Fluoride Crystal Structures. Part 34.[1] Antimony Pentafluoride–Iodine Trifluoride Dioxide

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The structure of the title adduct has been determined by the heavy-atom method from 1 451 diffractometer reflections and refined by full-matrix least-squares methods to R 0.074. Crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 5.72(1), b = 9.96(1), c = 12.56(2) Å, β = 101.7(2)°. The solid adduct exists as dimers with two antimony and two iodine atoms at the corners of a rhombus, linked by asymmetric, angular oxygen bridges, with Sb–O 2.05 and I–O 1.80 Å. Both the SbF_4O_2 and IF_4O_2 units have distorted octahedral geometries with *cis* oxygen bridges, and with a greater distortion in the antimony unit. This can be correlated with a contribution to the structure from the ionic form $[SbF_4]^+[IF_4O_2]^-$. The adduct has a very similar structure to pentafluorides typified by RuF_5, based on an approximate hexagonal close-packing of the light atoms.

THERE have been three previous spectroscopic studies of the adduct of antimony pentafluoride and iodine trifluoride dioxide. Engelbrecht *et al.*[2] interpreted the ^{19}F n.m.r. spectrum of the molten compound in terms of a polymeric linking of IF_4O_2 and SbF_4 groups, with both *cis* and *trans* oxygen bridges. On the basis of Raman and ^{121}Sb Mössbauer spectra Aubke and his co-workers[3] concluded that IF_3O_2 acted as an oxygen-donor ligand, while retaining its associated structure, with a donor strength less than that of SO_2, for example. In the most recent report, Gillespie and Krasznai[4] proposed from Raman and ^{19}F n.m.r. studies that the adduct is an oxygen-bridged polymer in the molten state or in solution, with alternating IF_4O_2 and SbF_4O_2 groups.

We have now determined the crystal structure of the adduct to obtain details of the degree of polymerisation and of the bridging interaction.

EXPERIMENTAL

Iodine trifluoride dioxide was prepared by a modification of the method of Engelbrecht and Peterfy.[5] Sulphur trioxide vapour, derived from heated 25% oleum, was condensed onto tetrafluoro-orthoperiodic acid, and pale yellow crystals of IF_3O_2 were sublimed from the mixture. The compound was purified by passing the vapour first over dry potassium sulphate and then over phosphorus pentaoxide. Antimony pentafluoride (Ozark Mahoning) was purified by repeated vacuum distillation.

Preparation of the Adduct.—Excess of SbF_5 was distilled onto IF_3O_2 in a rigorously dried Pyrex glass apparatus. On gentle warming the IF_3O_2 dissolved. Excess of SbF_5 was removed by pumping under vacuum at room temperature. The white crystalline product was sublimed directly into thin-walled Pyrex capillaries attached to the evacuated apparatus. Single crystals were grown by sublimation in a temperature gradient and sealed into small lengths of tube using a microflame. Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

Crystal Data.—F_8IO_2Sb, $M = 433$, Monoclinic, $a = 5.72(1)$, $b = 9.96(1)$, $c = 12.56(2)$ Å, $\beta = 101.7(2)°$, $U = 701$ Å^3, $Z = 4$, $D_c = 4.10$ g cm^{-3}, $F(000) = 736$, space group $P2_1/c$ (C^5_{2h}, no. 14) from systematic absences $h0l$ for $l \neq 2n$, $0k0$ for $k \neq 2n$, Mo-K_α radiation, λ 0.710 7 Å, μ 79 cm^{-1}.

The density of the crystals was not measured but $Z = 4$ was assumed, since the volume per light atom was then 17.5 Å^3, comparable with the usual value of 18 Å^3.

Structure Determination.—Intensity data were collected about the b axis (layers $h0$—$12l$) with a Stoe two-circle computer-controlled diffractometer as described previously.[6] Within the range $0.1 < (\sin\theta)/\lambda < 0.65$, 1 451 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarisation factors but not for absorption.

TABLE 1

Final positional parameters ($\times 10^2$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
I	0.223 9(2)	−0.008 6(1)	0.317 3(1)
Sb	0.502 3(2)	0.251 7(1)	0.492 0(1)
O(1)	0.597 6(24)	0.153 2(12)	0.637 0(10)
O(2)	0.299 1(20)	0.085 8(10)	0.441 7(9)
F(1)	0.459 7(20)	0.060 0(10)	0.259 4(8)
F(2)	−0.042 1(21)	−0.077 0(11)	0.354 0(9)
F(3)	0.034 7(22)	0.124 8(12)	0.252 3(9)
F(4)	0.127 8(21)	−0.092 9(11)	0.190 0(9)
F(5)	0.754 9(20)	0.168 9(10)	0.447 6(9)
F(6)	0.388 2(22)	0.328 1(11)	0.354 9(10)
F(7)	0.245 8(19)	0.310 7(10)	0.548 0(8)
F(8)	0.690 9(22)	0.394 6(11)	0.550 1(10)

The structure was solved by conventional Patterson–Fourier techniques. Scattering factors used were those for neutral atoms[7] with corrections for the effects of anomalous dispersion.[8] Refinement by full-matrix least-squares methods was carried out initially with layer-scale factors refined separately, with unit weights, and with all atoms vibrating isotropically. In these early stages both heavy atoms were assigned iodine scattering factors and all light atoms those for fluorine.

After this refinement was complete (R 0.079) the two bridge atoms were found to have higher temperature factors than the other light atoms and were assigned oxygen scattering factors. The two heavy atoms were assigned antimony and iodine scattering factors alternately, and the final model reported here gave much closer agreement for temperature factors than the alternative. The introduction of anisotropic thermal parameters gave no significant improvement in R. In the final stages of refinement the weighting scheme $w = [\sigma^2|F_o| + (0.002\,5|F_o|)^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. Final parameter shifts were $<0.1\sigma$, the final R was 0.074, and $R'\{=[\Sigma w(|F_o|-|F_c|)^2]^{\frac{1}{2}}\}$ 0.080. The calculations were carried out on an ICL 1906A computer at Birmingham University Computer Centre using the program SHELX-76.[9] Observed and calculated structure factors and isotropic thermal parameters are listed in Supplementary Publication No. SUP 22806 (11 pp.),* final positional parameters with their estimated standard deviations in Table 1, and interatomic distances and angles in Table 2.

DISCUSSION

The structure analysis has shown that the adduct exists in the solid state as dimers, $(SbF_5{\cdot}IF_3O_2)_2$. In the tetranuclear dimer unit, shown in Figure 1, two antimony atoms and two iodine atoms are at opposite corners of a rhombus. Although the analysis of thermal vibrations discussed above has indicated a distinction between the iodine and antimony atoms, and between the oxygen and fluorine atoms, these assignments have been confirmed by a comparison of the final geometry with that of related compounds.

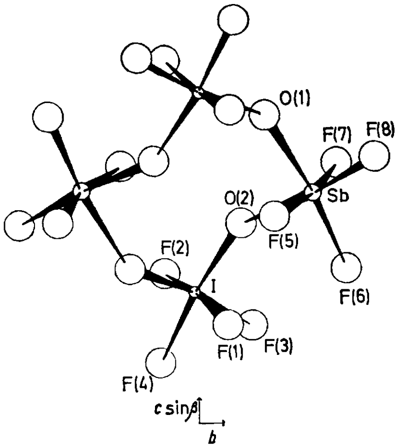

FIGURE 1 The dimer unit $(SbF_5{\cdot}IF_3O_2)_2$ shown in projection down [100]

For the co-ordination around the iodine atom the distances to all six light atoms in the distorted octahedral arrangement are the same, within experimental error, and average 1.80 Å. The angular distortions in the octahedron can be rationalised on the assumption that the two bridging atoms are oxygen atoms, with a greater spatial requirement due to their multiple bonding to iodine. Thus the angle between them O(2)–I–O(1$^{\rm I}$) of 96.8° is the largest in the octahedron, and all the O–I–F angles [except O(1$^{\rm I}$)–I–F(4)] are greater than 90°, averaging 92°. The F–I–F angles are correspondingly less than 90°, averaging 86°. This assignment is confirmed by comparison with the recently reported structure [10] of the adduct of IF_3O with IF_3O_2, which also has a tetranuclear structure, where the co-ordination of the iodine(VII) atom is almost identical (Table 3).

TABLE 2

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

(*a*) Distances			
I–F(1)	1.79(1)	Sb–F(5)	1.85(1)
I–F(2)	1.81(1)	Sb–F(6)	1.88(1)
I–F(3)	1.80(1)	Sb–F(7)	1.85(1)
I–F(4)	1.79(1)	Sb–F(8)	1.84(1)
I–O(1$^{\rm I}$)	1.80(1)	Sb–O(1)	2.05(1)
I–O(2)	1.80(1)	Sb–O(2)	2.05(1)
F(1) · · · F(3)	2.50(2)	F(6) · · · F(5)	2.70(2)
F(1) · · · F(4)	2.45(2)	F(6) · · · F(8)	2.78(2)
F(2) · · · F(3)	2.47(2)	F(5) · · · F(8)	2.65(2)
F(2) · · · F(4)	2.46(2)	F(6) · · · F(7)	2.72(2)
F(3) · · · F(4)	2.40(2)	F(7) · · · F(8)	2.67(2)
F(1) · · · O(1$^{\rm I}$)	2.55(2)	F(5) · · · O(1)	2.71(2)
F(2) · · · O(1$^{\rm I}$)	2.63(2)	F(7) · · · O(1)	2.62(2)
F(4) · · · O(1$^{\rm I}$)	2.48(2)	F(8) · · · O(1)	2.74(2)
F(1) · · · O(2)	2.65(2)	F(5) · · · O(2)	1.72(2)
F(2) · · · O(2)	2.60(2)	F(6) · · · O(2)	2.74(2)
F(3) · · · O(2)	2.58(2)	F(7) · · · O(2)	2.66(1)
O(1$^{\rm I}$) · · · O(2)	2.69(2)	O(1) · · · O(2)	2.77(2)
(*b*) Angles			
O(2)–I–O(1$^{\rm I}$)	96.8(5)	O(2)–Sb–O(1)	85.4(5)
O(2)–I–F(1)	95.0(5)	O(2)–Sb–F(5)	88.6(4)
O(2)–I–F(2)	92.3(5)	O(2)–Sb–F(6)	88.6(5)
O(2)–I–F(3)	91.4(5)	O(2)–Sb–F(7)	85.9(4)
O(1$^{\rm I}$)–I–F(1)	90.7(5)	O(1)–Sb–F(5)	88.4(5)
O(1$^{\rm I}$)–I–F(2)	93.9(5)	O(1)–Sb–F(7)	84.4(5)
O(1$^{\rm I}$)–I–F(4)	87.7(5)	O(1)–Sb–F(8)	89.4(5)
F(1)–I–F(3)	88.1(5)	F(5)–Sb–F(6)	93.2(5)
F(1)–I–F(4)	86.3(5)	F(5)–Sb–F(8)	91.9(5)
F(2)–I–F(3)	86.2(5)	F(6)–Sb–F(7)	93.7(5)
F(2)–I–F(4)	85.9(5)	F(6)–Sb–F(8)	96.7(5)
F(3)–I–F(4)	83.9(5)	F(7)–Sb–F(8)	92.9(5)
F(1)–I–F(2)	170.9(5)	F(5)–Sb–F(7)	171.3(4)
I–O(2)–Sb	135.3(6)	Sb–O(1)–I$^{\rm I}$	134.7(6)
O(2)–I–F(4)	175.1(5)	O(1)–Sb–F(6)	173.7(5)
O(1$^{\rm I}$)–I–F(3)	171.6(5)	O(2)–Sb–F(8)	174.7(4)
(*c*) Contacts <3Å			
F(5) · · · F(1)	2.83(2)	F(6) · · · F(1)	2.99(2)
F(6) · · · F(3)	2.97(2)	F(5) · · · O(2$^{\rm I}$)	2.94(2)
F(5) · · · F(2$^{\rm I}$)	2.84(2)	F(6) · · · F(1$^{\rm II}$)	2.94(2)
F(7) · · · F(1$^{\rm III}$)	2.98(2)	F(8) · · · F(3$^{\rm IV}$)	2.89(2)
F(7) · · · F(2$^{\rm V}$)	2.98(2)		

Roman numerals as superscripts refer to atoms in the positions: I $1-x, -y, 1-z$; II $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; III $x, \frac{3}{2}-y, \frac{3}{2}+z$; IV $1+x, \frac{3}{2}-y, \frac{3}{2}+z$; V $-x, -y, 1-z$.

The co-ordination arrangement for the antimony atom is a more distorted octahedron. There are four equivalent bonds to terminal fluorine atoms, averaging 1.86 Å, and two bonds to the bridging oxygen atoms of 2.05 Å. The octahedron is distorted in the opposite sense to that around iodine, with the O–Sb–O angle of 85.4° being the smallest, and the fluorine atoms moved towards the more weakly bonded oxygen atoms, giving average O–Sb–F

TABLE 3

Comparison of dimensions in $SbF_5{\cdot}IF_3O_2$, $IF_3O{\cdot}IF_3O_2$, and $Cs_3[Sb_3O_3F_{12}]$

	$SbF_5{\cdot}IF_3O_2$	$IF_3O{\cdot}IF_3O_2$	$[Sb_3O_3F_{12}]^{3-}$
(*a*) Distances (Å)			
I$^{\rm VII}$–O	1.80	1.80	
I$^{\rm VII}$–F	1.80	1.83	
Sb–O	2.05		1.92
Sb–F	1.86		1.86
(*b*) Angles (°)			
O–I–O	96.8	100	
O–I–F	92	92	
F–I–F	86	85	
O–Sb–O	85.4		101.9
O–Sb–F	87.3		90.0
F–Sb–F	93.7		87.5

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

and F–Sb–F angles of 87.3 and 93.7° respectively. The arrangement around antimony is very similar to that in the trimeric anion [11] in $Cs_3[Sb_3O_3F_{12}]$. The Sb–F distances are the same in both cases but the Sb–O distance in the symmetrically bridged anion is smaller than that in the adduct (Table 3).

The I–O–Sb angles average 135°, which is very close to the theoretical value of 132° for the angle involving adjacent octahedral holes in a hexagonal close-packed array. The approximate close-packing of the light atoms is shown in Figure 2 with the layers running parallel to [101]. This arrangement of tetranuclear units to give a hexagonal close-packed array of light atoms is the same as that found for the transition-metal pentafluorides [12,13] MF_5 (M = Ru, Os, Rh, Ir, or Pt). The cell dimensions of these pentafluorides are very similar to those of the adduct: for example, for RhF_5, $a = 5.52$, $b = 9.92$, $c = 12.34$ Å, and $\beta = 100.4°$ for space group $P2_1/c$.

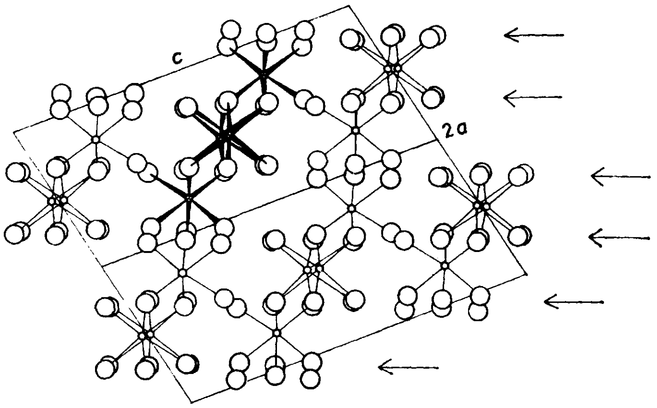

FIGURE 2 Projection of the structure down [010]; two unit cells are shown. One dimer unit is depicted with full lines for bonds and the arrows indicate planes of approximately close-packed atoms

The previous conclusions, based on spectroscopic measurements, that the oxygen atoms were more strongly bonded to the iodine than to the antimony atom have now been confirmed. The asymmetric bridges in the adduct give a considerably closer approach of oxygen to iodine. From the symmetric bridges in the structures of the $[Sb_3O_3F_{12}]^{3-}$ anion [11] and the dimer [14] of IF_3O_2 itself, distances of 1.92 and 1.94 Å can be deduced to correspond to single Sb–O and I–O bonds respectively. Thus the sum of these single bond distances is 3.86 Å, about the same as the 3.85 Å for the sum of Sb–O and I–O in the adduct. There has therefore been a redistribution of the bonding in the bridge system, and this can be described in terms of an ionic contribution from the form $[SbF_4]^+$-$[IF_4O_2]^-$ to the predominantly covalent linking in the tetranuclear unit. The I–O distance of 1.80 Å can be usefully compared with the I–O(terminal) distance of 1.74 Å in the IF_3O_2 dimer, to which it is closer than to the symmetric I–O(bridge) bond of 1.94 Å. This is in agreement with the bond order of *ca.* 1.7 derived from Raman spectra.[4]

Although the mechanism of interaction of IF_3O_2 and SbF_5 needs to be considered, as has been discussed previously,[4] it appears formally from the structural results that IF_3O_2 is a stronger fluoride-ion acceptor than SbF_5, and this adduct contains the closest approach yet to the $[SbF_4]^+$ ion. The F–Sb–F angles of 96.7 and 170.9° can be considered to be moving towards the tetrahedral angle of 109.5° expected for such a cation from the 90 and 180° in the octahedron.

This fluoride-ion acceptor strength is consistent with the fluoride-ion affinities of the iodine [15] and antimony [16] compounds which have been determined recently; $\Delta H_F(IF_3O_2, c) = -625$, $\Delta H_F(SbF_5, l) = -468$ kJ mol^{-1}.

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