665. *Co-ordination Compounds Formed by Tetrafluorides of the Sulphur Sub-group.*

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Fluoride ion acceptors form co-ordination compounds with the tetrafluorides of Group VIB elements. The sulphur compounds can be converted easily into their selenium analogues. These conversions are useful for the convenient generation of sulphur tetrafluoride and its purification. The nature of the bonding in the adducts is discussed.

IN a preliminary communication,[1] we described new co-ordination compounds formed by the tetrafluorides of sulphur, selenium, and tellurium. Sulphur tetrafluoride complexes are convertible into selenium analogues by displacement of the more volatile base and we have outlined a method [2] of purifying sulphur tetrafluoride, based on this. The recent development of a convenient preparative method [3] for sulphur tetrafluoride and the demonstration of its synthetic value as a fluorinating agent [4] has stimulated further interest in its derivatives.

Sulphur tetrafluoride, mixed with thionyl fluoride or other sulphur fluorides, can easily be isolated by first making the boron trifluoride adduct, SF_4,BF_3, from which the other

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[1] Bartlett and Robinson, *Chem. and Ind.*, 1956, 1351.

[2] Bartlett and Robinson, *Proc. Chem. Soc.*, 1957, 230.

[3] Tullock, Fawcett, Smith, and Coffman, *J. Amer. Chem. Soc.*, 1960, **82**, 539.

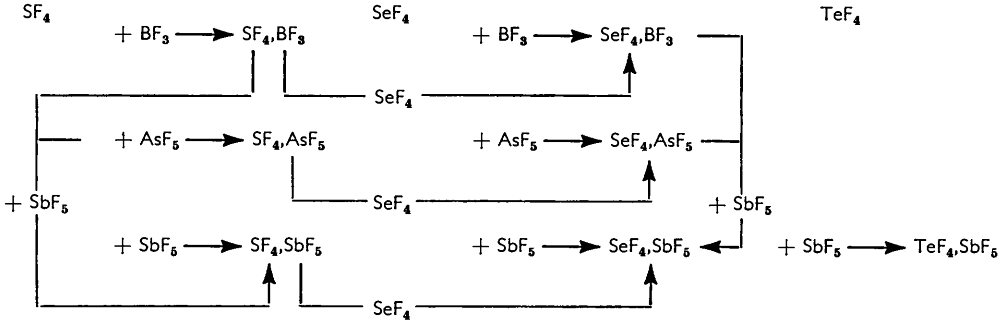
[4] Hasek, Smith, and Engelhardt, *J. Amer. Chem. Soc.*, p. 543; Smith, Tullock, Smith, and Engelhardt, *ibid.*, p. 551.

fluorides can readily be removed. This compound is also formed when boron–sulphur mixtures are fluorinated at low temperatures and when sulphur tetrafluoride fluorinates borosilicate glass. In the latter reaction, which occurs above 300°, the formation of the adduct is accompanied by deposition of sulphur, probably produced in the disproportionation $3SF_4 \longrightarrow 2SF_6 + S$. Boron trifluoride is formed in the reaction $6SF_4 + 2B_2O_3 \longrightarrow 4BF_3 + 6SOF_2$.

The arsenic pentafluoride complex, SF_4,AsF_5, which is much less volatile than SF_4,BF_3, can be stored indefinitely in Pyrex glass ampoules, as can the antimony pentafluoride complex; this is, however, more troublesome to prepare. Selenium tetrafluoride will displace sulphur tetrafluoride from all these complexes: $SeF_4 + SF_4,A \longrightarrow SeF_4,A + SF_4$. It is probable that other basic liquid fluorides such as arsenic trifluoride, iodine pentafluoride, and bromine trifluoride will also liberate sulphur tetrafluoride from its adducts. Boron trifluoride can be removed from SF_4,BF_3 by passing the vapour over sodium fluoride at 240°: $SF_4,BF_3 + NaF \longrightarrow SF_4 + NaBF_4$. But this is a less convenient and efficient preparative method for sulphur tetrafluoride than displacement with liquid bases.

The more volatile acid can also be displaced by a less volatile one, so that boron trifluoride and arsenic pentafluoride complexes can be converted by antimony pentafluoride into SF_4,SbF_5 and SeF_4,SbF_5. The former is more easily prepared in this way than by direct combination. Interconversions which can easily be made are shown schematically.

Inter-relationships between the complexes of SF_4, SeF_4, *and* TeF_4.



Neither sulphur tetrafluoride nor selenium tetrafluoride forms a co-ordination complex with platinum dichloride; this indicates that they are unlikely to be electron-pair donors. It is significant that phosphorus trifluoride, although it forms a co-ordination complex with platinum dichloride involving donation of the phosphorus " lone pair,"[5] does not combine with boron trifluoride.[6]

The adduct SF_4,BF_3 is completely dissociated in the vapour phase and the enthalpy of dissociation is consistent with the ionic formulation $SF_3^+BF_4^-$. Table 1 gives present thermodynamic data for the adduct together with the values of Cotton and George[7] and Seel and Detmer;[8] enthalpies of dissociation of other boron trifluoride derivatives (cf. ref. 9) are included for comparison. The enthalpy of formation for the arsenic pentafluoride adduct is greater than for SF_4,BF_3.

Nuclear magnetic resonance measurements by Cotton and George[10] and by Muetterties

[5] Chatt and Williams, *J.*, 1951, 3061.
[6] Booth and Walkup, *J. Amer. Chem. Soc.*, 1943, **65**, 2334.
[7] Cotton and George, *J. Inorg. Nuclear Chem.*, 1960, **12**, 386.
[8] Seel and Detmer, *Z. anorg. Chem.*, 1959, **301**, 113.
[9] Greenwood and Martin, *Quart. Rev.*, 1954, **8**, 1.
[10] Cotton and George, *J. Inorg. Nuclear Chem.*, 1958, **7**, 397.

and his co-workers[11] indicate that the bonding in SF_4,BF_3 is either ionic or by fluorine bridging. It is evident, however, that sulphur tetrafluoride is a poor acceptor since it does not combine with nitryl fluoride[12] or with cæsium fluoride. The tendency, therefore, for the sulphur atom to attain a pseudo-octahedral co-ordination, such as it would have in the bridged structure, must be small; and the pseudo-tetrahedral co-ordination of the SF_3^+ ion may well be preferred. Possibly fluorine bridging may be more important in selenium tetrafluoride derivatives since this tetrafluoride can act as a fluoride ion acceptor to form the SeF_5^- ion[13] in which the selenium is presumed to attain a pseudo-octahedral co-ordination.

TABLE 1.

Compound	van't Hoff equation	Enthp. of dissn. (kcal. mole^{-1})	Reference
SF_4,BF_3	$\log p_{\text{mm.}} = 12{\cdot}8 - 3230/T$	29·6	7
SF_4,BF_3	$\log p_{\text{mm.}} = 11{\cdot}34 - 2783/T$	25·5	8
SF_4,BF_3	$\log p_{\text{mm.}} = 11{\cdot}11 - 2716/T$	24·8 ± 0·2	Present work
$CsBF_4$		26·9	9
$RbBF_4$		27·0	9
KBF_4		28·9	
SF_4,AsF_5	$\log p_{\text{mm.}} = 10{\cdot}26 - 3376/T$	31·0 ± 0·8	Present work

X-Ray powder photographs of the sulphur tetrafluoride derivatives are simpler than those of their selenium analogues. The pattern of SF_4,SbF_5 only has been indexed; in the simple cubic unit cell, $a = 5{\cdot}625 \pm 0{\cdot}002$ Å, there is one molecule. The structure determination has not been completed, but the symmetry is suggestive of an ionic formulation $SF_3^+SbF_6^-$.

Enhancement of the electrical conductivity of selenium tetrafluoride by antimony pentafluoride indicates considerable ionisation of the complex: $SeF_4,SbF_5 \longrightarrow SeF_3^+ + SbF_6^-$.

When a mixture of potassium chloride with the adduct SeF_4,SbF_5 is heated in a vacuum, a volatile, thermally unstable product is obtained which rearranges to a mixture of the tetrafluoride and tetrachloride of selenium. It is probable that this initial product, which is a pale yellow liquid, may be selenium trifluorochloride:

$$SeF_3,SbF_6 + KCl \longrightarrow SeF_3Cl + KSbF_6;\ 4SeF_3Cl \longrightarrow 3SeF_4 + SeCl_4$$

Selenium tetrafluoride derivatives of platinum tetrafluoride, $(SeF_4)_2PtF_4$ [previously given[14] as $(SeF_4)_2PtF_2$] and of gold trifluoride, SeF_4,AuF_3, are thermally more stable than the bromine trifluoride acids $(BrF_3)_2PtF_4$[15] and BrF_3,AuF_3,[16] from which they are derived by displacement of the bromine trifluoride with an excess of selenium tetrafluoride. Selenium tetrafluoride and bromine trifluoride do not react in the liquid phase.

$$(BrF_3)_2PtF_4 + 2SeF_4 \longrightarrow (SeF_4)_2PtF_4 + 2BrF_3$$
$$BrF_3,AuF_3 + SeF_4 \longrightarrow SeF_4,AuF_3 + BrF_3$$

High-temperature decomposition of these complexes gives rise to platinum and gold since the selenium tetrafluoride acts as a reducing agent:

$$(SeF_4)_2PtF_4 = 2SeF_6 + Pt\ (350^\circ)$$
$$3SeF_4,AuF_3 = AuF_3 + 2Au + 3SeF_6\ (350^\circ)$$

Bartlett, Lohmann, and Quail[17] have shown that the platinum adduct $(SeF_4)_2PtF_4$ is isomorphous with the complexes $(SeF_4)_2GeF_4$ and $(SeF_4)_2PdF_4$.

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[11] Oppegard, Smith, Muetterties, and Engelhardt, *J. Amer. Chem. Soc.*, 1960, **82**, 3836.
[12] Hetherington, Ph.D. Thesis, Durham, 1955.
[13] Aynsley, Peacock, and Robinson, *J.*, 1952, 1231.
[14] Hair and Robinson, *J.*, 1960, 3419.
[15] Sharpe, *J.*, 1950 3444.
[16] Sharpe, *J.*, 1949, 2901.
[17] Bartlett, Lohmann, and Quail, unpublished work.

It has not been possible to isolate sulphur and tellurium analogues of $(SeF_4)_2PtF_4$ and SeF_4,AuF_3. The pale pink solid, formed when ruthenium pentafluoride is mixed with sulphur tetrafluoride, is probably SF_4,RuF_5 which would be analogous to SF_4,OsF_5 and SF_4,IrF_5, but a ruthenium pentafluoride analogue of SeF_4,OsF_5 and SeF_4,IrF_5 [18] cannot be isolated, although the ruthenium and selenium fluorides are miscible.

The higher melting point of tellurium tetrafluoride prevents the preparation of boron trifluoride and arsenic pentafluoride derivatives by direct addition; but antimony pentafluoride dissolves the tetrafluoride, and removal of the solvent leaves TeF_4,SbF_5. In contrast to the sulphur and selenium analogues and unlike antimony pentafluoride itself, hydrolysis of this adduct is slow, although exothermal, and is accompanied by the precipitation of tellurium dioxide: $TeF_4,SbF_5 + 2H_2O \longrightarrow TeO_2 + H^+ + SbF_6^- + 3HF$. Although this could be interpreted as indicative of an ionic formulation, there is no structural evidence on the point. The *X*-ray powder pattern was not indexed.

Boron trichloride does not form adducts with the sulphur or selenium tetrafluorides but interacts very energetically thus:

$$3SF_4 + 4BCl_3 \longrightarrow 3SCl_2 + 3Cl_2 + 4BF_3$$
$$3SeF_4 + 4BCl_3 \longrightarrow 3SeCl_4 + 4BF_3$$

EXPERIMENTAL

Purification of Sulphur Tetrafluoride.—(*a*) Sulphur tetrafluoride, made as described by Brown and Robinson [19] and containing silicon tetrafluoride and other fluorides of sulphur, was mixed at ~−180° with an equal bulk of boron trifluoride. The excess of boron trifluoride, sulphur hexafluoride, thionyl fluoride, and other sulphur fluorides was removed at −75° under a vacuum. The adduct SF_4,BF_3 remained. Selenium tetrafluoride, prepared as described by Aynsley, Peacock, and Robinson,[13] was distilled under a vacuum on to the SF_4,BF_3; on warming to room temperature the mixture evolved sulphur tetrafluoride. The gaseous product was passed through a Podbielniak fractionation column, all distilling at −40·4°/1 atm., the b. p. for the pure tetrafluoride.[19] Vapour-density measurements indicated $M = 108{\cdot}9 \pm 1{\cdot}0$ (Calc. for SF_4: $M = 108{\cdot}1$).

When too little selenium tetrafluoride to displace the sulphur tetrafluoride was used, SeF_4,BF_3, m. p. 50°, remained after the excess of SF_4,BF_3 had been removed at 20° under a vacuum.

(*b*) We are indebted to a Referee for suggesting that the reaction of SF_4,BF_3 with ethyl ether mentioned on p. 3422 was probably $SF_4,BF_3 + Et_2O \longrightarrow Et_2O,BF_3 + SF_4$ and that, if so, then readily accessible ether could be used in place of selenium tetrafluoride in our purification of sulphur tetrafluoride through the SF_4,BF_3 compound. We have found that the reaction goes smoothly when well dried ether is condensed on to SF_4,BF_3 at −190° and the mixture allowed to rise in temperature. A clear liquid is formed which evolves sulphur tetrafluoride. This was condensed at −190° and a specimen of the vapour gave infrared absorption peaks at 728vs, 870vs, 890vs, 1280m cm.$^{-1}$ (cf. 728vs, 867vs, 889vs, 1281m cm.$^{-1}$; ref. 20. The only impurities detected were traces of silicon tetrafluoride and thionyl fluoride which probably arose from moisture on the sodium chloride windows of the cell, since their peaks were weaker on a second filling. Neither boron trifluoride nor sulphur hexafluoride was present.

Preparation of SF_4,BF_3.—(a) SF_4 *with* BF_3. Both sulphur tetrafluoride and boron trifluoride are gases and can be manipulated volumetrically. The volumes were measured in a 1-l. bulb to which were attached a mercury manometer and two condensation limbs, one with a tap. After the pressure of the sulphur tetrafluoride had been measured in the bulb; it was condensed in the limb with the tap, which was then closed. The boron trifluoride was measured in the same way and condensed in the other limb. The sulphur tetrafluoride was condensed on to the boron trifluoride and the mixture allowed to react at about −100°. When the two initial gas pressures were equal the pressure for the product was independent of them. Clearly the vapour pressure or dissociation pressure of the co-ordination

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[18] Hepworth, Robinson, and Westland, *Chem. and Ind.*, 1955, 1516.
[19] Brown and Robinson, *J.*, 1955, 3147.
[20] Dodd and Woodward, *Trans. Faraday Soc.*, 1956, **52**, 1055.

compound was being registered, for an excess of either reactant led to a final pressure greater than this. Whatever the proportions, however, the properties of the solid were always the same, and it was concluded that one co-ordination compound only is formed, namely SF_4,BF_3. Typical results from equimolar proportions at 19° were:

Pressure of each gas (mm.)	206	285	410
Pressure of compound (mm.)	99	107	110

(b) *Fluorination of boron–sulphur mixtures.* Fluorination at room temperatures failed to produce the adduct, even with dilute fluorine. At $-75°$, however, a mixture of 95—97% boron and sulphur gave SF_4,BF_3 which slowly crystallised on the walls of the vessel. This sublimed at ~60° and qualitative tests confirmed its nature.

(c) *Fluorination of borosilicate glass with* SF_4. Reaction did not occur until ~350°; the heating flame was then coloured by the hot glass and there was marked etching. Sulphur was deposited just beyond the hot zone and, further away, acicular white crystals of SF_4,BF_3. Some sulphur hexafluoride was also formed.

Dissociation Pressure of SF_4,BF_3.—Vapour pressures were measured with a simple isoteniscope to which a tap-bottle containing freshly prepared material could be attached. This was of exaggerated wine-bottle form, to give minimum volume with maximum surface exposed to the bath liquid and to shorten the time required for thermal equilibrium. Its tap was spring-loaded to prevent seepage of water when, at higher temperatures, the grease had softened a little. It was connected to one side of the small differential mercury gauge by an A10 cone-and-socket joint secured by lugs and springs. This side of the gauge could be evacuated through a tap to a vacuum-line, and the other was connected to a mercury manometer and, by a two-way tap, separately to the vacuum-line and a fine capillary. The arrangement was sufficiently small to allow the bottle, the tap to the vacuum line, and the differential gauge to be submerged in water in a 5-l. beaker. All joints and taps were lubricated with stiff fluorocarbon grease. Manometer levels were measured with a cathetometer. The dissociation pressure increased as the material approached the working temperature and was balanced by admitting air through the capillary. Sufficient pressure–temperature readings were taken to ensure reliable results (Table 2). Between measurements the material was cooled at $-75°$ and the apparatus was evacuated.

TABLE 2.

Temp. (K)	273·2°	291·2°	294·2°	298·2°	301·2°	303·2°	308·2°	311·2°	313·2°	314·2°
Pressure (mm.)	20	59	74	94	119	133	187	237	291	295
Temp. (K)	317·2°	319·2°	321·2°	323·2°	324·2°	326·2°	327·2°	329·2°	330·2°	
Pressure (mm.)	340	401	437	478	534	589	647	692	755	

Vapour Density of SF_4,BF_3.—A thin-walled glass bulb of about 50 c.c. capacity was filled with gaseous SF_4,BF_3 in equilibrium with the solid. Its volume was found by weighing the bulb full of water. Measurements were made at 39·5° and 19·5° (Table 3). Clearly the pressures are the dissociation pressures of SF_4,BF_3 which dissociates thus: $s \longrightarrow g + g$, so that $K_p = \frac{1}{4}(P_{atm.})^2$.

TABLE 3.

Temp. (°C)	Observed density	Calc. density for a 1 : 1 mixture of SF_4 and BF_3	Calc. density for SF_4,BF_3
39·5°	44·1	43·7	87·5
19·5	43·1	43·7	87·5

Thermodynamic Data for SF_4,BF_3.—The vapour pressure–temperature measurements can be expressed by:

$$\log_e K_{P_{atm.}} = -\frac{12{\cdot}51 \times 10^3}{T(°K)} + 36{\cdot}50$$

$$\Delta G = 2{\cdot}483 \times 10^4 - 72{\cdot}50T \text{ cal. mole}^{-1}$$

Now $\Delta G = \Delta H - T\Delta S$, so $\Delta H = +24{\cdot}83$ kcal. mole^{-1}, and $\Delta S = 72{\cdot}50$ cal. per degree per mole.

Reactions of SF_4,BF_3.—When the adduct was vaporised in a stream of nitrogen over sodium fluoride at 240—250°, boron trifluoride combined with the salt to give sodium tetrafluoroborate, and sulphur tetrafluoride passed on.

Water, ethyl alcohol, and ethyl ether reacted vigorously and exothermally with the adduct; the resulting clear aqueous solution reduced permanganate and gave a precipitate with nitron. In carbon tetrachloride, trichloroethylene, carbon disulphide, and liquid sulphur dioxide, the adduct was insoluble. In 100% sulphuric acid, it dissolved with the vigorous evolution of boron trifluoride, and, after considerable additions of the solid, gave acicular white crystals which may have been SF_4,SO_3, analogous to SeF_4,SO_3.[21]

Preparation of SF_4,AsF_5. Arsenic pentafluoride, made by fluorinating "AnalaR" arsenious oxide in a nickel tube, was mixed with sulphur tetrafluoride in the apparatus used in the synthesis of SF_4,BF_3. From equal volumes of the two gases at the same temperature and pressure, the vapour pressure of the product was always very small, and an excess of either increased the final pressure. The evidence suggested that SF_4,AsF_5 was the only compound formed. It was initially white but rapidly became pale blue. Typical results at 19° were:

SF_4	AsF_5	Resultant pressure
1 vol., 138·2 mm.	1 vol., 138·2 mm.	5 mm.
2 vols., 31·7 mm.	1 vol., 31·7 mm.	33 mm.

When residual gas was pumped off, the solid showed a very low vapour pressure at 20°.

Properties. The adduct sublimed when warmed in a vacuum, and the vapour pressure was about an atmosphere at 180°. Vapour pressure–temperature measurements are expressed by $\ln K_{\text{P atom}} = -(15{\cdot}55 \times 10^3)/T + 32{\cdot}60$. $\Delta H = 31{\cdot}0 \pm 0{\cdot}8$ kcal. mole^{-1}, $\Delta S = 65{\cdot}0$ cal. degree^{-1} mole^{-1}.

Selenium tetrafluoride dissolved the solid, sulphur tetrafluoride being evolved. Removal of the excess of selenium tetrafluoride left the white solid, SeF_4,AsF_5. Water reacted vigorously with the adduct, and the clear solution gave a precipitate of nitron fluoroarsenate with nitron acetate. Hydrogen sulphide precipitated sulphur and, after the solution had been boiled with hydrochloric acid, arsenic sulphide. Ethyl alcohol and ethyl ether reacted vigorously, but the adduct was insoluble in carbon tetrachloride.

Preparation of SF_4,SbF_5.—Antimony pentafluoride, made by Woolf and Greenwood's method,[22] was used to prepare SF_4,SbF_5 in three ways:

(*a*) An excess of sulphur tetrafluoride was condensed on to antimony pentafluoride in a bulb with a break-seal, which was cooled to −180° and sealed under a vacuum. Since antimony pentafluoride is a glass at −40° and viscous even at 20°, the mixture had to be raised to room temperature to secure reaction. Repeatedly the bulb was cooled to −180° and the container was shaken to break up the solid which was formed at the interface between the two fluorides. After two days, when the reaction was judged to be complete, the excess of sulphur tetrafluoride was removed under a vacuum through the break-seal, leaving a white solid, m. p. 245°.

A sample of this product was dissolved in sodium hydroxide, and the antimony determined by acidification with hydrochloric acid, reduction with sulphur dioxide, boiling to remove the excess, and titration with potassium bromate and Methyl Red. Fluorine was precipitated as lead chlorofluoride in the distillate from sulphuric acid at 132—138°; the composition was checked by dissolving the solid *adduct* in dilute nitric acid and precipitating the chloride as silver chloride. Sulphur was precipitated as barium sulphate from a solution oxidised with hydrogen peroxide (Found: Sb, 38·9; S, 9·1; F, 52·1. SF_4,SbF_5 requires Sb, 37·5; S, 9·9; F, 52·6%).

(*b*) It is much more convenient to use the reaction $SbF_5 + SF_4,BF_3 \longrightarrow SF_4,SbF_5 + BF_3$. A deficiency of the former reactant was distilled, under a vacuum, on to the latter, boron trifluoride being displaced as the antimony pentafluoride melted. The excess of SF_4,BF_3 was removed under a vacuum at room temperature, leaving a white residue melting slightly above 240° (Found: Sb, 36·0; F, 52·4%).

(*c*) A reaction similar to the last, but with SF_4,AsF_5, released arsenic pentafluoride and left SF_4,SbF_5.

X-*Ray Powder Photographs of* SF_4,SbF_5.—Thin-walled, 0·5 mm. capillaries were filled with the adduct in a dry box and sealed off with a very small flame. Photographs were taken at 18° ± 2° on a 19 cm. Unicam camera with crystal-reflected Fe-K_α radiation from a lithium fluoride monochromator. The reflexions were indexed on a simple cubic unit cell: $a = 5{\cdot}625 \pm 0{\cdot}002$ Å, $U = 178$ Å^3, $D_n = 3{\cdot}1 \pm 0{\cdot}1$, $Z = 1$, $D_c = 3{\cdot}03$. The density was determined in a

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[21] Peacock, *J.*, 1953, 3617.

[22] Woolf and Greenwood, *J.*, 1950, 2200.

1 ml. density bottle with a ground glass cap; this was loaded in a dry box. Carbon tetrachloride was the displacement fluid.

Miscellaneous reactions of SF_4,SbF_5.—Selenium tetrafluoride dissolved it at about 30°, sulphur tetrafluoride being evolved and SeF_4,SbF_5 left. Water reacted vigorously and nitron acetate precipitated nitron fluoroantimonate from the clear solution, but hydrogen sulphide gave only sulphur until the solution had been evaporated with hydrochloric acid; then antimony sulphide could be precipitated.

Other Reactions of Sulphur Tetrafluoride.—Platinum dichloride. Platinous chloride, prepared by heating platinic chloride at 500° in chlorine, reacted readily with phosphorus trifluoride, as described by Chatt and Williams,[5] to give $PtCl_2,2PF_3$, but not at all with sulphur tetrafluoride between $-40°$ and 200°.

Boron trichloride. Equal volumes of boron trichloride and sulphur tetrafluoride were mixed. On warming they reacted violently; a little red liquid and some chlorine were formed. The final pressure at 18° was greater than the sum of the initial pressures and compatible with $4SF_4(g) + 4BCl_3(g) \longrightarrow 4BF_3(g) + 3SCl_2(l) + 3Cl_2(g) + SF_4(g)$; an amount of trichloride necessary to satisfy the reaction $3SF_4(g) + 4BCl_3(g) \longrightarrow 4BF_3(g) + 3SCl_2(l) + 3Cl_2(g)$ led to almost the same final pressure. The respective pressures (mm. at 18°) were:

Pressure of SF_4	60·5	Pressure of SF_4	60·5
Pressure of BCl_3	60·5	Pressure of BCl_3	80·5
Resultant pressure after mixing of equal volumes	146·5	Resultant pressure after mixing of equal volumes	145·7

The red liquid, b. p. 60°, was hydrolysed slowly in water, precipitating sulphur, and was sulphur dichloride (b. p. 59°).

Ruthenium pentafluoride [23] at its m. p. (108°) gave, with sulphur tetrafluoride vapour, a pinkish-white solid which melted with decomposition at 150° to a port-wine-coloured liquid. This lost gas rapidly under a vacuum, reverting to ruthenium pentafluoride. The viscosity of the latter made complete reaction impossible, and the compound was not identified.

Molybdenum hexafluoride,[24] when mixed with sulphur tetrafluoride, gave, at $-40°$ and below, an intensely yellow solid which decomposed above that temperature.

Chlorine did not react with sulphur tetrafluoride at room temperature.

Cæsium fluoride showed no evidence of combination at any temperature between $-40°$ and 220°.

Preparation of SeF_4,BF_3.—Selenium tetrafluoride and a large excess of boron trifluoride were distilled into a trap at $-180°$ and allowed to come to room temperature under dry air. The excess of boron trifluoride was evolved and a white solid, m. p. 50°, remained. It was dissolved in sodium hydroxide, and the selenium determined by reduction with sulphurous acid in hydrochloric acid. Fluoroborate was precipitated from a solution of the *adduct* in a dilute acetic acid, with nitron (Found: Se, 34·9; BF_4^-, 38·5. SeF_4,BF_3 requires Se, 35·9; BF_4^-, 39·0%).

Preparation by the action of selenium tetrafluoride on SF_4,BF_3 is easier.

The adduct melted to a clear liquid at 50° and began to liberate boron trifluoride at 60°. Water decomposed it vigorously; it was freely soluble in ether without evident reaction, but was insoluble in carbon tetrachloride. Antimony pentafluoride displaced boron trifluoride to give SeF_4,SbF_5.

Preparation of SeF_4,AsF_5.—Selenium tetrafluoride was melted with an excess of arsenic pentafluoride under pressure. As the former absorbed the latter it became warm and viscous and granular crystals slowly appeared. Eventually the vessel was warmed and the uncombined selenium tetrafluoride was removed under a vacuum. White crystals, m. p. 118—120°, of the *adduct* remained which evolved a little gas on melting. They were dissolved in sodium hydroxide, and selenium and fluorine were determined. Arsenic was found by titrating the boiled filtrate from the selenium with potassium bromate solution against Methyl Red (Found: Se, 25·1; As, 22·7; F, 48·0. SeF_4,AsF_5 requires Se, 24·3; As, 23·1; F, 52·6%).

Water reacted violently with this product, and the clear solution gave a precipitate of nitron fluoroarsenate with nitron acetate. Antimony pentafluoride displaced arsenic pentafluoride.

[23] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.

[24] Dodd and Robinson, "Experimental Inorganic Chemistry," Elsevier Publ. Co., Amsterdam, 1954, p. 221.

Preparation of SeF_4,SbF_5.—Mixing selenium tetrafluoride and antimony pentafluoride produced much heat and large white crystals separated as the liquid cooled. When the excess of tetrafluoride was removed under a vacuum at 120°, the crystals melted sharply at 122° to a colourless liquid. The *product* was stable up to 200° and could be distilled unchanged in a vacuum. It was dissolved in sodium hydroxide and analysed (Found: Se, 21·3; Sb, 32·8; F, 45·9. SeF_4,SbF_5 requires Se, 21·2; Sb, 32·8; F, 46·0%).

The electrical conductivity of a solution of SeF_4,SbF_5 in selenium tetrafluoride was determned in a U-shaped silica cell charged by rotating a trap containing the solution about a cone-and-socket joint. The liquid was received into a reservoir from which some of it could be poured over a weir into the smaller electrode chamber. The resistance between platinum electrodes was measured with a bridge circuit of a modified Kohlrausch type. The resistance remained constant for 15 min. and did not change when the liquid in the electrode chamber was re-mixed with that in the reservoir. All measurements were made at 25° ± 0·01°.

The concentration was found by running the liquid into potassium hydroxide and determining the selenium and antimony; it was 271 g. of antimony pentafluoride per kg. of selenium tetrafluoride, approximately 1 mole per kg. The cell constant was found with a known potassium chloride solution, the specific conductivities of Jones and Bradshaw [25] being employed:

SbF_5,SeF_4 (1 mole/1000 g. of SeF_4), $\kappa = 5{\cdot}6 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ at 25°.
SbF_5, $\kappa = 1{\cdot}2 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$ at 25° (cf. ref. 22).
SeF_4, $\kappa = \sim 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 25° (cf. ref. 26).
KCl (standard), $\kappa = 0{\cdot}012836$ ohm^{-1} cm.$^{-1}$; resistance 42·4 ohms.
The resistance of the SeF_4–SbF_5 solution was 97·5 ohms.

Preparation of $(SeF_4)_2PtF_4$.—The complex fluoride, $(BrF_3)_2PtF_4$, was prepared as described by Sharpe.[15] When this was warmed with selenium tetrafluoride, bromine trifluoride was evolved and an orange-yellow solid remained in suspension. The mixture was refluxed for some time and the volatile material distilled off under a vacuum. The residual solid showed no evidence of decomposition even at 248° under a vacuum. At about 350° under atmospheric pressure, it decomposed rapidly and left a black residue which an *X*-ray photograph showed to be metallic platinum. The *salt* was decomposed in aqueous sodium hydroxide: a little of the platinum was precipitated as the hydrated dioxide; this was filtered off and ignited to metal. Selenium and fluorine were determined, and the platinum in the boiled filtrate from the selenium was precipitated with zinc [Found: Pt, 32·7; Se, 26·9; F, 39·6. $(SeF_4)_2PtF_4$ requires Pt, 33·6; Se, 27·2; F, 39·2%].

Preparation of SeF_4,AuF_3.—The complex BrF_3,AuF_3, prepared as described by Sharpe,[16] was dissolved in hot selenium tetrafluoride, and the bromine trifluoride was displaced by refluxing. When the solvent was distilled off under a vacuum, a yellow solid remained, from which an *X*-ray photograph showed auric fluoride to be absent. The *adduct* was hydrolysed in moist air to auric hydroxide and dissolved in dilute hydrochloric acid to a clear yellow solution. From this gold and selenium were precipitated with sulphur dioxide. Fluorine was determined on a separate sample decomposed in alkali (Found: Au + Se, 67·5; F, 31·5. SeF_4,AuF_3 requires Au + Se, 67·5; F, 32·5%). When the adduct was heated under atmospheric pressure to 210°, a little selenium tetrafluoride condensed on the cooler parts of the vessel. The residue had become khaki-coloured, but analysis showed that it was still largely unchanged complex. The slight residue from treatment with hydrochloric acid was presumably gold, since it dissolved only in aqua regia. At 350°, however, decomposition to gold was rapid.

Other Reactions of Selenium Tetrafluoride.—Boron trichloride reacted vigorously with an excess of selenium tetrafluoride when the latter melted, liberating boron trifluoride and leaving a cream-coloured solid when this and the excess of boron trichloride were removed under a vacuum. This was sublimable under a vacuum and proved to be selenium tetrachloride (Found: Se, 35·4; Cl, 63·0. Calc. for $SeCl_4$: Se, 35·7; Cl, 64·3%).

Ruthenium pentafluoride gave a green solution in selenium tetrafluoride, from which it was recovered unchanged when the solvent was distilled off at 20° under a vacuum.

Platinum dichloride reacted with neither the liquid tetrafluoride nor its vapour up to 200°.

Preparation of TeF_4,SbF_5.—Tellurium tetrafluoride [27] dissolved in antimony pentafluoride

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[25] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.
[26] Hub and Robinson, unpublished result.
[27] Campbell and Robinson, *J.*, 1956, 785.

at 40° and a white solid crystallised as the solution cooled. It was recovered by pumping off the solvent at 100°. The *adduct*, m. p. 206°, reacted very quietly with water, tellurium dioxide being precipitated. It was dissolved in potassium hydroxide and the tellurium was precipitated with sulphurous acid and hydrazine hydrate after acidification with hydrochloric acid (Found: Te, 28·5; F, 41·2. TeF_4,SbF_5 requires Te, 30·2; F, 40·7%).

Boron trifluoride did not react with solid or liquid tellurium tetrafluoride.

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