Caesium Pentafluorohydroxoantimonate

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Abstract. $Cs[SbF_5OH]$, rhombohedral, $R3$ (hexagonally indexed), $a = 7.94$ (1), $c = 8.28$ (1) Å, $Z = 3$, $D_c = 4.04$, $D_m = 3.96$ Mg m^{-3}, $M_r = 367$, $V = 452$ Å^3. The compound was prepared from caesium hexafluoroantimonate by hydrolysis. As a result of the space-group symmetry the OH group was indistinguishable from the F atoms.

Introduction. Small colourless needles were recrystallized from methanol and a crystal $0.08 \times 0.10 \times 0.40$ mm was chosen for the data collection. 383 reflections were collected on the Philips PW 1100 four-circle diffractometer at the NPRL, CSIR, with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) for $3 \leq \theta \leq 31°$ [ω–2θ scan, scan width $0.9°$ (θ), scan speed $0.03°$ (θ) s^{-1}]. 55 reflections were considered to be unobserved with $I < 1.65\sigma$. The intensities were corrected for background, Lorentz and polarization effects but not for extinction or absorption ($\mu = 9.88$ mm^{-1}, $\mu R = 0.49$). The structure was solved by Patterson and Fourier methods. All computations were carried out with the XRAY 76 system (Stewart, 1976). Full-matrix least-squares refinement of the positional and anisotropic thermal parameters of the Cs, Sb and two F atoms led to a final R of 0.051, with unit weights for the 328 observed reflections. Scattering factors are those of Cromer & Mann (1968). The final positional

parameters are given in Table 1. Table 2 lists the interatomic distances and angles.†

Discussion. The crystallographic study was undertaken to investigate the effect on the space group (and therefore on the vibration spectra) of replacing an F atom in $Cs[SbF_6]$ by an OH group. The preparation of $Cs[SbF_5OH]$ from $Cs[SbF_6]$ has been described by Kolditz & Rehak (1959). The antimony was determined using the method described by Mazeika & Neumann (1966) in which Sb^V oxidizes KI in about 3 mol l^{-1} hydrochloric acid and the iodine liberated is titrated with standard thiosulphate solution. Boric acid is added to eliminate complications caused by the fluoride ion. The fluorine was determined by the methods described by Palmer (1970) and Vogel (1961) in which the fluoride is precipitated as PbClF. The chlorine was determined by Volhard's method from which the fluorine content can be calculated. An Sb:F value of 1:5.07 was found.

* This investigation was part of the work for a PhD thesis in the Department of Chemistry of the University of South Africa.

Table 1. *Positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
Sb	0	0	0
Cs	0	0	4999 (8)
F(1)	795 (38)	2099 (45)	1514 (31)
F(2)	2162 (36)	1616 (33)	−1187 (35)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Sb–F(1)	1.922 (3)	F(1)–F(2)	2.60 (1)
Sb–F(2)	1.832 (2)	F(2)–F(1)*	2.80 (1)
Cs–F(1)	3.23 (1)	F(1)–F(2)*	3.37 (1)
Cs–F(1)*	3.15 (1)	F(1)–F(1)*	2.52 (1)
Cs–F(2)*	3.15 (1)	F(2)–F(2)*	2.68 (1)
F(2)–Sb–F(1)	87.5 (1)	F(2)–Sb–F(1)*	169.6 (1)
F(1)–Sb–F(1)*	82.1 (1)	F(2)*–Sb–F(1)	96.3 (1)
F(2)–Sb–F(2)*	93.9 (1)		

* Related by symmetry operations allowed by the space group.

The molecule consists of a discrete cation and anion and the shortest distance between an F and the Cs atom is 3·15 (1) Å. The Sb atom occupies the special position (0,0,0) and is octahedrally coordinated by six atoms, five of which must be F atoms and the other an O atom according to analytical results and infrared spectroscopy. However, since the Sb atom is situated on a threefold rotation axis, the presence of one bonded atom generates another two atoms at equivalent positions and the OH group can therefore not be uniquely determined. By specifying the positions of two independent F atoms, the six atoms surrounding Sb are obtained, distinguishable only as two groups of three atoms each. The Sb—F lengths of 1·83 (1) and 1·92 (1) Å differ by 0·09 Å. This seems to imply that the O atom is not randomly distributed between the two groups, as Sb—F and Sb—O (as in Sb—O—H) distances are reported to be 1·84 (Kruger, Pistorius & Heyns, 1976) and 2·05 Å (Beauchamp, Bennett & Cotton, 1969) respectively. Therefore it appears likely that one group consists of three F atoms (giving an Sb—F length of 1·83 Å) and the other of two F atoms and one O atom (giving an average bond length of 1·92 Å). It is interesting to note that (1·84 + 1·84 + 2·05)/3 = 1·91 Å. However, the values of the bonding parameters can be affected by absorption, and since these were not included in the data reduction it would be unwise to draw definite conclusions about the position of the O atom or the significance of the difference between the bond lengths. Application of absorption corrections was considered unnecessary because the OH group could not be structurally characterized among the five neighbouring F atoms as a result of the symmetry considerations. Attempts to locate the H atom would

already have been difficult in the presence of the heavy atoms and become meaningless under the present circumstances.

The choice of the space group $R3$ rather than $R\bar{3}$ was initially based on the assumption that a threefold equivalence of F atoms would be a better description of the real situation of five F atoms and one O atom than a sixfold equivalence of F atoms would be. In order to confirm this choice the refinement was repeated in $R\bar{3}$. The Hamilton (1965) test was then applied to the hypothesis that the space group is $R\bar{3}$ rather than $R3$. In Table 3 the pertinent parameters are given. For 328 observed reflections the number of degrees of freedom is 304 and the dimension of the hypothesis is 10. From Hamilton's table $R_{10,304,0·005} = 1·042$ but

$$\frac{R_2}{R_1} = \frac{0·057}{0·051} = 1·1177 > R_{10,304,0·005}.$$

Therefore the hypothesis that the space group is $R\bar{3}$ rather than $R3$ can be rejected at the 0·005 level.

Table 4 summarizes the structures of a few fluoroantimonates and hydroxofluoroantimonates. Cs[SbF$_4$(OH)$_2$] is presently under investigation and its symmetry appears to be orthorhombic. Because little work has been done on the hydroxo compounds, no definite pattern emerges from the tabulated data about the effect of substitution of F by OH on the space group and dimensions. A change to lower space-group symmetry is indicated for the addition of OH groups, in keeping with the symmetry changes of the anion.

The presence of Sb—F, Sb—O and O—H bonds was confirmed by infrared spectroscopy (Table 5). At low temperatures (83 K) no phase transition was observed in the infrared spectrum. A low-temperature study

Table 3. *Pertinent parameters for the Hamilton test*

Space group	Parameters	R
R3	24	0·051 (R_1)
R̄3	14	0·057 (R_2)

Table 5. *Infrared spectra of* Cs[SbF$_5$OH]

Sb—O	56·0 mm^{-1}
Sb—F	63·0
O—H	323·0

Table 4. *Structures of a few fluoroantimonates and hydroxofluoroantimonantes*

Compound	Parameters		Symmetry and possible space groups	References
LiSbF$_6$	$a = 5·473$ Å	$\alpha = 58·09°$	Rhombohedral	i
NaSbF$_6$	$a = 8·18$		Cubic	i
NaSbF$_4$(OH)$_2$	$a = 5·24$	$c = 10·00$ Å	Hexagonal ($P\bar{3}1c$)	ii 2-0444
AgSbF$_6$	$a = 4·96$	$c = 9·61$	Tetragonal	i
TlSbF$_6$	$a = 5·16$	$\alpha = 96·0°$	Rhombohedral	i
RbSbF$_6$	$a = 5·11$	$\alpha = 96·5$	Rhombohedral	i
KSbF$_6$	$a = 5·16$	$c = 10·07$ Å	Tetragonal ($P\bar{4}2m$)	iii
CsSbF$_6$	$a = 7·90$	$c = 8·25$	Rhombohedral ($R3m$)	ii 15-808
CsSbF$_5$OH	$a = 7·94$	$c = 8·28$	Rhombohedral ($R3$)	Present study

References: (i) Kemmitt, Russell & Sharp (1963). (ii) *Index to Powder Diffraction Files* (1971). (iii) Kruger, Pistorius & Heyns (1976).

would thus reveal no more about the position or the bonding of the OH group. Comparison with the data for Cs[SbF$_6$] (*Index to Powder Diffraction Files*, 1971) shows only a slight change in the cell dimensions, which is not unexpected since F and O atoms are of comparable size. The similarity in space groups, however, is surprising and does not account for the presence of the OH group as the infrared spectra do.

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Structure of Iron Selenide 3C-Fe₇Se₈

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Abstract. 3C-Fe$_7$Se$_8$ (a high-temperature form) trigonal, $P3_121$, $a = 7\cdot2613$ (9), $c = 17\cdot675$ (5) Å, $Z = 3$, $D_x = 6\cdot31$ Mg m^{-3}. The structure of synthetic 3C-Fe$_7$Se$_8$ has been refined on the assumption of twinning of domains with $P3_121$ and $P3_221$ by rotation about the c axis. The weighted R factor converged to 0·036 for 1550 intensities generated from the 527 observed. The average Fe—Se bond length is 2·57 Å. 3C-Fe$_7$Se$_8$ is isostructural with 3C-Fe$_7$S$_8$.

Introduction. Single crystals of Fe$_{1-x}$Se have been studied systematically by Okazaki & Hirakawa (1956) and Okazaki (1961). These authors proposed a defect NiAs-type structure of 3C-Fe$_7$Se$_8$ based on the inspection of the X-ray photographs of single crystals. Here 3C refers to the number of times the NiAs-type subcell repeats along the c axis. The present study has been undertaken using precise intensity data collected by a four-circle diffractometer in order to elucidate atomic shifts and correlations in the structure of 3C-Fe$_7$Se$_8$.

Small chips were taken from a large synthetic crystal, heated for 12 h at 573 K in evacuated silica-glass capsules, quenched in ice water and then crushed. Because the Laue symmetry is 6/mmm and 00*l* reflections appear only when $l = 3n$, the space group is apparently $P6_222$ (or $P6_422$). A small specimen was

chosen for intensity measurements; it had an almost triangular-prismatic form and was about 0·1 mm in height and on edge. 1054 intensities in two dependent sectors were collected with the ω–2θ scan technique ($2\theta_{max} = 60°$) and Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å), monochromatized by pyrolytic graphite. Weak intensities with $F_o < 2\sigma(F_o)$ were measured three times. After averaging the equivalent reflections the data set contained 527 independent reflections of which 113 had zero intensity. A spherical absorption correction ($\mu r = 2\cdot1$) was made on the assumption that the specimen crystal was spherical.

The observed symmetry of 6/mmm is inconsistent with the possible ordering of vacancies in the defect NiAs-type superstructure for the 3C type which gives space group $P3_121$ (or $P3_221$). It has been assumed that the observed symmetry arises from the twinning of small domains, with point symmetry 32, related by 180° rotation about the c axis. This would give apparent symmetry 622. Since the anomalous-dispersion term for Se is large ($f'' = 2\cdot223$), the observed symmetry 6/mmm [in which $I(hkl) = I(\bar{h}\bar{k}\bar{l})$] has been attributed to the existence of two enantiomorphs ($P3_121$ and $P3_221$) in the specimen crystal. This is equivalent to reflection across (100) which transforms symmetry 622 to 6/mmm. Accordingly, the