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Structures of the MF_5E Type. The Crystal Structure of Ammonium Pentafluoroantimonate(III)[1]

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The crystal structure of ammonium pentafluoroantimonate(III), $(NH_4)_2SbF_5$, has been determined by a three-dimensional single crystal X-ray diffractometer study. A full-matrix least-squares refinement using 505 observed reflections resulted in a final unweighted R value of 2.4%. The structure was refined in the orthorhombic space group *Cmcm*. The cell constants are $a = 6.497$ (3), $b = 14.162$ (5), and $c = 6.772$ (2) Å with $d_{\text{calcd}} = 2.69$ g/cm^3 for $Z = 4$ and $d_{\text{measd}} = 2.68$ g/cm^3. The structure consists of isolated SbF_5^{2-} ions which approximate a square pyramid. The apical Sb–F distance is 1.916 (4) Å; the average basal distance is 2.075 (2) Å. The geometry of the SbF_5^{2-} ion is compared with that of other isoelectronic ions in the series MF_5E, where M = Sb, Te, I, and Xe and E is a stereochemically active lone pair of electrons.

Introduction

Considerable interest has recently been shown in the structures and packing characteristics of ions in the isoelectronic series MF_5E where M = Sb,[2] Te,[3,4] I,[5] and Xe[6–8] and E is a stereochemically active lone pair of electrons. This interest has been stimulated partially because of the existence of the XeF_5^+ ion in the crystal structures of XeF_6[7,8] and partially because accurate structural information on the series shows interesting trends in the relationship between F–F and F–E interactions.

The structure of the SbF_5^{2-} ion has previously been determined in the compound K_2SbF_5[2] which is isotypic with $(NH_4)_2SbF_5$. This study was based on partial sets of film data and the atomic positions were determined by two-dimensional Fourier syntheses. The results of a subsequent least-squares refinement of this data are shown in Table II. The refinement converged to an F(axial)–Sb–F(equatorial) angle of 83 (2)° and, furthermore, the axial and equatorial distances could not be said to be significantly different. Both of these observations would indicate that F–E interactions are less important relative to F–F interactions in this ion than they are in the remainder of the series. Such a result contradicts the structural trends established for the remainder of the series. For these reasons a more accurate X-ray study on a compound containing the SbF_5^{2-} ion was deemed worthwhile.

Experimental Section

Crystals of a quality and size suitable for X-ray studies were obtained by recrystallization of a commercial sample of $(NH_4)_2SbF_5$ from anhydrous HF. A crystal of dimensions 0.104 × 0.046 × 0.046 mm was selected for the study and was mounted on a glass fiber approximately along the a axis. The developed faces were of the prism {011} and of the pinacoids {010} and {100}. Precession photographs (Mo Kα radiation) showed orthorhombic symmetry, with systematic absences hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, indicating possible space groups *Cmcm*, *C2cm*, and *Cmc*2$_1$. After alignment of the crystal on an automated Picker diffractometer, 12 reflections with $2\theta \geq 50°$ were centered using the Mo Kα_1 component of the incident X-ray beam (takeoff angle of 2°, λ 0.70930 Å); these reflections were used in a least-squares refinement of the cell parameters and the orientation matrix. The room-temperature (23°) cell constants and their standard deviations are $a = 6.497$ (3), $b = 14.162$ (5), and $c = 6.772$ (2) Å. For $Z = 4$, $d_{\text{calcd}} = 2.69$ g/cm^3. The density measured by flotation methods was 2.68 g/cm^3.

Intensities were collected using Mo Kα radiation, a single-crystal graphite monochromator (002 plane), and takeoff angle of 5°. The count was taken using a θ–2θ scan over a 2θ range of 2° in 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 measured for all hkl and $\bar{h}kl$ planes for which $2\theta < 60°$, resulting in 976 measurements. The redundant (assuming *Cmcm*) reflections were averaged, resulting in 505 reflections 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, B the estimated background, and $f(t)$ a time dependent correction factor determined as described below. The quantity σ_s^2 was taken to be 2.5×10^{-4}, a number which we feel to be a reasonable estimate of the normalized variance of a reflection due to random variations other than counting statistics. The R index estimated by comparison of equivalent F's was 0.015.

The intensity of a standard reflection, measured after every 50 reflections, was found to decrease by approximately 7% during the course of data collection. Multiplicative correction factors $[f(t)]$ for the data were determined by fitting a polynomial to the intensity measurements of the standard reflection. The order of the polynomial was determined from significance tests based on the sum of the squares of the residuals.[9] 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 α is the angle the beam makes with the monochromator. The absorption corrections were made by the Busing and Levy method using Burnham's program as modified by Larson, Cromer, and Roof.[10] The linear absorption coefficient for Mo Kα radiation is 45 cm^{-1} and the calculated transmission varied from 0.77 to 0.88.

Structure factors were calculated using the scattering factors of Doyle and Turner[11] for the neutral atoms antimony, fluorine, and nitrogen and the dispersion terms of Cromer and Liberman;[12] *i.e.*, Sb, $\Delta f' = -0.816$ and $\Delta f'' = 1.546$.

Refinement of the Structure

Refinement was carried out, using all observed reflections, by full-matrix least-squares techniques[13] using Byström and Wil-

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

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TABLE I

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	0	0.4364 (5)	$^1/_4$	138 (12)	49 (3)	131 (11)	0	0	0
N(2)	0	0.755 (5)	$^1/_4$	161 (13)	38 (3)	192 (14)	0	0	0
Sb	0	0.08854 (3)	$^1/_4$	100 (1)	26 (2)	116 (1)	0	0	0
F(1)	0	0.2238 (3)	$^1/_4$	247 (12)	27 (2)	248 (11)	0	0	0
F(2)	0.2256 (5)	0.1155 (2)	0.0406 (5)	405 (10)	72 (2)	370 (9)	−53 (7)	552 (17)	−62 (7)

[a] Thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ and are multiplied by 10^4.

helmi's structure as a starting model for the nonhydrogen positions. The function minimized was $\Sigma w(|F_o| - |F_c^*|)^2$ where w is the weight defined as $1/\sigma^2(F_o)$ and

$$F_c^* = kF_c/\left\{1 + 2g\left(\frac{e^2}{mc^2V}\right)^2 Lp \times \left[\frac{(1 + \cos^2 2\alpha)(\cos^2 2\alpha + \cos^4 2\theta)}{(\cos^2 2\alpha + \cos^2 2\theta)^2}\right]^2 F_c^2\right\}^{1/4}$$

in which k is a scale constant, Lp is the Lorentz-polarization factor, g is the extinction coefficient,[14] V is the unit cell volume, and F_c is the structure factor calculated in the usual way.

The structure was refined in the centric space group *Cmcm* to an unweighted R value, $R = \Sigma||F_o| - |F_c^*||/\Sigma|F_o|$, of 0.058 with isotropic temperature factors for all nonhydrogen positions. A difference Fourier map calculated at this point could not be interpreted in terms of meaningful hydrogen positions.

Further refinement with anisotropic temperature factors for all nonhydrogen atoms reduced the R value to 0.024.[15] Hamilton's significance tests reject the hypotheses (1) that extinction is not present, (2) that only the heavy atoms vibrate anisotropically, and (3) that our model is not significantly different from that of Byström and Wilhelmi, all at better than the 0.005 confidence level.

Because of the deviation of the SbF_5^{2-} ion from C_{4v} symmetry (see Discussion), the structure was refined in both $Cmc2_1$ and $C2cm$ starting from a model which was distorted from the structure in *Cmcm* in such a way as to destroy one of the mirror planes (site symmetry of the SbF_5^{2-} ion is *mm* in *Cmcm*). Neither refinement resulted in a significantly improved R value.

A final difference Fourier map showed residuals centered around the antimony atom positions; these ranged from −0.3 to +0.8 e/Å^3. Residuals elsewhere in the map ranged from −0.2 to +0.6 e/Å^3 with $\sigma(\rho)$ = 0.1 e/Å^3. These residuals are centered about F(2) and may be due to the failure of the model adequately to describe the thermal motion.

Discussion

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) IN $(NH_4)_2SbF_5$

Sb–F(1)	1.916 (4)	2.00 (9)[a]
Sb–F(2)	2.075 (3)	2.04 (9)[a]
F(1)–F(2)	2.552 (4)	
F(2)–F′(2)	2.836 (6)	
F(2)–F″(2)	2.932 (6)	
F(1)–Sb–F(2)	79.4 (1)	83 (2)[a]
F(2)–Sb–F′(2)	86.2 (2)	
F(2)–Sb–F″(2)	89.9 (2)	
N(1)–F(2)	2.755 (3)	
N(2)–F(2)	3.016 (5)	

[a] Distances and angles resulting from a least-squares refinement of the Byström and Wilhelmi data for K_2SbF_5.[2]

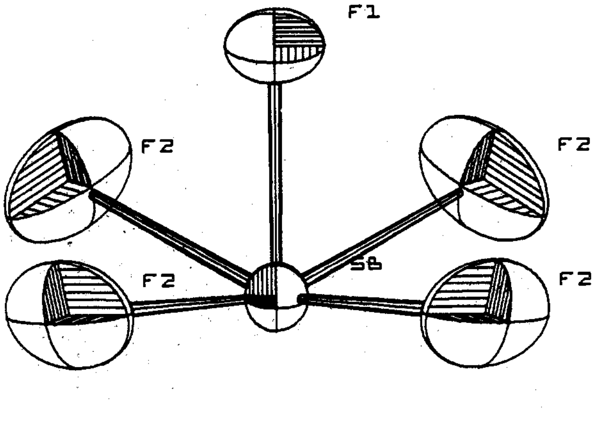

Figure 1.—Projection of the SbF_5^{2-} ion.

Table II lists pertinent interatomic distances and angles. The structure contains isolated pentafluoroantimonate ions whose geometry is approximately square pyramidal (see Figure 1). The crystallographic symmetry of the ion is *mm* with the Sb atom 0.382 Å below the plane of the basal fluorine atoms.

N(1) is surrounded by four fluorine atoms at a distance of 2.755 (3) Å and one fluorine at a distance of 3.011 (8) Å forming a rectangular pyramid. It may be inferred from inspection of the packing diagram (Figure 2) that two lone pairs of electrons occupy coordination points opposite the apical fluorine atom. The coordination of N(2) consists of two sets of four fluorine atoms at distances of 3.016 (5) and 3.062 (5) Å to form a distorted square prism. The lone pair on the antimony atom points at the larger of the two faces having *mm* symmetry. The "hole" in the structure which apparently contains the lone pair of electrons is surrounded in one plane by an antimony atom and three nitrogen atoms. In a perpendicular plane are four fluorine atoms.

The structure of the SbF_5^{2-} ion is compared to that of the other existing members of the series in Table III.

TABLE III

DISTANCES (Å) AND ANGLES (DEG) IN IONS AND MOLECULES ISOELECTRONIC WITH SbF_5^{2-} AVERAGED TO C_{4v} SYMMETRY FOR COMPARISON

	SbF_5^{2-}	TeF_5^{-} [a]	IF_5[b]	XeF_5^{+} [c]
M–F(1)	1.916 (4)	1.862 (4)	1.817 (10)	1.81 (8)
M–F(2)	2.075 (3)	1.952 (4)[d]	1.873 (5)	1.88 (8)
F(1)–F(2)	2.552 (4)	2.424 (6)[d]	2.395 (9)	
F(2)–F(2)	2.884[d]	2.708 (7)[d]	2.615 (8)	
F(1)–M–F(2)	79.4 (1)	78.8 (2)[d]	80.9 (2)	80 (4)[d]
F(2)–M–F(2)	88.0[d]	87.8 (2)[d]	88.6 (2)	88 (4)[d]

[a] Reference 4. [b] Reference 5. [c] Reference 6. [d] Average values—errors are largest of the individual values.

It is now well-established that the axial fluorine distance is significantly shorter in this isoelectronic series than is the basal fluorine distance. This observation can be adequately rationalized in terms of the Gillespie and

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[14] (a) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); (b) A. C. Larson, *ibid.*, **23**, 664 (1967).

[15] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2322. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

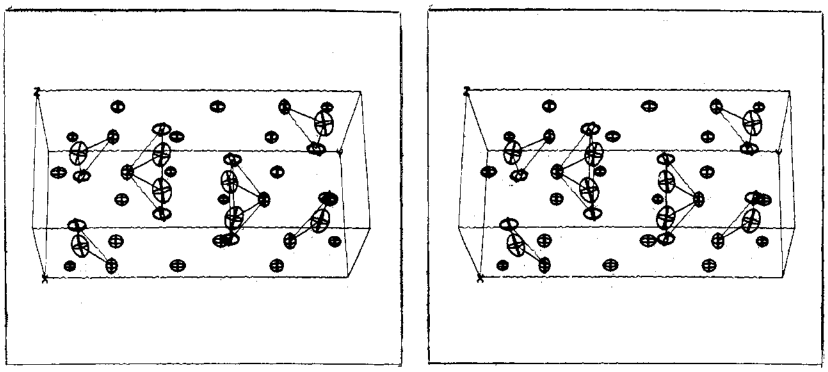

Figure 2.—Stereoview of the unit cell contents.

Nyholm theory.[16,17] The point to be made by Table III is that the equatorial M–F_e distance decreases by 0.20 Å as one proceeds to the right in the table while the axial M–F_a distance decreases by only 0.10 Å and the F_e–Sb–F_a angle remains about the same. (The results for XeF_5^+ are not included in this discussion because of the relatively large errors associated with that structure.) The decrease of 0.10 Å for the axial distance is approximately equal to the contraction of the ionic radius for the series Sb^{5+}, Te^{6+}, and I^{7+} (these radii are 0.62, 0.56, and 0.50 Å[18]) in which the stereochemically active lone pair of electrons is not present. These observations can be rationalized by invoking a decrease in the importance of lone pair–fluorine bond interactions relative to fluorine bond–fluorine bond interactions as one proceeds to the right in the periodic table.

This behavior can be accounted for in a pictorial way by consideration of a simple molecular orbital scheme in which the basis set is comprised only of the *n*s and *n*p orbitals on the central atom and σp orbitals on each of the fluorines. Assuming idealized C_{4v} symmetry, the highest occupied orbital has a_1 symmetry, is antibonding, and is comprised primarily of the *n*s and np_z central atom. In such an orbital the electrons are "localized" in a region opposite the axial fluorine and below the equatorial plane. This localization is maximized when s and p_z participate equally in the orbital. As one proceeds to the right in the periodic table, the *n*s orbital is more tightly bound, thereby decreasing its participation in the a_1 antibonding orbital and simultaneously decreasing the localization in this region. A similar situation exists in simple MO calculations on XeF_6 where O_h symmetry is predicted only if the 5s orbital is omitted from the calculation;[19] *i.e.*, the s orbital is apparently important in accounting both for the distortion in XeF_6 and for the trends in F–E interactions under discussion here.

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