all memory of its origin. It has often been assumed that a fundamental criterion for the demonstration of a five-coordinate intermediate is that the steric course[13] and all other consequences of the subsequent reaction of the reactive intermediate (discrimination, competition, etc.) are independent of the nature of the leaving group, but, while this provides an operational definition of a dissociative mechanism that is readily open to experimental examination, it diverts attention from the mechanistically important part of the process, namely, the transition state for the slow step. A five-coordinate intermediate whose lifetime is so short that it combines with a component of the environment that it inherited from the parent substrate before this environment can fully reequilibrate is as much the product of a dissociative reaction as the longer lived species. In such a case

(13) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).

one would expect to find that the reactions of the intermediate were influenced by the nature of the leaving group.

The considerable difference between the steric courses of the spontaneous and mercuric ion induced reactions of the *trans*-(*SS*)-Co(trien)Cl$_2$$^+$ cation is extremely difficult to understand in the light of the normal behavior of the 2,3,2-tet analog. It is possible that the steric crowding and the subsequent loosening of the chloride by the attachment of Hg^{2+} is sufficient to cause dissociation without conjugative assistance from the *trans* chloride so that the trigonal bipyramid need not be formed. The square pyramid as suggested by Sargeson[12] would lead to substitution with retention of configuration.

The Relationship between Base Hydrolysis and Racemization at the Asymmetric Nitrogen Center in Cobalt(III) Complexes of 4-(Aminoethyl)-1,4,7,10-tetraazadecane. π Stabilization in the Sn1CB Intermediate

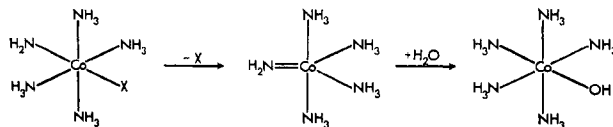BY D. A. BUCKINGHAM, P. A. MARZILLI, AND A. M. SARGESON

The structures of *sym*-Co(trenen)Cl^{2+}, *sym*-Co(trenen)N$_3$$^{2+}$, and *sym*-Co(trenen)OH$_2$$^{3+}$ ions [trenen = 4-(aminoethyl)-1,4,7,10-tetraazadecane] are assigned along with the base hydrolysis and racemization rate constants of the optically active complexes. For the hydrolysis of the chloro complex some racemization occurs in the deprotonated reactant and in the hydroxo product. For the intervening steps, however, the reaction occurs with retention of configuration. This result eliminates for this complex the possibility of an sp^2 N center Co=N< *trans* to the leaving group. The general validity of π stabilization of the five-coordinate intermediate is discussed. The results also imply that inversion and conformational interchange are synchronous.
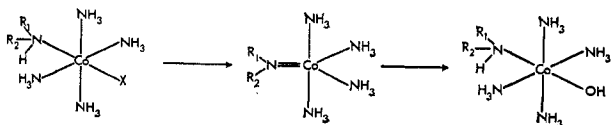
Introduction

In the past few years the evidence in favor of the Sn1CB mechanism for the base hydrolysis of substituted cobalt(III)–ammine type complexes has been substantial.[1-3] Competition and stereochemical studies have established some of the properties of the intermediates of reduced coordination number[2,3] but their stereochemistry is still obscure. In the original proposal for this mechanism Basolo and Pearson[4] accounted for the rapid rate of base hydrolysis (relative to aquation of ions of the same charge as the deprotonated reactant) by invoking the possibility of π bonding in the reaction intermediate: "This π bonding is of the type in which electrons move from ligand to metal" by overlap of a filled p orbital on the deprotonated N center with the vacant d$_{x^2-y^2}$ orbital on cobalt. The movement aids

the loss of leaving group and stabilizes the five-coordinate intermediate

The proposal can be tested provided the center at which deprotonation occurs is optically active. The mode of stabilization of the intermediate requires the N center to adopt an sp^2 configuration with a plane of symmetry and the resulting hydroxo product must be racemic.

Recently three complexes have been prepared[5] which have the required asymmetry to test this proposal,

(1) F. Basolo and R. G. Pearson "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.
(2) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).
(3) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6654 (1968).
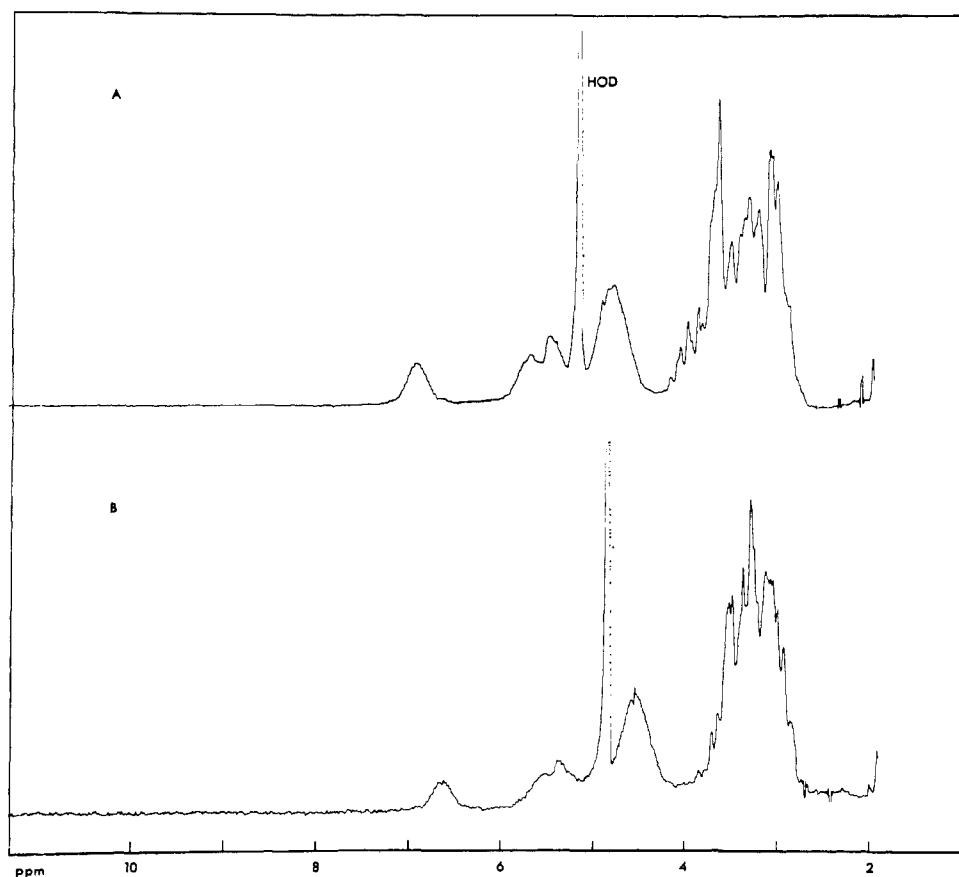(4) R. G. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956).
(5) P. A. Marzilli, to be submitted for publication.

Figure 1.—The 100-Mc pmr spectra of (A) [Co(trenen)Cl]Cl$_2$ in 1.0 N DCl solution with [Co] = 0.62 M and (B) [Co(trenen)N$_3$]Cl$_2$ in 0.28 N DCl solution with [Co] = 0.37 M. (Spectra were recorded with t-butyl alcohol as an internal reference, and chemical shifts are quoted here relative to TMS.)

namely, the chloro-, azido-, and aquo-4-(aminoethyl)-1,4,7,10-tetraazadecanecobalt(III) ions, and this article describes their structure, proton-exchange properties, racemization, and the route for base hydrolysis of the chloro complex. An abbreviated name for the complicated ligand is clearly indicated, and "trenen" has been chosen since it is an unambiguous description of the ligand if it is considered to be composed of the elements "tren" (tris(2-aminoethyl)amine) and "en" (ethylenediamine).

Experimental Section

The preparation and resolution of the complexes used in this study will be described shortly along with several cobalt(III)–tetraethylenepentamine complexes. However, to characterize the complexes the analytical data for the chloro, aquo, and azido isomers are given along with visible, rotatory dispersion, and pmr spectra (Figures 1, 5, 6, 7). *Anal.* Calcd for (±)[Co(C$_8$H$_{23}$N$_5$)-Cl](ClO$_4$)$_2$: C, 19.91; H, 4.80; N, 14.51. Found: C, 19.9; H, 4.6; H, 14.6. Found for (+)$_{520}$[Co(C$_8$H$_{23}$N$_5$)Cl](ClO$_4$)$_2$: C, 19.6; H, 4.5; N, 14.6. Calcd for (−)$_{500}$[Co(C$_8$H$_{23}$N$_5$)N$_3$]-(NO$_3$)$_2$: C, 23.19; H, 5.60; N, 33.82. Found: C, 22.9; H, 5.5; N, 34.1. Calcd for (+)$_{520}$[Co(C$_8$H$_{23}$N$_5$)(OH$_2$)](ClO$_4$)$_3$: C, 17.02; H, 4.46; N, 12.41. Found: C, 17.3; H, 4.7; N, 12.3.

Pmr and Proton Exchange.—The pmr spectra were obtained using a Varian HA 100 spectrometer. The complexes (∼0.3 M) were dissolved in 0.1–1.0 M DCl and D$_2$SO$_4$ (98%) was added to move the HOD signal as required. The exchange reactions were followed for ∼5$t_{1/2}$ in DCl solutions at 34° using t-butyl alcohol as an internal reference.

Racemization.—(−)$_{500}$[Co(trenen)N$_3$](NO$_3$)$_2$ [2.06 mg; [M]$_{500}$

−4080° (M^{-1} cm^{-1})] was dissolved in Tris–HClO$_4$ buffers (10 ml, 0.05 M) made up to μ = 1.0 M with NaClO$_4$. Racemization was followed at 436 mμ, and rotatory dispersion curves were recorded at intervals. At the end of the reaction no activity remained at any wavelength (620–400 mμ). After each kinetic run the visible spectrum was recorded on a Cary 14 spectrophotometer and the spectrum (ϵ_{497} 493 M^{-1} cm^{-1}) was essentially that of the starting material (ϵ_{497} 491 M^{-1} cm^{-1}).

(+)$_{520}$[Co(trenen)(OH$_2$)](ClO$_4$)$_3$ (0.01 g; [M]$_{520}$ +1130°; 90% active) was dissolved in buffer (10 ml, 0.05 M) previously equilibrated at 25°. Racemization was followed at 436 mμ and RD curves were also recorded at intervals. Rates from both sets of data at different wavelengths were consistent (±2%). The optical rotation of the solution decayed to zero at all wavelengths (620–400 mμ), and the visible spectra before and after racemization were consistent (ϵ_{493} 167 ± 2 M^{-1} cm^{-1}).

Base hydrolysis was followed spectrophotometrically (Cary 14) and polarimetrically (Cary 60) at 25 ± 0.05° in buffer solutions (0.05 M, 2,4,6-collidine–HClO$_4$, Tris–HClO$_4$, and pyridine–HClO$_4$, at μ = 1 with NaClO$_4$). The complex (1.1 × 10^{-3} M for spectrophotometric and 1–2 × 10^{-3} M for polarimetric rates) was dissolved in the equilibrated buffer and changes in optical rotation or optical density were followed in 5- or 10-cm thermostated cells. The spectrum was scanned frequently during the reaction from 650 to 300 mμ and RD curves were also recorded from 600 to 300 mμ.

In one experiment, (+)$_{520}$[Co(trenen)Cl](ClO$_4$)$_2$ ([M]$^{25}_{520}$ +1005°; 93% active; 0.0500 g finely ground) was dissolved in collidine–HClO$_4$ buffer of pH 8.03 (0.05 M, μ = 1.0, 25°, 100 ml). The solution was maintained at 25 ± 0.1° for 14.7 min and then was quickly acidified (<20 sec) and diluted (two times), and the complexes were sorbed on a cation-exchange column (Bio-Rad Analytical Resin, Dowex 50-WX2, 200–400 mesh,
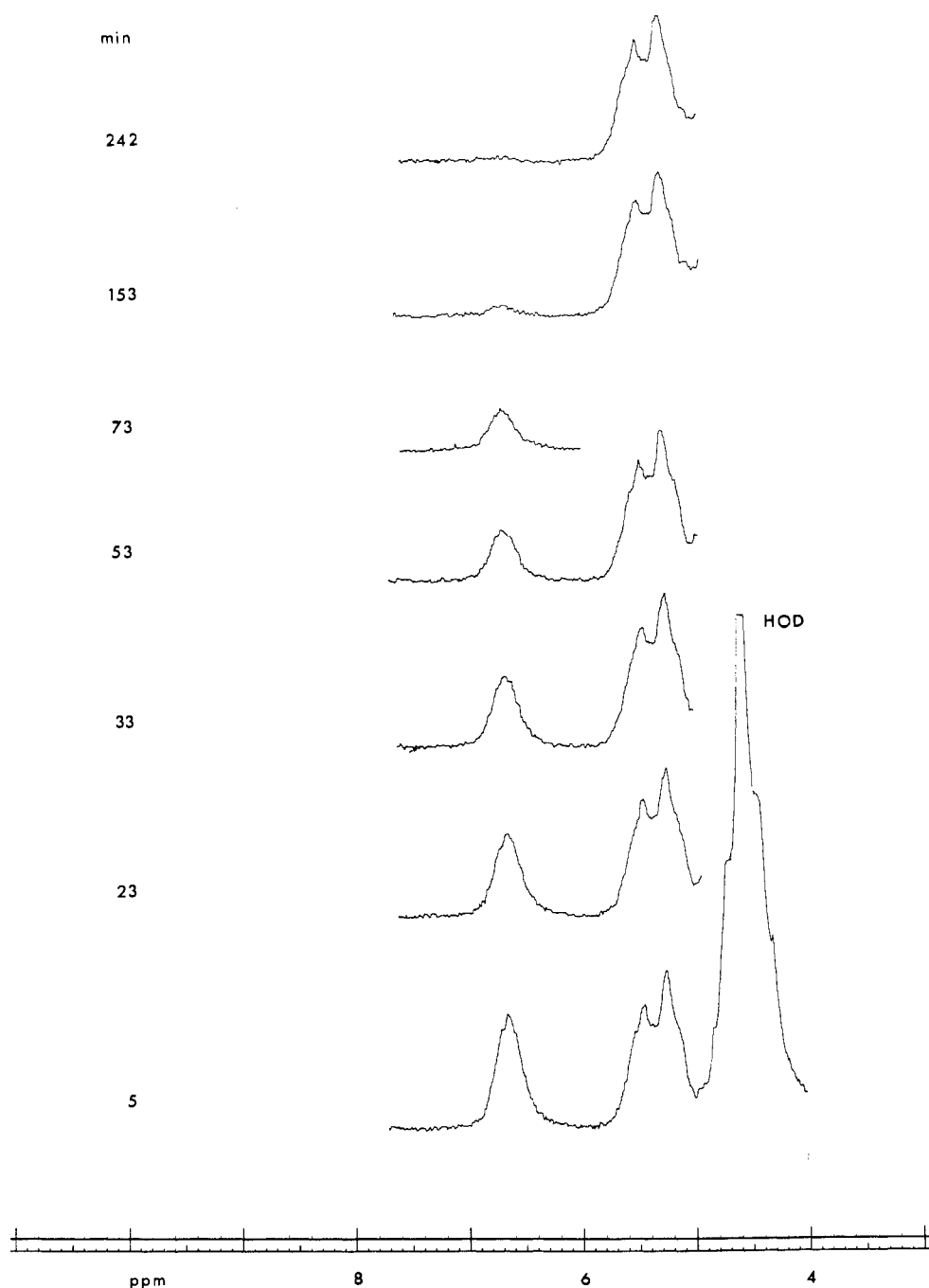
Figure 2.—Proton-exchange reaction of [Co(trenen)Cl]Cl$_2$ in 0.15 N DCl; k_{obsd} (34°) = 2.6 × 10^{-4} sec^{-1} for N–H resonance at 6.7 ppm *vs.* TMS.

~9 × 1 cm). The column was washed with water and eluted with 1 M NH$_4$Cl to collect the unreacted chloro complex followed by 3 M HCl to collect the aquo complex. The product concentrations were determined spectrophotometrically and their optical rotatory power was measured: aquo complex, α_{436} −0.029° (for a 1.19 × 10^{-3} M solution in a 1-dm tube); chloro complex, α_{436} −0.008° (for a 4.0 × 10^{-4} M solution in a 1-dm tube).

Results

Proton Exchange.—The 100-Mc pmr spectra of the chloro and azido complexes are given in Figure 1. The three signals due to the NH and NH$_2$ groups are clearly evident and integrate for 1:2:4 protons. The methy-

lene region is complex and so far has not yielded any information concerning the conformational structure of the complex.

The proton excange in these complexes was followed by collapse of the NH signals when exchange occurred in dilute DCl solutions. Plots of log (integrated peak)$_t$ against time were linear over at least 3 half-lives. The same result was achieved by plotting log (peak height)$_t$ against time, and it is clear from Figure 2 that for the chloro complex exchange was complete for the signal at lowest field. The observed rate constants (Table I) were plotted against [OD$^-$], a procedure

which revealed that a small term (k_{D_2O}) independent of pH contributed to the rate. The results are consistent with the rate law

$$-\frac{d[H]}{dt} = \{k_{OD^-}[OD^-] + k_{D_2O}\}[H]$$

The second-order rate constants are also given in Table I. That for the base-catalyzed path is about four times greater for the chloro complex ($k_{OD^-} = 5.6 \times 10^9\ M^{-1}$ sec^{-1}) than for the azido complex ($k_{OD^-} = 1.3 \times 10^9$ M^{-1} sec^{-1}). The rate constants for the acid-independent paths were 1.2×10^{-4} and 6.3×10^{-5} sec^{-1} for the chloro and azido ions, respectively. The activation enthalpy for exchange in the chloro complex was 28 ± 1 kcal/mol.

TABLE I
RATE CONSTANTS FOR PROTON EXCHANGE IN
[Co(trenen)N$_3$]Cl$_2$[a] AND [Co(trenen)Cl]Cl$_2$[b]

[DCl], N[c]	10^{13}[OD$^-$], M[d]	$10^4 k_{obsd}$, sec^{-1}	$10^{-9}k_{OD^-}$, M^{-1} sec^{-1}
		Co(trenen)N$_3$$^{2+}$	
0.0043	8.84	12	1.3[e]
0.0172	2.21	3.6	1.3[e]
0.0380	1.00	1.9	1.3[e]
		Co(trenen)Cl^{2+}	
0.0172	2.21	14	5.7[f]
0.0319	1.19	8.0	5.7[f]
0.0380	1.00	6.8	5.6[f]
0.152	0.250	2.6	5.6[f]
0.0363		6.9	
0.0363[g]		29	

[a] Temperature 34°, [Co] $\approx 0.4\ M, \mu = 0.8\ M$. [b] Temperature 34°, [Co] $\approx 0.6\ M, \mu = 1.2\ M$. [c] Normality determined by titration. [d] [OD$^-$] $= K_{D_2O}/[D^+]$; K_{D_2O} (34°) $= 3.80 \times 10^{-15}$: W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936). [e] $k_{OD^-} = (k_{obsd} - k_{D_2O})/[OD^-]$; $k_{D_2O} = 6.3 \times 10^{-5}$ sec^{-1}. [f] $k_{OD^-} = (k_{obsd} - k_{D_2O})/[OD^-]$; $k_{D_2O} = 1.2 \times 10^{-4}$ sec^{-1}. [g] Temperature 45°.

An experiment, carried out in 0.0017 N DCl at 34° over a much longer time, showed that the remaining protons in the chloro complex were less than half-exchanged in 5 days ($k_D < 10^{-6}$ sec^{-1}). Both sets of protons appeared to exchange at roughly the same rate, which was less than that for aquation of the Cl$^-$ group ($k = 1.6 \times 10^{-6}$ sec^{-1} at 34°). Aquation prevented quantitative measurement of the exchange and it is likely that exchange at these sites arose primarily from a faster exchange in the more highly charged aquo product.

Racemization.—Proton exchange at the asymmetric N center also leads to racemization of the complex. This was followed for the azido and the aquo complexes in a series of buffer solutions. Plots of log $\alpha°$ against time were linear for 4 half-lives and the rate constants obtained are listed in Tables II and III.

For the aquo complex the rate was essentially independent of pH in the range 7–8.7; $k_{obsd} = 6.8 \times 10^{-4}$ sec^{-1} at 25°, $\mu = 1.0$ (NaClO$_4$). The rate decreased at lower pH however and increased rapidly above pH 10. The pK_a for the aquo complex was 5.99 ± 0.04 at 25°, $\mu = 1.0$ (NaClO$_4$). The rate constants were inde-

TABLE II
RATE DATA FOR THE RACEMIZATION OF THE
$(+)_{500}$Co(trenen)OH^{2+} ION[a]

Sample[b]	pH[c]	$10^4 k_{obsd}$, sec^{-1}	Sample[b]	pH[c]	$10^4 k_{obsd}$, sec^{-1}
Cl	12.0[d]	Fast	OH$_2$	8.16 (T)	6.8
Cl	9.04 (T)	9.5	Cl	8.12 (T)	7.3
Cl	8.69 (T)	6.6	Cl	7.93 (C)	7.3
OH$_2$	8.69 (T)	6.6	OH$_2$	7.59 (T)	5.1
Cl	8.42 (C)	7.0	OH$_2$	6.92 (C)	6.1
Cl	8.36 (C)	6.7	OH$_2$	5.30 (P)	1.4
Cl	8.16 (T)	7.3			

[a] At 25° using 0.05 M buffers, $\mu = 1.0\ M$ (NaClO$_4$). [b] Sample dissolved in buffer: Cl $= (+)_{520}$[Co(trenen)Cl](ClO$_4$)$_2$, rate observed after hydrolysis of Cl$^-$; OH$_2 = (+)_{500}$[Co(trenen)OH$_2$]-(ClO$_4$)$_3$. [c] C = collidine–HClO$_4$; P = pyridine–HClO$_4$; T = Tris–HClO$_4$. [d] In 0.01 N NaOH.

TABLE III
RATE DATA FOR THE RACEMIZATION OF
$(-)_{500}$[Co(trenen)N$_3$](NO$_3$)$_2$ IN TRIS BUFFERS
(0.05 M) AT 25° AND UNIT IONIC STRENGTH
($\mu = 1.0\ M$, NaClO$_4$)

pH	$10^4 k_{obsd}$, sec^{-1}	k_{calcd},[a] M^{-1} sec^{-1}
8.16	2.28	165
8.46	4.81	167
9.11	21.8	169
8.44[b]	30.4[b]	566[b]

[a] $k_{calcd} = k_{obsd}/[OH^-]$. [b] Rate measured at 34°.

pendent of the buffers 2,4,6-collidine–HClO$_4$ and Tris–HClO$_4$ (0.05 M, $\mu = 1.0\ M$) but showed a small dependence on the collidine buffer concentration in the range 0.05–0.2 M at constant ionic strength.

For the azido complex (Table III) racemization was observed in the pH range 8–9 and base hydrolysis of the azido group was not a competing reaction under these conditions. The activation energy found for this process was 36 ± 1 kcal/mol.

The rate constant–pH profile for the racemization of the Co(trenen)OH$_2$$^{3+}$ complex is consistent with two superimposed rates, a larger rate constant for the aquo ion and a smaller rate constant for the hydroxo complex. Assuming that both the aquo and hydroxo species obey the same rate law, $R = k$[complex][OH$^-$] for racemization, the following reaction scheme can account for the results

$$(+)\text{Co(trenen)OH}^{2+} + \text{OH}_2 \underset{}{\overset{K_b}{\rightleftharpoons}} (+)\text{Co(trenen)OH}_2{}^{3+} + \text{OH}^-$$

$$\text{OH}^- \downarrow k_2 \qquad\qquad\qquad \text{OH}^- \downarrow k_1$$

$$\text{racemate} \qquad\qquad\qquad \text{racemate}$$

The derived rate law takes the form

$$k_{obsd} = \frac{k_1 K_b[OH^-] + k_2[OH^-]^2}{K_b + [OH^-]}$$

and p$K_b = 8.01 \pm 0.04$. When [OH$^-$] $\gg K_b$, $k_{obsd} = k_1 K_b + k_2[OH^-]$, and the constant rate observed in the pH range 7–8.7 is due to the small contribution of the k_2 term. It follows that $k_1 K_b = 6.8 \times 10^{-4}$ sec^{-1} and $k_1 = 6.8 \times 10^4\ M^{-1}$ sec^{-1}. At pH 9.04, however, the k_2 term becomes significant and indicates a value for k_2 of 27 M^{-1} sec^{-1}. At pH 5.30 only the k_1 term is important and the derived rate law requires k_{obsd} to be

1.1×10^{-4} sec^{-1} compared to the measured value of 1.4×10^{-4} sec^{-1}.

Base Hydrolysis.—The rate of base hydrolysis was followed spectrophotometrically and polarimetrically. The loss of Cl$^-$ from the complex was established spectrophotometrically, and plots of log $(D - D_\infty)$ against time were linear for at least 3 half-lives at each pH. The rate constants are listed in Table IV. There is a first-order dependence on hydroxide ion concentration and the reaction obeys the rate law $-$d[Co(trenen)-Cl^{2+}]/dt = k[Co(trenen)Cl^{2+}][OH$^-$]. The data show no dependence on the nature of the buffer.

Table IV

Base Hydrolysis of [Co(trenen)Cl](ClO$_4$)$_2$
Followed Spectrophotometrically in 0.05 M
Collidine–HClO$_4$ Buffers at 25° and
μ = 1.0 M (NaClO$_4$)

pH	$10^4 k_{obsd}$, sec^{-1}	k_b,^{a} M^{-1} sec^{-1}
8.42^{b,c}	23.1	878
8.36	20.3	887
8.03^b	9.09	885
7.93	7.36	865
7.17	1.31	885

^{a} k_b = k_{obsd}/[OH$^-$]. ^{b} Optically active sample used for spectrophotometric rate. ^{c} Using 0.05 M Tris–HClO$_4$ buffer.

An example of the change of optical rotation with time at pH 7.45 is given in Figure 3. It is evident that there are at least two rate processes, and these were separated by plotting log $\alpha°$ against time at $\sim$460 mμ (zero rotation and isorotatory point for the second reaction) and then at 436 mμ. The rate constants obtained from this procedure are given in Table V. The first process has a rate constant considerably larger than that for base hydrolysis (obtained spectrophotometrically) while the second process has a rate constant close to that for the racemization of the aquo complex under the same conditions.

Table V

Base Hydrolysis of [Co(trenen)Cl](ClO$_4$)$_2$
Followed Polarimetrically at 460 mμ in
0.05 M Collidine–HClO$_4$ at 25° and
μ = 0.1 M (NaClO$_4$)

pH	$10^3 k_{obsd}$, sec^{-1}	$10^{-3} k_b$,^{a} M^{-1} sec^{-1}	$10^4 k_R^{OH}$,^{b} sec^{-1}
7.98	3.64	3.8	8
7.85	2.82	4.0	6
7.45	1.16	4.1	6
6.85	0.210	3.0	

^{a} k_b = k_{obsd}/[OH$^-$]. ^{b} At 436 mμ.

More accurate data for the second rate associated with the chloro complex are given in Table II and the agreement with the values for the isolated aquo species is evident. These rate constants were obtained at 436 mμ for the latter part of the rate plot, log α against t, which was linear. At this wavelength rate constants for the first reaction were variable and reliable data were obtained for this process only at the wavelength where the hydroxo product had zero rotation (*i.e.*, $\sim$460 mμ).

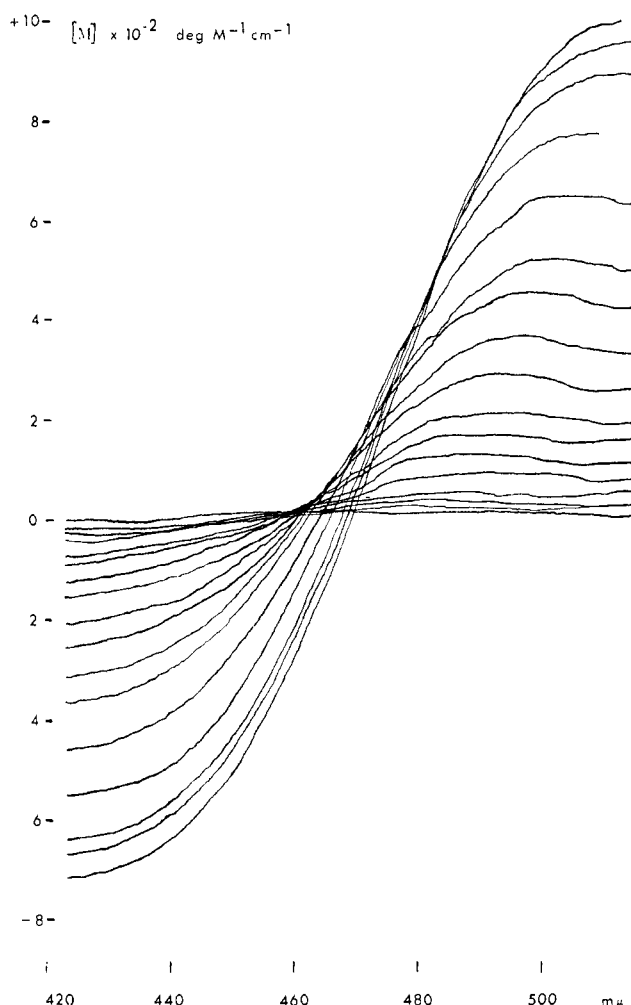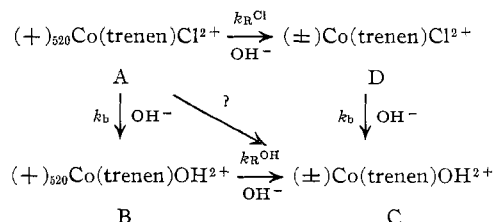Figure 3.—Continuous rotatory dispersion curves for $(+)_{520}$-[Co(trenen)Cl](ClO$_4$)$_2$ in 0.05 M collidine–HClO$_4$ buffer, pH 7.45, at 25° and μ = 1.0 M; t (min) reading upward at 460 mμ: 2.5, 4.5, 6.5, 11.5, 17.5, 25.5, 30.5, 44.5, 54, 61, 70, 80, 95, 108, 121.

It is required then that the first polarimetric rate include base hydrolysis of Cl$^-$ and some racemization, and the rates and products accordingly have been analyzed on the basis of the reaction scheme

$$(+)_{520}\text{Co(trenen)Cl}^{2+} \xrightarrow[\text{OH}^-]{k_R^{Cl}} (\pm)\text{Co(trenen)Cl}^{2+}$$

$$\text{A} \qquad\qquad\qquad\qquad \text{D}$$

$$k_b \downarrow \text{OH}^- \qquad \searrow^? \qquad k_b \downarrow \text{OH}^-$$

$$(+)_{520}\text{Co(trenen)OH}^{2+} \xrightarrow[\text{OH}^-]{k_R^{OH}} (\pm)\text{Co(trenen)OH}^{2+}$$

$$\text{B} \qquad\qquad\qquad\qquad \text{C}$$

Racemization of the parent chloro complex and of the active hydroxo product can account for the loss of activity qualitatively but it is possible that activity is lost by a path (+)chloro → ($\pm$)hydroxo. Assuming that this path was negligible, the concentration of $(+)_{520}$Co(trenen)OH^{2+} at time t was calculated using the expressions

$$A_t = A_0 e^{(-k_R^{Cl} - k_b)t}$$

$$B_t = \frac{A_0 k_b}{k_R^{OH} - k_R^{Cl} - k_b} [e^{(-k_R^{Cl} - k_b)t} - e^{(-k_R^{OH})t}]$$

$$D_t = A_0 [e^{-k_b t} - e^{(-k_b - k_R^{Cl})t}]$$

The base hydrolysis rate constant k_b was obtained from the spectrophotometric experiment, and the first polarimetric rate constant gave $(k_b + k_R^{Cl})$, whence $k_R^{Cl} = 3.8 \times 10^3 \ M^{-1} \ \text{sec}^{-1}$. Racemization of the hydroxo complex gave $k_R^{OH} = 6.8 \times 10^4 \ \text{sec}^{-1}$ in the pH region required. The following experiment was then carried out.

The salt $(+)_{520}[Co(trenen)Cl](ClO_4)_2$ was allowed to react in collidine–HClO$_4$ buffer (0.05 M, pH 8.03, 25°) for 14.9 min ($\sim t_{1/2}$ for base hydrolysis) and then acidified (pH 1) before the solution was sorbed onto a cation-exchange column. The chloro (43 ± 1%) and aquo (57 ± 1%) complexes were eluted separately and their relative concentrations were determined spectrophotometrically. The chloro complex was partly active (25 ± 12% dextro) and the aquo complex was 22 ± 5% active. The uncertainty in the rotations arises largely from the dilute solutions obtained from the ion-exchange separations. This leads to a final product analysis of 11 ± 6% $(+)_{520}$chloro, 32% $(\pm)$chloro, 13 ± 2% $(+)_{500}$aquo, and 44% $(\pm)$aquo which is to be compared with the calculated values of 4.7% $(+)$chloro, 38.1% $(\mp)$chloro, 14.3% $(+)$aquo, and 42.9% $(\mp)$ aquo. The agreement between the total chloro and total aquo complex calculated and isolated is excellent. The poor agreement between calculated and found values for $(+)_{520}$chloro is attributed to the inaccuracy in the small rotation (α_{436} −0.008°) found for the isolated species. However, the larger rotation measured for the $(+)_{500}$aquo complex (α_{436} −0.029°) allows its concentration to be estimated with more certainty.

Discussion

Structure.—The structure[6] of the *sym*-Co(trenen)N$_3^{2+}$ ion is depicted in Figure 4 and the structure analysis and determination of the absolute configuration of $(+)_{520}$*sym*-[Co(trenen)Cl](ClO$_4$)$_2$ is in progress.[7]

Structural features of interest are the conformations of the coupled chelate rings in orthogonal planes and the asymmetric configuration about the N atom *trans* to N$_3$. The conformations of the chelates in each coupled pair are essentially mirror images and if inversion at the N center *trans* to N$_3$ occurs, the ion racemizes. Conformational inversion is then required for the chelate rings attached to this center but the conformations of the other coupled pair are maintained.

In the absence of the X-ray structural analyses for the aquo and chloro complexes we need to deduce their relationship to the azido complex by chemical means. This can be done by comparing the reactions of the optical isomers of the two species. The $(+)_{520}$Co-(trenen)Cl^{2+} ion treated with Hg^{2+} ion in dilute acid gave the optically active aquo complex with the same RD curve as that obtained by treating $(+)_{500}$Co-(trenen)N$_3^{2+}$ with NO$^+$ in the same acidic conditions. The spectra and rotatory dispersion curves of the chloro, azido, aquo, and hydroxo complexes are given in
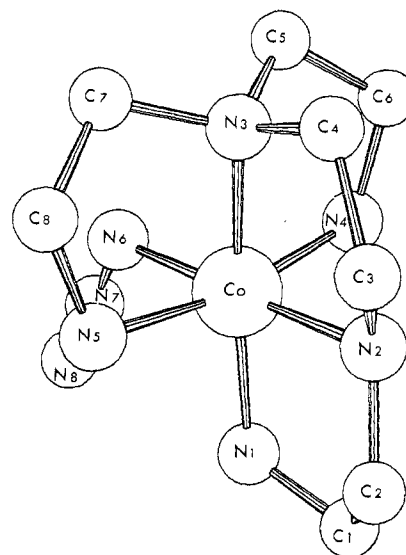

Figure 4.—Crystal structure of racemic *sym*-[Co(trenen)N$_3$]-(NO$_3$)$_2$.[6]

Figures 5–7. In cobalt(III)–pentaammine chemistry, in general, these reactions are known to occur with full retention of the original configuration[3,8,9] and we deduce therefore that the $(+)_{520}$chloro, $(+)_{500}$azido, and $(+)_{500}$aquo ions all have the same configuration. Under the acidic conditions used, proton exchange at the asymmetric N center does not occur and inversion therefore is not possible. In addition, when the aquo complex derived from the azido ion was heated with HCl (10 N) the chloro complex was obtained with the same spectrum as an authentic sample of *sym*-Co-(trenen)Cl^{2+}. These anation reactions are also known to occur with retention of configuration[3,8,9] for penta-ammine-type compounds.

The existence and properties of other geometrical isomers containing the trenen ligand will be discussed at a later date. It is sufficient to say now that they do not occur in this investigation in detectable quantities.

Proton Exchange.—Deuteration at the N centers was followed by the collapse of the three NH signals (4,2,1 protons) observed in the 100-Mc pmr spectra. Despite the lack of symmetry in the complex these signals may be related to specific protons by applying parallels which are observed in related pentaammine complexes.[10] In the (NH$_3$)$_5$CoCl^{2+} ion the signal for the *trans*-NH$_3$ groups is upfield from that for the *cis* ammonias. Moreover, the protons on the group *trans* to the substituent exchange faster ($k = 3 \times 10^6 \ M^{-1} \ \text{sec}^{-1}$, 25°) than those on the *cis* species ($k = 5 \times 10^4 \ M^{-1} \ \text{sec}^{-1}$, 25°, $\mu = 0.1$).[10] In the *trans*-Co(en)$_2$NH$_3$Cl^{2+} ion the NH$_3$ signal upfield from the NH$_2$ groups exchanges its protons much faster (300 times) than the latter, all of which exchange at the same rate despite the fact that the two protons on each N atom are in different environments.[10] In the less symmetrical *cis*-Co(en)$_2$-

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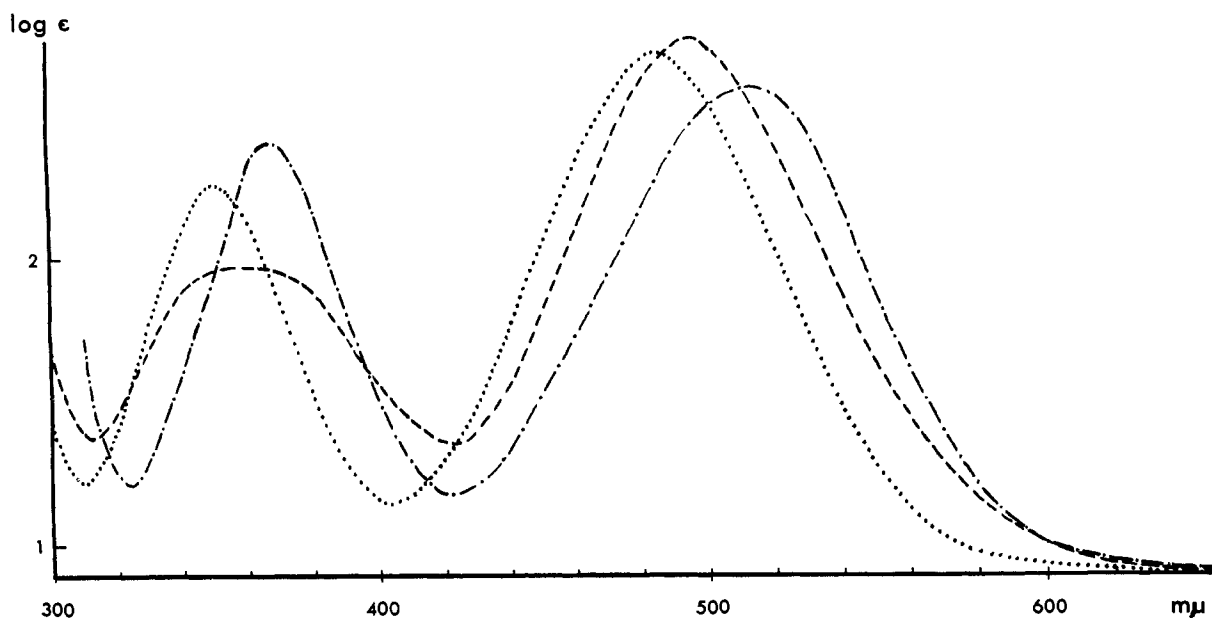
(10) I. I. Olsen, to be submitted for publication.

Figure 5.—Visible absorption spectra (log ϵ vs. λ) of Co(trenen)Cl²⁺ in 0.11 N HClO₄ (–·–·–·), Co(trenen)OH²⁺ in 0.01 N NaOH (————), and Co(trenen)OH₂³⁺ in 0.11 N HClO₄ (······).

Figure 6.—Rotatory dispersion curves ([M] in deg M^{-1} cm⁻¹ vs. λ in mμ) for [Co(trenen)Cl](ClO₄)₂ in 1.0 N HClO₄ (–·–·–·) and [Co(trenen)OH₂](ClO₄)₃ in 1.0 N HClO₄(······).

NH₃Cl²⁺ ions three exchange rates were observed for the four NH signals in the 100-Mc pmr spectra: one NH₂ group, the NH₃ and one NH₂ group, and two NH₂ groups in the rate ratio of ∼200:2:1, respectively.[10] We assume on the basis of the more symmetrical compounds that the fastest rate is due to the NH₂ group *trans* to the Cl⁻ ion. The NH₂ and NH₃ groups *trans* to each other exchange at the same rate and the two NH₂ groups *trans* to each other with the same chemical shift exchange slowest. The last groups are the most nearly equivalent and it is not surprising that they have the same chemical shift.

On the basis of this analysis, the downfield signal for the NH in the chloro trenen complex which exchanges most rapidly with solvent is assigned to the NH *trans* to the Cl⁻ ion. The two-proton signal is ascribed to
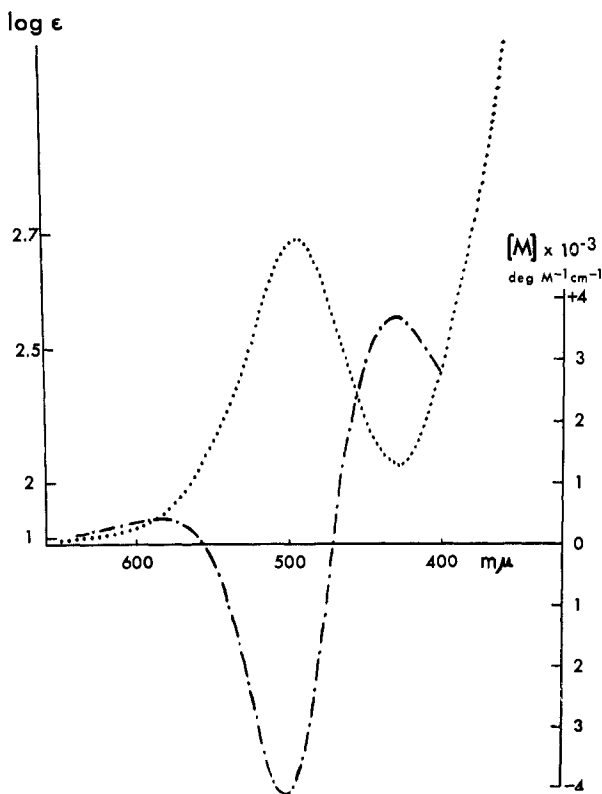

Figure 7.—Visible absorption (·····) spectrum (log ϵ vs. λ in mμ) and rotatory dispersion (–·–·–·) curve ([M] in deg M^{-1} cm⁻¹ vs. λ in mμ) for [Co(trenen)N₃](NO₃)₂ in dilute acetic acid.

the NH₂ *trans* to the tertiary N, and the four-proton signal to the two NH₂ groups which are most nearly equivalent.

The two-path rate law for the exchange of the *trans*-NH proton, $k_{obsd} = k_{D_2O} + k_{OD}\text{-}[OD^-]$, is attributed to both D₂O and OD⁻ catalyzing the proton exchange. The rate constants $k_{D_2O} = 1.2 \times 10^{-4}$ sec⁻¹ and $k_{OD}\text{-} = 5.6 \times 10^9$ M^{-1} sec⁻¹ at 34° are large in relation

to the rate constants for cobalt(III)–amine or –ammine complexes of the same charge. Usually the constant for the acid-dependent path is in the vicinity of 10^5–10^6 M^{-1} sec^{-1} and the acid-independent path is not observed. The results constitute some evidence for general-base catalysis in the H exchange for cobalt(III)–amine complexes. The absence of general-base catalysis in this type of exchange reaction has been puzzling and the above results suggest that the reason is due to the low proton dissociation constants for the amine complexes. In the present instance one proton is considerably more acidic than usual and bases other than the most efficient OH$^-$ are able to effect the reaction.

The remaining NH protons exchanged with solvent D$_2$O more slowly ($<10^5$ M^{-1} sec^{-1}) and at approximately the same rate. This rate could not be followed with certainty because aquation of Cl$^-$ interfered ($k = 1.6 \times 10^{-6}$ sec^{-1}, 34°) with the measurement and it is likely that the exchange rate observed is due to the more rapid NH exchange in the more highly charged product sym-Co(trenen)OH$_2{}^{3+}$. A rate increase of ~ 10 times would be expected for the change in charge from 2+ to 3+. It follows that the difference between the exchange rate for the $trans$-NH and the other protons for the chloro complex under the same conditions is of the order 10^5. This is considerably greater than the difference observed[10] for exchange of N protons cis and $trans$ to Cl$^-$ in $trans$-Co(en)$_2$NH$_3$Cl^{2+}.

The pK_a of NH in these cobalt complexes is too large to measure in aqueous solution and kinetic measurements are used as an estimate of relative acidity for the proton dissociation. There is evidence to suggest that the rate measurements reflect the pK of the center,[4,11–13] and an extraordinarily constant factor in these rates is $\Delta H^{\pm}$ for the deprotonation (28 ± 1 kcal/mol). Using this criterion for acidity we deduce that the $trans$-NH in sym-Co(trenen)Cl^{2+} is $\sim 10^5$ times more acidic than the other NH protons and clearly in the base-hydrolysis media the major deprotonated species in solution will be that deprotonated $trans$ to the chloride.

A similar set of results was observed for sym-Co(trenen)N$_3{}^{2+}$ where one NH proton exchanged with solvent D$_2$O very much faster than the others. Again a two-term rate law was found, $k_{obsd} = k_{D_2O} + k_{OD^-}$[OH$^-$], where $k_{D_2O} = 6.3 \times 10^{-5}$ sec^{-1} and $k_{OD^-} = 1.3 \times 10^9$ M^{-1} sec^{-1} at 34° and the same deductions regarding general-base catalysis apply. The behavior was also analogous to that observed for the isomerization and mutarotation of some Co(trien)(OH$_2$)$_2{}^{2+}$ ions.[14]

Racemization of $(-)_{500}sym$-Co(trenen)N$_3{}^{2+}$.—Under conditions where the sym-Co(trenen)Cl^{2+} is hydrolyzed

(pH 7), the azido group is inert and the secondary N center equilibrates with the solvent protons. In these circumstances racemization of sym-Co(trenen)N$_3{}^{2+}$ was observed with a rate law of the form $R = k_R$[complex]·[OH$^-$], where $k_R = 167$ M^{-1} sec^{-1}. The ratio of exchange to racemization (k_D/k_R) is 2.3×10^6, which is larger than the previous highest value obtained for the Co(NH$_3$)$_4$Meen^{3+} ion, $\sim 120,000$[13] (Meen = N-methylethylenediamine). Such an increase might be accounted for by the coupled chelate conformations. Dreiding molecular models imply that both conformations invert if inversion at the N center occurs and that the conformational interchange must be synchronous with inversion at the N center. In the Co(NH$_3$)$_4$Meen^{2+} ion this was not required and it was not established if the conformational change occurred before, during, or after inversion at nitrogen. If conformational interchange is synchronous with inversion, a higher activation energy for the process would be expected than for that where interchange preceded or anteceded the event. The activation energy for the present system is 36 ± 1 kcal/mol which is to be compared with that for the Co(NH$_3$)$_4$Meen^{3+} ion of 37 ± 1 kcal/mol. The similarity implies that in the latter ion inversion at the N center and conformational interchange coincide.

Racemization of $(+)_{500}sym$-Co(trenen)OH$_2{}^{3+}$.—The lack of dependence on pH for racemization of this ion in the region pH 7–8.7 is accounted for by the greater reactivity of the aquo species relative to the hydroxo form toward OH$^-$ even when the complex is substantially in the hydroxo condition. The large difference between the racemization rate constants for the aquo and hydroxo complexes ($k_{aquo} = 6.8 \times 10^4$ M^{-1} sec^{-1} and $k_{hydroxo} = 27$ M^{-1} sec^{-1} at 25°) can be attributed to the effect of the groups with different electronegativity $trans$ to the asymmetric center. This correlation extends to the chloro and azido complexes where the order for k_R is OH$_2$ > Cl > N$_3$ > OH, essentially that for decreasing electronegativity.

Base Hydrolysis of $(+)_{520}sym$-Co(trenen)Cl^{2+}.—The release of Cl$^-$ showed a normal base hydrolysis rate law $k_{obsd} = k_{OH}$[OH$^-$], where $k_{OH} = 8.8 \times 10^2$ M^{-1} sec^{-1} at 25°. The more interesting results, Table V and Figure 3, were obtained from the polarimetric data. Clearly two rates were observed; one of these is first order in [OH$^-$] ($k_b = 3.8 \times 10^3$ M^{-1} sec^{-1}) and ~ 4 times faster than the base hydrolysis rate. The second rate is considerably slower than the first and is largely independent of [OH$^-$]. It corresponds to the rate and rate law for the racemization of $(+)sym$-Co(trenen)-OH$_2{}^{3+}$ or the hydroxo complex. The polarimetric rate which is ~ 4 times faster than base hydrolysis consists of two processes: $(+)$chloro → $(\mp)$chloro and $(+)$chloro → $(+)$hydroxo. The rate constant for the latter is 8.8×10^2 M^{-1} sec^{-1} and therefore the racemization rate constant for the chloro complex is 2.9×10^3 M^{-1} sec^{-1}. This is to be compared with 1.7×10^2 M^{-1} sec^{-1} for the analogous azido complex.

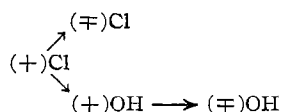The important result which obtains is that some

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(13) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967).

(14) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

optical activity is retained in the product, and if the maximum value is calculated assuming the paths

$$
(+)Cl \begin{array}{c} \nearrow (\mp)Cl \\ \searrow \\ (+)OH \longrightarrow (\mp)OH \end{array}
$$

and using the observed rate constants, ~14% activity should appear at ~$t_{1/2}$ for the base hydrolysis rate. This is close to the observed value and requires that the reaction (+)chloro → (∓)hydroxo cannot contribute significantly to the reaction. The racemic hydroxo product arises almost exclusively from the competitive racemization and hydrolysis reaction (+)chloro → (∓)chloro → (∓)hydroxo.

The results require that the deprotonated five-coordinate intermediate be asymmetric and that it react with retention of configuration. The possibility of dπ-pπ stabilization of the intermediate is questionable for this complex if the reactive intermediate arises from the reactant which is deprotonated *trans* to the leaving group. In this context it is difficult to imagine that the reactive species is that deprotonated *cis* to the leaving group which is ~10^5 times less abundant. Moreover, this would be required to be ~10^6 times more reactive than the species deprotonated *trans* to account for the majority of the reaction by this route. The large difference between the acidities of the protons leads to an interesting possibility, which may establish the position of deprotonation in the conjugate base prior to loss of halide and in the intermediate. With the chloro complex the base hydrolysis rate is only ~10 times less than the proton-exchange rate for the "slow" protons, but for a better leaving group such as NO_3 it is likely that base hydrolysis will be faster than proton exchange for the "slow" protons. It follows that under suitable conditions recovery of the hydroxo product should show exchange at the site *trans* while the *cis*-NH protons should be substantially unaffected. This aspect of the problem is now being pursued.

The significance of the chelate conformations in relation to retention of activity in the hydroxo product needs some discussion. The anticipated stereochemistry of the chelates for the postulated[4] deprotonated intermediate is depicted in Figure 8. It is apparent that the species is still asymmetric in this form, by virtue of the chelate conformations. The lifetime of the intermediate is probably close to diffusion-controlled 10^{-10} sec, whereas the rate constants for conformational inversion and inversion at the N center are estimated to be in the vicinity of 10^2–10^4 sec^{-1} by analogy with previous studies[12,13] and systems in organic chemistry. Excluding the possibility of π stabilization, it is not surprising in this analysis that the activity is retained in the product.

Formation of the π-stabilized intermediate as it was formulated originally[4] and in the Introduction requires the chelate rings to be in the symmetrical eclipsed form, Figure 9, which is a conformationally less stable condition and is clearly eliminated by the results. Some π stabilization with retention of the asymmetry
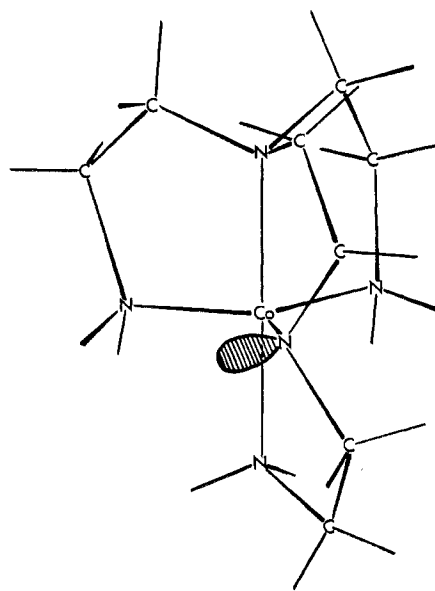

Figure 8.—Stereochemistry of the chelate conformations in the proposed deprotonated intermediate Co(trenen-H)$^{2+}$.

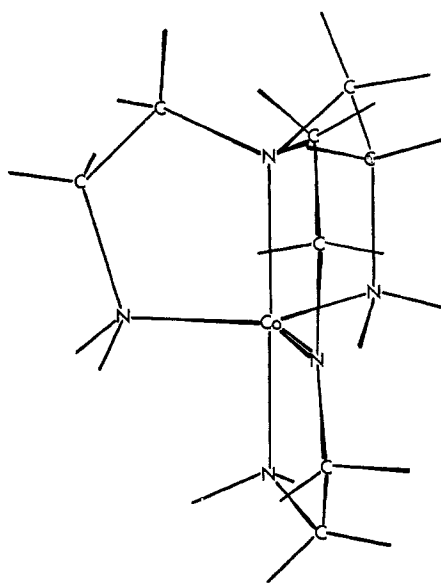Figure 9.—Possible symmetrical form[4] of the Co(trenen-H)$^{2+}$ intermediate showing π stabilization and eclipsed chelate rings.

might be achieved by partial or poor overlap of the filled sp^3 orbital on the deprotonated N atom with an empty lobe of the $d_{x^2-y^2}$ orbital. The situation would require that this intermediate be less stable relative to the parent complex than the corresponding Co(NH$_3$)$_4$-NH$_2^{2+}$ ion relative to its parent where the full degree of stabilization is allowed.[4] A decrease in rate might be expected therefore for the relatively destabilized system. However a much faster base hydrolysis rate for *sym*-Co(trenen)Cl^{2+} was observed under the same conditions. This difference of ~10^3 is largely accounted for by the different acidities of the two complexes as gauged from their proton-exchange rates. The concentration of trenen deprotonated reactant is ~10^3 times greater than that for the deprotonated penta-

ammine. This indicates a similar reaction rate for the two deprotonated reactants and indicates that π stabilization[4] is not a dominating feature in the base hydrolysis of the chloropentaamminecobalt(III) ion.

The extreme labilizing effect of NR_2 (R = H, alkyl) relative to other anionic species such as Cl^- and OH^- for the aquation of Cl^- in these cobalt(III) systems might then be accounted for by the alternative pro-

posal[4] invoking the base strengths of the substituents which promoted the loss of Cl^-. Under these circumstances the rate order should be $NR_2 > OH^- > Cl^-$ which is the order usually observed.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
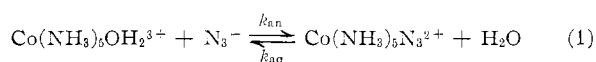THE UNIVERSITY OF CALGARY, CALGARY 44, ALBERTA, CANADA

Kinetics and Equilibria of the Reaction of the Aquopentaamminecobalt(III) Ion with Aqueous Azide Ion–Hydrazoic Acid Buffer
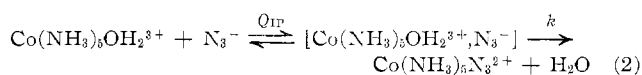
By T. W. SWADDLE and G. GUASTALLA

Anation of $Co(NH_3)_5OH_2^{3+}$ by N_3^- at pH $\sim$4 follows the rate law $d[Co(NH_3)_5N_3^{2+}]/dt = k_{an}[Co(NH_3)_5OH_2^{3+}]$; k_{an} is essentially independent of $[HN_3]$ and pH and is proportional (within experimental error) to $[N_3^-]$, up to $[N_3^-] = 0.4$ M. Typically, $k_{an} = 6.1 \times 10^{-5}[N_3^-]$ sec^{-1} and $\Delta H^* = 26.9$ kcal mol^{-1} at 50° and ionic strength $I = 0.5$ M. However, detailed investigation over a wider $[N_3^-]$ range shows that ion-pair formation precedes anation and that the rate of entry of N_3^- equals the rate of water exchange for $Co(NH_3)_5OH_2^{3+}$. A specific interaction between N_3^- and the aquo ligand is suggested. The formation quotient for $Co(NH_3)_5N_3^{2+}$ is 830 M^{-1} at 25° and $I = 0.5$ M; the azido complex fits the Langford linear free energy relationship for the aquation of $Co(NH_3)_5X^{2+}$ species.

We have previously commented[1] upon the extraordinarily high entropy of activation (ΔS^*) associated with the acid-independent aquation pathway of the azidopentaamminecobalt(III) ion[2] and have suggested[1,3] that this may result from the specific involvement of a water molecule through hydrogen bonding to the N_3 ligand, leading in the transition state to the production of HN_3 and $Co(NH_3)_5OH^{2+}$ rather than the more electrostrictive "normal" products N_3^- and $Co(NH_3)_5H_2O^{3+}$. We now report on our attempts to clarify the situation by analysis of the kinetics and equilibria of the reverse reaction ("anation")

$$Co(NH_3)_5OH_2^{3+} + N_3^- \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} Co(NH_3)_5N_3^{2+} + H_2O \quad (1)$$

with particular attention to the influence of the ion-pairing preequilibrium[4]

$$Co(NH_3)_5OH_2^{3+} + N_3^- \underset{}{\overset{Q_{IP}}{\rightleftharpoons}} [Co(NH_3)_5OH_2^{3+},N_3^-] \overset{k}{\longrightarrow}$$
$$Co(NH_3)_5N_3^{2+} + H_2O \quad (2)$$

and to the properties of the azido complex with respect to Langford's[5] linear free energy relationship (LFER) between log k_{aq} and $-\log Q$ (where the stability constant $Q = k_{an}/k_{aq}$) for the complexes $Co(NH_3)_5X^{2+}$.

The latter aspect is of interest in another context; a similar LFER (of lower slope) exists[6] for the aquation of

most ions of the series $Cr(H_2O)_5X^{2+}$, and this correlation includes the complex $Cr(H_2O)_5F^{2+}$, despite the anomalously high ΔS^* which is found[3,7] for the acid-independent aquation of this species. One might therefore ask whether complexes with anomalously high ΔS^* values in aquation *should* fit an LFER, in which case $Co(NH_3)_5N_3^{2+}$ will correlate with the other $Co(NH_3)_5X^{2+}$, or whether the apparent fit of $Cr(H_2O)_5F^{2+}$ in the Cr(III) LFER is fortuitous.

Experimental Section

Materials.—Distilled water was further purified by passage through Barnstead organic-removal and demineralizer cartridges, before use as solvent in the experiments described below.

Aquopentaamminecobalt(III) perchlorate was prepared by the method of Taube and Rutenberg[8] and checked for purity by microanalysis (*Anal.* Calcd for $CoN_5H_{17}O_{13}Cl_3$: N, 15.2; H, 3.5. Found: N, 15.2; H, 3.7) and by the absorption spectrum of the aqueous solution (ϵ 47.2 M^{-1} cm^{-1} at 490 nm; *cf.* 47.1 M^{-1} cm^{-1} reported elsewhere[9]).

Azidopentaamminecobalt(III) perchlorate was made by a procedure based on that described[10] for the chloride salt and was microanalyzed. *Anal.* Calcd for $CoN_8H_{15}Cl_2O_8$: N, 29.2; H, 3.9. Found: N, 28.8; H, 4.0. An aqueous solution of the complex had absorption maxima at 516 nm (ϵ 266) and 302 nm (ϵ 7810); these data compare favorably with those reported,[2] 520 nm (ϵ 262) and 302 nm (ϵ 7870).

Fisher and BDH Laboratory grade sodium azide was purified by recrystallization from water, washed with alcohol and then with ether, dried at 100°, and stored in a desiccator over phos-

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(3) T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).
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