862. *The Simple Fluorides of Iridium, including the New Trifluoride.*

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The hexafluoride and tetrafluoride of iridium have been re-investigated, and improved methods of preparing the latter developed. Some new reactions of the hexafluoride are described. These have led to the isolation of new compounds, including IrF_5,SF_4, IrF_5,SO_2, $(NO)_2IrF_6$, $(NO_2)_2IrF_6$, $(NO)_2IrF_5$, and $(NO_2)_2IrF_5$. No evidence of the formation of a pentafluoride has been secured; but the trifluoride, hitherto unknown, has been prepared and characterised. The iridium fluorides are briefly considered in relation to the simple fluorides of other members of Group VIII.

Observations by Hepworth, Robinson, and Westland,[1] during isolation of the hexafluoroiridates(v) and hexafluoroiridates(iv), prompted a re-investigation of the simple fluorides of iridium. The available information about them is a paper by Ruff and Fischer,[2] published twenty-seven years ago; in this the hexafluoride, IrF_6, and tetrafluoride, IrF_4, were characterised and the possibility of a still lower fluoride was mooted. In the work described here, the formation of the hexa- and tetra-fluoride has been confirmed and both have now been extensively studied; in addition the occurrence of a third fluoride has been established and it is shown to be the trifluoride, IrF_3.

Iridium Hexafluoride.—This is best prepared directly from the elements at 300—400°, is bright yellow, melts at 44° and boils at 53°. The vapour is dense and deep yellow and is stable up to red heat. It is the only compound in which iridium is unequivocally in the sexavalent condition, and measurements of its magnetic moment, made for us by Professor Nyholm, are in conformity with an octahedral distribution of the bonds about the metal, and show that Hund's rules of maximum multiplicity are obeyed in this valency state. Table 1 illustrates the outer electronic configuration of iridium(vi) and its similarity to those of rhenium and osmium in the isoelectronic ReF_6^{2-} and OsF_6^- ions (the octahedral shape of the molecule has recently been deduced from its infrared spectrum [3]). The effective magnetic moment as measured, 3·3 B.M., is appreciably lower than the value calculated, 3·88 B.M., owing presumably to a Russell–Saunders type of coupling between the resultant spin and orbital angular momenta. The presence of this *L–S* coupling would be established by a temperature-susceptibility study of the compound.

Table 1.

Compound	Valency	Outer electronic configuration 5*d*	 6*s*	 6*p*	Magnetic moment (B.M.) Found	 Calc.
K_2ReF_6 ...	iv	[↓][↓][↓][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	3·2 [a]	3·88
$KOsF_6$	v	[↓][↓][↓][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	3·2 [b]	3·88
IrF_6	vi	[↓][↓][↓][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	3·3 [c]	3·88

[a] Weise, *Z. anorg. Chem.*, 1956, **283**, 377. [b] Hepworth, Robinson, and Westland, *J.*, 1954, 4268. [c] Present work.

Although very stable, the hexafluoride is extremely active chemically and behaves as a strong fluorinating agent, in which respect it is comparable with osmium octafluoride (see Ruff and Tschirch [4]). Contrary, however, to the findings by Ruff and Fischer [2] this reactivity does not prevent the hexafluoride from being handled in glass at temperatures

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[1] Hepworth, Robinson, and Westland, *J.*, 1954, 4269.
[2] Ruff and Fischer, *Z. anorg. Chem.*, 1929, **179**, 161.
[3] Mattraw, Hawkins, Carpenter, and Sabol, *J. Chem. Phys.*, 1955, **23**, 985.
[4] Ruff and Tschirch, *Ber.*, 1913, **46**, 929.

below 150°, provided the glass has been rigorously dried. In this connection, we have found no evidence for the oxyfluoride, $IrOF_4$, which Ruff and Fischer thought was formed when the hexafluoride is left in contact with glass. All our experiments which might conceivably have led to the isolation of such a substance, for example, keeping the hexafluoride in a glass vessel for several months, and repeated fluorination of iridium dioxide, IrO_2, failed to give a sign of an oxyfluoride.

Since sexavalent iridium readily acquires electrons, the reactions of the hexafluoride naturally involve its reduction to one of the lower valency states.

Quinquevalent iridium, as found in the anion IrF_6^-, is the stable state of the element in a liquid fluoride medium, such as bromine trifluoride. When the fluoride solvent is itself susceptible of further fluorination, the iridium hexafluoride is reduced to the quinquevalent condition; thus, for example, Hepworth, Robinson, and Westland [5] have shown that in selenium tetrafluoride the product is the " acid " SeF_3,IrF_6. We find a similar reaction takes place even more readily with the sulphur tetrafluoride, SF_4, recently made available.[6] In this instance, the resulting material has the empirical composition IrF_5,SF_4, though whether it should have a formulation analogous to the corresponding selenium compound must await more evidence on the existence of the SF_3^+ cation. Liquid sulphur dioxide also appears to bring about a reduction to the quinquevalent condition, giving a product represented by IrF_5,SO_2.

Quadrivalent iridium is the result of most reductions of the hexafluoride, the compound isolated depending upon the reducing agent employed. Thus hydrogen, chlorine, and iodine under appropriate conditions produce the tetrafluoride, IrF_4, being themselves fluorinated in the process. On the other hand, both nitric oxide and gaseous dinitrogen tetroxide combine readily with the hexafluoride to give nitrosonium hexafluoroiridate(IV), $(NO)_2IrF_6$, and nitronium hexafluoroiridate(IV), $(NO_2)_2IrF_6$, which separate in the pure condition as pale yellow and white solids respectively. That these compounds are nitrosonium and nitronium salts is demonstrated by their reaction with water to form a mixture, in the first instance, of nitrous acid and, in the second, of nitric acid, with hexafluoroiridic acid, H_2IrF_6. The mechanism of their formation is most probably an electron-transfer from the oxide to the fluoride; certainly, although these were looked for in the experiments, nitrosyl fluoride, nitryl fluoride, and iridium tetrafluoride were not detected. Thermal degradation of the salts results in the loss of a fluorine atom from each and in compounds having the compositions $(NO)_2IrF_5$ and $(NO_2)_2IrF_5$ respectively.

Liquid sulphur trioxide also reacts, though slowly, with iridium hexafluoride to give an ill-defined, dark blue product with a composition approximating to $IrF_4,3SO_3$.

We investigated qualitatively a variety of other reactions of the hexafluoride; in many of these, reduction reaches the stage of the free element which manifests itself in the *X*-ray powder photographs. Thus carbon monoxide and ammonia each reduced it vigorously to the metal. Phosphorus trifluoride, which we had hoped would co-ordinate to give an identifiable derivative, produces dark green solids of variable composition always heavily contaminated with the free element.

Iridium Tetrafluoride.—This compound is to be regarded as the parent of the hexafluoroiridates(IV). Methods for its preparation all involve reduction of the hexafluoride. Ruff and Fischer [2] used iridium metal in a sealed quartz tube at 150° for this purpose; the method gives an almost quantitative yield. However, a little above 200° the hexafluoride attacks glass readily and is thereby reduced to tetrafluoride; the temperature at which this occurs is quite well defined and the reaction forms the most convenient way of preparing the tetrafluoride. Finally, we find that the pure tetrafluoride is formed, though in poor yield, in the photolysis of iridium hexafluoride by ultraviolet light.

When pure, iridium tetrafluoride is a yellow solid, melting at 106—107° to a dark yellow liquid which boils above 300°. It is very sensitive to moisture, being rapidly hydrolysed to hydrated iridium dioxide and hydrofluoric acid; it is a poor fluorinating agent, in which respect it rather resembles ruthenium pentafluoride, RuF_5. Like the hexafluoride, it is

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[5] Hepworth, Robinson, and Westland, *Chem. and Ind.*, 1955, 1516.

[6] Brown and Robinson, *J.*, 1955, 3147.

reduced to the metal by carbon monoxide; but it does not react with nitric oxide to give a nitrosonium salt.

Iridium Trifluoride.—Ruff and Fischer[2] noticed that when iridium tetrafluoride was strongly heated, their black residues varied in composition, the iridium : fluorine atomic ratio ranging from 1 : 1 to 1 : 4. An examination of the formulæ of the lower fluorides of Group VIII, given in Table 2, shows *two* trifluorides in the iron and *three* in the ruthenium triad; and we early felt that, should there be a third fluoride of iridium, it ought to belong to this class. Our thermal decompositions of the tetrafluoride in glass within a certain temperature range do actually give black solids which are pure iridium trifluoride, but the method is tedious and the yields small. By heating iridium tetrafluoride in an atmosphere of sulphur tetrafluoride a slightly better yield of trifluoride is more easily obtained. With a view to further improving the yield other reactions were examined, but all give impure products; among these may be cited the reaction of iridium on iridium hexafluoride, and the reduction of iridium tetrafluoride severally with iodine, sulphur, and hydrogen.

Iridium trifluoride is a brownish-black to black solid, insoluble in and unaffected by water, and attacked only slowly by concentrated acids and alkalis. In these respects it resembles the ruthenium and the rhodium trifluoride with which it is isostructural; the rhombohedral unit cell contains two molecules and has the dimensions $a = 5{\cdot}42$ Å, $\alpha = 54{\cdot}3°$. Structural details will be published elsewhere.[7] Thermally the trifluoride is not very stable; above 250° it begins to lose fluorine and give iridium metal. This probably accounts for the variable composition observed by Ruff and Fischer.

TABLE 2.*

FeF_2	CoF_2	NiF_2
FeF_3	CoF_3	
		$[PdF_2]$
RuF_3	RhF_3	PdF_3
	RhF_4	
RuF_5 : m. p. 106°; b. p. 313°		
	IrF_3	
$[OsF_4]$	IrF_4 : m. p. 106—107°; b. p. >300° [c]	PtF_4
OsF_6 : m. p. 74·5°; b. p. 200° [a]	IrF_6 : m. p. 44·4°; b. p. 53° [d]	
OsF_8 : m. p. 34°; b. p. 47° [b]		

* Compounds given in brackets cannot be held to be established with certainty.

[a] Hepworth, Ph.D. Thesis, Durham, 1956, p. 55. [b] Ruff and Tschirch, *Ber.*, 1913, **46**, 929. Present work. [d] Ruff and Fischer, *Z. anorg. Chem.*, 1929, **179**, 161.

We have sought to settle the question of the existence of a pentafluoride of iridium—the hypothetical parent of the hexafluoroiridates(v)—but all our evidence points to its absence from the series; as with osmium the simple pentafluoride does not seem to occur.

The now known simple fluorides of the Group VIII elements are listed in Table 2. When a group is set out in this way resemblances between the elements are generally to be sought in a vertical direction though these are not particularly marked in Group VIII. In this respect, however, the new iridium trifluoride provides a link between the third and earlier triads. In its fluorine chemistry iridium also exhibits certain similarities to the diagonally placed ruthenium and to the horizontally disposed osmium. In particular, these elements all form isostructural complex fluorides of the types $K_2M^{IV}F_6$ and $KM^{V}F_6$, and we can trace this relationship back to likenesses between the simple fluorides. For instance, iridium tetrafluoride and ruthenium pentafluoride display a marked similarity in chemical properties and, as an examination of Table 2 shows, the relation extends to some of their physical properties. Again, the essentially covalent iridium hexafluoride lies physically and chemically closer to osmium octafluoride than it does to osmium hexafluoride.

EXPERIMENTAL

Preparation of Iridium Hexafluoride.—To prepare iridium hexafluoride Ruff and Fischer[2] fluorinated iridium metal in a fluorite tube and fractionated the product in a quartz apparatus.

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[7] Hepworth, Jack, and Westland, unpublished work.

We found that the hexafluoride was indifferent to Pyrex glass up to about 150°, provided the surface had been rigorously freed from moisture, and that it could be conveniently handled in this glass. These conditions were achieved by baking-out the apparatus at 300—400° at about 10^{-3} mm., and having well-cooled "guard" traps. Fluorine, freed from hydrogen fluoride by passage over sodium fluoride pellets followed by a trap at $-180°$, and diluted with nitrogen, was passed over iridium in an alumina boat at 300—400°. The temperature at which reaction began depended on the history and state of division of the metal. The bright yellow hexafluoride vapour was collected at $-65°$ in a Pyrex-glass train, and there subjected to a trap-to-trap distillation in a vacuum. Still under a vacuum, it was either transferred to a break-seal vessel for storage, or used directly in an all-glass apparatus. The absence of greased joints and taps was essential, since we found that iridium hexafluoride attacked, and suffered contamination from, all the greases tried.

Preparation of Iridium Tetrafluoride.—(a) *Reduction of iridium hexafluoride by iridium metal.* This was effected by carrying the fluoride in a slow stream of dry nitrogen over the metal in a nickel boat in a heated Pyrex-glass tube. At 100° reduction was slow, but between 150° and 170° it was much quicker and practically quantitative. The tetrafluoride condensed to a yellow-brown oil beyond the heated zone, and was purified by fractional distillation at 120—140°/10^{-2} mm. The vapour passed directly into a solid at the cooled surface; this solid, when pure, consisted of yellow, needle-shaped crystals. The valency of the iridium was established by allowing it to react with potassium iodide (2%) in N-sulphuric acid and estimating the iodine with thiosulphate. One equivalent of iodine was liberated per equivalent of iridium which was itself reduced to the tervalent state, indicating a valency of four in agreement with the value found by Ruff and Fischer.[2] The crystalline material melted sharply at 106—107° to a dark yellow liquid which, on cooling, set to a glass that crystallised only on very long storage. The b. p. was found to be above 300°; a more precise estimate was impossible because of decomposition and attack on the glass. Pure iridium tetrafluoride could be kept indefinitely in glass under dry air, but in moist air it fumed and was rapidly hydrolysed to a hydrated oxide and hydrofluoric acid. With excess of water, it reacted vigorously to form a purple solution containing colloidal oxide and hydrofluoric acid.

(b) *Reduction of iridium hexafluoride by glass.* This was attained by passing the fluoride through a heated Pyrex tube in a slow stream of dry nitrogen. Below 190° there was no visible attack or decomposition; but, at 250°, an almost quantitative yield of the tetrafluoride was obtained, again as a yellow-brown oil. This was purified as already described (Found: Ir, 71·4. Calc. for IrF_4: Ir, 71·7%). The silicon tetrafluoride, boron trifluoride, and alkali fluorides simultaneously formed were easily separated from the product.

(c) *Photolysis of iridium hexafluoride.* 1 G. portions of the fluoride were sealed in transparent silica bulbs furnished with break-seals. These were irradiated at the ambient temperature for 6 days with ultraviolet light from a mercury-vapour lamp at a distance of 6 in. The yield of yellow crystalline solid was poor (30% conversion), but was pure tetrafluoride. The unchanged iridium hexafluoride, silicon tetrafluoride, and oxygen were removed under a vacuum. Presumably the photolysis, $IrF_6 \longrightarrow IrF_4 + F_2$, released fluorine which slowly reacted with the silica ($SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$).

Preparation of Iridium Trifluoride.—(a) *Reduction of iridium tetrafluoride by glass.* This was brought about by heating the fluoride in a glass vessel under dry air. At 280° there was only a slight darkening of the liquid and inappreciable decomposition, but at 430—450° a solid appeared and continued to be formed. After 12—18 hr., the resulting black mass was found to contain, besides an insoluble portion, some residual tetrafluoride. The latter was removed by washing the whole with water followed by 15% hydrochloric acid until the runnings were no longer coloured; afterwards water, alcohol, and ether were used, and finally the solid was dried at 40°. It proved to be *iridium trifluoride* (Found: Ir, 77·0. IrF_3 requires Ir, 77·2%). The identity of the new compound was settled by Debye *X*-ray powder photographs which showed it to be free from iridium metal and dioxide, and to be isostructural with palladium and rhodium trifluorides. The lattice was rhombohedral and contained two molecules per unit cell with $a = 5{\cdot}42$ Å and $\alpha = 54{\cdot}3°$.

(b) *Reduction of iridium tetrafluoride by sulphur tetrafluoride.*[6] This was effected by passing the vapour of sulphur tetrafluoride over the iridium compound in a heated glass tube. At about 100° the iridium tetrafluoride absorbed some sulphur tetrafluoride, becoming brown; then, at 350—400°, a rapid reaction produced brownish-black iridium trifluoride, only slightly contaminated with the tetrafluoride. The latter was removed as before. The yield was better, without apparent decrease in purity. Furthermore, sulphur tetrafluoride appeared to inhibit the decomposition of iridium trifluoride to metal and fluorine, for even heating to 550—600° in sulphur tetrafluoride left the compound largely intact.

In the absence of iridium tetrafluoride, the trifluoride was decomposed into its elements when heated above 250° in alumina under dry air. The decomposition was slow at 250°, but became faster before 450° was reached, being then complete in 30 min. Hence, in the preparation, the necessity for stopping heating before all the iridium tetrafluoride was spent, and for controlling the temperature to avoid either a too tedious preparation or a product adhering to the glass. It has been mentioned that the trifluoride was insoluble in water and dilute acids: even with concentrated acids attack was slow.

The Supposed Oxyfluoride of Iridium.—(a) *Action of iridium hexafluoride on glass.* When handling iridium hexafluoride in glass, a careful watch was kept for non-volatile residues. These, usually cream to pale yellow, were always in insignificant quantities—quite insufficient for characterisation. When treated with water, traces of gas, probably oxygen, were evolved and colourless to pale yellow solutions were left. This suggested that these residues, and probably the material which Ruff and Fischer supposed to be $IrOF_4$, were complex salts of quinquevalent iridium of the type $M^IIrF_6(v)$, resulting, very feasibly, from the reaction between iridium hexafluoride and the alkali of the glass. Keeping the hexafluoride in a well-dried vessel at room temperature for several months did not appreciably increase the residues, nor did limited additions of moisture stimulate their formation. The effect of the latter was to produce at first some tetrafluoride and, finally, hydrated iridium oxide and hydrogen fluoride.

(b) *Fluorination of iridium dioxide.* Iridium dioxide was prepared by fusing sodium hexachloroiridate(IV) with fusion mixture in a platinum dish, extracting the melt with hot water, and washing the black residue with more hot water followed by dilute hydrochloric acid to remove adsorbed alkali. Subsequent heating for 4 hr. at 600° in a stream of dry oxygen yielded pure anhydrous iridium dioxide, as was shown by its Debye *X*-ray photograph. Fluorine, very well diluted with oxygen, was passed over this material in a nickel boat in a transparent silica tube. The temperature was slowly raised without evidence of reaction until 350°; at this point the oxide was rapidly and completely converted directly into hexafluoride.

Reactions of Iridium Hexafluoride.—(a) *Hydrogen.* The gas, dried by cooling to −180°, reacted quietly with iridium hexafluoride vapour at 60° giving yellow-brown, oily droplets of the tetrafluoride and hydrogen fluoride. At 100°, however, the reduction proceeded further and more rapidly, producing metallic iridium, as shown by an *X*-ray of the black product. There did not appear to be an intermediate stage in the reduction from the four to the zero valency state.

(b) *Iridium metal.* The residue remaining in the boat after preparation of iridium tetrafluoride (see above) was principally unchanged metal together with a little trifluoride. But when the reaction was carried out at about 500° in an all-nickel apparatus, and the product was allowed to cool in iridium hexafluoride vapour, the material contained up to 50% of the trifluoride. A complete conversion of the metal into trifluoride by this reaction was probably impossible; first, because an initial protective layer of the trifluoride effectively hindered further attack and, secondly, because this trifluoride layer, in the presence of a large excess of iridium hexafluoride, was further fluorinated to the tetrafluoride: thus iridium metal and tetrafluoride tended to be the ultimate products.

(c) *Halogens.* (i) Chlorine, diluted (1 : 1) with dry nitrogen, reacted quietly with iridium hexafluoride vapour at 55—60° to give dark green, oily droplets and a chlorine fluoride, the latter being carried out of the reaction zone by the chlorine–nitrogen stream. Distillation of the liquid in a vacuum at 120—140° yielded a chlorine-free sublimate of yellow iridium tetrafluoride.

(ii) Purified dry iodine, in amount calculated for $5IrF_6 + I_2 \longrightarrow 5IrF_4 + 2IF_5$, gave, at room temperature, a product identical in appearance with iridium tetrafluoride; however, it retained traces of iodine pentafluoride even after distillation at 10^{-2} mm. It reacted vigorously with more iodine at 120°; the black products, after being heated in a vacuum at 100° for 24 hr., varied in composition. One specimen approximated to $Ir_2F_6I_3$ (Found: Ir, 43·0; F, 11·9. Calc. for $Ir_2F_6I_3$: Ir, 43·8; F, 12·9%) and the *X*-ray photograph showed neither iridium trifluoride nor metal, indeed no identifiable pattern. It was insoluble in water and dilute hydrochloric acid, but dissolved in aqueous potassium hydroxide forming a chocolate-coloured solution which became reddish-violet when boiled. Heated dry to 400°, it gave iridium metal. Since both iodine and iridium hexafluoride dissolve in iodine pentafluoride, solutions of each were mixed at room temperature, and, after the supernatant liquid had been boiled, the precipitate was removed and heated to 150° in a vacuum. The solid was dark purple, slightly hygroscopic, decomposed to metal at 400°, and approximated to $IrF_3,0{\cdot}2I$ (Found: Ir, 70·5; F, 20·3. Calc. for $IrF_3,0{\cdot}2I$: Ir, 70·1; F, 20·7%), but could not be identified by *X*-ray investigation.

(d) *Sulphur trioxide.* Specially prepared sulphur trioxide which had been kept over phosphoric oxide for several hours was purified by repeated trap-to-trap distillation and condensed on to solid iridium hexafluoride. The latter proved to be insoluble and the ensuing reaction slow as the solid changed through yellow, green, and brown to blue. After 1—2 hours' refluxing and removal of the sulphur trioxide in a vacuum, a deep blue solid with the composition $IrF_4,3SO_3$ was left (Found: Ir, 38·0; SO_3, 47·1. $IrF_4,3SO_3$ requires Ir, 37·9; SO_3, 47·2%). The iridium had a valency of four. The *compound* was hygroscopic in moist air, and in water dissolved to give a deep blue solution which slowly became blue-violet and, when boiled, reddish-violet. Dwyer and Gyarfas[8] obtained dark blue, ill-defined solids from oxidised solutions of iridium(III) sulphate, perchlorate, and nitrate and suggested that the colours were due to the $[IrO{\cdot}OH]^+$ ion (blue-violet) and IrO^{++} ion (reddish-violet). We were able to show that iridium was present as a cation in the deep blue solution by passing it through an exchange resin (hydrogen-charged): the blue material was absorbed. In concentrated sulphuric acid the blue colour was stable for several days.

(e) *Sulphur tetrafluoride.* Iridium hexafluoride reacted quietly with liquid sulphur tetrafluoride at −60° to give a precipitate which, after the removal of supernatant reactant under a vacuum at room temperature, appeared as a light brown powder (Found: Ir, 48·5; F, 42·1; S, 8·5. IrF_5,SF_4 requires Ir, 48·7; F, 43·2; S, 8·1%). With water this *compound* was hydrolysed completely to colloidal iridium oxide and sulphurous and hydrofluoric acid; there was no evidence of the IrF_6^{--} ion. The compound, IrF_5,SF_4, when heated at 10^{-2} mm. melted at 125—130°, with decomposition and release of sulphur tetrafluoride, to a brown oil. But even after refluxing at 150° until no further evolution of vapour was observed, the liquid still contained much sulphur tetrafluoride (cf. the reaction between iridium hexafluoride and selenium tetrafluoride; Hepworth, Robinson, and Westland[5]).

(f) *Sulphur dioxide.* Pure liquid sulphur dioxide dissolved iridium hexafluoride to form a deep orange-red solution which, after the removal of the solvent in a vacuum at room temperature, left orange-brown crystals of a *compound* IrF_5,SO_2 (Found: Ir, 55·5; F, 26·9; SO_2, 17·1%; equiv., 355. IrF_5O_2S requires Ir, 54·8; F, 27·0; SO_2, 18·2%; equiv., 352). In water, this was hydrolysed immediately to colloidal iridium oxide, sulphur dioxide, and hydrofluoric acid, and, in a vacuum at 40°, decomposed to an unidentified gas and iridium tetrafluoride.

(g) *Nitric oxide.* This was prepared by the action of dilute nitric acid on copper, freed from nitrogen peroxide by bubbling through 10% sodium hydroxide solution, and stored over air-free water. Before use, the nitric oxide was led in a stream of oxygen-free nitrogen through traps at −75° and over phosphoric oxide to remove moisture and easily condensed impurities. Reaction between solid iridium hexafluoride and nitric oxide began at −75°, was completed by heating to 60° for 15 min., and left a pale yellow powder, *nitrosonium hexafluoroiridate*(IV) [Found: Ir, 52·5; F, 31·7; NO, 16·5. $(NO)_2IrF_6$ requires Ir, 52·6; F, 31·1; NO, 16·3%]. (There was no sign of a concurrent formation of iridium tetrafluoride or nitrosonium fluoride.) This reacted vigorously with water, evolving oxides of nitrogen and forming hexafluoroiridic(IV) acid, H_2IrF_6. The structure of the latter was proved by the precipitate of white barium hexafluoroiridate(IV) (identified by a Debye *X*-ray photograph) produced by aqueous barium nitrate. The nitrosonium salt was stable up to 250°, above which it darkened and finally melted to a black viscous liquid which could be distilled unchanged at 250—300° in a vacuum. On cooling, the liquid readily solidified to a black *product* having the composition $(NO)_2IrF_5$ [Found: Ir, 56·5; F, 27·9; NO, 17·0. $(NO)_2IrF_5$ requires Ir, 55·5; F, 27·3; NO, 17·2%]. Its reactions suggested the complex fluoride of tervalent iridium $(NO^+)_2IrF_5^{--}$. It dissolved completely in water, evolving oxides of nitrogen and forming a red solution which, when boiled, gave a precipitate of an iridium oxide. When passed through a cation-exchange resin the red material was absorbed, leaving the solution dark olive-green. Aqueous potassium hydroxide precipitated dark green iridium oxide and turned the solution green, indicating the presence of tervalent iridium (cf. Peacock[9]).

(h) *Dinitrogen tetroxide.* Dinitrogen tetroxide was condensed on to phosphoric oxide at −20° and purified by trap-to-trap distillation in a stream of dry oxygen. Liquid dinitrogen tetroxide was first tried but in it, as in sulphur trioxide, the hexafluoride proved to be insoluble; the reaction was slow, and the product obviously heterogeneous. Homogeneity was attained by

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[8] Dwyer and Gyarfas, *J. Proc. Roy. Soc. New South Wales*, 1950, **84**, 123.

[9] Peacock, *J.*, 1955, 3291.

employing the vapours. Each, carried by nitrogen, was led into a 150 ml. bulb. Reaction was immediately evinced by formation of a white solid on the walls near the point of mixing. Analysis showed this to be *nitronium hexafluoroiridate*(IV) [Found : Ir, 48·4; F, 28·6. $(NO_2)_2IrF_6$ requires Ir, 48·4; F, 28·6%]. It reacted with water to form nitric acid and hexafluoroiridic(IV) acid, the latter being characterised by the precipitation of barium hexafluoroiridate(IV). When heated in a vacuum, nitronium hexafluoroiridate(IV), analogously to nitrosonium hexafluoroiridate(IV), formed a *compound* $(NO_2)_2IrF_5$ [Found : Ir, 50·1; F, 25·4. $(NO_2)_2IrF_5$ requires Ir, 50·8; F, 25·0%]. The reactions of this compound were similar to those of the corresponding nitrosonium compound, $(NO)_2IrF_5$, except that with water the nitronium fragment gave nitric acid.

Analysis.—Iridium and fluorine were determined as metal and lead chlorofluoride, respectively, by the methods described by Hepworth, Robinson, and Westland.[1]

Sulphur was determined as barium sulphate in the filtrate after removal of the iridium and oxidation of any sulphite by the addition of a few ml. of hydrogen peroxide (100-vol.), the solution being made 2N with hydrochloric acid to prevent precipitation of barium fluoride.

For determination of nitrogen, the individual compounds were decomposed in 10% aqueous sodium hydroxide and, after boiling, the solutions were filtered from iridium oxide. The nitrogen was determined in aliquot parts of the filtrate by reducing the nitrate or nitrite to ammonia with Devarda's alloy, absorbing the ammonia in 2% boric acid solution, and titrating it with 0·01N-hydrochloric acid, following the method of Kieselbach.[10]

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[10] Kieselbach, *Ind. Eng. Chem.*, *Anal.*, 1944, **16**, 764.