

The Pentachlorothallium(III) and Pentachloroindium(III) Ions

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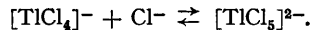
For the Group IV elements a series of monomeric halide species, MX_4 , MX_5^- , and MX_6^{2-} , are well established but an analogous series is lacking in Group III, where only tetrahedral and octahedral halide complexes are known.¹ Compounds with empirical formulae appropriate for five co-ordinated anions [e.g. $(\text{Et}_4\text{N})_2\text{InCl}_5$] 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_6 .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 $[\text{Et}_4\text{N}][\text{InCl}_4]$ 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, $\text{M}_2\text{Cl}_{10}^{4-}$, and double salts containing the known anions, MCl_4^- , $\text{M}_2\text{Cl}_9^{3-}$, and MCl_6^{3-} must also be considered. For the pentachlorothallate species, i.r. absorptions occur at 121sh, 125s, 250sh, 255vs, ~ 300 vvw 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}), $[\text{Et}_4\text{N}]_2[\text{TlCl}_5]$ 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 (7.66×10^{-3} M) and 180 (4.12×10^{-3} M) for the pentachlorothallate (calc. 642), and 178 (2.17×10^{-2} M) and 132 (6.79×10^{-3} M) for the indium compound (calc. 553). Although $i \sim 3.0$ 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 $[\text{Et}_4\text{N}]_2[\text{TlCl}_5]$ in nitromethane shows two strong peaks of nearly equal intensity at 277 and 310 cm^{-1} , both highly polarised also indicating considerable dissociation to $[\text{TlCl}_4^-]$ has occurred. After addition of a large excess of $[\text{Et}_4\text{N}]\text{Cl}$ to the solution only one band at 279 cm^{-1} was observed. A Raman study of the solution equilibrium using $[\text{Bu}_4\text{N}][\text{TlCl}_4]$ and $[\text{Bu}_4\text{N}]\text{Cl}$ gave a value of $K = 4.6 \pm 1.0$ l.mole⁻¹ at $26 \pm 1^\circ$ for the equilibrium,



Equilibrium constants calculated using the alternative ions suggested above, show greater variation and these species can therefore be discounted. A nitromethane solution of $[\text{Bu}_4\text{N}][\text{TlCl}_4]$, 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-} ($\text{M} = \text{In}$ 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 $[(\text{Et}_4\text{N})_2][\text{InCl}_5]$.

¹ However, pentaco-ordinate neutral complexes are known for Group III, as are the five-co-ordinate anions RTlCl_4^{2-} and $\text{R}_2\text{TlCl}_3^{2-}$ (R. Barbieri, B. L. Pepe, L. R. Fiorani, and G. Furaglia, *J. Organometallic Chem.*, 1967, **10**, 363).

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