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MACROCYCLE-METAL AND -NON METAL CATION, FLUOROANION SALTS

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Mononuclear cations which are solvated by acetonitrile and which have complex fluoro-counter-anions, are convenient source materials for investigations of non-aqueous coordination chemistry [1]. Complexes between N_4 -macrocyclic ligands, for example [12]-ane N_4 , [14]-ane N_4 or [15]-ane N_4 , and copper(II), iron(II) or iodine(I) fluoroanion salts have been isolated by this route. Although macrocycle, metal cation complexes are well known [e.g. 2], the iodine complexes [I(L)][MoF_6], L = [14]-ane N_4 or [15]-ane N_4 , appear to be the first examples of isolable I^I species. Quantum mechanical calculation of the I⁺ radius using a double zeta basis set yields the value 1.30 Å, suggesting that the [14]-ane N_4 ligand in [I(L)]⁺ may have a folded conformation. Cyclic voltammetry studies indicate considerable stabilization of the I^I oxidation state through complexation with N_4 -macrocycles. Elemental I₂ does not react with the weak oxidizing agent PF₅ in MeCN but reaction does occur in the presence of N_4 -macrocycles to give isolable complexes.

- 1 L. McGhee, R.M. Siddique and J.M. Winfield, <u>J. Chem. Soc.</u>, <u>Dalton</u> <u>Trans.</u>, 1309 (1988); R.M. Siddique and J.M. Winfield, <u>Can. J. Chem</u>., in press.
- 2 D.D. Watkins, jr., D.P. Riley, J.A. Stone and D.H. Busch., <u>Inorg. Chem.</u>, <u>15</u>, 387 (1976).