Isolation of the Pentacyanohydridocobalt(III) Ion

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REACTIONS with H_2 provide one of the striking examples of the remarkable reactivity, and often catalytic activity, of metal complexes, since at room temperature H_2 is usually extremely inert kinetically even when the reaction is thermodynamically very favourable (*cf.*, N_2O [1]). The fastest reaction of this type appears to be the reaction of H_2 with aqueous solutions of cobalt(II) cyanide complexes.[2] In spite of considerable work the identity of the product(s) has not been established and no reduced complex has been isolated in the solid state. Here we report our results on equilibria in solution and the isolation of the complex $[Co^{III}(CN)_5H]^{3-}$ in the solid state.

Experiments in solution showed that the reaction between H_2 and solutions containing cobalt(II) and cyanide ions, where the main complex has recently[3] been shown to be $[Co^{II}(CN)_5H_2O]^{3-}$, gives at least three products: (A) the main product under the usual conditions with CN : Co = 5 (determined by titration of free cyanide after hydrogenation), the spectrum showing a band at 305 mμ, $\epsilon_{\text{molar}} = 620$ (*cf.* ref. 4, 5). Recent n.m.r. measurements[5] show that this is a diamagnetic hydride complex. Both results taken together are evidence for the structure $[Co^{III}(CN)_5H]^{3-}$, which has often been assumed but without adequate experimental support. (B) CN : Co < 5 (from titration of cyanide with cobalt during hydrogenation), $\lambda \leqslant 300$ mμ, $\epsilon_{\text{molar}} \geqslant 700$. (C) CN : Co = 6 (from the effect of cyanide concentration on the amount of [$Co^{II}(CN)_5H_2O$] remaining unchanged at equilibrium). (A) and probably (B) and (C) are also produced when borohydride or sodium amalgam is used as the reducing agent instead of H_2. The situation is therefore more complicated than previously assumed; this may explain some of the apparent discrepancies in the literature.

If an aqueous solution of $CoCl_2$ and NaCN is treated under nitrogen with sodium amalgam and a solution of CsCl then added, a white precipitate forms fairly rapidly. This is stable as a solid, but difficult to recrystallise because of its reactivity. Analysis (C, N, H by microanalysis; Na by atomic absorption spectrophotometry; Cs and Co by *X*-ray fluorescence) agrees with the formula $NaCs_2Co(CN)_5H$, with 10% $Na_2CsCo(CN)_5H$; an analogous partial replacement of one alkali-metal cation by another is found in the insoluble salts of the hexanitrocobalt(III)ate ion, $[Co(NO_2)_6]^{3-}$.[6] The infrared spectra (KCl discs) of samples prepared from H_2O and D_2O showed strong bands at 1840 and 1340 cm.$^{-1}$ (Co–H/D stretch) and 774 and 610 cm.$^{-1}$, respectively (Co–H/D bend), which establishes the presence of a hydride ligand, and identifies the complex as [$Co^{III}(CN)_5H$]. The cyanide bands occur at 2113 and 535 cm.$^{-1}$ in both compounds. The spectrum of the solution in water shows a strong band at 305 mμ, $\epsilon_{\text{molar}} = 620$, *i.e.*, the same as that of the complex already studied in solution. (B) and (C) may be $[Co^{III}(CN)_4H_2]^{3-}$ and $[Co^{I}(CN)_6]^{5-}$ respectively.

Much of our knowledge of the effects of ligands on the spectra and other properties of octahedral complexes relates to cobalt(III) complexes. [$Co^{III}(CN)_5H$] is, therefore, a key hydride complex, which will permit a direct comparison of H^- with other, more usual ligands; studies on the physical properties of the complex will be reported later.

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