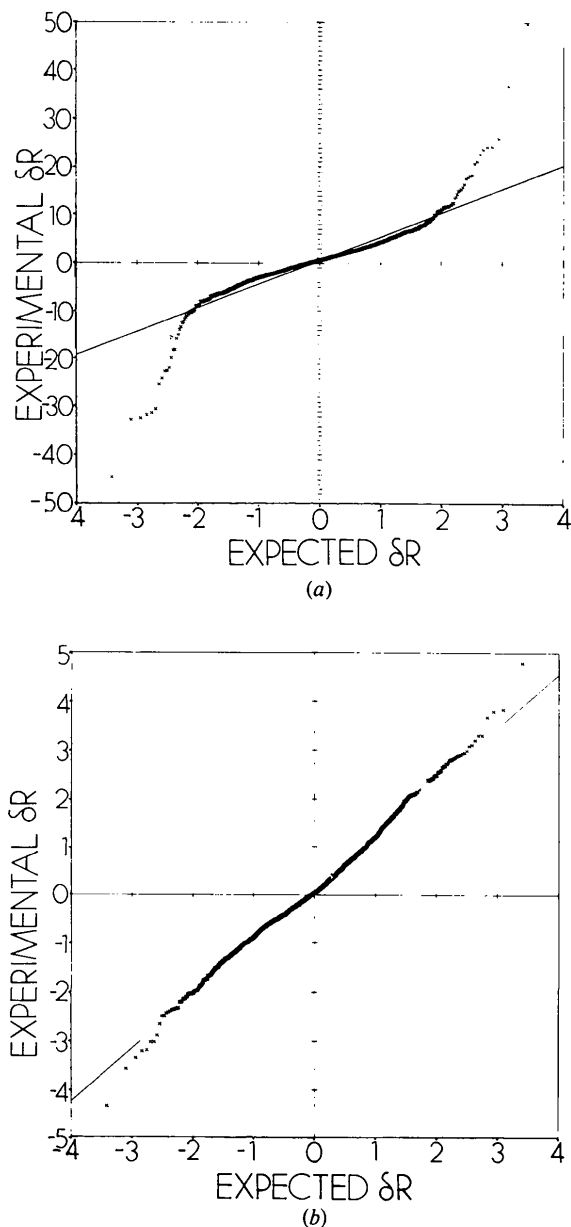


Fig. 1. Half-normal probability plots for, as an example, $\text{Cd}_5(\text{AsO}_4)_3\text{Br}$ (a) before and (b) after incorporation of σ_x (see text).

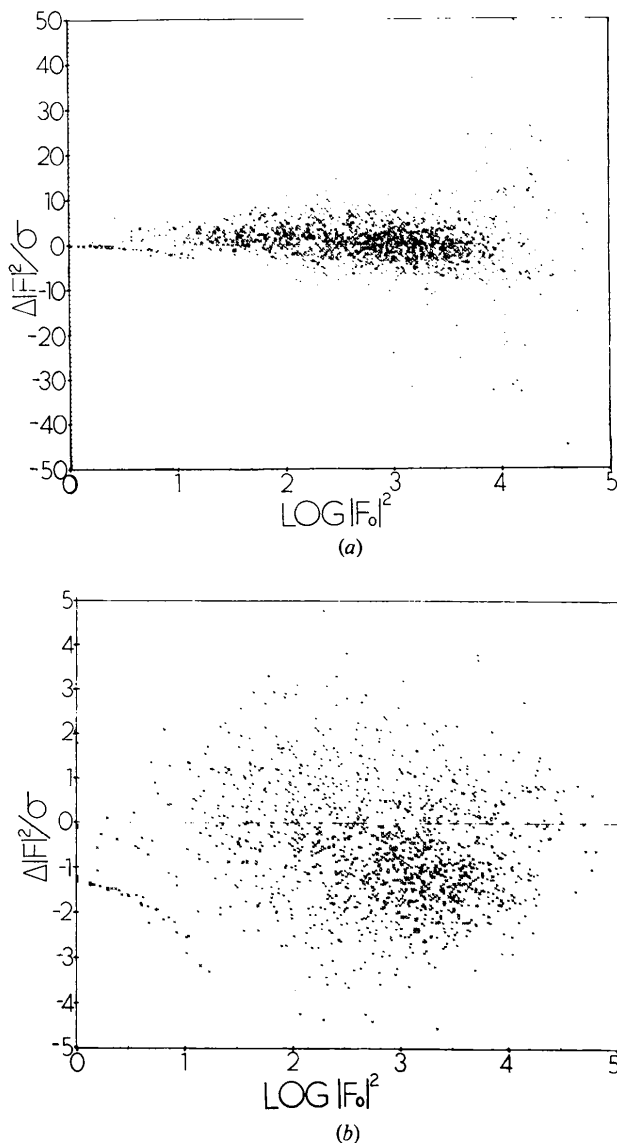


Fig. 2. Correlation plots for, as an example, $\text{Cd}_5(\text{AsO}_4)_3\text{Br}$ (a) before and (b) after $\sigma_x = 0.05|F|^2$ was incorporated in the weights. The appearance of several points falling on a particular curve at low $|F|^2$ does not occur in the plots vs $(\sin \theta)/\lambda$.

Table 2. Final R values

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$R_2 = \frac{\sum |F_o|^2 - |F_c|^2}{\sum |F_o|^2}$$

$$wR_2 = \left[\frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^4} \right]^{1/2}$$

	Number of reflections	R_1	R_2	wR_2
$\text{Cd}_5(\text{VO}_4)_3\text{I}$	1770	0.043	0.057	0.107
$\text{Cd}_5(\text{PO}_4)_3\text{Br}$	1234	0.040	0.050	0.105
$\text{Cd}_5(\text{AsO}_4)_3\text{Br}$	1500	0.024	0.032	0.077
$\text{Cd}_5(\text{VO}_4)_3\text{Br}$	1587	0.039	0.046	0.074
$\text{Cd}_5(\text{PO}_4)_3\text{Cl}^*$	1671	0.058	0.094	0.105

* New refinement with data of Sudarsanan, Young & Donnay (1973) and the multiple-halogen model.

Results and discussion

All these cadmium apatites were found to be more or less isostructural. The final R values are given in Table 2. The positional parameters are listed in Table 3 and the bond angles and interatomic distances in Table 4.* The PO_4 groups and Cd ions occupy much the same structural locations as in calcium apatites. In these four newly studied apatites, the MO_4 tetrahedra are distorted from perfect tetrahedral symmetry similarly both to one another and to other apatites for which detailed structure refinements have been reported.

The least-squares refinements with the halogens at $(0,0,\frac{1}{4})$ showed abnormally high values for the temperature factors (β_{33}) along the c direction (Table 5). Placing the halogen anywhere on the hexad axis $(0,0,z)$ does not result in any halogen-to-nonhalogen interatomic distance shorter than the sum of the ionic radii. The determination of the actual statistical distributions of the halogens about $(0,0,\frac{1}{4})$ and the determination of the amounts of halogen present became special tasks in themselves. They are the subject matter of part II (Wilson, Sudarsanan & Young, 1977).

A substantial correlation exists between the X -ion deficiency as determined from results of least-squares refinement and the degree to which the c dimension is shorter than the sum of the X -ion radii, as shown in Table 6, whether ionic radii or crystal radii were used. These indications of halogen deficiency, on the one hand, and of the possible indeterminacy of the halogen position along the hexad axis, on the other hand, led to consideration of a chain-packing model. In this model, normal halogen-halogen distances are maintained within a chain. The center of each chain is in some modal position and ions in succeeding half-cells deviate farther and farther from this modal position until, finally, the steric strain is relieved by the occurrence of a vacancy. A new chain then begins. Analogous phenomena have been described for iodine in dextran iodide (Borchert, 1952; Dietrich & Cramer, 1954), for cerium in $(\text{Pu,Ce})_5\text{Co}_3$ (Larson, Roof & Cromer, 1964), and for cobalt in $\text{Pt}_2\text{Co}_{1.7}$ (Schweizer, Strnat & Tsui, 1971).

* The anisotropic thermal parameters refined to normal values for all non-halogen ions. Those for halogen ions in the multiple-halogen model (Table 3) were fixed at inferred reasonable values of 28, 28, 100, 14, 0 and 0 ($\times 10^{-4}$), respectively, for β_{11} , β_{22} , β_{33} , β_{12} , β_{13} , and β_{23} . Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32647 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

As a first effort to characterize the distributions of the halogen ions along the axis, halogen ions were placed in the model at intervals along the axis, their thermal parameters were fixed at 'reasonable' values

Table 3. Positional parameters

All values are multiplied by 10^4 except those given as fractions. Standard deviations are given within parentheses for parameters varied.

	Site occupancy	x	y	z
$\text{Cd}_5(\text{VO}_4)_3\text{I}$				
O(1)	10000	3652 (3)	5223 (3)	$\frac{1}{4}$
O(2)	10000	6076 (3)	4598 (3)	$\frac{1}{4}$
O(3)	10000	3430 (3)	2697 (3)	$\frac{1}{4}$ (3)
V	10000 (64)	4113 (1)	3850 (1)	$\frac{1}{4}$
Cd(1)	9699 (48)	$\frac{1}{2}$	$\frac{3}{4}$	37 (1)
Cd(2)	8994 (44)	-436 (1)	2458 (1)	$\frac{1}{4}$
I(1)	900 (30)	0	0	2500
I(2)	2364 (42)	0	0	2000
I(3)	1602 (36)	0	0	1500
I(4)	1524 (36)	0	0	1000
I(5)	984 (36)	0	0	500
I(6)	-30 (36)	0	0	0
$\text{Cd}_5(\text{PO}_4)_3\text{Br}$				
O(1)	10000	3547 (5)	5042 (5)	$\frac{1}{4}$
O(2)	10000	5903 (5)	4569 (5)	$\frac{1}{4}$
O(3)	10000	3480 (4)	2696 (4)	$\frac{1}{4}$ (4)
P	10000	4056 (1)	3779 (1)	$\frac{1}{4}$
Cd(1)	9630 (48)	$\frac{1}{2}$	$\frac{3}{4}$	54 (1)
Cd(2)	9650 (44)	-202 (1)	2562 (1)	$\frac{1}{4}$
Br(1)	1218 (54)	0	0	2500
Br(2)	3534 (90)	0	0	2000
Br(3)	2130 (84)	0	0	1500
Br(4)	864 (84)	0	0	1000
Br(5)	408 (90)	0	0	500
Br(6)	144 (60)	0	0	0
$\text{Cd}_5(\text{AsO}_4)_3\text{Br}$				
O(1)	10000	3573 (3)	5164 (2)	$\frac{1}{4}$
O(2)	10000	6017 (2)	4654 (2)	$\frac{1}{4}$
O(3)	10000	3469 (2)	2634 (2)	$\frac{1}{4}$ (3)
As	10000 (34)	4072 (1)	3817 (1)	$\frac{1}{4}$
Cd(1)	9900 (24)	$\frac{1}{2}$	$\frac{3}{4}$	39 (1)
Cd(2)	9802 (18)	-325 (1)	2469 (1)	$\frac{1}{4}$
Br(1)	3132 (48)	0	0	2500
Br(2)	4158 (78)	0	0	2000
Br(3)	1224 (72)	0	0	1500
Br(4)	690 (72)	0	0	1000
Br(5)	48 (78)	0	0	500
Br(6)	0 (48)	0	0	0
$\text{Cd}_5(\text{VO}_4)_3\text{Br}$				
O(1)	10000	3622 (3)	5203 (3)	$\frac{1}{4}$
O(2)	10000	6089 (3)	4620 (3)	$\frac{1}{4}$
O(3)	10000	3419 (3)	2669 (3)	$\frac{1}{4}$ (3)
V	10000	4096 (1)	3830 (1)	$\frac{1}{4}$
Cd(1)	9798 (33)	$\frac{1}{2}$	$\frac{3}{4}$	30 (1)
Cd(2)	9668 (45)	-383 (1)	2424 (1)	$\frac{1}{4}$
Br(1)	3420 (36)	0	0	2500
Br(2)	3534 (60)	0	0	2000
Br(3)	1140 (54)	0	0	1500
Br(4)	630 (54)	0	0	1000
Br(5)	18 (60)	0	0	500
Br(6)	0 (48)	0	0	0

Table 3 (cont.)

Site occupancy	x	y	z
$Cd_5(PO_4)_3Cl^*$			
O(1)	10000	3511 (2)	5019 (1)
O(2)	10000	5908 (1)	4596 (2)
O(3)	10000	3444 (1)	2668 (1)
P	10000 (40)	4046 (1)	3772 (1)
Cd(1)	9957 (21)	$\frac{1}{3}$	$\frac{2}{3}$
Cd(2)	10026 (20)	-188 (1)	2534 (1)
Cl(1)	6192 (60)	0	0
Cl(2)	2886 (90)	0	0
Cl(3)	-318 (72)	0	0
Cl(4)	-222 (72)	0	0
Cl(5)	-66 (102)	0	0
Cl(6)	-18 (66)	0	0

* Results of refinement with multiple-halogen model and data of Sudarsanan, Young & Donnay (1973).

(β_{11} and β_{22} were taken from the least-squares refinement results obtained with only one halogen position per half-cell; β_{33} was taken from values found in analogous compounds), and the site-occupancy factors were refined along with the parameters of all the nonhalogen ions in least-squares refinements. The results, given in Table 3 as for differently numbered halogens, show that the halogens are distributed along the axis and that the widths of the distributions do differ among the compounds. Because of effects of missing terms and of termination (which do affect least-squares refinements as well as Fourier maps), however, any further simplistic interpretation of the results could be very misleading. The analysis of what further inter-

Table 5. Halogen site-occupancy factors and temperature factors with the halogens at $(0,0,\frac{1}{4})$

	Site-occupancy	Thermal parameters* ($\times 10^4$)	
		β_{11}	β_{33}
$Cd_5(VO_4)_3I$	0.800 (11)	30 (1)	3304 (55)
$Cd_5(PO_4)_3Br$	0.838 (11)	26 (2)	1981 (46)
$Cd_5(AsO_4)_3Br$	0.911 (6)	26 (1)	807 (12)
$Cd_5(VO_4)_3Br$	0.880 (8)	29 (1)	681 (11)
$Cd_5(PO_4)_3Cl^\dagger$	0.836 (10)	24 (1)	222 (3)

* $\beta_{22} = \beta_{11}$, $\beta_{12} = \frac{1}{2}\beta_{11}$, $\beta_{13} = 0$ and $\beta_{23} = 0$.

† From Sudarsanan, Young & Donnay (1973).

pretation is allowable, and comparative results of other analytical methods for determining the distribution details, therefore, form the subject matter of part II (Wilson, Sudarsanan & Young, 1977).

The major remaining questions are the extent of the halogen deficiency and the mechanism of charge balance. The results from the least-squares refinements were re-scaled to set the site occupancies of the MO_4 groups at stoichiometric values as an appropriate reference point. The refinements made then gave two direct estimates of the halogen content: (1) the site-occupancy factor when only one halogen position per half-cell was used in the model (Table 5), and (2) the sum of the site-occupancy factors when six halogen positions were used (Table 6, column 5). The corresponding halogen deficiencies are given in Table 6, together with their standard deviations. The agreement between these two direct estimates is well within

Table 4. Bond angles ($^\circ$) and interatomic distances (\AA)

M represents P, As or V as appropriate. O'(3) is related to O(3) by reflection in m at $z = \frac{1}{4}$. A doubly primed symbol designates an atom with coordinates $(-y, x - y, z)$ and a triply primed symbol that with coordinates $(x - y, x, \frac{1}{2} + z)$, where (x, y, z) are those given in Table 3. The number of asterisks indicates the number of times the distance is repeated for symmetry-related sites of the second atom. Calculations were made with ORFFE3 (Busing, Johnson, Thiesen & Levy, 1973).

	$Cd_5(VO_4)_3I$	$Cd_5(PO_4)_3Br$	$Cd_5(AsO_4)_3Br$	$Cd_5(VO_4)_3Br$
O(1)-M-O(2)	111.9 (1)	110.9 (2)	111.4 (1)	111.1 (1)
O(2)-M-O(3)	106.6 (1)	106.2 (2)	104.6 (1)	106.9 (1)
O(1)-M-O(3)	112.9 (1)	113.2 (1)	115.3 (1)	113.0 (1)
O(3)-M-O'(3)	105.2 (2)	106.5 (2)	104.2 (1)	105.5 (2)
M-O(1)	1.702 (3)	1.544 (4)	1.669 (2)	1.689 (3)
M-O(2)	1.770 (3)	1.563 (4)	1.711 (2)	1.768 (2)
M-O(3)*	1.706 (2)	1.535 (3)	1.686 (2)	1.703 (2)
O(1)-O(2)	2.878 (4)	2.559 (6)	2.793 (3)	2.852 (4)
O(2)-O(3)*	2.788 (3)	2.478 (5)	2.589 (2)	2.788 (3)
O(3)-O(1)*	2.842 (3)	2.571 (4)	2.836 (2)	2.829 (3)
O(3)-O'(3)	2.711 (4)	2.461 (5)	2.662 (4)	2.711 (4)
Cd(1)-O(1)**	2.318 (2)	2.315 (3)	2.304 (1)	2.312 (2)
Cd(1)-O(2)**	2.358 (2)	2.372 (3)	2.379 (1)	2.357 (2)
Cd(1)-O(3)**	3.075 (3)	2.880 (4)	2.958 (2)	3.039 (3)
Cd(2)-O(1)	3.723 (3)	3.212 (4)	3.492 (2)	3.618 (3)
Cd(2)-O(2)	2.253 (2)	2.254 (4)	2.285 (2)	2.278 (3)
Cd(2)-O'''(3)*	2.198 (2)	2.206 (2)	2.220 (2)	2.198 (2)
Cd(2)-O''(3)*	2.506 (3)	2.487 (3)	2.467 (2)	2.486 (2)
Cd(2)-Cd''(2)*	4.823 (1)	4.500 (1)	4.629 (1)	4.645 (1)

Table 6. Comparison of estimates of halogen-ion deficiencies (figures in parentheses are standard deviations)

	$D = X\text{-ion diameter (Å)}$		$c/2$ (Å)	$X\text{-ion site-occupancy factor}‡$	$X\text{-ion deficiencies (%)}$				
	(ionic*)	(crystal†)			From dimensions $(D - c/2)/D$		From site occupancies		From chemical assay (Engel, 1971)
					(with ionic D)	(with crystal D)	(six positions)	(one position)	
$\text{Cd}_5(\text{VO}_4)_3\text{I}$	4.40	4.12	3.248	0.734 (9)	26	21	27 (1)	20 (1)	—
$\text{Cd}_5(\text{PO}_4)_3\text{Br}$	3.92	3.64	3.234	0.830 (19)	17	11	17 (2)	16 (1)	7 (2)
$\text{Cd}_5(\text{AsO}_4)_3\text{Br}$	3.92	3.64	3.260	0.925 (16)	17	10	7.5 (2)	9 (1)	5 (2)
$\text{Cd}_5(\text{VO}_4)_3\text{Br}$	3.92	3.64	3.266	0.874 (12)	17	10	13 (1)	12 (1)	4 (2)
$\text{Cd}_5(\text{PO}_4)_3\text{Cl}$	3.62	3.34	3.242	0.845 (19)	10	3	15.5 (2)	16 (1)	—

* From Shannon & Prewitt (1969), confirmed by Shannon (1976).

† From Shannon (1976).

‡ Multiple-halogen model used in structure refinements.

Table 7. Cadmium deficiency

Crystal ($M-X$)	Observed (%)		Required to compensate halogen deficiency* (%)	
	Cd(2)	All Cd	Cd(2)	All Cd
V—I	10.1 (0.4)	7.2 (0.5)	4.3	2.6
P—Br	3.5 (0.4)	3.6 (0.5)	2.8	1.7
As—Br	2.0 (0.1)	1.6 (0.1)	2.7–1.3	1.6–0.7
V—Br	3.3 (0.3)	2.8 (0.2)	2.7–2.2	1.6–1.3
P—Cl	–0.3 (0.2)	0.0 (0.1)	1.1–1.5	0.6–0.9

* As calculated in Table 6.

statistical expectation for all but $\text{Cd}_5(\text{VO}_4)_3\text{I}$. In addition, an indirect estimate is obtained from the discrepancy between the halogen-ion diameter and the half-length of the hexad axis (Table 6) with the assumption that each halogen is in contact with two others.

Since ionic diameters are somewhat variable it is difficult to assess the accuracy of the deficiency calculated in this way; if the ionic diameters are correct the estimate should be a lower limit. In view of these uncertainties the agreement with the site-occupancy estimates may be regarded as satisfactory.

The Cd(2) ions have halogen ions in their immediate environment, whereas the Cd(1) ions have only O ions. One might, therefore, expect that charge balance would be maintained chiefly by Cd(2) vacancies. Table 3 shows a large excess of Cd(2) vacancies in $\text{Cd}_5(\text{VO}_4)_3\text{I}$ [10%, compared with 3% for Cd(1)], but for the other compounds the difference is much less. The cadmium-ion deficiencies corresponding to the observed halogen-ion deficiencies are given in Table 7, both on the assumption that charge balance involves both types of Cd ion, and on the assumption that only Cd(2) ions are involved. Except for $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, which is stoichiometric in Cd within the statistical limits, the total cadmium-ion deficiency is about twice that required to balance the halogen-ion deficiency indicated by the other estimates, and there is thus an unsolved problem

of (apparent) charge balance for all five compounds. There is, of course, no assurance that the assumption that there are no vacancies or substitutions among the MO_4 groups is correct, nor is there a firm confirmation that all the halogen deficiency is due to vacancies rather than, in part, the substitution of other ions, such as F. In view of these possibilities, and the semi-quantitative agreement between the estimates based on halogen-site occupancies and ionic diameters, the apparent charge-balance discrepancies are not regarded as serious. Further discussion and a more detailed analysis of the halogen deficiencies (which do not alter these semi-quantitative results) are in part II (Wilson, Sudarsanan & Young, 1977).

The authors are indebted to Professor H. Wondratschek and D. G. Engel (Universität, Karlsruhe) for kindly supplying the specimens and for helpful discussions, to Dr Engel for communicating his chemical-analysis results for the bromides, and to Derrold W. Holcomb for the infrared-spectroscopy survey. This work has been supported mainly by the US Public Health Service through NIH-NIDR grant DE-01912. AJCW is indebted also to the Royal Society and the William Waldorf Astor Foundation for travel and subsistence expenses, and to the University of Birmingham for leave of absence.

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The Structures of Some Cadmium 'Apatites' $Cd_5(MO_4)_3X$.

II. The Distributions of the Halogen Atoms in $Cd_5(VO_4)_3I$, $Cd_5(PO_4)_3Br$, $Cd_5(AsO_4)_3Br$, $Cd_5(VO_4)_3Br$ and $Cd_5(PO_4)_3Cl$

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(Received 21 December 1976; accepted 6 April 1977)

Many cadmium 'apatites' are 10 to 20% halogen deficient, with the halogen atoms distributed over a range of positions on the hexad axis instead of occupying the ideal positions $\pm(0,0,\frac{1}{2})$. Direct determination of the probability distribution of their positions has been attempted in three ways: (i) Fourier atomic-center density syntheses, (ii) least-squares refinement of the occupancy factors of a multiplicity of sites uniformly spaced along the c axis, and (iii) fitting of postulated distribution functions to the 'observed' structure factors corresponding to halogen centers only. All three methods are limited similarly by the resolving power afforded by the reflections in the accessible volume of reciprocal space. The results from all three methods are consistent with a 'chain' model in which the center of each chain occupies the modal position $(0,0,\frac{1}{2})$ or $(0,0,\frac{3}{2})$. Being 'oversize' (diameter $>\frac{1}{2}c$), halogen ions in succeeding half-cells are forced to deviate further and further from this modal position, until finally the steric strain is relieved by the occurrence of a vacancy, after which a new chain begins. Qualitative agreement is achieved with a uniform distribution of atomic centers over a range, δ , on each side of the modal positions, with δ varying from 0.04 in the chloride to 0.2 in the iodide. No other simple distribution tried, such as Cauchy or Gaussian, was applicable to all compounds.

1. Introduction

The structures of five cadmium apatites have been described in earlier papers (Sudarsanan, Young & Donnay, 1973; Sudarsanan, Young & Wilson, 1977).

Normalized to full occupancy of the oxygen sites in a structure of the fluorapatite type, they are halogen and cadmium deficient, with formulae $Cd_{1-x}(MO_4)_3X_{1-2x}$, and no definite positions on the hexad axis can be ascribed to the halogen atoms. These appear to be