SHORT COMMUNICATIONS

A New Monocyano Cobalt(III) Complex

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Previously, dicyano-cobalt(III) complex, K-$[Co(CN)_2dg_2]\cdot 3/2H_2O$, was reported to have been prepared and reduced to a cobalt(I) complex polarographically.[1,2]

In the present communication, the preparation of the monocyanobis(dimethylglyoximato)ammine-cobalt(III) complex, $[Co(CN)dg_2(NH_3)]\cdot 1/2H_2O$ (trans-form), is described and was found to undergo stepwise reduction to a cobalt(0) complex at the dropping mercury electrode (DME).

The complex was prepared by the following method: To 15.0 g of $[Co(CN)(OH_2)(NH_3)_4]Cl_2$[3] in 150 m*l* of water was added 14.4 g dimethylglyoxime. The mixture was heated on a water bath (85°C) for three hours. The reaction proceeds, evolving ammonia, according to the following:

$$[Co(CN)(OH_2)(NH_3)_4]^{2+} + 2dgH \rightarrow [Co(CN)dg_2(NH_3)] + 3NH_3.$$

Every half hour during the reaction, 5—7 g of ammonium acetate was added to the solution. In total, 20 g of ammonium acetate was used. Lustrous orange-yellow needle-shaped crystals (17.2 g) separated from solution when it was allowed to stand. The product was filtered and washed with 80% ethanol to eliminate traces of unreacted dimethylglyoxime. The yield was above 82%. The complex was recrystallized from hot water (85°C) containing acetic acid.

Found: Co, 17.41; C, 32.08; N, 24.83; H, 5.43%. Calcd for $[Co(CN)dg_2(NH_3)]\cdot 1/2H_2O$: Co, 17.37; C, 31.83; N, 24.77; H, 5.64%.

The complex gave rise to the well-defined waves of three steps in 0.5 M sodium sulfate supporting electrolyte containing 0.007% Triton X100 at the DME (Fig. 1). For each, the limiting current was diffusion-controlled. The diffusion current and the concentration of the complex was linearly related in the concentration range between $5\cdot 10^{-4}$ and 10^{-3} M. The first, second and third waves, each corresponding to an acceptance of one electron, represents the reduction of Co(III)→Co(II), Co(II)→Co(I) and of Co(I)→Co(0), respectively. Table 1 shows the half-wave potentials of the waves for the cobalt(III) complexes of the mono-cyano-series in 0.5 M sodium sulfate solution. The oscillopolarogram obtained with a Polaroscope P 576 indicates three cuts on both the cathodic and anodic branches. Namely, the process of oxidation occurs in three steps, almost the same as in reduction. This implies that the cobalt(0) complex exists in solution.

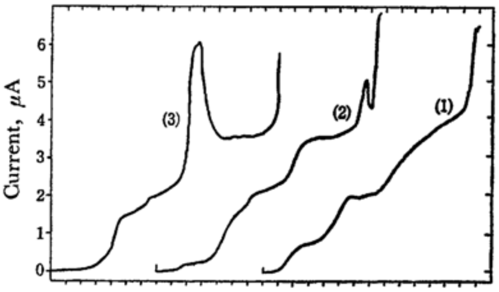

Fig. 1. The current-potential curves for the $[Co(CN)dg_2(NH_3)]$ complex obtained at 10^{-3} M in 0.5 M Na_2SO_4 solution (25°C).
(1) No suppressor
(2) In the presence of 0.0035% Triton X100
(3) 0.0070% Triton X100
Measured from -0.40 V *vs.* SCE.

TABLE 1. HALF-WAVE POTENTIALS OF THE WAVES FOR THE MONOCYANO-COBALT(III) COMPLEXES (25°C)

Complex	$E_{1/2}$ of 1st wave	$E_{1/2}$ of 2nd wave	$E_{1/2}$ of 3rd wave
$[Co(CN)dg_2(NH_3)]$*	-0.65	-0.80	-1.05
$[Co\,dg_2(NH_3)_2]^+$	-0.43	-0.83	-1.05
$[Co(CN)_2dg_2]^-$	$-1.12(Co^{III}\rightarrow Co^{I})$		

* 0.0035% TritonX100 V *vs.* SCE.　0.5 M Na_2SO_4 supporting salt

The net processes of the electrode reaction in the following are considered to be most plausible:

$$\begin{tikzcd}
{[Co^{III}(CN)dg_2(NH_3)]} \arrow[d] & \\
{[Co^{II}(CN)dg_2(NH_3)]^-} \arrow[r] \arrow[d] & {[Co^{I}(CN)dg_2(NH_3)]^{2-}} \arrow[d] \\
{[Co^{II}(CN)dg_2(OH_2)]^-} \arrow[r] & {[Co^{0}dg_2]^{2-}} \arrow[d] \\
 & Co
\end{tikzcd}$$

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[1] N. Maki, This Bulletin, **38**, 2013 (1965).
[2] N. Maki, *Nature,* **188**, 227 (1960).
[3] H. Siebert, *Z. anorg. u. allgem. Chem.*, **327**, 63 (1964).