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The Crystal Structure of $Hg_2FeF_5(OH)_2 \cdot H_2O$

E. COURANT, J. L. FOURQUET, AND R. DE PAPE

Laboratoire des Fluorures et Oxyfluorures Ioniques, UA 449, Faculté des Sciences du Mans, Route de Laval, 72017 Le Mans Cédex, France

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The new compound $Hg_2FeF_5(OH)_2 \cdot H_2O$ was prepared by evaporation of an aqueous 40% HF solution containing HgO and FeF_3 in the stoichiometric ratio. The material is orthorhombic, space group *Cmmm*, with $a = 7.505(1)$ Å, $b = 11.823(3)$ Å, $c = 3.941(2)$ Å, and $Z = 2$. The crystal structure was determined from single crystal intensity data obtained by means of an automated four-circle diffractometer and refined to the conventional values $R = 0.0621$ and $R_w = 0.0566$ for 451 observed reflections. The structure is characterized by infinite straight chains of FeF_6 octahedra sharing *trans* F atoms in the direction [001]. These chains are linked by rutile-type chains of $HgF_4(OH)_2$ octahedra also running along [001]. Water molecules are statistically distributed on half of the 4*i* positions; they are off-centered in the channels parallel to [001] allowing O–H · · · F bonding. The structure is compared to that of $HgFeF_5 \cdot 2H_2O$ and to that of the hexagonal tungsten bronze.

Introduction

Very few fluorinated compounds of mercury and metal atoms are known (*1–2*). So we started a systematic study of such compounds, both with Hg^I and Hg^{II}, in an attempt to find new structural types. We report here the structure of the complex $Hg_2FeF_5(OH)_2 \cdot H_2O$.

Experimental Part

Single crystals of $Hg_2FeF_5(OH)_2 \cdot H_2O$ are obtained by slow evaporation of an aqueous 40% HF solution containing HgO and FeF_3 in the molar ratio 2/1. The crystals are small, elongated, pink needles with a pseudohexagonal section. Standard chemical analysis gives Hg 62.7%, Fe 9.1%, F 17.7%; the theoretical values are 66.4%, 9.2%, and 15.7%, respectively. The dehydration of the compound begins at 100°C when heated under vacuum with a slow heating under flowing dry argon. Heating to 170°C leads to total irreversible dehydration. Before 600°C, the anhydrous complex decomposes and gives 2HF + 2HgO + FeF_3. The presence of OH^- is confirmed by preparation of the anhydrous compound by heating HgOHF and FeF_3 (2/1 ratio) in a sealed silver tube at 400°C.

Crystallographic Study and Data Collection

A standard photographic analysis by X-ray diffraction on single crystals revealed the *mmm* Laue group and the systematic absences $h + k \neq 2n$ lead to five possible space groups: *Cmmm*, *Cmm2*, *C222*, *C2mm* and *Cm2m*. The last two space groups are nonstandard settings of the space group

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TABLE I

STRUCTURAL PARAMETERS OF $Hg_2FeF_5(OH)_2 \cdot H_2O$

Atom	Position	t^a	x	y	z	$u_{11}{}^b$	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}	B (Å^2)
Hg	4*f*	1.0	0.25	0.25	0.5	59(4)	130(5)	133(4)	0.0	0.0	−5(1)	0.847
Fe	2*a*	1.0	0.0	0.0	0.0	1(11)	53(12)	51(11)	0.0	0.0	0.0	0.276
F(1)	2*d*	1.0	0.0	0.0	0.5	355(82)	359(76)	71(53)	0.0	0.0	0.0	2.06
F(2)	8*p*	1.0	0.1784(10)	0.1137(6)	0.0	260(41)	313(39)	211(37)	0.0	0.0	−230(30)	2.06
O(1)	4*j*	1.0	0.0	0.3228(8)	0.5	127(49)	138(44)	335(66)	0.0	0.0	0.0	1.58
O(2)	4*i*	0.5	0.0	0.4729(24)	0.0	262(165)	87(107)	1110(387)	0.0	0.0	0.0	3.8

[a] *t*: occupancy factor.

[b] All values are $\times 10^4$. The vibrational coefficients are relative to the expression $T = \exp[-2\pi^2(h^2a^{*2}u_{11} + k^2b^{*2}u_{22} + l^2c^{*2}u_{33} + 2klb^*c^*u_{23} + 2hla^*c^*u_{13} + 2hka^*b^*u_{12})]$.

*Amm*2. The powder diffractogram was readily indexed on the basis of the orthorhombic unit cell: $a = 7.505(1)$ Å, $b = 11.823(3)$ Å, and $c = 3.941(2)$ Å ($Z = 2$). A small crystal, $V \simeq 6.5 \times 10^{-3}$ mm^3 (section ~ 0.029 mm^2 and length ~ 0.225 mm), was chosen for the data collection. Intensities were measured on an automated Nonius CAD4 diffractometer with graphite-monochromated MoK_α radiation. A total of 2492 reflections satisfying the conditions $0 \leq h \leq 11$, $-18 \leq h \leq 18$, and $-6 \leq l \leq 6$ were explored with an ω–2θ scanning technique in the range $1.5 < \theta < 35°$. After correction for the Lorentz polarization effect the data were averaged ($R_{int} = 0.1043$) (*3*) and it was not judged necessary to apply an absorption correction because of the badly defined dimensions of the boundary faces. The data were reduced to 451 independent observations with $\sigma(I)/I < 0.333$. All the calculations needed for the resolution of the structure were performed with SHELX 76 (*3*). Atomic scattering factors and $\Delta f'$ and $\Delta f''$ values were those from "International Tables for X-Ray Crystallography" (*4*).

Structure Resolution

The calculations were first done using *Cmmm*, the most symmetrical space group. The Patterson function analysis gave the positions of the four Hg atoms and the two Fe atoms in the 4*f* and 2*a* positions, respectively. Fourier synthesis calculations revealed 14 anions (OH^- or F^-) on the 2*d*, 8*p*, and 4*j* positions. At this stage of the solution and with the isotropic thermal motion approximation, the values of the conventional R indexes (*3*) were $R = 0.088$ and $R_w = 0.078$ where w is defined by $w = k/(\sigma(F)^2 + |g|\,|F|^2)$ with k and g refined. A Fourier difference synthesis then revealed a residual electronic density on 4*i* positions, this was interpreted by a statistical half-occupancy of these sites by two water molecules (called O(2)). Final calculations, with the anisotropic thermal motion approximation gave $R = 0.0621$ and $R_w = 0.0566$ ($k = 10.3596$, $g = 0.001344$). The values of the atomic coordinates, the u_{ij}, and the equivalent isotropic thermal parameters are listed in Table I.

The OH^- (called O(1)) and F^- ions were distinguished on the basis of the Hg–O and Hg–F distances found in HgOHF (*5*) and in $Hg_2FeF_5 \cdot 2H_2O$ (*2*): the distances Hg–O(1) and Hg–F(2) are 2.064(4) and 2.601(4)Å, respectively, they agree well on the one hand with the mean short distances Hg–O in HgOHF and with the Hg–O distance in $HgFeF_5 \cdot 2H_2O$ −2.100 and 2.107(3) Å, respectively, and on the other hand, with the mean Hg–F distances in the same structures −2.493 and 2.496 Å, respectively.

TABLE II

INTERATOMIC DISTANCES (Å) IN $Hg_2FeF_5(OH)_2 \cdot H_2O$

Octahedron FeF_6	Octahedron $HgF_4(OH)_2$	Water molecules environment
Fe–F(1) : 1.970(1)	Hg–F(2) : 2.601(4)	2× short O(2)–O(1) : 2.652(20)
Fe–F(2) : 1.898(6)	Hg–O(1) : 2.064(4)	2× O(2)–O(1) : 3.117(20)
		2× short O(2)–F(2) : 2.622(20)
		2× O(2)–F(2) : 2.932(20)

Calculations with the two groups *Cmm*2 and *C*222 did not significantly improve the results. The space groups *C*2*mm* and *Cm*2*m* are nonstandard settings of *Amm*2. This case was interesting because it alone should allow an ordering of the water molecules on the 2*a* positions. Calculations using this model did not give any significant improvement in the *R* values. It should also be noticed that the second harmonic generation test was negative.[1]

Structure Description

Figure 1 shows the projection of the structure on the (001) plane. The structure contains infinite straight chains of FeF_6 octahedra sharing *trans* F(1) atoms in the direction [001]. These chains are linked by rutile-type chains of $HgF_4(OH)_2$ octahedra running along [001]. The connections between the two kinds of chains are achieved by the F(2) atoms.

Table II reports the different interatomic distances.

For the FeF_6 octahedron, the mean Fe–F distance is 1.922 Å, very close to the sum of ionic radii—1.93 Å (*6*). For the very distorted $HgF_4(OH)_2$ octahedron, Hg–O(1) and Hg–F(2) distances are close to those observed in HgOHF and $HgFeF_5 \cdot 2H_2O$ as discussed above. The two water molecules are statistically distributed in the channels parallel to [001] and occupy off-centered

[1] F_o and F_c values may be obtained on request to J.L.F.

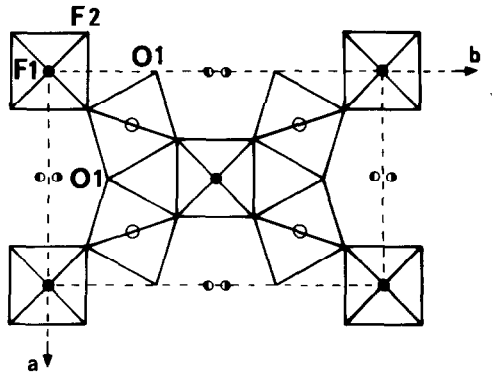

FIG. 1. Projection of the structure of $Hg_2FeF_5(OH)_2 \cdot H_2O$ on (001). Full circles are Fe atoms ($z = 0$), open circles are Hg atoms ($z = \frac{1}{2}$). The positions of water molecules –O(2)–, shown by half full circles, are statistically half occupied ($z = 0$). F(1) are at $z = 0.5$, F(2) at $z = 0$, O(1) at $z = \frac{1}{2}$.

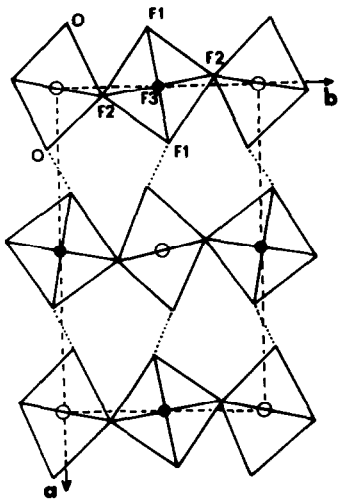

FIG. 2. Projection of the structure of $HgFeF_5 \cdot H_2O$ on (001). Fe atoms: full circles ($z = \frac{1}{2}$); open circles: Hg atoms ($z = 0$). F(1): $z = \frac{1}{2}$; F(2): $z = \frac{1}{2}$; F(3): $z = 0$; and O: $z = 0$. Dotted lines show hydrogen bonding involving H_2O at $z = 0$ and F(1) at $z = 0.5$.

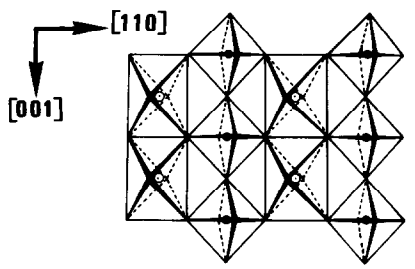

FIG. 3. Projection of a layer in $Hg_2FeF_5(OH)_2 \cdot H_2O$. Full and open circles show Fe and Hg atoms, respectively.

positions which allow O–H · · · F bonding; the shortest O(2)–F(2) distances lie in the range 2.56–2.86 Å characteristic of O–H · · · F hydrogen bonding in crystalling hydrates of metal fluorides (*7*).

As in the case of $HgFeF_5 \cdot 2H_2O$ (*2*), the structure of which is presented in Fig. 2, the present structure can be described in terms of layers constituted by FeF_6 and $HgF_4(OH)_2$ octahedra as shown in Fig. 3. In the case of $HgFeF_5 \cdot 2H_2O$, the layers are connected to each other by O–H · · · F bonding, and in $Hg_2FeF_5(OH)_2 \cdot H_2O$, these layers are connected by rutile-type chains of $HgF_4(OH)_2$ octahedra formed by the supplementary Hg atoms. These layers are interconnected and parallel to (110) and $(\bar{1}10)$.

The network of $Hg_2FeF_5(OH)_2 \cdot H_2O$ looks strikingly like the hexagonal tungsten bronze one, but it differs nevertheless by the presence of the rutile-type chaining of the $HgF_4(OH)_2$ octahedra.

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