CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO 87544

# The Geometry of the Heptafluorodiantimonate Ion. The Crystal Structure of Cesium Heptafluorodiantimonate(III)[1]

BY R. R. RYAN,*[2] S. H. MASTIN, AND ALLEN C. LARSON

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The crystal structure of $CsSb_2F_7$ has been determined by a three-dimensional single-crystal X-ray study. The crystals are monoclinic, space group $C2/c$, with $a = 19.315$, $b = 6.878$, $c = 5.594$ Å, and $\beta = 90.09°$. For $Z = 4$, $d_c = 4.54$ g/cm³ compared with $d_m = 4.54$ g/cm³. The structure was refined by full-matrix least-squares techniques using 1019 observed reflections to an unweighted $R$ value of 0.020. The idealized geometry of the dimeric $Sb_2F_7^-$ can be described as two trigonal bypyramids (including the lone pair of electrons contained in the equatorial plane in each bipyramid) joined by an axial corner. The axial bridging fluorine is on a crystallographic twofold axis and the Sb–F–Sb angle is 125.3°. Distances and angle relationships as well as the overall conformation of the anion are in accord with electron-pair repulsion theory. The coordination number of the cesium ion is 10.

## Introduction

Several recent reviewers have cited the structure of $CsSb_2F_7$ as an example of a dimeric anion containing five-coordinate antimony (including the stereochemically active lone pairs). The geometry around the antimony has been described as a trigonal bipyramid with the lone pair occupying an equatorial site,[3] a trigonal bipyramid with the lone pair occupying an apical site,[4,5] or a distorted square pyramid with the lone pair at a basal site.[5]

The reference for the above remarks is a single-crystal investigation by Byström and Wilhelmi[6] in which they described the ion as a pair of tetrahedrally coordinated antimony atoms that share a fluorine.

In connection with nmr studies currently being carried out in this laboratory we have reexamined the structures of several antimony fluoride salts using the published data. In the case of $CsSb_2F_7$, least-squares calculations using the published parameters to define the starting model failed to converge in the light-atom positions. A difference Fourier map phased on the heavy-atom positions showed no meaningful light-atom peaks. In addition a recent X-ray study of $KSb_2F_7$[7] showed that structure to contain $SbF_4^-$ ions and $SbF_3$ molecules rather than a $Sb_2F_7^-$ ion. The apparent interest in the structure of the $Sb_2F_7^-$ ion and our inability to verify the published structure prompted us to collect diffractometric data and reexamine the problem.

## Experimental Section

Crystals of $CsSb_2F_7$, prepared as described by Byström and Wilhelmi,[6] invariably were twinned. However, a single crystal was found upon optical examination of several hundred crystals which had been recrystallized from saturated solutions of the material in dilute (*ca.* 5% *M*) HF at refrigerator temperatures. The needlelike crystal was cleaved perpendicular to the needle direction and the resulting 84 × 163 × 157 μ crystal was mounted with the $c$ axis nearly parallel to the $\varphi$ axis of the goniometer and was used both for preliminary investigations and for data collection.

Precession photographs taken with Mo K$\alpha$ radiation showed monoclinic symmetry with extinctions: $hkl$, $h + k$ odd; $h0l$, $l$ odd. These observations are consistent with space groups $C2/c$ and $Cc$. The developed faces of the crystal were of the forms {100}, {010}, and {001}. A twinned crystal was also examined and was found to be twinned across a plane perpendicular to the $a^*$ axis.

The cell constants were determined by least-squares refinement, using as observations the setting angles of 12 reflections that had been centered on an automated four-circle Picker X-ray diffractometer using Mo K$\alpha_1$ radiation ($\lambda$ 0.70930 Å). The values thus determined are $a = 19.315$ (8), $b = 6.878$ (5), $c = 5.594$ (3) Å, and $\beta = 90.09$ (4)° where the number in parentheses is the least-squares standard error of the least significant digit. The calculated density for $Z = 4$ is 4.54 g/cm³; the density measured by pycnometer is 4.54 g/cm³.

Intensity data were collected on the Picker diffractometer using Mo K$\alpha$ radiation, a single-crystal graphite monochromator (reflecting from the 002 plane), and a takeoff angle of 3°. The count was taken using a $\theta$–$2\theta$ scan over a $2\theta$ range of 2° (plus the $\alpha_1$–$\alpha_2$ dispersion), 0.05° steps for 2 sec at each step; stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan. Intensities were collected for all $hkl$ planes in the hemisphere of the reciprocal cell with $k \geq 0$ and $2\theta \leq 60°$. Of the 2179 reflections so measured, 181 were lost due to problems with the paper tape punching equipment. No attempt was made to recover the lost information. Of the remaining 1998 reflections, 1850 were judged to be observed according to the criterion $I \geq 3\sigma(I)$, where $\sigma^2(I) = f^2(t)(T + B) + \sigma_s^2(T - B)^2$, $T$ being the total count and $B$ the estimated background; $f(t)$ is a time-dependent correction factor determined as below. The quantity $\sigma_s^2$ was taken to be $2.5 \times 10^{-4}$, a number which we feel to be a reasonable estimation of the normalized variance of a reflection due to random variations other than counting statistics. Average values of $E$ (0.774) and $E^2 - 1$ (1.05) indicated the structure to be centric. The redundant reflections were averaged, resulting in 1019 "observed" data points.

The intensity of a standard reflection, measured after every 50 reflections, was found to decrease by approximately 5% during the course of data collection. Multiplicative correction factors [$f(t)$] for the data were determined by least-squares fitting a fifth-order polynomial to the intensity measurements. The order of the polynomial was determined from significance tests based on the sum of the squares of the residuals.[8] Corrections were made for the Lorentz and polarization factors. The graphite crystal in the monochromator was assumed to be of perfect mosaicity giving the following form for the polarization factor: $(\cos^2 2\alpha + \cos^2 2\theta)/(1 + \cos^2 2\alpha)$, where $\alpha$ is the angle the beam makes with the monochromator. The absorption corrections were made using the Busing and Levy[9] method using Burnham's[10] program as modified by Larson, Cromer, and Roof.[11] The linear absorption coefficient for Mo K$\alpha$ radiation is

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] Address correspondence to this author.

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TABLE I

FRACTIONAL COORDINATES AND THERMAL PARAMETERS ($\times 10^4$)[a]

|  | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cs | 0.25 | 0.25 | 0.5 | 13.7 (1) | 126.0 (7) | 170.4 (11) | −13.6 (3) | −1.0 (4) | 10.8 (11) |
| Sb | 0.58197 (1) | 0.26733 (3) | 0.53504 (5) | 9.3 (1) | 71.1 (5) | 149.7 (9) | −2.2 (2) | −0.8 (3) | −1.7 (8) |
| F(1) | 0 | 0.0831 (4) | 0.25 | 16 (1) | 107 (6) | 285 (12) | 0 | 47 (5) | 0 |
| F(2) | 0.8682 (1) | 0.0240 (3) | 0.3062 (4) | 16 (1) | 121 (4) | 178 (7) | −26 (2) | 4 (3) | −63 (8) |
| F(3) | 0.4190 (1) | 0.1182 (3) | 0.6715 (4) | 27 (1) | 147 (5) | 252 (8) | −14 (3) | 15 (4) | −154 (10) |
| F(4) | 0.3230 (1) | 0.1668 (3) | 0.0052 (4) | 11 (1) | 160 (5) | 315 (9) | −20 (2) | −2 (3) | 59 (11) |

[a] Thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

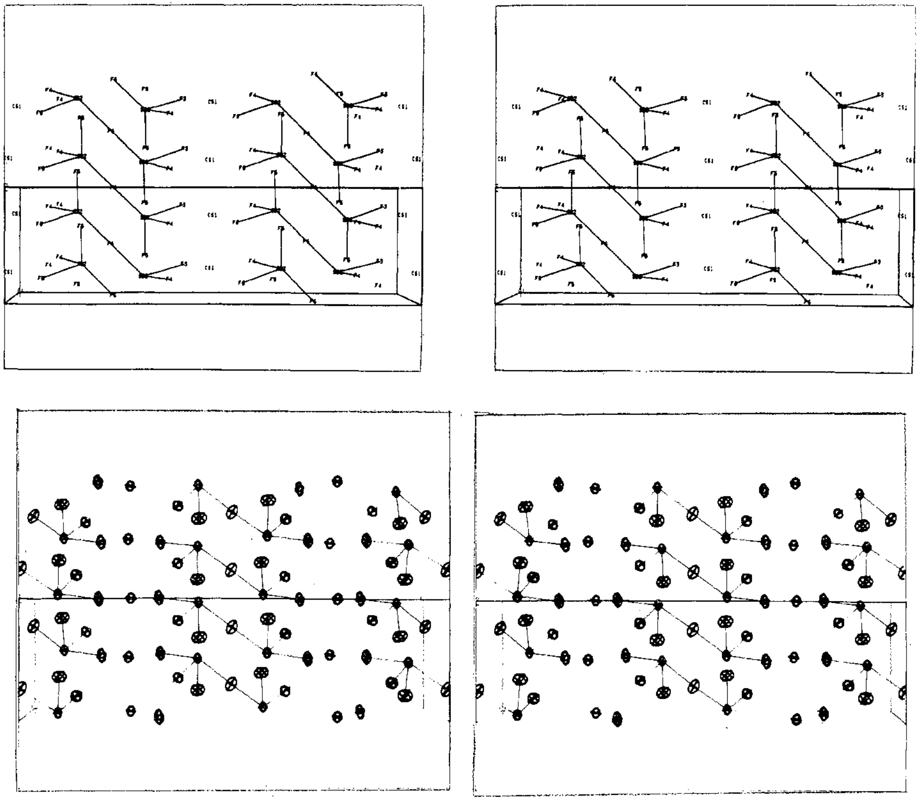

Figure 1.—Stereoview of $CsSb_2F_7$ looking down the *b* axis. The top view is the structure as proposed by Byström and Wilhelmi. The bottom view is the present structure.

123 cm$^{-1}$ and the calculated transmission varied from 0.16 to 0.36.

Structure factors were calculated using the scattering factors of Doyle and Turner[12] for the neutral atoms cesium, antimony, and fluorine with appropriate dispersion corrections[13] for potassium and antimony.

The major features of the Patterson function could be interpreted either in terms of a Cs atom on the twofold axis at the special position 4e at *ca.* 0, 0.22, 0.25 in $C2/c$ and a Sb atom in the general position at *ca.* 0.17, 0.25, 0.75 (as Byström and Wilhelmi did) or with the Cs on the $\bar{1}$ position (4d) and the Sb atom with general coordinates of *ca.* 0.42, 0.27, 0.96. Refinement of the structure with the first choice of coordinates resulted in an $R$ index of 0.40 where $R = \Sigma(|F_o| - |F_c^*|)/\Sigma|F_o|$. A subsequent refinement of the second choice reduced the $R$ index to 0.15. A difference Fourier map phased on the two heavy atoms showed four unique peaks, all of which could be reasonably assigned as fluorines. The least-squares refinement, including fluorines and anisotropic temperature factors for all atoms, converged to an $R$ index of 0.020.

Refinement was carried out using Larson's[14] full-matrix least-squares program. The function minimized was $\Sigma w_i(|F_o| - |F_c^*|)^2$, where $w_i$ is the weight defined as $1/\sigma^2(F_o)$ and

$$F_c^* = kF_c\left\{1 + gLp\left[\frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2}\right]F_c^2\right\}^{-1/2}$$

in which $k$ is a scale constant, $Lp$ is the Lorentz-polarization factor, $g$ is the extinction coefficient,[15,16] and $F_c$ is the structure factor calculated in the usual way.

The structure refined to a Hamilton's $R_H$ index, $R_H = (\Sigma w_i \cdot ||F_o| - F_c^*|^2/\Sigma w_i|F_o|^2)^{1/2}$, of 0.026 with all atoms anisotropic and an extinction correction. The $R_H$ index with only the heavy atoms anisotropic was 0.038 and with no extinction correction was 0.038. The hypothesis that the light atoms vibrate isotropically can thus be rejected at the 0.005 confidence level as can the hypothesis that extinction is not present. Parameter shifts in the last refinement were less than $0.001\sigma$ for all parameters. The final difference Fourier map showed residuals near the heavy-atom position ranging in value from −0.5 to +1.2 e$^-$/Å$^3$; the largest residuals elsewhere were *ca.* 0.5 e$^-$/Å$^3$ with $\sigma(\rho)$ = 0.2 e$^-$/Å$^3$ elsewhere. The final parameters are given in Table I.[17]

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(12) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).

(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(14) A. C. Larson, unpublished programs.

(15) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967).

(16) A. C. Larson, *ibid.*, **23**, 664 (1967).

(17) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

## Discussion

As can be seen in Figure 1, the structure consists of layers of $Sb_2F_7^-$ dimers separated by layers of $Cs^+$ ions. Also shown is the structure as proposed by Byström and Wilhelmi. Comparison of the two structures shows the metric relationships between the heavy atoms to be approximately the same, but the fluorine positions are grossly different. Table II shows the distances for cesium coordination.

TABLE II
DISTANCES FOR THE CESIUM COORDINATION (Å)[a]

| | | | |
|---|---|---|---|
| Cs–F(2) | 3.153 | Cs–F′(4) | 3.208 |
| Cs–F′(2) | 3.247 | Cs–F″(4) | 3.161 |
| Cs–F(4) | 3.195 | | |

[a] Least-squares errors are 0.002 Å.

Figure 2 shows the distances and angles in the $Sb_2F_7^-$ ion. The idealized geometry of the ion can be described as two trigonal bipyramids joined by an axial corner. The lone pairs of electrons are apparently contained in the equatorial plane. The closest nonbonded Sb–F distance is 2.77 Å.

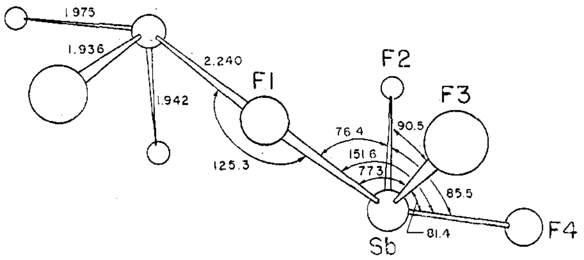

Figure 2.—Distances and angles in the $Sb_2F_7^-$ ion.

The $F_{ax}$–Sb–$F_{ax}$ angle of 151.6° and the $F_{eq}$–Sb–$F_{eq}$ angle of 90.5° are both drastically distorted from the values for an ideal trigonal bipyramid in such a way as to minimize lone-pair–bond repulsions, Sb–$F_{ax}$ is significantly longer than the average Sb–$F_{eq}$ distance, and the overall conformation of the ion minimizes lone-pair–lone-pair repulsions. All of these observations are in accord with the electron-pair repulsion theory of Gillespie and Nyholm,[18,19] and indeed these features of the geometry have been predicted by others in various attempts to reinterpret the results by Byström and Wilhelmi. The bridging fluorine on the crystallographic twofold axis has an included angle of 125.3° between the antimony atoms at 2.240 Å. The lack of an obvious stereochemical reason for the bent fluorine bridge supports the thesis that these bridges tend to be bent in the absence of $\pi$ bonding.[20] The nonlinear angle about the fluorine can be rationalized either in the MO scheme in terms of a three-center two-electron bond in which the fluorine orbitals involved are primarily p orbitals or in the valence-bond scheme in terms of the resonance structures $[F_3Sb{:}F]^-SbF_3 \rightleftarrows F_3Sb[F{:}SbF_3]^-$ again in which p orbitals on the fluorines are the chief participants.

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CONTRIBUTION FROM THE ANORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT, GÖTTINGEN, GERMANY

# The Crystal Structure of Tellurium Tetrachloride

BY BRUNO BUSS AND BERNT KREBS*

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The crystal structure of tellurium tetrachloride has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $C2/c$ of the monoclinic system with $a$ = 17.076, $b$ = 10.404, $c$ = 15.252 Å, $\beta$ = 116.82°. The unit cell contains 16 formula units of $TeCl_4$. Calculated and observed densities are 2.959 and 2.96 g/cm$^3$, respectively. The data have been collected for a twinned crystal and have been reduced according to the kind of twinning. The structure has been refined by least-squares methods to a final $R$ factor of 0.061 for 2948 nonequivalent reflections. The structure consists of isolated tetramers, $Te_4Cl_{16}$, which have a cubane-like structure with approximate $T_d$ symmetry and with Te and Cl atoms occupying alternating corners of the cubane skeleton. Every Te atom has three neighboring terminal Cl atoms with an average distance of 2.311 Å. With these it is forming an equilateral trigonal pyramid. The coordination of the Te is completed to a distorted octahedron by three bridging chlorine atoms with much longer Te–Cl bond lengths (average 2.929 Å). In the polar limiting case the structure may be described, in a rough approximation, as an arrangement of $TeCl_3^+$ ions with nearly $C_{3v}$ symmetry and of $Cl^-$ ions. The structure data suggest possible concentration of the nonbonding Te electrons toward the center of the cubane skeleton. From the unexpected crystal structure some unexplained properties of solid tellurium(IV) chloride (correctly formulated tetra-$\mu_3$-chloro-tetrakis[trichlorotellurium(IV)]) can be understood.

## Introduction

In the last few years a large number of papers on possible structures of the solid selenium and tellurium tetrachlorides and -bromides have been published, but in the absence of direct X-ray structure determinations it was impossible to give an unequivocal interpretation of the partly controversial results.

According to an early electron diffraction investigation[1] tellurium tetrachloride is monomeric in the vapor

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