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Polarographic Study of Metal Complexes. X.[1] The Disulfitotetracyanocobaltate(III) Complex[2]

Nobufumi Maki and Kouei Yamamoto[*1]

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

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The sodium disulfitotetracyanocobaltate(III), $Na_5[Co^{III}(SO_3)_2(CN)_4]\cdot 3H_2O$, was found to be irreversibly reduced in one step to the cobalt(I) state in a 0.5M Na_2SO_3 aqueous solution at the dropping mercury electrode (DME). As for the resulting cobaltate(I) complex, neither further reduction to the metal nor oxidation was observed in the potential range of 0—−2.0 V (*vs.* SCE). Above 40°C, a partial reduction to the metal was observed to take place at about −1.9 V (*vs.* SCE). The reduction was interpreted as being of the "*inert-inert*" type, as shown below:

$$trans\text{-}[Co^{III}(SO_3)_2(CN)_4]^{5-} \xrightarrow{2e} trans\text{-}[Co^{I}(SO_3)_2(CN)_4]^{7-}.$$

Here, the disulfito complex was presumed to take a *trans*-configuration rather than that of a *cis*-form on the evidence of its polarographic behavior and the absorption spectrum. That is, the tetracyano complexes with a *cis*-configuration are considered to be reduced to the metal, whereas those with a *trans*-configuration are reduced to the cobalt(I) state, and not to the metal polarographically, at the DME.

In earlier papers,[3] we reached some significant conclusions about the electrode reaction of the tetracyanocobaltate(III) complex, $K[Co^{III}(CN)_4en]\cdot H_2O$ (*cis*-form). Namely, the *cis*-$[Co(CN)_4en]^-$ ion gave rise to an apparent one-step wave of a three-electron reduction, representing a direct reduction from the cobalt(III) complex to the metal in aqueous solutions at the DME. In the presence of ethylenediamine (2M), however, the *cis*-$[Co(CN)_4en]^-$ ion was reduced to the metal *via* the cobaltate(I) complex. The hexa-coordinated cobalt(I) ion $[Co^I(CN)_4en]^{3-}$, was presumed to be able to exist under the conditions where aquation is prevented.

Recently, in examining the *cis*-dicyanobis(ethylenediamine)cobalt(III) complex polarographically, we ascertained the binuclear tetracyanocobaltate(II) ion,[4] $[Co^{II}(CN)_4\text{-en-}Co^{II}(CN)_4]^{4-}$, to be formed in the course of reductions by the rearrangement of cyanide ligands; the ion undergoes the step-by-step reduction of Co(II)→Co(I)→Co(0) at the DME.[5]

In connection with these results, several kinds of pentacyanocobaltate(III) complexes of the $[Co^{III}X(CN)_5]$-type have also been reported to be all reduced to the cobalt(I) state in aqueous solutions at the DME.[6-8] Neither further reduction of the pentacyanocobaltate(I) complex to the metal nor oxidation from the cobalt(I) state was observed in the potential range of 0—−2.0 V (*vs.* SCE).

The present paper is concerned with the behavior of the disulfitotetracyanocobaltate(III) complex, $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$, in aqueous solutions.

Experimental

Apparatus. A Yanagimoto Polarograph, Model P8-DP, was used for the measurements of the d.c. polarograms. The *iR* drop was corrected automatically with a compensator for the liquid resistances, Yanagimoto Model P8-PT. The other experimental set-up and the measurements were the same as those employed previously.[3,5] The characteristics of the capillary used were as follows: $m=1.38$ mg/sec, $t=4.50$ sec, both measured on an open circuit in a 0.5M Na_2SO_3 aqueous solution (25°C).

The absorption spectra in the visible and ultraviolet regions were determined manually with a Beckmann DU spectrophotometer.

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[1] Previous paper of this series: N. Maki, Y. Ishiuchi and S. Sakuraba, This Bulletin, **42**, 3166 (1969).

[2] Briefly reported in part: N. Maki and R. Tsuchida, This Bulletin, **34**, 891 (1961).

[*1] Present address: K. Y., Hamamatsu TV company Inc., Ichino-cho, Hamamatsu.

[3] N. Maki and K. Okawa, *J. Electroanal. Chem.*, **8**, 262 (1964); This Bulletin, **37**, 1233 (1964).

[4] R. Ripàn, A. Farcăs and O. Piringer, *Z. Anorg. Allgem. Chem.*, **346**, 211 (1966).

[5] N. Maki, K. Yamamoto, H. Sunahara and S. Sakuraba, This Bulletin, **42**, 3159 (1969).

[6] D. N. Hume and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **71**, 867 (1949).

[7] N. Maki, J. Fujita and R. Tsuchida, *Nature*, **183**, 458 (1959); N. Maki, *ibid.*, **185**, 682 (1960).

[8] N. Maki, Proceeding 3rd International Congress of Polarography, Vol. 1, ed. by G. J. Hills, MacMillan & Co., London (1966), p. 505.

Materials. The complex, $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$,*[2] was prepared by the method of Rây and Chackrabarty9) and purified according to the directions of Chen *et al.*10) The purifications were essential for obtaining the pure aimed-at complex and were carried out five times here. The complex thus obtained has this formula: $Na_5[Co(SO_3)_2(CN)_4]\cdot 12H_2O$ (orange-yellow); it is efflorescent in an open state and the crystallization water is lost partly in the air. The anhydrous salt, which had been dried *in vacuo* at 100—110°C (in an Abderhalden apparatus) for six hours, assumed a brown color and was very hygroscopic. Hence, the trihydrate salt used for the polarographic measurements was obtained by drying it *in vacuo* at 60°C overnight. Found: Co, 11.57; C, 10.03; N, 11.30; H, 1.35%. Calcd for $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$: Co, 11.98; C, 9.76; N, 11.39; H, 1.23%.

The diaquotetracyanocobaltate(III) complex, $K[Co(OH_2)_2(CN)_4]\cdot \frac{3}{4}H_2O$, was also prepared by the method of Rây and Chackrabarty9) according to the following reaction of scheme:

$$Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O \xrightarrow{HNO_3}$$

$$[Co(SO_4)_2(CN)_4]^{5-} \xrightarrow{H_2O} [Co(OH_2)_2(CN)_4]^-$$

$$\xrightarrow{AgNO_3} Ag[Co(OH_2)_2(CN)_4]\ \text{ppt.} \xrightarrow{KI}$$

$$K[Co(OH_2)_2(CN)_4]\cdot \tfrac{3}{4}H_2O.$$

The diaquo complex can not be stored for more than two weeks, because it decomposes gradually even in the solid state to yield an unknown product insoluble in water. The causes of this deterioration are not clear, but probably it is due to the polymerization of the complex. Therefore, the elementary analyses and the polarographic measurements were always carried out on a freshly-prepared complex. Found: Co, 24.09; C, 19.83; N, 22.97; H, 1.62%. Calcd for $K[Co(OH_2)_2(CN)_4]$: Co, 24.75; C, 20.18; N, 23.53; H, 1.69%.

The sulfitopentacyanocobaltate(III) complex, $K_4[Co(SO_3)(CN)_5]\cdot 3H_2O$, was prepared from the $K_3[CoBr(CN)_5]$ complex by the method of Fujita and Shimura.11) Found: Co, 12.26; C, 12.38; N, 14.77; H, 1.32%. Calcd for $K_4[Co(SO_3)(CN)_5]\cdot 3H_2O$: Co, 12.29; C, 12.52; N, 14.61; H, 1.26%. The other complexes used in this work were lots prepared in our previous experiments.3,5)

Results and Discussion

The disulfito complex, $Na_5[Co^{III}(SO_3)_2(CN)_4]\cdot 3H_2O$, gave rise to a well-defined wave of one step at the DME in a 0.5M sodium sulfite supporting electrolyte. This wave, corresponding to a gain of two electrons, represents the reduction from the cobalt(III) to the cobalt(I) state. No further reduction to the metal was found over the potential range of 0—−2.0 V (*vs.* SCE). Figure 1 shows the dependence of the current-potential curves upon the concentration of the complex in the 10^{-2}—10^{-3}M range in a 0.5M Na_2SO_3 aqueous solution. In the figure, the current-scale is individually curtailed, lest it should change with the concentration of the complex. Scarcely no changes were found in the

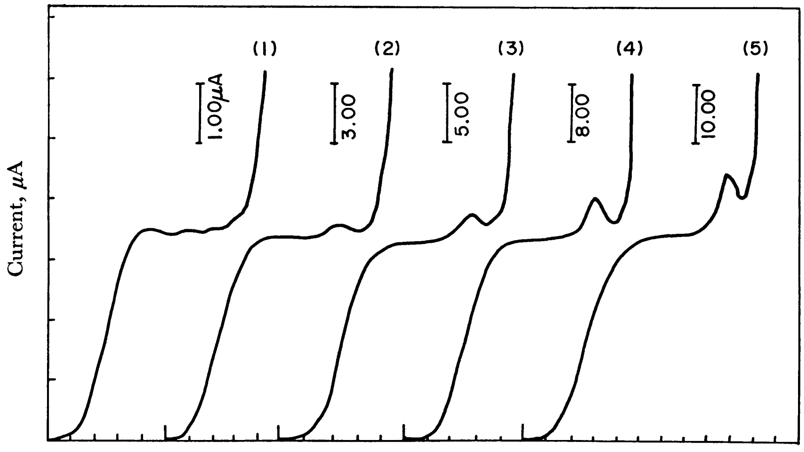

Fig. 1. The dependence of the current-potential curves upon the concentration of the complex, $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$, in a 0.5M Na_2SO_3 aqueous solution (25°C). Concentration of the complex, (1) 10^{-3}; (2) $3\cdot 10^{-3}$; (3) $5\cdot 10^{-3}$; (4) $8\cdot 10^{-3}$; (5) 10^{-2}M; recorded from −1.00 V (*vs.* SCE).

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*[2] The sulfite ion, OSO_2^{2-}, can be bound to the cobalt either by the oxygen or by the sulfur atom; the former is named the sulfito complex, and the latter, the sulfono complex.

9) P. R. Rây and S. Ch. Chackrabarty, *Z. Anorg. Allgem. Chem.*, **211**, 173 (1933).

10) H. H. Chen, M-S. Tsao, R. W. Gaver, P. H. Tewari and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).

11) J. Fujita, Ph. D. thesis (1959); J. Fujita and Y. Shimura, This Bulletin, **36**, 1281 (1963).

TABLE 1. THE RELATIONSHIP BETWEEN THE HEIGHT OF THE MERCURY RESERVOIR AND THE LIMITING CURRENT

$h_{corr.}$ (cm)	i_l (μA)	$i_l/\sqrt{h_{corr.}}$
92.0	18.5	1.93
82.0	17.3	1.92
72.0	16.5	1.93
62.0	15.1	1.92
52.0	13.7	1.90
42.0	12.3	1.89

Concentration of the complex: $5.0\cdot10^{-3}$M in a 0.5M Na_2SO_3 i_l=the limiting current at −1.50 V *vs.* SCE (25°C)

shape of the wave with the concentration. The limiting current and the concentration of the complex were ascertained to be strictly linearly related in the concentration range of 10^{-4}—10^{-2}M.

Table 1 shows that the limiting current is proportional to the root of the height of the mercury reservoir; the values $i_l/\sqrt{h_{corr.}}$ are almost constant, irrespective of the mercury pressure.

Figure 2 shows the temperature-dependence of the limiting current in the range of 0—60°C. Above 40°C, the current values were seen to deviate from the straight line of the plot; the current increases remarkedly with the temperature, indicating a kinetically-controlled feature. This seems to be due to the disruption of the cobaltate(I) complex in solution. Below 40°C, the current increases linearly with the temperature; its coefficient was 1.70%/degree at 25°C. Figure 3 shows the temperature-dependence of the current-potential curves in a 0.5M Na_2SO_3 supporting electrolyte. On the whole, scarcely no deformations of the wave with the temperature were observed, but the partial reduction to the metal could be discerned to appear at around −1.98 V (*vs.* SCE) above 50°C.

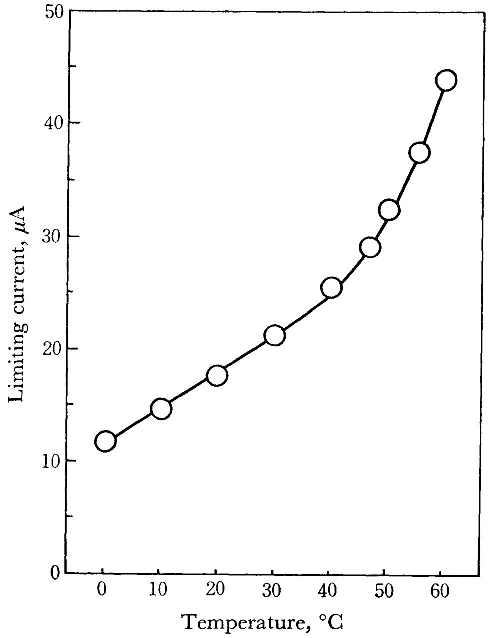

Fig. 2. The relationship between the limiting current and the temperature for the $Na_5[Co(SO_3)_2(CN)_4]\cdot3H_2O$ complex in a 0.5M Na_2SO_3 solution (25°C).

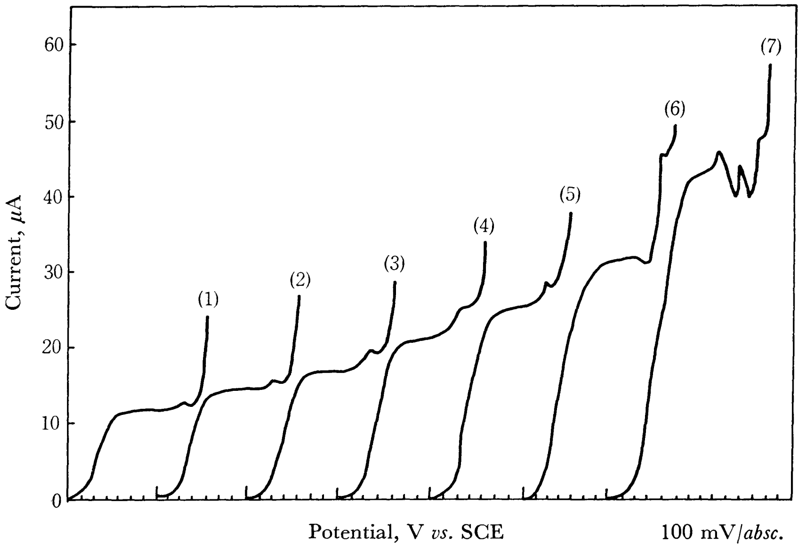

Fig. 3. The temperature-dependence of the current-potential curves for the $Na_5[Co(SO_3)_2(CN)_4]\cdot3H_2O$ complex in a 0.5M Na_2SO_3 solution. The concentration of the comeplx, $5\cdot10^{-3}$M, the temperature, (1) 0; (2) 10; (3) 20; (4) 30; (5) 40; (6) 50; (7) 60°C. Recorded from −1.00 V (*vs.* SCE).

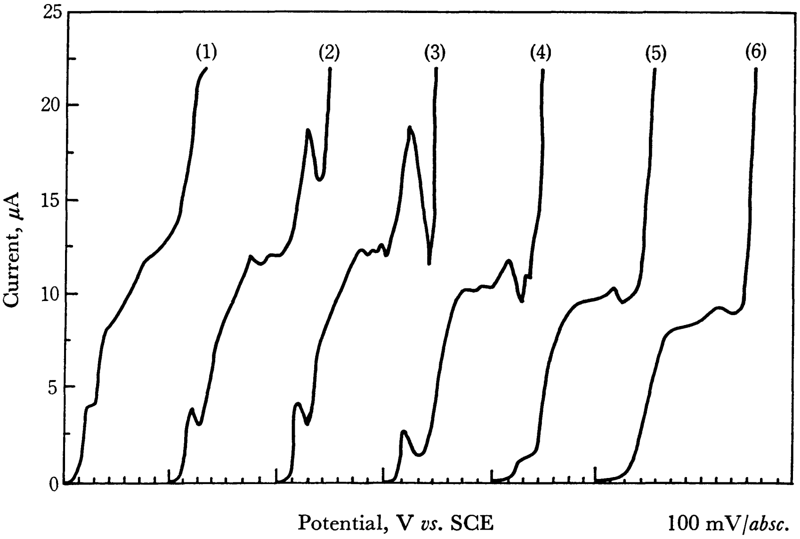

Fig. 4. The effect of sulfite ions upon the current-potential curves for the complex, $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_3O$, under a unit ionic strength ($Na_2SO_3+Na_2SO_4$). The concentration of SO_3^{2-} ions, (1) 0; (2) 0.005; (3) 0.01; (4) 0.05; (5) 0.1; (6) 0.5M. Recorded from −0.90 V (*vs.* SCE).

From these results, the limiting current may well be concluded to be diffusion-controlled below 40°C.

Figure 4 shows the effect of sulfite ions on the current-potential curves in solution under a unit ionic strength. The disulfitotetracyano complex has previously been described as not being able to exist stably in solution unless sulfite ions are present in excess. That is, the cobaltate(III) complex in solution decomposes with time to yield unknown yellow precipitates insoluble in water. Polarographic measurements were, however, practically possible on the freshly-prepared solution. The limiting current decreases with the increase in the concentration of the sulfite ions by about 15%.

Figure 5 shows oscillopolarograms of the Heyrovský-Forejt type photographed for the disulfito-, diaquo-tetracyanocobaltate(III), and sulfitopentacyanocobaltate(III) complexes in aqueous solutions. For the sulfito- and disulfito-complexes, only one incision was observed, at −1.26 or at −1.24 V (*vs.* Hg pool) respectively on the cathodic branch of the d*E*/d*t* - *E* curves, whereas no incision was found on the anodic branch; this is in agreement with the findings on the aquopentacyanocobaltate(I) ion by Kolthoff and Hume.[6] Moreover, in the solution not containing an excess of sulfite ions, the disulfitotetracyano complex also exhibited oscillopolarographic behavior quite similar to that in the presence of sulfite ions; neither further reduction to the metal nor oxidation from the tetracyanocobaltate(I) complex was found on the oscillopolarogram. On the other hand, for the diaquotetracyano complex, two incisions were recorded, at −0.59 and −1.39 V (*vs.* Hg pool) on the cathodic branch, while no incision was found on the anodic branch, just as above. The former two incisions correspond to the

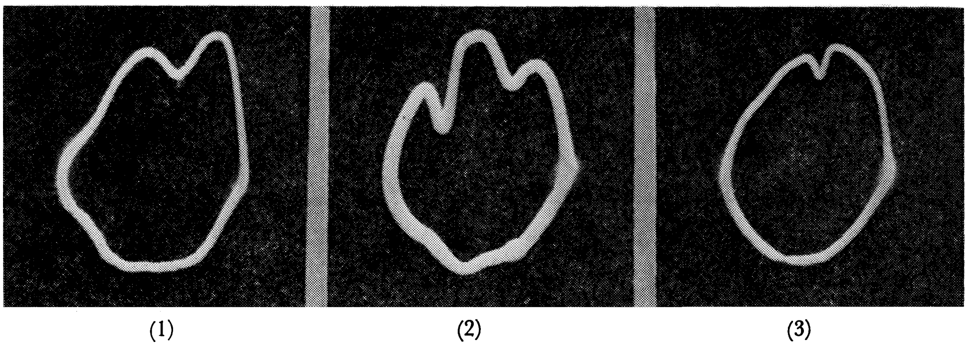

Fig. 5. The current-controlled oscillopolarograms of d*E*/d*t*-*E* curves measured at $5\cdot 10^{-3}$M complex ion (25°C). (1) $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$ in 0.5M Na_2SO_3 aqueous solution; (2) $K[Co(OH_2)_2(CN)_4]\cdot \frac{3}{4}H_3O$ in 0.5M Na_2SO_4 aqueous solution: (3) $K_4[Co(SO_3)(CN)_5]\cdot 3H_2O$ in 0.5M Na_2SO_4 aqueous solution. Voltage unit: V *vs.* Hg pool.

double wave in the conventional polarography, as will be described later. Therefore, we may conclude that the tetracyanocobaltate(I) complexes for these disulfito and diaquo complexes as well as for the sulfitopentacyano complex do not electrochemically take any oxidation at the DME.

From these results, it seems to be most likely that the following process of electrode reaction takes place at the DME:

$$\underset{inert}{trans\text{-}[\mathrm{Co^{III}(SO_3)_2(CN)_4}]^{5-}} \xrightarrow{2e} \underset{inert}{trans\text{-}[\mathrm{Co^{I}(SO_3)_2(CN)_4}]^{7-}}.$$

The cobaltate(III) and cobaltate(I) complexes may be considered to take a *trans*-configuration rather than that of a *cis*-form on the following evidence.

The diaquo complex, $\mathrm{K[Co^{III}(OH_2)_2(CN)_4]\cdot\frac{3}{4}H_2O}$, which had been prepared from the disulfito complex was found to be reduced in two steps to the cobalt(I) state, but not to the metal at the DME, in a 0.5M Na_2SO_4 aqueous solution.

$$trans\text{-}[\mathrm{Co^{III}(OH_2)_2(CN)_4}]^{-} \xrightarrow{e} trans\text{-}[\mathrm{Co^{II}(OH_2)_2(CN)_4}]^{2-} \xrightarrow{e} trans\text{-}[\mathrm{Co^{I}(OH_2)_2(CN)_4}]^{3-}.$$

On the other hand, the ethylenediaminetetracyano complex, $\mathrm{K[Co^{III}(CN)_4en]\cdot H_2O}$ (*cis*-form), was found to be reduced directly to the metal in the same supporting electrolyte of a 0.5M Na_2SO_4 aqueous solution; no cobalt(II) and cobalt(I) states were detected by means of conventional polarography in the course of reductions.[3] The cobalt(I) state was detectable only in the presence of an excess of ethylenediamine, *i.e.*, under conditions where the aquation was prevented. In other words, the resulting cobaltate(I) ion, *cis*-$\mathrm{[Co^{I}(CN)_4en]^{3-}}$, certainly aquates rapidly, unless an excess of ethylenediamines is present in the solution, to yield the *cis*-diaquo complex ion, *cis*-$\mathrm{[Co^{I}(OH_2)_2(CN)_4]^{3-}}$. This diaquo-cobaltate(I) complex with a *cis*-form is immediately reduced to the metal at the DME.

Figure 6 shows the current-potential curves of the disulfitotetracyano and its related mixed cyanocobaltate(III) complexes measured in an aqueous solution under the same conditions, employing the same capillary, concentration, height of mercury head and temperature. Since the limiting currents to be investigated here are all diffusion-controlled, we can ascertain the number of electrons participating in the electrode process from the ratio of the wave-heights.

The electrode process for the tetracyano complex with a *cis*-form may be speculated to be as follows:

$$cis\text{-}[\mathrm{Co^{III}(CN)_4en}]^{-} \xrightarrow{2e} cis\text{-}[\mathrm{Co^{I}(CN)_4en}]^{3-} \xrightarrow{\text{aquation}} cis\text{-}[\mathrm{Co^{I}(CN)_4(OH_2)_2}]^{3-} \xrightarrow{e} \mathrm{Co}(\textit{metal}).$$

in a 0.5M Na_2SO_4 aqueous solution.

In the dimethyl sulfoxide (DMSO), however,

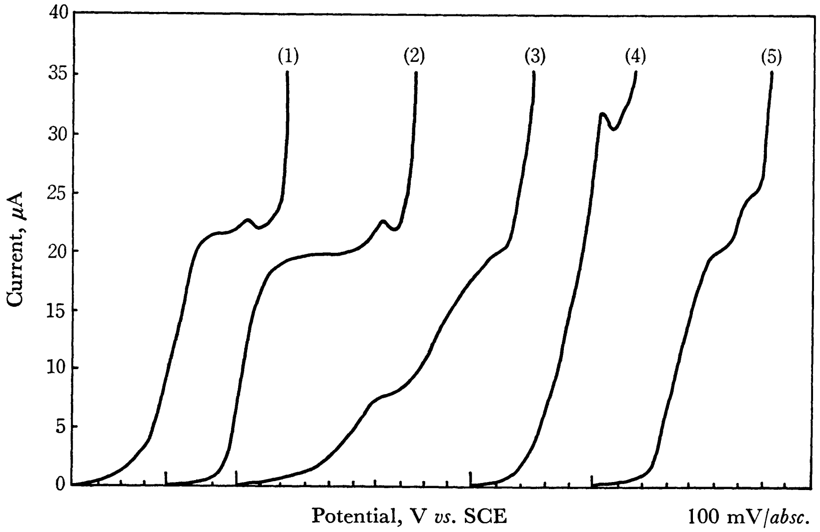

Fig. 6. The current-potential curves of the mixed cyano cobaltate(III) complexes at $5\cdot10^{-3}$ M complex ion measured under the same experimental conditions (25°C). The cobaltate(III) complexes are as follows: (1) $\mathrm{K_4[Co(SO_3)(CN)_5]\cdot3H_2O}$, recorded from −1.10 V; (2) $\mathrm{Na_5[Co(SO_3)_2(CN)_4]\cdot3H_2O}$ in 0.5M Na_2SO_3 solution, from −0.90 V; (3) $\mathrm{K[Co(OH_2)_2(CN)_4]\cdot\frac{3}{4}H_2O}$, from −0.60 V; (4) $\mathrm{Na[Co(CN)_4en]\cdot3.5H_2O}$, recorded from −0.80 V; (5) $\mathrm{Na[Co(CN)_4en]\cdot3.5H_2O}$, in 0.5M Na_2SO_4 solution containing 1M ethylenediamine, recorded from −0.80 V (*vs.* SCE). The supporting electrolyte is an aqueous solution of 0.5M Na_2SO_4, except the cases (2) and (5).

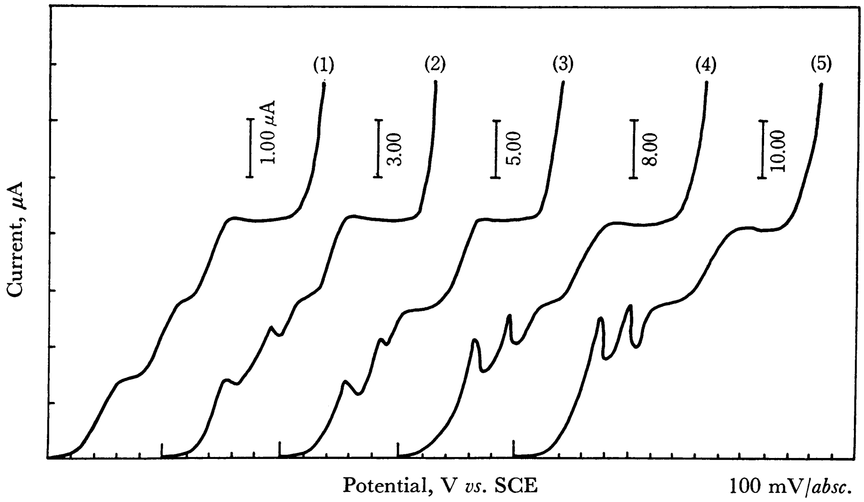

Fig. 7. The dependence of the current-potential curves upon the concentration of the complex, Na[Co(CN)$_4$en]·3.5H$_2$O, in the DMSO (100%) solution containing 0.1M [(C$_2$H$_5$)$_4$N]ClO$_4$(25°C). The concentration of the complex, (1) 10^{-3}; (2) $3\cdot10^{-3}$; (3) $5\cdot10^{-3}$; (4) $8\cdot10^{-3}$; (5) 10^{-2}M. Recorded from −1.40 V (*vs.* SCE).

the *cis*-tetracyano complex, $Na[Co^{III}(CN)_4en]\cdot3.5H_2O$,[*3] taking up three electrons, one by one, undergoes the step-by-step reduction of Co(III)→Co(II)→Co(I)→Co(*metal*) at the DME. In an aprotic non-aqueous solvent such as DMSO, it may be considered that all the cobalt complexes of the oxidized and reduced-forms are of the "*inert*" type for substitution, unlike those in aqueous solutions. Therefore, the cobaltate(III) complex may be presumed to be reduced, as it were, without any accompanying structural changes throughout the reduction; neither the aquation nor the rearrangements of ligands need be considered during reductions in DMSO. Hence, the *cis*-$[Co^I(CN)_4en]^{3-}$ ion of the "*inert*" type is interpreted as undergoing subsequent reduction to the metal in DMSO.

Figure 7 shows the dependence of the current-potential curves upon the concentration of the complex in the DMSO(100%) containing 0.1M $[(C_2H_5)_4N]ClO_4$. The following net processes of the electrode reaction are considered to be most reasonable:

$$\underset{inert}{cis\text{-}[Co^{III}(CN)_4en]^-} \xrightarrow{e} \underset{inert}{cis\text{-}[Co^{II}(CN)_4en]^{2-}} \xrightarrow{e}$$

$$\underset{inert}{cis\text{-}[Co^{I}(CN)_4en]^{3-}} \xrightarrow{e} Co(metal).$$

From the above-mentioned results, it would not be out of the way to assume that the tetracyanocobaltate(III) complexes with a *cis*-configuration are finally reduced to the metal *via* the cobalt(I) state, while those with a *trans*-configuration are reduced to the cobalt(I) state, but not to the metal at the DME. This difference in their polarographic behavior may be understood in terms of the configuration of four cyanides, which exerts a considerable effect on the stability of a cobalt(I) state, since the d^8-complexes of the univalent cobalt tend to get a coplanar structure with a *trans*-form rather than an octahedral configuration with a *cis*-form, a structure similar to that of nickel(II) complexes,

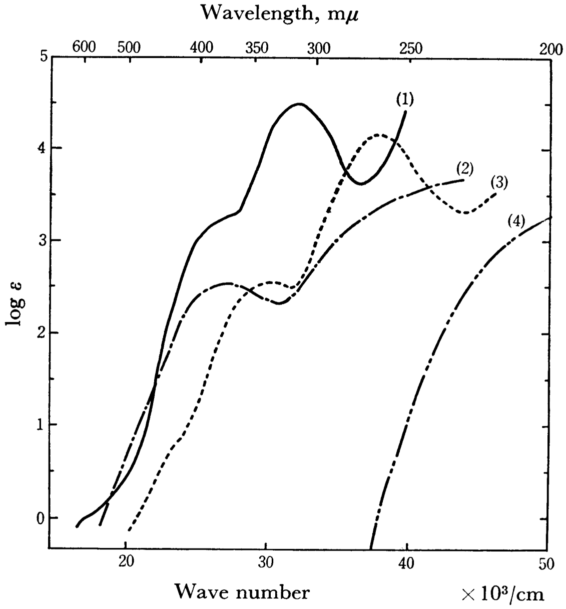

Fig. 8. The absorption spectra of the cyano cobaltate(III) complexes in water solutions (25°C). (1) ——— $Na_5[Co(SO_3)_2(CN)_4]\cdot3H_2O$ in 0.5M Na_2SO_3; (2) -·-·-·- $K[Co(OH_2)_2(CN)_4]\cdot\frac{3}{4}H_2O$ in 0.1M HNO_3; (3) -------- $K_4[Co(SO_3)(CN)_5]\cdot3H_2O$ in H_2O; (4) -··-··- Na_2SO_3 in H_2O.

[*3] The sodium salt was used here, since it is more soluble in a DMSO solvent than the potassium salt.

through a dsp^2-hybridization. Taking account of the Jahn-Teller effect, it might happen that, in solution, the coordinate bonds of the fifth and the sixth sulfite ligands became longer at the cobalt(I) state than those for the cobaltate(III) complex.

Figure 8 shows the absorption spectra of the tetracyano- and pentacyano-cobaltate(III) complexes in the visible and ultraviolet regions in water. Since the disulfito- and diaquo-complexes both gradually decompose even in a crystal state, the spectrum had to be measured in the solution of a freshly-prepared complex. The spectrum revealed that the disulfito complex can not be stored in the pure state for more than two weeks. In fact, the spectrum of the disulfito complex, $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$, does not necessarily coincide in detail with that reported in 1941 by Kiss *et al.*[12]

Table 2 summarizes the absorption maxima and intensities of the cyano cobaltate(III) complexes measured in water. The first d–d transition band shifts towards a shorter wavelength in the following order of ligands: OH_2, SO_3, en. According to Shimura and Tsuchida,[13] however, the spectrochemical series for both the *cis*-tetrammine- and *cis*-bis(ethylenediamine)-cobalt(III) complexes of the $[CoX_2(NH_3)_4]$- and $[CoX_2en_2]$-types is in this order of ligands: OH_2, en, SO_3. Hence, the order for the *cis*-type complexes does not agree with that for the tetracyano complexes. This disagreement seems likely to be due to the *trans*-configuration of the disulfito complex. Since the diaquotetracyano complex was prepared from the disulfito complex, and since it exhibited quite different polarographic behavior from that of the aquated species of the *cis*-ethylenediaminetetracyano

TABLE 2. ABSORPTION MAXIMA AND INTENSITIES OF THE CYANO-COBALTATE(III) COMPLEXES

Compound	I-Band	II-Band
$K[Co(OH_2)_2(CN)_4]\cdot \frac{3}{4}H_2O$	27.03(2.56)	—*
$Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$	27.30(3.23)	31.95(4.52)
$K[Co(CN)_4en]\cdot H_2O$	28.43(2.26)	36.13(2.28)
$K_4[Co(SO_3)(CN)_5]\cdot 3H_2O$	29.87(2.59)	37.87(4.16)

* shoulder band kK (10^3 cm^{-1})

TABLE 3. HALF-WAVE POTENTIALS OF THE WAVES FOR THE TETRACYANO- AND PENTACYANO-COBALTATE(III) COMPLEXES (25°C)

Complex compound	$E_{1/2}$	$E_{1/2}$	Supporting electrolyte
trans-$K[Co(OH_2)_2(CN)_4]\cdot \frac{3}{4}H_2O$	−1.03 $(Co^{III}\rightarrow Co^{II})$	−1.41 $(Co^{II}\rightarrow Co^{I})$	0.5M Na_2SO_4 aq. soln.
trans-$Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$	*ca* −1.21 $(Co^{III}\rightarrow Co^{I})$		0.5M Na_2SO_4
	−1.22 $(Co^{III}\rightarrow Co^{I})$		0.5M Na_2SO_3
cis-$Na[Co(CN)_4en]\cdot 3.5\ H_2O$	−1.17 $(Co^{III}\rightarrow Co^{0})$		0.5M Na_2SO_4
	−1.12 $(Co^{III}\rightarrow Co^{I})$	−1.39 $(Co^{I}\rightarrow Co^{0})$	0.5M Na_2SO_4+1M en
	−1.59 $(Co^{III}\rightarrow Co^{II})$	−1.78 −2.09 $(Co^{II}\rightarrow Co^{I})$ $(Co^{I}\rightarrow Co^{0})$	DMSO(100%) containing 0.1M $[(C_2H_5)_4N]ClO_4$
$K_4[Co(SO_3)(CN)_5]\cdot 3H_2O$	−1.55 $(Co^{III}\rightarrow Co^{I})$		0.5M Na_2SO_4 aq. soln.

Volt *vs.* SCE

TABLE 4. APPARENT KINETIC PARAMETERS OF THE ELECTRODE PROCESS FOR THE $Na_5[Co(SO_3)_2(CN)_4]\cdot 3H_2O$ COMPLEX IN A 0.5M Na_2SO_3 SOLUTION

T°K	288	293	298	303	313
$E_{1/2}$ (V *vs.* NHE)	− 0.969	− 0.976	− 0.980	− 0.993	− 1.003
i_d (μA)	1.80	2.02	2.18	2.50	3.04
αn	0.55	0.56	0.53	0.57	0.61
D_{ox} (cm$^2\cdot$sec^{-1})	$3.13\cdot 10^{-6}$	$3.96\cdot 10^{-6}$	$4.62\cdot 10^{-6}$	$6.10\cdot 10^{-6}$	$9.00\cdot 10^{-6}$
$\log k_f^a$	−12.57	−12.48	−12.28	−12.18	−12.04
k_f^a (cm/sec)	$2.67\cdot 10^{-13}$	$3.32\cdot 10^{-13}$	$5.29\cdot 10^{-13}$	$6.56\cdot 10^{-13}$	$9.12\cdot 10^{-13}$

Characteristics of capillary: $m=0.54$ mg$\cdot$sec^{-1}, $t=4.00$ sec $\Delta H^{\ddagger}=4.7$ kcal/mol

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[12] P. Pascal (ed.), "Nouveau Traite de Chimie Minerale," Tome XVIII, Masson et Cie, Editeurs, Paris (1959), pp. 697—698; A. Kiss, G. Auer and E. Major, *Z. Anorg. Allgem. Chem.*, **246**, 28 (1941).

[13] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

TABLE 5. APPARENT KINETIC PARAMETERS OF THE ELECTRODE PROCESS FOR THE $K_4[Co(SO_3)(CN)_5]\cdot 3H_2O$ COMPLEX IN A 0.5M Na_2SO_4 SOLUTION

T°K	283	288	293	303
$E_{1/2}$ (V *vs.* NHE)	−1.305	−1.305	−1.299	−1.286
i_d (μA)	1.64	1.78	1.94	2.01
αn	0.59	0.56	0.61	0.61
D_{ox} ($cm^2\cdot cm^{-1}$)	$2.37\cdot 10^{-6}$	$2.82\cdot 10^{-6}$	$3.31\cdot 10^{-6}$	$3.57\cdot 10^{-6}$
$\log k^a{}_f$	−16.78	−16.51	−16.18	−15.82
$k^a{}_f$ (cm/sec)	$1.66\cdot 10^{-17}$	$3.06\cdot 10^{-17}$	$6.62\cdot 10^{-17}$	$15.03\cdot 10^{-17}$

The same capillary in Table 4 was employed. $\Delta H^{\neq}=20.8$ kcal/mol

complex, it may also be interpreted as getting a *trans*-configuration rather than a *cis*-form.

Table 3 summarizes the half-wave potentials and the corresponding electrode processes of the cyano cobaltate(III) complexes in various kinds of supporting electrolytes. Since the disulfito-, diaquotetracyano, and sulfitopentacyano complexes are quite insoluble in such organic solvent as DMSO, acetonitrile (AN), dimethylformamide (DMF), and ethanol, it was impossible for us to obtain the reduction waves of these complexes in such aprotic solvents.

Tables 4 and 5 show the apparent kinetic parameters for the irreversible electrode process of Co(III)→Co(I) in an aqueous solution, such parameter having been determined by a method described previously;[8] the terms have their usual significance. Here, the so-called "Frumkin's correction" was not taken into consideration in estimating these data. Since a plot of $\log k^a{}_f$ (apparent rate constant) against $1/T$ should be linear with a slope equal to $\Delta H^*/2.303\ R$, the activation energies at a constant pressure ($\Delta H^{\neq}$) can be calculated; these values are shown below the respective tables. The $\Delta H^{\neq}$ value for the disulfito complex was found to be far smaller than that for the sulfitopentacyano complex, although it is noteworthy that these parameters have, ultimately, only a relative meaning.[14]

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14) R. Tamamushi, *Rev. Polarography* (Kyoto), **10**, 1 (1962).