

## I-11

ReF<sub>7</sub> AND ReOF<sub>5</sub> AS FLUORIDE ION DONORS

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Salts containing the ReF<sub>6</sub><sup>+</sup> ion have been prepared by one-electron oxidation of ReF<sub>6</sub> using KrF<sup>+</sup> salts. The compounds ReF<sub>6</sub><sup>+</sup>MF<sub>6</sub><sup>-</sup> (M = Au, Sb) are of moderate stability, tending to decompose to ReF<sub>7</sub> and the corresponding pentafluoride. This gives rise to isolated ReF<sub>7</sub> and MF<sub>5</sub> molecules within the ionic lattice, whose presence is demonstrated by Raman spectroscopy. Interaction of ReF<sub>6</sub> and PtF<sub>6</sub> produced not the salt ReF<sub>6</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup> (1), but rather the deep red (PtF<sub>5</sub>)<sub>4</sub> when PtF<sub>6</sub> was present in excess, and PtF<sub>4</sub> when ReF<sub>6</sub> was in excess. ReF<sub>6</sub> and IrF<sub>6</sub> appear to be in equilibrium with ReF<sub>7</sub> and (IrF<sub>5</sub>)<sub>4</sub>, possibly via an ionic intermediate ReF<sub>6</sub><sup>+</sup>(IrF<sub>6</sub>·xIrF<sub>5</sub>)<sup>-</sup>.

The salts ReOF<sub>4</sub><sup>+</sup>MF<sub>6</sub><sup>-</sup> (M = As, Au, Sb) have been characterized. In contrast to the behaviour of IOF<sub>5</sub> and IF<sub>7</sub>, ReOF<sub>5</sub> is a better fluoride ion donor than ReF<sub>7</sub>.

- 1 E. Jacob and M. Fahnle, Angew. Chem. **88**, 190, (1976).

## I-12

FLUORIDE ION DONOR PROPERTIES IN UOF<sub>4</sub>

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Recently the adducts UOF<sub>4</sub>·nSbF<sub>5</sub> (n = 1-3) were obtained from the reaction of UOF<sub>4</sub> with SbF<sub>5</sub> in SbF<sub>5</sub> or HF solvents and the structure of the 1:2 compound was described in terms of a fluorine-bridged network but with some contribution to the bonding from the ionic formulation [U<sup>VI</sup>OF<sub>2</sub>][Sb<sup>V</sup>F<sub>6</sub>]<sub>2</sub>.

Reaction of UOF<sub>4</sub> with the Lewis Acid pentafluorides, BiF<sub>5</sub>, TaF<sub>5</sub> and NbF<sub>5</sub>, in anhydrous HF solvent or by fusing together UOF<sub>4</sub>/MF<sub>5</sub> mixtures, also yields fluorine-bridged adducts, UOF<sub>4</sub>·2BiF<sub>5</sub>, UOF<sub>4</sub>·3TaF<sub>5</sub> and UOF<sub>4</sub>·3NbF<sub>5</sub>, and it has been shown that, in these complexes too, UOF<sub>4</sub> exhibits weak fluoride ion donor properties.

The ternary adducts UOF<sub>4</sub>·mSbF<sub>5</sub>·nCH<sub>3</sub>CN (m = 1,2; n = 2,6 respectively) and UF<sub>5</sub>·xSbF<sub>5</sub>·yCH<sub>3</sub>CN (x = 1,2; y = 2,5 respectively) have been prepared by the reaction of dry acetonitrile with the appropriate binary adduct.