Acta Cryst. (1977). B33, 232–234

Tin Difluoride–Arsenic Pentafluoride (1:1)

BY LJUBO GOLIČ AND IVAN LEBAN
Chemistry Department, University of Ljubljana, 61000 *Ljubljana, Yugoslavia*

(*Received* 6 *July* 1976; *accepted* 15 *August* 1976)

Abstract. $SnF_2.AsF_5$, F.W. 326·6, rhombohedral, space group $R32$ [hexagonal axes, $a = 9{\cdot}123$ (2), $c = 16{\cdot}983$ (5) Å], $V = 1224{\cdot}3$ Å^3, $D_x = 3{\cdot}986$ g cm^{-3}, $Z = 9$, at 20 (1) °C. The structure consists of discrete cyclic $(Sn{-}F)_3^{3+}$ cations and octahedral AsF_6^- anions arranged along threefold axes. The final R value was 0·039 for the 292 reflexions used in the analysis.

Introduction. Tin difluoride, SnF_2, reacts with the strong fluoride-ion acceptor arsenic pentafluoride, AsF_5, to give a 1:1 complex. On the basis of its vibrational and ^{119}Sn Mössbauer spectra, this compound was formulated as a salt of the polyfluoro cation $(Sn{-}F)_n^{n+}$ with $nAsF_6^-$ anions as counterions (Birchall, Dean & Gillespie, 1971). It has also been suggested that there is some covalent interaction between these ions (Gantar, 1975). Therefore, the crystal structure of this 1:1 complex was investigated to determine the geometry of the $(Sn{-}F)_n^{n+}$ cation and the possible distortions of the octahedral AsF_6^- groups due to covalent interactions. It is of interest to compare this structure with that of $XeRuF_7$, which contains discrete XeF^+ and RuF_6^- species (Bartlett, Gennis, Gibler, Morrell & Zalkin, 1973).

Crystals suitable for X-ray analysis were obtained by D. Gantar, J. Stefan Institute, Ljubljana, Yugoslavia, and J. H. Holloway, Department of Chemistry, The University, Leicester, England, by reacting SnF_2 with excess AsF_5 in anhydrous HF at room temperature. The detailed method of preparation will be published elsewhere. Since the compound is highly sensitive to moisture, a crystal of nearly spherical shape (average radius 0·026 cm) was sealed in a *ca* 0·5 mm quartz capillary. The systematically absent reflexions (hkl: $-h + k + l = 3n$) on precession photographs and the acentric distribution of $|E|$ values ($\langle E^2\rangle = 1{\cdot}000$; $\langle|E^2 - 1|\rangle = 0{\cdot}746$; $\langle|E|\rangle = 0{\cdot}879$) indicate the space group $R32$ (No. 155, hexagonal setting), which had also been implied by the Patterson function and was borne out by the structure analysis. Unit-cell dimensions were obtained from a least-squares fit of the 2θ values of 15 high-order reflexions measured on a CAD-4 diffractometer, with Mo $K\alpha_1$ radiation, $\gamma = 0{\cdot}70926$ Å, $t = 20$ (1) °C. The value $Z = 9$ was deduced assuming a close-packed fluoride lattice, the effective volume per fluorine atom being 19·4 Å^3 (Zachariasen, 1948). Intensity data were collected on an automatic computer-controlled Enraf–Nonius CAD-4 four-circle diffractometer by an ω–2θ scan technique with a variable scan rate. Details of both data collection and reduction are shown in Table 1.

The data were corrected for variation in standards, Lorentz and polarization effects, and absorption, assuming the crystal to be a sphere. For the θ range covered and for $\mu R = 2{\cdot}9$, A^* varied from 35·0 to 21·1 (*International Tables for X-ray Crystallography*, 1959).

The position of the Sn atom was deduced from a Patterson map. All the remaining atoms were revealed in a subsequent electron density map phased on Sn. The structure refinement was by full-matrix least squares, minimizing the function $\Sigma\, w(F_o - F_c)^2$, where the weighting function was determined empirically: $w = w_F w_S$, where $w_F(|F_o| < 75{\cdot}0) = (|F_o|/75{\cdot}0)^{1/2}$, $w_F(|F_o| > 150{\cdot}0) = (150{\cdot}0/|F_o|)^4$, $w_F(75{\cdot}0 < |F_o| < 150{\cdot}0) = 1{\cdot}0$; and $w_S(\sin\theta < 0{\cdot}28) = (\sin\theta/0{\cdot}28)^3$, $w_S(\sin\theta > 0{\cdot}38) = (0{\cdot}38/\sin\theta)$, $w_S(0{\cdot}28 < \sin\theta < 0{\cdot}38) = 1{\cdot}0$. Final refinement parameters are given

Table 1. *Data collection summary*

Temperature (°C)	20 (1)
Diffractometer	CAD-4 automatic 4-circle
X-radiation (Å)	Mo $K\alpha$ ($\bar{\lambda} = 0{\cdot}71069$)
Monochromator	Graphite crystal
Scan method	ω–2θ (moving-crystal moving-counter)
2θ scan width (°)	$0{\cdot}8 + 0{\cdot}2 \tan\theta$
Scan rate (deg min^{-1})	min. 3·4, max. 20·1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{max}$ (°)	50
Maximum scan time (s)	30
Aperture (mm)	$2{\cdot}5 + 0{\cdot}9 \tan\theta$
Intensity decrease (%)	2·5
Measured reflexions	1663 ($\pm h$, $\pm k$, $\pm l$)
Averaged reflexions	292
Mean discrepancy on I (%)	7·8 for 1509 reflexions
Observed reflexions	277
Unobserved reflexions	15 [$I < 3{\cdot}0\,\sigma(I)$]
$\sigma(I)$ based on	Counting statistics
Linear absorption coefficient (cm^{-1})	111·5 for Mo $K\alpha$
Corrections	Lp and absorption for a sphere ($\mu R = 2{\cdot}9$)

in Table 2. The atomic scattering factors used for neutral Sn, As and F were those of Cromer & Mann (1968). The real and imaginary parts of the dispersion correction for Sn, As and F were those of Cromer & Liberman (1970). An isotropic extinction parameter (g) was also included in the final stage of the refinement (Larson, 1967). All calculations were carried out on the CDC Cyber 72 computer at RRC Ljubljana. The X-RAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used.

Table 2. *Refinement summary*

Final refinement cycle	
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0·039
$R_w = [\Sigma\, w(\Delta F)^2/\Sigma\, wF_o^2]^{1/2}$	0·039
Average shift/error	0·038
Maximum shift/error	1·056
Data(m)-to-variable(n) ratio	6·5
$[\Sigma\, w(\Delta F)^2/(m-n)]^{1/2}$	3·3
Final difference map	
Maximum $\Delta\rho$ (e Å^{-3})	2·5 [near As(2)]
Extinction parameter (g)	$2 \cdot 2 \times 10^{-3}$

Table 3 lists the final fractional coordinates and anisotropic thermal factors.*

Discussion. The crystal structure is built up of discrete cyclic $(Sn{-}F)_3^{3+}$ cations and AsF_6^- anions; thus the structural formula of the complex is better represented by $(SnF)_3.3AsF_6$. A stereoscopic view of the cation with the environment of the Sn atom is shown in Fig. 1.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32048 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Final fractional coordinates and thermal parameters with standard deviations in parentheses*

Coordinates are multiplied by 10^4. The anisotropic temperature factors are expressed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \cdots)]$ in units of 10^{-4} Å^2.

	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	9(e)	2601 (1)	0	$\frac{1}{2}$	326 (7)	$=2U_{12}$	465 (8)	205 (5)	3 (3)	$=2U_{13}$
As(1)	3(a)	0	0	0	$=2U_{12}$	$=2U_{12}$	376 (14)	171 (5)	0	0
As(2)	6(c)	0	0	2989 (1)	$=2U_{12}$	$=2U_{12}$	337 (10)	181 (4)	0	0
F(1)	18(f)	851 (26)	1730 (16)	592 (6)	1282 (112)	594 (64)	694 (49)	261 (78)	−8 (84)	−291 (50)
F(2)	18(f)	1538 (13)	1512 (13)	2414 (5)	627 (58)	621 (59)	497 (39)	242 (48)	159 (40)	178 (40)
F(3)	18(f)	39 (11)	1558 (10)	3588 (5)	617 (48)	398 (41)	499 (38)	305 (37)	−2 (35)	−51 (32)
F(4)	9(e)	1760 (12)	$=x$	$\frac{1}{2}$	398 (41)	$=U_{11}$	416 (45)	219 (45)	−3 (20)	$=-U_{13}$

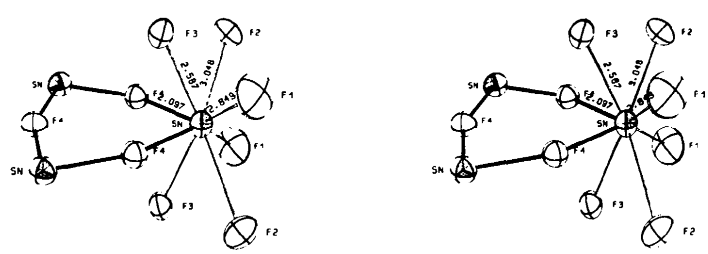

Fig. 1. A stereoscopic view of the $(Sn{-}F)_3^{3+}$ cation with the coordination sphere around the Sn atom. The atoms are represented by thermal ellipsoids drawn at the 50% probability level (Johnson, 1965).

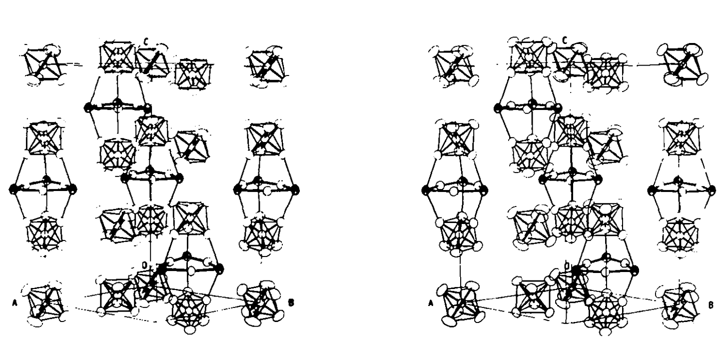

Fig. 2. A stereoscopic view of the unit cell viewed approximately along [110].

Table 4. *Some important interatomic distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

(*a*) $(Sn-F)_3^{3+}$ environment

Sn—F(4)^{a,b}	2·097 (8)	F(4)—Sn—F(3)^{b}	74·2 (2)
Sn—F(3)^{b,c}	2·587 (8)	F(4)—Sn—F(4)^{b}	83·0 (4)
Sn—F(1)^{d,e}	2·849 (9)	F(3)^{b}—Sn—F(3)^{c}	136·0 (3)
Sn—F(2)^{d,e}	3·048 (5)	Sn—F(4)—Sn^{f}	157·0 (3)

(*b*) AsF_6 octahedron (D_3 symmetry)

As(1)—F(1)^{a,b,f,g,h,i}	1·696 (11)
F(1)—As(1)—F(1)^{f}	88·4 (7)
F(1)—As(1)—F(1)^{g}	92·1 (8)
F(1)—As(1)—F(1)^{h}	90·9 (7)
F(1)—As(1)—F(1)^{i}	179·2 (9)

(*c*) AsF_6 octahedron (C_3 symmetry)

As(2)—F(2)^{a,b,f}	1·701 (8)
As(2)—F(3)^{a,b,f}	1·733 (7)
F(2)—As(2)—F(3)	90·1 (5)
F(2)—As(2)—F(2)^{f}	90·2 (5)
F(2)—As(2)—F(3)^{b}	90·6 (5)
F(3)—As(2)—F(3)^{b}	89·1 (5)
F(2)—As(2)—F(3)^{f}	179·1 (4)

Symmetry code

(*a*)	x,	y,	z	(*f*)	$-y$,	$x-y$,	z
(*b*)	$y-x$,	$-x$,	z	(*g*)	y,	x,	$-z$
(*c*)	y,	x,	$1-z$	(*h*)	$-x$,	$y-x$,	$-z$
(*d*)	$\frac{2}{3}-y$,	$\frac{1}{3}-y+x$,	$\frac{1}{3}+z$	(*i*)	$x-y$,	$-y$,	$-z$
(*e*)	$\frac{1}{3}-x$,	$-\frac{1}{3}-x+y$,	$\frac{2}{3}-z$				

Fig. 2 provides a stereo view of the packing in the unit cell. Some important interatomic distances and angles are given in Table 4.

The cation $(Sn-F)_3^{3+}$ has D_{3h} symmetry with a Sn—F(4) distance of 2·097 (8) Å and the angles F(4)—Sn—F(4) and Sn—F(4)—Sn are 83·0 (4) and 157·0 (3)° respectively. Each Sn atom is surrounded within 3·1 Å by eight F atoms. Four [two F(4) at 2·097 and two F(3) at 2·587 Å] are at one side of the Sn atom in a nearly square-pyramidal arrangement. The distance 2·097 Å within the cation is very close to the 2·12 Å expected for a pure covalent Sn—F bond, and the value 2·587 Å is not far off the value 2·55 Å expected for a pure ionic bond between Sn and F (Wells, 1975). On the opposite side of the Sn there are four more distant F atoms [two F(1) at 2·849 and two F(2) at 3·048 Å]. There are two different kinds of AsF_6^- octahedra in the structure. One of these, around As(1), exhibits D_3 symmetry with six equivalent As(1)—F(1) distances of 1·696 (11) Å and angles within 88·4 (7)–92·1 (8)°. The other, around As(2), possesses C_3 symmetry with three equivalent As(2)—F(2) and As(2)—F(3) distances of 1·701 (8) and 1·733 (7) Å respectively. This distortion is probably due to the ionic interaction of the AsF_6^- anion with the $(Sn-F)_3^{3+}$ cation. The angles in the second octahedron vary from 89·1 (5) to 90·6 (5)°.

We are indebted to B. Frlec, J. Stefan Institute, Ljubljana, for useful discussions. The financial support of the Research Community of Slovenia is also gratefully acknowledged.

References

BARTLETT, N., GENNIS, M., GIBLER, D. D., MORRELL, B. K. & ZALKIN, A. (1973). *Inorg. Chem.* **12**, 1717–1721.

BIRCHALL, T., DEAN, P. A. W. & GILLESPIE, R. J. (1971). *J. Chem. Soc.* (*A*), pp. 1777–1782.

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.

GANTAR, D. (1975). M.Phil. Thesis, Univ. of Ljubljana, Ljubljana, Yugoslavia.

International Tables for X-ray Crystallography (1959). Vol. II, pp. 302–303. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

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

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972. Technical Report TR-192, Computer Science Center, Univ. of Maryland.

WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., pp. 236–259. Oxford: Clarendon Press.

ZACHARIASEN, W. H. (1948). *J. Amer. Chem. Soc.* **70**, 2147–2151.