Reactions of Complex Fluorides of Some 3*d* Metals in Anhydrous Hydrogen Fluoride

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Summary Elemental fluorine is generated chemically, and xenon is fluorinated, by certain fluorometallates in HF solution; solvolysis of MnF_6^{2-} and NiF_6^{2-} with AsF_5 in HF gives MnF_4 and NiF_3.

ANHYDROUS HF is an attractive solvent for high-oxidation-state fluorides and fluoro-complexes, *e.g.* XeF_6[1] and NF_4^+ salts.[2] Indeed there has been no report as yet of a chemical oxidation of the solvent, although attack on fluorinated plastic vessels by certain solutes[1,3] in HF is known. A number of the complexes investigated in this study cause cracking of moulded Kel-F (polychlorotrifluoroethylene) tubes; however, FEP (fluorinated ethylene–propylene) was more inert.

We have investigated the behaviour of a number of hexafluorometallate complexes, $K_3M^{III}F_6$ (M = Mn, Co, Ni, Cu), $K_2M^{IV}F_6$ (M = Mn, Ni), and Cs_2CoF_6, in HF. Three of these (K_3CuF_6, K_2NiF_6, and Cs_2CoF_6) are outstandingly reactive in HF solution; the copper and cobalt complexes are sufficiently reactive to cause elemental fluorine, identified by its reaction with mercury, to be evolved above 0°. Solutions of the nickel(IV) complex are known to be inert towards solvent oxidation;[4] however, we find that it reacts with xenon at *ca.* 0°. Xenon difluoride, containing traces of XeF_4, was isolated and identified by ^{19}F n.m.r. spectroscopy in HF solutions. The nickel(III) complex behaves similarly on account of its disproportionation[3] to NiF_6^{2-} and brown $NiF_{2\cdot3}$ ($\mu_{eff.}$ 2·5 BM at 20°). The copper(III) and cobalt(IV) complexes also fluorinate xenon at or below room temperature, but these reactions are less efficient owing to the competing reaction with the solvent. Since the low-pressure dark reaction of xenon with fluorine is immeasurably slow[5] and is unaffected by the addition of liquid HF, it seems likely that fluorination of xenon occurs by an electron-transfer reaction, at least in the case of NiF_6^{2-}. The hexafluoronickelate(IV) ion has been postulated as an intermediate in Simons' electrochemical fluorinations (using Ni anodes);[3] it would be interesting to find out whether Xe is electrochemically oxidisable.[6]

The kinetically inert d^3 and d^6 hexafluorometallates, MnF_6^{2-} and NiF_6^{2-}, were solvolysed by adding AsF_5 to the HF solutions. Manganese(IV) fluoride,[7] along with $KAsF_6$, was produced but not NiF_4. Spontaneous reduction of Ni^{IV} occurred generating black NiF_3 ($\mu_{eff.}$ 2·41 BM at 20°). This new binary fluoride of nickel could not be isolated pure; it decomposed to NiF_2 when the co-precipitated $KAsF_6$ was extracted with HF.

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[6] Referee's comment.

[7] Previously prepared only by high temperature fluorination method, *e.g.* H. Roesky and O. Glemser, *Angew. Chem.*, 1963, **2**, 626.