

The Structure of Mercury Hexafluoroantimonate $\text{Hg}_{3-\delta}\text{SbF}_6$

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(Received 29 December 1981; accepted 18 March 1982)

Abstract

$\text{Hg}_{3-\delta}\text{SbF}_6$ [$\delta = 0.10$ (2) at 293 K], $M_r = 817$ (4), tetragonal, space group $I4_1/amd$, $a = 7.711$ (2), $c = 12.641$ (2) Å, $V_{\text{cell}} = 751.6$ (5) Å³, $Z = 4$, $D_x = 7.22$ (4) Mg m⁻³. The structure was refined from 248 unique diffractometer-measured reflections to a final $R_w = 0.036$. The compound is isostructural with $\text{Hg}_{3-\delta}\text{AsF}_6$ with Sb–F = 1.86 Å (averaged) and Hg–Hg = 2.66 (2) Å. The F atoms show apparent anisotropic thermal motions which probably reflect disorder induced by interaction with the neighbouring Hg chains. The Hg chains show lateral displacements of 0.036 (5) Å that are related to the requirements of packing.

Introduction

Although the structure and the electrical properties of the infinite linear-chain compound $\text{Hg}_{3-\delta}\text{AsF}_6$ have been studied extensively over the past few years (see Brown, Datars & Gillespie, 1982), very few studies have been published on the isostructural compound $\text{Hg}_{3-\delta}\text{SbF}_6$. The structure of $\text{Hg}_{3-\delta}\text{AsF}_6$ was first determined by Brown, Cutforth, Davies, Gillespie, Ireland & Vekris (1974) using X-ray diffraction and refined by Schultz, Williams, Miro, MacDiarmid & Heeger (1978) using neutron diffraction. They observed two distinct features in the precession photographs. One is a well defined lattice of Bragg reflections which shows the symmetry and absences characteristic of the space group $I4_1/amd$. The other is a series of sheets of diffuse scattering with a spacing which is incommensurate with the spacing of Bragg peaks. The sheets are arranged perpendicular to the a^* and b^* axes and can be seen as lines in the $hk0$ precession photographs. (The $hk0$ precession photograph of $\text{Hg}_{3-\delta}\text{SbF}_6$ is shown in Fig. 1.) From this unusual diffraction pattern Brown *et al.* (1974) concluded that the structure contains two incommensurate components, a host lattice of AsF_6^- ions in space group $I4_1/amd$ and two sets of parallel Hg chains running along the non-intersecting tunnels formed by the host lattice.

For the present work, crystals of $\text{Hg}_{3-\delta}\text{SbF}_6$ were supplied by Dr R. J. Gillespie of this University. The precession photographs indicate that $\text{Hg}_{3-\delta}\text{SbF}_6$ is isostructural with $\text{Hg}_{3-\delta}\text{AsF}_6$. The spacing between the sheets measured from the photographs corresponds to an Hg–Hg distance of 2.66 (2) Å.

Details of the measurements of the X-ray Bragg reflections of the SbF_6^- lattice, which also contain contributions from the Hg chains, and of the structure refinement are given in Table 1. The structure was determined using data set (I). Data set (II) was used only to determine the absorption correction which was calculated as follows. A two-circle optical goniometer was used to measure the orientations and the distances (from an arbitrarily chosen point inside the crystal) of the faces of the crystal used for intensity measurements. Because of the low magnifying power of the microscope attached to the goniometer the distance measurements were not very accurate. The distances were therefore varied to minimize the internal agree-

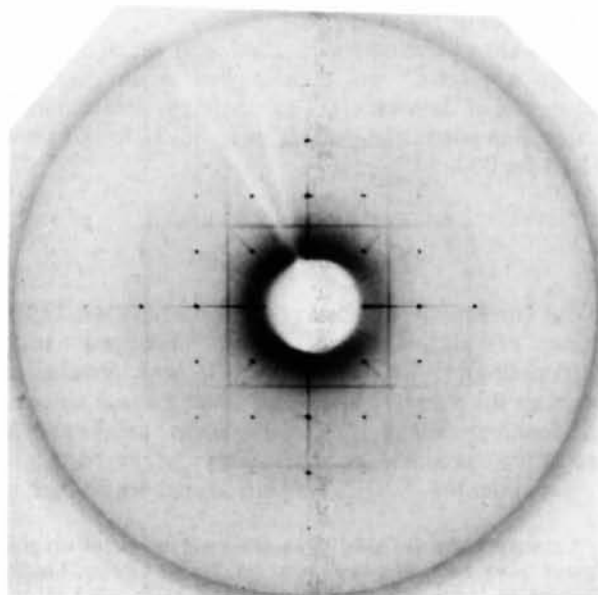


Fig. 1. The $hk0$ precession photograph of $\text{Hg}_{3-\delta}\text{SbF}_6$ showing the Bragg reflections from the lattice and the sheets of scattering from the Hg chains.

Table 1. *Summary of structure determination*

Diffractionmeter: Nicolet P21.
Graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$.
Lattice constants determined from 15 well centred reflections having $10^\circ < 2\theta < 29^\circ$.
Linear absorption coefficient $\mu = 64 \text{ mm}^{-1}$.

Data set (I)

Maximum 2θ : 55°
 $0 \leq h, k \leq 10, -16 \leq l \leq 16$
Standard reflections: 015 and 024
Number of reflections measured: 993
Number of unique reflections: 248
Number of unobserved reflections measured ($I < 3\sigma_I$): 571

Data set (II)

$-3 \leq h, k, l \leq 3$
Standard reflections: 015 and 024
Number of reflections measured: 144
Number of unique reflections: 14

Final $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.036$ (all reflections)
Weighting scheme: $w = [\sigma^2(\text{counting}) + (0.0135F_o)^2]^{-1}$
Standard deviation of an observation of unit weight: 1.36
Maximum shift/error in final cycle: 0.12
Average shift/error in final cycle: 0.03
Secondary-extinction correction (Larson, 1967): $g = 1.1(2) \times 10^{-7}$
Number of variables refined: 21
Scattering factors: neutral atoms from *International Tables for X-ray Crystallography* (1974)
Maximum residual electron density: $\pm 1.9 \text{ e \AA}^{-3}$; positive peaks at F(1)

ment factor between the symmetry-related reflections of data set (II) which had been specially measured to include all the equivalent reflections for a selected number of medium to strong reflections. The best correction obtained reduced the internal agreement factor from 0.096 to 0.037.

This absorption correction, details of which are given in the Appendix,* was then applied to the measured intensities of data set (I). The maximum and minimum absorption correction factors were 30.31 for 011 and 11.67 for 097.

Structure refinement

After correction for absorption the equivalent reflections of data set (I) were averaged using $[\sigma(\text{counting})]^{-2}$ as the weights. It was possible to estimate the standard error σ_A of each average since up to four equivalent reflections were measured. A weighting scheme of the form $w = \sigma_{\text{total}}^{-2} = [\sigma^2(\text{counting}) + k^2 F_o^2]^{-1}$ was introduced adjusting k so

* The Appendix and a list of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36843 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic positional coordinates and thermal parameters ($\text{\AA}^2 \times 10^3$)*

The positional coordinates are based on the centrosymmetric setting of space group $I4_1/amd$. Thermal parameters are those given in the expressions $\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$ and $\exp(-2\pi^2 \sum U_{ij} \times h_i h_j a_i^* a_j^*)$.

		<i>x</i>	<i>y</i>	<i>z</i>	Occupation number	<i>U</i>
Hg(1)†	16(<i>h</i>)	0	$\frac{1}{2}$	0.0000 (11)	0.182	51 (1)
Hg(2)†	16(<i>h</i>)	0	$\frac{1}{2}$	-0.0002 (8)	0.182	50 (1)
Hg(3)†	16(<i>h</i>)	0	$\frac{1}{2}$	0.0013 (7)	0.182	48 (1)
Hg(4)†	16(<i>h</i>)	0	$\frac{1}{2}$	0.0028 (4)	0.182	47 (1)
Sb	4(<i>b</i>)	0	$\frac{1}{2}$	$\frac{1}{2}$	1.0	‡
F(1)	8(<i>e</i>)	0	$\frac{1}{2}$	0.2295 (10)	1.0	‡
F(2)	16(<i>g</i>)	0.6723 (17)	$x + \frac{1}{4}$	$\frac{1}{2}$	1.0	‡

† Partial Hg atoms are used to simulate the Hg chains.

‡ Anisotropic thermal parameters:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	32 (2)	U_{11}	20 (1)	0	0	0
F(1)	57 (12)	149 (19)	18 (7)	0	0	0
F(2)	42 (8)	U_{11}	85 (8)	-13 (5)	3 (9)	$-U_{13}$

Table 3. *Bond lengths (\AA) in $\text{Hg}_{3-\delta}\text{AsF}_6$ (Schultz *et al.*, 1978) and $\text{Hg}_{3-\delta}\text{SbF}_6$*

	$\text{Hg}_{3-\delta}\text{AsF}_6$	$\text{Hg}_{3-\delta}\text{SbF}_6$
As,Sb-F(1)	1.702 (2)	1.84 (1) \times 2
As,Sb-F(2)	1.720 (2)	1.88 (1) \times 4
Hg-Hg (inrachain)	2.64 (2)	2.66 (2)
Chain-chain*	3.24 (2)	3.23 (1)
F(1)-chain†	2.87 (1)	2.86 (1) \times 1
F(2)-chain†	2.981 (5)	2.98 (1) \times 2

* The closest contact distance between the two neighbouring perpendicular chains which is greater than $c/4$ by $2u_o$.

† Shortest distance to the neighbouring chain.

that σ_{total} was equal on average to σ_A . The value of k obtained in this way was 0.0135.

The parameters of the initial model were those of $\text{Hg}_{3-\delta}\text{AsF}_6$. The chains were represented by a string of partial Hg atoms placed about 0.5 \AA apart.

The final atomic positional and thermal parameters are shown in Table 2. Selected interatomic distances are given in Table 3.

Discussion

$\text{Hg}_{3-\delta}\text{SbF}_6$ is isostructural with $\text{Hg}_{3-\delta}\text{AsF}_6$ (Brown *et al.*, 1974; Schultz *et al.*, 1978). The SbF_6 octahedra are slightly flattened with two axial Sb-F(1) distances of 1.84 (1) \AA and four equatorial Sb-F(2) distances of 1.88 (1) \AA . Brown *et al.* (1982) have pointed out that the distortion can be attributed to the different cationic environments of the F atoms; the axial F(1) atoms have a single neighbouring Hg chain at a distance of 2.86 \AA while the equatorial F(2) atoms have two such chains at 2.98 \AA .

The influence of the Hg chains on the SbF_6^- ions can be seen in the anisotropic temperature factors (Table 2). The r.m.s. displacements of Sb and F(1) are equal in the z direction (0.14 Å) but very different in the other two directions. In particular, the r.m.s. displacement of F(1) parallel to the neighbouring Hg chain is very large (0.39 Å) (see Fig. 2). This is consistent with a static disorder of the F(1) atom produced by the different positions of the Hg atoms in different unit cells. Since the Hg–Hg distance is incommensurate with the SbF_6^- lattice, every F(1) atom will have a different arrangement of Hg neighbours. If the distribution of Hg atoms is symmetric about the Sb–F(1) bond, then F(1) will lie at its apparent equilibrium position. But, in general, the distribution will not be symmetric and, as a result, F(1) will be slightly displaced from this position. We therefore expect to find a large value of U_{22} for F(1).

If the SbF_6^- ion is rigid the static disorder of F(1) will result in a rotational disorder of the ion which will appear as an apparent thermal libration (see Fig. 2). The temperature factors indicate that there are two symmetry-related libration centres for this disorder, one 0.75 Å above the Sb atom for libration about an axis parallel to **a** and the other 0.75 Å below the Sb atom for libration about an axis parallel to **b**. In both cases, the r.m.s. angle of apparent libration is about 8°. In addition, the temperature factors indicate that the ion undergoes isotropic translational vibrations with an amplitude of 0.14 Å and a libration around the F(1)–Sb–F(1) axis of 6°. These three effects account for the observed temperature factors within experimental error. Using neutron diffraction Schultz *et al.* (1978) observed similar features in the temperature factors of $\text{Hg}_{3-\delta}\text{AsF}_6$.

The Hg chains show undulation in the z direction with the period of the host lattice. The maximum

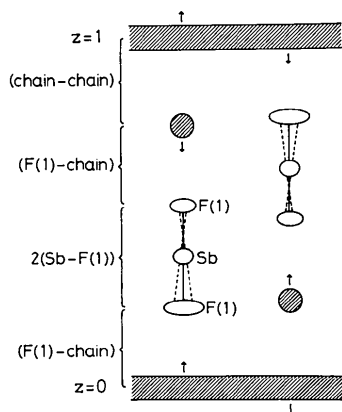


Fig. 2. A section of $\text{Hg}_{3-\delta}\text{SbF}_6$ in the plane $x = 0$. The shaded sections represent Hg chains seen end on (circles) or side on (bars). The displacement of the Hg chains in the z direction is too small to show on this scale but occurs in the directions of the arrows.

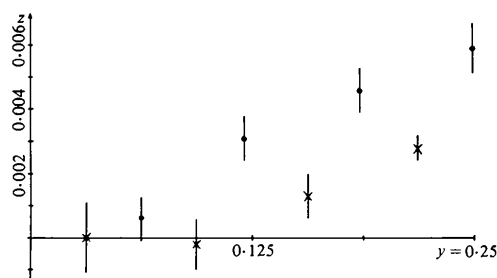


Fig. 3. Displacement of the Hg chains in the z direction as a function of y . Circles: $\text{Hg}_{3-\delta}\text{AsF}_6$, crosses: $\text{Hg}_{3-\delta}\text{SbF}_6$.

displacement, u_o , of the chains from the linear position is 0.036 (5) Å and it occurs at the crossings with the neighbouring perpendicular chains. Because of the undulation, the closest contact distance between the perpendicular chains is 3.23 (1) Å, rather than $c/4 = 3.16$ Å. Schultz *et al.* (1978) have observed similar undulation of the chains in $\text{Hg}_{3-\delta}\text{AsF}_6$ with a maximum displacement about twice that observed in $\text{Hg}_{3-\delta}\text{SbF}_6$. Fig. 3 shows that the undulations of the Hg chains are sigmoidal in shape with a straight section between the crossing points.

The differences in u_o in the two compounds can be understood by considering the bonding along the c axis. Fig. 2 shows all the atoms and chains contained in the z direction. It can be seen that the c -axis length is given by

$$c = 2[\text{F(1)-chain}] + 2[\text{Sb-F(1)}] + (\text{chain-chain}), \quad (1)$$

where

$$(\text{chain-chain}) = \frac{c}{4} + 2u_o. \quad (2)$$

Table 4. Predicted [and observed] parameters for Hg chain compounds

	$\text{Hg}_{3-\delta}\text{PF}_6$	$\text{Hg}_{3-\delta}\text{AsF}_6$	$\text{Hg}_{3-\delta}\text{SbF}_6$	$\text{Hg}_{3-\delta}\text{BiF}_6$
a (Å)	7.41	7.53	7.72	7.85
c (Å)	12.09	[7.540 (4)]	[7.711 (2)]	12.85
u_o^* (Å)	0.104	[12.393 (7)]	[12.641 (2)]	0.009
δ	0.21	[0.07 (1)]	[0.036 (5)]	0.05
		[0.17	[0.10	
		[0.16 (2)]	[0.10 (2)]	

Assuming chain-chain = 3.23 Å, Hg–Hg (intrachain) = 2.66 Å

F(1)-chain	2.86 Å	F(2)-chain	2.98 Å
P–F(1)	1.57	P–F(2)	1.61
As–F(1)	1.70	As–F(2)	1.72
Sb–F(1)	1.84	Sb–F(2)	1.88
Bi–F(1)	1.95	Bi–F(2)	2.00

* The maximum displacement of the chain from the straight configuration.

Similarly the a -axis length is given by

$$a = 2\{[\text{F}(2)\text{-chain}]^2 - (c/8)^2\}^{1/2} + \sqrt{2}[\text{Sb-F}(2)] \quad (3)$$

and from a the value of δ can be calculated.

Since the Hg–Hg intrachain distance, chain–chain distance and F–chain distances are the same in both $\text{Hg}_{3-\delta}\text{AsF}_6$ and $\text{Hg}_{3-\delta}\text{SbF}_6$ (Table 3), the values of a , c , u_0 and δ should depend only on the size of the anion. Table 4 shows that good predictions of these quantities can be made on this assumption. Prediction can also be made for all the positional coordinates as well as for the structural parameters expected for the hypothetical $\text{Hg}_{3-\delta}\text{PF}_6$ and $\text{Hg}_{3-\delta}\text{BiF}_6$ compounds. The small value of δ expected for the latter suggests that it might exist in a stoichiometric form.

We wish to thank Dr Gillespie for supplying the crystals and the Natural Sciences and Engineering

Research Council of Canada for an operating grant. One of us (ZT) would like to thank McMaster University for a scholarship.

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Acta Cryst. (1982). **B38**, 2324–2328

Single-Crystal Neutron Diffraction Study of Ammonium Nitrate Phase III

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(Received 16 November 1981; accepted 19 March 1982)

Abstract

The crystal structure of ammonium nitrate phase III has been studied at room temperature by neutron diffraction using a single crystal containing 5% KNO_3 in solid-solution form. The space group is $Pnma$, with $a = 7.6772$ (4), $b = 5.8208$ (4), $c = 7.1396$ (5) Å, $Z = 4$. The final residual after full-matrix least-squares refinement was $R = 0.042$ for 348 observed reflections. The ammonium ions are thermally disordered into two orientations, displaced by an angle of approximately 42° about an axis parallel to the c axis.

Introduction

Ammonium nitrate (AN), NH_4NO_3 , crystallizes in five different polymorphic forms, phase I, II, III, IV, V with transition temperatures of 398, 357, 305, and 255 K respectively. The crystal structures of phase IV (Choi,

Mapes & Prince, 1972), phase II (Lucas, Ahtee & Hewat, 1979) and phase I (Ahtee, Kurki-Suonio, Lucas & Hewat, 1979) have been completely determined by neutron diffraction. The structure of phase III has also been determined for the non-hydrogen atoms by three independent studies: an X-ray single-crystal study by Holden & Dickinson (1975); a neutron powder diffraction study by Choi, Prask & Prince (1980); and a neutron powder diffraction study (ND_4NO_3) by Lucas, Ahtee & Hewat (1980). However, the orientation of the ammonium group was not clearly determined. The orientation of the ammonium group as reported by Lucas *et al.* (1980) has one of the 4 axes of the ammonium ion parallel to the unit-cell a axis, but that reported by Choi *et al.* (1980) shows the $\bar{4}$ axis parallel to the c axis. This study is aimed at clarifying the disputed orientation of the ammonium group by using the single-crystal neutron diffraction method. Since the crystal structures of AN, in all solid phases except phase I, contain hydrogen bonds, the orientation of the NH_4 group is particularly important for understanding AN phase transitions.

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