

## SHORT STRUCTURAL PAPERS

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## Refinement of Mercury Fluoride Hydroxide

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**Abstract.** HgF(OH), orthorhombic, space group  $P2_12_12_1$ ,  $a = 4.9568$  (6),  $b = 5.9042$  (7),  $c = 6.8630$  (11) Å,  $V = 200.85$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 7.82$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 77.8$  mm<sup>-1</sup>. For 441 observed reflections the final  $R = 0.066$ . The structure is built up of endless zig-zag chains of formula  $[\text{Hg}(\text{OH})]_n^{2+}$  with Hg–O = 2.10 and 2.12 Å. The chains are connected by O–H···F hydrogen bonds of 2.52 Å and weak Hg–F and Hg–O contacts.

**Introduction.** A refinement of the structure of HgF(OH) (Grdenić & Sikirica, 1973) has been performed as the earlier determination, based on a fairly limited number of intensities, resulted in rather large e.s.d.'s in the interatomic distances and high temperature factors for O and F.

Pale-yellow crystals of HgF(OH) were obtained by dissolving yellow HgO in 10% HF and concentrating the solution on a water bath at 343 K. A prismatic single crystal, 0.10 × 0.12 × 0.20 mm, was used in the diffractometer work. For the determination of the cell parameters and collection of the intensities a CAD-4 diffractometer was used with Zr-filtered Mo  $K$  radiation. The lattice parameters were determined by least-squares analysis of the  $\theta$  values for 50 reflections. The intensities were collected with the  $\omega$ - $2\theta$  scan technique and a peak scan interval  $\Delta\omega = (0.70 + 0.70 \tan \theta)^\circ$ . The maximum time spent on a reflection was 4.5 min. In one octant of reciprocal space all reflections with  $3^\circ < \theta \leq 30^\circ$  were measured. If  $30^\circ < \theta \leq 37.5^\circ$  only those with  $I > \sigma(I)$  were measured.  $I$  and  $\sigma(I)$  were calculated from fast prescans. Every second hour five standard reflections were measured. A decrease in their intensities was detected, but as it was irregular and the variation only between 2 and 7% during the two days of data collection, no correction was made. In the structure analysis 441 reflections with  $I > 3\sigma(I)$  were used. Corrections were applied for Lorentz–polarization and absorption effects ( $\mu = 77.8$  mm<sup>-1</sup>). The transmission factors, evaluated by numeri-

cal integration, varied between 0.005 and 0.047. The position of Hg, found by the Patterson method, was refined by least-squares calculations. As the resulting  $x$  coordinate was close to  $\frac{1}{4}$ , two peaks ( $x, y, z; \frac{1}{2} - x, y, z$ ) of nearly the same height were found for each of the O and F atoms in the difference syntheses. In the refinements, the lowest  $R$  was obtained with the coordinates given in Table 1, which thus represent the true structure. Considerably larger  $R$  values were found when the Hg coordinate was shifted to  $\frac{1}{2} - x$ , combined with the earlier positions of O and F, as chosen by Grdenić & Sikirica (1973). The refinements were performed by full-matrix least-squares calculations with anisotropic temperature factors for Hg and isotropic ones for O and F. The H atom of the OH group was included with fixed parameters, the fractional coordinates derived from geometrical considerations, assuming an  $sp^3$ -hybridized O atom. In the final refinement a parameter to correct for secondary extinction (Zachariasen, 1967) was included. The form factors for Hg, F and O were those of Doyle & Turner (1968) and for H that of Stewart, Davidson & Simpson (1965). An anomalous-dispersion correction for Hg (Cromer & Liberman, 1970) was also used. The refinement converged to  $R = 0.066$  and  $R_w = 0.077^*$  with the

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34159 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and isotropic temperature factors

	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Hg	0.2436 (2)	0.5070 (1)	0.6152 (1)	
F	0.408 (4)	0.108 (3)	0.635 (2)	2.1 (3)
O	0.035 (4)	0.398 (3)	0.864 (3)	2.0 (3)
H	–0.149	0.471	0.868	3

isotropic extinction parameter  $g = 0.20(3) \times 10^4$ . Slightly larger  $R$  values and e.s.d.'s were obtained with reversed signs on the coordinates. The function minimized was  $\sum w_i(|F_o| - |F_c|)^2$ , with  $w_i^{-1} = \sigma^2(F_o) + (0.035|F_o|)^2$ . The final parameters are given in Table 1.

**Discussion.** A stereoview of the structure is shown in Fig. 1. The structure is built up of infinite chains of formula  $[\text{Hg}(\text{OH})]_n^{n+}$ , connected by hydrogen bonds to the F atoms. The description is in good agreement with that given by Grdenić & Sikirica (1973); they had, however, based it on an incorrect structure determination. Some of the bond distances differ considerably from those in the earlier work and furthermore the present e.s.d.'s are much smaller (Table 2).

Endless chains of different geometries and compositions are found in a number of oxygen-containing inorganic  $\text{Hg}^{\text{II}}$  compounds (Aurivillius & Stålhandske, 1974). The  $[\text{Hg}(\text{OH})]_n^{n+}$  chains in the present structure

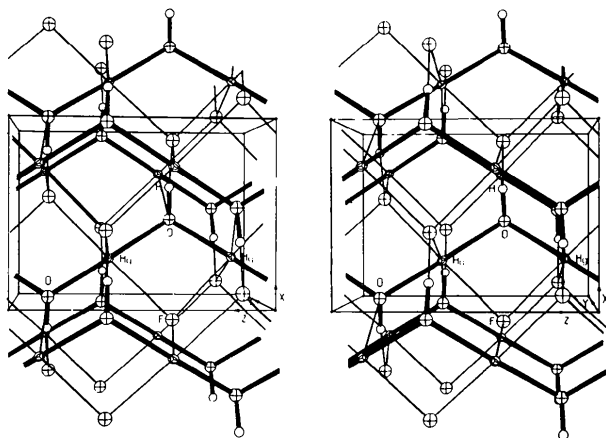


Fig. 1. Stereoscopic illustration of the crystal structure of  $\text{HgF}(\text{OH})$ . Covalent bonds  $\text{Hg}-\text{O}$  and  $\text{O}-\text{H}$  are drawn with heavy lines, the acceptor distances  $\text{H}\cdots\text{F}$  of the hydrogen bonds and the weak contacts  $\text{Hg}-\text{O}$  and  $\text{Hg}-\text{F}$  with thin lines.

Table 2. Selected interatomic distances (Å) and angles ( $^\circ$ )

In brackets are given values according to Grdenić & Sikirica (1973).

$\text{Hg}-\text{O}$	2.10 (2)	[2.11 (6)]	$\text{O}-\text{Hg}-\text{O}^{\text{I}}$	177.2 (1)	[176 (2)]
$-\text{O}^{\text{I}}$	2.12 (2)	[2.06 (6)]	$\text{O}^{\text{IV}}-\text{Hg}-\text{F}^{\text{II}}$	85.8 (6)	[89 (2)]
$-\text{F}^{\text{II}}$	2.49 (2)	[2.60 (8)]	$\text{F}^{\text{II}}-\text{Hg}-\text{F}$	89.9 (4)	[86 (2)]
$-\text{F}$	2.50 (2)	[2.26 (8)]	$\text{F}-\text{Hg}-\text{F}^{\text{III}}$	87.8 (4)	[93 (2)]
$-\text{F}^{\text{III}}$	2.50 (2)	[2.48 (8)]	$\text{F}^{\text{III}}-\text{Hg}-\text{O}^{\text{IV}}$	96.6 (6)	[92 (3)]
$-\text{O}^{\text{IV}}$	2.69 (2)	[2.75 (6)]	$\text{Hg}-\text{O}-\text{Hg}^{\text{V}}$	109.0 (9)	[111 (3)]
$\text{O}\cdots\text{F}^{\text{IV}}$	2.52 (3)	[2.76 (10)]	$\text{Hg}-\text{O}-\text{F}^{\text{IV}}$	106.2 (8)	[104 (3)]
$\cdots\text{F}$	2.97 (3)	[2.80 (10)]			

Symmetry code

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

can be compared with the planar endless zig-zag chains  $[\text{Hg}-\text{O}]_n$ , originally found in orthorhombic  $\text{HgO}$  (Aurivillius, 1956). The  $\text{Hg}-\text{O}$  distances within the chain in  $\text{HgF}(\text{OH})$  are 2.10 and 2.12 Å with angles  $\text{Hg}-\text{O}-\text{Hg}$  and  $\text{O}-\text{Hg}-\text{O}$  of 108.9 and 174.2°. Chains of the same type are also formed in the isostructural compounds  $\text{HgClO}_3(\text{OH})$  (Weiss, Lyng & Weiss, 1960) and  $\text{HgBrO}_3(\text{OH})$  (Björnlund, 1971) and in  $\text{HgNO}_3(\text{OH})$  (Matković, Ribar, Prelesnik & Herak, 1974); a finite chain of similar geometry is found in  $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  (Björnlund, 1974; Aurivillius & Stålhandske, 1976). In  $\text{HgBrO}_3(\text{OH})$  the  $\text{Hg}-\text{O}-\text{Hg}$  and  $\text{O}-\text{Hg}-\text{O}$  angles are 123 and 175°, in  $\text{HgNO}_3(\text{OH})$  119.6 and 171.6°. Corresponding values for  $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  are 114.4 and 180°. Comparing the angles  $\text{Hg}-\text{O}-\text{Hg}$  in the compounds it is seen that the value of  $\text{HgF}(\text{OH})$ , 108.9°, is closest to 109°, characteristic of  $sp^3$  hybridization and found in  $\text{HgO}(\text{orth.})$ .

The chains in  $\text{HgF}(\text{OH})$  are, as suggested by Polishchuk, Khmeleva, Zadneprovskii, Kaidalova & Kuptsova (1970) from IR measurements, linked by rather strong hydrogen bonds. The distance  $\text{O}-\text{H}\cdots\text{F}$  is 2.52 Å. Assuming an  $\text{O}-\text{H}$  distance of 1.00 Å and  $sp^3$  hybridization of the O atom, the  $\text{H}\cdots\text{F}$  distance is 1.52 Å and the angle  $\text{O}-\text{H}\cdots\text{F}$  173°. The chains are furthermore linked by four weak contacts; three  $\text{Hg}-\text{F}$  distances are 2.49–2.50 Å and one  $\text{Hg}-\text{O}$  is 2.69 Å to an adjacent chain. All those distances are shorter than the sum of the corresponding van der Waals radii.

$\text{HgF}_2 \cdot 2\text{H}_2\text{O}$  (Bukvetskii, Polishchuk & Simonov, 1976) is prepared in the same way as  $\text{HgF}(\text{OH})$  but from a more concentrated HF solution. This compound is described as built up of linked deformed Archimedean antiprisms with six  $\text{Hg}-\text{O}$  and  $\text{Hg}-\text{F}$  bonds of 2.27–2.40 Å and two  $\text{Hg}-\text{O}$  contacts of 2.81 Å. The polyhedra are further connected by hydrogen bonds  $\text{O}-\text{H}\cdots\text{F}$  of 2.51 and 2.65 Å. The coordination of  $\text{Hg}^{\text{II}}$  in  $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$  deviates from the more common one, the deformed octahedron, found in  $\text{HgF}(\text{OH})$ .

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## Structure of Tetraphenylarsonium *trans*-Dichlorobis(2,4-pentanedionato)rhenate(III), [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>][Re(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]

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**Abstract.** [C<sub>24</sub>H<sub>20</sub>As]<sup>+</sup>. [C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub>Re]<sup>-</sup>, *M<sub>r</sub>* = 838.69, monoclinic, *P*2<sub>1</sub>/c, *a* = 7.874 (2), *b* = 26.953 (9), *c* = 15.511 (4) Å, β = 102.37 (2)°, *Z* = 4, *V* = 3215.4 Å<sup>3</sup>, *D<sub>c</sub>* = 1.73, *D<sub>o</sub>* = 1.70 Mg m<sup>-3</sup>. Refinement by full-matrix least squares based on 4226 reflections gave *R* = 0.068 and *R<sub>w</sub>* = 0.053. The Re atom has pseudo-octahedral coordination to four O atoms of the acetylacetonate groups [range Re–O, 1.996 (9) to 2.016 (12) Å] and two *trans* Cl atoms [Re–Cl, 2.385 (5), 2.425 (5) Å].

**Introduction.** Courier (1971) first showed that the reaction of reducing agents with *trans*-dichlorobis(2,4-pentanedionato-*O,O*)rhenium(IV) (*A*) produced a blue-green species in solution. Later it was possible to isolate this species as a potassium salt and show that it was the one-electron reduction product of *A*, and, further, that the same salt could be produced by the reduction of the *cis* form of *A* (Lock, Murphy & Turner, 1979). Subsequent experiments suggested that the potassium salt contained the *trans* form of the reduction product, but it was of interest to confirm this by X-ray crystallography. Also, a fairly accurate X-ray study of *A* had been made (Brown, Lock & Wan, 1973), so that it may be possible to determine how the extra electron modified the molecular structure. Attempts to produce crystals of the potassium salt suitable for X-ray studies were unsuccessful, but the corresponding tetraphenylarsonium salt did give suitable crystals.

The title compound was prepared by the reaction of aqueous solutions of K[Re(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] (Lock, Murphy & Turner, 1979) with [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]Cl. The product precipitated immediately, and was purified by dissolving it in dichloromethane followed by precipitation with diethyl ether. Crystals suitable for X-ray

diffraction studies were prepared by the vapour-diffusion technique, allowing diethyl ether vapour to diffuse into a dichloromethane solution of the title compound over several days:

A roughly spherical blue-green crystal of 0.2 mm diameter was used for the X-ray diffraction studies. Precession photographs revealed the systematic absences *h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1. Accurate lattice parameters were obtained from a Syntex P1 diffractometer by a least-squares fit to 15 well centered reflections with 19 < 2θ < 26° [Mo Kα radiation, λ(*K*α) = 0.71069 Å]. Crystal density was measured by flotation in an aqueous ZnBr<sub>2</sub> solution. The intensities of 4700 reflections with 2θ ≤ 45° were measured on the same diffractometer; of these, 2420 had *I* > 3σ<sub>*I*</sub>. The stability of the system was monitored by measuring three standard reflections after every 47 reflections. The standard errors of the 113, 151, and 202 reflections were 1.9, 2.2 and 1.6% respectively. All reflections were corrected for Lorentz, polarization and absorption (spherical correction, μ = 1.32 mm<sup>-1</sup>; absorption correction factor, *A*<sup>\*</sup>, range 2.08 to 2.05). Equivalent reflections were averaged and those systematically absent were removed to give 4226 independent intensities of which 2219 had *I* > 3σ<sub>*I*</sub>.

A Patterson map gave the position of the Re atom and subsequent difference syntheses revealed all the other non-hydrogen atoms. The structure was refined using the full-matrix least-squares program CUDLS which minimized ∑ w(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup>, where w = [σ<sub>*F*</sub><sup>2</sup> + (*kF*)<sup>2</sup>]<sup>-1</sup> except for reflections for which *F<sub>c</sub>* < *F<sub>o</sub>* and *I* < 3σ<sub>*I*</sub> for which w = 0 (σ<sub>*I*</sub> and σ<sub>*F*</sub> are the standard errors in *I* and *F*, respectively, based on counting statistics). The value of *k* = 0.01 in the weighting scheme was chosen to make ⟨w(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup>⟩