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

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(Received December 24, 1958)

In the earlier papers of this series[1,3] the orders of the polarographic stability were determined for cobalt(III) complexes of pentammine and bisethylenediamine series, $[Co(NH_3)_5X]$, $[Co\ en_2X_2]$ or $[Co\ en_2Y]$. For the same purpose, the comparison of the half-wave potentials of the first waves has been carried out for the cobalt(III) complexes of tetrammine series, $[Co(NH_3)_4X_2]$ or $[Co(NH_3)_4Y]$, which has been briefly reported in the present paper. Some studies[4-10] were found in literature for the hexammine and the tetrammine cobalt(III) complexes of $[Co(NH_3)_4X_2]$ type, but few reports were found on the $[Co(NH_3)_4Y]$ type[10].

Experimental

A Yanagimoto model 104 polarograph similar to that previously described[1] was used to obtain the polarograms. The rate of flow of mercury, *m*, and the drop time, *t*, of the dropping mercury electrode were 0.635 mg./sec. and 6.92~7.32 sec., respectively, being measured in the solution of 0.1 F potassium chloride or 0.5 F potassium sulfate at an open circuit with a mercury head of 66.5 cm. A saturated calomel electrode (S.C.E.) was used for a reference electrode and connected to the cell solution through an agar bridge. The cell temperature was maintained at 25±0.1°C by means of a water thermostat. For accurate evaluation of curves and half-wave potentials the method previously described[10] was used. The oxygen dissolved in solution was expelled by passing a stream of nitrogen through the cell solution for an hour prior to each electrolysis. The reversibilities of the electrode reactions were examined by determining the slopes of $\log i/(i_d-i)$ vs. potential. The slopes of the log plots indicated irreversible reduction throughout.

The complex compounds studied were prepared by the methods described in literature. (The references are given in Tables I and II.) Each solution for 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 litre. No maximum suppressor was used for the purpose of comparing the half-wave potentials of the complexes with one another. The presence of the maximum suppressor causes the lowering of the diffusion current and the shift of the half-wave potential to the negative direction. For instance, the half-wave potential of the first wave of the complex,

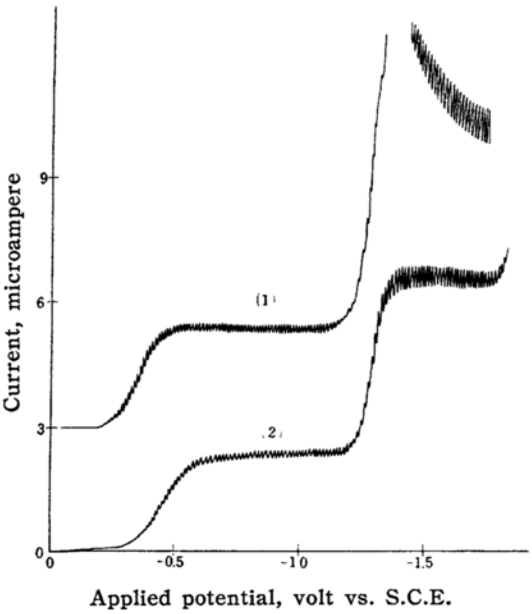

Fig. 1. The polarograms of alaninatotetramminecobalt(III) complex, $[Co(NH_3)_4 alan]SO_4$, obtained in 0.5 F K_2SO_4 solution at the concentration of 0.001 F.

1. In the absence of the maximum suppressor.
   $E_{1/2}$ of 1st wave $= -0.32$ V.
2. In the presence of 0.0032% Tween-80.
   $E_{1/2}$ of 1st wave $= -0.44_5$ V.
   $E_{1/2}$ of 2nd wave $= -1.28_3$ V.

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[1] Part IV of this series; N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 150 (1959).

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

[3] N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **32**, 23 (1959).

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

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

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

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

[8] H. A. Laitinen, J. C. Bailar, H. F. Holtzclaw, Jr. and J. V. Quagliano, *J. Am. Chem. Soc.*, **70**, 2999 (1948).

[9] H. A. Laitinen, A. J. Frank and P. Kivalo, ibid., **75**, 2865 (1953).

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

TABLE I. HALF-WAVE POTENTIALS OF COBALT(III) COMPLEXES OF $[Co(NH_3)_4X_2]$ TYPE

Complex	Supporting electrolyte 0.5 F K_2SO_4			Supporting electrolyte 0.1 F KCl		
	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the wave of aquated species Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the wave of aquated species Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)
$NH_4[Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$[11]	-0.63		——**	-0.57		-1.25
cis-$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3\cdot 3H_2O$[12]	-0.48_5		——**	-0.40_2		-1.25
$[Co(NH_3)_6](ClO_4)_3$[13]	-0.43_8		-1.28	-0.23_5		*prewave*
trans-$[Co(NH_3)_4(NO_2)_2]ClO_4$[14]	-0.20_7*		-1.28_1*	-0.21		
cis-$[Co(NH_3)_4(NO_2)_2]ClO_4$[14]	-0.04_3*		-1.28_3*	-0.04_8		
trans-$[Co(NH_3)_4Cl_2]Cl$[15]	+	-0.42	——**	+	-0.40	——**
cis-$[Co(NH_3)_4Cl_2]Cl$[16]	+	-0.42	——**	+	-0.40	——**
$[Co(NH_3)_4(IO_3)_2]IO_3\cdot HIO_3$[17]	+		*hydrogen wave*	+		*hydrogen wave*

The concentration of complex: 0.001 gram complex ion per litre. Potential unit: V. vs. S.C.E. Temp.: 25°C.

* The data quoted from J. B. Willis, J. A. Friend and D. P. Mellor, *J. Am. Chem. Soc.*, **67**, 1680 (1945).

** Maximum wave

TABLE II. HALF-WAVE POTENTIALS OF TETRAMMINE COBALT(III) COMPLEXES CONTAINING ONLY ONE CHELATE RING

Complex	Supporting electrolyte 0.5 F K_2SO_4		Supporting electrolyte 0.1 F KCl	
	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)	$E_{1/2}$ of the 1st wave Co(III)→Co(II)	$E_{1/2}$ of the 2nd wave Co(II)→Co(0)
$[Co(NH_3)_4en]_2(SO_4)_3\cdot 4H_2O$[18]	-0.44	——*	-0.27	——*
$[Co(NH_3)_4gly]SO_4\cdot H_2O$[19]	-0.40_5	——*	-0.23_4	——*
$[Co(NH_3)_4CO_3]_2SO_4\cdot 3H_2O$[20]	-0.37	-1.28	-0.30_5	-1.24
$[Co(NH_3)_4alan]SO_4$[19]	-0.32	——*	-0.20_5	——*
$[Co(NH_3)_4ox]Cl$[21]	-0.29_5	——*	-0.19	——*
$[Co(NH_3)_4leuc](ClO_4)_3$[22]	-0.25_5	——*	——*	——*
$[Co(NH_3)_6](ClO_4)_3$[13]	-0.43_8	*prewave*	-0.23_5	*prewave*

The concentration of complex: 0.001 gram complex ion per litre. Potential unit: V. vs. S.C.E. Temp.: 25°C.

* Maximum wave

$[Co(NH_3)_4alan^*]SO_4$, shifts towards the negative direction by -0.12_5V. (vs. S.C.E.) in the presence of 0.0032% Tween-80**, as is shown in Fig. 1.

The supporting electrolytes used are 0.1 F potassium chloride and 0.5 F potassium sulfate.

Results and Discussion

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

All the compounds are reduced irreversibly in two steps at the dropping mercury electrode in 0.1 F potassium chloride or 0.5 F potassium sulfate except the complexes which aquate easily in solution. The ratio of the height of the first wave to that of the second is approximately 1:2. The heights of the first and the second waves are roughly proportional to the concentration of the complex ion at the concentration of $5\times10^{-3}\sim10^{-4}$ gram complex ion per litre. Consequently, it is considered that the first wave, corresponding to a gain of one electron, represents the reduction to cobalt(II) state and the second, corresponding to two electrons, represents the reduction to the metal. The half-wave potentials of the latter are always close to that of the hexaquocobalt(II) ion, $[Co(OH_2)_6]^{2+}$. ($E_{1/2}=-1.428$ V. vs. S.C.E. in 0.5 F K_2SO_4 solution[4].)

The reduction processes of tetrammine cobalt(III) complexes are considered as follows:

$$[Co(NH_3)_4X_2]^{(3-2n)+}+e^- \rightarrow [Co(NH_3)_4X_2]^{(2-2n)+}$$

$$[Co(NH_3)_4X_2]^{(2-2n)+}+mH_2O \xrightarrow[\text{rapidly}]{}$$

$$\begin{cases} [Co(OH_2)_6]^{2+}+2X^{n-}+4NH_3 \\ [Co(OH_2)_5X]^{(2-n)+}+X^{n-}+4NH_3 \\ [Co(OH_2)_4X_2]^{(2-2n)+}+4NH_3 \\ \text{etc.} \end{cases}$$

$$\begin{cases} [Co(OH_2)_6]^{2+}+2e^- \rightarrow Co+6H_2O \\ [Co(OH_2)_5X]^{(2-n)+}+2e^- \rightarrow Co+5H_2O+X^{n-} \\ [Co(OH_2)_4X_2]^{(2-2n)+}+2e^- \rightarrow Co+4H_2O+2X^{n-} \\ \text{etc.} \end{cases}$$

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

The polarographic stability of the cobalt(III) complexes of tetrammine series increases in the following order of the ligands; for the complexes of $[Co(NH_3)_4X_2]$ type,

IO_3^-, $Cl^- < NO_2^- < NH_3 < OH_2 < SO_3^{2-}$

(supporting electrolyte; 0.5 F K_2SO_4)

and for the complexes of $[Co(NH_3)_4Y]$ type,

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

(supporting electrolyte; 0.5 F K_2SO_4)

The order of the stability for the latter type was found to be altered between carbonate and ethylenediamine in the supporting electrolyte of 0.1 F potassium chloride.

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

(supporting electrolyte; 0.1 F KCl).

No special relation between the orders of the polarographic stability and that of the spectrochemical series could be found.

The half-wave potentials of the first waves for the complexes of the tetrammine series, $[Co(NH_3)_4X_2]$ or $[Co(NH_3)_4Y]$, exhibit always less negative values than those of the corresponding complexes of bisethylenediamine series, $[Co\ en_2X_2]$ or $[Co\ en_2Y]$, as is shown in Table III. This means that the two ethylenediamine chelate rings have the ability of forming the more stable cobalt(III) complexes against the polarographic reduction than the coordination of the corresponding four ammonia ligands. The result is quite in agreement with that obtained in the previous paper[10].

Fig. 2 shows the polarograms of *cis*-diaquotetramminecobalt(III) ion, $[Co(NH_3)_4(OH_2)_2]^{3+}$, in neutral supporting electrolyte. The slope of the tangent at the half-wave potential of the first wave is very small and the current rising gradually near the zero potential just like a residual current was observed as well as in the case of

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* The following abbreviations are used; gly, $NH_2CH_2COO^-$; alan, $NH_2CH(CH_3)COO^-$; leuc, $(CH_3)_2CHCH_2CH(NH_2)COO^-$; ox, $(COO)_2^{2-}$; en, $NH_2CH_2CH_2NH_2$.

** Polyoxyethylene sorbitane monooleate.

11) A. Werner and H. Grüger, *Z. anorg. Chem.*, **16**, 398 (1898).

12) S. M. Jörgensen, ibid., **2**, 279 (1892).

13) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

14) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 455 (1898).

15) S. M. Jörgensen, ibid., **14**, 404 (1897).

16) C. Duval, *Compt. rend.*, **182**, 636 (1926).

17) N. I. Lobanov, *Obschei Neorg. Khim., Akad. Nauk S. S. S. R.*, **28**, 277 (1954), *Chem. Abstr;* **49**, 14555e.

18) Y. Shimura, This Bulletin, **31**, 311 (1958).

19) Y. Shimura, ibid., **31**., 173 (1958).

20) S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 279 (1892).

21) S. M. Jörgensen, ibid., **11**, 416 (1896).

22) Y. Shimura, This Bulletin, **31**, 315 (1958).

TABLE III. COMPARISON OF THE HALF-WAVE POTENTIALS OF THE FIRST WAVES IN THE COBALT(III) COMPLEXES OF BISETHYLENEDIAMINE SERIES AND OF THE CORRESPONDING TETRAMMINE SERIES

Complex	Supporting electrolyte 0.5 F K_2SO_4 $E_{1/2}$ of the 1st wave Co(III)→Co(II)	Supporting electrolyte 0.1 F KCl $E_{1/2}$ of the 1st wave Co(III)→Co(II)
$[Co\ en_2CO_3]Cl\cdot H_2O$	-0.45_5	-0.40
$[Co(NH_3)_4CO_3]_2SO_4\cdot 3H_2O$	-0.37	-0.30_5
$[Co\ en_2\ gly]Cl_2\cdot H_2O$	-0.41	-0.36
$[Co(NH_3)_4gly]SO_4$	-0.40_5	-0.23_4
$[Co\ en_2ox]Cl$	-0.31	-0.32
$[Co(NH_3)_4ox]Cl$	-0.29_5	-0.19
$[Co\ en_2leuc](ClO_4)_2$	-0.30_5	-0.33_5****
$[Co(NH_3)_4leuc](ClO_4)_2$	-0.25_5	——*
cis-$[Co\ en_2(OH_2)_2](NO_3)_3$	-0.50	-0.42
cis-$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3\cdot 3H_2O$	-0.48_5	-0.40_2
trans-$[Co\ en_2(NH_3)_2]Cl_3\cdot H_2O$	-0.45	-0.31
cis-$[Co\ en_2(NH_3)_2](ClO_4)_3$	-0.45	-0.31
$[Co(NH_3)_6](ClO_4)_3$	-0.43_8	-0.23_5
trans-$[Co\ en_2(NO_2)_2]Cl$	-0.26	-0.27***
trans-$[Co(NH_3)_4(NO_2)_2]ClO_4$	-0.20_7**	-0.21
cis-$[Co\ en_2(NO_2)_2]ClO_4$	-0.25	-0.24***
cis-$[Co(NH_3)_4(NO_2)_2]ClO_4$	-0.04_3**	-0.04_8

The data for the cobalt(III) complexes of bisethylenediamine series were quoted from N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, 32, 150 (1959). The concentration of complex: 0.001 gram complex ion per litre. Potential unit: V. vs. S.C.E.

* Maximum wave

** The data quoted from J. B. Willis, J. A. Friend and D. P. Mellor, *J. Am. Chem. Soc.*, 67, 1680 (1945).

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

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

diaquobisethylenediaminecobalt(III) complex[1] and could not be diminished only by the removal of the oxygen dissolved in solution. In perchloric acid, on the other hand, the first wave becomes steeper as is shown in Fig. 3. The reason for this is considered to be quite similar to the case of *cis*-diaquobisethylenediaminecobalt(III) complex. Namely, in neutral aqueous solution, the hydroxytetramminecobalt(III) ions are formed by the following ligandolysis.

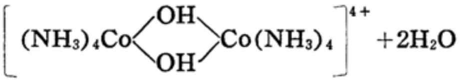
$$[Co(NH_3)_4(OH_2)_2]^{3+} \rightleftarrows [Co(NH_3)_4(OH_2)(OH)]^{2+} + H^+$$

$$[Co(NH_3)_4(OH_2)(OH)]^{2+} \rightleftarrows [Co(NH_3)_4(OH)_2]^{+} + H^+$$

The monohydroxymonoaquo complex ions formed here polymerize to the various kinds of the polynuclear cobalt(III) complex with the lapse of time, as was verified by the spectrochemical studies of Rasmussen et al.[23]

For instance,

$$2\ cis\text{-}[Co(NH_3)_4(OH_2)(OH)]^{2+} \rightarrow$$



$$\left[(NH_3)_4Co\begin{matrix}OH\\ OH\end{matrix}Co(NH_3)_4\right]^{4+} + 2H_2O$$

Accordingly, in neutral solution the several kinds of these cobalt(III) complexes having similar structures are considered to be reduced almost at the same time.

The above mechanism well explains the fact that the overlapped waves of small slope are obtained for the diaquotetramminecobalt(III) complex. In perchloric acid, on the other hand, the above equilibrium is markedly shifted to the left hand due to the presence of an overwhelming hydrogen ion. Hence, the polymerization is quite inhibited and only the original ion is present in solution. Consequently, the wave of steep slope was obtained.

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

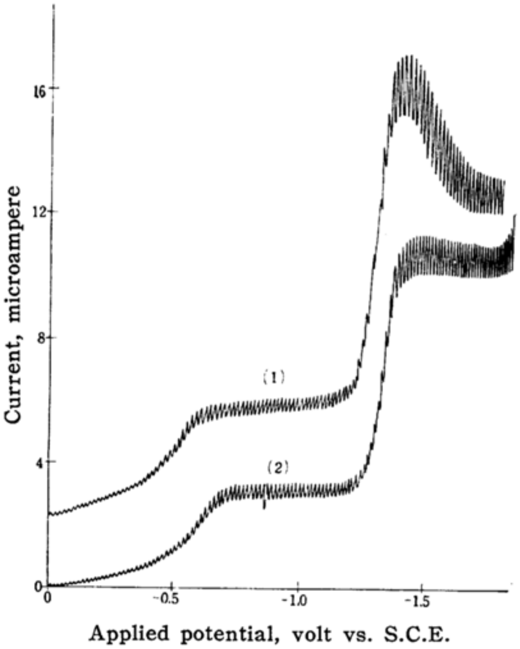

Fig. 2. The polarograms of *cis*-diaquotetramminecobalt(III) complex, $[Co(NH_3)_4(OH_2)_2](SO_4)_3 \cdot 3H_2O$, obtained at the concentration of 0.001 gram complex ion per litre in 0.5 F K_2SO_4 solution.

1. In the absence of the maximum suppressor.
2. In the presence of 0.0032% Tween-80.

Sensitivity: 0.08 μA/mm. Damping: 200.

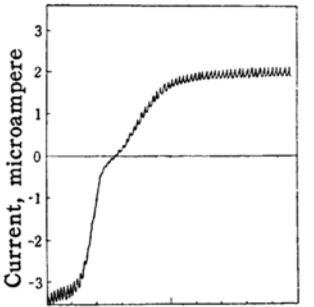

Fig. 3. The polarogram of *cis*-diaquotetramminecobalt(III) ion, $[Co(NH_3)_4(OH_2)_2]^{3+}$, obtained in 1 F perchloric acid at the concentration of 0.001 gram complex ion per litre.

The wave of *cis*- or *trans*-dichlorotetramminecobalt(III) ion which appeared at around -0.42 V. (vs. S.C.E.) is considered to correspond to the reduction of the aquated species such as $[Co(NH_3)_4(OH_2)Cl]^{2+}$ and $[Co(NH_3)_4(OH_2)_2]^{3+}$, since the half-wave potential is in proximity to that of diaquotetramminecobalt(III) ion. ($E_{1/2} = -0.40_2$ V. vs. S.C.E. in 0.1 F KCl). Judging from the wavelet, the reduction wave of the original ion is believed to be in the positive region of potential.

As to the wave of diiodatotetramminecobalt(III) complex, $[Co(NH_3)_4(IO_3)_2]IO_3 \cdot HIO_3$, the half-wave potential of the first wave is in the positive region of potential and the second wave is covered by the reduction wave of the hydrogen ion liberated from iodic acid.

Summary

1. All the cobalt(III) complexes of tetrammine series, $[Co(NH_3)_4X_2]$ or $[Co(NH_3)_4Y]$, were reduced irreversibly in two steps at the dropping mercury electrode. The first wave, corresponding to a gain of one electron, represents the reduction of Co(III)→Co(II) and the second, corresponding to two electrons, represents the reduction of Co(II)→Co(0).

2. The polarographic stability of the cobalt(III) complexes of tetrammine series are ranked in the following order of the ligand; for the complexes of $[Co(NH_3)_4X_2]$ type,

$$IO_3^-,\ Cl^- < NO_2^- < NH_3 < OH_2 < SO_3^{2-}$$

(supporting electrolyte; 0.5 F K_2SO_4),

and for the complexs of $[Co(NH_3)_4Y]$ type,

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

(supporting electrolyte; 0.5 F K_2SO_4).

3. The half-wave potentials of the reduction step of Co(III)→Co(II) for all the tetrammine cobalt(III) complexes exhibit always more positive values than those of the corresponding bisethylenediamine cobalt(III) complexes.

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