Polarography of the Dicyano Cobalt(III) Complexes

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It has been found that several kinds of pentacyano- and tetracyano-cobaltate(III) complexes can be reduced to or through the cobalt(I) state in an aqueous solution at the dropping mercury electrode (DME).[1] The stabilization of the cobalt (I) state can certainly be ascribed to the contribution of the "back donation" at the bonds of four or five cyanide ligands.

In the present communication, however, the dicyano-tetrammine- and bis(ethylenediamine)-cobalt(III) complexes have been found still to undergo a step-by-step reduction of $Co^{III} \rightarrow Co^{II} \rightarrow Co^{I} \rightarrow Co^{0}$, as it were, at the DME in dimethyl sulfoxide (DMSO); it has hitherto been considered impossible for the cobalt(I) states of these complexes with only two cyanides to exist in solution during the course of reduction. That is, the complex ions, *cis*- and *trans*-$[Co^{III}(CN)_2en_2]^+$, and *trans*-$[Co^{III}(CN)_2(NH_3)_4]^+$, gave rise to well-defined waves of three steps in DMSO (100%) containing 0.1 M $[(C_2H_5)_4N]ClO_4$. The waves, each corresponding to an acceptance of one electron, represent the reductions of $Co^{III} \rightarrow Co^{II}$, $Co^{II} \rightarrow Co^{I}$, and $Co^{I} \rightarrow Co^{0}$ respectively.

Each of the limiting currents was proportional to the concentration of the complex in the range of 10^{-4}—10^{-2} M, and also proportional to the square root of the mercury pressure on the DME; the values of $i_l/\sqrt{h_{corr.}}$ are almost constant, irrespective of the mercury pressure. The instantaneous current-time curves during a one-drop growth of the DME at a constant potential exhibit a normal shape except that of the third step for the tetrammine complex; the current varies with time to the powers of 0.19—0.22 at the potentials, at which potential the current reaches a limiting plateau. This result, combined with the finding in relation to the mercury head, supports the conclusion regarding the diffusion-controlled features of all the waves except that of the third step for the ammine complex. The third wave for the tetrammine complex, involving a somewhat kinetic character in its current, expresses the partial disruption of the cobalt(I) complex during the reduction of $Co^{I} \rightarrow Co^{0}$ at the DME.

The following processes of the electrode reaction are considered to be the most probable:

$$\begin{tikzcd}
{[Co^{III}(CN)_2(NH_3)_4]^+} \arrow[r, "e"] & {} \\
{[Co^{II}(CN)_2(NH_3)_4]} \arrow[r, "e"] & {[Co^{I}(CN)_2(NH_3)_4]^-} \arrow[dl] \arrow[d, "e"] \\
{[Co^{I}(CN)_2(NH_3)_{4-n}(dmso)_n]^-} \arrow[r, "e"] & Co(\mathit{metal}).
\end{tikzcd}$$

Table 1 summarizes the half-wave potentials of the dicyano cobalt(III) complexes in DMSO. The addition of a small amount of water to the DMSO solution immediately causes the disruption of the cobalt(II) complex, thus permitting further direct reduction to the metal to take place; no cobalt(I) state can exist upon the reduction in water.

TABLE 1. THE HALF-WAVE POTENTIALS OF THE DICYANO COBALT(III) COMPLEXES IN THE DMSO (100%) CONTAINING 0.1 M $[(C_2H_5)_4N]ClO_4$ (25°C)

Compound	1st Wave ($Co^{III} \rightarrow Co^{II}$)	2nd Wave ($Co^{II} \rightarrow Co^{I}$)	3rd Wave ($Co^{I} \rightarrow Co^{0}$)
trans-$[Co(CN)_2(NH_3)_4]NO_3 \cdot H_2O$	−0.71	−1.06	−1.57
trans-$[Co(CN)_2en_2]NO_3$	−0.97	−1.52	−1.99
cis-$[Co(CN)_2en_2]NO_3$	−0.95	−1.48	−1.99
cis-$[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$	−0.48	−1.16	−1.96
cis-$[Co(CN)_2phen_2]NO_3 \cdot 6H_2O$	−0.39	−1.28	−1.94

Volt *vs.* SCE

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[1] N. Maki, "Proceedings of the 3rd International Congress of Polarography," Vol. 1, ed. by G. J. Hills, Macmillan & Co., London (1966), p. 505.