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The Crystal Structure of Xenon(II) Fluoride Fluorosulfate, $FXeOSO_2F$

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Received August 23, 1971

The crystal structure of xenon(II) fluoride fluorosulfate has been determined from three-dimensional X-ray data. The compound crystallizes in the orthorhombic system, with eight molecules in a unit cell of dimensions a = 9.88 (1), b = 10.00 (1), and c = 10.13 (1) Å. The space group is *Pbca* and refinement has proceeded satisfactorily in this space group, with a final conventional R factor of 0.045 for 838 nonzero reflections. The structure analysis has established the existence of discrete $FXeOSO_2F$ molecules. The xenon atom is approximately linearly coordinated by an oxygen atom of the fluorosulfate group and a fluorine atom. The angle F–Xe–O is 177.4 (3)°, and the interatomic distances are Xe–F = 1.940 (8) and Xe–O = 2.155 (8) Å. The fluorosulfate group is similar to that observed in the alkali salts, with the difference that, in this structure, the group is distorted as a consequence of one oxygen atom being linked to the xenon atom. This oxygen atom is longer bonded to the sulfur atom and subtends lower angles to its neighboring atoms of the $-OSO_2F$ group than the other oxygen atoms.

Introduction

Xenon difluoride can act as a fluoride ion donor, forming salts with strong fluoride ion acceptors, such as arsenic pentafluoride and metal pentafluorides.[2-5] It also forms 1:1 molecular addition compounds with xenon tetrafluoride,[6] iodine pentafluoride,[7] and xenon oxide tetrafluoride.[8] A third type of complex is obtained by the interaction of the difluoride with fluorosulfonic and perchloric acids.[9] The last type of XeF_2 derivative was the subject of an earlier communication[10] in which we briefly reported the preparation and some properties of $FXeOSO_2F$, $Xe(OSO_2F)_2$, $FXeOClO_3$, and $Xe(OClO_3)_2$. In this paper we give our detailed X-ray single-crystal structural analysis for $FXeOSO_2F$. The related compounds are discussed in a forthcoming paper.[11]

Experimental Section

Xenon(II) fluoride fluorosulfate was prepared by treating XeF_2 with the correct molar quantity of fluorosulfonic acid at −75°,[11] the hydrogen fluoride, formed in the reaction, being removed under vacuum at temperatures below −30°. Material, powdered at ∼−10°, was sealed in thin-walled quartz capillaries. Crystals were grown by sublimation at room temperature.

Crystal Data.—Crystals of $FXeOSO_2F$, mol wt 249.4, are orthorhombic with $a = 9.88 \pm 0.01$, $b = 10.00 \pm 0.01$, $c = 10.13 \pm 0.01$ Å, $V = 1001$ Å^3, $Z = 8$, $d_{calcd} = 3.30 \pm 0.02$ g cm^{-3}, and $F(000) = 896$. Single-crystal precession photographs of the $h0l$, $h1l$, $0kl$, hkk, and hhl levels showed absences for $0kl$, with k odd, $h0l$ with l odd, $hk0$ with h odd, $0k0$ with k odd, and $00l$ with l odd. This indicated that the most probable space group was $Pbca = D_{2h}^{15}$. Complete indexing of the power data, on the basis of the single-crystal parameters, proved that the crystals were representative of the bulk material.

X-Ray Measurements.—Data were recorded, at a temperature of 0 ± 2°, using a manually operated single-crystal orienter, with a low-temperature attachment,[12] on a GE diffractometer using Zr-filtered Mo Kα radiation, λ 0.7107 Å. The crystal was without well-defined faces, edges, or corners and was roughly spherical, the diameter at the outset being ∼0.13 mm. It was mounted with the (001) direction parallel to the ϕ axis of the orienter. High-order $h00$, $0k0$, and $00l$ reflections were used to determine the unit cell constants. Intensities were measured, for both reflections and background, by the stationary-crystal, stationary-counter technique with 10-sec counts. The background measurements were taken at ±1.0° 2θ for reflections up to 20° 2θ and ±2° 2θ beyond this point. Counting rates were kept below 10,000 counts/sec by the use of zirconium filters of known attenuation. Measurements were made on 1453 unique reflections occurring in the range $2\theta \leq 60°$, of which 849 were considered to be observable above the background. The criterion for presence of a reflection was $I > 3\sigma(I)$, where $\sigma(I)$ was determined from counting statistics, *i.e.*, $\sigma(I) = \sqrt{C_P + C_B}$ where C_P is the peak count and C_B is the background counts. Several standard reflections were monitored during the experiment at frequent intervals. There was an overall intensity decrease of about 20% during the collection period. The raw data were divided into eight batches and each batch was corrected by a different scale factor. The eight experimental scale factors were taken directly proportional to the monitored intensities measured at eight different time intervals. The data were then refined as a single problem, yielding a single R value. However, eight scale factor parameters were included in the refinement to serve as a measure of the appropriateness of the original choice of relative scale factors. At the end of the refinement the scale parameters had the following values: 0.7248972, 0.7683301, 0.7608877, 0.7318397, 0.7841719, 0.7549182, 0.7309175, 0.7207349. The chronology of the experimental data is from first to last. The parameters have a mean of 0.7470872, maximum deviation from the mean of 0.0370847, and standard deviation of 0.0216772. There is no systematic trend in the deviation which is as it should be if we have treated the problem properly. The standard deviation is only 2.9% of the mean. We consider this to be a very satisfactory resolution of a difficult experimental problem. The small size and near-spherical nature of the crystal permitted a spherical sample absorption correction to be applied, for which μr was taken to be ≤0.5.

Structure Analysis.[13]—The position of the xenon atom was

(1) (a) University of California at Berkeley. (b) Princeton University. (c) Bell Laboratories.

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

(3) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

(4) V. M. McRae, R. D. Peakcock, and D. R. Russell, *Chem. Commun.*, 62 (1969).

(5) J. G. Knowles and J. H. Holloway, *J. Chem. Soc. A*, 756 (1969).

(6) J. H. Burns, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **18**, 11 (1965).

(7) (a) G. R. Jones, R. D. Burbank, and N. Bartlett, *Inorg. Chem.*, **9**, 2264 (1970); (b) N. Bartlett and F. O. Sladky, *J. Chem. Soc. A*, 2188 (1969).

(8) N. Bartlett and M. Wechsberg, *Z. Anorg. Allg. Chem.*, **385**, 5 (1971).

(9) N. Bartlett and F. O. Sladky, paper presented at 2nd European Fluorine Chemistry Symposium, Gottingen, West Germany, Aug 28–31, 1968.

(10) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones, and R. D. Burbank, *Chem. Commun.*, 703 (1969).

(11) M. Wechsberg, P. A. Bulliner, F. O. Sladky, R. Mews, and N. Bartlett, submitted for publication in *Inorg. Chem.*

(12) R. D. Burbank and S. S. DeBalla, to be submitted for publication.

(13) Programs employed during the analysis included FOUR (C. J. Fritchie, unpublished, modified by L. Guggenberger and P. B Jameison), ORFLS (W. R. Busing, K. O. Martin, and H. A. Levy, ORNL, Department TM-305, 1962, modified by B. B. Cetlin and W. C. Hamilton), ORFFE (W. R. Busing, K. O. Martin, and H. A. Levy, ORNL, Department TM-306, 1964), and ORTEP (C. K. Johnson, ORNL, Department 3794, 1965, modified by R. L. Kornegay). All computations were carried out on a GE 635 computer.

TABLE I
FINAL POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Xe	0.6757 (1)[b]	0.4519 (1)	0.6686 (1)	0.0071 (1)	0.0070 (1)	0.0086 (1)	−0.0008 (1)	0.001 (1)	−0.1007 (1)
S	0.5340 (3)	0.2269 (3)	0.4849 (3)	0.0075 (3)	0.0062 (3)	0.0080 (3)	−0.0002 (2)	0.001 (3)	−0.1001 (3)
F_1	0.8095 (8)	0.5394 (9)	0.7791 (9)	0.0112 (10)	0.0139 (1)	0.0169 (12)	−0.0027 (9)	−0.0023 (9)	−0.0033 (10)
F_2	0.4555 (9)	0.1398 (9)	0.5842 (9)	0.0156 (12)	0.0123 (10)	0.0142 (11)	−0.0056 (1)	0.0013 (10)	0.0039 (9)
O_1	0.5205 (9)	0.3618 (8)	0.5484 (9)	0.0077 (9)	0.0059 (8)	0.0139 (12)	0.0012 (7)	−0.0014 (9)	−0.0030 (8)
O_2	0.6701 (9)	0.1784 (9)	0.4886 (11)	0.0094 (10)	0.0099 (10)	0.0151 (13)	0.0024 (9)	−0.0028 (11)	−0.0022 (10)
O_3	0.4598 (9)	0.2206 (9)	0.3656 (8)	0.0102 (10)	0.0125 (12)	0.0078 (9)	0.001 (9)	−0.0029 (9)	−0.0026 (9)

[a] The form of the anisotropic thermal ellipsoid is $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$. [b] Number in parentheses is the estimated standard deviation in the least significant digit.

derived from the three-dimensional Patterson function, and six cycles of full-matrix, least-squares refinement of the scale, positional, and thermal parameters for this atom in an eightfold position gave a value of 0.29 for the conventional R factor for all reflections. A three-dimensional electron density summation showed the position of the sulfur atom and subsequent refinement for Xe and S yielded $R = 0.21$. The light-atom positions were obtained from a three-dimensional difference synthesis. Refinement by least-squares methods was continued, with scattering factors for neutral Xe, S, F, and O obtained from ref 14. A correction for the real part of the anomalous dispersion effect[14] was made for xenon. The longer bonded terminal ligand of the SO_3F group was assumed to be the fluorine atom. In the final stages of refinement, anisotropic temperature factors were introduced for all atoms and the unobserved reflections were given zero weight in the analysis. The criteria for the latter were $I_{unobsd} = 1.5\sigma(I)$. There were 604 unobserved reflections in a total of 1453. Nine weak, high-order reflections, which appeared to be greatly in error, and two strong, low-order reflections, which were probably subject to extinction effects, were discarded. The final parameter shifts were all less than 0.1σ and the final agreement for 838 observed reflections was $R = 0.0448$ and $R' = 0.0441$ where $R' = \sqrt{\Sigma w(F_o - F_c)^2}/\sqrt{\Sigma w F_o^2}$. Unit weights were used throughout, except when the unobserved reflections were discarded (given zero weight). The standard deviation of an observation of unit weight with this weighting scheme was 2.36. The positional and thermal parameters are listed in Table I. [The F_o and F_c data (Table VI) are given in the microfilm version of this paper. Rms components of thermal displacements (Table VII) are also given in the microfilm edition.[15]]

TABLE II
INTERMOLECULAR CONTACTS LESS THAN 4.0 Å

Xe···F(1^{VIII})[b]	3.760 (8)[a]	Xe···O(2^{III})	3.283 (9)
Xe···F(1^{IX})	3.949 (9)	Xe···O(2^{IV})	3.494 (10)
Xe···F(2^{II})	3.879 (9)	Xe···O(3^{II})	3.313 (9)
Xe···F(2^{V})	3.388 (8)	Xe···O(3^{IV})	3.392 (9)
Xe···O(1^{I})	3.473 (9)		
S···O(2^{X})	3.728 (10)	S···O(3^{IV})	3.960 (10)
F(1)···F(2^{III})	3.209 (13)	F(1)···O(2^{III})	3.262 (14)
F(1)···F(2^{V})	3.127 (12)	F(1)···O(2^{VII})	3.536 (13)
F(1)···O(1^{VI})	3.249 (12)	F(1)···O(2^{IV})	3.338 (13)
F(1)···O(1^{VII})	3.352 (13)	F(1)···O(3^{II})	3.334 (12)
F(2)···F(2^{XI})	3.392 (19)	F(2)···O(3^{IV})	3.173 (13)
F(2)···O(2^{X})	3.435 (14)	F(2)···O(3^{XI})	3.735 (13)
F(2)···O(2^{XI})	3.494 (12)		
O(1)···O(3^{IV})	3.370 (13)	O(1)···O(2^{X})	3.506 (13)
O(1)···O(1^{I})	2.961 (16)		
O(2)···O(3^{II})	3.376 (13)		

[a] Estimated standard deviations in parentheses. [b] The crystal chemical unit is at x, y, z and the Roman numerals refer to equivalent positions: I $(1 - x, 1 - y, 1 - z)$, II $(^1/_2 + x, ^1/_2 - y, 1 - z)$, III $(1^1/_2 - x, ^1/_2 + y, z)$, IV $(x, ^1/_2 - y, ^1/_2 + z)$, V $(1 - x, ^1/_2 + y, 1^1/_2 - z)$, VI $(^1/_2 + x, y, 1^1/_2 - z)$, VII $(1^1/_2 - x, 1 - y, ^1/_2 + z)$, VIII $(x - ^1/_2, y, 1^1/_2 - z)$, IX $(1^1/_2 - x, 1 - y, z - ^1/_2)$, X $(x - ^1/_2, ^1/_2 - y, 1 - z)$, XI $(1 - x, y, 1 - z)$.

(14) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 216.

Discussion

The structural analysis shows that crystals of $FXeOSO_2F$ each consist of an ordered assembly of the monomer units illustrated in Figure 1. None of the

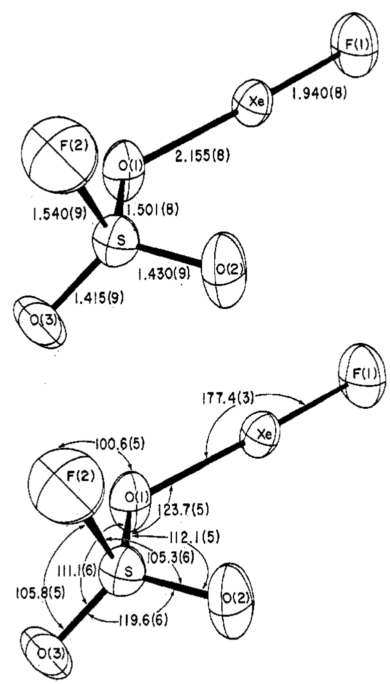


Figure 1.—The $FXeOSO_2F$ molecule (distances in ångströms and angles in degrees).

(shorter) intermolecular contacts listed in Table II are short enough to demand special comment. All distances are compatible with the close packing of somewhat dipolar molecules. The arrangement of the molecules in the lattice is illustrated in Figure 2.

The molecule of $FXeOSO_2F$ consists of a xenon atom approximately linearly coordinated to a fluorine atom on one side and an approximately tetrahedral fluorosulfate group on the other. The fluorosulfate group is coordinated to the Xe atom by way of an oxygen atom. The bond distances and angles are given in Table III.

The near-linear arrangement of F(1)–Xe–O(1) is typical of the coordination geometry previously ob-

(15) Tables VI and VII will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1124. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

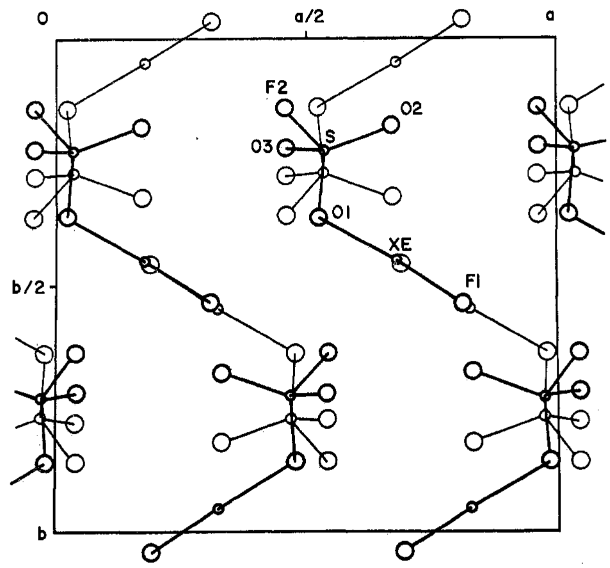


Figure 2.—A view of the molecular arrangement in $FXeOSO_2F$.

TABLE III
INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG) FOR $FXeOSO_2F$

Xe–F(1)	1.940 (8)	Xe–O(1)	2.155 (8)
S–O(1)	1.501 (8)	S–O(2)	1.430 (9)
S–O(3)	1.415 (9)	S–F(2)	1.540 (9)
F(2)–O(1)	2.340 (11)	F(2)–O(2)	2.363 (13)
F(2)–O(3)	2.359 (12)	O(1)–O(2)	2.432 (11)
O(1)–O(3)	2.405 (12)	O(2)–O(3)	2.459 (13)
F(1)–Xe–O(1)	177.4 (0.3)	Xe–O(1)–S	123.7 (0.5)
O(1)–S–O(2)	112.1 (0.5)	O(1)–S–O(3)	111.1 (0.6)
O(1)–S–F(2)	100.6 (0.5)	F(2)–S–O(2)	105.3 (0.6)
F(2)–S–O(3)	105.8 (0.5)	O(2)–S–O(3)	119.6 (0.6)

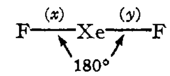
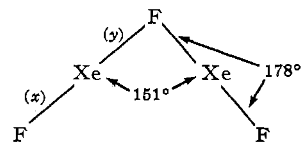
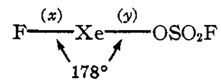
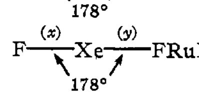
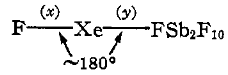
served in Xe(II) compounds. Relevant structural features of xenon difluoride and some of its derivatives are given in Table IV. Although the Xe–F bond in $FXeOSO_2F$ is shorter than in XeF_2 it is larger than the terminal bonds in $Xe_2F_3^+$. The Xe–F bond is evidently much more XeF_2-like than in any of the other derivatives listed.

It is generally agreed that the Xe–F bond in XeF_2 is less than an electron pair bond. The simple molecular orbital bonding model, given first by Pimentel[16a] and Rundle,[16b] depicts the three atoms as bound by one electron pair. In a formally different model, Bilham and Linnett[17] have represented the binding of *each* fluorine atom to the xenon atom by a single electron bond. The valence-bond treatment advocated by Coulson[18] presents a similar picture. Coulson argued that the major canonical forms in the resonance hybrid for XeF_2 are $(F–Xe)^+F^-$ and $F^-(Xe–F)^+$ (both ion species are classical octet species). Again, one bonding electron pair serves for all three atoms. As with the other models mentioned, the valence-bond representation suggests high bond polarity; indeed $^{0.5-}F–Xe^{+}–F^{0.5-}$ appears to be at least an approximate representation. The valence-bond approach is probably the most suitable one for the discussion of the $FXeOSO_2F$ structure.

It is reasonable to assume that the major canonical

(16) (a) G. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951); (b) R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 112 (1963).
(17) J. Bilham and J. W. Linnett, *Nature (London)*, **201**, 1323 (1964).
(18) C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).

TABLE IV
COMPARISON OF THE Xe(II) COORDINATION IN XeF_2 AND SOME OF ITS DERIVATIVES

	(x), Å	(y), Å	Ref
	2.01 (1)	2.01 (1)	*a*
	1.90 (2)	2.14 (1)	*b*
	1.94 (1)	2.16 (1)	Present work
	1.88 (2)	2.19 (2)	*c*
	1.84 (2)	2.35 (2)	*d*

[a] H. A. Levy and P. A. Agron, *J. Amer. Chem. Soc.*, **85**, 241 (1963). [b] Reference 2. [c] N. Bartlett, D. Gibler, M. Gennis, and A. Zalkin, to be submitted for publication. [d] Reference 4.

forms in the $FXeOSO_2F$ resonance hybrid are $(F–Xe)^+(SO_3F)^-$ and $^-F(XeOSO_2F)^+$. The bond length of 1.94 Å for Xe–F suggests that the $(Xe–F)^+$ weight is greater than in XeF_2 and therefore indicates that $(F–Xe)^+(SO_3F)^-$ is more dominant than $F^-(Xe–OSO_2F)^+$ in the resonance hybrid. A more quantitative measure of this dominance is of interest and can be derived from consideration of the Xe–F and Xe–O bond lengths.

The shortest observed[4] Xe(II)–F bond is the terminal bond in the compound $FXeFSb_2F_{10}$. This bond, which has a length of 1.84 Å, is shorter than the bond in the I–F molecule, which is reported[19a] to be 1.906 Å. Furthermore, the stretching frequency ν(Xe–F) = 621 cm^{-1} in $FXeFSb_2F_{10}$ is greater than given[19b] for ν(I–F) = 610 cm^{-1}. This suggests that the Xe–F species in $FXeFSb_2F_{10}$ is, at least approximately, the cation $(Xe–F)^+$. (The cation is isoelectronic with I–F.) Both of these species may be represented in conventional bonding models, as electron pair bonded octet species. If we assign the electron pair bond as possessing bond order unity, then the bond order in $(Xe–F)^+$ is 1 and in XeF_2 it is 0.5.[3]

Although the relationship between bond order and bond length is not easily resolved from purely theoretical considerations, Pauling has given[20] an empirical relationship for fractional bonds: $D(n) = D(1) - 0.60 \log n$, where $D(n)$ is the bond length for bond of order n and $D(1)$ is the bond length for order unity. Solving for the latter, assuming (from the XeF_2 data) $D(0.5) = 2.01$ Å, the Xe–F bond length $D(1) = 1.83$ Å, which is in excellent agreement with our hypothesis. Continuing on this basis, the bond order in the terminal Xe–F bond in $FXeFSb_2F_{10}$ is 0.96, whereas the terminal bonds in $Xe_2F_3^+$ have a bond order of 0.76. The XeF bond order in $FXeOSO_2F$ is only 0.63. If this result and our assumptions concerning the major canonical forms are valid, the canonical form $(F–Xe)^+(OSO_2F)^-$ has a 63:37 dominance over the $^-F(XeOSO_2F)^+$ form.

The Xe–O bond lenth is larger than any Xe–O bond

(19) (a) L. G. Cole and G. W. Elverum, Jr., *J. Chem. Phys.* **20**, 1543 (1952); R. A. Durie, *Proc. Roy. Soc., Ser. A*, **207**, 388 (1951).
(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 255.

previously described, but a treatment analogous to that given in the Xe–F case cannot be made, since this is the first case of a Xe(II)–O bond length. It should be noted, however, that the bond lengths in both XeO_3 and XeO_4, which are 1.76 and 1.74 Å, respectively,[21,22] are much shorter than the bond observed here. The Xe–O bonds in XeO_3 and XeO_4 can either be described as double bonds (*i.e.*, ($Xe{=}O_3$ and $Xe{=}O_4$) or as semiionic bonded species (*i.e.*,$(Xe^+{:}{\rightarrow}O^-)_3$ and $(Xe^+{:}{\rightarrow}O^-)_4$). Either representation indicates that it would not be realistic to take 1.74 Å as the bond length for bond order unity. It is however possible to make a rough estimate of the bond order if we assume[23] that the bond length in Xe:O is akin to that in isoelectronic I:F, namely, 1.91 Å. On this basis, the 2.16-Å Xe–O bond in $FXeOSO_2F$ has a bond order of 0.38. This is in close agreement with the dominance of the $(F\text{–}Xe)^+(OSO_2F)^-$ canonical form derived earlier.

The fluorosulfate geometry is compatible with the partial ionic bonding just discussed. It should first be noted that the shape of the $-OSO_2F$ group is fully consistent with the assignment of the fluorine atom to the position shown. The F(2)–S bond is not only the longest in the $-OSO_2F$ group, but the bond angles, which this bond subtends to the other bonds in this group, are in the range 100–106°, and are, on the whole, less than the angles subtended by the other bonds to adjacent bonds. It is also impressive that the plane defined by the atoms F(2), S, and O(1) is not significantly different from a mirror plane, as far as the $-OSO_2F$ group is concerned. The F–Xe–O(1) group of atoms does not lie in the plane just defined, but there is no reason to anticipate restricted rotation about either the Xe–O(1) or O(1)–S bonds. Therefore the disposition adopted in this lattice is presumably one which results from the best packing and crystal energy.

The greater bond angles for O–S–O (*e.g.*, 120°) compared with O–S–F (106°) may be atrributed to the greater repulsive effect of oxygen atoms. This may either be due to double bonding of oxygen to sulfur (*i.e.*, to four-electron bonding) or be due to high bond polarity (a consequence of a semiionic linkage $S^+{:}{\rightarrow}O^-$). Many object to the major involvement of sulfur 3d orbitals in bonding.[24] For them, the latter model for the S–O bond is appropriate. With this representation, each of the terminal S–O bonds is a semiionic linkage (involving one electron pair) and the S–F bond is an electron pair (covalent) bond. Clearly, for the isolated SO_3F^- group we should anticipate three equivalent, semiionic S–O bonds and this appears to be the case in KSO_3F[25] and NH_4SO_3F.[26] Such a situation is not observed in $FXeOSO_2F$. We see, rather, that the third oxygen ligand of the sulfur atom (O(1)) subtends smaller angles to the other oxygen atoms (112, 111°) than they do to one another (120°). Furthermore, the fluorine atom (F(2)), subtends smaller angles to O(1) (101°) than to the other oxygen ligands (105.8, 105.3°). This means that the repulsive effect of O(1) is less than for O(2) or O(3), although evidently greater than for F(2). This is compatible with a decrease in the net negative charge borne by the ligands in the sequence O(2) = O(3) > O(1) > F(2). The greater polarity of the S–O(terminal) bonds compared with S–O(bridge) may also account for the former bonds being significantly shorter than the latter.

It is instructive to compare the $-OSO_2F$ group observed here with the SO_3F^- ion observed in the potassium[25] and ammonium[26] salts. Although there is evidently disordering of the O and F placement of the sulfur ligands in the anion in the potassium salt and partial disordering in the ammonium salt, ion dimensions were determined for each case, assuming C_{3v} symmetry[25,26] of the disordered ion.

The $-OSO_2F$ and SO_3F^- species are compared in Table V. Evidently the S–F and S–O(terminal) bonds in the xenon compound are essentially the same as in the simple salts. Indeed even the bond angles are remarkably akin, except for those subtended by the S–O(1) bond. Departure of the $-OSO_2F$ group geometry from the ionic (SO_3F^-) ideal may be attributed solely to a change in the character of the oxygen atom O(1) linked to xenon. The atom O(1) has evidently lost electron density to the Xe–F group. This fits rather conveniently into the description of the SO_3F^- species as a sulfur atom semiionic bonded ($S^+{:}{\rightarrow}O^-$) to each oxygen atom and electron pair bonded to the F atom (S:F). But in the xenon compound, atom O(1) possesses less electron density, as a consequence of the contributing canonical form $(FO_2SO\text{–}Xe)^+F^-$, in which O(1) is bicovalent.

TABLE V

COMPARISON OF THE $-OSO_2F$ DIMENSIONS (Å AND DEG) WITH THOSE OF SO_3F^- IN KSO_3F[a] AND NH_4SO_3F[b]

	$-OSO_2F$		SO_3F^-
F(2)–S	1.54 (1)	F–S	1.58 (2)[a]; 1.55 (1)[b]
O(2)–S	1.43 (1)	O–S	1.43 (1)[a]; 1.45 (1)[b]
O(3)–S	1.42 (1)		
O(1)–S	1.50 (1)		
F(2)–S–O(3)	105.8 (5)	F–S–O	106.0 (5)[a]; 105.8 (7)[b]
F(2)–S–O(2)	105.3 (6)		
F(2)–S–O(1)	100.6 (5)		
O(2)–S–O(3)	119.6 (6)	O–S–O	112.9 (7)[a]; 113.0 (5)[b]
O(2)–S–O(1)	112.1 (5)		
O(3)–S–O(1)	111.1 (6)		

[a] Reference 25. [b] Reference 26.

Acknowledgment.—The authors are grateful to the National Science Foundation for Grant GP-7153X, for support of that part of this work which was carried out at Princeton University.

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