Polarographic Studies of Metallic Complexes. I. Oxalato-ammine, Glycinato-ammine and Ethylenediamine-ammine Series of Cobalt(III) Complexes[1]

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There have been reported some polarographic researches concerning the relation between the structures of cobalt(III) complexes and the half-wave potentials of their $Co^{III}\rightarrow Co^{II}$ reduction. For instance, Willis, Friend and Mellor[2] studied nitro-ammine series of cobalt(III) complexes and found the following order of the half-wave potentials:

$[Co(NO_2)_6]^{3-}$, $[Co(NH_3)_3(NO_2)_3]$,
cis-$[Co(NH_3)_4(NO_2)_2]^+$,
$[Co(NH_3)_2(NO_2)_4]^-$,
trans-$[Co(NH_3)_4(NO_2)_2]^+$,
$[Co(NH_3)_5NO_2]^{2+}$, $[Co(NH_3)_6]^{3+}$
(from positive to negative).

It was also reported by Brigando[3] that the polarographic stability of luteo-type cobalt(III) complexes increased as unidentate ligands were replaced by polydentate ligands. Thus the half-wave potentials of the luteo-type cobalt(III) complexes were in the order of

$[Co(NH_3)_4(NH_2CH_3)_2]^{3+}$, $[Co(NH_3)_6]^{3+}$,
$[Co\ en_3]^{3+}$, $[Co\ dien_2{}^*]^{3+}$.

Recently, Holtzclaw et al.[4-6] reported that the *cis* isomer exhibited a less negative half-wave potential than the corresponding *trans* isomer for the cobalt(III) complexes containing negative ligands on two of the coordination positions and neutral ligands on the other four. The complexes which contain only one or no negative ligands scarcely ever show such a trend.

The present paper deals with the polarography of oxalato-ammine, glycinato-ammine and ethylenediamine-ammine series of cobalt(III) complexes. The main purpose of this study is to examine the relation between the polarographic stabilities of these complexes and their structures.

Experimental

Apparatus.—A Heyrovsky-Shikata type polarograph was employed with the circuit for extendable and adjustable e.m.f. An H-cell with a saturated calomel electrode was used. The capillary used had an m-value of 5.828 mg./sec. and a drop time of 4.00 sec./drop in distilled water at the mercury height of 96 cm. with an open circuit. All measurements were carried out in a thermostat of 18.0±0.1°C.

The half-wave potentials were determined from the enlarged polarograms by "plotting method". The potential values were calibrated for iR drop, using the minimum value of the cell resistance.

Materials.—The complex compounds studied were prepared by the method described in the literature[7-17] (the references are given in Tables I-III). The concentration of the solution was 0.001 gram complex ion per liter.

The supporting electrolytes used were potassium chloride, potassium sulfate or ammonium oxalate. The concentration of each supporting electrolyte was 0.1 F.

Oxygen was removed from the solutions for electrolysis by bubbling nitrogen gas through them for about half an hour, preventing the evaporation. Polarographic measurements were made as soon as possible after the removal of oxygen.

No maximum suppressor was used because it was feared that the presence of it might cause

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[1] Presented at the Tenth Annual Meeting of the Chemical Society of Japan, Tokyo, April 6, 1957.

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

[3] J. Brigando, *Compt. rend.*, **236**, 708 (1953).

* dien=$NH_2CH_2CH_2NHCH_2CH_2NH_2$

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

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* Polyoxyethylene sorbitan monooleate.

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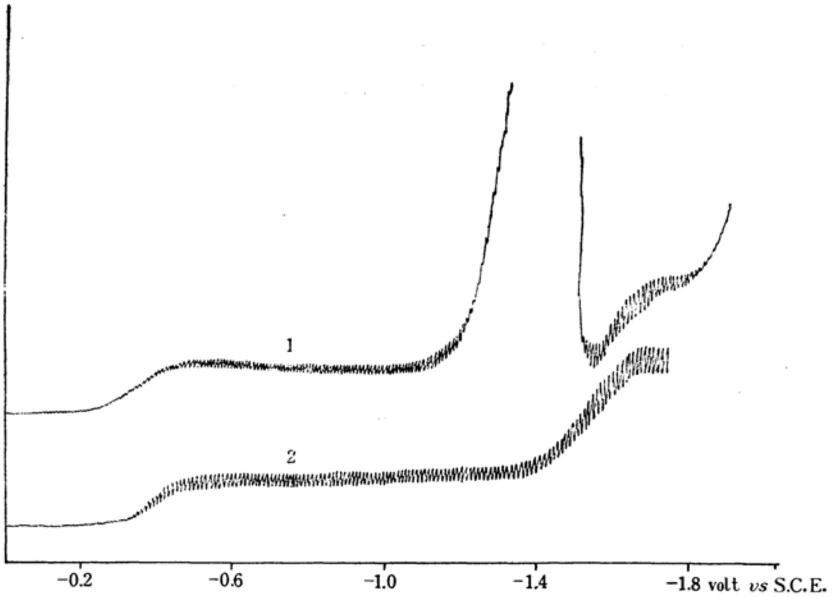

Fig. 1. (1) Polarogram of $[Co\ en_2\ gly]Cl_2 \cdot H_2O$ in the absence of suppressor. (2) Polarogram of $[Co\ en_2\ gly]Cl_2 \cdot H_2O$ in the presence of 0.02 % Tween-80. Supporting electrolyte is 0.1 F KCl.

TABLE I

HALF-WAVE POTENTIALS OF OXALATO-AMMINE SERIES OF Co(III) COMPLEXES

(Supporting electrolyte: 0.1 F $(NH_4)_2C_2O_4$ or 0.1 F KCl).

Compound	First wave (volt *vs.* S. C. E.)		Second wave (volt *vs.* S. C. E.)	
	in $(NH_4)_2C_2O_4$	in KCl	in $(NH_4)_2C_2O_4$	in KCl
$K_3[Co\ ox_3]$[7]	+		No reduction	
$NH_4[Co(NH_3)_2ox_2] \cdot H_2O$[8]	−0.03	−0.03	−1.58	−1.23
$[Co(NH_3)_4ox]NO_3$[9]	−0.21	−0.21	−1.46	−1.25
$[Co(NH_3)_6]SO_4 \cdot Cl \cdot 3H_2O$[10]	—	−0.24	—	−1.23
$[Co\ en_2\ ox]Cl$[11]	−0.32	—	−1.35	—

TABLE II

HALF-WAVE POTENTIALS OF GLYCINATO-AMMINE SERIES OF Co(III) COMPLEXES

(Supporting electolyte: 0.1 F KCl or 0.1 F K_2SO_4)

Compound	First wave (volt *vs.* S. C. E.)		Second wave (volt *vs.* S. C. E.)	
	in KCl	in K_2SO_4	in KCl	in K_2SO_4
α-$[Co\ gly_3]$[12]	−0.14	−0.07	*	*
$[Co(NH_3)_2\ gly_2]Cl$[13]	-0.23_0	−0.28	−1.24	−1.31
$[Co(NH_3)_4\ gly]SO_4$[13]	-0.23_4	−0.36	−1.26	*
$[Co(NH_3)_6](ClO_4)_3$[14]	−0.24**	−0.43	−1.25**	−1.26
$[Co\ en_2\ gly]Cl_2 \cdot H_2O$[15]	−0.36	−0.41	*	*

* Maximum wave

** The data of the chloride sulfate, $[Co(NH_3)_6]Cl \cdot SO_4 \cdot 3H_2O$.

the lowering of the limiting current and the shift of the half-wave potential to negative direction. For example, 0.02 % Tween-80* shifted the half-wave potential of the first wave of glycinato-diethylenediamine cobalt(III) complex to the negative direction by −0.03 V (Fig. 1).

Results and Discussion

The half-wave potentials of the oxalato-ammine, glycinato-ammine and ethylenediamine-ammine series of cobalt(III) complexes measured are given in Tables I-III.

TABLE III
HALF-WAVE POTENTIALS OF ETHYLENEDIAMINE-AMMINE SERIES OF Co(III) COMPLEXES
(Supporting electrolyte: 0.1 F KCl)

Compound	First wave (volt *vs.* S.C.E.)	Second wave (volt *vs.* S.C.E.)
$[Co\ en_3](ClO_4)_3$ [14]	−0.43	*
cis-$[Co\ en_2(NH_3)_2](ClO_4)_3$ [16]	−0.31	*
trans-$[Co\ en_2(NH_3)_2]Cl_3 \cdot H_2O$ [17]	−0.31	*
$[Co\ en\ (NH_3)_4]_2(SO_4)_3 \cdot 4H_2O$ [13]	−0.27	*
$[Co(NH_3)_6](ClO_4)_3$	−0.24	−1.23

* Maximum wave

All the compounds examined are reduced polarographically in two steps except in the case of the trioxalato complex, $[Co\ ox_3]^{3-}$, in the presence of an excess of $C_2O_4^{2-}$. On plotting $\log i/(i_d-i)$ against $E_{d.e.}$ for these three series of cobalt(III) complexes, straight lines were usually obtained. Only in a few cases, lines, having slight inflection were obtained. The reciprocal slopes of such lines for all the complexes showed that every reduction was irreversible.

The ratio of the height of first wave to that of the second is approximately 1 : 2. Consequently, it is concluded that the first wave, corresponding to a gain of one electron, apparently represents the reduction to cobalt(II) state, and the second, corresponding to two electrons, represents the reduction to the metal. The half-wave potential of the latter is always very near to that of hexaaquo cobalt(II) $[Co(OH_2)_6]^{2+}$ ion (−1.428 V *vs.* S. C. E. in 1 F K_2SO_4 solution[2]).

As regards the process of the reduction of hexammine cobalt(III) $[Co(NH_3)_6]^{3+}$, Laitinen et al.[18] offered the following mechanism:

$$[Co(NH_3)_6]^{3+} + e^- \longrightarrow [Co(NH_3)_6]^{2+}$$

$$[Co(NH_3)_6]^{2+} + 6H_2O \xrightarrow{\text{very rapid}} [Co(OH_2)_6]^{2+} + 6NH_3$$

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

The similar mechanism of reduction is probably true for the oxalato-ammine and glycinato-ammine series of cobalt(III) complexes. In the case of the trisoxalato complex, $[Co\ ox_3]^{3-}$, no reduction wave is observed below the final current rise in solutions containing an excess of oxalate ion. This fact has already been reported by Watters and Kolthoff[19]. This is probably an indication of the presence of a stable cobalt(II) oxalato-complex in the solution such as dioxalatodiaquo cobaltate (II) $[Co\ ox_2(OH_2)_2]^{2-}$ or a similar one.

All the second waves of the ethylenediamine-ammine complexes have maxima, which can be easily suppressed by a capillary active substance. According to Kivalo[20], the product of the first reduction of trisethylenediamine cobalt(III) $[Co\ en_3]^{3+}$ is an equilibrium mixture of aquo-ethylenediamine cobalt(II) complexes. The second waves of the ethylenediamine-ammine cobalt(III) complexes are, therefore, due to the similar aquo-ethylenediamine cobalt(II) complexes.

As to the relation between the half-wave potential of the first wave of these complexes and their structure, the authors are led to the following conclusion. As the ammonia molecules in hexa-ammine cobalt(III) $[Co(NH_3)_6]^{3+}$ are replaced with ethylenediamine, the half-wave potential of the first wave shifts to the negative direction. If the ammonia molecules in $[Co(NH_3)_6]^{3+}$ are replaced by glycinate the first wave shifts to the positive direction. similarly, by successive replacements of the ammonia molecules in $[Co(NH_3)_6]^{3+}$ with oxalate, the first wave shifts to further more positive. Since the half-wave potential of the first wave of trisoxalato cobaltate(III) $[Co\ ox_3]^{3-}$, a chelate produced by exhaustive replacement with oxalate, is in the positive region of applied potential *vs.* S. C. E., it is hardly possible to measure its value at

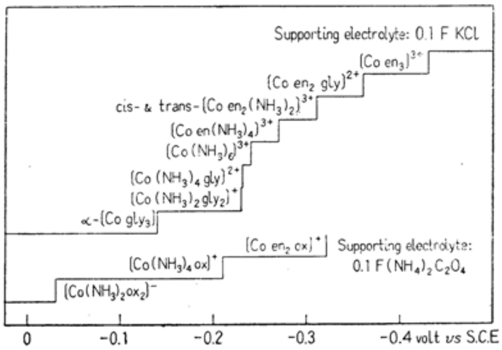

Fig. 2. Half-wave potentials of the first wave of oxalato-ammine, glycinato-ammine and ethylenediamine-ammine series of Co(III) complexes.

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the dropping mercury electrode.

Eventually, the polarographic stability of cobalt(III) complexes increases in the following order of the ligands (see Fig. 2): ox^{2-}, gly^{-}, NH_3, en. The half-wave potential of $[Co\ en_2\ gly]^{2+}$ is more negative than that of $[Co\ en_2\ (NH_3)_2]^{3+}$. This is an exception of the order above mentioned. As is also seen from the work of Willis et al.[2] on the nitro-ammine cobalt(III) complexes, it is suggested that many factors affect the position of the first wave of cobalt(III) complexes.

In agreement with the observation of Holtzclaw et al.[5], *cis*- and *trans*-forms of $[Co\ en_2(NH_3)_2]^{3+}$ have identical values of the half-wave potential of the first wave.

Summary

The ions $[Co\ ox_n(NH_3)_{6-n}]^{(2n-3)-}$, $[Co\ gly_n(NH_3)_{6-n}]^{(3-n)+}$, $[Co\ en_n(NH_3)_{6-n}]^{3+}$, $[Co\ en_2\ gly]^{2+}$ and $[Co\ en_2\ ox]^{+}$ were all reduced irreversibly in two steps at the dropping mercury electrode.

The first diffusion current corresponds to the reduction, $Co^{III} \rightarrow Co^{II}$ and the second to the reduction, $Co^{II} \rightarrow Co^{0}$. The diffusion current and the concentration were linearly related.

The half wave potential of the first wave of the cobalt(III) complexes shifts to negative direction in the following order of the ligands: ox^{2-}, gly^{-}, NH_3, en.

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