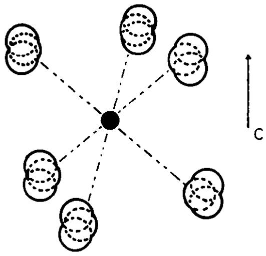

Fig. 3. The average picture of a $CuCl_6$ octahedron as described by model *A*. The *c* axis of the unit cell is indicated.

Jahn–Teller distorted structure in α-$CsCrCl_3$, α-$CsCrI_3$ and α-$CsCuCl_3$, we can also generalize that the high-temperature structures of $RbCuCl_3$, $CsCrBr_3$, *etc.*, are isostructural.

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The Structure of Dimercury(I) Aluminium(III) Fluoride Dihydrate

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Abstract

Single crystals of $Hg_2AlF_5.2H_2O$ are tetragonal with $a = 9{\cdot}353\ (5)$, $c = 7{\cdot}241\ (6)$ Å, *I4cm*, $Z = 4$, $D_c = 5{\cdot}86$ Mg m^{-3}. The final $R = 0{\cdot}0365$ ($R_w = 0{\cdot}0391$) for 383 independent reflections. The network of *trans* chains of AlF_6 octahedra parallel to the *c* axis is closely related to similar arrangements found in $Cs_2MnF_5.H_2O$ and several $M^{I}_{2}AlF_5.H_2O$ compounds. Between the chains, the structure contains the quasi-linear $[H_2O—Hg—Hg—OH_2]^{2+}$ cation, with an Hg—Hg distance of 2·511 (1) Å and equivalent Hg—O distances of 2·144 (9) Å. Cooperative hydrogen bonding is discussed.

Introduction

Only very few crystal structures of fluorinated compounds containing Hg^I are known: Hg_2F_2 (Grdenić & Djordjević, 1956), $Hg_2SiF_6.2H_2O$ (Dorm, 1971). The present work on $Hg_2AlF_5.2H_2O$ forms part of a research programme on inorganic fluorinated compounds containing monovalent mercury.

Preparation

Single crystals were prepared in HF (5 *M*) solutions at 423 K under 15 MPa from Hg_2F_2 and AlF_3 in

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stoichiometric proportions. Attempts to prepare the compound directly from HF solutions under atmospheric pressure did not succeed. The crystals are small, colourless needles elongated along **c**. Standard chemical analysis confirms the Hg/Al ratio; the exact water content of the cell was found at the end of the structure determination. DTA measurements showed a strong decomposition peak at 508 ± 5 K.

Crystallographic study and data collection

Laue photographs reveal that $Hg_2AlF_5.2H_2O$ belongs to Laue group $4/mmm$. Systematic absences hkl with $h + k + l \neq 2n$ and $h0l$ with $h \neq 2n$ lead to three possible space groups, $I4/mcm$, $I\bar{4}c2$ and $I4cm$. The cell parameters were refined from powder data; data collection was performed on a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation from a single crystal with boundary faces $\pm\{001\}$ ($L = 0{\cdot}225$ mm) and $\pm\{100\}$, $\pm\{010\}$, $\pm\{110\}$, $\pm\{\bar{1}10\}$ which were equally developed ($L = 0{\cdot}045$ mm). 2413 reflections satisfying the conditions $-16 < h < 16$, $0 < k < 16$ and $-12 < l < 12$ were explored with an ω–2θ scanning technique. After correction for Lorentz–polarization and absorption effects ($\mu = 48{\cdot}579$ mm^{-1}), the data were averaged and reduced to 383 independent observations [$\sigma(I)/I < 0{\cdot}333$].

Structure solution

All calculations were performed with *SHELX* (Sheldrick, 1976). The presence of a second-harmonic-generation signal indicated the noncentrosymmetric character of the compound. But in the absence of any other structural information we first tried direct methods in the centrosymmetric space group $I4/mcm$. The best solution gave the positions of eight Hg atoms [8(h)] arranged in pairs (Hg—Hg = 2·52 Å) at $z = 0$ and $\frac{1}{2}$, and of four Al atoms [4(a)] symmetrically surrounded at 1·82 Å by 16 F atoms [16(j)], denoted F_{eq}, at $z = \frac{1}{4}$ and $\frac{3}{4}$. After a few cycles of refinement of the atomic coordinates of the Hg atoms, a Fourier synthesis revealed the four remaining F atoms [4(c)], denoted F_{ax}, at $z = 0$ and $\frac{1}{2}$ and eight water molecules which appeared to be statistically distributed over the 16(l) positions near the $z = 0$ and $\frac{1}{2}$ levels.

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

The isotropic extinction parameter x (Sheldrick, 1976) takes the value 163 (11) × 10^{-5}.

	Position	x	y	z	B_{eq} (Å^2)
Hg	8(c)	0·9051 (1)	0·4051 (1)	0	1·82 (2)
Al	4(a)	0	0	0·2674 (18)	0·82 (15)
F_{ax}	4(a)	0	0	0·0055 (56)	2·50 (36)
F_{eq}	16(d)	0·8100 (7)	−0·0273 (7)	0·2600 (16)	1·66 (28)
O	8(c)	0·7442 (10)	0·2442 (10)	−0·0359 (18)	1·44 (30)

Atomic coordinates and anisotropic thermal parameters were refined by full-matrix least squares to $R = 0{\cdot}0427$ ($R_w = 0{\cdot}0461$). Calculations were then made for the two noncentrosymmetric space groups which gave $R = 0{\cdot}0390$ ($R_w = 0{\cdot}0415$) for $I\bar{4}c2$ and $R = 0{\cdot}0365$ ($R_w = 0{\cdot}0391$) for $I4cm$. We finally chose $I4cm$; Table 1 lists final atomic parameters.* This choice is supported by the following considerations concerning the water molecules:

– The final Fourier synthesis of the structure determination ($R = 0{\cdot}04$) shows peaks significantly out of the (001) plane. The water molecules are thus in the 8(c) positions (x, $\frac{1}{2} + x$, z) of space group $I4cm$. This is confirmed by the final value of the z parameter and its e.s.d. In $I\bar{4}c2$, corresponding positions are 8(h) (x, $\frac{1}{2} + x$, 0).

– If we consider that covalent bonding occurs between Hg and the O atom [Hg—O 2·144 (9) Å], the 8(c) positions (point symmetry m) fit the expected stereochemistry of the water molecule (Fig. 2). In $I\bar{4}c2$, the point symmetry of the 8(h) positions, 2, is inconsistent with the stereochemistry of the water molecule bonded to Hg.

Description of the structure

Fig. 1 shows the projection along the c axis.

The structure consists of infinite straight chains of alternately rotated AlF_6 octahedra parallel to the c axis, each octahedron sharing two *trans* F atoms (F_{ax}). There are *trans* chains of linked octahedra in $Cs_2MnF_5.H_2O$ (Kaučič & Bukovec, 1978) and they also occur, slightly kinked, in several Al compounds, $Rb_2AlF_5.H_2O$, $Tl_2AlF_5.H_2O$ (Fourquet, Plet & De Pape, 1981) and $K_2AlF_5.H_2O$ (Brosset, 1942). The imprecision of the z coordinate of F_{ax} prevents consideration of the difference found between the two Al—F_{ax} distances [1·896 (42) and 1·724 (42) Å]. The mean Al—F_{ax} distance is 1·810 Å while the Al—F_{eq} distance is 1·796 (6) Å, very close to the sum of the ionic radii, 1·82 Å (Shannon, 1976).

Between the chains, at the $z = 0$ and $\frac{1}{2}$ levels, lies the quasi-linear cation $[H_2O—Hg—Hg—OH_2]^{2+}$. The

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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 36127 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Hg–Hg distance is indistinguishable from those in similar compounds (Grdenić, 1956; Johansson, 1966; Dorm, 1971).

Table 2 presents characteristic distances for the structure.

Fig. 2 shows the environment of the $[Hg_2(H_2O)_2]^{2+}$ ion.

Water molecules have an (8 + 2 + 1) coordination number: eight F_{eq}, two F_{ax} and one Hg. The shortest F_{eq}–O distances [2·584 (13) Å] lie in the range 2·56–2·86 Å, characteristic of O–H···F hydrogen bonds in crystalline hydrates of metal fluorides (Simonov & Bukvetsky, 1978). In $Rb_2AlF_5.H_2O$ (Fourquet, Plet & De Pape, 1981) the corresponding distances are 2·729 (7) Å. Cooperative hydrogen bonding plays a very important part here; it is clearly responsible for the stabilization of the *trans*-chain network of octahedra and for the alternate rotations around the *c* axis, observed for the F_{eq} atoms. Another type of cooperative hydrogen bonding was previously found and discussed in the *trans*-chain compound $Rb_2AlF_5.H_2O$ (Fourquet, Plet & De Pape, 1981).

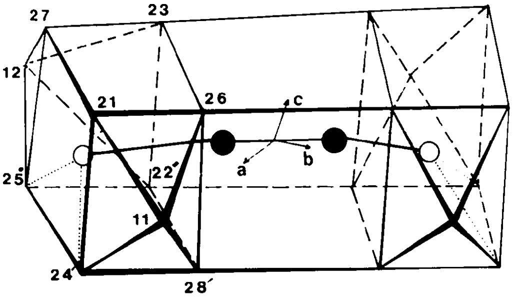

Fig. 2. Environment of the $[H_2O–Hg–Hg–OH_2]^{2+}$ cation. Full circles: Hg atoms, open circles: O atoms. F atoms are labelled as in Table 2. Dotted lines indicate hydrogen bonding.

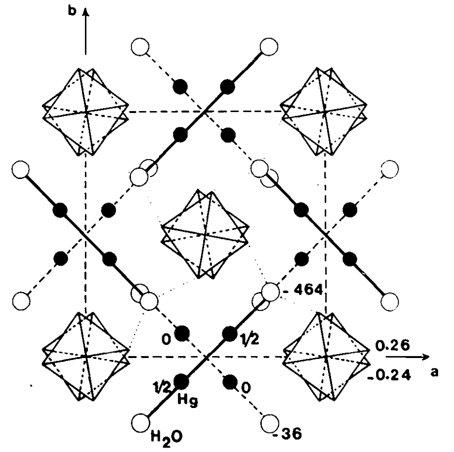

Fig. 1. Projection of the structure on the (001) plane. Full circles: Hg atoms, open circles: O atoms. Al atoms are on the fourfold axis of the octahedra at $z = 0·26$ and 0·76. Dashed lines indicate $[Hg_2(H_2O)_2]^{2+}$ cations at $z = 0$. The z coordinates of the O atoms are $\times 10^3$. Dotted lines show hydrogen bonding involving H_2O near $z = 0·5$.

Table 2. *Characteristic distances* (Å)

Mercury coordination		Water coordination	
Hg–Hg	2·511 (1)	O–Hg	2·144 (9)
Hg–O	2·144 (9)	O–F(24′) O–F(25′)	2·584 (13)
Hg–F(26) Hg–F(23′)	2·827 (9)	O–F(26) O–F(23′)	3·068 (14)
Hg–F(28′) Hg–F(22′)	2·894 (8)	O–F(28′) O–F(22′)	3·074 (13)
		O–F(11) O–F(12)	3·321 (10)
		O–F(21) O–F(27)	3·379 (14)

F atoms are assigned two digits. The first refers to the type of F: 1 for F_{ax}, 2 for F_{eq}. The second defines the coordinates of the equivalent position, as follows:

F(11)	$0,0,z$	F(24′)	$(\frac{1}{2}+x, \frac{1}{2}-y, z) + (\frac{1}{2},\frac{1}{2},\frac{1}{2})$
F(12)	$\frac{1}{2},\frac{1}{2},z$	F(25′)	$(\bar{y},x,z) + (\frac{1}{2},\frac{1}{2},\frac{1}{2})$
F(21)	x,y,z	F(26)	$y,\bar{x},z$
F(22′)	$(\bar{x},\bar{y},z) + (\frac{1}{2},\frac{1}{2},\frac{1}{2})$	F(27)	$\frac{1}{2}+y, \frac{1}{2}+x, z$
F(23′)	$(\frac{1}{2}-x, \frac{1}{2}+y, z) + (\frac{1}{2},\frac{1}{2},\frac{1}{2})$	F(28′)	$(\frac{1}{2}-y, \frac{1}{2}-x, z) + (\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

The Hg atom has an octahedral environment composed of four F_{eq}, another Hg (forming the Hg_2^{I} doublet) and a water molecule.

$Hg_2AlF_5.2H_2O$ should, therefore, be looked upon as an ionic structure with $[H_2O–Hg–Hg–OH_2]^{2+}$ cations inserted in the familiar $[AlF_4F_{2/2}]^{2-}$ *trans*-chain network of octahedra stabilized by strong hydrogen bonding.

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