

SYNTHESES AND SOME PROPERTIES OF BINARY FLUORIDES OF SILVER, COPPER AND NICKEL

B. Žemva, K. Lutar
 Institut "Jožef Stefan", 61111 Ljubljana (Slovenija)

W.J. Casteel, Jr. and N. Bartlett
 Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley CA 94720 (USA)

Thermally unstable highest-oxidation-state transition metal polymeric fluorides (e.g. AgF_3 , NiF_4) are precipitated from anhydrous hydrogen fluoride (AHF) solutions of their salts by addition of fluoroacids (A) such as BF_3 , PF_5 or AsF_5 [1]: $\text{MF}_x^+ + y\text{A} \rightarrow \text{MF}_{(x-y)} + y\text{AF}^-$. Red, diamagnetic AgF_3 precipitated by AsF_5 from AHF solutions of AgF_4^- salts is reduced with excess of AsF_5 by following equation: $\text{AgF}_3 + \text{AsF}_5 \rightarrow \text{AgFAsF}_6 + 1/2\text{F}_2$. While such reduction does not occur with BF_3 this acid is therefore preferred for the preparation of stoichiometric AgF_3 . Silver trifluoride is thermodynamically unstable and loses F_2 in contact with AHF according to the equation: $3\text{AgF}_3 \rightarrow \text{Ag}_3\text{F}_8 + 1/2\text{F}_2$. The formation of Ag_3F_8 by the interaction of one mole of Ag(II) and two moles of Ag(III) confirmed that the material formed in the degradation of AgF_3 is a mixed valence material $\text{Ag(II)Ag(III)}_2\text{F}_8$. Interaction of AgF^+ with AgF_4^- (1:1) in AHF yields maroon Ag(II)Ag(III)F_5 . Silver trifluoride is isostructural with AuF_3 . Its powerful oxidizing properties are in accord with the tight binding of its valence shell d orbital electrons. CuF_6^{3-} salts interact quantitatively with liquid AHF already at -60°C yielding bright red CuF_3 : $\text{CuF}_6^{3-} + 3\text{xHF} \rightarrow \text{CuF}_3 + 3\text{F}^-(\text{HF})_x^-$. The oxidizing properties of above-mentioned fluorides will be discussed.

1. B. Žemva, K. Lutar, A. Jesih, W.J. Casteel, Jr., and N. Bartlett, J. Chem. Soc., Chem. Commun., 346 (1989)