A Polarographic Study of the Tetracyanomono(ethylenediamine)cobaltate(III) Complex

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Previously, the $[Co^{III}(CN)_4(SO_3)_2]^{5-}$ ion (probably the trans-form) was found to be reduced in one step to the cobaltate(I) complex in a sulfite medium at the dropping mercury electrode (DME).[1]

In the present report, the tetracyanomono(ethylenediamine)cobaltate(III) complex, $K[Co^{III}(CN)_4\,en] \cdot H_2O$ (cis-form)[2], will be found to be reduced irreversibly to the metal through the cobaltate(I) complex in a 0.5 M sodium sulfate solution containing 2 M ethylenediamine.

More specifically, the $[Co^{III}(CN)_4\,en]^-$ ion gave rise to well-defined two-step waves at the DME. The ratio of the height of the first wave to that of the second was roughly 2 : 1. The first wave, corresponding to an acceptance of two electrons, represents the reduction from the cobalt(III) to the cobalt(I) state, while the second, corresponding to a gain of one electron, represents the reduction to the metal.

The limiting current of both waves was proportional to the concentration of the complex in the range between 10^{-2} and 10^{-4} F and was diffusion-controlled.

In the absence of excess ethylenediamine, the wave of apparently one step, corresponding to a three-electron reduction, was obtained.

Figure 1 shows the d.c. polarograms for this complex in the presence or in the absence of excess ethylenediamine. For the sake of comparison, the wave of the two electron-reduction of the dicyanobis(dimethylglyoximato)cobaltate(III) complex, whose resulting cobaltate(I) complex was ascertained by isolation in vacuo[3] is also shown. It can be seen that the wave-height is roughly proportional to the electron-number of the reduction process.

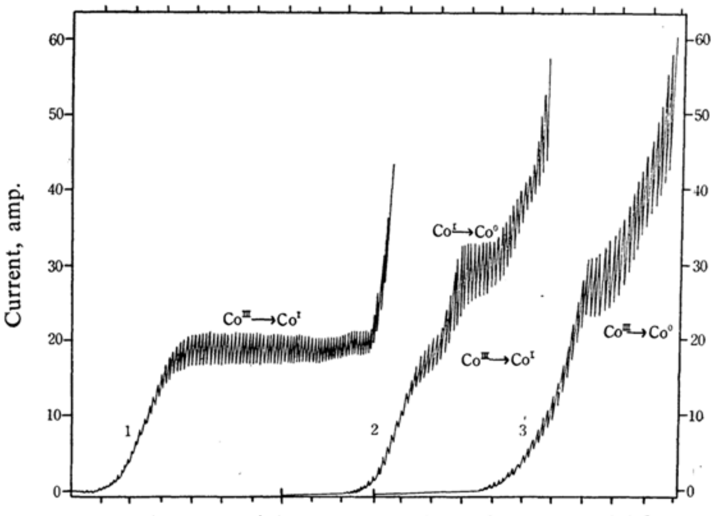

Fig. 1. D.C. polarograms of cyano-cobaltate(III) complexes obtained at the concentration of $5 \cdot 10^{-3}$F/1(25°C).

1) $K[Co^{III}(CN)_2dg_2] \cdot 3/2\ H_2O$ in 0.5 F Na_2SO_4 aq. soln. Recorded from −0.90 V. vs. SCE. $E_{1/2} = -1.10_5$ V. vs. SCE.
2) $Na[Co^{III}(CN)_4\,en] \cdot 3.5\ H_2O$, in 0.5 F Na_2SO_4 + 2 M en + 0.0078% Triton X 100. Recorded from −1.00 volt vs. SCE.
3) $Na[Co^{III}(CN)_4\,en] \cdot 3.5\ H_2O$, in 0.5 F Na_2SO_4 aq. soln. Recorded from −0.50 V. vs. SCE.

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[1] N. Maki and R. Tsuchida, This Bulletin, **34**, 891 (1961).

[2] J. Fujita and K. Okawa, unpublished.

[3] N. Maki, *Nature*, **188**, 227 (1960).

TABLE I. HALF-WAVE POTENTIALS OF THE CYANO-COBALT(III) COMPLEXES (25°C)

Compund	$E_{1/2}$ of 1st wave Co(III) → Co(I)	$E_{1/2}$ of 2nd wave Co(I) → Co(0)	Supporting electrolyte
$Na[Co(CN)_4\ en]\cdot 3.5\ H_2O$	-1.36_4	-1.51	$0.5\ \mathrm{F}\ Na_2SO_4 + 2\ \mathrm{M}$ en 0.0078% Triton X 100*
$Na_5[Co(CN)_4(SO_3)_2]$	-1.36	No reduction	$0.5\ \mathrm{F}\ Na_2SO_3$
$K_4[Co(CN)_5SO_3]\cdot 2\ H_2O$	-1.53_5	No reduction	$1\ \mathrm{F}$ KCl

* Triton X 100=Alkyl-aryl-polyether alcohol (Rohm & Haas Inc.)
Voltage unit: volt vs. SCE. Concentration of the complex: $5\cdot 10^{-3}$ F/l

These overall processes of the electrode reaction are considered to be most plausible:

$$\begin{tikzcd}
{[Co^{III}(CN)_4\,en]^-} \arrow[r, "e"] & {[Co^{II}(CN)_4\,en]^{2-}} \arrow[r, "e", "(A)"'] \arrow[d, "(B)"'] & {[Co^{I}(CN)_4\,en]^{3-}} \arrow[d, "e"] \\
 & {[Co^{II}(CN)_4(OH_2)_2]^{2-},\ \text{etc.}\ \text{(aquated species)}} \arrow[r, "2e"] & {[Co^{0}(CN)_4]^{4-}} \arrow[d] \\
 & & \text{Co(metal)}
\end{tikzcd}$$

The reaction takes place in two ways. When the aquation of the cobalt(II) ion is prevented, the reaction proceeds mainly along path A rather than along path B. Otherwise, the aquated cobalt(II) ions would all be reduced to the metal directly, not through the cobalt(I) state.

Therefore, the resulting cobalt(I) complex was presumed to have the hexacoordinate formula, $[Co^{I}(CN)_4\,en]^{3-}$, in solution, judging from the properties of the other tetracyano complexes.[1,4]

This is the first time that the type of polarographic reduction Co(III)→Co(I)→Co(0) has been observed for the cobalt(III) complexes.

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[4] G. W. Watt and R. J. Thompson, *J. Inorg. Nucl. Chem.*, 9. 311 (1959).