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Mechanism of the Deoxygenation and the Ligand-Substitution Reactions of μ -Peroxo-bis[amminebis(ethylenediamine)cobalt(III)] Ions in Aqueous Solution

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Kinetics of the three apparently different reactions of $[(en)_2(NH_3)Co^{III}(\mu-O_2^2-)Co^{III}(NH_3)(en)_2]^{4+}$ (**1**) (*en* = ethylenediamine) have been studied in aqueous solutions at $I = 0.1 \text{ mol dm}^{-3}$ ($NaClO_4$) and at 15–25 °C, i.e., (i) decomposition to Co^{II} and O_2 (pH 1.1–10.2), (ii) spontaneous conversion into $[(en)_2Co^{III}(\mu-OH,O_2^2-)Co^{III}(en)_2]^{3+}$ (**2**) (pH 8.4–9.9), and (iii) reaction with NO_2^- to give *trans*- $[(en)_2(NO_2)Co^{III}(\mu-O_2^2-)Co^{III}(NO_2)(en)_2]^{2+}$ (**3**) (pH 8.4–9.8). Rates of all the reactions are almost identical and are first order with respect to the concentration of **1** and independent of the concentrations of other species in the solution including $[H^+]$, $[NO_2^-]$, and $[EDTA]$. The common first-order rate constant is $(4.9 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$ at 25 °C with activation parameters $\Delta H^\ddagger = 132 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 151 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$. The common rate-determining step for all three reactions is suggested to be the decomposition of **1** to Co^{II} and O_2 . **2** and **3** should be formed rapidly from the cobalt(II) complexes and O_2 .

Peroxo-bridged dicobalt(III) complexes are often regarded as models of biological oxygen carriers.^{1–3} The following μ -peroxo complexes will appear in this paper:⁴ $[(L)(NH_3)Co^{III}(\mu-O_2^2-)Co^{III}(NH_3)(L)]^{4+}$, $L = 2 \text{ en}$ (**1**), 2 R-pn (**4**), **trien** (**5**), **tren** (**6**); $[(L)Co^{III}(\mu-OH,O_2^2-)Co^{III}(L)]^{3+}$, $L = 2 \text{ en}$ (**2**), 2 R-pn (**7**), **trien** (**8**), **tren** (**9**); $[(en)_2(NO_2)Co^{III}(\mu-O_2^2-)Co^{III}(NO_2)(en)_2]^{2+}$ (**3**); $[(\text{tren})Co^{III}(\mu-O_2^2-,\text{tren})Co^{III}(\text{tren})]^{4+}$ (**10**); $[(\text{tren})(CH_3NH_2)Co^{III}(\mu-O_2^2-)Co^{III}(CH_3NH_2)(\text{tren})]^{4+}$ (**11**). These dicobalt(III) complexes undergo ligand-substitution reactions that are unusually rapid for substitution-inert cobalt(III) complexes.^{5–11} The complexes $[(L)(NH_3)Co^{III}(\mu-O_2^2-)Co^{III}(NH_3)(L)]^{4+}$ lose coordinated NH_3 in aqueous basic solution to give $[(L)Co^{III}(\mu-OH,O_2^2-)Co^{III}(L)]^{3+}$ within ca. 1 h at room temperature.^{5,7,8} The complex **10** also loses its bridging **tren** ligand to give **9**.⁹ Shibahara and Mori reported that NO_2^- or NCS^- readily substitutes for the NH_3 molecules in **1** and isolated the products.⁶ The geometrical structure of **1** is not known. However, the location of NO_2^- in **3** was revealed by X-ray crystallography to be *trans* to the bridging peroxide.¹² This is interesting since OH^- and O_2^{2-} in **2** are obviously *cis* to each other.

Fallab and his co-workers found that the rate of the conversion of **6** into **9** in basic solution is almost identical with that of the rate of the decomposition of **6** to Co^{II} and O_2 in acid solution.⁹ Very recently they showed that the rate of O_2 exchange of **11** with dioxygen in water is identical with that of its conversion into **9**.¹¹ They thus concluded that the rate-determining step for the reaction **11** \rightarrow **9** is the decomposition of **11** to Co^{II} and O_2 rather than the direct substitution at the Co^{III} center of **11**.¹¹

We have been studying the kinetics of the "unusually rapid substitution reactions" of **1** as well as its decomposition to Co^{II} and O_2 and have reached the conclusion that the rate-determining step for the "substitution reactions" is the decomposition to Co^{II} and O_2 .

Experimental Section

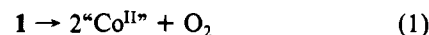
Materials. μ -Peroxo-bis[amminebis(ethylenediamine)cobalt(III)] perchlorate dihydrate, $[(en)_2(NH_3)Co^{III}(\mu-O_2^2-)Co^{III}(NH_3)(en)_2](ClO_4)_4 \cdot 2H_2O$, and μ -peroxo-bis[ammine(triethylenetetramine)cobalt(III)] perchlorate, $[(\text{trien})(NH_3)Co^{III}(\mu-O_2^2-)Co^{III}(NH_3)(\text{trien})](ClO_4)_4$, were prepared as stated previously.^{5,13} *R-pn* and *R-chxn*⁴ were obtained as in the literature.^{14,15}

Measurements. Ultraviolet and visible absorption spectra were recorded with a Hitachi 323 spectrophotometer and with a Hitachi 124 spectrophotometer with a Hitachi QPD-34 recorder. The latter was used also for the kinetic runs. A Metrohm Herisau E300B pH meter was used for the measurement of pH values. Circular dichroism spectra were recorded with a JASCO J-40A spectropolarimeter.

Kinetic Runs. Solutions containing appropriate amounts of reagents were thermostated for at least 20 min. The weighed μ -peroxo complex was quickly dissolved, and the change in absorbance was followed at a given wavelength (between 295 and 400 nm). The reaction cell was shaken quickly at appropriate time intervals to remove the bubbles of dioxygen formed by the reaction. In the presence of excesses of Co^{II} and *en*, the procedure was carried out under nitrogen atmosphere.

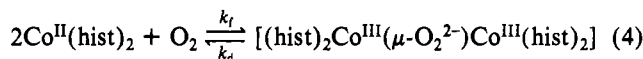
Results and Discussion

Reactions 1–3 were studied. The reaction (1) was observed



in acidic aqueous solutions. The initial product may be $[Co^{II}(en)_2(NH_3)(H_2O)]^{2+}$, which rapidly undergoes ligand-substitution reactions to give a variety of cobalt(II) complexes shown by " Co^{II} " in (1), depending on the conditions. **1** undergoes reaction 2 in basic solutions. However, in the presence of EDTA,¹⁶ **1** undergoes the reaction (1) instead of (2). The reaction (3) occurs in the presence of an excess of nitrite ions in a basic solution without EDTA.

Reaction 1. a. Procedures for the Kinetic Measurement. Simplicio and Wilkins measured the k_d and k_f of the reaction (4).^{4,17} The equilibrium (4) is shifted to the right-hand side



in a basic solution, and the μ -peroxo complex is not formed

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Table I. First-Order Rate Constants, k_d , for the Reaction (1) in Aqueous Solution, $I = 0.1$ M (NaClO_4), Followed at 295 nm

temp/ $^{\circ}\text{C}^a$	pH ^b	[1]/ 10^{-4} M	[EDTA]/ 10^{-3} M	$k_d/10^3$ s^{-1}
15.0	8.8	1.00	1.00	0.69
	9.9	1.00	1.00	0.70
20.0	3.6	0.61	0	1.95 ^c
	1.1	0.89	0	2.05 ^c
21.0	8.5	0.98	1.00	1.99
	8.5	1.00	1.00	1.83
	9.1	1.05	1.00	1.89
	9.6	1.05	1.00	1.87
	10.2	0.94	1.00	1.89
	8.6	1.81	1.00	1.94 ^d
	8.8	4.46	1.00	1.97 ^e
	8.9	1.00	0.20	2.09
	8.9	1.01	0.40	2.01
	8.2	1.00	2.00	1.83
	8.9	1.02	1.00	1.99 ^f
25.0	8.9	1.00	1.00	2.06 ^g
	8.4	0.96	1.00	4.87 ^h
	8.7	1.10	1.00	4.89
	9.8	0.86	1.00	4.68
	4.8	0.68	0	4.95 ^d
	3.6	2.09	0	5.10 ^d
	3.6	1.00	0	4.87 ^c
	1.1	0.78	0	4.76 ^c

^a ± 0.3 $^{\circ}\text{C}$. ^b Buffers: pH 8.2–10.2, ammonia buffer (0.01 M); pH 3.6–4.8, acetate buffer (0.02 M); pH 1.1, 0.1 M HClO_4 . ^c At 300 nm. ^d At 360 nm. ^e At 400 nm. ^f Buffer concentration 5.1×10^{-2} M. ^g Buffer concentration 3×10^{-2} M. ^h At 310 nm.

at all in an acidic solution. They measured the k_d in basic solution, by use of dithionate ions and EDTA for scavenging O_2 and Co^{II} , respectively. Addition of aqueous acid to the neutral solution of $[(\text{hist})_2\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{hist})_2]$ also resulted in the deoxygenation.¹⁷ The concentrations of dithionate ions, EDTA, and H^+ (pH 3–5) did not affect the deoxygenation rate. The first-order rate constants obtained by the three methods were almost identical with one another. The last two methods were applied to the measurement of the deoxygenation rate of $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{NH}_3)_5]^{4+}$.^{18,19}

The rate of deoxygenation of **1** was successfully measured in a wide range of pH by the EDTA and the "acidification" methods.

b. Kinetics. The first-order plot of $\log(D_{\infty} - D_t)$ vs. t (D_{∞} and D_t refer to the absorbances at infinite time and time t , respectively) is straight except for a first few minutes. The perchlorate salt of **1** dissolves in water very slowly, which brought about the initial deviation from the straight line. First-order rate constants (k_d) were obtained from the linear part of the plots and are summarized in Table I. It is seen that k_d is independent of pH (1.1–10.2). The pH in basic solutions was adjusted by the use of $\text{NH}_3\text{-NH}_4^+$ buffer. The k_d is independent of [EDTA] ($(0.2\text{--}2.0) \times 10^{-3}$ M) ($M = \text{mol dm}^{-3}$), $[\text{NH}_3] + [\text{NH}_4^+]$ ($(1\text{--}5) \times 10^{-2}$ M), the initial concentration of the complex ($(1.0\text{--}4.5) \times 10^{-4}$ M), and the wavelength at which the kinetics was followed (295–400 nm). Insensitivity of k_d to such factors clearly indicates that the measured rates correspond to the decomposition of **1** to Co^{II} and O_2 . The average values of k_d at 15, 21 and 25 $^{\circ}\text{C}$ are $(6.9 \pm 0.1) \times 10^{-4}$, $(1.9 \pm 0.1) \times 10^{-3}$, and $(4.9 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$, respectively. The activation parameters are $\Delta H^{\ddagger} = 132 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = 151 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$.

The k_d was constant over the wide range of pH also for the decomposition of $[(\text{hist})_2\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{hist})_2]$ ¹⁷ and $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{NH}_3)_5]^{4+}$.^{18,19} It is generally understood for the decomposition of the μ -peroxo-dicobalt com-

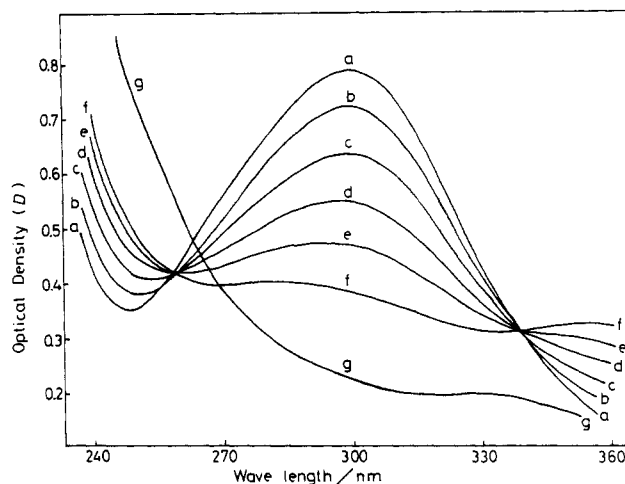


Figure 1. Change in absorption spectra of 8×10^{-5} M $[(\text{en})_2\text{-(NH}_3\text{)Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{NH}_3)(\text{en})_2]^{4+}$ in 0.01 M NaClO_4 solution at ca. 17 $^{\circ}\text{C}$: (a) immediately after dissolution; (b) after 10 min; (c) after 20 min; (d) after 35 min; (e) after 55 min; (f) after 2 h; (g) after 2 days.

plexes^{1,17-19} that the rate-determining step is the formation of uninuclear $\text{Co}^{\text{III}}\text{-O}_2^-$ complex and Co^{II} rather than the successive decomposition of the hyperoxo complex to Co^{II} and O_2 . Such a conclusion seems to be applicable to the present reaction, since there is no spectroscopic or kinetic evidence for the accumulation of a detectable amount of intermediate uninuclear $\text{Co}^{\text{III}}\text{-O}_2^-$ complex, which should therefore decompose rapidly.

The elementary reaction at the rate-determining step can be either the electron transfer from O_2^{2-} to one of the Co^{III} atoms in **1** or the following break of the $\text{Co}^{\text{II}}\text{-O}_2^-$ bond. The bond break would be liable to pH dependence, since the conjugate-base pathway involving the deprotonation of coordinated amines is likely in a basic solution particularly at a high pH. Therefore the rate-controlling factor must be the ease with which an electron is transferred intramolecularly from peroxide to one of the Co^{III} ions.¹⁹

Reaction 2. a. Preliminary Observations. The change in absorption spectrum of an aqueous solution (no buffer added) of **1** is shown in Figure 1. The peak of **1** at 295 nm slowly disappears, and a new peak appears at 360 nm corresponding to the formation of **2**.⁵ An isosbestic point is observed at 337 nm except at the very initial stage. Another isosbestic point is less clear at ca. 260 nm. Slow dissolution of the perchlorate of **1** in water should be responsible at least partly for the absence of an isosbestic point at 337 nm at the initial stage. Slow deviation at the later stage (curve g in Figure 1) must correspond to the decomposition of **2** to uninuclear Co^{III} complexes.^{20,21} Both influences would be responsible for the less clear isosbestic point at ca. 260 nm.

The pH of the aqueous solution of **1** changed as shown in Figure 2 (15 $^{\circ}\text{C}$). The pH first increases sharply, then stays almost constant for ca. 15 min, and finally starts to decrease almost linearly with time. Since the decrease in pH proceeded for more than 100 min, it should correspond to the decomposition of **2** to uninuclear Co^{III} complexes. The conversion of **1** into **2** is accompanied by a small change in pH. The initial sharp increase in pH may suggest that the effective formation of **2** from **1** requires a pH as high as ca. 9 (vide infra).

Quantitative kinetic study of the reaction (2) was difficult at a constant pH, since buffer components affected the reaction. The buffer components interact most probably with

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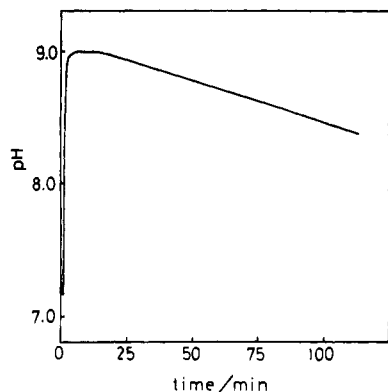


Figure 2. pH change of a solution of 1.26×10^{-4} M $[(en)_2(NH_3)Co^{III}(\mu-O_2^{2-})Co^{III}(NH_3)(en)_2]^{4+}$ during the course of spontaneous conversion into $[(en)_2Co^{III}(\mu-OH,O_2^{2-})Co^{III}(en)_2]^{3+}$ at 15 °C ($I = 0.01$ M $(NaClO_4)$).

Table II. First-Order Rate Constants, k_{OH} , for the Reaction (2) in Aqueous Basic Solutions, $I = 0.1$ M $(NaClO_4)$, Followed at 360 nm

temp/ °C	[1]/ 10^{-4} M	k_{OH} / 10^{-3} s^{-1}	remarks
15.0	2.24	0.71	pH 9.3 (borate buffer, 10^{-3} M) ^a
	2.49	0.75	pH 9.3 (borate buffer, 10^{-3} M) ^a
	2.40	0.73	no buffer ^{a,c}
	2.60	0.74	no buffer ^{a,c}
21.0	1.03	2.1	no buffer ^c
	1.05	2.2	no buffer ^{a,c}
	0.96	4.9	pH 8.4 (ammonia buffer, 10^{-2} M) ^b
25.0	0.96	4.7	pH 8.9 (ammonia buffer, 10^{-2} M) ^b
	0.85	5.2	pH 9.9 (ammonia buffer, 10^{-2} M) ^b
	0.95	5.0	10^{-5} M NaOH soln
	0.77	5.2	no buffer ^c
	0.95	4.8	no buffer ^c

^a $I = 0.01$ M. ^b 0.0018 M ethylenediamine added. ^c Where no buffer was used, the pH of the solution changed from ca. 7 to ca. 9 (see Figure 2).

the Co^{II} state formed by the decomposition of **1** and affect the quantitative formation of **2** in various degrees and ways depending on the conditions. When the phosphate or borate concentration was more than 10^{-3} M, **2** was not quantitatively produced. The conversion of **1** into **2** is favored by the decrease in concentration of $[NH_3] + [NH_4^+]$ at a given pH and by the increase in pH at a given buffer concentration. **2** is formed at pH > 8 in 0.01 M ammonia buffer and at pH > 7 in 10^{-4} M buffer. The absorption peak at ca. 300 nm remained at higher buffer concentrations, but its location changed slightly depending on pH and the buffer concentration. Since the peak at ca. 300 nm is characteristic of a single-bridged μ -peroxo structure,^{2,5} a part of coordinated en must be replaced by NH_3 under such a condition.

b. Kinetics. The rate of conversion of **1** into **2** was followed in aqueous solution mainly without buffer. The absorbance at infinite time was obtained sometimes with difficulty, particularly when the reaction was followed at lower wavelength (<300 nm). This owes to the slow conversion of **2** into un-nuclear cobalt(III) complexes. The first-order rate constant was thus evaluated by the Guggenheim method.²² The plot of $\log(D_{t+\Delta t} - D_i)$ vs. t (Δt is 2–3 times the half-life of the reaction) gave a reasonable straight line except for the initial period. The deviation is due to the slow dissolution of the complex in aqueous solutions as mentioned for the reaction (1). The first-order rate constant (k_{OH}) is given in Table II.

Table III. First-Order Rate Constants, $k_{NO_2^-}$, for the Reaction (3) in Aqueous Solution ($I = 0.1$ M $(NaClO_4)$, Ammonia Buffer (10^{-2} M), $[en] = 0.002$ M) at 25 °C

pH	[1]/ 10^{-5} M	$[NO_2^-]/10^{-2}$ M	$k_{NO_2^-}/10^{-3}$ s^{-1}
8.4	7.1	1.39	4.91 ^a
8.4	8.3	0.28	4.88 ^b
8.4	5.9	1.39	4.68 ^b
9.8	5.3	1.39	4.64 ^b

^a The reaction was followed at 320 nm. ^b At 360 nm. ^c en = ethylenediamine.

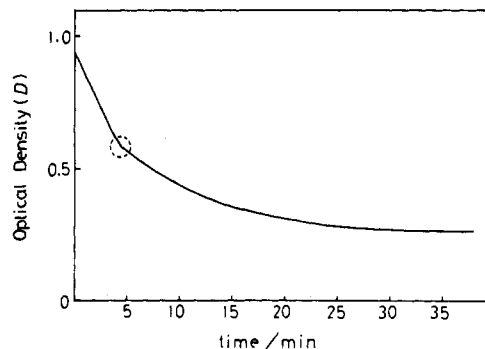


Figure 3. Change in optical density at 295 nm of a solution containing 1×10^{-4} M $[(en)_2(NH_3)Co^{III}(\mu-O_2^{2-})Co^{III}(NH_3)(en)_2]^{4+}$ and 1×10^{-4} M EDTA ($I = 0.1$ M $(NaClO_4)$) at pH 8.8 (ammonia buffer, 0.01 M) and room temperature. A dotted circle shows the point at which the reaction pattern changed (see text).

Although **2** is formed almost quantitatively in ammonia buffer (0.01 M, pH 9.6), the rate constant was considerably smaller than those obtained without buffer. Addition of en or en and Co^{II} (ca. 10^{-3} M) to the buffered solution, however, gave rate constants similar to those in the absence of buffer. Ammonia coordinates to a part of Co^{II} ions produced by the decomposition of **1**. Such Co^{II} species rapidly produce singly bridged μ -peroxo-dicobalt(III) complexes instead of **2**.¹⁷ These single-bridged species are in equilibrium with Co^{II} species, and eventually all the Co turned to **2** irreversibly. These “side reactions” cause an apparent decrease of the rate of conversion of **1** into **2**. If an excess of en is added, the coordination sites of Co^{II} are occupied by en instead of ammonia and the rate of the conversion becomes normal.

The k_{OH} values (normal) were independent of pH (8.4–9.9) in ammonia buffer (10^{-2} M) containing 0.0018 M en. The k_{OH} at 25 °C is $(5.0 \pm 0.2) \times 10^{-3} s^{-1}$, and the activation parameters are $\Delta H^\ddagger = 134 \pm 8$ kJ mol⁻¹ and $\Delta S^\ddagger = 158 \pm 26$ J K⁻¹ mol⁻¹.

Reaction 3. The absorption spectrum of **1** (ca. 5×10^{-5} M) slowly changed in aqueous solution containing $NaNO_2$ (ca. 10^{-2} M). The final spectrum is similar to that of **3**.^{6,12} The first-order rate constant ($k_{NO_2^-}$) for this reaction was obtained in ammonia buffer containing 0.002 M en (Table III). The $k_{NO_2^-}$ value is independent of $[NO_2^-]$ (0.0028–0.014 M) and pH (8.4–9.8). **2** is formed instead of **3** at lower concentrations of NO_2^- (<0.001 M).

Mechanism of the Ligand-Substitution Reactions of 1. Since k_{OH} and $k_{NO_2^-}$ are almost identical with k_d , all the three reactions should have a common rate-determining step. We conclude from the following observation as well as the kinetic results that the rate-determining step for the reactions (2) and (3) is the decomposition of **1** to give Co^{II} and O_2 (reaction 1).

2 and **3** were not produced at all in the presence of EDTA. When the molar ratios of EDTA to **1** were 1:1 and 1:2 ($[1] = 1 \times 10^{-4}$ M), the yields of **2** were 50 and 75%, respectively, at pH 9. The change in absorbance of the 1:1 solution at 300 nm (Figure 3) indicates that **2** is formed after EDTA is

consumed completely by the Co^{II} produced by the decomposition of **1**. When an excess of EDTA was added to the basic solution of **2**, no spectral change was observed within the time scale of the reaction (1).¹ Addition of EDTA to the solution of **3** gave only slow decomposition to Co^{II} and O_2 (1 day to complete at room temperature).²³ Therefore **2** and **3** cannot be the intermediates of the decomposition of **1** in the presence of EDTA. When **1** was converted into a μ -hydroxo- μ -peroxo complex in the presence of an excess of *R*-pn, $\Delta\Delta\text{-}[(R\text{-pn})_2\text{Co}^{\text{III}}(\mu\text{-OH}, \text{O}_2^{2-})\text{Co}^{\text{III}}(R\text{-pn})_2]^{3+}$ was quantitatively formed.⁵ Similarly $\Delta\Delta\text{-}[(R\text{-chxn})_2\text{Co}^{\text{III}}(\mu\text{-OH}, \text{O}_2^{2-})\text{Co}^{\text{III}}(R\text{-chxn})_2]^{3+}$ was formed when an excess of *R*-chxn was added to a solution of **1**. Addition of *R*-pn or *R*-chxn to a solution of **2** did not cause ligand substitution within the time scale of the conversion of **1** into **2**.

All the above observations strongly support the mechanism that the rate-determining step for the reactions (2) and (3) is the decomposition of **1** to Co^{II} and O_2 and exclude the mechanism involving the direct ligand substitution of **1** with rate-determining ammonia liberation. Once **1** is decomposed to Co^{II} and O_2 , rapid ligand substitution should take place on Co^{II} . Concentration of NH_3 produced by the decomposition of **1** would not be sufficiently high to give $[\text{Co}^{\text{II}}(\text{en})_2(\text{NH}_3)(\text{H}_2\text{O})]^{2+}$. Hence $[\text{Co}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ must be the main species that reacts with O_2 to give **2** rapidly.¹ In the presence of NO_2^- , $[\text{Co}^{\text{II}}(\text{NO}_2)(\text{en})_2(\text{H}_2\text{O})]^{2+}$ must be the main intermediate species that reacts with O_2 to give **3**. The "memory" of the geometrical structure of **1** must be lost in the labile Co^{II} state. The present mechanism is similar to that proposed recently by Fallab et al. for the conversion of the tren complex, **11**, into **9**.⁹

The conversion of **1** into **2** produces two ammonia molecules and consumes one hydroxide ion, so that the pH should increase as the conversion proceeds. The pH increases initially, however, and then remains almost constant during the con-

version reaction in an aqueous solution without buffer (Figure 2). Such a behavior indicates that **2** is formed from Co^{II} and O_2 with difficulty at $\text{pH} < 9$. The reaction takes place appreciably after the pH reaches ca. 9 by the decomposition of **1** to give the basic ligands en and NH_3 . Once the reaction starts, the free en and NH_3 act as buffer to keep the pH almost constant.

An alternative explanation for the pH change in Figure 2 may be that the coordinated ammonia molecules in **1** are rapidly lost to give a diaqua complex, $[(\text{en})_2(\text{H}_2\text{O})\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{H}_2\text{O})(\text{en})_2]^{4+}$, which then spontaneously decomposes to Co^{II} and O_2 . This mechanism is excluded, however, by the comparison with the behavior of trien complexes. We observed that the single-bridged trien-ammonia complex **5** was converted into a μ -hydroxo- μ -peroxo-trien complex, **8**, in aqueous solution at a rate similar to that of the decomposition of **5** to Co^{II} and O_2 . The first-order rate constant was evaluated with difficulty since **5** consists of more than two geometrical isomers but is in the magnitude of 10^{-3} s^{-1} at 25°C . The change in pH of the solution during the conversion of **5** into **8** is similar to that in Figure 2. Therefore, the mechanisms of the reactions of **1** and **5** should be similar to each other. There are some discrepancies in the literature as to the formation and the lifetime of the diaqua complex $[(\text{en})_2(\text{H}_2\text{O})\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{H}_2\text{O})(\text{en})_2]^{4+}$ from the reaction of $[\text{Co}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ with O_2 to give **2**.^{1,24} On the contrary, $[(\text{trien})(\text{H}_2\text{O})\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{H}_2\text{O})(\text{trien})]^{4+}$ is very likely formed on the reaction of $[\text{Co}^{\text{II}}(\text{trien})(\text{H}_2\text{O})_2]^{2+}$ with O_2 .²⁵ $[(\text{trien})(\text{H}_2\text{O})\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{H}_2\text{O})(\text{trien})]^{4+}$ is, however, converted into **8** within the time scale of the stopped-flow technique.²⁵ Therefore it cannot be the intermediate formed at the initial stage of the slow conversion of **5** into **8**. Such a discussion based on the comparison with the trien system clearly denies the participation of the diaqua complex, $[(\text{en})_2(\text{H}_2\text{O})\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{H}_2\text{O})(\text{en})_2]^{4+}$, as an intermediate in the conversion of **1** into **2**.

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(23) Shibahara et al. reported that **3** in acidic solution gave *trans*- $[\text{Co}^{\text{III}}(\text{NO}_2)(\text{H}_2\text{O})(\text{en})_2]^{2+}$ and $[\text{Co}^{\text{III}}(\text{NO}_2)(\text{HO}_2)(\text{en})_2]^{2+}$ as primary products at a rate much greater than that of the decomposition to Co^{II} and O_2 in basic solution (Shibahara, T.; Kuroya, H.; Mori, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2834.). When a basic solution of **3** was set aside for a few days, slow spectral change was observed. A peak appeared at 360 nm, and the intensity of the peak at ca. 315 nm of **3** decreased. The change seems to correspond to the conversion of **3** into **2**, since addition of EDTA to such an aged solution resulted in complete disappearance of the peak at ca. 315 nm and no change of a peak at 360 nm after a day.

(24) Miller, F.; Simplicio, J.; Wilkins, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 1962.

(25) Miller, F.; Wilkins, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 2687.