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Polarographic Study of Metal Complexes. IX.[1] Halogeno- and Aquo-bis(dimethylglyoximato)amminecobalt(III) Complexes[2]

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The halogeno- and aquo-bis(dimethylglyoximato)amminecobalt(III) complexes of the *trans*-$[\mathrm{Co^{III}X\ dg_2(NH_3)}]$-type have been found to be reduced to the metal through the cobalt(I) state in a 0.5M Na_2SO_4 aqueous solution at the dropping mercury electrode (DME), where the ligand, X, denotes the ion, Cl^-, Br^-, or I^-, or the molecule, OH_2. The aquation of the halogeno complexes is found to take place more rapidly in solution in this order: $Cl^- < Br^- < I^-$. The diaquobis(dimethylglyoximato)cobalt(III) ion, $[Co(OH_2)_2dg_2]^+$, has also been ascertained to undergo a step-by-step reduction to the metal through the cobalt(I) state at the DME.

In previous papers,[3-5] the dicyanobis(dimethylglyoximato)cobaltate(III) complex, *trans*-$K[Co(CN)_2dg_2]\cdot 3\frac{1}{2}H_2O$, was found to be reduced down to the cobaltate(I) complex in a 0.5M Na_2SO_4 solution at the dropping mercury electrode (DME). The resulting cobaltate(I) complex was isolated as an almost black soid *in vacuo* by the reduction of a 3% sodium amalgam. The aqueous solution of the cobaltate(I) complex assumed a deep blue color.

The bis(dimethylglyoximato)diamminecobalt(III) complex, $[Codg_2(NH_3)_2]Cl\cdot 5H_2O$ (efflorescent crystals), has been reported to undergo the step-by-step reduction of Co(III)→Co(II)→Co(I)→Co(0) at the DME in a neutral Na_2SO_4 solution.[3] In connection with these complexes, the cyanobis(dimethylglyoximato)amminecobalt(III), *trans*-$[Co(CN)dg_2(NH_3)]\cdot \frac{1}{2}H_2O$,[5] has also been found to be reduced to a cobalt(0) complex through the cobalt(I) state in the same supporting electrolyte. It is of interest that this complex, with both the cyanide ion and an ammonia ion, has a configuration similar to that of cyanocobalamine (vitamin B_{12})[6] in the coordination sphere around the cobalt. The stabilization of such lower oxidation states of the central cobalt can be interpreted as being due to the strong π-bonding character, *i. e.*, the "back donation" in the coordinate-bonds of the cyanide ions and of a pair of dimethylglyoximes with two hydrogen bonds.

The purpose of this study is to determine if the oxidation state of a cobalt(I) can be detected in a solution or not for the halogeno- and aquo-ammine complexes, in which the contribution of the π-bonding character at the fifth and the sixth ligands is regarded as being absent.

Experimental

The experimental details of the measurements have been described previously.[7] The current-time curves were recorded on a Yanagimoto Polarovision, Model PE 20, equipped with a National X-Y recorder, Model VR 301. The characteristics of the capillary used were as follows: $m=1.42$ mg/sec, $t=4.80$ sec, both measured at an open circuit in a 0.5M Na_2SO_4 water solution.

Materials. The chloro-ammine complex, $[CoCldg_2(NH_3)]$ (anhydrous) was prepared according to the directions of Tschugaeff.[8] Found: Co, 17.28; C, 28.03; N, 20.39; H, 5.21%. Calcd for $[CoCldg_2(NH_3)]$: Co, 17.25; C, 28.13; N, 20.50; H, 5.02%.

Preparation of *trans*-$[\mathbf{Co\ Br\ dg_2(NH_3)}]$. The bromo- and iodo-bis(dimethylglyoximato)amminecobalt(III) complexes were prepared analogously to the method of Tschugaeff.[8]

Twenty grams of $[CoBr(NH_3)_5]Br_2$[9] dissolved in 400 m*l* of water were heated on a water bath for two hours with 12.1 g of dimethylglyoxime and 50 g of ammonium acetate. During the reaction, 15 m*l* of

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[1] Previous paper of this series: N. Maki, K. Yamamoto, H. Sunahara and S. Sakuraba, This Bulletin, **42**, 3159 (1969).

[2] Presented at the 14th Symposium on Polarography, held at Hiroshima, October 8, 1968.

[3] N. Maki, "Proceedings of the 3rd International Congress of Polarography", ed. by G. J. Hills, Vol. 1, Macmillan & Co., London (1966), p. 505.

[4] N. Maki, This Bulletin, **38**, 2013 (1965).

[5] N. Maki, T. Itoh and S. Sakuraba, *ibid.*, **41**, 529 (1968).

[6] M. Brezina and P. Zuman, "Polarography in Medicine, Biochemistry and Pharmacy", Interscience Publ. Inc., New York, N. Y. (1958), pp. 397—401.

[7] N. Maki and K. Okawa, *J. Electroanal. Chem.*, **8**, 262 (1964).

[8] L. Tschugaeff, *Ber.*, **39**, 2694 (1906); *ibid.*, **40**, 3499 (1907).

[9] S. M. Jϕrgensen, *J. prakt. Chem.*, 2 **19**, 49 (1879); *Z. Anorg. Allgem. Chem.*, **17**, 463 (1898).

glacial acetic acid were added to the solution in small portions. The reaction took place, evolving ammonia, to yield a brown solution. When the temperature of the solution went down, lustrous brown crystals were deposited from the solution, these were filtered and washed with cold water, ethanol and ether. The crude product was recrystallized from hot water containing acetic acid. Found: Co, 15.37; C, 24.99; N, 18.04; H, 4.64%. Calcd for $[\mathrm{Co\,Br\,dg_2(NH_3)}]$: Co, 15.26; C, 24.89; N, 18.14; H, 4.44%.

Preparation of *trans*-$[\mathrm{CoIdg_2(NH_3)}]$.$^{10)}$ Twenty grams of $[\mathrm{CoI(NH_3)_5](NO_3)_2}$$^{11)}$ and 50 g of ammonium acetate were dissolved in 400 m*l* of water, and the mixture was heated on a water bath with 9.5 g of dimethylglyoxime. During the reaction, 15 m*l* of acetic acid were stirred into the solution. After the solution had then been allowed to stand overnight, dark brown crystals were separated from the solution; they were filtered and washed with water, ethanol, and ether. The crude product was purified by recrystallization from hot water containing acetic acid. Found: Co, 13.54; C, 22.09; N, 16.02; H, 4.16%. Calcd for $[\mathrm{CoIdg_2(NH_3)}]$: Co, 13.61; C, 22.19; N, 16.17; H, 3.96%.

Preparation of *trans*-$[\mathrm{Co(OH_2)dg_2(NH_3)]OCOCH_3}$. Ten grams of $[\mathrm{CoCldg_2(NH_3)}]$$^{8)}$ and about 6 g of wet $\mathrm{Ag_2O}$ were well mixed together in 50 m*l* of distilled water under ice cooling, then the mixture was allowed to stand for three hours below 0°C. The exothermic reaction took place gently to yield the hydroxo complex, $[\mathrm{Co(OH)dg_2(NH_3)}]$. No smell of ammonia could be discerned during the reaction. The suspension was filtered, and the filtrate was concentrated to one-fifth its volume by evaporation *in vacuo* with a rotatory evaporator after 15 m*l* of acetic acid had been added to it. On cooling, bright yellow crystals separated from the solution; they were filtered and washed with ethanol and ether. Recrystallizations were carried out from hot water containing acetic acid. The yield was 48% of theory. The complex has no water of crystallization. Found: Co, 15.21; C, 31.11; N, 18.28; H, 5.85%. Calcd for $[\mathrm{Co(OH_2)dg_2(NH_3)]OCOCH_3}$: Co, 15.38; C, 31.34; N, 18.27; H, 5.79%. The complex is soluble in water, while the corresponding salt of nitrate, $[\mathrm{Co(OH_2)dg_2(NH_3)]NO_3}$, is insoluble in water. The absorption spectra of this and the diammine complex in the visible and ultraviolet regions are shown in Fig. 1. The first spin-allowed band is located at a longer wavelength than that of the corresponding diammine cobalt(III) complex, $[\mathrm{Codg_2(NH_3)_2]Cl\cdot 5H_2O}$, though the first d–d band is hidden by the foot of the charge-transfer bands of dimethylglyoximes.

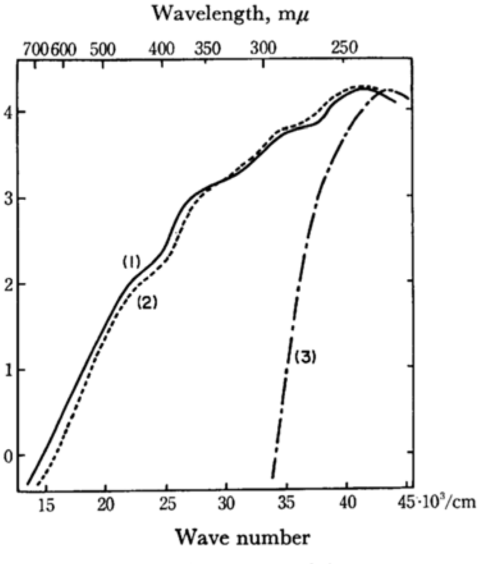

Fig. 1. The absorption spectra of the aquo-ammine and the diammine cobalt (III) complexes obtained in water.

(1) —— *trans*-$[\mathrm{Co(OH_2)dg_2(NH_3)]OCOCH_3}$ (a new compouund)

(2) ------ *trans*-$[\mathrm{Co\,dg_2(NH_3)_2]Cl\cdot 5H_2O}$

(3) —·—· dimethylglyoxime (dgH) in methanol

Results and Discussion

The halogenobis(dimethylglyoximato)amminecobalt(III) complexes, $[\mathrm{Co^{III}Xdg_2(NH_3)}]$, gave rise to four step waves in a 0.5M $\mathrm{Na_2SO_4}$ aqueous solution at the DME, where the ligand, X, is the ion, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, or $\mathrm{I^-}$. The first two steps, corresponding to a total acceptance of one electron, represent the reductions from the cobalt(III) and the aquated cobalt(III) species to a cobalt(II) state, while the following two steps represent the reduction of $\mathrm{Co^{II}} \rightarrow \mathrm{Co^{I}}$ and of $\mathrm{Co^{II}} \rightarrow \mathrm{Co^{0}}$ respectively. The waves of the second, the third, and the fourth step for halogeno complexes agree completely with those of the aquo-complex, $[\mathrm{Co(OH_2)dg_2(NH_3)]OCOCH_3}$. Therefore, the aquation of the halide ligands is considered to be almost completely finished in lower oxidation states. Judging from the wave-height of the first wave, it can be said that the aquation proceeds more rapidly in a solution according to this order of the ligands: $\mathrm{Cl} < \mathrm{Br} < \mathrm{I}$.

Figure 2 shows the current-potential curves of the halogeno- and the aquo-ammine complexes under the same experimental conditions. The two-electron reduction wave of *trans*-$\mathrm{K[Co(CN)_2dg_2]\cdot \frac{3}{2}H_2O}$ under the same conditions is given for the sake of comparison. It may be seen that the total height of the first and the second steps for halogeno complexes is approximately equal to that of the first step for the aquo-complex. The ratio of the wave-heights corrected for drop time is given in Table 1.

Each of the limiting currents of the waves was proportional to the concentration of the complex in the range of $2.5\cdot 10^{-3}$—$5\cdot 10^{-4}$M for halogeno complexes and in the ragne of 10^{-2}—$5\cdot 10^{-4}$M for

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10) *Cf.* "Gmelins Handbuch der anorganischen Chemie," Nr. 58, Teil B Kobalt-Ergänzungsband, Verlag Chemie, GmbH, Berlin (1964), p. 724.

11) J. Sand and G. Böckman, *Ber.*, **40**, 4497 (1907); "Gmelins Handbuch der anorgenischen Chemie," Nr. 58, Teil B Kobalt, Verlag Chemie, GmbH, Berlin (1930), p. 179.

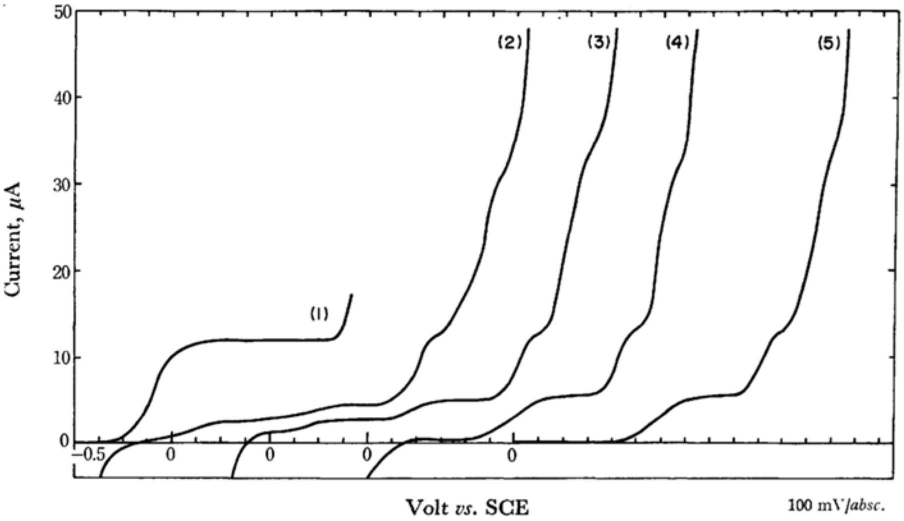

Fig. 2. The current-potential curves of the bis(dimethylglyoximato)cobalt(III) complexes obtained at the concentration of the complex, $2.0 \cdot 10^{-3}$M in 0.5M Na_2SO_4 under the same experimental conditions.
(1) *trans*-$K[Co(CN)_2dg_2] \cdot \frac{3}{2}H_2O$ (the two-electron reduction wave); (2) *trans*-$[CoCldg_2(NH_3)]$ (anhydrous); (3) *trans*-$[CoBrdg_2(NH_3)]$; (4) *trans*-$[CoIdg_2(NH_3)]$; (5) *trans*-$[Co(OH_2)dg_2(NH_3)]OCOCH_3$; recorded from 0 V (*vs.* SCE) for the halogeno- and aquo-complexes, (2)—(5), and from −0.50 V (*vs.* SCE) for the dicyano complex, (1).

TABLE I. THE RATIO OF THE WAVE-HEIGHTS OBTAINED FOR THE HALOGENO- AND AQUO-BIS(DIMETHYLGLYOXIMATO)COBALT(III) COMPLEXES (25°C)

Compound	1st Wave	2nd Wave	3rd Wave	4th Wave
trans-$[CoCldg_2(NH_3)]$	0.41	0.59	1.10	2.44
trans-$[CoBrdg_2(NH_3)]$	0.38	0.62	1.14	2.53
trans-$[CoIdg_2(NH_3)]$	0.09	0.91	1.20	2.57
trans-$[Co(OH_2)dg_2(NH_3)]OCOCH_3$	1		1.15	2.18

The wave-heights corrected for drop time were measured at the concentration of $2 \cdot 10^{-3}$M in 0.5M Na_2SO_4 solution.

the aquo-ammine complex, $[Co(OH_2)dg_2(NH_3)]OCOCH_3$.

The limiting currents of the first, the second, and the third steps (named from positive to negative potentials) were found to be proportional to the square root of the mercury pressure on the DME, whereas that of the fourth step was not proportional for all the halogeno complexes, the value of $i_{1(4)}/\sqrt{h_{\mathrm{corr.}}}$ becoming smaller with the increase in the mercury pressure. Table 2 shows the dependence of the limiting currents on the mercury pressure obtained for the chloro-ammine complex. The results for the aquo-ammine complex quite agree with the above results obtained for the waves following the second step of the halogeno-ammine complexes. Accordingly, hereafter the polarographic data for the halogeno complexes only will be described, unless otherwise stated, since the three waves following the second step of the halogeno complexes coincide completely with those of the aquo-ammine complex.

TABLE 2. THE RELATIONSHIP BETWEEN THE LIMITING CURRENT AND THE HEIGHT OF THE MERCURY RESERVOIR (25°C)

$h_{\mathrm{corr.}}$	i_1 (μA)	i_2 (μA)	i_3 (μA)	i_4 (μA)	$i_1/\sqrt{h_{\mathrm{corr.}}}$	$i_2/\sqrt{h_{\mathrm{corr.}}}$	$i_3/\sqrt{h_{\mathrm{corr.}}}$	$i_4/\sqrt{h_{\mathrm{corr.}}}$
90.0	0.89	3.60	6.26	13.00	0.09	0.38	0.66	1.37
83.0	0.82	3.56	6.19	12.90	0.09	0.38	0.68	1.42
76.0	0.78	3.31	6.18	12.00	0.09	0.38	0.71	1.38
69.0	0.75	3.15	6.06	11.70	0.09	0.38	0.73	1.41
62.0	0.79	3.00	5.76	10.30	0.10	0.38	0.73	1.30
55.0	0.74	2.73	5.62	9.80	0.10	0.37	0.76	1.33

For the iodo-ammine complex, $[CoIdg_2(NH_3)]$: $2.5 \cdot 10^{-3}$M in 0.5M Na_2SO_4 containing $2.3 \cdot 10^{-3}$ % of Triton X 100.

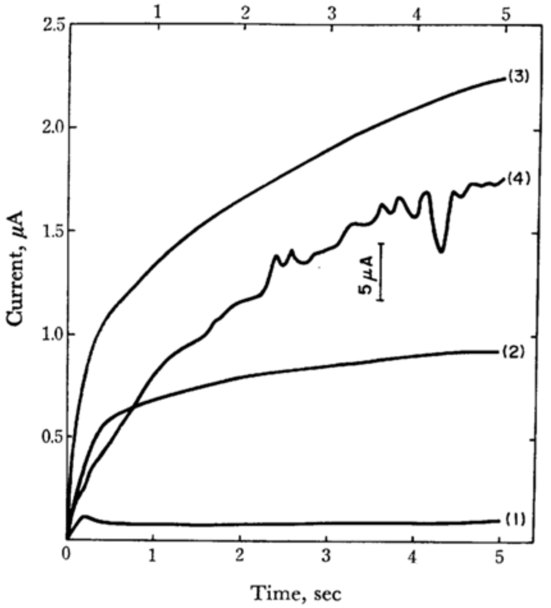

Fig. 3. The current-time curves obtained at the constant potentials.
(1) −0.40; (2) −0.85; (3) −1.15; (4) −1.33 V *vs.* SCE. Concn. of the complex: $1\cdot10^{-3}$M; Supporting electrolyte: 0.5M Na_2SO_4 soln. The current scale of the curve (4) only is curtailed, as indicated in the figure.

The temperature coefficients of the first, the second, the third, and the fourth steps were 1.2, 1.5, 2.4, and 2.5%/deg respectively at 25°C for all the halogeno complexes, and 1.5, 2.4, and 2.4%/deg respectively at 25°C for the aquo-ammine complex (in this case, the first step is absent).

Figure 3 shows the current-time curves observed during the life of a mercury drop at various potentials for the iodo-ammine complex. At the potentials of −0.85 and −1.15 V (*vs.* SCE), at which the current reaches the limiting plateaus of the second and third steps, the exponents (τ) of the drop time (t) in the Ilkovič equation, $i_d=kt^\tau$, were 0.21 and 0.33 respectively (25°C); the value of the former falls within 0.16—0.22, a range characteristic of diffusion-controlled values, but the value of the latter did not because of the disruption of the resulting cobalt(I) complex in solution. At the potentials of −0.40 and −1.33 V (*vs.* SCE), at which the current reaches the limiting plateaus of the first and fourth steps, the current-time curves show an abnormal shape. At the former potential, the current is quenched with time to some extent, this distinctive quenching may be attributed to the adsorption of the halogeno complex at the DME. The electrocapillary curve also indicated that the adsorption was taking place and so supported this interpretation. At the latter potential, the oscillations observed on the abnormal curve are undoubtedly connected with the time involved in the formation and adherence of the disruption species of dimethylglyoximes insoluble in an aqueous solution at the DME. In a 40% methanolic solution containing 1M LiCl, no oscillations were observed.

Thus, the limiting current of the second step only may be concluded to be strictly diffusion-controlled, whereas those of the other three steps involve, more or less, a kinetic character, though the polarographic data of the others presented above indicate the rate-determining step of the first three steps to be by diffusion.

The half-wave potentials of each of the steps for halogeno- and their related complexes are summarized in Table 3. The half-wave potentials of the waves following the second step for halogeno complexes agree approximately with those of the aquo-complex $[Co(OH_2)dg_2(NH_3)]^+$ and do not coincide with those of the diaquo-complex $[Co(OH_2)dg_2(OH_2)]^+$. Therefore, the ammonia ligand for the halogeno- and aquo-ammine complexes may be concluded not to aquate in the lower oxidation states of the cobalt in a solution.

On the other hand, Figs. 4 and 5 show the dependences of the current-potential curves on the concentration of excess ammonia in a solution for the aquo-ammine and the diammine cobalt(III)

TABLE 3. THE HALF-WAVE POTENTIALS OF THE WAVES FOR THE BIS(DIMETHYLGLYOXIMATO)COBALT(III) COMPLEXES (25°C)

Compound	1st Wave $Co^{III}\rightarrow Co^{II}$	2nd Wave $Co^{III}\rightarrow Co^{II}$	3rd Wave $Co^{II}\rightarrow Co^{I}$	4th Wave $Co^{I}\rightarrow Co^{0}$	Supporting electrolyte
trans-$[CoCldg_2(NH_3)]$	+	−0.58	−1.03	−1.20	0.5M Na_2SO_4
trans-$[CoBrdg_2(NH_3)]$	+	−0.58	−1.03	−1.20	0.5M Na_2SO_4
trans-$[CoIdg_2(NH_3)]$	+	−0.59	−1.01	−1.23	0.5M Na_2SO_4
trans-$[Co(OH_2)dg_2(NH_3)]OCOCH_3$		−0.58	−1.03	−1.22	0.5M Na_2SO_4
		−0.78	−0.94	−1.25	0.5M Na_2SO_4+1M NH_3
trans-$[Co(NH_3)dg_2(NH_3)]Cl\cdot5H_2O$		−0.60	−1.03	−1.23	0.5M Na_2SO_4
		−0.78	−0.94	−1.27	0.5M Na_2SO_4+1M NH_3
trans-$[Co(OH_2)dg_2(OH_2)]^+$		+	−0.75	−0.99	0.5M Na_2SO_4

Voltage unit: volt *vs.* the saturated calomel electrode (SCE)

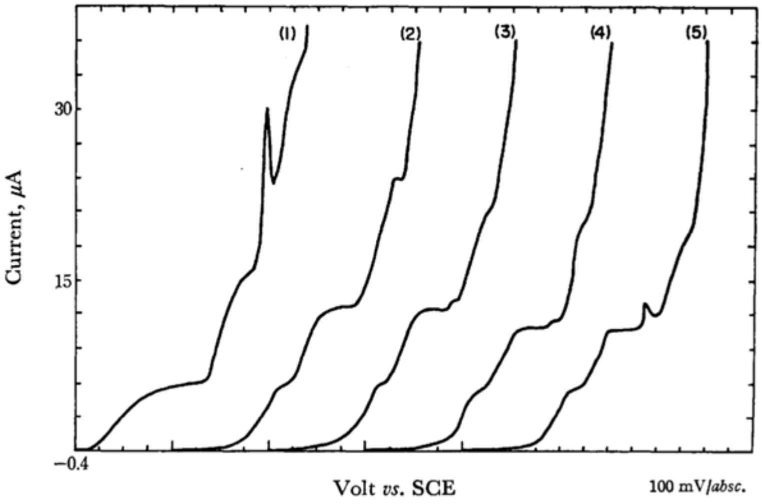

Fig. 4. The dependence of the current-potential curves upon the concentration of excess ammonia in a solution.
(1) 0; (2) 0.1; (3) 0.5; (4) 1.0; (5) 1.5M; obtained for the complex, *trans*-$[Co(OH_2)dg_2(NH_3)]OCOCH_3$, at the concentration of the complex, $2.5 \cdot 10^{-3}$M in 0.5M Na_2SO_4 (25°C).

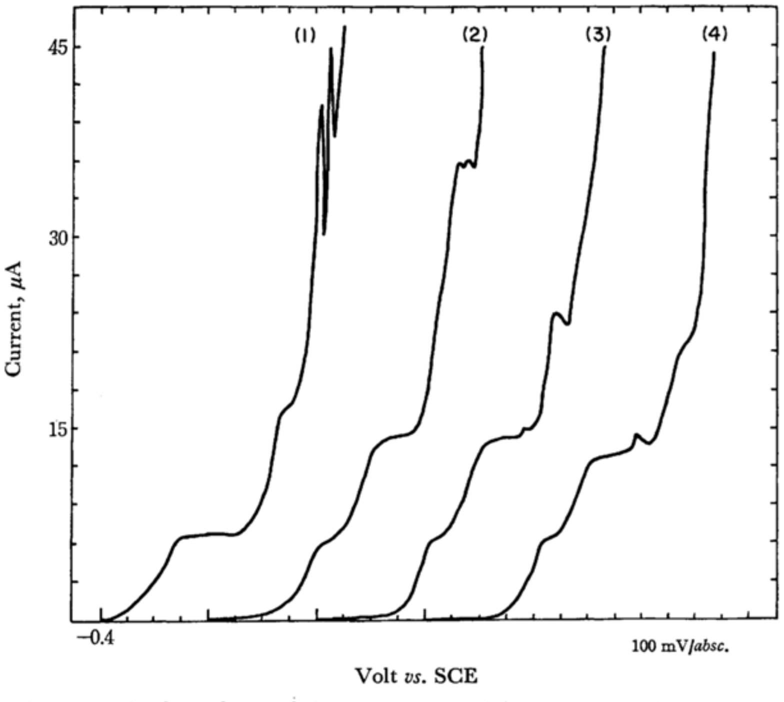

Fig. 5. The dependence of the current-potential curves upon the concentration of excess ammonia in a solution.
(1) 0; (2) 0.1; (3) 0.5; (4) 1.0M; obtained for the complex, *trans*-$[Codg_2(NH_3)_2]Cl \cdot 5H_2O$, at the concn. of the complex, $2.5 \cdot 10^{-3}$M in 0.5M Na_2SO_4 (25°C).

complexes respectively. In Figs. 4 and 5, the shapes of the waves for the aquo-ammine and the diammine complexes are seen to come to resemble each other with the increase in the concentration of ammonia, especially in the shapes of the last steps. This suggests that the ammine complexes tend to aquate in a solution in the absence of excess ammonia, especially in the last step of reduction

($Co^I \rightarrow Co^0$). Nevertheless, the fifth ligand of ammonia or, at least, one of ammonia ligands is not replaced with a water molecule in a neutral Na_2SO_4 solution throughout the reductions, taking account of the half-wave potentials for the diaquo-complex (see Table 3).

Accordingly, the overall processes of the electrode reaction given below may be considered to be the most plausible:

$$\begin{tikzcd}
trans\text{-}[Co^{III}Xdg_2(NH_3)] \arrow[r, "e"] \arrow[d, "\text{aquation}"] & {[Co^{II}Xdg_2(NH_3)]^-} \arrow[r, "2e"] \arrow[d, "\text{aquation}"] & Co\ (\textit{metal}) \\
trans\text{-}[Co^{III}(OH_2)dg_2(NH_3)]^+ \arrow[r, "e", "(a)"'] & {[Co^{II}(OH_2)dg_2(NH_3)]} \arrow[r] \arrow[d, "e"] & {[Co^{II}(OH_2)_2dg_2]} \arrow[d, "e"] \\
 & {[Co^{I}dg_2(NH_3)]^-} \arrow[d, "e"', "(a)"] & {[Co^{I}dg_2]^-} \arrow[dl, "e"'] \\
 & Co\ (\textit{metal}). &
\end{tikzcd}$$

The electrode reaction in a 0.5M Na_2SO_4 solution is considered to proceed mainly along the (a) path rather than along the other paths. The contribution of the other paths, accompanied by the disruption of the cobalt(I) complexes, is considered to be one of the reasons why the limiting currents of the last two steps exhibit some kinetic character. From the view point of the electronic structure, the cobalt(I) complex might have the tetra-coordinate formula, $[Co^Idg_2]^-$, even in solutions.

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