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A Kinetic Study of the Anation Reactions of Some Cobalt(III) Complexes Containing Macrocyclic Quadridentate Amine Ligands

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The kinetics of the anation of *trans*-$[Co(OH)(N_4)(H_2O)]^{2+}$ by acetate ions (OAc^-) have been studied at 25 °C and at an ionic strength of 0.10 mol dm^{-3} ($LiClO_4$), and over the pH range from 3.62 to 5.17; N_4 represents a macrocyclic ligand. The reaction is considered to proceed through a dissociative mechanism. The rate constants of the loss of the coordinated water of $[Co(OH)(N_4)(H_2O)]^{2+}$ are estimated to be $(1.4\pm0.2)\times10^{-2}\,s^{-1}$, $(8.9\pm1.6)\times10^{-2}\,s^{-1}$, $(1.0\pm0.1)\times10^{-1}\,s^{-1}$, and $(4.0\pm0.1)\times10^{-1}\,s^{-1}$ for [14]aneN_4,[†] Me_6[14]4,11-dieneN_4, *ms*-Me_6[14]aneN_4, and *rac*-Me_6[14]aneN_4 complexes respectively. These represent the steric acceleration by the methyl groups of the macrocyclic ligands. The anation of the [14]aneN_4 complex by chloride and bromide ions in acetate-buffer solutions has also been investigated. The relative effectiveness of entering groups for the coordination to the pentacoordinate intermediate follows the order: $H_2O < OAc^- < Cl^- < Br^-$. The substitution reaction of $[Co(OH)(N_4)(H_2O)]^{2+}$ is slower than the ascorbate reduction of this complex reported previously. It is concluded that the electron-transfer reaction does not proceed through an inner-sphere mechanism, but through an OH-bridged mechanism.

In a previous paper,1) we reported that the ascorbate reduction of *trans*-diaqua cobalt(III) complexes containing macrocyclic quadridentate amine ligands (Fig. 1) proceeds through an outer-sphere mechanism; however, it has not yet been determined whether *trans*-aquahydroxo complexes are reduced through a substitution-limited inner-sphere mechanism or through an OH-bridged mechanism. The substitution reaction is an important factor in determining the electron-transfer mechanism.

Extensive investigations have been carried out on the kinetics of substitution reactions of cobalt(III) complexes of the type *trans*-$[CoX_2(N_4)]^{n+}$ (N_4=a macrocyclic quadridentate amine ligand and X=a replaceable group such as Cl^-, Br^-, or NO_2^-).2) These reactions are considered to proceed through a dissociative mechanism; the increase of the steric crowding of methyl groups of the macrocyclic ligands accelerates the loss of the leaving group. The kinetics of the substitution reactions of the diaqua and aquahydroxo macrocyclic cobalt(III) complexes, however, have rarely been investigated except for porphyrin complexes.3)

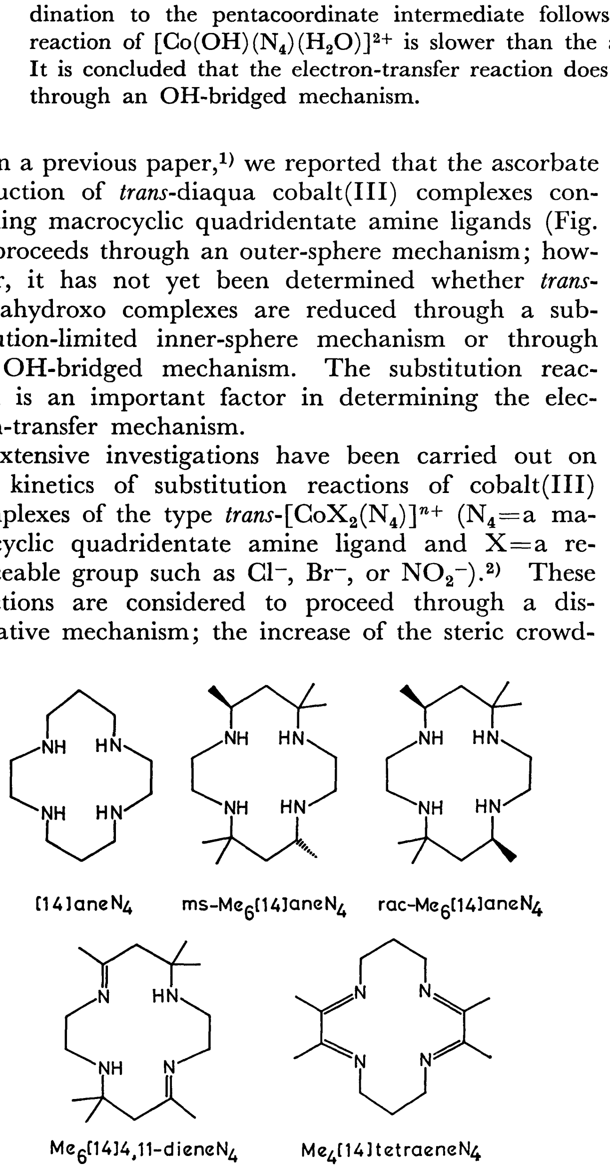

Fig. 1. Structures of tetraazamacrocycles (N_4).

In this paper we report the kinetics of the anation reaction of *trans*-$[Co(OH)(N_4)(H_2O)]^{2+}$ by an acetate ion (OAc^-), Cl^-, or Br^- and estimate the rate constants of the loss of the coordinated water of these complexes. The mechanism of the ascorbate reductions of the aquahydroxo complexes is discussed.

Experimental

Reagents. The *trans*-diaqua complexes [Co([14]aneN_4)$(H_2O)_2$]$(ClO_4)_3$,4) [Co(*ms*-Me_6[14]aneN_4)$(H_2O)_2$]$(ClO_4)_3$,5,6) [Co(*rac*-Me_6[14]aneN_4)$(H_2O)_2$]$(ClO_4)_3$,5,6) [Co(Me_6[14]4,11-dieneN_4)$(H_2O)_2$](ClO)$_3$,6) and [Co(Me_4[14]tetraeneN_4)$(H_2O)_2$]$(ClO_4)_3\cdot2.5H_2O$7) were prepared as has been described elsewhere. The acetate-buffer solutions and the $LiClO_4\cdot3H_2O$ were obtained according to the procedure reported previously.8) All the solutions used for the measurements were prepared from redistilled water. All the other reagents used were of guaranteed grade from Wako Pure Chemical Industries, Ltd.

Kinetic Measurements. Solutions containing a cobalt(III) complex and $LiClO_4$ were added to an optical cell, which was then sealed with a serum cap. After the solution had been purged with a nitrogen atmosphere for 15 min, the reaction was initiated by the injection of the acetate-buffer solution (or the solution containing the acetate buffer and lithium halide for the anation by halide ions). The change in the absorbance with the time was followed with either a Hitachi 200-20 or a Shimadzu UV 140-02 spectrophotometer. The wavelengths used for the measurements were 290 nm ([Co(Me_4[14]tetraeneN_4)$(H_2O)_2$]$^{3+}$), 310 nm ([Co(*rac*-Me_6[14]aneN_4)$(H_2O)_2$]$^{3+}$), 320 nm ([Co([14]aneN_4)$(H_2O)_2$]$^{3+}$ and [Co(*ms*-Me_6[14]aneN_4)$(H_2O)_2$]$^{3+}$), and 345 nm ([Co(Me_6[14]4,11-dieneN_4)$(H_2O)_2$]$^{3+}$). In order to ensure a pseudo-first-order condition, acetate or lithium halide was used in at least a 10^2 fold excess over the cobalt(III) complexes.

The temperature was controlled at 25.0±0.1 °C, and the ionic strength (*I*) was adjusted to 0.10 mol dm^{-3} with

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[†] [14]aneN_4=1,4,8,11-Tetraazacyclotetradecane; *ms*- and *rac*-Me_6[14]aneN_4=*meso*- and *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Me_6[14]4,11-dieneN_4= 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; Me_4[14]tetraeneN_4= 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

lithium perchlorate. The pH of the solution was measured on a Hitachi-Horiba F-7 pH meter. The $[H^+]$ was computed from the pH, using a value of 0.83 for the activity coefficients of H^+.[9)]

Acid-dissociation Constants. The acid-dissociation constants of the diaqua ligands of $[Co(\textit{ms}\text{-}Me_6[14]aneN_4)(H_2O)_2]^{3+}$ and $[Co(\textit{rac}\text{-}Me_6[14]aneN_4)(H_2O)_2]^{3+}$ were determined by pH titrations with a standard sodium hydroxide solution at 25 °C and $I=0.10$ mol dm^{-3} ($LiClO_4$) under a nitrogen atmosphere. The pK values thus obtained are listed in Table 1 along with those in the literature.

Results

Reactions of $[Co(OH)(N_4)(H_2O)]^{2+}$ *with Acetate.* The spectral changes observed during the reaction of $[Co(OH)([14]aneN_4)(H_2O)]^{2+}$ with acetate gave four isosbestic points over the range from 370 to 700 nm (Fig. 2). The absorption maxima of the spectra after the reaction was completed were 360 nm ($\varepsilon=79$ dm^3 mol^{-1} cm^{-1}), 443 nm ($\varepsilon=34$ dm^3 mol^{-1} cm^{-1}), and 565 nm ($\varepsilon=41$ dm^3 mol^{-1} cm^{-1}), which agreed with those of the species separated by the use of an SP-Sephadex C-25 column (H^+ form). This product, which has a 2+ charge in 0.1 mol dm^{-3} $HClO_4$, is considered to be $[Co(OAc)([14]aneN_4)(H_2O)]^{2+}$. In the case of the $Me_6[14]4,11\text{-}dieneN_4$ complex, two isosbestic points (at 549 nm and 630 nm) were observed at pH 4.17. The absorption maximum of the reaction product in this system was 567 nm ($\varepsilon=37$ dm^3 mol^{-1} cm^{-1}). The reaction product in the *ms*-$Me_6[14]aneN_4$ system, on the other hand, had the absorption maxima at 468 nm ($\varepsilon=40$ dm^3 mol^{-1} cm^{-1}) and 577 nm ($\varepsilon=42$ dm^3 mol^{-1} cm^{-1}). These results indicate that the reactions of these complexes with acetate can be represented as follows:

$$[Co(OH)(N_4)(H_2O)]^{2+} \text{ (or } [Co(N_4)(H_2O)_2]^{3+}) + OAc^- \longrightarrow [Co(OAc)(N_4)(H_2O)]^{2+} + H_2O. \tag{1}$$

Table 1. pK values of *trans*-$[Co(N_4)(H_2O_2]^{3+}$ at 25 °C

$$[Co(N_4)(H_2O)_2]^{3+} \overset{K_1}{\rightleftharpoons} [Co(OH)(N_4)(H_2O)]^{2+} + H^+$$

$$[Co(OH)(N_4)(H_2O)]^{2+} \overset{K_2}{\rightleftharpoons} [Co(OH)_2(N_4)]^+ + H^+$$

N_4	pK_1	pK_2	Ref.
$[14]aneN_4$	$2.9 \pm 0.1^{a)}$	$7.2 \pm 0.1^{a)}$	10
ms-$Me_6[14]aneN_4$	$2.7 \pm 0.05^{b)}$	$6.4 \pm 0.05^{b)}$	11
	$3.32 \pm 0.05^{c)}$	$6.6 \pm 0.1^{c)}$	This work
rac-$Me_6[14]aneN_4$	$3.46 \pm 0.05^{c)}$	$7.1 \pm 0.1^{c)}$	This work
$Me_6[14]4,11\text{-}dieneN_4$	$4.02 \pm 0.01^{b)}$	$8.2 \pm 0.1^{b)}$	11
	$3.93 \pm 0.02^{c)}$	$8.6 \pm 0.1^{c)}$	1

a) $I=0.50$ mol dm^{-3} ($NaClO_4$). b) $I=1.0$ mol dm^{-3} ($NaClO_4$). c) $I=0.10$ mol dm^{-3} ($LiClO_4$).

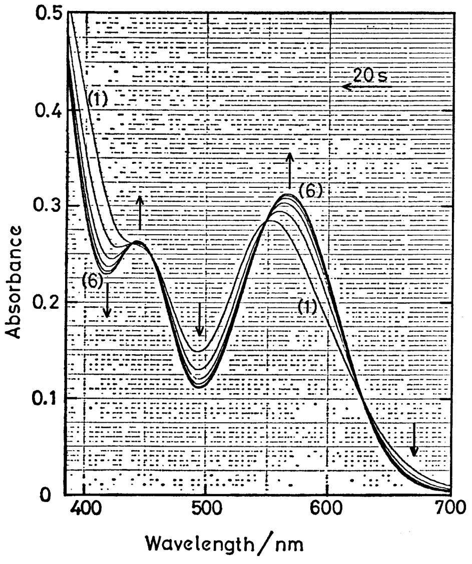


Fig. 2. Spectral changes during the reaction of $[Co([14]aneN_4)(H_2O)_2]^{3+}$ with acetate at $[Co(III)]_0=7.66\times10^{-3}$ mol dm^{-3}, $[OAc]_T=0.250$ mol dm^{-3}, pH=4.17, 25 °C, and $I=0.08$ mol dm^{-3}: (1) 45 s; (2) 4 min 25 s; (3) 8 min 25 s; (4) 12 min 25 s; (5) 17 min 25 s; (6) 25 min 25 s after the reaction. The time given are for the start of scan at 700 nm.

The kinetics of the reactions were studied in various concentrations of acetate (0.020—0.25 mol dm^{-3}), cobalt(III) ((1.00—2.40)$\times10^{-4}$ mol dm^{-3}), and hydrogen ions ((0.82—8.15)$\times10^{-5}$ mol dm^{-3}). The plots of $-\ln(A_\infty - A_t)$ *vs.* the time were linear for at least 90% completion; here A_∞ and A_t represent the absorbance at infinity and time t respectively. The pseudo-first-order rate constant, k_{obsd}, increased with a decrease in the acidity when the total concentrations of acetate ($[OAc]_T$) were fixed. The acid dependency of the rate in the $[14]aneN_4$ system was analyzed as the occurrence of Reactions 2—7:

$$[Co(N_4)(H_2O)_2]^{3+} \overset{K_1}{\rightleftharpoons} [Co(OH)(N_4)(H_2O)]^{2+} + H^+, \tag{2}$$

$$HOAc \overset{K_a}{\rightleftharpoons} H^+ + OAc^- \quad (pK_a=4.53^{12)}), \tag{3}$$

$$[Co(N_4)(H_2O)_2]^{3+} + OAc^- \xrightarrow{k_1} \text{products}, \tag{4}$$

$$[Co(N_4)(H_2O)_2]^{3+} + HOAc \xrightarrow{k_1^H} \text{products}, \tag{5}$$

$$[Co(OH)(N_4)(H_2O)]^{2+} + OAc^- \xrightarrow{k_2} \text{products}, \tag{6}$$

$$[Co(OH)(N_4)(H_2O)]^{2+} + HOAc \xrightarrow{k_2^H} \text{products}. \tag{7}$$

Then, Eq. 8 can be derived for k_{obsd}:

$$k_{obsd} = \frac{k_1^H K_a{}^{-1} + (k_1 + k_2^H K_1 K_2{}^{-1})[H^+]^{-1} + k_2 K_1 [H^+]^{-2}}{(1+K_1[H^+]^{-1})(1+[H^+]K_a{}^{-1})[H^+]^{-1}}. \tag{8}$$

The plots of the values of $k_{obsd}(1+K_1[H^+]^{-1})(1+[H^+]K_a{}^{-1})[H^+]^{-1}$ *vs.* $[H^+]^{-1}$ gave a quadratic curve and the intercept was nearly zero. On the other hand, the plots of the values of $k_{obsd}(1+K_1[H^+]^{-1})\times(1+[H^+]K_a{}^{-1})$ *vs.* $[H^+]^{-1}$ gave a straight line (Fig. 3) and the intercept was very small. Therefore, both k_1 and k_2^H terms can be neglected under the present experimental conditions.[13)] The pseudo-first-order rate constants showed nonlinear dependency on the total concentrations of acetate. The rate law was as follows:

$$-\frac{d[Co(III)]}{dt} = \frac{c[OAc]_T}{a+b[OAc]_T}[Co(III)], \tag{9}$$

where $k_{obsd}=c[OAc]_T/(a+b[OAc]_T)$. The plots of $k_{obsd}{}^{-1}$ *vs.* $[OAc]_T{}^{-1}$ gave straight lines (Fig. 4). The values of a/c and of b/c are obtained from the slope

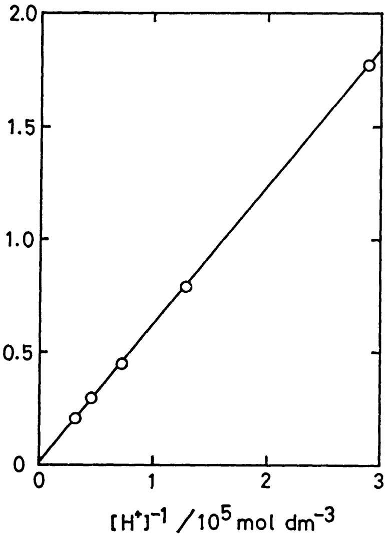


Fig. 3. Plots of $k_{obsd}(1+K_1[H^+]^{-1})(1+[H^+]K_a^{-1})$ *vs.* $[H^+]^{-1}$ for the $[Co([14]aneN_4)(H_2O)_2]^{3+}$–acetate system at $[Co(III)]_0=2.20\times10^{-4}$ mol dm^{-3}, $[OAc]_T=0.100$ mol dm^{-3}, 25 °C, and $I=0.10$ mol dm^{-3} ($LiClO_4$).

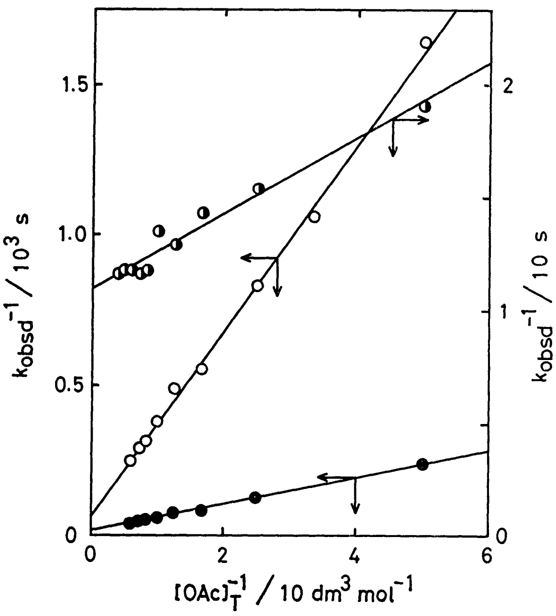


Fig. 4. Plots of k_{obsd}^{-1} *vs.* $[OAc]_T^{-1}$ for the $[Co(N_4)(H_2O)_2]^{3+}$–acetate system at $[Co(III)]_0=2.30\times10^{-4}$ mol dm^{-3}, 25 °C, and $I=0.10$ mol dm^{-3} ($LiClO_4$). ○: The $[14]aneN_4$ complex at pH 4.71, ●: the Me_6-$[14]4,11$-dieneN$_4$ complex at pH 4.71, ◑: the *ms*-$Me_6[14]aneN_4$ complex at pH 4.35.

and the intercept of this straight line respectively. These are explained by either a dissociative mechanism (D-mechanism):

$$[Co(OH)(N_4)(H_2O)]^{2+} \underset{k^{H_2O}}{\overset{k_d}{\rightleftharpoons}} [Co(OH)(N_4)]^{2+} + H_2O, \tag{10}$$

$$[Co(OH)(N_4)]^{2+} + OAc^- \xrightarrow{k_1^{OAc}} [Co(OH)(OAc)(N_4)]^+, \tag{11}$$

$$[Co(OH)(OAc)(N_4)]^+ + H^+ \rightleftharpoons [Co(OAc)(N_4)(H_2O)]^{2+}, \tag{12}$$

or an interchange mechanism (I-mechanism):

$$[Co(OH)(N_4)(H_2O)]^{2+} + X^- \overset{Q^X}{\rightleftharpoons} \{[Co(OH)(N_4)(H_2O)]^{2+}\cdot X^-\} \xrightarrow{k_2^X} \text{products}. \tag{13}$$

These mechanisms lead to Eqs. 14a and 14b respectively (X=OAc):

$$\frac{1}{k_{obsd}}=\frac{1+[H^+]K_1^{-1}}{k_d} + \frac{k^{H_2O}(1+[H^+]K_1^{-1})(1+[H^+]K_a^{-1})}{k_dk_1^{OAc}}\times\frac{1}{[OAc]_T}, \tag{14a}$$

$$\frac{1}{k_{obsd}}=\frac{1}{k_2^{OAc}}+\frac{(1+[H^+]K_1^{-1})(1+[H^+]K_a^{-1})}{k_2^{OAc}Q^{OAc}}\times\frac{1}{[OAc]_T}, \tag{14b}$$

The values of k_d and k_1^{OAc}/k^{H_2O} or of k_2^{OAc} and Q^{OAc} obtained by means of the plots of k_{obsd}^{-1} *vs.* $[OAc]_T^{-1}$ are listed in Table 2.

The pseudo-first-order rate constants for the reactions of the $Me_4[14]$tetraeneN$_4$ complex with acetate and bromide ions are 1.2×10^{-6} s^{-1} at 0.10 mol dm^{-3} acetate and pH 5.17, and 6.3×10^{-7} s^{-1} at $[Br^-]=0.050$ mol dm^{-3}, $[OAc]_T=0.060$ mol dm^{-3}, and pH 5.17.

Reaction of $[Co(OH)([14]aneN_4)(H_2O)]^{2+}$ *with* Cl^-. The title reaction was examined in the presence of acetate. The plots of $-\ln(A_\infty-A_t)$ *vs.* the time were linear for at least 90% completion, when $[OAc]_T \gg [Cl^-]$.[14] Since the anation of $[CoCl([14]aneN_4)(H_2O)]^{2+}$ by Cl^- is very slow ($k=7.6\times10^{-7}$ dm^3 mol^{-1} s^{-1} at 25 °C),[15] the following parallel reactions are considered to occur:

$$[Co(OH)([14]aneN_4)(H_2O)]^{2+} + OAc^- \longrightarrow [Co(OH)(OAc)([14]aneN_4)]^+ + H_2O, \tag{15}$$

$$[Co(OH)([14]aneN_4)(H_2O)]^{2+} + Cl^- \longrightarrow [CoCl(OH)([14]aneN_4)]^+ + H_2O. \tag{16}$$

The pseudo-first-order rate constants show nonlinear dependency on the concentrations of Cl^- ions (Fig. 5). If the following reactions occur in addition to Reactions 10—12;

$$[Co(OH)(N_4)]^{2+} + Cl \xrightarrow{k_1^{Cl}} [CoCl(OH)(N_4)]^+, \tag{17}$$

$$[CoCl(OH)(N_4)]^+ + H^+ \rightleftharpoons [CoCl(N_4)(H_2O)]^{2+}, \tag{18}$$

Eq. 19 can be derived:

$$\frac{1}{k_{obsd}-k_{obsd}^{OAc}}=\frac{1}{k'-k_{obsd}^{OAc}}+\frac{k''}{k'-k_{obsd}^{OAc}}\times\frac{1}{[Cl^-]}. \tag{19}$$

Here k_{obsd}^{OAc} is the pseudo-first-order rate constant in the absence of Cl^-, $k'=k_d/(1+[H^+]K_1^{-1})$, and $k''=k_1^{OAc}/k_1^{Cl}+k_1^{OAc}[OAc]_T/k_1^{Cl}(1+[H^+]K_a^{-1})$. The plots of the left-hand side of Eq. 19 *vs.* $[Cl^-]^{-1}$ gave a linear relation (Fig. 5). The values of k_d and k_1^{OAc}/k_1^{Cl} were determined from the intercept and the slope of this straight line respectively. In the I-mechanism (Reaction 13), k' and k'' correspond to k_2^{Cl} and (1+

TABLE 2. KINETIC DATA OF THE SUBSTITUTION REACTIONS OF $[Co(OH)(N_4)(H_2O)]^{2+}$ AT 25 °C AND $I=0.10$ mol dm^{-3} ($LiClO_4$)

N_4	X	D-Mechanism		I-Mechanism	
		$\frac{k_d}{10^{-2}\ s^{-1}}$	k_1^X/k^{H_2O} a)	$\frac{k_2^X}{10^{-2}\ s^{-1}}$	$\frac{Q^X}{dm^3\ mol^{-1}}$
[14]aneN_4	OAc^-	1.4 ± 0.2	$(2.5\pm0.5)\times10^2$	1.3 ± 0.2	4.7 ± 1.1
	Cl^-	2.1 ± 0.2	$(2.4\pm0.3)\times10^3$	2.0 ± 0.2	$(4.4\pm0.7)\times10$
	Br^-	4.2 ± 2.3	$(4.4\pm2.1)\times10^3$	4.2 ± 2.3	$(8.1\pm4.0)\times10$
ms-Me_6[14]aneN_4	OAc^-	10 ± 1	$(1.2\pm0.2)\times10^4$	9.0 ± 0.3	$(2.4\pm0.3)\times10^2$
rac-Me_6[14]aneN_4	OAc^-	40 ± 2	$(1.9\pm0.4)\times10^3$	27 ± 5	$(5.2\pm2.0)\times10$
Me_6[14]4,11-dieneN_4	OAc^-	8.9 ± 1.6	$(2.9\pm0.7)\times10^2$	7.7 ± 1.9	6.2 ± 1.7

a) These are multiplied by 55.5 to make a correction for the concentration of the water.

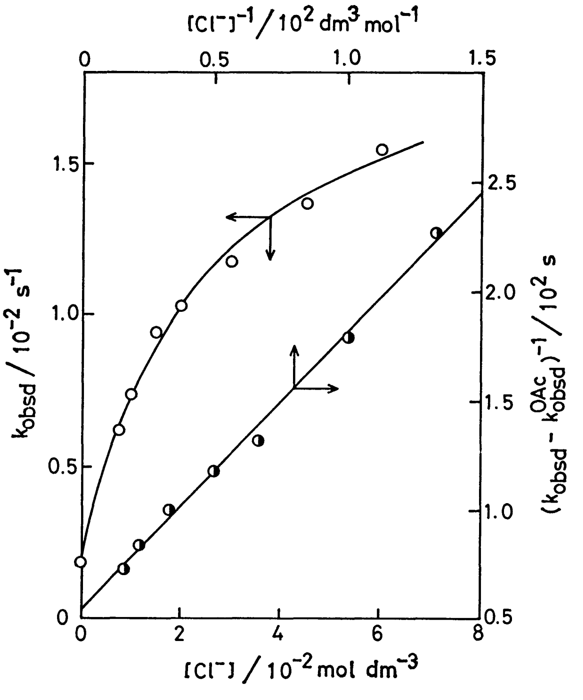


Fig. 5. Plots of k_{obsd} *vs.* $[Cl^-]$ and of $(k_{obsd}-k_{obsd}^{OAc})^{-1}$ *vs.* $[Cl^-]^{-1}$ for the $[Co(N_4)(H_2O)_2]^{3+}$–Cl^- system at $[OAc]_T=0.060$ mol dm^{-3}, pH 4.71, 25 °C, and $I=0.10$ mol dm^{-3} ($LiClO_4$).

$[H^+]K_1^{-1})/Q^{Cl}+Q^{OAc}[OAc]_T/Q^{Cl}(1+[H^+]K_a^{-1})$ respectively. The data thus obtained are given in Table 2.

Reaction of $[Co(OH)([14]aneN_4)(H_2O)]^{2+}$ *with* Br^-. Figure 6 shows an example of the change in the absorbance at 320 nm against the time and of the consecutive reaction treatment[1] for the evaluation of the pseudo-first-order rate constants, k_1^{obsd} and k_2^{obsd}, for the first and second stages of the reaction. The second-stage rate constant, k_2^{obsd}, is given by the slope of the linear portion observed by means of a plot of $-\ln(A_\infty-A_t)$ *vs.* t:

$$-\ln(A_\infty-A_t) = k_2^{obsd}t - \ln C_2. \tag{20}$$

Using the values of k_2^{obsd} and C_2 thus obtained, a plot of the left-hand side of Eq. 21 against the time for the first-stage reaction gives k_1^{obsd} as a slope:

$$-\ln\{A_\infty-A_t-C_2\exp(-k_2^{obsd}t)\} = k_1^{obsd}t - \ln C_1, \tag{21}$$

where C_1 and C_2 are constant. The first-stage rate constant, k_1^{obsd}, depends on $[Br^-]$, while k_2^{obsd} does not (Fig. 7). Therefore, the first-stage reaction is considered to be the simultaneous occurrence of Reactions 15 and 22:

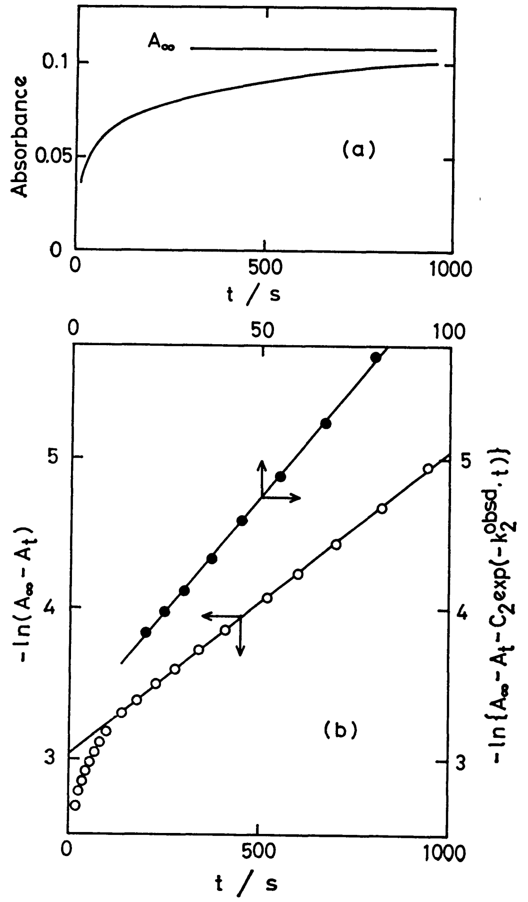


Fig. 6. Reactions of $[Co([14]aneN_4)(H_2O)_2]^{3+}$ with bromide ion at $[Co(III)]_0=7.98\times10^{-4}$ mol dm^{-3}, $[Br^-]=0.060$ mol dm^{-3}, $[OAc]_T=0.060$ mol dm^{-3}, pH, 4.71, 25 °C, and $I=0.10$ mol dm^{-3} ($LiClO_4$) followed at 320 nm: (a) absorbance-time profile; (b) resolution of the kinetic data into two component exponentials.

$$[Co(OH)([14]aneN_4)(H_2O)]^{2+} + Br^- \longrightarrow [CoBr(OH)([14]aneN_4)]^+ + H_2O \tag{22}$$

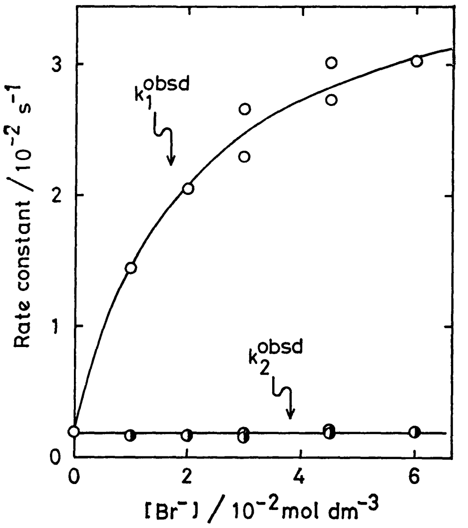


Fig. 7. Plots of k_1^{obsd} *vs.* [Br$^-$] and of k_2^{obsd} *vs.* [Br$^-$] for the [Co([14]aneN$_4$)(H$_2$O)$_2$]$^{3+}$–bromide system.

Discussion

Anation of trans-*[Co(OH)(N$_4$)(H$_2$O)]$^{2+}$ Ions.* There are two possible mechanisms for the anation of the [Co(OH)(N$_4$)(H$_2$O)]$^{2+}$ ions: (i) a dissociative mechanism (Eqs. 10—12) and (ii) an interchange mechanism (Eq. 13). The D-mechanism is more likely than the I-mechanism, because, if the reaction proceeds via the interchange mechanism, the large values of the ion-association constants cannot be explained (Q^{OAc} for the *ms-* and *rac-*Me$_6$[14]aneN$_4$ complexes or Q^{Cl} and Q^{Br} for the [14]aneN$_4$ complex); the expected value for a 2:1 electrolyte in water at 25 °C is about 2 dm^3 mol^{-1}. Poon[2] has demonstrated that the substitution reactions of [CoX$_2$([14]aneN$_4$)]$^+$ (X=a replaceable group such as Cl$^-$, Br$^-$, or NO$_2^-$) proceed through a dissociative mechanism.

The rate constants of the loss of the coordinated water of [Co(OH)(N$_4$)(H$_2$O)]$^{2+}$ range from 10^{-2} to 10^{-1} s^{-1} and increase in the following order: [14]aneN$_4$ < Me$_6$[14]4,11-dieneN$_4$ $\simeq$ *ms-*Me$_6$[14]aneN$_4$ < *rac-*Me$_6$-[14]aneN$_4$. This order is similar to that of the hydrolysis of dichloro and dibromo complexes.[2] This similarity suggests that the methyl groups of the macrocyclic ligands accelerate the loss of the coordinated water. The increasing order of $k_1^{\mathrm{X}}/k^{\mathrm{H_2O}}$ (X=OAc$^-$), [14]aneN$_4$ $\leqslant$ Me$_6$[14]4,11-dieneN$_4$<*rac-*Me$_6$[14]aneN$_4$< *ms-*Me$_6$[14]aneN$_4$, is coincident with the inference that [14]aneN$_4$ is more hydrophilic than the others and that its $k^{\mathrm{H_2O}}$ is larger. The relative effectiveness of the entering group for the coordination to the pentacoordinate intermediate follows the order: H$_2$O< OAc$^-$<Cl$^-$<Br$^-$.

The anation of the Me$_4$[14]tetraeneN$_4$ complex by OAc$^-$ and Br$^-$ is very slow. We have not found any reactions which signaled the rapid anation by means of a stopped-flow apparatus. However, it does not necessarily follow that the loss of the coordinated water of this complex is slow, because the Me$_4$[14]-tetraeneN$_4$ complex may have less affinity to OAc$^-$ and Br$^-$.

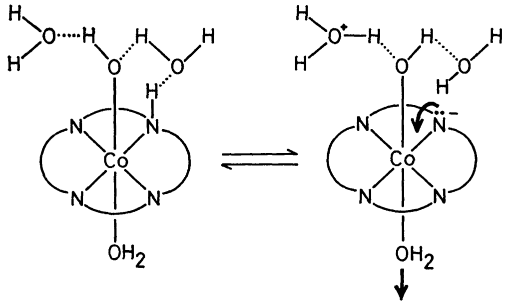
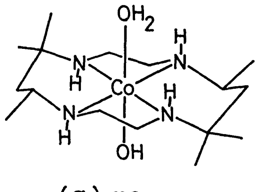


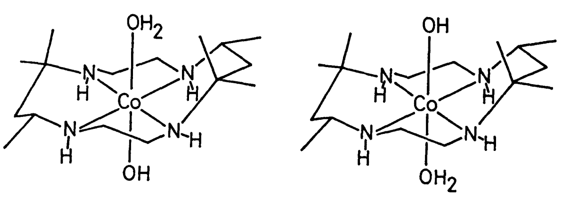
Fig. 8. Internal $S_{\mathrm{N}}1$ conjugate-base mechanism.

The substitution reaction of *trans-*[Co(OH)(N$_4$)-(H$_2$O)]$^{2+}$ obtained in this work is much faster than that of other cobalt(III) complexes;[2] this is explained by the "internal $S_{\mathrm{N}}1$ conjugate-base mechanism" proposed by Mok and Poon.[16] As is shown in Fig. 8, the amido group, >N$^-$, can facilitate a dissociative reaction and may stabilize a tetragonal-pyramidal intermediate. The rate of the aquation of [CoCl(OH)-([14]aneN$_4$)]$^+$ is comparable with that of the loss of the coordinated water of [Co(OH)([14]aneN$_4$)(H$_2$O)]$^{2+}$ (2.1×10^{-2} s^{-1} at 25 °C);[15] therefore, the rate of the formation of the pentacoordinated intermediate may be independent of the nature of the leaving group. Interestingly, k_{d} of *trans-*[Co(OH)([14]aneN$_4$)(H$_2$O)]$^{2+}$ agrees with the rate constant of the N–H proton exchange of this complex (2×10^{-2} s^{-1} at 21 °C and I= 0.50 mol dm^{-3}).[10] These facts suggest that the N–H protons play a significant role in the substitution reactions of the macrocyclic cobalt(III) complexes.

Possible Structure of trans-*[Co(OH)(*rac*-M$_6$[14]aneN$_4$-(H$_2$O)]$^{2+}$.* Since the *trans-*[Co(*ms-*Me$_6$[14]aneN$_4$)-(H$_2$O)$_2$]$^{3+}$ complex has a center of symmetry with respect to the cobalt atom, there is only one possible structure for the aquahydroxo species (Fig. 9a). The *trans-*[Co(OH)(*rac-*Me$_6$[14]aneN$_4$)(H$_2$O)]$^{2+}$ complex, on the other hand, has two possible structures (Figs. 9b and 9c),[17] because *rac-*Me$_6$[14]aneN$_4$ has no axis of symmetry. We propose that the predominant structure of the *rac-*complex is (b) rather than (c). The *ms-* and *rac-*isomers are very similar in the first aciddissiciation constants, pK_1 (Table 1). The pK_2 of the *ms-*isomer, however, is smaller than that of the



(a) ms

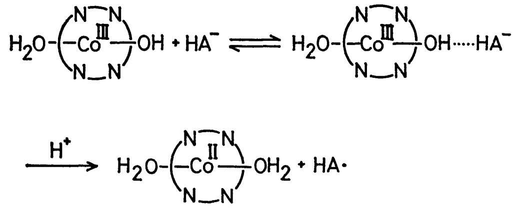


(b) rac (c) rac

Fig. 9. Proposed structures of *trans-*[Co(OH)(Me$_6$[14]-aneN$_4$)(H$_2$O)]$^{2+}$.

rac-isomer; that is, the *ms*-dihydroxo species is more stable than the *rac*-dihydroxo species. The OH^- ligand, which faces the N–H proton, can make a chain of hydrogen bonds with the N–H proton through solvent water molecules (Fig. 8). In the *ms*-isomer two OH^- ligands are possible to make such a hydrogen bonding; in the *rac*-isomers, only one OH^- ligand is possible. Since the electronic effect of these ligands is identical, the difference in pK_2 can be ascribed to the stabilization by the hydrogen bonding. In the aquation of *trans*-$[CoCl_2(N_4)]^+$,[18] the loss of the coordinated chloride is accelerated by the increase of the steric crowding of methyl groups. The k_d of the *rac*-isomer is larger than that of the *ms*-isomer. This can be explained as the steric acceleration. The fact that k_1^{OAc}/k^{H_2O} of the *rac*-isomer is much smaller than that of the *ms*-isomer can also be explained as the steric hindrance.

Mechanism of Electron-transfer Reactions of trans-*$[Co(OH)(N_4)(H_2O)]^{2+}$ with Ascorbic Acid.* We have reported that the rate constants of the reactions of $[Co(OH)(N_4)(H_2O)]^{2+}$ with ascorbate (HA^-) range from 2.9×10 to 1.3×10^3 dm^3 mol^{-1} s^{-1}.[1] If the reaction proceeds through an inner-sphere mechanism, the substitution reaction of $[Co(OH)(N_4)(H_2O)]^{2+}$ must be faster than the electron-transfer reaction. The kinetic data for the substitution reaction of the aquahydroxo complexes obtained in this work show that the ascorbate reduction of these complexes is faster than the substitution reaction. Therefore, an inner-sphere mechanism can be ruled out and the ascorbate reduction of *trans*-$[Co(OH)(N_4)(H_2O)]^{2+}$ is considered to proceed through an OH-bridged mechanism:



(23)

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14) When $[Cl^-]$ is larger than $[OAc]_T$, a subsequent reaction is found to occur; it is much slower than the first-stage reaction.

15) The rate constant was calculated by the use of the equilibrium constant and the rate constant of the aquation: C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, **1967**, 2069.

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