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Proton Transfer and Nitrogen Inversion in the Base-Catalyzed Hydrolysis of *trans*-Dichloro[(R,R(S,S))-1,9-diamino-3,7-diazanonane]cobalt(III) Chloride

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The base hydrolysis of *trans*-[Co(RR(SS)-2,3,2-tet)Cl₂]⁺ (2,3,2-tet = 1,9-diamino-3,7-diazanonane; *RR* and *SS* indicate that the racemate containing these enantiomeric forms of the coordinated ligand has been used without resolution) has been studied using fully N-deuterated material. It has been shown that the rate-determining step is the removal of the proton from one of the secondary nitrogens and the amido conjugate base thus formed is at least 20 times more likely to undergo dissociative aquation than to be reprotonated. Every act of base hydrolysis leads to the formation of the meso isomer *trans*-[Co(RS-2,3,2-tet)(OH)Cl]⁺. The high lability of the conjugate base is thereby shown to be due to π-donor stabilization of the five-coordinate intermediate by the amido ligand, which becomes planar at this stage of the reaction.

Introduction

The base-catalyzed hydrolysis of certain octahedral amine complexes of cobalt(III) has been shown to involve the removal of a proton from nitrogen followed by the dissociative solvolysis of the amido species.[1,2] This mechanism, labeled SN1cb or Dcb, requires that the amido conjugate base must be many orders of magnitude more reactive than the original substrate (10^5–10^8 times more reactive). The original explanation of this labilization, in terms of π interaction between the lone pair of electrons on the amido nitrogen and the vacated orbital on the metal which stabilizes the five-coordinate intermediate by maintaining an 18-electron valence shell about the central atom,[3] has been questioned by Sargeson, *et al.*[4] They found that the unique secondary amine proton in *sym*-[Co(trenen)Cl]²⁺ (trenen = 1,8-diamino-3-(β-aminoethyl)-3,6-diazaoctane), which is trans to the chlorine, was extremely labile with respect to exchange and, by studying a resolved sample and investigating the relationship between the base hydrolysis and racemization of this complex, showed conclusively that no racemization could be associated with the act of base hydrolysis. They concluded that the labilizing power of the amido nitrogen could not arise from a π donation of charge from the nitrogen to the cobalt because this would require that the nitrogen concerned became planar in the five-coordinate intermediate. However, at no stage in the investigation did they show that the labeled nitrogen was in fact the site of the active conjugate base. Recently[5] it was shown that certain complexes of the type *trans*-[Co(L₄)Cl₂]⁺ (where L is an amine donor from a bidentate or a quadridentate ligand) undergo base hydrolysis at rates that do not differ greatly from those of proton exchange thus making it possible to label the amines with deuterium and use this label to locate the site of deprotonation. In the case of *trans*-[Co(RS-2,3,2-tet)Cl₂]⁺ (2,3,2-tet = 1,9-diamino-3,7-diazanonane, and *RS* denotes the configurations of the secondary nitrogen atoms) it was shown conclusively that the active conjugate base was formed by deprotonation of a secondary amine group. This paper reports similar studies on the isomeric *trans*-[Co(RR(SS)-2,3,2-tet)Cl₂]⁺ cation where preliminary work had indicated that base hydrolysis

was accompanied by inversion of configuration at the secondary nitrogen.

Experimental Section

Preparations. 1,9-Diamino-3,7-diazanonane (2,3,2-tet) was prepared by Van Alphen's method.[6]

trans-Dichloro[(R,S)-1,9-diamino-3,7-diazanonane]cobalt(III) chloride was prepared by the method of Bosnich.[7] *Anal.* Calcd for C₇H₂₀N₄Cl₃Co: C, 25.8; H, 6.1; N, 17.2; Cl, 32.8. Found: C, 25.6; H, 6.0; N, 17.0; Cl, 32.6.

β-*cis*-Carbonato[(R,R(S,S))-1,9-diamino-3,7-diazanonane]cobalt-(III) perchlorate was prepared from *trans*-[Co(RS-2,3,2-tet)Cl₂]Cl by the method of Niththyananthan.[8] *Anal.* Calcd for C₈H₂₀N₄O₇-ClCo: C, 25.4; H, 5.3; N, 14.8; Cl, 9.4. Found: C, 25.3; H, 5.3; N, 14.8; Cl, 9.1.

trans-Dichloro[(R,R(S,S))-1,9-diamino-3,7-diazanonane]cobalt-(III) Perchlorate. β-*cis*-[Co(RR(SS)-2,3,2-tet)CO₃]ClO₄ (2 g) was dissolved in water (40 ml), concentrated hydrochloric acid (4 ml) was added, and the mixture was set aside for 1 hr. Perchloric acid (2 ml, 72%) was then added and the solution was warmed on a hot plate until the color had changed from red to violet. On cooling, green needles of the required complex separated leaving, eventually, an almost colorless mother liquor. The product was filtered off, washed with ethanol and ether, and air-dried. The ¹H nmr spectrum of a solution in dimethyl sulfoxide showed no signal at τ 4.60, indicating that less than 2% of the *RS* isomer was present. *Anal.* Calcd for C₇H₂₀N₂O₄Cl₃Co: C, 21.6; H, 5.2; N, 14.4; Cl, 27.2. Found: C, 21.7; H, 5.2; N, 14.5; Cl, 26.4.

trans-Dichloro[(R,R(S,S))-1,9-diamino-3,7-diazanonane]cobalt-(III) Chloride. The racemic dichloro perchlorate (0.4 g) was dissolved in dimethyl sulfoxide (10 ml) that had been acidified with 1 drop of concentrated hydrochloric acid. A solution of lithium chloride (0.08 g) in dimethyl sulfoxide (10 ml) was added and acetone was slowly dropped into the stirred solution. The walls were scratched to induce crystallization and the mixture was set aside for 30 min. The chloride was filtered off, washed with acetone and ether, and air-dried. *Anal.* Calcd for C₇H₂₀N₄Cl₃Co: C, 25.8; H, 6.1; N, 17.2; Cl, 32.8. Found: C, 25.8; H, 6.2; N, 17.1; Cl, 32.4.

β-*cis*-Carbonato{[N,N,N′,N″,N‴,N‴′-²H₆]-(R,R(S,S))-1,9-diamino-3,7-diazanonane}cobalt(III) Perchlorate. β-*cis*-[Co(RR(SS)-2,3,2-tet)CO₃]ClO₄ (2 g) was dissolved in the minimum amount of warm D₂O and the solution was set aside to crystallize overnight. The product was filtered off and the process was repeated three more times with fresh D₂O in order to obtain the fully N-deuterated complex in which the peaks assigned to the N–H stretches at 3290, 3228, and 3128 cm⁻¹ have been replaced by a new set at 2460, 2420, 2400, 2370, and 2320 cm⁻¹. *Anal.* Calcd for C₈H₁₄D₆N₄O₇ClCo: C, 25.0; N, 14.2; Cl, 9.2. Found: C, 24.9; N, 14.5; Cl, 9.3.

trans-Dichloro{[N,N,N′,N″,N‴,N‴′-²H₆]-(R,R(S,S))-1,9-diamino-3,7-diazanonane}cobalt(III) perchlorate was prepared from the fully deuterated carbonato complex by the method used for the normal complex, except that D₂O was used instead of normal water; yield 1.98 g. The peaks at 3305, 3256, and 3125 cm⁻¹, assigned to the N–H stretches in the normal complex, have been replaced by a new

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 177.

(2) See M. L. Tobe, *Accounts Chem. Res.*, 3, 377 (1970), for more recent references.

(3) R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, 78, 4878 (1956).

(4) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 8, 1595 (1969).

(5) G. Marangoni, M. Panayotou, and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1989 (1973).

(6) J. Van Alphen, *Recl. Trav. Chim. Pays-Bas*, 55, 835 (1936).

(7) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).

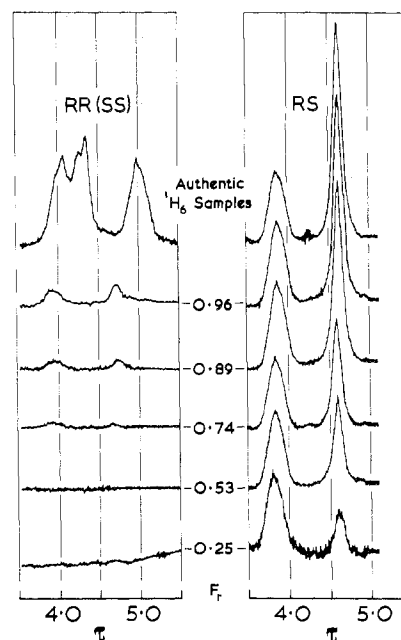(8) R. Niththyananthan, Ph.D. Thesis, London, 1970, p 186.

set at 2480, 2400, and 2330 cm^{-1}. *Anal.* Calcd for C$_7$H$_{14}$D$_6$N$_4$O$_4$-Cl$_3$Co: C, 21.3; N, 14.2; Cl, 26.9. Found: C, 21.4; N, 14.2; Cl, 27.0.

The N-deuterated perchlorate was converted to the chloride in the same way as the normal salt. *Anal.* Calcd for C$_7$H$_{14}$D$_6$N$_4$Cl$_3$-Co: C, 25.4; N, 16.9. Found: C, 25.2; N, 16.6.

Isotope-Exchange Studies. The buffer solution was prepared by adding 0.10 *M* nitric acid to a 0.300 *M* solution of 2,6-dimethyl-pyridine in water until the pH had reached the required value. Aliquot portions of this solution were brought to the reaction temperature and a weighed amount of *trans*-dichloro-{[*N,N,N',N'',N''',N'''*-^{2}H$_6$]-(*R,R*(*S,S*))-1,9-diamino-3,7-diazanonane}cobalt(III) chloride (sufficient to produce a 0.030 *M* solution) was added to each to start the reaction. At the appropriate time, the contents of the reaction vessel were poured into excess ice-cold dilute perchloric acid (10^2 mol of acid/mol of complex) and the mixture was set aside in ice for 2 hr to ensure complete precipitation of the dichloro perchlorate.[9] This was filtered off, washed with a small amount of ice-cold perchloric acid (0.1 *M*) followed by ethanol and then ether, and finally air-dried. The filtrate was treated with a few milliliters of concentrated hydrochloric acid and warmed on a water bath for 2–3 hr, during which time the aquo species were converted to a *trans*-dichloro complex which crystallized out as its insoluble perchlorate on cooling. This too was filtered off and washed and dried as before. There was no evidence that the perchlorate of the protonated buffer amine contaminated either of these recovered materials. The extent of amine proton exchange was determined by dissolving a known amount of the perchlorate (generally 0.0300 g) in 5.00 ml of dimethyl sulfoxide containing benzene (5% by weight) as an internal standard. The ^{1}H nmr spectrum was measured with a Varian HA 100 instrument and the areas under the appropriate peaks were integrated by standard means. The number of amine protons present in the complex was deduced by comparison of these areas with that under the benzene peak.

Results

The nature and extent of hydrogen exchange accompanying the base hydrolysis of *trans*-[Co(*RR*(*SS*)-2,3,2-tet)Cl$_2$]$^+$ was studied by dissolving the fully N-deuterated complex in a buffer solution of pH within the range 6.0–6.5, allowing the reaction to proceed for a known period of time, and then pouring the mixture into an excess of perchloric acid. This served to stop the base hydrolysis as well as any parallel or subsequent proton exchange and also precipitated the unreacted substrate as its insoluble perchlorate. The reaction product, present in solution as soluble diaquo species, was converted, by warming with hydrochloric acid, to a *trans*-dichloro complex which was obtained as its insoluble perchlorate. The extent of replacement of ^{2}H by ^{1}H could be measured quantitatively by means of ^{1}H nmr studies of the solution of these perchlorates in dimethyl sulfoxide, in which they are extremely soluble. The part of the ^{1}H nmr spectrum of a normal sample of *trans*-[Co(*RR*(*SS*)-2,3,2-tet)-Cl$_2$]ClO$_4$ in dimethyl sulfoxide that can be assigned to the amine protons is shown in Figure 1. Three peaks of equal intensity appear at τ 4.05; 4.23, 4.32; 4.95. They are typically broad and are absent in the spectrum of the fully N-deuterated material. The middle peak is split and the τ 4.95 peak is unsymmetrical; on examining the spectrum at 60 MHz, the doublet is broadened and the downfield part overlaps the τ 4.05 peak. The protons producing the middle peak are therefore coupled individually to a single proton, $J = 9$ Hz. The peak at τ 4.95 is further broadened at 60 MHz but still not properly resolved into a doublet; nevertheless, spin decoupling experiments show that irradiation at the τ 4.95 peak causes the doublet at τ 4.23, 4.32 to be replaced by a sharp singlet at τ 4.29. These observations are all consistent with the following assignment. The peak at

(9) The *RR*(*SS*) *trans*-dichloro perchlorate is somewhat more soluble in water than the *RS* isomer,[5] but independent studies showed that 96% of the complex was precipitated as the perchlorate when a freshly prepared 0.030 *M* solution of the chloride was treated with perchloric acid under the conditions used in the separation.

Figure 1. The 100-MHz ^{1}H nmr spectra (in dimethyl sulfoxide solution) of the amine protons in the recovered unreacted material (left-hand side) and the recovered and reanated reaction product (right-hand side) of the base hydrolysis of *trans*-[Co(*RR*(*SS*)-2,3,2-tet)Cl$_2$]Cl in aqueous 2,6-dimethylpyridine–nitric acid buffer, pH 6.40, at 26.6°. The authentic spectra of the normal isomers are shown at the top.

τ 4.05 comes from the equivalent pair of secondary amine protons, the doublet centered on τ 4.29 comes from two equivalent primary amine protons, one on each nitrogen, and the broad peak at τ 4.95 belongs to the other pair of equivalent primary amine protons. If one assumes, as was suggested by Hamilton and Alexander,[10] that the six-membered chelate ring adopts a skew configuration and the five-membered rings are gauche, then the secondary amine protons are symmetrically equivalent. If the *SS* enantiomer is considered, these five-membered rings would adopt the δ conformation[11] which leaves the four primary amine protons equivalently sited with respect to the CoN$_4$ plane and the axial chlorines. However, the structure is loose enough for the λ conformations to be adopted without strain. The rings are not strictly gauche but this conformation leaves one primary amine proton in a pseudoaxial position and the other in a pseudoequatorial position. The axial and equatorial protons cannot exchange their positions without an inversion of the configuration of the secondary nitrogen. It is suggested that the contribution from the λ conformation therefore makes the average environments of the two types of primary amine protons different, that with τ 4.29 having a pseudoaxial contribution (analogous to the secondary amine protons) and that with τ 4.95 having a pseudoequatorial contribution. The two protons on the same nitrogen are coupled with $J = 9$ Hz. Similar reasoning will account for the spectrum of the simpler *RS* isomer (Figure 1) where the secondary amines are even more axially constrained and the chemical shift is even further downfield at τ 3.83, while the four primary amine protons are interchangeable with respect to the pseudoaxial and pseudoequatorial positions and appear as a single sharp peak at τ 4.60, halfway between

(10) H. G. Hamilton and M. D. Alexander, *J. Amer. Chem. Soc.*, **89**, 5065 (1967).

(11) See *Inorg. Chem.*, **9**, 1 (1970), for details of this nomenclature.

Table I. Exchange of Deuterium in the Base Hydrolysis of the *trans*-Dichloro{[N,N,N',N'',N''',N'''-^{2}H$_6$]-($R,R(S,S)$)-1,9-diamino-3,7-diazanonane}cobalt(III) Cations in Aqueous Soltuion[a]

| | | No. of deuterium atoms exchanged | | | |
| | | Unreacted | | Reacted | |
Time, sec	$F_{reaction}$	–NH$_2$	>NH	–NH$_2$	>NH
		(A) Initial pH 6.19, Temperature 25.0°			
120	0.20	0.0	0.0	0.43	1.3
210	0.31	0.0	0.0	0.87	1.4
390	0.46	0.0	0.0	1.19	2.0
720	0.62	0.0	0.0	1.61	2.0
1200	0.74	0.0	0.0	1.96	2.0
1980	0.84	0.0	0.0	2.28	2.0
		(B) Initial pH 6.40, Temperature 26.0°			
90	0.25	0.0	0.0	0.37	1.5
180	0.39	0.0	0.0	0.73	1.6
360	0.53	0.0	0.0	1.49	2.0
720	0.74	0.0	0.0	2.02	2.0
1200	0.89	0.0	0.0	0.67	2.0

[a] Using 0.30 M 2,6-dimethylpyridine–nitric acid buffer; [complex] = 0.03 M.

the peaks of the primary amine protons in the $RR(SS)$ isomer. It is implied in this reasoning and assignment that the axial chloride ligands make a major contribution to the chemical shifts of the amine protons.

The ^{1}H nmr spectra of the unreacted dichloro complexes recovered at different stages of the base hydrolysis are shown in Figure 1, where it will be seen that (a) no proton signal appears until after 80% has reacted and (b) when the signal does appear, it does so at chemical shifts characteristic of the RS isomer. The spectra of the recovered reaction products are characteristic of the RS isomer in which there has been parital replacement of the N-D by N-H. As in the case of the product of base hydrolysis of the RS dichloro isomer[5] the exchange has progressed further in the secondary amine proton signal (τ 3.83). The extent of exchange, as determined from the areas under the peaks, is given in Table I. An experiment was carried out in which the isotopically normal *trans*-[Co($RR(SS)$-2,3,2-tet)Cl$_2$]Cl complex was allowed to undergo base hydrolysis in the presence of 0.50 M sodium chloride. Only the recovered "unreacted material" was examined and the ^{1}H nmr spectra used to determine the relative amounts of $RR(SS)$ and RS dichloro isomers present. The results are collected in Table II.

The isomeric composition of the ^{2}H$_6$ unreacted material obviously cannot be determined in this way by ^{1}H nmr and the differences in the visible or infrared absorption spectra of the $RR(SS)$ and RS isomers, while quite noticeable, are too small to be of use in any accurate analysis. This, nevertheless, could be done quite conveniently by making use of the widely different stereochemistries of the acid hydrolyses of the two dichloro isomers. If a solution of the complex in 0.01 N HNO$_3$ is allowed to reach aquation equilibrium, the *trans*-[Co(RS-2,3,2-tet)Cl$_2$]$^+$ complex gives only *trans*-[Co-(RS-2,3,2-tet)(H$_2$O)Cl]$^{2+}$ product (ϵ_{520} 19 M^{-1} cm^{-1}) while the *trans*-[Co($RR(SS)$-2,3,2-tet)Cl$_2$]$^+$ isomer, in a two-stage reaction, gives the β-*cis*-[Co($RR(SS)$-2,3,2-tet)(H$_2$O)Cl]$^{2+}$ cation (ϵ_{520} 85 M^{-1} cm^{-1}).[12] Thus, the spectrum of a 0.01 M nitric acid solution of the isomer mixture (which has been allowed to aquate for 7 half-lives) of the less labile complex is a sensitive method of assessing the relative amounts of the $RR(SS)$ and RS isomers present in a sample of the dichloro material. The method was checked against synthetic mix-

Table II. Isomeric Composition of the "Unreacted" *trans*-[Co(2,3,2-tet)Cl$_2$]$^+$ Cations Recovered in the Course of the Base Hydrolysis of *trans*-Dichloro[($R,R(S,S)$)-1,9-diamino-3,7-diazanonane]cobalt(III) Chloride in Aqueous Solution at pH 6.19 in the Presence of 0.50 M NaCl[a]

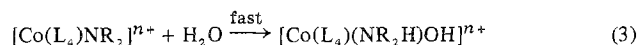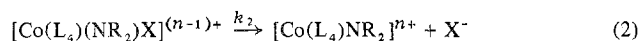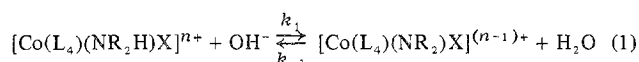| Time, sec	Fraction of dichloro complex recovered	% $RR(SS)$	% RS
180	0.54	94	6
360	0.45	80	20
720	0.34	44	56
1200	0.38	0	100
1800	0.43	0	100

[a] Temperature 25.2°; [2,6-dimethylpyridine–nitric acid buffer] = 0.30 M; [complex] = 0.03 M.

tures and also against the ^{1}H nmr method for the normal complexes. Using this method it was shown that the recovered unreacted material that was still fully deuterated was completely in the $RR(SS)$ form and that no measurable amount of the unexchanged $RR(SS)$ material (undetectable by the ^{1}H nmr method) was present in the recovered reaction product, even at the earliest stages of the reaction.

Discussion

The kinetics and products of the aqueous solvolysis of the RS and $RR(SS)$ isomers of *trans*-[Co(2,3,2-tet)Cl$_2$]$^+$ depend very much upon the pH of the solution. The acid hydrolysis is slow and independent of pH, the RS species giving the RS *trans*-aquochloro product and the $RR(SS)$ species giving a 1:1 mixture of $RR(SS)$ *trans*- and β-*cis*-chloroaquo complex.[12] The $RR(SS)$ *trans*-chloroaquo species isomerizes quite rapidly to the β-*cis* form. For pH >5 the base-catalyzed hydrolysis studied in this paper becomes important. In the region 5 < pH < 9, the relatively slow loss of the first chloride is followed by a relatively rapid, pH-independent solvolysis of the chloroaquo product,[5,13] the final product being the pH-determined equilibrium mixture of the hydroxoaquo and dihydroxo complexes. Above pH 9, the loss of the first chloride becomes faster than the second and the two stages can be examined separately.

The S$_N$1cb (or Dcb) mechanism for the base hydrolysis reaction can be written in general terms as

$$[Co(L_4)(NR_2H)X]^{n+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(L_4)(NR_2)X]^{(n-1)+} + H_2O \quad (1)$$

$$[Co(L_4)(NR_2)X]^{(n-1)+} \overset{k_2}{\longrightarrow} [Co(L_4)NR_2]^{n+} + X^- \quad (2)$$

$$[Co(L_4)NR_2]^{n+} + H_2O \overset{fast}{\longrightarrow} [Co(L_4)(NR_2H)OH]^{n+} \quad (3)$$

Assuming that no intermediate ever achieves significantly large concentrations, this mechanism and the stationary-state approximation give the rate law

$$-d[[Co(L_4)(NR_2H)X]^{n+}]/dt =$$

$$k_B[[Co(L_4)(NR_2H)X]^{n+}][OH^-]$$

where $k_B = k_1k_2/(k_{-1} + k_2)$ [or $nk_1k_2/(k_{-1} + k_2)$ in the general case when there are n equivalent amine protons in the complex].

It has been suggested that, in the normal base hydrolysis reaction, the specific base catalysis by hydroxide indicates that the proton-transfer steps establish a preequilibrium in (1) before there is any significant base hydrolysis.[14] This re-

(12) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).

(13) E. Ahmed, M. L. Tucker, and M. L. Tobe, *Inorg. Chem.*, in press.
(14) See ref 1, p 183.

quires that $k_{-1} \gg k_2$ which is eminently reasonable although the number of actual systems for which the proton-exchange rate constants and the base hydrolysis rate constants are known is few indeed. For [Co(NH$_3$)$_5$Cl]$^{2+}$, $k_B(25°) = 0.85$ M^{-1} sec^{-1} [15] and $k_1 = 1.5 \times 10^5 M^{-1}$ sec^{-1} at 25°.[16] Assuming 15 equivalent protons, since Palmer and Basolo gave no indication that more than one exchange process is occurring,[17] $k_{-1}/k_2 = nk_1/k_B = 15 \times 1.5 \times 10^5/0.85 = 2.6 \times 10^6$. Previously reported studies[5] have shown quite clearly that in the base hydrolysis of *trans*-[Co(en)$_2$Cl$_2$]⁺ the ratio of k_{-1}/k_2 lies between 4 and 10, while in the base hydrolysis of *trans*-[Co(*RS*-2,3,2-tet)Cl$_2$]⁺ the ratio is even smaller.[18]

The analogous study of the *trans*-[Co(*RR*(*SS*)-2,3,2-tet)-Cl$_2$]⁺ isomer now reported shows quite clearly that the limiting situation has been reached and that $k_2 \gg k_{-1}$. Using the expression $N_u = 2[1 - (1 - F_r)^{k_{-1}/2k_2}]$ for the relationship between the number of exchanged protons appearing in the unreacted material, N_u recovered after the fraction F_r had been converted to product, and the ratio of rate constants, k_{-1}/k_2,[5,19] it is possible to estimate that, since N_u is less than 0.1 at $F_r = 0.85$, $k_2/k_{-1} > 20$. The appearance of some partially exchanged *trans*-[Co(*RS*-2,3,2-tet)Cl$_2$]⁺ in the recovered unreacted material at the late stages of the reaction does not arise from competition for the conjugate base between the k_{-1} and k_2 paths. The experiment carried out in the presence of 0.50 *M* NaCl was originally designed to look for evidence for competition between water and chloride ions for the five-coordinate intermediate generated in step 2. Under these circumstances, the rate of formation of *trans*-[Co(*RS*-2,3,2-tet)Cl$_2$]⁺ would be maximum at the early stages of the reaction as soon as the steady-state condition had been reached; however, the data in Table II indicate quite clearly that there is an induction period and that the formation of the *RS* dichloro species is only important at the late stages of the reaction. It is probable that the *RS* dichloro species is formed after the reaction mixture has been acidified as a result of anation of the *RS* diaquo species by the chloride present and that its presence in the "unreacted material" is nothing more than a limitation of the method of separation when only small quantities of genuine unreacted material remain and a relatively large amount of chloride is present. This is also consistent with the observation (Table II) that the amount of recovered "unreacted material" starts to *increase* at the later stages of the reaction. The effect will be far less important when the only chloride present is that which has been displaced from the complex, but it will be enough to account for the observed formation of *RS* *trans*-dichloro species in the recovered unreacted material. This type of test cannot be applied to the analogous studies of the N-deuterated *trans*-[Co(*RS*-2,3,2-tet)Cl$_2$]⁺ [5] and it is possible

that a part of the observed exchange in the recovered unreacted material is due to this separation-induced anation. This would suggest that the ratio k_{-1}/k_2 might be smaller than the value quoted in that paper.

Since there is no significant exchange of the protons in the unreacted *RR*(*SS*) material before the act of base hydrolysis, it follows that any exchange that is observed in the isolated product must occur during the act of base hydrolysis or subsequent to it. The secondary amine protons are fully exchanged in all samples separated after 50% reaction, and although the accuracy of the measurement of the extent of exchange of the secondary amine protons did not allow a fully quantitative treatment, it can be stated unambiguously that the observation of less than full exchange at the earlier stages of the reaction is real and not attributable to incomplete separation of the unreacted (unexchanged) substrate from the fully exchanged reaction product since no *RR*(*SS*) isomer, exchanged or nonexchanged, was found in the isolated reaction product. An attempt to fit the exchange data to the expression $N_{\text{exch}} = N_1 + (2 - N_1)\{1 - (\alpha - 1)^{-1} \cdot [\alpha(1 - F_r) - (1 - F_r)^{\alpha}]F_r^{-1}\}$,[20] where $\alpha = k_D/k_B$ (k_D being the rate constant for exchange after base hydrolysis) indicates that N_1 (the number of secondary amine protons exchanged in the actual act of base hydrolysis) is 1 and $\alpha = 7 \pm 2$. This is fully consistent with the S$_N$1cb mechanism which requires that the act of base hydrolysis causes the exchange of one amine proton and indicates that the act of deprotonation to produce the labile conjugate base takes place on the secondary amine group. The value of α indicates that k_D for the secondary amine protons is $(1.2 \pm 0.4) \times 10^{-2}$ sec^{-1} under the experimental conditions used. The relatively small difference in the pH between the two experiments and the wide range of error do not permit us to say whether or not this rate constant is pH dependent.[21,22] The exchange of the primary amine protons can be treated in the same way, bearing in mind that there are four such protons. Here the data indicate that $N_1 = 0$, *i.e.*, no exchange results from the act of base hydrolysis, and $k_D/k_B = 0.9 \pm 0.1$. The calculated curves, assuming $N_1 = 0$, for various values of α are presented in Figure 2; also included are the data for the corresponding experiment starting from the *trans*-[Co(*RS*-2,3,2-tet)Cl$_2$]⁺ complex, taken from ref 5. These are consistent with $k_D/k_B = 2.5$. Inserting values for k_B in both cases it is possible to show that $k_D = (1.5 \pm 0.2) \times 10^{-3}$ and $(1.0 \pm 0.2) \times 10^{-3}$ sec^{-1}, respectively, for the products derived from the (*RR*(*SS*)- and the (*RS*-2,3,2-tet)Cl$_2$⁺ cations. The rate of exchange of these primary amine protons is sufficiently slow under these conditions for it to be quite certain that the process is occurring in *trans*-[Co(*RS*-2,3,2-tet)(H$_2$O)-OH]$^{2+}$ or the corresponding dihydroxo species.

One of the most important observations to come out of this work is that the act of base hydrolysis converts the *trans*-[Co(*RR*(*SS*)-2,3,2-tet)Cl$_2$]⁺ cation directly into *RS* product. The experiments in buffer solution, while confirming that the secondary nitrogen atom is the site of deprotonation to

(15) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

(16) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).

(17) Unpublished results of I. I. Olsen, quoted in ref 4, indicate that the protons on the nitrogen trans to the chlorine exchange much faster ($k_1^t = 3 \times 10^6 M^{-1}$ sec^{-1} at 25°) than the others ($k_1^c = 5 \times 10^4 M^{-1}$ sec^{-1} at 25°). This would give the ratio $k_{-1}/k_2 = 3 \times 3 \times 10^6/0.87 = 1 \times 10^7$ if trans deprotonation gave the active conjugate base and $12 \times 5 \times 10^4/0.85 = 7 \times 10^5$ if cis deprotonation formed the active conjugate base. In any event, the assumption that $k_{-1} \gg k_2$ is valid.

(18) A reexamination of the experimental data in the light of experience of the work in this paper and recognition of the importance of chloride anation at the later stages of the reaction suggests that the ratio is closer to the lower end of the range of values quoted, *i.e.*, 0.5.

(19) Note that, in this case, there are two equivalent secondary amine protons that can be removed to give the active amido conjugate base.

(20) This equation is derived simply from that given in ref 5 by replacing t by $-k_B^{-1} \ln(1 - F_r)$ and assuming that N_{exch} contains contributions from the act of base hydrolysis (N_1) as well as the subsequent exchange. Account is also taken of the fact that there are only two secondary amine protons.

(21) It is possible that the loss of the second chloride, which occurs at a rate that is independent of pH in this region ($k = 3.0 \times 10^{-2}$ sec^{-1} at 13.5° for the fully protonated species[13]), goes by way of an internal conjugate base mechanism[22] with the internal transfer of a proton from N-H to O. The similarities of the rate constants for aquation of *trans*-[Co(*RS*-2,3,2-tet)(OH)Cl]⁺ and the exchange of the secondary amine protons are not in conflict with this mechanism.

(22) C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968).
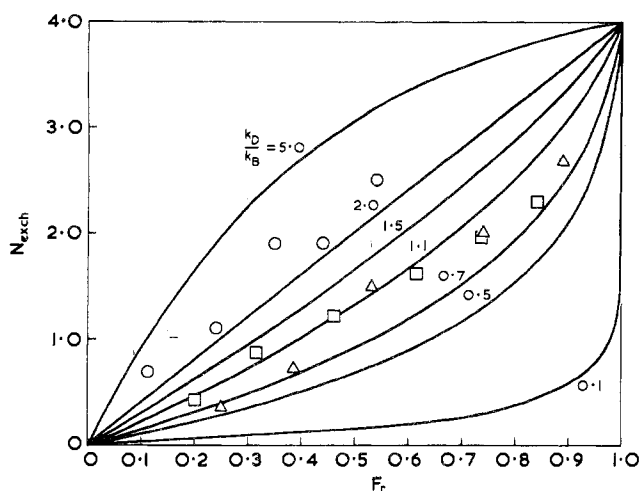
Figure 2. Plot of the number of primary amine protons per mole appearing as a result of exchange in the recovered and reanated product of the base hydrolysis of *trans*-[Co(RR(SS)-2,3,2-tet)Cl$_2$]$^+$ at pH 6.19 ($\square$) and 6.40 ($\triangle$) and of *trans*-[Co(RS-2,3,2-tet)Cl$_2$]$^+$ at pH 6.19 from ref 5 ($\bigcirc$). Lines are calculated for the indicated values of $k_D/k_B = \alpha$ using the equation described in the text.

form the reactive amido conjugate base, do not determine unambiguously which of the two stages of loss of chloride is associated with nitrogen inversion, although the total absence of RR(SS) material in the reaction product, even at the earliest stages of the reaction, would suggest that inversion accompanies the loss of the first chloride. A simple rapid mixing and killing experiment, in which *trans*-[Co(RR(SS)-2,3,2-tet)Cl$_2$]$^+$ is mixed with a twofold molar excess of 0.01 M sodium hydroxide, the mixture being acidified within 5 sec after mixing, shows that only one chloride has been released and yet the reaction product anates back directly to the RS dichloro complex. This complex, identified by its ^{1}H nmr spectrum and by its aquation behavior, indicates that the inversion of nitrogen configuration accompanies the fast base-catalyzed displacement of the first chloride.

Thus it has been shown that, in the base hydrolysis of *trans*-[Co(RR(SS)-2,3,2-tet)Cl$_2$]$^+$, the rate-determining step is the removal of the proton from one of the secondary amine nitrogens. In the subsequent dissociative solvolysis, the configuration of one of the two secondary nitrogens is inverted. The RS isomer also undergoes base hydrolysis as a consequence of deprotonation of a secondary amine nitrogen, but in this case there is no inversion and the product has the RS configuration.[5] It can also be noted at this point that, whereas the site of deprotonation has not yet been determined, it has been shown that β-*cis*-[Co(RR(SS)-2,3,2-tet)Cl$_2$]$^+$ also gives *trans*-[Co(RS-2,3,2-tet)(OH)$_2$]$^+$ as product of base hydrolysis.[8] These results can be readily understood if all three reactions possess a common intermediate and this can best be visualized in terms of the sequence represented in Figure 3. The original complexes and their deprotonated conjugate bases are represented by the same diagram since the lone pair maintains the configuration of the nitrogen during the lifetime of the conjugate base. There is ample evidence that the configurational stability of the nitrogen in a cobalt(III)–amido complex is sufficient for this purpose. Sargeson has compared the rates of proton exchange and racemization of a number of coordinated secondary amines and shown that the rate constant for exchange, in aqueous solution, is generally many orders of magnitude greater than that for racemization,[4,23–27] but in all the cases studied the central metal ion remained octahedral through-
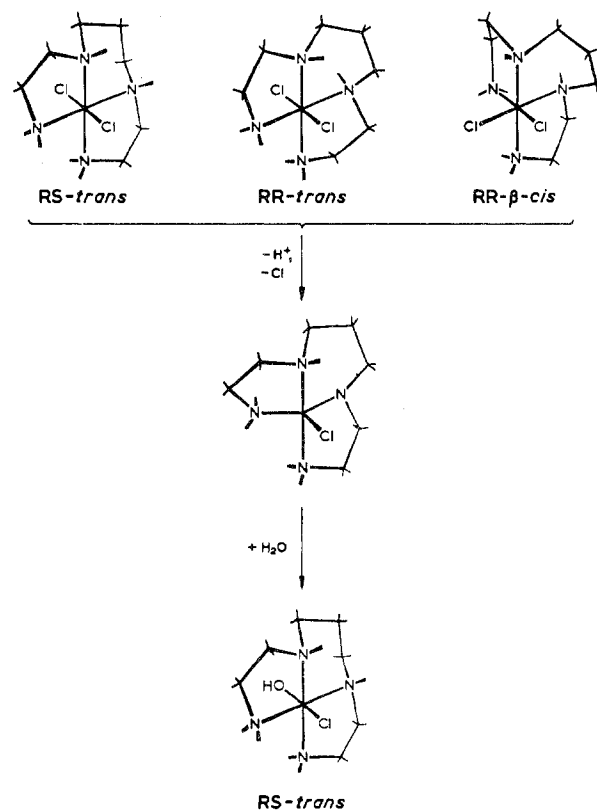
Figure 3. Diagrammatic representation of the base hydrolysis of *trans*-[Co(RS-2,3,2-tet)Cl$_2$]$^+$, *trans*-[Co(RR-2,3,2-tet)Cl$_2$]$^+$, and β-*cis*-[Co(RR-2,3,2-tet)Cl$_2$]$^+$ showing the formation and consequences of a common trigonal-bipyramidal intermediate with a planar amido nitrogen in the trigonal plane.

out. If the dissociation of the chloride from the conjugate base is accompanied by a change in geometry from octahedral to trigonal bipyramidal with the amido group in the trigonal plane and the nitrogen planar in order to function adequately as a π donor to cobalt, then all three substrates will give the same intermediate, once the chelate rings have had time to equilibrate their conformations. The subsequent reaction with water will give the same hydroxychloro product, which should be the most stable isomeric form of all the possibilities. This therefore represents the first demonstration of planarity in the amido nitrogen in the five-coordinate intermediate generated in the base-catalyzed hydrolysis of cobalt(III)–amine complexes. These conclusions differ from those of Sargeson[4] but it is likely that, in the base-catalyzed hydrolysis of *sym*-[Co(trenen)Cl]$^{2+}$, the most labile nitrogen with respect to proton exchange is not the site of the active amido group in the conjugate base and the fate of the stereochemical label at that point gives no information about the labilizing role of the amido nitrogen.

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(24) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 825 (1967).
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(26) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **90**, 6028 (1968).
(27) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **91**, 5227 (1969).