Fluoride Crystal Structures. Part XXIV.[1] Tetrafluoroiodine(V) μ-Fluoro-bis[pentafluoroantimonate(V)]

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Crystals of the title compound are monoclinic, space group $P2_1/c$, a = 8.52(1), b = 14.82(2), c = 9.98(1) Å, β = 112.7(3)°. The structure was solved by Patterson and Fourier methods and refined by three-dimensional least-squares methods to R 0.089 for 1 299 reflections measured photographically. The atomic arrangement can be described by the ionic formulation $[IF_4]^+[Sb_2F_{11}]^-$, but there is strong interionic fluorine bridging giving fluorine neighbours to the iodine at 2.51, 2.55, 2.83, and 2.94 Å, in addition to the four bonded atoms with mean I–F 1.80 Å.

IODINE pentafluoride has been reported to react with antimony pentafluoride to form a 1 : 1 adduct. In a brief report of the crystal structure of this adduct[2] an ionic formulation $[IF_4]^+[SbF_6]^-$ was suggested but accurate details of the cation were not obtained owing to disorder, with two different cation orientations.

We observed that on heating the 1 : 1 adduct under vacuum, iodine pentafluoride was evolved and the residue crystallised with a different habit from the characteristic square plates of the original material. Although no single crystal could be isolated from this system, a colourless crystal of similar habit was isolated during a concurrent investigation of the interaction of chromyl fluoride and antimony pentafluoride in the presence of iodine pentafluoride. This crystal has been characterised by X-ray single-crystal structure analysis as the previously unreported title compound, the 1 : 2 adduct $IF_5{\cdot}2SbF_5$.

EXPERIMENTAL

Iodine and antimony pentafluorides were prepared by direct fluorination of the elements. Chromyl fluoride, mixed with iodine pentafluoride, resulted from the interaction of iodine pentafluoride and chromium trioxide, and this mixture was distilled on a sample of antimony pentafluoride in a rigorously dried Pyrex glass apparatus. On warming to room temperature, and removing excess of antimony pentafluoride by pumping, an orange-red solution was produced which had negligible vapour pressure Samples of this orange liquid were transferred into thin-walled Pyrex capillaries, and sealed under vacuum. No single crystals of the orange adduct of chromyl fluoride with antimony pentafluoride could be obtained, but one colourless crystal formed, which the present structure analysis has shown to be the title compound.

Crystal Data.—$F_{15}ISb_2$, M = 656, Monoclinic, a = 8.52(1), b = 14.82(2), c = 9.98(1) Å, β = 112.7(3)°, U = 1 163 Å^3, Z = 4, D_c = 3.75 g cm^{-3}, $F(000)$ = 1 160. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$. Mo-K_α (λ = 0.7107 Å, μ = 75.7 cm^{-1}) radiation. Single-crystal precession and Weissenberg photographs.

No density measurement could be made for the single crystal, but Z = 4 was assumed since the volume per fluorine atom is then 19.4 Å^3, similar to that (18.6 Å^3)[3] for $[TeF_3]^+[Sb_2F_{11}]^-$.

Structure Determination.—Integrated intensities were collected about the b axis (layers $h0$—$13l$) by use of Mo-K_α radiation and a Nonius integrating camera. The relative intensities of 1 299 independent reflections were measured with a photometer of similar design to that described by Jeffery,[4] and were corrected for Lorentz and polarisation factors. Since the crystal was small, and approximated to a needle of uniform cross-section, elongated parallel to the b axis, no absorption corrections were applied.

A three-dimensional Patterson synthesis was calculated and the positions of three heavy atoms in general positions derived. Structure factors were calculated using scattering factors for neutral atoms from ref. 5, with the three atoms given antimony scattering factors, for simplicity, at this stage. Least-squares refinement of these parameters and layer scale factors gave R 0.19.

The positions of fifteen independent fluorine atoms were derived from three-dimensional electron-density and difference maps and the identity of the iodine atom and the formulation of the compound verified from the geometry of the fluorine atom co-ordination. Refinement of the posi-

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[1] Part XXIII, J. C. Dewan, A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, preceding paper.

[2] H. W. Baird and H. F. Giles, *Acta Cryst.*, 1969, **A25**, S 115.

[3] A. J. Edwards and P. Taylor, *J.C.S. Dalton*, 1973, 2150.

[4] J. W. Jeffery, *J. Sci. Instr.*, 1963, **40**, 494.

[5] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, p. 202.

tional and isotropic temperature parameters, with the iodine-atom scattering factor assigned, and layer scale factors, was continued by full-matrix least-squares methods. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised, at first with unit weights and, in the final stages of the refinement with $\sqrt{w} = 1$ when $|F_o| \leqslant 95$ and $\sqrt{w} = 95/|F_o|$ when $|F_o| > 95$. Final parameter shifts were $< 0.1\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$ was satisfactory. The final R was 0.089. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21397 (9 pp., 1 microfiche),* final positional parameters and isotropic temperature factors, with their estimated standard deviations, in Table 1, and interatomic distances and angles in Table 2.

TABLE 1

Final atomic positional and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/Å^2$
I	−0.3055(3)	0.3897(2)	0.1953(2)	2.29(5)
Sb(1)	0.0986(3)	0.2452(2)	0.1127(2)	1.94(4)
Sb(2)	−0.1981(3)	0.0485(2)	0.1455(2)	2.14(4)
F(1)	−0.269(4)	0.484(3)	0.086(4)	5.8(7)
F(2)	−0.482(4)	0.455(2)	0.188(3)	4.4(5)
F(3)	−0.419(3)	0.343(2)	0.020(3)	4.1(5)
F(4)	−0.414(3)	0.303(2)	0.255(3)	4.5(5)
F(5)	0.257(3)	0.159(2)	0.103(3)	4.2(5)
F(6)	0.191(4)	0.346(2)	0.058(3)	4.6(5)
F(7)	−0.071(3)	0.314(2)	0.135(2)	3.1(4)
F(8)	−0.058(3)	0.220(1)	−0.074(2)	2.2(3)
F(9)	0.231(3)	0.260(2)	0.314(3)	4.2(5)
F(10)	−0.018(3)	0.142(2)	0.173(3)	3.6(5)
F(11)	−0.024(3)	−0.036(2)	0.168(3)	3.9(5)
F(12)	−0.358(4)	−0.040(2)	0.116(3)	4.5(5)
F(13)	−0.228(3)	0.049(2)	−0.053(2)	3.0(4)
F(14)	−0.133(4)	0.059(2)	0.345(4)	5.2(6)
F(15)	−0.340(4)	0.146(3)	0.112(4)	5.9(7)

TABLE 2

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

(*a*) Distances

I–F(1)	1.87(4)	I ··· F(7)	2.55(2)
I–F(2)	1.76(3)	I ··· F(13$^{\mathrm{I}}$)	2.51(2)
I–F(3)	1.78(3)	I ··· F(8$^{\mathrm{I}}$)	2.94(2)
I–F(4)	1.82(3)	I ··· F(11$^{\mathrm{II}}$)	2.83(3)
Sb(1)–F(5)	1.88(3)	Sb(2)–F(11)	1.89(3)
Sb(1)–F(6)	1.86(3)	Sb(2)–F(12)	1.83(3)
Sb(1)–F(7)	1.85(2)	Sb(2)–F(13)	1.90(2)
Sb(1)–F(8)	1.87(2)	Sb(2)–F(14)	1.85(3)
Sb(1)–F(9)	1.90(3)	Sb(2)–F(15)	1.83(4)
Sb(1)–F(10)	2.03(3)	Sb(2)–F(10)	2.01(3)
F(1) ··· F(2)	2.44(4)	F(1) ··· F(7)	2.96(5)
F(1) ··· F(3)	2.41(5)	F(3) ··· F(7)	2.77(3)
F(2) ··· F(3)	2.56(4)	F(2) ··· F(13$^{\mathrm{I}}$)	2.65(4)
F(2) ··· F(4)	2.36(4)	F(4) ··· F(13$^{\mathrm{I}}$)	2.95(4)
F(3) ··· F(4)	2.40(4)	F(10) ··· F(8$^{\mathrm{I}}$)	3.37(3)
F(1) ··· F(11$^{\mathrm{II}}$)	2.76(4)	F(4) ··· F(8$^{\mathrm{I}}$)	2.87(3)
F(6) ··· F(5)	2.82(4)	F(12) ··· F(11)	2.69(4)
F(6) ··· F(7)	2.67(4)	F(12) ··· F(13)	2.69(4)
F(6) ··· F(8)	2.75(4)	F(12) ··· F(14)	2.77(4)
F(6) ··· F(9)	2.76(4)	F(12) ··· F(15)	2.75(5)
F(10) ··· F(5)	2.70(4)	F(10) ··· F(11)	2.63(4)
F(10) ··· F(7)	2.59(4)	F(10) ··· F(13)	2.66(3)
F(10) ··· F(8)	2.62(3)	F(10) ··· F(14)	2.59(4)
F(10) ··· F(9)	2.69(4)	F(10) ··· F(15)	2.58(4)
F(5) ··· F(8)	2.73(3)	F(11) ··· F(13)	2.55(3)
F(5) ··· F(9)	2.67(4)	F(11) ··· F(14)	2.68(4)
F(7) ··· F(8)	2.56(3)	F(15) ··· F(13)	2.63(4)
F(7) ··· F(9)	2.63(4)	F(15) ··· F(14)	2.65(5)
F(8) ··· F(13)	2.96(3)	F(3) ··· F(15)	3.06(5)
F(4) ··· F(15)	2.92(5)	F(7) ··· F(15)	3.34(4)

TABLE 2 (*Continued*)

(*b*) Angles

F(5)–Sb(1)–F(6)	97.6(1.3)	F(11)–Sb(2)–F(12)	92.9(1.2)
F(7)–Sb(1)–F(6)	91.8(1.2)	F(13)–Sb(2)–F(12)	92.4(1.1)
F(8)–Sb(1)–F(6)	95.1(1.1)	F(14)–Sb(2)–F(12)	97.4(1.3)
F(9)–Sb(1)–F(6)	94.3(1.2)	F(15)–Sb(2)–F(12)	97.7(1.4)
F(5)–Sb(1)–F(10)	87.0(1.3)	F(11)–Sb(2)–F(10)	85.0(1.1)
F(7)–Sb(1)–F(10)	83.6(1.2)	F(13)–Sb(2)–F(10)	85.9(1.1)
F(8)–Sb(1)–F(10)	84.3(1.2)	F(14)–Sb(2)–F(10)	84.2(1.2)
F(9)–Sb(1)–F(10)	86.1(1.3)	F(15)–Sb(2)–F(10)	84.3(1.3)
F(5)–Sb(1)–F(8)	93.4(1.0)	F(11)–Sb(2)–F(13)	84.7(1.0)
F(5)–Sb(1)–F(9)	89.5(1.2)	F(11)–Sb(2)–F(14)	91.6(1.2)
F(7)–Sb(1)–F(8)	86.8(0.9)	F(15)–Sb(2)–F(13)	89.6(1.3)
F(7)–Sb(1)–F(9)	88.8(1.1)	F(15)–Sb(2)–F(14)	92.2(1.5)
F(1)–I–F(4)	160.3(1.2)	F(2)–I–F(3)	92.4(1.2)
F(1)–I–F(2)	84.1(1.4)	F(4)–I–F(2)	82.6(1.4)
F(1)–I–F(3)	82.5(1.4)	F(4)–I–F(3)	83.7(1.4)
F(7)–I–F(13$^{\mathrm{I}}$)	117.7(1.0)	F(7)–I–F(3)	77.2(1.1)
F(13$^{\mathrm{I}}$)–I–F(2)	74.5(1.2)	F(7)–I–F(1)	82.5(1.3)
F(7)–I–F(4)	108.0(1.3)	F(13$^{\mathrm{I}}$)–I–F(1)	105.8(1.4)
F(13$^{\mathrm{I}}$)–I–F(4)	84.5(1.2)	F(8$^{\mathrm{I}}$)–I–F(11$^{\mathrm{II}}$)	63.7(1.0)
F(8$^{\mathrm{I}}$)–I–F(4)	69.9(1.0)	F(11$^{\mathrm{II}}$)–I–F(1)	68.4(1.2)
F(8$^{\mathrm{I}}$)–I–F(7)	63.3(0.7)	F(8$^{\mathrm{I}}$)–I–F(13$^{\mathrm{I}}$)	65.3(0.9)
F(11$^{\mathrm{II}}$)–I–F(13$^{\mathrm{I}}$)	62.9(0.8)	F(11$^{\mathrm{II}}$)–I–F(7)	64.2(1.0)

(*c*) Contacts <3.5 Å

F(1) ··· F(2$^{\mathrm{III}}$)	2.89(4)	F(1) ··· F(6$^{\mathrm{III}}$)	3.10(4)
F(1) ··· F(14$^{\mathrm{I}}$)	3.11(4)	F(1) ··· F(14$^{\mathrm{II}}$)	3.40(5)
F(2) ··· F(6$^{\mathrm{V}}$)	3.05(4)	F(2) ··· F(13$^{\mathrm{VI}}$)	2.66(4)
F(2) ··· F(12$^{\mathrm{VII}}$)	2.78(4)	F(3) ··· F(6$^{\mathrm{V}}$)	3.49(4)
F(3) ··· F(4$^{\mathrm{I}}$)	3.43(4)	F(3) ··· F(9$^{\mathrm{VIII}}$)	3.28(4)
F(4) ··· F(5$^{\mathrm{V}}$)	3.38(4)	F(4) ··· F(6$^{\mathrm{V}}$)	3.24(4)
F(4) ··· F(9$^{\mathrm{V}}$)	3.36(4)	F(4) ··· F(8$^{\mathrm{VI}}$)	2.88(3)
F(4) ··· F(13$^{\mathrm{VI}}$)	2.95(4)	F(4) ··· F(15$^{\mathrm{I}}$)	3.46(4)
F(5) ··· F(15$^{\mathrm{V}}$)	3.41(4)	F(5) ··· F(11$^{\mathrm{IV}}$)	3.24(4)
F(5) ··· F(12$^{\mathrm{IV}}$)	3.18(4)	F(5) ··· F(13$^{\mathrm{IV}}$)	3.12(4)
F(5) ··· F(9$^{\mathrm{I}}$)	3.04(4)	F(6) ··· F(9$^{\mathrm{I}}$)	3.02(4)
F(6) ··· F(14$^{\mathrm{I}}$)	3.10(4)	F(6) ··· F(12$^{\mathrm{II}}$)	3.46(4)
F(6) ··· F(14$^{\mathrm{II}}$)	3.40(5)	F(7) ··· F(8$^{\mathrm{I}}$)	2.90(3)
F(7) ··· F(14$^{\mathrm{I}}$)	3.32(4)	F(7) ··· F(11$^{\mathrm{II}}$)	2.87(4)
F(8) ··· F(9$^{\mathrm{I}}$)	3.08(3)	F(8) ··· F(11$^{\mathrm{IV}}$)	3.05(4)
F(8) ··· F(14$^{\mathrm{I}}$)	3.39(4)	F(9) ··· F(12$^{\mathrm{II}}$)	3.14(4)
F(11) ··· F(13$^{\mathrm{IV}}$)	2.80(3)	F(12) ··· F(12$^{\mathrm{IX}}$)	2.88(6)
F(12) ··· F(13$^{\mathrm{IX}}$)	3.34(3)	F(12) ··· F(15$^{\mathrm{IX}}$)	3.12(4)

Roman numerals as superscripts refer to atoms in the positions:

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

DISCUSSION

Although the 1 : 1 adduct of IF_5 and SbF_5 is well characterised,[2] the existence of the previously unreported 1 : 2 adduct, $IF_5 \cdot 2SbF_5$, has been established by the present crystal-structure analysis. A similar 1 : 2 adduct has been characterised [6] for BrF_5 and SbF_5, but for BrF_5 no 1 : 1 adduct has been reported.

In the atomic arrangement (Figure 1) the nearest fluorine atom neighbours to the iodine and antimony atoms define the ions $[IF_4]^+$ and $[Sb_2F_{11}]^-$. Interionic fluorine bridging then gives a more complex co-ordination to the iodine atom, with four extra contacts, and leads to a complex three-dimensional structural network.

The shape of the $[IF_4]^+$ cation is as predicted by VSEPR theory, with the four fluorine atoms at four of

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[6] M. D. Lind and K. O. Christe, *Inorg. Chem.*, 1972, **11**, 608.

the corners of a distorted trigonal bipyramid and with the fifth position assumed to be filled by the non-bonding electron pair. The equatorial I–F bonds to F(2) and F(3) (mean 1.77 Å) are shorter than those in the axial positions (mean 1.84 Å) as expected, but the difference is only possibly statistically significant. Corresponding distances [2] in $[IF_4]^+[SbF_6]^-$ are 1.79 and 1.83 Å. Repulsion between the non-bonding electron pair and the bond pairs leads to a decrease in the angle between the axial bonds from the theoretical value of 180 to 160°, and of that between the equatorial bonds correspondingly from 120 to 92°. These two angles for the $[IF_4]^+$ cation are similar to those found for the $[GeF_4]$ unit in the structure [7] of GeF_2 (163 and 92°), for the $[AsF_4]$ unit in that [8] of AsF_3,SbF_5 (164 and 92°), and for [9] TeF_4 (161 and 89°). The corresponding angles reported, without estimated standard deviations, for $[IF_4]^+[SbF_6]^-$ are 148 and 107°, but the accuracy is probably low (*R* 0.15).

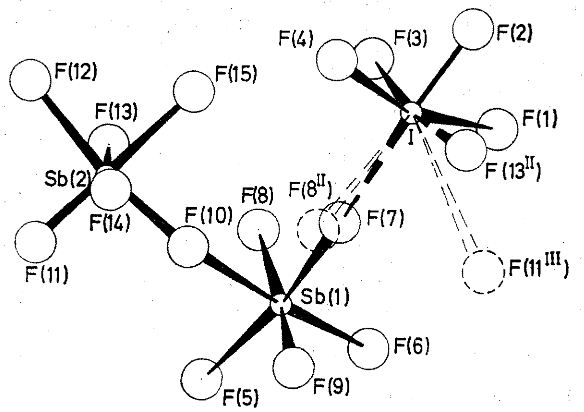

FIGURE 1 Projection of the structural unit down [001] showing the atom numbering and the iodine atom co-ordination

The shape of the IOF_3 molecule [10] is similar to that of $[IF_4]^+$ with an oxygen atom substituted for one of the equatorial fluorine atoms. The effect of the oxygen atom is to increase the angles in the structure to 166 and 100°.

The I–F distances in IOF_3 [1.84 (equatorial) and 1.90 Å (axial)] are in the same ratio as those for $[IF_4]^+$, but the mean (1.87 Å) is 0.06 Å larger than that (1.81 Å) for the cation. This increase can be correlated with the change in overall charge of the species, and the effect is also observed for the neutral IF_5 molecule [11] with mean I–F 1.86 Å.

The structure determination [6] for $[BrF_4]^+[Sb_2F_{11}]^-$ is not of sufficient accuracy for any detailed comparisons of cation geometry to be made; the reported axial and equatorial Br–F distances (1.85 and 1.77 Å) are the same as the corresponding I–F distances reported here.

The two shorter bridging contacts to the iodine atom (2.51 and 2.55 Å) give a distorted octahedral co-ordination of fluorine atoms around iodine. This arrangement is similar to that found [3] around the tellurium atom in $[TeF_3]^+[Sb_2F_{11}]^-$ where three long contacts to tellurium complete the co-ordination. The strength of the bridging interactions appears to be similar in the two cases, as the ratio M–F(bridge) : M–F(terminal) is almost identical: 1.41 for $[TeF_3]^+$ and 1.40 for $[IF_4]^+$. The position attributed to the non-bonding pair is different for the two ions. For $[TeF_3]^+$ it is considered to complete a seven-co-ordinate monocapped octahedral geometry, whereas for $[IF_4]^+$ it is between the two long contacts, at the midpoint of the longest edge of the octahedron, giving a distorted pentagonal bipyramidal arrangement.

The co-ordination of the iodine atom is completed by the two longer contacts at 2.83 and 2.94 Å. The ratios M–F(bridge) : M–F(terminal) for these contacts are 1.56 and 1.62, and the interactions are much weaker. These two contacts are symmetrically arranged, with the two shorter contacts, about the assumed non-bonding electron-pair position, and the total co-ordination of the iodine atom by eight fluorine atoms can be described on the basis of a greatly distorted cube.

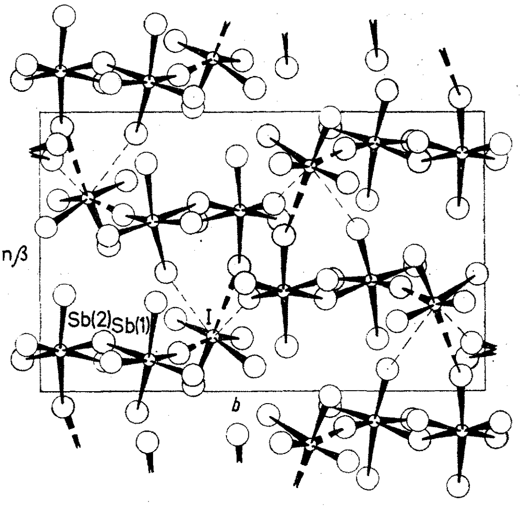

FIGURE 2 Projection of the structure down [100]

The bromine atom in $[BrF_4]^+[Sb_2F_{11}]^-$ has a distorted octahedral geometry similar to that of the iodine atom in the present case, but without the two extra, longer, contacts, which may reflect the greater size of the iodine atom. The extra contacts may also be a significant factor in the difference in linking together of the 'ions' in the two cases. Thus in $[BrF_4]^+[Sb_2F_{11}]^-$ the two bridges give a planar zigzag chain arrangement whereas

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[7] J. Trotter, M. Akhtar, and N. Bartlett, *J. Chem. Soc.* (*A*), 1966, 30.

[8] A. J. Edwards and R. J. C. Sills, *J. Chem. Soc.* (*A*), 1971, 942.

[9] A. J. Edwards and F. I. Hewaidy, *J. Chem. Soc.* (*A*), 1968, 2977.

[10] A. J. Edwards and P. Taylor, *J. Fluorine Chem.*, 1974, **4**, 173.

[11] R. D. Burbank and G. R. Jones, *Inorg. Chem.*, 1974, **13**, 1071; G. R. Jones, R. D. Burbank, and N. Bartlett, *ibid.*, 1970, **9**, 2264; A. G. Robiette, R. H. Bradley, and P. N. Brier, *Chem. Comm.*, 1971, 1567.

for the iodine compound the chain is much more complex (Figure 2).

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