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Platinum Metal Fluorides

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The properties of the simple fluorides, oxide fluorides, and dioxygenyl compounds of the platinum metals have been reviewed. The most important fields of application and directions of study in the field of platinum metal fluorides have been outlined. The bibliography contains 185 references.

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I. INTRODUCTION

The platinum metals are now widely used in chemical technology, chiefly as catalysts in petroleum reforming, and also in electrical technology, jewellery, and laboratory practice. The use of platinum metals as alloy components makes it possible to improve considerably the mechanical properties and increase the corrosion resistance of alloys, compared with the pure metals.

The fields of application of the platinum metal fluorides are determined directly by their physicochemical properties. The development of fluoride metallurgy is extending the possible applications of the volatile platinum metal fluorides in one of the most promising fields—the preparation of coatings, powders, alloys, or articles by reducing the volatile fluorides with hydrogen. For example, the preparation of iridium coatings by reducing IrF_6 with hydrogen has been described[1,2]. The simultaneous reduction of fluorides can be used to prepare alloys of platinum metals with refractory metals. The use of platinum metal fluorides to regenerate spent catalysts in the petrochemical industry appears promising[3].

Increasing quantities of platinum metals are accumulating in spent nuclear fuel, which can possibly be processed by subliming the fluorides. It has been estimated[4] that for 3% burnout, one ton of nuclear fuel gives 500 g of Rh and 1500 g of Pd. By the year 2000, the quantity of palladium produced in the reactors of atomic power stations will be about 250 tons, close to the required quantity of this metal. The quantities of rhodium and ruthenium obtained by nuclear fission will exceed the expected demand. Here it is necessary to solve the problem of removing the radioactive isotope ^{103}Ru,[5] and then the problem of isolating the other platinum metals.

The electronic configuration of the atoms Ru ($4d^75s^1$), Rh ($4d^85s^1$), Pd ($4d^{10}$), Os ($5d^66s^2$), Ir ($5d^76s^2$), and Pt ($5d^96s^1$) makes possible a variety of fluoride compounds, in which the oxidation state of the metal varies from +2 to +8. Simple platinum metal fluorides have coordination numbers from 2 to 7.

Thus platinum metal fluorides are already of considerable interest in both technology and chemistry.

Published reviews of the properties of platinum metal fluorides[6,7] are based on 15–20-year-old publications, and require to be bought up to date. A number of recent books and reviews have dealt with platinum metal fluorides among other fluorides[8–12], but they deal mainly with the properties of the fluorides of individual platinum metals, for example ruthenium,[9,12] iridium,[10] and osmium.[11] Data on the properties of fluorides are given in a number of reference books[13–16], but even the most complete of these[16] includes original publications only up to 1973.

The aim of the present review was to systematise the methods of synthesis, review published data on the physicochemical properties of the platinum metal fluorides, and define the most important directions of studies in this field.

II. SIMPLE FLUORIDES

1. Higher Fluorides

Among the platinum metals, a heptafluoride is known only for osmium. The higher fluoride OsF_7 was obtained by treating osmium powder with fluorine at 573–683 K and a pressure of 350–400 atm in a nickel bomb[17]. Osmium heptafluoride is obtained as a pale-yellow extremely hygroscopic powder, which partly loses fluorine at temperatures above 173 K, and on prolonged standing at room temperature decomposes quantitatively to OsF_6 and fluorine. Osmium heptafluoride has been characterised by mass spectrometry, magnetic susceptibility, and EPR and infrared spectroscopy at 93 K. The wavenumbers of vibrational bands in the infrared spectrum of OsF_7 are 715, 550, 483, 366, 336, and 282 cm^{-1}. Analysis of the infrared spectrum indicates that the OsF_7 molecule has D_{5h} symmetry[17]. A comparison of the enthalpies of formation of the fluorides of the elements from Hf to Re has been used to estimate the enthalpies of formation of gaseous OsF_7 and the hypothetical OsF_8: −1140 kJ $mole^{-1}$ and −980 kJ $mole^{-1}$ respectively[18].

The reported formation of RuF_8 [19] by the fluorination of ruthenium and its dioxide has not been confirmed. A study of the hydrolysis of ruthenium fluorides and the fluorination of ruthenium hydroxides revealed the formation of a volatile substance[20], whose infrared spectrum showed bands at 389 cm^{-1} and 1030 cm^{-1}, previously assumed erroneously[19] to be ruthenium octafluoride. This substance is the adduct $RuO_4(HF)_{10}$, which volatilises at temperatures above 273 K and an HF pressure above 150 mmHg.[20]

The most fully characterised platinum metal fluorides are the hexafluorides, of which only palladium hexafluoride was isolated only recently[21] and has been little studied. A general method for obtained the hexafluorides of ruthenium[22], rhodium[23], osmium[24], and iridium[25] involves the action of fluorine, diluted with nitrogen, on the metal powders, heated to 550–700 K, with subsequent rapid cooling of the reaction products. Platinum hexafluoride is obtained similarly, but under more severe conditions, by heating platinum wire electrically in a stream of fluorine to 1150–1300 K.[26,27] The synthesis of PtF_6 by the action of fluorine on spongy platinum at a pressure of 15 atm and a temperature of 470 K and a molar

ratio Pt : F_2 = 1 : 15, which gives a yield of 75%, has also been proposed[28].

A method for obtaining platinum metal hexafluorides in solution in KrF_2, anhydrous HF, or BrF_5 has been successfully developed and applied[29]. The solution of the metals, oxides, or lower fluorides in KrF_2 gives complexes $KrF_2.MF_5$ (M = Pt, Ru, Rh) and $KrF_2.2MF_5$ (M = Pt, Ru), which when heated slightly decompose vigorously with the quantitative formation of the corresponding metal hexafluorides, Krypton difluoride has a high fluorinating power, and acts as a fluoride ion donor, stabilising the higher oxidation states of the elements.

An effective method for the synthesis of thermally unstable platinum metal hexafluorides involves the use of atomic fluorine[30], which takes part in chemical reactions with an activation energy close to zero. The reaction of atomic fluorine with palladium powder at room temperature was in fact used to prepare PdF_6.[21] The fluorination of the platinum metals by atomic fluorine at low temperatures (below 370 K) is rapid. The yield of hexafluorides decreases in accordance with their thermal stability in the order $OsF_6 > IrF_6 > PtF_6 > RuF_6 > RhF_6$, and also depends on the composition of the starting material. The limiting stage of the fluorination of the platinum metals by atomic fluorine is the conversion of the pentafluorides to the hexafluorides. The fluorination of osmium and iridium oxides by atomic fluorine also gives the hexafluorides of these metals.

Table 1. Physical properties of platinum metal hexafluorides.

Property	RuF_6 [22, 34]	PhF_6 [23, 34]	OsF_6 [18, 24, 34, 35]	IrF_6 [25, 34, 35]	PtF_6 [27]
Colour*	dark brown	black	yellow	pale yellow	dark red
M.p., K	327	343	305.2 306.55	317.25	334.45
B.p., K	—	346.65	320.65	326.75	342
$T_{p.t.}$, K	275.65	250.2	272.75	271.95 273.55	276.45
ΔH^0 of formation in the gaseous state at 298.15 K, kJ mole^{-1}	—	—	−1080 ** [18]	−850 ** [37]	−600 *** [36]
ΔH°_{fusion}, kJ mole^{-1}	—	—	7.4 ****	5.0	4.5
$\Delta H^\circ_{volatilisation}$, kJ mole^{-1}	—	—	28.1	30.9	29.5
$\Delta H^\circ_{phase\ transformation}$, kJ mole^{-1}	—	—	8.2	7.1	9.6
$\Delta H^\circ_{sublimation}$, kJ mole^{-1}:					
above the phase transformation	38.5	41.0	35.5	35.9	38.9
below the phase transformation	—	—	43.7	43.0	47.9
ΔS°_{fusion}, J mole^{-1}K^{-1}	—		23.9 ****	15.6	13.4
$\Delta S^\circ_{volatilisation}$, J mole^{-1}K^{-1}	—	121	87.9	94.6	86.2
$\Delta S^\circ_{phase\ transformation}$, J mole^{-1}K^{-1}	—	—	30.1	26.0	32.6

*PdF_6 is dark red[21]. **Estimated data. ***At 915 K, ****These data are probably too high.

Note. Numbers in square brackets denote references (Ed. of Translation).

A study of the kinetics of the reaction of compact Ir and Pt with atomic fluorine in the range 1000–1450 K for iridium and 600–1430 K for platinum at a partial pressure of atomic fluorine of 0.005–0.06 mmHg [31] showed that the condensed films of lower fluorides of iridium and platinum formed on the metal surfaces do not decrease the rate of fluorination. The fluorination of osmium powder by molecular fluorine[32] takes place in two stages, and is described satisfactorily by the equation for a contracting sphere. The activation energy is 55.5 ± 2.1 kJ mole^{-1} for the first stage, and 17.4 ± 5.4 kJ mole^{-1} for the second. The order of the reaction is 0.5, so that it is assumed that the limiting stage of the fluorination of osmium is the dissociative adsorption of fluorine on the metal surface. The kinetics of the fluorination of ruthenium powder by molecular fluorine[33] in the temperature range 543 to 583 K at a fluorine partial pressure of 22.5–60 mmHg differs from that of the fluorination of osmium. This process is a single-stage process, the activation energy is 79.5 ± 7.1 kJ mole^{-1}, and the order of the reaction with respect to fluorine is 1. The rate of fluorination of ruthenium increases if the metal powder is heated beforehand in hydrogen.

The principal physical properties of the platinum metal hexafluorides are given in Table 1. The boiling points (T) and the enthalpies (ΔH^0) and entropies (ΔS^0) of fusion, volatilisation, phase transformation, and sublimation of the hexafluorides were obtained from the temperature dependence of the vapour pressure.

Linear correlations have been established between the enthalpies of fusion and volatilisation of the hexafluorides of W, Re, Os, Ir, and Pt and their melting and boiling points respectively[37,38]. The correlation of the enthalpy of fusion with the melting point indicates that the value of the enthalpy of fusion of OsF_6 given in Table 1 (7.5 kJ mole^{-1}) is about 2.7 kJ mole^{-1} too high. The value of the entropy of fusion of OsF_6 is also apparently too high. The correlation of the logarithms of the absolute values of the enthalpies of formation of the gaseous hexafluorides of W, Re, Os, and Pt with the stretching vibration frequency ν_1 was used[37] to estimate the enthalpy of formation of gaseous IrF_6 at 298.15 K—approximately −850 kJ mole^{-1}.

The hexafluorides crystallise in a body-centred cubic lattice at room temperature, and in an orthorhombic lattice at low temperatures[34]. The low-temperature form has the YF_3 structure, space group *Pnma*, and the number of formula units Z in the unit cell is 4. The high-temperature form (298 K) is isostructural with the cubic MoF_6 phase, Z = 2. The lattice parameters and densities for both phases of each hexafluoride are given in Table 2.

Table 2. Structural characteristics and densities of the crystals of the platinum metal hexafluorides[34].

Substance	Calculated density of the crystal, kg m^{-3}		Lattice parameters, A	
	cubic phase	orthorhombic phase	cubic phase	orthorhombic phase
RuF_6	3130	3500	6.11±0.01	*a* 9.44 *b* 8.59 *c* 4.98
RhF_6	3130	3620	6.13±0.02	*a* 9.40 *b* 8.54 *c* 4.96
OsF_6	4130	4770	6.25±0.02	*a* 9.59 *b* 8.75 *c* 5.04
IrF_6	4200	4820	6.23±0.02	*a* 9.58 *b* 8.73 *c* 5.04
PtF_6	4280	4900	6.21±0.02	*a* 9.55 *b* 8.71 *c* 5.03

The saturated vapour pressure over RuF_6 at 273.2, 277.8, 281.8, 284.2, 287.6, and 290.8 K has the values 23, 32, 40, 46, 56, and 67 mmHg,[22] and that over RhF_6 at 273, 278, 284, 289, and 293 K has the values 15, 19, 29, 40, and 49.5 mmHg respectively[23]. The vapour pressure (p, mmHg) is described

by the equations

for OsF_6 [35] $\lg p = 10.290 - 2284/T$ $(233.15 \leqslant T \leqslant 272.75$ K)
$\lg p = 8.726 - 1857.7/T$ $(272.75 \leqslant T \leqslant 307.15$ K)
$\lg p = 7.470 - 1472.8/T$ $(307.15 \leqslant T \leqslant 320.65$ K)

for IrF_6 [35] $\lg p = 10{,}000 - 2245.7/T$ $(223.15 \leqslant T \leqslant 273.55$ K)
$\lg p = 8.618 - 1867.5/T$ $(273.55 \leqslant T \leqslant 317.15$ K)
$\lg p = 7.952 - 1656.5/T$ $(317.15 \leqslant T \leqslant 327.15$ K)
for PtF_6 [27] $\lg p = 27.7758 - 3147.6/T - 6.09 \lg T$
$(250.2 \leqslant T \leqslant 276.15$ K)
$\lg p = 20.6280 - 2528.7/T - 4.080 \lg T$
$(276.15 \leqslant T \leqslant 334.45$ K)
$\lg p = 89.1496 - 5685.8/T - 27.485 \lg T$
$(334.45 \leqslant T \leqslant 354.9$ K).

The vibrational spectra of the platinum metal hexafluorides have been the subject of a large number of experimental studies[23,39-42]. All the platinum metal hexafluorides have a regular octahedral configuration (O_h symmetry). For RuF_6 and OsF_6 the ν_2 and ν_5 frequencies are anomalously low, because of the dynamic Jahn–Teller effect[39-41]. The non-perturbed values of these frequencies were calculated for the first time[43] by interpolation from the dependence of the vibrational frequencies on the number of non-bonded electrons in the hexafluorides.

In this and later papers[44-47], the infrared and Raman spectroscopic data for the platinum metal hexafluorides were analysed and systematised.

The calculated vibrational frequencies in the infrared and Raman spectra of the platinum metal hexafluorides[43] and the interatomic distances (r_{M-F}), determined using Badger's rule[48,54], are given to Table 3. The force constants and mean-square amplitudes of the vibrations of the M–F bonds have been calculated[48,50-55].

Table 3. Calculated molecular constants of platinum metal hexafluorides[43].

Substance	Vibrational wavenumbers in the spectra of MF_6, cm^{-1}						r_{M-F}, Å
	ν_1 (a_{1g})	ν_2 (e_g)	ν_3 (f_{1u})	ν_4 (f_{1u})	ν_5 (f_{2g})	ν_6 (f_{2u})	
RuF_6	675	624	735	275	283	186	1.8775
RhF_6	634	595	724	283	269	192	1.8738
PdF_6	590	525	711*	280	258	191	1.87
OsF_6	730.7	668	720	268	276	205	1.831 (1.831±0.008 **)
IrF_6	701.7	645	719	276	267	206	1.833 (1.830±0.008 **)
PtF_6	656.4	601	705	273	242	211	1.829

*This band has been detected in the infrared spectrum of PdF_6.[21]
**Determined by electron diffraction in the gaseous state[49].

The ^{19}F NMR spectra of the hexafluorides of osmium, iridium, and platinum[56,57] show that in the low-temperature orthorhombic phase there is tetragonal distortion of the octahedra of the hexafluorides, and the chemical shifts of the axial and equatorial F atoms in PtF_6 are apparently the highest for all known fluoride compounds.

Thermochemical data[58,59] indicate that the electron affinity increases in the order $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$, and for PtF_6 it is greater than 653 kJ $mole^{-1}$ (6.8 eV); the difference between two neighbouring terms is approximately constant, 84 kJ $mole^{-1}$ (0.9 eV). The spectra of the charge-transfer complexes between IrF_6 and liquid xenon in the near infrared range[60] have been used to estimate the electron affinity of IrF_6, 548.1 kJ $mole^{-1}$ (5.7 eV), which is close to the value obtained by other workers[58,59]. The electron affinity of PtF_6 at 0 K, calculated from effusion measurements, lies between 5.14 eV and 7.9 eV.[36] The physical properties and bonds in the molecules of the hexafluorides of osmium, iridium, and platinum have been studied theoretically[61-63]; earlier measurements of the electron affinity were examined critically, and new measurements of this quantity carried out[63]. The calculated values of the electron affinity and ionisation potentials of OsF_6, IrF_6, and PtF_6 are given in Tables 4 and 5. The values of the ionisation potentials of OsF_6 [62] are close to the data previously obtained from the photoelectron spectra[64].

Table 4. Electron affinity of MF_6, eV.

M	Model I (Ref.62)	Model II (Ref.62)	Published data (Ref.63)
Os	6.17	5.97	7.19 *
Ir	6.96	6.86	8.24 *
Pt	7.59	8.55	9.3

*Values calculated assuming a constant increment per unit increase in the atomic number[65].

Table 5. Ionisation potentials of MF_6, eV.

Configuration	OsF_6		IrF_6 [62]	PtF_6 [62]
	[62]	[64]		
$2t_{2g}$	12.93	14.1	13.72	15.28
$1t_{1g}$	15.48	14.8	15.40	16.18
$3t_{1u}$	15.80	15.5	15.75	16.45
$1t_{2u}$	15.99		15.88	16.65
$2t_{1u}$	16.39	16.5	16.40	17.09
$2a_{1g}$	17.16	16.9	17.21	17.68
$1t_{2g}$	18.55	18.7	18.85	20.16
$2e_g$	20.17	19.6	20.40	21.53

In spite of the fact that the hexafluorides of the platinum metals are often considered as a whole, their chemical properties show significant differences[66]. The hexafluorides of all the platinum metals except Os and Ir are thermally unstable and begin to decompose even at room temperature with the liberation of fluorine[22,23,67,68]; the rate of decomposition of PdF_6 under these conditions is much greater than that of the other hexafluorides, and amounts to 30% h^{-1}.[21] The tendency for the hexafluorides to decompose increases with increase in atomic number in each series, and the stability decreases more rapidly in the second than in the third series[6,69].

RuF_6 and RhF_6 react with Pyrex even at room temperature; the reaction with quartz is slower[22,23]; when heated with Pyrex, OsF_6 apparently forms OsO_3F and OsO_2F_2;[70] IrF_6 does not react with Pyrex up to 420 K,[25] but at 620 K it is reduced quantitatively by finely divided glass to iridium pentafluoride[68]; PtF_6 also decomposes slowly in contact with Pyrex or quartz[26].

The platinum metal hexafluorides are readily hydrolysed by even traces of moisture, undergoing disproportionation or reduction to give various products. For RuF_6 the chief product is $RuO_2.nH_2O$;[22] the hydrolysis of PdF_6 also gives the hydrated dioxide $PdO_2.nH_2O$, with the liberation of oxygen and ozone[21]. OsF_6 is hydrolysed according to equations[24]:

$$2OsF_6 \rightarrow OsF_6^{2-} + Os^{8+} + 6F^-,$$
$$OsF_6 + H_2O \rightarrow OsF_6^{2-} + 0.5O_2 + 2H^+.$$

The hydrolysis of IrF_6 gives $IrO_2.nH_2O$, with the liberation of ozone[25]; a PtF_6 specimen weighing less than 200 mg gives a yellow solution of H_2PtF_6 ($PtF_6 + H_2O \rightarrow H_2PtF_6 + 0.5O_2$), and quantities of more than 1 g give a black precipitate[27].

A study of the hydrolysis of solutions of platinum metal hexafluorides in hydrogen fluoride by accurately measured quantities of H_2O [71] showed that the products are the oxide tetrafluoride $OsOF_4$ for OsF_6, and for RuF_6, IrF_6, and PtF_6 the hydroxonium salts $H_3O^+MF_6^-$, or $(H_3O^+)_2PtF_6^{2-}$ for PtF_6 in an excess of H_2O. The hydrolysis of RhF_6 gives an unstable product, which could not be characterised. The difference between the results of the hydrolysis of OsF_6 and the hexafluorides of ruthenium, iridium, or platinum can be attributed to the greater electron affinity of the latter[71].

The reaction of the platinum metal hexafluorides with NO and NOF in most cases gives the ionic compounds $NO^+MF_6^-$.[58,72] In an excess of NOF, RhF_6 and PtF_6 give the salts $(NO)_2RhF_6$ and $(NO)_2PtF_6$.[72] With NO_2F and N_2O_4 with slow heating from 77 K to 298 K, platinum hexafluoride gives NO_2PtF_6 and $N_2O_3PtF_6$ respectively[73].

A study of the behaviour of the hexafluorides of osmium, iridium, ruthenium, and rhodium in redox reactions showed that OsF_6 and IrF_6 react vigorously with PF_3 with considerable liberation of heat to give mixtures of the metals, lower fluorides, and volatile PF_5.[74,75] In anhydrous HF at low temperatures, $Os(PF_3)_2F_4$ and IrF_4 were obtained, and for ruthenium the polymeric compound $[Ru(PF_3)_4]_n$ The hexafluorides OsF_6, IrF_6, and RuF_6 in anhydrous HF oxidise AsF_3 to AsF_5, forming adducts; Os is reduced to Os^V, and Ir and Ru to Ir^{IV} and Ru^{IV}. Unlike OsF_6, which does not react with SbF_3, iridium and ruthenium hexafluorides oxidise it at room temperature to SbF_5, and are converted mainly to the corresponding pentafluorides. Ruthenium hexafluoride oxidises BiF_3 to BiF_5 (this does not take place with OsF_6 and IrF_6) and oxidises ClF_3 to ClF_5, giving a mixture of $ClF_3.RuF_5$ and $ClF_5.RuF_5$.[75] The hexafluorides of osmium, iridium, and ruthenium react with CS_2 to give CF_4 and SF_4; and with hydrogen or the corresponding metal in anhydrous HF to give the pentafluorides; when heated to 370 K they are reduced by hydrogen in the presence of anhydrous HF to the metals[75]. RuF_6 also reacts with xenon[76]; with B_2O_3, ruthenium and iridium hexafluorides give the corresponding pentafluorides, and OsF_6 gives the oxide tetrafluoride $OsOF_4$.[77]

The few chemical reactions reported for RhF_6 do not make it possible to distinguish its oxidising power from that of RuF_6; however, since rhodium hexafluoride is thermally less stable than RuF_6,[6] it may be expected that it will be a stronger oxidising agent. Summarising all the above reactions, Burns and O'Donnell[75] arranged the hexafluorides in order of decreasing oxidising power: $RhF_6 > RuF_6 > IrF_6 > OsF_6$. This trend, which can be explained from thermodynamic data and an examination of the physical properties[6, 65,69,78,79], is confirmed by the data of other workers[74–77]. The oxidising power also increases in the transition metal sub-groups: $RuF_6 > OsF_6$; $RhF_6 > IrF_6$ (RhF_6 oxidises Xe,[76] but IrF_6 does not). PdF_6, prepared only recently, is also a very strong oxidising agent, apparently stronger than PtF_6 and RhF_6. Palladium hexafluoride is rapidly reduced on metal surfaces, and oxidises oxygen and xenon[21].

Platinum hexafluoride occupies a unique position, since it was used to synthesise the ionic compound $O_2^+PtF_6^-$ for the first time[80,81]. Bartlett, drawing attention to the similarity in the ionisation and potentials of xenon and oxygen, carried out the reaction of PtF_6 with Xe and obtained the yellow ionic solid $Xe^+PtF_6^-$, and discovered the chemistry of the noble gases[82]. Platinum hexafluoride reacts with KrF_2 at 273 K to give $KrF^+PtF_6^-$, whose Raman spectrum confirms its ionic structure[83]. The plutonium fluorides PuF_3 and PuF_4, when treated with PtF_6 below room temperature, are converted into PuF_6,[84] ClF_3 into ClF_5,[85] BrF_3 into BrF_5, and Np into NpF_6.[27] An infrared and NMR spectroscopic study of the solid product of the reaction of PtF_6 with $XeOF_4$ [86] showed that this reaction is accompanied by the formation of XeF_5^+, and the oxygen displaced from $XeOF_4$ is converted into O_2^+.

$OsCl_5$ was obtained for the first time by the reaction of OsF_6 with an excess of BCl_3 below room temperature[87]. The reaction of OsF_6 with liquid Br_2 gives solid $Br_2^+OsF_6^-$, and the dissolution of OsF_6 in liquid Cl_2 at 195 K gives a blue solution, from which a green solid of unknown composition separates on cooling[88].

The platinum metal hexafluorides are soluble in anhydrous HF; at 298 K the solubility of OsF_6 in hydrogen fluoride is 0.97 mole in 1000 g.[89]

An EPR study of the homogeneous recombination of fluorine atoms in OsF_6 and IrF_6 molecules at 293 K showed that the rate of recombination in these hexafluorides is the same as that of fluorine atoms in the MF_6 molecules for M = Os, Ir, and W.[90]

The reaction of volatile fluorides with graphite is now attracting considerable interest. Thus treatment of pyrolytic graphite with osmium and iridium hexafluorides gives the compounds $C_8^+OsF_6^-$ and $C_8^+IrF_6^-$, and the insertion of PtF_6 into graphite gives $C_{12}^{2+}PtF_6^{2-}$.[91] The electrical conductivity of the products of the insertion of OsF_6 and IrF_6 along the basal plane of graphite is a maximum for a composition of approximately $C_{24}MF_6$, for which it is 10 times that for the starting material; further insertion leads to a marked decrease in the electrical conductivity (the electrical conductivity of C_8MF_6 is comparable with that of the original graphite). This behaviour differs from that of graphite–AsF_5 systems, in which there is a steady increase in conductivity along the basal plane of graphite with increase in the AsF_5 concentration. The products of the insertion of PtF_6 into graphite are weakly conducting[91]. Examination of structural data and the physicochemical properties of platinum metal hexafluorides shows that they resemble to a considerable extent the hexafluorides of such metals as molybdenum, technetium, tungsten, and rhenium, they all form cubic crystals at room temperature, and orthorhombic crystals on cooling, with similar lattice parameters. The enthalpies of fusion and volatilisation have similar values (kJ $mole^{-1}$): 4.3 and 28.0 respectively for MoF_6; 4.5 and 30 for TcF_6; 4.1 and 25.9 for WF_6; and 4.5 and 28.3 for ReF_6.[16] All these hexafluorides have a regular octahedral configuration and approximately the same interatomic distances (from 1.82 Å in MoF_6 to 1.877 Å in RuF_6).

The main difference between the platinum metal hexafluorides and the corresponding compounds of molybdenum, technetium, tungsten, and rhenium is the higher reactivity of the former. This is revealed in the thermal instability of the platinum metal hexafluorides and in their more extensive hydrolysis (the platinum metal hexafluorides react with water to form the M^{IV} oxides, and MoF_6 and WF_6 give MoO_3 and WO_3 respectively). The platinum metal hexafluorides are also stronger oxidising agents than MoF_6, TcF_6, WF_6, and ReF_6; thus RuF_6, RhF_6, PtF_6, and PdF_6 oxidise even Xe, and platinum and palladium hexafluorides also oxidise oxygen.

2. Pentafluorides

The methods used to prepare the pentafluorides to a large extent are specific for each platinum metal. Pure ruthenium pentafluoride was first obtained by decomposing in a vacuum at 390 K the compound $RuBrF_8$, formed by the reaction of metallic ruthenium with BrF_3 at room temperature[92]. Ruthenium pentafluoride has also been synthesised by the direct fluorination of ruthenium powder with a mixture of F_2 and N_2 at 550–570 K,[93] by a mixture of HF and F_2 diluted with N_2,[94] and by fluorine at 470 K and a pressure of 4–5 atm in a nickel bomb[95].

The pentafluorides of ruthenium, osmium, and iridium have been obtained by the reaction of a solution of XeF_2 in anhydrous HF with $RuCl_3$ or RuO_2, or metallic Os or Ir.[96]

Rhodium pentafluoride is formed, together with RhF_6 and RhF_3, when rhodium wire burns in fluorine, and pure RhF_5 is obtained at a fluorine pressure of 6 atm and a temperature of 670 K.[97]

The reaction of $W(CO)_6$ with an excess of OsF_6 at 273 K gives a mixture of OsF_5, OsF_4, and Os, which can be separated by vacuum distillation (OsF_5 distils at 390 K).[67] Osmium pentafluoride is obtained by reducing OsF_6 with a solution of iodine in IF_5 [67,98] or by tungsten heated to a dull red heat[99].

IrF_5 and OsF_5 have been obtained in 100% yield by reducing IrF_6 and OsF_6 by hydrogen or Si powder in anhydrous HF at 298 K.[100–102] The rate of the process is increased when Pt gauze and ultraviolet irradiation are used. Iridium pentafluoride has been obtained[68] by heating a stoichiometric mixture of the elements in a Monel bomb; the bottom of the bomb was heated to 620–650 K, and yellow crystals of IrF_5 condensed on the lid of the reaction vessel.

Table 6. Physical properties of platinum metal pentafluorides.

Substance	RuF_5 [91, 105]	RhF_5 [97]	OsF_5 [67, 106]	IrF_5 [68]	PtF_5 [103, 107–109]
Colour	emerald-green	dark red	greenish-blue	yellow	dark red
M.p., K	358	368,65	343	378	353
B.p., K	500 *, 503	—	499 *, 506	—	573–578
$\Delta H^\circ_{formation}$, kJ mole^{-1}	−892.9±1.5**	—	—	—	−545 ***
$\Delta H^\circ_{volatilisation}$, kJ mole^{-1}	56.5	—	59.4	—	—
$\Delta S^\circ_{volatilisation}$, kJ mole^{-1}	113.0	—	119.1	—	—
Magnetic moment at room temperature μ, B.M.	3.6	2.93	2.06	1.3	2.05

*Determined by extrapolation from the temperature dependence of the vapour pressure.

**For crystalline RuF_4 at 298.15 K.

***At 915 K.[36]

The fluorination of spongy platinum or $PtCl_2$ by fluorine at 620 K gives PtF_5, which is readily separated from the more volatile O_2PtF_6 by vacuum distillation at 370 K.[80,103] The fluorination can be carried out under pressure[104].

The principal physical properties of the platinum metal pentafluorides are given in Table 6.

All the platinum metal pentafluorides form monoclinic crystals with the RuF_5 structure, space group $P2_1/c$, $Z = 8$. The unit cell parameters and densities of the crystalline platinum metal pentafluorides are given in Table 7.

X-Ray diffraction has shown that the structural unit of the platinum metal pentafluorides is an $(MF_5)_4$ tetramer with bridging F atoms in the *cis*-position. The metal has distorted octahedral coordination; each M atom is surrounded by six F atoms, but two *cis*-F atoms in the MF_6 group are joined to other M atoms. The average M–F distances for the terminal and bridging fluorine atoms are 1.81 Å and 2.01 Å respectively, and the MFM angle is 135°.[95,97,98,110,111] An analysis of the ^{19}F NMR spectra of the platinum metal pentafluorides in the temperature range 77–296 K confirmed that these compounds are polymeric[112].

Table 7. Structural characteristics and densities of the crystals of the platinum metal pentafluorides.

Substance	RuF_5 [98]	RhF_5 [97]	OsF_5 [98]	IrF_5 [98]
Lattice parameters, A angle F-M-F, °	*a* 5.42 * *b* 10.01, *s* 12.47 β 99.82	*a* 5.48 ** *b* 9.85, *c* 12.28, β 99.2	*a* 5.53 *b* 9.91, *c* 12.59, β 99.5	*a* 5.43 *b* 9.98, *c* 12.27, β 99.87
Calculated density of the crystal, kg m^{-3}	3920	4018	5570	5815

*Refinement of Ref. 110.

**According to Ref. 111, the lattice parameters of RhF_5 are: $a = 5.5173$, $b = 9.9177$, $c = 12.3376$ Å; $\beta = 100.42°$; density of the crystals 3950 kg m^{-3}.

The vapour pressure (p, mmHg) is described by the equations:

for RuF_5 (Ref. 94) $\lg p = 9.54 - 3329/T$ ($363.15 \leqslant T \leqslant 433.15$ K),
for OsF_5 (Ref. 106) $\lg p = 9.75 - 3429/T$ ($343.15 \leqslant T \leqslant 453.15$K).

The mass-spectrometric study of the composition of the saturated vapour of the platinum metal pentafluorides has shown[104,113,114] that close to room temperature, RuF_5, RhF_5, and IrF_5 form dimers, trimers, and tetramers, and OsF_5 and PtF_5 for dimers and trimers.

The vibrational frequencies of the two possible structural forms of the platinum metal pentafluorides, and the thermodynamic functions in the temperature range 298–3200 K, have been calculated[115]. The infrared spectrum of solid RuF_5, recorded in the range 400–1000 cm^{-1},[116] shows bands at 525, 645, 670, 715, and 750 cm^{-1}.

The chemical properties of the platinum metal pentafluorides have been less extensively studied. Ruthenium pentafluoride can be kept for a long time in nickel and quartz containers at room temperature, but begins to react slowly with Pyrex even at 370 K. When dissolved in water, RuF_5 is hydrolysed instantly to give a brownish–black solution and a precipitate of $RuO_2.nH_2O$; disproportionation also leads to the partial liberation of volatile RuO_4.[94] OsF_5 behaves similarly, forming $OsO_2.nH_2O$ and OsO_4 on hydrolysis[67]. Rhodium pentafluoride also reacts vigorously with H_2O, but the hydrolysis products could not be identified[97]. When PtF_5 is dissolved in water, PtO_2 is formed (25% of the total Pt), and the solution contains the rest of the platinum as the PtF_6^{2-} ion; in addition, O_2 is liberated[107].

The reaction of RuF_5 with CO in a flow system at 470 K gives a non-volatile solid product with the composition $Ru(CO)F_{3.5}$.[117] Iridium pentafluoride at 530–550 K reacts with CO to give a product with the composition $Ir(CO)_{2-3}F_2$.[118]

The reactions of molten XeF_2 with osmium and ruthenium pentafluorides give coloured crystalline adducts with the composition $XeF_2.OsF_5$, $XeF_2.RuF_5$, and $XeF_2.2RuF_5$.[119] The adducts $2XeF_2.MF_5$ and $XeF_2.MF_5$ (M = Ru, Os, Ir, Pt) and also $XeF_2.2MF_5$ (M = Ru, Ir, Pt) were obtained by the reaction of the corresponding platinum metal pentafluorides with a solution of XeF_2 in BrF_5.[120] Iridium pentafluoride forms adducts $2XeF_6.IrF_5$ and $XeF_6.IrF_5$.[121] The reaction of an equimolar mixture of Xe and PtF_5 with fluorine under pressure at a temperature of 450–490 K gave crystals of $XeF_5^+PtF_6^-$ and $Xe_2F_{11}^+PtF_6^-$.[109,122] A study of the crystal structure of these compounds[116,119–123] confirmed that they are ionic. The reaction of RuF_5 with KrF_2 in anhydrous HF also gives relatively stable adducts, as confirmed by the Raman spectra[124].

Osmium[106] and platinum[107] pentafluorides when heated disproportionate according to the equation

$$2MF_5 \rightarrow MF_4 + MF_6.$$

Platinum pentafluoride shows the properties of a relatively strong Lewis acid; it forms $NOPtF_6$ with NOF,[72] $2BrF_3.PtF_6$ with BrF_3, $2SeF_4.PtF_4$ with SeF_4, and $IF_5.PtF_5$ with IF_5.[107]

Comparison of the platinum metal pentafluorides with other known rare metal pentafluorides indicates that their properties are closer to those of the pentafluorides of molybdenum, niobium, and tantalum. The structural unit of all these pentafluorides is the tetramer $(MF_5)_4$, with bridging fluorine atoms in the *cis*-position and octahedral coordination of the metal. The average $M-F_{terminal}$ and $M-F_{bridging}$ distances in the tetramers of the pentafluorides of the platinum metals and molybdenum, niobium, or tantalum are similar; the values for the latter are 1.77 Å and 2.06 Å. These compounds are also polymerised in the gaseous state, and the platinum metal pentafluorides are also polymerised in the liquid state. The melting points and boiling points of MoF_5, NbF_5, and TaF_5 (340 and 487, 353.15 and 508, and 370.1 and 502 K respectively) and enthalpies of volatilisation (47.4, 51.0, and 54.3 kJ $mole^{-1}$) [16] are close to those for the platinum metal pentafluorides.

3. Tetrafluorides

All the platinum metals form tetrafluorides. The sandy-yellow RuF_4 is obtained by the reaction of an excess of RuF_5 with iodine in IF_5 [125] or by reducing RuF_5 with hydrogen in anhydrous HF.[75] The purple–red RhF_4 is obtained by the action of liquid BrF_3 on $RhBr_3$ or $RhCl_3$ with subsequent thermal decomposition of the adducts[126]. Red–brown PdF_4 has been synthesised by fluorinating PdF_3 with fluorine at a pressure of 7 atom and a temperature of 570–620 K.[127] Yellow–brown OsF_4 is formed, together with OsF_5, by the reaction of OsF_6 with $W(CO)_6$, and can be separated from the more volatile OsF_5 by vacuum distillation[67]. Osmium and iridium tetrafluorides are obtained by reducing their pentafluorides with hydrogen or powdered Si in anhydrous HF.[100,101] The rate of the process is increased by using Pt gauze or ultraviolet irradiation.

The reduction of IrF_6 using an electrically heated tungsten or iridium spiral in a Pyrex reaction vessel with walls cooled to 230 K gave red–brown IrF_4.[128] IrF_4 has also been synthesised by the reaction of IrF_6 with PF_3 in anhydrous HF.[74] Other reports of the synthesis of IrF_4 [25,129] have been refuted[68].

The action of an excess of BrF_3 on $PtCl_4$ or $PtBr_4$ at room temperature gives the adduct $(BrF_3)_2PtF_4$, which when heated in a vacuum to 450–470 K gives pale-brown PtF_4.[126] In this case, however, BrF_3 is not completely removed even by heating to 570 K, and further increase in temperature leads to decomposition of PtF_4. BrF_3 has been removed completely by treatment with fluorine at a low temperature[107]. The same paper described a method for preparing PtF_4 by heating $PtCl_2$ to 470–520 K in a stream of HF diluted with nitrogen. Platinum tetrafluoride is obtained by fluorinating spongy Pt and $PtCl_2$ with fluorine in a quartz apparatus at temperatures below 470 K.[103] The pure tetrafluoride is obtained by heating a $PtF_6 + PtF_x$ ($4 < x < 5$) mixture at 470 K for several hours and then removing the excess of fluorine in a vacuum[28].

There is almost no published information on the physical properties of the platinum metal tetrafluorides. RuF_4 does not melt up to 550 K.[125] OsF_4 melts at 403 K.[67] Iridium tetrafluoride begins to sublime at 450 K, and decompose at 670 K; the mass spectrum of IrF_4 showed that it is not associated in the vapour[128]. A thermodynamic study of gaseous PtF_4, formed by introducing fluorine into the effusion compartment of a mass spectrometer at 518–960 K, showed that for the reaction $Pt(solid) + 2F_2(gas) \rightleftharpoons PtF_4(gas)$ at 793 K, the change in the Gibbs free energy is −158 kJ $mole^{-1}$, and the enthalpy of formation of gaseous PtF_4 at 793 K is −214 kJ $mole^{-1}$.[130] A similar method in the temperature range 860–980 K using exchange reactions in the $MnF_2–MnF_3–Pt$ system gave the enthalpy of formation of gaseous PtF_4. At 298 K, ΔH^0[form. $PtF_4(gas)$] = −410 ± 40 kJ $mole^{-1}$, and the dissociation energy $D^0(PtF_2–F_2)$ = 330 ± 40 kJ $mole^{-1}$.[131] The magnetic moments of RuF_4 [125] and RhF_4 [132] at 291 K are 3.04 B.M. and 1.1 B.M. respectively; PdF_4 and PtF_4 are diamagnetic[127,107].

An X-ray diffraction study of PdF_4, IrF_4, and PtF_4 [133] showed that they form monoclinic crystals, $Z = 8$, space group $Fdd2$ with lattice parameters $a = 9.35$, $b = 9.25$, $c = 5.84$ Å, $\beta = 90.7°$; $a = 9.61$, $b = 9.28$, $c = 5.71$ Å, $\beta = 92.0°$; $a = 9.64$, $b = 9.25$, $c = 5.67$ Å, $\beta = 92.7°$ respectively. A later and more accurate neutron diffraction study of PdF_4 [134] indicated that PdF_4 forms orthorhombic crystals ($Z = 8$, space group $Fdd2$, lattice parameters $a = 9.339$, $b = 9.240$, $c = 5.828$ Å) and is isostructural with IrF_4, previously studied by X-ray diffraction[133,135]. The Pd atom shows octahedral coordination; four F atoms are bridging (Pd–F distances 1.91 Å and 2.00 Å), and two are terminal, with the *cis*-arrangement (Pd–F distance 1.94 Å). The bridging angle PdFPd (134.0°) is close to the ideal value of 135° required for hexagonal closest packing of the octahedra. The ^{19}F NMR spectra of platinum and palladium tetrafluorides confirmed[136] that they show only octahedral coordination with non-equivalent F atoms. The crystal structure of RhF_4 has been studied[137]. The lattice parameters are $a = 9.71$, $b = 9.05$, $c = 5.63$ Å, $Z = 8$. According to Ref.133, RhF_4 is not isomorphous with PdF_4, PtF_4, and IrF_4, and the structure of RuF_4 is different from those of all the above tetrafluorides. The calculated densities of PdF_4 and PtF_4 crystals[16] are 4790 kg m^{-3} and 7070 kg m^{-3} respectively, and that of IrF_4 [133] is 7050 kg m^{-3}.

The vibrational frequencies of the platinum metal tetrafluorides have been calculated assuming T_d symmetry and M–F distances equal to those in the hexafluorides[115]. The experimentally determined vibrational frequencies in the infrared spectra of OsF_4 and IrF_4 are 719, 702, 660, 532 cm^{-1} and 691, 688, 545 cm^{-1} respectively[101]. According to Ref.74, the infrared spectrum of IrF_4 show bands at 685, 660, 609, 558, and 460 cm^{-1}.

The tetrafluorides of ruthenium[125], rhodium[126], and palladium[127] react vigorously with water to give $RuO_2.nH_2O$ and $RhO_2.nH_2O$ (the hydrolysis products of PdF_4 have not been identified). Osmium tetrafluoride dissolves in water to give a transparent yellow solution[67], and PtF_4 is hydrolysed slowly

to give a precipitate of PtO_2 and a solution containing the PtF_6^{2-} ion[107].

Rhodium tetrafluoride oxidises HCl to Cl_2; it does not react with ether or CCl_4 at room temperature[126]. Heating RhF_4 with an excess of SeF_4 gives $(RhF_4)_2SeF_4$.[138] The reaction of RhF_4 with CO gives $Rh(CO)_2F_3$, and the action of CO under pressure on PtF_4 gives the compound $Pt(CO)_2F_8$.[139]

Platinum tetrafluoride is reduced to the metal by hydrogen at 370 K, reacts with BrF_3 to give $(BrF_3)_2PtF_4$, and does not react with IF_5 and is insoluble in it. Evaporation of a solution of PtF_4 in SeF_4 in a vacuum gives $(SeF_3)_2PtF_6$.[107] Platinum tetrafluoride in acetone reacts at 273 K with a small quantity of H_2O, forming $H_2Pt(OH)_4F_2$, and with CH_3OH in acetone it forms the substance $PtF_2(OCH_3)_2$, which is explosive at 360 K.[140] Liquid XeF_2 at 410–420 K oxidised PtF_4, forming $Xe_2F_3PtF_6$.[141] A DTA study of the BrF_3–PtF_4 system detected the incongruently melting compounds $2BrF_3.PtF_4$ and $7BrF_3.PtF_4$.[142]

Palladium tetrafluoride is readily reduced to PdF_3, and decomposes to give the same compound when heated in a vacuum[127]. Compounds of different composition are formed by the reaction of PdF_4 with XeF_6 and XeF_2.[133,141]

4. Trifluorides

Brown RuF_3 has been obtained by reducing ruthenium pentafluoride with an excess of iodine at 420 K or with sulphur at 470 K.[143] Red RhF_3, contaminated by metallic rhodium, was first obtained by fluorinating rhodium or $RhCl_3$ with fluorine at a dull red heat (below 770 K).[144,145] Pure RhF_3 was synthesised by the reaction of RhI_3 with fluorine at 670–770 K.[146] Iridium trifluoride (black) was obtained by reducing IrF_6 with metallic iridium[146].

The physical characteristics of the platinum metal trifluorides have not been studied. An X-ray diffraction study of RuF_3, RhF_3, and IrF_3 [146] showed that they form orthorhombic crystals with the VF_3 structure, space group $R\bar{3}c$, $Z = 2$. The orthorhombic cell corresponds to a hexagonal pseudo-cell. The structural characteristics and densities of the crystalline platinum metal trifluorides are given in Table 8.

Table 8. Structural characteristics and densities of the crystals of the platinum metal trifluorides[146].

Trifluoride	Lattice parameters, Å, and angle F–M–F, °			Calculated density of the crystals, kg m^{-3}
	bimolecular rhombohedral cell	hexagonal cell, $Z = 6$	monomolecular rhombohedral cell	
RuF_3	a 5.408±0.001; α 54.67±0.01	a 4.967, c 13.756	a 3.672, α 85.13	5350 *
RhF_3	a 5.330±0.001; α 54.42±0.01	a 4.874, c 13.579	a 3.611, α 84.89	5690 *
IrF_3	a 5.418±0.002; α 54.13±0.03	a 4.940, c 13.819	a 3.666, α 84.72	8520

*Calculated in Ref. 12.

There are almost no published data on the chemical properties of the platinum metal trifluorides. RuF_3 is hydrolysed in water, but insoluble in it; it is also insoluble in dilute acids or alkalis[143]. When heated in a stream of fluorine, RuF_3 gives RuF_5.[147] Rhodium trifluoride is not hygroscopic, insoluble in water, and almost unaffected by hot concentrated HCl, HNO_3, HF (40%), or NaOH. When heated, it is reduced exothermally by H_2, NH_3, SO_2, P, Si, Fe, Al, Na, and Mg.[144,145]

Palladium trifluoride has been obtained by dissolving $PdBr_2$ or PdI_2 in bromine trifluoride, followed by thermal decomposition in a vacuum of the resulting adduct $PdF_3.BrF_3$,[126] or by fluorinating metallic palladium and its halides with fluorine[146]. Its magnetic properties were explained by assuming that this substance does not contain Pd^{III} but is $Pd^{2+}Pd^{4+}F_6$, whose effective magnetic moment (2.88 B.M.) corresponds to the moment of the d^8 configuration of Pd^{2+}.[127]

Measurements of the enthalpy of the reaction $PdPdF_6$(solid) + $3PF_3$(gas) = $3PF_5$(gas) + 2Pd in a bomb calorimeter gave ΔH^0(form.$PdPdF_6$(solid) 298.15 K) = −967.4 ± 7.3 kJ mole^{-1}.[148]

$PdPdF_6$ forms rhombohedral crystals, space group $R\bar{3}c$, $Z = 2$, with lattice parameters: $a = 5.5234 \pm 0.0005$ Å, $\alpha = 53.925 \pm 0.005°$. The calculated and measured densities of PdF_3 are 5315 kg m^{-3} and 5060 kg m^{-3} respectively. The structure of $PdPdF_6$ is related to the $LiSbF_6$ structure, and contains Pd^{II} and Pd^{IV} atoms surrounded octahedrally by F atoms (Pd^{II}–F distance 2.17 Å, Pd^{IV}–F distance 1.90 Å).[146,149]

A study of the influence of high pressure (up to 9×10^4 atm) on the properties of $PdPdF_6$ showed[150,151] that with increase in pressure there is a marked increase in the electrical conductivity, probably due to the electron transfer $Pd^{2+} + Pd^{4+} \rightarrow Pd^{3+}$. At 410–420 K, $PdPdF_6$ is oxidised by liquid XeF_2 to $XePdF_6$.[141]

A study of the reaction of Pt powder with fluorine at different temperatures established[152] that at 670–720 K the product is the fluoride $Pt^{2+}Pt^{4+}F_6$, which at 570–620 K is present in a mixture with PtF_4. The yellow hygroscopic $PtPtF_6$ powder decomposes to the elements at 460 K. The rhombohedral lattice parameters have been determined by X-ray diffraction: $a = 5.56$ Å, $\alpha = 53.85°$, space group $R\bar{3}$, density of the crystals (calculated) 7977 kg m^{-3}, $LiSbF_6$ structure.

5. Dichlorides

Only palladium difluoride is known and has been reliably characterised. Heating $BrF_3.PdF_3$ with SeF_4 gives $(SeF_3)_2.PdF_6$, which at 430 K decomposes rapidly to pale-violet PdF_2.[153,154] It can also be obtained by the direct reduction of $PdPdF_6$ with boiling SeF_4.[154] Fluorination of Pd powder gives a mixture of Pd and PdF_2, further treatment of which with fluorine at 770–1020 K gives PdF_2.[155]

Palladium difluoride crystallises with the tetragonal rutile structure, space group $P4_2/mnm$, $a = 4.956$ Å, $c = 3.389$ Å, $Z = 2$,[153,156] density of the crystals (calculated) 5760 kg m^{-3}.[16] At a pressure of 6×10^4 atm and 720 K in an argon atmosphere, the product is the violet–brown cubic form of PdF_2 (space group $Pa3$, $CdPdF_4$ structure, $a = 5.32$ Å), which is metastable at normal pressure[157]. PdF_2 obtained by the solid-phase reaction of a stoichiometric mixture of $PdPdF_6$ and dispersed Pd in an evacuated Pd tube at 870 K and a pressure of up to 9×10^4 atm undergoes a polymorphic transformation to give a phase isostructural with fluorite[151,158]. The electrical conductivity increases sharply (by a factor of 10^5).

Palladium difluoride is rapidly hydrolysed in moist air, and is decomposed exothermally by water[153].

ΔH^0[form. 198.15 K, PtF_2(gas)] = −80 ± 42 kJ mole^{-1}, and the dissociation energy $D^0(Pt–F_2)$ = 644 ± 42 kJ mole^{-1}.[130,131]

III. PLATINUM METAL OXIDE FLUORIDES

The platinum metals can form various oxide fluorides (Table 9), but these are known for only three metals—OsO_3F_2, OsO_2F_3, $OsOF_5$, $OsOF_4$, $RuOF_4$, and $PtOF_3$. The hypothetical $PtOF_4$ [101] was found to be O_2PtF_6.[80]

Orange OsO_3F_2 powder was first obtained by the reaction of Os with a mixture of F_2 and O_2 (2 : 1).[159] OsO_3F_2 has also been synthesised by heating a mixture of F_2 and OsO_4 (2 : 1, 570 K, 50 h).[70] OsO_3F_2 melts at 443–446 K.[79,159] The magnetic susceptibility and mass spectra of OsO_3F_2 have been recorded[160]. The principal vibrational frequencies in the infrared and Raman spectra of matrix-isolated OsO_3F_2 have been determined and assigned[161]: $\nu_1(A_1') = 946.5$, $\nu_2(E') = 928.5$, $\nu_3(A_2'') = 646$, $\nu_4(A_1') = 619$, $\nu_5(E'') = 348$, $\nu_6(E') = 316.5$, $\nu_7(A_2'') = 258$, and $\nu_8(E') = 206$ cm^{-1}. OsO_3F_2 has D_{3h} symmetry. The force constants of OsO_3F_2 have been calculated in a Urey–Bradley force field[162]. The thermodynamic functions of gaseous OsO_3F_2 in the temperature range 298–6000 K have been calculated in the rigid rotator–harmonic oscillator approximation[163]. The values of the heat capacity (C_p^0) and S^0, calculated at 298.15 K, are 96.631 J mole^{-1} K^{-1} and 327.18 J mole^{-1} K^{-1} respectively.

Table 9. Platinum metal oxide fluorides.

Oxidation state of the metal			
M (VIII)	M (VII)	M (VI)	M (V)
MO_3F_2	(MO_3F)	(MO_2F_2)	(MO_2F)
(MO_2F_4)	MO_2F_3	MOF_4	MOF_3
—	MOF_5	—	—

Note. Compounds whose existence is assumed are given in bracket.

Of the chemical properties of OsO_3F_2 it is known that it does not decompose on Pyrex, but is rapidly hydrolysed in the presence of moisture to OsO_4 and HF.[159]

Yellow-green OsO_2F_3 has been synthesised from an equimolar mixture of OsO_4 and OsF_6 (420 K, 17 h), and also from $OsOF_4$ and OsO_3F_2 (370 K, 12 h).[70,160] The magnetic susceptibility, mass spectrum, and EPR and Raman spectra of OsO_2F_3 have been recorded, and the vibrational frequencies assigned[160]. Solid OsO_2F_3 is polymeric, and probably has a structure containing tetrameric groups in which Os atoms with formal charges of 6+ and 8+ are joined by F-bridges.

OsO_2F_3 is sensitive to moisture, and is comparatively stable at room temperature, but it disproportionates at 330 to 350 K to give a mixture of $OsOF_4$ and OsO_3F_2; above 380 K, the equilibrium mixture also contains OsF_6 and OsO_4.[160]

The most fully studied platinum metal oxide fluoride is the emerald-green osmium oxide pentafluoride. It was obtained by heating Os in a stream of a mixture of O_2 and F_2 (1 : 2 by volume), and also by passing F_2, diluted with N_2, over OsO_2 and by heating Os in a Monel bomb with a mixture of O_2 and F_2 (1.0 : 2.5) at 570 K.[164,165] In all cases the product was a mixture of $OsOF_5$ (yield ~ 50%) and OsF_6, from which the more volatile OsF_6 was removed by vacuum distillation. $OsOF_5$ was obtained in more than 90% yield by the action of a slight excess of F_2 on anhydrous OsO_2 at 520 K.[165] $OsOF_5$ has also been synthesised by treating Os, placed in the atomic fluorine generation zone, with a mixture of O_2 and F_2 (1 : 3 by volume).[166]

The physical properties of $OsOF_5$ are given in Table 10.

The X-ray diffraction study of $OsOF_5$ [164,165,168] has shown that below 306 K it has the orthorhombic YF_3 structure, space group *Pnma*, $Z = 4$, density of the crystals (calculated) 4820 kg m^{-3}, lattice parameters $a = 9.540$, $b = 8.669$, $c = 5.019$ Å; above 306 K it is converted into a cubic form, $Z = 2$, $a = 6.14$ Å. Comparison of the structural data for $OsOF_5$ and the platinum metal hexafluorides (see Table 2) shows that they are isostructural. The fact that all the bonds formed by Os with neighbouring atoms in $OsOF_5$ are shorter than the Os–F bonds in the OsF_6 molecule (1.831 Å) is apparently due to the greater polarisation by Os in the first case[168].

Table 10. Physical properties of $OsOF_5$.[165]

Property	Value
M.p., K	332.35
B.p., K	373.75
$T_{p.t.}$, K	305.65
ΔH^0_{fusion}, kJ mole^{-1}	6.8
$\Delta H^0_{volatilisation}$, kJ mole^{-1}	36.6
$\Delta H^0_{sublimation}$, kJ mole^{-1}	43.4
ΔS^0_{fusion}, J mole^{-1}K^{-1}	22.1
$\Delta S^0_{volatilisation}$, J mole^{-1}K^{-1}	98
C_p^0 for the gas at 298.15 K, J mole^{-1}K^{-1}	118 *
S^0 for the gas at 298.15 K, J mole^{-1}K^{-1}	356 *
Magnetic moment μ, B.M.	1.47

*According to Ref. 167.

The $OsOF_5$ molecule has a slightly distorted octahedral structure with interatomic distances $r(Os{-}O) = 1.74$, $r(Os{-}F_{ax}) = 1.76$, and $r(Os{-}F_{eq}) = 1.80$ Å. The thermodynamic properties of $OsOF_5$ are also close to those of the platinum metal hexafluorides (Tables 1 and 10).

The vapour pressure (p, mmHg) of $OsOF_5$ is given by the equations[165]:

$$\lg p = 9.064 - 2266/T \quad (305 \leqslant T \leqslant 332\text{K}),$$
$$\lg p = 7.994 - 1911/T \quad (332 \leqslant T \leqslant 378\text{K}).$$

The infrared, Raman, and ^{19}F NMR spectra indicate that the $OsOF_5$ molecule belongs to the symmetry group C_{4v} [165,166,169,170]. The frequencies required for this configuration have been determined for gaseous $OsOF_5$: 962.6, 716.4, 644, 280.5, 645, 210, 332, 700.6, 263, 367, and 167 cm^{-1}.[170] The presence in the infrared spectrum of solid $OsOF_5$ of a band at 530 cm^{-1}, characteristic of the vibration of the Os–F–Os bridging bond, indicates that $OsOF_5$ is polymerised in the solid state[166]. The ^{19}F NMR spectrum indicates that the non-bonded *d* electrons are localised in the equatorial plane of the molecule[169].

$OsOF_5$ is stable in dry air, but decomposes in the presence of moisture to give OsO_4.[164] The oxidising properties of $OsOF_5$ are similar to those of OsF_6, but the former is a much weaker F^- acceptor[59].

Osmium oxide tetrafluoride was obtained by reducing $OsOF_5$ on an electrically heated tungsten wire[171] or by the reaction of OsF_6 with OsO_4 (2.5 : 1.0) at 450 K.[70] A general method for the synthesis of transition metal oxide fluorides, including $OsOF_4$, has been described, based on the exchange reaction of the corresponding hexafluorides with finely divided B_2O_3. A convenient method for synthesising $OsOF_4$ involves the hydrolysis of OsF_6 in hydrogen fluoride with an accurately measured quantity of H_2O.[71] $OsOF_4$ can be obtained by reducing $OsOF_5$ with finely dispersed Si powder in anhydrous HF.[166] The last two methods of obtaining $OsOF_4$ are preferred, since they do not require additional operations to remove the OsF_5 which usually accompanies it.

The orthorhombic lattice parameters of $OsOF_4$ [171] are $a = 5.56$, $b = 9.56$, $c = 12.83$ Å, the density of the crystals (measured) 5500 kg m^{-3}, $Z = 8$, space group $P2_122_1$.

The infrared spectrum of crystalline $OsOF_4$ has been studied[77,166]. According to Ref.166, the spectrum contains bands at 1010, 958, 707, 672, 649, and 535 cm^{-1}. The 1010 cm^{-1} band was assigned to the Os=O stretch, and the bands at 600–750 cm^{-1} to bridging Os–F–Os stretches. These bands in the range 500–600 cm^{-1} are characteristic of other transition metal oxide tetrafluorides and oxide pentafluorides[172], and indicate that they have a polymeric structure, in agreement with X-ray diffraction[171] and Raman spectroscopic[160] data. An electron diffraction study of $OsOF_4$ [166] showed best agreement with an equilibrium configuration with symmetry C_{4v} (a tetragonal pyramid with the oxygen atom in the axial position), previously established for $ReOF_4$ and WOF_4.[173] The existence of the four-fold axis in the $OsOF_4$ molecule was confirmed by photoelectron spectroscopy[174]. Analysis of the photoelectron spectra of the oxide tetrafluorides of tungsten, rhenium, and osmium shows an increase in the ionic character of the M–F bond in this order, and indicates that the multiplicity of the M–O bond must be close to 3, since the covalent bonding involves not 2 but 3 electron pairs, $(5a_1)^2$, $(5e)^4$. The last conclusion is confirmed by the results of electron diffraction studies[166] [r(Os–O) = 1.625, r(Os–F) = 1.835, r(O–F) = 2.825, r(F–F) = 2.466 Å], from which it follows that the Os–O bond in $OsOF_4$ is 0.115 Å shorter than the Os–O bond in $OsOF_5$. $OsOF_4$ is extremely sensitive to moisture, and dissolves in water and alkali solutions to give transparent yellow solutions with an odour of ozone (OsO_4 is apparently liberated)[77]. The fluorination of $OsOF_4$ at 450 K gives $OsOF_5$,[70] and heating an equimolar mixture of $OsOF_4$ and OsO_3F_2 at 370 K gives OsO_2F_3.[160]

The preparation of $RuOF_4$ by the reaction of metallic Ru with a mixture of BrF_3 and Br_2 (1 : 1) at room temperature has been described[94]. The source of oxygen was the wall of the reaction vessel. When the reaction was complete, BrF_3 was removed in a vacuum at 390 K, and the residue was heated in a sealed evacuated glass tube for 3–5 weeks at 310 K. According to Ref.94, $RuOF_4$ is a colourless substance, coloured pale green by impurities, which melts at 388 K, boils at 457 K, and has a heat of volatilisation of 50 kJ $mole^{-1}$. The vapour pressure (p, mmHg) is given by the equations

$$\text{for } RuOF_4\ [94]\ \lg p = 9.22 - 2857/T\ (293 \leqslant T \leqslant 373\text{K})$$
$$\lg p = 8.60 - 2616/T\ (393 \leqslant T \leqslant 433\text{K}).$$

Japanese workers who studied the behaviour of ruthenium during the sublimation of the fluorides to solve the problems of processing irradiated nuclear fuel[175–178] consider that the data in Ref.94 are erroneous, for the following reasons: 1) a stoichiometric reaction component ratio with respect to oxygen was not observed; 2) the presence of oxygen in the final products was not confirmed, and 3) the components of the gas phase were not analysed before the vapour pressure was measured. A study of the kinetics of the reaction of RuO_2 with fluorine in a flow reactor in the range 523–773 K at a fluorine partial pressure of 150 mmHg [175] showed that at temperatures above 670 K, RuO_2 is completely converted to $RuOF_4$, whose formation was confirmed by chemical analysis and from the mass and infrared spectra. The thermal decomposition of $RuOF_4$ was studied[176] by gas chromatography at 290–670 K, combined with chemical analysis and an infrared spectroscopic study of the solid residue and measurement of the vapour pressure by a transpiration method. Solid $RuOF_4$ decomposes to give O_2 and solid RuF_4, and the process takes place even at 293 K. With increase in temperature to 340 K, the decomposition rate increases to a maximum, and with further increase in temperature it decreases, although a small quantity of O_2 is liberated even at 670 K.

The authors cited[176] consider that the static method of measuring the vapour pressure of $RuOF_4$, used in Ref.94, is not suitable, because of errors associated with the liberation of oxygen. Moreover, at temperatures above 340 K, the RuF_4 formed prevents the normal volatilisation of $RuOF_4$. According to Ref.176, the equilibrium vapour pressure of $RuOF_4$ in the range 273–343 K is described by the equation $\lg p$ (mmHg) = 8.48 – 2740/T. It is pointed out that $RuOF_4$ vapour is stable, and that the instability of solid $RuOF_4$ is apparently related to the fact that the Ru^{VI} corresponds to an excited state. The bands at 1040 cm^{-1} and 720 cm^{-1} in the infrared spectrum of gaseous $RuOF_4$ were assigned to the Ru=O and Ru–F vibrations respectively. The spectrum of solid $RuOF_4$ does not show a band at 1040 cm^{-1}, but shows bands at 720, 630, and 520 cm^{-1}. The first of these was assigned to Ru–F stretches, the second to single bond Ru–O stretches, and the last to bridging Ru–F–Ru vibrations.

The fluorination of Ru with a mixture of F_2 and O_2 at 570–670 K gives RuF_5 (76–84%), $RuOF_4$ (16–24%), and small quantities of RuO_4.[178] These results differ from earlier data[19,179], and require confirmation.

Mass spectrometry, infrared spectroscopy, DTA, and TGA have established that at room temperature, a series of reactions involving the hydrolysis of $RuOF_4$, RuF_4, and RuF_5 followed by treatment of the hydrolysis products (mainly ruthenium hydroxides) with gaseous fluorine is accompanied by their almost complete conversion into RuO_4:[177]

$$Ru(OH)_4 \cdot n H_2O + (2+n) F_2 \rightarrow RuO_4 + 2(2+n) HF + n/2 O_2.$$

Platinum oxide fluoride has been obtained by fluorinating PtO_2 at 470 K; it is nonvolatile, is slowly hydrolysed in moist air, and its behaviour towards water is the same as that of PtF_4.[107]

IV. DIOXYGENYL COMPOUNDS OF THE PLATINUM METALS

Dioxygenyl hexafluoroplatinate O_2PtF_6 was first obtained[103] by fluorinating spongy platinum or $PtCl_2$ at 620 K in a quartz apparatus, but was erroneously assumed to be $PtOF_4$. The true composition of the compound was determined soon afterwards[80].

Methods for preparing O_2PtF_6 have been described[81]. They include fluorination in quartz, the action of a mixture of F_2 and O_2 on Pt at 720 K, the reaction of OF_2 with Pt above 670 K, and the reaction of equimolar quantities of PtF_6 and O_2 at room temperature. The compounds O_2RuF_6 and O_2RhF_6 were obtained by heating the corresponding powdered metal with a mixture of F_2 and O_2 (3 : 1 and 4 : 1) for a long time (up to 60 h) at 570–770 K.[180] The fluorination of oxides of Ru, Rh, and Pt by atomic fluorine also gives dioxygenyl compounds[30]. According to Ref.21, the reaction of PdF_6 with O_2 gives an orange compound, apparently O_2PdF_6.

An X-ray diffraction study of O_2PtF_6 [80,81] showed that it forms cubic or orthorhombic crystals. The high-temperature cubic form, obtained by the reaction of OF_2 with Pt at a temperature above 673 K, has lattice parameter a = 10.032 ± 0.002 Å, space group $Ia3$, Z = 8, and calculated and measured densities 4480 kg m^{-3} and 4200 kg m^{-3} respectively. For the low-temperature orthorhombic form, obtained by the reaction of PtF_6 with O_2 in liquid N_2, a = 4.96 Å, α = 97.5°, density 4725 kg m^{-3}. For the cubic O_2RuF_6 lattice, a = 10.004 Å, and for rhombohedral O_2RhF_6, a = 5.05 Å, α = 97°.[180]

The chemical properties and infrared and ultraviolet absorption spectra indicate that dioxygenyl hexafluoroplatinate has an ionic structure. The lattice energy of $O_2^+PtF_6^-$ is about 500 kJ $mole^{-1}$. The composition of the compounds O_2MF_6 (M = Ru, Rh, Pt) was confirmed by the Raman and mass spectra[180,181].

O_2PtF_6 reacts vigorously with H_2O to give a pale-yellow solution containing PtF_6^{2-} ions and a black solid residue containing metallic platinum, with the liberation of oxygen and a gas with the odour of ozone[81]. The hydrolysis of O_2PtF_6 and O_2RuF_6 in 40% NaOH takes place according to the equation[182]:

$$O_2MF_6 + 2OH^- \rightarrow 1.5O_2 + MF_6^{3-} + H_2O.$$

O_2PtF_6 reacts with BrF_3, SeF_4, IF_5, and ClF_3 at room temperature to form various adducts[81]. The reaction of O_2RuF_6 at 298 K and of O_2RhF_6 and O_2PtF_6 at 379 K with an excess of NOF gives the nitrosyl compounds $NORuF_6$, $(NO)_2RhF_6$, and $(NO)_2PtF_6$.[72]

V. SUMMARY

The chemistry of the platinum metal fluorides has developed rapidly in the last 25 years. Discoveries such as the synthesis of O_2PtF_6 and $XePtF_6$ have been among the most significant in inorganic chemistry in recent decades. Nevertheless, the physicochemical properties and methods of synthesis of the platinum metal fluorides examined in the present review show that there are many "blank spots" in this field.

The most important task is still the development of simple and reliable methods for preparing platinum metal fluorides of sufficient purity. Existing methods are complicated by the fact that the isolation of individual substances requires a large number of additional operations to separate the compounds formed. High demands are also made of the purity of the starting materials, since for example traces of oxygen in the metal or fluorine leads to contamination of the hexafluorides with oxide fluorides[37]. Here, promising methods involve the use of solutions of KrF_2 and XeF_2 in anhydrous hydrogen fluoride, the use of atomic fluorine[29,30,96], and the use of selective sorption and selective reduction.

The lower fluorides of the platinum metals have been very little studied, and there are practically no data on their structure and chemical and thermal properties.

The most important problems in the field of platinum metal fluorides include the determination of the thermodynamic parameters, the lack of which makes it difficult to solve problems associated with the application of the platinum metal fluorides.

From the practical viewpoint, the platinum metal fluorides are of interest because of their high volatility and the consequent possibility of their use in processes of fluoride metallurgy[183,184]. This technology in principle has all the advantages of non-aqueous methods, and can simplify the existing multi-stage schemes for separating and purifying the platinum metals. The demand and the price of the platinum metals continue to increase[185], so that a change to short technological schemes and the associated marked decrease in losses are undoubtedly justified.

Fluorination may also prove extremely promising for the analysis of the platinum metals, which are difficult to dissolve quantitatively.

The present review has not examined the large number of complex fluorides of the platinum metals, which are also interesting materials for scientific study and which may find practical application, for example for the separation and purification of the platinum metals.

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