diamagnetism with the appropriate Pascal's constants. The conductivities of the complexes in 10^{-3}M solution in anhydrous ethyl alcohol were measured with a WTW (Wissenschaftlich Technische Werkstatten) LBR conductivity bridge at 25 °C. Carbon, nitrogen, and hydrogen were determined using a Perkin-Elmer 240 elemental analyzer.

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Registry No. Co(bpy)$_2$(PhSeO$_2$)$_2$, 63714-24-9; Co(bpy)$_2$(*p*-ClPhSeO$_2$)$_2$, 63714-25-0; Co(bpy)$_2$(*m*-ClPhSeO$_2$)$_2$, 63714-26-1; Co(bpy)$_2$(*p*-BrPhSeO$_2$)$_2$, 63714-27-2; Co(bpy)$_2$(*m*-BrPhSeO$_2$)$_2$, 63714-28-3; Co(bpy)$_2$(*p*-CH$_3$PhSeO$_2$)$_2$, 63743-87-3; Co(bpy)$_2$(*p*-NO$_2$PhSeO$_2$)$_2$, 63743-88-4; Co(*o*-phen)$_2$(PhSeO$_2$)$_2$, 63714-29-4; Co(*o*-phen)$_2$(*p*-ClPhSeO$_2$)$_2$, 63714-30-7; Co(*o*-phen)$_2$(*m*-ClPhSeO$_2$)$_2$, 63714-31-8; Co(*o*-phen)$_2$(*p*-BrPhSeO$_2$)$_2$; 63714-32-9; Co(*o*-phen)$_2$(*m*-BrPhSeO$_2$)$_2$, 63714-33-0; Co(*o*-phen)$_2$(*p*-CH$_3$PhSeO$_2$)$_2$, 63714-34-1; Co(*o*-phen)$_2$(*p*-NO$_2$PhSeO$_2$)$_2$, 63714-35-2; Ni(bpy)$_2$(PhSeO$_2$)$_2$, 63743-89-5; Ni(bpy)$_2$(*p*-ClPhSeO$_2$)$_2$, 63714-13-6; Ni(bpy)$_2$(*m*-ClPhSeO$_2$)$_2$, 63714-14-7; Ni(bpy)$_2$(*p*-BrPhSeO$_2$)$_2$, 63714-15-8; Ni(bpy)$_2$(*m*-BrPhSeO$_2$)$_2$, 63714-16-9; Ni(bpy)$_2$(*p*-CH$_3$PhSeO$_2$)$_2$, 63714-17-0; Ni(*o*-phen)$_2$(PhSeO$_2$)$_2$, 63714-18-1; Ni(*o*-phen)$_2$(*p*-ClPhSeO$_2$)$_2$, 63714-19-2; Ni(*o*-phen)$_2$(*m*-ClPhSeO$_2$)$_2$, 63714-20-5; Ni(*o*-phen)$_2$(*p*-BrPhSeO$_2$)$_2$, 63714-21-6; Ni(*o*-phen)$_2$(*m*-BrPhSeO$_2$)$_2$, 63714-22-7; Ni(*o*-phen)$_2$(*p*-CH$_3$PhSeO$_2$)$_2$, 63714-23-8; Co(H$_2$O)$_2$(PhSeO$_2$)$_2$, 55060-50-9; Co(H$_2$O)$_2$(*p*-ClPhSeO$_2$)$_2$, 55060-51-0; Co(H$_2$O)$_2$(*m*-ClPhSeO$_2$)$_2$, 55060-52-1; Co(H$_2$O)$_2$(*p*-BrPhSeO$_2$)$_2$, 55060-53-2; Co(H$_2$O)$_2$(*m*-BrPhSeO$_2$)$_2$, 55060-54-3; Co(H$_2$O)$_2$(*p*-CH$_3$PhSeO$_2$)$_2$, 55060-55-4; Co(H$_2$O)$_2$(*p*-NO$_2$PhSeO$_2$)$_2$, 55060-56-5; Co(PhSeO$_2$)$_2$, 63743-85-1; Co(*p*-ClPhSeO$_2$)$_2$, 63714-01-2; Co(*m*-ClPhSeO$_2$)$_2$, 63714-02-3; Co(*p*-BrPhSeO$_2$)$_2$, 63714-03-4; Co(*m*-BrPhSeO$_2$)$_2$, 63714-04-5; Co(*p*-CH$_3$PhSeO$_2$)$_2$, 63714-05-6; Co(*p*-NO$_2$PhSeO$_2$)$_2$, 63714-06-7; Ni(H$_2$O)$_2$(PhSeO$_2$)$_2$, 55060-72-5; Ni(H$_2$O)$_2$(*p*-ClPhSeO$_2$)$_2$, 55060-73-6; Ni(H$_2$O)$_2$(*m*-ClPhSeO$_2$)$_2$, 55060-74-7; Ni(H$_2$O)$_2$(*p*-BrPhSeO$_2$)$_2$, 55060-75-8; Ni(H$_2$O)$_2$(*m*-BrPhSeO$_2$)$_2$, 55060-76-9; Ni(PhSeO$_2$)$_2$, 63714-07-8; Ni(*p*-ClPhSeO$_2$)$_2$, 63714-08-9; Ni(*m*-ClPhSeO$_2$)$_2$, 63714-09-0; Ni(*p*-BrPhSeO$_2$)$_2$, 63714-10-3.

Supplementary Material Available: Tables containing analytical data and other physical properties, substituent absorption and out-of-plane ring bending frequencies of the benzeneseleninato ligands, most important infrared bands of 2,2′-bipyridyl and 1,10-phenanthroline derivatives (1700–200 cm^{-1}), and a comparison of the effective positive charges Z^* (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Hahn-Meitner-Institut für Kernforschung Berlin GmbH,
Bereich Strahlenchemie, D 1000 Berlin 39, Germany

Kinetics and Mechanism of Ligand Dissociation of Cobalt(II)–Polyamine Complexes in Aqueous Solution

N. SHINOHARA, J. LILIE,* and M. G. SIMIC

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The kinetics of dissociation of Co(II)–polyamine (en, ethylenediamine; dien, diethylenetriamine; trien, triethylenetetramine), which were formed by the reaction of hydrated electrons e_{aq}^- with the corresponding Co(III) complexes, have been investigated by conductometric pulse radiolysis in weakly acid aqueous solutions. The dissociation (detachment) rate constants for all ligands examined increase with increasing hydrogen ion concentration and attain a limiting value: $[\mathrm{Co(en)_3}]^{2+}$, 1.5×10^4 s^{-1}; $[\mathrm{Co(en)_2(OH_2)_2}]^{2+}$, 1.4×10^3 s^{-1}; $[\mathrm{Co(en)(OH_2)_4}]^{2+}$, 1.7×10^2 s^{-1}; $[\mathrm{Co(dien)_2}]^{2+}$, 1.8×10^4 s^{-1}; $[\mathrm{Co(dien)(OH_2)_3}]^{2+}$, 8.7×10^2 s^{-1}; $[\mathrm{Co(trien)(OH_2)_2}]^{2+}$, 2.1×10^3 s^{-1}. The dissociation of these multidentates proceeds by a proton-catalyzed mechanism in which the first N–Co(II) bond rupture is the rate-determining step. A proton adds to this released amino group and accelerates further dissociation of the rest of the donor groups. The enhancement ratios of rate constants with increasing number of N donors in Co(II)–ammine complexes are larger for dissociation (~7 for the first two NH$_3$) than for formation (~2).

I. Introduction

The kinetics of the stepwise "unwrapping" (peeling off) of multidentate amino ligands from nickel(II)[1-5] and chromium(III)[6-9] have been well investigated in aqueous solution. However, few kinetic data exist on the dissociation of labile chelate complexes containing cobalt(II) as the central atom.

In our preceding paper[10] the dissociation rate constants of some ammine- and polyaminecobalt(II) complexes formed by the reduction with hydrated electrons, e_{aq}^-, were determined. In the case of Co(II)–ammine complexes such as $[\mathrm{Co(NH_3)_6}]^{2+}$, $[\mathrm{Co(NH_3)_5Cl}]^+$, etc., the first three ligands are detached very rapidly ($k > 7 \times 10^5$ s^{-1}) whereas the last three ligands $[\mathrm{Co(NH_3)_3(OH_2)_3}]^{2+}$ are detached successively with rate constants of 6.4×10^4, 8.6×10^3, and 1.1×10^3 s^{-1}. The rate constants are independent of pH in the pH range 3–4.5. On the other hand, Co(II)–polyamine complexes such as ethylenediamine and triethylenetetramine dissociate more slowly and the dissociation rates depend on pH. Further we present the data for the dissociation of Co(dien)$_2^{2+}$ (dien = diethylenetriamine) and discuss the dissociation kinetics and mechanisms in more detail.

II. Experimental Section

$[\mathrm{Co(en)_3}]\mathrm{Br_3}$,[11] $[\mathrm{Co(dien)_2}](\mathrm{ClO_4})_3$,[12] and *cis*-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$[13] were prepared according to the literature and $[\mathrm{Co(en)_3}]\mathrm{Br_3}$ was

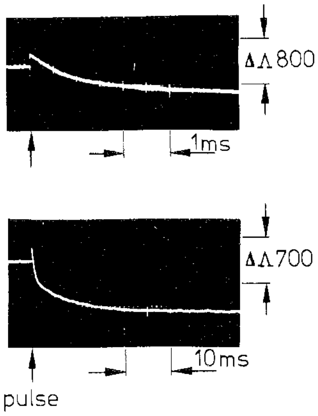


Figure 1. Oscilloscope traces of conductivity vs. time for the dissociation of Co(dien)$^{2+}$ ion at pH 3.5.

changed to the perchlorate salt with silver perchlorate. Other chemicals were A.R. grade and were used without further purification. Perchloric acid was used for pH adjustment. Oxygen in solutions was eliminated by purging the solutions with O_2-free argon. The apparatus and experimental technique have been described previously.[10]

We employed a 10-MHz ac conductivity cell with two pairs of platinum electrodes, one serving as a compensatory pair. The cell was irradiated with 0.5-μs electron pulses from a Van de Graaff generator. The dose per pulse and the cell constant were determined before each series of experiments with tetranitromethane solution. The dose was between 0.5 and 1 krad/pulse which corresponds to $(1.3-2.6) \times 10^{-6}$ M of hydrated electrons. The ionic strength was between 5.0×10^{-3} and 3×10^{-2}.

From the reactive species (e_{aq}^-, OH radicals and H atoms) which are produced by irradiation, the OH radicals and H atoms were scavenged with 0.2 M *tert*-butyl alcohol.

$$C_4H_9OH + OH \rightarrow \cdot C_4H_8OH + H_2O \qquad (1)$$

$$C_4H_9OH + H \rightarrow \cdot C_4H_8OH + H_2 \qquad (2)$$

The resulting *tert*-butyl alcohol radicals do not react with Co(III)-polyamine complexes[15] and do not show any acid-base properties in the pH region investigated. On the other hand, e_{aq}^- reacts with the complexes rapidly ($k \sim 8 \times 10^{10}$ M^{-1} s^{-1}).[16] Thus only the Co(II)-polyamine formed by reaction 3 causes changes in conductivity.

$$\text{Co(III)-polyamine} + e_{aq}^- \rightarrow \text{Co(II)-polyamine} \qquad (3)$$

The data were digitized and transferred to the PDP 11/40 computer by a Biomation 8100 transient recorder and a CAMAC interface. The data analysis was done on line using a Tectronix 4010 interactive graphic display. After checking that there was no dose effect on the rate (the same half-life with a change of the dose per pulse by a factor of 10 was measured), first-order kinetics was applied. When the rates of the different reaction steps were sufficiently different ($k_1/k_2 > 10$), the steps were treated as separate reactions and the end levels for the exponential fit were determined by the calculated change in conductivity ($G = 2.7$, $\Delta\Lambda = -275$ Ω^{-1} cm^2 mol^{-1} for one hydrolysis step) or the Guggenheim method[14] was used which needs no end level. In other cases the differential equations were integrated numerically by the Runge-Kutta method and the calculated curves were fitted to the experimental by variation of the k values.

III. Results and Discussion

(1) pH Dependence of Dissociation. Figure 1 shows a typical oscillogram of the conductance resulting from pulse irradiation of an aqueous 5 mM [Co(dien)$_2$]$^{3+}$ solution. Two steps of first-order kinetics are apparent. The extent of conductivity change for each step of [Co(dien)$_2$]$^{2+}$ dissociation depends on pH. The change for the first step at pH 3 corresponds to the uptake of three protons. Figure 2 shows the pH dependence of the conductivity change for the first step together with the relative fraction of dien species calculated from the pK_a of dien.[17] The change for the second step is smaller than that for the first step. The observed half-lives, $t_{1/2}$, of the dissociation for the first step are shown as a function of pH in Figure 3b. The results clearly demonstrate that the dissociation rates depend on pH.

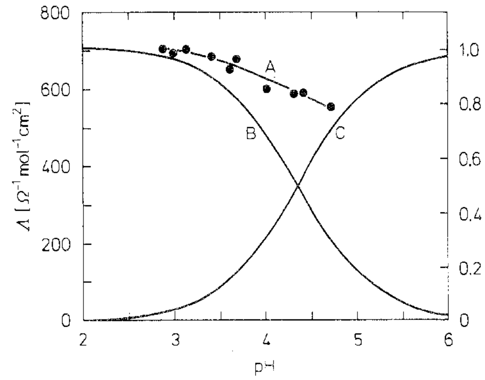


Figure 2. pH dependence of conductivity change for the first step of Co(dien)$_2{}^{2+}$ together with the relative abundance of dien species: A, conductivity; B, the fraction of dienH$_3{}^{3+}$; C, the fraction of dienH$_2{}^{2+}$.

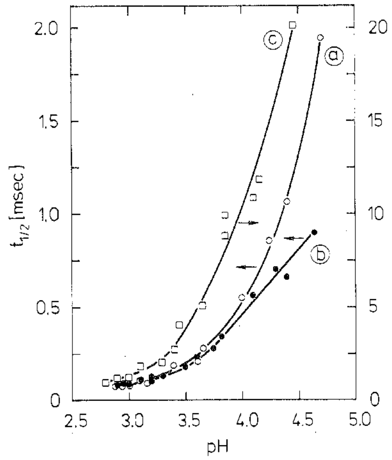


Figure 3. Half-lives vs. pH for the first step of dissociation: (a) [Co(en)$_3$]$^{2+}$, (b) [Co(dien)$_2$]$^{2+}$, (c) [Co(trien)]$^{2+}$.

For [Co(en)$_3$]$^{2+}$ the conductivity vs. time consists of three first-order steps. The extent of conductivity change for each step is pH independent (2.5-4.5) and corresponds to the consumption of two protons. Figure 3a shows the typical relationship between half-lives and pH for the first step of dissociation of [Co(en)$_3$]$^{2+}$. For the dissociation of [Co(trien)Cl$_2$], the two labile Cl$^-$ ligands are released very rapidly ($k > 3 \times 10^5$ s^{-1}) to give [Co(trien)(OH$_2$)$_2$]$^{2+}$. Two steps are observed for the dissociation of [Co(trien)(OH$_2$)$_2$]$^{2+}$ which are of first order. The extent of conductivity change for the first step is almost pH independent (there is a small decrease at higher pH) and corresponds to the consumption of three protons ($\Delta\Lambda = 850$ Ω^{-1} mol^{-1} cm^2). The change for the second step is smaller ($\Delta\Lambda < 150$ Ω^{-1} mol^{-1} cm^2) and depends on pH. The observed half-life for the first step is shown as a function of pH in Figure 3c.

(2) Kinetics and Mechanism of Dissociation. (a) [Co(en)$_3$]$^{2+}$. Three steps were observed for dissociation of [Co(en)$_3$]$^{2+}$, which we assigned[10] to reactions 4, 5, and 6 (for simplicity,

$$[Co(en)_3]^{2+} + 2H^+ \rightarrow [Co(en)_2]^{2+} + enH_2{}^{2+} \qquad (4)$$

$$[Co(en)_2]^{2+} + 2H^+ \rightarrow [Co(en)]^{2+} + enH_2{}^{2+} \qquad (5)$$

$$[Co(en)]^{2+} + 2H^+ \rightarrow Co^{2+} + enH_2{}^{2+} \qquad (6)$$

coordinated water molecules are hereafter neglected). Complete dissociation is in agreement with reported stability constants. Two mechanisms are possible for the acid-catalyzed dissociation of multidentate ligands, depending on whether a proton attaches itself to the donor atoms[1-4,18-20] or to other basic groups in the ligand.[21-26] Since the coordinated poly-

Scheme I

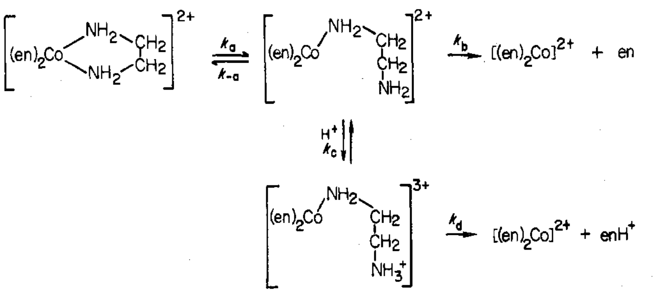


Table I. Rate Constants for Dissociation of Co(II)–Polyamine Complexes at 25 °C

	k_a, s^{-1}	$k_b/(k_{-a} + k_b)$	k_c/k_{-a}
$Co(en)_3^{2+}$	1.5×10^4	2.0×10^{-2}	9.9×10^2
$Co(en)_2^{2+}$	1.4×10^3	7.9×10^{-3}	1.6×10^2
$Co(en)^{2+}$	1.7×10^2	2.0×10^{-3}	5.0×10^3
$Co(dien)_2^{2+}$	1.8×10^4	8.0×10^{-3}	7.2×10^2
$Co(dien)^{2+}$	8.7×10^2	3.4×10^{-3}	1.0×10^3
$Co(trien)^{2+}$	2.1×10^3	7.9×10^{-3}	3.6×10^2

amines have no readily available electrons for bond-attaching protons, only the first mechanism is viable for the investigated Co(II)–polyamine complexes. Hence, the proton reacts with the released amino group of the multidentate ligand only when it becomes detached from the metal ion. Thus Scheme I is suggested for the first step of dissociation of $[Co(en)_3]^{2+}$. Similar schemes were proposed previously for the dissociation of $Ni(en)^{2+}$[1] and $[Co(bpy)]^{2+}$.[20] In Scheme I the intermediates containing monodentated ethylenediamine are assumed to be short-lived as explained later. The released ethylenediamine and monoprotonated ethylenediamine would be protonated, relative to other steps, very rapidly under our experimental conditions ($t_{1/2} < 10^{-5}$ s).

$$en + 2H^+ \rightarrow enH_2^{2+} \tag{7}$$

$$enH^+ + H^+ \rightarrow enH_2^{2+} \tag{8}$$

According to this reaction scheme and considering stationary-state kinetics for the half-bonded unprotonated species the observed rate constant for the consumption of H$^+$, k_{obsd}, will be given by

$$k_{obsd} = \frac{k_a(k_b + k_c[H^+])}{k_{-a} + k_b + k_c[H^+]} \tag{9}$$

A limiting rate will be obtained at sufficiently low pH's; i.e., $k_{obsd} = k_a$ in strong acid media. With the technique used we were unable to measure the limiting rate constant directly; however, it was possible to obtain the extrapolated k_a values by the following procedure. Equation 9 can be rearranged to

$$\frac{1}{k_{obsd}} = \frac{1}{k_a} + \frac{k_{-a}}{k_a(k_b + k_c[H^+])} \tag{9a}$$

At lower pH where $k_b \ll k_c[H^+]$, a plot of $1/k_{obsd}$ vs. $1/[H^+]$ is linear, and k_a is derived by extrapolation to $1/[H^+] = 0$. The graph for the first step of the dissociation of $[Co(en)_3]^{2+}$ is shown in Figure 4 and all pertinent values are given in Table I. k_b is also included; however, its contribution is very small. When a limiting rate constant is reached at higher hydrogen ion concentration, the proton acts as an effective scavenger for the detached amino group in a dynamic equilibrium but it does not catalyze the rate of this release directly.

The effects can be further accounted for by rearranging eq 9 in the following manner

$$\frac{1}{k_a - k_{obsd}} = \frac{k_{-a} + k_b}{k_a k_{-a}} + \frac{k_c}{k_a k_{-a}}[H^+] \tag{9b}$$

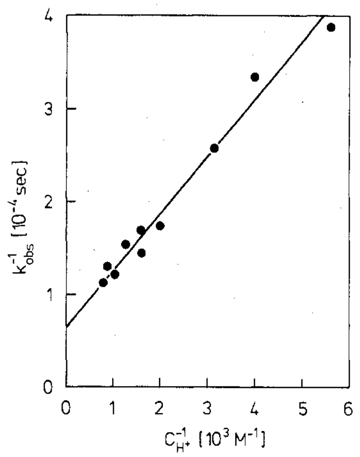


Figure 4. Plot of $1/k_{obsd}$ vs. $1/[H^+]$ for the first step of $[Co(en)_3]^{2+}$ dissociation.

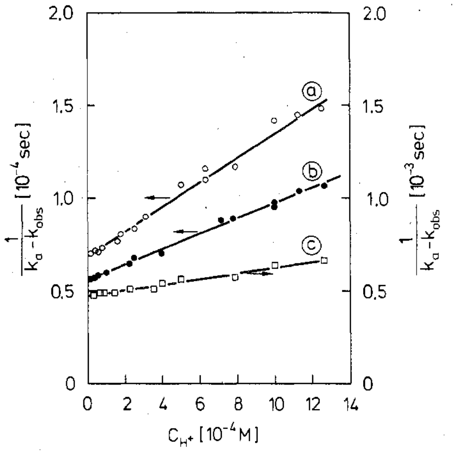


Figure 5. Dependence of $1/(k_a - k_{obsd})$ upon hydrogen ion concentration for the first step of dissociation of Co(II)–polyamine: (a) $[Co(en)_3]^{2+}$, (b) $[Co(dien)_2]^{2+}$, (c) $[Co(trien)]^{2+}$.

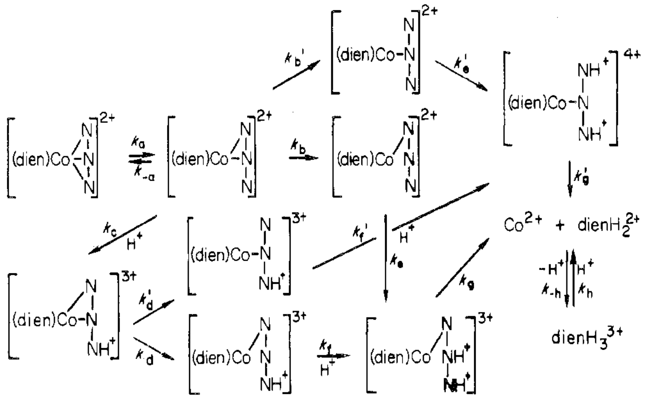
Figure 5a shows the plots of $1/(k_a - k_{obsd})$ vs. $[H^+]$, which is linear as expected from eq 9b. The corresponding values of the rate constants derived from the intercepts and the slopes are listed in Table I.

To summarize briefly, the monoprotonated intermediate $(en)_2Co^{II}NH_2CH_2CH_2NH_3^+$ will decompose very rapidly by the accelerating effect of a charge placed near the reacting donor center. At low hydrogen ion concentration, the free amino group produced by the Co–N bond rupture (reaction a) has a chance to re-form the chelate ring before protonation can occur. However, the probability of re-forming the chelate increases with decreasing hydrogen ion concentration. At lower pH values a limiting value of k is attained, when the detached amino group is scavenged with protons before it can re-form the bond with the metal (intermediates are present mainly as protonated species). Thus there is no rebuilding of the chelate ring and the first bond rupture is the rate-determining step for the dissociation. Furthermore, reaction Scheme I also holds for the dissociation of $[Co(en)_2]^{2+}$ and $[Co(en)]^{2+}$ and the kinetic values for the second and third ligand are also given in Table I.

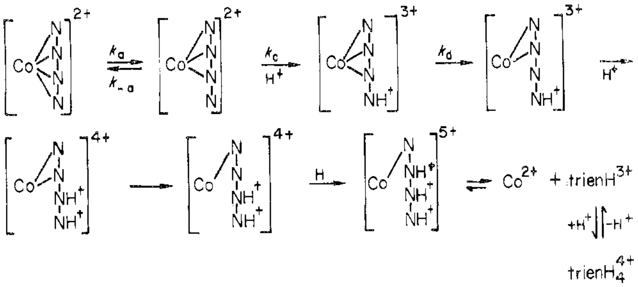
For the dissociation of *trans*-$[Co(en)_2Cl_2]$ which is reduced by e_{aq}^-, the two Cl$^-$ ligands detach rapidly[10] ($k > 3 \times 10^5$ s^{-1}). The dissociation of the resulting $Co(en)_2^{2+}$ corresponds to the second step of $[Co(en)_3]^{2+}$ and in fact the same rate constant values were obtained within experimental error.

(b) $[Co(dien)_2]^{2+}$ Ion. Dissociation of $[Co(dien)_2]^{2+}$ exhibits two steps in the pH region investigated. These two steps can be attributed to the dissociation of a ligand from $[Co(dien)_2]^{2+}$

Scheme II



Scheme III



and $[Co(dien)]^{2+}$ while the steps for dissociation of a single ligand were not resolvable. The limiting rate constants at low pH's are shown in Table I, which are obtained by a similar method as that described for the Co–en system. Considering that the first Co–N bond cleavage of $[Co(dien)_2]^{2+}$ is slow and that the subsequent Co–N bond cleavages are relatively rapid, a reaction scheme similar to the Co–en system can also be applied to this system. However, the kinetics of a dien complex is more complicated due to the length and the increased number of donor groups in the ligand. Rupture of the Co–N bond of a secondary amino group is more difficult than the rupture of the Co–N bond of a primary amino group, especially if the steric factors are taken into consideration. Thus first Co–N bond rupture would involve the primary amino group. The possible reaction paths for the dissociation of the $[Co(dien)_2]^{2+}$ complex are shown in Scheme II (dien and N–N–N stand for $NH_2–CH_2–CH_2–NH–CH_2–CH_2–NH_2$). Assuming stationary-state kinetics for unprotonated bidentated species, eq 9 can be used, with $k_b = k_b + k_b'$. The plots of $1/(k_a - k_{obsd})$ vs. $[H^+]$ for the first step gave a straight line as shown in Figure 5b and the corresponding rate constants are listed in Table I. The results show that reaction c is predominant and the contributions of reactions b and b′ are very small. However, we have no means to decide which of the two reactions is predominant.

The behavior of the free amino group produced by the first Co–N bond rupture (reaction a) will be similar to that in the Co–en system (reaction a in Scheme I) (at higher pH the released amino group can re-form the chelate ring easily). After the first proton addition to the still-bound ligand, the released amino group from the second Co–N bond rupture will be able to rotate away from the central metal ion under the influence of the charged group and become protonated rapidly. Wilkins et al.[3,27] have demonstrated an effect of charge by comparing nickel complexes of $NH_2CH_2CH_2NHCH_2CH_2CH_3$ and $NH_2CH_2CH_2NHCH_2CH_2NH_3^+$ as well as of $NH_2CH_2NMe_3^+$ and NH_3. The second Co–N bond rupture takes place from an unsymmetrical bidentate complex which is in part protonated. If the second bond rupture would involve the Co–N bond of the remaining primary end amino group, the rate should be comparable to the first step and one would observe two steps for the dissociation of one dien molecule.

Hence, the dissociation mechanism of the Co–dien complex is similar to that of the Co–en complex. After protonation of the first released amino group, the subsequent two Co–N bond ruptures proceed rapidly by the electrostatic accelerating effect. Thus the main paths for the dissociation will be c, d, and f.

The height of the conductivity signal for the first step of $Co(dien)_2^{2+}$ dissociation is very similar to that expected from the protonation of dien species calculated by pK_a[17] of dien, as shown in Figure 2. At higher pH the contribution of equilibrium k_h/k_{-h} in Scheme II must be considered. Data analysis appears to be easier at lower pH values. However, due to the fact that protons are good scavengers of e_{aq}^- ($H^+ + e_{aq}^- = H$, $k = 2.3 \times 10^{10}$ M^{-1} s^{-1})[28] an investigation in this pH region (pH <3) is not feasable. For the second step of the dissociation of $[Co(dien)]^{2+}$, we can apply the same reaction scheme. However, the conductivity change for the second step was smaller than that of the first step. This means that equilibrium g for the second step will be shifted toward the complex side because of the higher stability constant of $Co(dien)^{2+}$ compared to that of $Co(dien)_2^{2+}$ and higher concentration of the free dien (one dien released).

(c) $[Co(trien)]^{2+}$ Ion. Two steps were observed in the complete dissociation of $Co(trien)^{2+}$. The main overall dissociation reactions for the first and second step can be attributed to reactions 10 and 11, respectively. The linear plot

$$[Co(trien)]^{2+} + 3H^+ \rightarrow [Co(trien)H_3]^{5+} \quad (10)$$

$$[Co(trien)H_3]^{5+} + H^+ \rightarrow Co^{2+} + trienH_4^{4+} \quad (11)$$

of $1/(k_a - k_{obsd})$ vs. $[H^+]$ for the first step is shown in Figure 5c and the corresponding rate constants are reported in Table I. The results are very similar to the values from the Co–dien system and therefore an equivalent scheme is suggested. The main paths are shown in Scheme III where the path without protonation of the intermediates (k_b) is neglected because of its very small contributions.

As expected from the pK of trien,[29] the threefold protonated intermediate $[Co(trien)H_3]^{5+}$ will be attained by reaction Scheme III similar to that of the Co–dien system. Since the pK of this intermediate is likely to be less than that of $trienH_4^{4+}$ (pK = 3.32),[29] the free amino group of the intermediate will be formed to a high degree as the unprotonated form and the tendency to rearrange the chelate ring is greater than that of further bond rupture. Thus the dissociation rate for the last dissociation can be expected to be slower than for the first ones.

(3) Factors Affecting Ligand Kinetics. Comparison of rate constants for ligand detachment provides essential information concerning the mechanism of dissociation of metal complexes. The rate constants for Co(II) complexes were in most cases too fast to measure by classical techniques. So far, the best understood systems have been the Ni(II) complexes which have relatively slower dissociation rates. Wilkins et al.[3] have reported that for the dissociation of Ni(II)–polyamine complexes in the limiting acid region (where all released amino groups are scavenged by protons) the rupture of the second Ni–N bond is slower than that of the first, and the rupture of the last Ni–N bond is unmeasurably rapid. On the other hand, Margerum, Rorabacher, and Clarke[5] concluded on the basis of indirect evidence that the rupture of the last Ni–N bond is the rate-determining step in the dissociation of the Ni(trien)$^{2+}$ complex.

For the dissociation of Co–en and Co–dien complexes at lower pH (3–5) the first Co–N bond rupture represents the rate-determining step, and it can be expected that complete dissociation even of $Co(trien)^{2+}$ proceeds in one step in stronger acidic media (pH <3).

Table II. Comparison of Rate Constants for Dissociation and Formation and Enhancement Ratios of Ammine Complexes of Co(II) and Ni(II)

Complex	k_d, s^{-1} [a]	k_n/k_{n-1}	k_f, M^{-1} s^{-1} [b]	k_n/k_{n-1}
$Co(NH_3)^{2+}$	1.1×10^3	7.8	1.1×10^5	2.6
$Co(NH_3)_2{}^{2+}$	8.6×10^3	7.5	2.9×10^5	2.0
$Co(NH_3)_3{}^{2+}$	6.4×10^4	>11	5.8×10^5	>5.3
$Co(NH_3)_4{}^{2+}$	$>7 \times 10^5$		$>3 \times 10^6$	
$Ni(NH_3)^{2+}$	5.8[c]		5×10^3 [d]	

[a] From M. G. Simic and J. Lilie, *J. Am. Chem. Soc.*, 96, 291 (1974), and ref 10. [b] Calculated from the formation constants of J. Bjerrum in "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen, 1957, p 188, and footnote *a*. [c] From ref 27. [d] From D. B. Rorabacher, *Inorg. Chem.*, 5, 1891 (1966).

Our conclusion that the initial ring opening is the rate-determining step in the limiting acid region is strongly supported by the following facts. The rate constants k of the first Co–N bond rupture in complexes with the same number of Co–N bonds are the same, e.g., in $[Co(dien)_2]^{2+}$ and $[Cotrien]^{2+}$ are similar to those of $[Co(en)_3]^{2+}$ and $[Co(en)_2]^{2+}$, respectively, and the k_a for $[Co(dien)]^{2+}$ is between those of $[Co(en)_2]^{2+}$ and $[Co(en)]^{2+}$. The successive dissociation steps of $[Co(en)_3]^{3+}$ to the final product Co^{2+} are progressively slower which is similar to the case of $[Ni(en)_3]^{2+}$. The relative rates are 88:8.2:1 for the Co–en system and 600:36:1 for the Ni–en system and can be explained by the labilizing effect of the N donors.[30,31]

The dissociation rate constant of $Co(II)–NH_3$ in ammino complexes was independent of pH[10] in agreement with the mechanism proposed for Co(II)–polyamine complexes. The detached end of the polyamine ligand will remain near Co(II) and can easily re-form the chelate ring if a proton does not add to it. On the other hand in Co(II)–ammino complexes the detached NH_3 can easily, without any constraint, leave the metal ion.

The dissociation rate of $Co(NH_3)_3{}^{2+}$ to $Co(NH_3)_2{}^{2+}$ (Table II) is ca. 30 times more rapid than that of the first ring rupture of $Co(dien)^{2+}$, the complex with the same degree of hydration, and the rate of $Co(NH_3)_2{}^{2+}$ to $Co(NH_3)^{2+}$ is ca. 50 times more rapid than that of the first bond rupture of $Co(en)^{2+}$. This comparison of kinetic data clearly demonstrates a greater barrier for the opening of the chelate ring than for detachment of a monodentate ligand. This could be attributed to the necessary rotation of the chelate ring in the "peeling off" process. On the other hand, ammonia forms hydrogen bonds with water more easily than polyamine ligands which may also favor its replacement by water.

The ratio $k_b/(k_{-a} + k_b)$ in Table I is a measure of the probability for complete dissociation of a ligand once the first Co–N bond has dissociated. For Co(II)–polyamine complexes the ratio is small as shown in Table I. The values are similar to that of $Co(bpy)_3{}^{2+}$ (<0.0045)[20] while for $Fe(bpy)_3{}^{2+}$ the value is much larger (0.16).[19] At low acidity the partly dissociated ligands of Co(II)–polyamine complexes will re-form the chelate ring with a much greater frequency that that of $Fe(bpy)_3{}^{2+}$. The ratios k_c/k_{-a} were larger than 360 for all complexes investigated. This means that at high acidity hydrolysis, k_c, involving protonation is much faster than k_{-a}, thus the dissociation of Co(II)–polyamine complexes mainly proceeds through reaction c. On the other hand, the ratio for $Co(bpy)_3{}^{2+}$ is 1.16. This fact suggests that for the Co(II)–polyamine complexes the protonation reaction of an uncoordinated ligand can occur much more easily than for $Co(bpy)_3{}^{2+}$. This may be attributed to the fact that uncoordinated groups of polyamine–$CH_2CH_2NH_2$ can rotate more easily away from the metal ion than that of bipyridine, while the releasing of the ligands occurs more frequently in the case of the bulky bipyridine ligands than in the case of the more flexible polyamines.

Both formation and dissociation rate constants for Co(II)–ammine complexes are higher than the respective rate constants for Ni(II) complexes (Table II). The trend of change of these rate constants with the number of n donors in Co(II) complexes is in accordance with the exchange enhancement observed for Ni(II)[30,31] and Co(II) complexes.[10] It is interesting to note, though, that the enhancement for dissociation of reaction 12 is about 2 or 3 times larger than

$$Co(NH_3)_n(OH_2)_m \rightleftharpoons Co(NH_3)_{n-1}(OH_2)_{m+1}{}^{2+} + NH_3 \qquad (12)$$

for the formation (see Table II). The enhancement ratios appear to increase with increasing number of N donors. However, the lack of kinetic information beyond four N donors does not allow us to generalize the finding. Further confirmation of stronger labilization of N donor than water molecules by N donors is necessary in other complexes, although the choice is rather limited in view of additional complexities associated with multidentates.

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Registry No. $[Co(en)_3]^{2+}$, 14878-41-2; $[Co(dien)_2]^{2+}$, 18703-28-1; $[Co(trien)(OH_2)_2]^{2+}$, 29871-98-5.

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