

I₁₉OXIDATION OF I₂, Br₂ AND Cl₂ BY MoF₆ and UF₆ IN ACETONITRILE

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I₂ is oxidized by both MoF₆ and UF₆ in MeCN to give [I(NCMe)₂][MF₆], M = Mo or U. The cation is a good oxidizing and electrophilic iodinating agent (G.M.Anderson and J.M.Winfield, J.Chem.Soc.,Dalton Trans., 1986, 337). Iodine and molybdenum EXAFS studies (in collaboration with C.D. Garner and A. Steel, SERC Daresbury Laboratory) indicate the presence of discrete [I(NCMe)₂]⁺ and [MoF₆]⁻ ions in both solid and solution. The N-I-N skeleton is linear, I-N = 2.18Å. MoF₆⁻ is octahedral, Mo-F = 1.77Å. Br₂ is oxidized by UF₆, but not by MoF₆, under similar conditions to give a bromine salt. This does not contain the [Br(NCMe)₂]⁺ cation; low temperature ¹³C n.m.r. spectroscopy indicates that a complex mixture of species is formed, which are believed to result from solvent oligomerization and cyclization reactions. However the salt is a powerful brominating agent towards aromatic organic compounds, and appears to be a more powerful oxidizing agent than [I(NCMe)₂]⁺. The reaction of UF₆ with Cl₂ in MeCN is apparently similar to that with Br₂, however under some conditions UF₅, NCMe rather than UF₆⁻ is formed.