Formation of Thallium–Cobalt Bonds from $\mathrm{Tl^{I}}$ Ions in Aqueous Solution

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Summary $\mathrm{Tl^{I}}$ ions react with pentacyanocobaltate(II) ion in aqueous solution to give the dimeric complex $[(CN)_5Co\text{–}Tl\text{–}Co(CN)_5]^{5-}$.

THE equilibria and rates and products of reaction of aqueous solutions of the pentacyanocobaltate(II) ion $[Co^{II}(CN)_5]^{3-}$ depend to a marked degree on the nature of the alkali metal cation present, and the formation of ion-pairs has been quantitatively established.[1–3] We have now extended our study of the effect of univalent cations to include $\mathrm{Tl^{I}}$ and find that it behaves quite differently from the alkali metal cations.

Solutions of TlCl or $TlNO_3$ react very rapidly with aqueous solutions of the pentacyanocobaltate(II) ion, prepared by mixing solutions of $CoCl_2$ and KCN, to give a new complex (A), characterised by an intense charge transfer band at 389 nm. The complex decomposes in dilute solution (10^{-5}—10^{-2}M) to give unknown products, while one experiment using concentrated solutions (0·2M-Tl and 0·4M-Co) produced thallium metal. We have not yet been able to obtain (A) as a pure solid, and its empirical formula has been determined in solution.

Titration of $CoCl_2$ with KCN (*cf.* ref. 2) in the presence and absence of excess of $TlNO_3$ gave CN : Co = 4·98 for the complex (X); apparent ϵ (389 nm.) $2{\cdot}9 \times 10^4$ cm.$^{-1}$ M^{-1}(Co) in the presence of excess of thallium and $5{\cdot}7 \times 10^4$

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cm.$^{-1}$M^{-1}(Tl) in the presence of excess of cobalt; Beer's Law was obeyed in both cases. The ratio of extinction coefficients gives Co : Tl = 2·0. The empirical formula of (A) is, therefore, $[Co_2Tl(CN)_{10}]$; if we neglect any formation of ion-pairs and assume that no reduction of H_2O or CN^- has occurred, then (A) carries five negative charges. Solutions of (A) underwent no colour change on freezing to −180° C, and the frozen solutions gave no e.s.r. signal; (A) can therefore be considered to be diamagnetic. Its stoicheiometry, diamagnetism, and intense charge-transfer band in the visible region are paralleled by other bridged dimeric complexes of the type $[(CN)_5Co–X–Co(CN)_5]$; see, in particular, the complex where X = $SnCl_2$, which has an intense band at 405 nm. (ϵ *ca.* 10^4) and whose structure is assumed to contain Co–Sn–Co bonds.[4] X can therefore be written with the analogous structure $[(CN)_5Co–Tl–Co(CN)_5]^{5-}$.

Compounds containing bonds between Tl and another metal are rare. The only compounds previously reported appear to be $Tl[Co(CO)_4]_n$ where n = 1 and 3, which also contain Co–Tl bonds; their synthesis involves the use of cobalt metal with CO at high pressure or either $TlCl_3$ or Tl^I acetylacetonate and cobalt carbonyl compounds in tetrahydrofuran.[5,6] The new complex (A) not only provides another example of a metal–metal bond involving Tl but its mode of formation represents the first case in which a heteronuclear metal–metal bond is formed by the reaction of a simple aquated cation (Tl^+) in aqueous solution. The only parallel is the formation of the homonuclear metal–metal bond in the mercury(I) cation (Hg_2^{2+}) by the reaction of the aquated mercury(II) cation with mercury metal.

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