Crystal Structure of Chlorodifluoro-oxosulphur(VI) Hexafluoroarsenate(V) $OSClF_2^+AsF_6^-$

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The crystal structure of the title compound has been determined from three-dimensional diffractometer data. Crystals are monoclinic, space group $P2_1/n$, with unit cell dimensions: $a = 9{\cdot}96(1)$, $b = 8{\cdot}94(1)$, $c = 8{\cdot}295(9)$ Å, $\beta = 95{\cdot}70(5)°$, and $Z = 4$. The atomic parameters were refined by block-diagonal least-squares to R 0·045 for 304 observed reflections. The structure consists of discrete $OSClF_2^+$ and AsF_5^- ions. The $OSClF_2^+$ group is a distorted tetrahedron, the S–Cl bond distance is the shortest so far reported, 1·86(1) Å. The fluorine and oxygen positions cannot be determined uniquely owing to disorder by rotation about the S–Cl axis. There is a short inter-ionic contact Cl · · · F(AsF_5^-) of 2·67(2) Å.

RECENTLY various compounds containing $OSClF_2^+$ have been prepared.[1] The vibrational spectra of these salts indicated that the S–O, S–F, and S–Cl bond strengths were the largest so far reported, except for S–O and S–F in OSF_3^+,[2] and that the compounds were essentially ionic. We have therefore determined the crystal structure of $OSClF_2^+AsF_6^-$.

EXPERIMENTAL

Crystal Preparation.—$OSClF_2^+AsF_6^-$ was prepared and manipulated in apparatus described in ref. 1. This salt (*ca.* 0·3 g) was dissolved in anhydrous hydrogen fluoride in a Kel-F trap at room temperature and solvent gradually removed by slightly opening the valve while pumping through a soda-lime trap for *ca.* 1 h. Needle crystals formed and the vessel was further evacuated for another hour to remove all traces of volatile materials. Crystals were mounted in a dry-box in silica capillaries (o.d. 0·3 mm) which were quickly sealed by a small hot flame.

Crystal Data.—$OSClF_2^+AsF_6^-$, monoclinic, $M = 310{\cdot}4$, $a = 9{\cdot}96(1)$, $b = 8{\cdot}94(1)$, $c = 8{\cdot}295(9)$ Å, $\beta = 95{\cdot}70(5)°$, $U = 735{\cdot}3$ Å^3, $Z = 4$, $D_c = 2{\cdot}81$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 55·7 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5).

Unit-cell dimensions and their estimated standard deviations were obtained from a least-squares evaluation of the positions of 8 independent reflections. Assuming the volume of a chlorine atom to be twice that of a fluorine, and an oxygen volume equal to that of fluorine, then four molecules of $OSClF_2^+AsF_6^-$ in the unit cell corresponds to an approximate volume per fluorine atom of 16·8 Å^3, which satisfies Zachariasen's [3] criterion for close packing.

X-Ray Data.—Intensity data were collected on a Picker computer-controlled four-angle diffractometer by use of β-filtered Mo-K_α radiation. The crystal was needle shaped along a with dimensions, 0·16 × 0·08 × 0·08 mm. The two octants hkl and $\bar{h}kl$ were explored to a maximum 2θ of

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[1] C. Lau and J. Passmore, *Chem. Comm.*, 1971, 950; C. Lau and J. Passmore, preceding paper.

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

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

36°. In the region used, there were **506** accessible reflections of which **304** were taken to be observed. No corrections were made for absorption or extinction.

Structure Analysis.—The arsenic atoms were located from a three-dimensional Patterson synthesis. All other atom positions were obtained from subsequent Fourier syntheses, and are in general positions. The structure was refined by successive cycles of block-diagonal least-squares using 3 × 3 matrices for the positional parameters and 6 × 6 matrices for the anisotropic thermal parameters of each atom. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ for the observed reflections only using the weighting function $w = \{1 + [(|F_o| - P_2)/P_1]^4\}^{-1}$, with $P_1 = 45$ and $P_2 = 53$. Scattering-factor curves used were taken from ref. 4 with anomalous dispersion corrections for arsenic, chlorine, and sulphur.[5]

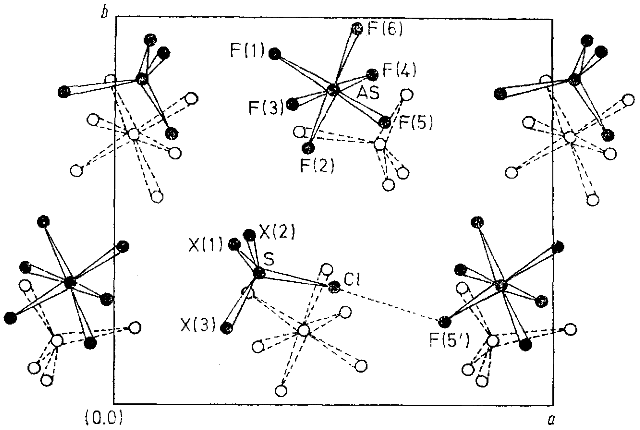
TABLE 1

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As	5576(3)	8116(4)	7550(4)	71(3)	75(3)	88(3)	−3(4)	−5(3)	−5(4)
Cl	5583(7)	3036(10)	7180(8)	77(8)	160(12)	77(10)	13(10)	17(8)	12(11)
S	3782(8)	3371(11)	7456(10)	113(10)	135(12)	118(12)	−7(10)	40(10)	21(10)
X(1) †	3142(15)	4095(20)	6010(20)	94(20)	126(25)	72(22)	44(19)	−9(16)	−2(19)
X(2) †	3698(16)	4392(20)	8735(21)	117(22)	109(24)	118(25)	26(21)	−24(19)	49(22)
X(3) †	3131(17)	1988(21)	7755(23)	137(23)	96(24)	207(31)	−51(26)	28(22)	15(23)
F(1)	4202(16)	9045(24)	6794(25)	110(22)	222(33)	240(38)	77(28)	59(24)	58(24)
F(2)	4958(19)	6559(19)	6661(22)	234(29)	87(24)	163(26)	−36(21)	73(23)	−97(23)
F(3)	4774(16)	7696(22)	9177(20)	120(21)	195(31)	99(21)	24(20)	37(17)	35(20)
F(4)	6390(15)	8518(20)	5895(18)	120(21)	172(29)	107(24)	30(20)	87(19)	−2(21)
F(5)	6933(16)	7181(29)	8335(23)	105(21)	333(45)	175(29)	87(29)	43(21)	95(26)
F(6)	6185(25)	9702(28)	8403(29)	297(40)	238(37)	208(37)	−105(32)	66(30)	−88(35)

* In the form: $\exp[-2\pi^2(a^{*2}h^2U_{11} + \ldots 2b^*c^*klU_{23} + \ldots)]$. † Atoms labelled X represent the oxygen and the two fluorine atoms attached to the sulphur, treated as (1/3O + 2/3F).

The oxygen and fluorine atoms attached to the sulphur could not be distinguished from each other in the Fourier synthesis, either by electron-density distribution or bond distances and angles. Models were refined with the oxygen atom in each of the three possible positions with no significant differences in the agreement residual or the final atomic parameters. A model using a weighted average scattering curve $(1/3f_O + 2/3f_F)$ was also used with the same result. The final R was 0·045 for this model. In the final cycle no parameter shift was $>0{\cdot}25\sigma$. A final difference-Fourier synthesis showed some residual electron density near the $OSClF_2^+$ oxygen and fluorine atom positions, but was nowhere $>0{\cdot}5$ eÅ^{-3}.



The contents of the unit cell viewed down c^*: full circles atoms near z = 3/4, open circles atoms near z = 1/4

A set of structure factors for the final parameters given in Table 1 are listed in Supplementary Publications No. SUP 20771 (3 pp., 1 microfiche).*

DISCUSSION

The arrangement of the atoms in the unit cell is shown in the Figure. Interatomic distances and angles are given in Table 2. Atoms labelled as X are the oxygen and fluorine atoms attached to sulphur. The structure consists of a close-packed arrangement of discrete $OSClF_2^+$ and AsF_6^- ions. The shortest distances between ions are Cl · · · F(5′) 2·67(2), X(1) · · · F(2) 2·87(2), X(2) · · · F(3′) 2·88(3), and X(3) · · · F(1)

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

S–Cl	1·86(1) [1·86] *	Cl · · · X(1)	2·70(2)
S–X(1)	1·45(2)	Cl · · · X(2)	2·67(2)
S–X(2)	1·41(2)	Cl · · · X(3)	2·70(2)
S–X(3)	1·43(2)	X(1) · · · X(2)	2·29(2)
		X(1) · · · X(3)	2·38(3)
As–F(1)	1·67(2) [1·70]	X(2) · · · X(3)	2·35(3)
As–F(2)	1·67(2) [1·69]		
As–F(3)	1·68(2) [1·69]	Cl · · · F(5′)	2·67(2) [2·70]
As–F(4)	1·70(2) [1·71]	X(1) · · · F(2)	2·87(2)
As–F(5)	1·67(2) [1·70]	X(2) · · · F(3′)	2·88(3)
As–F(6)	1·67(2) [1·71]	X(3) · · · F(1)	2·98(3)
		S–Cl · · · F(5′)	172·2(6)

(*b*) Angles

Cl–S–X(1)	108·7(8)	F(1)–As–F(6)	89·2(11)
Cl–S–X(2)	109·1(9)	F(2)–As–F(3)	89·1(9)
Cl–S–X(3)	110·0(9)	F(2)–As–F(4)	90·2(8)
X(1)–S–X(2)	106·2(11)	F(2)–As–F(5)	90·2(10)
X(1)–S–X(3)	111·1(11)	F(3)–As–F(5)	90·3(9)
X(2)–S–X(3)	111·6(11)	F(3)–As–F(6)	91·8(10)
		F(4)–As–F(5)	89·3(9)
F(1)–As–F(2)	89·8(9)	F(4)–As–F(6)	88·9(10)
F(1)–As–F(4)	91·8(9)	F(5)–As–F(6)	90·8(11)

* Values in square brackets are corrected for libration.

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* For details 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).

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

[5] Ref. 4, Table 3.3.2C.

2·98(3) Å. The Cl $\cdots$ F(5′) distance corrected for libration[6] is 2·70 Å, significantly shorter than the van der Waals distance 3·15 Å.[7] Other chlorine–fluorine interionic distances are all >3·15 Å. Neither the S–Cl nor the As–F(5′) bonds seem to be weakened by this short interaction. The shortest sulphur–fluorine interionic distance is 3·16(2) Å.

The arsenic atom is surrounded octahedrally by six fluorine atoms. The mean As–F distance is 1·68 Å (1·70 Å corrected for libration), and the mean F–As–F angle is 90·0°. Similar As–F distances have been obtained from the structures of other recently determined salts containing AsF_6^-.[8-11]

The $OSClF_2^+$ ion is a distorted tetrahedron. The expected bond lengths for S–O and S–F should be slightly longer than the values 1·35 and 1·44 Å found in $OSF_3^+AsF_6^-$.[8] The mean S–X distance (1·43 Å) is consistent with this prediction. The S–Cl bond distance [1·86(1) Å] is significantly shorter than that in O_2SCl_2,[12] [2·011(6) Å] and is the shortest S–Cl distance so far reported. Similar contractions of S–F bond distances are observed on replacement of oxygen by fluorine atoms.[8] It has been estimated that[13,14] a unit positive charge on an atom of atomic number Z, should lead to a decrease in the covalent radii of *ca.* 2/3 of the difference between the covalent radii of atoms of atomic number Z and $Z + 1$. A contraction of the S–Cl distance in $OSClF_2^+$ of *ca.* 0·04 Å would then be expected if the positive charge were located totally on the sulphur atom. The bond contraction is greater than this, and can perhaps be accounted for, in valence-bond terms, by a contribution of the resonance structure $\overset{+}{Cl}{=}SOF_2$. The partial positive charge, and availability of empty d orbitals on the chlorine, may account for the short interionic Cl–F(5′)(AsF_5) distance. It is also possible that dissociation of the salt may proceed by transfer of fluoride ion across this interaction. However, intermolecular interactions have been detected in solid $OPCl_3$,[15] and $OPBr_3$[16] [O–Cl 3·053(11) and O–Br 3·065(27) Å]. The expected van der Waals[7] separations are 3·20 and 3·35 Å respectively.

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