Phenylantimony(V) Fluoride Halides: Isolation and Crystal Structures of $SbPh_2Br_2F{\cdot}SbPh_2Br_3$, $(SbPh_2BrF)_2O$ and $SbPh_3Cl_{1.8}F_{0.2}$†

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Oxidation of diphenylantimony fluoride with chlorine leads to diphenylantimony trichloride as the only isolable product, while the corresponding reaction with bromine gives, in addition to $SbPh_2Br_3$, the bromide fluorides, $Sb_2Ph_4Br_5F$, $SbPh_2Br_2F$, $Sb_2Ph_4Br_3F_3$ and $SbPh_2BrF_2$. The structure of the first compound has been confirmed by X-ray diffraction as a fluorine-bridged diantimony compound, $SbPh_2Br_2F{\cdot}SbPh_2Br_3$, where the antimony atoms are, respectively, in trigonal-bipyramidal and distorted-octahedral co-ordination. Hydrolysis during attempts to obtain crystals of the second compound produced the oxygen-bridged $(SbPh_2BrF)_2O$, which contains a strong intramolecular fluorine bridge, again giving antimony atoms in both trigonal-bipyramidal and octahedral co-ordination. As an alternative approach to the preparation of mixed chloride fluorides, reactions between diphenylantimony trichloride and KF, AgF and arsenic trifluoride were investigated. There was no reaction with the first two reagents but the product with arsenic trifluoride was a disordered mixed halide, shown by X-ray crystallography to be $SbPh_3Cl_{1.8}F_{0.2}$.

Although organoantimony(V) fluorides such as SbR_4F and SbR_3F_2, where R is an alkyl or aryl group are well established,[1] less is known about compounds containing only two organic groups. Diphenylantimony trifluoride, for example, has been mentioned as a monohydrate from the reaction of antimony(V) fluoride and benzene[2] and as the anhydrous compound when diphenylantimony fluoride is treated with either xenon difluoride[3] or $PhIF_2$[4] or when sulfur tetrafluoride reacts with $SbPh_2O(OH)$.[5] The dimethyl analogue is also mentioned without detail as resulting from the reaction of dimethylantimony trichloride with silver fluoride in ethanol.[6]

We were interested in the structures of $SbPh_2F_3$ and related fluoride halides, which are likely to differ substantially from those of analogues containing only heavier halogens[7,8] because of the high bridging capacity of fluorine. Our attempts to prepare these compounds used two approaches: (*a*) oxidation of $SbPh_2F$ with either chlorine or bromine to produce $SbPh_2FX_2$ and (*b*) reaction of $SbPh_2Cl_3$ with a range of fluorinating agents to obtain $SbPh_2Cl_{3-n}F_n$. Previous work has shown that all members of the diphenylantimony trihalide series, $SbPh_2Br_nCl_{3-n}$, can be obtained by oxidising either $SbPh_2Cl$ or $SbPh_2Br$ with chlorine or bromine.[9]

Results

Oxidation of Diphenylantimony Fluoride.—Although simple oxidation of antimony(III) to antimony(V) was expected to occur when the stoichiometric amount of chlorine was added to diphenylantimony fluoride suspended in dichloromethane at −97 °C, the white solid obtained on concentrating the solution was identified by analysis, IR and mass spectrometry, and X-ray diffraction as diphenylantimony trichloride.[7] Attempts to isolate further products, presumably containing a higher ratio of fluorine to phenyl groups, by concentrating the mother-liquor were unsuccessful. A similar reaction with 1 mol of bromine led to decolorisation on warming the solution from −97 to −40 °C, and on concentrating the solution and cooling again to −97 °C a white precipitate (m.p. 171 °C) was obtained. This was identified as $SbPh_2Br_3$ from the analytical data and by comparison with the IR and mass spectra of an authentic sample.[9] Fractional crystallisation of the mother-liquor led to five further white solids, which showed an increase in carbon and hydrogen content and a decrease in bromine content with increasing solubility in dichloromethane (see Experimental section).

From its IR spectrum, fraction 1 (m.p. 162 °C) appears to be a mixture of $SbPh_2Br_3$ with a small amount of fraction 2. The IR spectrum of fraction 2 (m.p. 168 °C) shows major new features at 533 and 510 cm^{-1}, in the region expected for Sb–F···Sb stretching and at *ca.* 360 cm^{-1}, tentatively assigned as an Sb–F deformation. Fraction 3 (m.p. 161 °C) again shows new IR features with the Sb–F bands moving to higher energies at 584 and 552 cm^{-1}. There is a strong similarity between the IR spectra of fractions 3 and 4 (m.p. 158 °C), while that of fraction 5 (m.p. 141 °C) is more complex. In line with the analytical results, the IR spectra show a general increase in the intensity of bands due to Sb–F stretching and a decrease in bands at *ca.* 220 cm^{-1}, associated with Sb–Br stretching.

Little definitive information was obtained from the mass spectra of fractions 1–5, which produced similar fragments, but there were marked changes in their relative intensities, confirming an increase in fluorine and decrease in bromine content with increasing solubility. Fragment ions containing bromine were observed even for the most soluble fraction. Attempts to identify the products by ^{19}F NMR spectroscopy were unsuccessful, probably because of the quadrupole moment of the antimony nucleus.

On the basis of this information, it is possible to assign the following formulae to fractions 2–5 respectively: $Sb_2Ph_4Br_5F$, $SbPh_2Br_2F$, $Sb_2Ph_4Br_3F_3$ and $SbPh_2BrF_2$. Crystals suitable for X-ray diffraction were obtained by slowly cooling dichloromethane solutions of fractions 2 and 3, but crystals could not be obtained either by this method or by vapour diffusion for the more fluorine-rich fractions.

Structure of Fraction 2.—Fraction 2 was identified by X-ray diffraction as a diantimony species, $SbPh_2Br_2F{\cdot}SbPh_2Br_3$, where the two molecules are joined by a fluorine bridge.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

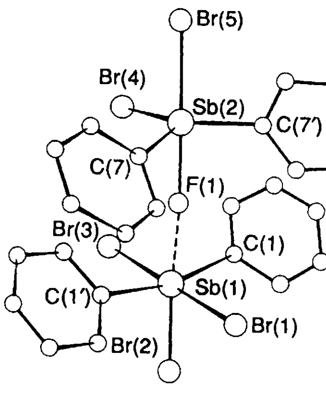

Fig. 1 Structure of $SbPh_2Br_2F{\cdot}SbPh_2Br_3$, showing the atom numbering scheme

Table 1 Important bond lengths (Å) and angles (°) for $SbPh_2Br_2F{\cdot}SbPh_2Br_3$, with estimated standard deviations (e.s.d.s) in parentheses *

Sb(1)–Br(1)	2.626(2)	Sb(2)–Br(4)	2.449(2)
Sb(1)–Br(2)	2.510(2)	Sb(2)–Br(5)	2.531(2)
Sb(1)–Br(3)	2.600(2)	Sb(2)–F(1)	2.077(7)
Sb(1)–C(1)	2.132(8)	Sb(2)–C(7)	2.103(9)
Sb(1) ··· F(1)	2.343(7)	Sb(2) ··· Br(3″)	3.982(2)

Br(1)–Sb(1)–Br(2)	89.96(7)	Br(4)–Sb(2)–Br(5)	91.98(6)
Br(1)–Sb(1)–Br(3)	177.92(7)	Br(4)–Sb(2)–C(7)	113.2(2)
Br(1)–Sb(1)–C(1)	89.3(3)	Br(4)–Sb(2)–F(1)	84.0(2)
Br(1)–Sb(1) ··· F(1)	85.0(2)	Br(4)–Sb(2) ··· Br(3″)	166.36(6)
Br(2)–Sb(1)–Br(3)	92.12(7)	Br(5)–Sb(2)–C(7)	96.4(2)
Br(2)–Sb(1)–C(1)	99.8(2)	Br(5)–Sb(2)–F(1)	175.9(2)
Br(2)–Sb(1) ··· F(1)	174.9(2)	Br(5)–Sb(2) ··· Br(3″)	74.38(5)
Br(3)–Sb(1)–C(1)	90.4(3)	C(7)–Sb(2)–F(1)	85.3(2)
Br(3)–Sb(1) ··· F(1)	92.9(2)	C(7)–Sb(2) ··· Br(3″)	69.3(2)
C(1)–Sb(1) ··· F(1)	80.1(2)	C(7)–Sb(2)–C(7′)	131.2(5)
C(1)–Sb(1)–C(1′)	160.3(5)	F(1)–Sb(2)–Br(3″)	109.7(2)
Sb(1) ··· F(1)–Sb(2)	174.6(4)		
Sb(1″)–Br(3″) ··· Sb(2)	178.74(7)		

* Atoms carrying primes and double primes are related to unprimed atoms by the symmetry operations x, $0.5 - y$, z and $x - 0.5$, $0.5 - y$, $0.5 - z$, respectively.

The structure is shown together with the atom numbering scheme in Fig. 1. A preliminary report has already been published.[10] In addition to the two antimony atoms, all six halogen atoms also lie on a mirror plane and the two phenyl groups attached to each antimony are related by this mirror plane. Important bond distances and angles are listed in Table 1.

The Sb(2) molecule, $SbPh_2Br_2F$, has basically trigonal-bipyramidal geometry with two phenyl groups and Br(4) in equatorial positions and Br(5) and the fluorine atom in the axial sites. Trigonal-bipyramidal geometry would also be expected for the Sb(1) molecule as an isolated entity with the equatorial plane passing through the two phenyl groups and Br(2), but donation from the fluorine atom raises the co-ordination to distorted octahedral. Donation takes place in the equatorial plane of the Sb(1) molecule, *trans* to Br(2) [F(1) ··· Sb(1)–Br(2) 174.9°], increasing the C(1)–Sb(1)–C(1′) angle from 120 to 160.3°. There is a compensating reduction in the other equatorial angles, maintaining planarity in the SbC_2Br system. The fluorine bridge is almost linear [Sb(1) ··· F(1)–Sb(2) 174.6°] but very asymmetric [Sb(2)–F(1) 2.077, Sb(1) ··· F(1) 2.343 Å]. Angles at bridging fluorine atoms are usually high, but generally the fluorine atoms are placed more centrally than in this example.[11]

The shortest antimony–bromine distance (2.449 Å) is that in the equatorial plane at Sb(2), the shortness a consequence of the enhanced Lewis acidity at Sb(2) due to fluorine substitution and the usual shortening of equatorial over axial bonds in trigonal bipyramids. Fluorine substitution also affects the bromine atom at Sb(1) *trans* to the fluorine bridge, which forms the second shortest bond [Sb(1)–Br(2) 2.510 Å].

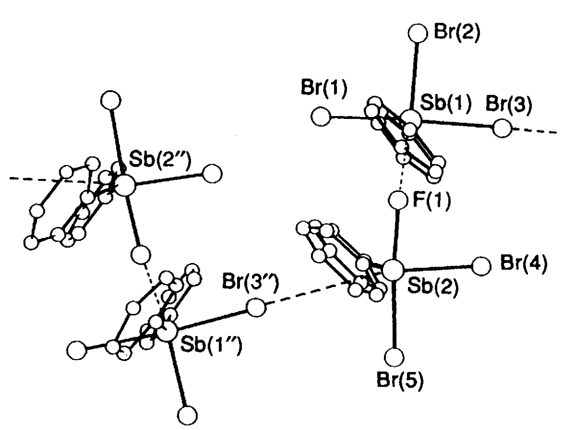

Fig. 2 Projection of the $SbPh_2Br_2F{\cdot}SbPh_2Br_3$ structure down the *b* axis, showing weak intermolecular contacts

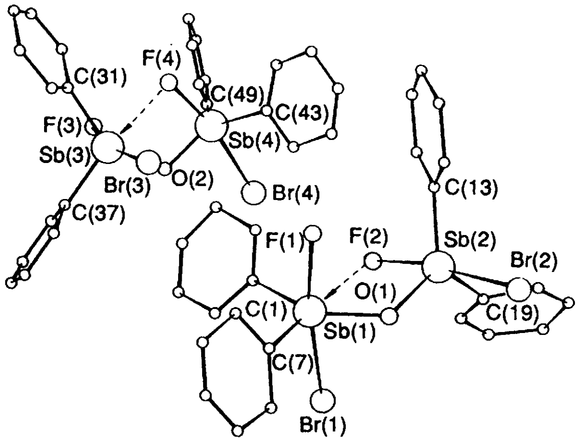

Fig. 3 Relative orientations of the two independent molecules in the structure of $(SbPh_2BrF)_2O$

Finally, the structure is completed by weak intermolecular interactions between Sb(2) and a symmetry related Br(3) atom, linking the dimeric molecules into zigzag chains parallel to the *a* axis (see Fig. 2). This interaction is *trans* to Br(4) and, like the fluorine bridging discussed above, is between the equatorial phenyl groups [Br(4)–Sb(2) ··· Br(3′) 166.4 and Sb(1″)–Br(3″) ··· Sb(2) 178.7°]. Here the C(7)–Sb(2)–C(7′) angle is only opened by 11.2° and the interaction is clearly much weaker, [Sb(2) ··· Br(3″) 3.982 Å, *cf.* 4.2 Å for the sum of the van der Waals radii].

Structure of Fraction 3.— An X-ray investigation of crystals of fraction 3 showed the unit cell contained two independent molecules of an oxygen-bridged diantimony species $(SbPh_2BrF)_2O$, which presumably arises from partial hydrolysis of $SbPh_2Br_2F$ during crystallisation. The structure and relative orientations of the two molecules are shown in Fig. 3 and important bond parameters are listed in Table 2. There are no interactions between the individual molecules closer than 5.5 Å.

Co-ordination about one antimony in each molecule, *i.e.* Sb(2) and Sb(4), is trigonal bipyramidal with two phenyl groups and the bridging oxygen atom occupying the equatorial plane and a bromine and a fluorine atom in the axial sites. Angles in the equatorial planes are close to the ideal values, but those between the axial atoms are reduced to 168.9 and 167.7° at Sb(2) and Sb(4) respectively, as a result of intramolecular F(2) ··· Sb(1) and F(4) ··· Sb(3) interactions at 2.78 and

Table 2 Important bond lengths (Å) and angles (°) for $(SbPh_2BrF)_2O$, with e.s.d.s in parentheses

Sb(1)–O(1)	1.93(2)	Sb(2)–O(1)	1.93(2)	Sb(3)–O(2)	1.95(2)	Sb(4)–O(2)	1.90(2)
Sb(1)–Br(1)	2.567(4)	Sb(2)–Br(2)	2.549(4)	Sb(3)–Br(3)	2.579(4)	Sb(4)–Br(4)	2.528(5)
Sb(1)–F(1)	2.13(2)	Sb(2)–F(2)	1.99(2)	Sb(3)–F(3)	2.12(2)	Sb(4)–F(4)	2.00(2)
Sb(1)–C(1)	2.13(3)	Sb(2)–C(13)	2.03(3)	Sb(3)–C(31)	2.13(3)	Sb(4)–C(43)	2.11(3)
Sb(1)–C(7)	2.09(3)	Sb(2)–C(19)	2.03(3)	Sb(3)–C(37)	2.05(3)	Sb(4)–C(49)	2.05(3)
Sb(1) ··· F(2)	2.78(2)	Sb(2) ··· F(1)	3.46(2)	Sb(3) ··· F(4)	2.58(2)	Sb(4) ··· F(3)	3.58(2)
		Sb(2) ··· Sb(1)	3.354(3)			Sb(4) ··· Sb(3)	3.327(3)
O(1)–Sb(1)–Br(1)	85.6(6)	O(1)–Sb(2)–Br(2)	85.5(6)	O(2)–Sb(3)–Br(3)	85.8(6)	O(2)–Sb(4)–Br(4)	86.4(6)
O(1)–Sb(1)–F(1)	85.3(7)	O(1)–Sb(2)–F(2)	83.4(7)	O(2)–Sb(3)–F(3)	84.7(8)	O(2)–Sb(4)–F(4)	81.3(8)
O(1)–Sb(1)–C(1)	138.3(9)	O(1)–Sb(2)–C(13)	118.4(9)	O(2)–Sb(3)–C(31)	146.2(10)	O(2)–Sb(4)–C(43)	118.6(10)
O(1)–Sb(1)–C(7)	107.2(9)	O(1)–Sb(2)–C(19)	118.5(10)	O(2)–Sb(3)–C(37)	102.9(10)	O(2)–Sb(4)–C(49)	119.1(11)
O(1)–Sb(1) ··· F(2)	64.5(7)	O(1)–Sb(2) ··· F(1)	52.5(6)	O(2)–Sb(3) ··· F(4)	66.6(7)	O(2)–Sb(4) ··· F(3)	49.1(7)
Br(1)–Sb(1)–F(1)	168.7(4)	Br(2)–Sb(2)–F(2)	168.9(5)	Br(3)–Sb(3)–F(3)	165.8(5)	Br(4)–Sb(4)–F(4)	167.7(5)
Br(1)–Sb(1)–C(1)	93.9(7)	Br(2)–Sb(2)–C(13)	97.2(8)	Br(3)–Sb(3)–C(31)	93.5(8)	Br(4)–Sb(4)–C(43)	98.3(8)
Br(1)–Sb(1)–C(7)	97.6(8)	Br(2)–Sb(2)–C(19)	92.9(9)	Br(3)–Sb (3)–C(37)	99.5(9)	Br(4)–Sb(4)–C(49)	94.8(9)
Br(1)–Sb(1) ··· F(2)	89.3(3)	Br(2)–Sb(2) ··· F(1)	107.5(3)	Br(3)–Sb(3) ··· F(4)	86.4(4)	Br(4)–Sb(4)–F(3)	113.5(3)
F(1)–Sb(1)–C(1)	88.4(8)	F(2)–Sb(2)–C(13)	88.8(9)	F(3)–Sb(3)–C(31)	88.6(10)	F(4)–Sb(4)–C(43)	88.3(9)
F(1)–Sb(1)–C(7)	91.6(9)	F(2)–Sb(2)–C(19)	91.6(10)	F(3)–Sb(3)–C(37)	92.9(10)	F(4)–Sb(4)–C(49)	90.6(10)
F(1)–Sb(1) ··· F(2)	80.7(5)	F(2)–Sb(2) ··· F(1)	66.0(5)	F(3)–Sb(3) ··· F(4)	80.1(6)	F(4)–Sb(4) ··· F(3)	58.1(5)
C(1)–Sb(1)–C(7)	114.0(10)	C(13)–Sb(2)–C(19)	122.8(11)	C(31)–Sb(3)–C(37)	110.6(12)	C(43)–Sb(4)–C(49)	121.4(12)
C(1)–Sb(1) ··· F(2)	73.8(8)	C(13)–Sb(2) ··· F(1)	68.6(8)	C(31)–Sb(3) ··· F(4)	79.6(9)	C(43)–Sb(4) ··· F(3)	74.2(8)
C(7)–Sb(1) ··· F(2)	169.0(8)	C(19)–Sb(2) ··· F(1)	155.7(9)	C(37)–Sb(3) ··· F(4)	167.7(10)	C(49)–Sb(4) ··· F(3)	146.1(9)
Sb(1)–O(1)–Sb(2)	120.8(10)			Sb(3)–O(2)–Sb(4)	119.6(10)		
Sb(1) ··· F(2)–Sb(2)	87.8(6)			Sb(3) ··· F(4)–Sb(4)	92.2(6)		

Table 3 Important fragments in the mass spectra of $SbPh_3Cl_2$, $SbPh_3F_2$ and $SbPh_3Cl_{1.8}F_{0.2}$ (intensities as % total ion current, t = trace)

Fragment ion	$SbPh_3Cl_2$	$SbPh_3F_2$	$SbPh_3Cl_{1.8}F_{0.2}$
$[SbPh_3Cl_2]^+$	2.2		0.9
$[SbPh_3ClF]^+$			0.4
$[SbPh_3F_2]^+$		2.8	0.9
$[SbPh_3Cl]^+$	2.0		1.0
$[SbPh_3F]^+$		2.1	0.4
$[SbPh_3]^+$	0.3	0.3	0.4
$[SbPh_2Cl_2]^+$	8.7		8.5
$[SbPh_2ClF]^+$			0.9
$[SbPh_2F_2]^+$		10.2	0.8
$[SbPh_2Cl]^+$	2.8		2.5
$[SbPh_2F]^+$		2.9	1.4
$[SbPh_2]^+$	4.4	4.1	4.3
$[SbPhCl_2]^+$	1.9		1.8
$[SbPhClF]^+$			0.1
$[SbPhF_2]^+$		2.4	0.1
$[SbPhCl]^+$	6.8		5.3
$[SbPhF]^+$		8.9	1.4
$[SbPh]^+$	10.6	11.8	9.2
$[SbC_4H_3]^+$	0.1	0.2	0.2
$[(C_6H_5)_2]^+$	31.6	26.9	29.2
$[SbCl]^+$	3.1		2.5
$[SbF]^+$		4.2	1.3
$[(C_4H_3)_2]^+$	t	0.1	t
$[Sb]^+$	1.1	1.7	1.2
$[PhCl]^+$	0.3		0.5
$[PhF]^+$		0.7	0.2
$[Ph]^+$	19.2	15.4	21.4
$[C_5H_3]^+$	3.4	3.6	2.8
$[C_4H_3]^+$	1.2	0.9	0.2

2.58 Å, respectively (*cf.* 3.55 Å for the sum of the van der Waals radii). The structure is unusual as bromine rather than the more electronegative oxygen occupies an axial position, but this arrangement allows for intramolecular Sb ··· F bonding with consequent additional stabilisation.

The strength of intramolecular interaction is clearly greater at Sb(3) than at Sb(1), leading to greater distortion from trigonal-bipyramidal geometry, *e.g.* the O(2)–Sb(3)–C(31) equatorial angle increases to 146.2°, while the corresponding O(1)–Sb(1)–C(1) angle increases to 138.3°. In each case the equatorial moiety remains planar by appropriate reductions in the other two angles and, as the donor fluorine lies in the same plane, it is probably more accurate to describe the geometry at Sb(1) and Sb(3) as distorted octahedral.

Angles at the bridging oxygen atoms are close to 120° and within the accuracy of the determination, the bridge in each case is symmetrical (mean Sb–O distance 1.93 Å). Bridging oxygen angles in antimony systems vary quite widely, from 106° in $Sb_3Cl_9F_4O$[12] to 139.9° in $(SbPh_3N_3)_2O$,[13] but in the present case the oxygen bond angle will be that which maximises Sb ··· F bonding without bringing into play Sb ··· Sb repulsions. The Sb ··· Sb separations are in fact *ca.* 3.3 Å, compared with 4.4 Å for the van der Waals separation for two antimony atoms.

Fluorination of Diphenylantimony Trichloride.—Attempts to substitute the chlorine atoms in $SbPh_2Cl_3$ using either anhydrous potassium fluoride in methanol or silver fluoride in acetonitrile were unsuccessful and only starting materials were recovered. On the other hand, reaction did take place with arsenic trifluoride giving a white solid after removal of volatiles. Microanalytical data pointed to more than two phenyl groups per antimony atom, and although the results were close to those for $SbPh_3Cl_2$, the product melted at 103 °C, compared with 142 °C for authentic $SbPh_3Cl_2$.[14] There were also significant differences in the IR and mass spectra of the dichloride and the fluorination product, which persisted after repeated crystallisations of the product from ethanol. There was no change in the melting point and the product appears to be a stable entity. Its IR spectrum contains a broad peak at 501 cm^{-1}, not present for $SbPh_3Cl_2$, suggesting that fluorination had taken place. In support, bands at 509 and 490 cm^{-1} assigned to Sb–F stretching are observed for $SbPh_3F_2$.[15] Confirmation of the presence of fluorine came from the mass spectrum, which showed parent ion peaks for $SbPh_3Cl_2$, $SbPh_3F_2$ and $SbPh_3ClF$. The mass spectral data are summarised in Table 3, which also contains data for pure $SbPh_3Cl_2$ and $SbPh_3F_2$. Ions in the series $SbPh_2X_2$, $SbPhX_2$, $SbPh_2X$, SbPhX and SbX were observed for all three compounds, but the arsenic trifluoride product showed fragments containing both halogens, with higher intensities for the chlorine containing fragments.

The product then is clearly a triphenylantimony chloride fluoride, but it is not stoichiometric with analysis pointing to replacement of approximately 10% of the chlorine atoms in $SbPh_3Cl_2$ by fluorine. The product does however maintain its

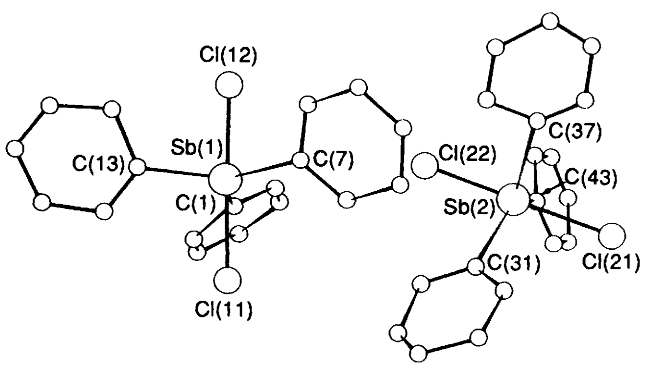

Fig. 4 Structure of $SbPh_3Cl_{1.8}F_{0.2}$; the Cl(12) position contains 26% F and Cl(22) 15% F

Table 4 Important bond lengths (Å) and angles (°) for $SbPh_3Cl_{1.8}F_{0.2}$ with e.s.d.s in parentheses

Sb(1)–Cl(11)	2.433(8)	Sb(2)–Cl(21)	2.491(7)
Sb(1)–Cl(12)	2.383(8)	Sb(2)–Cl(22)	2.415(7)
Sb(1)–C(1)	2.04(3)	Sb(2)–C(31)	2.13(3)
Sb(1)–C(7)	2.08(3)	Sb(2)–C(37)	2.08(3)
Sb(1)–C(13)	2.11(3)	Sb(2)–C(43)	2.07(3)
Cl(11)–Sb(1)–Cl(12)	175.4(4)	Cl(21)–Sb(2)–Cl(22)	176.5(3)
Cl(11)–Sb(1)–C(1)	88.2(6)	Cl(21)–Sb(2)–C(31)	90.1(7)
Cl(11)–Sb(1)–C(7)	90.9(7)	Cl(21)–Sb(2)–C(37)	90.7(7)
Cl(11)–Sb(1)–C(13)	92.6(9)	Cl(21)–Sb(2)–C(43)	86.9(7)
Cl(12)–Sb(1)–C(1)	88.2(6)	Cl(22)–Sb(2)–C(31)	92.3(7)
Cl(12)–Sb(1)–C(7)	88.7(7)	Cl(22)–Sb(2)–C(37)	90.5(7)
Cl(12)–Sb(1)–C(13)	91.6(9)	Cl(22)–Sb(2)–C(43)	89.7(7)
C(1)–Sb(1)–C(7)	122.8(9)	C(31)–Sb(2)–C(37)	115.9(9)
C(1)–Sb(1)–C(13)	117.4(9)	C(31)–Sb(2)–C(43)	126.1(9)
C(7)–Sb(1)–C(13)	119.8(9)	C(37)–Sb(2)–C(43)	117.9(7)

integrity on successive recrystallisations and to investigate the problems further an X-ray structure determination was carried out.

Structure of $SbPh_3Cl_{1.8}F_{0.2}$.—Two complete molecules make up the asymmetric unit and a diagram showing the structure is given in Fig. 4. Important bond distances and angles are collected in Table 4.

The two independent molecules are both trigonal bipyramidal with axial halogen and equatorial phenyl groups. The equatorial angles at Sb(1) are 117.4, 119.8 and 122.8°, while those at Sb(2) vary more widely from the ideal angles at 115.9, 117.9 and 126.1°. In the initial stages of refinement the axial atoms were considered to be chlorine but the isotropic thermal parameters indicated that, although the Cl(11) and Cl(21) positions were indeed occupied by chlorine atoms, the electron density at Cl(12) and Cl(22) was lower indicating chlorine–fluorine disorder. Refinement of the occupation factors for these atoms gave values of 0.88 and 0.93 respectively, implying a random distribution of 74% $SbPh_3Cl_2$ and 26% $SbPh_3ClF$ for the Sb(1) molecule and 85% $SbPh_3Cl_2$ and 15% $SbPh_3ClF$ for the Sb(2) molecule. The overall molecular formula is thus $SbPh_3Cl_{1.8}F_{0.2}$, in agreement with the analytical data. Even though mass spectrometry shows the presence of $SbPh_3F_2$ ions, there is no evidence for fluorine occupancy at the Cl(11) and Cl(21) positions and it seems unlikely that this compound is present. Cases are known where rearrangements take place in the ion source of the mass spectrometer and this is the most likely explanation here.

Axial bond distances reflect the different fluorine contents and there is also an effect on the lengths of the Sb–Cl bonds *trans* to the disordered atoms. Due to the higher inductive effect, the Sb(1)–Cl(11) distance is shorter than that from Sb(2) to Cl(21). In $SbPh_3Cl_2$ itself, the Sb–Cl distances are 2.484 Å,[14] and although data are not available for the corresponding fluoride, in $SbMe_3F_2$ the Sb–F distances are 1.993 and 2.004 Å.[16]

The SbC_3 equatorial units are close to planarity with Sb(1) lying 0.02 Å out of the C(1)C(7)C(13) plane in the direction of Cl(11); Sb(2) is similarly displaced 0.03 Å from the C(31)C(37)C(43) plane toward Cl(21), again towards the purely chlorine position. The phenyl groups in the two molecules are oriented slightly differently: those in the Sb(1) molecule make angles of 145.7, 54.8 and 86.5° with the SbC_3 plane while for the Sb(2) molecule, the corresponding angles are 148.1, 51.2 and 66.3°.

The greater deviation of the equatorial angles in the Sb(2) molecule from 120° might result from intra- or inter-molecular interaction between a fluorine-containing axial halogen and antimony at a position between the C(31) and C(43) phenyl groups. Intramolecular interactions of this kind are known, for example in $SbPh_3(O_2CMe)_2$, where one of the equatorial angles is increased to 148.2°.[17] This does not appear to be the case here, as the angle between the axial atoms is smaller in the Sb(1) molecule than in the more distorted Sb(2) molecule. Intermolecular interactions also seem unlikely as the closest Sb–Cl contacts are between Sb(1) and a symmetry related Cl(22) at 5.45 Å and Sb(2) and a symmetry related Cl(12) atom at 5.54 Å.

Discussion

These experiments show that it is not possible to prepare individual diphenylantimony fluoride halides by methods that are successful for the heavier mixed halides. Oxidation of either diphenylantimony bromide or chloride with the stoichiometric amount of free chlorine or bromine occurs cleanly to the appropriate trihalide, although with an excess of chlorine, bromine is displaced from $SbPh_2Br$ to give $SbPh_2Cl_3$.[9] Rather surprisingly, only $SbPh_2Cl_3$ was isolated in the oxidation of $SbPh_2F$ with chlorine, and although more highly fluorinated products must be present, none could be isolated. The situation with bromine is more complicated, and although simple products were not obtained, it is possible to see how the reaction may occur.

Clearly, isolation of $SbPh_2Br_2F{\cdot}SbPh_2Br_3$ indicates that the likely first stage is oxidation to the expected product, $SbPh_2Br_2F$. Some of this product must undergo halogen reorganisation to give $SbPh_2Br_3$ and more highly fluorinated products such as $SbPh_2BrF_2$. Reorganisation, on the other hand, cannot be as complete or as rapid as in the chlorine case as there is evidence that fraction 3 is $SbPh_2Br_2F$ and the monofluoride can be stabilised as an adduct with $SbPh_2Br_3$ (fraction 2).

The X-ray determination showed, however, that the material obtained by slow recrystallisation of fraction 3 was not $SbPh_2Br_2F$, but μ-oxo-bis(diphenylantimony bromide fluoride), arising from partial hydrolysis by adventitious water during crystallisation. At present there is no further information on the nature of fractions 4 and 5 but the formulae suggested above, *i.e.* the fluorine-bridged diantimony compound $SbPh_2BrF_2{\cdot}SbPh_2Br_2F$ and $SbPh_2BrF_2$, respectively, are not unreasonable.

It is surprising that $SbPh_2Cl_3$ could not be fluorinated by conventional reagents such as KF and AgF and that arsenic trifluoride leads to a rearrangement product containing only a small amount of fluorine. We have previously observed a related rearrangement in the fluorination of diphenylantimony chloride with arsenic trifluoride where, although chlorine is completely replaced, the product is $SbPh_3F_2$ and not the expected $SbPh_2F$.[18] Phenyl group mobility is particularly well established in a number of antimony(III) systems,[19] but fewer examples are known with Sb^V.

The most likely first stage in the reaction with arsenic trifluoride is formation of $SbPh_2Cl_2F$ [equation (1)], which could then bridge *via* fluorine to a molecule of the starting material. Phenyl–fluorine exchange, *via* a four-centre intermediate, would then give $SbPh_3Cl_2$ and $SbPhCl_3F$ [equation (2)]. A less probable alternative, which also could occur, is

Table 5 Characterising data for fractions obtained upon oxidation of diphenylantimony fluoride with bromine

		Analysis * (%)			
Fraction	M.p. (°C)	C	H	Br	Possible formula
1	162	29.0	2.1	43.8	Mixture
2	168	29.6	2.1	41.1	$C_{24}H_{20}Br_5FSb_2$
		(29.7)	(2.1)	(41.2)	
3	161	31.9	2.4	35.2	$C_{12}H_{10}Br_2FSb$
		(31.7)	(2.2)	(35.2)	
4	158	33.4	3.2	28.2	$C_{24}H_{20}Br_3F_3Sb_2$
		(34.0)	(2.4)	(28.8)	
5	141	35.1	3.5	21.9	$C_{12}H_{10}BrF_2Sb$
		(36.8)	(2.5)	(20.3)	

* Required values are given in parentheses.

Table 6 Fractional atomic coordinates ($\times 10^4$) for $SbPh_2Br_2F \cdot SbPh_2Br_3$, with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	1993.9(6)	2500	320.5(7)
Sb(2)	1424.0(6)	2500	3686.5(7)
Br(1)	211(1)	2500	24(1)
Br(2)	2243(2)	2500	−1607(1)
Br(3)	3749(1)	2500	686(1)
Br(4)	3103(1)	2500	3751(1)
Br(5)	1306(1)	2500	5646(1)
F(1)	1622(5)	2500	2090(5)
C(1)	1940(6)	1081(5)	597(7)
C(2)	2436(7)	709(6)	1407(7)
C(3)	2342(8)	−213(7)	1603(9)
C(4)	1768(8)	−725(6)	1020(10)
C(5)	1297(8)	−348(6)	200(10)
C(6)	1374(7)	561(6)	−12(9)
C(7)	862(6)	3793(6)	3461(6)
C(8)	254(7)	3933(6)	2671(8)
C(9)	−112(8)	4782(8)	2560(10)
C(10)	140(10)	5485(8)	3190(10)
C(11)	740(10)	5332(8)	3980(10)
C(12)	1108(9)	4478(7)	4141(9)

the formation of an analogous chlorine-bridged diantimony species, which by phenyl–chlorine exchange would give $SbPh_3ClF$ and $SbPhCl_4$ [equation (3)]. The tetrahalide by-products are unstable, decomposing [equations (4) and (5)] *via* a second phenyl group migration to $SbPh_2Cl_3$ and antimony(V) halides. In this way it would be possible to obtain the mixed $SbPh_3(Cl/F)_2$ product.

$$3SbPh_2Cl_3 + AsF_3 \longrightarrow 3SbPh_2Cl_2F + AsCl_3 \quad (1)$$

$$SbPh_2Cl_2F + SbPh_2Cl_3 \longrightarrow SbPh_3Cl_2 + SbPhCl_3F \quad (2)$$

$$SbPh_2Cl_2F + SbPh_2Cl_3 \longrightarrow SbPh_3ClF + SbPhCl_4 \quad (3)$$

$$SbPhCl_4 \longrightarrow SbPh_2Cl_3 + SbCl_5 \quad (4)$$

$$SbPhCl_3F \longrightarrow SbPh_2Cl_3 + SbCl_4F \quad (5)$$

Pure $SbPh_3ClF$ does not appear to have been isolated, but it has been observed in a ^{19}F NMR study of the equilibrium between $SbPh_3Cl_2$ and $SbPh_3F_2$.[20] A small amount must be produced during fluorination, which in the $SbPh_3Cl_2$ structure lowers the melting point (103 °C) below that of either of the pure dihalides (142 °C for $SbPh_3Cl_2$,[14] and 112 °C for $SbPh_3F_2$ [21]). Pure $SbPh_3Cl_2$ and $SbPh_3Cl_{1.8}F_{0.2}$ both crystallise in the same space group, but a small amount of unequally distributed fluorine at one of the axial positions leads to two independent molecules and a doubling of the unit cell volume.

Experimental

Diphenylantimony bromide, chloride[20] and fluoride[18,22] were prepared by literature methods. Chlorine was dried over P_2O_5 then calcium oxide, before fractionation on a vacuum line and bromine was distilled from anhydrous potassium bromide, washed with water and dried over P_2O_5 before use. Solvents were dried by conventional desiccants.

Oxidation of Diphenylantimony Fluoride with Chlorine.—Diphenylantimony fluoride (1.47 g, 5 mmol) was suspended in dry dichloromethane (50 cm^3) and purified chlorine (0.35 g, 5 mmol) was added at −97 °C from a weighted Carius tube. Warming to −40 °C gave a clear solution and reduction of the volume to 20 cm^3 gave white crystals. Yield 0.9 g, 2.4 mmol, m.p. 172 °C (Found: C, 37.8; H, 2.5; Cl, 26.2. Calc. for $C_{12}H_{10}Cl_2FSb$: C, 39.4; H, 2.8; Cl, 19.4; $C_{12}H_{10}Cl_3Sb$: C, 37.7; H, 2.6; Cl, 27.8%). It was not possible to obtain further product by concentration and cooling of the mother-liquor.

Oxidation of Diphenylantimony Fluoride with Bromine.—Diphenylantimony fluoride (2.95 g, 10 mmol) was suspended in dry dichloromethane (100 cm^3) and purified bromine (1.60 g, 10 mmol) was added with stirring at −97 °C. As with the chlorine experiment above, warming to −40 °C gave a clear solution and the bromine was decolourised. Concentration of the solution to 70 cm^3 and cooling to −97 °C gave crystals, m.p. 171 °C (Found: C, 27.9; H, 2.0; Br, 45.9. Calc. for $C_{12}H_{10}Br_2FSb$: C, 30.4; H, 2.6; Br, 33.8; $C_{12}H_{10}Br_3Sb$: C, 27.9; H, 2.0; Br, 46.5%). Fractional crystallisation of the mother liquor gave five further fractions (Table 5).

Crystal Structure of Fraction 2.—*Crystal data.* $C_{24}H_{20}Br_5FSb$, $M = 970.2$, orthorhombic, space group *Pnma* from systematic absences and subsequent refinement, $a = 14.573(6)$, $b = 14.807(6)$, $c = 12.884(5)$ Å, $U = 2779.3$ Å^3, $Z = 4$, $D_c = 2.32$ g cm^{-3}, $F(000) = 1800$, Mo-Kα radiation, μ(Mo-Kα) = 96.5 cm^{-1}, crystal size 0.1 × 0.1 × 0.2 mm.

Structure determination. Data were collected for 2143 reflections with $I > 3\sigma(I)$ and corrected for Lorentz and polarisation effects and for absorption using the ABSORB program.[23] Crystallographic calculations used the CRYSTALS programs[24] and scattering factors for neutral atoms.[25] The structure was solved by Patterson and Fourier difference methods and refined by full-matrix least squares to $R = 0.102$ with isotropic and $R = 0.055$ with anisotropic thermal parameters. Placing the hydrogen atoms at their calculated positions and application of a four-coefficient Chebyshev weighting scheme gave final convergence at $R = 0.051$. Final atomic coordinates are listed in Table 6.

Crystal Structure of Fraction 3.—*Crystal data.* $C_{24}H_{20}Br_2F_2OSb_2$, $M = 765.5$, monoclinic, space group $P2_1/c$, $a = 17.843(7)$, $b = 18.072(7)$, $c = 15.520(6)$ Å, $\beta = 90.29(3)$, $U = 5003.1$ Å^3, $Z = 8$, $D_c = 2.03$ g cm^{-3}, $F(000) = 2896$, Mo-Kα radiation, μ(Mo-Kα) = 56 cm^{-1}, crystal size 0.1 × 0.1 × 0.1 mm.

Structure determination. Data were collected and treated as above for 2292 observed reflections. The four antimony atoms in the asymmetric unit were located using the MULTAN programs[26] and the remaining non-hydrogen atoms were located by a series of Fourier difference syntheses. Refinement by full-matrix least squares, blocked for each independent molecule, converged at $R = 0.085$ with isotropic thermal parameters and at $R = 0.065$ with anisotropic thermal parameters and the hydrogen atoms placed at their calculated positions. Unit weighting was most appropriate. The final atomic coordinates are listed in Table 7.

Crystal Structure of the Arsenic Trifluoride Product.—*Crystal data.* $C_{18}H_{15}Cl_{1.8}F_{0.2}Sb$, $M = 420.5$, orthorhombic, space group $P2_12_12_1$, $a = 9.104(4)$, $b = 17.048(7)$, $c = 22.121(9)$ Å,

Table 7 Fractional atomic coordinates (× 10^3) for $(SbPh_2BrF)_2O$, with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	565.4(1)	84.1(1)	764.5(1)	Sb(3)	61.8(1)	62.4(1)	214.2(1)
Br(1)	661.1(2)	74.2(2)	642.1(2)	Br(3)	151.8(2)	81.8(2)	342.7(2)
F(1)	488.4(9)	115.3(9)	862(1)	F(3)	−14.9(8)	75.4(9)	111(1)
O(1)	621(1)	170(1)	800(1)	O(2)	116(1)	143(1)	159(1)
C(1)	472(1)	58(1)	684(2)	C(31)	−30(2)	32(2)	294(2)
C(2)	409(2)	91(2)	696(2)	C(32)	−102(2)	54(2)	273(2)
C(3)	343(2)	68(2)	648(2)	C(33)	−159(2)	27(2)	324(3)
C(4)	358(2)	15(2)	585(2)	C(34)	−145(2)	−11(2)	399(2)
C(5)	419(2)	−19(2)	574(2)	C(35)	−73(2)	−34(2)	416(2)
C(6)	481(2)	2(2)	623(2)	C(36)	−13(2)	−8(2)	365(2)
C(7)	604(2)	−5(2)	838(2)	C(37)	110(2)	−30(2)	160(2)
C(8)	676(2)	−36(2)	828(2)	C(38)	159(2)	−75(2)	207(2)
C(9)	694(2)	−98(2)	880(3)	C(39)	194(2)	−138(2)	169(2)
C(10)	647(2)	−126(2)	937(2)	C(40)	175(2)	−150(2)	89(3)
C(11)	585(2)	−100(2)	943(2)	C(41)	134(2)	−108(2)	32(2)
C(12)	555(2)	−35(2)	891(2)	C(42)	102(2)	−46(2)	76(2)
Sb(2)	580.9(1)	268.5(1)	781.9(1)	Sb(4)	80.6(1)	241.8(1)	171.3(1)
Br(2)	675.9(2)	309.4(2)	895.4(3)	Br(4)	183.7(2)	277.0(2)	68.5(3)
F(2)	515.0(9)	217.4(9)	696(1)	F(4)	8.5(9)	191.3(9)	250(1)
C(13)	487(2)	298(1)	847(2)	C(43)	−12(2)	276(2)	96(2)
C(14)	484(2)	299(2)	935(2)	C(44)	−77(2)	286(2)	135(2)
C(15)	419(2)	317(2)	978(2)	C(45)	−139(2)	314(2)	89(3)
C(16)	354(2)	332(2)	937(2)	C(46)	−130(2)	329(2)	4(3)
C(17)	356(2)	332(2)	849(3)	C(47)	−68(2)	320(2)	−31(2)
C(18)	422(2)	314(2)	804(2)	C(48)	−5(2)	293(2)	12(2)
C(19)	627(2)	333(2)	689(2)	C(49)	120(2)	305(2)	271(2)
C(20)	645(2)	405(2)	703(2)	C(50)	75(2)	338(2)	329(3)
C(21)	672(2)	455(2)	640(2)	C(51)	95(2)	379(2)	397(3)
C(22)	677(2)	431(2)	558(2)	C(52)	173(2)	386(2)	409(2)
C(23)	648(2)	361(2)	537(3)	C(53)	223(2)	356(2)	364(2)
C(24)	624(2)	316(2)	603(2)	C(54)	199(2)	311(2)	291(2)

Table 8 Fractional atomic coordinates (× 10^3) for $SbPh_3Cl_{1.8}F_{0.2}$, with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	159.4(2)	226.1(1)	195.24(8)	Sb(2)	927.4(2)	954.4(1)	978.39(7)
Cl(11)	240(1)	117.5(5)	258.4(4)	Cl(21)	1009.4(8)	833.1(4)	925.5(3)
Cl(12)	66(1)	325.9(5)	130.4(4)	Cl(22)	833(1)	1070.4(4)	1027.4(4)
C(1)	−52(3)	192(1)	211.2(9)	C(31)	1043(3)	919(2)	1058(1)
C(2)	−155(4)	178(1)	166(1)	C(32)	1007(3)	945(2)	1113(2)
C(3)	−292(3)	160(2)	176(1)	C(33)	1090(5)	916(3)	1162(1)
C(4)	−351(3)	159(2)	235(2)	C(34)	1196(6)	883(3)	1160(3)
C(5)	−249(4)	173(2)	282(2)	C(35)	1237(6)	851(3)	1103(2)
C(6)	−106(4)	191(2)	271(1)	C(36)	1157(4)	872(2)	1051(1)
C(7)	282(3)	184(1)	123(1)	C(37)	1045(3)	1023(1)	918(1)
C(8)	346(3)	234(2)	82(1)	C(38)	1111(3)	1091(2)	937(1)
C(9)	428(4)	206(2)	33(1)	C(39)	1187(4)	1138(2)	897(1)
C(10)	442(4)	130(2)	25(1)	C(40)	1188(4)	1120(2)	838(1)
C(11)	390(3)	77(2)	62(2)	C(41)	1129(5)	1057(2)	818(1)
C(12)	308(4)	103(2)	113(1)	C(42)	1053(4)	1004(2)	857(1)
C(13)	251(5)	310(2)	254(1)	C(43)	715(3)	923(1)	955(1)
C(14)	232(5)	393(2)	236(2)	C(44)	633(3)	977(2)	921(1)
C(15)	293(8)	445(2)	280(2)	C(45)	490(3)	953(2)	904(1)
C(16)	365(5)	423(4)	331(2)	C(46)	429(4)	885(2)	919(1)
C(17)	371(5)	348(3)	345(2)	C(47)	506(4)	834(2)	953(2)
C(18)	310(4)	290(2)	306(2)	C(48)	648(3)	854(2)	969(1)

U = 3433.2 Å^3, Z = 8, D_c = 1.63 g cm^{-3}, $F(000)$ = 1652, Mo-Kα radiation, μ(Mo-Kα) = 19.2 cm^{-1}, crystal size *ca.* 0.2 × 0.2 × 0.2 mm.

Structure determination. Intensities for 2199 observed reflections were corrected for Lorentz and polarisation effects but an absorption correction was not considered necessary. Positions for the two independent antimony atoms in the asymmetric unit were obtained from a three-dimensional Patterson synthesis and the other heavy atoms were revealed by successive Fourier difference syntheses. Refinement with the axial positions occupied by chlorine atoms converged at R = 0.076 with isotropic thermal parameters and at R = 0.065 with anisotropic thermal parameters and the phenyl hydrogen atoms placed at calculated positions. Thermal parameters at the Cl(12) and Cl(22) were higher than at the Cl(11) and Cl(21) positions, implying fluorine–chlorine disorder, and in the next refinement cycles the occupation factors of the chlorine atoms were allowed to refine. After three cycles there was no significant deviation of the factors for Cl(11) and Cl(21) from 1.0 and their occupancy was fixed at that value. Further refinement reduced the occupation factors at Cl(12) and Cl(22) to 0.88(2) and 0.93(2), respectively and the final R value was 0.058. Final atomic coordinates are listed in Table 8.

Additional material available for all structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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Received 12*th February* 1992; *Paper* 2/00762B