Formation of Chlorobisethylenediaminecobalt(III)-μ-cyano-pentacyanocobalt(III) and the High Apparent Nucleophile Efficiency of the Cyanide Ligands of Hexacyanocobaltate(III)†

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Summary At 25 °C with a pH of 7–8 and in concentrations of *ca.* 10^{-2} M, $[Co(CN)_6]^{3-}$ competes successfully with solvent H_2O in the substitution of Cl^- in *trans*-$[Co(en)_2Cl_2]^+$ to give mainly $[Co(en)_2Cl(\mu\text{-}CN)Co(CN)_5]^-$ (en = ethylenediamine); at higher temperatures polymeric species are also formed.

THE cyanide ion is well known to form bridged complexes either as stable species[1] or as intermediates in electron transfer processes.[2] It has also been shown[3,4] that the cyanide ion, even when bound as a ligand, can still engage in a substitution reaction by displacing an aquo-group from a cobalt centre and thus form a dimeric cyanide bridged complex. We have now found that a cyanide ligand from $[Co(CN)_6]^{3-}$ can behave as though it were a more efficient nucleophile than solvent water, virtually eliminating the aquation reaction in favour of cyanide bridge formation in the substitution of Cl^- in *trans*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine). This property is apparently retained by a cyanide ligand in the product so that a mixture of cyanide bridged polynuclear cobalt anions are eventually produced at higher reactant concentrations and temperatures.

At 25 °C in an aqueous solution buffered at pH 7·5 by a standard[5] $(OHCH_2)_3CNH_2$–HCl mixture, 0·01 M *trans*-$[Co(en)_2Cl_2]^+$ and 0·02 M $[Co(CN)_6]^{3-}$ react with a half-life of *ca.* 4 min to yield mainly *trans*-$[Co(en)_2Cl(\mu\text{-}CN)Co(CN)_5]^-$. The product was isolated by evaporation of the solution at 40 °C after all the cationic species had been removed by hydrogen ion exchange. The identity of the compound which crystallised as $[H\{$*trans*-$[Co(en)_2Cl(\mu\text{-}CN)Co(CN)_5]\}\text{-}3H_2O]$ was confirmed by microanalysis. The number of moles of water of crystallisation was confirmed by dehydration *in vacuo*, (H_2O, found 13; calc. 11%). The i.r. spectrum showed a bridging cyanide band[5] at 2207 cm^{-1} and four other bands at 2166, 2148, 2134, and 2128 cm^{-1} typical of terminal cyanide bands.[6] The bands at 1600 cm^{-1} and below were similar in position and relative intensity to those given by the ethylenediamine ligands in *trans*-$[Co(en)_2Cl_2]^+$. The complex apparently polymerised on prolonged heating, afterwards having a similar but greatly broadened i.r. spectrum with only two cyanide bands at 2180 and 2122 cm^{-1}. The acid complex was titrated (titrable hydrogen ion: found $2{\cdot}08 \times 10^{-3}$; calc. for univalent acid of dimer anion, $2{\cdot}13 \times 10^{-3}$%), and the formula weight was determined by 'Salzkryoskopie'[7] (found, 520; calc., 485). Conductivity, vapour pressure osmometry in water, and electrophoresis experiments all confirmed that the product was a 1:1 electrolyte containing an unusually large anion of low charge.

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† No reprints available.

The kinetics of the reaction [equation (1)] were studied

$$[Co(en)_2Cl_2]^+ + [Co(CN)_6]^{3-} \rightarrow [Co(en)_2(\mu\text{-}CN)Co(CN)_5]^- + Cl^- \quad (1)$$

by the disappearance of the band at 618 nm due to $[Co(en)_2Cl_2]^+$. At 25 °C, the reaction was first order with respect to the concentration of $[Co(CN)_6]^{3-}$ below 0·02 M but it became zero order above 0·03 M. The reaction mixture was of unit ionic strength supported by potassium chloride and was adjusted to give a nominal pH of 7·5 by a $(OHCH_2)_3CNH_2$–HCl buffer. The limiting rate above 0·03 M was a factor of 17 times faster than the normal base catalysed aquation reaction [equation (2)] under the same conditions, ($k_2 = 4{\cdot}3 \times 10^{-4}\ s^{-1}$). The large difference in rate makes

$$[Co(en)_2Cl_2]^+ + H_2O \xrightarrow{OH^-} [Co(en)_2Cl(H_2O)]^{2+} + Cl^- \quad (2)$$

the aquo-complex an unlikely intermediate in the formation of the dimer.

The products of reaction (1) under these conditions were almost entirely anionic since almost no cobalt complex apart from the starting material was retained by a cation exchange column (Zeocarb 225, 10 × 1·7 cm). Continuous sampling during reaction and separation of the anionic and cationic complexes present showed that there was no induction period in the formation of the dimer and that it was therefore a primary reaction product. The reaction showed a well defined isosbestic point at 401 nm markedly different from that of the aquation reaction (2) which was at 417 nm. The other isosbestic points at 582, 439, and 352 nm all closely resembled those of the aquation reaction (588, 443, and 356 nm). Separation of the anionic products by a gel permeation column (Bio-gel P-2, 94 × 1·7 cm), showed that although the major product was the dimer, detectable amounts of other anionic products were also formed. As the pH was changed from 7 to 8, the reaction rate increased and, although clearly defined isosbestic points were still observed, the spectra showed slight but distinct changes in absorption maxima, intensities, and isosbestic points. In strong acid or alkali (0·1 M HCl or 0·05 M KOH), aquation occurred with only slight degree of anion formation. At reactant concentrations of the order of 10^{-1} M or at higher temperatures, a mixture of cationic aquation products and cyanide-bridged anions together with some insoluble polymer were formed.

These experiments show the unusually strong nucleophile character of $[Co(CN)_6]^{3-}$ in the substitution reactions of $[Co(en)_2Cl_2]^+$. The extension of the chain which occurs at higher concentrations or temperatures suggests that terminal $-Co(CN)_5{}^{2-}$ and $-Co(en)_2Cl^{2+}$ can still react as did the parent $[Co(CN)_6]^{3-}$ and *trans*-$[Co(en)_2\text{-}Cl_2]^+$ ions.

At pH 7·5 *trans*-$[Co(en)_2Cl_2]^+$ aquates mainly by a S_N1CB mechanism[8] in which the amido-intermediate, being uncharged, seems unlikely to bind $[Co(CN)_6]^{3-}$ by electrostatic ion-pairing forces. Despite this, some form of interaction[9] binding the cyanide adjacent to the site of the departing chloride ligand seems the most plausible explanation both for the nucleophilic efficiency of $[Co(CN)_6]^{3-}$ and also for the change from first to zero order at higher concentrations. Conductivity measurements on solutions of $[Co(en)_2Cl_2]_3[Co(CN)_6]$ below 10^{-3} M suggest that the degree of ion association is much greater than that expected for electrostatic binding and thus support the hypothesis of non-electrostatic outer-sphere co-ordination[10] for this class of ions.

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