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The Reduction of Cobalt(III) Complexes by Ascorbic Acid. II.[1] The Kinetics and Mechanisms of the Reactions of Diaqua and Aquahydroxo Macrocyclic N_4 Complexes

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The kinetics of the reductions of several macrocyclic N_4 cobalt(III) complexes by L-ascorbic acid (H_2A) have been studied at 25.0 °C, at an ionic strength of 0.10 mol dm^{-3} ($LiClO_4$), and over the pH range from 1.64 to 3.47. The second-order rate constants in $dm^3\ mol^{-1}\ s^{-1}$ are 3.4 ± 0.6 (Me_6[14]4,11-dieneN_4),† $(4.2\pm0.2)\times10$ (Me_4[14]tetraeneN_4), and $(4.2\pm0.1)\times10$ (*ms*-Me_6[14]aneN_4) for the reactions of $[Co(N_4)(H_2O)_2]^{3+}$ with HA^- ions and $(1.1\pm0.1)\times10^2$ (Me_6[14]4,11-dieneN_4), $(1.3\pm0.1)\times10^3$ (Me_4[14]tetraeneN_4), $(5.5\pm0.1)\times10$ (*ms*-Me_6[14]aneN_4), and $(2.9\pm0.6)\times10$ ([14]aneN_4) for the reactions of $[Co(OH)(N_4)(H_2O)]^{2+}$ with HA^- ions. The mechanisms of these reactions are discussed, and it is concluded that the lack of saturation of macrocyclic ligands facilitates the electron-transfer reaction between cobalt(III) and ascorbic acid.

L-Ascorbic acid plays a significant role in biological redox systems.[2] Kinetic studies of the ascorbate reductions of metal complexes may be useful in understanding the role of ascorbic acid.

The reactions of metal complexes with ascorbic acid, as with the other organic reducing agents, are classified into three categories:[3] (i) outer-sphere electron transfer, (ii) inner-sphere electron transfer, which occurs subsequent to the substitution of a ligand for ascorbate, and (iii) a bridging mechanism in which ascorbate is bound at a ligand of the complex prior to electron transfer.

In a previous paper we reported the outer-sphere electron-transfer reactions of cobalt(III) complexes ligating 1,10-phenanthroline or 2,2′-bipyridine with ascorbic acid.[1] Cobalt(III) tetraazamacrocyclic and porphyrin complexes have a soft character, and it is expected that ascorbic acid, which is a π donor, interacts with these complexes; consequently, Mechanism (ii) or Mechanism (iii) may be possible. In this paper we will report on the ascorbate reductions of diaqua and aquahydroxo cobalt(III) complexes containing tetraazamacrocycles, Me_4[14]tetraeneN_4, Me_6-[14]4,11-dieneN_4, *ms*-Me_6[14]aneN_4, and [14]aneN_4 (Fig. 1), whose cobalt(II) complexes are low-spin species in an aqueous solution.

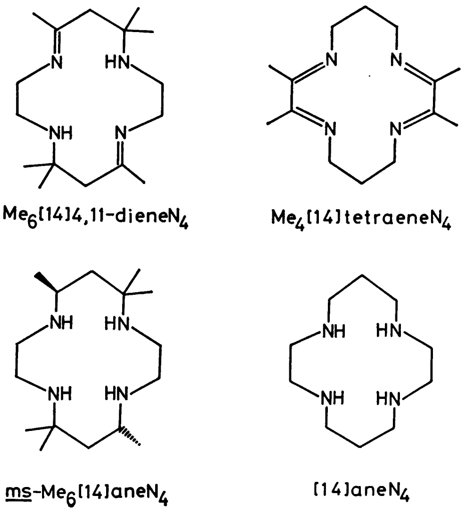

Fig. 1. Structures of tetraazamaclocycles (N_4).

Experimental

Reagents. The complexes, $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2](ClO_4)_3$,[4] $[Co(Me_4[14]\text{tetraene}N_4)(H_2O)_2](ClO_4)_3\cdot2.5H_2O$,[5] $[Co(ms\text{-}Me_6[14]\text{ane}N_4)(H_2O)_2](ClO_4)_3$,[4,6] and $[Co([14]\text{ane}N_4)(H_2O)_2](ClO_4)_3$,[7] were prepared as reported in the literature. All the complexes are *trans* isomers. The L-ascorbic acid and sodium L-ascorbate were supplied by Wako Pure Chemical Industries. The $LiClO_4\cdot3H_2O$ was obtained according to the procedure reported previously.[8] All the solutions used for the measurements were prepared using water obtained by the distillation of alkaline permanganate solutions. A solution of ascorbic acid was freshly prepared under a nitrogen atmosphere which had been scrubbed twice with alkaline potassium pyrogallate.

Kinetic Measurements. All the measurements were made under a nitrogen atmosphere. The reaction was initiated by injecting a solution of ascorbic acid into a solution containing the required amounts of a complex and lithium perchlorate. The change in the absorbance with the time was followed with a Hitachi 200-20 spectrophotometer. The wavelengths used for the measurements were 320 nm ($[Co(ms\text{-}Me_6[14]\text{ane}N_4)(H_2O)_2]^{3+}$), 340 nm ($[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$), 500 nm ($[Co([14]\text{ane}N_4)(H_2O)_2]^{3+}$), and 540 nm ($[Co(Me_4[14]\text{tetraene}N_4)(H_2O)_2]^{3+}$). In order to ensure a pseudo-first order condition, ascorbic acid was used in at least a twentyfold excess over the cobalt(III) complexes. In an aqueous solution of $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$ ions[9] or $[Co(Me_4[14]\text{tetraene}N_4)(H_2O)_2]^{3+}$ ions, a dimerization was gradually observed. In order to minimize this dimerization, the concentrations of the complexes were restricted below 4×10^{-4} mol dm^{-3} and the solution was used within 20 min after preparation.

The temperature was controlled at 25.0 ± 0.1 °C, and the ionic strength (I) was adjusted to 0.10 mol dm^{-3} with lithium perchlorate. The pH of the solution was adjusted with sodium ascorbate or perchloric acid and was measured on a Hitachi-Horiba F-7 pH meter with a 3.33 mol dm^{-3} NaCl solution as a junction. The hydrogen-ion concentrations were computed from the pH, using a value of 0.83 for the activity coefficient of H^+.[10]

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† Abbreviations: 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, *ms*-Me_6[14]aneN_4 = *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, [14]ane-N_4 = 1,4,8,11-tetraazacyclotetradecane.

Stoichiometric Determinations. The stoichiometry of the reaction of $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$ with ascorbic acid was determined spectrophotometrically. The reaction was initiated by mixing solutions of the complex and of ascorbic acid under a nitrogen atmosphere ($[Co(III)]_0 = 1.20\times10^{-2}$ mol dm^{-3} and $[H_2A]_0 = (0.136\text{–}1.32)\times10^{-2}$ mol dm^{-3}). Then the reaction was monitored with a Shimadzu UV 140-02 spectrophotometer until no spectral changes were observed. After the hydrogen-ion concentrations of the solutions had been adjusted to 0.10 mol dm^{-3} with perchloric acid under a nitrogen atmosphere, the absorbance at 445 nm (absorption maximum of Co(II) complex) was recorded.

Acid-dissociation Constants. The acid-dissociation constants of the diaqua ligands of $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$ were determined by pH titrations with a standard sodium hydroxide solution at 25 °C and $I = 0.1$ mol dm^{-3} ($LiClO_4$) under a nitrogen atmosphere. The pK values thus obtained were 3.93 ± 0.02 and 8.6 ± 0.1, compared with the literature values of 4.02 ± 0.01 and 8.2 ± 0.1 at 25 °C and $I = 1.0$ mol dm^{-3} ($NaClO_4$).11) The acid-dissociation constants of the diaqua ligands of the other complexes and of ascorbic acid were used of the literature values for the analysis of the rate constants without any correction of the ionic strength: the pK values at 25 °C are 3.5 ± 0.1 and 6.5 ± 0.1 ($I = 0.50$ mol dm^{-3}) for $[Co(Me_4[14]\text{tetraene}N_4)(H_2O)_2]^{3+}$,12) 2.7 ± 0.05 and 6.4 ± 0.05 ($I = 1.0$ mol dm^{-3}) for $[Co(ms\text{-}Me_6[14]\text{ane}N_4)(H_2O)_2]^{3+}$,11) 2.9 ± 0.1 and 7.2 ± 0.1 ($I = 0.50$ mol dm^{-3}) for $[Co([14]\text{ane}N_4)(H_2O)_2]^{3+}$,13) and 4.04 and 11.3 ($I = 0.10$ mol dm^{-3}) for H_2A.14)

Results

The Reactions of $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$, $[Co(Me_4[14]\text{tetraene}N_4)(H_2O)_2]^{3+}$, and $[Co(\text{ms-}Me_6[14]\text{ane}N_4)(H_2O)_2]^{3+}$ with Ascorbic Acid. Spectrophotometric titrations confirm to the following stoichiometry for the reaction of $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$ with ascorbic acid ($[Co(III)]/[H_2A] = 1.96\pm0.04$):

$$2Co(III) + H_2A = 2Co(II) + \text{dehydroascorbic acid}. \quad (1)$$

The spectral changes observed during the reaction of $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$ with ascorbic acid gave three isosbestic points over the range from 370 to 650 nm (Fig. 2). The spectrum at infinity corresponds to that of $[Co^{II}(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{2+}$.15) In the reactions of $[Co(Me_4[14]\text{tetraene}N_4)(H_2O)_2]^{3+}$ and $[Co(ms\text{-}Me_6[14]\text{ane}N_4)(H_2O)_2]^{3+}$, the spectra at infinity also agree with those of the corresponding cobalt(II) complexes.15,16)

The kinetics of the title reactions were studied in various concentrations of ascorbic acid ($(0.380\text{–}2.10)\times10^{-2}$ mol dm^{-3}), cobalt(III) ($(1.42\text{–}3.41)\times10^{-4}$ mol dm^{-3}), and hydrogen ions ($4.08\times10^{-4}\text{–}1.19\times10^{-2}$ mol dm^{-3}). The plots of $-\ln(A_t - A_\infty)$ *vs.* time were linear for at least 90% completion (A_t and A_∞ represent the absorbance at time t and infinity respectively). The observed first-order rate constants (k_{obsd}) obtained from the slope of this straight line were also linearly dependent on the initial concentrations of ascorbic acid (Fig. 3). Thus, the rate law was described as follows:

$$-\frac{1}{2}d[Co(III)]/dt = k[Co(III)][H_2A]_0. \quad (2)$$

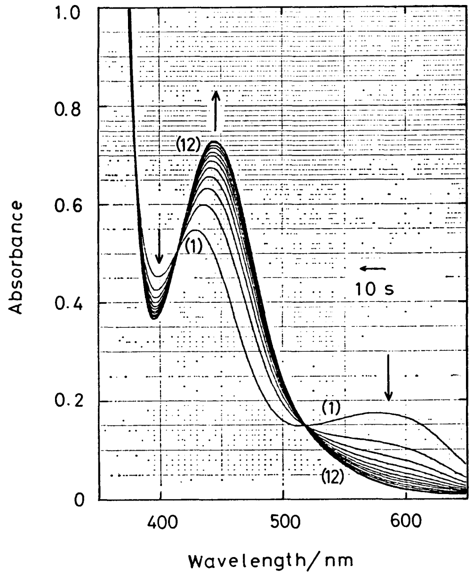


Fig. 2. Spectral changes during the reaction of $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$ with ascorbic acid at $[H_2A]_0 = 1.00\times10^{-1}$ mol dm^{-3}, $[Co(III)]_0 = 8.40\times10^{-3}$ mol dm^{-3}, pH=2.60, 25.0 °C, and $I = 0.50$ mol dm^{-3}: (1) 15 s; (2) 3 min; (3) 5 min 40 s; (4) 8 min 20 s; (5) 11 min 10 s; (6) 14 min; (7) 17 min; (8) 20 min; (9) 25 min; (10) 30 min; (11) 40 min; (12) 50 min after the reaction. The times given are for the start of scan at 650 nm.

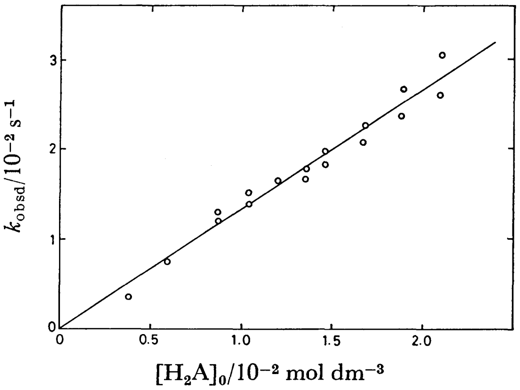
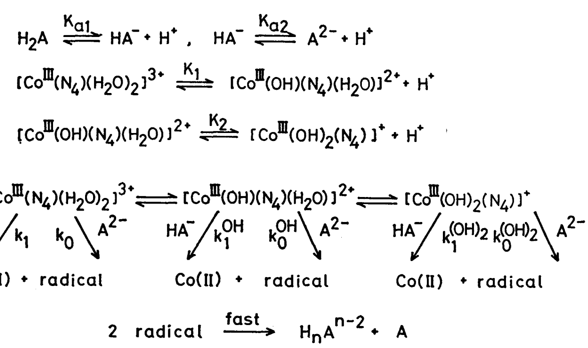


Fig. 3. Plots of k_{obsd} *vs.* $[H_2A]_0$ for the $[Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2]^{3+}$-ascorbic acid system at $[Co(III)]_0 = 2.34\times10^{-4}$ mol dm^{-3}, pH=3.12, 25.0 °C, and $I = 0.10$ mol dm^{-3} ($LiClO_4$).

The second-order rate constants obtained from $k_{obsd}/[H_2A]_0$ increased with a decrease in the acidity (Fig. 4). The dependence of k on the hydrogen-ion concentrations may be explained by Scheme 1, considering that cobalt(III) complexes are not reduced by H_2A species.1) The above mechanism leads to Eq. 3 for the second-order rate constant:

$$\begin{aligned}k = \{&k_1K_{a1} + (k_0K_{a1}K_{a2} + k_1^{OH}K_1K_{a1})[H^+]^{-1}\\ &+ k_0^{OH}K_1K_{a1}K_{a2} + k_1^{(OH)_2}K_1K_2K_{a1})[H^+]^{-2}\\ &+ k_0^{(OH)_2}K_1K_2K_{a1}K_{a2}[H^+]^{-3}\}/\alpha(H)\beta(H)[H^+], \quad (3)\end{aligned}$$

where the symbols are abbreviated as in Scheme 1 and where $\alpha(H) = 1 + K_{a1}[H^+]^{-1} + K_{a1}K_{a2}[H^+]^{-2}$ and $\beta(H) = 1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2}$. The plots of the values of $k\alpha(H)\beta(H)[H^+]$ *vs.* $[H^+]^{-1}$ gave a straight



Scheme 1.

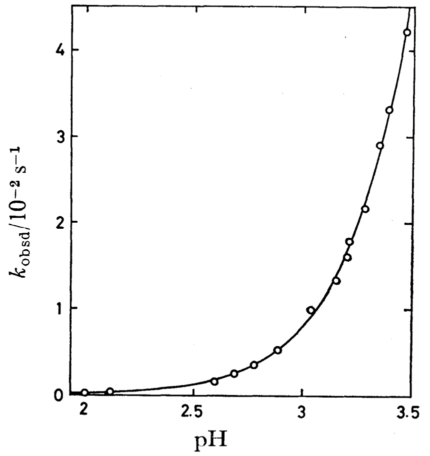


Fig. 4. Plots of k_{obsd} *vs.* pH for the [Co(Me$_6$[14]4,11-dieneN$_4$)(H$_2$O)$_2$]$^{3+}$-ascorbic acid system at [H$_2$A]$_0$= 1.00×10^{-2} mol dm^{-3}, [Co(III)]$_0$=(2.30—3.41)×10^{-4} mol dm^{-3}, 25.0 °C, and I=0.10 mol dm^{-3} (LiClO$_4$).

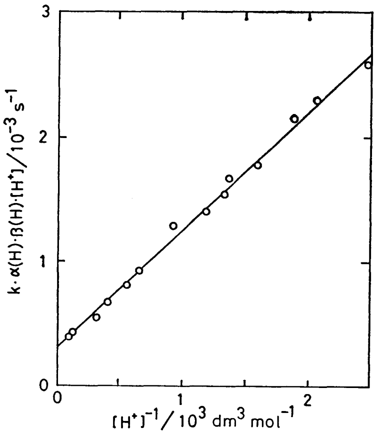


Fig. 5. Plots of $k\alpha(\mathrm{H})\beta(\mathrm{H})[\mathrm{H}^+]$ *vs.* [H$^+$]$^{-1}$ for the [Co(Me$_6$[14]4,11-dieneN$_4$)(H$_2$O)$_2$]$^{3+}$-ascorbic acid system.

line (Fig. 5), showing that the k_0^{OH}, $k_1^{(\mathrm{OH})_2}$, and $k_0^{(\mathrm{OH})_2}$ paths do not contribute under the present experimental conditions. The values of k_1K_{a1} and of $(k_0K_{\mathrm{a1}}K_{\mathrm{a2}}+k_1^{\mathrm{OH}}K_1K_{\mathrm{a1}})$ are obtained from the intercept and the slope of this straight line respectively. In order to be comparable to the k_1^{OH} term, k_0 must exceed 10^{10} dm^3 mol^{-1} s^{-1}, which is in excess of the highest previously reported second-order rate constants. Therefore, the k_0 term does not contribute to the present reaction $(k_0K_{\mathrm{a1}}K_{\mathrm{a2}} \ll k_1^{\mathrm{OH}}K_1K_{\mathrm{a1}})$. The second-order rate constants, k_1 and k_1^{OH}, were obtained by the use of the values of K_1, K_{a1}, and K_{a2}. The same analysis was also employed for the Me$_4$[14]tetraeneN$_4$ and the *ms*-Me$_6$[14]aneN$_4$ systems (Fig. 6). The values of k_1 and k_1^{OH} are listed in Table 1.

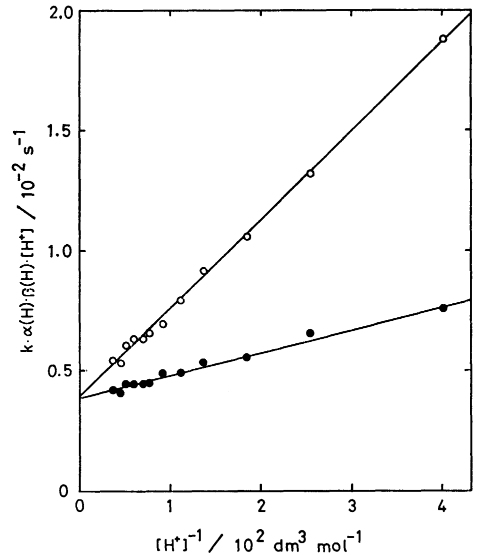


Fig. 6. Plots of $k\alpha(\mathrm{H})\beta(\mathrm{H})[\mathrm{H}^+]$ *vs.* [H$^+$]$^{-1}$ for the [Co(Me$_4$[14]tetraeneN$_4$)(H$_2$O)$_2$]$^{3+}$ and [Co(*ms*-Me$_6$-[14]aneN$_4$)(H$_2$O)$_2$]$^{3+}$-ascorbic acid system at [H$_2$A]$_0$= 1.00×10^{-2} mol dm^{-3}, 25.0 °C, and I=0.10 mol dm^{-3} (LiClO$_4$).
○: [Co(Me$_4$[14]tetraeneN$_4$)(H$_2$O)$_2$]$^{3+}$ ([Co(III)]$_0$= (1.42—2.00)×10^{-4} mol dm^{-3}), ●: [Co(*ms*-Me$_6$[14]-aneN$_4$)(H$_2$O)$_2$]$^{3+}$ ([Co(III)]$_0$=(3.06—3.43)×10^{-4} mol dm^{-3})

TABLE 1. SECOND-ORDER RATE CONSTANTS OF THE REACTIONS OF [Co(N$_4$)(H$_2$O)$_2$]$^{3+}$ WITH ASCORBIC ACID AT 25.0 °C AND I=0.10 mol dm^{-3} (LiClO$_4$)

N$_4$	k_1 / dm^3 mol^{-1} s^{-1}	k_1^{OH} / dm^3 mol^{-1} s^{-1}
Me$_4$[14]tetraeneN$_4$	(4.2±0.2)×10	(1.3±0.1)×10^3
Me$_6$[14]4,11-dieneN$_4$	3.4±0.6	(1.1±0.1)×10^2
ms-Me$_6$[14]aneN$_4$	(4.2±0.1)×10	(5.5±0.1)×10
[14]aneN$_4$	≈0	(2.9±0.6)×10

The Reactions of [Co([14]aneN$_4$)(H$_2$O)$_2$]$^{3+}$ with Ascorbic Acid. Figure 7 shows an example of the change in the absorbance at 500 nm against the time and of the consecutive reaction treatment 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 title reaction.[17] The absorption spectra at infinity in the second stage at pH>3 show those of the [Co$^{\mathrm{II}}$-([14]aneN$_4$)(H$_2$O)$_2$]$^{2+}$ ion, but not at pH<2. The situation for the biphasic kinetics under the pseudo-first-order conditions can be represented by the following sequence:

$$\mathrm{A} \xrightarrow{k_1^{\mathrm{obsd}}} \mathrm{B} \xrightarrow{k_2^{\mathrm{obsd}}} \mathrm{C}. \qquad (4)$$

Equation 5 describes the change in the absorbance with the time, where ε_{A}, ε_{B}, and ε_{C} are the molar ab-

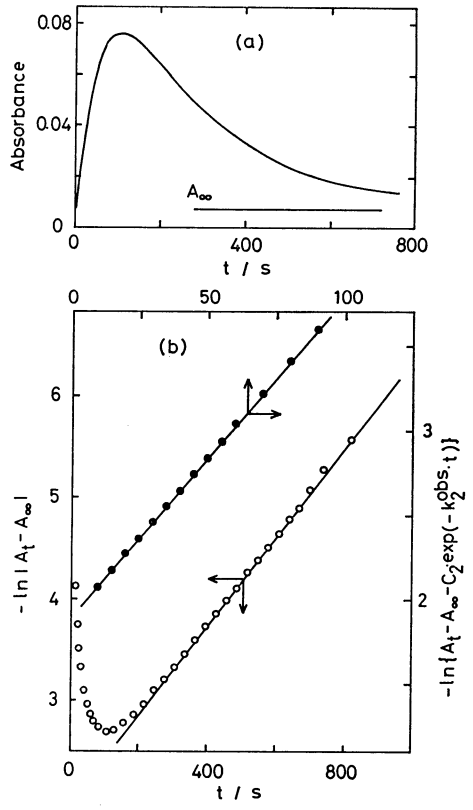


Fig. 7. Reaction of $[Co([14]aneN_4)(H_2O)_2]^{3+}$ with ascorbic acid at $[H_2A]_0=1.04\times10^{-2}$ mol dm^{-3}, $[Co(III)]_0=1.70\times10^{-4}$ mol dm^{-3}, pH=3.14, 25.0 °C, and I=0.10 mol dm^{-3} ($LiClO_4$) followed at 500 nm: (a) absorbance-time profile; (b) resolution of the kinetic data into its two component exponentials.

sorption coefficients of the species and where $[A]_0$ is the initial concentration of A:

$$A_t - A_\infty = C_1 \exp(-k_1^{obsd}t) + C_2 \exp(-k_2^{obsd}t), \tag{5}$$

$$C_1 = \frac{[A]_0\{k_1^{obsd}(\varepsilon_A-\varepsilon_B)-k_2^{obsd}(\varepsilon_A-\varepsilon_C)\}}{k_1^{obsd}-k_2^{obsd}}, \tag{6}$$

$$C_2 = \frac{[A]_0 k_1^{obsd}(\varepsilon_B-\varepsilon_C)}{k_1^{obsd}-k_2^{obsd}}. \tag{7}$$

The second-stage rate constant, k_2^{obsd}, is given by the slope of the linear portion observed by means of a plot of $-\ln(A_t-A_\infty)$ *vs.* t:

$$-\ln(A_t-A_\infty) = k_2^{obsd}t-\ln C_2. \tag{8}$$

A plot of the left-hand side of Eq. 9 against the time gives the first-stage rate constant, k_1^{obsd}, as a slope:

$$-\ln\{A_t-A_\infty-C_2\exp(-k_2^{obsd}t)\} = k_1^{obsd}t - \ln C_1. \tag{9}$$

The values of k_1^{obsd} and k_2^{obsd} at various concentrations of ascorbic acid and hydrogen ions are listed in Table 2. It is found that $k_1^{obsd}=a[H_2A]_0$ and that $k_2^{obsd}=b+c[H_2A]_0$, where the constants a, b, and c depend on the hydrogen-ion concentrations.

TABLE 2. OBSERVED RATE CONSTANTS OF THE FIRST AND THE SECOND STAGES FOR THE $[Co([14]aneN_4)(H_2O)_2]^{3+}$-ASCORBIC ACID SYSTEM AT 25.0 °C AND I=0.10 mol dm^{-3} ($LiClO_4$)

$[Co(III)]_0$ / 10^{-4} mol dm^{-3}	$[H_2A]_0$ / 10^{-2} mol dm^{-3}	pH	k_1^{obsd} / 10^{-3} s^{-1}	k_2^{obsd} / 10^{-3} s^{-1}
3.01	1.00	2.34	0.940	0.630
3.01	1.00	2.48	2.09	0.640
4.04	1.00	2.68	3.55	0.900
1.82	1.00	2.89	5.05	1.39
1.67	1.00	3.00	7.30	1.74
1.74	1.00	3.15	16.0	2.11
1.50	1.00	3.28	24.4	1.91
1.82	0.594	3.14	5.30	1.36
1.91	0.872	3.14	8.10	1.88
1.70	1.04	3.14	9.50	2.20
1.74	1.20	3.14	12.2	2.38
1.60	1.36	3.14	11.9	2.48
1.78	1.68	3.14	15.8	3.40

The reaction products were examined by the use of an SP-Sephadex C-25 column (Na^+ form). The reaction was initiated by mixing solutions of $[Co([14]aneN_4)(H_2O)_2]^{3+}$ ((1.0—2.0) × 10^{-2} mol dm^{-3}) and of H_2A (1.0×10^{-2} mol dm^{-3}) at pH 4 and 25.0 °C under a nitrogen gas, an argon gas, or air. The reaction was monitored with a Hitachi 200-20 spectrophotometer. The first increase in absorption was observed over the range from 400 to 700 nm in each case ($\lambda_{max}\approx440$ nm and $\lambda_{sh}\approx550$ nm); thereafter, the absorbance decreased. After the first-stage reaction had been completed, the solution was poured into a Sephadex column and three species were separated with a 0.1 mol dm^{-3} $NaClO_4$ solution–violet, violet, and brown from the bottom to the top of the column. The first violet band turned green when treated with a 0.2 mol dm^{-3} $HClO_4$ solution, and the green species may have a 2+ charge (λ_{max} 620±5 nm, λ_{max} 525±5 nm, and λ_{sh} 420 nm). It has not yet been identified. The second violet band also turned green when treated with a 0.2 mol dm^{-3} $HClO_4$ solution; the green species was identified as $[Co([14]aneN_4)(H_2O)_2]^{3+}$. The last brown species have a 4+ charge and changed to $[Co([14]aneN_4)(H_2O)_2]^{3+}$ when treated with a 0.4 mol dm^{-3} $HClO_4$ solution. The brown species was identified as $[\{(H_2O)Co([14]aneN_4)\}_2O_2]^{4+}$.[18] A $[Co^{II}([14]aneN_4)(H_2O)_2]^{2+}$ ion is very sensitive to a trace of oxygen;[18–20] therefore, it is concluded that the biphasic behavior in the present system is ascribable to a trace of oxygen in a nitrogen or an argon gas. Accordingly, the present reaction is considered to be represented as follows:

$$\begin{aligned}&[Co([14]aneN_4)(H_2O)_2]^{3+} \text{ or}\\ &\quad[Co(OH)([14]aneN_4)(H_2O)]^{2+} + HA^-\\ &\quad\longrightarrow [Co([14]aneN_4)(H_2O)_2]^{2+} + HA\cdot\end{aligned} \tag{10}$$

$$\begin{aligned}&2[Co([14]aneN_4)(H_2O)_2]^{2+} + O_2\\ &\quad\longrightarrow [\{(H_2O)Co([14]aneN_4)\}_2O_2]^{4+}\end{aligned} \tag{11}$$

$$(k=4\times10^9 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \text{ at } 25\,^\circ\text{C}^{20)})$$

$$[\{(H_2O)Co([14]aneN_4)\}_2O_2]^{4+} + HA^- \xrightarrow{\text{reduction}} \tag{12a}$$

$$[\{(H_2O)Co([14]aneN_4)\}_2O_2]^{4+} + H^+ \xrightarrow{\text{decomposition}} \tag{12b}$$

The first-stage reaction (Eq. 10) was only analyzed in detail on the basis of Scheme 1. The plot of $k\alpha(H)\beta(H)[H^+]$ *vs.* $[H^+]^{-1}$ ($k=k_1^{obsd}/[H_2A]_0$) gave a straight line, with an intercept of nearly zero (Fig.

Table 3. Second-order rate constants of the reductions of $[Co(N_4)(H_2O)_2]^{3+}$ and $[Co(OH)(N_4)(H_2O)]^{2+}$

Oxidant	Rate contant/$dm^3\ mol^{-1}\ s^{-1}$		
	Reductant		
	HA^- a)	$[Ru(NH_3)_6]^{2+}$ b)	$[V(H_2O)_6]^{2+}$ b)
$[Co(Me_4[14]tetraeneN_4)(H_2O)_2]^{3+}$	4.2×10	1.9×10^4	1.0×10^3
$[Co(OH)(Me_4[14]tetraeneN_4)(H_2O)]^{2+}$	1.3×10^3	—	—
$[Co(Me_6[14]4,11\text{-}dieneN_4)(H_2O)_2]^{3+}$	3.4	8×10^2	2.4×10^2
$[Co(OH)(Me_6[14]4,11\text{-}dieneN_4)(H_2O)]^{2+}$	1.1×10^2	1.0×10^2	8.5×10^2
$[Co(ms\text{-}Me_6[14]aneN_4)(H_2O)_2]^{3+}$	4.2×10	3.0×10^3	1.8×10^3
$[Co(OH)(ms\text{-}Me_6[14]aneN_4)(H_2O)]^{2+}$	5.5×10	5×10^2	8.5×10^3
$[Co([14]aneN_4)(H_2O)_2]^{3+}$	—	—	—
$[Co(OH)([14]aneN_4)(H_2O)]^{2+}$	2.9×10	—	—

a) 25 °C and $I=0.10\ mol\ dm^{-3}$; this work. b) 25 °C and $I=1.0\ mol\ dm^{-3}$; Refs. 5 and 9.

Table 4. Comparison between the observed rate constants and the calculated ones from the Marcus cross relationships for the reactions of $[Co(N_4)(H_2O)_2]^{3+}$ with HA^- ions at 25 °C and $I=0.10\ mol\ dm^{-3}$ a)

N_4	E°_{22} b) / V	k_{22} / $dm^3\ mol^{-1}\ s^{-1}$	k_{12}(calcd) / $dm^3\ mol^{-1}\ s^{-1}$	k_{12}(obsd) / k_{12}(calcd)
$Me_4[14]tetraeneN_4$	0.56 d)	6×10^{-2} e)	2.7	16
$Me_6[14]4,11\text{-}dieneN_4$	0.56 d)	3×10^{-5} e)	0.065	52
$ms\text{-}Me_6[14]aneN_4$	0.54 f)	$\approx10^{-3}$ g)	≈0.2	≈200
$[14]aneN_4$	0.44 h)	7.8×10^{-4} i)	0.021	—

a) $E^\circ_{11}(HA\cdot/HA^-)=0.88\ V$ and $\Delta G^*_{11}=17\ kJ\ mol^{-1}$; Ref. 23. b) The redox potential for the $[Co(N_4)(H_2O)_2]^{3+/2+}$ couple. c) The rate constant of the self-exchange reaction for the $[Co(N_4)(H_2O)_2]^{3+/2+}$ couple. d) Ref. 24. e) Ref. 25. f) The mean value between 0.49 V in Ref. 19 and 0.59 V in Ref. 9. g) Estimated value from the $[V(H_2O)_6]^{2+}$ reduction. h) Ref. 19. i) Ref. 20.

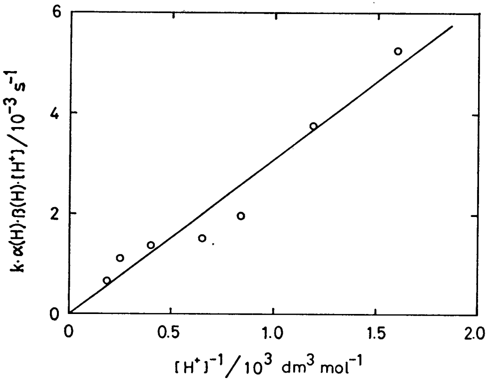


Fig. 8. Plots of $k\alpha(H)\beta(H)[H^+]$ *vs.* $[H^+]^{-1}$ for the first-stage reaction of $[Co([14]aneN_4)(H_2O)_2]^{3+}$ with ascorbic acid at $[H_2A]_0=1.00\times10^{-2}\ mol\ dm^{-3}$, $[Co(III)]_0=(1.50—4.04)\times10^{-4}\ mol\ dm^{-3}$, 25.0 °C, and $I=0.10\ mol\ dm^{-3}$ ($LiClO_4$).

8). The second-order rate constant, k_1^{OH}, is obtained from the slope of this straight line.

Discussion

The rate constants of the reactions of $[Co(N_4)(H_2O)_2]^{3+}$ and $[Co(OH)(N_4)(H_2O)]^{2+}$ with HA^- ions are summarized in Table 3, along with the data for the other reducing agents.

The Reactions of the $[Co(N_4)(H_2O)_2]^{3+}$ Ions. The trend in the relative rates of the reactions is Me_4-tetraene$N_4\simeq ms$-$Me_6[14]aneN_4>Me_6[14]4,11$-diene$N_4\gg[14]aneN_4$, similar to that for a $[Ru(NH_3)_6]^{2+}$ or $[V(H_2O)_6]^{2+}$ reduction, which proceeds by means of an outer-sphere mechanism.[5,9] As the water-exchange reactions of the $[Co(N_4)(H_2O)_2]^{3+}$ species may be very slow,[21] the water molecules of the $[Co(N_4)(H_2O)_2]^{3+}$ ions may not be replaced by the HA^- ions prior to electron transfer. Therefore, the reactions of the diaqua complexes are considered to proceed by an outer-sphere electron-transfer mechanism.

The rate constants of the reactions of $[Co(N_4)(H_2O)_2]^{3+}$ with HA^- are calculated on the basis of the Marcus cross relationships[22] in the way reported previously:[1]

$$\Delta G^*_{12} = \lambda(1+\Delta G^{\circ\prime}_{12}/\lambda)^2/4, \tag{13}$$

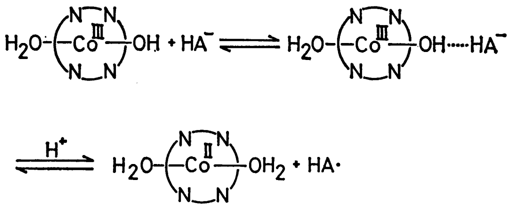
$$k_{12} = Z\exp(-\Delta G^*_{12}/RT), \tag{14}$$

$$\lambda = 2(\Delta G^*_{11}+\Delta G^*_{22}), \tag{15}$$

where Z is the collision frequency in solution ($10^{11}\ dm^3\ mol^{-1}\ s^{-1}$), where ΔG^*_{11} and ΔG^*_{22} refer to the self-exchange reactions of the reagents, and where $\Delta G^{\circ\prime}_{12}$ is the free-energy change in the reactions. The calculated rate constants are listed in Table 4. All the observed rate constants exceed the calculated ones by a factor of 10—10^2. This may be ascribable, at least in part, to the work terms neglected or to the small effect of the bond-length changes from Co^{III}–OH_2 to Co^{II}–OH_2.[25] The latter is considered to be a significant factor in the self-exchange reaction of the cobalt(III)/(II) couple.[25]

The Reactions of the $[Co(OH)(N_4)(H_2O)]^{2+}$ Ions.

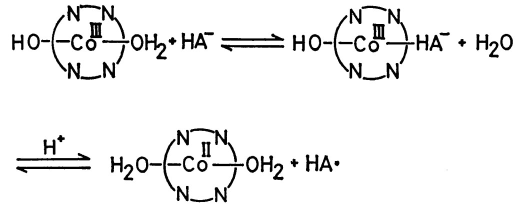
The rate constants of these reactions tend to decrease in the following order: $Me_4[14]tetraeneN_4 >$ $Me_6[14]4,11\text{-}dieneN_4 > ms\text{-}Me_6[14]aneN_4 > [14]aneN_4$; the ratios of k_1^{OH}/k_1 are 31 for $Me_4[14]tetraeneN_4$, 32 for $Me_6[14]4,11\text{-}dieneN_4$, 1.3 for $ms\text{-}Me_6[14]aneN_4$, and $\gg 29$ for $[14]aneN_4$. These results are in contrast to those of typical outer-sphere electron-transfer reactions; for example, $k_1 > k_1^{OH}$ for a cobalt(III) porphyrin–dithionite system.[26] It is suggested that the reactions of $[Co(OH)(N_4)(H_2O)]^{2+}$ with HA^- proceed *via* an OH-bridged mechanism:



(16)

The trend in the relative rate of this reaction corresponds to the extent of the lack of saturation of the macrocyclic ligands. As the polarizability of the central cobalt(III) ion is expected to be enhanced with an increase in the extent of electronic delocalization between the cobalt(III) ion and the macrocyclic ligand, an electron of ascorbic acid, which is a π-donor, may be more easily transferred to the cobalt (III) moiety, which has an unsaturated ligand. The small difference in reactivity between $Me_6[14]4,11\text{-}dieneN_4$ and $ms\text{-}Me_6[14]aneN_4$ is probably due to the steric hindrance of methyl groups.

These reactivities can also be explained by an alternative pathway which is a substitution-limited inner-sphere mechanism:



(17)

It is expected that the OH^- ligand accelerates the dissociation of the water molecule in the trans position; in fact, the dissociation of the water molecule of $[Co(OH)([14]aneN_4)(H_2O)]^{2+}$ is not slow ($k_d = (1.4 \pm 0.3) \times 10^{-2}\ s^{-1}$ at 25 °C and $I = 0.1\ mol\ dm^{-3}$ [21])). Studies of the kinetics of the water displacement of these macrocyclic complexes are in progress in order to establish the mechanism of the reactions of $[Co(OH)(N_4)(H_2O)]^{2+}$ with ascorbic acid.

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