Hg$_3$AlF$_6$O$_2$H, a structure with a short interpolyhedral O···O distance

Matthias Weil

Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, Getreidemarkt 9/171, A-1060 Vienna, Austria
Correspondence e-mail: mweil@mail.zserv.tuwien.ac.at

The crystal structure of Hg$_3$AlF$_6$O$_2$H, trimercury(II) aluminium hydrogen hexafluoride dioxide, can be derived from a slightly distorted cubic close-packed (ccp) arrangement of the metal atoms, where three quarters of the positions are occupied by Hg atoms and one quarter by Al atoms. The F and O atoms are considerably dislocated from the tetrahedral voids of this arrangement, thus forming [HgO$_2$F$_6$] polyhedra, with two short Hg—O distances, two intermediate Hg—F distances and four longer Hg—F distances, and nearly ideal [AlF$_6$] octahedra. The H atoms are presumably located close to the inversion centre. Their positions were derived from crystal chemical arguments, and they take part in the formation of O—H···O hydrogen bonds between two O atoms, with an O···O distance of 2.562 (9) Å.

Comment

Only a few crystal structures of fluorinated and hydrated compounds containing Hg in different oxidation states are known, namely HgF(OH) (Stålhandske, 1979), HgF$_2$(H$_2$O)$_2$ (Bukvetskii *et al.*, 1976), Hg$_2$AlF$_5$(H$_2$O)$_2$ (Fourquet *et al.*, 1981), Hg$_2$SiF$_6$(H$_2$O)$_2$ (Dorm, 1971), Hg$_2$(OH)$_2$SiF$_6$(H$_2$O)$_2$ (Golovastikov, 1984), HgFeF$_5$(H$_2$O)$_2$ (Fourquet *et al.*, 1985) and Hg$_2$FeF$_5$(OH)$_2$(H$_2$O) (Courant *et al.*, 1985). The present work on Hg$_3$AlF$_6$O$_2$H forms part of a project to prepare such phases under different conditions.

The crystal structure of the title compound can be derived from a cubic close-packed (ccp) arrangement of the metal atoms, where three quarters of the positions are occupied by Hg atoms and one quarter by Al atoms. The appropriate rhombohedral cell, with lattice parameters a = 5.4491 Å and α = 83.572°, corresponds to a slight distortion of the cubic close packing. F and O atoms are considerably dislocated from the tetrahedral voids of this arrangement, thus forming [HgO$_2$F$_6$] polyhedra and [AlF$_6$] octahedra (Fig. 1). The corresponding coordination polyhedron around the Hg atom (coordination number = 8) might be described as being between a distorted cube and a triangulated dodecahedron (Fig. 2).

The bond lengths in the title compound agree with those found in other fluorinated and hydrated Hg compounds, where the Hg—O bonds are considerably shorter than the Hg—F bonds. The [AlF$_6$] group has a nearly perfect octahedral geometry, with bond lengths within the typical range for other fluoroaluminates and in good agreement with the mean Al—F value of 1.801 Å for the more irregular [AlF$_6$] octahedron observed in Hg$_2$AlF$_5$(H$_2$O)$_2$ (Fourquet *et al.*, 1981). The F atoms are surrounded by one Al and three Hg atoms, resulting in a strongly distorted tetrahedral arrangement. The O atoms are three-coordinate and are located
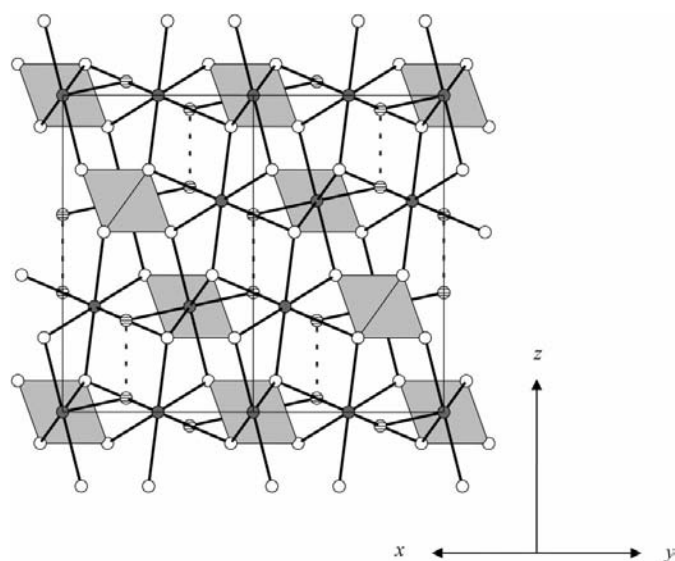

Figure 1
A projection of the crystal structure of Hg$_3$AlF$_6$O$_2$H along [110]. Hg atoms are plotted as dark-grey spheres, F atoms as white spheres and O atoms as hatched spheres. The [AlF$_6$] octahedra are light grey. The assumed hydrogen bonding between two O atoms is indicated with dashed bonds.
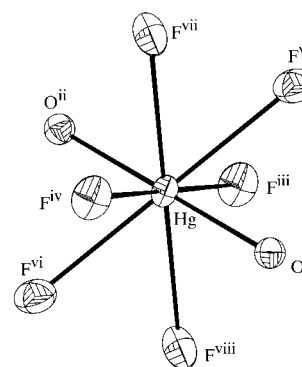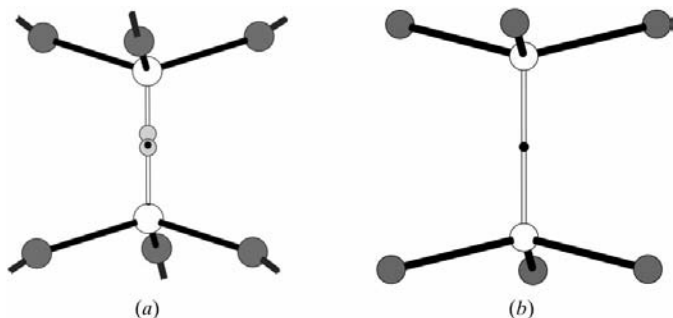

Figure 2
A plot of the [HgO$_2$F$_6$] polyhedron, with displacement ellipsoids drawn at the 75% probability level [symmetry codes: (i) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (ii) $\frac{1}{3} + x, y - \frac{1}{3}, z - \frac{1}{3}$; (iii) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$; (iv) $\frac{1}{3} - x + y, -\frac{1}{3} - x, z - \frac{1}{3}$; (v) $-x, -y, -z$. (vi) $1 + x, y, z$; (vii) $-y, x - y, z$; (viii) $1 + y, y - x, -z$].

Figure 3
A diagram of the [Hg₃O] pyramids in (*a*) eglestonite (Mereiter *et al.*, 1992) and (*b*) Hg₃AlF₆O₂H. Hg atoms are dark grey, O atoms are white and H atoms are light grey. The inversion centre is denoted by a small black point. The broken bonds in (*a*) correspond to the connection to neighbouring Hg atoms of the Hg_2^{2+} dumb-bell.

at the apices of trigonal [OHg₃] pyramids [Hg—O—Hg = 115.55 (8)°].

Tests on the occupancy factors of Hg, Al, F and O did not indicate the presence of vacancies. Taking into account the fact that, if only the atoms given in the chemical formula were present, the charge sum would be negative, and that the remaining electron-density map showed no significant peaks corresponding to other atoms, we are led to the conclusion that H atoms must be present in the structure. However, it was not possible to determine the position(s) of the H atom(s) unambiguously by difference Fourier syntheses of the present X-ray data.

Even though the interpolyhedral F···O distance is within the range for the formation of a weak hydrogen bond, it is rather a normal distance between non-bonded O and F atoms. On the other hand, the O···O distance is too short to be an ordinary interpolyhedral contact. Moreover, this is an ideal length for strong hydrogen bonding. Since this distance is too long for the formation of a symmetrical O—H···O bond, with O—H = 1.28 Å and the H atom situated at the inversion centre (position 3*a*, with site symmetry $\bar{3}m$ and full occupancy), it is most likely that the H atom lies along the O···O line on position 6*c* (00*z*) with half occupancy, to form an asymmetrical O—H···O hydrogen bond with a linear O—H···O angle.

The bond-valence sums for the atoms, calculated using the bond-valence parameters provided by Brese & O'Keefe (1991), are 1.88 for Hg, 2.98 for Al, 1.87 for O and 0.814 for F. This does not strongly support the suggested model, but it has to be considered that the Hg—F parameters are not well tested and therefore the valences of the Hg—F bonds are unreliable.

Another common method to derive the position(s) of the H atom(s) within the structure is the application of IR spectroscopy. A very useful correlation of O—H stretching frequencies and O—H···O hydrogen-bond length has recently been published (Libowitzky, 1999), and therefore conventional IR measurements on a powder specimen using the KBr and KCl technique, and single-crystal measurements

of selected crystals, were performed. However, although they were expected to give useful results, these IR experiments were not evaluable because of the reaction of the powder with the matrix and the small size of the measured single crystals.

A comparison between Hg₃AlF₆O₂H and the mineral eglestonite, (Hg₂)₃Cl₃O₂H (Mereiter *et al.*, 1992), shows a similar situation concerning the hydrogen bonding. In the latter mineral, short O···O distances [2.494 (11) Å] and the location of the O atoms at the apices of trigonal [OHg₃] pyramids [Hg—O—Hg = 113.7 (1)°; Fig. 3] are also observed. The H-atom position in eglestonite was determined by means of neutron measurements performed on a microcrystalline sample and, by considering half occupancy for the H atom, it was refined close to the inversion centre, thus resulting in asymmetric hydrogen bonding with a linear O—H···O angle.

Further studies to determine the H-atom position(s) of the title compound experimentally, preferably by means of neutron scattering, need to be carried out in the future.

Experimental

Single crystals of Hg₃AlF₆O₂H were prepared under hydrothermal conditions. Stoichiometric amounts of Hg(NO₃)₂·2H₂O (Merck, p.A.) and AlF₃ (Merck, Patinal; milled before application), with an Hg:Al molar ratio of 1:1, were placed in a 5 ml Teflon inlay which was two-thirds filled with 32wt% HF solution (Merck, p.A.). The inlay was then closed, placed in a steel autoclave and heated in a laboratory furnace at 543 K for 10 d. Besides small light-yellow plates of Hg₃AlF₆O₂H with mostly hexagonal habit, unreacted AlF₃ and yellow hexagonal columns of an as yet unknown compound were obtained. The latter could be indexed with hexagonal lattice parameters of $a = 6.9705\ (4)$ Å and $c = 7.2809\ (4)$ Å. Thermal analysis of selected crystals of this compound and subsequent X-ray powder diffraction analysis of the remaining solid provided an Hg:Al molar ratio of approximately 3:1, but due to the poor quality of the single crystals, a structure solution has not so far been possible. By working in more dilute HF solutions (24wt%), mainly colourless tetragonal columns of Hg₂AlF₅(H₂O)₂ (Fourquet *et al.*, 1981) and unreacted AlF₃ were observed.

Crystal data

Hg₃AlF₆O₂H	Mo $K\alpha$ radiation
$M_r = 775.76$	Cell parameters from 1547
Trigonal, $R\bar{3}m$	reflections
$a = 7.2621\ (6)$ Å	$\theta = 3.8–29.8°$
$c = 10.4415\ (9)$ Å	$\mu = 72.47$ mm^{-1}
$V = 476.89\ (7)$ Å^3	$T = 293\ (2)$ K
$Z = 3$	Plate, light yellow
$D_x = 8.104$ Mg m^{-3}	$0.14 \times 0.08 \times 0.08$ mm

Table 1
Selected interatomic distances (Å).

Hg—O^i	2.1461 (10)	Al—F	1.804 (2)
Hg—F^{ii}	2.526 (3)	F—O^{iv}	2.772 (3)
Hg—F^{iii}	2.6703 (19)	O—O^v	2.562 (9)

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

Data collection

Siemens SMART CCD area-detector diffractometer	192 independent reflections
	192 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.048$
Absorption correction: numerical using indexed crystal faces (*SHELXTL*; Siemens, 1995)	$\theta_{max} = 30°$
	$h = -9 \rightarrow 10$
	$k = -9 \rightarrow 10$
$T_{min} = 0.034$, $T_{max} = 0.496$	$l = -14 \rightarrow 14$
1744 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0134P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.014$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.027$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.19$	$\Delta\rho_{max} = 1.71$ e Å^{-3}
192 reflections	$\Delta\rho_{min} = -1.10$ e Å^{-3}
17 parameters	Extinction correction: *SHELXL*97
H-atom parameters are not defined	Extinction coefficient: 0.00150 (12)

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1998); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1353). Services for accessing these data are described at the back of the journal.

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