Attempted Synthesis of Osmium(VI) and Iridium(VI) Thiofluorides; the Preparation of $OsF_5{\cdot}SF_4$ and $IrF_5{\cdot}SF_4$

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The interaction of OsF_6 or IrF_6 with ZnS or B_2S_3 at elevated temperature yields the adducts $OsF_5{\cdot}SF_4$ and $IrF_5{\cdot}SF_4$ rather than the transition-metal thiofluorides. Infrared and *X*-ray powder diffraction studies indicate that the adducts have contributions to the bonding from the ionic formulations $[SF_3]^+[OsF_6]^-$ and $[SF_3]^+[IrF_6]^-$ and there is also ^{19}F n.m.r. evidence for the latter in solution in anhydrous HF.

Whereas oxofluorides of the transition metals, which span Groups 3A—8, have been well understood for many years[1] successful preparation, isolation, and characterisation of thio- and seleno-fluorides has taken place only recently.[2–17] So far, known species occur only in Groups 3A, 6A, and 7A. In the present study attempts to obtain osmium and iridium thiofluorides by methods similar to those used for tungsten, molybdenum, and rhenium species have resulted in the preparation of the previously identified and isostructural adducts $OsF_5{\cdot}SF_4$[18] and $IrF_5{\cdot}SF_4$.[18,19] These have been fully characterized and have contributions to their bonding from the ionic forms $[SF_3]^+$ $[OsF_6]^-$ and $[SF_3]^+$ $[IrF_6]^-$.

Results and Discussion

Attempts to prepare the compounds MF_4S (M = Os or Ir) by the direct reaction of the appropriate hexafluoride with ZnS or B_2S_3 at elevated temperature resulted in the formation of the adducts $MF_5{\cdot}SF_4$ (M = Os or Ir), sulphur fluorides, the metal (Os or Ir), and, in the experiments where B_2S_3 was used, BF_3 (see Table 1). The main solid products of the reactions were characterized as $[SF_3]^+[OsF_6]^-$ and $[SF_3]^+[IrF_6]^-$ by comparing their i.r. spectra (Table 2) with those of the solid products of the reactions of the appropriate hexafluorides with SF_4, which are known to produce these adducts, and *X*-ray powder diffraction patterns (Table 3) with data published earlier.[18] It seems likely that substantial interaction between the ions occurs through fluorine bridging as in the case of $[SeF_3]^+$-$[Nb_2F_{11}]^-$.[20]

These same compounds also appear to exist in solution as ionic species since a broad singlet characteristic of the $[SF_3]^+$ ion is observed in the ^{19}F n.m.r. spectrum of solutions of the iridium adduct in anhydrous HF (Table 4).

Efforts to prepare the osmium and iridium thiofluorides by the reactions of the appropriate hexafluorides with Sb_2S_3 in anhydrous hydrogen fluoride at room temperature gave only lower oxidation-state fluorides, SbF_3 and unreacted Sb_2S_3 (see Table 5).

Table 1. Thermal reactions

			Products	
Reactions	Temp./°C	Duration/h	Volatiles[a]	Solids[b]
IrF_6 + ZnS	300	7–11	SF_4, SF_6, S_2F_{10}	$IrF_5{\cdot}SF_4$, Ir
OsF_6 + ZnS	300	7–11	SF_4, SF_6, S_2F_{10}	$OsF_5{\cdot}SF_4$, Os
3 IrF_6 + B_2S_3	210	4–6	SF_4, SF_6, S_2F_{10}, BF_3	$IrF_5{\cdot}SF_4$, Ir
3 OsF_6 + B_2S_3	210	4–6	SF_4, SF_6, S_2F_{10}, BF_3	$OsF_5{\cdot}SF_4$, Os

[a] Identified by their i.r. spectra in comparison with those in R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, 1952, **52**, 1052 and K. O. Christe, W. Sawodny, and P. Pulay, *J. Mol. Struct.*, 1974, **21**, 158, for SF_4; J. Gaunt, *Trans. Faraday Soc.*, 1953, **49**, 1122, for SF_6; D. Eclelsen, *J. Am. Chem. Soc.*, 1952, **74**, 262 and J. K. Wilmhurst and H. J. Bernstein, *Can. J. Chem.*, 1957, **35**, 191, for S_2F_{10}. [b] Characterised by i.r. spectra and *X*-ray powder diffraction patterns.

Table 2. Comparison of i.r. spectra of solid products of reactions of MF_6(M = Os or Ir) and ZnS or B_2S_3 with those of $MF_5{\cdot}SF_4$ resulting from reactions of MF_6 with SF_4 (frequencies are in cm^{-1})[a]

				Assignments	
From OsF_6 + ZnS or B_2S_3	$OsF_5{\cdot}SF_4$	From IrF_6 + ZnS or B_2S_3	$IrF_5{\cdot}SF_4$	$[SF_3]^{+b}$	$[MF_6]^-$
922ms	925s,br	920s,br	920s,br	ν_1, ν_3	
	705w,m				ν_3
640s	~620vs,br	635ms,br	633s,br		
590w(sh)					
525ms	528s	522s	522s	ν_2	
	400s	400m	400ms	ν_4	

[a] w = Weak, m = medium, s = strong, v = very, br = broad. [b] Assigned by comparison with spectra published for $SF_4{\cdot}BF_3$ and $SF_4{\cdot}MF_5$ (M = P, As, or Sb) in M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, 1969, **47**, 4159.

Table 3. Comparison of *d* spacings for $OsF_5{\cdot}SF_4$ and $IrF_5{\cdot}SF_4$

This work			Ref. 18		
$OsF_5{\cdot}SF_4$	$IrF_5{\cdot}SF_4$	Relative intensity *	$OsF_5{\cdot}SF_4$	$IrF_5{\cdot}SF_4$	Relative intensity
5.584	5.582	6	5.564	5.581	8
3.932	3.930	10	3.934	3.934	10
3.211	3.209	3	3.204	3.202	6
2.786	2.786	3	2.781	2.776	5
2.484	2.482	4	2.486	2.482	6
2.273	2.271	6	2.273	2.267	7
1.974	1.972	3	1.970	1.966	5
1.849	1.850	4	1.856	1.855	7
1.758	1.759	4	1.763	1.758	5
1.682	1.680	1	1.679	1.678	4

* Visual estimations.

Table 4. Fluorine-19 chemical shifts (p.p.m. from $CFCl_3$)[a]

		Chemical shift	
Solute	*T*/°C	$[SF_3]^+$	HF
$BF_3{\cdot}SF_4$	-50^b	26.7	-194.2^b
$2AsF_5{\cdot}SF_4$	-60^b	26.8	-198^b
$SbF_5{\cdot}SF_4$	-60^b	27.1	-178.3^b
$IrF_5{\cdot}SF_4$	-29^c	31.0^c	-196^c

[a] A positive chemical shift denotes a positive frequency, and *vice versa*, with respect to the designated reference substance. [b] See reference cited in footnote *b* of Table 2. [c] This work.

Table 5. Reactions in anhydrous HF at room temperature

Reactants	Products
$3\ IrF_6 + Sb_2S_3$	SbF_3,[a] involatile brown powder which contains iridium, antimony, and sulphur[b]
$3\ OsF_6 + Sb_2S_3$	SbF_3, OsF_5, and unreacted Sb_2S_3[a]

[a] Determined by *X*-ray powder photography. [b] Determined by *X*-ray fluorescence spectroscopy.

Conclusions

The transition-metal hexafluorides increase in oxidant strength with increasing atomic number across any period of the Periodic Table.[21] The trend for the third-row transition series is: $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$.

The greater electron affinity of PtF_6 compared with that of WF_6 correlates with the greater charge on the platinum and with the poor shielding of this charge from the ligands by the formally non-bonded t_{2g} electrons. Since the non-bonding t_{2g} valence-electron configurations are: $WF_6 = 0$, $ReF_6 = 1$, $OsF_6 = 2$, $IrF_6 = 3$, $PtF_6 = 4$, a regular increase in oxidizing power may be anticipated. Thus, while WF_6 and ReF_6 can substitute sulphur to give WF_4S and ReF_4S respectively it is not surprising that OsF_6 readily oxidatively fluorinates B_2S_3 or ZnS to give SF_4 and that the reduced osmium species, OsF_5, then combines with this to give $OsF_5{\cdot}SF_4$ and that the analogous $IrF_5{\cdot}SF_4$ adduct is formed even more readily.

Experimental

Reagents.—The hexafluorides of osmium and iridium were prepared by direct high-pressure fluorination of the respective hydrogenated metal (Johnson Matthey, Spec. Pure grade) at *ca.* 300 °C. The resulting hexafluorides were purified by trap-to-trap distillation and final purities monitored by gas-phase i.r. spectroscopy and mass spectrometry. The reagents ZnS (Johnson Matthey, Puratronic), Sb_2S_3 (B.D.H., Technical Grade), and B_2S_3 (Ventron GmbH), were degassed prior to use. Anhydrous HF (B.D.H., 99.8%) was used directly from the cylinder.

Reactions of MF_6 (M = Os *or* Ir) *with* ZnS *or* B_2S_3.—Thermal reactions were carried out using between 0.8 and 3.0 mmol of the hexafluoride (5% excess) in pre-fluorinated stainless-steel reactors fitted with stainless-steel valves (Autoclave Engineers, 30VM Series). Appropriate amounts of ZnS or B_2S_3 were loaded into the reactors in a nitrogen-filled dry-box (Vacuum Atmospheres, Dri Lab.) and, after evacuation, the hexafluoride was introduced at liquid-nitrogen temperature *via* a vacuum manifold. Reactions involving anhydrous HF were carried out in pre-fluorinated FEP-Teflon (tetrafluoroethylene–perfluoropropylene co-polymer) reactors fitted with Teflon valves (Chemcon type, Production Techniques Ltd.), the reactants and anhydrous HF solvent being introduced as outlined above.

Reactions of MF_6 (M = Os *or* Ir) *with* SF_4.—Reactions were carried out in FEP-Teflon tubes fitted with Teflon needle valves. An approximately four-fold excess of SF_4 was distilled onto the appropriate hexafluoride (1—3 mmol) at liquid-nitrogen temperature and the mixture was warmed to −78 °C (solid CO_2 acetone bath). In the IrF_6 case reaction was immediate and vigorous. The reaction involving OsF_6 did not take place until further warming to −30 °C (ice–salt bath) had occurred and the reaction was complete only after 48 h. However, reaction was immediate at room temperature. In both the reactions of OsF_6 and IrF_6 fine crystalline products (Os, lilac; Ir, pale yellow) were obtained after removal of excess of SF_4.

Monitoring of the reactions by mass balance showed that 1 mol of hexafluoride reacts with 1 mol of SF_4 in each case. This result was confirmed by elemental analysis [Found: F, 42.1; Os, 47.9; S, 7.7. Calc. for $OsF_5{\cdot}SF_4$: F, 43.5; Os, 48.4; S, 8.1% Found: F, 43.6; Ir, 47.9; S, 7.6. Calc. for $IrF_5{\cdot}SF_4$: F, 43.3; Ir, 48.6; S, 8.1%].

Characterisation.—I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Solid samples were analysed as finely ground powders between KBr discs. Volatile samples were examined in a 10-cm path-length copper gas cell fitted with AgCl windows. Mass spectra were recorded on a V.G. Micromass 16B instrument, the samples being introduced directly into the ionization chamber. N.m.r. spectra were run in 5-mm outside diameter Kel-F (chlorotrifluoroethylene) tubes on a JEOL JNM-PS-100 instrument operating at 94.08 MHz. *X*-Ray powder patterns were recorded photographically on a Philips camera (diameter 11.46 cm) using Cu-K_α filtered radiation. Elemental analysis was performed by a commercial analyst.

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