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The Polarographic Behavior of Tris(1, 10-phenanthroline)cobalt Complexes and the Univalent Phenanthroline-Cobalt Complex.*1

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The oxidation-reduction behavior of tris(1, 10-phenanthroline)cobalt complexes at a dropping mercury electrode has been studied by the d. c. and a. c. polarographic methods. The trivalent cobalt-phenanthroline complex ion is reduced in two steps in 1 M sodium sulfate in a quite similar way as the trivalent cobalt-dipyridyl complex ion. Both electrode processes, cobalt(III)→cobalt(II) and cobalt(II)→cobalt(I), are considered to be reversible. The univalent cobalt-phenphenanthroline complex has been obtained as a black powder by the reduction of the divalent cobalt complex with sodium borohydride; the atomic ratio of nitrogen to cobalt has been found to be close to six. The ethanolic solution is brown-black, in remarkable contrast with that of the corresponding dipyridyl complex, deep blue.

It is well known that the lower valency states of transition metals can be stabilized by coordinating ligands, such as carbonyl, cyanide, and dipyridyl which are likely to form bonds of a partly double-bond character between a central metal ion and the ligands.[1] A polarographic method has been proved to be very useful for detecting such abnormal valency states in many metal complex compounds.[2-9] From polarographic studies of cobalt-dipyridyl complexes, it has been shown that the tris(2, 2′-dipyridyl)cobalt(III) complex ion is reduced in two steps, from cobalt(III) to cobalt(II) and from cobalt(II) to cobalt(I). The isolation of the univalent cobalt complex has also been reported.[4,6] The cobalt complexes of phenanthroline, however, in spite of its strong resemblance to dipyridyl as a ligand, have never been studied in detail by the polarographic method. Therefore, the present authors have investigated the polarographic behavior of the tris(1, 10-phenanthroline)cobalt(III or II) ion in a 1 M sodium sulfate medium and found a great similarity between the d. c. polarogram of the tris(1, 10-phenanthroline)cobalt ion and that of the tris-(2, 2′-dipyridyl)cobalt ion, which has been reported on in a previous short communication.[10] They have also attempted to isolate the univalent cobalt complex and define its formula. The results will be presented in the present paper.

Experimental

Direct-current (d. c.) and alternating-current (a. c.) polarograms were recorded with a Yanagimoto model PS-52 photorecording polarograph and a Yanagimoto model PA-101 pen-recording polarograph respectively. A Yanagimoto controlled-potential electrolyzer was also used in an attempt to prepare and to identify the univalent cobalt complex in a solution. The absorption spectra were measured using a Hitachi EPU 2 spectrophotometer. The cell equipment used for the polarographic measurements was the same as has been reported on previously except that the saturated calomel electrode was replaced by the saturated mercurous sulfate electrode.[11] The dropping mercury electrode employed had an m value of 0.855_9 mg./sec. and a drop-time of 8.52 sec. when measured in distilled water at a 58.2 cm. height of the mercury reservoir with an open circuit. The cell temperature was maintained at 25 ± 0.1°C by means of a water thermostat. The oxygen dissolved in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution. $[Co(phen)_3](ClO_4)_2$ and $[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$ (phen=1, 10-phenanthroline) were prepared according to the procedures described in the literature.[12] A 1 M sodium sulfate solution was used as a supporting electrolyte, while no maximum suppressor was added. Solutions

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2) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, **71**, 867 (1949).
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4) A. A. Vlček, ibid., **180**, 753 (1957); *Z. phys. Chem.*, Sonderheft, 143 (1958).
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TABLE I. DEPENDENCE OF LIMITING CURRENTS ON A MERCURY COLUMN HEIGHT FOR 0.2_9 mM $[Co(phen)_3]^{3+}$ IN 1 M Na_2SO_4

H_{corr} cm.	i_{l_1}* μamp.	$i_{l_1}/\sqrt{H_{corr}}$	i_a* μamp.	$i_a/\sqrt{H_{corr}}$	i_{l_2}* μamp.	$i_{l_2}/\sqrt{H_{corr}}$
64.1	0.425	0.053	0.074	0.009_2	0.425	0.053
56.1	0.387	0.051	0.060	0.008_0	0.385	0.051
48.1	0.369	0.053	0.051	0.007_1	0.360	0.052
41.1	0.332	0.051	0.042	0.006_0	0.323	0.050

* i_{l_1}, i_a and i_{l_2} represent the limiting current for the first wave, the prewave and the total limiting current for the second wave including the prewave, respectively.

TABLE II. CHARACTERISTICS OF D. C. WAVES FOR $[Co(phen)_3]^{3+}$ IN 1 M Na_2SO_4

Concentration of depolarizer	1st reduction wave		2nd reduction wave			
	i_d	$E_{1/2}$	i_d*	i_a**	$E_{1/2}$**	E_d***
mM	μamp.	V. vs. SCE	μamp.	μamp.	V. vs. SCE	V. vs. SCE
1.27	1.61	$+0.08_6$	1.59	0.04_6	−0.83	−0.98
0.86	1.05	$+0.09_8$	1.03	0.05_9	−0.84	−1.00
0.63	0.83_1	$+0.10_1$	0.82_1	0.06_5	−0.84	−1.03
0.32	0.44_3	$+0.10_4$	0.42_4	0.06_5	−0.83	−1.08
0.12	0.17_5	$+0.08_5$	0.13_5	0.05_8	−0.83	−1.13

* The total diffusion current including the prewave
** The values for the prewave
*** The decomposition potential for the main second wave

containing the divalent cobalt complex were carefully prepared in order to prevent it from oxidation. All the chemicals used were of guaranteed reagent grade.

Results and Discussion

On the D. C. and A. C. Polarograms.—$[Co(phen)_3]^{3+}$ ions are reduced in two steps in 1 M sodium sulfate, as has been shown in Fig. 1 of a previous paper.[10] The first wave appears around +0.10 V. vs. SCE, and the second one accompanying a small prewave appears around −1.0 V. vs. SCE. A small minimum was observed on the plateau of the first wave. $[Co(phen)_3]^{2+}$ ions show an oxidation wave and a reduction wave at the respective potentials corresponding to the first and the second waves of $[Co(phen)_3]^{3+}$ ions. Since the solubility of $[Co\ phen_3]\ (ClO_4)_2$ was very low, the reduction waves of the $[Co(phen)_3]^{3+}$ ion were studied under varied conditions. The dependence of the limiting current on the mercury column height is given in Table I. The characteristics of the d. c. polarograms at various concentrations of the depolarizer are given in Table II.

A typical example of the logarithmic plot for the first reduction wave with 0.6_3 mmol./l. $[Co(phen)_3]^{3+}$ is shown in Fig. 1. The reciprocal slope in the upper part decreases with the increase in the depolarizer concentration up to 1.5 mmol./l. Beyond that point, the d. c. polarogram is distorted to a greater extent with an increase in the concentration. The main second wave has a discontinuity at its beginning, and the decomposition potential shifts to a more positive potential with an incerase

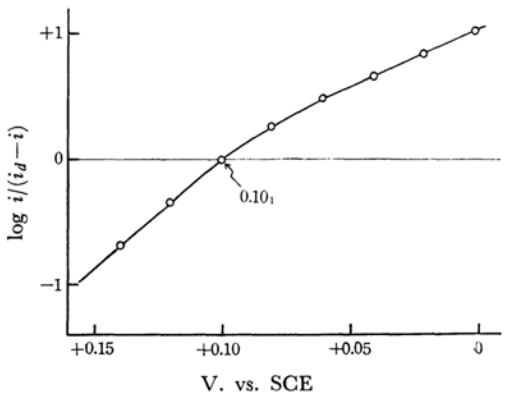

Fig. 1. Logarithmic plot for the reduction wave of 0.6_3 mM $[Co(phen)_3](ClO_4)_3$ in 1 M Na_2SO_4.

in the depolarizer concentration. The first and the second (including the prewave) waves are concentration-dependent and are evidently diffusion-controlled. The prewave has the characteristic of an adsorption wave in that its height is independent of the depolarizer concentration.[13] Since adsorption phenomena seem to play an important role over a wide potential range, the drop time was measured at different potentials. The results are shown in Fig. 2. The irregularity of the electrocapillary curve is exactly reflected in the d. c. and a. c. polarograms. The a. c. polarograms at various concentrations of the depolarizer are shown in Fig. 3, together with the a. c. polarograms obtained in the presence of gelatine.

13) R. Brdička, *Z. Elektrochem.*, **48**, 278 (1942).

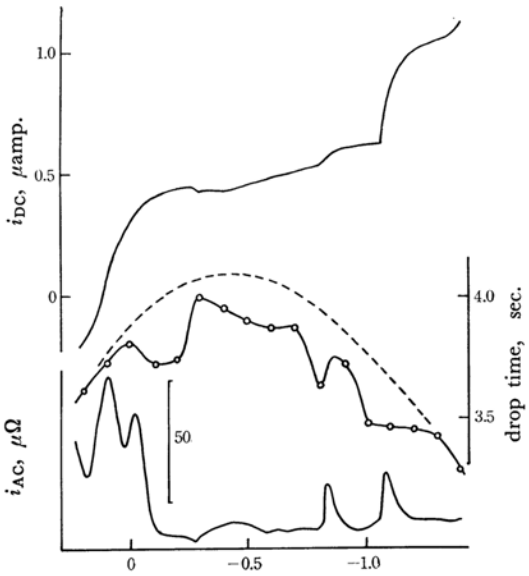

Fig. 2. Electrocapillary curve and d.c. and a.c. polarograms of 0.3 mM $[Co(phen)_3](ClO_4)_3$ in 1 M Na_2SO_4.

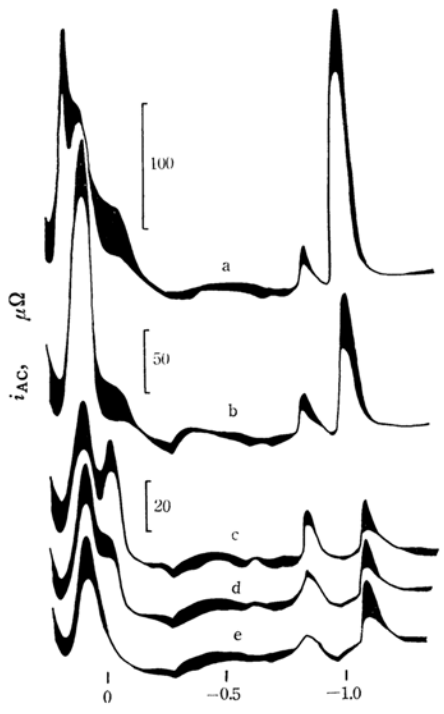

Fig. 3. A. c. polarograms of $[Co(phen)_3](ClO_4)_3$ in 1 M Na_2SO_4. The concentration of $[Co(phen)_3](ClO_4)_3$: a) 1.5 mM, b) 0.9 mM, c) 0.3 mM, d) 0.3 mM (+0.01% gelatine) and e) 0.3 mM (+0.03% gelatine).

It should be noted that the a. c. peak height corresponding to the first d. c. wave is not proportionate to the concentration of the depolarizer, and that the two a. c. peaks are observed at the potential for the first d. c. wave with 0.3 mmol./l. $[Co(phen)_3]^{3+}$.

On the Reduction Mechanism.—From the diffusion current constants for the first and the second waves, the first wave can be attributed to the reduction of cobalt from a trivalent to a divalent state and the second, to the reduction of divalent to univalent cobalt. A similar reduction process has been already proposed for several cobalt complexes.[4-7] In the case of the tris(dipyridyl) complex, Waind and Martin[6] concluded that the first reduction wave is reversible, while Vlček[4] pointed out that the second reduction wave is reversible.

The inflection of the logarithmic plot at the upper part for the first step and the appearance of a minimum on the d. c. polarogram may be explained qualitatively by assuming the following electrode reaction:

$$[Co(phen)_3]^{3+} + e^- \rightarrow [Co(phen)_3]^{2+}$$
$$\downarrow\uparrow$$
$$\text{Hg-phen complex} + e^- \leftarrow Hg + phen + [Co(phen)_2]^{2+}$$

The $[Co(phen)_3]^{2+}$ ion produced at the electrode surface, because of its lower stability, dissociates partly to the lower complex, liberating phenanthroline; the phenanthroline is very likely to be adsorbed onto the electrode surface, where it will interfere with the passage of the current and cause a minimum. At a certain potential dependent on the depolarizer concentration, the free phenanthroline adsorbed on the surface accelerates the dissolution of mercury through the formation of a mercury-phenanthroline complex; this oxidation process will compensate for a part of the reduction current, thus causing an inflection of the logarithmic plot and also a distinct deformation of the d. c. polarograms with an increase in the depolarizer concentration. These reduction and oxidation processes give the two peaks around +0.1 V. on an a. c. polarogram.

The peak at a negative potential is confirmed to correspond to the oxidation process since its peak height increases when a small amount of excess free phenanthroline is added. At higher concentrations of the depolarizer, the two opposite processes take place at almost the same potential, resulting in an apparent lowering of the a. c. peak height. If a more strongly adsorbable substance than phenanthroline covers the electrode surface, the dissolution of mercury will be hindered. This expectation can be fully realized by adding 0.03% gelatine to the electrolytic solution, as has been shown in Fig. 3. In spite of the addition of gelatine, however, the polarographic reversibility is very high, as is shown in Table III. The polarographic

Table III. Values of $i_p/(ni_d\sqrt{\tau})$

Electrolyte	Electrode reaction	$i_p/(ni_d\sqrt{\tau})$ kΩ amp^{-1}sec$^{-1/2}$
0.3 mM$[Co(phen)_3]^{3+}$+1 M Na_2SO_4 +0.03% gelatine	Co(III) ⟷ Co(II)	0.052_0
	Co(II) ⟷ Co(I)	0.03*
0.3 mM Tl^++1 M Na_2SO_4	Tl(I) ⟷ Tl(Hg)	0.054_0
0.3 mM Cd^{2+}+1 M Na_2SO_4	Cd(II) ⟷ Cd(Hg)	0.052_5
0.3 mM Zn^{2+}+1 M NaCl +0.001% gelatine	Zn(II) ⟷ Zn(Hg)	0.020_1
0.3 mM$[Co(NH_3)_6]^{3+}$+1 M Na_2SO_4	Co(III) ⟷ Co(II)	0.007_0

* 0.05 with 0.8 mM$[Co(phen)_3]^{3+}$

reversibility is defined as $i_p/(ni_d\sqrt{\tau})$, where i_p, i_d and τ represent an a. c. peak height, a limiting diffusion current of the d. c. polarogram and a drop time respectively.[14] Also, from the approximate coincidence of the half-wave potential values for the oxidation of cobalt(II) (aver. +0.093 V.) and the reduction of cobalt(III) (aver. +0.095 V.), it can be concluded that the electrode process for the reduction of cobalt(III) to cobalt(II) is highly reversible in the phenanthroline system.

The prewave of the second wave can be attributed to the adsorption of the cobalt(I)-complex produced through the following electrode reaction:

$$[Co(phen)_{2-3}]^{2+} + e^- \rightarrow [Co(phen)_{2-3}]^+$$

The uncommon univalent cobalt complex ion can be produced in solution by the controlled-potential electrolysis method. The existence of the cobalt(I)-complex can be shown by the oxidation curve, as is shown in Fig. 4. From the polarographic reversibility and the constancy of the half-wave potential for the redox waves, the reduction of cobalt(II) to cobalt(I) is also considered

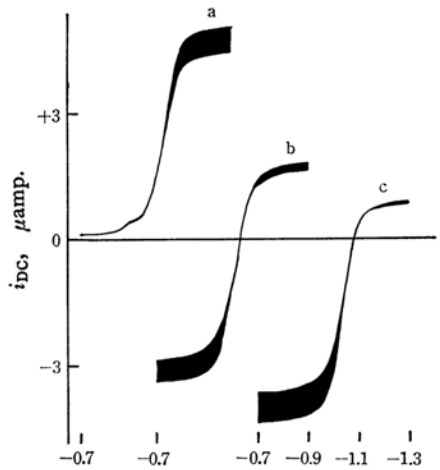

Fig. 4. D. c. polarograms obtained with a 1 : 3 mixture of cobalt(II) and phenanthroline in 0.5 M LiCl ethanolic solution: (a) 0, (b) 0.5 and (c) more than 3 hr. after controlled-potential electrolysis was started.

to be reversible in the present system.

From the above results, it can definitely be concluded that the polarographic behavior of the tris-(1,10-phenanthroline)cobalt complex is quite similar to that of the tris(dipyridyl) complex as regards both the mechanism and the reversibility of the electrode reaction.

On the Composition of the Univalent Cobalt Complex.—In the case of the dipyridyl complex, two formulas, $[Co(dipy)_3]ClO_4$ and $[Co(dipy)_2]$-ClO_4, have been proposed for the univalent cobalt complex by different authors.[4,6] Therefore, the present authors attempted to isolate the univalent cobalt phenanthroline complex in a pure state and to determine its chemical composition. Since the controlled-potential electrolysis method proved unsuccessful in its isolation, a reduction method similar to that employed in the preparation of the dipyridyl complex was used; $[Co(phen)_3](ClO_4)_2$ suspended in an ice-cold methanol (20%)-water mixture was reduced by slowly adding a cold aqueous solution of sodium borohydride in an atmosphere of nitrogen. The black solid which had precipitated was filtered, washed with cold water, and dried in a vacuum desiccator. It is highly sensitive to oxidation and turns brown-black on exposure to the air. Chemical analysis gave the atomic ratio of Co : N : Cl = 1 : 5.75 : 0.90. (Found: Co, 8.2; N, 11.20; ClO_4, 12.4%). Preliminary measurements revealed that the magnetic moment is much less than the value to be expected for a complex of octahedral symmetry, with its central metal ion having a d^8-electron configuration. From these results and from the fact that the prolonged electrolysis did not completely diminish the reduction wave of divalent cobalt, it may be supposed that the univalent cobalt complex obtained by the above method is not in a pure state. The color of the solid and the solution also suggests the possibility that the product is either entirely or partly a polynuclear complex. This situation leads to the conclusion that the authors are unable to decide definitely whether the univalent cobalt complex is $[Co(phen)_3]^+$ or $[Co(phen)_2]^+$,

14) M. Senda, M. Senda and I. Tachi, *J. Electrochem. Soc. Japan (Denki Kagaku)*, **27**, 83 (1959).

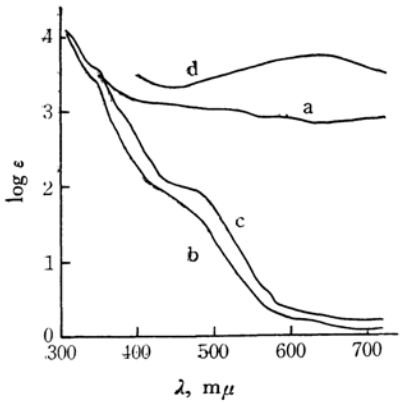

Fig. 5. Absorption spectra.
(a) $[Co(phen)_{2-3}]^{+}$, (b) $[Co(phen)_3]^{2+}$, (c) $[Co(phen)_3]^{3+}$, (d) $[Co(dipy)_3]^{+}$ plotted from the data obtained by Waind and Martin.[6]

although the atomic ratio of nitrogen to cobalt is close to six.*

The brown-black solution obtained by electrolyzing the 1 : 3 mixture of cobalt(II) and phenanthroline in a 0.5 M lithium chloride ethanolic solution (50% by volume) was used to measure the absorption spectrum. No definite absorption maxima are observed on the absorption curve, as is shown in Fig. 5. The color of the solution is in remarkable contrast with that of the dipyridyl complex, which has been shown to be a deep blue, its λ_{max} being 640 mμ.[6] Although the color of the solution and that of the solid are quite similar, there still remains some uncertainty with regard to the identity of the primary electrode reaction product and the solid obtained above. More detailed studies are needed.

* Independent of the present work, it has been reported that the phenanthroline cobalt(I) perchlorate is the hexacoordinated complex, $[Co(phen)_3]ClO_4$. N. Maki, M. Yamagami and H. Itatani, *J. Am. Chem. Soc.*, **86**, 514 (1964).

Summary

Tris(1, 10-phenanthroline)cobalt(III) complex ions are reduced in two steps in 1 M sodium sulfate. The first wave, which appears around +0.10 V. vs. SCE, corresponds to the reduction of cobalt from a trivalent state to a divalent, while the second, which appears around −1.0 V. vs. SCE, corresponds to the reduction of divalent to univalent cobalt. Tris(1, 10-phenanthroline)cobalt(II) ions show an oxidation wave and a reduction wave at the respective potentials corresponding to the first and the second waves of trivalent cobalt complex ions. A small minimum is observed on the plateau of the first wave, and a small prewave is accompanied by the second wave. Both electrode processes are considered to be reversible.

The univalent cobalt-phenanthroline complex has been prepared by the reduction of the divalent cobalt complex with sodium borohydride. It is a black powder, and the atomic ratio of nitrogen to cobalt is found to be nearly six, though not exactly six.

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