Polarographic Studies of Metallic Complexes. IV.[1] *Bisethylenediamine Series of Cobalt(III) Complexes*[2]

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There have been reported, heretofore, some polarographic studies on the ethylenediaminecobalt(III) complexes[3-10]. Holtzclaw et al.[3-5] studied several kinds of *cis*- and *trans*-bisethylenediaminecobalt (III) complex and found that the *trans*-isomer having two negative ligands in its coordination sphere exhibits a little more negative half-wave potential than the corresponding *cis*-isomer. This fact was explained as being due to the stabilization of the complex compound by the trans effect of the two negative ligands. On the other hand the *trans*-isomer containing one or two neutral ligands in its coordination sphere showed almost the same half-wave potential as the corresponding *cis*-isomer.

As regards the reduction wave of trisethylenediaminecobalt(III) ion, Kivalo[8] and Laitinen et al.[7] obtained the following results. The ion, $[\mathrm{Co\ en_3}]^{3+}$, is reduced reversibly to $[\mathrm{Co\ en_3}]^{2+}$ ion in the presence of an excess of 0.1~0.5 F ethylenediamine. ($E_{1/2}=-0.456$ V. vs. S.C.E) However, in the absence of an excess of ethylenediamine the irreversible wave of $[\mathrm{Co\ en_3}]^{3+}$ was given. This fact was considered to be due to the following reason. The apparent irreversibility of the reduction is due to the aquation of the reduction product, or to the decrease in the coordination number of cobalt(II) complex ion, though the electron transfer reaction for $[\mathrm{Co\ en_3}]^{3+}+e^-\rightarrow[\mathrm{Co\ en_3}]^{2+}$ is fast enough to be reversible. While the reversible electrode reaction in the presence of excessive ethylenediamine was explained as being due to the existence of the stable ion, $[\mathrm{Co\ en_3}]^{2+}$, which is in equilibrium with an excess of ethylenediamine, being different from the reduction product of hexamminecobalt(III) ion. The latter ion gave an irreversible wave, even if an excess of ammonia was present in solution.

However, Doležal[9] obtained a somewhat different result recently. Namely, his polarographic and oscillopolarographic studies showed that the redox system, $[\mathrm{Co\ en_3}]^{3+}/[\mathrm{Co\ en_3}]^{2+}$, is not perfectly reversible. It was found that the difference of the half-wave potentials between the anodic and the cathodic wave was 30 mV. under equal conditions. The dependence of the cathodic wave on the pH value of the solution and on the concentration of ethylenediamine and of gelatin was also different from that of the anodic wave. The anodic wave approaches reversibility more perfectly than the cathodic wave.

In the previous work of this series[1] the present authors determined the order of the polarographic stability for the cobalt (III) complexes of pentammine series, $[\mathrm{Co(NH_3)_5X}]$. For the same purpose, a comparison of the half-wave potentials of the first waves has been carried out for the cobalt(III) complexes of bisethylenediamine series, $[\mathrm{Co\ en_2X_2}]$ or $[\mathrm{Co\ en_2Y}]$. The polarographic behavior of these complexes has also been dealt with in the present paper.

Experimental

Apparatus.—A Yanagimoto model 104 polarograph with the sensitivity of galvanometer of $2\times10^{-9}\mu$A/mm./m. was used. For the accurate evaluation of curves and half-wave potentials the method described previously was used[10]. As an electrolysis cell an H-type vessel with a saturated calomel electrode was employed. The capillary used had a rate of flow of mercury, 0.615 mg. /sec. and a drop time of 7.42~6.98 sec./drop in the solution of 0.5 F potassium sulfate and of 0.1 F potassium chloride at an open circuit with a mercury head of 65.5 cm.. The capillary was

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[1] Part III of this series; N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 23 (1959).

[2] Presented in part at the Eleventh Annual Meeting of the Chemical Society of Japan, Tokyo, April 6, 1958.

[3] H. F. Holtzclaw, Jr., *J. Am. Chem. Soc.*, **73**, 1821 (1951).

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[5] H. F. Holtzclaw, Jr., *J. Phys. Chem.*, **59**, 300 (1955).

[6] J. B. Willis, J. A. Friend and D. P. Mellor, *J. Am. Chem. Soc.*, **67**, 1680 (1945).

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[9] J. Doležal, *Coll. Czech. Chem. Communs.*, **21**, 113 (1956).

[10] N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **30**, 909 (1957).

connected to the mercury reservoir by a tube of polyvinylchloride. All the measurements were made at 25±0.1°C, the temperature being maintained by a water thermostat. The reversibility of the electrode reaction was examined by determining the slope of $\log i/(i_d - i)$ vs. potential. Slopes of the log plots indicated irreversible reaction throughout.

Material.—The complex compounds studied were prepared by the method described in literature[11-27,30]. (The references are given in Tables I, II and III.) Each solution for the electrolysis was made freshly from the dry crystalline cobalt(III) complexes before use and the polarographic measurements were made as soon as possible after the removal of oxygen. The concentration of the solution was 0.001 gram complex ion per liter.

In order to remove the dissolved oxygen, a vigorous stream of nitrogen which was purified from oxygen by means of an alkaline solution of pyrogallol, was passed through the cell solution for an hour prior to each electrolysis, preventing the evaporation.

In order to compare the half-wave potentials with each other, no maximum suppressor was used, because its presence at the concentration which is enough to suppress the maxima of the second waves of bisethylenediaminecobalt(III) complxes, causes lowering of the diffusion current, shift of the half-wave potential of the first wave towards negative direction, and sometimes deformation of the wave. The supporting electrolytes used are 0.5 F potassium sulfate and 0.1 F potassium chloride.

Results and Discussion

In Tables I and II are shown the half-wave potentials of the cobalt(III) complexes of bisethylenediamine series.

All the compounds are reduced irreversibly in two steps at the dropping mercury electrode in the solution of 0.1 F potassium chloride or 0.5 F potassium sulfate except the case of the complexes which aquate easily in solution. The complex ions such as $[\mathrm{Co\ en_2S_2O_3}]^{+}$, $[\mathrm{Co\ en_2gly}]^{2+}$*, $[\mathrm{Co\ en_2leuc}]^{2+}$* show two waves in 0.5 F potassium sulfate at the potential corresponding to the reduction of cobalt(III) → cobalt(II). The height of the second wave was very close to twice that of the first wave in the presence of Tween-80**, a maximum suppressor. The height of the first wave was proportional to the concentration of the complex ion in the range of the concentration $1\times10^{-2}\sim5\times10^{-4}$ F. In the case of the mixed solution of a complex ion and its aquated species, the total height of the waves of the original ion and of the aquated species was roughly proportional to the original concentration of the cobalt(III) complex. Hence, the first wave, corresponding to a gain of one electron, represents the reduction of cobalt(III) to cobalt(II) and the second, corresponding to two electrons, represents the reduction of cobalt(II) to metallic state.

In the solution of a non-complexing supporting electrolyte such as potassium chloride or potassium sulfate, the reduction processes of bisethylenediaminecobalt(III) complexes are considered to be in the following:

$$[\mathrm{Co\ en_2X_2}]^{(3-2n)+} + \mathrm{e}^- \rightarrow [\mathrm{Co\ en_2X_2}]^{(2-2n)+}$$

$$[\mathrm{Co\ en_2X_2}]^{(2-2n)+} + m\mathrm{H_2O} \rightarrow$$

$$\left\{\begin{array}{l} [\mathrm{Co\ en_2(OH_2)_2}]^{2+} + 2\mathrm{X}^{n-} \\ [\mathrm{Co\ en_2(OH_2)X}]^{(2-n)+} + \mathrm{X}^{n-} \\ [\mathrm{Co\ en(OH_2)_4}]^{2+} + 2\mathrm{X}^{n-} + \mathrm{en} \\ \text{etc., etc.} \end{array}\right.$$

$$[\mathrm{Co\ en_2(OH_2)_2}]^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Co} + 2\mathrm{H_2O} + 2\mathrm{en}$$

$$[\mathrm{Co\ en_2(OH_2)X}]^{(2-n)+} + 2\mathrm{e}^- \rightarrow \mathrm{Co} + \mathrm{H_2O} + \mathrm{X}^{n-} + 2\mathrm{en}$$

$$[\mathrm{Co\ en(OH_2)_4}]^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Co} + 4\mathrm{H_2O} + \mathrm{en}\ \text{etc.}$$

From the scheme of the reduction processes, it may be seen that the first step in the polarographic reduction of these cobalt(III) complexes corresponds to the disruption of the cobalt(III) complexes, resulting in the formation of aquo-ethylenediaminecobalt(II) ions such as $[\mathrm{Co\ en_2(OH_2)_2}]^{2+}$, $[\mathrm{Co\ en_2(OH_2)X}]^{(2-n)+}$ and $[\mathrm{Co\ en(OH_2)_4}]^{2+}$, so its half-wave potential may be regarded as a measure of the stability toward polarographic reduction.

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* The following abbreviations are used; gly, $\mathrm{NH_2CH_2COO^-}$; leuc, $\mathrm{NH_2CH(COO^-)CH_2CH(CH_3)_2}$; ox, $\mathrm{(COO^-)_2}$.

** Polyoxyethylene sorbitan mono-oleate (Atlas Powder Co. in U. S. A.).

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TABLE I

HALF-WAVE POTENTIALS OF COBALT(III) COMPLEXES OF [Co en$_2$X$_2$] type

Compound	Supporting electrolyte; 0.5 F K$_2$SO$_4$		Supporting electrolyte; 0.1 F KCl	
	$E_{1/2}$ of 1st wave [Co(III)→Co(II)]	$E_{1/2}$ of wave of aquated complexes [Co(III)→Co(II)]	$E_{1/2}$ of 1st wave [Co(III)→Co(II)]	$E_{1/2}$ of wave of aquated complexes [Co(III)→Co(II)]
[Co en$_2$(CN)$_2$]Cl[11]	-0.85	—	-0.80	-0.61
cis-[Co en$_2$(OH$_2$)$_2$](NO$_3$)$_3$[12]	-0.50	—	-0.42	—
trans-[Co en$_2$(NH$_3$)$_2$]Cl$_3$·H$_2$O[13]	-0.45	—	-0.31	—
cis-[Co en$_2$(NH$_3$)$_2$](ClO$_4$)$_3$[14]	-0.45	—	-0.31	—
trans-[Co en$_2$(NO$_2$)$_2$]Cl[15]	-0.26	-0.5	-0.27***	-0.40***
cis-[Co en$_2$(NO$_2$)$_2$]ClO$_4$[16]	-0.25	-0.5	-0.24***	-0.41***
trans-[Co en$_2$(NCS)$_2$]Cl·H$_2$O[17]	+	-0.51**	+	*
cis-[Co en$_2$(NCS)$_2$]Cl·H$_2$O[17]	+	-0.51**	+	*
trans-[Co en$_2$Cl$_2$]Cl[18]	+	*	+	*
cis-[Co en$_2$Cl$_2$]Cl[19]	+	*	+	*
trans-[Co en$_2$Br$_2$]Br[20]	+	*	+	*
cis-[Co en$_2$Br$_2$]Br[20]	+	*	+	*

1) The concentration of the complex ion; 0.001 F.

2) The characteristics of capillary used; $\begin{cases} m=0.615 \text{ mg./sec.} \\ t=7.42\sim6.98 \text{ sec./drop.} \end{cases}$

3) Potential unit; V. vs. S. C. E.

4) Temp., 25°C.

* Maximum wave.

** The data obtained in the presence of 0.0016% Tween-80.

*** The data adopted from H. F. Holtzclaw, Jr. and D. P. Sheetz, *J. Am. Chem. Soc.*, **75**, 3053 (1953).

TABLE II

HALF-WAVE POTENTIALS OF COBALT(III) COMPLEXES OF [Co en$_2$Y] TYPE

Compound	Supporting electrolyte; 0.5 F K$_2$SO$_4$		0.1 F KCl	
	$E_{1/2}$ of 1st wave Co(III)→Co(II)	$E_{1/2}$ of wave of aquated complexes Co(III)→Co(II)	$E_{1/2}$ of 1st wave Co(III)→Co(II)	$E_{1/2}$ of wave of aquated complexes Co(III)→Co(II)
[Co en$_3$](ClO$_4$)$_3$[21]	-0.51	—	-0.41	—
[Co en$_2$CO$_3$]Cl·H$_2$O[22]	-0.45_5	—	-0.40	—
[Co en$_2$SO$_3$]Cl·3H$_2$O[23]	-0.43	*	*	*
[Co en$_2$S$_2$O$_3$]Br·3H$_2$O[24]	—	-0.49_5	—	**
[Co en$_2$gly]Cl$_2$·H$_2$O[25]	-0.41	-0.5	-0.36	—
[Co en$_2$ox]Cl[26]	-0.31	-0.5	-0.32****	—
[Co en$_2$leuc](ClO$_4$)$_2$[27]	-0.30_5	-0.5	-0.33_5***	—

1) The experimental conditions are the same as mentioned in Table I.

2) Potential unit; V. vs. S. C. E.

* The waves of the original complex ion and of the aquated species are so near located that both the waves cannot be discriminated one another. However, it was noticed that the half-wave potential shifted towards negative direction with the decreasing concentration due to the aquation of the complex ion.

** Maximum wave.

*** The data obtained in the presence of 0.0016% Tween-80.

**** The data obtained in the solution of 1 F (NH$_4$)$_2$C$_2$O$_4$.

The polarographic stability of the cobalt (III) complexes of [Co en$_2$X$_2$] type increases in the following order of the ligand X;

$$\text{Br}^-,\ \text{Cl}^- < \text{NCS}^- < \text{NO}_2^- < \text{NH}_3 < \text{OH}_2 < \text{CN}^-$$

(Supporting electrolyte; 0.5 F K$_2$SO$_4$)

The same order was also obtained in 0.1 F potassium chloride. For the complexes of [Co en$_2$X$_2$] type the difference of the half-wave potentials between *cis*- and *trans*-isomer is far smaller than that among the other kinds of the complex of this series, hence the difference between *cis*- and *trans*-isomer need not be taken into consideration in this case.

The order of stability of [Co en_2Y] type complexes was in the following order of the ligands;

$$leuc^- < ox^{2-} < gly^- < SO_3^{2-} < CO_3^{2-} < en$$

(0.5 F K_2SO_4 or 0.1 F KCl as supporting electrolyte)

No relation between the above orders of the polarographic stability and that of the spectrochemical series[28] could be found in accordance with the result obtained in the previous paper[1].

Polarographic Behavior of Individual Complexes.—The second waves of all the bisethylenediaminecobalt(III) complexes indicated the maxima which could be suppressed by the maximum suppressor, Tween-80, except the case of dicyanobisethylenediaminecobalt(III) ion, [Co $en_2(CN)_2]^+$. Trisethylenediaminecobalt(III) and monoethylenediamine-tetramminecobalt(III) ions have also the maxima in the second step of the reduction, which was reported briefly in an earlier communication[10]. Therefore, it can be said that all the cobalt(III) complexes containing one or more ethylenediamine in their coordination sphere show the maxima at the second wave corresponding to the reduction for Co(II)→Co(0).

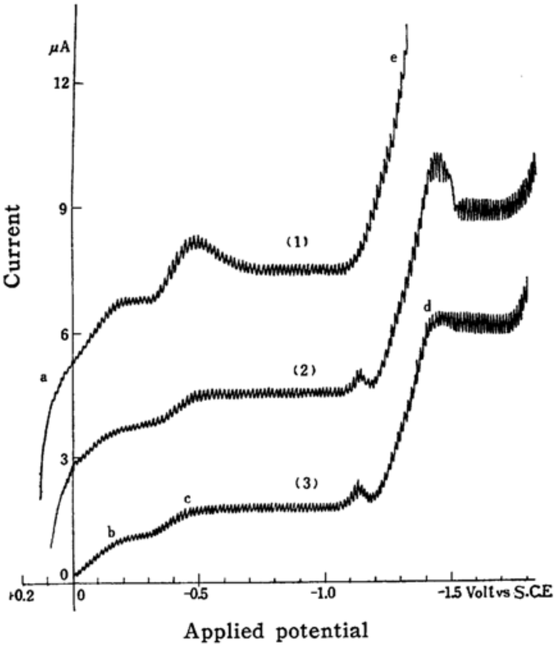

Fig. 1. The polarograms of *trans*-[Co $en_2(NCS)_2]Cl\cdot H_2O$ obtained at the concentration of 0.001 F in the solution of 0.1 F KCl.

1) In the absence of maximum suppressor
2) In the presence of 0.0016% Tween-80
3) In the presence of 0.0032% Tween-80
   a Anodic wave
   b The first wave of *trans*-[Co $en_2(NCS)_2]^+$
   c The reduction wave of the aquated complexes
   d The second wave of *trans*-[Co $en_2(NCS)_2]^+$
   e Maximum wave

Sensitivity; 0.06 μA/mm., Damping; 200

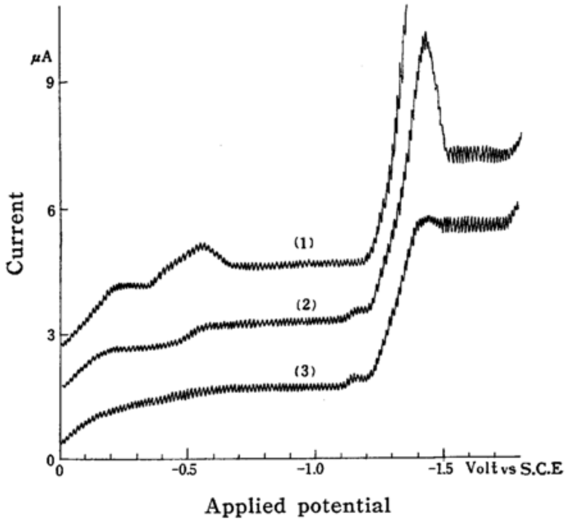

Fig. 2. The polarograms of *cis*-[Co $en_2(NCS)_2]Cl\cdot H_2O$ obtained at the concentration of 0.001 F in the solution of 0.5 F K_2SO_4.

1) In the absence of maximum suppressor
2) In the presence of 0.0016% Tween-80
3) In the presence of 0.0032% Tween-80

Sensitivity; 0.06 μA/mm., Damping; 200

Figs. 1 and 2 show the polarograms of *cis*- and *trans*-diisothiocyanato-bisethylenediaminecobalt(III) ions, [Co $en_2(NCS)_2]^+$, respectively. It is expected that these ions aquate to some extent in solution. In fact, for *trans*-[Co $en_2(NCS)_2]^+$ ion, the small maximum wave was given at around −0.4 V. (vs. S. C. E.), which could be suppressed in the presence of 0.0016% Tween-80. The half-wave potential of this small wave is near to that of diaquobisethylenediamine-cobalt(III) ion, [Co $en_2(OH_2)_2]^{3+}$. ($E_{1/2} = -0.44$ V. vs. S. C. E. in 0.1 F KCl) Therefore, this small wave is considered to correspond to the reduction wave of the aquated species such as [Co $en_2(NCS)OH_2]^{2+}$ and [Co $en_2(OH_2)_2]^{3+}$. Similarly, for *cis*-[Co $en_2(NCS)_2]^+$ ion, the small wave of the aquated cobalt(III) ions was given at around −0.51 V. (vs. S. C. E.)

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[28] Y. Shimura and R. Tsuchida, ibid., **29**, 311 (1956).

in a solution of 0.5 F potassium sulfate. The half-wave potential of $[\mathrm{Co\ en_2(OH_2)_2}]^{3+}$ ion is −0.50 V. in 0.5 F potassium sulfate.

In a dilute supporting electrolyte, a similar wave of the aquated cobalt(III) complex ions was found for the following ions;

$[\mathrm{Co\ en_2Cl_2}]^+$, $[\mathrm{Co\ en_2Br_2}]^+$
$[\mathrm{Co\ en_2(NCS)_2}]^+$, $[\mathrm{Co\ en_2ox}]^+$
$[\mathrm{Co\ en_2gly}]^{2+}$, $[\mathrm{Co\ en_2S_2O_3}]^+$
$[\mathrm{Co\ en_2(CN)_2}]^+$

Among these ions it was noticed that the height of the wave of the aquated species increases gradually with time for some complex ions, but does not for the others. This is considered to be due to the variety of the rate of the aquation. Namely, the aquation of some ions is comparatively slow, compared with the time of the polarographic measurement, while for the others, the aquation is so rapid that the usual polarographic method can not detect and trace the change of the height of the wave. The ions, $[\mathrm{Co\ en_2(CN)_2}]^+$, $[\mathrm{Co\ en_2SO_3}]^+$ belong to the former and the ions, $[\mathrm{Co\ en_2Cl_2}]^+$, $[\mathrm{Co\ en_2Br_2}]^+$ to the latter.

In a solution of 0.1 F potassium chloride dicyano-bisethylenediaminecobalt(III) ion, $[\mathrm{Co\ en_2(CN)_2}]^+$ showed the wave of the aquated complexes at around −0.80 V., but did not show anything in 0.5 F potassium sulfate. It seemed that the wave of the aquated species was probably covered by the wave of the original ion in the solution of potassium sulfate, because the waves of the original and the aquated ions were located very near to each other. The reduction potential of the aquated ions of $[\mathrm{Co\ en_2(CN)_2}]^+$ did not coincide with that of $[\mathrm{Co\ en_2(OH_2)_2}]^{3+}$ ion, so it is considered that the main species of the aquated ions is a partly aquated complex ion, $[\mathrm{Co\ en_2(CN)OH_2}]^{2+}$. (Fig. 3)

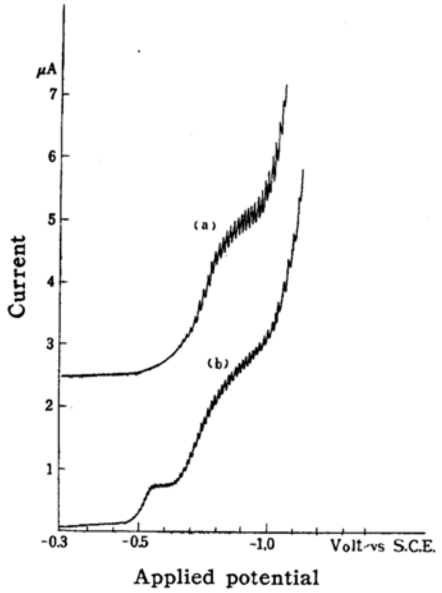


Fig. 3. The polarograms of $[\mathrm{Co\ en_2(CN)_2}]\mathrm{Cl}$ obtained at the concentration of 0.001 F.
a) In the solution of 0.5 F $\mathrm{K_2SO_4}$
b) In the solution of 0.1 F KCl
Sensitivity; 0.04 μA/mm., Damping; 100

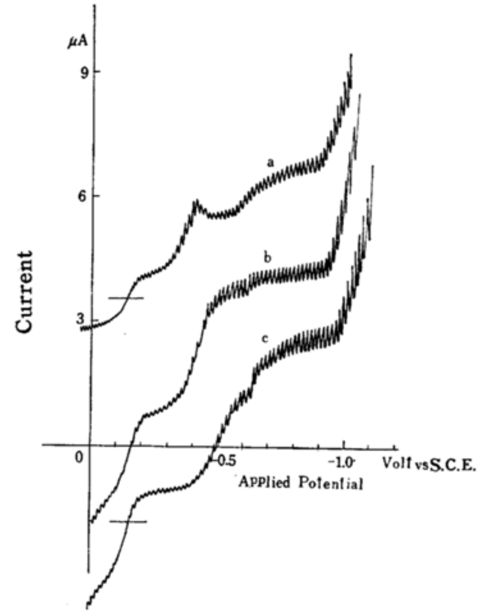


Fig. 4. The polarograms $[\mathrm{Co\ en_2S_2O_3}]\mathrm{Br\cdot 3H_2O}$.
a) obtained at the concentration of 0.001 F complex ion in the solution of 0.1 F KCl
b) obtained at the concentration of 0.005 F complex ion in the solution of 0.1 F KCl
c) obtained at the concentration of 0.005 F complex ion in the solution of 0.5 F $\mathrm{K_2SO_4}$
Sensitivity; 0.06 μA/mm., Damping; 200

In 0.1 F potassium chloride, thiosulfato-bisethylenediaminecobalt(III) ion, $[\mathrm{Co\ en_2S_2O_3}]^+$ has the small maximum wave which could be suppressed in the presence of 0.0016% Tween-80. (Fig. 4) The half-wave potential of the first wave of this ion could not be determined owing to the interference of the anodic wave of the thiosulfate ion liberated from the original complex by the aquation.

Fig. 5 shows the polarogram of the first wave of *cis*-diaquo-bisethylenediamine-cobalt(III) ion, $[\mathrm{Co\ en_2(OH_2)_2}]^{3+}$ in 0.5 F potassium sulfate. The wave has always

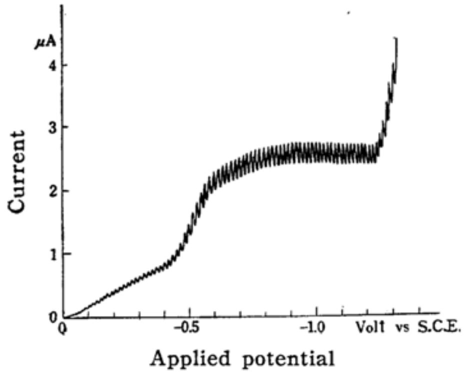


Fig. 5. The polarogram of cis-$[Co\ en_2(OH_2)_2]^{3+}$ obtained in the solution of 0.5 F K_2SO_4 at the concentration of 0.001 F complex ion.
Sensitivity; 0.04 μA/mm., Damping; 200

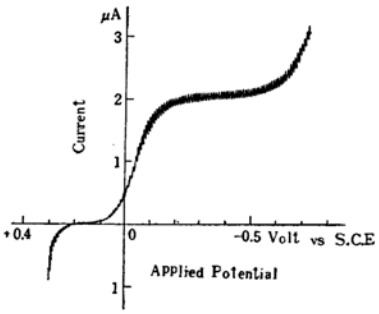


Fig. 6. The polarogram of cis-$[Co\ en_2(OH_2)_2]^{3+}$ obtained in 1 F $HClO_4$ at the concentration of 0.001 F complex ion.
Sensitivity; 0.04 μA/mm., Damping; 200
$E_{1/2}=-0.01$ V. (vs. S. C. E.)
$i_d=2.09$ μA.

a slower slope at the half-wave potential than that of the other complex ions of bisethylenediamine series. A gradually rising current near the zero potential was observed. However, it can not necessarily be said that this current is a residual current, since the diffussion current reaches a plateau parallel to the axis of the potential. (Usually, the diffusion current, runs parallel to the residual current, not to the axis of the potential.) Moreover in 1 F perchloric acid, a well-defined wave is obtained, which has a steep slope at the half-wave potential. (Fig. 6) One of the reasons for this is the presence of an equilibrium between the aquo-bisethylenediaminecobalt(III) ion and hydroxo-bisethylenediaminecobalt(III) ion.

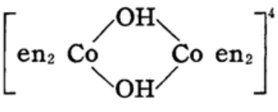
$$[Co\ en_2(OH_2)_2]^{3+} \rightleftarrows [Co\ en_2(OH_2)OH]^{2+} + H^+$$

$$[Co\ en_2(OH_2)OH]^{2+} \rightleftarrows [Co\ en_2(OH)_2]^{+} + H^+$$

In perchloric acid the above equilibrium is markedly shifted to the left hand. Consequently, the steep wave of diaquo-bisethylenediaminecobalt(III) ion could be obtained.

Another reason for this is the polymerization of diaquo-bisethylenediaminecobalt (III) ion in neutral solution. Namely, as verified by the spectrochemical studies of Rasmussen et al.[29], various kinds of polynuclear cobalt(III) complex are formed in solution. For instance,

2 cis-$[Co\ en_2(OH_2)OH]^{2+} \rightarrow$



$+2H_2O$

It is also considered that in perchloric acid, the polymerization is inhibited due to the presence of an overwhelming

TABLE III
HALF-WAVE POTENTIALS OF AQUO-AMMINE AND DIAQUO-BISETHYLENEDIAMINE COBALT(III) COMPLEXES

Complex	Supporting electrolyte; 0.5 F K_2SO_4 $E_{1/2}$ of 1st wave [Co(III)→Co(II)]	1 F $HClO_4$ $E_{1/2}$ of 1st wave [Co(III)→Co(II)]
$[Co(NH_3)_6](ClO_4)_3$	-0.43_8	—
$[Co(NH_3)_5OH_2]_2(SO_4)_3\cdot 2H_2O$[30]	-0.47_5	-0.06
cis-$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3\cdot 3H_2O$[30]	-0.48_5	$+0.14$
$[Co(NH_3)_3(OH_2)_3]^{3+}$	-0.24_9*	—
cis-$[Co\ en_2(OH_2)_2](NO_3)_3\cdot H_2O$[12]	-0.50	-0.01

1) The concentration of the complex ion; 0.001 gram complex ion per liter.
2) Potential unit; V. vs. S. C. E.
3) Temp., 25°C.
* The data adopted from J. B. Willis, J. A. Friend and D. P. Mellor, *J. Am. Chem. Soc.*, **67**, 1680 (1945).

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[29] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

[30] S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 461 (1898).

hydrogen ion. Consequently, only the original ion is present in solution. Therefore, the steep well-defined wave of this ion was obtained in perchloric acid.

A similar behavior was observed for the aquo-ammine cobalt(III) complexes, which were shown in Table III.

Summary

1. Most of the cobalt(III) complex ions of bisethylenediamine series, $[Co\ en_2X_2]^{(3-2n)+}$ or $[Co\ en_2Y]^{(3-m)+}$ are reduced irreversibly in two steps at the dropping mercury electrode. The first diffusion current corresponds to the reduction, Co(III)→Co(II) and the second to the reduction, Co(II)→Co(0). The second step always exhibits the maximum wave.

2. The polarographic stability of $[Co\ en_2X_2]$ type complexes increases in the following order of the ligands;

Br^-, $Cl^- < NCS^- < NO_2^- < NH_3 < OH_2 < CN^-$

(Supporting electrolyte; 0.5 F K_2SO_4)

Similarly, the order of the stability of $[Co\ en_2Y]$ type complexes is as follows;

$leuc^- < ox^{2-} < gly^- < SO_3^{2-} < CO_3^{2-} < en$

(Supporting electrolyte; 0.5 F K_2SO_4)

These orders are independent of the kind of supporting electrolyte such as potassium chloride or potassium sulfate. The orders of the polarographic stability did not agree with that of the spectrochemical series.

3. In perchloric acid the well-defined wave of steep slope was obtained for diaquo-bisethylenediaminecobalt(III) ion, $[Co\ en_2(OH_2)_2]^{3+}$, while the ion gave a modified wave in the neutral solution of 0.1 F potassium chloride and of 0.5 F potassium sulfate. This phenomena was explained as being due to the inhibition of the dissociation and polymerization of the complex in the presence of an overwhelming hydrogen ion. A similar behavior was observed in the aquo-ammine cobalt (III) complexes.

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