

Iridium Pentafluoride

By NEIL BARTLETT and P. R. RAO

(The Chemistry Department, The University of British Columbia, Vancouver 8, B.C., Canada)

ALTHOUGH a number of complex fluorides of quinquivalent iridium, (*e.g.* KIrF_6) are known, previous attempts^{1,2} to establish the simple fluoride have failed. The absence of a pentafluoride of iridium has become increasingly anomalous as the pentafluorides of the neighbouring elements, rhenium,³ osmium,⁴ and platinum⁵ have been prepared. Previous work^{1,2} indicated that reactions which might have yielded the pentafluoride gave the tetrafluoride instead. The physical properties of this tetrafluoride. (m.p. $106\text{--}107^\circ$; b.p. $> 300^\circ$),² however, resembled those of a pentafluoride or oxide tetrafluoride. This indicated that iridium tetrafluoride differed structurally from its neighbouring tetrafluorides.

We have now established the pentafluoride of iridium and believe that the previously reported tetrafluoride was the pentafluoride.

The pentafluoride was prepared by heating iridium metal in fluorine gas, the elements being in the required stoichiometric ratio. The container was a Monel metal vessel the lid of which was cooled by air, the base of the reactor being maintained at $350\text{--}380^\circ$. Yellow crystalline pentafluoride m.p. 104.5° collected on the lid [Found: F, 33.3; Ir, 66.3. IrF_5 requires: F, 33.1; Ir, 66.9%]. Following a method given previously² for the preparation of iridium tetrafluoride, iridium hexafluoride was heated at 350° in the reactor with powdered glass. A major product of the reaction, which also produced oxygen, silicon tetrafluoride, and involatile iridium-containing residues, was a yellow-green sublimate, m.p. $104\text{--}105^\circ$, which gave an identical X-ray powder pattern to that exhibited by authentic pentafluoride. The physical properties and appearance

¹ O. Ruff and J. Fischer, *Z. anorg. Chem.*, 1929, **179**, 161.

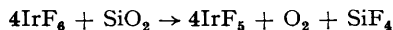
² G. J. Westland and P. L. Robinson, *J. Chem. Soc.*, 1956, 4481.

³ G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1960, 1099.

⁴ G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1960, 2618.

⁵ N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 1964, 619.

are similar to those ascribed to the tetrafluoride. It is surmised that the pentafluoride producing reaction is as follows:



The magnetic susceptibility of the pentafluoride has been measured over the temperature range

Table 2 gives some of the physical properties of the known pentafluorides. Iridium pentafluoride is isomorphous and nearly isodimensional with ruthenium pentafluoride and presumably has the nonlinear fluorine-bridged tetrameric molecular structure, reported⁸ by Holloway, Peacock, and Small for that fluoride. In this arrangement the

TABLE 1. *Magnetic susceptibility data for IrF₅*

Temp (°K)	77	90.6	105	123	154.7	172.6
10 ⁶ χ _A (CG/mole)	885	868	845	845	836	836
Temp (°K)	181.5	205.4	221	235.6	260	296
10 ⁶ χ _A (CG/mole)	833	805	782	759	727	727

TABLE 2. *Known pentafluorides of the second and third transition-series metals*

Compound	NbF ₅	MoF ₅	TcF ₅	RuF ₅		
m.p.; b.p. (°C)	80; 235 ¹¹	67; 213.6 ¹⁰	50 ¹² ;—	86.5; 230 ⁹		
crystal class	monoclinic (I) ¹²	monoclinic (I) ¹⁴	orthorhombic ¹³	monoclinic (II) ⁸		
a; b; c; (Å)	9.62; 14.43; 5.12	9.61; 14.22; 5.16	5.8; 7.6; 16.7	12.47; 10.01; 5.42		
β(°)	96.1	94.3		99.82		
Compound	TaF ₅		ReF ₅	OsF ₅	IrF ₅	PtF ₅
m.p.; b.p. (°C)	95; 229 ¹¹		48; 221.3 ¹⁰	70; 225.9 ¹⁰	105; —	80 ⁵ ;—
crystal class	monoclinic (I) ¹²		orthorhombic ⁸	monoclinic(II) ⁸	monoclinic (II)	
a; b; c; (Å)	9.64; 14.45; 5.12				12.5; 10.0; 5.4	
β(°)	96.3				99.8	

77—296°K and the behaviour is typical of a *d*⁴ electronic configuration in octahedral or near octahedral third-transition-series metal fluorides.⁶ The data, given in Table 1, is similar to that reported for hexafluoro-osmates(IV) and hexafluoroiridates(V), and to that found recently⁷ in these laboratories for platinum hexafluoride.

metal atoms are approximately octahedrally coordinated. Osmium pentafluoride has also been reported⁸ to be isomorphous with the ruthenium analogue.

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⁶ A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, *J. Chem. Soc.*, 1961, 3132.

⁷ N. Bartlett and N. K. Jha, Unpublished observation.

⁸ J. H. Holloway, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1964, 644.

⁹ J. H. Holloway and R. D. Peacock, *J. Chem. Soc.*, 1963, 527.

¹⁰ G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.*, 1961, 1568.

¹¹ F. Fairbrother and W. C. Frith, *J. Chem. Soc.*, 1951, 3051; F. Fairbrother, W. C. Frith, and A. A. Woolf, *J. Chem. Soc.*, 1954, 1031.

¹² A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

¹³ J. Edwards, D. Hugill, and R. D. Peacock, cited in *Proc. Chem. Soc.*, 1963, 205.

¹⁴ A. J. Edwards, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1962, 4486.