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Structural Studies of Trifluorosulfur(IV)yl, $[SF_3]^+$, Salts Including the Crystal Structure of $[SF_3]^+[BF_4]^-$

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Received February 14, 1972

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 with $a = 9.599$ (3) Å, $b = 5.755$ (3) Å, $c = 8.974$ (3) Å, $V = 495.7$ Å^3, $Z = 4$, and $d_{\text{calcd}} = 2.36$ 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–F(1)(twice) = 1.495 (2) Å and S–F(2) = 1.499 (2) Å and bond angles F(1)–S–F(1) = 97.62 (7)° and F(2)–S–F(1)(twice) = 97.39 (12)° and effectively C_{3v} symmetry. The BF_4 group is slightly distorted from tetrahedral symmetry with B–F(3) = 1.397 (4) Å, B–F(4) = 1.393 (5) Å, B–F(5)(twice) = 1.377 (3) Å, F(4)–B–F(5) = 108.58 (17)°, F(3)–B–F(4) = 107.63 (25)°, F(5)–B–F(5) = 111.37 (14)°, and F(3)–B–F(5)(twice) = 110.29 (16)°. 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 C_{3v} symmetry cations with tetrahedral anions. The bond length in the cation is the shortest observed hitherto in any sulfur fluoride and is ~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. $[SF_3]^+[AsF_6]^-$ is orthorhombic with $a = 20.375$ (3) Å, $b = 8.508$ (3) Å, $c = 11.224$ (3) Å, $V = 1945.7$ Å^3, $Z = 12$, and $d_{\text{calcd}} = 2.85$ g cm^{-3}. The observed extinctions indicate *Cmc*2$_1$, *C*2*cm*, and *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_α/r^2, 0.85; $f_{\alpha'}/r^2$, 0.12 mdyn Å^{-1}.

Introduction

Many of the nonmetal fluorides interact with strong fluoride ion acceptors, such as BF_3 and the metal pentafluorides, to form adducts. Work in these laboratories had indicated that such adducts of the xenon and iodine fluorides may be adequately formulated as salts, *e.g.*, $[XeF]^+[RuF_6]^-$, $[Xe_2F_3]^+[AsF_6]^-$, $[XeF_5]^+[RuF_6]^-$, $[IF_4]^+[SbF_6]^-$, and $[IF_6]^+[AsF_6]^-$.[1-5]

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 Robinson.[6] The $SF_4 \cdot BF_3$ adduct has attracted considerable attention.[7-11] Bartlett and Robinson had initially proposed[6] that the compound might be a Lewis adduct, but their later finding,[12] that the $SF_4 \cdot SbF_5$ 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 infrared and conductivity studies) for salt formulations was given by Seel and Detmer.[8] Muetterties and his coworkers,[7] while admitting the validity of an ionic formulation, also allowed, on the basis of solution nmr studies, that the $SF_4 \cdot BF_3$ adduct could be a fluorine-bridged dimer or polymer. Cotton and George[9] reviewed theoretical considerations suggesting an ionic formulation. More recently from vibrational spectroscopic studies,[11] 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 $SeF_4 \cdot NbF_5$ and $SeF_4 \cdot 2NbF_5$ reported by Edwards and his coworkers.[13] Although the structures are suggestive of salt formulations ($[SeF_3]^+[NbF_6]^-$ and $[SeF_3]^+[Nb_2F_{11}]^-$, respectively), each cation has three anion contacts at <2.5 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[12] 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 with those of 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 $SF_4 \cdot MF_5$ compounds[12,14,15] (M = 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[10] from single-crystal studies of $SF_4 \cdot BF_3$. Al-

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[1] N. Bartlett, D. Gibler, and A. Zalkin, to be submitted for publication.

[2] F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968).

[3] B. Morrell, M.S. Thesis, University of California, Berkeley, Calif., L.B.L. Report No. 156, Sept 1971.

[4] N. Bartlett, D. Gibler, and D. Hall, unpublished work.

[5] S. P. Beaton, Ph.D. Thesis, University of British Columbia, 1966.

[6] N. Bartlett and P. L. Robinson, *Chem. Ind. (London)*, 1351 (1956).

[7] A. L. Oppegaard, W. L. Smith, E. L. Muetterties, and V. A. Engelhard, *J. Amer. Chem. Soc.*, **82**, 3835 (1960).

[8] F. Seel and O. Detmer, *Z. Anorg. Allg. Chem.*, **301**, 113 (1959).

[9] F. A. Cotton and J. W. George, *J. Inorg. Nucl. Chem.*, **7**, 397 (1958); **12**, 386 (1960).

[10] L. D. Calvert and J. R. Morton, *Acta Crystallogr.*, **17**, 617 (1964).

[11] M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, **47**, 4159 (1969).

[12] N. Bartlett and P. L. Robinson, *J. Chem. Soc. A*, 3417 (1961).

[13] A. J. Edwards and G. R. Jones, *ibid.*, 1491 (1970).

[14] The salts $[SF_3]^+[MF_6]^-$ (M = Os, Ir) are simple cubic, both with $a_0 = 5.581 \pm 0.004$ Å, $Z = 1$, $V = 173.8$ Å^3: N. K. Jha, Ph.D. Thesis, University of British Columbia, 1965.

[15] $[SF_3]^+[RuF_6]^-$ has a tetragonal cell, with $a = 5.37 \pm 0.01$ Å, $c = 5.93 \pm 0.01$ Å, $Z = 1$, and $V = 171.5$ Å^3, which is related to the cubic cells of $[SF_3]^+[MF_6]^-$ (M = Sb, Os, Ir): R. Surfass, Senior Thesis, Princeton University, Princeton, N. J., 1967.

though the latter workers suggested that the $SF_4 \cdot BF_3$ structure might be the anti NH_4IO_3 structure,[16a] they did not undertake a complete analysis.[16b]

Experimental Section

Crystal Preparation.—The adduct $SF_4 \cdot BF_3$ was prepared by cocondensation 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. ω scans of representative diffraction peaks from the crystal finally chosen for data collection revealed a major peak with two satellites. The satellites contributed ~10% toward the total intensity for the most unfavorable of several reflections scanned. The crystal was roughly rectilinear with dimensions $0.4 \times 0.2 \times 0.2$ mm.

The $SF_4 \cdot AsF_5$ adduct was also investigated and was prepared by cocondensing 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. Although no obvious systematic discrepancies were observed between the two data sets, large and irregular backgrounds gave us little confidence in the quality of the data sets.

Crystal Data.—SBF_7 (mol wt 175.86) is orthorhombic with $a = 9.599\ (3)$ Å, $b = 5.755\ (3)$ Å, $c = 8.974\ (3)$ Å, $V = 495.8$ Å^3, $Z = 4$, $d_{\text{calcd}} = 2.34$ cm^{-3}, and F(000) = 336.52. The unit cell volume satisfies Zachariasen's criterion for close-packed fluoride lattices, since the effective volume per fluorine atom is 17.7 Å^3.[17] Single-crystal photographs confirmed the diffraction symmetry found for $SF_4 \cdot BF_3$ by Calvert and Morton.[10] The structure was successfully refined in the centrosymmetric space group *Pnma*.

$SAsF_9$ (mol wt 277.89) is orthorhombic with $a = 20.375\ (3)$ Å, $b = 8.508\ (3)$ Å, $c = 11.224\ (3)$ Å, $V = 1945.7$ Å^3, $Z = 12$, $d_{\text{calcd}} = 2.84$ g cm^{-3}, and $F(000) = 781.6$. The effective volume per fluoride ion is 18 Å^3. Single-crystal precession photographs were obtained for the zero, first, second, and third layers along each of the principal axes. Systematic absences noted were the following: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$ which is consistent with the space groups $Cmc2_1$, $C2cm$, 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 ω scans of the crystal were not entirely satisfactory. Accurate cell dimensions were obtained by determining the 2θ angle for the Mo Kα_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 1°/min. The poor mosaic quality of the crystal required a scan width of 2°. Background counts were offset from the scan limits by 0.5° and each count lasted 10 sec. The radiation was monochromatized with a graphite crystal ($2\theta = 11.8°$). Automatic attenuators were inserted when the beam intensity exceeded 10,000 counts/sec. Three standards were checked every 100 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

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

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

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

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

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

in which S is the scaling factor in the equation

$$F_o = (SI/Lp)^{1/2}$$

For cases in which $I \leq \sigma(I)$, $\sigma(F) = [S\sigma(I)Lp]^{1/2}$ 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

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

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 factors[18] for neutral sulfur, boron, and fluorine were used. The anisotropic temperature factor has the form $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl]$. The B_{ij} values reported are related to the β's in the above expression

$$B_{ij} = \frac{4\beta_{ij}}{a^*_i a^*_j}$$

in which a^*_i is the ith reciprocal cell length.

A complete set of $\bar{h}kl$ reflections was collected to a 2θ of 65° and a portion of the hkl set also. A sorted and averaged set of 980 unique reflections was obtained from 1240 intensity measurements. Of these 700 were given nonzero 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[19] to check statistical inequalities. These were not conclusive but indicated strongly that *Pnma* (No. 62), the centric group, was correct. A set of E values produced by this program was subsequently used in MULTAN,[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 (fourfold) position indicated by the Patterson synthesis, along with an eightfold set and a fourfold set of fluorine atoms. A Fourier synthesis, produced with the phases generated by this refinement,

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(16) (a) C. H. MacGillavry and C. L. Panthaleon Van Eck, *Recl. Trav. Chim. Pays-Bas*, **62**, 729 (1943). (b) The space group of NH_4IO_3 was recently shown to be $Pna2_1$, not *Pbnm* as suggested in ref 16a: G. R. Crane, J. G. Bergman, Jr., and A. M. Glass, *J. Amer. Ceram. Soc.*, **52**, 655 (1969).

(17) W. H. Zachariason, *Acta Crystallogr.*, **2**, 388 (1949).

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

(19) Computer programs used were as follows: 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, Department of Physics, University of York, York, England, and Gabriel Germain, University of Louvain, Loueven, 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.

TABLE I

FINAL PARAMETERS FOR $[SF_3]^+[BF_4]^-$

Atom	x	y	z	B_{xx} (Å²)	B_{yy} (Å²)	B_{zz} (Å²)	B_{xy} (Å²)	B_{xz} (Å²)	B_{yz} (Å²)	RMSD[a]
S	0.28168 (8)	$^1/_4$	0.11259 (10)	2.40 (3)	2.80 (3)	2.75 (3)		0.44 (3)		0.1833
B	0.48346 (40)	$^3/_4$	0.17658 (44)	2.43 (12)	2.74 (13)	3.09 (15)		0.33 (11)		0.1867
F(1)	0.19529 (17)	0.05453 (31)	0.05347 (21)	4.35 (7)	4.28 (7)	4.84 (8)	−1.43 (6)	0.46 (6)	−0.88 (6)	0.2385
F(2)	0.22481 (26)	$^1/_4$	0.26822 (26)	4.06 (10)	4.13 (10)	3.17 (9)		1.31 (8)		0.2190
F(3)	0.62818 (23)	$^3/_4$	0.15984 (28)	2.60 (8)	4.53 (11)	4.09 (10)		0.35 (7)		0.2176
F(4)	0.42490 (30)	$^3/_4$	0.03457 (33)	4.31 (12)	7.81 (18)	4.39 (13)		−0.97 (10)		0.2640
F(5)	0.44087 (19)	0.55238 (33)	0.25011 (21)	4.69 (8)	3.78 (8)	5.79 (10)	−0.49 (7)	0.81 (7)	1.16 (7)	0.2454

[a] Average root-mean-square displacement along the principal axes of the thermal ellipsoids.

revealed that the fourfold 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/Å³, 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 is 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 SF_3AsF_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 poor quality of the data may be responsible for our failure to solve this structure. The two crystals we examined may have been disordered, as suggested by the large and irregular backgrounds.

The Patterson synthesis indicated that the space group *C2cm* (No. 40) was unlikely since this requires fourfold sets of As and S atoms to be at $Z = ^1/_4, ^3/_4$ or $0, ^1/_2$ and appropriate vectors were not observed. An ordered arrangement in space group $Cmc2_1$ (No. 36) and disordered arrangements in *Cmcm* (No. 63) 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 a conventional R factor of 0.37. The positional parameters for these atoms are given in Table II.

TABLE II

SULFUR AND ARSENIC POSITIONAL PARAMETERS FOR $[SF_3]^+[AsF_6]^-$ ($Cmc2_1$, No. 36)

Atom	No.	x	y	z
As(1)	4	0	−0.0177 (7)	0.0002 (3)
As(2)	8	0.1632 (2)	0.4922 (7)	0.4909[a]
S(1)	4	0	0.4091 (20)	0.3138 (15)
S(2)	8	0.3346 (3)	0.4031 (10)	0.1773 (8)

[a] Fixed value.

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[11] show that the $[SF_3]^+$ has essentially the same character as in $[SF_3]^+[BF_4]^-$.

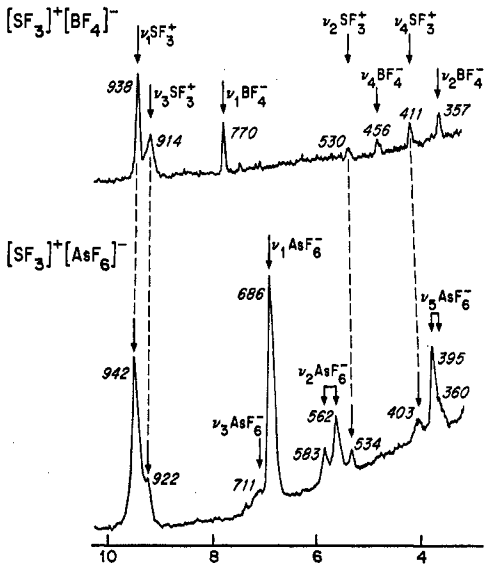

Figure 1.—The Raman spectra of $[SF_3]^+[BF_4]^-$ and $[SF_3]^+$-$[AsF_6]^-$.

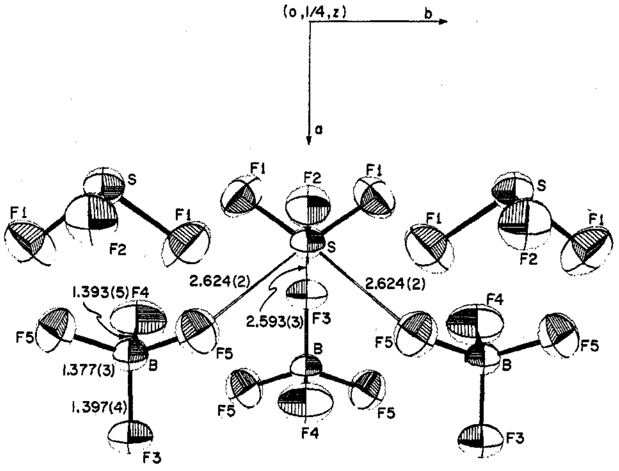

Figure 2.—The atomic arrangement in $[SF_3]^+[BF_4]^-$.

Raman Spectra.—Raman spectra of the powdered adducts $SF_4 \cdot BF_3$ and $SF_4 \cdot AsF_5$ were excited at 4880 Å using a 100-mW 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 ±3 cm⁻¹.

Spectroscopic Results.—The Raman spectra which we obtained for solid $SF_4 \cdot BF_3$ and $SF_4 \cdot AsF_5$ 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 $SF_4 \cdot AsF_5$. 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

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[20] 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 Street, N.W., Washington D. C. 20036, by referring to code number INORG-72-2325. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

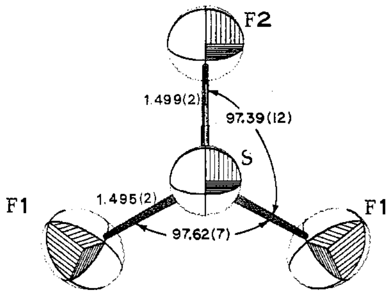

Figure 3.—The shape of the $[SF_3]^+$ ion in $[SF_3]^+[BF_4]^-$.

$SF_4 \cdot BF_3$ [$\nu_1(a_1)$, 938; $\nu_2(a_1)$, 530; $\nu_3(e)$, 914; $\nu_4(e)$, 411 cm^{-1}] were analyzed to 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 mdyn 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_s 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 four close F atom neighbors, is C_s, the BF_4 group is approximately tetrahedral. The chemically significant interatomic distances and angles are given in Table III.

TABLE III

INTERATOMIC DISTANCES[a] (Å) AND ANGLES (DEG) FOR $[SF_3]^+[BF_4]^-$

S–2F(1)	1.495 (2), [1.518]	F(3)···2F(5)	2.277 (3)
S–F(2)	1.499 (2), [1.514]	F(4)···2F(5)	2.249 (3)
S···F(3)	2.593 (3)	F(5)···F(5)	2.275 (4)
S···2F(5)	2.624 (2)	B···2F(1)	3.456 (4)
S···B	3.438 (4)		
S···F(4)	3.111 (3)	F(1)–S–F(1)	97.62 (7)
S···2F(4)	3.265 (2)	F(1)–S–F(2)	97.39 (12)
B–F(3)	1.397 (4), [1.410]	F(3)–B–F(4)	107.63 (25)
B–F(4)	1.393 (5), [1.428]	F(3)–B–F(5)	110.29 (16)
B–2F(5)	1.377 (3), [1.404]	F(4)–B–F(5)	108.58 (17)
F(2)···2F(1)	2.249 (3)	F(5)–B–F(5)	111.37 (14)
F(1)···F(1)	2.250 (4)	S···F(3)–B	115.66 (17)
F(3)···F(4)	2.252 (4)	S···F(5)–B	119.69 (17)

[a] Values in brackets are thermally corrected distances based on in-phase motion of the atoms.

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 three of the four F atoms of the BF_4 species (F(3) and F(5) (twice)) make these closer approaches to S atoms. The closest approach which the fourth F atom of this species, F(4), 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 F(3), which makes the closest approach to a S atom (2.593 (3) Å), the B–F(3) distance is 1.397 (4) Å. This is not significantly different from B–F(4) = 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.

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 nonbonding valence electron pair of S(IV) will provide appreciable screening on the threefold axis, if, as might be expected, it occupies a spatially directed orbital (*e.g.*, an sp^3 hybrid). Such steric activity of the "nonbonding 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 three (of three separate BF_4^- 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) Å (mean 1.386 (6) Å) 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 ± 0.005 Å), KBF_4[22] (1.386 (6) Å), and NH_4BF_4[23] (1.382 (6) Å).

TABLE IV

SHAPE COMPARISON OF ISOELECTRONIC CATION AND MOLECULE PAIRS

	Cation	Molecule
	SF_3^+ [b]	PF_3[a]
M–F, Å	2 at 1.495 (2) 1 at 1.499 (2)	3 at 1.5700 ± 0.0012
F–M–F, deg	2 at 97.39 (12) 1 at 97.62 (07)	3 at 97.8 ± 0.2
	SeF_3^+ [d]	AsF_3[c]
M–F, Å	1.67 (2) 1.64 (2) 1.66 (2)	3 at 1.7063 ± 0.0006
F–M–F, deg	94.9 (1.7) 93.9 (1.7) 94.6 (1.7)	3 at 96.2 ± 0.2
	XeF_5^+ [f]	IF_5[e]
M–F, Å, ax	1.793 (8)	1.817 (10)
eq	2 at 1.841 (8) 2 at 1.848 (8)	4 at 1.873 (5)
F_{ax}–M–F_{eq}, deg	2 at 78.59 (43) 2 at 79.43 (50)	4 at 80.9 (2)

[a] Reference 24. [b] This work. [c] F. B. Clippard and L. S. Bartell, *Inorg. Chem.*, **9**, 805 (1970). [d] Reference 13. [e] Reference 3. [f] N. Bartlett, R. D. Burbank, and G. R. Jones, *Inorg. Chem.*, **9**, 2264 (1970).

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

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S–F interatomic distance being 0.07 Å shorter than the P–F distance. The maintainance of constant shape, despite bond length change, appears to be the rule for cation and isoelectronic neutral molecule pairs, as Table IV illustrates.

The similarity of shape among isoelectronic species may be ascribed to characteristic orbital hybridization of the central atom, the hybridization being characteristic of the period of the periodic table to which the related central atoms belong. On the other hand, molecular shape is often discussed in terms of the mutual repulsions of valence electron pairs, particularly those of the central atom. From this standpoint, the shape of SF_3^+ and PF_3 is fixed by repulsions involving one nonbonding electron pair and three bonding electron pairs about the central atom. This electron-pair arrangement is pseudotetrahedral. Evidently the greater effective nuclear charge of the central atom in SF_3^+ causes the bonding electron pairs to be closer to the central atom than in PF_3, since the bond lengths are significantly shorter in the former than in the latter. However, since the bond angles are the same for SF_3^+ and PF_3, the shapes of the valence electron pair pseudotetrahedra must be similar. Thus if we accept the repulsion model, it seems, at least *for isoelectronic* species, that *increase or decrease of effective nuclear charge at the central atom nucleus has a similar effect on all electrons of the valence shell, whether they are bonding or nonbonding electrons.*

The full refinement of the crystal structure of $[SF_3]^+[BF_4]^-$ and the partial solution of the structure of $[SF_3]^+[AsF_6]^-$ 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 [$\nu_2(e_g)$ of AsF_6^-] and the breakdown of gross selection rules so that $\nu_3(t_{1u})$ of AsF_6^- is observed in the Raman spectrum of $[SF_3]^+[AsF_6]^-$, as are $\nu_1(a_1)$ and $\nu_2(e)$ of BF_4^- in the infrared spectrum of $[SF_3]^+[BF_4]^-$.[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 tetrafluoroborates.[25] 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 possibly 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 (~0.05 Å) than the equatorial bond in SF_4 (1.545 Å), it is dramatically shorter (~0.15 Å) than the axial bonds in the latter (1.646 Å).[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 bonds.[28] (Donation of fluoride ion, $SF_4 \rightarrow SF_3^+ + F^-$, 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 mdyn Å^{-1}, which is comparable with the value of 5.2 mdyn Å^{-1} for the S–F equatorial stretching force constant of SF_4 and approximately twice the value of 2.8 mdyn Å^{-1}, derived for the axial bonds in that molecule.[29]

Acknowledgment.—This work was supported by the United States Atomic Energy Commission, under Contract No. W-7405-eng-48. C. J. A. thanks the Commonwealth Fund of New York for the award of a Harkness Fellowship.

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