Crystal Structure of μ-Fluorosulphato-bis[fluoroxenon(II)] Hexafluoroarsenate(V)

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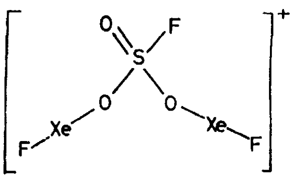
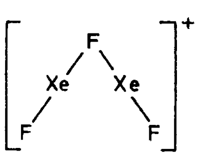
The crystal structure of $[(XeF)_2SFO_3][AsF_6]$ has been determined from three-dimensional *X*-ray counter data. Crystals are monoclinic with $a = 11.178(5)$, $b = 8.718(5)$, $c = 11.687(6)$ Å, $\beta = 91.28(4)°$, $U = 1\,132$ Å^3, $Z = 4$, and $D_c = 3.45$ g cm^{-3}. The structure has been refined in the space group $P2_1/n$ to a final conventional R' of 0.87 for 1 147 independent reflections. The structure consists of discrete $[(XeF)_2SFO_3][AsF_6]$ units with no cation–anion contact less than 3.0 Å. The cation consists of a nearly tetrahedral fluorosulphate group having a Xe–O bond to each Xe–F group. The two linear F–Xe–O groups are slightly staggered with respect to each other.

THE salt $[(XeF)_2SFO_3][AsF_6]$ was prepared and studied spectroscopically by Bartlett and his co-workers,[1] Gillespie and Schrobilgen,[2] and Schrobilgen and his co-workers.[3] It was concluded from Raman,[1,2] ^{19}F n.m.r.,[2] and ^{129}Xe n.m.r. data [3] that the cation had the fluorosulphate-bridged structure (1), analogous to the fluoride-bridged cation $[Xe_2F_3]^+$, structure (2).[4] We now report a detailed single-crystal structure analysis of this salt.



(1)



(2)

EXPERIMENTAL

Materials.—Details of the techniques used for the preparation of $[(XeF)_2SFO_3][AsF_6]$ are described elsewhere.[2]

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[1] M. Wechsberg, P. A. Bulliner, F. O. Sladky, R. Mews, and N. Bartlett, *Inorg. Chem.*, 1972, **11**, 3063.

[2] R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1974, **13**, 1694.

[3] J. H. Holloway, G. J. Schrobilgen, P. Granger, and C. Brevard, *Compt. rend.*, 1976, **282**, 519.

[4] N. Bartlett, B. G. DeBoer, F. J. Hollander, F. O. Sladky, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1974, **13**, 780.

The salt was prepared by the reaction of stoicheiometric amounts of $HSFO_3$ with $[Xe_2F_3][AsF_6]$ in HF solution. Crystals were grown by subliming the bulk material under dynamic vacuum at 35 to 40 °C in a Pyrex glass tube (15 cm × 8 mm internal diameter) for 30 min. Single crystals were selected and transferred to dry quartz capillaries in a dry-box and sealed. A Raman spectrum of the single crystal used for the X-ray structure determination showed it to be identical with the bulk material.

TABLE 1

Positional and thermal parameters ($\times 10^4$) for $[(XeF)_2SFO_3][AsF_6]$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Xe(1)	1 487(2)	1 774(3)	−1 108(2)	741(17)	518(15)	643(16)	−110(14)	192(13)	−29(13)
Xe(2)	−3 794(2)	0 809(3)	−2 078(2)	664(16)	441(13)	745(17)	24(13)	38(12)	−13(13)
As	−1 919(3)	3 144(4)	636(3)	629(24)	396(22)	571(24)	−42(19)	233(19)	73(20)
S	−926(10)	945(12)	−2 689(9)	770(76)	568(66)	784(78)	−108(58)	137(58)	−197(59)

	x/a	y/b	z/c	U		x/a	y/b	z/c	U
O(1)	−2 107(20)	1 661(29)	−2 825(20)	607(66)	F(4)	−1 667(28)	2 259(37)	1 851(27)	1 253(104)
O(2)	−43(22)	2 091(30)	−2 306(21)	672(73)	F(5)	−533(29)	3 718(39)	737(28)	1 341(110)
O(3)	−883(26)	−423(38)	−2 084(26)	907(94)	F(6)	−2 086(24)	4 039(33)	−603(23)	1 054(86)
F(1)	−614(22)	637(31)	−3 939(22)	941(78)	F(7)	−2 592(32)	4 597(43)	1 356(30)	1 487(125)
F(2)	−3 300(31)	2 431(41)	487(29)	1 430(122)	F(8)	2 793(23)	1 583(32)	−96(22)	1 011(82)
F(3)	−1 384(25)	1 581(35)	−134(24)	1 129(92)	F(9)	−4 754(23)	−152(32)	+1 494(22)	989(84)

Anisotropic temperature factors U_{ij} are given by the expression: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}]$.

Crystal Data.—$AsF_9O_3SXe_2$, Monoclinic, $a = 11.178(5)$, $b = 8.718(5)$, $c = 11.687(6)$ Å, $\beta = 91.28(4)°$, $U = 1\,132$ Å^3, $Z = 4$, $D_c = 3.45$ g cm^{-3}, $F_w = 588.5$, $F(000) = 1\,036$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, and $\mu(\text{Mo-}K_\alpha) = 95$ cm^{-1}. The unit-cell parameters were obtained from a least-squares refinement of 15 reflections in the region $20 < 2\theta < 25°$. Preliminary precession and Weissenberg photographs indicated that reflections were absent for $h0l$ when $h + l = 2n + 1$, and $0k0$ when $k = 2n + 1$. These absences are characteristic of the space group $P2_1/n$, an alternative orientation of $P2_1/c$ (no. 14).[5] Equivalent positions for the non-standard space group are: x, y, z; $-x, -y, -z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

X-*Ray Measurements.*—A crystal of approximate dimensions 0.4 × 0.2 × 0.2 mm was examined on a four-circle Syntex $P\bar{1}$ diffractometer with a fine-focus molybdenum anode tube and graphite monochromator. The crystal was mounted with its b axis approximately coincident with the ϕ axis of the diffractometer. Data were collected in a manner similar to that described previously.[6] A total of 1 529 reflections were measured within a quadrant with $2\theta < 45°$. Subsequent averaging resulted in a total of 1 147 independent reflections, of which 832 had intensities greater than three times their standard deviation based on counting statistics. Structure factors were computed by application of Lorentz and polarization corrections. The absorption correction was computed with $\mu R = 1.0$, assuming the crystal to be cylindrical.

Solution and Refinement of the Structure.—The positions of two xenon, an arsenic, and a sulphur atom were obtained from the three-dimensional Patterson function. Two cycles of least-squares refinement using an overall scale factor and positional and isotropic thermal parameters gave R 0.19. Scattering curves for neutral atoms were corrected for anomalous dispersion using values for the real and imaginary parts given in the International Tables.[7] A three-dimensional electron-density map, phased on the heavy-atom positions, gave the locations of all the light atoms. Since it is not possible to distinguish between oxygen and fluorine by X-ray methods, *all the light atoms* around sulphur were assumed to be oxygen. Full-matrix least-squares refinement gave an R of 0.128. The sulphur–terminal-atom distances of 1.39 and 1.53 Å were assumed to correspond to an S=O and an S–F bond respectively.[8] The appropriate scattering curves were applied and anisotropic

TABLE 2

Interatomic bond lengths (Å) and bond angles (°)

(*i*) Interatomic distances <2.3 Å			
Xe(1)–F(8)	1.86(3)	As–F(2)	1.67(3)
Xe(1)–O(2)	2.20(2)	As–F(3)	1.75(3)
Xe(2)–F(19)	1.86(3)	As–F(4)	1.63(3)
Xe(2)–O(1)	2.22(2)	As–F(5)	1.63(3)
S–O(1)	1.47(3)	As–F(6)	1.65(3)
S–O(2)	1.47(3)	As–F(7)	1.71(3)
S–O(3)	1.39(3)		
S–F(1)	1.53(3)		
(*ii*) Contacts <3.5 Å to Xe			
Xe(1)–S	3.31(1)	Xe(2)–S	3.30(1)
Xe(1)–O(3)	3.44(3)	Xe(2)–O(3)	3.43(3)
Xe(1)–F(3)	3.43(3)	Xe(2)–O(3^{V})	3.44(3)
Xe(1)–F(3^{I})	3.27(3)	Xe(2)–F(2)	3.35(3)
Xe(1)–F(4^{II})	3.30(3)	Xe(2)–F(5^{III})	3.29(3)
Xe(1)–F(7^{II})	3.38(4)	Xe(2)–F(6^{V})	3.45(3)
Xe(1)–F(7^{IV})	3.41(4)	Xe(2)–O(3^{V})	3.20(3)
(*iii*) Angles			
F(8)–Xe(1)–O(2)	178(1)	F(2)–As–F(3)	89(2)
F(9)–Xe(2)–O(1)	177(1)	F(2)–As–F(4)	93(2)
O(1)–S–O(2)	110(1)	F(2)–As–F(5)	176(2)
O(1)–S–O(3)	116(2)	F(2)–As–F(6)	90(2)
O(1)–S–F(1)	101(1)	F(2)–As–F(7)	85(2)
O(2)–S–O(3)	114(2)	F(3)–As–F(4)	91(1)
O(2)–S–F(1)	104(1)	F(3)–As–F(5)	87(2)
O(3)–S–F(1)	109(2)	F(3)–As–F(6)	87(1)
Xe(1)–O(2)–S	128(2)	F(3)–As–F(7)	174(2)
Xe(2)–O(1)–S	126(1)	F(4)–As–F(5)	86(2)
		F(4)–As–F(6)	177(1)
		F(4)–As–F(7)	89(2)
		F(5)–As–F(6)	90(1)
		F(5)–As–F(7)	100(2)
		F(6)–As–F(7)	92(2)

Roman numeral superscripts refer to atoms in the positions:

I $-x, -y, -z$
II $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
III $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
IV $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
V $-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$

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[5] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1965, vol. 1.

[6] P. Boldrini, R. J. Gillespie, P. R. Ireland, and G. J. Schrobilgen, *Inorg. Chem.*, 1974, **13**, 1690.

[7] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

[8] N. Bartlett, M. Wechsberg, G. R. Jones, and R. D. Burbank, *Inorg. Chem.*, 1972, **11**, 1124.

temperature factors were introduced for the heavy atoms. A final R' index, based on unit weights, of 0.087 was obtained. The final R was 0.078 and the largest shift, Δ/σ, was 0.1 in the final cycle of refinement. A final difference-Fourier map showed no peak greater than 0.5 eÅ^{-3}. Final positional and thermal parameters are in Table 1 and interatomic distances and angles in Table 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21997 (7 pp.).*

DISCUSSION

The structural unit (Figure 1) consists of $[(XeF)_2SFO_3]^+$ cations and $[AsF_6]^-$ anions. The cation consists of an approximately tetrahedral SFO_3 group bonded to two XeF groups by means of two oxygen atoms. The S–F distance (1.53 Å) is close to that found in the related $XeF(SFO_3)$ molecule (1.54 Å),[8] and the S–O(3) bond length (1.39 Å) is close to the corresponding S–O distance in $XeF(SFO_3)$ (1.42 Å).[8] In both cases these S–O bonds can be regarded as having a bond order of *ca.* 2. The S–O(1) and S–O(2) bond lengths are much longer (1.47 Å), although somewhat shorter than expected for a single S–O bond and slightly shorter than the corresponding S–O bond in $XeF(SFO_3)$ (1.50 Å).[8] The bond lengths about the sulphur are consistent with a description of the cation in terms of the valence-bond structures (3).

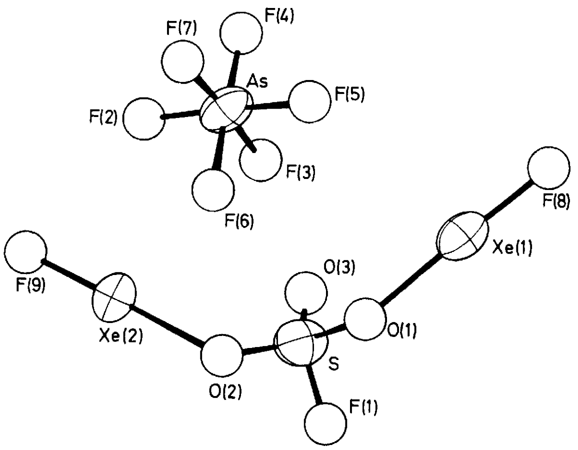
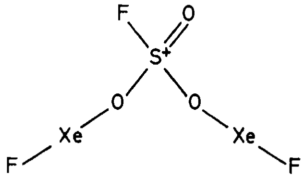


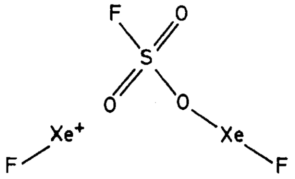
FIGURE 1 Projection of the asymmetric unit down the c axis

The angles about sulphur are also of interest. The O–S–O bond angles lie in the range 110—116° whereas the F–S–O angles lie in the range 101—109°. This is consistent with the greater electronegativity of fluorine and also with the greater bond order of the S–O bonds compared with the S–F bond.[9] A similar difference in the O–S–O and F–S–O bond angles was found in $XeF(SFO_3)$.[8]

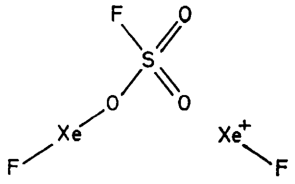
The F–Xe–O angles are close to 180° which is expected for an AX_2E_3 system.[9] The mean Xe–F bond length (1.86 Å) is somewhat shorter than that found in $XeF(SFO_3)$ (1.94 Å),[8] but longer than that in $[XeF][Sb_2F_{11}]$ (1.82 Å).[10] We may, therefore, reasonably describe the bonding in $[(XeF)_2SFO_3]^+$ in terms of the 'covalent' structure (3a) together with an important contribution from the 'ionic' structures (3b) and (3c). Furthermore, the Xe–O distances of 2.21 Å in $[(XeF)_2SFO_3]^+$ are much too short to allow us to suppose that this cation can be described as an $[SFO_3]^-$ ion weakly bonded to two essentially free $[XeF]^+$ ions [*cf.* Xe–O in $XeF(SFO_3)$ is 2.16 Å, and the Xe–O contact distance for a pure 'ionic' structure which may be taken to be the sum of the van der Waals radii, *i.e.* 3.7 Å]. We may conclude that the interaction between the XeF and the SFO_3 groups is more 'ionic' in $[(XeF)_2SFO_3]^+$ than in $XeF(SFO_3)$ but less 'ionic' than the interaction between the XeF and Sb_2F_{11} groups in $FXe\cdots FSb_2F_{10}$. This view is supported by recent studies of the ^{129}Xe and ^{19}F chemical shifts of xenon(II) species in solution, which have demonstrated that both the ^{19}F and ^{129}Xe chemical shifts[3] of the $[(XeF)_2SFO_3]^+$ cation ($HSFO_3$ and BrF_5 solution) are approximately intermediate between those of $XeF(SFO_3)$ ($HSFO_3$ and BrF_5 solution) and $[XeF]^+$ ($HSFO_3$ and SbF_5 solution).



(3a)



(3b)



(3c)

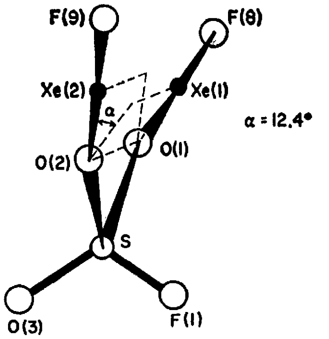


FIGURE 2 The $[(XeF)_2SFO_3]^+$ cation

The dihedral angle (α) Xe(1)O(1) ··· O(2)Xe(2) is

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* See Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[9] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand Reinhold Co., London, 1972.

[10] J. Burgess, C. J. W. Fraser, V. M. McRae, R. D. Peacock, and D. R. Russell, Suppl. to *J. Inorg. Nuclear Chem.*, eds. J. J. Katz and I. Sheft, Pergamon, Oxford, 1976, p. 183.

12.4° (Figure 2); thus the cation has C_1 rather than C_s symmetry as was assumed in an earlier Raman-spectroscopic investigation.[2] The $[AsF_6]^-$ ion is a slightly distorted octahedron with a mean As–F distance of 1.67 Å which is similar to that found in $[Xe_2F_3][AsF_6]$ (1.63 Å).[4]

The Raman spectrum contained four strong lines at *554*, *566*, *571*, and 582 cm^{-1} which have been assigned to factor-group-split in-phase and out-of-phase Xe–F stretching modes. On the basis of the observed crystal space and molecular-point groups, the correlation diagram for the $[(XeF)_2SFO_3]^+$ modes (*cf.* the correlation diagram for $[XeF_3]^+$, C_{2v} symmetry, and the identical space group in ref. 11), shows that in principle each normal mode of the cation should give rise to two Raman-active modes, an a_g and a b_g mode. The Xe–F stretching modes are evidently much more strongly coupled in the unit cell than the other vibrational modes of the cation. Similar strong factor-group splittings of symmetric Xe–F and Kr–F stretching modes have also been observed in $[KrF]^+$, $[XeF]^+$, and $[XeF_3]^+$ compounds.[11,12]

Packing of the $[(XeF)_2SFO_3][AsF_6]$ structural units is illustrated in Figure 3. There are no interionic contacts less than 3.0 Å and we may conclude that there are no interionic fluorine-bridge interactions and that the structure of $[(XeF)_2SFO_3][AsF_6]$ is satisfactorily described as ionic. This is consistent with the Raman spectrum observed for the $[AsF_6]^-$ anion [2] which consists of only three Raman-active lines which can be readily assigned to the a_{1g}, e_g, and t_{2g} modes of an undistorted $[AsF_6]^-$ ion possessing O_h symmetry.

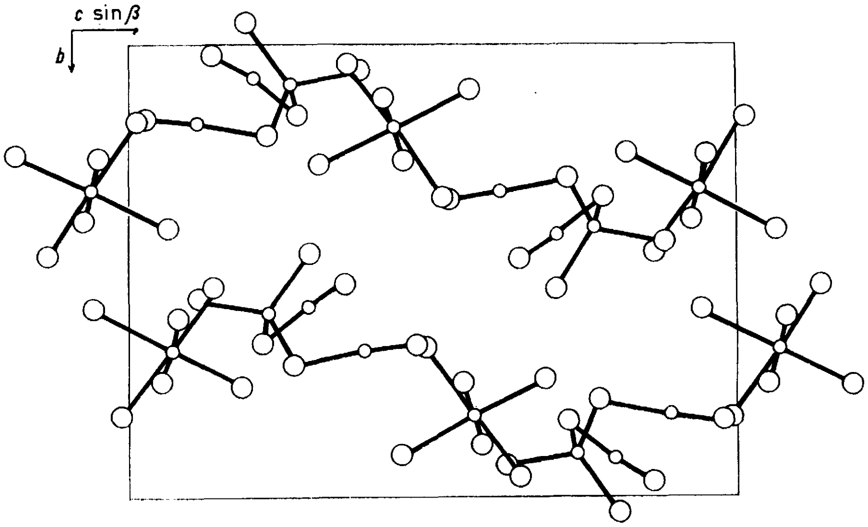

FIGURE 3 Projection of the structure down the *a* axis

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[6/1970 *Received, 25th October*, 1976]

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[11] R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 1256.

[12] R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 22.