π molecular orbitals, these are believed to be less effective in establishing a magnetic exchange interaction.

The intramolecular bond lengths and angles correspond well with the results of previous structural studies of compounds containing the TTF^+ (Kistenmacher, Phillips & Cowan, 1974) and $MS_4C_4(CF_3)_4^-$ units (Schmitt, Wing & Maki, 1969) and are generally consistent with the conclusion that complete one-electron charge transfer has occurred in this compound.

References

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
DAVISON, A., EDELSTEIN, N., HOLM, R. H. & MAKI, A. H. (1964). *Inorg. Chem.* **3**, 814–823.
JACOBS, I. S., INTERRANTE, L. V. & HART, H. R. JR (1975). *Magnetism and Magnetic Materials* – 1974, AIP Conf. Proc. No. 24, pp. 355–356, American Institute of Physics, New York.
KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* **B30**, 763–768.
SCHMITT, R. D., WING, R. M. & MAKI, A. H. (1969). *J. Amer. Chem. Soc.* **91**, 4394–4401.

Potassium Hexafluoroantimonate (I)

BY G. J. KRUGER AND C. W. F. T. PISTORIUS*

National Physical Research Laboratory, CSIR, Pretoria, South Africa

AND A. M. HEYNS†

Department of Chemistry, University of South Africa, Pretoria 0001, South Africa

Abstract. $KSbF_6$ (I), tetragonal, $P\bar{4}2m$, $a = 5 \cdot 16$ (1), $c = 10 \cdot 07$ (2) Å, $V = 267 \cdot 86$ Å^3, $Z = 2$, $D_c = 3 \cdot 407$ g cm^{-3}. In $KSbF_6$ (I), which is stable above $\sim 16°C$, the Sb is surrounded by six F atoms in a slightly distorted octahedral configuration. The average Sb–F distance is 1·844 Å and the mean deviation of the F–Sb–F bond angles from the ideal octahedral values is 3·3°. The F–F distances in the coordination octahedra vary between 2·544 and 2·736 Å, with a mean of 2·605 Å. The K atoms are surrounded by eight F atoms, forming a slightly distorted dodecahedron, at distances between 2·618 and 3·204 Å. The coordination octahedra and dodecahedra are connected by sharing of corners.

Introduction. $KNbF_6$ and $KTaF_6$ have been reported to be cubic, space group $Ia3$ (Cox, 1956) or tetragonal, space group $P\bar{4}c2$ ($Z = 2$) (Bode & von Döhren, 1958). $KSbF_6$ has been reported to possess the same structure as cubic $KNbF_6$ and $KTaF_6$ (Bode & Voss, 1951). The structures and space groups of these compounds have not been established unambiguously since the reported structures are based primarily on the positions of the heavy atoms. It was also shown that the powder pattern of $KSbF_6$ (I), which is stable above $\sim 16°C$, can be fully indexed on the basis of a tetragonal unit cell, but the correct space group could

* Deceased 12 December, 1975.
† To whom correspondence should be addressed.

not be convincingly established (Heyns & Pistorius, 1976). In the same study, low-temperature $KSbF_6$ (II) was reported to be cubic.

Crystals of $KSbF_6$ (I) were obtained by recrystallization of a commercial sample of $KSbF_6$ from a methanol solution at 30°C. A multi-faceted, roughly spherical crystal with a diameter of 0·28 mm was used. Accurate cell parameters were determined and intensities collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The intensities were collected in the ω–2θ scan mode over a scan width of 1·5° in θ and at a scan rate of 0·05° s^{-1}. A unique set of 282 reflexions with a maximum $\sin\theta/\lambda$ of 0·7 was measured of which 53 were considered to be unobserved with $I < 1 \cdot 650\sigma(I)$. The background was counted for half the total scanning time on each side of a reflexion. Lorentz–polarization and absorption corrections for a spherical crystal were applied.

The apparent systematic absences: $0kl$ for $l = 2n + 1$ indicated space groups $P\bar{4}c2$, $P4cm$ and $P4_2/mcm$. Closer inspection of the $0kl$ reflexions revealed, however, that they are definitely not systematically absent when l is odd. Several $0kl$ and $00l$ reflexions, although very weak, were clearly discernible above background, especially when the scans were traced on a recorder. The possible space groups with Laue symmetry $4/mmm$ and no systematic absences are: $P4/mmm$, $P422$, $P4mm$, $P\bar{4}m2$ and $P\bar{4}2m$.

Crystal-packing considerations were used to deter-

mine the correct space group. The six F atoms in the $[SbF_6]^-$ ion are expected to be situated at the vertices of an octahedron at a distance of about 1·9 Å. The hkl reflexions with $l \neq 2n+1$ are systematically weak and the fact that $Z=2$ requires that the K and Sb atoms lie on the fourfold axes. In the first three space groups above, the presence of the fourfold rotation axes forces the octahedron to be placed with four corners in a plane perpendicular to (001). This would result in an impossibly short F···F distance of about 1·3 Å and so these space groups can be ruled out. The inversion tetrad in $P\bar{4}m2$ and $P\bar{4}2m$ allows the octahedron to be tilted so that only two corners are required to be in the same plane, perpendicular to (001), as the Sb. The mirror planes in $P\bar{4}m2$, however, force these two F atoms into the same short contact of about 1·3 Å. $P\bar{4}2m$ satisfies all the packing requirements and is thus indicated as correct.

The fact that the $0kl$ reflexions with l odd are extremely weak indicates that the structure of $KSbF_6$ is very close to that of $KNbF_6$ and $KTaF_6$ and therefore the trial structure chosen is as follows: $1K$: (b) $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; $1K$: (d) $\frac{1}{2},\frac{1}{2},0$; $2Sb$: (g) $0,0,z$; $3 \times 4F$: (n) x,x,z.
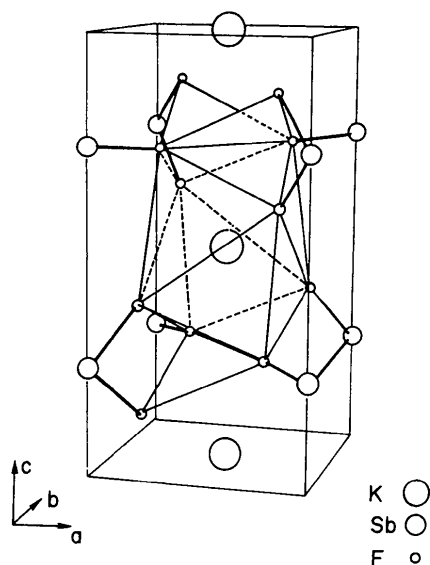

Fig. 1. Perspective view of the unit cell and contents of $KSbF_6$ showing the dodecahedral configuration of the F atoms surrounding the K atoms.

The structure was refined by full-matrix least squares with the X-RAY system (1972). In the final stages of refinement the thermal parameters of all the atoms were allowed to vary anisotropically and a variable isotropic extinction correction (Larson, 1967) was introduced. $R=\sum\Delta F/\sum F_o$ and $R_w=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$ converged to 0·035 and 0·043 respectively. The function minimized was $\sum w(\Delta F)^2$ with $1/\sigma_F^2$ weights.

The scattering factors for Sb^{5+}, K^+ and F^- were generated from the analytical expressions of Cromer & Mann (1968) and the corrections applied for anomalous dispersion were taken from Cromer & Liberman (1970). The final values of the atomic parameters are given in Table 1.‡ Interatomic distances and angles are listed in Table 2.

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

Sb——F(1)	1·841 (8)	F(2)–F(2)*	2·545 (7)
Sb——F(2)	1·841 (6)	F(2)–F(3)*	2·544 (11)
Sb——F(3)	1·849 (5)		
K(1)–F(1)	2·618 (7)	F(1)–Sb–F(2)	88·3 (3)
K(1)–F(3)	3·204 (7)	F(1)–Sb–F(3)	92·6 (4)
K(2)–F(2)	2·653 (6)	F(1)–Sb–F(1)*	96·0 (4)
K(2)–F(3)	2·991 (13)	F(1)–Sb–F(2)*	175·7 (3)
F(1)–F(2)	2·565 (13)	F(1)–Sb–F(3)*	92·6 (4)
F(1)–F(3)	2·669 (10)	F(2)–Sb–F(3)	87·2 (4)
F(1)–F(1)*	2·736 (7)	F(2)–Sb–F(2)*	87·4 (3)
F(1)–F(3)*	2·669 (12)	F(2)–Sb–F(3)*	87·2 (4)
F(2)–F(3)	2·544 (9)	F(3)–Sb–F(3)*	172·2 (6)

* Related by twofold rotation axis (symmetry code: $-x, -x, z$).

Discussion. The structure of $KSbF_6$ is illustrated by the perspective drawings of the unit cell and contents in Figs. 1 and 2 (Johnson, 1971). The Sb is surrounded by six F ions in a slightly distorted octahedral configuration. The average Sb–F distance is 1·844 Å and the mean deviation of the F–Sb–F bond angles from the ideal octahedral values is 3·3°. The F–F distances

Table 1. *Final atomic parameters* ($\times 10^4$) *for* $KSbF_6$

Thermal parameters are of the form $T=\exp[-2\pi^2(a^{*2}h^2U_{11}+\ldots+2b^*c^*klU_{23})]$.
Refinement was based on extinction parameter $g=5\cdot3 \times 10^{-4}$. Estimated standard deviations are in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	5000	5000	0	646 (28)	646†	542 (40)	0	0	0
K(2)	5000	5000	5000	231 (12)	231†	417 (25)	0	0	0
Sb	0	0	2504 (1)	350 (4)	350†	387 (5)	−75 (4)	0	0
F(1)	1876 (12)	1876†	1280 (10)	941 (50)	941†	746 (55)	−556 (76)	115 (34)	115†
F(2)	1745 (12)	1745†	3825 (7)	1128 (53)	1128†	399 (39)	−670 (73)	−109 (32)	−109†
F(3)	2529 (11)	−2529†	2630 (15)	608 (29)	608†	2202 (128)	128 (34)	−312 (67)	312†

† Parameters related by symmetry.

in the coordination octahedron vary between 2·544 and 2·736 Å with a mean of 2·605 Å.

Eight F atoms, forming a slightly distorted dodecahedron, surround the K atoms at distances between 2·618 and 3·204 Å. The F atoms lying at $z \sim \frac{1}{8}$ and $\frac{3}{8}$ are closer to K than those lying at $z \sim \frac{1}{4}$.

The coordination octahedra and dodecahedra are connected by sharing of corners. The dodecahedra lie in channels at $(\frac{1}{2}, \frac{1}{2}, z)$ and are connected by the sharing of one edge at $z \sim \frac{1}{4}$.

References

BODE, H. & VON DÖHREN, H. (1958). *Acta Cryst.* **11**, 80–82.

BODE, H. & VOSS, E. (1951). *Z. anorg. allgem. Chem.* **264**, 144–150.

COX, J. (1956). *J. Chem. Soc.* pp. 876–878.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

HEYNS, A. M. & PISTORIUS, C. W. F. T. (1976). *Spectrochim. Acta*, **32A**, 535–545.

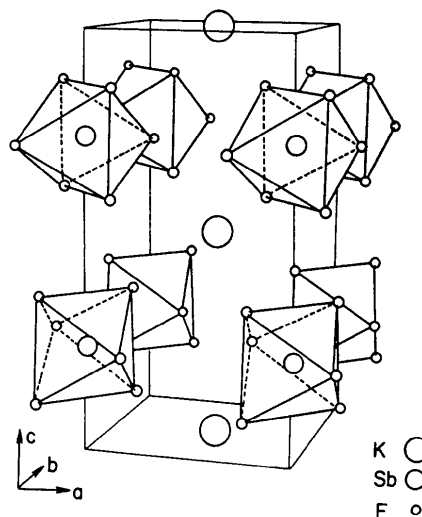JOHNSON, C. K. (1971). *ORTEP*-II. Oak Ridge National Laboratory Report ORNL-3794.

Fig. 2. Orientation of the Sb coordination octahedra in KSbF$_6$.

LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.

X-RAY system (1972). Edited by J. M. STEWART, G. J. KRUGER, H. L. AMMON, C. DICKINSON & S. R. HALL. Tech. Rep. 192, Computer Science Center, Univ. of Maryland.