Contribution from the Department of Chemistry,
Boston University, Boston, Massachusetts 02215

Crystallographic Studies of Tin(II) Compounds. I. Crystal Structure of Tin(II) Fluoride, SnF_2

ROBERT C. McDONALD, HERBERT HO-KUEN HAU, and KLAAS ERIKS*[1]

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The crystal structure of stannous fluoride, SnF_2, has been determined using 1114 reflections collected from a single crystal with a semiautomated x-ray diffractometer. The crystals are monoclinic, with space group $C2/c$ with $a = 13.353$ (1) Å, $b = 4.9090$ (4) Å, $c = 13.787$ (1) Å, $\beta = 109.11$ (1)°, $V = 853.9$ Å^3, $Z = 16$ molecules/cell, d(obsd) = 4.84(4) g cm^{-3}, and d(calcd) = 4.88 g cm^{-3}. Least-squares refinement with anisotropic thermal parameters gave a final R value of 0.057 for all observed reflections. The lattice contains cyclic Sn_4F_8 tetramers, held to each other by weaker Sn–F interactions. The tetramers are puckered eight-membered rings with alternating tin and fluorine atoms, strongly bonded together. Four more fluorine atoms are strongly bonded externally to the four tin atoms of the ring. Sn–F–Sn angles in the ring are 132.1 and 170.4°. Each tin forms the apex of a trigonal pyramid with three near fluorine atoms at the base. Average Sn–F distances in the pyramids are 2.14 Å and average F–Sn–F angles are 84°.

Introduction

Studies of the coordination of main-group elements with an ns^2 valence electron configuration have shown a marked tendency for these elements to exhibit distortions from centric symmetry. The distortions and the general bonding principles have been treated by several investigators[2-6] but lack of accurate structural information has hampered attempts to describe and explain trends, if indeed they exist, in these distortions. Very early structure determinations may well be incorrect, particularly in those cases where a heavy element (atomic number >45) is combined with light elements (O, F, Cl, S). In such cases the heavy element can easily be assigned to a position of incorrect site symmetry, by placing it in a convenient special position. This was the case in the earlier structural interpretation of SnF_2 by Bergerhoff[7] and it appears to be true in several other structures as well.

As part of a more extensive study of the coordination geometry of Sn(II) we decided to reexamine the structure of SnF_2, partly in view of the special properties of this compound in dental caries prevention.

Experimental Section

(A) Preparation and Physical Properties. Solid SnF_2 was obtained commercially (No. 2291, K & K Laboratories) and was recrystallized from water that had been slightly acidulated with HF. The clear, colorless crystals were washed with ethanol. They were of a size suitable for x-ray diffraction study, displayed a large number of crystal faces and had roughly the shape of a biaxial ellipsoid. Anal. Calcd for SnF_2: Sn, 75.75; F, 24.25. Found: Sn, 75.47; F, 25.14. The pure solid showed a weight loss of 0.84% upon heating to 160 °C. Since an orthorhombic form had been reported to crystallize[8] along with the usual monoclinic form, the solid was examined by differential scanning calorimetry. No phase changes were detected between room temperature and 210 °C, at which temperature the solid began to decompose.

The density of SnF_2 was determined using a micropycnometric technique described by Syromyatnikov.[9] Using bromoform as the immersion liquid the density was found to be 4.84 ± 0.04 g cm^{-3} at 25 °C.

From Weissenberg photographs of a single crystal a monoclinic cell was deduced. Systematic absences were hkl with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$. The possible space groups are Cc or $C2/c$, the latter being proved correct by the structure determination. Unit cell parameters, determined from a powder diagram taken at 25 °C, were found to be identical with those reported by the National Bureau of Standards.[10] All crystal data are given in Table I, along with those reported by Bergerhoff.[7] In the entry marked "crystal dimensions" the first dimension corresponds to the b axis, which is the axis along which the crystal was mounted.

(B) X-Ray Data Collection. Reflection intensities were determined using a Supper-Pace automated diffractometer (SPAD). Details of the geometry of this instrument and of the procedures for data collection have been described elsewhere.[11] Zones $h0l$ through $h5l$ were collected using Zr-filtered Mo Kα radiation (λ 0.71069 Å). A total of 1114 independent nonzero reflections were measured, out to $2\theta_{max} = 60°$. One check reflection was determined within each zone after every 50 general reflections. The check reflections varied by less than 5% in intensity.

Table I. Crystal Data for SnF_2 (Space Group $C2/c$)

	This study	Bergerhoff[7]
a, Å	13.353 (1)	13.46
b, Å	4.9090 (4)	4.92
c, Å	13.787 (1)	13.86
β, deg	109.11 (1)	109.5
Temp, °C	25	
d(measd), g cm^{-3}	4.84 (4)	4.57
d(calcd), g cm^{-3}	4.88	
V, Å^3	853.9	
Z, molecules/cell	16	
Crystal dimensions, cm^3	0.016 × 0.017 × 0.010	

The mass absorption coefficient of SnF_2 is 118 cm^2 g^{-1} for Mo Kα radiation. For the crystal used for data collection the absorption factor A^* could therefore vary from 2.55 to 5.05. An absorption correction was applied assuming an ellipsoidal shape of the crystal and using Wuensch and Prewitt's program.[12] Scattering factors for Sn^{2+} and F^- were taken from ref 13. Anomalous dispersion corrections were included as well, using values for $\Delta f'$ and $\Delta f''$ from ref 14.

(C) Structure Determination and Refinement. The vector map for SnF_2 shows a pseudo-body-centered arrangement for the tin atoms. Bergerhoff[7] consequently placed these atoms in the following combination of special and general positions in the space group $C2/c$: 4 Sn at (b); 0, $^1/_2$, 0; 4 Sn at (c), 0, y, $^1/_4$, with $y \approx 0$; 8 Sn at (f), x, y, z, with $x = 0.242$, $y = 0.980$, $z = 0.121$. Appreciable time was spent in trying to refine the structure with these positions, but all efforts failed. In retrospect this should have been apparent from the start, since the site symmetries of the tin atoms in the special positions would give rise to entirely unacceptable tin coordination. An alternate pseudo-body-centered arrangement of tin atoms can be obtained by moving the origin to the position $^1/_8$, 0, $^3/_{16}$ of Bergerhoff's model, as shown in Figure 1. All tin atoms then occupy general positions xyz and no restraints on coordination exist. The dashed lines in Figure 1 outline one body-centered tin subcell. A difference-Fourier map based on these revised tin positions showed all of the fluorine atoms unambiguously and least-squares refinement with isotropic thermal parameters proceeded smoothly to an unweighted R value of 0.125. The subsequent refinement with anisotropic thermal parameters gave physically unreasonable temperature factors for some of the fluorine atoms, which were not resolved until a correction for secondary extinction was introduced of the form

$$F_c^* = k|F_c|\left(1 + \frac{2gAP\bar{T}|F_c|^2}{V^2}\right)^{-1/4}$$

where k, A, P, $\bar{T}$, and V are constants and g is a variable parameter.[15,18] With g determined at (2.44 ± 0.19) × 10^{-3} all thermal parameters became positive definite. The final least-squares refinement with anisotropic thermal parameters resulted in an unweighted R value[16] of 0.057 and a R_w value[16] of 0.074 using all 1114 observed reflections. The function minimized in all cases was $\sum w(F_o - F_c)^2$. Of the total

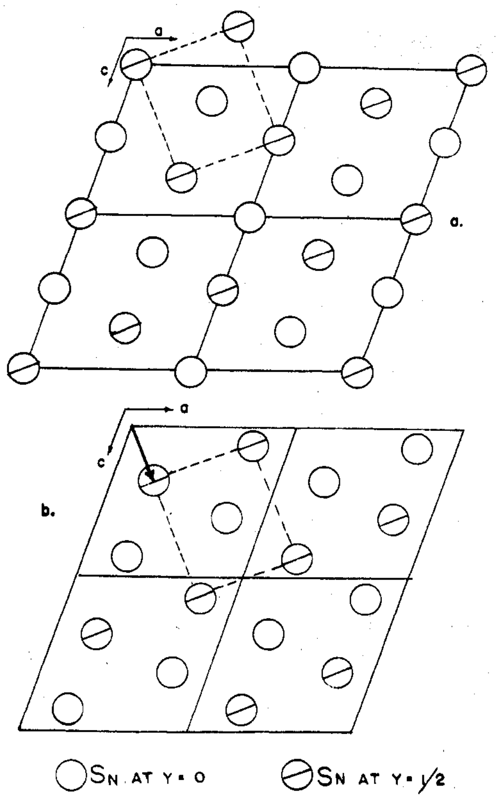

Figure 1. Pseudo-body-centered arrangements of Sn atoms in SnF_2: (a) Bergerhoff model; (b) revised model.

Table II. SnF_2 Final Positional and Thermal Parameters[a]

	x	y	z
Sn(1)	0.3724 (1)	0.4900 (4)	0.0574 (1)
Sn(2)	0.1183 (1)	0.4825 (3)	0.1867 (1)
F(1)	0.2606 (10)	0.2376 (30)	0.3077 (12)
F(2)	0.3852 (11)	0.2195 (31)	0.1787 (11)
F(3)	0.1749 (11)	0.3391 (30)	0.0406 (10)
F(4)	0.4717 (11)	0.3259 (32)	0.4157 (12)

	U_{11}	U_{22}[b]	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	2.31 (7)	2.05	1.96 (7)	0.18 (5)	0.73 (4)	0.01 (5)
Sn(2)	1.72 (7)	1.85	2.20 (7)	−0.22 (7)	0.53 (4)	−0.12 (7)
F(1)	1.71 (53)	3.28	4.92 (81)	0.34 (52)	0.59 (53)	0.59 (64)
F(2)	3.70 (60)	3.75	3.13 (66)	0.23 (61)	1.39 (57)	1.50 (59)
F(3)	3.60 (68)	3.27	2.97 (62)	−0.23 (58)	1.43 (56)	−0.99 (56)
F(4)	2.70 (66)	3.49	5.33 (88)	−1.46 (58)	0.59 (63)	−1.62 (68)

[a] Anisotropic temperature factor is of the form $\exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Standard deviation of the last significant number in parentheses. Values of U have been multiplied by 10^2.
[b] Standard deviations indeterminate because of high correlation (see text).

1114 reflections, 419 had a value less than 3 times their average background, (BK1 + BK2)/2, and were assigned a weight of 0.05 in the refinement. The remaining 695 had a weight of unity. The average shift per error in the last refinement cycle was 0.03 and the maximum shift per error was 0.54. A high correlation was found between the scale factors for the individual levels and the anisotropic thermal parameters U_{22}. Consequently these variables were refined in alternate cycles. Final atomic parameters are listed in Table II. A table of the final F_o and F_c values is available.[17] All crystallographic computations except the absorption correction were carried out using the program "X-Ray 72".[18]

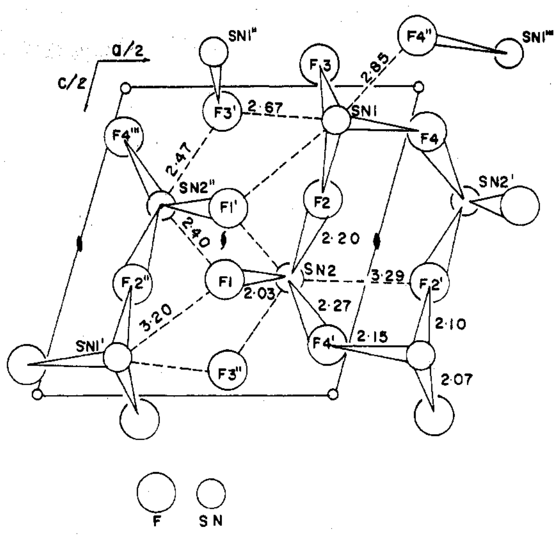

Figure 2. SnF_2 asymmetric unit, projected along the b axis.

Table III. SnF_2 Interatomic Distances (Å) and Angles (deg)[a]

A. Distances within the Sn_4F_8 Group			
Sn(1)–F(3)	2.07 (1)	Sn(2)–F(1)	2.03 (1)
Sn(1)–F(2)	2.10 (2)	Sn(2)–F(2)	2.20 (2)
Sn(1)–F(4)	2.15 (2)	Sn(2)–F(4′)	2.27 (1)
F(3)–F(4)	2.82 (2)	F(1)–F(2)	2.81 (2)
F(2)–F(3)	2.87 (2)	F(1)–F(4′)	2.76 (2)
F(2)–F(4)	2.69 (2)	F(2)–F(4′)	3.13 (2)
F(2)–F(2′)	3.05 (2)	Sn(2)–F(2′)	3.29 (2)

B. Distances between the Sn_4F_8 Group			
Sn(1)–F(3′)	2.67 (1)	Sn(2)–F(1′)	2.40 (1)
Sn(1)–F(4″)	2.85 (2)	Sn(2)–F(3″)	2.47 (2)
Sn(1)–F(1′)	3.20 (2)	Sn(2)–F(4)*	3.56 (1)
Sn(1)–F(1)*	3.54 (1)	Sn(2)–F(2)*	3.83 (2)
Sn(1)–F(3)*	3.54 (2)	Sn(2)–F(4)*	3.91 (1)
Sn(1)–F(2)*	3.93 (2)	Sn(2)–F(1)*	3.99 (1)
Sn(1)–F(2)*	4.02 (1)	F(4)–F(4″)	2.78 (2)
F(3)–F(3′)	2.74 (2)	F(1)–F(1′)	2.89 (2)
F(3′)–F(4‴)	3.27 (2)	F(1)–F(2″)	3.11 (2)
F(3)–F(4″)	3.37 (2)	F(1)–F(2″)	3.25 (2)
F(2)–F(3′)	2.89 (2)	F(1′)–F(3′)	2.78 (2)

C. Angles within the Sn_4F_8 Group			
F(2)–Sn(1)–F(3)	87.3 (6)	F(1)–Sn(2)–F(2)	83.2 (6)
F(2)–Sn(1)–F(4)	78.6 (6)	F(1)–Sn(2)–F(4′)	76.6 (5)
F(3)–Sn(1)–F(4)	83.9 (5)	F(2)–Sn(2)–F(4′)	88.8 (6)
Sn(1)–F(2)–Sn(2)	170.4 (9)	Sn(1)–F(4)–Sn(2′)	132.1 (8)
Sn(2)–F(2′)–Sn(2′)	93.9 (5)	Sn(1)–F(2)–Sn(2′)	94.7 (6)

D. Angles between the Sn_4F_8 Groups			
F(2)–Sn(1)–F(1′)	72.3 (5)	F(1)–Sn(2)–F(1′)	81.0 (5)
–F(3′)	73.5 (5)	–F(2′)	121.2 (5)
–F(4″)	144.4 (5)	–F(3″)	75.7 (6)
F(3)–Sn(1)–F(1′)	124.5 (5)	F(2)–Sn(2)–F(1′)	84.7 (5)
–F(3′)	69.2 (5)	–F(2′)	64.0 (4)
–F(4″)	84.9 (5)	–F(3″)	158.8 (5)
F(4)–Sn(1)–F(1′)	137.0 (5)	F(4′)–Sn(2)–F(1′)	160.0 (5)
–F(3′)	141.7 (5)	–F(2′)	54.2 (5)
–F(4″)	66.1 (5)	–F(3″)	87.0 (6)
Sn(2)–F(1)–Sn(1′)	97.5 (4)	Sn(1)–F(3′)–Sn(1″)	110.8 (7)
Sn(2)–F(1)–Sn(2″)	140.9 (8)	Sn(2″)–F(3′)–Sn(1″)	130.0 (7)
Sn(1)–F(1′)–Sn(2″)	109.3 (6)	Sn(1)–F(4)–Sn(1‴)	113.9 (6)
Sn(1)–F(3′)–Sn(2″)	114.0 (5)	Sn(2′)–F(4)–Sn(1‴)	113.0 (6)

[a] Primes correspond to those in Figure 2; asterisks indicate atoms not represented in Figure 2.

Description of the Structure

The structure consists of discrete tetramers Sn_4F_8, as shown in Figure 2, which represents one asymmetric unit of the cell projected along the b axis. In this figure short and long Sn–F distances are indicated by cones and dashed lines, respectively, the sum of the ionic radii (2.27 Å) being selected to distinguish between the two types. A listing of pertinent interatomic distances and angles is given in Table III.

The tetramer exists as a puckered eight-membered ring in which Sn and F atoms alternate. Four additional F atoms are bonded to the four tin atoms at short distances, pointing outward. These latter fluorine atoms provide most of the weaker interactions with tin atoms of adjacent rings. The rings possess actual crystallographic symmetry C_2 from the twofold

Table IV. Bond Distances and Angles for Various Tin(II)-Fluorine Compounds

Compd	Sn-X distances, A			X-Sn-X angles, deg			Ref
SnF_2 1	2.07	2.10	2.15	78.6	83.9	87.3	This study
2	2.03	2.21	2.27	79.6	83.2	88.8	
Sn_3F_8	2 10	2.17	2.25	77.8	81.9	85.5	19
$NaSn_2F_5$	2.07	2.08	2.22	81.2	84.1	89.3	20
$(Sn_2F_3)Cl$	2.11	2.11	2.16	79.1	81.6	81.6	21
$KSnF_3 \cdot {}^1/_2H_2O$	2.01	2.04	2.27	78.5	85.5	89.7	22
NH_4SnF_3	2.05	2.10	2.21	83.1	85.3	85.9	23
$SnCl_2$	2.66	2.78	2.78				24
$K_2SnCl_4 \cdot H_2O$	2.54	2.54	2.63	88	88	91	25

axis of the unit cell, and they almost have C_{2v} symmetry. The average Sn–F distances within the ring are 2.18 Å, while the external ones average 2.05 Å. The Sn–F–Sn angles in the ring are 170.4 and 132.1°.

The tin atoms form an only slightly distorted body-centered lattice, as already shown in Figure 1, with repeat distances 4.91 Å in the [010], 4.22 Å in the $[20\bar{1}]$, and 5.13 Å in the [203] direction. The two structurally different tin atoms each form three bonds with fluorine atoms that are shorter than the sum of ionic radii of 2.27 Å. This choice of a critical distance may seem somewhat arbitrary, but Brown[6] used in his discussion a rather similar distance (~2.2 Å) as a cutoff between bonds of high and intermediate strength. Accepting the 2.27-Å value, the geometry of the Sn(II) coordination is a trigonal pyramid with tin at the apex and with all F–Sn–F angles less than 90°. The angles range from 78.6 to 88.8° and average 83.3° for Sn(1) and 83.8° for Sn(2). Sn–F distances average 2.10 Å for Sn(1) and 2.17 for Sn(2). At distances ranging from 2.40 up to 4.0 Å each tin is surrounded by seven additional fluorine atoms, as shown in Table III. Following again the criteria of Brown,[6] any distances above 3.4 Å would not be considered and thus the environment of each tin would be a highly distorted octahedron. Two points seem quite clear, viz. (a) that Sn(1) and Sn(2) differ significantly in their distances to the nearer fluorine atoms (further discussed below) and (b) that there is no indication whatever for tetrahedral coordination of the tin atoms, since no fluorine is located on or near the pseudothreefold axis, on the side opposite to the base plane of the trigonal pyramid.

Each fluorine atom is trifurcated with a very wide range of Sn–F–Sn angles (94–170.5°). There are two structurally different types: F(1) and F(3), the external fluorines, with one short Sn–F distance and two longer Sn–F distances, and F(2) and F(4), the ring fluorines, with two short Sn–F distances and one longer Sn–F distance. Interestingly, the average F–Sn distances for the four F atoms are 2.54 Å for F(1), 2.53 Å for F(2), 2.40 Å for F(3), and 2.42 Å for F(4), so that there is no significant difference between the two types as far as average Sn–F distance is concerned.

Discussion

The Sn^{II}–F bond distances and angles agree well with those found in other tin(II) fluoride compounds. A number of these are listed in Table IV, along with some other tin(II) halides. All of the compounds presented in the table have in common a trigonal-pyramidal coordination of the Sn(II) ion. In all cases the three short Sn–X distances are equal to or less than the sum of ionic radii (2.27 Å for Sn–F and 2.74 Å for Sn–Cl) and the apical angles of the pyramid are less than 90°. The same configuration exists also in $SnCl_2 \cdot 2H_2O$[26] where one of the coordinating atoms is oxygen (Sn–Cl = 2.59 Å (two times), Sn–O = 2.16 Å; angles 83, 85, 87°), in SnS[27] (Sn–S = 2.62, 2.68 Å (two times); angles 88, 88, 96°), and in $SnSO_4$[28] (Sn–O = 2.33, 2.40 Å (two times); angles 74, 76, 76°). This coordination is not quite followed in $Na_4Sn_3F_{10}$,[29] which contains $Sn_3F_{10}{}^{4-}$ chains in which each Sn(II) is four-coordinated in a distorted tetragonal pyramid with Sn at the apex. Still all but one of the Sn–F distances are below the sum of ionic radii, and the F–Sn–F angles, with one exception, are less than 90°.

It can be concluded therefore that, at least with the lighter elements, Sn(II) has a strong tendency toward trigonal-pyramidal coordination, an observation already made earlier by Rundle and Olsen.[4] Without doubt the region above the apex, i.e., on the side of Sn opposite to the plane of the ligands, is occupied by the nonbonding pair of 5s electrons. This accounts for the cavities and channels that frequently occur in the structures of these compounds and for the fact that no ligands approach Sn directly from that side.

In combination with heavier elements, specifically Br and I, this tendency does not persist. The structures of $2SnBr_2 \cdot H_2O$,[30] $3SnBr_2 \cdot H_2O$,[31] $6SnBr_2 \cdot 5H_2O$,[32] and SnI_2[33] all have a trigonal prism as the basic coordination geometry of Sn, with varying numbers of atoms capping the prism faces. The tin coordination in these cases is seven- or eightfold.

The structure can also be analyzed using Brown's[6] bond valence concept. Distances above 3.4 Å are disregarded because they correspond to a bond valence $S \leq 0.08$ vu (valence unit). Each tin atom therefore has six near neighbors. Sn(1) is found to have three strong and three weak bonds, corresponding to Brown's configuration C, with Sn–F bond valences of 0.54, 0.51, 0.46, 0.23, 0.18, and 0.12 vu, respectively, adding to a total bond valence of 2.04 vu for Sn(1). This tin atom is similar to the ones in $Sn_2F_5{}^-$ and the terminal tin atoms in $Sn_3F_{10}{}^{4-}$. Sn(2), on the other hand, can be described as having one strong bond, four intermediate bonds, and one weak bond, corresponding most closely to Brown's configuration E except for large deviations from octahedral angles. The Sn–F bond valences in this case are 0.58, 0.43, 0.39, 0.32, 0.29, and 0.10 vu, respectively, and the total Sn(2) bond valence is 2.11 vu. No similar configuration is listed in Brown's paper, nor do there appear to be analogies in Table IV, judging from the reported distances.

Fluoride structures containing cyclic tetramers are not unknown. Recently this configuration was reported for RhF_5[34] and the isomorphous OsF_5 and RuF_5. The rings in these cases are rather different from that in SnF_2, in that (a) Rh is octahedrally coordinated, (b) the Rh–F–Rh angles in the ring are 134.3 and 135.7°, while those in SnF_2 are 132.1 and 170.4°, and (c) the ring is more puckered in SnF_2 than in RhF_5. All of these effects appear to be a consequence again of the lone pair of 5s electrons on Sn(II) which tend to be as far removed from each other as possible. The Sn–F–Sn angle of 170° is the highest found so far in these systems of interconnected (SnF_3) pyramids.

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Registry No. Sn_4F_8, 57738-90-6.

Supplementary Material Available: Final values of $|F_o|$ and $|F_c|$ for 1114 reflections (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada, L8S 4M1

Preparation and Crystal Structures of Ditellurium Octaselenium Bis(hexafluoroarsenate)–Sulfur Dioxide, $Te_2Se_8(AsF_6)_2{\cdot}SO_2$, and "Tetratellurium Hexaselenium" Bis(hexafluoroarsenate), $Te_{3.7}Se_{6.3}(AsF_6)_2$

P. BOLDRINI, I. D. BROWN, R. J. GILLESPIE,* P. R. IRELAND, W. LUK, D. R. SLIM, and J. E. VEKRIS

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The compound $Te_2Se_8(AsF_6)_2{\cdot}SO_2$ has been prepared by the reaction of elemental tellurium with octaselenium bis(hexafluoroarsenate), $Se_8^{2+}(AsF_6^-)_2$, in liquid SO_2. The crystal structure has been determined by direct methods from three-dimensional x-ray counter measurements. Crystals are monoclinic with a = 7.337 (2) Å, b = 8.545 (3) Å, c = 36.030 (2) Å, and β = 91.52 (5)°. The structure, which has been refined in space group $P2_1/c$ to a final agreement index, R_2, of 0.094 for 1409 independent reflections, is made up of discrete $Te_2Se_8^{2+}$ and AsF_6^- ions and an SO_2 molecule. The $Te_2Se_8^{2+}$ cation may be regarded as a bicyclic cluster formed by a six-membered ring fused with an eight-membered ring, with the two Te atoms in the three-coordinate positions. The compound $Te_{3.7}Se_{6.3}(AsF_6)_2$ has been prepared by a reaction of a 1:1 Se–Te "alloy" with AsF_5 in liquid SO_2. The crystal structure has been determined by direct methods from three-dimensional x-ray counter measurements. Crystals are orthorhombic with a = 14.840 (6) Å, b = 10.828 (5) Å, and c = 13.345 (5) Å. The structure has been refined in space group $Pbcn$ to a final agreement index, R_2, of 0.128 for 2477 independent reflections. It is composed of discrete AsF_6^- ions and of "$Te_{3.7}Se_{6.3}^{2+}$" ions with some positional and occupational disorder. The cation is a bicyclic cluster with a structure similar to that of $Te_2Se_8^{2+}$.

Introduction

It has been shown recently that sulfur can be oxidized by a number of oxidizing agents such as sulfuric acid, oleum, AsF_5, and SbF_5 to form the homonuclear polyatomic cations S_{16}^{2+}, S_8^{2+}, and S_4^{2+}.[1] It has also been shown that the reactions of elemental selenium and of elemental tellurium with the same oxidizing agents lead to the formation of the cations Se_8^{2+}, Se_4^{2+}, and Te_4^{2+}, respectively, as well as other cations that have been less well characterized.[1] The cations S_8^{2+} and Se_8^{2+} have been shown to have very similar nonplanar cyclic structures with an exo–endo conformation and a rather long and weak cross-ring bond.[2,3] The tetraatomic cations S_4^{2+}, Se_4^{2+}, and Te_4^{2+} all have the same square-planar structure.[4–6]

We have extended this investigation to interchalcogen compounds and we now report the preparation and crystal structures of the compounds $Te_2Se_8^{2+}(AsF_6^-)_2{\cdot}SO_2$ and $Te_{3.7}Se_{6.3}^{2+}(AsF_6^-)_2$. These compounds both contain interchalcogen cations with similar bicyclic structures not previously encountered among the homonuclear cations of sulfur, selenium, and tellurium.

Experimental Work

(a) Preparation of $Te_2Se_8(AsF_6)_2{\cdot}SO_2$. In a typical experiment, anhydrous SO_2 (40 ml) was distilled at −78 °C onto a mixture of powdered Te (0.002 mol, 0.255 g) and $Se_8(AsF_6)_2$ (0.001 mol, 1.009 g) which was prepared from the reaction of Se and AsF_5 as described previously.[7,8] The mixture was allowed to warm up to room temperature and stirred. The dark green color of the Se_8^{2+} species was found to diminish rapidly as the reaction proceeded. After stirring of the mixture for 12 h a light brown solution with a dark brown solid was obtained. The solution was filtered at −20 °C and allowed to stand at room temperature. Dark brown crystals were formed after 1 day. More product could be obtained by extracting the solid part of the original product with SO_2. As the solubility of the product in SO_2 is rather limited, a number of extractions were required in order to obtain a good yield of product. The dark brown crystalline material was quite stable at room temperature but was readily decomposed by the moisture of the atmosphere to give a mixture of the elements and other products. The crystals were handled in a drybox or in sealed tubes. Anal. Calcd for $Te_2Se_8As_2F_{12}SO_2$: Te, 19.20; Se, 47.54; As, 11.28; F, 17.15. Found: Te, 19.31; Se, 48.03; As, 12.24; F, 17.14.

(b) Preparation of $Te_{3.7}Se_{6.3}(AsF_6)_2$. Equimolar amounts of finely powdered selenium and tellurium were placed in a Pyrex glass tube. The contents of the tube were pumped to dryness for 24 h on a vacuum line and the tube was sealed. The materials were thoroughly mixed by shaking the tube which was then placed in a furnace and heated to 530 °C and maintained in the molten state for 12 h. On cooling a metallic looking material was produced which was pulverized in a porcelain mortar.

In a typical experiment AsF_5 (3 mol) was condensed onto 1 mol of Se–Te "alloy" and 40 ml of SO_2 at −196 °C. On warming to room temperature the color of the solution became red and the color intensified as stirring was continued. After 24 h of stirring a very dark red, almost black, solution was obtained. This solution was filtered and allowed to stand at room temperature for several days. A large quantity of black crystals of a variety of shapes and sizes was obtained but the most prominent crystal forms present were (312), (010), (100).