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A LOW TEMPERATURE ROUTE TO BINARY FLUORIDES EXEMPLIFIED BY NiF_4, AgF_3, RuF_4, OsF_4 AND ReF_4

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The interaction between some binary fluorides and the combination of krypton difluoride and xenon hexafluoride in anhydrous hydrogen fluoride (AHF) provides an effective synthetic route to new xenon(VI) fluorometalates with each metal in a high oxidation state (e.g. $(Xe_2F_{11}^+)_2NiF_6^{2-}$; $(XeF_5^+)_2NiF_6^{2-}$; $XeF_5^+AgF_4^-$). Fluoride-ion capture from such high oxidation-state-metal anions in AHF solution by strong fluoride ion acceptors (e.g. AsF_5) provides a general approach to the synthesis of polymeric and (in AHF) insoluble binary fluorides. This is particularly advantageous in the synthesis of thermally unstable highest-oxidation-state transition metal polymeric fluorides (e.g. NiF_4, AgF_3). AgF_3 prepared in this way is a bright red diamagnetic solid apparently isostructural with AuF_3. The hexagonal unit cells are: AgF_3: a_o, 5.088(10); c_o, 15.43(3) Å; V, 346 Å^3; AuF_3: a_o, 5.149(2); c_o, 16.26 (1) Å; V 373 Å^3, the AgF_3 formula unit being 4.5 Å^3 smaller than for AuF_3. These structural features imply that the d_{z^2} electron pair of Ag(III) is highly contracted and in conformity with its chemistry, tightly bound. Less powerfully oxidizing binary fluorides have also been made by this new approach and include RuF_4, OsF_4 and ReF_4, all of which have structures related to that of PdF_4.