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Kinetics and Mechanism of Aquation of Cobalt(II)–Glycine Complexes in Aqueous Solutions: A Pulse Radiolytic Study

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The kinetics of aquation of tris(glycinato)cobaltate(II), $[Co(gly)_3]^-$, formed by the reaction of the corresponding Co(III) complex with hydrated electrons, has been investigated by conductometric pulse radiolysis in aqueous solutions. The rate of the reactions leading to the loss of each of the three glycinate ions in $[Co(gly)_3]^-$ were well separated from each other and were studied as a function of pH. The observed rate constants are given by $k^0 + k^H[H^+]$. For the glycinate ion dissociation from the Co(II) complexes with one, two, and three glycinate ions, k^0 were 4.9×10, 3.5×10^2, and 4.2×10^3 s^{-1}, respectively and k^H were 2.1×10^4, 8.1×10^5, and 2.7×10^7 M^{-1} s^{-1}, respectively. The kinetics and mechanism of the aquation reaction of $[Co(gly)_3]^-$ are discussed and compared to those for the aquation of $[Co(en)_3]^{2+}$ and $[Co(acac)_3]^-$.

Introduction

The kinetic conductivity technique coupled to pulse radiolysis has been useful in the study of the kinetics of ligand dissociation in labile complexes.[2-8] The technique is based on the very rapid reduction of an inert complex to produce a labile complex. In the case of $[Co(NH_3)_6]^{2+}$, it was found that the dissociation of the first three NH$_3$ groups is too fast to measure by pulse radiolysis, and the remaining NH$_3$ are lost via pH-independent, consecutive first-order reactions.[2,4] The release of the second and third NH$_3$ groups was measured by conductometric laser photolysis.[9] The dissociation rates of polyamine from labile Co(II) complexes with ligands such as ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), etc.[4-6] and acetylacetonate ion (acac$^-$)[8] were found to be considerably slower and acid-catalyzed. The rate constants of the acid-independent dissociation of glycinate ions from $[Co(gly)_3]^-$ (gly$^-$ = NH$_2$CH$_2$COO$^-$) were measured by a temperature jump method.[10]

In the present work, we report the dissociation rates of glycinate ions from labile Co(II)–gly$^-$ complexes. The reactions were found to proceed via acid-independent and acid-catalyzed pathways, which were greatly dependent on the number of glycinate ions on metal. The kinetics and mechanisms of the aquation reaction of $[Co(gly)_3]^-$ are discussed and compared to those for the aquation reactions of $[Co(en)_3]^{2+}$ and $[Co(acac)_3]^-$.

Experimental Section

Tris(glycinato)cobalt(III) complex, *mer*-$[Co(gly)_3]$·2H$_2$O, was prepared by the method described in the literature[11] and recrystallized. Other chemicals were analytical reagent grade. All the solutions were prepared with triply distilled water or water purified by a Millipore Super-Q system. The pH of such solutions was adjusted with HClO$_4$ or NaOH solution. Air was removed from the solution either by repeated freezing, evacuation to <10^{-5} mmHg pressure, and thawing, or by passing oxygen-free argon through the solution. The apparatus and experimental technique for the transient conductivity measurement have been described previously.[2-4] The irradiations were performed with 0.5-μs electron pulses from a 1.6-MeV Van de Graaf generator or with a 2000 Ci cobalt-60 γ source. The dose per pulse and the cell constant were determined before each series of experiments with a tetranitromethane solution.[12] All
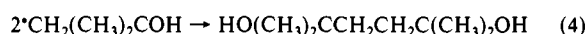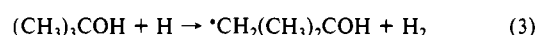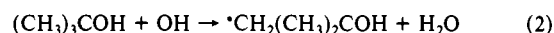
experiments were carried out at about 25 °C. All the points obtained experimentally were the average of three to five measurements. Hydrogen and nitrogen were determined volumetrically or gas chromatographically. The data obtained by the conductivity method were digitized and analyzed with a PDP 11/40 computer.

Results and Discussion

Dissociation of $[Co(gly)_3]^-$. The radiolysis of water can be summarized by eq 1. The following G values (the number of product molecules

$$H_2O \rightsquigarrow e_{aq}^-, OH, H, H_2, H_2O_2, H^+, OH^- \qquad (1)$$
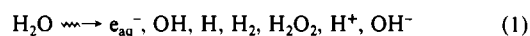
formed by the absorption of 100 eV by the solution) were used; $G(e_{aq}^-)$ = 2.7, $G(OH)$ = 2.7, $G(H)$ = 0.55, $G(H_2O_2)$ = 0.75, $G(H_2)$ = 0.45, and $G(H_3O^+)$ = $G(e_{aq}^-)$ + $G(OH^-)$.[13,14] Argon-saturated solutions containing $[Co(gly)_3]$ and *tert*-butyl alcohol were irradiated in the pH region 3.0–4.6. The reaction of $[Co(gly)_3]$ with H atoms is relatively slow (k = 3.3 × 10^6 M^{-1} s^{-1}).[15] Therefore, under our experimental conditions, OH radicals and about 70% of the H atoms were scavenged by *tert*-butyl alcohol (k_2 = 5 × 10^8 M^{-1} s^{-1},[16] and k_3 = 1.0 × 10^5 M^{-1} s^{-1}[17]). The resulting *tert*-butyl alcohol radicals disappear through reaction 4 (k_4 = 1.3 × 10^9 M^{-1} s^{-1}[18]). Therefore, the main reducing agent is e_{aq}^-, which

$$(CH_3)_3COH + OH \rightarrow \text{·}CH_2(CH_3)_2COH + H_2O \qquad (2)$$

$$(CH_3)_3COH + H \rightarrow \text{·}CH_2(CH_3)_2COH + H_2 \qquad (3)$$

$$2\text{·}CH_2(CH_3)_2COH \rightarrow HO(CH_3)_2CCH_2CH_2C(CH_3)_2OH \qquad (4)$$

reacts with $[Co(gly)_3]$ complex very rapidly (reaction 5). We estimated

$$[Co(gly)_3] + e_{aq}^- \rightarrow [Co(gly)_3]^- \qquad (5)$$

$$N_2O + e_{aq}^- \xrightarrow{H^+} N_2 + OH \qquad (6)$$
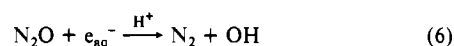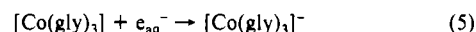
the rate constant to be 2.5 × 10^{10} M^{-1} s^{-1} with a competitive reaction between reactions 5 and 6, taking k_6 = 8.7 × 10^9 M^{-1} s^{-1}.[19]

Figure 1 shows typical oscillograms of the conductivity change after a pulse irradiation of an argon-saturated $[Co(gly)_3]$ solution containing *tert*-butyl alcohol. In weak acidic media, there was an immediate increase in conductivity ($\Delta\Lambda \approx 430$ Ω^{-1} cm^2 mol^{-1}) at the end of the pulse (curve A in Figure 1). The addition of N$_2$O, which is an effective scavenger of e_{aq}^-, eliminated the occurrence of the immediate increase

(1) (a) Yokohama City University, (b) Hahn-Meitner-Institut Berlin GmBH.
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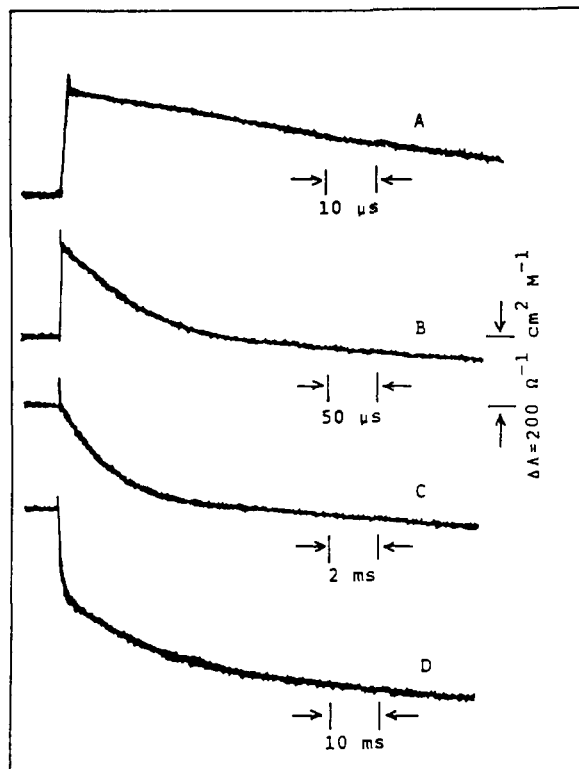(19) Gordon, S.; Hart, E. J.; Matheson, M. S.; Rabani, J.; Thomas, J. L. *Discuss. Faraday Soc.* 1963, 36, 193.

Figure 1. Typical oscillograms of conductivity change with time resulting from a pulse irradiation of an argon-saturated 3.0×10^{-3} M [Co(gly)$_3$] solution containing 0.2 M *tert*-butyl alcohol at pH 3.4.

in conductivity, indicating that it resulted from a reaction involving e_{aq}^-. Part of the increase in conductivity in the argon system decayed rapidly to a lower level as shown in curve A in Figure 1 (the spike at the beginning). This fast process is attributed to a very rapid neutralization reaction of OH$^-$ and H$^+$ formed by eq 1.[14,20] A similar process was observed in the pulse radiolysis of [Co(acac)$_3$].[8] The neutralization reaction is over within less than 1 μs; thus, the conductivity change, $\Delta\Lambda_0$ = 400 Ω^{-1} cm^2 mol^{-1}, observed at the higher pH region after neutralization corresponds to the formation of H$^+$ and [Co(gly)$_3$]$^-$ (reactions 1 and 5). If we assume Λ(Co(gly)$_3^-$) is 40 Ω^{-1} cm^2 mol^{-1}, the expected value is $\Delta\Lambda_0 = \Lambda$(H$^+$) + Λ(Co(gly)$_3^-$) = 350 + 40 = 390 Ω^{-1} cm^2 mol^{-1}, which is in very good agreement with the observed value. The Λ values for [Co(gly)$_3$]$^-$ and [Co(gly)]$^+$ are unknown but are expected to be smaller than Λ(Co$_{aq}^{2+}$) = 55 Ω^{-1} cm^2 mol^{-1}. Thus, the Λ(Co(gly)$_3^-$) and Λ(Co(gly)$^+$) values of about 40 Ω^{-1} cm^2 mol^{-1} are reasonable. $\Delta\Lambda_0$ decreases with the decrease in pH, as shown in Figure 2. Part of the decrease in conductivity in the lower pH region examined is attributed to a contribution of reaction 7 ($k_7 = 2.2 \times 10^{10}$ M^{-1} s^{-1} [17]). About 25% of the e_{aq}^- moieties are transformed into H atoms at pH = 3 via reaction 7 instead of reaction 5. Although a fraction of H atoms (~70%) react

$$H^+ + e_{aq}^- \rightleftharpoons H \quad (7)$$

$$[Co(gly)_3] + H \rightleftharpoons [Co(gly)_2(gly')] + H_2 \quad (8)$$
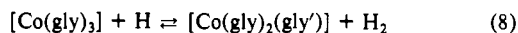
with *tert*-butyl alcohol as stated above, about 30% of the H atoms react with the [Co(gly)$_3$] complex by reaction 8. In eq 8, gly′ denotes a degraded glycinate ion that finally decomposes to NH$_3$, CO$_2$ and other products.[15] Shagisultanova et al.[15] detected H$_2$ in the reaction of [Co(gly)$_3$] with H atoms. We also obtained G(H$_2$) = 0.85 and 4.0 in the γ-radiolysis of [Co(gly)$_3$] in neutral and acidic aqueous solutions, respectively, suggesting that the reaction of [Co(gly)$_3$] with H atoms proceeds via reaction 8. $\Delta\Lambda_0$ in the lower pH region is somewhat smaller than that expected from the mechanism stated above. This lower value may be due to the contribution of equilibrium reaction 9. The pK_a of

$$[Co(gly)_3]^- + H^+ \rightleftharpoons H[Co(gly)_3] \quad (9)$$
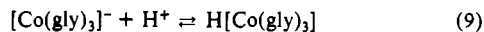
the equilibrium is expected to be smaller than 3.0 from the curve of pH vs $\Delta\Lambda_0$ in Figure 2. Similar species, H[Co(acac)$_3$], H[Cr(acac)$_3$], and H[Ru(acac)$_3$], were assumed in the study of the acetylacetonate ions dissociation from the complexes with acetylacetonate ions.[8]

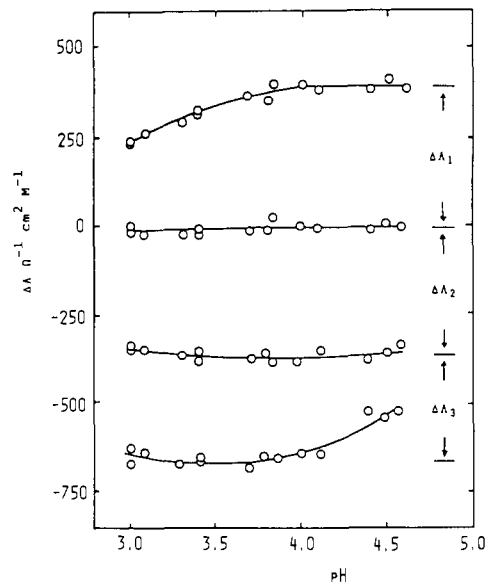**Figure 2.** pH dependence of conductivity changes for the glycinate ion dissociation of [Co(gly)$_3$]$^-$. $\Delta\Lambda_1$, $\Delta\Lambda_2$, and $\Delta\Lambda_3$ denote the conductivity change for the first, second, and third steps of the dissociation, respectively.
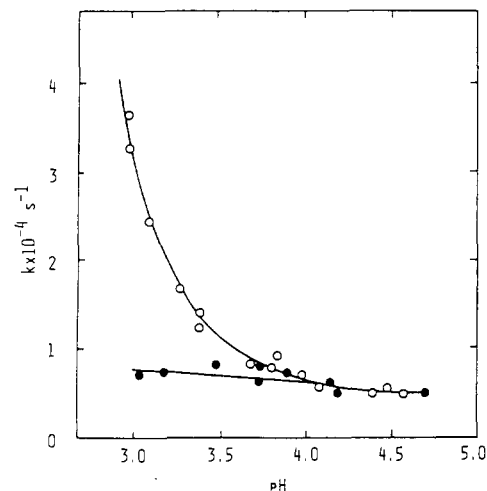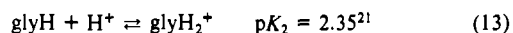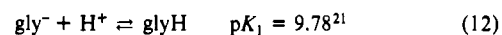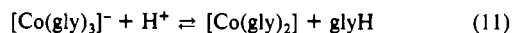

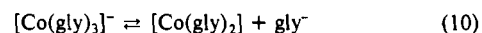**Figure 3.** Rate constants vs. pH for the first step of the glycinate ion dissociation of [Co(gly)$_3$]$^-$: (O) 3.0×10^{-3} M [Co(gly)$_3$] + 0.2 M *tert*-butyl alcohol; (●) N$_2$O-saturated 5.0×10^{-4} M [Co(gly)$_3$].

After the initial increase, conductivity decreased in three steps, which are attributed to the stepwise dissociation of the coordinated three glycinate ions (curves B, C, and D in Figure 1). The changes in the conductivity signals for the first step obeyed first-order kinetics, and the rate constants increased with the decrease in pH, as shown in Figure 3. The first step can be explained by reactions 10–13 (coordinated water molecules are hereafter neglected for simplicity). In the pH region examined, the contribution of reaction 13 is small. The observed rate constants are given by eq 14. The plot of the observed rate constant, k_{obs}, vs [H$^+$]

$$[Co(gly)_3]^- \rightleftharpoons [Co(gly)_2] + gly^- \quad (10)$$

$$[Co(gly)_3]^- + H^+ \rightleftharpoons [Co(gly)_2] + glyH \quad (11)$$

$$gly^- + H^+ \rightleftharpoons glyH \quad pK_1 = 9.78^{21} \quad (12)$$

$$glyH + H^+ \rightleftharpoons glyH_2^+ \quad pK_2 = 2.35^{21} \quad (13)$$

$$k_{obs} = k^0 + k^H[H^+] \quad (14)$$

for the first step gives a straight line. k^H ($= k_{11}$) was estimated to be 2.7 $\times 10^7$ M^{-1} s^{-1} from the slope, and k^0 ($= k_{10}$) = 4.2×10^3 s^{-1} was obtained from the intercept. The changes in the conductivity for second and third steps (curves C and D in Figure 1) also obeyed first-order kinetics and

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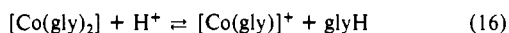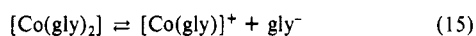(21) King, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 155.

Table I. Kinetic Data for the Aquation Reactions of $[Co(gly)_3]^-$, $[Co(acac)_3]^-$, $[Co(en)_3]^{2+}$, and $[Ni(gly)_3]^{2+}$

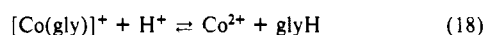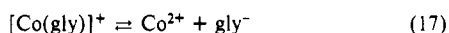| param	$[Co(gly)_3]^{-a}$	$[Co(acac)_3]^{-b}$	$[Co(en)_3]^{2+c}$	$[Ni(gly)_3]^{2+d}$
$k_{3L}^{0,e}$ s^{-1}	4.2×10^3 (3.3×10^3)	8.0×10^3	6.8×10^2	1.1×10
$k_{3L}^{H,e}$ M^{-1} s^{-1}	2.7×10^7	7.2×10^8	6.6×10^6	
k_{2L}^0, s^{-1}	3.5×10^2 (3.3×10^2)	3.0×10	5.0×10	0.93
k_{2L}^H, M^{-1} s^{-1}	8.1×10^5	3.1×10^6	1.4×10^6	
k_L^0, s^{-1}	4.9×10 (3.4×10)	3	1.4×10	0.057
k_L^H, M^{-1} s^{-1}	2.1×10^4	7.5×10^4	3.2×10^5	

[a] The values in parentheses were obtained by a temperature jump method.[10b] [b] Reference 8. [c] Calculated from the original data in the ref 5 (please also see ref 8). [d] Reference 10b. [e] k_{iL}^0 and k_{iL}^H are the non acid catalytic and acid catalytic dissociation rate constants for the ith ligand respectively.

the rate increased with the decrease in pH. The dissociations of glycinate ions can be expressed as follows:

for the second step

$$[Co(gly)_2] \rightleftharpoons [Co(gly)]^+ + gly^- \qquad (15)$$

$$[Co(gly)_2] + H^+ \rightleftharpoons [Co(gly)]^+ + glyH \qquad (16)$$

for the third step

$$[Co(gly)]^+ \rightleftharpoons Co^{2+} + gly^- \qquad (17)$$

$$[Co(gly)]^+ + H^+ \rightleftharpoons Co^{2+} + glyH \qquad (18)$$

In this scheme, reactions 15 and 17 are followed by reaction 12. The plots of k_{obs} vs $[H^+]$ for the second and third steps are linear as in the case of the first step. The rate constants are summarized in Table I.

When the solution was saturated with N_2O, the initial increase in conductivity was not observed. Under these conditions, e_{aq}^- is converted into OH radical (reaction 6), which degrades one coordinated glycinate ion of $[Co(gly)_3]^-$, and the rate constant for the reaction of $[Co(gly)_3]$ with OH radicals was estimated to be 1.5×10^8 M^{-1} s^{-1}. The dissociation rate constant of the degraded glycinate ions was independent of pH (Figure 3). The observed kinetics for the dissociation of the remaining two glycinate ions was very similar to those of the second and third steps in the argon-saturated *tert*-butyl alcohol system.

The magnitude of conductivity change for the first step, $\Delta\Lambda_1$, is shown as a function of pH in Figure 2. In the higher pH region, the observed value $\Delta\Lambda_1 = -410$ Ω^{-1} cm^2 mol^{-1} was in good agreement with the value -390 Ω^{-1} cm^2 mol^{-1} ($=-\Lambda(H^+) - \Lambda(Co(gly)_3^-)$) expected from reactions 10–12. $\Delta\Lambda_1$ decreases with the decrease in pH for the contribution of reactions 7 and 13. If we assume reactions 15, 16, and 12 for the second step and reactions 17, 18, and 12 for the third step, $\Delta\Lambda$ for the second and third steps are expected to be $\Delta\Lambda_2 = -\Lambda(H^+) + \Lambda(Co(gly)^+) = -310$ Ω^{-1} cm^2 mol^{-1} and $\Delta\Lambda_3 = -\Lambda(H^+) - \Lambda(Co(gly)^+) + \Lambda(Co^{2+}) = -280$ Ω^{-1} cm^2 mol^{-1}, respectively. In this calculation, 55 Ω^{-1} cm^2 mol^{-1} is taken as the conductivity of Co^{2+} ion. The observed values were $\Delta\Lambda_2 = -350$ Ω^{-1} cm^2 mol^{-1} and $\Delta\Lambda_3 = -305$ Ω^{-1} cm^2 mol^{-1} (Figure 2). These results indicate that the reactions proposed for each step indeed occur but cause somewhat larger than the expected changes in $\Delta\Lambda$. The difference may be attributed to the contribution of reaction 8.

$\Delta\Lambda_1 = -414$ Ω^{-1} cm^2 mol^{-1}, $\Delta\Lambda_2 = -457$ Ω^{-1} cm^2 mol^{-1}, and $\Delta\Lambda_3 = -401$ Ω^{-1} cm^2 mol^{-1} have been reported for the stepwise dissociation of $[Co(acac)_3]^-$ (the $\Delta\Lambda$ values were the average of values obtained at different $[H^+]$).[8] $\Delta\Lambda_1$ for $[Co(acac)_3]^-$ is very close to that for $[Co(gly)_3]^-$. However, $\Delta\Lambda_2$ and $\Delta\Lambda_3$ for $[Co(acac)_3]^-$ are greater than those for $[Co(gly)_3]^-$ by about 100 Ω^{-1} cm^2 mol^{-1}, indicating that a reaction of $[Co(acac)_3]^-$ with *tert*-butyl alcohol radical partially occurs as suggested by Meisel et al.[8] In the $[Co(gly)_3]^-$ system, $\Delta\Lambda_i$ (the conductivity changes for the dissociation of ith ligand) can be explained reasonably by assuming that e_{aq}^- and part of the H atoms reduce $[Co(gly)_3]^-$ (reactions 5 and 8).

Figure 4 shows typical oscillograms of the conductivity change resulting from a pulse irradiation of an argon-saturated alkaline $[Co(gly)_3]$ solution containing *tert*-butyl alcohol. There was an immediate decrease in conductivity ($\Delta\Lambda_0 = -167$ Ω^{-1} cm^2 mol^{-1}) at the end of the pulse (curve A in Figure 4), which was independent of pH. The decrease is due to the neutralization reaction of H^+ with OH^- and reaction 5 ($\Delta\Lambda_0 = -\Lambda(OH^-) + \Lambda(Co(gly)_3^-) = -198 + 40 = -158$ Ω^{-1} cm^2 mol^{-1}). After the immediate decrease in conductivity, an increase was observed as shown in Figure 4. The first step (curve A) was well separated in time from the second one (curve B), but the third step was not observed clearly. The dissociation reactions of glycinate ions can be explained by assuming reactions 10 and 19 for the first step and reactions 15 and 19
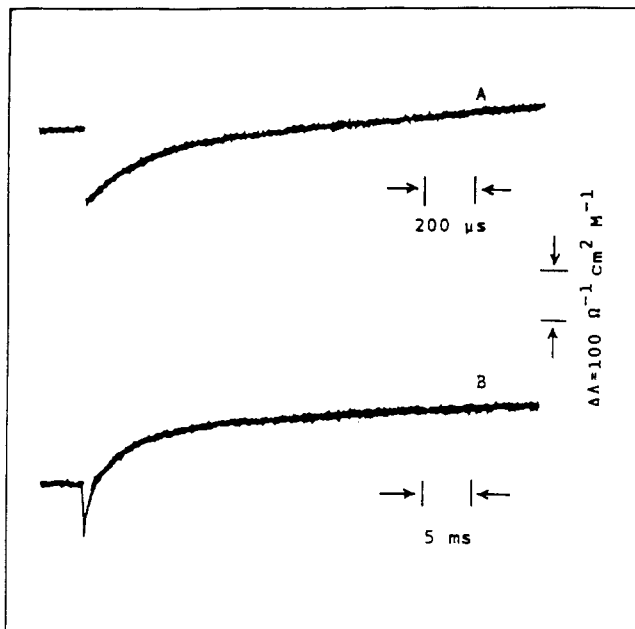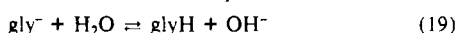
$$gly^- + H_2O \rightleftharpoons glyH + OH^- \qquad (19)$$

Figure 4. Typical oscillograms of conductivity change with time resulting from a pulse irradiation of an argon-saturated 3.0×10^{-3} M $[Co(gly)_3]$ solution containing 0.2 M *tert*-butyl alcohol at pH 8.5.

for the second step. The rate constants for the first and second steps were 4.0×10^3 s^{-1} and 3.3×10^2 s^{-1}, respectively, which were independent of pH, as expected. These rate constants are very close to the k_{3L}^0 and k_{2L}^0 values obtained in acidic medium. Of course, $\Delta\Lambda_i$ for $[Co(gly)_3]^-$ system decreased with the increase in pH for the contribution of equilibrium 19 in the alkaline solution.

Comparison of Dissociation Rates with Those for Some Other Complexes. Two mechanisms are possible for the dissociation of multidentate ligands, depending on whether a proton attaches itself to the donor atoms or to other basic groups in the ligand. The dissociation of Co(II)–en complexes occurs via the former and that of Co(II)–gly⁻ complexes occurs via the latter. In the dissociation of ethylenediamine from $[Co(en)_3]^-$, the free amino group produced by Co–N bond rupture has a chance to re-form the chelate ring at a lower $[H^+]$ before protonation occurs.[5,22] However, a probability of re-forming the chelate decreases with the increase of $[H^+]$, for the protonation of the released amino groups, where the rate law is given by eq 14.[23] The coordinated ethylenediamines have no readily available electrons for bond-attacking protons. Thus, the decomposition will be initiated by the ring opening.[5] In the dissociation of glycinate ion from $[Co(gly)_3]^-$, a coordinated glycinate ion has an attacking point that is the carbonyl of glycinate ion; therefore, the carboxylate end is probably released first. A similar mechanism was suggested for the dissociation mechanism of Ni(II)–gly⁻ complexes.[25a] The following mechanism for the dissociation reactions of $[Co(gly)_3]^-$ would explain the experimental results:
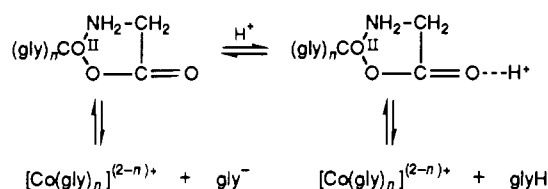
The observed rates were expressed with k_{iL}^0 and k_{iL}^H as stated above, and the values of k_{iL}^0 were in agreement with those obtained by temperature jump method[10] (Table I). Pearson et al.[22] also obtained a similar k_{3L}^0 value for $[Co(gly)_3]^-$ by using an NMR line-broadening method. The magnitudes of k_{iL}^0 and k_{iL}^H for $[Co(gly)_3]^-$ and $[Co(acac)_3]^-$

(22) Pearson, R. G.; Lanier, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 765.
(23) The rate law for the mechanism given for the ligand dissociation of $[Co(en)_3]^{2+}$ in ref 5 simplifies to $k_{obs} = K_a$ ($k_b + k_c[H^+]$) $= k^0 + k^H[H^+]$ in a lower $[H^+]$ region. A similar mechanism and the kinetic treatment for the ligand dissociation of nickel complex are given in ref 24.
(24) Childers, R. F.; Wentworth, R. A. D. *Inorg. Chem.* **1969**, *8*, 2218.
(25) (a) Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408. (b) Ahmed, A. K. S.; Wilkins, R. G. *Proc. Chem. Soc., London* **1959**, 399.

strongly depend on the number of ligand molecules on the metal (Table I). The rate constant for the dissociation of the glycinate ion from [Ni(gly)$_3$]$^-$ is independent of pH from pH 7 to 3.5 and becomes enhanced at pH <3.[25b] Similar dependence of k_{fL}^0 on the number of glycinate ions was observed for Ni(II)–gly$^-$ complexes[10,25] as shown in Table I.

Useful information can be obtained by comparing the rate constants. $k_{fL}^0/k_{(f-1)L}^0$ (=7–12) or $k_{fL}^H/k_{(f-1)L}^H$ (=33–40) for both Co(II)–gly$^-$ and Co(II)–acac$^-$ complexes are roughly constant with the exception of k_{3L}^0/k_{2L}^0 (=270) or k_{3L}^H/k_{2L}^H (=230) for the acetylacetonate system. k_{3L}^0/k_{2L}^0 or k_{3L}^H/k_{2L}^H for the acetylacetonate system is much larger than that for the glycinate system. It is also known that [Co(acac)$_2$(H$_2$O)$_2$] in a solid state is a trans form.[26] These facts suggest that [Co(acac)$_2$] is more stable than [Co(gly)$_2$] against dissociation, and the geometry change of the [Co(acac)$_2$] complexes upon dissociation might be important. $k_{fL}^0/k_{(f-1)L}^0$ (=12–16)[10b] and $k_{fL}^H/k_{(f-1)L}^H$ (=11–49)[25b] for Ni–gly$^-$ complexes are similar to those of Co-gly$^-$ complex. However, k_{fL}^0 for the nickel complex is smaller than that for the cobalt complex by more than 2 orders of magnitude.

k_{fL}^0(gly)/k_{fL}^0(en) depends little upon the number of ligand molecules on the metal (k_{3L}^0(gly)/k_{3L}^0(en) = 6.2, k_{2L}^0(gly)/k_{2L}^0(en) = 7.0, and k_L^0(gly)/k_L^0(en) = 3.5), on the other hand, k_{fL}^H(gly)/k_{fL}^H(en) depends significantly upon the number of the ligand molecules on the metal

(k_{3L}^H(gly)/k_{3L}^H(en) = 4.1, k_{2L}^H(gly)/k_{2L}^H(en) = 0.58, and k_L^H(gly)/k_L^H(en) = 0.066). This observation might be attributed to the fact that the total charge of the Co(II)–gly$^-$ complex changes in going from [Co(gly)$_3$]$^-$ to [Co(gly)]$^+$, which alters the ease of attack by proton, whereas the charge on Co(II)–en complexes is independent of the number of ligand. From the dissociation rate constants of [Co(gly)$_3$]$^-$ and [Co(acac)$_3$]$^-$, the following ratios of the rates were obtained: k_{3L}^0(acac)/k_{3L}^0(gly) = 1.9, k_{2L}^0(acac)/k_{2L}^0(gly) = 0.09, and k_L^0(acac)/k_L^0(gly) = 0.06 for the acid-independent reactions and k_{3L}^H(acac)/k_{3L}^H(gly) = 27, k_{2L}^H(acac)/k_{2L}^H(gly) = 3.8, and k_L^H(acac)/k_L^H(gly) = 3.6 for the acid-catalytic reactions. These results show that k_{fL}^0(acac) is smaller than k_{fL}^0(gly) by more than 1 order of magnitude with the exception of k_{3L}^0(acac), and k_{fL}^H(acac) is larger than k_{fL}^H(gly). This observation indicates that the dissociation of acetylacetonate ion in [Co(acac)$_3$]$^-$ is more acid catalytic than that in [Co(gly)$_3$]. The mechanism suggested for the aquation reactions of the Co(II)–acac$^-$ complex is that the complex opens one end and the second end dissociates with the assistance of protons[8]. Although the mechanism is different from that of the Co(II)–gly$^-$ complex, the kinetic behavior of [Co(acac)$_3$]$^-$ is very similar to that of [Co(gly)$_3$]$^-$, indicating that the charge of the ligand more strongly influences kinetic behavior rather than the presence or absence of an attacking point for protons on the ligand.

(26) Bullen, R. J. *Acta Crystallogr.* **1959**, *12*, 703.

Synthesis, Electrochemistry, and Kinetic Investigations of Low-Spin Ferrous Bis(difluoroboryl)bis(dioximate) Complexes[1,2]

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The synthesis of new *trans*-Fe(dioxBF$_2$)$_2$(CH$_3$CN)$_2$ complexes (diox = dimethylglyoxime, naphthoquinone dioximate, benzoquinone dioximate) complexes and their conversion to a variety of Fe(dioxBF$_2$)$_2$TL complexes (T or L = acetonitrile, 1-methylimidazole, pyridine, tributyl phosphite, tributylphosphine, *tert*-butyl isocyanide, tosylmethyl isocyanide, carbon monoxide) is described. These complexes display MLCT spectra and rate constants for axial ligation similar to those of the analogous Fe(dioxH)$_2$TL complexes but have Fe(III/II) redox potentials 500 mV greater and ν_{CO} for the carbonyl derivatives some 60 cm^{-1} higher. Kinetic and equilibrium data for the CH$_3$CN derivatives obtained by spectrophotometric and flash-photolysis methods in acetonitrile solution and in toluene are compared with data for other FeN$_4$ systems.

Introduction

Extensive rate and equilibrium data for dissociative axial ligation reactions of complexes of the form *trans*-FeN$_4$TL (where N$_4$ is a planar tetradentate ligand such as bis(dioxime),[3] phthalocyanine,[4] or other macrocyclic ligand[5] and T and L are mono-

(1) Given in part at the 72nd Canadian Chemical Conference and Exhibition, University of Victoria, Victoria, British Columbia, Canada, June 4–8, 1989.

(2) Abbreviations: dmgH, dimethylglyoximate; dmgBF$_2$, (difluoroboryl)dimethylglyoximate; dmgB(Ph)$_2$, (diphenylboryl)dimethylglyoximate; bqdH, benzoquinone dioximate; bqdBF$_2$, (difluoroboryl)benzoquinone dioximate; npqH, naphthoquinone dioximate; npqBF$_2$, (difluoroboryl)-naphthoquinone dioximate; Me$_4$[TIM], 2,3,9,10-tetramethyl-1,2,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; Ph$_4$[TIM], 2,3,9,10-tetraphenyl-1,2,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; Pc, phthalocyanine; TPP, tetraphenylporphyrin; PpIX, protoporphyrin IX dimethyl ester; TAAB, tetrabenzo[*b*,*f*,*j*,*n*]-1,5,9,13-tetraazacyclohexadecane; [14]aneN$_4$, *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; MeIm, 1-methylimidazole; Im, imidazole; BuNC, *n*-butyl isocyanide; TMIC, (*p*-tolylsulfonyl)methyl isocyanide (tosylmethyl isocyanide); py, pyridine; CH$_3$CN, acetonitrile; P(OBu)$_3$, tributyl phosphite; MLCT, metal to ligand charge transfer. Rate constants are designated by k_{-L}^T for dissociation of the ligand L trans to T and by k_{+E}^T for addition of a ligand to the pentacoordinate intermediate trans to T. Equilibrium constants K_{LE}^T are for replacement of L by E trans to T. The shortened forms N (MeIm), PO (P(OBu)$_3$), and A (CH$_3$CN) are used as superscripts and subscripts.

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dentate axial ligands such as imidazoles, pyridines, CO, RNC, PR$_3$, etc.) provide a rich source of quantitative information on metal–ligand bonding involving low-spin Fe(II). The neutral Fe(dioxH)$_2$TL complexes (diox = dmg, npq, bqd) are soluble in noncoordinating solvents but generally have axial labilities orders of magnitude more inert than those of their heme counterparts.[3]

The availability of derivatives containing weaker axial ligands such as acetonitrile could significantly extend the chemistry of these systems. Such complexes may be useful in applications that require high lability and/or high binding constants such as CO scrubbing, catalysis, or possibly dioxygen binding.[6] While cationic Fe(N$_4$)(CH$_3$CN)$_2$$^{2+}$ derivatives are known for N$_4$ = Me$_4$[TIM],[7]

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