Crystal Structure of Trifluoro-oxosulphur(VI) Hexafluoroarsenate(V), $OSF_3^+AsF_6^-$

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The crystal structure of the title compound has been determined from three-dimensional diffractometer data. Crystals are orthorhombic, unit cell dimensions: a = 10·88(1), b = 7·366(7), and c = 8·473(9) Å, Z = 4, space group *Pnma*. The atomic parameters were refined by block-diagonal least-squares to R 0·046 for 331 observed reflections. The structure consists of discrete OSF_3^+ and AsF_6^- ions. The OSF_3^+ group is a distorted tetrahedron with bond lengths (corrected for libration in parentheses) S–O 1·35(1) (1·37), S–F(5) 1·44(1) (1·45), and S–F(6) 1·45 (1) (1·46) Å; bond angles F(6)–S–O 116·3(6), F(5)–S–O 115·5(6), and F(5)–S–F(6) 102·0(5)°. The S–F bond length is the shortest so far reported. The S–O bond length is also shorter than those determined previously, but is not significantly different from the axial S–O in S_3O_9. The structure of OSF_3^+ is compared with those of some related species.

Solid 1 : 1 complexes of OSF_4 and BF_3, AsF_5, and SbF_5 were first prepared[1] in 1959. More recently it was shown,[2] on the basis of conductivity measurements in HF, ^{19}F n.m.r. spectra, and laser Raman spectroscopy, that the AsF_5 and SbF_5 adducts contained the OSF_3^+ cation. The S–O and S–F stretching frequencies were found to be the highest so far recorded. In the course of studying the thermal decomposition of $OSClF_2^+$-AsF_6^-, we found that crystals of $OSF_3^+AsF_6^-$ were readily grown by sublimation.[3] We therefore determined the crystal structure of $OSF_3^+AsF_6^-$ in order to establish the extent of any anion–cation interaction, and to find the exact configuration of the OSF_3^+ ion, of interest in terms of current theories of bonding[4-7] and stereochemistry.[8]

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[1] F. Seel and O. Detmer, *Z. anorg. Chem.*, 1959, **301**, 113.

[2] M. Brownstein, P. A. W. Dean, and R. J. Gillespie, *Chem. Comm.*, 1970, 9.

[3] C. Lau and J. Passmore, *J.C.S. Dalton*, 1973, 2528.

[4] D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.

[5] R. E. Rundle, *Record Chem. Progr.*, 1962, **23**, 195.

[6] K. A. R. Mitchell, *Chem. Rev.*, 1969, **69**, 157.

[7] J. I. Musher, *Angew. Chem. Internat. Edn.*, 1969, **8**, 54.

[8] R. J. Gillespie, *Angew. Chem. Internat. Edn.*, 1967, **6**, 819, and refs. therein.

EXPERIMENTAL

Crystal Preparation.—$OSF_3^+AsF_6^-$ was prepared by the reaction of OSF_4 and AsF_5 in apparatus described in ref. 3. Small lumps of the compoundwere placed, in a dry-box, into carefully dried thin-walled silica capillaries [o.d. 0·3 mm], which were quickly sealed off, by a small hot flame. A number of such capillaries were placed on the bottom of a beaker, with one end of each capillary propped up by a small piece of plasticine and left on the top of an oven for several weeks. The crystals were periodically examined under the polarizing microscope, until a suitable single crystal was formed.

TABLE 1

Distribution and statistics of the normalized structure factors $|E|$

	Calc. Centric	Calc. Non-Centric	Obs.
$\langle\|E\|\rangle$	0·798	0·886	0·872
$\langle\|E\|^2\rangle$	1·000	1·000	1·021
$\langle\|E^2 - 1\|\rangle$	0·968	0·736	0·875
$\|E\| > 3·0$	0·27%	0·01%	0·15%
$\|E\| > 2·5$	1·24%	0·19%	0·46%
$\|E\| > 2·0$	4·55%	1·83%	3·71%
$\|E\| > 1·8$	7·19%	3·92%	6·80%
$\|E\| > 1·6$	10·96%	7·73%	10·82%
$\|E\| > 1·4$	16·15%	14·09%	15·61%
$\|E\| > 1·2$	23·01%	23·69%	23·18%
$\|E\| > 1·0$	31·73%	36·79%	30·45%

Crystal Data.—$OSF_3^+AsF_6^-$, $M = 294·0$, Orthorhombic, $a = 10·88(1)$, $b = 7·366(7)$, $c = 8·473(9)$ Å, $U = 678·7$ Å^3, $Z = 4$, $D_c = 3·0$ gm cm^{-3}. Space group *Pnma* (D_{2h}^{16}) or $Pn2_1a$, (C_{2v}^9). Mo-K_α radiation, $\lambda = 0·7107$ Å; μ(Mo-K_α) = 59·76 cm^{-1}. Unit-cell dimensions and their estimated standard deviations were obtained from a least-squares evaluation of 12 independent reflections. U satisfies Zachariasen's criterion [9] for close-packed fluoride lattices, since the effective mean volume for a fluorine atom is 17·0 Å^3 (oxygen atoms treated as fluorine).

TABLE 2

Final positional ($\times 10^4$) and thermal parameters ($\times 10^3$) * with estimated standard deviations in parentheses

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As	0118(1)	2500	2066(2)	74(1)	75(1)	100(2)	0	5(2)	0
F(1)	−0025(22)	2500	0099(17)	615(50)	182(22)	150(16)	0	−213(26)	0
F(2)	0351(17)	2500	4036(14)	446(39)	270(27)	84(14)	0	14(21)	0
F(3)	1207(7)	0868(10)	1907(9)	164(10)	103(9)	212(13)	36(10)	63(10)	55(8)
F(4)	−0919(8)	4148(14)	2300(18)	144(10)	151(13)	620(31)	1(21)	74(18)	75(11)
S	3033(4)	2500	8371(5)	95(4)	88(5)	88(5)	0	13(4)	0
O	2328(11)	2500	7065(14)	146(16)	133(17)	133(19)	0	−68(16)	0
F(5)	4339(8)	2500	8099(11)	98(10)	110(11)	115(13)	0	16(10)	0
F(6)	2887(7)	4032(11)	9423(8)	164(10)	118(10)	122(9)	−33(8)	37(8)	28(9)

* In the form: $\exp[-2\pi^2(a^{*2}h^2U_{11} + \ldots 2b^*c^*klU_{23} + \ldots)]$.

X-Ray Data.—Intensity data were collected on a Picker computer-controlled four-angle diffractometer with a θ—2θ scan with β-filtered Mo-K_α radiation. The two octants hkl and $\bar{h}kl$ were explored to a maximum 2θ of 50° and averaged. Of 647 accessible independent reflections, 331 were considered observed. The crystal was elongated along b with dimensions $0·26 \times 0·08 \times 0·08$ mm. No corrections were made for absorption or extinction.

Structure Analysis.—A three-dimensional Patterson synthesis established the arsenic atoms in special positions 4*c* of space group *Pnma*. The remaining atoms were located from a Fourier synthesis using the arsenic phases. The sulphur, oxygen, and fluorine atoms F(1), F(2), and F(5) are in special positions 4*c*, and the fluorine atoms F(3), F(4), and F(6) in general positions 8*d*.

Refinement was carried out by minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$ for observed reflections only using successive cycles of block-diagonal least-squares with 3×3 matrices for atomic co-ordinates and 6×6 matrices for anisotropic thermal parameters for each of the atoms. The weighting function used was $w = \{1 + [(|F_o| - P_2)/P_1]^4\}^{-1}$ with $P_1 = 26$ and $P_2 = 36$. Scattering-factor curves were taken from ref. 10 with corrections for anomalous dispersion for arsenic and sulphur.[11] The final R was 0·046. In the last cycle no parameter shift was $> 0·1\sigma$. A difference-Fourier synthesis showed no residual peaks $> 0·3$ eÅ^{-3}.

The choice of space group *Pnma* is supported by examination of the normalized structure-factor table (Table 1) which shows that the structure is nearer to centrosymmetric. Refinement of the structure in the noncentric space group $Pn2_1a$ was attempted but successive cycles of least squares were not convergent. A set of structure factors for the final parameters given in Table 2 are listed in Supplementary Publication No. SUP 20767 (4 pp., 1 microfiche).*

DISCUSSION

Interatomic distances and angles are given in Table 3. Figure 1 shows the structure projected on the (010) plane. The structure consists of a close-packed arrangement of discrete OSF_3^+ and AsF_6^- ions, the shortest distances between ions being: S · · · F(3) 2·89(1), O · · · F(3) 2·95(1), and O · · · F(4) 2·96(1) Å. Other interionic SF distances are all $> 3·42(1)$ Å.

The structure is cubic close-packed with respect to oxygen and fluorine atoms, with arsenic atoms in 1/10 of the octahedral holes and sulphur in 1/20 of the tetrahedral holes. Using PTOT nomenclature [12] the structure is $3·8PT_{1/20}O_{1/10}T_{1/20}$, where in 24 layers corresponding to the orthorhombic cell of four molecules, 36 fluorines + 4 oxygens occupy the six P layers, 4 arsenic atoms in the six O layers with occupancy 4/40, and 4 sulphur atoms in the twelve T layers with occupancy 4/80.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[9] W. H. Zachariasen, *Acta Cryst.*, 1949, **2**, 388.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968, Table 3.3.1A.

[11] Ref. 10, Table 3.3.2C.

[12] S. M. Ho and B. E. Douglas, *J. Chem. Educ.*, 1969, **46**, 207.

The octahedral AsF_6^- ion has a mean As–F bond length of 1·68 Å (1·73 corrected for libration[13]), and a mean F–As–F bond angle of 90·4°. Similar As–F bond distances have been found in other recently determined structures of salts containing AsF_6^-.[14,15] The OSF_3^+ ion is a distorted tetrahedron with mean bond lengths and angles (values corrected for libration in parentheses) S–O 1·35 (1·37), S–F 1·44 (1·455) Å; F–S–F 102·3 and F–S–O 115·9°. The corrections for librational motion are quite large, a reflection of the high temperature factors for fluorine and oxygen.

TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses; values corrected for libration are in square brackets

(*a*) Distances

As–F(1)	1·67(1) [1·74]	S–O	1·35(1) [1·37]
As–F(2)	1·69(1) [1·74]	S–F(5)	1·44(1) [1·45]
As–F(3)	1·69(1) [1·71]	S–F(6)	1·45(1) [1·46]
As–F(4)	1·67(1) [1·73]		

(*b*) Angles

F(1)–As–F(3)	89·2(6)	F(4)–As–F(4′)	93·4(6)
F(1)–As–F(4)	93·1(7)	F(5)–S–O	115·5(6)
F(2)–As–F(3)	88·5(5)	F(6)–S–O	116·3(6)
F(2)–As–F(4)	89·1(6)	F(5)–S–F(6)	102·0(5)
F(3)–As–F(3′)	90·5(4)	F(6)–S–F(6′)	102·6(5)
F(3)–As–F(4′)	88·0(5)		

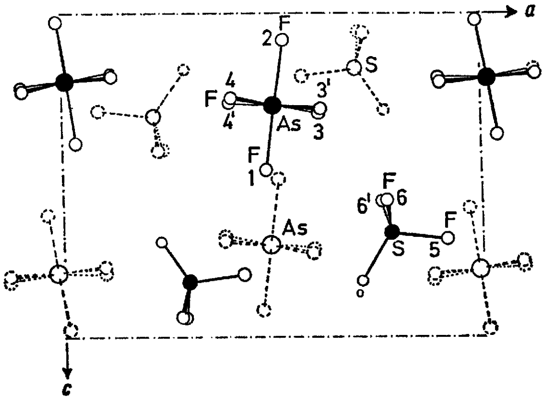

FIGURE 1 Projection along the *b* axis. Arsenic and sulphur atoms in the mirror plane at $y = 1/4$ are represented by closed, and those at $y = 3/4$ by open circles

The ionic formulation for the compound is therefore confirmed. The S···F(3) distance [2·89(1) Å] is somewhat less than the sum of the van der Waals radii of sulphur and fluorine (3·20 Å).[16] It would be expected that the contact distance for sulphur in this environment and oxidation state, should be less than that in S_8. However, it is possible that dissociation of the salt into OSF_4 and AsF_5 takes place by transfer of fluoride ion from AsF_6^- to the sulphur atom across this interaction.

The pairs of unique S–F bond distances [1·44(1) and 1·45(1) Å], O–S–F bond angles [115·5(6) and 116·3(6)°], and F–S–F angles [102·0(5) and 102·6(5)°] are essentially equal. Thus OSF_3^+ has C_{3v} symmetry, confirming the spectroscopic results.[2]

The observed S–F bond distances are the shortest so far reported (Table 4), as is the S–O bond distance, relative to other reliably determined values, except for the axial S–O bond distances[18] in S_3O_9. However, standard deviations are too large to allow a distinction between the S–O distance in OSF_3^+, and axial bonds in S_3O_9. The S–O stretching frequencies however would indicate that the S–O bond lengths should be less in OSF_3^+: OSF_3^+, ν(SO) 1535,[2] terminal S–O in S_3O_9 ν(SO), 1250 and 1502 cm^{-1}.[19]

TABLE 4

Comparison of structure of OSF_3^+ with those of some related species

Compound	Bond lengths/Å [a]			Bond angles/°.	
SO_4^{2-}	S–O	1·44—1·48			
SO_3F^- [b]	S–O	1·42(1)	[1·43]	O–S–O	112·9(7)
	S–F	1·57(2)	[1·58]	F–S–O	105·8(7)
O_2SF_2 [c, d]	S–O	1·405(3)		O–S–O	124·0(2)
	S–F	1·530(3)		F–S–O	108·2(2)
				F–S–F	96·1(2)
OSF_3^+	S–O	1·35(1)	[1·37]	F(5)–S–O	115·6(6)
	S–F(5)	1·44(1)	[1·45]	F(6)–S–O	116·3(6)
	S–F(6)	1·45(1)	[1·46]	F(5)–S–F(6)	102·0(5)
				F(6)–S–F(6′)	102·6(5)
SO_3^{2-} [e]	S–O(1)	1·528(6)	[1·532]	O(1)–S–O(2)	105·4(4)
	S–O(2)	1·513(6)	[1·520]	O(1)–S–O(3)	104·4(4)
	S–O(3)	1·532(6)	[1·535]	O(2)–S–O(3)	104·6(4)
SF_3^+ [f]	S–F(1)	1·495(2)	[1·518]	F(1)–S–F(1)	97·62(7)
	S–F(2)	1·499(2)	[1·514]	F(1)–S–F(2)	97·39(12)
OSF_2 [c, g]	S–O	1·412(1)		F–S–F	92·8(1)
	S–F	1·585(1)		F–S–O	106·8(1)
$OSMe_3^+$ [h]	S–O	1·45(1)		O–S–C(1)	112·1(5)
				O–S–C(2)	114·8(6)
				C(1)–S–C(1)	105·8(7)
				C(1)–S–C(2)	105·7(5)
O_2SMe_2 [i, j]	S–O	1·43(2)			
$OSMe_2$ [i, k]	S–O	1·47(3)			

[a] Values in square brackets are corrected for libration. [b] K. O'Sullivan, R. C. Thompson, and J. Trotter, *J. Chem. Soc.* (*A*), 1967, 2024. [c] Microwave. [d] D. R. Lide, D. E. Mann, and R. M. Fristrom, *J. Chem. Phys.*, 1957, **26**, 734. [e] L. F. Battelle and K. W. Trueblood, *Acta Cryst.*, 1965, **19**, 531. [f] Ref. 17. [g] R. C. Ferguson, *J. Amer. Chem. Soc.*, 1954, **76**, 850. [h] C. L. Coulter, P. K. Gantzel, and J. D. McCullough, *Acta Cryst.*, 1963, **16**, 676. [i] Electron diffraction. [j] R. E. Rundle, Dissertation, California Inst. Technol., Pasadena, California, 1941. [k] O. Bastiansen and H. Viervoll, *Acta Chem. Scand.*, 1948, **2**, 702.

Table 4 compares the structure of OSF_3^+ with those of some related species. The S–F and S–O bond distances decrease in the series SO_4^{2-}, O_3SF^-, O_2SF_2, and

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[13] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

[14] R. F. Dunphy, C. Lau, H. Lynton, and J. Passmore, preceding paper.

[15] C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, 1971, **10**, 2781.

[16] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 120.

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[18] W. S. McDonald and D. W. J. Cruickshank, *Acta Cryst.*, 1967, **22**, 48.

[19] R. J. Gillespie and E. A. Robinson, *Canad. J. Chem.*, 1961, **39**, 2189.

OSF_3^+. Replacement of a lone pair by oxygen gives rise to bond shortening, *e.g.* SO_3^{2-}, SO_4^{2-}; OSF_2, O_2SF_2; SF_3^+, OSF_3^+. Replacement of a methyl group by fluorine also results in a S–O bond decrease, *e.g.* $OSMe_3^+$, OSF_3^+; O_2SMe_2, O_2SF_2; $OSMe_2$, OSF_2. The bond distances in OSF_3^+ are therefore consistent with these trends.

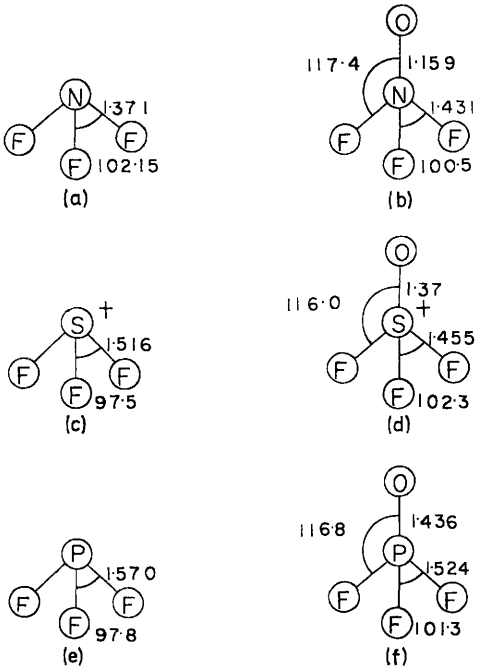

FIGURE 2 Comparison of some MF_3 and OMF_3 species, distances (Å), angles (°). (a) J. Sheridan and W. Gordy, *Phys. Rev.*, 1950, 79, 513; (b) V. Plato, W. D. Hartford, and K. Hedberg, *J. Chem. Phys.*, 1970, **53**, 3488; (c) mean values, corrected for vibrational motion, from ref. 17; (d) mean values, corrected as in (c), present work; (e) Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, 1969, **8**, 867; (f) T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, 1971, **10**, 344.

The changes in bond angles can be accounted for by valence-shell electron-pair repulsion theory.[8] The wide range of sulphur–oxygen distances has received much attention [20] and has been interpreted [4,20] to imply the existence of p_π–d_π bonding. Sulphur–fluorine bond lengths also span a wide range. The contraction in the S–F bond length relative to that in O_2SF_2 (0·075 Å) may be due to the presence of positive charge [21,22] on the sulphur atom and to some increase in p_π–d_π bonding. The high electronegativity of the sulphur atom carrying a formal positive charge, coupled with the highly electronegative environment provides very favourable conditions for such bond formation to occur. The bonding in OSF_3^+ may perhaps be described in valence-bond terms by the resonance structures $O{=}\overset{+}{S}F_3$, $\overset{+}{O}{\equiv}SF_3$, and three of the type $\overset{+}{F}{=}SOF_2$, $O{=}\overset{+}{S}F_3$ having the greatest importance.

The similarity of the bond angles in SF_3^+ and PF_3, and some other isoelectronic cation and molecule pairs has been pointed out [17] (Figure 2). The angles in OSF_3^+ and OPF_3 are also similar, and the relationship between the geometries of SF_3^+ and OSF_3^+ parallels that of PF_3 and OPF_3. The bond angles in OSF_3^+ are also similar to those in ONF_3, but the relationship between NF_3 and ONF_3 differs from that of SF_3^+ and OSF_3^+. It is probable that the bonding in the nitrogen compounds differs from the phosphorus and sulphur analogues, and that the similarity of the OSF_3^+ and ONF_3 bond angles is fortuitous.

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[3/281 *Received, 7th February,* 1973]

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[21] L. Pauling and J. Sherman, *Z. Krist.*, 1932, **81**, 1.

[22] D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, 1942, 642.