The Pentachlorothallium(III) and Pentachloroindium(III) Ions

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FOR the Group IV elements a series of monomeric halide species, MX_4, MX_5^-, and MX_6^{2-}, are well established but an analogous series is lacking in Group III, where only tetrahedral and octahedral halide complexes are known.[1] Compounds with empirical formulae appropriate for five co-ordinated anions [*e.g.* $(Et_4N)_2InCl_5$] have been reported and a species with a chloride to indium ratio of five is indicated by solvent extraction studies.[2] However, there is no evidence to show that these are simple pentaco-ordinated anions rather than analogues of the pentahalogeno-aquo-complexes which are well established for indium and thallium in aqueous solution, or halogen-bridged polymers like Tl_2AlF_5.[3]

Addition of an acetonitrile solution of thallic chloride to one containing 50% excess of tetraethylammonium chloride followed by evaporation of the mixture gave white crystals of tetra-ethylammonium pentachlorothallate, decomposing at 250—255°. A similar preparation using $[Et_4N][InCl_4]$ gave the analogous indium compound, decomposing at 264—267°. Both products were characterised by complete elemental analysis. The crystals are soluble in nitromethane and slightly soluble in ethanol. *X*-Ray powder photographs show the indium and thallium compounds to be isomorphous.

Although the compounds have empirical formulae which agree with the five-co-ordinate species, MCl_5^{2-}, the dimer, $M_2Cl_{10}^{4-}$, and double salts containing the known anions, MCl_4^-, $M_2Cl_9^{3-}$, and MCl_6^{3-} must also be considered. For the pentachlorothallate species, i.r. absorptions occur at 121sh, 125s, 250sh, 255vs, ~300vvw cm.$^{-1}$ (Nujol mull), while Raman peaks are found at 40w, 99m, 113m, 153w, 171vw, 260sh, 275vvs cm.$^{-1}$ (solid pellet). The indium complex has i.r. 141s, 150sh,vbr, 272s, 282s, 295sh cm.$^{-1}$; Raman 106m, 123m, 167m, 194w, 287sh, 294s cm.$^{-1}$.† In the higher frequency region (400—3000 cm.$^{-1}$), $[Et_4N]_2[TlCl_5]$ shows only absorptions characteristic of the cation. These i.r. and Raman spectra, by comparison with published data,[5] rule out the alternatives suggested above, in particular the metal–chlorine stretching and deformation bands are well separated with no sign of bridging-chloride frequencies, which are expected to be intermediate.

Molecular weights in ethanol at 37·3° were 215 ($7{\cdot}66 \times 10^{-3}$ M) and 180 ($4{\cdot}12 \times 10^{-3}$ M) for the pentachlorothallate (calc. 642), and 178 ($2{\cdot}17 \times 10^{-2}$ M) and 132 ($6{\cdot}79 \times 10^{-3}$ M) for the indium compound (calc. 553). Although $i \sim 3{\cdot}0$ in the more concentrated solutions, indicating a 2 : 1 electrolyte, considerable dissociation is evident at the lower concentrations. Similarly the Raman spectrum of a saturated solution of $[Et_4N]_2[TlCl_5]$ in nitromethane shows two strong peaks of nearly equal intensity at 277 and 310 cm.$^{-1}$, both highly polarised also indicating considerable dissociation to $[TlCl_4^-]$ has occurred. After addition of a large excess of $[Et_4N]Cl$ to the solution only one band at 279 cm.$^{-1}$ was observed. A Raman study of the solution equilibrium using $[Bu_4N][TlCl_4]$ and $[Bu_4N]Cl$ gave a value of $K = 4{\cdot}6 \pm 1{\cdot}0$ l.mole^{-1} at 26 ± 1° for the equilibrium,

$$[TlCl_4]^- + Cl^- \rightleftarrows [TlCl_5]^{2-}.$$

Equilibrium constants calculated using the alternative ions suggested above, show greater variation and these species can therefore be discounted. A nitromethane solution of $[Bu_4N][TlCl_4]$, with large excess of Bu_4NCl, had a Raman spectrum equivalent to that of the solid pentachlorothallate indicating that the same five-co-ordinate monomer MCl_5^{2-} (M = In or Tl) occurs both in solution and the solid state.

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† Adams *et al.*, ref. 2 (c), reported 267, 281sh cm.$^{-1}$ for $[(Et_4N)_2][InCl_5]$.

[1] However, pentaco-ordinate neutral complexes are known for Group III, as are the five-co-ordinate anions $RTlCl_4^{2-}$ and $R_2TlCl_3^{2-}$ (R. Barbieri, B. L. Pepe, L. R. Fiorani, and G. Furaglia, *J. Organometallic Chem.*, 1967, **10**, 363).

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