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A Contribution from The Lawrence Berkeley Laboratory and the Department of Chemistry, The University of California, Berkeley, California 94720

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

by

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ABSTRACT

The crystal structure of trifluorosulfur(IV)-yl tetrafluoroborate, $[\text{SF}_3]^+[\text{BF}_4]^-$ has been determined from three dimensional X-ray data. The compound is orthorhombic, $a = 9.599(3)$, $b = 5.755(3)$, $c = 8.974(3)\text{\AA}$, $V = 495.7\text{\AA}^3$, $z = 4$, $d_c = 2.36\text{ g cm}^{-3}$. 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 $\text{S-F1}(\text{twice}) = 1.495(2)$ and $\text{S-F2} = 1.499(2)\text{\AA}$ and bond angles $\text{F1-S-F1} = 97.62(7)$ and $\text{F2-S-F1}(\text{twice}) = 97.39(12)^\circ$ and effectively C_{3v} symmetry. The BF_4 group is slightly distorted from tetrahedral symmetry with $\text{B-F3} = 1.397(4)$, $\text{B-F4} = 1.393(5)$, $\text{B-F5}(\text{twice}) = 1.377(3)\text{\AA}$, $\text{F4-B-F5} = 108.58(17)$, $\text{F3-B-F4} = 107.63(25)$, $\text{F5-B-F5} = 111.37(14)$ and $\text{F3-B-F5}(\text{twice}) = 110.29(16)^\circ$. Each SF_3 group is so oriented that the sulfur atom makes short contacts of $2.624(2)(\text{twice})$ and $2.593(3)\text{\AA}$ 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 C_{3v} symmetry cations with tetrahedral anions. The bond length in the cation is the shortest observed hitherto in any sulfur fluoride and is $\sim 0.07 \text{ \AA}$ 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 .

$[SF_3]^+[AsF_6]^-$ is orthorhombic with $a = 20.375(3)$, $b = 8.508(3)$, $c = 11.224(3) \text{ \AA}$, $V = 1945.7 \text{ \AA}^3$, $z = 12$, $d_c = 2.85 \text{ g cm}^{-3}$. The diffraction symmetry (m.c.c) indicates $Cmc2_1$, $C2cm$ and $Cmcm$ as possible space groups.

(close up) 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_{α}/r^2 , 0.85; $f_{\alpha'}/r^2$, 0.12 mdyne $\text{\AA}^{-1}$.

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.,

A simple example, which appeared to belong to this class was the 1:1 $SF_4 \cdot BF_3$ adduct, first reported (along with other SF_4 , SeF_4 , and TeF_4

adducts) by Bartlett and Robinson⁶. The $\text{SF}_4 \cdot \text{BF}_3$ adduct has attracted considerable attention^{7,8,9,10,11}. Bartlett and Robinson had initially proposed⁶ that the compound might be a Lewis adduct, but their later finding¹², that the $\text{SF}_4 \cdot \text{SbF}_5$ adduct possesses a primitive cubic lattice, led them to favor a salt formulation, involving the SF_3^+ ion, for all of the SF_4 adducts. More convincing experimental evidence (including infra-red and conductivity studies) for salt formulations was given by Seel and Detmer⁸. Muetterties and his coworkers⁷, 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 George⁹ reviewed theoretical considerations suggesting an ionic formulation. More recently from vibrational spectroscopic studies¹¹, Gillespie and his coworkers concluded that the SF_4 adducts with BF_3 , AsF_5 , and SbF_5 were essentially 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 SeF_4 adducts, $\text{SeF}_4 \cdot \text{NbF}_5$ and $\text{SeF}_4 \cdot 2\text{NbF}_5$ reported by Edwards and his coworkers¹³. 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 $< 2.5 \text{ \AA}$. These short fluorine-bridge contacts may indicate some covalency (multicenter bonding), as Edwards and his coworkers have suggested. Indeed, Bartlett and Robinson had argued¹² that fluorine bridging might be more important in the SeF_4 adducts, than in those of SF_4 , since SeF_4 is superior to SF_4 as a fluoride ion acceptor; also the higher fusion temperatures of the SF_4 adducts compared to their 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 $\text{SF}_4 \cdot \text{MF}_5$ compounds,^{12,14,15} ($\text{M} = \text{Sb}, \text{Os}, \text{Ir}, \text{Ru}$), 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 coworkers¹⁰ from single crystal studies of $\text{SF}_4 \cdot \text{BF}_3$. Although the latter workers suggested that the $\text{SF}_4 \cdot \text{BF}_3$ structure might be the anti NH_4IO_3 structure¹⁶ they did not undertake a complete analysis.

EXPERIMENTAL

Crystal Preparation.- The adduct $\text{SF}_4 \cdot \text{BF}_3$ 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 $\sim 60^\circ$. 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 $\sim 10\%$ 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 $\text{SF}_4 \cdot \text{AsF}_5$ adduct was also investigated and was prepared by co-condensing SF_4 (excess) and AsF_5 , in a Monel can fitted with a teflon-gasketed lid, warming to ambient temperature and removing excess SF_4 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.- SBF_7 (mol wt 265.56) is orthorhombic with $a = 9.599(3)$, $b = 5.755(3)$, $c = 8.974(3)$ Å, $V = 495.8$ Å³, $z = 4$, $d_c = 2.34$ g cm³ 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 Å³¹⁷. Single crystal photographs confirmed the diffraction symmetry found for $\text{SF}_4 \cdot \text{BF}_3$ by Calvert et al.¹⁰ The structure was successfully refined in the centrosymmetric space group Pnma .

SAsF_9 (mol wt 277.89) is orthorhombic with $a = 20.375(3)$, $b = 8.508(3)$, $c = 11.224(3)$ Å, $V = 1945.7$ Å³, $z = 12$, $d_c = 2.84$ g cm³ 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 (close up) consistent with the space groups $\text{Cmc}2_1$, $\text{C}2\text{cm}$, and Cmcm .

X-ray Measurements, SF_3BF_4 .- 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 $\text{MoK}\alpha_1$ peak of the reflection of 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 ($2\theta = 11.8^\circ$). 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

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

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

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

unless σ_{ave} is less than the scatter of the N reflections in which case the formula applied was

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

in which Δ_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

$$\sigma(F) = F_o - [F_o^2 - S \sigma(I)/Lp]^{\frac{1}{2}}$$

in which S is the scaling factor in the equation

$$F_o = \left(\frac{SI}{Lp} \right)^{\frac{1}{2}}$$

For cases in which $I \leq \sigma(I)$, $\sigma(F) = [S\sigma(I)/Lp]^{\frac{1}{2}}$ in which L and p are the Lorentz and polarization corrections. The least squares program used in the structure refinements minimizes the function R_2^2

$$R_2^2 = \sum w(\Delta F)^2 / \sum w F_o^2$$

in which F_o and F_c are observed and calculated structure factors and ΔF 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 factors¹⁸ for neutral sulfur, boron, and fluorine were used. The anisotropic temperature factor has the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{12}hl - 2\beta_{23}kl)$. The B_{ij} values reported are related to the Betas in the above expression:

$$B_{ij} = \frac{4\beta_{ij}}{a_i^* a_j^*}$$

in which a_i^* is the i^{th} reciprocal cell length.

A complete set of $-hkl$ reflections was collected to a 2θ 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 $R = .50$ ($R = \sum |(F_o) - (F_c)| / \sum (F_o)$). We were still not certain of the space group at this point and so ran WILSON¹⁹ 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 MULTAN¹⁹, 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 $0.96 \text{ e}/\text{\AA}^3$, 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 ²⁰.

A Partial Solution of the Structure SF₃AsF₆. - 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 spectra¹¹ 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;¹¹ 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 $\nu_3(t_{1u})$ of the AsF_6^- anion. Using a simple valence force field and the geometry established in this work, the fundamentals of SF_3^+ in $SF_4 \cdot BF_3$ [$\nu_1(a_1)$, 938 cm^{-1} ; $\nu_2(a_1)$, 530 cm^{-1} ; $\nu_3(e)$, 914 cm^{-1} ; $\nu_4(e)$, 411 cm^{-1}] were analysed to yield the following force constants: f_r , 5.67 mdyne $\text{\AA}^{-1}$; $f_{r'}$, 0.19 mdyne $\text{\AA}^{-1}$; f_{α}/r^2 , 0.85 mdyne $\text{\AA}^{-1}$; $f_{\alpha'}/r^2$, 0.12 mdyne $\text{\AA}^{-1}$.

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 $\underline{C}_s$ has, effectively, symmetry $\underline{C}_{3v}$, 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 $\underline{C}_s$, 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) $\text{\AA}$. 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) $\text{\AA}$. 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) $\text{\AA}$) the B-F3 distance is 1.397(4) $\text{\AA}$. This is not significantly different from B-F4 = 1.393(5) $\text{\AA}$ where S...F4' is 3.111(3) $\text{\AA}$.

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 $^{16}NH_4^+IO_3^-$ 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 spacially 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 BF_4^- departs slightly from the tetrahedral ideal, the B-F interatomic distances 1.377(3) (twice), 1.393(5) and 1.397(4) (mean 1.386(6)) are not significantly different within the set, and are in excellent agreement with the mean values (uncorrected for librational motion) for NaBF_4 ²¹ ($1.389 \pm 0.005 \text{ \AA}$) KBF_4 ²² (1.386(6)) and NH_4BF_4 ²³ (1.382(6)).

The SF_3^+ species is very similar to its isoelectronic relative PF_3 ²⁴ (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 $\text{\AA}$ 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 [$\nu_2(\underline{e}_g)$ of AsF_6^-] and the breakdown of gross selection rules so that $\nu_3(\underline{t}_{1u})$ of AsF_6^- is observed in the Raman spectrum of $[\text{SF}_3]^+[\text{AsF}_6]^-$, as

are $\nu_1(\underline{a}_1)$ and $\nu_2(\underline{e})$ of BF_4^- in the infrared spectrum of $[\text{SF}_3]^+[\text{BF}_4]^-$.¹¹ 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;¹¹ we note that comparable "site effects" are seen in the spectra of the alkali metal tetrafluoroborates²⁵. Neither our crystallographic nor spectroscopic studies of the SF_4 adducts reveal the signally deformed anions evident in adducts of BrF_3 ²⁶ with fluoride-acceptors, which are possible caused by fluorine bridging to the strongly polarizing BrF_2^+ cation.

The bond length in the 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 SF_3^+ is even shorter ($\sim 0.05 \text{ \AA}$) than the equatorial bond in SF_4 ($1.545 \text{ \AA}$) it is dramatically shorter ($\sim 0.15 \text{ \AA}$) than the axial bonds in the latter ($1.646 \text{ \AA}$)²⁷. These findings are in harmony with the view that the axial SF_4 bonds are effectively single-electron bonds, and the equatorial bonds, electron-pair bonds²⁸. (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 SF_3^+ we find to be $5.67 \text{ md \AA}^{-1}$, which is comparable to the value of $5.2 \text{ md \AA}^{-1}$ for the S-F equatorial stretching force constant of SF_4 and approximately twice the value of $2.8 \text{ md \AA}^{-1}$, derived for the axial bonds in that molecule²⁹.

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

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B_{xx}</u> (Å ²)	<u>B_{yy}</u> (Å ²)	<u>B_{zz}</u> (Å ²)	<u>B_{xy}</u> (Å ²)	<u>B_{xz}</u> (Å ²)	<u>B_{yz}</u> (Å ²)	R.M.S.D. (a)
S	.28168(8)	1/4	.11259(10)	2.40(3)	2.80(3)	2.75(3)		.44(3)		.1833
B	.48346(40)	3/4	.17658(44)	2.43(12)	2.74(13)	3.09(15)		.33(11)		.1867
F1	.19529(17)	.05453(31)	.05347(21)	4.35(7)	4.28(7)	4.84(8)	-1.43(6)	.46(6)	-0.88(6)	.2385
F2	.22481(26)	1/4	.2682 2(26)	4.06(10)	4.13(10)	3.17(9)		1.31(8)		.2190
F3	.628180(23)	3/4	.15984(28)	2.60(8)	4.53(11)	4.09(10)		.35(7)		.2176
F4	.42490(30)	3/4	.03457(33)	4.31(12)	7.81(18)	4.39(13)		-0.97(10)		.2640
F5	.44087(19)	.55238(33)	.25011(21)	4.69(8)	3.78(8)	5.79(10)	-0.49(7)	.81(7)	1.16(7)	.2454

(a) Average root-mean-square displacement along the principle axes of the thermal ellipsoids (Å).

Table II

SULFUR AND ARSENIC POSITIONAL PARAMETERS

FOR $[\text{SF}_3]^+[\text{AsF}_6]^-$ (CmC₂₁ - No. 36)

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

* fixed value.

Table III
(a)
INTERATOMIC DISTANCES (Å) AND ANGLES (°)

S-2F1	1.495(2), [1.518]	F3...2F5	2.277(3)
S-F2	1.499(2), [1.514]	F4...2F5	2.249(3)
S...F3	2.593(3)	F5...F5	2.275(4)
S...2F5	2.624(2)	B... 2F1	3.456(4)
S...B	3.438(4)	F1-S-F1	97.62(7)
S...F4	3.111(3)	F1-S-F2	97.39(12)
S...2F4	3.265(2)	F3-B-F4	107.63(25)
B-F3	1.397(4), [1.410]	F3-B-F5	110.29(16)
B-F4	1.393(5), [1.428]	F4-B-F5	108.58(17)
B-2F5	1.377(3), [1.404]	F5-B-F5	111.37(14)
F2...2F1	2.249(3)	S...F3-B	115.66(17)
F1...F1	2.250(4)	S...F5-B	119.69(17)
F3...F4	2.252(4)		

(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

	<u>Cation</u>	<u>Molecule</u>
	$\text{SF}_3^+ \text{ (b)}$ ---3	$\text{PF}_3 \text{ (a)}$ ---3
M-F(Å)	$\left\{ \begin{array}{l} 2 \text{ at } 1.495(2) \\ 1 \text{ at } 1.499(2) \end{array} \right.$	3 at 1.5700 ± 0.0012
F-M-F(°)	$\left\{ \begin{array}{l} 2 \text{ at } 97.39(12) \\ 1 \text{ at } 97.62(07) \end{array} \right.$	3 at 97.8 ± 0.2
	$\text{SeF}_3^+ \text{ (d)}$ ----3	$\text{AsF}_3 \text{ (c)}$ ----3
M-F(Å)	$\left\{ \begin{array}{l} 1.67(2) \\ 1.64(2) \\ 1.66(2) \end{array} \right.$	3 at 1.7063 ± 0.0006
F-M-F(°)	$\left\{ \begin{array}{l} 94.9(1.7) \\ 93.9(1.7) \\ 94.6(1.7) \end{array} \right.$	3 at 96.1 ± 0.05
	$\text{XeF}_5^+ \text{ (f)}$ -----5	$\text{IF}_5 \text{ (e)}$ -----5
axial	1.793(8)	1.817(10)
M-F(Å)	$\left\{ \begin{array}{l} 2 \text{ at } 1.841(8) \\ 2 \text{ at } 1.848(8) \end{array} \right.$	4 at 1.873(5)
equilat.		
F _{axial} -M-F _{eq} (°)	$\left\{ \begin{array}{l} 2 \text{ at } 78.59(43) \\ 2 \text{ at } 79.43(.50) \end{array} \right.$	4 at $80.9(0.2)$

References for Table IV

- (a) Ref. 24.
- (b) This work.
- (c) F. B. Clippard, and L. S. Bartell, Inorg. Chem., 9, 805 (1970).
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- (e) Ref. 3.
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FIGURE CAPTIONS:

FIGURE 1: The Raman spectra of $[\text{SF}_3]^+[\text{BF}_4]^-$ and $[\text{SF}_3]^+[\text{AsF}_6]^-$.

FIGURE 2: The atomic arrangement in $[\text{SF}_3]^+[\text{BF}_4]^-$.

FIGURE 3: The shape of the $[\text{SF}_3]^+$ ion in $[\text{SF}_3]^+[\text{BF}_4]^-$.

Fig. 1

XBL7110-4512

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

TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (SF3119F4)

FOR FCA		3715		5 63 64		8 91 101		7 7 10		12 30 22		8 30 30		11 19 6		5 48 49		7 24 25		1 101 102		H,K= 9, 2		0 78 74		H,K= 12, 0	
1	FOR FCA	3	315 320	5	63 64	8	91 101	7	7 10	12	30 22	8	30 30	11	19 6	5	48 49	7	24 25	1	101 102	H,K= 9, 2	0	78 74	H,K= 12, 0		
H,K= 0, 0	4	21 3	6	11 8	10	46 46	9	38 41	H,K= 4, 1	H,K= 4, 7	1	10 11	5	5	5	148 155	8	30 17	2	120 120	1	154 159	1	8 16	0	136 128	
2	344 319	5	378 383	7	35 34	10	46 46	9	38 41	H,K= 4, 1	H,K= 4, 7	1	10 11	5	5	5	148 155	8	30 17	2	120 120	1	154 159	1	8 16	0	136 128
3	243 216	5	157 151	8	30 23	11	48 43	10	21 25	0	442 425	0	54 57	2	89 93	8	66 72	10	0 3	4	25 21	2	150 152	3	30 30	2	7 15
4	366 351	7	140 147	H,K= 1, 8	H,K= 2, 5	11	40 36	1	518 503	1	48 52	3	16 5	9	0 9	11	25 29	5	24 24	4	44 42	4	133 131	3	79 80		
5	144 144	4	150 155	1	29 39	0	79 95	12	49 54	2	57 62	2	67 58	4	35 31	10	40 42	H,K= 7, 3	6	35 24	5	94 97	5	60 65	4	74 75	
6	6 60	9	63 62	2	44 43	1	345 350	H,K= 3, 3	3	161 165	3	26 26	5	100 97	11	0 7	1	148 148	7	78 84	6	49 47	6	23 2	5	41 35	
7	26 28	10	37 43	3	17 24	2	20 16	1	131 143	4	182 171	4	83 81	6	101 107	H,K= 6, 4	2	293 290	4	30 32	7	10 1	7	37 36	6	17 20	
8	1 73	1	11 36	31	4 14	9	78 76	2	290 269	5	20 30	5	15 12	7	11 7	0	120 127	3	28 24	9	20 4	8	14 10	6	33 38	7	56 51
H,K= 0, 1	30	73	12 19	3	5 14	4	195 189	3	6 4	6	15 10	6	24 2	8	53 50	1	156 155	4	23 12	10	26 13	7	66 64	H,K= 10, 4	H,K= 12, 1		
1	30 73	12 19	3	5 14	4	195 189	3	6 4	6	15 10	6	24 2	8	53 50	1	156 155	4	23 12	10	26 13	7	66 64	H,K= 10, 4	H,K= 12, 1			
2	244 281	13	62 61	H,K= 2, 0	5	88 91	4	166 173	7	146 140	7	53 50	9	43 42	2	44 45	5	16 14	H,K= 8, 3	3	10 29	29	0	47 50	0	78 76	
3	244 281	13	62 61	H,K= 2, 0	5	88 91	4	166 173	7	146 140	7	53 50	9	43 42	2	44 45	5	16 14	H,K= 8, 3	3	10 29	29	0	47 50	0	78 76	
4	119 93	H,K= 1, 2	0	582 549	6	69 71	5	181 182	8	95 95	H,K= 4, 8	10	60 54	H,K= 5, 6	4	16 5	6	93 95	0	130 132	H,K= 9, 3	3	1 28	25	1 43	40	
5	390 306	1	548 543	1	177 160	7	94 97	6	39 46	9	43 45	0	51 50	H,K= 5, 6	4	16 5	6	93 95	0	130 132	H,K= 9, 3	3	1 28	25	1 43	40	
6	16 7	2	18 28	2	542 501	8	19 23	7	72 62	10	54 57	1	41 41	1	48 46	5	126 130	8	57 51	2	66 63	2	107 108	3	48 47	3	56 54
7	110 107	3	84 78	3	270 276	9	35 28	8	38 42	11	45 43	2	0 5	2	61 64	6	54 62	9	19 23	3	121 124	3	66 70	4	46 45	4	92 88
8	7 10	3	67 65	4	410 436	10	41 34	9	90 89	12	36 33	3	36 31	3	76 77	7	62 56	10	33 33	4	182 190	4	56 51	5	45 45	5	0 8
H,K= 0, 2	550 544	6	360 355	6	234 213	0	126 128	11	31 27	0	118 118	1	318 279	5	67 57	8	40 34	H,K= 7, 4	5	78 87	5	0 2	6	0 7	5	20 44	
1	550 544	6	360 355	6	234 213	0	126 128	11	31 27	0	118 118	1	318 279	5	67 57	8	40 34	H,K= 7, 4	5	78 87	5	0 2	6	0 7	5	20 44	
2	59 42	7	43 37	7	216 204	1	22 20	12	29 19	1	363 354	2	321 329	6	62 62	10	16 15	2	41 25	7	36 32	7	18 11	H,K= 10, 5	H,K= 12, 2		
3	496 494	9	42 81	8	69 69	2	31 33	3	19	4	211 116	3	306 337	7	0 7	H,K= 6, 5	3	23 31	9	46 44	8	68 72	0	87 90	0	60 61	
4	175 181	2	53 46	9	43 38	3	15 13	1	88 95	3	180 171	4	36 36	8	14 5	0	92 93	4	70 78	23	18	3	32 40	1	56 49	1	23 25
5	143 140	10	71 71	10	66 61	4	82 78	2	212 203	4	64 63	5	157 166	H,K= 5, 7	1	28 20	5	89 95	10	42 49	H,K= 9, 4	2	12 24	2	22 22		
6	101 91	11	0 1	11	88 88	5	19 5	3	84 91	5	78 84	6	126 138	1	0 14	2	66 74	6	24 20	H,K= 8, 4	1	72 78	3	28 25	3	83 80	
7	29 28	12	132 13	12	64 66	6	63 62	4	84 83	6	130 129	7	77 80	2	73 75	3	35 26	7	0 3	0	21 36	2	49 55	4	53 59	4	79 79
H,K= 0, 3	403 385	H,K= 1, 3	13 12	10	7	64 64	5	89 90	7	174 172	8	40 45	3	14 6	4	166 162	8	14 15	1	25 25	3	105 104	5	25 21	5	35 38	
1	403 385	H,K= 1, 3	13 12	10	7	64 64	5	89 90	7	174 172	8	40 45	3	14 6	4	166 162	8	14 15	1	25 25	3	105 104	5	25 21	5	35 38	
2	59 42	7	43 37	7	216 204	1	22 20	12	29 19	1	363 354	2	321 329	6	62 62	10	16 15	2	41 25	7	36 32	7	18 11	H,K= 10, 5	H,K= 12, 2		
3	496 494	9	42 81	8	69 69	2	31 33	3	19	4	211 116	3	306 337	7	0 7	H,K= 6, 5	3	23 31	9	46 44	8	68 72	0	87 90	0	60 61	
4	175 181	2	53 46	9	43 38	3	15 13	1	88 95	3	180 171	4	36 36	8	14 5	0	92 93	4	70 78	23	18	3	32 40	1	56 49	1	23 25
5	143 140	10	71 71	10	66 61	4	82 78	2	212 203	4	64 63	5	157 166	H,K= 5, 7	1	28 20	5	89 95	10	42 49	H,K= 9, 4	2	12 24	2	22 22		
6	101 91	11	0 1	11	88 88	5	19 5	3	84 91	5	78 84	6	126 138	1	0 14	2	66 74	6	24 20	H,K= 8, 4	1	72 78	3	28 25	3	83 80	
7	29 28	12	132 13	12	64 66	6	63 62	4	84 83	6	130 129	7	77 80	2	73 75	3	35 26	7	0 3	0	21 36	2	49 55	4	53 59	4	79 79
H,K= 0, 3	403 385	H,K= 1, 3	13 12	10	7	64 64	5	89 90	7	174 172	8	40 45	3	14 6	4	166 162	8	14 15	1	25 25	3	105 104	5	25 21	5	35 38	
1	403 385	H,K= 1, 3	13 12	10	7	64 64	5	89 90	7	174 172	8	40 45	3	14 6	4	166 162	8	14 15	1	25 25	3	105 104	5	25 21	5	35 38	
2	59 42	7	43 37	7	216 204	1	22 20	12	29 19	1	363 354	2	321 329	6	62 62	10	16 15	2	41 25	7	36 32	7	18 11	H,K= 10, 5	H,K= 12, 2		
3	496 494	9	42 81	8	69 69	2	31 33	3	19	4	211 116	3	306 337	7	0 7	H,K= 6, 5	3	23 31	9	46 44	8	68 72	0	87 90	0	60 61	
4	175 181	2	53 46	9	43 38	3	15 13	1	88 95	3	180 171	4	36 36	8	14 5	0	92 93	4	70 78	23	18	3	32 40	1	56 49	1	23 25
5	143 140	10	71 71	10	66 61	4	82 78	2	212 203	4	64 63	5	157 166	H,K= 5, 7	1	28 20	5	89 95	10	42 49	H,K= 9, 4	2	12 24	2	22 22		
6	101 91	11	0 1	11	88 88	5	19 5	3	84 91	5	78 84	6	126 138	1	0 14	2	66 74	6	24 20	H,K= 8, 4	1	72 78	3	28 25	3	83 80	
7	29 28	12	132 13	12	64 66	6	63 62	4	84 83	6	130 129	7	77 80	2	73 75	3	35 26	7	0 3	0	21 36	2	49 55	4	53 59	4	79 79
H,K= 0, 3	403 385	H,K= 1, 3	13 12	10	7	64 64	5	89 90	7	174 172	8	40 45	3	14 6	4	166 162	8	14 15	1	25 25	3	105 104	5	25 21	5	35 38	
1	403 385	H,K= 1, 3	13 12	10	7	64 64	5	89 90	7	174 172	8	40 45	3	14 6	4	166 162	8	14 15	1	25 25	3	105 104	5	25 21	5	35 38	
2	59 42	7	43 37	7	216 204	1	22 20	12	29 19	1	363 354	2	321 329	6	62 62	10	16 15	2	41 25	7	36 32	7	18 11	H,K= 10, 5	H,K= 12, 2		
3	496 494	9	42 81	8	69 69	2	31 33	3	19	4	211 116	3	306 337	7	0 7	H,K= 6, 5	3	23 31	9	46 44	8	68 72					

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