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LEWIS ACIDITY AND SYNTHESIS IN ANHYDROUS HYDROGEN FLUORIDE

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Much of the Melbourne work on Lewis acidity in anhydrous hydrogen fluoride (AHF) has been directed towards identifying Lewis acids capable of generating unusual cationic species in AHF and then isolating these cations in crystalline solids for structure determination. The ideal Lewis acid would be strong and, unlike the familiar examples SbF_5 and AsF_5, weakly or non-oxidizing. We have used conductometry to compare the strengths of ReF_5, TaF_5, $ReOF_4$, WOF_4 and $MoOF_4$ with those of SbF_5 and AsF_5 and we have Raman spectroscopic and some X-ray structural evidence for dimerization of anions in most cases. The very weak acid GeF_4 has proved very effective as a precipitant in AHF.

Careful selection of the type and concentration of Lewis acid allows the generation in AHF of metal cations in unusually low oxidation states e.g. U^{3+}, Ti^{2+} and Sm^{2+}, which yielded the solid $SmGeF_6$. U^{3+} had been shown to disproportionate on increasing the solution basicity. Also homopolyatomic cations of non-metals such as iodine and sulphur disproportionate in a controllable way with increase in AHF basicity.

We have exploited the reversal of these disproportionations by controlling both the reation stoichiometry and the AHF acidity levels to produce solutions and solids containing several polyatomic cations of iodine and sulphur by oxidation of I_2 with IF_5 and of S_8 with SF_4 .

In order to develop further the general nature of this synthetic approach, work has been commenced on the generation in AHF, and the subsequent isolation of solids, of polyatomic metal cations M_y^{x+} where M = Cd, Ag, Bi, Pb etc.