BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3422—3426 (1973)

Polarographic Studies of the Rates of the Dissociation Reactions of Cobalt(II)-Iminodiacetate, -Aspartate, and -2,2′-Ethylenedioxydi(ethylamine)-*N*,*N*,*N*′,*N*′-tetraacetate Complexes

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(Received March 22, 1973)

The cobalt(II)-IDA, -Asp, and -GEDTA complexes produce kinetic wave due to their dissociation preceding the electron-transfer step at the electrode surface. From an experimental examination of the nature of these kinetic waves, the dissociation mechanisms were determined to be:

i) IDA and Asp systems,

$CoX_2^{2-} \rightleftarrows CoX^0 + X^{2-}$ rate-determining step

$CoX^0 + 2e^- + Hg \rightleftarrows Co(Hg) + X^{2-}$

ii) GEDTA system,

$CoY_2^{6-} \rightleftarrows CoY^{2-} + Y^{4-}$ in a rapid equilibrium

$CoY^{2-} \rightleftarrows CoY^{2-*}$ rate-determining step

$CoY^{2-*} + 2e^- + Hg \rightleftarrows Co(Hg) + Y^{4-}$

where CoY^{2-*} is the electroactive cobalt(II)-GEDTA complex produced upon the partial dissociation of the normal cobalt(II)-GEDTA complex with a 1 : 1 composition. From the relative rate constants for these complexes, the detailed structures of the reaction intermediates in their dissociation were also obtained.

In earlier papers,[1,2] we reported systematic studies of the polarographic behavior of the nickel(II)–iminodiacetate (IDA), –aspartate (Asp), and –glutamate (Glut) complexes and those of the nickel(II), zinc(II), and cadmium(II)–2,2′-ethylenedioxydi(ethylamine)-*N*,*N*,*N*′,*N*′-tetraacetate (GEDTA) complexes. All these complexes produce kinetic waves as a result of their dissociation at the electrode surface. From an experimental examination of the nature of these kinetic waves, we concluded that (1) the kinetic waves observed in the polarography of the nickel(II)–IDA,

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[1] M. Kodama, H. Nunokawa, and N. Oyama, This Bulletin, **44**, 2387 (1971).

[2] M. Kodama and N. Oyama, *ibid.*, **45**, 2169 (1972).

–Asp, –Glut, and –GEDTA complexes and of the zinc(II)–GEDTA complex can be ascribed to the reduction of the metal(II) aquo ions formed upon the dissociation of the metal(II)-aminopolycarboxylate complexes, whereas (2) the kinetic wave in the cadmium(II)–GEDTA system may be ascribed to the reduction of the cadmium(II)–GEDTA complex formed by the partial dissociation of the original complex. The cobalt(II)–IDA, –Asp, and –GEDTA complexes also produce kinetic waves as a result of their dissociation. In this paper, we will report a systematic study of the nature of the above-mentioned kinetic waves and will determine the dissociation mechanism and rates. Furthermore, from a comparison of the dissociation rate constants with those estimated on the basis of the proposed reaction intermediates, the structure of the reaction intermediates will be described in detail.

Experimental

Reagents. The procedure used to prepare the standard cobalt(II) nitrate solution was described previously.[1] L-Aspartic acid (Asp), iminodiacetic acid (IDA), and 2,2′-ethylenedioxydi(ethylamine)-*N*,*N*,*N*′,*N*′-tetraacetic acid (GEDTA) were recrystallized from their aqueous solutions by adding pure ethanol and hydrochloric acid. The standard solutions of Asp, IDA, and GEDTA were prepared by dissolving known amounts of recrystallized Asp, IDA, and GEDTA in redistilled water. All the other chemicals used were of analytical-reagent grade and were used without further purification.

Apparatus and Experimental Procedures. All the DC current-voltage curves were measured by using a manual polarograph similar to that of Kolthoff and Lingane[3] or a Yanagimoto pen-recording polarograph, PA-102. The characteristic feature of the dropping mercury electrode used in this study was described previously.[4] All the other apparatus and the experimental procedures employed were also described in the above-mentioned paper.[4] The ionic strength of the solution was adjusted to 0.30 by adding an appropriate amount of pure sodium perchlorate. In this study, no buffer mixture was used, because the sample solutions always contained a large excess of uncomplexed Asp, IDA, or GEDTA and, hence, may be considered to have a sufficient buffer capacity over the entire pH range covered ($8.10 < \mathrm{pH} < 9.70$ in the IDA system, $8.45 < \mathrm{pH} < 10.40$ in the Asp system, and $7.80 < \mathrm{pH} < 8.50$ in the GEDTA system).

Results and Discussion

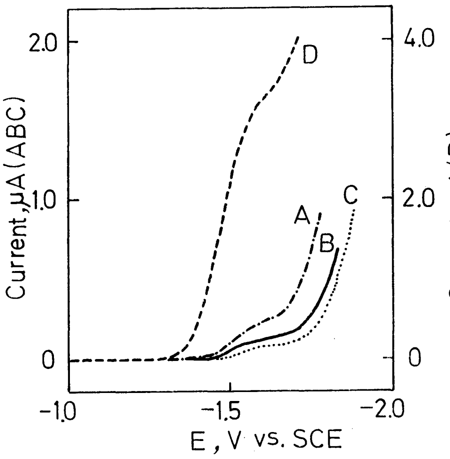

Fig. 1. Polarograms of the cobalt(II)–GEDTAcomplex, 25.0 °C, μ=0.30.
A) Concentration of cobalt(II) ion=1.0 mM
Concentration of GEDTA=11.8 mM
pH=7.85
B) Concentration of cobalt(II) ion=1.0 mM
Concentration of GEDTA=39.4 mM
pH=7.86
C) Concentration of cobalt(II) ion=1.0 mM
Concentration of GEDTA=11.8 mM, pH=8.35
D) Concentration of cobalt(II) ion=0.53_2 mM
Concentration of GEDTA=20.0 mM
Concentration of acetate ion=0.06 M, pH=5.45

Polarographic Behavior of the Cobalt(II)–GEDTA Complex. In an acetate buffer solution containing a large excess of GEDTA, the cobalt(II)–GEDTA complex gives a single well-defined reduction wave, one which is diffusion-controlled in nature. Its half-wave potential is located at far more negative potentials than that of the cobalt(II) aquo ion. Therefore, the polarographic step observed in the acetate buffer solution can be ascribed to the direct reduction of the cobalt(II)–GEDTA complex. As is shown by the polarograms in Fig. 1, the wave-height decreases appreciably with increases in the solution pH and in the concentration of uncomplexed GEDTA; finally, the polarographic wave shows a kinetic-controlled nature. By examining the nature of the above kinetic wave with the aid of the well-known relation employed by Koryta in the polarographic study of the cadmium(II)–nitrilotriacetate complex,[5] the reaction mechanism was studied. As is clear from the Koryta equation, if the cobalt(II) ion forms only a 1 : 1 ratio complex with GEDTA and if its dissociation at the electrode surface is rate-determining, the following relation can be derived for the kinetic wave:

$$\mathrm{CoY^{2-}} \overset{k_\mathrm{d}}{\rightleftarrows} \mathrm{Co^{2+}} + \mathrm{Y^{4-}} \quad \text{rate-determining step} \tag{1}$$

$$\frac{i_\mathrm{k}}{i_\mathrm{d}-i_\mathrm{k}} = 0.886\sqrt{\frac{k_\mathrm{d}\cdot(\alpha_\mathrm{H})_\mathrm{Y}\cdot t}{K_\mathrm{CoY}\cdot[\mathrm{Y}]_\mathrm{f}}} \tag{2}$$

where K_CoY, $[\mathrm{Y}]_\mathrm{f}$, and $(\alpha_\mathrm{H})_\mathrm{Y}$ are the formation constant of a 1 : 1 composition cobalt(II)–GEDTA complex, the concentration of uncomplexed GEDTA, and the (α_H) value of GEDTA respectively. Here, i_d in Eq. (2) is the hypothetical diffusion current. Previously,[6,7] we mentioned finding in our polarographic study that the nickel(II), copper(II), and cadmium(II) ions can form 1 : 1 and 1 : 2 ratio complexes with GEDTA under normal experimental conditions. If the cobalt(II) ions also form a 1 : 2 ratio complex with GEDTA, and if the dissociation of the 1 : 1 ratio complex is rate-determining, we can hypothesize the following mechanism(I):

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[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York (1952), p. 297.

[4] M. Kodama, Y. Fujii, and T. Ueda, This Bulletin, **43**, 2085 (1970).

[5] J. Koryta, *Collect. Czech. Chem. Commun.*, **24**, 3057 (1959).

[6] M. Kodama and T. Ueda, *Nippon Kagaku Zasshi*, **91**, 138 (1970).

[7] M. Kodama and Y. Tominaga, This Bulletin, **42**, 394 (1964).

$$\text{(I)}\quad \begin{array}{ll} \mathrm{CoY_2^{6-}} \underset{}{\overset{K_2}{\rightleftharpoons}} \mathrm{CoY^{2-}} + \mathrm{Y^{4-}} & \qquad (3) \\ \mathrm{CoY^{2-}} \overset{k_d}{\rightleftharpoons} \mathrm{Co^{2+}} + \mathrm{Y^{4-}} \quad \text{rate-determining step} & \qquad (4) \end{array}$$

For the above reaction mechanism, one can derive Eq. (5) for the kinetic wave:

$$\frac{i_k}{i_d-i_k} = 0.886\sqrt{\frac{k_d\cdot(\alpha_H)_Y\cdot t}{K_{CoY}\cdot[Y]_f}}\,\frac{1}{1+K_2'\cdot[Y]_f} \qquad (5)$$

where K_2' is the conditional second successive formation constant of the cobalt(II)–GEDTA complex.

On the other hand, if the partial dissociation of the 1:1 ratio cobalt(II)-GEDTA complex, which is in a rapid equilibrium with the 1:2 ratio complex, is rate-determining, and if the resulting complex, CoY^{2-*}, is reducible at the electrode (Mechanism II), the following relation can be derived:

$$\frac{i_k}{i_d-i_k} = 0.886\sqrt{\frac{k_d\cdot t}{K}}\cdot\frac{1}{1+K_2'\cdot[Y]_f} \qquad (6)$$

where K is the equilibrium constant for (7).

$$\text{(II)}\quad \begin{array}{ll} \mathrm{CoY_2^{6-}} \rightleftharpoons \mathrm{CoY^{2-}} + \mathrm{Y^{4-}} \quad \text{in a rapid equilibrium} & \qquad (3) \\ \mathrm{CoY^{2-}} \overset{k_d}{\rightleftharpoons} \mathrm{CoY^{2-*}} \quad \text{rate-determining step} & \qquad (7) \end{array}$$

Furthermore, if the cobalt(II) ion forms only a 1:1 ratio complex with GEDTA, and if its partial dissociation (7) is slow-step, the $i_k/(i_d-i_k)$ value should be independent of the concentration of uncomplexed GEDTA, $[Y]_f$, and the solution pH. As has been stated above, the i_k value, however, decreases with increases in the $[Y]_f$ value and in the solution pH. Therefore, the above reaction mechanism can be eliminated. As is shown in Fig. 2, only the plot of $(i_d-i_k)/i_k$ against the $[Y]_f/(\alpha_H)_Y$ yielded a linear relation for the cobalt(II)–GEDTA system. As is clear from the foregoing discussion, this indicates that the cobalt(II) ion forms 1:1 and 1:2 ratio complexes with GEDTA and that the reaction mechanism can be represented by (II). With the aid of Eq. (6), the second successive formation constant, K_2, was determined to be $7.8_4\times10^3$ from the ratio of the slope to the intercept of the straight line in Fig. 2. By using the K_2 value thus estimated, the effects of the concentration of uncomplexed GEDTA and the solution pH on the $i_k/(i_d-i_k)$ value were examined. The plot of $i_k/(i_d-i_k)$ against $1/(1+K_2'\cdot[Y]_f)$ yielded a linear relation passing through the point of origin (Fig. 3). The k_d value obtained from the slope of the straight line (A) agreed well with that obtained from the slope of the straight line (B). This agreement also lends strong support to the reaction mechanism proposed by the present author for the cobalt(II)–GEDTA system.

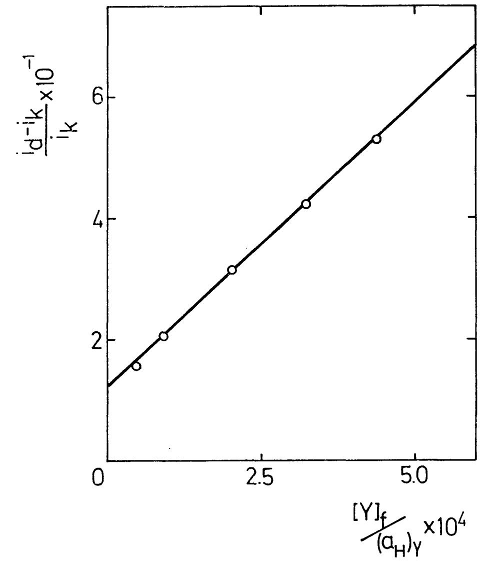

Fig. 2. Plot of $(i_d-i_k)/i_k$ against $[Y]_f/(\alpha_H)_Y$, GEDTA system, 25.0 °C, μ=0.30.
Concentration of cobalt(II) ion=1.0 mM
Concentration of GEDTA=10.8 mM

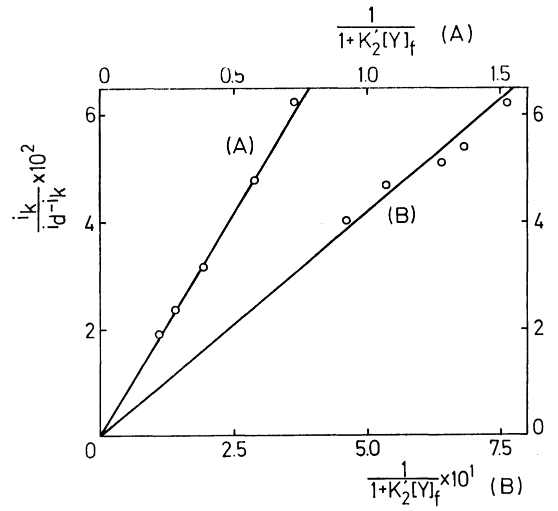

Fig. 3. Plot of $i_k/(i_d-i_k)$ against $1/(1+K_2'\cdot[Y]_f)$, GEDTA system, 25.0 °C, μ=0.30.
Concentration of cobalt(II) ion=1.0 mM
A) Concentration of GEDTA=10.8 mM
pH ranged from 7.80 to 8.50
B) GEDTA concentration ranged from 10.0 mM to 40.0 mM. pH=7.82.

Polarographic Behavior of Cobalt(II)–IDA and –Asp Complexes. Both cobalt(II)–IDA and –Asp com-

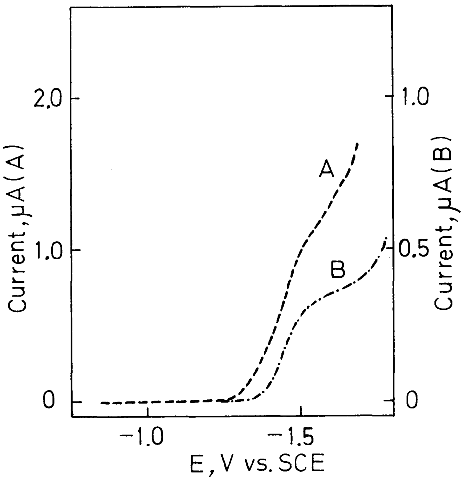

Fig. 4. Polarograms of the cobalt(II)-Asp and-IDA complexes, 25.0 °C, μ=0.30.
Concentration of cobalt(II) ion=1.0 mM
A) Aspartate concentration=38.0 mM, pH=9.23
B) Iminodiacetate concentration=18.0 mM, pH=8.58

plexes also produced kinetic waves in alkaline solutions containing excess IDA or Asp. Typical polarograms are given in Fig. 4. In both cases, the plot of the $i_k/(i_d-i_k)$ value against $(\alpha_H)_X^{1/2}$ (at constant uncomplexed IDA or Asp, $[X]_f$) or $(\alpha_H)_X^{1/2}\cdot[X]_f^{1/2}$ yielded a linear relation passing through the point of origin (Figs. 5 and 6). Here, $(\alpha_H)_X$ is the (α_H) value of IDA or Asp. In considering that the cobalt(II) ion can form 1 : 1 and 1 : 2 ratio complexes with IDA and Asp under the present experimental conditions, the above fact evidently implies that the reaction mechanism for the kinetic currents of cobalt(II)-IDA and -Asp complexes can be expressed as:

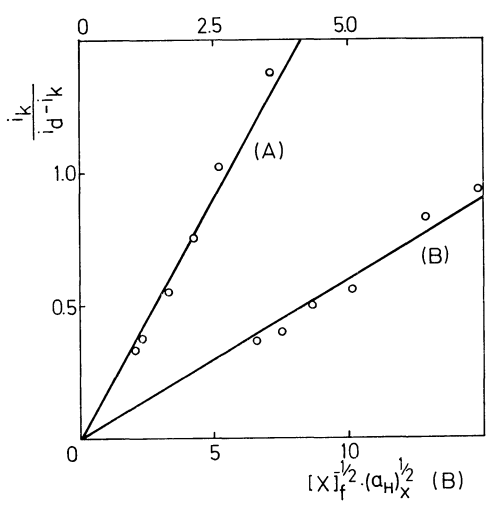

Fig. 5. Plot of $i_k/(i_d-i_k)$ against $(\alpha_H)_X^{1/2}$ or $(\alpha_H)_X^{1/2}[X]_f^{-1/2}$, Aspartate system, 25.0 °C, μ=0.30.
A) $i_k/(i_d-i_k)$ vs. $(\alpha_H)_X^{1/2}$ plot
Aspartate concentration=28.0 mM
B) $i_k/(i_d-i_k)$ vs. $(\alpha_H)_X^{1/2}[X]_f^{-1/2}$ plot

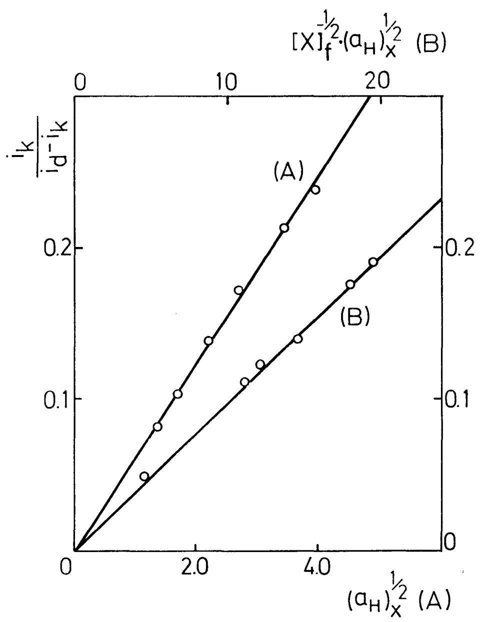

Fig. 6. Plot of $i_k/(i_d-i_k)$ against $(\alpha_H)_X^{1/2}$ or $(\alpha_H)_X^{1/2}[X]_f^{-1/2}$, Iminodiacetate system, 25.0 °C, μ=0.30.
A) $i_k/(i_d-i_k)$ vs. $(\alpha_H)_X^{1/2}$ plot
Iminodiacetate concentration=23.0 mM
B) $i_k/(i_d-i_k)$ vs. $(\alpha_H)_X^{1/2}[X]_f^{-1/2}$ plot

$$\text{(III)}\quad \begin{array}{l} CoX_2^{2-} \rightleftharpoons CoX^0 + X^{2-} \quad \text{rate-determining step} \\ CoX^0 + 2e^- + Hg \rightleftharpoons Co(Hg) + X^{2-} \end{array}$$

corresponding to the following relation:

$$\frac{i_k}{i_d-i_k} = 0.886\sqrt{\frac{k_d\cdot(\alpha_H)_X\cdot t}{K_2[X]_f}} \tag{8}$$

The dissociation rate constant, k_d, was determined from the slope of the linear relation between the $i_k/(i_d-i_k)$ value and $(\alpha_H)_X^{1/2}$ or $(\alpha_H)_X^{1/2}\cdot[X]_f^{-1/2}$. In both systems, the k_d value determined from the slope of the linear relation between the $i_k/(i_d-i_k)$ and $(\alpha_H)_X^{1/2}$ agreed well with that determined from the slope of the linear relation between the $i_k/(i_d-i_k)$ and $(\alpha_H)_X^{1/2}\times[X]_f^{-1/2}$. All the k_d values determined in this study are listed in Table 1, together with other numerical values.[8]

TABLE 1. DISSOCIATION RATE CONSTANTS OF THE COBALT-(II)-AMINOPOLYCARBOXYLATE COMPLEXES
25.0 °C, μ=0.30

System	Asp	IDA	GEDTA
$\log K_2$	4.34	5.34	3.74 3.86[a)]
$\log K_{st}$	0	0.30	0.30
$\Delta\log k_d$ calcd	0.69	0	1.60
$\Delta\log k_d$ obsd	0.56	0	0.45
k_d[b)]	27.0	7.5	20.7
k_f	$10^{5.77}$	$10^{6.21}$	$10^{5.18}$

a) Determined in this study.
b) In the case of GEDTA system, this corresponds to k_d in Eq. (7).

As was discussed in connection with the dissociation reactions of nickel(II)-IDA and -Asp complexes,[1] it is reasonable to believe that (1) less than three bond breakages are involved in the rate-determining step, (2) the cobalt(II)-oxygen (carboxylate) bond breakage is much faster than the cobalt-nitrogen (amine) bond breakage, and (3) the five-membered chelate ring is less substitution-labile than the six-membered chelate ring in the dissociation of the cobalt(II)-aminopolycarboxylate complex. Therefore, one can assume the reaction intermediates I and II in Fig. 7 for the dis-

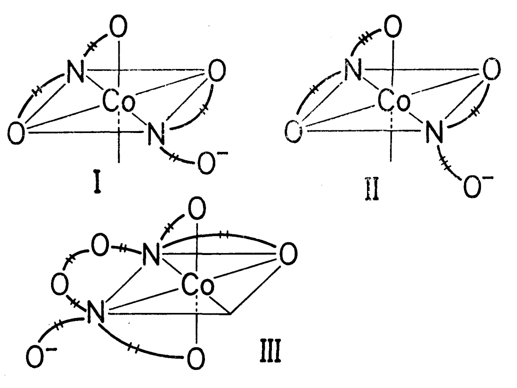

Fig. 7. Reaction intermediates.

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[8] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," 2nd ed., The Chemical Society, London (1964).

sociation of cobalt(II)–IDA and –Asp complexes respectively. In general, the observed rate constant can be related to the rate constant for breaking X^{2-} away from the reaction intermediate, k_{rds}, the stability constant of the reaction intermediate, K_{inter}, and the K_{MX} value in the following manner:[1)]

$$k_{\text{d}} = k_{\text{rds}} \cdot \frac{K_{\text{inter}}}{K_{\text{MX}}} \cdot K_{\text{st}} \cdot K_{\text{elec}} \qquad (9)$$

Since, in the above reaction intermediates, both IDA and Asp anions are bonded to the cobalt(II) ion through a glycinate chelate ring, K_{inter} can be approximated by the formation constant of the cobalt(II)–glycinate complex, $K_{\text{Co-gly}}$. K_{MX} in Eq. (9) should be the second successive formation constant of the cobalt(II)–IDA or –Asp complex, K_2. The above relation suggests that, provided that the k_{rds} value for the IDA system is equal to that for the Asp system, the observed rate constant should be inversely proportional to the second successive formation constant corrected for the statistical factor.[9)] The observed rate constant ratio was successfully compared with the ratio calculated by means of Eq. (9) (Table 1). In this study, we discovered that the cobalt(II) ion can also form a 1:2 ratio complex with the GEDTA anion. In sharp contrast with the EDTA anion, where two iminodiacetate groups are separated by two carbon atoms, the two nitrogen atoms of the GEDTA anion, where two iminodiacetate groups are separated by six carbon atoms and two oxygen atoms, have nearly identical protonation constants.[10)] All these facts may mean that, under most conditions, the two iminodiacetate groups act as if they were unrelated entities in the complex formation with metal(II) ions. Therefore, it is not unreasonable to believe that the GEDTA anion in the electroactive cobalt(II)–GEDTA complex, $\text{CoY}^{2-}*$, is coordinated to the cobalt(II) ion through one iminodiacetate group, and that, hence, the dissociation of the first IDA group of the GEDTA anion is the rate-determining step. When the two IDA groups act as if they were functionally independent, the K value in Eq. (6) must be equal to $K_{\text{CoY}}/(K_{\text{CoY}})_{\text{IDA}} \times 2$. Here, 2 is the statistical factor. With the aid of the above relation, K was calculated to be $10^{3.74}$. This value agrees well with the K_2 value determined in this study, showing the validity of the estimation of the K value. In the above calculation, the cobalt(II)–*N*-(2-hydroxyethyl)iminodiacetate complex was employed as a model. The fact that the overall formation constant for the cobalt(II)–IDA complex, $\text{CoX}_2{}^{2-}$, is nearly identical with that of the 1:2 cobalt(II)–GEDTA complex also gives strong support to the above explanation. By using the K value thus estimated, the k_{d} value was calculated to be 2.07×10^1. This is about ten times smaller than that predicted from the reciprocal of the K value on the basis of the reaction intermediate III (see Table 1). However, the discrepancy between the rate constant ratio observed and that calculated can be explained in terms of the rotational barrier of the dissociating iminodiacetate group around the C–C or C–O bond.[9)] The formation rate constants, k_{f}'s, were also calculated from the $K_2 = k_{\text{f}}/k_{\text{d}}$ relation by using the k_{d} values determined in this study. The estimated k_{f} values for the IDA, Asp, and GEDTA systems are nearly identical with the characteristic water exchange rate constant of the cobalt(II) ion, $k_{\text{Co}}^{-\text{H}_2\text{O}}$ (Table 1).[11)] Because the complexation reaction which involves the formation of an equilibriated outer-sphere complex, preceding the loss of a coordinated water molecule as the rate-determining step, the rate constant, k_{f}, can be written as the product of the outer-sphere association constant, K_{OS}, and $k_{\text{Co}}^{-\text{H}_2\text{O}}$. As predicted by the Fuoss equation,[12)] the K_{OS} value for the outer-sphere association process, in which one of the reacting species is uncharged, is smaller than unity. Therefore, in considering that the coordinated ligand tends to increase the exchange rate of the remaining coordinated water,[13,14)] the rate constant for the formation of the higher complex from the uncharged lower complex, which proceeds through the common water-loss mechanism, must be nearly identical with the characteristic water exchange rate. Thus, the above fact that the k_{f} values for the IDA and Asp systems are nearly identical with the $k_{\text{Co}}^{-\text{H}_2\text{O}}$ value can be explained by assuming a reaction mechanism where an outer-sphere complex formation between CoX^0 and X^{2-} precedes the loss of a coordinated water molecule from the CoX^0 as the rate-determining step. In the case of the GEDTA system, the fact that the k_{f} value is nearly identical with the $k_{\text{Co}}^{-\text{H}_2\text{O}}$ value can also be accounted for by assuming a reaction mechanism which involves the dissociation of water from the $\text{CoY}^{2-}*$ as the rate-determining step following the initial weak association (outer-sphere association in nature) between the free IDA group of the GEDTA anion in $\text{CoY}^{2-}*$ and the formally-uncharged cobalt(II) coordinated by the IDA group.

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9) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

10) a) R. W. Schmidt and C. N. Reilley, *Anal. Chem.*, **29**, 264 (1957). b) G. Schwarzenbach, H. Senn, and G. Anderegg, *Helv. Chim. Acta*, **40**, 1886 (1957).

11) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

12) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

13) D. W. Margerum and H. M. Rosen, *ibid.*, **89**, 1088 (1967).

14) J. P. Jones, E. J. Billow, and D. W. Margerum, *ibid.*, **92**, 1875 (1970).