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D. D. Gibler, C. J. Adams, M. Fischer
Allan Zalkin and Neil Bartlett

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Structural Studies of Trifluorosulfur(IV)-yl, [SF$_3$]$^+$, Salts including the Crystal Structure of [SF$_3$]$^+$[BF$_4$]$^-$

by

D. D. Gibler, C. J. Adams, M. Fischer
Allan Zalkin and Neil Bartlett

ABSTRACT

The crystal structure of trifluorosulfur(IV)-yl tetrafluoroborate, [SF$_3$]$^+$[BF$_4$]$^-$ has been determined from three dimensional X-ray data. The compound is orthorhombic, $a = 9.599(3)$, $b = 5.755(3)$, $c = 8.974(3)$ Å, $V = 495.7$ Å$^3$, $z = 4$, $\rho_c = 2.36$ g cm$^{-3}$. Refinement has proceeded satisfactorily in the space group Pnma, with a final conventional $R$ factor of 0.043 for 700 reflections. The structure consists of discrete SF$_3$ and BF$_4$ groups. The SF$_3$ has site symmetry $C_s$ with interatomic distances S-F1(twice) = 1.495(2) and S-F2 = 1.499(2) Å and bond angles F1-S-F1 = 97.62(7) and F2-S-F1(twice) = 97.39(12)$^\circ$ and effectively $C_{3v}$ symmetry. The BF$_4$ group is slightly distorted from tetrahedral symmetry with B-F3 = 1.397(4), B-F4 = 1.393(5), B-F5(twice) = 1.377(3) Å, F4-B-F5 = 108.58(17) F3-B-F4 = 107.63(25), F5-B-F5 = 111.37(14) and F3-B-F5(twice) = 110.29(16)$^\circ$. Each SF$_3$ group is so oriented that the sulfur atom makes short contacts of 2.624(2)(twice) and 2.593(3) Å with fluorine atoms of the three closest BF$_4$ groups. Each sulfur atom is in a trigonally distorted octahedral...
environment of fluorine atoms. The entire arrangement is consistent with close packing of \( \text{C}_3 \text{V} \) symmetry cations with tetrahedral anions. The bond length in the cation is the shortest observed hitherto in any sulfur fluoride and is \( \sim 0.07 \) Å shorter than the P-F bond in PF\(_3\). The bond angle in SF\(_3^+\) is not significantly different from that observed in PF\(_3\).

\[ \text{[SF}_3^+\text{][AsF}_6^-] \] is orthorhombic with \( a = 20.375(3), b = 8.508(3), c = 11.224(3) \) Å, \( V = 1945.7 \) Å\(^3\), \( z = 12, d_c = 2.65 \) g cm\(^{-3}\). The diffraction symmetry \( \text{mC.c} \) indicates \( \text{Cmc2}_1, \text{C}2\text{cm} \) and \( \text{Cmcm} \) as possible space groups.

The arsenic and sulfur atoms are essentially in a nickel arsenide lattice with each arsenic atom approximately octahedrally surrounded by sulfur atoms and each sulfur lying approximately at the center of a trigonal prism defined by arsenic atoms. The poor quality and limited extent of the intensity data did not permit significant placement of the many fluorine atoms in the asymmetric unit. Simple valence force field calculations for the SF\(_3^+\) ion yield the following force constants: \( f_r, 5.67; f_r', 0.19; f_{\alpha}/r^2, 0.85; f_{\alpha}/r^2, 0.12 \) mdyne Å\(^{-1}\).

**INTRODUCTION**

Many of the non-metal fluorides interact with strong fluoride ion acceptors, such as BF\(_3\) and the metal pentafluorides, to form adducts. Work in these laboratories has indicated that such adducts of the xenon and iodine fluorides may be adequately formulated as salts, e.g.,

\[ \text{[XeF]}^+\text{[RuF}_6^-], \text{[Xe}_2\text{F}_3]^+\text{[AsF}_6^-], \text{[XeF}_3]^+\text{[RuF}_6^-], \text{[IF}_4]^+\text{[SbF}_6^-], \text{[IF}_6]^+\text{[AsF}_6^-]. \]

A simple example, which appeared to belong to this class was the 1:1 SF\(_4\)·BF\(_3\) adduct, first reported (along with other SF\(_4\), SeF\(_4\), and TeF\(_4\).
adducts) by Bartlett and Robinson. The $\text{SF}_4 \cdot \text{BF}_3$ adduct has attracted considerable attention. Bartlett and Robinson had initially proposed that the compound might be a Lewis adduct, but their later finding, that the $\text{SF}_4 \cdot \text{SbF}_5$ adduct possesses a primitive cubic lattice, led them to favor a salt formulation, involving the $\text{SF}_3^+$ ion, for all of the $\text{SF}_4$ adducts. More convincing experimental evidence (including infrared and conductivity studies) for salt formulations was given by Seel and Detmer. Muettterties and his coworkers, while admitting the validity of an ionic formulation, also allowed, on the basis of solution-nmr studies, that the $\text{SF}_4 \cdot \text{BF}_3$ adduct could be a fluorine-bridged dimer or polymer. Cotton and George reviewed theoretical considerations suggesting an ionic formulation. More recently from vibrational spectroscopic studies, Gillespie and his coworkers concluded that the $\text{SF}_4$ adducts with $\text{BF}_3$, $\text{AsF}_5$, and $\text{SbF}_5$ were essentially $\text{SF}_3^+$ salts; however, they interpreted deviations of the observed spectra from the idealized behavior in terms of fluorine bridging between the oppositely charged species. Fluorine bridging between the oppositely charged ions is indicated in the structures of the $\text{SeF}_4$ adducts, $\text{SeF}_4 \cdot \text{NbF}_5$ and $\text{SeF}_4 \cdot 2\text{NbF}_5$ reported by Edwards and his coworkers. Although the structures are suggestive of salt formulations ($[\text{SeF}_3]^+ [\text{NbF}_6]^-$ and $[\text{SeF}_3]^+ [\text{Nb}_2\text{F}_{11}]^-$ respectively), each cation has 3 anion contacts at $< 2.5 \, \text{Å}$. These short fluorine-bridge contacts may indicate some covalency (multicenter bonding), as Edwards and his coworkers have suggested. Indeed, Bartlett and Robinson had argued that fluorine bridging might be more important in the $\text{SeF}_4$ adducts, than in those of $\text{SF}_4$, since $\text{SeF}_4$ is superior to $\text{SF}_4$ as a fluoride ion acceptor; also the higher fusion temperatures of the $\text{SF}_4$ adducts compared to their $\text{SeF}_4$ relatives, suggested...
greater ionicity in the SF$_4$ compounds.

Full crystallographic studies of the SF$_4$ adducts were clearly of interest.

Apart from the limited information provided by the powder data of SF$_4$·MF$_5$ compounds ($M = \text{Sb, Os, Ir, Ru}$), the only other crystallographic data on the SF$_4$ adducts, at the outset of this work, was the space group information provided by Calvert and his coworkers from single crystal studies of SF$_4$·BF$_3$. Although the latter workers suggested that the SF$_4$·BF$_3$ structure might be the anti NH$_4$IO$_3$ structure they did not undertake a complete analysis.

**EXPERIMENTAL**

**Crystal Preparation.** - The adduct SF$_4$·BF$_3$ was prepared by co-condensation of SF$_4$ (excess) and BF$_3$ in a Monel can provided with a teflon-gasketed lid. Sulfur tetrafluoride was obtained from Ozark-Mahoning Co., Tulsa, Okla., and BF$_3$ from Matheson Co., Inc., East Rutherford, N.J. Both were used without purification. The colorless solid was transferred to quartz capillaries in a Vacuum Atmospheres Corp. Dri-Lab with a nitrogen atmosphere. The capillaries were sealed by drawing down in a small flame. Crystals were grown by sublimation, by establishing small temperature gradients in the capillaries at ~ 60°. Most of the crystals grown by this technique proved to be twinned when examined under the polarizing microscope. Even crystals which appeared to be satisfactory under microscopic examination showed poor mosaic quality when examined on the diffractometer. Omega scans of representative diffraction peaks from the crystal finally chosen for data collection revealed a major peak with two satellites. The satellites contributed ~ 10% towards the total...
intensity for the most unfavorable of several reflections scanned. The crystal was roughly rectilinear with dimensions .4 x .2 x .2 mm.

The SF₄·AsF₅ adduct was also investigated and was prepared by co-condensing SF₄ (excess) and AsF₅, in a Monel can fitted with a teflon-gasketed lid, warming to ambient temperature and removing excess SF₄ under vacuum. Single crystals were grown by sublimation in quartz capillaries. Two crystals were indexed and a complete set of intensity data was gathered on each. No obvious systematic discrepancies were observed between the two data sets.

Crystal Data.- SBF₇ (mol wt 265.56) is orthorhombic with a = 9.599(3), b = 5.755(3), c = 8.974(3) Å, V = 495.8 Å³, z = 4, d₀ = 2.34 g cm⁻³ and F(000) = 336.52. The unit cell volume satisfies Zachariason's criterion for close-packed fluoride lattices, since the effective volume per fluorine atom is 17.7 Å³. Single crystal photographs confirmed the diffraction symmetry found for SF₄·BF₃ by Calvert et al. The structure was successfully refined in the centrosymmetric space group Pnma.

SAsF₉ (mol wt 277.89) is orthorhombic with a = 20.375(3), b = 8.508(3), c = 11.224(3) Å, V = 1945.7 Å³, z = 12, d₀ = 2.84 g cm⁻³ and F(000) = 781.6. The effective volume per fluoride ion is 18 Å³. Single crystal precession photographs were obtained for the zero, first, second and third layers along each of the principle axes. Systematic absences noted were: hkl, h + k = 2n; h0l, l = 2n which is consistent with the space groups Cmc2₁, C2cm, and Cmcm.

X-ray Measurements, SF₄·BF₃.- Diffraction data were collected on a Picker automatic four circle diffractometer equipped with a fine focus Mo anode tube. As previously noted, the omega scans of the crystal were not entirely
satisfactory. Accurate cell dimensions were obtained by determining the 
2θ angle for the MoKa peak of the reflection of the highest angle 
observable along each of the principal axes. Intensity data were collected 
by the θ-2θ scan technique at a scan rate of one degree per minute. The 
poor mosaic quality of the crystal required a scan width of two 
degrees. Background counts were offset from the scan limits by 0.5 
degrees, and each count lasted 10 seconds. The radiation was monochromatized 
with a graphite crystal (2θ = 11.8°). Automatic attenuators were inserted 
when the beam intensity exceeded 10,000 counts per second. Three standards 
were checked every one hundred reflections.

The data were corrected for Lorentz and polarization effects. The 
net intensity was calculated from

\[ I = C - (B_1 + B_2)(T_c/2T_b) \]

in which \( C \) is the total recorded counts in scan time \( T_c \) and \( B_1 \) and \( B_2 \) are background counts for time \( T_b \) each. The standard deviation of \( I \) is

\[ \sigma(I) = \sqrt{[C + (T_c/2T_b)^2(B_1 + B_2) + (qI)^2]}^{1/2} \]

in which \( q \) is an arbitrary factor of 0.06 used to prevent the relative 
error for large counts becoming unrealistically small. The standard 
development used for the average of \( N \) reflections was

\[ \sigma_{\text{AVE}} = \left( \frac{1}{N} \sum_{i=1}^{N} \sqrt[4]{\sigma(I)^2} \right)^{1/2} \]

unless \( \sigma_{\text{ave}} \) is less than the scatter of the \( N \) reflections in which case the 
formula applied was

\[ \sigma(I)_{\text{AVE}} = \left( \frac{1}{n} \sum_{i=1}^{N} \Delta_i^2 \right)^{1/2}/(n - 1) \]

in which \( \Delta_i \) is the difference between the average of \( n \) reflections and
reflection i.

The standard deviation of the structure factor, by the method of finite differences is taken as
\[ \sigma(F) = F_o - \left[ F_o^2 - S \sigma(I)/Lp \right]^{\frac{1}{2}} \]
in which \( S \) is the scaling factor in the equation
\[ F_o = \left( \frac{SI}{Lp} \right)^{\frac{1}{2}} \]
For cases in which \( I \leq \sigma(I) \), \( \sigma(F) = \left[ 3\sigma(I)/Lp \right]^{\frac{1}{2}} \) in which \( L \) and \( p \) are the Lorentz and polarization corrections. The least squares program used in the structure refinements minimizes the function \( R^2 \)
\[ R^2 = \sum w(\Delta F)^2 / \sum wF_o^2 \]
in which \( F_o \) and \( F_c \) are observed and calculated structure factors and \( \Delta F \) is their difference. The weighting factor \( w \) is \( 1/[\sigma(F)]^2 \) except that it has been arbitrarily set to zero for cases in which \( I \leq 2\sigma(I) \). Scattering factors for neutral sulfur, boron, and fluorine were used. The anisotropic temperature factor has the form \( \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hl - 2\beta_{13}hk - 2\beta_{23}kl) \). The \( B_{ij} \) values reported are related to the Betas in the above expression:
\[ B_{ij} = \frac{4\sigma_{ij}}{a^*_i a^*_j} \]
in which \( a^*_i \) is the \( i^{th} \) reciprocal cell length.

A complete set of \(-hkl\) reflections was collected to a 20 of 65° and a portion of the \( h-k-l \) set also. A sorted and averaged set of 980 unique reflections was obtained from 1240 intensity measurements. Of these 700 were given non-zero weighting in the least-squares refinement.

Structure Refinement.- A Patterson synthesis revealed the position of the
sulfur atom but the least-squares refinement, with the sulfur atom alone, gave $R = 0.50$ ($R = \Sigma |F_o - F_c|/\Sigma F_o$). We were still not certain of the space group at this point and so ran WILSON\textsuperscript{19} to check statistical inequalities. These were not conclusive but indicated strongly that Pnma (No. 62 in the International Tables), the centric group, was correct. A set of E values produced by this program were subsequently used in MULTAN\textsuperscript{19}, a recently developed direct methods program. Two sets of phases generated by the program looked promising and a Fourier synthesis was produced from each, neither of which indicated a full structure. Several trial structures, indicated by these Fourier syntheses, were refined by least-squares. The best refinement $R = 0.43$ was achieved using the sulfur (four fold) position indicated by the Patterson synthesis, along with an eight-fold set and a four-fold set of fluorine atoms. A Fourier synthesis, produced with the phases generated by this refinement, revealed that the four-fold fluorine atom set was misplaced, but the positions of the other atoms were clearly indicated. Subsequent isotropic refinement gave $R = 0.10$ and incorporation of anisotropic temperature factors, for all atoms, reduced $R$ to 0.043. The largest residual density revealed by a difference Fourier at this point was 0.96 e/Å\textsuperscript{3}, near the S atom position. The positional and thermal parameters and the average root-mean-square displacements from this refinement are reported in Table I. The final value of $R_2 = 0.058$, and $R$ (including zero weighted data) = 0.063. The standard deviation of an observation of unit weight was 1.32. The largest shift of any parameter, divided by the estimated standard deviation on the last cycle, was less than 0.0003\textsuperscript{20}.

A Partial Solution of the Structure SF\textsubscript{3}AsF\textsubscript{6}. A set of single crystal
data was averaged to give 1530 unique reflections of which, however, only 487 proved to be greater than 3σ. The paucity and poor quality of the data may be responsible for our failure to solve this structure. It may be that the 2 crystals we examined may have been twinned although it is also possible that the structure may be disordered.

The Patterson synthesis indicated that the space group C2cm (No. 40 in The International Tables) was unlikely since this requires four-fold sets of As and S atoms to be at \( z = \frac{1}{4}, \frac{3}{4} \) or \( 0, \frac{1}{2} \) and appropriate vectors were not observed. An ordered arrangement in space group Cmc2\(_1\) (No. 36 in The International Tables) and disordered arrangements in Cmcm (No. 63 in The International Tables), were allowable. An ordered arrangement of the sulfur and arsenic atoms, derived from a solution of the Patterson map, refined by least-squares to yield conventional R factor of 0.37. The positional parameters for these atoms are given in Table II. The arsenic and sulfur atom arrangement associated with this solution is essentially that of a nickel arsenide lattice. Each sulfur atom is approximately at the center of a trigonal prismatic arrangement of arsenic atoms and each arsenic atom is approximately at the center of an octahedron of sulfur atoms. Although subsequent Fourier and least-squares calculations, in which all atoms were included, yielded small conventional R factors, it became evident that a chemically significant location of the fluorine atoms was unlikely to result from the available data.

The trigonal prismatic arrangement of the [AsF\(_6\)]\(^-\) ions about the [SF\(_3\)]\(^+\) species suggests that disordering of the cation, equivalent to inversion along the threefold axis, might be a feature of this structure. It should be noted that the [SF\(_3\)]\(^+\)[MF\(_6\)]\(^-\) (M = Sb, Os, Ir) salts\(^{12,14}\) are simple cubic (\( z = 1 \)) and must therefore be appreciably disordered, since
the vibrational spectra show that the \([\text{SF}_3]^+\) has essentially the same character as in \([\text{SF}_3]^+\)\([\text{BF}_4]^-\).

**Raman Spectra.** Raman spectra of the powdered adducts of \(\text{SF}_4 \cdot \text{BF}_3\) and \(\text{SF}_4 \cdot \text{AsF}_5\) were excited at 4880 Å using a 100 m.W C.R.L. argon-ion laser and were recorded with a Cary 83 spectrometer. The Raman spectrum of indene was used for calibration, and the accuracy of the reported frequencies is \(\pm 3\ \text{cm}^{-1}\).

**Spectroscopic Results.** The Raman spectra which we obtained for solid \(\text{SF}_4 \cdot \text{BF}_3\) and \(\text{SF}_4 \cdot \text{AsF}_5\) and our assignments of the lines contained therein (Figure 1) are in essential agreement with those reported by earlier workers; except that we observe an additional weak feature at 711 cm\(^{-1}\) in the spectrum of \(\text{SF}_4 \cdot \text{AsF}_5\). This new feature is attributable to a
fundamental transition in the formally Raman-inactive mode $v_3(t_{1u})$ of the AsF$_6^-$ anion. Using a simple valence force field and the geometry established in this work, the fundamentals of SF$_3^+$ in SF$_4^·$BF$_3$ [$v_1(a_1)$, 938 cm$^{-1}$; $v_2(a_1)$, 530 cm$^{-1}$; $v_3(e)$, 914 cm$^{-1}$; $v_4(e)$, 411 cm$^{-1}$] were analysed to yield the following force constants: $f_r$, 5.67 mdyne Å$^{-1}$; $f_r''$, 0.19 mdyne Å$^{-1}$; $f_{r/r}$, 0.85 mdyne Å$^{-1}$; $f_{a/r}$, 0.12 mdyne Å$^{-1}$.

Description of [SF$_3^+$][BF$_4^-$]. - The atomic arrangement in [SF$_3^+$][BF$_4^-$] is illustrated in Figure 2. The sulfur atoms and the boron atoms lie in mirror planes. Each sulfur atom has three close neighbor fluorine atoms which define an SF$_3$ group, which although of required symmetry $C_3$, has, effectively, symmetry $C_{3v}$, as Figure 3 illustrates. Likewise, although the site symmetry of the group of atoms, defined by each boron atom and its 4 close F atom neighbors, is $C_3$, the BF$_4$ group is approximately tetrahedral. The chemically significant interatomic distances and angles are given in Table III.

Each sulfur atom is approximately equidistant from three fluorine atoms of three different BF$_4$ species, these interatomic distances (or shortest interionic contacts) being 2.624(2) (twice) and 2.593(3) Å. Only 3 of the 4 F atoms of the BF$_4$ species (F3 and F5 (twice)) make these closer approaches to S atoms. The closest approach which the fourth F atom of this species (F4) makes to a S atom is 3.111(5) Å. It should be noted particularly that there is no simple correlation between the closeness of approach of the F atom of the BF$_4$ species to the S atom and the B-F interatomic distance. Thus for F3, which makes the closest approach to a S atom (2.593(3) Å) the B-F3 distance is 1.397(4) Å. This is not significantly different from B-F4 = 1.393(5) Å where S...F$_4^·$ is 3.111(3) Å.
Indeed, the entire arrangement appears to be simply dictated by the closest packing of $C_{3v}$ symmetry SF$_3$ species and tetrahedral BF$_4$ species, the slight angle distortions in the latter being a consequence of the close packing with the SF$_3$ group.

It should be noted that this structure is not the anti-type of the reported $^{16}\text{NH}_4^+\text{IO}_3^-$ as had been supposed by Calvert et al.~10.

**DISCUSSION**

On chemical grounds we can formulate the sulfur species as SF$_3^+$ and the boron species as BF$_4^-$ and furthermore, we can anticipate that the sulfur atom of the SF$_3$ group will be the effective center of positive charge.

Since fluorine atoms are highly electron attracting, they should be neutral if not slightly negative in net charge, even in the SF$_3^+$ ion. On the F atom side of the SF$_3^+$ ion it is therefore reasonable to suppose that the positive charge would be more effectively screened than on the sulfur side. However, the non-bonding valence electron pair of S(IV) will provide appreciable screening on the three-fold axis, if, as might be expected, it occupies a spatially directed orbital (e.g., an sp$^3$ hybrid). Such steric activity of the 'non-bonding pair' suits the arrangement observed in this structure, since the F ligands of the BF$_4^-$ make their close approach, to the sulfur atom, well off the C$_3$ axis, and also avoid the F ligands of the SF$_3^+$ to the maximum extent. The fluorine atom arrangement about each sulfur atom is therefore that of a trigonally distorted octahedron, with three F atoms bound and 3 (of 3 separate BF$_3$ ions) attracted electrostatically.
Although the \( \text{B F}_4^- \) departs slightly from the tetrahedral ideal, the B-F interatomic distances 1.377(3) (twice), 1.393(5) and 1.397(4) (mean 1.396(6)) are not significantly different within the set, and are in excellent agreement with the mean values (uncorrected for librational motion) for \( \text{NaBF}_4 \), \( 1.389 \pm 0.005 \, \text{Å} \) \( \text{KBF}_4 \) (1.386(6)) and \( \text{NH}_4\text{BF}_4 \).

The \( \text{SF}_3^+ \) species is very similar to its isoelectronic relative \( \text{PF}_3 \) (see Table IV). The most striking feature of this resemblance is the equality of the apical angles F-S-F and F-P-F. Presumably the higher nuclear charge of the sulfur atom is responsible for the S-F interatomic distance being 0.07 Å shorter than the P-F distance. The maintenance of constant shape, despite bond length change, appears to be the rule for cation and isoelectronic neutral molecule pairs, as Table IV illustrates. It is not surprising that the non-bonding valence electron pair in the cation should be more contracted, and hence have greater repulsive-interaction effect, than in the neutral molecule, but the preservation of constant shape indicates that the bonding electrons are affected to a like extent.

The full refinement of the crystal structure of \( [\text{SF}_3]^+\text{[BF}_4^-] \) and the partial solution of the structure of \( [\text{SF}_3]^+\text{[AsF}_6^-] \) each show the anion occupying a lattice site of symmetry lower than \( T_d \) and \( O_h \), respectively. The anionic vibrational frequencies of these two compounds lie close to those found for the anions in other salts or in solution, but the spectra clearly show "site effects", viz. the splitting of degenerate fundamentals \( [\nu_2(e_g) \text{ of AsF}_6^-] \) and the breakdown of gross selection rules so that \( \nu_3(t_{1u}) \) of \( \text{AsF}_6^- \) is observed in the Raman spectrum of \( [\text{SF}_3]^+\text{[AsF}_6^-] \), as
are $v_1(a_1)$ and $v_2(e)$ of $\text{BF}_4^-$ in the infrared spectrum of $[\text{SF}_3]^+[\text{BF}_4]^-$. These effects are small, and certainly originate in unit-cell dynamics and in the slight deviation of the ions from structural regularity rather than in extensive interionic fluorine-bridging interactions, as proposed by Gillespie.\textsuperscript{11} We note that comparable "site effects" are seen in the spectra of the alkali metal tetrafluoroborates.\textsuperscript{25} Neither our crystallographic nor spectroscopic studies of the $\text{SF}_4$ adducts reveal the signally deformed anions evident in adducts of $\text{BrF}_3$ with fluoride-acceptors, which are possible caused by fluorine bridging to the strongly polarizing $\text{BrF}_2^+$ cation.

The bond length in the $\text{SF}_3^+$ species is the shortest recorded so far for a S-F bond. This, at least in part, may be attributed to appreciable net positive charge of the sulfur atom, and the low coordination number (hence weaker interligand repulsions). Although the bond in $\text{SF}_3^+$ is even shorter ($\sim 0.05 \, \text{Å}$) than the equatorial bond in $\text{SF}_4$ (1.545 Å) it is dramatically shorter ($\sim 0.15 \, \text{Å}$) than the axial bonds in the latter (1.646 Å).\textsuperscript{27} These findings are in harmony with the view that the axial $\text{SF}_4$ bonds are effectively single-electron bonds, and the equatorial bonds, electron-pair bonds. (Donation of fluoride ion: $\text{SF}_4 \rightarrow \text{SF}_3^+ + \text{F}^-$, generates a cation, in which all bonds are electron pair bonds.) Indeed the bond stretching force constants give further support to these views.

The S-F stretching force constant for $\text{SF}_3^+$ we find to be 5.67 md$^2$Å$^{-1}$, which is comparable to the value of 5.2 md$^2$Å$^{-1}$ for the S-F equatorial stretching force constant of $\text{SF}_4$ and approximately twice the value of 2.8 md$^2$Å$^{-1}$, derived for the axial bonds in that molecule.\textsuperscript{29}
1. N. Bartlett, D. Gibler, and A. Zalkin, to be published.
14. The salts $[\text{SF}_3]^+[\text{MF}_6]^-$ (M = Os, Ir) are simple cubic, both with $a_0 = 5.581 \pm 0.004 \text{ Å}$, $z = 1$, $V = 173.8 \text{ Å}^3$. M. K. Jha, Ph.D. Thesis, University of British Columbia, Canada (1965).
15. $[\text{SF}_3]^+\text{RuF}_6^- \text{ has a tetragonal cell: } a = 5.37 \pm 0.01, c = 5.93 \pm 0.01 \text{ Å}, z = 1, V = 171.5 \text{ Å}^3$, which is related to the cubic cells of $[\text{SF}_3]^+[\text{MF}_6]^-$ (M = Sb, Os, Ir). R. Surfass, Senior Thesis, Princeton University, Princeton, New Jersey (1967).


19. Computer programs used were: WILSON, a Wilson plot and E calculating program of H. S. and M. L. Maddox revised by B. G. DeBoer and A. Zalkin for local use; MULTAN, a program for the automatic solution of crystal structures by Peter Main and Michael M. Woolfson, Dept. of Physics, University of York, York, England, and Gabriel Germain, University of Louvain, Louven, Belgium; ORTEP, Oak Ridge thermal ellipsoid plot program by C. K. Johnson; FORDAP, Fourier plot program of A. Zalkin; LESQ, unpublished least-squares-refinement program of A. Zalkin.

20. 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, A.C.S. Publications, 1155 Sixteenth Street, N.W., Washington, D.C., 20036, by referring to author, title of article, volume and page number. Remit $3.00 for photocopy or $2.00 for micro.


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Table I

FINAL PARAMETERS \([\text{SF}_3]^+[\text{BF}_4]^-

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(B_{xx}(\AA^2))</th>
<th>(B_{xy}(\AA^2))</th>
<th>(B_{xz}(\AA^2))</th>
<th>(B_{yy}(\AA^2))</th>
<th>(B_{yz}(\AA^2))</th>
<th>(B_{yz}(\AA^2))</th>
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<td>.28168(8)</td>
<td>1/4</td>
<td>.11253(10)</td>
<td>2.40(3)</td>
<td>2.80(3)</td>
<td>2.75(3)</td>
<td>.14(3)</td>
<td>.1633</td>
<td></td>
<td></td>
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<tr>
<td>B</td>
<td>.48346(40)</td>
<td>3/4</td>
<td>.17658(44)</td>
<td>2.43(12)</td>
<td>2.74(13)</td>
<td>3.09(15)</td>
<td>.33(11)</td>
<td>.1867</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>.19529(17)</td>
<td>0.0543(31)</td>
<td>.05347(21)</td>
<td>4.35(7)</td>
<td>4.28(7)</td>
<td>4.84(8)</td>
<td>-1.43(6)</td>
<td>.46(6)</td>
<td>-0.88(6)</td>
<td>.2385</td>
</tr>
<tr>
<td>F2</td>
<td>.2248(2)</td>
<td>1/4</td>
<td>.2682(26)</td>
<td>4.06(10)</td>
<td>4.13(10)</td>
<td>3.17(9)</td>
<td>1.31(8)</td>
<td>.2190</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>.628180(23)</td>
<td>3/4</td>
<td>.15984(28)</td>
<td>2.60(8)</td>
<td>4.53(11)</td>
<td>4.09(10)</td>
<td>.35(7)</td>
<td>.2176</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F4</td>
<td>.42490(30)</td>
<td>3/4</td>
<td>.03457(33)</td>
<td>4.31(12)</td>
<td>7.81(18)</td>
<td>4.39(13)</td>
<td>-0.97(10)</td>
<td>.2640</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>.44087(19)</td>
<td>.55238(33)</td>
<td>.25011(21)</td>
<td>4.69(8)</td>
<td>3.78(8)</td>
<td>5.79(10)</td>
<td>-0.49(7)</td>
<td>.81(7)</td>
<td>1.16(7)</td>
<td>.2454</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Average root-mean-square displacement along the principle axes of the thermal ellipsoids (Å).
Table II
SULFUR AND ARSENIC POSITIONAL PARAMETERS
FOR [SF$_3$][AsF$_6$] (CmC2$_1$ - No. 36)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Number</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As1</td>
<td>4</td>
<td>0</td>
<td>-.0177(7)</td>
<td>.0002(3)</td>
</tr>
<tr>
<td>As2</td>
<td>8</td>
<td>.1632(2)</td>
<td>.4922(7)</td>
<td>.4909$^*$</td>
</tr>
<tr>
<td>S1</td>
<td>4</td>
<td>0</td>
<td>.4091(20)</td>
<td>.3138(15)</td>
</tr>
<tr>
<td>S2</td>
<td>8</td>
<td>.3346(3)</td>
<td>.4031(10)</td>
<td>.1773(8)</td>
</tr>
</tbody>
</table>

* fixed value.
Table III
(a).
INTERATOMIC DISTANCES (Å) AND ANGLES (°)

\[ [\text{SF}_3]^+ [\text{BF}_4]^- \]

<table>
<thead>
<tr>
<th></th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-2F1</td>
<td>1.495(2), [1.518]</td>
<td>F3···2F5</td>
</tr>
<tr>
<td>S-F2</td>
<td>1.499(2), [1.514]</td>
<td>F4···2F5</td>
</tr>
<tr>
<td>S···F3</td>
<td>2.593(3)</td>
<td>F5···F5</td>
</tr>
<tr>
<td>S···2F5</td>
<td>2.624(2)</td>
<td>B···2F1</td>
</tr>
<tr>
<td>S···B</td>
<td>3.43(3)</td>
<td>F1-S-F1</td>
</tr>
<tr>
<td>S···F4</td>
<td>3.111(3)</td>
<td>F1-S-F2</td>
</tr>
<tr>
<td>S···2F4</td>
<td>3.265(2)</td>
<td>F3-B-F4</td>
</tr>
<tr>
<td>B-F3</td>
<td>1.397(4), [1.410]</td>
<td>F3-B-F5</td>
</tr>
<tr>
<td>B-F4</td>
<td>1.393(5), [1.428]</td>
<td>F4-B-F5</td>
</tr>
<tr>
<td>B-2F5</td>
<td>1.377(3), [1.404]</td>
<td>F5-B-F5</td>
</tr>
<tr>
<td>F2···2F1</td>
<td>2.249(3)</td>
<td>S···F3-B</td>
</tr>
<tr>
<td>F1···F1</td>
<td>2.250(4)</td>
<td>S···F5-B</td>
</tr>
</tbody>
</table>

(a)

Values in square brackets are thermally corrected distances based on in phase motion of the atoms.
Table IV
SHAPE COMPARISON OF ISOELECTRONIC CATION AND MOLECULE PAIRS

<table>
<thead>
<tr>
<th>Cation</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₃⁺ (b)</td>
<td>PF₃⁻ (a)</td>
</tr>
<tr>
<td>M-F(Å)</td>
<td></td>
</tr>
<tr>
<td>2 at 1.495(2)</td>
<td>3 at 1.5700 ± 0.0012</td>
</tr>
<tr>
<td>1 at 1.499(2)</td>
<td></td>
</tr>
<tr>
<td>F-M-F(°)</td>
<td></td>
</tr>
<tr>
<td>2 at 97.39(12)</td>
<td>3 at 97.8 ± 0.2</td>
</tr>
<tr>
<td>1 at 97.62(07)</td>
<td></td>
</tr>
<tr>
<td>SeF₃⁺ (d)</td>
<td>AsF₅ (c)</td>
</tr>
<tr>
<td>M-F(Å)</td>
<td></td>
</tr>
<tr>
<td>{1.67(2)}</td>
<td>3 at 1.7063 ± 0.0006</td>
</tr>
<tr>
<td></td>
<td>3 at 1.7063 ± 0.0006</td>
</tr>
<tr>
<td>F-M-F(°)</td>
<td></td>
</tr>
<tr>
<td>94.9(1.7)</td>
<td>3 at 96.1 ± 0.05</td>
</tr>
<tr>
<td>93.9(1.7)</td>
<td></td>
</tr>
<tr>
<td>XeF₅⁺ (f)</td>
<td>IF₅ (e)</td>
</tr>
<tr>
<td>axial</td>
<td></td>
</tr>
<tr>
<td>1.793(8)</td>
<td>1.817(10)</td>
</tr>
<tr>
<td>M-F(Å)</td>
<td></td>
</tr>
<tr>
<td>equilat.</td>
<td></td>
</tr>
<tr>
<td>2 at 1.841(8)</td>
<td>4 at 1.873(5)</td>
</tr>
<tr>
<td>2 at 1.848(8)</td>
<td></td>
</tr>
<tr>
<td>F axial-M-F eq (°)</td>
<td></td>
</tr>
<tr>
<td>2 at 78.59(43)</td>
<td>4 at 80.9(0.2)</td>
</tr>
<tr>
<td>2 at 79.43(50)</td>
<td></td>
</tr>
</tbody>
</table>
References for Table IV

(a) Ref. 24.
(b) This work.
(d) Ref. 13.
(e) Ref. 3.
FIGURE CAPTIONS:


Fig. 1
$F_1 - 1.499(2) - S - 97.39(12)$

$F_1 - 1.495(2) - F_1 - 97.62(7)$

XBL7110-4597
NOTE TO PRINTER: Place the following heading on the attached glossy print which is supplementary material for the microfilm edition only.

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[S\text{F}_3]^+[B\text{F}_4]^-$. 
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