Table 2. *Distances* (Å) *and angles* (°)

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

(*a*) Cs—O distances <3·7 Å; e.s.d.'s 0·013–0·019 Å

Cs(1)	O(3)	3·05	$O(2^{i})$	3·12	$Aq(1^{i})$	3·16
	$O(5^{i})$	3·20	$O(4^{i})$	3·31	O(4)	3·31
	O(5)	3·41	O(6)	3·47	$Aq(2^{i})$	3·54
Cs(2)	$O(6^{ii})$	3·02	$O(1^{iii})$	3·18	O(7)	3·21
	$O(2^{iii})$	3·22	O(4)	3·24	$Aq(2^{iv})$	3·25
	$O(7^{ii})$	3·30	O(2)	3·63	O(1)	3·64
Cs(3)	$O(1^{v})$	3·05	$O(3^{v})$	3·08	$O(7^{ii})$	3·12
	O(6)	3·16	O(1)	3·16	$Aq(2^{vi})$	3·19
	O(4)	3·31	$Aq(1^{vii})$	3·54		
Cs(4)	$O(2^{viii})$	3·07	O(5)	3·13	$O(3^{viii})$	3·15
	$O(5^{i})$	3·14	$O(7^{i})$	3·19	O(6)	3·28
	$Aq(1^{viii})$	3·31	$O(3^{ix})$	3·52		

(*b*) Aq—O distances (Å) and O—Aq—O angles (°) for possible hydrogen bonds; e.s.d.'s 0·02 Å and 0·7°

$Aq(1)—O(2^{i})$	2·70	$Aq(2)—O(6^{iv})$	2·69
$Aq(1)—O(1^{x})$	2·74	Aq(2)—O(5)	2·78
$O(2^{i})—Aq(1)—O(1^{x})$	103·9	$O(5)—Aq(2)—O(6^{iv})$	97·3

Aq(1) and Aq(2) (both 0·302) show that these O atoms belong to water molecules, and those of O(1), O(2), O(5) and O(6) (range 1·795–1·879) correspond to the fact that these take part in hydrogen bonds. For the other O atoms, the sum of bond valences is in the range 1·891–2·150.

References

Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* B**32**, 1957–1959.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE.* Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Hawthorne, F. C. & Calvo, C. (1978). *J. Solid State Chem.* **26**, 345–355.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Kato, K. & Takayama, E. (1983). *Acta Cryst.* C**39**, 1480–1482.

Sakurai, T. (1967). *Universal Crystallographic Computation Program System.* Tokyo: The Crystallographic Society of Japan.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1985). C**41**, 165–167

Structure of Mercury(II) Iron(III) Fluoride Dihydrate, $HgFeF_5.2H_2O$

By J. L. Fourquet and E. Courant

Laboratoire des Fluorures et Oxyfluorures Ioniques, Faculté des Sciences du Mans, Equipe de Recherche Associée au CNRS n° 609, *Route de Laval, BP* 535, 72017 *Le Mans CEDEX, France*

P. Chevalier

Laboratoire de Chimie des Solides, UER de Chimie, Laboratoire Associé au CNRS n° 279, 2 *rue de la Houssinière,* 44072 *Nantes CEDEX, France*

and R. De Pape

Laboratoire des Fluorures et Oxyfluorures Ioniques, Faculté des Sciences du Mans, Equipe de Recherche Associée au CNRS n° 609, *Route de Laval, BP* 535, 72017 *Le Mans CEDEX, France*

(*Received* 4 *June* 1984; *accepted* 2 *October* 1984)

Abstract. $M_r = 387{\cdot}5$, orthorhombic, $Pbam$, $a = 10{\cdot}711\,(2)$, $b = 6{\cdot}638\,(1)$, $c = 4{\cdot}008\,(1)$ Å, $U = 285{\cdot}0$ Å^3, $Z = 2$, $D_x = 4{\cdot}53$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 29{\cdot}483$ mm^{-1}, $F(000) = 342$, $T = 293$ K. Final $R = 0{\cdot}0291$ for 413 independent observed reflections. The structure consists of chains of *trans*-linked FeF_6 octahedra and rutile-type chains of $HgF_4(H_2O)_2$ octahedra running along [001], forming layers parallel to (100). These layers, related to the $MnAlF_5$ structure type, are connected to each other along [100] by strong O—H···F bonding.

Introduction. Very few inorganic and fluorinated compounds of mercury are known (Fourquet, Plet & De Pape, 1981). The present work on $HgFeF_5.2H_2O$ forms part of a research programme on such phases.

Experimental. Powdered samples are prepared from HgOHF and FeF_3 (1/1 ratio) in HF solutions (40%) at 473 K under 15 MPa or simply at ambient pressure, by evaporation of a saturated HF solution of HgOHF and FeF_3. Curiously, the best crystals were grown in HF solution (40%) at 473 K under 15 MPa from Hg_2F_2

0108-2701/85/020165-03$01.50

and FeF_3 (1/1 ratio); they were always mixed with opalescent crystals of $Hg_2FeF_5.2H_2O$. Crystals of the title compound are small, colourless and transparent parallelepipeds elongated along **c**. Standard chemical analysis confirmed the Hg/Fe ratio; the exact water content of the cell was established by the structure determination.

Laue photographs show Laue group *mmm*; systematic absences $0kl$ with $k \neq 2n$ and $h0l$ with $h \neq 2n$ lead to two possible space groups, *Pbam* and *Pba*2; cell parameters refined from powder data; data collection on Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation from a single crystal with boundary faces $\pm\{001\}$ ($L = 0{\cdot}135$ mm), $\pm\{100\}$ ($L = 0{\cdot}045$ mm) and $\pm\{010\}$ ($L = 0{\cdot}072$ mm). 2617 reflections measured, $0 < h < 16$, $-10 < k < +10$, $-6 < l < +6$, ω–2θ scans between 1·5 and 35° θ. After each block of 40 reflections three standard reflections measured, relative variations $< 0{\cdot}09$; data corrected for Lorentz–polarization and absorption effects with *SHELX*76 (Sheldrick, 1976), max. and min. transmission factors 0·2922 and 0·1470; data averaged to 481 unique reflections ($R_{\text{int}} = 0{\cdot}0334$); 413 independent observations retained for analysis [$\sigma(I)/I < 0{\cdot}333$]. All calculations performed with *SHELX*76 (Sheldrick, 1976). Atomic scattering factors and f' and f'' values from *International Tables for X-ray Crystallography* (1974). Hg and Fe atoms located from Patterson function, remaining atoms from subsequent Fourier-difference synthesis; atomic coordinates and anisotropic thermal parameters refined, using F magnitudes, by full-matrix least squares; $w = k/[\sigma^2(F) + |q|F^2]$, where $k = 1{\cdot}0000$ and $q = 0{\cdot}003721$; refinement leads to $R = 0{\cdot}0291$ ($R_w = 0{\cdot}0298$) for *Pbam* and to $R = 0{\cdot}0292$ ($R_w = 0{\cdot}0296$) for *Pba*2; max. least-squares shift/error ratio $< 0{\cdot}005$; in final difference synthesis max. and min. electron densities 3·14 and −3·53 e Å^{-3}; isotropic extinction parameter (Sheldrick, 1976) = 151 (46) × 10^{-5}.

Discussion. Final atomic parameters are in Table 1.*

Fig. 1 shows the projection on (001). The structure consists essentially of infinite linear chains of FeF_6 octahedra running along [001], each octahedron sharing two *trans* F(3) atoms. Two $[FeF_5]^{2-}_{\infty}$ chains are connected by rutile-type chains of $HgF_4(H_2O)_2$ octahedra also running along [001]. For the FeF_6 octahedron the distances are Fe—F(1) = 1·922 (7), Fe—F(2) = 1·897 (6) and Fe—F(3) = 2·004 (1) Å, the mean Fe—F distance being 1·941 Å, close to the sum of ionic radii, 1·93 Å (Shannon, 1976). For the $HgF_4(H_2O)_2$ octahedron the distances are Hg—O = 2·107 (3) and Hg—F(2) = 2·496 (4) Å; these distances are close to those in HgOHF (Nozik, Fykin, Bukin & Laptash, 1979) built from $HgF_3(OH)_3$ octahedra, mean Hg—F = 2·493 Å and mean short Hg—O = 2·100 Å.

The structure can also be described as built from infinite puckered layers of octahedra parallel to (100) as shown in Fig. 2. The layers are linked approximately along [100] by strong O—H···F bonding, the interlayer

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (*Willis & Pryor*, 1975), *with e.s.d.'s in parentheses*

	Position	x	y	z	B_{eq} (Å^2)
Hg	2(*a*)	0	0	0	1·537 (15)
Fe	2(*d*)	0	$\frac{1}{2}$	$\frac{1}{2}$	0·85 (3)
F(1)	4(*h*)	0·1765 (6)	0·5526 (13)	$\frac{1}{2}$	2·03 (24)
F(2)	4(*h*)	0·0309 (7)	0·2186 (9)	$\frac{1}{2}$	1·85 (24)
F(3)	2(*c*)	0	$\frac{1}{2}$	0	1·80 (27)
O	4(*g*)	0·3071 (9)	0·4376 (16)	0	2·13 (27)

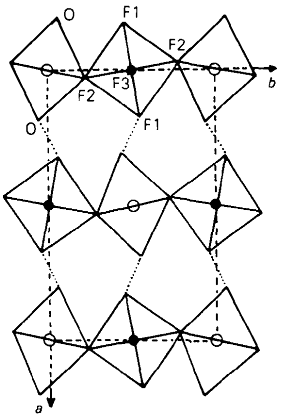

Fig. 1. Projection of the structure on (001). Full circles: Fe atoms, open circles: Hg atoms. Dotted lines show hydrogen bonding involving H_2O at $z = 0$ and F(1) at $z = 0{\cdot}5$.

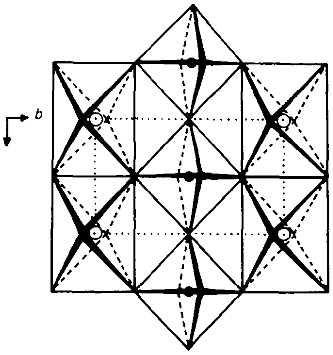

Fig. 2. Projection of a layer in $HgFeF_5.2H_2O$ on (100). Full and open circles show Fe and Hg atoms respectively. The linkage between the *trans* chains of FeF_6 octahedra and the rutile-type chains of $HgF_4(H_2O)_2$ octahedra is indicated. The dotted lines show the unit cell.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39806 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

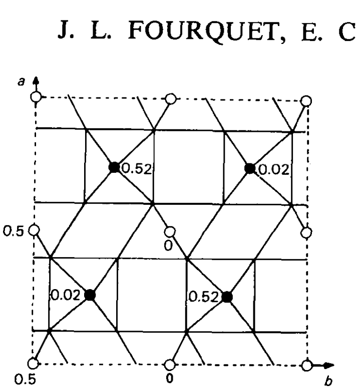

Fig. 3. Projection of the $MnAlF_5$ structure on (001). Full circles: Al atoms, open circles: Mn atoms.

distances O—F(1) [2·560 (8) Å] lying in the range 2·56–2·86 Å, characteristic of O—H···F hydrogen bonds in crystalline hydrates of metal fluorides (Simonov & Bukvetsky, 1978).

The organization of these layers may be compared to that of the octahedra in $MnAlF_5$ (Rimsky, Thoret & Freundlich, 1970); considering the layers shown in Fig. 1, if we remove all the water molecules, apply a **c**/2 translation and connect adjacent layers by means of the F(1) atoms, we obtain the $MnAlF_5$ three-dimensional network (Hg^{2+} for Mn^{2+} and Fe^{3+} for Al^{3+}) shown in Fig. 3.

We thank Professor G. Ferey for fruitful discussions.

References

FOURQUET, J. L., PLET, F. & DE PAPE, R. (1981). *Acta Cryst.* B**37**, 2136–2138.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

NOZIK, YU. Z., FYKIN, L. E., BUKIN, V. I. & LAPTASH, N. M. (1979). *Koord. Khim.* **5**(2), 276–278.

RIMSKY, A., THORET, J. & FREUNDLICH, W. (1970). *C.R. Acad. Sci. Sér. C*, **270**, 407–409.

SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SIMONOV, V. I. & BUKVETSKY, B. V. (1978). *Acta Cryst.* B**34**, 355–358.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Acta Cryst. (1985). C**41**, 167–168

Structure of Mercury(I,II) Iodide Oxide, Hg_2OI

BY C. STÅLHANDSKE,* K. AURIVILLIUS† AND G.-I. BERTINSSON

Inorganic Chemistry, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

(*Received* 15 *June* 1984; *accepted* 10 *October* 1984)

Abstract. $M_r = 544·08$, monoclinic, $C2/c$, $a = 17·603$ (8), $b = 6·981$ (5), $c = 6·701$ (5) Å, $\beta = 101·61$ (2)°, $V = 807$ (1) Å^3, $Z = 8$, $D_x = 8·96$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 853$ cm^{-1}, $F(000) = 1768$, $T = 295$ K. Single crystals obtained by hydrothermal synthesis at 470 K. Final $R = 0·036$ for 979 unique reflections. The structure is built up of layers with bond distances Hg^I—Hg^I 2·534, Hg—O 2·13–2·16 and Hg—I 3·05–3·14 Å. The layers are connected by Hg—O bonds (2·47 Å) to form a three-dimensional structure.

Introduction. Mercury(I,II) compounds are rare and only $Hg_4O_2Cl_2$, the mineral terlinguaite, has been structurally investigated (Ščavničar, 1956; Aurivillius & Folkmarsson, 1968). In this structure there are linearly coordinated Hg^{II} atoms and Hg_3 groups, forming equilateral Hg triangles, with a formal oxidation number of $\frac{4}{3}$ for each Hg. The Hg—Hg distance within the triangle is 2·708 Å, much longer than the Hg—Hg bonds of 2·48–2·54 Å found in Hg^I compounds, but considerably shorter than $Hg^{II}\cdots Hg^{II}$ contacts (> 3·4 Å) and even shorter than the closest Hg—Hg distance of 2·99 Å found in α-Hg (Barrett, 1957).

In order to investigate further mercury(I,II) compounds two new oxide halides have been synthesized, Hg_2OI and $Hg_8O_4Br_3$ (Stålhandske, 1983). It has so far not been possible to prepare a bromide oxide with the same stoichiometry as terlinguaite.

Experimental. Crystals grown by hydrothermal synthesis at 450 K from a stoichiometric mixture of yellow HgO and Hg_2I_2. Plate-shaped dark-red crystal 0·22 × 0·11 × 0·04 mm. CAD-4 diffractometer, graphite-monochromatized Mo K radiation, ω–2θ scan, width (0·60 + 0·50 tanθ)°, max. recording time 180 s. Three standard reflections, no significant variations. Lattice

---

* To whom correspondence should be addressed.

† Deceased.

0108-2701/85/020167-02$01.50