

# The Fluorine Compounds of the Platinum Metals

## THE NATURE AND IMPORTANCE OF RECENT WORK

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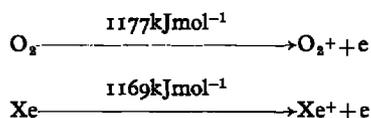
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*This review summarises some of the chemistry of the platinum metal fluorides and outlines the part they have played in developments in inorganic chemistry. A number of new compounds in this field have been identified only recently for the first time.*

The last fifteen years has seen a revision and considerable extension of the fluorine chemistry of the platinum metals. In the earlier part of the period the new hexafluorides PtF<sub>6</sub> (1), RuF<sub>6</sub> (2) and RhF<sub>6</sub> (3) were reported and the fluoride previously thought to be OsF<sub>8</sub> was shown to be OsF<sub>6</sub> (4). More recently OsF<sub>7</sub> itself has been prepared and characterised and the possible existence of OsF<sub>8</sub> has been suggested (5). Unusual polymeric structures have been found in the crystalline pentafluorides of ruthenium (6), osmium (7), rhodium (8), iridium (9), and platinum (10), all of which have been either discovered or properly characterised for the first time since 1960. The first oxide fluorides have been discovered, but so far only RuOF<sub>4</sub> (11), OsO<sub>3</sub>F<sub>2</sub> (12), OsOF<sub>5</sub> (13), OsOF<sub>4</sub> (14), and PtOF<sub>3</sub> (15) have been reported and some of these are still not well characterised.

In 1962 a compound of formula PtO<sub>2</sub>F<sub>6</sub> (16) was found among the products of the reaction of platinum and platinum salts with fluorine in glass and silica apparatus. Subsequently it was shown that this same substance could be synthesised by oxidising molecular oxygen with an equimolar quantity of PtF<sub>6</sub> vapour (16, 17) and that the correct formulation is O<sub>2</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup> (17). This discovery is without doubt one of the most

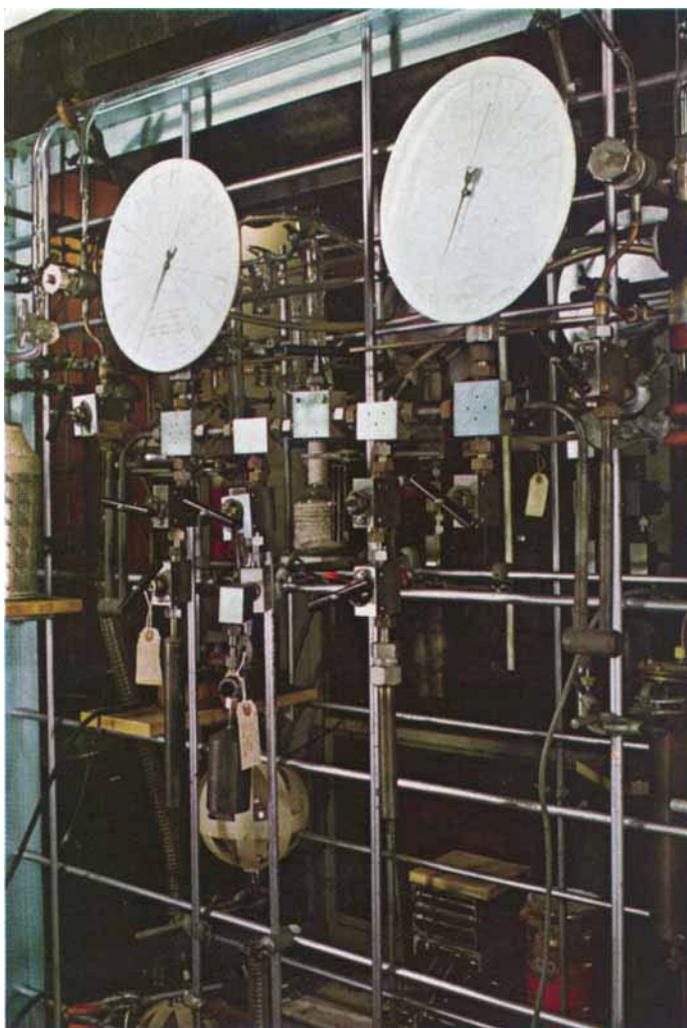
historically significant in inorganic fluorine chemistry in the last sixty years. In order to form this type of compound an electron must be removed from oxygen and transferred to PtF<sub>6</sub>. The surprising thing about the reaction is that the first ionisation potential for oxygen is quite high. Until O<sub>2</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup> was made no compound containing O<sub>2</sub><sup>+</sup> had ever been reported. The discoverer of this unique compound, Neil Bartlett, realised that the first ionisation potential of xenon is almost identical with that of molecular oxygen:



This led him to wonder if the reaction of platinum hexafluoride with xenon would produce a xenon compound analogous to the oxygen compound. A simple experiment, the mixing of xenon with PtF<sub>6</sub> vapour, confirmed that it did (18). This first compound of xenon, Xe<sup>+</sup>PtF<sub>6</sub><sup>-</sup>, was the precursor to the discovery of the whole new chemistry of the noble gases (19). Now compounds of krypton, xenon and radon are known (19) and there are hints (20) that argon compounds may be discovered soon.

Perhaps the most interesting recent aspect of platinum metal fluoride chemistry has

*Fig. 1 The hexafluorides of the platinum metals are highly volatile and extremely corrosive. Consequently their discovery awaited the development of special Monel and nickel vacuum and high-pressure systems for handling them under anhydrous conditions and such apparatus is shown here*



been the discovery of a new class of compounds, the transition metal carbonyl fluorides. Carbonyl fluorides of molybdenum (21) and ruthenium (22) have been claimed but only the ruthenium compound, difluorotricarbonylruthenium(II) (22) has been fully characterised and this has been shown to have a closely related structure to those of the platinum metal pentafluorides (see later).

### **Binary Fluorides**

Because the six platinum metals are usually referred to as a single "group", it is often assumed that they are chemically similar.

The variety of types of oxide fluoride and the fact that oxide fluorides are known only for three metals are indications that this is not the case. In fact, the chemistry of the platinum metals is quite diverse. This is well illustrated by the fluorides, and trends are best determined by considering the elements as members of the second and third transition series (See Table I). As is usual with transition elements each exhibits a variety of oxidation states. Through the series up to the first members of Group VIII the highest attainable oxidation state is equal to the group number. Ruthenium and osmium both exhibit octavalence in their

Group	IIIA	IVA	VA	VIA	VIIA	VIII		IB	
Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Electronic Configuration	4d <sup>1</sup> 5s <sup>2</sup>	4d <sup>2</sup> 5s <sup>2</sup>	4d <sup>4</sup> 4s <sup>1</sup>	4d <sup>5</sup> 4s <sup>1</sup>	4d <sup>6</sup> 4s <sup>1</sup>	4d <sup>7</sup> 4s <sup>1</sup>	4d <sup>8</sup> 5s <sup>1</sup>	4d <sup>10</sup>	4d <sup>10</sup> 5s <sup>1</sup>
Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
Electronic Configuration	5d <sup>1</sup> 6s <sup>2</sup>	5d <sup>2</sup> 6s <sup>2</sup>	5d <sup>3</sup> 6s <sup>3</sup>	5d <sup>4</sup> 6s <sup>2</sup>	5d <sup>5</sup> 6s <sup>2</sup>	5d <sup>6</sup> 6s <sup>2</sup>	5d <sup>7</sup> 6s <sup>2</sup>	5d <sup>9</sup> 6s <sup>1</sup>	5d <sup>10</sup> 6s <sup>1</sup>

tetroxides and some hint of the existence of OsF<sub>8</sub> has also been obtained (5). Beyond these first members of Group VIII, however, the oxidation state maximum diminishes dramatically from Ru to Ag and from Os to Au in spite of the availability of the necessary numbers of valence electrons. There is no firm evidence for Rh(IX) and Ir(IX) compounds or for decavalent palladium or platinum. Indeed, even hepta- and octavalent states for the elements beyond ruthenium and osmium have not been attained.

In Table II the known fluorides and oxide fluorides of the platinum metals are listed along with the highest oxidation-state oxides. A number of interesting features are at once apparent. For example, although RhF<sub>6</sub> is known RhO<sub>3</sub> is not; the highest known fluoride of ruthenium is RuF<sub>6</sub> in spite of the fact that RuO<sub>4</sub> exists. Some explanations for observations such as these have been derived from thermodynamic considerations (23).

### Octafluorides and Heptafluorides

In spite of the demise of so-called "OsF<sub>8</sub>" in 1958 (4) there has always been hope that a higher osmium fluoride than OsF<sub>6</sub> might be formed since, unlike RuF<sub>6</sub>, OsF<sub>6</sub> is stable and the preceding element in the third transition series forms a heptafluoride.

In 1966, Glemser and his co-workers (5) succeeded in preparing OsF<sub>7</sub> by heating osmium plus fluorine mixtures at high temperatures (500 to 600°C) and pressures (350 to 400 atm.). As expected the pale yellow compound loses fluorine at room temperature to give OsF<sub>6</sub>. Osmium hepta-

<b>Ru</b>	RuF <sub>6</sub> RuF <sub>5</sub> RuF <sub>4</sub> RuF <sub>3</sub>  RuOF <sub>4</sub> RuO <sub>4</sub>	<b>Rh</b>	RhF <sub>6</sub> RhF <sub>5</sub> RhF <sub>4</sub> RhF <sub>3</sub>   RhO <sub>2</sub>	<b>Pd</b>	  PdF <sub>4</sub> PdF <sub>3</sub> PdF <sub>2</sub>   Pd <sub>2</sub> O <sub>3</sub>
<b>Os</b>	OsF <sub>7</sub> OsF <sub>6</sub> OsF <sub>5</sub> OsF <sub>4</sub>  OsO <sub>3</sub> F <sub>3</sub> OsOF <sub>5</sub> OsOF <sub>4</sub> OsO <sub>4</sub>	<b>Ir</b>	 IrF <sub>6</sub> IrF <sub>5</sub> IrF <sub>4</sub> IrF <sub>3</sub>   IrO <sub>3</sub>	<b>Pt</b>	     PtF <sub>6</sub> PtF <sub>5</sub> PtF <sub>4</sub>   PtOF <sub>3</sub>   PtO <sub>3</sub>

fluoride was shown to have a pentagonal bipyramidal ( $D_{5h}$  symmetry) structure.

During these experiments mass spectro-metric, magnetic susceptibility, e.s.r. and i.r. evidence was accumulated which suggested the possible existence of some  $OsF_8$  in the reaction product. However no conclusive evidence for  $OsF_8$  has yet been obtained.

## Hexafluorides

The discovery of the hexafluorides  $RuF_6$  (2),  $OsF_6$  (4),  $RhF_6$  (3), and  $PtF_6$  (1) was the work of one research group under the leadership of Bernard Weinstock at Argonne National Laboratory in the U.S.A. Their success came largely through their development of special Monel and nickel vacuum and high-pressure systems for the handling of these highly volatile and corrosive materials. (Similar apparatus is shown in Fig. 1.) With the exception of palladium then, a hexafluoride is known for each of the platinum metals. The physical properties of some of these molecules have been carefully studied but very little is known of their chemistry (24, 25). Although there are no good heat of formation data available, fundamental vibration frequencies for the  $a_{1g}$  mode in the infrared and Raman spectra (26, 23) indicate a decrease in bond strength from left to right in each series and this is confirmed by the increasing tendency for the hexafluoride to dissociate to lower fluoride and fluorine with increasing atomic number. This decrease in stability has been explained in terms of there being an increase in the electron withdrawing power of the central atom across each series (23).

## Pentafluorides and Lower Fluorides

Unusual tetrameric structures were discovered in the crystalline pentafluorides of Ru (6), Os (7), Rh (8), Ir (9), and Pt (10) (see Fig. 2a) in the early 1960s. In these tetramers the metal atoms lie at the corners of a rhombus and there are non-linear bridging fluorine atoms between the metals.

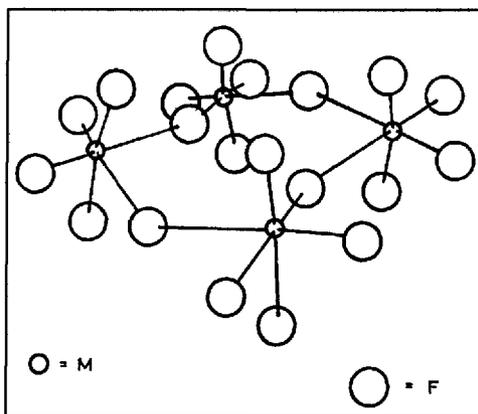


Fig. 2a (above)

Fig. 2b (below)

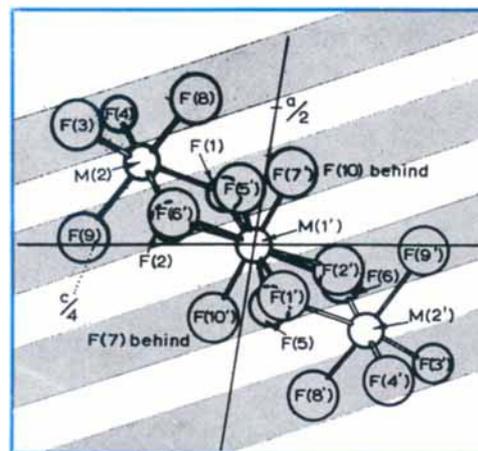


Fig. 2 (a) Tetrameric crystalline pentafluorides of the platinum metals with metal atoms  $M$  at the corners of a rhombus and with non-linear bridging fluorine atoms between the metals.  $F$  = fluorine atom

(b) The tetramer from the side showing clearly the close packed layers of fluorine atoms

The structures are based on a hexagonal close-packed arrangement of fluorine atoms, and the tetramer seen from the side clearly shows the close packed layers of fluorine atoms (see Fig. 2b).

Other recent interesting aspects of platinum metal pentafluoride chemistry include adduct formation of  $RuF_5$  and  $OsF_5$  with  $XeF_2$ . The  $MF_5 \cdot XeF_2$ ,  $MF_5 \cdot (XeF_2)_2$  ( $M = Ru$  or  $Os$ ) and  $(RuF_5)_2 \cdot XeF_2$  adducts are known and may be prepared in  $BrF_5$  solution (28) or, in most cases, directly from the parent

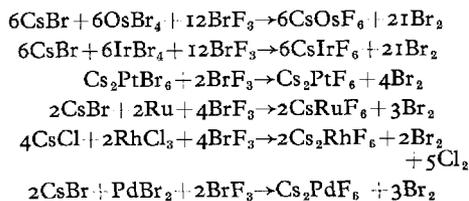
fluorides (27). X-ray evidence on the  $\text{OsF}_5$ ,  $(\text{XeF}_2)_2$  compound has been interpreted on the basis of an ionic formulation containing the  $\text{Xe}_2\text{F}_3^+$  cation (28) and it has been assumed that the remaining adducts can be formulated in terms of similar ionic adducts  $[\text{XeF}]^+[\text{MF}_6]^-$  or  $[\text{XeF}]^+[\text{M}_2\text{F}_{11}]^-$ .

Generally speaking the lower fluorides can be most readily prepared when the related higher fluorides are least stable, e.g.,  $\text{PdF}_2$  is known but  $\text{PdF}_6$  has not been made; attempts to make  $\text{PtF}_3$  and  $\text{PtF}_2$  have failed (29). Little is known of the properties of these compounds though the structures for some of the trifluorides are known (30) and the "trifluoride" of palladium has been shown to be  $\text{Pd}^{2+}[\text{PdF}_6]^{2-}$ , palladium(II) hexafluoropalladate(IV) (31).

## Complex Fluorides

Bartlett has drawn much attention to the reactivity of the higher fluorides of the platinum metals by reference to their complex formation with such things as nitric oxide (23). He has shown that the electron affinity of the hexafluorides increases with atomic number and that  $\text{PtF}_6$  is the only hexafluoride capable of oxidising oxygen (i.e. to give  $\text{O}_2^+\text{PtF}_6^-$  (17)). This correlates well with the increased readiness of hexafluorides to dissociate to fluorine and a lower fluoride with increasing atomic number.

He has also shown that the quinquevalent state is increasingly difficult to attain as atomic number is increased across each series, as the following reactions illustrate (23).



In fact, this decrease in the maximum attainable oxidation state with increasing atomic number parallels the case of the simple fluorides.

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