Cadmium Fluoride Hydroxide

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Abstract. CdF(OH), orthorhombic, $P2_12_12_1$, $a = 4.8320\ (7)$, $b = 5.5159\ (7)$, $c = 6.8559\ (10)$ Å, $V = 182.73$ Å^3, $Z = 4$, $D_x = 5.15$ Mg m^{-3}, μ(Mo $K\alpha$) = 11.5 mm^{-1}. For 690 observed reflections the final $R = 0.031$. The structure is of the rutile type, but with c doubled. It is built up of columns of edge-sharing almost regular CdF$_3$O$_3$ octahedra with Cd—F,O bonds varying between 2.26 and 2.28 Å. The F and O atoms are statistically distributed and hexagonally close packed.

Introduction. CdF(OH) is isomorphous with HgF(OH) (Zadneprovskii, Kaidalova & Polishchuk, 1971). The coordination polyhedron around Hg in HgF(OH) (Stålhandske, 1979) is a distorted octahedron with two strong Hg—O bonds of 2.10 and 2.12 Å and four weaker ones; three Hg—F distances are 2.49–2.51 Å and one Hg—O is 2.69 Å. This irregularity is prevalent for Hg^{II} compounds, but not usually found in Cd structures. In a recent structural proposal for CdF(OH) (Volkova, Samarets, Polishchuk & Laptash, 1978) the compound is described as composed of very distorted octahedra with Cd—O and Cd—F distances ranging from 2.00 to 2.71 Å. The structure solution was based on an earlier determination of HgF(OH) (Grdenić & Sikirica, 1973) and refined from only 22 independent powder diffractometer reflections. The present reinvestigation was started to ascertain the structure of CdF(OH) for a comparison of the coordination of Cd and Hg. Work is also in progress on the isomorphous HgSO$_4$ and CdSO$_4$ (Aurivillius & Stålhandske, 1979).

CdF(OH) in microcrystalline form was precipitated from an aqueous solution of NH$_4$F and CdO (Feitknecht & Bucher, 1943). The white powder was at first air-dried at room temperature and then heated in gold capsules at 2.0–2.5×10^8 Pa. In the range 773–923 K colourless transparent crystals were grown; most of these were rather small, but a few larger ones were also found with very irregular shapes. One of these, $0.25 \times 0.14 \times 0.10$ mm, was used in the data collection performed on a CAD-4 diffractometer with Zr-filtered Mo K radiation. The ω–2θ scan technique was used with variable scan speeds and peak scan

intervals $\Delta\omega = (1.00 + 0.50 \tan \theta)°$. The maximum time spent on a reflection was 5 min. In one quadrant of reciprocal space all reflections with $3° < \theta \le 35°$ were collected. Every second hour three standard reflections were measured but no systematic variation in their intensities was detected. Reflections with *l* odd were all weak indicating that the structure could nearly be described in a cell with *c* halved. Of the 915 measured reflections, 690 with $I > 3\sigma(I)$ were used in the analysis. Corrections were applied for Lorentz–polarization and absorption effects. The transmission factors, evaluated by numerical integration, varied between 0.22 and 0.34. A preliminary least-squares calculation, with the positional parameters taken from the refinement of HgF(OH), converged. Full-matrix refinement was then performed with anisotropic thermal parameters and a parameter to correct for secondary extinction (Zachariasen, 1967). Difference syntheses, calculated to locate the H atoms, showed electron densities in the O—F direction close to both the F and O atoms, indicating that they are statistically distributed. The H atoms, found in the difference syntheses, were included with half-occupied positions and fixed parameters in the final refinement, which gave $R = 0.031$, $R_w = 0.044$, $S = 0.98$ and the extinction parameter $g = 0.11\ (2) \times 10^4$. Slightly larger R factors were obtained with reversed signs on the coordinates. The form factors for Cd and $\frac{1}{2}$(F + O) were those of Doyle & Turner (1968) and for H that of Stewart, Davidson & Simpson (1965). The anomalous-dispersion

Table 1. *Fractional coordinates*

The values for HgF(OH) are given in square brackets.

	x	y	z
Cd	0.24697 (5)	0.50289 (5)	0.62383 (10)
[Hg]	[0.2436 (2)]	[0.5070 (1)]	[0.6152 (1)]
FO(1)	0.4880 (6)	0.1470 (5)	0.6273 (8)
[F]	[0.408 (4)]	[0.108 (3)]	[0.635 (2)]
FO(2)	−0.0098 (6)	0.3571 (5)	0.8732 (9)
[O]	[0.035 (4)]	[0.398 (3)]	[0.864 (3)]
H(1)	0.31	0.10	0.63
H(2)	−0.19	0.41	0.89
[H]	[−0.15]	[0.47]	[0.87]

correction for Cd was taken from Cromer & Liberman (1970). The function minimized was $\sum w_i(|F_o| - |F_c|)^2$, with $w_i^{-1} = \sigma^2(F_o) + (0.025|F_o|)^2 + 0.40$. The final parameters are given in Table 1.*

Cell dimensions were determined from powder photographs for a sample heated to 773 K at 2.0×10^8 Pa. A Guinier–Hägg focusing camera was used with Cu $K\alpha_1$ radiation ($\lambda = 1.54050$ Å) and KCl ($a = 6.2928$ Å) as an internal standard.

Discussion. CdF(OH) is isomorphous with HgF(OH), but with the F and O atoms statistically distributed. The two structures are of the rutile type, built up of edge-sharing octahedra forming columns, parallel to [001], which are corner-shared to each other. In CdF(OH) and HgF(OH) c is, however, twice that of rutile. The columns are also rotated relative to one another in such a way that a good approximation to hexagonal close packing (h.c.p.) of the anions is obtained. A similar distortion of rutile is found in InO(OH) (Lehmann, Larsen, Poulsen, Christensen & Rasmussen, 1970). These structures, all projected along **c**, are shown in Fig. 1. In this projection the octahedra are superimposed in CdF(OH), but somewhat twisted in HgF(OH). Although the rotation of the columns can be considered to be a result of the hydrogen bonds, more important is probably the achievement of h.c.p., since the same type of distortion is found in CaCl$_2$ (Bever & Nieuwenkamp, 1935). In the marcasite (FeS$_2$) structure (Buerger, 1937), the tendency to form the short S–S bond (2.21 Å) extends
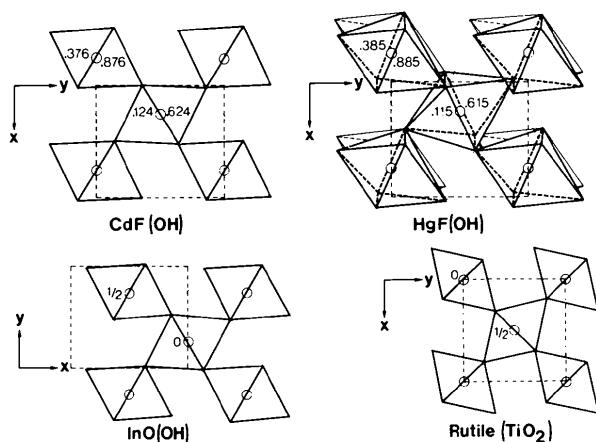

Fig. 1. The structures of CdF(OH), HgF(OH), InO(OH) and TiO$_2$ projected along **c**. The z coordinates of the metal atoms are given. The unit cells are indicated with light dashed lines, hydrogen bonds with dotted lines.
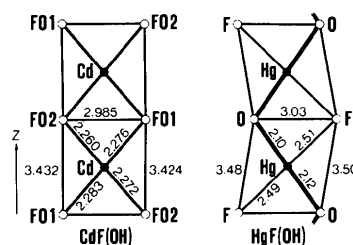

Fig. 2. Sections through the columns of edge-sharing octahedra in CdF(OH) and HgF(OH). In HgF(OH) the endless zigzag chains –O–Hg–O–Hg–O– are drawn with heavy lines.

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Cd–FO(2)	2.260 (5)	FO(1)–H(1)	0.90
–FO(2)^i	2.265 (3)	FO(2)–H(2)	0.93
–FO(2)^{ii}	2.272 (5)	FO(1)···FO(2)^v	2.810 (4)
–FO(1)^{iii}	2.276 (5)		
–FO(1)	2.283 (5)		
–FO(1)^{iv}	2.283 (5)		

FO(1)–Cd–FO(1)^{iv}	88.6 (1)	FO(1)^{iii}–Cd–FO(2)	82.3 (2)
–FO(1)^{iii}	90.3 (1)	–FO(2)^{ii}	97.7 (2)
–FO(2)	88.1 (1)	–FO(2)^i	88.7 (1)
–FO(2)^{ii}	90.9 (1)	FO(2)–Cd–FO(2)^{ii}	178.9 (1)
–FO(2)^i	178.9 (1)	–FO(2)^i	91.3 (1)
FO(1)^{iv}–Cd–FO(1)^{iii}	178.9 (1)	FO(2)^{ii}–Cd–FO(2)^i	89.8 (1)
–FO(2)	98.1 (2)		
–FO(2)^{ii}	81.9 (2)		
–FO(2)^i	92.4 (1)		

Symmetry code

(i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$
(ii) $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$
(iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$
(iv) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
(v) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$

this rotation even beyond h.c.p. In rutile the O atoms are triangularly coordinated by three Ti atoms. To obtain h.c.p. in CdF(OH) the anions are forced 0.41 and 0.42 Å out of the planes of three nearest Cd neighbours.

The CdF$_3$O$_3$ octahedra are nearly regular with Cd–F,O bonds of 2.260–2.283 Å (Table 2). Rather small changes in the positional parameters of F and O give the HgF(OH) structure, built up of more deformed octahedra with two short Hg–O bonds of 2.10 and 2.12 Å and four longer Hg–F and Hg–O distances of 2.49–2.69 Å. If only the shorter distances are considered, HgF(OH) can be described in terms of endless zigzag chains of formula $[\text{Hg(OH)}]_n^{n+}$, running in the z direction. Sections through the columns of edge-sharing octahedra in CdF(OH) and HgF(OH) are compared in Fig. 2. As in rutile the lengths of the shared edges for CdF(OH) are considerably shorter (2.985 Å) than those of the unshared edges (3.158–3.432 Å). The Cd–Cd distances in the columns are 3.428 Å; all other Cd–Cd distances are >4.0 Å. The
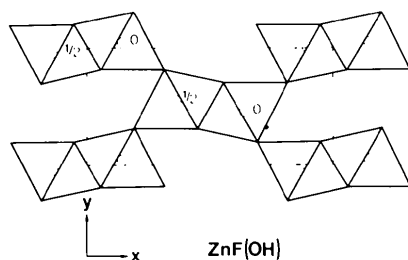
Fig. 3. The structure of ZnF(OH) projected along c. The z coordinates of the Zn atoms are given. The unit cell is indicated with dashed lines.

hydrogen bonds $O \cdots F$ in CdF(OH) (2·81 Å) are weaker than those in HgF(OH) (2·52 Å) and in InO(OH) ($O \cdots O$ 2·54 Å).

CdF(OH) differs from both CdF_2, with the fluorite (CaF_2) structure, and the layer structures CdCl(OH) (Hoard & Grenko, 1934) and $Cd(OH)_2$ (Natta, 1928). ZnF_2 has the rutile structure, but ZnF(OH) (Volkova, Samarets, Polishchuk & Laptash, 1978), shown in Fig. 3, has the diaspore [AlO(OH)] structure (Busing & Levy, 1958), which is of the rutile type, but with the columns of octahedra doubled.

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The Structure of Trieuropium Tetraarsenide*

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Abstract. Eu_3As_4, orthorhombic, $Fdd2$, a = 14·6419 (7), b = 17·6357 (5), c = 5·8866 (2) Å, U = 1520 Å^3, FW = 755·6, D_m = 6·42, Z = 8, D_x = 6·60 Mg m^{-3}, μ(Mo $K\alpha$) = 42·7 mm^{-1}, $F(000)$ = 2568. Diffractometer data gave R = 3·8% for 1800 independent observed hkl, for the model described below, when refined by full-matrix least-squares procedures. The structure consists of a continuous network of $[Eu_6]$ trigonal prisms. Two-thirds of the prisms contain As atoms which form As_4 chains (As–As = 2·47, 2·56 Å, As–As–As = 115·9°) and thus the structure can be considered to be polyanionic. Both Eu atoms are 16-coordinated (to 8 Eu and 8 As) with average distances Eu–Eu = 4·19 and Eu–As = 3·19 Å, consistent with metallic Eu^{2+}.

Introduction. This study was undertaken to characterize a new phase in the Eu–As system (Ono, Hui, Despault, Calvert & Taylor, 1971; Taylor, Calvert, Utsunomiya, Wang & Despault, 1978) which had a composition in the range 43–45 at.% Eu. Intensity data were collected on a four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·70926 Å) using local programs (for details see Wang, Gabe, Calvert & Taylor, 1976; Larson & Gabe, 1978). The crystal used was a fragment 0·1 × 0·04 × 0·04 mm from an Eu–As alloy