

1005. *Fluorides of the Noble Metals. Part II.* Dioxygenyl
Hexafluoroplatinate(v), $O_2^+[PtF_6]^-$.*†

By NEIL BARTLETT and D. H. LOHMANN.

Dioxygenyl hexafluoroplatinate(v) has been made from oxygen and platinum hexafluoride and by fluorinating platinum or platinum salts in the presence of oxygen. It is a red, dimorphic, paramagnetic solid which sublimates without decomposition in a vacuum above 90°. A lower-temperature, rhombohedral form is isomorphous with potassium hexafluoroplatinate(v); a higher-temperature, cubic form is isomorphous and nearly isostructural with potassium hexafluoroantimonate(v). The pentapositive platinum complexes, $KPtF_6$, ClF_3 , PtF_5 , and IF_5 , PtF_5 have been derived from it.

THE fluorine chemistry of the platinum metals has recently been extended and revised. To this Weinstock and his co-workers have contributed significantly. The volatile

* Presented at the Second International Symposium on Fluorine Chemistry, Estes Park, Colorado, 1962. The paper by Bartlett and Quail, *J.*, 1961, 3728, is considered Part I of this series.

† Dioxygenyl is preferred to dioxygenium, to indicate the removal of one electron from dioxygen (O_2) since the suffix -yl is usual for cations or radicals containing oxygen (*e.g.*, nitrosyl and chlorosyl), whereas -ium is often used to indicate the addition of a proton.

hexafluorides of platinum,^{1,2} ruthenium,³ and rhodium⁴ which they prepared are of particular interest as the first unambiguously sexivalent compounds of these elements. All appear to dissociate slowly at room temperature to fluorine and the respective lower fluorides¹⁻³ (PtF₄, RuF₅, and RhF₅). This oxidation of combined fluorine shows that these hexa-positive metals have extremely high electron affinities and should accordingly be powerful oxidising agents.

That platinum hexafluoride is able to oxidise molecular oxygen to form dioxygenyl hexafluoroplatinate(v), has been recently demonstrated by us.⁵ The compound has special interest as the first salt in which the dioxygenyl ion, O₂⁺, has been observed. Moreover, it is the first hexafluoroplatinate(v) salt to have been made. Potassium, difluorochlorinium (ClF₂⁺), and tetrafluoroiodinium (IF₄⁺) hexafluoroplatinate(v) have been derived from it.

EXPERIMENTAL

Preparation of Dioxygenyl Hexafluoroplatinate(v).—(a) It is conveniently prepared by the action at 450° of a mixture of fluorine and oxygen on platinum sponge presented in a nickel boat in a thick-walled silica tube. This was joined, by graded seals, to a train of Pyrex U traps, provided with break-seals, which served to collect the volatile products. The apparatus was evacuated and dried, the traps were cooled in liquid oxygen, and an oxygen-fluorine mixture was passed over the platinum which was slowly raised to 425–450°. The platinum glowed as it reacted and dioxygenyl hexafluoroplatinate(v) was deposited as a deep red film beyond the reaction zone and as a fine orange-red powder in the traps. It was purified by vacuum-sublimation at 100°.

(b) Oxygen difluoride reacts with platinum sponge at 350° to produce platinum tetrafluoride. Above 400° dioxygenyl hexafluoroplatinate(v) is formed.

(c) Dioxygenyl hexafluoroplatinate(v) is produced in the fluorination of other platinum compounds (PtCl₂, PtCl₄, PtBr₄, PtI₄) when the temperature is >400° and oxygen is present. Oxygen for this purpose was produced by the attack of fluorine on Pyrex or silica at this temperature.

(d) The compound is formed at room temperature during the tensimetric titration of oxygen with platinum hexafluoride. The platinum hexafluoride was prepared by igniting platinum strips in fluorine (~760 mm.) with nitrogen as carrier gas. It condensed as an almost black solid, in traps cooled at -75°, and was purified by vacuum-sublimation from traps held at 0° into a Pyrex break-seal bottle cooled in liquid oxygen. Oxygen for the titration was dried by passing it slowly through U traps cooled in liquid oxygen. The break-seal bottle containing the hexafluoride was joined to a 100-ml. Pyrex bulb which had two bellows-type Hoke valves (type A434), one (A) opening to a condensation limb, the other (B) to a nickel diaphragm pressure gauge. Another valve (C) on the gauge opened to the vacuum system and the oxygen supply.

The diaphragm gauge had a sensitivity ±2 mm. and was used as a null instrument. After the apparatus had been well dried and evacuated, valves A and C were closed and the hexafluoride was admitted to the bulb. The pressure, actually 25 mm., was balanced by admitting air to the other side of the diaphragm. The vapour was deep red-brown. The hexafluoride was transferred to the condensation limb by cooling it with liquid oxygen. Valve A was closed and oxygen admitted to the bulb through valves C and B, to a pressure of 25 mm. Mixing the hexafluoride and oxygen by opening valve A precipitated a red solid; the red vapour disappeared and the pressure fell to zero. An X-ray powder photograph of the red solid formed in the cold condensation limb showed two patterns, one cubic and identical with that of the oxyfluorination product, the other rhombohedral and very similar to the pattern of potassium hexafluoroplatinate(v). The diffuse lines of the rhombohedral pattern indicated that the phase was poorly crystalline, and the difficulty of locating high-angle reflexions prevented an accurate determination of cell dimensions. A comparison of the photograph with

¹ Weinstock, Claasen, and Malm, *J. Amer. Chem. Soc.*, 1957, **79**, 5832.

² Weinstock, Malm, and Weaver, *J. Amer. Chem. Soc.*, 1961, **83**, 4310.

³ Claasen, Selig, Malm, Chernick, and Weinstock, *J. Amer. Chem. Soc.*, 1961, **83**, 2390.

⁴ Chernick, Claasen, and Weinstock, *J. Amer. Chem. Soc.*, 1961, **83**, 3165.

⁵ Bartlett and Lohmann, *Proc. Chem. Soc.*, 1962, 115.

one of potassium hexafluoroplatinate(v) proved that the unit cell was very similar to that of the potassium salt. Pictures of sublimed material disclosed only the cubic pattern.

Hydrolysis of Dioxygenyl Hexafluoroplatinate(v).—(a) *By liquid water.* The solid reacted violently with liquid water, contact between the solid and the liquid often being accompanied by the emission of light. Oxygen and gas smelling of ozone was evolved, a pale yellow solution was produced, and a black solid remained. The last, very finely divided, was shown by X-ray powder photographs, to contain metallic platinum. The rest of the solid was amorphous and soluble in hydrochloric acid. The pale yellow solution contained the fluoroplatinate(iv) ion. The gas evolved on treatment of the dioxygenyl salt with water was totally adsorbed by alkaline pyrogallol and was shown to be oxygen by mass-spectrometric analysis.

(b) *By water vapour.* The new compound reacted with water vapour to give oxygen, an orange yellow precipitate of hydrated platinum dioxide, and a golden-yellow solution containing the fluoroplatinate(iv) ion. This reaction was followed quantitatively, the arrangement used being similar to that described by Emeléus and Woolf.⁶ Two evacuated break-seal bulbs, one containing a known weight of the fluoride and the other a sample of degassed water, were attached to a vacuum-system provided with a Töpler pump. The dioxygenyl salt was exposed to water vapour and when reaction was complete both bulbs were cooled in liquid oxygen and any residual gas was removed with the Töpler pump. There was some attack on the mercury of the pump but an analysis of the gas by mass spectrum showed only oxygen. Results were: (i) 0.8872 g. of O_2PtF_6 gave 70.5 ml. of oxygen at N.T.P. (1 mole gave 27.1 l.); (b) 0.1908 g. of O_2PtF_6 gave 14.8 ml. of oxygen at N.T.P. (1 mole gave 26.5 l.).

Analysis.—Decomposition in aqueous alkali proved to be unsuitable analytical procedure for dioxygenyl hexafluoroplatinate(v), giving consistently low values for fluorine. Platinum analysis required two determinations, one of the mixture of metallic platinum and hydrated platinum oxides, the other of the solution of hexafluoroplatinate(iv). The precipitate was reduced to the metal in hydrogen. Platinum in the solution was precipitated by zinc. The total-platinum figures were not very concordant and always higher than that required for O_2PtF_6 .

Pyrohydrolysis.—(a) Consistent analyses were, however, obtained by a modification of the pyrohydrolytic techniques described by Welsh and Parker and by Rushmere and Mason.⁷ The apparatus consisted of a silica tube, 40 × 2 cm., a 35/20 B.S. socket at one end, and a B.10 cone at the other; to the last a Pyrex condenser was fitted. The steam-preheater and steam-trap, of ¼ in. copper tubing, were linked to the 35/20 B.S. socket by means of a brass ball, machined to fit. The silica tube was heated in an electric furnace, and its temperature was measured with a thermometer. The steam was generated in a three-necked 1-l. flask provided with an air-inlet, an air-steam outlet, and a thermometer.

Dioxygenyl hexafluoroplatinate (~0.2 g.) was transferred to a platinum boat in a dry-box, weighed, and quickly transferred to the cold silica tube. Moist air was first passed over the sample, then the temperatures of the boiler-water and the furnace were both slowly raised until the water was boiling and the tube was at 300°. The products were collected in 50 ml. of water, and finally washings from the condenser were added. The fluoride was titrated with 0.1N-sodium hydroxide to phenolphthalein and as a check the fluoride was precipitated and weighed as lead chloride fluoride.

For the determination of platinum, the condenser was replaced by a 1 cm. silica tube which tapered to 5 mm. The apparatus was flushed with nitrogen; then hydrogen was passed through it, the emergent gas being burnt. The platinum residue was heated to constant weight (Found: F, 32.4; Pt, 57.5. PtO_2F_6 requires F, 33.4; Pt, 57.2%).

The platinum boat was always weighed in a horizontal weighing bottle with a ground-glass stopper.

(b) *Sodium fusion.* About 0.3 g. of material in a gelatine capsule was placed in a Parr bomb, together with ~0.2 g. of metallic sodium, all the operations being carried out in a dry-box. The bomb was heated for 1 hr. over a Meker burner, cooled, and opened at room temperature, and the excess of sodium was destroyed by boiling with absolute alcohol. Sodium fluoride was extracted from the residue with water and the fluorine determined as lead chloride fluoride (Found: F, 32.7%).

⁶ Emeléus and Woolf, *J.*, 1950, 164.

⁷ (a) Welsh and Parker, U.K.A.E.A. unclassified report WSL-R-36, 1959; (b) Rushmere and Mason, *ibid.*, SCS-R-392, ARDC/P-84, 1959.

(c) Platinum was determined by igniting a known weight in a platinum crucible under hydrogen (Found: Pt, 57.4%).

(d) Oxygen was determined by displacing it with bromine trifluoride in the apparatus used for the hydrolysis (Found: O, 10.4. PtO_2F_6 requires O, 9.4%).

Properties.—The salt separating from its vapour is orange-red, as are thin films, but in mass the sublimed material appears black. It sublimes readily at pressures below 10^{-2} mm. at above 90° . Attempts to determine the vapour pressure–temperature relationship failed because pressures developed below 130° are small in comparison with the probable error, and the compound reacts with the glass container above that temperature. When heated in a sealed tube it melts to a viscous liquid at 219° and evolves a little gas. But decomposition is incomplete at this temperature since X-ray photographs still show the characteristic cubic phase.

Spectra.—The infrared spectrum was recorded with the material sublimed on to cold potassium bromide windows sealed to a gas-tight glass cell with an epoxy resin. The deposit could not be sublimed from the windows without some attack on the bromide and thus it is possible that spurious peaks may be present in the spectrum. The observed peaks are: 631vs, 680w, 725vw, and 1308 cm^{-1} .

For the ultraviolet and visible region material was sublimed on to the windows of a quartz cell. The absorption steadily rose as the wavelength fell, rising sharply at 4000 \AA and showing a single maximum at 3500 \AA .

Magnetic Properties.—The magnetic susceptibility was measured, on an instrument previously described,⁸ between 88 and 300°K . Mercury(II) tetrathiocyanatocobaltate(III), recommended by Figgis and Nyholm,⁹ was used as the standard. The molar susceptibilities (see Table 1) were corrected for diamagnetic contributions, $\Delta\chi_M$ being taken as 100×10^{-6} c.g.s. units. Throughout this temperature range the susceptibility obeys the Curie–Weiss law, the molecular field constant being $+45^\circ$.^{*} The susceptibility is independent of the field strength. The effective magnetic moment $\mu_{\text{eff}} = 2.57$ B.M.

TABLE 1.

		Corrected molar susceptibilities of O_2PtF_6 .								
Temp. (K) ...	88°	116°	133°	146°	175°	204°	233°	261°	271°	294°
$10^6\chi_M$	6166	4909	4390	4207	3770	3309	2901	2657	2598	2413

Reactions.—(a) *With bromine trifluoride.* Bromine trifluoride at 23° dissolved the solid with the evolution of oxygen. Removal of the excess of the reagent and volatile material left a pale orange platinum tetrafluoride–bromine trifluoride adduct, $(\text{BrF}_3)_2\text{PtF}_4$, which was identified by X-ray photography. The oxygen evolved was determined in order to find the oxygen content of the dioxygenyl hexafluoroplatinate(v).

(b) *With selenium tetrafluoride.* The compounds reacted with vigorous effervescence at room temperature and ordinary pressure, to give a pale yellow solution and a deeper yellow solid. Removal of the reagent under a vacuum left a pale yellow solid shown by X-ray photography to be mainly a selenium tetrafluoride–platinum tetrafluoride adduct, $(\text{SeF}_4)_2\text{PtF}_4$. There was also the faint pattern of another phase. The infrared spectrum of the gaseous product, 664w, 717vw, 780vs, 842m, 925m, 1030s, 1182w, 1286mw, 1438s, 1484s cm^{-1} , indicates much selenium hexafluoride¹⁰ since it accounts for all peaks except for that of silicon tetrafluoride¹¹ at 1030 cm^{-1} . This was confirmed by mass-spectrometric analysis. The vapour density, however, was 25.0 and since SeF_6 requires $\rho = 96.15$, oxygen was probably present. The gas evolved in the reaction was measured with the Töpler pump (Found: 0.134 g. of O_2PtF_6 gave 18.0 ml. of gas at N.T.P.; i.e., 1 mole gave 45.8 l.).

(c) *With iodine pentafluoride.* The new compound and iodine pentafluoride did not react at room temperature but at 35° gas was slowly evolved and a deep red solution formed, which became paler as the reaction proceeded. Removal of the excess of iodine pentafluoride, under

* In our preliminary communication an error was made in estimating the molecular field constant.

⁸ Clark and O'Brien, *Canad. J. Chem.*, 1961, **39**, 1030.

⁹ Figgis and Nyholm, *J.*, 1958, 4190.

¹⁰ Gaunt, *Trans. Faraday Soc.*, 1953, **49**, 1122.

¹¹ Jones, Kirby-Smith, Woltz, and Nielson, *J. Chem. Phys.*, 1951, **19**, 242.

a vacuum, at room temperature, left an orange solid, a platinum pentafluoride-iodine pentafluoride adduct (Found: F, 34.2; Pt, 38.9. $\text{IF}_5, \text{PtF}_5$ requires F, 37.1; Pt, 38.1%). This was paramagnetic, with $\mu = 0.64$ B.M. at 23°.

(d) *With potassium fluoride.* Potassium fluoride (0.093 g.) and dioxygenyl hexafluoroplatinate(v) (0.534 g.) reacted in liquid iodine pentafluoride. There was slow evolution of gas and to complete the reaction the cloudy red solution was refluxed for 15 min. A mustard-yellow solid remained when the iodine pentafluoride was removed under vacuum, which X-ray photography showed to be isomorphous and nearly isodimensional with potassium hexafluororuthenate(v). Analysis by pyrohydrolysis to 300° gave: F, 32.0; residue 69.0% (KPtF_6 requires F, 32.7; K, 11.3; Pt, 56.0%).

Potassium fluoride forms a deep yellow solid when the oxyfluoride is sublimed over it. X-Ray photography showed this to be potassium hexafluoroplatinate(v) with a little potassium hexafluoroplatinate(iv) and residual potassium fluoride.

(e) *With chlorine trifluoride.* When chlorine trifluoride was condensed on to the dioxygenyl salt and the mixture was warmed, there was vigorous evolution of gas. The solution, first deep red, became paler and finally pale orange. The system was cooled in liquid oxygen, and volatile materials were pumped off for mass-spectrometry. Although oxygen difluoride, fluorine, and ozone were also looked for, oxygen alone was found. When the excess of chlorine trifluoride was distilled from the solution it carried with it a deep red, volatile material, possibly chlorine dioxide. The pale orange residue was a 1:1 chlorine trifluoride-platinum pentafluoride adduct. Analysis by pyrohydrolysis to 300° gave: F, 38.4; Pt, 51.9% ($\text{ClF}_3, \text{PtF}_5$ requires Cl, 9.3; F, 39.7; Pt, 51.0%).

(f) *With organic solvents.* The solid reacted violently with benzene, cyclohexane, and pyridine, but not with carbon tetrachloride in which it is insoluble.

Structure of O_2PtF_6 (cub.).—Thin-walled, 0.5 mm. quartz capillaries were charged in a dry-box with the sublimed material, and sealed. A 14.32 cm. General Electric precision camera (Straumanis loading) and Cu- K_α radiation from a nickel filter were used. The photographs were indexed on a cubic unit cell with $a = 10.032 \pm 0.002$ Å, $V = 1010$ Å³, $D_m = 4.20$, $Z = 8$, $D_c = 4.48$. The density was determined in a 2-ml. density bottle with a ground-glass cap; this was loaded in a dry-box and carbon tetrachloride was the displacement fluid. Accurate

TABLE 2.
X-Ray powder data for O_2PtF_6 (cub.).

<i>hkl</i>	$1/d^2$		<i>I</i> (estd.)	<i>hkl</i>	$1/d^2$		<i>I</i> (estd.)
	calc.	obs.			calc.	obs.	
110	0.0199	—	—	822, 660	0.7154	0.7190	6
200	0.0398	0.0413	8	662	0.7552	0.7582	4
211	0.0597	—	—	840	0.7949	0.7984	5
220	0.0795	0.0818	10	842	0.8347	0.8381	6
222	0.1193	0.1217	5	664	0.8744	0.8761	4
321	0.1391	0.1410	1	844	0.9539	0.9558	3
400	0.1590	0.1614	4	10,0,0; 860	0.9938	0.9957	4
411	0.1789	0.1808	2	10,2,0; 862	1.0340	1.0361	7
420	0.1988	0.2020	7	10,2,2; 666	1.0731	1.0768	4
332	0.2187	0.2216	2	10,4,0; 864	1.1526	1.1549	6
422	0.2385	0.2415	9	10,4,2	1.1924	1.1936	5
431	0.2584	0.2606	1	880	1.2718	—	—
440	0.3180	0.3209	6	10,4,4; 882	1.3116	1.3134	4
600, 442	0.3578	0.3613	9	10,6,0; 866	1.3514	1.3525	4
620	0.3975	0.4010	7	10,6,2	1.3911	1.3925	4
622	0.4372	0.4406	6	12,0,0; 884	1.4309	1.4313	3
444	0.4770	0.4800	4	12,2,0	1.4706	1.4721	2
640	0.5167	0.5198	6	12,2,2; 10,6,4	1.5103	1.5118	5
642	0.5564	0.5600	9	12,4,0	1.5898	1.5902	3
800	0.6359	0.6390	2	12,4,2; 10,8,0; 886	1.6296	1.6300	6
820, 644	0.6757	0.6787	7				

cell dimensions were obtained by using the Nelson-Riley extrapolation function.¹² The calculated and the observed values for $1/d^2$ are in Table 2. Two films, one of long and the other of short exposure, were examined on a Hilger recording microphotometer (type L486.)

¹² Azaroff and Buerger, "The Powder Method," McGraw-Hill Book Co., Toronto, 1958, p. 238.

Relative intensities were obtained by counting squares under the recorded curves, the intensities for the strongest lines being taken from the short-exposure film.

The space group was assumed to be $Ia\bar{3}$ (T_h^7 , No. 206) with the atoms in the following positions: 8 Pt in 8(a) 0,0,0; etc., 16 in 16(c) n,n,n ; etc., 48 F in 48(e) x,y,z ; etc. To obtain parameters for the fluorine atoms the dioxygenyl ions were centered on $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, etc., with their long axes along the three-fold rotation axes, the value of n being estimated from the inter-

TABLE 3.

Observed and calculated intensities for $O_2^+[PtF_6]^-$ (cub.).

Atomic positions: 8 Pt at 0,0,0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; etc., 16 O at n,n,n ; $\bar{n}, \bar{n}, \bar{n}$; etc., 48 F at x,y,z ; etc.
 $n = 0.218 \pm 0.005$; $x = 0.09_1$; $y = 0.13_2$; $z = -0.06_3$.

Plane	I	I_o	Plane	I_o	I_o	Plane	I_o	I_o	Plane	I_o	I_o			
200	100	88	420	50.8	}96.5	103	600	11.6	}109.0	109	622	73.2	78	
211	0.5	—	240	45.7		442	97.4	631		0.8	0.8	—		
220	200	204	332	8.2	12	611	0.2	—	361	0.1	}0.9	—		
222	55	55	422	159	171	532	0.1	—	444	22.2		28		
321	0.4	}1.1	431	2.3	}6.4	9	352	0.7	}0.8	—	640	41.2	}75.0	73
231	0.7		341	4.1		620	44.2	83.0		92	460	33.8		
400	29.1	25	521	0.3	}2.4	vwv	260	38.8	—	642	64.4	}123.0	126	
411	8.1	8	251	2.1		vwv	541	0.03	vwv	462	58.6		8.5	
			440	80.0	83	451	2.0	vwv	800	10.3				
			433	0.2	—									

$$\frac{\sum |I_o - I_c|}{\sum I_o} = 0.062.$$

atomic distance reported for O_2^+ from spectroscopic work.¹³ The fluorine parameters were then varied to give the calculated intensities which agreed best with those observed. Because of the difficulty of assessing the temperature factor, the agreement was tested by a graphical method. For any line in a powder photograph, the intensity is given by

$$I = \text{Constant} \times F_{hkl}^2 \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta} pA \exp[-B(\sin \theta/\lambda)^2],$$

where the symbols have their usual meanings. The fluorine atom positions were obtained by plotting

$$\log e \sqrt{\frac{I_{\text{obs}}}{pA (1 + \cos^2 \theta) / (\sin^2 \theta \cos \theta)}} / F_{hkl}$$

against $\sin^2 \theta$ and varying the parameters (which changed F_{hkl} alone) until a straight line was obtained. Agreement was not improved by small parameter changes for the oxygen atoms. Table 3 gives the derived parameters, the calculated intensities, to which the temperature factor (obtained from the graph) has been applied, and the observed intensities. Scattering factors and Bradley's values for the absorption correction (absorption coefficient = 552.5 cm^{-1}) were taken from Sagel's book.¹⁴ The chemically significant interatomic distances are given in Table 4.

TABLE 4.

Interatomic distances for O_2PtF_6 (cub.) (in Å).

Pt-F	F-F	O ₂ -F	O-O
1.74	(3) 2.57	(6) 2.71	1.13
	(3) 2.99	(6) 3.74	

Materials.—"Pure Platinum Sponge" was used as supplied by Johnson, Matthey, and Mallory Ltd., Toronto. Fluorine was taken directly from a cylinder supplied by Allied Chemicals, New York, and used after hydrogen fluoride had been removed by passing it over sodium fluoride. Halogen fluorides, from the Mattheson Co. Inc., Illinois, were given a

¹³ "Interatomic Distances," Chem. Soc. Special Pub. No. 11, 1958, p. M69.

¹⁴ Sagel, "Tabellen zur Röntgenstrukturanalyse," Springer-Verlag, Berlin, 1958, pp. 106—119.

preliminary trap-to-trap distillation. Selenium tetrafluoride was prepared according to Aynsley, Peacock, and Robinson's directions.¹⁵

DISCUSSION

Although there are a number of possible formulations for a compound of empirical formula O_2PtF_6 , the preparative and physical evidence unambiguously points to its being the salt, dioxygenyl hexafluoroplatinate(v) $O_2^+[PtF_6]^-$.

Its rapid formation from the hexafluoride vapour and molecular oxygen makes it unlikely to be $Pt(OF)_2F_4$, $OF^+[PtF_5O]^-$, or $OPtF_6O$. The crystal symmetry, which in the rhombohedral form is isomorphous with potassium hexafluoroplatinate(v), and its insolubility in carbon tetrachloride, indicate an ionic lattice. Formulation as either

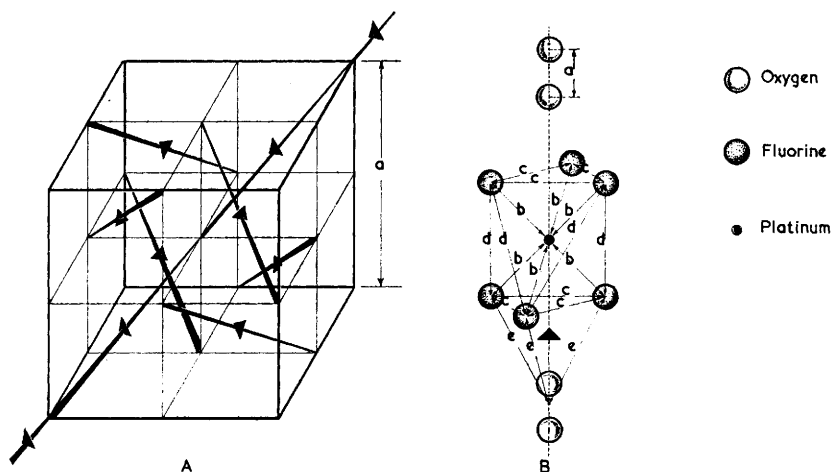
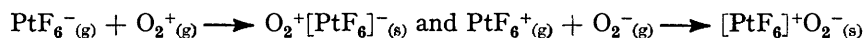


FIG. 1.

(A) Unit cell of $O_2^+[PtF_6]^-$ (cub.). $a = 10.032 \text{ \AA}$. [The units shown in (B) lie along the three-fold axis indicated.] (B) Contents of cubic pseudo-unit cell. $a = 1.13$, $b = 1.74$, $c = 2.99$, $d = 2.57$, $e = 3.74 \text{ \AA}$.

$O_2^+[PtF_6]^-$ or $PtF_6^+O_2^-$ is consistent with the crystal structure. Lattice-energy calculations, with Kapustinskii's equations,¹⁶ for the processes:



give values $\sim 120 \text{ kcal. mole}^{-1}$. But formulation as $[PtF_6]^+O_2^-$ would require $< 100 \text{ kcal. mole}^{-1}$ for the first ionisation of platinum hexafluoride, less energy than for the first ionisation of the potassium atom, since the molar enthalpy of formation of the superoxide ion,¹⁷ $O_{2(g)} + e \longrightarrow O_2^-(g)$, is $-19 \text{ kcal. mole}^{-1}$. On this evidence alone, the $PtF_6^+O_2^-$ formulation can be rejected. For the $O_2^+[PtF_6]^-$ formulation, since the energy for the first ionisation of molecular oxygen¹⁸ is $-281 \text{ kcal. mole}^{-1}$, the required minimum energy for the electron affinity of platinum hexafluoride is $-161 \text{ kcal. mole}^{-1}$. Although unusually high, the value is compatible with the spontaneous dissociation of the hexafluoride; it indicates that platinum hexafluoride is perhaps the strongest oxidising agent known.

¹⁵ Aynsley, Peacock, and Robinson, *J.*, 1952, 1231.

¹⁶ Kapustinskii, *Quart. Rev.*, 1956, 10, 283.

¹⁷ Evans and Uri, *Trans. Faraday Soc.*, 1949, 45, 217.

¹⁸ Field and Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957, pp. 114—116.

The good agreement between the X-ray line intensities and those calculated on the basis of the ionic formula $O_2^+[PtF_6]^-$ (Table 3) strongly supports this model. Since, however, the contribution which an atom makes to line intensity is roughly proportional to the square of the atomic number and since there are only two oxygen atoms ($Z = 8$), against six fluorine atoms ($Z = 9$), to every platinum atom ($Z = 78$), these intensities are insensitive to small changes in the parameters of the oxygen atom. The limited intensity data available did not, therefore, allow the dioxygenyl ion interatomic distance to be precisely determined and, as the O_2^+ (1.12 Å) and O_2^- (1.28 Å) ion interatomic distances¹³ are very similar, X-ray evidence could not disprove the $PtF_6^+O_2^-$ formulation.

The structure reveals that the PtF_6 octahedra, one of which is represented in Fig. 1, are compressed along the three-fold rotation axis along which the dioxygenyl ions lie. This trigonal distortion of the MF_6^- ion is similar to that previously observed in the rhombohedral potassium hexafluoro-osmate(v) structure.¹⁹ Each O_2^+ ion has twelve fluorine neighbours, six in a puckered ring and almost coplanar with the ion, the other six in sets of three, one above and one below this plane. The situation of the dioxygenyl ion with its long axis coincident with the three-fold rotation axis is more acceptable on the grounds of close packing than the alternative random orientation (equivalent to rotation) of the ion. Apart from the non-spherical nature of the cation, the structure is almost identical with that proposed for the potassium hexafluoroantimonate(v).²⁰

As the nitrosyl ion, NO^+ , is similar in size¹³ and shape to the dioxygenyl ion, O_2^+ , a resemblance of the dioxygenyl hexafluoroplatinate(v) diffraction patterns to those of nitrosyl hexafluoro-osmate(v), -ruthenate(v), and -antimonate(v) is expected. Moreover, since the first ionisation energy of the nitric oxide molecule²¹ is 62 kcal. mole⁻¹ lower than that of oxygen, nitrosyl salts are not uncommon. From the unit-cell sizes and molar

TABLE 5.

Unit-cell dimensions and molecular volumes for $O_2^+[PtF_6]^-$ and some $A^+[BF_6]^-$ compounds.

Structure type is indicated by: C (cubic), R (rhombohedral).					
	a (Å)	U (Å ³)		a (Å)	U (Å ³)
O_2PtF_6 C	10.032	126.3	O_2PtF_6 R	~4.96, 97.5	~119.9
(NO)RuF ₆ C *	10.087	128.3	KPtF ₆ R	~4.96, 97.4	~119.9
(NO)OsF ₆ C *	10.126	129.8	KRuF ₆ R ††	4.96, 97.5	119.9
(NO)SbF ₆ C *	10.193	132.4	KOsF ₆ R †	4.991, 97.18	121.6
KSbF ₆ C *	10.142	130.4			

* Bartlett and Jha, unpublished work. † Weise and Klemm, *Z. anorg. Chem.*, 1955, **279**, 74. ‡ Hepworth, Jack, and Westland, *J. Inorg. Chem.*, 1956, **2**, 79.

volumes of various salts (Table 5), the nitrosyl and dioxygenyl ions are both clearly similar in size and are no more than 2 Å³ bigger than the potassium ion. The hexafluoroplatinate(v) ion is the smallest MF_6^- ion among the platinum metals, because platinum has the largest nuclear charge; the non-bonding d_e -electrons have a negligible shielding effect.

The magnetic behaviour of the compound is unusual for a complex of an element of the third transition series, in that the susceptibility obeys the Curie-Weiss law, $\chi_M \propto 1/(T + \theta)$, where $\theta = +45^\circ$. This and the magnitude of the magnetic moment μ_{eff} (2.57 B.M.) are compatible with the effect of the d_e^5 -configuration of the Pt^{5+} and the unpaired electron associated with the dioxygenyl ion. Since, for the third transition series, the spin-orbit interaction is great,²² the magnetic moment associated with the

¹⁹ Hepworth, Jack, and Westland, *J. Inorg. Nuclear Chem.*, 1956, **2**, 79.

²⁰ Bode and Voss, *Z. anorg. Chem.*, 1951, **264**, 144.

²¹ Tate, Smith, and Vaughan, *Phys. Rev.*, 1935, **48**, 525; Hagstrum and Tate, *ibid.*, 1941, **59**, 354.

²² Earnshaw, Figgis, Lewis, and Nyholm, *Nature*, 1957, **179**, 1123.

d_e^5 -configuration is almost temperature-independent over the range used and is 1.73 B.M. It is also to be expected that the magnetic behaviour of the dioxygenyl ion will resemble that of nitric oxide, with which it is isoelectronic. Although the magnetic moment of nitric oxide does vary with temperature,²³ the variation is small in the range 110–300°K. The recorded values have been used in computing the magnetic moment for a nitric oxide

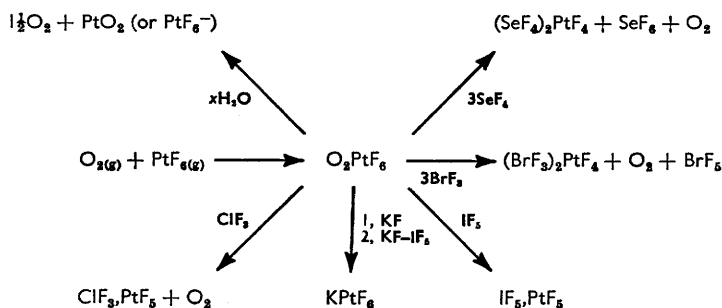


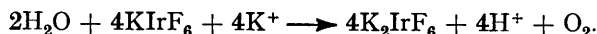
FIG. 2. Chemical relationships of O_2PtF_6 .

hexafluoroplatinate(v) ion combination, $\mu = 2.839\sqrt{[\chi_M(\text{NO}) + \chi_M(\text{PtF}_6^-) \times T]}$. The values $\chi_M(\text{PtF}_6^-)$ were assessed from $\mu = 1.73$ B.M. As may be seen from Table 6, the moments calculated in this way are similar to those found for the dioxygenyl salt.

TABLE 6.

Temp. (K)	113°	178°	300°
$\mu_{\text{calc.}}$ (B.M.)	2.31	2.40	2.56
$\mu_{\text{obs.}}$ (B.M.)	2.12	2.28	2.34

As chemically summarised in Fig. 2, the compound behaves as a powerful oxidising agent and as a derivative of platinum(v). Its hydrolysis by water vapour to oxygen, platinum dioxide, and hydrogen hexafluoroplatinate(iv) resembles that of osmium(v), iridium(v), and ruthenium(v) fluoro-salts, which are similarly reduced to the acids of their 4+ ions: ²⁴ *e.g.*,



The authors are indebted to Dr. David Frost for mass-spectrometric analyses and gratefully acknowledge support from the National Research Council, Ottawa, the Research Corporation, and the President's Research Fund, the University of British Columbia. One author (D. H. L.) also thanks the Consolidated Mining and Smelting Company of Canada Ltd. for a Cominco Fellowship.

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

[Received, May 21st, 1962.]

²³ Bhatnagar and Mather, "Physical Principles and Applications of Magnetochemistry," Macmillan and Co. Ltd., London, 1935, p. 174.

²⁴ Hepworth, Robinson, and Westland, *J.*, 1954, 4268.