Kinetics of the Acid Dissociation of Cyclic and Open-chain Tetramine Complexes of Cobalt(II): General Acid Catalysis with Co-ordinating Phosphate–Citric Acid Buffers†

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The kinetics of dissociation of the cobalt(II) complexes of the quadridentate ligands 1,4,8,11-tetraazacyclotetradecane (cyclam), triethylenetetramine (trien) and 2,2′,2″-triaminotriethylamine (tren) was followed spectrophotometrically in the ranges $10 < T < 50$ °C and $0.8 < \text{pH} < 4.0$ in perchloric acid and McIlvaine phosphate–citrate buffer system, an an ionic strength $I = 1.0$ mol dm^{-3}, NaClO$_4$. The complexes were prepared *in situ* in preaerated solutions under a nitrogen atmosphere, by the addition of a 10% excess of the ligand in the form of the free base to a solution of $CoCl_2 \cdot 6H_2O$. The ligand dissociation reaction was then initiated by the addition of perchloric acid or McIlvaine phosphate–citrate buffer. No dissociation was observed for the cyclam complex in perchloric acid media. It was, however, observed in the buffer and obeyed biphasic kinetics comprising two consecutive first-order steps. The action of the phosphate and/or citrate is attributed to their complexing ability and to their association through hydrogen bonding to the axial aqua ligand, thus bringing the proton closer to the dissociating nitrogen and hence catalysing the dissociation. The dissociation kinetics of the open-chain unbranched trien and the tripod tren was observed in perchloric acid as well as the McIlvaine buffer system. Except when too fast to follow by conventional spectrophotometry, the reaction obeyed biphasic kinetics comprising two consecutive first-order steps. The tren complex dissociates at a rate 5–10 times faster than that of trien, the first step being too fast to follow except at 10 °C in the buffer system. The observed rate dependence is explained on the basis of mechanisms involving solvation, specific acid catalysis and general acid catalysis. The cyclam complex dissociates at a rate 5–30 times slower than those of the two open-chain complexes. This is attributed to the stabilization due to the hindered rotation of the dissociating nitrogen (entropic effect) and to the higher ligand-field stabilization of the macrocycle (enthalpic effect). Mechanisms covering the entire range of pH studied and conforming to the observed rate laws are given.

Macrocyclic ligands[1] offer enhanced kinetics and thermodynamic stabilities of corresponding metal complexes over those observed for their open-chain counterparts. This effect has been termed the macrocyclic effect.[2] It was originally attributed to an entropic[3] effect arising from the restricted configuration that the macrocycle offers, and to an enthalpic[4] effect resulting from the diminished solvation of the free macrocyclic ligand[5–8] relative to the open-chain analogue. The two effects reflect a number of separate components[7,8–11] the magnitudes of which will vary from one system to another.

The kinetic and mechanisms of formation[12–15] and dissociation[16–20] of macrocyclic complexes is an area covering a wide range of behaviour. The details of a particular reaction often reflect the type of metal ion present and the structural features of the cyclic ligand. Thus the formation reactions of these complexes can be governed by the rate of solvent exchange, ligand rearrangement in the co-ordination sphere, steric and electrostatic effects as well as the possibility of ligand protonation.[14,21] On the other hand the dissociation kinetics reflects the kinetic macrocyclic effects (the inertness associated with the close fit of the ligand). The dissociation often requires energetically unfavourable rearrangements[22,23] such as folding within the co-ordination sphere before dissociation can occur.

In the present work we report the results of kinetic studies on the ligand dissociation of two open-chain (triethylenetetramine and 2,2′,2″-triaminotriethylamine) and one macrocyclic (1,4,8,11-tetraazacyclotetradecane, cyclam) polyamine complexes of cobalt(II) in the presence of perchloric acid and McIlvaine phosphate–citric acid buffers at an ionic strength $I = 1.0$ mol dm^{-3}, NaClO$_4$.

Experimental

Materials.—Except where indicated, reagent-grade chemicals were used without further purification. Doubly distilled water was used for the preparation of all solutions. 1,4,8,11-Tetraazacyclotetradecane (Fluka) and triethylenetetramine (trien) (Fluka) were used without further purification. 2,2′,2″-Triaminotriethylamine trihydrochloride (tren·3HCl) was obtained from Strem Chemicals. The free base was obtained by addition of 3 equivalents of carbonate-free standard NaOH solution.

Complexes.—The aqueous solutions of the complexes (ionic strength calculated to give a final value of 1.0 mol dm^{-3}, NaClO$_4$ in the kinetic experiments) were prepared by mixing prethermostatted stock solutions of $CoCl_2 \cdot 6H_2O$ and a 10% excess of the ligands. All solutions were deaerated by bubbling a stream of purified N_2 (g) for 15–20 min before mixing. The resulting solutions were left to stand for 10 min to complete complex formation and used for the kinetic experiments.

Buffer Solutions.—McIlvaine[24] phosphate–citric acid buffers were used for reactions at pH >2.0. Stock solutions of the buffers were prepared to give the desired pH value when diluted four times. Fresh buffer solutions were used in all experiments.

pH *Measurements.*—The pH measurements were made with an Orion Research model 601 A Digital Ion analyser equipped

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† Taken in part from the M.Sc. thesis of H. A. Gazzaz, King Abdulaziz University, 1991.

with an Orion combination electrode. The meter was standardized against commercially available standard buffers. The pH values of all kinetic runs were measured immediately after mixing the solutions and again when the kinetic measurements were completed. No noticeable pH change was observed. The hydrogen-ion concentration $[H^+]$ was calculated from the activity values, *i.e.* pH, using the relationship (1), on the basis

$$-\log [H^+] = pH + \log \gamma = pH - 0.15 \qquad (1)$$

of electrode calibration titrations[25,26] with standard NaOH and $HClO_4$, where γ is the mean activity coefficient and is consistent with the extended Debye–Huckel relationship[27] (2).

$$-\log \gamma = \frac{0.5Z^2I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.1\ I \qquad (2)$$

Rate Measurements.—All rate measurements were made at an ionic strength $I = 1.0$ mol dm^{-3}, $NaClO_4$, over the ranges $0.8 < pH < 4.0$ and $10 < T < 50$ °C. The pH was generated prior to use and the kinetics followed by UV/VIS methods. Kinetic runs were initiated by mixing freshly prepared solutions of the complexes $[Co(cyclam)]^{2+}$, $[Co(tren)]^{2+}$ or $[Co(trien)]^{2+}$ with a solution that contained the desired quantity of $HClO_4$. All solutions were thermostatted to the required temperature and deaerated by bubbling a stream of purified N_2 (g) for 15–20 min before mixing. The resulting solution was then well mixed and quickly transferred to a thermostatted quartz cell sealed with a Teflon stopper and placed in the thermostatted cell compartment of the spectrophotometer. The reaction was followed at a fixed wavelength dependent on the absorption maximum of the complex {400 and/or 460 nm for $[Co(cyclam)]^{2+}$, 350 nm for $[Co(trien)]^{2+}$ and 345 nm for $[Co(tren)]^{2+}$}. The kinetic experiment was then followed by utilizing the time-drive chart procedure of the spectrophotometer. In a number of experiments, spectrum *vs.* time curves were recorded over the range 650–250 nm. Spectral and kinetic measurements were done using a Shimadzu 260 and/or 160 UV/VIS spectrophotometer equipped with a thermostatted cell compartment.

Treatment of Data.—All ligand-dissociation kinetic data were found well fitted by the assumption of first-order kinetics or of two consecutive first-order steps. The observed pseudo-first-order rate constants were calculated from plots of $\ln[(A_t - A_0)/(A_0 - A_\infty)]$ *vs.* time, where A_0, A_t and A_∞ are the absorbances at time zero, t, and infinity respectively. The final values for the rate constants were obtained from linear least-squares fits of the data and are reported as the means of at least three measurements for the $[H^+]$-dependence study.

The biphasic kinetics data were well fitted by the assumption of two consecutive first-order steps. The rate constants were calculated[28,29] by the use of equation (3), which reduces to equation (4), with C and D representing the constant pre-exponential factors and A_I and A_P are the absorbancies of the intermediate and product respectively. On the assumption that

$$(A_t - A_P) = \left(A_R + \frac{A_Ik_1}{k_2 - k_1} + \frac{A_Pk_2}{k_1 - k_2}\right)e^{-k_1t} + \left(\frac{A_Ik_1}{k_1 - k_2} - \frac{A_Pk_1}{k_1 - k_2}\right)e^{-k_2t} \qquad (3)$$

$$(A_t - A_P) = C\,e^{-k_1t} + D\,e^{-k_2t} \qquad (4)$$

k_1 is larger than k_2, a plot of $\ln(A_t - A_P)$ *vs.* time should give a straight line at long times; a plot of $\ln(A_t - A_P - D\,e^{-k_2t})$ *vs.* time should give a straight line in the early stages of the reaction. Initial values of k_1 and k_2 were obtained graphically by this method, and these were used to get the final values with an iterative[30] least-squares treatment. The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were obtained from a linear least-squares fit of the $\ln(k/T)$ *vs.* $1/T$ data as given by Eyring's transition-state equation.[31–33]

Table 1 Temperature dependences and activation parameters for the dissociation rate constants of $[Co(H_2O)_2(cyclam)]^{2+}$ in McIlvaine buffers

T/°C	10^3k_{1obs}/s^{-1}	10^4k_{2obs}/s^{-1}
20	5.6 ± 0.6	5 ± 2
30	9.8 ± 0.9	3.7 ± 1
40	19 ± 9	8 ± 1
50		23 ± 2
$\Delta H^‡$/kJ mol^{-1}	44 ± 2	69 ± 6
$\Delta S^‡$/J K^{-1} mol^{-1}	−137 ± 0.5	−84 ± 4

Results and Discussion

Ligand Dissociation Kinetics of $[Co(H_2O)_2(cyclam)]^{2+}$.—The addition of a (10% excess) solution of cyclam to an aqueous solution of $CoCl_2{\cdot}6H_2O$ causes an immediate colour change from light pink to pale green, indicative of formation of the cobalt(II) cyclam complex.[34,35] Addition of perchloric acid protonates the excess of free ligand without decomposing the complex.[35,36] The visible spectrum of such solutions showed a maximum at $\lambda = 465$ nm, $\varepsilon = 22.5$ dm^3 mol^{-1} cm^{-1} and is in good agreement with that in the literature.[37] The resulting protonated species is very stable in solutions of perchloric acid and no evidence for ligand dissociation is observed. Thus, a solution of $[Co(H_2O)_2(cyclam)]^{2+}$ in 0.1 mol dm^{-3} $HClO_4$ was stable even after heating for 0.5 h at 90 °C. The use of higher acid concentrations resulted in the precipitation of a green solid with no evidence of decomposition.

It is known[2,38] that compounds containing a macrocyclic ligand co-ordinating coplanar to a metal ion resist stepwise dissociation in acid, in contrast to those containing linear ligands which undergo rapid dissociation in acid.

Many of the cobalt(II) complexes containing 14-membered tetradentate macrocycles having nitrogen-donor atoms are known from crystallographic determinations to have a six-co-ordinate geometry with the macrocycle occupying the equatorial positions.[39] The remainder of such complexes are surmised to possess similar geometries.[35] The restricted configuration that the macrocycle forms around the metal ion leads to a 'multiple juxtapositional fixedness'[40] which inhibits stepwise dissociation of the donor atoms from the metal ion.[2,3]

In contrast to the behaviour in perchloric acid solutions, addition of phosphate–citric acid buffer resulted in the dissociation of the complex and the formation of $Co(aq)^{2+}$ and the free ligand. The amount of $Co(aq)^{2+}$ was determined spectrophotometrically using thiocyanate in 50% aqueous acetone ($\lambda = 623$ nm, $\varepsilon = 1.84 \times 10^3$ dm^3 mol^{-1} cm^{-1}).[41] The reaction was thus studied in the buffer system in the range $2.0 < pH < 4.0$, $I = 1.0$ mol dm^{-3}, $NaClO_4$ at 20.0, 30.0, 40.0 and 50.0 ± 0.1 °C, under pseudo-first-order conditions in which the buffer concentration was at least 25 times greater than that of the complex. The reaction was followed spectrophotometrically for up to 5 half-lives at $\lambda = 400$ and 460 nm. In a number of experiments, spectrum *vs.* time curves were recorded over the range 650–300 nm. The reaction conformed to biphasic kinetics made up of two consecutive first-order steps. The corresponding observed rate constants k_{1obs} and k_{2obs} were independent of the pH of the buffer used over the pH range studied. The average values of k_{1obs} and k_{2obs} at the four temperatures studied are collected in Table 1, together with the corresponding activation parameters $\Delta H^‡$ and $\Delta S^‡$.

The above results show that the dissociation of the macrocyclic complex is initiated by the presence of the phosphate and/or citrate ions in the buffer system. These species are known for their great ability to co-ordinate to metal ions. The fact that no dissociation was observed in the presence of perchloric acid is indicative of the fact that the catalytic process of ring opening does not depend so much on acid strength, but rather on the ability of the acid to co-ordinate.

The acid-catalysed protonation and dissociation of deprotonated oligopeptides of copper(II) and nickel(II) was found[42] to proceed *via* a series of protonation steps, each of which involves a number of rate-determining steps, in the sense that water molecules, protons and the applied acid HB can induce the reaction.[18,20,43,44]

The contributions of the terms $k_H[H^+]$ and $k_{HB}[HB]$ are referred to as being specific acid catalysis and general acid catalysis respectively.[18,25] The extent of general acid catalysis depends strongly on the nature of HB. Thus sterically hindered acids such as the non-co-ordinating buffers 2-morpholinoethanesulfonic acid, piperazine-*N*,*N*′-bis(ethane-2-sulfonic acid), 2,6-dimethylpyridine-3-sulfonic acid, 3-acetyl-2,4,6-trimethylpyridine, *etc*., show very little or practically no acid catalysis.[25,45] Co-ordinating acids such as acetic acid, however, give rise to a substantial contribution to the dissociation process in the term $k_{HB}[HB]$.

The foregoing discussion shows that the ligand-cleavage kinetics of $[Co(H_2O)_2(cyclam)]^{2+}$ exhibits general acid catalysis, meaning that the presence of phosphate and/or citrate species in the reaction medium helps in activating the dissociation process. The reaction scheme can be represented by the sequence (5).

$$[Co(cyclam)]^{2+} \xrightarrow[HB]{k_{1obs}} [Co(Hcyclam)]^{3+} \xrightarrow[HB]{k_{2obs}} Co(aq)^{2+} + H_4cyclam^{4+} \quad (5)$$

As stated previously, the $[Co(cyclam)]^{2+}$ complex has a *trans*-octahedral arrangement in aqueous solution with the tetramine equatorial and the aqua groups axial. The generally accepted stepwise mechanism for the dissociation of tetramine macrocyclic ligand complexes is that suggested by Margerum and co-workers.[16,17] The complete detailed mechanism[46,47] is given in Scheme 1. For cleavage of the first cobalt–nitrogen bond there are three possible pathways: (1) solvation or solvent separation; (2) direct protonation, acid-assisted or specific acid catalysis, and (3) general acid catalysis. The dissociation or cleavage of the second cobalt–nitrogen bond has four possible mechanistic pathways: (1) solvation, (2) direct protonation, (3) intramolecular hydrogen bonding, and (4) general acid catalysis.

In the present system no evidence was found for the solvation or acid-catalysed pathways in either of the two steps, since solutions of $[Co(cyclam)]^{2+}$ are stable in perchloric acid for long periods of time. The only possible pathway is that of general acid catalysis.

Since the concentration of the general acid was kept virtually constant in all experiments one can write equations (6) and (7).

$$k_{1obs} = k_{1HB}[HB]_T \quad (6)$$

$$k_{2obs} = k_{2HB}[HB]_T \quad (7)$$

Given that $[HB]_T = 0.12$ mol dm^{-3}, values of 8.2×10^{-2} and 3.1×10^{-3} dm^3 mol^{-1} s^{-1} for k_{1HB} and k_{2HB} respectively are calculated at 30.0 °C. Since the weak acids are more effective than H_3O^+ in accelerating or bringing about dissociation of the $[Co(cyclam)]^{2+}$ complex, it is safe to assume that they react in a way so as to make proton transfer more efficient. The fact, however, remains that even at very high $[H^+]$ no dissociation was observed in the absence of the general acid. We have thus suggested (see general mechanism) that the general acid co-ordinates to the complex in such a way that the proton can be more readily transferred to the donor. In addition, the co-ordination of the general acid to the metal ions removes electron density from the bonding region to the co-ordinated nitrogen *cis* to the co-ordinated general acid. This labilizes the bond and helps in its cleavage.[48] Similar enhanced general acid catalysis has been observed for the cleavage of metal–peptide nitrogen bonds in the presence of co-ordinating acids such as $HC_2O_4^-$, $H_2PO_4^{2-}$, HCO_3^-, H_2trien^{2+}, *etc.*[19,43,49,50] Finally since the relative concentrations of the phosphate and citrate ions vary from one buffer to the other without changing the values of k_{obs}, it appears that the demetallation process is a combined effect and that both ions behave kinetically in a similar fashion.

Table 2 Observed first-order rate constants for the dissociation of $[Co(H_2O)_2(trien)]^{2+}$ in perchloric acid

10 °C			30 °C	
$10^2[H^+]$/mol dm^{-3}	10^2k_{1obs}/s^{-1}	10^3k_{2obs}/s^{-1}	$10^2[H^+]$/mol dm^{-3}	10^2k_{2obs}/s^{-1}
22.9	1.70 ± 0.08	1.50 ± 0.1	22.9	1.29 ± 0.02
20.9	1.68 ± 0.08	1.70 ± 0.1	20.9	1.21 ± 0.02
17.4	1.80 ± 0.07	1.36 ± 0.07	17.4	0.99 ± 0.02
13.8	1.35 ± 0.06	1.14 ± 0.06	13.8	0.81 ± 0.02
11.2	1.33 ± 0.05	1.22 ± 0.06	11.2	0.79 ± 0.02
5.4	1.13 ± 0.05	1.15 ± 0.06	5.4	0.49 ± 0.03
1.9	0.74 ± 0.03	0.79 ± 0.02	1.9	0.38 ± 0.02
20 °C			40 °C	
$10^2[H^+]$/mol dm^{-3}	10^2k_{1obs}/s^{-1}	10^3k_{2obs}/s^{-1}	$10^2[H^+]$/mol dm^{-3}	10^2k_{2obs}/s^{-1}
25.7	3.37 ± 0.05	5.21 ± 0.06	25.7	3.7 ± 0.3
18.6	4.1 ± 0.3	4.8 ± 0.4	18.6	2.8 ± 0.2
13.8	2.58 ± 0.07	3.4 ± 0.1	13.8	2.15 ± 0.04
13.5	3.5 ± 0.1	4.5 ± 0.2	12.0	1.97 ± 0.02
12.0	1.67 ± 0.09	2.4 ± 0.2	8.5	1.51 ± 0.03
5.4	1.3 ± 0.3	1.9 ± 0.8	6.8	1.14 ± 0.02
2.8	1.08 ± 0.04	1.61 ± 0.07	2.8	0.58 ± 0.01

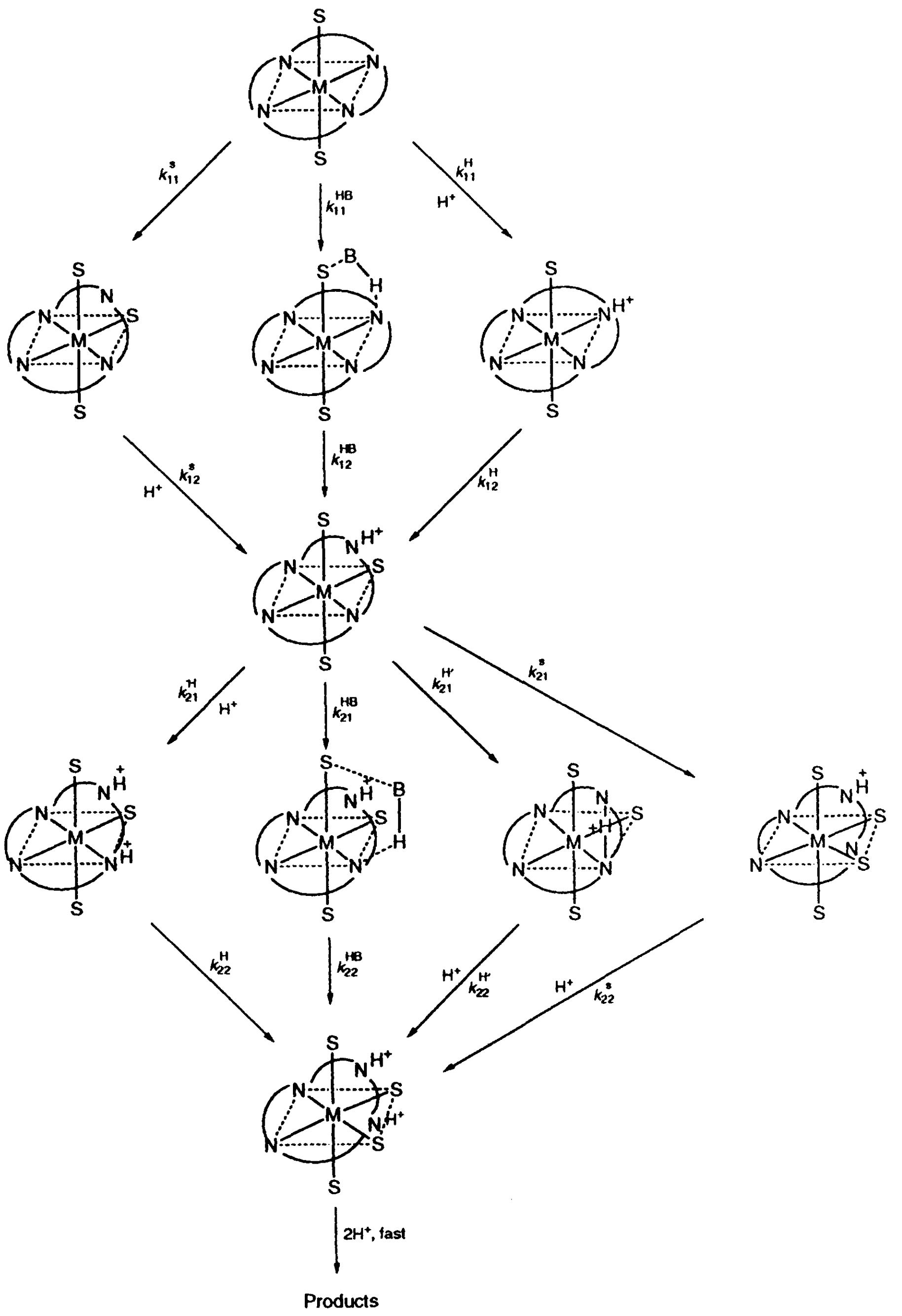
Table 3 Final rate and activation parameters for the dissociation of $[Co(H_2O)_2(trien)]^{2+}$ in perchloric acid

	k_{1obs}/s^{-1}		k_{2obs}/s^{-1}	
T/°C	$10^2k_{11}^{H_2O}$/s^{-1}	$10^2k_{12}^{H}$/dm^3 mol^{-1} s^{-1}	$10^3k_{21}^{H_2O}$/s^{-1}	$10^2k_{22}^{H}$/dm^3 mol^{-1} s^{-1}
10	0.8 ± 0.1	4.5 ± 0.6	0.72 ± 0.09	0.38 ± 0.05
20	0.8 ± 0.2	10 ± 1	1.0 ± 0.3	1.7 ± 0.2
30	—	—	2.4 ± 0.4	4.5 ± 0.2
40	—	—	2.7 ± 0.4	13.6 ± 0.3
$\Delta H^\ddagger$/kJ mol^{-1}		55	31 ± 2	84 ± 3
$\Delta S^\ddagger$/J K^{-1} mol^{-1}		−77	−197 ± 8	5 ± 0.6

Ligand Dissociation Kinetics of $[Co(H_2O)_2(trien)]^{2+}$.—The dissociation kinetics of the trien complex was followed in a similar fashion to that for the cyclam complex, in the ranges $0.02 < [H^+] < 0.25$ mol dm^{-3} $HClO_4$ and $2 < pH < 4$, using McIlvaine phosphate–citric acid buffers at $I = 1.0$ mol dm^{-3}, $NaClO_4$ and at 10.0, 20.0, 30.0 and 40.0 ± 0.1 °C. Except where the first step was too fast to follow the reaction conformed to biphasic kinetics made up of two consecutive first-order steps. The rate constants k_{1obs} and k_{2obs} in perchloric acid are given in Table 2 and those in the phosphate–citric acid media in Table 4.

The perchloric acid data were found to be linear functions of $[H^+]$ and were thus fitted by equations (8) and (9) where k^{H_2O}

$$k_{1obs} = k_{11}^{H_2O} + k_{12}^{H}[H^+] \quad (8)$$



Scheme 1 Stepwise mechanism for the dissociation of metal–tetradentate macrocycle complexes (S = solvent molecule)

$$k_{2\text{obs}} = k_{21}^{H_2O} = k_{22}^{H}[H^+] \qquad (9)$$

and k^H refer to the water- and proton-induced dissociation respectively. Values for these constants together with their activation parameters are given in Table 3. The rate constant $k_{11}^{H_2O}$ did not show any temperature dependence in the narrow range studied.

Scheme 2 gives a mechanism which conforms to the rate equations (8) and (9). The observed rate constant for each of the two biphasic steps corresponding to Scheme 2 takes the forms (10) and (11). Equations (10) and (11) reduce to the experimentally observed rate constants given that $K_1[H^+]$, $K_2[H^+] \ll 1$, since the pK value of the intermediate is likely to be less than that of H_4trien^{4+} (pK = 3.32).[51] Under these conditions we have $k_{11}^{H_2O} = k_{11}$, $k_{12}^{H} = k_{12}K_1$, $k_{21}^{H_2O} = k_{21}$ and $k_{22}^{H} = k_{22}K_2$.

$$k_{1\text{obs}} = \frac{k_{11} + k_{12}K_1[H^+]}{1 + K_1[H^+]} \qquad (10)$$

$$k_{2\text{obs}} = \frac{k_{21} + k_{22}K_2[H^+]}{1 + K_2[H^+]} \qquad (11)$$

An alternative mechanism for the dissociation of the trien complex is given in Scheme 3. This mechanism is a modification of that given by Lilie and co-workers[52] for the dissociation of cobalt(II) polyamines formed by the reaction of hydrated electrons e(aq)$^-$ with the corresponding cobalt(III) complexes. The essential feature of the mechanism in Scheme 3 is that the rupture of the first Co^{II}–N bond takes place *via* a rate-determining reversible step. The detached end of the polyamine ligand will remain near Co^{II} and can easily reform the chelate ring if a proton does not add to it. Our experimental conditions and method do not allow for the establishment of the number of protons actually involved in each step. The fact still remains that

Table 4 Observed first-order rate constants for the dissociation of $[Co(H_2O)_2(trien)]^{2+}$ in McIlvaine buffers

10 °C

$10^4[H^+]$/mol dm^{-3}	10^2k_{1obs}/s^{-1}	10^4k_{2obs}/s^{-1}
53.7	1.14 ± 0.05	16.9 ± 0.5
22.4	0.98 ± 0.04	12.8 ± 0.3
11.2	0.71 ± 0.03	7.9 ± 0.1
4.7	0.24 ± 0.03	5.5 ± 0.5
1.7	0.49 ± 0.01	5.1 ± 0.4

20 °C

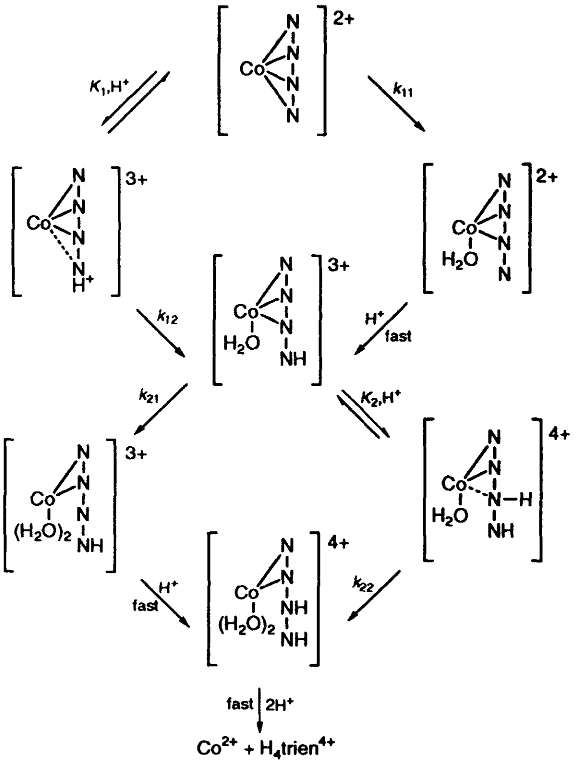
$10^4[H^+]$/mol dm^{-3}	10^2k_{1obs}/s^{-1}	10^3k_{2obs}/s^{-1}
85.1	1.90 ± 0.04	4.06 ± 0.09
35.5	1.67 ± 0.05	3.80 ± 0.09
14.1	1.36 ± 0.05	2.61 ± 0.06
7.1	0.89 ± 0.02	1.67 ± 0.03
2.6	0.70 ± 0.03	1.13 ± 0.03

30 °C

$10^4[H^+]$/mol dm^{-3}	10^2k_{1obs}/s^{-1}	10^3k_{2obs}/s^{-1}
85.1	2.3 ± 0.2	5.7 ± 0.6
36.3	1.8 ± 0.1	4.7 ± 0.5
17.8	1.14 ± 0.05	3.0 ± 0.3
8.9	1.10 ± 0.04	3.0 ± 0.1
2.7	0.56 ± 0.03	1.6 ± 0.1

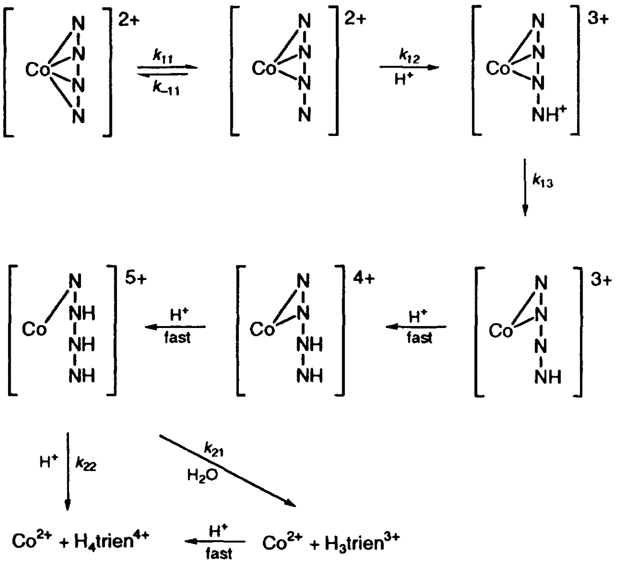
40 °C

$10^4[H^+]$/mol dm^{-3}	10^2k_{2obs}/s^{-1}
85.1	1.27 ± 0.02
53.7	1.01 ± 0.02
37.2	0.77 ± 0.01
14.5	0.56 ± 0.01
5.2	0.43 ± 0.01
4.7	0.41 ± 0.01
2.5	0.16 ± 0.01



Scheme 2 Mechanism involving acid- and solvent-assisted pathways for the dissociation of $[Co(H_2O)_2(trien)]^{2+}$

in their case, as in ours, the rate-determining step involves only one hydrogen ion in each of the two consecutive steps. Whether the rate-determining steps are the rupture of the first and last cobalt(II)–nitrogen bonds, or the first and second, is open to question. Melson and Wilkins[53] reported that for the dissociation of nickel(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 fast. On the other hand, Margerum *et al.*[54] 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 $[Ni(trien)]^{2+}$. Apart from this controversey, however, which cannot be resolved by the techniques used in this or the above authors works, the mechanism in Scheme 3 gives, after consideration of steady-state kinetics for the half-bonded unprotonated species, expressions (12) and (13).



Scheme 3 Alternative mechanism involving steady-state intermediates for the dissociation of $[Co(H_2O)_2(trien)]^{2+}$

$$k_{1obs} = \frac{k_{11}k_{12}[H^+]}{k_{-11} + k_{12}[H^+]} \quad (12)$$

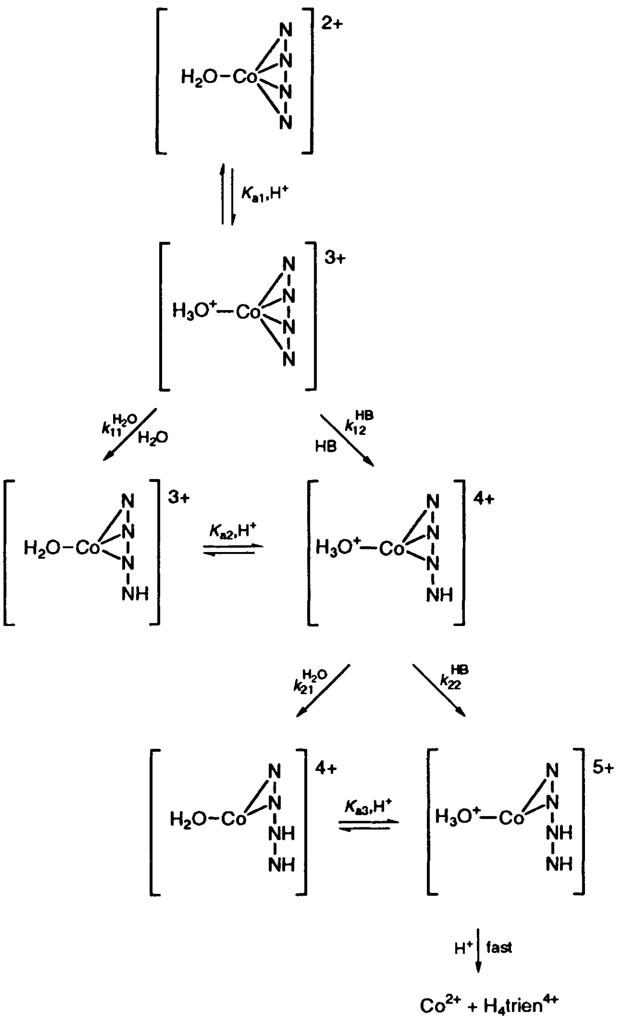
$$k_{2obs} = k_{21} + k_{22}[H^+] \quad (13)$$

Equation (13) for the second step is identical to that given by Scheme 2 with $k_{21}^{H_2O} = k_{21}$ and $k_{22}^{H} = k_{22}$. Rearranging equation (12) for the first step gives (14). A plot of $1/k_{1obs}$ *vs.*

$$\frac{1}{k_{1obs}} = \frac{1}{k_{11}} + \frac{k_{-11}}{k_{11}k_{12}[H^+]} \quad (14)$$

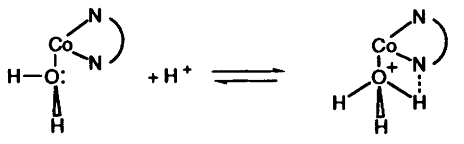
$[H^+]^{-1}$ should give a straight line with an intercept of $1/k_{11}$ and a slope of $k_{-11}/k_{11}k_{12}$. A least squares fit for the k_{1obs} data using equation (14) gave respectively for the slope and intercept the values 1.6 ± 0.1 s and 55.4 ± 2.8 mol dm^{-3} s^{-} at 10 °C and 2.1 ± 0.4 s and 24.4 ± 6.4 mol dm^{-3} s^{-1} at 20 °C.

A final note on the acid-catalysed pathway in the dissociation of polyamine complexes is pertinent. The co-ordinated trien molecule has no readily available electrons for bond-attacking protons. Thus the dissociation will be initiated by ring opening. It was suggested, however, by Margerum and co-workers[17,55] that protonation of the dissociating nitrogen can take place



Scheme 4 Mechanism for the general acid catalysis of the dissociation of $[Co(H_2O)_2(trien)]^{2+}$ in McIlvaine buffers

while it is still within the first co-ordination sphere. In this analysis the role of the water molecule occupying the co-ordination site *cis* to the dissociating nitrogen has been neglected. In fact these water molecules are capable of adding a proton *via* the available lone pair. This would result in a withdrawal of electron density from the Co^{II}–N bond, hence facilitating its rupture. In addition, as can be seen from the schematic representation (15), the protonated H_2O brings the



(15)

proton closer to the nitrogen atom resulting in a faster rate of rupture of the Co^{II}–N bond. The possibility thus manifests itself that it is this protonated species that undergoes dissociation *via* a water pathway and an acid-assisted pathway.

We thus conclude that three mechanisms are possible for the dissociation of multidentate ligands in acid solutions;[56,57] (1) a proton attaches itself to the donor atom, (2) a proton attaches itself to other basic groups in the ligand and (3) a proton attaches itself to a basic group occupying an adjacent co-ordination site to the dissociating donor atom.

The dissociation kinetics of the trien complex in presence of the phosphate–citrate buffer was studied at 10.0, 20.0, 30.0 and 40.0 ± 0.1 °C. Two steps each associated with two first-order rate constants were observed, except at 40 °C where only one step was realized. The data are presented in Table 4. The observed first-order rate constants were well fitted by the relationship (16). The kinetic behaviour is consistent with a

$$[H^+]/k_{obs} = a + b[H^+] \qquad (16)$$

mechanism in which rapid protonation of $[Co(trien)]^{2+}$ occurs prior to rate-limiting reactions with H_2O or with HB. The sequence of reaction steps is given in Scheme 4. This gives the relationships (17) and (18) which can be rearranged to give (19)

$$k_{1obs} = \frac{(k_{11}^{H_2O} + k_{12}^{HB})K_{a1}[H^+]}{1 + K_{a1}[H^+]} \qquad (17)$$

$$k_{2obs} = \frac{(K_{21}^{H_2O} + k_{22}^{HB})K_{a2}[H^+]}{1 + K_{a2}[H^+]} \qquad (18)$$

$$\frac{[H^+]}{k_{1obs}} = \frac{1}{(k_{11}^{H_2O} + k_{12}^{HB})K_{a1}} + \frac{[H^+]}{(k_{11}^{H_2O} + k_{12}^{HB})} \qquad (19)$$

$$\frac{[H^+]}{k_{2obs}} = \frac{1}{(k_{21}^{H_2O} + k_{22}^{HB})K_{a2}} + \frac{[H^+]}{(k_{21}^{H_2O} + k_{22}^{HB})} \qquad (20)$$

and (20). The various kinetic rate constants were obtained from a least-squares fit of the data by equations (19) and (20) and are given in Table 5. In arriving at the rate constants for the general acid pathway we subtracted the rate constants for the water pathway obtained from the perchloric acid data.

Table 5 Final rate and activation parameters for the first and second steps of the dissociation of $[Co(H_2O)_2(trien)]$ in McIlvaine buffers

T/°C	$10^3k_{12}^{HB}$/ s^{-1}	$10^{-3}K_{a1}$/ $dm^3\ mol^{-1}$	$10^3k_{22}^{HB}$/ s^{-1}	$10^{-3}K_{a2}$/ $dm^3\ mol^{-1}$
10	4.5 ± 0.9	2.6 ± 0.8	1.2 ± 0.1	1.6 ± 0.4
20	13 ± 2	1.9 ± 0.2	3.6 ± 0.1	1.5 ± 0.2
30	19 ± 2	0.9 ± 0.2	4.1 ± 0.4	1.1 ± 0.3
40	—	—	12 ± 1	0.75 ± 0.1
$\Delta H^{\ddagger}$/ kJ mol^{-1}	50 ± 7	—	48 ± 7	—
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−114 ± 7	—	−129 ± 7	—
ΔH°/ kJ mol^{-1}	—	−38 ± 6	—	−26 ± 1
ΔS°/J K^{-1} mol^{-1}	—	−71 ± 20	—	−30 ± 4
ΔG°_{298}/ kJ mol^{-1}	—	−59 ± 17	—	−17 ± 5

Ligand Dissociation Kinetics of $[Co(H_2O)_2(tren)]^{2+}$.—The ligand dissociation kinetics of the tren complex was followed in exactly the same fashion as that for the trien analogue. The complex was again prepared *in situ* by the addition of a deaerated (by the use of purified nitrogen gas) 10% excess of the free base to a deaerated solution of $CoCl_2{\cdot}6H_2O$. The free base was prepared from the trihydrochloride salt by the addition of 3 equivalents of NaOH.

The dissociation of the complex was initiated by the addition of perchloric acid or McIlvaine phosphate–citrate buffer. The reaction was followed up to 5 half-lives at 10.0, 20.0, 30.0 and 40.0 ± 0.1 °C. It was much faster than that of the trien analogue. Except at 10 °C in the buffer mixture, the first step was too fast to follow. Only the second step of dissociation was observed. The reaction thus conformed to first-order kinetics. The data for the ligand dissociation in perchloric acid are given in Table 6. The observed rate constant k_{2obs} data was well fitted by a linear function of $[H^+]$ of the form (21). Since this

$$k_{2obs} = k_{21}^{H_2O} + k_{22}^{H}[H^+] \qquad (21)$$

Table 6 Observed first-order rate constants for the dissociation of $[Co(H_2O)_2(tren)]^{2+}$ in perchloric acid

10 °C		30 °C		20 °C		40 °C	
$10^2[H^+]$/ mol dm^{-3}	10^2k_{2obs}/ s^{-1}	$10^2[H^+]$/ mol dm^{-3}	10^2k_{2obs}/ s^{-1}	$10^2[H^+]$/ mol dm^{-3}	10^2k_{2obs}/ s^{-1}	$10^2[H^+]$/ mol dm^{-3}	10^2k_{2obs}/ s^{-1}
34.7	5.0 ± 0.5	24.0	7.5 ± 0.7	34.7	7.7 ± 0.9	19.5	10.9 ± 0.5
28.2	4.2 ± 0.2	19.5	6.9 ± 0.5	28.2	6.4 ± 0.7	12.3	7.6 ± 0.1
24.0	3.6 ± 0.2	12.3	4.4 ± 0.3	24.0	5.5 ± 0.5	9.1	6.2 ± 0.3
19.5	2.9 ± 0.1	9.8	4.0 ± 0.1	19.5	4.9 ± 0.3	3.5	3.73 ± 0.04
12.6	2.31 ± 0.04	3.5	2.42 ± 0.02	12.3	3.5 ± 0.2		
8.9	1.60 ± 0.02			8.9	2.89 ± 0.04		
3.5	0.75 ± 0.01			3.5	1.82 ± 0.04		

Table 7 Final rate and activation parameters for the dissociation of $[Co(H_2O)_2(tren)]^{2+}$ in perchloric acid

T/°C	$10^3k_{21}^{H_2O}$/s^{-1}	k_{22}^{H}/dm^3 mol^{-1} s^{-1}
10	4.0 ± 0.8	0.135 ± 0.004
20	11.8 ± 0.6	0.186 ± 0.003
30	14 ± 2	0.26 ± 0.01
40	21.1 ± 0.3	0.45 ± 0.01
$\Delta H^‡$/kJ mol^{-1}	36 ± 7	27 ± 2
$\Delta S^‡$/J K^{-1} mol^{-1}	−161 ± 13	−168 ± 2

Table 8 Observed first-order rate constants for the dissociation of $[Co(H_2O)_2(tren)]^{2+}$ in McIlvaine buffers

10 °C			30 °C	
$10^4[H^+]$/ mol dm^{-3}	10^2k_{1obs}/ s^{-1}	10^3k_{2obs}/ s^{-1}	$10^4[H^+]$/ mol dm^{-3}	10^2k_{2obs}/ s^{-1}
354.8	3.7 ± 0.4	7.0 ± 0.3	354.8	2.54 ± 0.04
125.9	1.7 ± 0.2	4.0 ± 0.3	125.9	1.80 ± 0.02
56.2	1.8 ± 0.3	2.5 ± 0.2	56.2	1.20 ± 0.01
22.4	1.5 ± 0.1	1.42 ± 0.02	22.4	0.77 ± 0.01
4.3	1.2 ± 0.2	0.90 ± 0.01	4.2	0.51 ± 0.01
1.9	1.4 ± 0.1	0.56 ± 0.01	2.0	0.32 ± 0.01
20 °C			40 °C	
$10^4[H^+]$/ mol dm^{-3}		10^2k_{2obs}/ s^{-1}	$10^4[H^+]$/ mol dm^{-3}	10^2k_{2obs}/ s^{-1}
354.8		1.5 ± 0.01	301.2	4.6 ± 0.1
125.9		0.95 ± 0.01	125.9	3.14 ± 0.08
56.2		0.60 ± 0.01	44.7	2.2 ± 0.05
22.4		0.37 ± 0.01	24.5	1.55 ± 0.04
4.2		0.24 ± 0.01	7.7	1.06 ± 0.02
2.0		0.15 ± 0.01	2.0	0.72 ± 0.01

relationship is the same as that observed for trien, we suggest that the same mechanism applies, as given in Schemes 2 and 3. Whether or not the rate-determining step is cleavage of the second or last nitrogen is not answerable by our data. The final rate and activation parameters are given in Table 7 as obtained from linear least-squares fit of the data by the respective equations given above.

The rate constant data for the cleavage of tren in phosphate–citrate buffer are given in Table 8. It was possible only at 10 °C to obtain values for the observed first-order rate constant of the first step which were well fitted by equation (22). This relationship is the same as that observed for the trien analogue and hence it is predicted that the same mechanism given in Scheme 4 is applicable. The final rate parameters for the first rate constants for the second step obtained by the application of Scheme 4 together with the pertinent activation parameters are given in Table 9. The final parameters for the first step at 10 °C are $(k_{11}^{H_2O} + k_{12}^{HB}) = (3.3 \pm 0.4) \times 10^{-2}$ s^{-1} and $K_{a1} = (2.99 \pm 1.9) \times 10^2$ dm^3 mol^{-1}. Individual values for $k_{11}^{H_2O}$ and k_{12}^{HB} cannot be obtained because of the observation of only one step for the dissociation of the tren complex in perchloric acid.

$$[H^+]/k_{obs} = a + b[H^+] \qquad (22)$$

Table 9 Final rate and activation parameters for the dissociation of $[Co(H_2O)_2(tren)]^{2+}$ in McIlvaine buffers

T/°C	$10^3k_{22}^{HB}$/s^{-1}	$10^{-2}K_{a2}$/dm^3 mol^{-1}
10	4 ± 1	1.3 ± 0.4
20	5 ± 2	1.7 ± 0.5
30	13 ± 2	2.3 ± 0.6
40	32 ± 6	3 ± 1
$\Delta H^‡$/kJ mol^{-1}	68 ± 1	—
$\Delta S^‡$/J K^{-1} mol^{-1}	−57 ± 0.1	—
ΔH°/kJ mol^{-1}	—	22 ± 0.7
ΔS°/J K^{-1} mol^{-1}	—	118 ± 2
ΔG°_{298}/kJ mol^{-1}	—	−13 ± 0.4

Conclusion

The rate-determining step in the dissociation of metal chelates is the rupture of the metal–ligand bond. Three general mechanisms are possible for these systems in the presence of added acid, depending on whether the proton is attached to the donor atoms, to other basic groups in the ligand or to other basic ligands within the complex. Since co-ordinated amine has no readily available electrons for a bond-attacking proton, the dissociation of amine complexes would be expected to proceed by the first or last mechanism where the proton assists in the dechelation process either by hydrogen bonding to the donor atom during the ring-opening process or by hydrogen bonding to a basic group on a ligand *cis* to the dissociating ligand.

In the case of the cobalt(II) cyclam complex, the restrictions imposed by the ligand cyclization serve to hold the donor atom in the first co-ordination sphere leading to a much lower rate of dissociation in comparison to the open-chain complexes. In addition, the constraints of the cyclic structure decrease the distances between the ligand sites to be protonated and the metal ion, resulting in extremely large electrostatic repulsions. Therefore, the protonation pathway for cleavage of the Co–N bond in cyclam is highly hindered by electrostatic effects. Consequently, this complex does not dissociate in perchloric acid. Dissociation is only observed in presence of the phosphate–citrate buffer system.

The dissociation of the branched tripod tren proceeds at a rate much faster than that observed for the open-chain unbranched trien. There are three possible points of attack in comparison to only two points for the trien complex. In addition, the hindered dissociation observed for polydentate ligands due to the angular expansion of bond angles in the chelate ring and the hindered rotation of the chelating ligand[58] is smaller for tren compared to trien.

Finally, it should be noted that our experimental conditions and method do not allow for the establishment of the number of protons actually involved in each step. The fact still remains that in our case the rate-determining step involves only one hydrogen ion in each of the two consecutive steps. Whether the rate-determining steps are rupture of the first and last cobalt(II) nitrogen bonds or the first and second is open to question.

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