124. *Fluorides of the Noble Metals. Part III.[1] The Fluorides of Platinum.*

By Neil Bartlett and D. H. Lohmann.

Attempts to confirm the existence of platinum difluoride have been unsuccessful. Platinum tetrafluoride has been shown to be diamagnetic when pure. Although it is not isomorphous with any known tetrafluoride it is apparently related structurally to uranium tetrachloride. The quinque-positive oxidation state of platinum has been established in the simple fluoride, the salts potassium hexafluoroplatinate(v) and dioxygenyl hexa-fluoroplatinate(v), and in the adducts ClF_3,PtF_5 and IF_5,PtF_5. Platinum hexafluoride has been briefly investigated.

A TETRAFLUORIDE [2,3] and a hexafluoride [4] of platinum have been well characterized. Hexafluoroplatinic(IV) acid and its salts have been prepared and thoroughly investigated by several workers [5] and the 2 : 1 bromine trifluoride– and selenium tetrafluoride–platinum tetrafluoride adducts [3,6] briefly described. The difluoride, described by Moissan,[2] has not been confirmed and there has been no report of a trifluoride. We have now sought to confirm the existence of a difluoride, and to prepare a trifluoride, a pentafluoride, and complex hexafluoroplatinates(v). In addition the tetrafluoride and some of its adducts have been better characterized. One of the hexafluoroplatinates(v), namely dioxygenyl hexafluoroplatinate(v), was described in Part II.[1]

Platinum Difluoride.—Neither reliable chemical analyses nor structural evidence support the several reports [2,7,8] of the difluoride. Moissan [2] described it as a green-yellow, water-insoluble residue, formed together with the tetrafluoride, when platinum metal was heated in fluorine. We have been unable to confirm any of these observations and our attempts to prepare such a compound by reducing the tetrafluoride with selenium tetra-fluoride, sulphur tetrafluoride or powdered glass have failed; the action of hydrogen fluoride on the dichloride was also unsuccessful, the tetrafluoride and platinum being the sole products. Incidentally, Moissan [2] did not produce the difluoride by the thermal decomposition of a platinum tetrafluoride–phosphorus trifluoride adduct, and Sharp,[9] who heated platinum tetrafluoride with carbon monoxide under pressure, obtained only the volatile platinum carbonyl, $Pt(CO)_2F_8$, and metal without evidence of a lower fluoride.

Although the lattice energy for the difluoride, calculated from Kapustinskii's equation [10]

$$U = 287 \cdot 2 \sum n \frac{z_+ z_-}{r_+ + r_-} \left(1 - \frac{0 \cdot 345}{r_+ + r_-} \right)$$

with ionic radii $r_+ + r_-$ taken as equal to that for Pd–F in palladium difluoride [11] (= $2 \cdot 16$ Å), is ~ 670 kcal. mole^{-1}, from which the enthalpy of formation

$$\Delta H = I_{Pt^{2+}} + L_{Pt} - 2(E_F - 1/2D_{F_2}) - U = \sim 30 \text{ kcal. mole}^{-1}$$

[1] Part II, Bartlett and Lohmann, *J.*, 1962, 5253.
[2] Moissan, " Le fluor et ses composes," Steinheil, Paris, 1900.
[3] Sharpe, *J.*, 1950, 3444.
[4] (*a*) Weinstock, Claassen, and Malm, *J. Amer. Chem. Soc.*, 1957, **79**, 5832; (*b*) Weinstock, Malm, and Weaver, *ibid.*, 1961, **83**, 4310.
[5] (*a*) Schlessinger and Tapley, *J. Amer. Chem. Soc.*, 1924, **46**, 276; (*b*) Sharpe, *J.*, 1953, 197; (*c*) Perros and Naeser, *J. Amer. Chem. Soc.*, 1953, **75**, 2516; (*d*) Clarke and Perros, *ibid.*, p. 5734; (*e*) Wheller, Perros, and Naeser, *ibid.*, 1955, **77**, 2488; (*f*) Norr, Perros, and Naeser, *ibid.*, 1958, **80**, 5035.
[6] Bartlett and Robinson, *J.*, 1961, 3417.
[7] Poulenc, *Ann. Chim. Phys.*, 1894, **2**, 74.
[8] Ruff, *Ber.*, 1936, **69**A, 181.
[9] Sharp, *Proc. Chem. Soc.*, 1960, 317.
[10] Kapustinskii, *Quart. Rev.*, 1956, **10**, 284.
[11] Bartlett and Maitland, *Acta Cryst.*, 1958, **11**, 747.

it is nevertheless probable that the difluoride disproportionates readily ($2PtF_2 \longrightarrow PtF_4 +$ Pt) because of a high energy of formation of the tetrafluoride.

Platinum Trifluoride and Oxyfluorides of Platinum.—As for the difluoride, attempts to prepare a trifluoride by reduction of the tetrafluoride have failed. The black solid in the mixture, produced by the fluorination of platinum in the presence of powdered glass, is isomorphous with some noble metal trifluorides (Table 1). It is unlikely to be platinum trifluoride, and in view of the oxygen-rich environment necessary for its formation it is probably platinum oxide difluoride. Unfortunately, sufficiently pure material to settle this point was never obtained.

The black solid was always accompanied by a pale brown solid. This was obtained in much greater purity by fluorinating platinum dioxide; and analysis indicated that it was platinum oxide trifluoride.

TABLE 1.

Rhombohedral unit-cell dimensions of platinum metal trifluorides and PtO_xF_{3-x}.

	RuF_3 *	RhF_3 *	PdF_3 *	IrF_3 *	$PtO_xF_{(3-x)}$
a (Å), $\alpha°$	5·41(54·7)	5·33(54·4)	5·52(53·9)	5·42(54·1)	5·39(54·7)

* Hepworth, Jack, Peacock, and Westland, *Acta Cryst.*, 1957, **10**, 63.

Platinum Tetrafluoride.—Sharpe [3] observed that thermal decomposition of the 2 : 1 bromine trifluoride–platinum tetrafluoride adduct, under vacuum at 180°, produced the tetrafluoride contaminated with bromine. Nyholm and Sharpe [12] reported this material to be paramagnetic. Following Sharpe's procedure we found that the bromine was not entirely removed below 300° and that some decomposition to platinum and fluorine occurred above that temperature. The bromine could, however, be completely removed by low-temperature fluorination, and the product was a pale brown diamagnetic solid. The tetrafluoride thus conforms to the diamagnetism of Pt^{4+} salts. Possibly the bromine-containing material was paramagnetic through the presence of a bromine trifluoride-platinum trifluoride adduct, analogous to the palladium compound.[3]

Platinum tetrafluoride is monoclinic but the body-centred unit-cell, $a = b = 6·68$, $c = 5·71$ Å, $\gamma = 92·02°$, is similar to the body-centred tetragonal cell of uranium tetrachloride, $a = 8·30$, $c = 7·49$ Å, described by Mooney.[13] The similarity of the relative intensities of the low-angle powder lines of the tetrafluoride to those of the tetrachloride indicates a similar distribution of the heavy atoms in the two compounds. In uranium tetrachloride each uranium atom is co-ordinated by eight chlorine atoms arranged in two flattened tetrahedral sets, one at 2·41 Å, the other at 3·09 Å. As pointed out by Mooney,[13] this is consistent with the moderate volatility of uranium tetrachloride, since fission of the long, and hence weak, bonds liberates the formula unit. It is significant that platinum tetrafluoride is volatile above 300°. Because of the difficulty of locating light fluorine atoms in the presence of the highly scattering platinum atoms, the structure determination of platinum tetrafluoride was not attempted. Presumably the structure is similar to that of uranium tetrachloride. There is evidently some structural diversification with the tetrafluorides; cerium tetrafluoride, hafnium tetrafluoride, and the actinide tetrafluorides have the zirconium tetrafluoride structure,[14] but powder photographs of the tetrafluorides of platinum, tin, lead, and rhodium demonstrate the absence of any close structural relation of these fluorides with one another or with zirconium tetrafluoride.

Complex Fluorides of Platinum(IV).—Although hexafluoroplatinic(IV) acid cannot be synthesized in water, its hydrolysis is so slow that the alkali, alkaline-earth, and rare-earth salts have all been made from the acid in aqueous solution.[5] The crystal structure

[12] Nyholm and Sharpe, *J.*, 1952, 3579.
[13] Mooney, *Acta Cryst.*, 1949, **2**, 189.
[14] Zachariasen, *Acta Cryst.*, 1959, **12**, 388.

of the potassium salt[15] shows that the hexafluoroplatinate(IV) ion possesses the regular octahedral shape expected for a $d_{t2g}{}^6$ electron configuration.
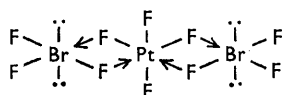
The 2 : 1 bromine trifluoride–platinum tetrafluoride adduct and the 2 : 1 selenium tetrafluoride–platinum tetrafluoride adduct have been formulated[3,6] as the salts $(BrF_2)_2PtF_6$ and $(SeF_3)_2PtF_6$. The compounds, although both diamagnetic, differ otherwise in their physical behaviour; the red-brown bromine trifluoride adduct, m. p. 136°, decomposes above its melting point, whereas the yellow selenium tetrafluoride compound decomposes, without fusion, at 350°. It is significant that the 2 : 1 selenium tetrafluoride–palladium tetrafluoride adduct can be prepared from the 1 : 1 bromine trifluoride–palladium trifluoride adduct:[16]

$$6BrF_3,PdF_3 + 12SeF_4 \longrightarrow 6(SeF_4)_2PdF_4 + Br_2 + 4BrF_3,$$
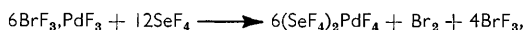
but a 2 : 1 bromine trifluoride–palladium tetrafluoride adduct cannot be made.[16] This behaviour of selenium tetrafluoride parallels that of potassium fluoride, which interacts with the bromine trifluoride–palladium trifluoride adduct to give potassium hexafluoropalladate(IV):[17]

$$6BrF_3,PdF_3 + 12KF \longrightarrow 6K_2PdF_6 + Br_2 + 4BrF_3.$$
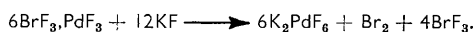
This suggests that selenium tetrafluoride is able to act as a fluoride-ion donor and that the adduct with palladium tetrafluoride is the salt $(SeF_3{}^+)_2[PdF_6]^{2-}$. Since the platinum tetrafluoride and germanium tetrafluoride[18] adducts are isomorphous with the palladium compound they should also be given the ionic formulation.

Evidently bromine trifluoride is not as good a fluoride-ion donor as selenium tetrafluoride and it is probable that in the platinum tetrafluoride–bromine trifluoride adduct the association is by bifluorine bridging, as represented in (I) or by monofluorine bridging to yield a polymeric structure.

Platinum Pentafluoride.—This is best prepared by the medium-temperature fluorination of platinum dichloride.[19] It is a deep red solid which melts at 80° to a viscous red liquid. The ready disproportionation, $2PtF_5 \longrightarrow PtF_6 + PtF_4$, prevents purification by distillation. Reliable boiling-point determination is not possible and our earlier value[19] must be rejected, since that observed was of tetrafluoride dissolved in pentafluoride.

Low melting point, high viscosity, and easy disproportionation are characteristics of several of the transition-metal pentafluorides;[20,21] in particular, those of rhenium and osmium resemble that of platinum. Peacock and his co-workers[22] have shown that molybdenum, ruthenium, and osmium pentafluorides are tetrameric fluorine-bridged structures, with distorted octahedral co-ordination of the transition-metal atoms. It is probable that the structure of platinum pentafluoride is similar. Although exact magnetic measurements on the pentafluoride are not available, it is known to be paramagnetic. If the platinum co-ordination is close to octahedral the electron configuration will be $d_{t2g}{}^5$. The chemical properties, which show the compound to be a powerful oxidizing agent, are represented schematically in the Figure. Bromine trifluoride and selenium tetrafluoride reduce the pentafluoride to the quadripositive state, whereas the pentafluorides of osmium and iridium form 1 : 1 adducts with them.[23,24]

[15] Mellor and Stephenson, *Austral. J. Sci. Res.*, 1951, **4**, *A*, 406.
[16] Part I, Bartlett and Quail, *J.*, 1961, 3728.
[17] Ref. 5 (*b*).
[18] Bartlett and Yu, *Canad. J. Chem.*, 1961, **39**, 81.
[19] Bartlett and Lohmann, *Proc. Chem. Soc.*, 1960, 14.
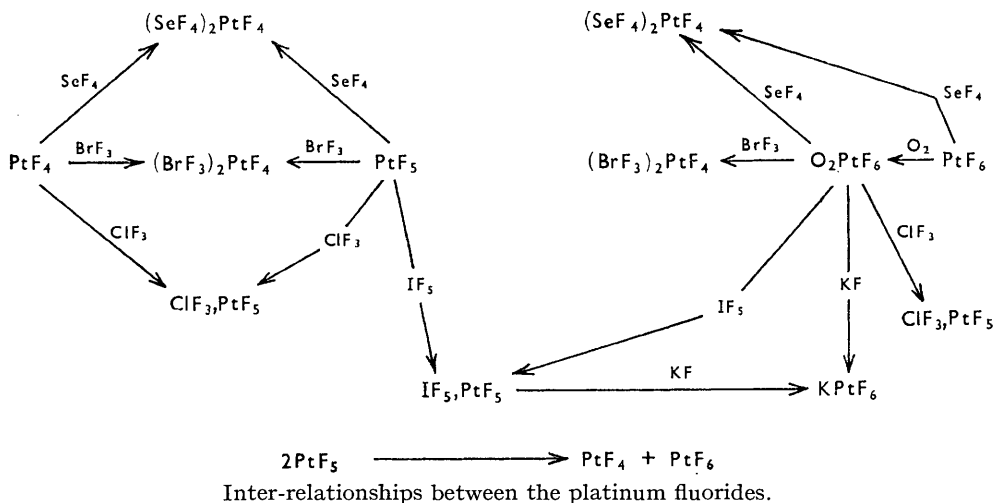[20] Hargreaves and Peacock, *J.*, 1960, 1099, 2618.
[21] Clark and Eméleus, *J.*, 1957, 2119.
[22] (*a*) Holloway and Peacock, *J.*, 1963, 528; (*b*) Edwards, Peacock, and Small, *J.*, 1962, 4486.
[23] Hepworth, Robinson, and Westland, *Chem. and Ind.*, 1955, 1516.
[24] (*a*) Hepworth, Ph.D. Thesis, Durham, England, 1956; (*b*) Westland, Ph.D. Thesis, Durham, England, 1957.

Complex Fluorides of Platinum(v).—The most convenient starting material for the preparation of hexafluoroplatinates(v) is dioxygenyl hexafluoroplatinate. This and some of the complex fluorides derived from it have been described in Part II;[1] the reactions are represented in the Figure.

$(SeF_4)_2PtF_4$ $(SeF_4)_2PtF_4$

SeF_4 SeF_4 SeF_4 SeF_4

PtF_4 $\xrightarrow{BrF_3}$ $(BrF_3)_2PtF_4$ $\xleftarrow{BrF_3}$ PtF_5 $(BrF_3)_2PtF_4$ $\xleftarrow{BrF_3}$ O_2PtF_6 $\xleftarrow{O_2}$ PtF_6

ClF_3 ClF_3 ClF_3

ClF_3,PtF_5 IF_5 KF ClF_3,PtF_5

IF_5

IF_5,PtF_5 $\xrightarrow{KF}$ $KPtF_6$

$2PtF_5 \longrightarrow PtF_4 + PtF_6$

Inter-relationships between the platinum fluorides.

Potassium hexafluoroplatinate(v), which is best made by the interaction of dioxygenyl hexafluoroplatinate(v) with potassium fluoride in iodine pentafluoride, is isomorphous with the analogues of the other platinum metals and is nearly isodimensional with potassium hexafluororuthenate(v). The rhombohedral unit-cell dimensions and volume for the platinum metal salts KM^VF_6 are given in Table 2.

TABLE 2.

Unit-cell dimensions (Å) and unit-cell volume (Å³) for KM^VF_6 salts.

Compound	$KOsF_6$ *	$KIrF_6$ *	$KPtF_6$	$KRuF_6$ *
a $(\alpha°)$	4·991(97·2)	4·98(97·4)	4·96(97·4)	4·97(97·4)
U	121·6	120·7	119·8	119·8

* Hepworth, Jack, and Westland, *J. Inorg. Nuclear Chem.*, 1956, **2**, 80.

The salt is paramagnetic, $\mu = 0·87$ B.M. (at 23°). This and the small molar volume are compatible with the electron configuration d_{t2g}^5. The decrease in molar volume in the series OsF_6^- (d_{t2g}^3), IrF_6^- (d_{t2g}^4), PtF_6^- (d_{t2g}^5) is probably due to an increase in the effective nuclear charge $(z - s)$ from osmium $(z = 76)$ to platinum $(z = 78)$. Since the d_{t2g} orbital electrons do not screen the ligands significantly, the screening factor (s) changes very little in this series.

The salt reacts rapidly with water precipitating some of the platinum as hydrated dioxide, most of it remaining in solution as hexafluoroplatinate(IV). This behaviour resembles the reductive interaction of the hexafluoro-rhenates(v)-osmates(v) and -iridates(v), with water [25] to give the quadripositive fluorosalts. Since the latter cannot be synthesized in aqueous media, they are probably thermodynamically unstable with respect to hydrolysis.[25] If so, evidently the hexafluoroplatinate(v) ion must remain intact during reduction to the hexafluoroplatinate(IV) ion.

The 1 : 1 chlorine trifluoride–platinum pentafluoride adduct, m. p. 171°, and the 1 : 1 iodine pentafluoride adduct, m. p. 140° resemble, in their physical properties, the selenium

[25] Peacock, in " Progress in Inorganic Chemistry," ed. Cotton, Interscience Pub. Inc., New York, 1960, p. 214.

tetrafluoride adducts of osmium pentafluoride (SeF_4,OsF_5, m. p. 158°) [23] and iridium pentafluoride (SeF_4,IrF_5, m. p. 133°).[23] They are probably bifluorine-bridged monomers:
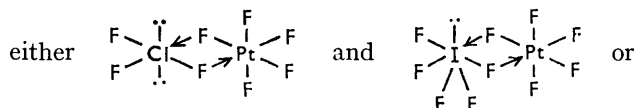
mono-fluorine-bridged polymers.

Platinum Hexafluoride.—This compound, first prepared and characterized by Weinstock and Malm and their co-workers,[4] is the most powerfully oxidizing one of the third transition series hexafluorides. It is the only one which will oxidize molecular oxygen: [1] $O_2 + PtF_6 \longrightarrow O_2{}^+[PtF_6]^-$. In contrast to the hexafluorides of osmium and iridium, which are reduced to the quinquepositive derivatives in interaction with selenium tetrafluoride,[23] the platinum fluoride is reduced to the quadripositive state: $PtF_6 + 3SeF_4 \longrightarrow$ $(SeF_4)_2PtF_6 + SeF_6$. Bromine trifluoride also reduces platinum hexafluoride to this oxidation state: [4] $PtF_6 + 3BrF_3 \longrightarrow (BrF_3)_2PtF_4 + BrF_5$.

The remarkable oxidizing properties and thermal instability [4] of the hexafluoride are compatible with the $d_{t2g}{}^4$ electron configuration suggested by the spectroscopic data.[26, 27] This electronic configuration exposes the fluorine ligands to a highly polarizing central atom. Evidently the polarizing power of the platinum is sufficient to remove bonding electrons from the fluorine ligands since the molecules dissociate at a measurable rate, above 150°, into platinum tetrafluoride and fluorine.[4] Moffitt *et al.*[26] concluded that for excited states involving $d_{t2g} \longrightarrow d_{eg}$ electron promotions the octahedron is considerably expanded. This is consistent with increased screening of the ligands by d_{eg} electrons, resulting in a marked reduction of the effective nuclear charge. Presumably molecules in these excited states are less likely to dissociate into fluorine and platinum tetrafluoride. It is probable that the hexafluoride is created in such excited states, in which the polarizing power is at a minimum. It is significant that good yields of the hexafluoride are obtained only if the molecule is quenched within a short time of its formation.

EXPERIMENTAL

Reaction of Platinum Dichloride with Anhydrous Hydrogen Fluoride.—Platinum dichloride, in a platinum boat contained in a nickel apparatus, was heated at 200—250°, in a stream of hydrogen fluoride diluted with nitrogen. An X-ray powder photograph of the product showed it to be a mixture of platinum tetrafluoride and platinum.

The Fluorination of Platinum in the Presence of Powdered Glass.—Fluorine, diluted with nitrogen, was passed in a slow stream over a heated mixture of powdered glass and platinum at 400° and a mixture of pale brown and black particles was left. X-Ray powder photographs showed these particles were two phases. A simple pattern, characteristic of the black material, was indexed on the basis of a rhombohedral unit-cell, $a = 5.39 \pm 0.02$ Å, $\alpha = 54.7 \pm 0.2°$, $U = 97$ Å³. Observed and calculated $1/d^2$ values are in Table 3. The complex pattern of the light brown phase was identical with that of platinum oxide trifluoride.

TABLE 3.

Calculated and observed X-ray data for PtO_xF_{3-x}.

	$1/d^2$		Rel.		$1/d^2$		Rel.
hkl	Calc.	Obs.	intensities	*hkl*	Calc.	Obs.	intensities
110	0·0764	0·0775	10	321	0·3568	0·3588	10
211	0·1402	0·1418	8	332	0·3954	0·3973	6
10$\bar{1}$	0·1654	0·1666	7	21$\bar{1}$	0·4072	0·4071	8
222	0·1914	0·1895	3	310	0·4710	0·4702	8
201	0·2133	0·2121	2	2$\bar{1}\bar{1}$	0·4962	0·4946	7
200	0·2418	0·2425	7	431	0·7262	0·7295	9
220	0·3056	0·3064	7	420	0·8530	0·8483	10

[26] Moffitt, Goodman, Fred, and Weinstock, *Mol. Phys.*, 1959, **2**, 109.
[27] Weinstock, Claassen, and Malm, *J. Chem. Phys.*, 1960, **32**, 181.

The Fluorination of Platinum Dioxide.—Platinum dioxide, in a nickel boat, was fluorinated at 200° until the product appeared to be homogeneous. It was analysed by pyrohydrolysis to 500° (Found: F, 21·4; Pt, 73·1. $PtOF_3$ requires F, 21·3; Pt, 72·8%). The complex X-ray powder photograph was not indexed. The involatile solid hydrolysed slowly in moist air; with water its hydrolysis was similar to that of platinum tetrafluoride.

Preparation of Platinum Tetrafluoride.—The platinum tetrafluoride–bromine trifluoride adduct was prepared by Sharpe's method [3] and heated to 180° under vacuum for 12 hr., which removed most of the bromine trifluoride. The remainder was displaced as bromine penta-fluoride by fluorinating with diluted fluorine at 250°. Platinum tetrafluoride prepared in this way was yellow-brown and crystalline. Analysis was by pyrohydrolysis to 300° (Found: F, 27·8; Pt, 71·7; Br, absent. Calc. for PtF_4: F, 28·0; Pt, 72·0%).

Physical properties. X-Ray powder photographs were indexed on the basis of a monoclinic unit-cell, $a = b = 6·68 \pm 0·005$, $c = 5·708 \pm 0·005$ Å, $\gamma = 92·02 \pm 0·005°$, $U = 253·5$ Å³,

TABLE 4.

X-Ray data for platinum tetrafluoride.

hkl	1/d² Calc.	1/d² Obs.	$I_{obs.}$	hkl	1/d² Calc.	1/d² Obs.	$I_{obs.}$	hkl	1/d² Calc.	1/d² Obs.	$I_{obs.}$
101	0·0532	0·0545	10	402	0·4826	—	—	105	0·7898	—	—
200	0·0899	0·0922	9	004	0·4910	0·4913	3	600	0·8095	0·8111	5
2̄11	0·1399	0·1425	8	3̄32	0·5131	0·5151	4	4̄32	0·8191	0·8216	5
211	0·1463	0·1483	8	332	0·5419	0·5420	6	503	0·8383	0·8403	1
1̄12	0·1661	0·1680	7	4̄22	0·5697	—	—	404	0·8508	0·8504	6
112	0·1693	0·1705	7	4̄31	0·5736	—	—	5̄11	0·8530	0·8549	6
2̄20	0·1735	0·1764	3	323	0·5781 ⎫	0·5800	7	433	0·8575	—	—
220	0·1863	0·1887	3	204	0·5809 ⎭			5̄32	0·8633	0·8654	3
202	0·2127	0·2141	2	501	0·5928	—	—	611	0·8722	0·8707	3
301	0·2331	0·2356	3	422	0·5953	0·5953	5	2̄15	0·8765		—
103	0·2987	0·3007	5	431	0·6120	0·6118	6	6̄20	0·8802	0·8̄806	2
3̄21	0·3134	0·3170	6	4̄13	0·6520	0·6529	3	215	0·8829		
321	0·3329	0·3348	5	2̄24	0·6646 ⎫			5̄23	0·9123	0·9127	5
3̄12	0·3429	0·3456	7	413	0·6648 ⎬	0·6663	5	620	0·9186	—	—
312	0·3525	0·3543	8	5̄21	0·6668 ⎭			5̄41	0·9206	—	—
4̄00	0·3598	0·3630	6	224	0·6784	—	—	532	0·9213	—	—
2̄13	0·3854	0·3873	5	521	0·6988 ⎫	0·7004	7	424	0·9279	0·9278	4
213	0·3918	0·3932	4	5̄12	0·6994 ⎭			602	0·9323	—	—
4̄11	0·4065	0·4104	6	3̄14	0·7111	—	—	523	0·9443	0·9435	3
411	0·4193	0·4205	6	512	0·7154	0·7163	9	424	0·9535	0·9504	3
4̄20	0·4369	0·4409	6	4̄40	0·7164	—	—	3̄05	0·9697	0·9655	1
420	0·4625	0·4639	4	3̄14	0·7207	—	—	541	0·9846	0·9819	4
303	0·4786	0·4802	3	440	0·7675	—	—				

$D_m = 6·12$ g. cm.$^{-3}$ (CCl_4 displacement), $Z = 4$, $D_c = 7·10$ g. cm.$^{-3}$. Observed and calculated $1/d^2$ values are in Table 4.

An infrared spectrum of the tetrafluoride in a Nujol mull, with sodium chloride and cæsium bromide plates, had peaks at 675 cm.$^{-1}$ (sharp) and at 576 cm.$^{-1}$ (broad). A magnetic sus-ceptibility measurement, at 23° by the Gouy technique, showed it to be diamagnetic.

Chemical properties. Water hydrolysed the solid platinum tetrafluoride slowly, some platinum being precipitated as dioxide and some remaining in solution as hexafluoroplatinate(iv) ion. Material from which all the bromine trifluoride had not been removed reacted much more vigorously. Hydrogen reduced the fluoride to platinum at 100°; below that temperature there was no reaction. Sulphur tetrafluoride was passed over platinum tetrafluoride heated to 300° in a closed glass apparatus. Chemical and X-ray analysis showed that the compound remained unchanged.

Selenium tetrafluoride partly dissolved the tetrafluoride to give a pale yellow solution and after being refluxed for 15 min. at $\sim$100° the platinum tetrafluoride was converted into a yellow solid, which was recovered by removal of the solvent under reduced pressure. Chemical analysis and X-ray powder photography showed it to be the 2 : 1 selenium tetrafluoride–platinum tetrafluoride adduct [6] [Found: F, 36·5; Pt, 34·9; Se, 25·5. Calc. for $(SeF_4)_2PtF_4$: F, 39·3; Pt, 33·5; Se, 27·2%]. It was diamagnetic. Thermal decomposition into platinum and selenium hexafluoride occurred, without fusion, at 350°. Water rapidly hydrolysed it,

some platinum being precipitated as dioxide but most remaining in solution as the hexafluoro-platinate(IV) ion. The X-ray powder pattern, which closely resembles those of the germanium [18] and palladium [16] analogues, has been indexed on the basis of a hexagonal unit-cell, $a = 15.74 \pm 0.03$ Å, $c = 4.93 \pm 0.01$ Å, $U = 1055$ Å^3, $Z = 4$, $D_c = 3.66$ g. cm.$^{-3}$.

Bromine trifluoride under reflux, dissolved the tetrafluoride to give a deep red solution. The red-brown solid which remained after vacuum distillation of the bromine trifluoride was the 2 : 1 bromine trifluoride–platinum tetrafluoride adduct [3] [Found: F, 35.1; Pt, 36.7. Calc. for $(BrF_3)_2PtF_4$: F, 34.9; Pt, 34.9%]. The diamagnetic solid melted with some decomposition at 136°. Its X-ray powder pattern was complex and no attempt was made to index it. Iodine pentafluoride neither dissolved nor reacted with the tetrafluoride even on prolonged refluxing at ~100°. Chlorine trifluoride, passed over the tetrafluoride at 300°, converted it into a yellow solid, m. p. 170°, of which the X-ray powder pattern was identical with that of the chlorine trifluoride–platinum pentafluoride adduct.[1]

Powdered glass, intimately mixed with the tetrafluoride was heated at increasing temperatures in a nickel boat under nitrogen. Samples were taken for X-ray examination at 50° intervals. There was no change below 350°, the photographs then indicated some decomposition to platinum. There was no evidence of lower fluorides.

Preparation of Platinum Pentafluoride.—Fluorine with nitrogen (3 : 1) was passed over platinum dichloride, in a platinum boat, in a quartz tube. At 350° a vigorous reaction yielded platinum pentafluoride as a deep red deposit beyond the reaction zone. Any dioxygenyl hexafluoroplatinate(V), formed concurrently, was removed by vacuum sublimation at 100°, after which the *pentafluoride* was collected by melting and pouring it into an adjacent silica tube. It was analysed by dissolution in aqueous alkali followed by the determination of fluorine, after a Willard and Winter distillation,[28] as lead chloride fluorides. Platinum was determined, as ammonium hexachloroplatinate, on a separate sample dissolved in hydrochloric acid [Found: F, 32.8; Pt, 65.0. PtF$_5$ requires F, 32.8; Pt, 67.2%]. The pentafluoride was formed by the fluorination of platinum tetrafluoride and other platinum salts; also by photolysis of the hexafluoride from whence it was recovered as a glass. Platinum pentafluoride melts at 80° to a viscous red liquid. When vacuum distillation was attempted at 130° it slowly disproportionated, the hexafluoride being evolved. The pale brown residue was shown by X-ray photography to be the tetrafluoride. Quantitative magnetic susceptibility measurements were not made on the pentafluoride, since a regularly packed specimen was not made; the qualitative examination showed it to be paramagnetic.

Chemical properties. Water reacted exothermally with the pentafluoride; a gas (probably oxygen) was evolved and about 25% of the platinum precipitated as the dioxide, the remainder went into solution as the hexafluoroplatinate(IV) ion.

Bromine trifluoride dissolved the pentafluoride to give a deep red solution. When the excess of solvent was removed under vacuum the residue was the 2 : 1 bromine trifluoride–platinum tetrafluoride adduct, which was identified by X-ray photography.

Iodine pentafluoride dissolved platinum pentafluoride, under reflux, to yield a deep red solution. When the excess of solvent was removed, under vacuum at 23°, a pale orange residue remained, which X-ray photography showed to be the 1 : 1 iodine pentafluoride–platinum pentafluoride adduct.[1]

Properties of the Iodine Pentafluoride–Platinum Pentafluoride Adduct.—The solid, m. p. 140°, begins to decompose at 180°; this is complete at 300° and the residue is platinum tetrafluoride. The adduct is paramagnetic, $\mu = 0.65$ B.M. (23°). The X-ray powder pattern was complex and no attempt was made to index it. Water reacted vigorously with it to give a solution containing the hexafluoroplatinate(IV) ion. Reaction with most organic solvents was exothermic and complex, but carbon tetrachloride neither reacted with nor dissolved it.

Preparation of Hexafluoroplatinates(V).—The 1 : 1 chlorine trifluoride–platinum penta-fluoride adduct and the salt, potassium hexafluoroplatinate(V), were prepared in quantity only from dioxygenyl hexafluoroplatinate as described in Part II.[1]

Properties of the 1 : 1 Chlorine Trifluoride–Platinum Pentafluoride Adduct.—The chlorine trifluoride–platinum pentafluoride adduct, m. p. 170—171°, sublimes in a good vacuum at 100°. It is paramagnetic and X-ray powder photographs show it has a low crystal symmetry. It reacts vigorously with water to liberate pungent gases and give a pale yellow solution. Spectroscopic examination of this solution proved the presence of the hexafluoroplatinate(IV) ion with

[28] Willard and Winter, *Ind. and Eng. Chem., Analyt.,* 1933, **5**, 7.

absorption peaks at 275 and 315 mμ and the absence of the hexachloroplatinate(IV) ion which has a peak at 263 mμ.

Properties of Potassium Hexafluoroplatinate(V).—This salt is mustard yellow. A sample containing some iodine, possibly as iodyl fluoride, was paramagnetic. The low value of the magnetic moment, $\mu = 0·87$ B.M. (at 23°), may, in part at least, be due to this impurity. An infrared spectrum, of a Nujol mull, recorded with sodium chloride and cæsium bromide optics, showed two broad, overlapping, absorption bands, with peaks at 590 and 640 cm.$^{-1}$. X-Ray powder photographs of the salt have been indexed on the basis of a rhombohedral unit-cell, $a = 4·96$ Å, $\alpha = 97·4°$, $U = 119·9$ Å^3. The observed and calculated values for $1/d^2$ are given in Table 5. The solid can be stored indefinitely in well-dried, sealed tubes but decomposes

TABLE 5.

Calculated and observed X-ray data for potassium hexafluoroplatinate(V), $KPtF_6$.

hkl	$1/d^2$ Calc.	$1/d^2$ Obs.	Rel. intensities	hkl	$1/d^2$ Calc.	$1/d^2$ Obs.	Rel. intensities
100	0·0421	0·0421	10	$3\bar{1}\bar{1}$	0·3986	—	—
$10\bar{1}$	0·0718	0·0717	10	$31\bar{1}$	0·4502	—	—
110	0·0971	0·0974	8	$22\bar{2}$	0·4536	—	—
$11\bar{1}$	0·1134	0·1139	7	310	0·4597	0·4591	6
111	0·1650	—	—	$30\bar{2}$	0·4699	0·4690	6
200	0·1684	0·1691	6	221	0·4821	—	—
$20\bar{1}$	0·1847	0·1850	3	$3\bar{1}2$	0·4991	0·5000	5
$2\bar{1}\bar{1}$	0·2139	0·2150	5	$31\bar{2}$	0·5249	0·5254	4
210	0·2363	—	—	311	0·5534	0·5521	1
$21\bar{1}$	0·2397	0·2396	9	$32\bar{1}$	0·6023 }		
$20\bar{2}$	0·2850	0·2867	4	$22\bar{3}$	0·6125 }	0·6061	2
211	0·3171	0·3180	2	320	0·6247	—	—
$21\bar{2}$	0·3273	0·3288	3	$30\bar{3}$	0·6417	—	—
$22\bar{1}$ }				222	0·6600 }		
300 }	0·3789 }	0·3811	7	$32\bar{2}$ }	0·6641 }	0·6639	3
$30\bar{1}$ }	0·3823 }			$40\bar{1}$ }			
220	0·3884	—	—	$4\bar{1}\bar{1}$	0·6675	—	—

in moist air with the smell of ozone. Reaction with water, which was exothermic, gave rise to the same smell and left a pale yellow solid. X-Ray photography showed this to contain potassium hexafluoroplatinate(IV).

Platinum Hexafluoride.—The preparation of this compound is given in Part II.[1]

Reaction of Selenium Tetrafluoride with Platinum Hexafluoride.—When selenium tetrafluoride and platinum hexafluoride were mixed in a silica bulb, there was an immediate and vigorous reaction at $-9°$, which evolved much gas, presumed to be selenium hexafluoride. Selenium tetrafluoride, which was present in a large excess, was removed by vacuum distillation. X-Ray examination showed the yellow residue to be the 2 : 1 selenium tetrafluoride–platinum tetrafluoride adduct.

Analyses.—The methods followed are described in Part II.

Special Reagents.—With the exception of sulphur tetrafluoride, obtained from E. I. duPont de Nemours and Co., Wilmington, Delaware, and anhydrous hydrogen fluoride, from Mattheson Co., Inc., Newark, the chemicals and reagents used have been the same as in Part II.

THE DEPARTMENT OF CHEMISTRY,
    THE UNIVERSITY OF BRITISH COLUMBIA,
        VANCOUVER 8, B.C. CANADA.

[Received, September 11th, 1962.]