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

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The relation between the structure of metallic complexes and their half-wave potentials has been studied to some extent[3-12]. For instance, Hall et al.[9] studied several kinds of platinum(IV) complex and found the following facts. Platinum (IV) complexes of halogenopentammine type were reduced irreversibly to platinum (II) complexes in one step and the half-wave potentials were at more positive values for halogenopentammineplatinum (IV) complexes than for hexammineplatinum(IV) ion, $[Pt(NH_3)_6]^{4+}$. The shift, however, was to a more negative value for hydroxypentammineplatinum(IV) complex. Namely the polarographic stability of the pentammineplatinum(IV) complexes, $[Pt(NH_3)_5X]$, increases in the following order of ligand X;

$$Br^- < Cl^- < NH_3 < OH^-$$

They also found that tris(ethylenediamine)-platinum(IV) complex ion was reduced irreversibly to $[Pt\,en_3]^{2+}$, through $[Pt\,en_3]^{3+}$, in two steps at a little more negative potential than the corresponding reduction of hexammineplatinum(IV) ion.

Brigando[11] reported that, on the basis of polarographic measurements and absorption spectra, the following complexes were ranked in order of increasing stability;

$[Co(NH_3)_4(NH_2CH_3)_2]Cl_3$

$[Co(NH_3)_6]Cl_3$, $[Co\,en_3]Cl_3$

$[Co(NH_2CH_2CH_2NHCH_2CH_2NH_2)_2]Cl_3$

The half-wave potentials for these complexes at the dropping mercury electrode in 0.6 F sodium perchlorate were respectively as follows; -0.215 V., -0.297 V., -0.392 V., and -0.420 V. (vs. S. C. E.).

For the same purpose, the present paper deals with the polarography of pentam minecobalt(III) complex ions, $[Co(NH_3)_5X]^{(3-n)+}$.

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[1] Part II of this series: N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **31**, 413 (1958).

[2] Partly presented at the Eleventh Annual Meeting of the Chemical Society of Japan, Tokyo, April 6, 1958.

[3] T. Uemura, K. Morinaga, H. Takesawa and H. Kobayashi, presented at the Symposium on Co-ordination Compounds, Tokyo, Nov. 13, 1951.

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[5] H. F. Holtzclaw, Jr., ibid., **73**, 1821 (1951).

[6] H. F. Holtzclaw, Jr. and D. P. Sheetz, ibid.. **75**, 3053 (1953).

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[9] J. R. Hall and R. A. Plowman, *Australian J. Chem.*. **8**, 158 (1955).

[10] J. R. Hall and R. A. Plowman, ibid., **9**, 143 (1956).

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

TABLE I

HALF-WAVE POTENTIALS OF PENTAMMINE SERIES OF COBALT(III) COMPLEXES

Complex compound	Supporting electrolyte; 0.1 F KCl		Supporting electrolyte; 0.5 F K_2SO_4	
	$E_{1/2}$ of 1st wave [Co(III)→Co(II)]	$E_{1/2}$ of 2nd wave [Co(II)→Co(0)]	$E_{1/2}$ of 1st wave [Co(III)→Co(II)]	$E_{1/2}$ of 2nd wave [Co(II)→Co(0)]
$[Co(NH_3)_5I]Cl_2$[13]	+	-1.24_5	+	—
$[Co(NH_3)_5Br]Br_2$[14]	+	-1.24_5	+	—
$[Co(NH_3)_5Cl]Cl_2$[15]	+	-1.24	+	—
$[Co(NH_3)_5NO_3](NO_3)_2$[16]	+	-1.25_5	-0.05_5	-1.28
$[Co(NH_3)_5N_3]Cl_2$[17]	+	-1.23	-0.12_5	-1.28_5**
$[Co(NH_3)_5SO_4]ClO_4$[18]	-0.10_5	-1.23_5	-0.24_5	-1.27_5
$[Co(NH_3)_5NO_2](ClO_4)_2$[19]	$-0{\cdot}12$	*	-0.26	-1.28_5
$[Co(NH_3)_5S_2O_3]Cl$[20]	-0.13	-0.96_5	about -0.12	*
$[Co(NH_3)_5C_2O_4]Br\cdot 1.5\,H_2O$[21]	-0.21	-1.23_5	-0.33	-1.29
$[Co(NH_3)_5OCOCH_3](ClO_4)_2$[22]	-0.22_5	-1.24	-0.37	-1.27
$[Co(NH_3)_6](NO_3)_3$	-0.23_5	-1.25_5	-0.43	-1.28
$[Co(NH_3)_5CO_3]NO_3$[23]	-0.38_2	-1.25	-0.50	*
$[Co(NH_3)_5HCO_3](NO_3)_2$[24]	—	—	-0.50_2	-1.28
$[Co(NH_3)_5OH_2]_2(SO_4)_3\cdot 3H_2O$[25]	-0.38	-1.24_5	-0.47	-1.27_5
$[Co(NH_3)_5OH]SO_4\cdot 1.5\,H_2O$[26]	-0.39	-1.25_5	-0.47_5	-1.27_5
$[Co(NH_3)_5CrO_4]Cl$[27]	+	*	+	*
$[Co(NH_3)_5NCS]SO_4\cdot 2\,H_2O$[28]	+	*	+	*

* Maximum wave.

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

1) The concentration of the complex; 0.001 gram complex ion per liter.

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

3) Temperature, 25°C.

Experimental

The experimental setup and technique are the same as in the previous work and have been described in the earlier communications[1,12]. The capillary had an *m*-value of 1.356 mg./sec. and a drop time of 5.82~6.23 sec./drop in 0.1 F potassium chloride or 0.5 F potassium sulfate at a potential of 0.0 V. against the saturated calomel electrode with the mercury head of 96 cm. All the measurements were made at 25±0.1°C, the temperature being maintained by a water thermostat. The reversibilities of the electrode reaction were examined by determining the slope of $\log i/(i_d-i)$ vs. potential. Slopes of the log plots indicated irreversible reaction throughout.

The complex compounds studied were prepared by the method described in previous literature[13-27]. (The references are given in Table I.) Each solution for the electrolysis was made freshly from the dry crystalline cobalt(III) complexes before use and polarographic measurements were made as soon as possible after the removal of oxygen dissolved in solution. No maximum suppressor was used except in the case of azidopentamminecobalt(III) ion. Regarding the complexes of pentammine type, the presence of the maximum suppressor causes the lowering of the diffusion current and the shift of the half-wave potential to negative direction. The supporting electrolytes used were 0.5 F potassium sulfate and 0.1 F potassium chloride.

Results and Discussion

In Table I are shown the half-wave potentials of the cobalt(III) complexes of pentammine series. All the compounds are irreversibly reduced in two steps at the dropping mercury electrode with two exceptions. One of the exceptions is the complexes which contain the ligand reducible by itself, such as chromate ion. The other is the complexes which aquate easily in solution.

From Table I it is seen that the first wave exhibits various half-wave potential

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14) H. H. Willard and D. Hall, ibid., **44**, 2220 (1922).

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25) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 461 (1898).

26) A. Werner, *Ber.*, **40**, 4104 (1907).

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28) A. Werner and A. Müller, *Z. anorg. Chem.*, **22**, 102 (1900).

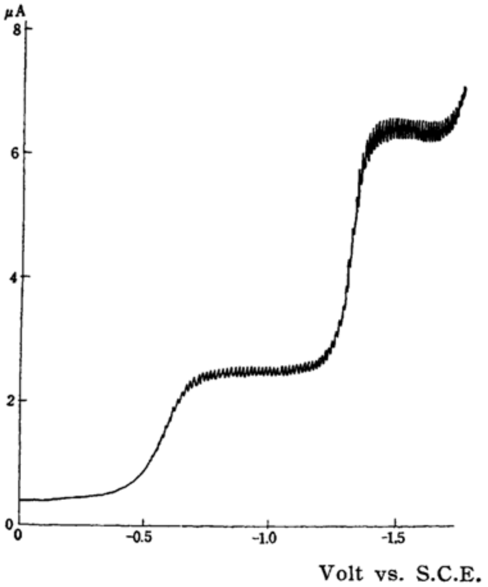

Fig. 1. The polarogram of $[Co(NH_3)_5CO_3]^+$ at the concentration of 0.001 F in the solution of 0.5 F K_2SO_4.
The first wave: $E_{1/2} = -0.50$ V., $i_d = 1.52$ μA.
The second wave: $E_{1/2} = -1.28$ V., $i_d = 3.04$ μA.

values from compound to compound, while the potentials of the second reduction are always in close proximity to that of hexaquocobalt(III) ion. (−1.428 V. vs. S. C. E. in 0.5 F potassium sulfate solution[4]). Fig. 1 shows the typical polarogram of the pentamminecobalt(III) complexes.

The height of the second wave was very close to twice that of the first wave. The heights of either waves were linearly related with the concentration of the complex ion in the range of $1\times10^{-2} \sim 5\times10^{-4}$ F. Accordingly the first wave, corresponding to a one-electron transfer, represents the reduction of cobalt(III) to cobalt(II), and the second, corresponding to a two-electron, represents the reduction of cobalt(II) to metallic state.

As regards the process of the reduction of pentamminecobalt(III) complexes in dilute solution, Willis et al.[4] proposed the following mechanism;

$$[Co(NH_3)_5X]^{n+} + e^- \longrightarrow [Co(NH_3)_5X]^{(n-1)+}$$

$$[Co(NH_3)_5X]^{(n-1)+} + 6\,H_2O \xrightarrow{\text{rapidly}} [Co(OH_2)_6]^{2+} + 5\,NH_3 + X^{-n+3}$$

$$[Co(OH_2)_6]^{2+} + 2e^- \longrightarrow Co + 6\,H_2O$$

From the reduction scheme, it may be seen that the first step in the polarographic reduction of the pentamminecobalt(III) complexes corresponds to the disruption of the complexes, so its half-wave potential of the first wave may be regarded as a measure of the stability against the polarographic reduction.

The polarographic stability of the pentammine series of cobalt(III) complexes increases in the following order of the ligands;

$$I^-, Br^-, Cl^-, CrO_4^{2-}, NCS^- < NO_3^- < SO_4^{2-} < NO_2^- < S_2O_3^{2-} < C_2O_4^{2-} < CH_3COO^- < NH_3 < CO_3^{2-} < OH_2 < OH^-$$

(Supporting electrolyte; 0.1 F potassium chloride).

This order of the stability varied scarcely by the kind of the supporting electrolyte. The reverse of the order is seen between carbonate and water molecule when 0.5 F potassium sulfate was used as a supporting electrolyte.

$$I^-, Br^-, Cl^-, CrO_4^{2-}, NCS^- < NO_3^- < N_3^- < SO_4^{2-} < NO_2^- < C_2O_4^{2-} < CH_3COO^- < NH_3 < OH_2 < OH^- < CO_3^{2-}, HCO_3^-$$

(Supporting electrolyte; 0.5 F potassium sulfate).

No relation between the above order of the polarographic stability and that of the spectrochemical series[29] could be found.

Polarographic Behavior of Individual Complexes.—Some cobalt(III) complexes of pentammine series gave a "prewave" which precedes the actual second

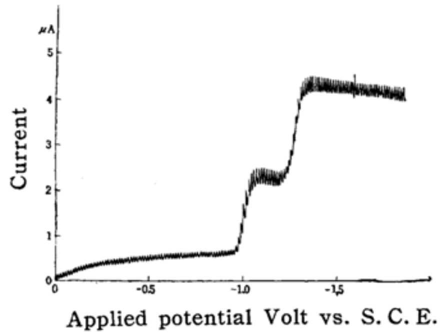

Fig. 2. The polarogram of $[Co(NH_3)_5Br]^{2+}$ at the concentration of 0.001 F in the solution of 0.1 F KCl.
The diffusion current of the second wave: 3.62 μA.
A prewave occurs at around −1.0 V.

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

wave. Brdička[30] explained the prewave as being due to the pentaquomonohydroxocobalt(II) ion formed by hydrolysis, the ion being in slow equilibrium with the hexaquocobalt(II) ion. Fig. 2 shows Brdička's prewave obtained in the reduction of bromopentamminecobalt(III) ion. Similar prewaves were found in the following ions;

$[Co(NH_3)_5I]^{2+}$, $[Co(NH_3)_5Br]^{2+}$
$[Co(NH_3)_5Cl]^{2+}$, $[Co(NH_3)_5SO_4]^{+}$
$[Co(NH_3)_5NO_2]^{2+}$, $[Co(NH_3)_5OH]^{2+}$
$[Co(NH_3)_5OH_2]^{3+}$, $[Co(NH_3)_5OCOCH_3]^{2+}$

On the other hand in the following ions the prewave was completely absent;

$[Co(NH_3)_5S_2O_3]^{+}$, $[Co(NH_3)_5SO_3]^{+}$
$[Co(NH_3)_5HCO_3]^{2+}$, $[Co(NH_3)_5CO_3]^{+}$
$[Co(NH_3)_5C_2O_4]^{+}$

The ion, $[Co(NH_3)_5NO_3]^{2+}$ shows a prewave in 0.1 F potassium chloride, but does not in 0.5 F potassium sulfate.

Thiosulfato- or sulfono-pentamminecobalt(III) ion[31] gave the first wave which had too small a slope at the reduction potential to determine its half-wave potential exactly. This is considered to be due to the aquation of the ion. In 1 F sodium sulfite a well-defined wave of the ion, $[Co(NH_3)_5SO_3]^{+}$ was obtained, because the presence of an overwhelming amount of sulfite ions causes an interruption of the aquation of the complex to some extent (Fig. 3).

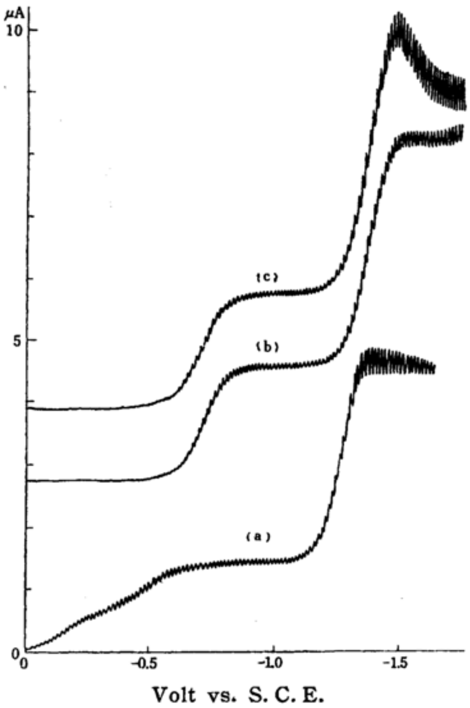

Fig. 3. The polarograms of $[Co(NH_3)_5SO_3]^{+}$ obtained at the concentration of 0.001 F in the solution of 0.5 F K_2SO_4 and of 1 F Na_2SO_3.
a) Supporting electrolyte: 0.5 F K_2SO_4
b) Supporting electrolyte: 1 F Na_2SO_3, in the presence of 0.0016% Tween-80.
c) Supporting electrolyte: 1 F Na_2SO_3, in the absence of the maximum suppressor.

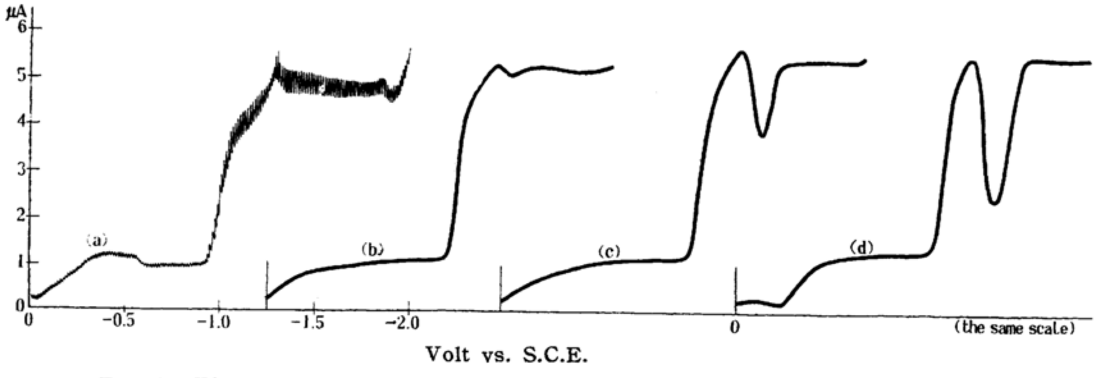

Fig. 4. The effects of maximum suppressor on the current-voltage curves of $[Co(NH_3)_5NCS]^{2+}$ at the concentration of 0.001 F in the solution of 0.5 F K_2SO_4.
a) The polarogram obtained in the absence of maximum suppressor.
b) Current-voltage curve taken in the presence of 0.0032% Tween-80.
c) In the presence of 0.0065% Tween-80.
d) In the presence of 0.0097% Tween-80.

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[30] R. Brdička, *Collection Czechoslov. Chem. Communs.*, 5, 113 (1933).

[31] The "sulfono group" is SO_3^{2-} radical bound to the central metal ion by the sulfur atom.

The reduction potential of the second step of thiosulfato-pentamminecobalt(III) ion, $[Co(NH_3)_5S_2O_3]^+$, is -0.965 V. vs. S. C. E. in 0.1 F potassium chloride. This value is quite different from that of the other pentamminecobalt(III) complexes. This fact means that through the reduction of the thiosulfatopentamminecobalt (III) ion, a cobalt(II) complex ion was formed, which was reducible more easily than hexaquocobalt(II) ion. The cobalt (II) complex is probably thiosulfatopentaquocobalt(II) ion or a similar one.

The first wave of isothiocyanatocobalt (III) ion has a small maximum wave which can easily be suppressed in the presence of 0.0032% Tween-80.* The effect of the maximum suppressor on the wave form of the ion, $[Co(NH_3)_5NCS]^{2+}$, are shown in Fig. 4. Chromatopentamminecobalt(III) ion shows many complicated waves. This may be an overlap of the waves of the cobalt(III) complexes and of chromate ion (Fig. 5).

In a neutral solution the first wave of aquopentamminecobalt(III) complex ion has always a smaller slope at the half-wave potential than the other pentamminecobalt(III) complexes (Fig. 6). On the other hand, in 1 F perchloric acid, a well-defined wave which had a sharp slope was obtained. One of the reasons for this is considered to be the shift of the equilibrium between the aquopentamminecobalt (III) ion and the hydroxopentamminecobalt(III) ion.

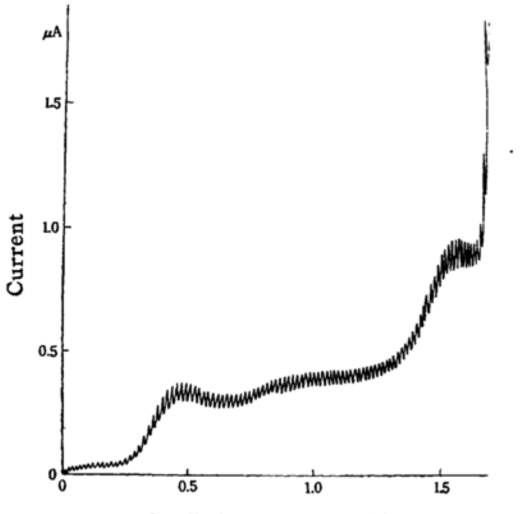

Fig. 5. The polarogram of $[Co(NH_3)_5CrO_4]^+$ obtained at the concentration of 0.001 F in the solution of 0.5 F K_2SO_4.

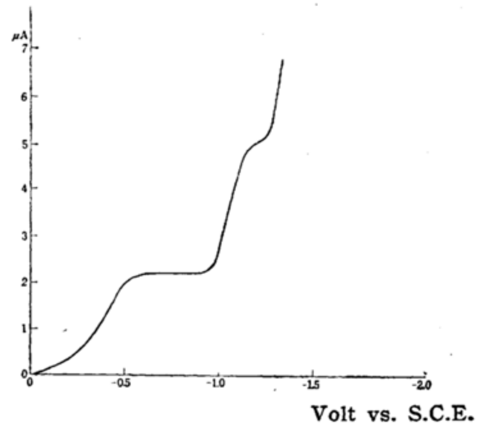

Fig. 6. Current-voltage curve of $[Co(NH_3)_5OH_2]^{3+}$ at the concentration of 0.001 F in the solution of 0.1 F KCl.

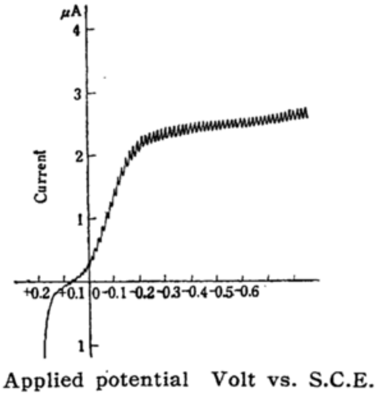

Fig. 7. The polarogram of $[Co(NH_3)_5OH_2]^{3+}$ obtained at 0.001 F in 1 F $HClO_4$. $E_{1/2}$ and i_d, respectively, -0.045 V. and 2.25 μA.

$$[Co(NH_3)_5OH_2]^{3+} \rightleftharpoons [Co(NH_3)_5OH]^{2+} + H^+$$

In perchloric acid the above equilibrium is markedly shifted to the left hand. Consequently the well-defined wave of the aquopentamminecobalt(III) ion could be obtained (Fig. 7).

Summary

1. Most of the cobalt(III) complex ions of pentammine series, $[Co(NH_3)_5X]^{(3-n)+}$, are reduced irreversibly in two steps at the dropping mercury electrode. The first diffusion current corresponds to the reduction, cobalt(III) → cobalt(II) and the second to the reduction, cobalt(II) → cobalt (0). The diffusion current and concentration were linearly related.

2. The polarographic stability of cobalt (III) complexes of the pentammine series increases in the following order of the ligands;

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* Polyoxyethylene sorbitan mono-oleate.

I^-, Br^-, Cl^-, CrO_4^{2-}, $NCS^- < NO_3^-$
$< N_3^- < SO_4^{2-} < NO_2^- < C_2O_4^{2-}$
$< CH_3COO^- < NH_3 < OH_2 < OH^-$
$< CO_3^{2-}$, HCO_3^-

(Supporting electrolyte; 0.5 F potassium sulfate).

The reverse of the order was found between carbonate and water molecule when 0.1 F potassium chloride was used as a supporting electrolyte. This order did not agree with that of the spectrochemical series of the pentamminecobalt(III) complexes.

3. In dilute perchloric acid the well-defined wave was obtained for aquopentamminecobalt(III) ion, $[Co(NH_3)_5OH_2]^{3+}$, while the ion gave a modified wave in the first reduction step in neutral supporting electrolyte, potassium chloride or potassium sulfate.

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