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# Primary Isotope Effects and General Base Catalysis in the Hydrolysis of *trans*-Dichloro(1,9-diamino-3,7-diazanonane)cobalt(III) Cations

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The kinetics of the base hydrolysis of *trans*-dichloro-(*RS*)- and *trans*-dichloro[(*RR*(*SS*))-1,9-diamino-3,7-diazanonane]cobalt(III) cations and their N-deuterated analogs have been studied in aqueous solution using sodium hydroxide or a substituted pyridine as base. For the reaction with hydroxide, $k_B^{OH} = 1.5 \times 10^4\ M^{-1}$ sec$^{-1}$ at 13.5° ($\mu = 0.05$) for the *RS* isomer and $3.0 \times 10^4\ M^{-1}$ sec$^{-1}$ for the *RR*(*SS*) isomer. In the latter case $\Delta H^\ddagger = 13.7$ kcal/mol and $\Delta S^\ddagger = +12$ cal deg$^{-1}$ mol$^{-1}$. The activation parameters reflect the rate-determining character of the deprotonation step. The primary isotope effect $k_B^{OH}(H)/k_B^{OH}(D) = 1.7$ and 1.5 for the *RR*(*SS*) and *RS* isomer, respectively and is, at first sight, rather small for such a rate-determining protonation but the behavior is rationalized in terms of the structure of the transition state. General base catalysis is observed with a Bronsted coefficient, $\beta = 0.67 \pm 0.07$.

## Introduction

The base-catalyzed hydrolysis of amine complexes of cobalt(III) involves a deprotonation of an amine ligand followed by a dissociative aquation of the amido conjugate base. Usually, the proton transfer is reversible and much faster than the overall base hydrolysis reaction but many complexes of the type, *trans*-$[CoL_4X_2]^+$, where $L_4$ is a four-nitrogen donor set and X is a halide, not only are extremely sensitive to base hydrolysis but also represent a situation where the proton-transfer reaction and the base hydrolysis have similar rates.[1,2] In a recent paper[3] it was shown that the base hydrolysis of *trans*-dichloro[(*RR*(*SS*))-1,9-diamino-3,7-diazanonane]cobalt(III) chloride (*R* and *S* refer to the configurations of the coordinated secondary nitrogen atoms, *RR*(*SS*) indicating the unresolved racemate species) represented the limit of the trend observed in *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(RS\text{-}2,3,2\text{-tet})Cl_2]^+$ [2] (2,3,2-tet = 1,9-diamino-3,7-diazanonane) in which the rate constant for the dissociation of the conjugate base "$k_2$" is considerably greater than that for its reprotonation, "$k_{-1}$". Consequently the deprotonation of the substrate becomes the rate-determining step for the base hydrolysis reaction. This should lead to a number of phenomena which are not normally associated with the base hydrolysis of octahedral complexes and which cannot be studied conveniently in these inorganic systems. This paper reports the general kinetics of base hydrolysis of the two isomers and examines the primary isotope effects associated with the deprotonation in the virtual absence of any secondary effects. It demonstrates a general base catalysis for the first time in reactions of this sort and shows how the temperature dependence of the rate constants might be used as a preliminary diagnostic tool for the identification of a rate-determining deprotonation in these systems.

## Experimental Section

The preparation and characterization of the normal and the N-deuterated complexes have been described in the previous paper.[3] Analytical, infrared, and $^1$H nmr criteria were used to establish their purity.

**Kinetics.** All reactions were followed spectrophotometrically but the technique used depended upon the rate of the change that was being studied. The slowest reactions, in buffer solutions, were followed by standard repetitive scanning techniques. The buffers were prepared by adding dilute nitric acid to an aqueous solution of the appropriate heterocyclic amine until the pH was approximately that required for the experiment. Sufficient sodium nitrate was then added to produce the desired ionic strength in the final reaction solution. In the experiments designed to study the effect of varying the concentration of the buffer a larger batch of buffer was made up at the highest concentration required and the appropriate dilution was made before the ionic strength was adjusted. The solution of the complex, as its chloride or perchlorate, and the solution of the buffer and the other reagents were separately brought to the reaction temperature and then mixed to start the reaction. When the *N*-deuterio complexes were being studied, a very small amount of acid was added to the solution of the complex in order to inhibit premature proton exchange. This did not significantly affect the final ionic strength or even the pH when the solutions were mixed. The reactions were carried out in a silica cell in the thermostated cell compartment of a Unicam SP 800 spectrophotometer. The temperature remained constant to within ±0.05° and was measured with a calibrated thermocouple inserted in the thermostat block (preliminary experiments with the thermocouple actually inserted in the solution in the cell showed that the temperature gradient was too small to measure), using a Solartron LM 1604 digital voltmeter to measure the emf. Spectra were scanned at the appropriate times and the course of the reaction could be deduced from the general changes in the form of these spectra. The kinetics were determined from the large change in absorbance at 335 nm. The pH of the reaction mixture was measured with a Radiometer PHM 26 pH meter using identical solutions at the same temperature as the spectrophotometrically studied mixtures. By using low concentrations of complex ($2.5 \times 10^{-4}\ M$) and concentrations of buffer mixtures at least 100 times greater than that of the complex the pH change in the course of the reaction was reduced to less than 0.05 unit. The ionic product of water at the appropriate temperature was obtained from the literature[4] and the appropriate activity coefficient corrections for the ionic strengths used were obtained from Harned and Owen.[5] The hydroxide concentration could then be calculated. In the more dilute solutions of complex the absorbance at wavelengths greater than 350 nm was very small and either the scanning was confined to a narrow part of the spectrum or else the change in absorbance at a single wavelength was recorded. The faster reactions in buffer solutions at higher pH were followed at a single wavelength using a Durrum D 110 stopped-flow spectrophotometer. In these reactions, sodium nitrate was present in the solution of the complex as well as that of the buffer in order to ensure that the ionic strength of the two reagent solutions was the same before mixing. The output of the photonmultiplier was displayed on the *Y* axis of a Servoscribe RE 511.20 potentiometric recorder. The pH of the reaction mixture was measured as before but the reaction was virtually complete before the measurement could be made. The fastest reactions between the complexes and sodium hydroxide were also followed with the stopped-flow technique. The output of the photonmultiplier was now observed on a storage oscilloscope in order to adjust the equipment but measurements were made by storing the data in a Datalab DL 905 transient recorder and then transferring the information to the Servoscribe pen recorder. When the reactions were carried out at temperatures significantly below that of the room, dry air was passed through the cold parts of the optical system in order to prevent misting on the windows and the mirrors. At temperatures below 13° the shrinkage of the pistons was sufficient to allow some of the solution to be forced back behind them and to allow premixing of the reagents. This was overcome by reducing the pressure of the driving air from 70 to 50 psi.

## Results

The change in spectrum accompanying the base-catalyzed hydrolysis of *trans*-$[Co(RS\text{-}2,3,2\text{-tet})Cl_2]^+$ in aqueous buffer solution in the pH range 5.7–7.0 is characteristic of a single process with well-defined isosbestic points at 592, 444, 423, and 352 nm. At lower pH the behavior is complicated by interference from the noncatalyzed aquation and the fact that the first product is present, in part, as the inert aquochloro species. At higher pH the change becomes too fast to monitor satisfactorily by repetitive scanning and there are also indications that the two stages of the reaction are starting to separate (the rate of the second stage is independent of pH up to 8.5). The *trans*-$[Co(RR(SS)\text{-}2,3,2\text{-tet})Cl_2]^+$ isomer behaves in a similar way with isosbestic points at 585, 455, 413, and 352 nm. In both cases the initial spectra are identical with those of the starting dichloro complex and the final spectra correspond to that of *trans*-$[Co(RS\text{-}2,3,2\text{-tet})(OH)H_2O]^{2+}$, changing to the dihydroxo complex at higher pH. If, at the end of the reaction, the solution is acidified with nitric acid and titrated with silver nitrate, it is found that all the chloride has been released. One can conclude that the rate-determining step is the displacement of the first chloride. The *RS* configuration of the ligand in the final product has been confirmed by $^1H$ nmr.[3]

At sufficiently high pH the two stages of displacement of chloride are separable and can be studied by stopped-flow techniques, using sodium hydroxide as the base. If a solution of either dichloro complex is mixed rapidly with a twofold molar excess of sodium hydroxide, the first stage of reaction is complete within a fraction of 1 sec and acidification within 5 sec of mixing will prevent significant amounts of the second stage from taking place. Only one of the two chlorides can be titrated with silver nitrate and the spectrum is consistent with that of a *trans*-aquochloro species.[6] The *RS* configuration of the secondary amine nitrogens in this complex has been confirmed by $^1H$ nmr.[3] Thus, it has been shown unambiguously that the two spectrophotometric changes that are observed correspond to Scheme I. Although it was possible to study the two stages of reaction in the same kinetic run, it was more convenient to examine them separately. The kinetics were followed at constant ionic strength and, where possible, in the presence of sufficient excess sodium hydroxide to ensure first-order conditions. When this was not possible, the rate constant was determined from the initial slope of the curved semilogarithmic plot of ln $(A_t - A_\infty)$ against time, where $A_t$ and $A_\infty$ are the absorbances at 530 nm at times "*t*" and at the end of the appropriate stage of the reaction. (Under first-order conditions the semilogarithmic plots are, of course, linear.) The appropriate first-order rate constants, $k_{\text{obsd}}$ and $k'_{\text{obsd}}$, for the first and second stages of the reaction, respectively, are collected in Table I. Plots of these rate constants against $[OH^-]$ are linear, those for the first stage passing through the origin. The slope of this line, $k_B^{OH}$ is also given in Table I. The slopes and intercepts of the second stage, $k'_B$ and $k'_0$ are also recorded. These reactions were carried out at a number of temperatures. The base hydrolyses of the fully N-deuterated *RS* and *RR*(*SS*) complexes were studied in a similar way, except that the complex was dissolved in 1 × $10^{-3}$ *M* perchloric acid in order to prevent exchange of the amine protons before the solution was mixed with sodium hydroxide. A correction was made to the concentration of sodium hydroxide to account for the neutralization of this acid. The rate constants are reported in Table II.

**Table I.** Pseudo-First-Order and Derived Second-Order Rate Constants for the Base Hydrolysis of the *RS* and *RR*(*SS*) Forms of the *trans*-Dichloro(1,9-diamino-3,7-diazanonane)cobalt(III) Cation in Aqueous Solution.[a,b]

| Temp, deg | [NaOH], *M* | $10^{-2} \cdot k_{\text{obsd}}$, $sec^{-1}$ | $10^{-4} \cdot k_B$, $M^{-1}$ $sec^{-1}$ | $10^2 \cdot k'_{\text{obsd}}$, $sec^{-1}$ | $10^2 \cdot k'_0$, $sec^{-1}$ | $k'_B$, $M^{-1}$ $sec^{-1}$ |
|---|---|---|---|---|---|---|
| | | *RS* Isomer | | | | |
| 13.5 | 0.0050 | 0.74 | 1.5 | | | |
| 13.5 | 0.0100 | 1.52 | | 6.3 | 2.7 | 3.4 |
| 13.5 | 0.0150 | 2.30 | | 7.9 | | |
| 13.5 | 0.0200 | 2.80 | | 8.5 | | |
| 13.5 | 0.0250 | | | 11.2 | | |
| 16.8 | 0.0025 | 0.48[c] | 2.1 | | | |
| 16.8 | 0.0030 | 0.59[c] | | | | |
| 16.8 | 0.0040 | 0.81[c] | | | | |
| 16.8 | 0.0050 | 1.00[c] | | | | |
| 19.9 | 0.0025 | 0.50[c] | 2.5 | | | |
| 19.9 | 0.0030 | 0.68[c] | | | | |
| 19.9 | 0.0040 | 1.00[c] | | | | |
| 19.9 | 0.0050 | 1.11[c] | | | | |
| | | *RR*(*SS*) Isomer | | | | |
| 6.8 | 0.0050 | 0.60 | 1.37 | | | |
| 6.8 | 0.0100 | 1.37 | | | | |
| 6.8 | 0.0200 | 2.74 | | | | |
| 10.4 | 0.0050 | 0.81 | 2.10 | | | |
| 10.4 | 0.0100 | 2.18 | | | | |
| 10.4 | 0.0200 | 4.03 | | | | |
| 13.5 | 0.0025 | 0.58 | 3.0 | | | |
| 13.5 | 0.0030 | 0.94 | | | | |
| 13.5 | 0.0040 | 1.14 | | | | |
| 13.5 | 0.0050 | 1.48 | | | | |
| 13.5 | 0.0100 | 3.0 | | 6.5 | 2.9 | 3.6 |
| 13.5 | 0.0150 | 4.8 | | 8.4 | | |
| 13.5 | 0.0200 | | | 10.0 | | |
| 13.9 | 0.0050 | 1.63 | 3.2 | | | |
| 13.9 | 0.0100 | 3.40 | | | | |
| 13.9 | 0.0200 | 6.02 | | | | |
| 19.9 | 0.0025 | 1.20[c] | 5.1 | | | |
| 19.9 | 0.0030 | 1.50[c] | | | | |
| 19.9 | 0.0040 | 2.1[c] | | | | |
| 19.9 | 0.0050 | 2.6[c] | | | | |

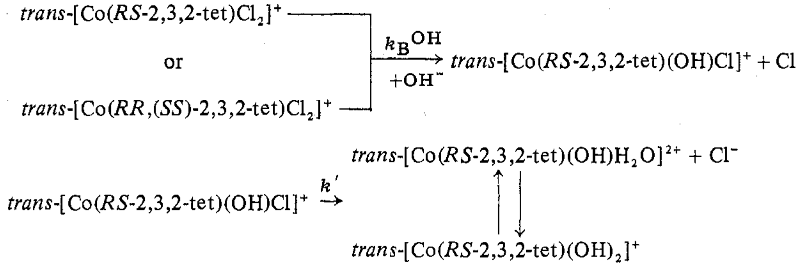
[a] Ionic strength 0.050 *M* ($NaNO_3$). [b] [Complex] = 1.0 × $10^{-3}$ *M*, except where indicated. [c] [Complex] = 2.5 × $10^{-4}$ *M*.

**Table II.** Pseudo-First-Order and Derived Second-Order Rate Constants for the Base Hydrolysis of the *RS* and *RR*(*SS*) Forms of *trans*-Dichloro($N,N,N',N'',N''',N'''$-$^2H_6$-1,9-diamino-3,7-diazanonane)cobalt(III) Cations in Water at 13.5°[a,b]

| *RS* | | | *RR*(*SS*) | | |
|---|---|---|---|---|---|
| [NaOH], *M* | $10^{-2} \cdot k_{\text{obsd}}$, $sec^{-1}$ | $k_B$, $M^{-1}$ $sec^{-1}$ | [NaOH], *M* | $10^{-2} \cdot k_{\text{obsd}}$, $sec^{-1}$ | $k_B$, $M^{-1}$ $sec^{-1}$ |
| 0.0045 | 0.41 | 1.0 × $10^4$ | 0.0045 | 0.85 | 1.8 × $10^4$ |
| 0.0095 | 0.88 | | 0.0095 | 1.76 | |
| 0.0195 | 2.20 | | 0.0195 | 3.53 | |

[a] Ionic strength 0.050 *M* ($NaNO_3$). [b] [Complex] = 1.0 × $10^{-3}$ *M*.

**Scheme I**



$$trans\text{-}[Co(RS\text{-}2,3,2\text{-tet})Cl_2]^+ \text{ or } trans\text{-}[Co(RR,(SS)\text{-}2,3,2\text{-tet})Cl_2]^+ \xrightarrow[+OH^-]{k_B{}^{OH}} trans\text{-}[Co(RS\text{-}2,3,2\text{-tet})(OH)Cl]^+ + Cl$$

$$trans\text{-}[Co(RS\text{-}2,3,2\text{-tet})(OH)Cl]^+ \xrightarrow{k'} trans\text{-}[Co(RS\text{-}2,3,2\text{-tet})(OH)H_2O]^{2+} + Cl^- \rightleftharpoons trans\text{-}[Co(RS\text{-}2,3,2\text{-tet})(OH)_2]^+$$

**Table III.** Pseudo-First-Order and Derived Second-Order Rate Constants for the Base Hydrolysis of the *RS* and *RR*(*SS*) Forms of the *trans*-Dichloro(1,9-diamino-3,7-diazanonane)cobalt(III) Cations as a Function of the Nature and Concentration of the Buffer[a-c]

| Buffer | [Free base], $M^{-1}$ | pH | $10^8[OH^-]$,[d] $M^{-1}$ | $10^4 k_{obsd}$, $sec^{-1}$ | $10^4 k_0$, $sec^{-1}$ | $k_B{}^{OH} = k_0/[OH^-]$, $M^{-1}\ sec^{-1}$ | $k_B{}^{am}$, $M^{-1}\ sec^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | *RS* Isomer | | | | |
| 3,5-Dimethylpyridine–$HNO_3$ | 0.025 | 6.26 | 3.72 | 6.54 | 6.62 | $1.8 \times 10^4$ | $2.1 \times 10^{-3}$ |
| | 0.050 | 6.26 | 3.72 | 8.10 | | | |
| | 0.100 | 6.26 | 3.72 | 9.03 | | | |
| | 0.200 | 6.26 | 3.72 | 10.5 | | | |
| 2,6-Dimethylpyridine–$HNO_3$ | 0.025 | 6.49 | 6.32 | 14.5 | 11 | $1.8 \times 10^4$ | $8 \times 10^{-3}$ |
| | 0.100 | 6.49 | 6.32 | 17.5 | | | |
| 2,4,6-Trimethylpyridine–$HNO_3$ | 0.025 | 7.52 | 67.8 | 142 | 109 | $1.6 \times 10^4$ | $1.4 \times 10^{-1}$ |
| | 0.050 | 7.52 | 67.8 | 179 | | | |
| | 0.100 | 7.52 | 67.8 | 245 | | | |
| | | | *RR*(*SS*) Isomer | | | | |
| 3,5-Dimethylpyridine–$HNO_3$ | 0.025 | 6.26 | 3.72 | 15.2 | 14.3 | $3.8 \times 10^4$ | $2.3 \times 10^{-3}$ |
| | 0.050 | 6.26 | 3.72 | 15.6 | | | |
| | 0.100 | 6.26 | 3.72 | 16.7 | | | |
| | 0.200 | 6.26 | 3.72 | 19.0 | | | |
| 2,4,6-Trimethylpyridine | 0.025 | 7.52 | 67.8 | 296 | 279 | $4.1 \times 10^4$ | $1.3 \times 10^{-1}$ |
| | 0.050 | 7.52 | 67.8 | 366 | | | |
| | 0.100 | 7.52 | 67.8 | 400 | | | |
| 2,4,6-Trimethylpyridine[e,f] | 0.032 | 8.095 | 80.4 | 370 | 322 | $4.0 \times 10^4$ | |
| 2,4,6-Trimethylpyridine[f,g] | 0.032 | 7.990 | 106 | 641 | 557 | $5.3 \times 10^4$ | |
| 2,4,6-Trimethylpyridine[f,h] | 0.032 | 7.915 | 124 | 970 | 843 | $6.8 \times 10^4$ | |
| 2,4,6-Trimethylpyridine[f,i] | 0.032 | 7.825 | 153 | 1650 | 1434 | $9.4 \times 10^4$ | |

[a] [Complex] = $2.5 \times 10^{-4}$ *M*. [b] $\mu = 0.25$ *M* ($NaNO_3$) except where otherwise indicated. [c] Temperature 25.7°. [d] Values for $K_w$ calculated from data in ref 4 and 5. [e] At 14.4°. [f] $\mu = 0.043$. [g] At 20.6°. [h] At 25.1° [i] At 30.4°.

The kinetics of the slower reactions in buffer solutions were monitored by the change in absorbance at 335 nm and the rate constants determined graphically as before. These are collected in Table III. In one group of reactions, three separate buffer bases were compared and, by keeping the buffer ratio, $[BH^+]/[B]$, and the ionic strength constant and varying the total buffer concentration, it was possible to examine the dependence of $k_{obsd}$ on the concentration of free base, [B]. At any particular pH the pseudo-first-order rate constant obeys the relationship $k_{obsd} = k_0 + k_B{}^{am}[B]$, in which $k_0$ is proportional to the hydroxide ion concentration. The derived values for $k_0$, $k_B{}^{am}$, and $k_B{}^{OH}$ ($=k_0/[OH^-]$) are also collected in Table III. In the other group of reactions the buffer concentration and ratio were held constant and the rate constant, $k_{obsd}$, was studied as a function of temperature. A small correction was made for the contribution from $k_B{}^{am}[B]$ in order to obtain $k_0$ (it was assumed that the relative correction did not change with temperature) and $[OH^-]$ was calculated from the measured pH and the appropriate value for the ionic product of water.[4,5] The second-order rate constant, $k_B{}^{OH}$, is also collected in Table III.

## Discussion

The two isomeric *trans*-$[Co(2,3,2\text{-tet})Cl_2]^+$ cations are members of the group of *trans*-$[CoL_4Cl_2]^+$ complexes that are unusually sensitive to base catalysis.[1] It is possible, with this pair of isomers, to examine the extent to which the configuration of the secondary nitrogen atoms affects the kinetics and steric course of base hydrolysis. This effect proves to be rather small, the two rate constants differ by a factor of 2, and the activation parameters are fairly similar. Both give the *trans*-hydroxochloro product and the only major difference in behavior is that the act of base hydrolysis causes the inversion of the configuration of the deprotonated nitrogen.[3] The existence of the common *trans*-(*RS*)-hydroxochloro product, which was demonstrated unequivocally by direct sampling experiments,[3] is confirmed by the observation that the rate constants associated with the second stage of base hydrolysis are the same for both dichloro substrates. This behavior is in contrast with the acid hydrolysis where, at 25°, the rate constants differ by a factor of 20, the entropies of activation differ by 11 cal $deg^{-1}$ $mol^{-1}$, and steric change is observed for the *RR*(*SS*) isomer only.[6] The reactivity toward base catalysis can be compared with other members of the series. For example, $k_B{}^{OH}$ for the 3,2,3-tet analog, which has been assigned an *RR*(*SS*) configuration,[7] is very similar to that of the corresponding 2,3,2-tet species, $2.6 \times 10^4$ $M^{-1}$ $sec^{-1}$ (13.5°, $\mu = 0.05$),[8] whereas that for the extremely strained *RR*-(*SS*)-2,2,2-tet complex is considerably greater, $1.4 \times 10^5$ $M^{-1}$ $sec^{-1}$ (13.5°, $\mu = 0.05$).[8] These observations are consistent with the conclusion based on the isotopic labeling experiments[2,3] that deprotonation of the secondary amine group is the rate-determining step in this reaction.

The clear-cut demonstration that virtually all acts of deprotonation of *trans*-$[Co(RR(SS)\text{-}2,3,2\text{-tet})Cl_2]^+$ lead to loss of chloride allows us, by following the base hydrolysis of the complex, to study a number of interesting aspects of the kinetics of this deprotonation. The reaction obeys virtually all of the requirements for the study of a pure primary isotope effect. There is no preequilibrium proton transfer, and so the base

($OH^-$) and the solvent ($H_2O$) are held constant, and the nitrogen to be deprotonated binds a single H (or D). The other amine protons in the complex, which will be of the same isotopic form as the one to be removed, are sufficiently remote from the site of reaction to have no significant effect in the reaction, other than through hydrogen-bonding solvation interactions. The N–H and N–D stretching frequencies observed for these complexes are to be found among the peaks at 3305, 3256, 3125 $cm^{-1}$ for N–H and 2480, 2400, and 2330 $cm^{-1}$ for N–D (no closer assignment has been made)[3] and so the difference in zero-point energy associated with isotopic substitution should be between 1.1 and 1.2 kcal/mol. Thus, the maximum primary kinetic isotope effect, arising from the absence of zero-point energy of this sort in the transition state, is expected to be in the region of $7.0 \pm 0.5$. It is generally accepted that the maximum isotope effect for a proton transfer will be observed when the basicities of the two species competing for the proton are closely matched. Bell and Goodall[9] have shown this quite clearly for isotope effects associated with carbon acids. Direct application of this reasoning to isotope effects associated with deprotonation of nitrogen in amine complexes of cobalt(III) is difficult since there are no directly measured $pK_a$ values associated with these systems. From a knowledge of certain of the rate constants it is possible to place limits upon the equilibrium constant for the process

$$trans\text{-}[CoCl_2\{NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2\}]^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} trans\text{-}[CoCl_2\{NH_2(CH_2)_2\ddot{N}(CH_2)_3NH(CH_2)_2NH_2\}] + H_2O$$

since the constant $K = k_1/k_{-1}$. The absence of any significant induction period and the maintenance of a strict first-order dependence on $[OH^-]$ even at the highest concentration studied ($2 \times 10^{-2}$ *M*) indicates that $K < 5\ M^{-1}$ and the lower limit is set by what is considered acceptable for the values of the rate constants $k_{-1}$ and $k_2$ (rate constant for the dissociation of the conjugate base). It has been shown that, for the *RR*(*SS*) complex, $k_2 > 20k_{-1}$,[3] and since $k_1 = 3.0 \times 10^4\ M^{-1}\ sec^{-1}$ at 13.5°, it would be necessary for $k_2$ to be greater than $20 \times 3.0 \times 10^4/10^{-3}\ sec^{-1}$, *i.e.*, $>6 \times 10^8\ sec^{-1}$ if $K < 10^{-3}\ M^{-1}$. Thus the basicity of the conjugate base of the amine complex is not very much greater than that of hydroxide, and, if nitrogen acids and carbon acids behaved similarly in this respect, we might expect to find a maximum primary isotope effect in this case. However, at 13.5° the ratio of the rate constants for the base hydrolysis of the normal and deuterated *RR*(*SS*) complexes is $k_B^{OH}(H)/k_B^{OH}(D) = 1.7$. A slightly smaller value, 1.5, is observed for the *RS* isomer, although the labeling experiments do not prove unambiguously in this case that $k_B^{OH}$ can be identified exactly with the deprotonation constant, $k_1$. Other unambiguous data relating to primary isotope effects involving N–H bonds are rare, and the information generally includes solvent effects as well as secondary isotope effects. In the case of *trans*-$[Co(en)_2Cl_2]^+$, where it is known that $k_1 > 4k_2$ and $k_B^{OH}$ is therefore a composite rate constant, the ratio $k_B^{OH}(H)/k_B^{OH}(D) = 2.1$ at 13.5° and decreases as the temperature increases.[2] Adamson and Basolo[10] showed that $k_B^{OH}(H)/k_B^{OH}(D)$ for the base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ is 1.7; however, in this case, not only is the rate constant composite and subject to secondary isotope effects but also the perdeuterated complex could only be studied in $D_2O$ with $OD^-$ as base, so that the observed isotope effect includes solvent effects and change of base effects. Similar objections apply to isotope effects obtained from a direct study of proton exchange. For example, the exchange of the unique secondary amine proton in $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ has an isotope effect of 3.0 at 34.3°,[11] but again the deuterated complex is studied in HCl($OH^-$ as base) while the normal complex has to be studied in DCl with $OD^-$ as base. In none of these cases is there any indication of a primary isotope effect of the magnitude that might be expected if the zero-point energy of the N–H (N–D) vibrations were lost in the transition state. An unusually low primary isotope effect is not an unusual occurrence in proton transfers between oxygen atoms, as for example in the mutarotation of glucose, although with oxygen, as with nitrogen, in normal organic systems, proton transfer to and from the solvent is fast and the separation of primary isotope effects from secondary isotope effects and solvent effects cannot be made experimentally. It is probable that a major difference between carbon acids on the one hand and nitrogen and oxygen acids on the other is that the latter pair can maintain a pseudotetrahedral geometry and have no need to delocalize the lone pair of electrons left after deprotonation in the way that seems to be necessary for carbon. Swain[12] has suggested that, in such circumstances, the proton jump is fast compared to the other nuclear motions involved in the reaction and so the antisymmetric $\overleftarrow{B}\cdots\overrightarrow{H}\cdots\overleftarrow{B}'$ vibration is no longer a translation through the reaction coordinate and has a finite frequency, a force constant, and a zero-point energy. Some years previously Bunton and Shiner[13] suggested that the low primary isotope effects that were thought to be observed in reactions involving proton transfer between electronegative atoms might be due to strong hydrogen bonding in the transition state, which took on some of the aspects of the bonding in the bifluoride ion, $[F\cdots H\cdots F]^-$, or else to a fast proton transfer between two slow steps, which seems not dissimilar to the Swain suggestion. The work that we have just described involving the base hydrolysis of *trans*-[Co(*RR*(*SS*)-2,3,2-tet)$Cl_2]^+$ complex appears to be one of the very few examples of a clear and unambiguous demonstration of the low primary isotope effect associated with the transfer of a proton from nitrogen to oxygen.

In view of the fact that proton transfer is rate determining in this system, a search was initiated for general base catalysis. For many years it was generally accepted that the absence of general base catalysis of the base hydrolysis reaction was a good indication that the proton-transfer stages rapidly established a preequilibrium.[14] Block and Gold[15] were unable to find general base catalysis (by acetate) of the proton-exchange reactions of $[Co(ND_3)_6]^{3+}$ and $[Co(ND_3)_4(C_2O_4)]^+$ and concluded that an ion pair between the complex cation and hydroxide was involved in the reaction. General base catalysis was observed in the base hydrolysis of *trans*-$[Co(cyclam)Cl_2]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane)[16] but the study was not pursued beyond the preliminary stages. The experiments with substituted pyridines clearly indicate that the base hydrolysis of both the *RS* and the *RR*(*SS*) forms of *trans*-[Co(2,3,2-tet)$Cl_2]^+$ is susceptible to general base catalysis. The purpose of this study was to establish the effect rather than to study it in depth and so the range of bases examined was too small to allow a proper examination of the catalytic constants for the various bases and their relationship with the properties of the bases such as basicity and steric hindrance. Nevertheless, if one includes $k_B^{OH}$ with the $k_B^{am}$ values, the Bronsted $\beta$ coefficient appears to be in the region of $0.67 \pm 0.07$.

The final point to be considered is the temperature dependence of the rate constants for base hydrolysis. It has been pointed out[1] that the enthalpy of activation of the base hydrolysis of complexes of the type $[Co(en)_2(A)Cl]^{n+}$ is even less sensitive to the nature of A than the rate constant and falls within the range $23 \pm 1$ kcal/mol. The variation in rate constant, when it is observed, arises mainly from differences in the entropies of activation, as for example in the comparison of *trans*-$[Co(en)_2(OH)Cl]^+$ with *trans*-$[Co(en)_2Cl_2]^+$ where the $10^4$-fold difference in rate constant arises almost entirely from a difference in $\Delta S^{\ddagger}$ of 18 cal deg$^{-1}$ mol$^{-1}$.[17] It was therefore of considerable interest to observe that the activation parameters for the base hydrolysis of *trans*-$[Co(cyclam)Cl_2]^+$, which was some 20 times more reactive than the corresponding ethylenediamine complex, did not fit this pattern at all [$\Delta H^{\ddagger}$ = 13.7 kcal/mol (22.7); $\Delta S^{\ddagger}$ = +12 cal deg$^{-1}$ mol$^{-1}$ (+35.0);[18] the corresponding values for the bis(ethylenediamine)complex are in parentheses], and it was suggested that this arose from a change in the rate-determining step of the base hydrolysis.[1] This suggestion is now confirmed and reinforced by the data for the analogous *RR*(*SS*)-2,3,2-tet complex, where $\Delta H^{\ddagger}$ = 13.6 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = +9 ± 3 cal deg$^{-1}$ mol$^{-1}$, and, although the data were only recorded over a narrow range of temperature, the *RS*-2,3,2-tet complex would appear to have similar activation parameters. The rate constant for the base hydrolysis reaction is normally a composite function, $k_B^{OH} = nk_1k_2/(k_{-1} + k_2)$,[2] where the individual constants have the significance already discussed in the text. For the *RR*-(*SS*)-2,3,2-tet complex it has been shown that $k_2 > 20k_{-1}$,[3] so that there $k_B^{OH} \simeq nk_1$ and therefore $\Delta H_B^{\ddagger} \simeq \Delta H_1^{\ddagger}$, whereas in the case of the bis(ethylenediamine) complex it was shown that $k_1 \geq 4k_2$,[2] so that $k_B^{OH}$ is approaching the limit $k_B^{OH} \simeq nk_1k_2/k_{-1}$. Under these circumstances, $\Delta H_B^{\ddagger} \simeq \Delta H_1^{\ddagger} + \Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger}$ (with a similar expression for the entropy of activation, taking account of the statistical factor $n$, which makes a contribution of $R \ln n$, cal deg$^{-1}$ mol$^{-1}$). Direct measurement of the activation parameters for proton exchange in substitutionally inert amine complexes (although direct comparisons are invalid because the reactions are carried out in $D_2O$ with $OD^-$ as base) indicate enthalpies of activation of 13.8 and 13.5 kcal/mol, respectively, for the exchange of the secondary amine proton in $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ and $[Co(NH_3)_4(sarc)]^{2+}$ [11] (sarc = *N*-methylglycinate). These exchanges are considerably faster than that observed in the unipositive dichloro complexes but the differences in rate appear to arise from the entropies of activation.

In the absence of accurate temperature dependence data for $k_1$ and for the $\Delta H°$ and $\Delta S°$ associated with deprotonation of the *trans*-$[Co(en)_2Cl_2]^+$ cation it is not possible to assign values to the activation parameters for the individual steps. However, in view of the invariance of $\Delta H_1^{\ddagger}$ within the range of secondary amines examined, it is unlikely that the 9 kcal/mol difference in the activation energies of the ethylenediamine and the *RR*(*SS*)-2,3,2-tet complexes arises from a major change in $\Delta H_1^{\ddagger}$ as a result of going from a primary to a secondary amine. It is more likely that this represents the contribution of $\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger}$ to the composite $\Delta H_B^{\ddagger}$ for the former complex, from which it follows that the dramatic change in the activation parameters is the consequence of a far less dramatic change in the relative magnitudes of $k_{-1}$ and $k_2$. We suggest that, provided the type of complex being examined is not changed too drastically, the magnitude of the observed enthalpy of activation for base hydrolysis should provide a good preliminary indication as to whether or not deprotonation is rate determining. One might also predict that, if 9 kcal/mol is the normal difference in the enthalpies of activation associated with the $k_{-1}$ and $k_2$ stages, the change from the $k_B^{OH} \simeq nk_1k_2/k_{-1}$ limiting case, which would be encountered if $k_1 > 5k_2$, to the $k_B^{OH} \simeq nk_1$ limit when $k_2 > 5k_{-1}$ would take place over a rise of temperature of approximately 60° centered on room temperature. Consequently a complex of this type with $k_{-1} \simeq k_2$ at 30° would show a very curved Arrhenius plot over the range 0–60°, the slope decreasing with increasing temperature. Such curvature has not yet been observed.

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**Registry No.** *trans*-[Co(*RS*-2,3,2-tet)$Cl_2]^+$, 46239-28-5; *trans*-[Co(*RR*(*SS*)-2,3,2-tet)$Cl_2]^+$, 46239-27-4; *trans*-{Co[(*N*,*N*,*N*',*N*'',*N*''',*N*'''-$^2H_6$)(*RS*-2,3,2-tet)]$Cl_2\}^+$, 52827-31-3; *trans*-{Co[(*N*,*N*,*N*',*N*'',*N*''',*N*'''-$^2H_6$)(*RR*(*SS*)-2,3,2-tet)]$Cl_2\}^+$, 52500-20-6.

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