

Polarographic Study of Metal Complexes. VIII.¹⁾ Dicyanobis-(ethylenediamine)cobalt(III) Complex with a *cis*-Configuration²⁾

Nobufumi MAKI, Kouei YAMAMOTO, Hiroshi SUNAHARA*¹ and Shukichi SAKURABA

Department of Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu

(Received November 12, 1968)

In an aqueous solution containing an excess of ethylenediamine, *i. e.*, under the conditions where the aquation is prevented, the dicyano-cobalt(III) complex, *cis*-[Co(CN)₂en₂]NO₃, has been found to be reduced in three steps at the dropping mercury electrode (DME). The first step, corresponding to the acceptance of one electron, represents the reduction from the cobalt(III) to the cobalt(II) state, while the second and the third step were interpreted as being due to the reduction of two kinds of the cobalt(II) species formed by the overall rearrangement of ligands in solution. One such kind of cobalt species is the binuclear tetracyanocobaltate(II) complex, [Co(CN)₄-en-Co(CN)₄]⁴⁻, which is reduced to the metal through the cobaltate(I) complex, while the other is the cobalt(II) complexes with ethylenediamines in an equilibrium state, which are reduced directly to the metal at the DME. Namely, the second step represents the reduction from the cobalt(II) complex of the former to the cobalt(I) state, while the third step, denoting the reduction to the metal, was observed only on the dE/dt - E curve of the oscillopolarogram, but not on the current-potential curve due to the maximum wave. In the non-aqueous solution of dimethyl sulfoxide, the dicyano-cobalt(III) complex, *cis*-[Co(CN)₂en₂]ClO₄, undergoes the step-by-step reduction of Co(III)→Co(II)→Co(I)→Co(0), as it were, at the DME. Neither aquation nor rearrangements of ligands take place throughout reductions under these experimental conditions, that is, even in lower oxidation states of the cobalt.

The ammine and amine cobalt(III) complexes have hitherto been well known to be reduced to the metal through the hexaquacobalt(II) ions at the dropping mercury electrode (DME). Namely, this kind of reduction type is regarded as belonging to the group of the "inert-labile" type according to the classification of Vlček.³⁾

On the other hand, the cyano-cobalt(III) complexes in general exhibit a reduction of the "inert-inert" type from the view-point of the lability of the complex. For example, the pentacyanocobaltate(III) complexes are reduced to the cobaltate(I) complex in one or two steps at the DME.^{4,5)}

The polarography of the tetracyano complexes, Na₅[Co(CN)₄(SO₃)₂] and K[Co(CN)₄en]·H₂O,

proves that the tetracyanocobaltate(I) complexes can exist stably in solution during reduction when such labile ligands as ethylenediamine and SO₃²⁻ ions are present in solution in an overwhelmingly large excess.⁶⁾ The net electrode processes of the tetracyanocobaltate(III) complexes are thus simplified under these conditions.^{1,6)}

As for the dicyano-cobalt(III) complexes, however, the aquation and the overall rearrangement of ligands are both involved in the electrode processes. Accordingly, in the presence of an excess of ethylenediamine, only the latter appears to take place through the electrode reduction. In the present work, most of our effort was devoted to elucidating the effects of the overall rearrangement of ligands on the current-potential curves.

On the other hand, the electrode processes are ultimately simplified in dimethyl sulfoxide (DMSO), since the dicyano-cobalt(II) and cobalt(I) complexes are regarded as "inert"-type complexes in such a non-aqueous solvent. Hence, the polarographic behavior in DMSO will be dealt with here briefly for the sake of comparison, because such simplified processes of the electrode reaction may serve to

1) Previous paper of this series: N. Maki and K. Okawa, *J. Electroanal. Chem.*, **8**, 262 (1964).

2) Presented at the 21st Annual Meeting of the Chem. Soc. Japan, held at Osaka, April 2, 1968.

*¹ H. S., Present address: Government Industrial Research Institute, Hirate-machi, Kita-ku, Nagoya.

3) A. A. Vlček, *Collection Czechoslov. Chem. Commun.*, **24**, 3572 (1959).

4) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, **71**, 867 (1949).

5) N. Maki, J. Fujita and R. Tsuchida, *Nature*, **183**, 458 (1959); N. Maki, *ibid.*, **195**, 682 (1960).

6) N. Maki and R. Tsuchida, *This Bulletin*, **34**, 891 (1961).

provide information which can then be used in interpreting more complicated processes of the polarographic reduction in an aqueous solution.

In the present paper, however, the polarographic reduction of the dicyano-cobalt(III) complex, $cis\text{-}[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$, was dealt with mainly in an aqueous solution containing ethylenediamine.

Experimental

Apparatus. The experimental details of the measurements have been described previously.¹⁾ The current-potential curves of the cobalt(II) complex in the presence of ethylenediamine were determined in a stream of nitrogen which had previously been passed through the same supporting electrolyte containing ethylenediamine. The current-time (i) curves were recorded on a Yanagimoto Polarovision model PE 20 equipped with a National X-Y recorder, model VR 301. The potential (E) - dE/dt curves were photographed on a Polaroscope P 576 of Kovo, Inc. The characteristics of the capillary used were as follows: $m=1.81$ mg/sec and $t=4.43$ sec (both of which values were measured in a 0.5M Na_2SO_4 solution containing 1M en), and $m=1.69$ mg/sec and $t=4.42$ sec in a 0.5M Na_2SO_4 aqueous solution only.

Materials. Twenty grams of $trans\text{-}[\text{CoCl}_2\text{en}_2]\text{NO}_3$,⁷⁾ were suspended in 700 ml of distilled water, mixed with 20 g of AgCN, and then heated on a water bath (90°C) for three hours. The color of the solution changed from green to yellow. The solution was then filtered, and the filtrate was concentrated by evaporation to one-third its former volume. When the solution was allowed to stand, silky-yellow crystals separated from the solution; these were filtered and washed with cold water, ethanol, and ether. The crude product was recrystallized from hot water.⁸⁾ Found: Co, 19.98; C, 24.49; N, 33.49; H, 5.63%. Calcd for $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$: Co, 20.10; C, 24.58; N, 33.44; H, 5.50%. The absorption spectrum in the visible and ultraviolet regions agrees with that reported by Ohkawa *et al.*⁹⁾

The perchlorate of the complex was analogously obtained by treating $trans\text{-}[\text{CoCl}_2\text{en}_2]\text{ClO}_4$ (20 g) with 22 g of AgCN instead of the nitrate of the praseo salt. Found: Co, 17.90; C, 21.78; N, 25.34; H, 4.90%. Calcd for $[\text{Co}(\text{CN})_2\text{en}_2]\text{ClO}_4$ (anhydrous): Co, 17.83; C, 21.80; N, 25.42; H, 4.88%. For making polarographic measurements in DMSO, the perchlorate of the complex is suitable; it was used since its solubility in DMSO is considerably larger than that of the corresponding nitrate.

The binuclear complex of potassium μ -ethylenediamine-bis[tetracyanocobaltate(II)] monohydrate was prepared according to the directions of Ripán *et al.*¹⁰⁾

7) S. M. Jørgensen, *J. Pr. Chem.*, **41**, 252 (1890); *Gmelins Handbuch der anorganischen Chemie*. Nr. 58, Teil B Kobalt, Verlag Chemie, GmbH, Berlin (1930), p. 239.

8) Briefly reported: N. Maki, T. Hamazaki and S. Sakuraba, *This Bulletin*, **41**, 1735 (1968); N. Maki and S. Sakuraba, *ibid.*, **42**, 1908 (1969).

9) K. Ohkawa, J. Fujita and Y. Shimura, *ibid.*, **38**, 66 (1965).

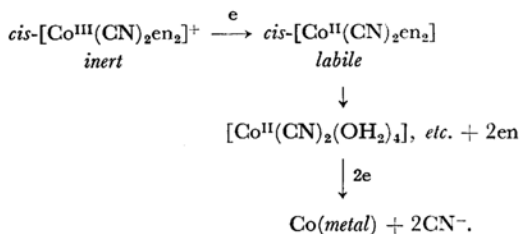
10) R. Ripán, A. Farcás and O. Piringer, *Z. anorg. u. allgem. Chem.*, **346**, 211 (1966).

Found: Co, 20.98; C, 21.22; N, 24.86; H, 1.91%. Calcd for $\text{K}_4[\text{Co}(\text{CN})_4\text{en-Co}(\text{CN})_4]\cdot\text{H}_2\text{O}$: Co, 21.03; C, 21.43; N, 24.99; H, 1.80%.

Results and Discussion

The $cis\text{-}[\text{Co}^{\text{III}}(\text{CN})_2\text{en}_2]^+$ ion behaves quite differently polarographically, depending upon the experimental conditions, especially on whether or not the supporting electrolyte contains an excess of ethylenediamine (en) and cyanide ions. Therefore, the electrode processes were studied and discussed in these four cases: (1) in an aqueous solution of 0.5M Na_2SO_4 only; (2) in a water solution containing 1M en and 0.5M Na_2SO_4 ; (3) in a water solution containing 1M en, 0.1M KCN and 0.45M Na_2SO_4 , and (4) in dimethyl sulfoxide (100%) containing 0.1M $[(\text{C}_2\text{H}_5)_4\text{N}]\text{ClO}_4$.

1) In an Aqueous Solution of 0.5M Na_2SO_4 Containing No Ethylenediamine. Here the $cis\text{-}[\text{Co}(\text{CN})_2\text{en}_2]^+$ ion gives rise to waves of two steps at the DME. The ratio of the height of the first wave to that of the second is approximately 1 : 2. The electrode process of the first step is of the "inert-labile" type and is considered to be quite similar to that of the usual ammine cobalt(III) complexes. That is, the resulting cobalt(II) complex of the "labile" type is broken up into several kinds of aquocobalt(II) species, which are subsequently reduced to the metal at the DME:



2) In an 0.5M Na_2SO_4 Aqueous Solution Containing 1M Ethylenediamine. Here the $cis\text{-}[\text{Co}(\text{CN})_2\text{en}_2]^+$ ion gives rise to the well-defined waves of two steps at the DME. The third or the last step is not distinct in conventional polarography,

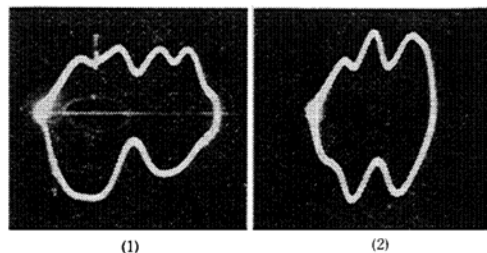


Fig. 1. The oscillograms of dE/dt - E curves of the $cis\text{-}[\text{Co}(\text{CN})_2\text{en}_2]^+$ ion (10^{-3}M) obtained; (1) in the 0.5M Na_2SO_4 aqueous solution containing 1M ethylenediamine; (2) in the 0.5M Na_2SO_4 solution only.

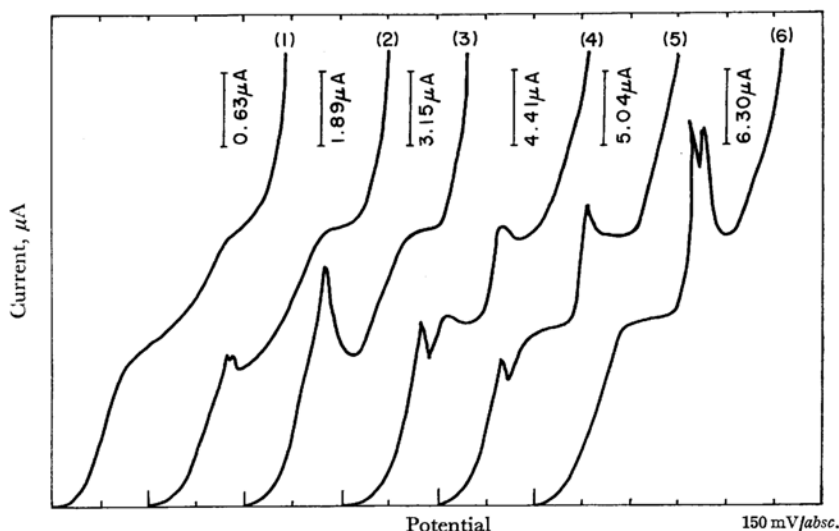


Fig. 2. The dependence of the current-potential curves on the concentration of the complex: (1) 10^{-3} ; (2) $3 \cdot 10^{-3}$; (3) $5 \cdot 10^{-3}$; (4) $7 \cdot 10^{-3}$; (5) $8 \cdot 10^{-3}$; (6) $10^{-2}M$ ($25^{\circ}C$).

Supporting electrolyte: $0.5M Na_2SO_4 + 1M en$

Recorded from $-0.60 V$ vs. SCE.

but it was seen to exist in the oscillogram of the Heyrovský-Foréjt type: indeed, the last step was covered completely with the large maximum, which could not be suppressed with a usual surface-active agent, such as Triton X 100*² or gelatin.

Figure 1 shows the $dE/dt - E$ (potential) curves photographed in the presence and the absence of excess ethylenediamine. In the former case three cuts were observed on the cathodic branch of the curve: the first two cuts correspond to the reduction waves of two steps in the classical d. c. polarogram, while the last cut may correspond to the last step of the maximum, which probably represents the reduction to the metallic cobalt, since only a cut ($Co \rightarrow Co^0$) was noticed on the anodic branch of the curve.

On the other hand, in the latter case two cuts

were seen to exist on the cathodic branch of the curve; these cuts correspond to the reductions of $Co(III) \rightarrow Co(II)$ and of $Co(II) \rightarrow Co(metal)$ respectively.

The limiting current of the first and the second wave is linearly related to the concentration of the complex in the range between $4 \cdot 10^{-4}$ and $2 \cdot 10^{-2}M$. The ratio of the height of the first wave to that of the second is approximately 1:0.5. The limiting current of each step was found to be proportional to the square root of the height of the mercury reservoir, as is shown in Table 1. The values of $i_1/\sqrt{h_{corr}}$ are independent of the increase in mercury pressure. Accordingly, the

TABLE 1. THE RELATIONSHIP BETWEEN THE CURRENT AND HEIGHT OF THE MERCURY RESERVOIR ($25^{\circ}C$)

h_{corr}	$i_1(\mu A)$	$i_2(\mu A)$	$i_1/\sqrt{h_{corr}}$	$i_2/\sqrt{h_{corr}}$
91.4	11.2	5.3	1.17	0.55
86.4	10.8	5.0	1.16	0.54
81.4	10.3	4.9	1.14	0.54
76.4	9.9	4.8	1.13	0.55
71.4	9.5	4.6	1.12	0.54
66.4	9.2	4.4	1.13	0.54
61.4	8.8	4.1	1.12	0.52

The concentration of the complex: $7 \cdot 10^{-3}M$;

Supporting electrolyte: $0.5M Na_2SO_4 + 1M en$

In the presence of 0.0021% Triton X 100

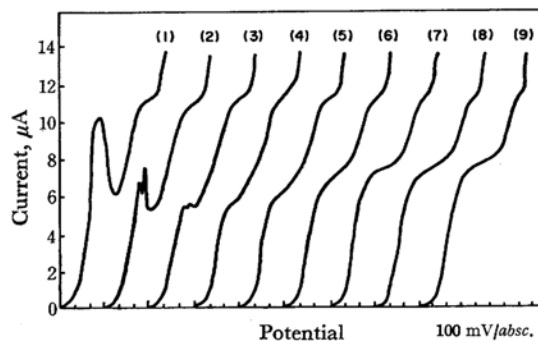


Fig. 3. The effect of Triton X 100 on the current-potential curves ($25^{\circ}C$).

The concentration of Triton X 100: (1) 0; (2) 0.00042%; (3) 0.00084%; (4) 0.00126%; (5) 0.00168%; (6) 0.00210%; (7) 0.00252%; (8) 0.00294%; (9) 0.00336%.

Supporting electrolyte: $0.5M Na_2SO_4 + 1M en$

Concn. of the complex: $5 \cdot 10^{-3}M$

Recorded from $-0.70 V$ vs. SCE

*² Triton X 100=Alkyl-aryl-polyether alcohol.

limiting current of both the waves is diffusion-controlled. This conclusion was also supported by the results of the analyses of $i-t$ curves coupled with the temperature-dependence of the limiting currents, as will be discussed hereafter.

Figure 2 shows the dependence of the current-potential curve on the concentration of the complex. In the figure, the current scale was individually curtailed, lest the current scale should change with the concentration of the complex. The two maxima observed at higher concentrations are considered to be due to the adsorption of the complex on the DME, judging from the electrocapillary curves measured. The maxima could be suppressed in the presence of Triton X 100 more than 0.0025%, as is shown in Fig. 3.

Figures 4 and 5 show the effect of Triton X 100 on the diffusion currents of both the waves obtained at the concentration of the complex of 10^{-3} and $5 \cdot 10^{-3}$ M. In the figure, at the steady state, *i. e.*, when Triton X 100 suppresses the maxima to exclude the adsorption of the complex on the DME, the height of the second wave is seen to become nearly a half of that of the first wave.

Figure 6 shows the effect of an excess of ethylenedi-

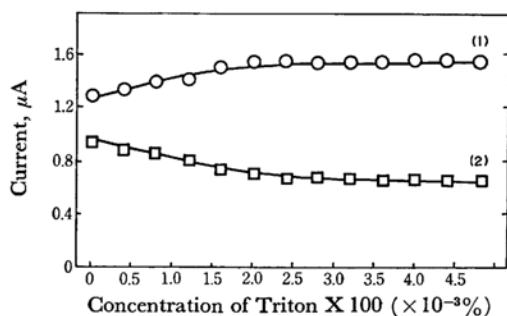


Fig. 4. The effect of Triton X 100 on the limiting currents of the first and the second wave obtained at 10^{-3} M complex ion: (1) 1st wave; (2) 2nd wave. Supporting electrolyte: $0.5\text{M Na}_2\text{SO}_4 + 1\text{M en}$ (25°C)

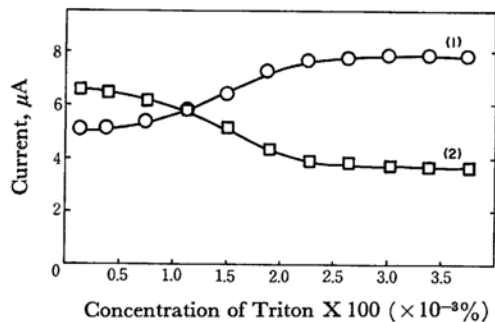


Fig. 5. The effect of Triton X 100 on the limiting currents of the first and the second wave obtained at $5 \cdot 10^{-3}$ M complex ion: (1) 1st wave; (2) 2nd wave. Supporting electrolyte: $0.5\text{M Na}_2\text{SO}_4 + 1\text{M en}$ (25°C).

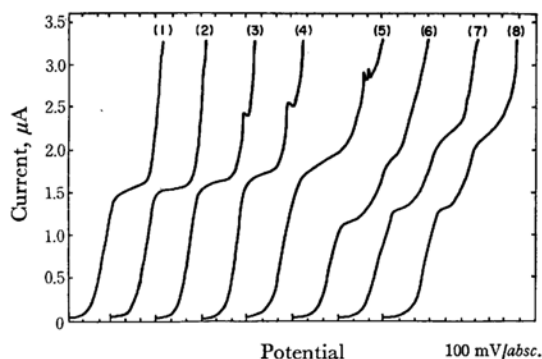
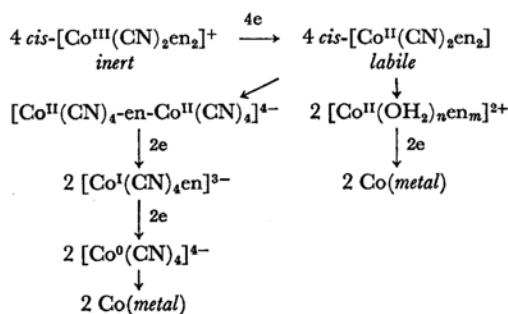


Fig. 6. The effect of the ethylenediamine on the current-potential curves obtained at 10^{-3} M complex ion in the $0.5\text{M Na}_2\text{SO}_4$ solution (25°C).

The concentration of ethylenediamine: (1) 0.00; (2) 0.01; (3) 0.03; (4) 0.05; (5) 0.06; (6) 0.07; (7) 0.09; (8) 0.10M

Recorded from -0.60 V vs. SCE

amine on the current-potential curve at the 10^{-3} M complex ion. At concentrations higher than 0.007M , the single wave is seen to split into the double wave. This fact suggests that the cobalt(II) complexes formed at the first step of the reduction react with each other in the presence of excess ethylenediamine to produce two kinds of stable new species. One of the species might be the binuclear tetracyanocobaltate(II) complex, $[\text{Co}(\text{CN})_4\text{-en-Co}(\text{CN})_4]^{4-}$, formed partly as a result of the overall rearrangement of ligands in solution, which is reduced in two steps to the metal through the cobaltate(I) complex; the other of the cobalt(II) species is a mixture of the aquocobalt(II) complexes with ethylenediamines in an equilibrium state, with all the elements being reduced directly to the metal at the DME. That is, the reduction of the former to a cobalt(I) state takes place at -1.18 V vs. SCE , while the reduction of the latter to the metal is not observed because of the maximum. In short, the former is polarographically active, but the latter is apparently inactive. Consequently, the fact that the wave-height of the second step, corresponding to an apparently $1/2$ electron reduction, is always a half of that of the first step can be explained in terms of the following processes of the electrode reaction:



In the previous paper,¹¹ the tetracyanocobaltate(I) complex, $[\text{Co}^{\text{I}}(\text{CN})_4\text{en}]^{3-}$, was speculated to be present stably in a solution containing ethylenediamine. Furthermore, Watt *et al.*^{11,12} have reported isolating two complexes, $\text{K}_3[\text{Co}^{\text{I}}(\text{CN})_4]$ and $\text{K}_4[\text{Co}^0(\text{CN})_4]$, as solids by the reduction of $\text{K}_3[\text{Co}(\text{CN})_6]$ in liquid ammonia with metallic potassium. Therefore, it would not be out of the way to assume that such tetracyanocobaltate(I) and cobaltate(0)

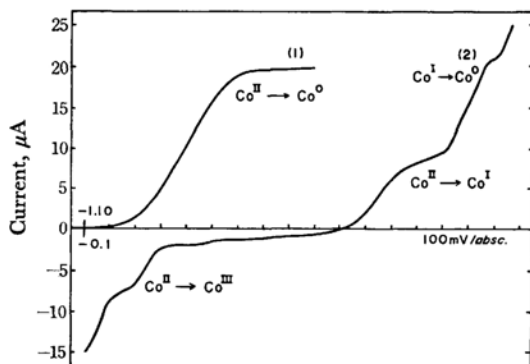


Fig. 7. The current-potential curves of the cobalt(II) complexes: (1) $[\text{Co}(\text{OH}_2)_6]^{2+}$ ion (10^{-2}M) in 0.5M Na_2SO_4 solution; Recorded from -1.10 V vs. SCE . (2) $\text{K}_4[\text{Co}(\text{CN})_4\text{-en-Co}(\text{CN})_4] \cdot \text{H}_2\text{O}$ ($5 \cdot 10^{-3}\text{M}$) in 0.5M Na_2SO_4 solution containing 1.5M ethylenediamine (25°C); Recorded from -0.10 V vs. SCE in a stream of nitrogen.

complexes are present in solution as intermediates in the reduction process.

Figure 7 shows the current-potential curve for $\text{K}_4[\text{Co}(\text{CN})_4\text{-en-Co}(\text{CN})_4] \cdot \text{H}_2\text{O}$ obtained in a stream of nitrogen. For comparison, the two-electron reduction wave of the hexaquo cobalt(II) ion is also shown in the figure. Both the curves were obtained at the same concentration of the cobalt(II). The $[\text{Co}(\text{CN})_4\text{-en-Co}(\text{CN})_4]^{4-}$ ion gave rise to waves of two steps: the first and the second wave, corresponding to a gain of one electron,

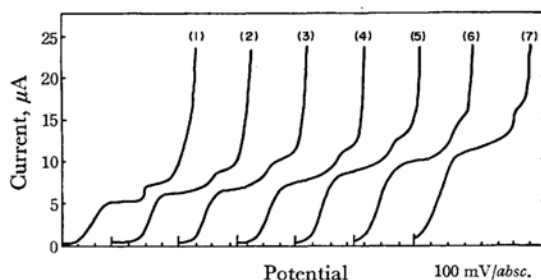


Fig. 8. The dependence of the current-potential curves upon the temperatures obtained at the concentration of the complex, $5 \cdot 10^{-3}\text{M}$, in the 0.5M Na_2SO_4 solution containing 1M ethylenediamine. The temperature of the electrolyte: (1) 0°C ; (2) 10°C ; (3) 20°C ; (4) 30°C ; (5) 40°C ; (6) 50°C ; (7) 60°C .

Recorded from -0.70 V vs. SCE

TABLE 2. THE HALF-WAVE POTENTIALS OF THE WAVES FOR THE MIXED CYANO COBALT(III) AND COBALT(II) COMPLEXES (25°C)

Compound	1st wave	2nd wave	3rd wave	Supporting electrolyte
<i>cis</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$	-0.95 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)		-1.38 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^0$)	0.5M Na_2SO_4 aq. soln.
	-0.86 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-1.18 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	*	0.5M $\text{Na}_2\text{SO}_4 + 1\text{M}$ en
	-0.78 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-1.33 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	*	0.00084% Triton X 100
			-1.99 ($\text{Co}^{\text{I}} \rightarrow \text{Co}^0$)	0.45M $\text{Na}_2\text{SO}_4 + 1\text{M}$ en
<i>cis</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{ClO}_4$	-0.95 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-1.48 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	-1.99 ($\text{Co}^{\text{I}} \rightarrow \text{Co}^0$)	$+0.1\text{M}$ KCN
<i>trans</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$	-0.87 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-1.20 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	*	DMSO(100%) + 0.1M $(\text{C}_2\text{H}_5)_4\text{NClO}_4$
			-1.99 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^0$)	0.5M $\text{Na}_2\text{SO}_4 + 1\text{M}$ en
	-0.78 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-1.31 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	*	0.45M $\text{Na}_2\text{SO}_4 + 1\text{M}$ en
<i>trans</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{ClO}_4$	-0.97 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-1.52 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	-1.99 ($\text{Co}^{\text{I}} \rightarrow \text{Co}^0$)	$+0.1\text{M}$ KCN
<i>cis</i> - $[\text{Co}(\text{CN})_2\text{dip}_2]\text{NO}_3 \cdot 7\text{H}_2\text{O}$	-0.43 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-0.87 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	-1.23 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^0$)	DMSO(100%) + 0.1M $(\text{C}_2\text{H}_5)_4\text{NClO}_4$
<i>cis</i> - $[\text{Co}(\text{CN})_2\text{phen}_2]\text{NO}_3 \cdot 6\text{H}_2\text{O}$	-0.42 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$)	-0.86 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	-1.22 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^0$)	0.5M Na_2SO_4 aq. soln.
$\text{K}_4[\text{Co}(\text{CN})_4\text{-en-Co}(\text{CN})_4] \cdot \text{H}_2\text{O}$	-0.32 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$)	-1.23 ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$)	-1.57 ($\text{Co}^{\text{I}} \rightarrow \text{Co}^0$)	0.5M $\text{Na}_2\text{SO}_4 + 1.5\text{M}$ en
$\text{K}[\text{Co}(\text{CN})_4\text{en}] \cdot \text{H}_2\text{O}^{11}$	-1.36 ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{I}}$)	-1.51 ($\text{Co}^{\text{I}} \rightarrow \text{Co}^0$)		0.00084% Triton X 100
				0.5M $\text{Na}_2\text{SO}_4 + 2\text{M}$ en
				0.0078% Triton X 100

Voltage unit: volt vs. SCE

* The maximum wave

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

12) G. W. Watt, J. L. Hall, G. R. Choppin and P. S. Gentile, *J. Am. Chem. Soc.*, **76**, 373 (1954); W. Hieber and C. Bartenstein, *Naturwissenschaften*, **13**, 300 (1952).

represent the step-by-step reduction of $\text{Co(II)} \rightarrow \text{Co(I)}$ and of $\text{Co(I)} \rightarrow \text{Co(0)}$ respectively. The half-wave potential (-1.23 V vs. SCE) of the first step ($\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$) is near that of the second wave for the $\text{cis-}[\text{Co}(\text{CN})_2\text{en}_2]^+$ ion, as Table 2 shows. Therefore, the second step for the $\text{cis-}[\text{Co}(\text{CN})_2\text{en}_2]^+$ ion may be concluded to represent the overall reduction from the binuclear tetracyanocobaltate(II) to the cobaltate(I) complex at the DME.

Figure 8 shows the temperature-dependence of the current-potential curves. The diffusion currents are linearly related with the temperature; the tangents of the lines for the first and the second wave-heights are 1.25 and 1.23% at 25°C respectively. The shape of the second wave at higher temperatures becomes more obvious than that at lower temperatures.

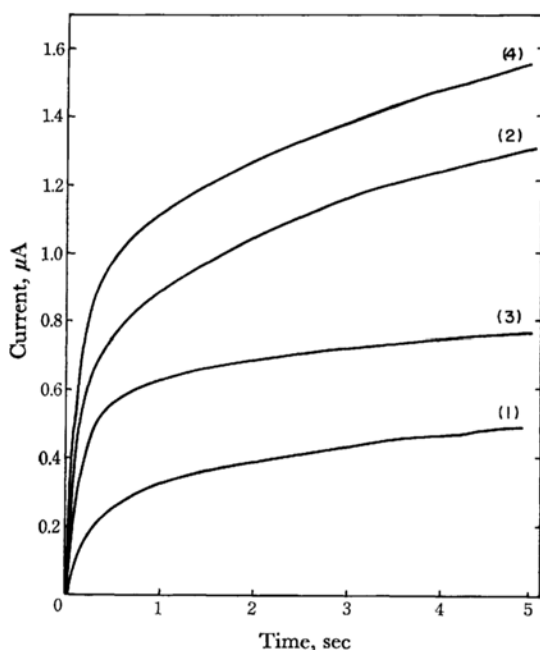


Fig. 9. The current-time curves of the $\text{cis-}[\text{Co}(\text{CN})_2\text{en}_2]^+$ ion recorded during one drop growth of DME at the potentials: (1) -0.85 ; (2) -1.00 ; (3) -1.18 ; (4) -1.35 V vs. SCE . Supporting electrolyte: $0.5\text{M Na}_2\text{SO}_4 + 1\text{M en}$ (25°C)

Figure 9 shows the current-time curves during a one-drop growth of DME obtained at a constant potential. The current varies with time to the powers of 0.17 and 0.19 at the potentials at which the first and the second step respectively exhibit the limiting currents. This result, combined with the above-mentioned finding in relation to the effect of the mercury head, supports the conclusion regarding the diffusion-controlled features of both the waves in a supporting electrolyte of this sort.

3) In a $0.45\text{M Na}_2\text{SO}_4$ Aqueous Solution Containing 0.1M KCN and $1\text{M Ethylenediamine}$.

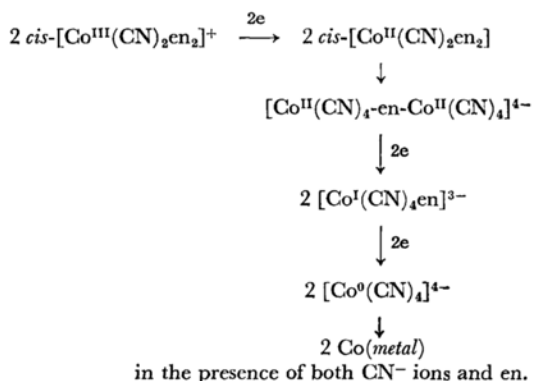
Here the $\text{cis-}[\text{Co}(\text{CN})_2\text{en}_2]^+$ ion similarly gave rise to well-defined waves of two steps at the DME. The second wave-height, however, increases twice as much as that in a solution containing no excess cyanide ions, that is, in a solution containing only excess ethylenediamine. More exactly, the ratio of the wave-heights of the first and the second waves was $1 : 1.03$ which had been corrected for the drop time. Undoubtedly, the cyanide ions in excess are available for producing the binuclear tetracyanocobaltate(II) complex through the rearrangement of ligands in solution.

The limiting currents of the two steps were found to be proportional to the square root of the mercury pressure on the DME; the limiting currents exhibit the diffusion-controlled feature.

In addition to these results, the d. c. polarogram of two steps for the $\text{K}_4[\text{Co}(\text{CN})_4\text{en-Co}(\text{CN})_4] \cdot \text{H}_2\text{O}$ (a pale yellow crystal) dissolved in a $0.45\text{M Na}_2\text{SO}_4$ solution containing both 0.1M KCN and $1\text{M ethylenediamine}$ agrees quite well with that of the hexaquocobalt(II) chloride dissolved in the same supporting electrolyte in the shape of the waves and in the half-wave potentials (see Table 2).

The presence of ethylenediamine in excess is essential for the existence of the $[\text{Co}(\text{CN})_4\text{en-Co}(\text{CN})_4]^{4-}$ ion in water solution, but the cyanide ions in excess are not necessary; the binuclear tetracyanocobaltate(II) complex should be regarded as "partly-labile."

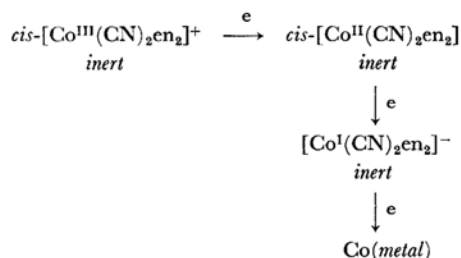
Accordingly, the net processes of the electrode reaction presented below may be considered to be the most plausible:



Thus, all the resulting cobalt(II) species of the $[\text{Co}^{\text{II}}(\text{CN})_2\text{en}_2]$ complex are presumed to be totally subject to the rearrangement of ligands to produce a binuclear tetracyanocobaltate(II) complex in solution; this is then reduced to the metal through the cobaltate(I) complex at the DME. Under these experimental conditions, no aquation occurs, and only the rearrangement of ligands is discerned to take place in solution.

4) In Dimethyl Sulfoxide (100%) Con-

taining 0.1M $[(C_2H_5)_4N]ClO_4$. Here the complex, $cis-[Co(CN)_2en_2]ClO_4$, gave rise to waves of three steps at the DME. The limiting current of each step is strictly diffusion-controlled. The diffusion currents of the first, the second, and the third wave, named from positive to negative potentials, are proportional to the concentration of the complex in the range between $5 \cdot 10^{-4}$ and $5 \cdot 10^{-3}M$. The first, the second, and the third wave, corresponding to an acceptance of one electron, represent the step-by-step reductions of $Co(III) \rightarrow Co(II)$, $Co(II) \rightarrow Co(I)$, and of $Co(I) \rightarrow Co(metal)$ respectively. The following processes of the electrode reaction seem to be the most plausible:¹³⁾



Thus, the dicyano-cobalt(III) complex is considered not to undergo any structural changes throughout the reductions and to undergo the step-by-step reductions, as it were, without disrupting the complex. In other words, neither the aquation nor the rearrangement of ligands takes place during the reductions.

Figure 10 shows the current-potential curves obtained in the four kinds of supporting electrolytes mentioned above. In the figure, the limiting currents of only three waves in a DMSO are relatively depressed to some extent compared with those of the other curves.

As far as the processes of the electrode reaction in these solutions are concerned, the processes in a DMSO are most simplified and can be best understood, an understanding of them evidently serves to provide information for interpreting more complicated processes in water solutions, since the polarographic reductions are regarded as of the "inert-inert" type in such a DMSO.

On the other hand, it is evident from the above-

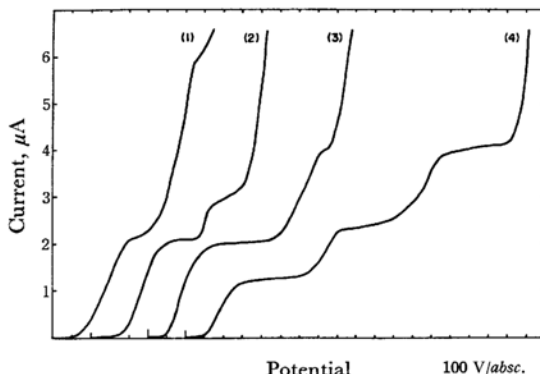


Fig. 10. The current-potential curves of the $cis-[Co(CN)_2en_2]^+$ ion measured at the concentration of the complex, $10^{-3}M$, in the various kinds of the supporting electrolytes: (1) in 0.5M Na_2SO_4 aqueous solution only; (2) in 0.5M Na_2SO_4 aqueous solution containing 1M ethylenediamine; (3) in 0.45M Na_2SO_4 aqueous solution containing 0.1M KCN and 1M ethylenediamine; (4) in dimethyl sulfoxide (100%) containing 0.1M $[(C_2H_5)_4N]ClO_4$ (25°C). The curves, (1), (2), and (3), were recorded from $-0.60V$ vs. SCE, while the curve of (4) was recorded from $-0.80V$ vs. SCE.

mentioned results that the dicyano-cobalt(II) complex in itself tends to be broken up and to turn into the more stable species of the tetracyano-cobaltate(II) complex as a result of the overall rearrangement of ligands in a water solution containing excess ethylenediamine. The rearrangement of ligands was also observed for the other dicyano-cobalt(III) complexes; for example, $cis-[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$, $cis-[Co(CN)_2phen_2]NO_3 \cdot 6H_2O$, $trans-[Co(CN)_2en_2]NO_3$, and $trans-[Co(CN)_2(NH_3)_4]NO_3 \cdot H_2O$. In a DMSO, even the $[Co^I(CN)_2(NH_3)_4]^-$ ion was found to be able to exist stably without disrupting the complex.

The merit of adopting a non-aqueous solvent lies not only in such a simplification of the electrode processes, but also in the stabilization of the lower oxidation states of the central metal ion from the point of view of the other side.

The authors wish to thank the Ministry of Education for the financial support granted this investigation.

13) More details in a non-aqueous solution are to be reported in the next paper of this series.