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A Polarographic Study of the Rates of the Dissociation Reactions of Aminopolycarboxylato-zinc(II), -lead(II), and -cadmium(II) Complexes

Mutsuo Kodama[1)], Kyoko Namekawa,* and Takashi Horiuchi*

Department of Chemistry, College of General Education, Hirosaki University, Bunkyo, Hirosaki 036

**Department of Chemistry, Ibaraki University, Bunkyo, Mito 310*

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The rates and the mechanisms of the dissociation reactions of aminopolycarboxylato zinc(II), lead(II), and cadmium(II) complexes were studied by analyzing their kinetic waves by conventional DC polarography. The dissociations of the zinc(II)–HIDA and –NTA complexes and the cadmium(II)– and lead(II)–HIDA complexes in an acetate buffer solution, and those of protonated lead(II)–EDTA and –EDTA–OH complexes were found to proceed through the following direct dissociation mechanisms:

i) HIDA and NTA systems

$$\mathrm{MX_2}^{2-2m} \rightleftharpoons \mathrm{MX}^{2-m} + \mathrm{X}^{m-} \qquad \text{in a rapid equil.}$$

$$\mathrm{MX}^{2-m} \rightleftharpoons \mathrm{M}^{2+} + \mathrm{X}^{m-} \qquad \text{r.d.s.}$$

ii) EDTA and EDTA-OH systems

$$\mathrm{MHY}^{3-n} \rightleftharpoons \mathrm{M}^{2+} + \mathrm{HY}^{1-n} \qquad \text{r.d.s.}$$

On the other hand, the dissociation of the zinc(II)–EDTA-OH and its protonated DTPA complexes gave this rate law: $-\mathrm{d}[\mathrm{MH}_i\mathrm{Y}^{2+i-m}]/\mathrm{d}t$ ($i=0$ or 1)$=k_\mathrm{d}^\mathrm{H}\cdot[\mathrm{H}^+]\cdot[\mathrm{MH}_i\mathrm{Y}^{2+i-m}]$. From a comparison of the observed rate constants, the zinc(II)-HIDA and -NTA, lead(II)- and cadmium(II)-HIDA and protonated lead(II)-EDTA and -EDTA-OH complexes are concluded to dissociate through a simple glycinate reaction intermediate, and the zinc(II)-EDTA-OH and its protonated DTPA complexes, through a glycinate reaction intermediate which includes polyfurcated hydrogen bonds.

The dissociation reactions of metal complexes have been studied by analyzing the kinetic waves by conventional polarography.[2~7)] Previously,[8~10)] we also studied the dissociation reactions of aminopolycarboxylato nickel(II) and cobalt(II) complexes in alkaline solutions by DC polarography. In this paper, the dissociation reactions of aminopolycarboxylato zinc(II), cadmium(II), and lead(II) complexes will be studied by DC polarography. The structure of the reaction intermediate and the reaction mechanism will be discussed in detail on the basis of a comparison of the observed rate constant with that calculated from the reaction intermediate proposed.

Experimental

Reagents. Our previous paper[11)] explained the preparation of standard zinc(II) and cadmium(II) solutions. The standard lead(II) solution was prepared by dissolving a known amount of pure lead(II) nitrate in redistilled water. EDTA, NTA, *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid (EDTA-OH), 2,2'-ethylenedioxydi(ethylamine)-*N*,*N*,*N'*,*N'*-tetraacetic acid (GEDTA), and diethylenetriaminepentaacetic acid (DTPA) were recrystallized from their aqueous solutions. *N*-(2-hydroxyethyl)iminodiacetic acid (HIDA) was synthesized from ethanolamine and monochloroacetic acid and recrystallized from its aqueous solution three times by adding pure hydrochloric acid, ethanol, and acetone. All the other chemicals were of analytical-reagent grades and were used without further purification.

Apparatus and Experimental Procedures. All the DC current-voltage curves were measured with a manual polarograph similar to Kolthoff and Lingane's or with a Yanagimoto pen-recording polarograph PA-102. The characteristic features of the DME used were described in a previous paper.[8)] All the other apparatuses and the experimental procedures were the same as those in that previous paper. In the HIDA, NTA, and GEDTA systems, an acetate buffer was used. For the EDTA, DTPA, and EDTA-OH systems, no buffer reagent was used, because the sample solutions contained a large excess of uncomplexed EDTA, EDTA-OH, or DTPA and had a sufficient buffer capacity in their pH ranges ($2.50 < \mathrm{pH} < 3.50$ in the EDTA-OH system, $2.00 < \mathrm{pH} < 3.00$ in the EDTA system, and $2.40 < \mathrm{pH} < 3.00$ in the DTPA system).

Results and Discussion

Reaction Rates and Mechanism. In an acetate buffer solution, zinc(II)–, cadmium(II)–, and lead(II)–HIDA complexes gave two step waves. The first waves were found to be kinetic waves due to the reduction of the aquo metal(II) ion and acetate complexes formed upon the slow dissociation of the metal(II) complexes, whereas the second waves, diffusion waves, were found to be the direct reduction of the metal(II) complexes. The zinc–(II)NTA complex also gave a kinetic wave due to its dissociation at the electrode surface. As was discussed in connection with the polarography of the aminopolycarboxylato cobalt(II) complexes,[10)] the reaction mechanism and dissociation rates were determined from the i_k and i_d values using the treatment employed by Koryta.[4)] Under the present experimental conditions, the Koryta equation for the kinetic waves of HIDA and NTA complexes could be formulated as:

$$\frac{i_\mathrm{k}}{i_\mathrm{d}-i_\mathrm{k}} = 0.886\cdot\sqrt{\frac{k_\mathrm{d}\cdot t\cdot(\alpha_\mathrm{H})_\mathrm{X}\cdot\beta_\mathrm{Ac}}{K_\mathrm{MX}\cdot[\mathrm{X}]_\mathrm{f}}}\;\frac{1}{1+\dfrac{K_2\cdot[\mathrm{X}]_\mathrm{f}}{(\alpha_\mathrm{H})_\mathrm{X}}} \tag{2}$$

corresponding to the (I) reaction mechanism:

$$(\mathrm{I})\quad\left\{\begin{array}{l}
\mathrm{MX_2}^{2-2m} \rightleftharpoons \mathrm{MX}^{2-m} + \mathrm{X}^{m-} \text{ in a rapid equil.}\\
\mathrm{MX}^{2-m} \overset{k_\mathrm{d}}{\rightleftharpoons} \mathrm{M}^{2+} + \mathrm{X}^{m-} \text{ (direct dissociation)}\\
\qquad\qquad\qquad\qquad\qquad (\mathrm{I_b}) \text{ r.d.s.}\\
\underbrace{\mathrm{M}^{2+} + i\mathrm{Ac}^- \rightleftharpoons \mathrm{MAc}_i{}^{2-i}}_{\substack{\mathrm{Hg}\Downarrow 2\mathrm{e} \\ \mathrm{M(Hg)}}} (\mathrm{I_c}) \text{ in a rapid equil.}
\end{array}\right.$$

The β_{Ac} in Equation (1) is defined as $\beta_{Ac}=1+K_1^{Ac}\cdot[Ac^-]+K_1^{Ac}\cdot K_2^{Ac}\cdot[Ac^-]^2+\cdots$, and $(\alpha_H)_X$, $[X]_f$, $[Ac^-]$, K_{MX}, K_2, and K_1^{Ac} are, respectively, the (α_H) value of HIDA or NTA, the concentration of uncomplexed HIDA or NTA, the concentration of the free acetate ion, the second successive formation constant of the HIDA or NTA complex, and the i-th successive formation constant of the metal(II)–acetate complex. From the slope of the linear relation between $i_k/(i_d-i_k)$ and $(\alpha_H)_X^{1/2}/(1+K_2'\cdot[X]_f)$ or $1/[X]_f^{1/2}\cdot(1+K_2'\cdot[X]_f)$, the k_d values were determined; they are listed in Tables 1, 2, and 3. The typical linear relations obtained are shown in Fig. 1. The lead(II)–EDTA-OH and –EDTA complexes in the pH range from 2.00 to 3.50 and the lead(II)–GEDTA complex in the pH range from 4.50 to 5.60 also gave kinetic waves due to their dissociations at the electrode surface. In the case of the EDTA-OH complex, we obtained a linear relation with an intercept of a finite value by plotting $((i_d-i_k)/i_k)\cdot(\alpha_H)_Y^{1/2}/[H^+]^{1/2}$ against the reciprocal of the hydrogen-ion concentration, $[H^+]^{-1}$ (at a given uncomplexed EDTA-OH concentration) (Fig. 2). This means that, under the present experimental conditions, the Koryta equation for the kinetic wave of the lead(II)–EDTA-OH complex may be expressed as:

$$\frac{i_k}{i_d-i_k}=0.886\cdot\sqrt{\frac{k_d\cdot t\cdot(\alpha_H)_Y}{K_{PbY}\cdot K^H\cdot[H^+]\cdot[Y]_f}}\frac{K^H\cdot[H^+]}{1+K^H\cdot[H^+]} \tag{2}$$

corresponding to the (II) reaction mechanism:

$$\text{(II)}\begin{cases}\text{PbY}^{2-m}+\text{H}^+ \rightleftharpoons \text{PbHY}^{3-m}\ (\text{II}_a)\ \text{in rapid equil.}\\ \text{PbHY}^{3-m} \xrightleftharpoons{k_d} \text{Pb}^+ + \text{HY}^{1-m}\ \text{(direct dissociation)}\\ \qquad\qquad (\text{II}_b)\ \text{r.d.s.}\\ \text{Pb}^{2+}+2\text{e}^-+\text{Hg} \rightleftharpoons \text{Pb(Hg)}\ (\text{II}_c)\end{cases}$$

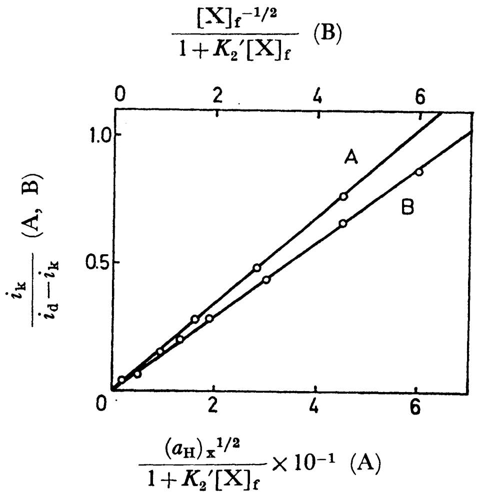

Fig. 1. The plot of $i_k/(i_d-i_k)$ against $(\alpha_H)_X^{1/2}/(1+K_2'[X]_f)$ or $(\alpha_H)_X^{1/2}/(1+K_2'\cdot[X]_f)\cdot[X]_f^{1/2}$
Cd(II)–HIDA system
25 °C, $\mu=0.30$
the concentration of cadmium(II) ion = 0.60 mM
the concentration of acetate ion = 0.06 M
A) The $i_k/(i_d-i_k)$ vs. $(\alpha_H)_X^{1/2}/(1+K_2/\cdot[X]_f)$ plot the concentration of HIDA = 30.0 mM
pH ranged from 4.80 to 5.82
B) The $i_k/(i_d-i_k)$ vs. $(\alpha_H)_X^{1/2}/(1+K_2'\cdot[X]_f)\cdot[X]_f^{1/2}$ plot the concentration of HIDA ranged from 10.0 mM to 50.0 mM
pH = 5.20

TABLE 1. DISSOCIATION AND FORMATION RATE CONSTANTS OF THE ZINC(II)-AMINOPOLYCARBOXYLATE COMPLEXES
25 °C, $\mu=0.30$

System		NTA	HIDA
$\log K_{MX}$[18]		10.0	8.06
$\log K_{st}$		0.48	0.30
$\log K_{elec}$		1.00	0.50
$\Delta \log k_d$	calcd	0	0.86
	obsd	0	0.86
k_d, s^{-1}		0.21	1.5
k_f, $M^{-1}\,s^{-1}$		2.1×10^9	2.7×10^8

TABLE 2. DISSOCIATION AND FORMATION RATE CONSTANTS OF THE CADMIUM(II)-AMINOPOLYCARBOXYLATE COMPLEXES
25 °C, $\mu=0.30$

System		NTA	EDTA (protonated)	HIDA
Reporter		13)	2)	present authors
$\log K_{MX}$		9.80	8.55	7.21
$\log K_{st}$		0.48	0.30	0.30
$\log K_{elec}$		1.00	0.50	0.50
$\Delta \log k_d$	calcd	0	0.90	1.91
	obsd	0	1.23	1.90
k_d, s^{-1}		~0.60	10.8	50
k_f, $M^{-1}\,s^{-1}$		$\sim4.0\times10^9$	6.0×10^9	8.1×10^8

TABLE 3. DISSOCIATION AND FORMATION RATE CONSTANT OF THE LEAD(II)-AMINOPOLYCARBOXYLATE COMPLEXES
25 °C, $\mu=0.30$

System		NTA	HIDA	EDTA-OH	EDTA	GEDTA
				protonated		
Reporter		13)	present authors			
$\log K_{MX}$		11.39	9.10	8.79	10.1	8.55
$\log K_{st}$		0.48	0.30	0.30	0.60	0.60
$\log K_{elec}$		1.00	0.50	0.50	0.50	0.50
$\Delta \log k_d$	calcd	0	1.61	2.74	1.74	2.98
	obsd	0	1.41	2.82	1.92	2.27
k_d, s^{-1}		~0.6	15.5	4.0×10^2	50	$1.0_5\times10^2$
k_f, $M^{-1}\,s^{-1}$		$\sim1.5\times10^{11}$	2.0×10^{10}	2.4×10^{11}	6.1×10^{11}	7.5×10^{10}

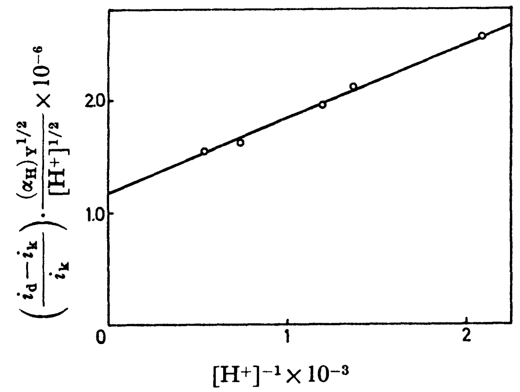

Fig. 2. The plot of $(i_d-i_k)\cdot(\alpha_H)_Y^{1/2}/i_k\cdot[H^+]^{1/2}$ against $[H^+]^{-1}$
Lead(II)-EDTA-OH system
25 °C, $\mu=0.30$
the concentration of lead(II) ion = 1.0 mM
the concentration of EDTA-OH = 14.0 mM
pH ranged from 2.60 to 3.50

Therefore, the ratio between the intercept and the slope of the above linear relation should correspond to the protonation constant of the lead(II)–EDTA-OH complex, K^H. From the above linear relation, the K^H value was determined to be 1.8×10^3. Although the formation of the protonated lead(II)–EDTA-OH complex has not yet been reported, if the pH dependence of the i_k value can be interpreted as due to the dissociation of the protonated lead(II)–EDTA-OH complex, the plot of the $i_k/(i_d-i_k)$ value against the $K^H\cdot[H^+]\cdot[\alpha_H]_Y^{1/2}/(1+K^H\cdot[H^+])[H^+]^{1/2}$ value (at a given $[Y]_f$) or the $[Y]_f^{-1/2}$ (at a given pH) should yield a straight line passing through the point of origin. These relations were examined successfully by using some typical experimental data (Fig. 3). The k_d value obtained from the slope of the above straight line is also listed in Table 3. In the GEDTA system, the straight line passing through the point of origin could be obtained by plotting $i_k/(i_d-i_k)$ against $K^H\cdot[H^+]\cdot(\alpha_H)_Y^{1/2}/(1+K^H\cdot[H^+])\cdot[H^+]^{1/2}$, $[Y]_f^{-1/2}$ or $\beta_{Ac}^{1/2}$, suggesting a reaction mechanism in which (II_b) is the slowest step. Therefore, the k_d value for the dissociation of the protonated lead(II)–GEDTA complex was determined from the slope of the above linear relation; it is listed in Table 3. In the case of the EDTA system, the plot of the $i_k^2\cdot[H^+]\cdot[(1+K^H\cdot[H^+])^2/(i_d-i_k)^2\cdot(\alpha_H)_Y\cdot(K^H\cdot[H^+])^2$ against $[H^+]$ gave a straight line with an intercept of a finite value. Furthermore, at a given pH, the plot of the $(i_k-(i_d-i_k))^2$ value against the $[Y]_f^{-1}$ value yielded a straight line passing through the point of origin. These facts evidently imply that the $i_k/(i_d-i_k)$ ratio is given by Eq. (3); hence, the dissociation of the protonated lead(II)–EDTA complex proceeds through (III_b) and (II_b):

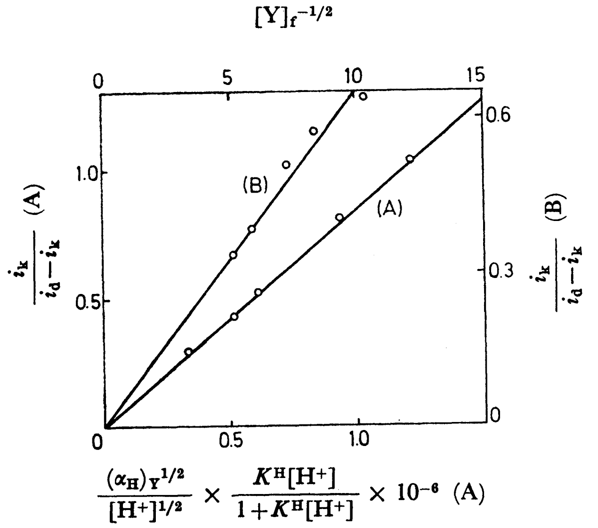

Fig. 3. The plot of $i_k/(i_d-i_k)$ against $(\alpha_H)_Y^{1/2}\cdot K^H\cdot[H^+]/[H^+]^{1/2}\cdot(1+K^H\cdot[H^+])$ or $[Y]_f^{-1/2}$
Lead(II)-EDTA-OH system
25.0 °C, $\mu=0.30$
the concentration of lead(II) ion = 1.0 mM
A) the $i_k/(i_d-i_k)$ *vs.* $(\alpha_H)_Y^{1/2}\cdot K^H\cdot[H^+]/[H^+]^{1/2}(1+K^H\cdot[H^+])$ plot. The concentration of EDTA-OH = 14.0 mM
pH ranged from 2.60 to 3.50
B) the $i_k/(i_d-i_k)$ *vs.* $[Y]_f^{-1/2}$ plot
the concentration of EDTA-OH ranged from 9.0 mM to 39.0 mM
pH = 3.09

$$\frac{i_k}{i_d-i_k}=0.886\cdot\sqrt{\frac{(k_d+k_d^H[H^+])\cdot t\cdot(\alpha_H)_Y}{K_{PbY}\cdot K^H\cdot[Y]_f\cdot[H^+]}}\,\frac{K^H\cdot[H^+]}{1+K^H\cdot[H^+]}\tag{3}$$

$$PbHY^{3-m}+H^+\overset{k_d^H}{\rightleftharpoons}Pb^{2+}+H_2Y^{2-m}\text{ (proton-assisted dissociation) }(III_b)\text{ r.d.s.}$$

The k_d and k_d^H values were determined from the intercept and the slope of the linear relation between $i_k^2\cdot(1+K^H\cdot[H^+])^2/(i_d-i_k)^2\cdot(\alpha_H)_Y\cdot K^{H^2}\cdot[H^+]$ and $[H^+]$ (Table 3). Although the results are not shown here, the effects of the solution pH and the uncomplexed ligand concentration on the half-wave potential of kinetic waves of the lead(II) and cadmium(II) complexes were also examined. The shifts of the half-wave potential, as calculated on the basis of the proposed reaction mechanism, agreed well with those observed.

The zinc(II)–EDTA-OH and –DTPA complexes in an acid solution also produced kinetic waves due to their dissociations at the electrode surface. From the systematic examination of the nature of the kinetic waves, the $i_k/(i_d-i_k)$ ratios for the EDTA-OH and DTPA systems were found to be $0.886\,(k_d^H\cdot t\cdot[H^+]\cdot(\alpha_H)_Y/K_{ZnY}\cdot[Y]_f]^{1/2}$ and $0.886\,[k_d^H\cdot t\cdot(\alpha_H)_Y/K_{ZnY}\cdot[Y]_f]^{1/2}$ respectively. In considering the fact that all the zinc(II)–DTPA complex exists in the form of $ZnHY^{2-}$ under the present experimental conditions, the above fact suggests that the dissociation reactions of the zinc(II)–EDTA-OH and –DTPA complexes are given by (IVa) and (IVb) respectively:

$$ZnY^-+H^+\overset{k_d^H}{\rightleftharpoons}Zn^{2+}+HY^{2-}\text{ (proton-assisted dissociation) }(IV_a)$$

$$ZnHY^{2-}+H^+\overset{k_d^H}{\rightleftharpoons}Zn^{2+}+H_2Y^{3-}\text{ (proton-assisted dissociation) }(IV_b)$$

TABLE 4. PROTON-ASSISTED DISSOCIATION AND FORMATION RATE CONSTANT OF THE ZINC(II)-AMINOPOLYCARBOXYLATE COMPLEXES
25 °C, $\mu=0.30$

System Reporter	NTA 13)	EDTA-OH present authors	EDTA 12)	DTPA (protonated) present authors
$\log K_{MX}$	10.0	14.0_5	15.9_1	13.2_0
$\log K_{st}$	0.30	0.30	0.60	0
$\log K_{elec}$	0.50	0.50	0.50	0
pK_a	1.86	5.26	5.97	4.10
$\log k_d^H$ calcd	1.50	0.85	0	−0.26
$\log k_d^H$ obsd	2.15	0.85	0	−0.26
k_d^H, $M^{-1}\cdot s^{-1}$	1×10^5	5×10^3	7×10^2	3.9×10^2
k_f, $M^{-1}\cdot s^{-1}$	—	1.7×10^8	5.7×10^8	1.1×10^8

The $k_d{}^H$ values for the zinc(II)–EDTA-OH and –DTPA systems were determined from the slope of the linear relation between $i_k/(i_d-i_k)$ and $[Y]_f^{-1/2}$ or that between $i_k/(i_d-i_k)$ and $(\alpha_H)_Y{}^{1/2}\cdot[H^+]^{1/2}$ (EDTA-OH system) or $(\alpha_H)_Y{}^{1/2}$ (DTPA system). They are listed in Table 4, together with the reported rate constants and EDTA and NTA systems.12,13)

Direct Dissociation. As has been stated above, metal(II)–HIDA and –NTA and protonated lead(II)–EDTA, –EDTA-OH, and –GEDTA complexes dissociate through the direct dissociation mechanism. As was discussed in connection with the dissociation reactions of nickel(II)–glutamate and –IDA complexes,8) it is hard to believe that, in the dissociation of the cadmium(II)–aminopolycarboxylate complexes, all the bond breakages are involved in the rate-determining step. Day and Reilley, in their NMR study of metal-aminopolycarboxylate complexes,14) mentioned that the breakage process of the cadmium(II)–nitrogen bond is much more sluggish than that of the cadmium(II) to the oxygen bond. Therefore, the dissociations of the cadmium(II)–HIDA and –NTA4) complexes should proceed through a reaction intermediate in which the leaving HIDA or NTA anion is bonded to the cadmium(II) ion through the glycinate or iminodiacetate chelate ring (glycinate or IDA mechanism). If both complexes dissociate through the glycinate reaction intermediate (Fig. 4), the rate constant ratio between HIDA and NTA systems, $(k_d)_{HIDA}/(k_d)_{NTA}$, must be given by $(K_{CdX})_{NTA}\times2\times3.16/(K_{CdX})_{HIDA}\times3\times10=10^{1.96}$ because the dissociation rate constant, k_d, is given by the well-known relation: $k_d=k_{rds}\cdot k_{inter}\cdot K_{st}\cdot K_{elec}/K_{MX}$.8) Here, the symbols used have their usual meanings, while $(K_{CdX})_{NTA}$ and $(K_{CdX})_{HIDA}$ are the formation constants of 1 : 1 ratio cadmium(II)–NTA and –HIDA complexes. On the other hand, if the IDA mechanism is operative here, the rate-constant ratio between the two systems should be $10^{2.11}$. The observed ratio of $10^{1.90}$ evidently excludes the IDA mechanism. The rate-constant ratio calculated on the basis of the other reaction intermediates showed no satisfactory agreement with the observed one. As is clear from the dissociation rate constants for the zinc(II)–acetate15) and –ammine complexes,16) the zinc(II)–nitrogen bond has a life span longer than that of the zinc(II)–oxygen bond. Therefore, the zinc(II)–aminopolycarboxylate complex seems to dissociate through a glycinate or IDA reaction intermediate produced by the partial dissociation of the original complex. Ogino17) suggested a water-loss mechanism for the formation of the zinc(II)–aminopolycarboxylate complex from the aquo zinc(II) ion and the aminopolycarboxylate anion. If the formation reaction of the zinc(II)-glycinate complex also has a water-loss mechanism, the dissociation rate constant of the zinc(II)-glycinate complex with a 1 : 1 ratio can be calculated by using the formation rate constant: $k_f=k_{Zn}^{-H_2O}\cdot K_{os}$ and the K_{ZnX} value for the zinc(II)-glycinate complex. By using the $k_{Zn}^{-H_2O}$ value of 5×10^7,13) the K_{os} value of 5, and the K_{ZnX} value of 7×10^4,18) the k_d value for the zinc(II)–glycinate complex was calculated to be 3.6×10^3 s^{-1}. Here, the zinc(II)–*N*-methyl-glycinate complex was employed as a model. By using the k_d value thus estimated as k_{rds}, the dissociation rate constant of the zinc(II)–NTA complex was calculated to be 0.1 on the basis of the glycinate dissociation mechanism. This value showed a satisfactory agreement with the observed k_d value (Table 1). None of the rate constants calculated on the basis of other reaction intermediates showed a satisfactory agreement with the observed one. The relative rate constant of the zinc(II)–HIDA system, calculated on the basis of the glycinate mechanism, is listed in Table 1 and compared with the observed one. The agreement between the observed and calculated rate constants can be regarded as satisfactory, lending strong support to the glycinate-mechanism explanation.

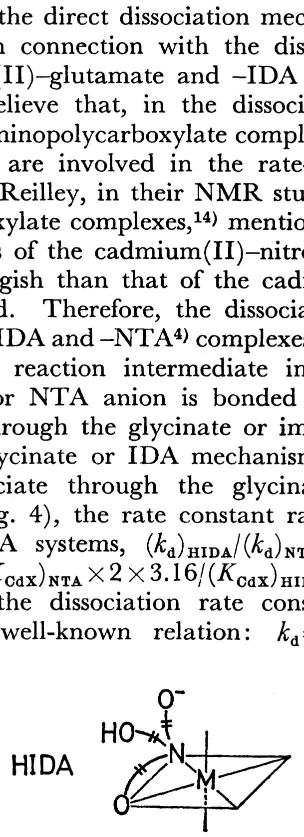

Fig. 4. Reaction intermediates for the direct dissociations of metal(II)-HIDA and -NTA complexes.

Rabenstein,13) in his NMR study of the reaction of the lead(II)–NTA complex, reported several features which support the conclusion that the lead(II)–NTA reaction also has a mechanism similar to those of the cadmium(II)- and zinc(II)–NTA reactions. Therefore it is natural to assume the glycinate mechanism for the dissociation of the lead(II)–aminopolycarboxylate complexes. As is shown by the data in Table 3, the relative dissociation rate constants evaluated on the basis of the glycinate mechanism agreed well with those observed. The dissociation rate constants of the protonated lead(II)–EDTA, -EDTA-OH, and -GEDTA complexes can also be understood in terms of the glycinate mechanism (Table 3). As is shown by the data in Table 3, the formation constant of the protonated complex evaluated from the K_{MY}, K^{H}, and pK_a values is always smaller than that of the corresponding normal complex, K_{MY}. This may mean that the formation of the protonated complex is always accompanied by the partial dissociation of the metal(II) ligand bonds in the original complex.[19] This would explain the dissociation of the protonated complex being more rapid than that of the normal complex. In exactly the same manner, the rapid dissociation of the protonated cadmium(II)–EDTA complex[2] can also be understood in terms of the glycinate mechanism.

Proton-Assisted Dissociation. As has been reported by several authors,[4,13] the proton-assisted dissociation of the metal(II)–aminopolycarboxylate complex proceeds much more rapidly than the corresponding direct dissociation. From a thermodynamic point of view, it can be said that when the metal complex of the polydentate ligand forms a binuclear complex with another metal ion through the free donor atom, its stability will increase appreciably. Therefore, it is reasonable to believe that, in the proton-assisted dissociation of the metal(II)–aminopolycarboxylate complex, the bond breakage in the course of the reaction intermediate formation always accompanied by the subsequent protonation at the freed donor atom, thus yielding a stable reaction intermediate. If the proton-assisted dissociations of zinc(II)–EDTA, -EDTA-OH, and -DTPA complexes proceed through the glycinate reaction intermediate, with the protonation occurring at the most basic free donor atom, one can estimate the relative rate constant by using the relation employed above. Here, the stability of the reaction intermediate, K_{inter}, should be the product of the stability constant of the zinc(II)-glycinate complex and the protonation constant of a free amino group, $K_h=1/K_a$. The relative rate constants calculated are listed in Table 4, together with the numerical values used in the calculation. The agreement between the calculated and observed values can be regarded as satisfactory. The rate constants for the proton-assisted dissociations of the lead(II)- and cadmium(II)–EDTA-OH, -EDTA, and -DTPA complexes also can be understood in terms of the glycinate reaction intermediate (Table 5). As is shown in Table 4 and 5, the rate constants for the proton-assisted dissociations of the zinc(II)-, lead(II)-, and cadmium(II)–NTA complex can also be understood by assuming a glycinate reaction intermediate where the carboxylate group is protonated (I in Fig. 5). If the reaction intermediates for the direct and proton-assisted dissociations of metal(II)–NTA complexes are given by the reaction intermediate in Fig. 4 and I in Fig. 5 respectively, the rate constant ratio between the two dissociation mechanisms should be 1 : 23.5. However, the observed ratios for the zinc(II)-,[13] lead(II)-,[13] and cadmium(II)–NTA[4,13,20] systems are $1:4\times10^4$, $1:5._5\times10^3$, and $1:1._3\times10^4$ respectively. As far as the $k_d=k_{rds}\cdot K_{inter}\cdot K_{st}\cdot K_{elec}/K_{MX}$ relation can be applied safely to the estimation of the relative dissociation rate constant, the above discrepancy would indicate that the protonation of the reaction intermediate results in not only an increase in the stability of the reaction intermediate, but also in an increase in the rate of the dissociation of the leaving ligand anion from the metal(II) ion. In order to describe the above effect, we propose an reaction intermediate with polyfurcated hydrogen bonds, shown by II in Fig. 5, in place of the simple binuclear complex, I. This structure can also explain why the zinc(II) system has a rate constant ratio different from those of the lead(II) and cadmium(II) systems. The rate constant for the proton-assisted dissociation of the nickel(II)–NTA complex[21] can also be understood by assuming the II reaction intermediate in Fig. 5. As is clear from the above discussion, it is not unreasonable to propose the III reaction intermediate in Fig. 5 for the proton-assisted dissociations of the metal(II) complexes of EDTA and its derivatives (Tables 4 and 5). The

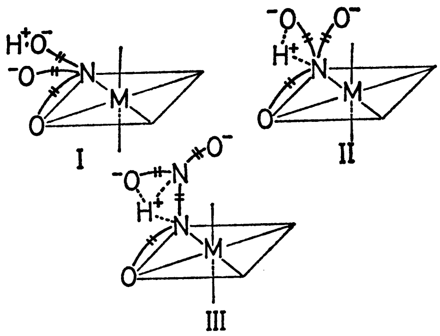

Fig. 5. Reaction intermediates for the proton-assisted dissociations of metal(II)-aminopolycarboxylate complexes.

TABLE 5. PROTON-ASSISTED DISSOCIATION RATE CONSTANTS OF CADMIUM(II)- AND LEAD(II)-AMINOPOLYCARBOXYLATE COMPLEXES

25 °C, $\mu=0.30$

A) Cadmium(II) system

System Ref.		NTA 4)	EDTA 12)	EDTA-OH 12)	DTPA 12)
$\log k_d^H$		5.40	3.05	5.60	1.60
$\Delta \log k_d^H$	calcd	0	−2.20	−0.05	−3.90
	obsd	0	−2.35	0.20	−4.00

B) Lead(II) system

System Ref.		NTA 3, 13)	EDTA-OH 12)	DTPA 12)
$\log k_d^H$		4.70	4.87	2.46
$\Delta \log k_d^H$	calcd	0	0.19	−1.53
	obsd	0	0.27	−2.24

rate constants for the direct and proton-assisted dissociations of the cobalt(II)–EDTA complex[22] can also be understood on the basis of the glycinate intermediate. However, in order to describe the precise role of the hydrogen ion in the dissociation of metal(II)–aminopolycarboxylate complexes, a further systematic investigation should be conducted.

Formation Reactions. The rate constants, k_f's, for the formation of the cadmium(II) complexes calculated with the aid of the $k_f=k_d \cdot K_{MX}$ relation were found to be slightly larger than the characteristic water-exchange rate constant of the cadmium(II) aquo ion[23] (Table 2). Since the equilibrium constant for the outer-sphere association of the cadmium(II) aquo ion with the aminopolycarboxylate anion, approximated by using the Fuoss exuation,[24] is expected to be larger than unity, the above fact can be taken as evidence for the usual water-loss mechanism. As in the case of cadmium(II) complex, the rate constants for the formation reactions of lead(II)– and zinc(II)–aminopolycarboxylate complexes, as calculated using the k_d values and the stability constants, can also be understood by assuming the usual water-loss mechanism (Tables 1 and 3).

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