but such data for perchloric acid solutions are not available. However, it is well known that both H_+ and H_- functions generally parallel the H_0 function (Rochester, pp 92–95).

(14) At $[H^+]$ = 2.0 M, the value of the quantity log ($k_{obsd} - k_0$) is subject to large errors since $k_{obsd} \sim k_0$, so this point may be ignored.

(15) D. J. Francis and G. H. Searle, *Aust. J. Chem.*, **27**, 269 (1974).

(16) A. J. Kernohan and J. F. Endicott, *J. Am. Chem. Soc.*, **91**, 6977 (1969).

(17) A. E. Martell and L. G. Sillen, Ed., *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

(18) The accepted view of all reactions of cobalt(III) complexes involving substitution on the metal ion is that they are dissociative in mechanism (either *D* or I_d); see T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).

(19) K. Kaas and A. M. Sørensen, *Acta Crystallogr., Sect. B*, **29**, 113 (1973).

(20) V. S. Sastri and G. M. Harris, *J. Am. Chem. Soc.*, **92**, 2943 (1970).

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Proton Exchange and Base Hydrolysis of β-*cis*-Dichloro(1,9-diamino-3,7-diazanonane)cobalt(III) Cations

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The kinetics of proton exchange of β-*cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]^+$ (2,3,2-tet = 1,9-diamino-3,7-diazanonane) have been studied in buffered aqueous solution. One primary and one secondary amine proton exchange rapidly ($k_1 = 2.7 \times 10^6$ and 3.6×10^6 M^{-1} s^{-1} at 20.0 °C, $\mu = 0.070$) and another primary amine proton exchanges somewhat more slowly ($k_1 = 9.5 \times 10^5$ M^{-1} s^{-1} at 20.0 °C, $\mu = 0.070$). It is presumed that these are the three protons on nitrogens that are trans to the chlorines. No exchange can be observed of the other three protons before the complex undergoes base hydrolysis. One of the labile protons must be involved in forming the reactive conjugate base, presumably the secondary amine proton since the immediate product is *trans*-$[Co(R,S\text{-}2,3,2\text{-tet})OH(Cl)]^+$. Exchange of the remaining three protons occurs after base hydrolysis, the secondary amine proton exchanging during or rapidly after the pH-independent loss of the second chlorine, while the primary amine protons exchange in the *trans*-$[Co(R,S\text{-}2,3,2\text{-tet})OH(H_2O)]^{2+}$–*trans*$[Co(R,S\text{-}2,3,2\text{-tet})(OH)_2]^+$ product at rates that do not depend strongly upon pH. The base hydrolysis of β-*cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]^+$ follows the usual second-order rate law with $k_B = 1.6 \times 10^4$ M^{-1} s^{-1} at 20.0 °C, $\mu = 0.04$; $\Delta H^\ddagger = 17.5 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = +19 \pm 3$ cal K^{-1} mol^{-1}. The β-*cis*-dichloro complex is compared with the *trans*-dichloro isomer where deprotonation is the rate-limiting step of base hydrolysis.

Introduction

The three known isomeric forms of $[Co(2,3,2\text{-tet})Cl_2]^+$ (2,3,2-tet = 1,9-diamino-3,7-diazanonane), namely, the *trans-R,S*, the *trans-R,R(S,S)*, and the β-*cis-R,R(S,S)* species, have all been shown to give the *trans-R,S*-$[Co(2,3,2\text{-tet})OH(Cl)]^+$ cation as the first product of base hydrolysis[1,2,3]. In the case of the two trans isomers it has been shown that the base hydrolysis involves the removal of the secondary amine proton in a slow, rate-determining step, followed by a rapid dissociative solvolysis of the amido conjugate base, in the course of which the deprotonated nitrogen becomes planar.[2,3] This is an unusual reversal of the normal pattern for the base hydrolysis of cobalt(III) amine complexes where proton transfer is usually fast compared to the overall rate of hydrolysis. The rate-determining deprotonation leads to general-base catalysis and the activation parameters of the reaction correspond to those expected for proton-exchange reactions.[4] It has long been known that proton exchange in octahedral cobalt(III) amine complexes is very sensitive inter alia to the nature of the trans ligand and that protons on nitrogens trans to chlorine could be some 2–3 orders of magnitude more labile than those on nitrogens trans to amine ligands[5–7] and so it was of some interest to see why the β-cis isomer, in spite of having one secondary amino group trans to a chlorine, did not undergo base hydrolysis significantly faster than the two trans isomers, where all amine groups are trans to nitrogen. This paper reports the proton-exchange rates of the amine groups of the β-*cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]^+$ cation and their relation to the base hydrolysis.

Experimental Section

β-*cis*-Dichloro[(*R*,*R*(*S*,*S*))-1,9-diamino-3,7-diazanonane]cobalt(III) Chloride. Finely powdered β-*cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})CO_3]ClO_4$, prepared by the method of Ahmed and Tobe[3] (0.6 g), was suspended in dry ethanol (15 ml) that was saturated with dry hydrogen chloride. The mixture effervesced and, when its color had changed from dark red to violet, it was cooled in ice and the violet product was filtered off and washed with ethanol and ether and dried in a stream of air (0.45 g, 78%).

Anal. Calcd for $C_7H_{20}N_4Cl_3Co$: C, 25.8; H, 6.19; N, 17.2; Cl, 32.7. Found: C, 25.8; H, 6.22; N, 17.1; Cl, 32.4.

β-*cis*-Dichloro[*N*,*N*,*N′*,*N″*,*N‴*,*N‴*-$^2H_6$]((*R*,*R*(*S*,*S*))-1,9-diamino-3,7-diazanonane)cobalt(III) chloride was prepared from the fully N-deuterated β-*cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})CO_3]ClO_4$[3] by the method described above for the normal complex. The peaks at 3255, 3180, and 3090 cm^{-1} found in the $^1H_6$ complex were absent and replaced by a new set at 2440, 2370, and 2285 cm^{-1}.

Anal. Calcd for $C_7H_{14}D_6N_4Cl_3Co$: C, 25.4; N, 16.9. Found: C, 25.3; N, 16.8.

All other reagents were AR or reagent grade and purified by recrystallization or distillation where necessary.

Proton-Exchange Kinetics. Buffer solutions were prepared by adding sufficient nitric acid (0.05 M) to a 0.1 M solution of 2,6-lutidine (pH 6.74 buffer) or 2,4,6-trimethylpyridine (pH 8.21 buffer) until the desired pH was reached. A weighed amount of β-*cis*-dichloro[*N*,*N*,*N′*,*N″*,*N‴*,*N‴*-$^2H_6$][(*R*,*R*(*S*,*S*))-1,9-diamino-3,7-diazanonane]cobalt(III) chloride was dissolved in 10^{-3} M hydrochloric acid (sufficient for a 0.03 M solution of the complex) previously brought to the reaction temperature and this was added as soon as possible to the thermostated buffer solution. After the required period of time the reaction was stopped by adding an excess of ice-cold perchloric acid and the mixture was set aside for 30 min in an ice bath. The β-*cis*-$[Co(2,3,2\text{-tet})Cl_2]ClO_4$ was filtered off, washed with ethanol and ether, and dried in a stream of air, and the ^1H NMR spectrum of the amine protons was measured in the way previously described.[2,3] The solubility of the *cis*-dichloro perchlorate in dilute perchloric acid is not low enough for this separation to be completely quantitative (only about 85% is precipitated under these conditions) but this only causes difficulties when one wishes to examine the nature and extent of isotopic exchange in the reaction product recovered in the early stages of base hydrolysis. Even there it is possible, with sufficient care, to minimize the interference to negligible amounts. In the experiments where the base hydrolysis was negligible the filtrate was discarded; otherwise a few milliliters of concentrated hydrochloric acid was added and the mixture was set aside at room temperature. Crystals of *trans*-$[Co(R,S\text{-}2,3,2\text{-tet})Cl_2]ClO_4$ separated slowly and were filtered off from time to time until sufficient sample was obtained for the subsequent examination. The *R*,*R*(*S*,*S*) trans isomer, formed by the anation and isomerization of the *cis*-$[Co(2,3,2\text{-tet})H_2O(Cl)]^{2+}$ species left behind after the separation of the *cis*-dichloro complex, separated more slowly and when this was detected in the recovered

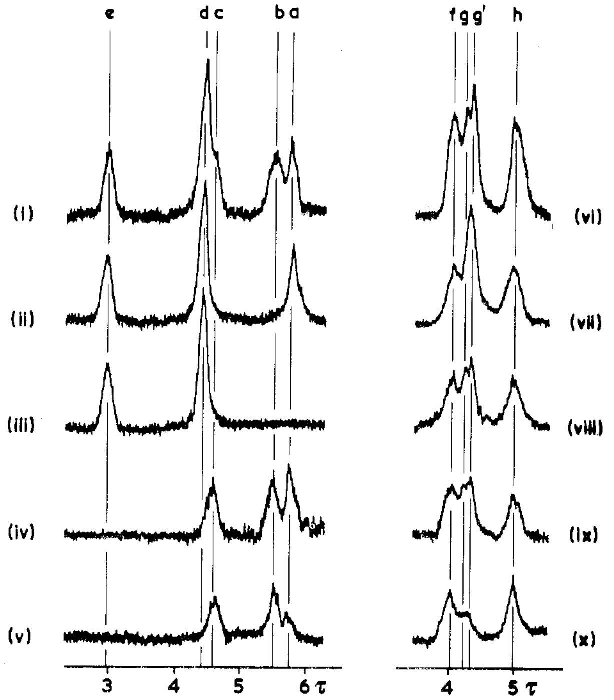

Figure 1. The 100-MHz ^1H NMR spectra of the amine protons in $[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]ClO_4$ measured in Me_2SO: (i)-(vi), *β-cis*-dichloro species [(i) $^1H_6$, (ii) $^1H_4{}^2H_2$, (iii) $^1H_3{}^2H_3$ derived from $^1H_6$, (iv) $^1H_3{}^2H_3$ derived from $^2H_6$, (v) $^1H_2{}^2H_4$]; (vi)-(x), *trans*-dichloro species derived from (i), (ii), (iii), (iv), and (v), respectively.

material, collection was stopped. The isomeric composition of the *trans*-dichloro perchlorate was determined from the spectrum of the product of aquation in acid solution;[3] the method is sensitive enough to detect more than 5% of the *R*,*R*(*S*,*S*) isomer. At the later stages of the base hydrolysis no *R*,*R*(*S*,*S*) species were present in the filtrate and a pure *trans*-(*R*,*S*)-dichloro perchlorate could be separated from a colorless mother liquor.

Conversion of *β-cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]ClO_4$ to the *R*,*R*(*S*,*S*) trans isomer was carried out by gently warming a solution in dilute hydrochloric acid. The green trans isomer that crystallized on cooling was free of the *R*,*S* isomer. An experiment with the $^2H_6$ species showed that no proton exchange occurred under these conditions.

Kinetics of Base Hydrolysis. The buffer solutions were prepared as before. A freshly prepared solution of *β-cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]Cl$ (ca. 10^{-2} M) was stored in ice and 0.10 ml was added to a 10.0-ml sample of the buffer solution previously brought to the reaction temperature in a 40-mm silica cell in the thermostated cell compartment of a Unicam SP 1800 spectrophotometer. The change in absorbance at 290 nm with time was recorded. The rate constant was determined by Guggenheim's method[8] because the subsequent aquation of the *trans*-$[Co(R,S\text{-}2,3,2\text{-tet})Cl(OH)]^+$ product interfered slightly, especially at the lower temperatures. At the end of each run the temperature was measured by inserting a thermometer into the reaction cell. The stock solution of *β-cis*-dichloro chloride was not kept for longer than 1 h.

Results and Discussion

(a) Kinetics of Proton Exchange. The ^1H NMR spectrum of a solution of *β-cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]ClO_4$ in dimethyl sulfoxide, Figure 1 (i), contains five peaks (relative areas in parentheses): τ 2.95, broad (1); τ 4.43, relatively sharp (2), overlapping with τ 4.63, broad (1); τ 5.53, broad (1); and τ 5.73, broad (1). These can be assigned to the amine protons since they are not present in the spectrum of the fully N-deuterated material. The ^1H NMR spectra of samples of the *β-cis*-dichloro perchlorate precipitated from solutions of the $^2H_6$-*β-cis*-dichloro chloride in aqueous buffer solution at pH 6.74 at 20.0 °C show only three peaks developing, those at τ 4.63 and 5.53 growing significantly faster than that at τ 5.73.

Table I. Rate Constants for the Exchange of Deuterium between *β-cis*-Dichloro[*N*,*N*,*N*′,*N*′′*N*′′′,*N*′′′-$^2H_6$][(*R*,*R*(*S*,*S*))-1,9-diamino-3,7-diazanonane]cobalt(III) Cations and H_2O at pH 6.74[a] at 20.0 °C

	Proton appearing at		
	τ 4.63	τ 5.53	τ 5.73
$k_{obsd}\,s^{-1}$	0.16	0.21	0.056
$10^{-6}k_2/M^{-1}\,s^{-1}$ [b]	2.7	3.6	0.95

[a] 0.05 M 2,6-dimethylpyridine-nitric acid buffer; [complex] = 0.03 M. [b] Using $K_w = 1.07 \times 10^{-14}\ M^2$ at 20.0 °C and $\mu = 0.08$ (calculated from data in ref 9 and 10).

Table II. Exchange of Deuterium between *β-cis*-Dichloro-[*N*,*N*,*N*′,*N*′′,*N*′′′,*N*′′′-$^2H_6$][(*R*,*R*(*S*,*S*))-1,9-diamino-3,7-diazanonane]cobalt(III) Cations and H_2O at pH 8.32[a] and the Isotopic Composition of the Recovered Reaction Product, at 20.0 °C.

		No. of deuterium atoms exchanged				
		Recovered unreacted *β-cis*-*R*,*R*(*S*,*S*)-dichloro complex: chemical shift of proton[b]			Recovered *R*,*S* trans product: type of proton	
Time/s	% reaction	τ 4.63	τ 5.53	τ 5.73	Primary	Secondary
5	20	0.96	0.97	0.95	2.10	1.10
10	31	1.06	1.05	0.95	2.11	1.16
15	55	1.10	1.07	1.07	2.30	1.20
25	82	1.20	1.04	1.00	2.30	1.20
180	>99				3.33	2.00

[a] 0.167 M 2,4,6-trimethylpyridine–nitric acid buffer; [complex] = 0.03 M. [b] No proton signal is detected where the other three protons of this complex absorb.

First-order rate constants were determined from a plot of ln $(A_\infty - A_t)$ against time (A_t is the area under the appropriate peak of the sample acidified and precipitated at time *t*, and A_∞ the area under the same peak of an authentic sample of the $^1H_6$ species at the same concentration and under the same measuring conditions). The rate constants are collected in Table I. No systematic study was made of the dependence of the rate of exchange upon pH, but at pH 4 there was no significant exchange in the few minutes available before the complex has aquated, and at pH 8.21 at 20.0 °C all three protons were fully exchanged within 5 s of mixing. It is assumed that, as with other amine complexes of this type, the rate of proton transfer is first order with respect to hydroxide ion concentration and second-order rate constants are also listed in this table. (No account was taken of the contribution from general-base catalysis by the buffer base but this is likely to be relatively small at the concentrations of buffer used.[4]) At pH 8.72 the dichloro complex undergoes base hydrolysis quite rapidly but it is possible to separate unreacted cis complex and examine its ^1H NMR spectrum. While all of the three labile hydrogens were fully exchanged in all samples, there was no signal indicating exchange of any of the other three amine hydrogens even after 80% of the starting material had been lost (Table II). In this respect the complex resembles the *trans*-$[Co(R,R(S,S)\text{-}2,3,2\text{-tet})Cl_2]^+$ cation.[3] The dichloro complex recovered after the chloride anation of the acidified reaction product of the base hydrolysis is a pure trans isomer and the ^1H NMR spectrum and its aquation behavior indicate that it has the *R*,*S* configuration. In the first sample of product, collected after 3 s of reaction (ca. 10% base hydrolysis), the areas under the peaks are in the ratio of 1:2 as in the normal $^1H_6$ sample but are only half the intensity expected. Consequently, only three of the six deuterium atoms originally present (one secondary and two primary) have been exchanged and it must be concluded that, since this exchange has already taken place in the unreacted material, the dissociatively active conjugate base (assuming that the D_{cB}

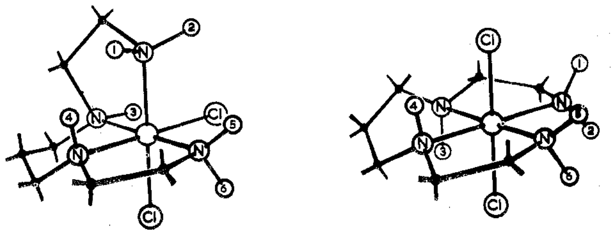

Figure 2. β-*cis*- and *trans*-[Co(*S*,*S*-2,3,2-tet)Cl_2]$^+$ showing the relationship between the amine protons if the latter is derived from the former by simple edge displacement of a terminal NH_2 group.

mechanism is sill operating) must be generated by the removal of one of these labile protons. It is not possible to use any labeling experiment to specify which this is but comparison with the trans isomers would suggest that the secondary nitrogen provides the labilizing effect.

(b) Assignment of the Amine Proton Peaks. The three peaks, labeled a, b, and c in the spectrum of the sample recovered during base hydrolysis of the $^{2}H_6$ species (Figure 1 (iv)) are assigned to the most labile protons in the complex which, as shown below, must include one attached to a secondary nitrogen and two attached to primary nitrogens. These peaks are absent from the spectrum of a sample of the normal ($^{1}H_6$) β-*cis*-dichloro complex that had been allowed to stand in D_2O solution before precipitation as its perchlorate, Figure 1(iii). Spectra (iii) and (iv) in this figure are essentially complementary and add up to give (i), that of the isotopically normal material. This indicates either that there is no coupling between individual amine protons or that such coupling that does exist, while unresolved, is not lost when three of the six protons are replaced. The β-*cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]$^+$ cation can be converted to the trans *R*,*R*(*S*,*S*) isomer under conditions where there is no proton exchange or nitrogen inversion and it is found that the two $^{1}H_3{}^{2}H_3$ cis species form trans products with identical ^{1}H NMR spectra (Figure 1(viii) and (ix)) in the amine proton region. In addition this spectrum is identical in position and shape with that of the normal $^{1}H_6$ *trans*-(*R*,*R*(*S*,*S*))-dichloro perchlorate, Figure 1(vi). However, the total areas under the peaks of equimolar solutions of the $^{1}H_6$ and the $^{1}H_3{}^{2}H_3$ species are in the ratio of 2:1 and, while the infrared spectra of the two $^{1}H_3{}^{2}H_3$ species are identical, they contain multiplets in the ν_{N-H} and ν_{N-D} regions (3305–3125 and 2480–2330 cm^{-1}, respectively) of roughly similar intensity; the latter is absent in the $^{1}H_6$ species. The trans complex, Figure 2, contains two sets of protons (1, 2, 4 and 3, 5, 6), each made up of a proton from a secondary nitrogen and the two protons from the primary nitrogen trans to it. The protons in the two sets are paired symmetrically as follows: $1 \equiv 6$; $2 \equiv 5$; $3 \equiv 4$. In the conversion of the β-cis complex to the trans isomer, the quadridentate ligand ensures that the two nitrogens that were trans to chlorine become trans to one another; consequently the protons in one of the sets in the trans complex derived in this way are on nitrogens that were originally trans to chlorine, while the other set contains protons that are on nitrogens that have been trans to each other throughout. The identity of the spectra (viii) and (ix) can be readily explained in terms of the markedly different lability of protons on nitrogens trans to chlorine and those on nitrogens trans to other nitrogens in the β-cis complex. Whether one starts from the $^{1}H_6$ complex in D_2O or the $^{2}H_6$ complex in H_2O, one set will be $^{1}H_3$ and the other will be $^{2}H_3$, and, in the trans complex, these two sets are equivalent. This is further support for the conclusion that the two sets of protons in the trans complex are independent of one another and that no coupling exists between them. In view of the strong trans-labilizing properties of coordinated chloride with respect to amine proton exchange[5–7] it is reasonable to assign the signals a, b, and c in Figure 1 to protons on nitrogens trans to chlorine. It would follow then that peak e at τ 2.95 belongs to the secondary amine proton (3) and that peak d at τ 4.43 belongs to the primary amine protons 5 and 6 (the coincidence of signals from one primary and one secondary amine proton in this relatively sharp peak seems improbable). In some respects these resemble the two amine proton peaks in the *trans*-[Co(*R*,*S*-2,3,2-tet)Cl_2]$^+$ cation [τ 3.83, broad (1); τ 4.60, sharp (2)].[2] A partial assignment of the remaining proton peaks can be made from the exchange behavior under less basic conditions. Proton a is less labile than protons b and c and so it is possible to obtain reasonably good samples of the $^{1}H_4{}^{2}H_2$ and the $^{1}H_2{}^{2}H_4$ species by careful control of pH and reaction time, starting with the $^{1}H_6$ complex in D_2O and the $^{2}H_6$ complex in H_2O, respectively. The spectra of these species, somewhat contaminated by $^{1}H_3{}^{2}H_3$ species, are shown in Figure 1(ii) and (v). The spectra of the trans *R*,*R*(*S*,*S*) isomers into which they can be converted without further proton exchange are given in Figure 1(vii) and (x). Comparison of spectra (v) and (x) for the $^{1}H_2{}^{2}H_4$ species shows quite clearly that signals a and g + g′ must come from the same proton. On the basis of spin-decoupling experiments[3] the peaks at g + g′ and h were assigned to primary amine protons in the trans complex and that at f to the secondary amine proton. It follows therefore that signal a must be assigned to one of the two protons on the primary nitrogen trans to chlorine [either 1 or 2]. The spectrum of the trans $^{1}H_4{}^{2}H_2$ species [Figure 1(vii)] is consistent with this assignment. This contains three peaks in the ratio 1:2:1 at τ 4.04, 4.29, and 4.95, respectively, and can be looked upon as the superposition of a sharp singlet at τ 4.29, arising from a single proton on the NHD group, upon the spectrum of the $^{1}H_3{}^{2}H_3$ species (protons 3, 5, and 6). This confirms that g + g′ and h can be assigned to protons on the same primary nitrogen and that the g–g′ splitting arises from a coupling, $J = 9$ Hz, between them. Peak h is not sufficiently resolved for this splitting to be seen. The assignment cannot be taken further without making assumptions about the relationship between the amine proton chemical shifts and their orientation with respect to the coordinated chlorine. It is clearly shown that two amine protons on the same nitrogen have markedly different exchange lability but it cannot be deduced with certainty which is the more labile.

(c) Relationship between Base Hydrolysis and Proton Transfer. In spite of the remaining ambiguities in the full assignment of the amine proton NMR spectrum it is clear that, in the β-*cis*-dichloro species, unlike its two trans isomers, exchange of three of the six amine protons is considerably faster than base hydrolysis. The first-order rate constants for the hydrolysis were determined at only one pH, but over a range of temperature, and are collected in Table III. Assuming that there is no general-base catalysis, the rate is first order with respect to hydroxide, and correcting for the background aquation, the second-order rate constants are also calculated and tabulated. Since the proton exchange has ceased to be rate limiting, k_{-1}, the rate constant for reprotonation of the amido conjugate base, must be very much greater than k_2, the rate constant for its dissociation, and the general expression relating the observed second-order rate constant for base hydrolysis, k_B, to the other rate constants, $k_B = nk_1k_2/(k_{-1} + k_2)$,[4] reverts to its usual form, $k_B = k_1k_2/k_{-1}$ (in view of the inversion of a secondary nitrogen configuration in the act of base hydrolysis of the cis isomer it is reasonable to assume that the labile secondary nitrogen is involved and therefore $n = 1$). The observed enthalpy of activation, 18 kcal/mol, is consistent with this observation, being some 4 kcal/mol greater than that for the trans isomer, where $k_2 \gg k_{-1}$ and $k_B = k_1$.[4] It is possible to estimate the

Table III. Second-Order Rate Constants for the Base Hydrolysis of *β-cis*-Dichloro[(*R*,*R*(*S*,*S*))-1,9-diamino-3,7-diazanonane]cobalt(III) Chloride in 2,4,6-Trimethylpyridine–Nitric Acid Buffer[a,b]

Temp/°C	pH	$10^{14}K_w/M^2$	$10^6[OH^-]/M$[c]	$10^2k_{obsd}/s^{-1}$	$10^2k_{obsd}(cor)$[d]$/s^{-1}$	$10^{-4}k_B/M^{-1}\ s^{-1}$
14.3	8.35	0.65	1.5	1.15	1.13	0.8
17.4	8.295	0.85	1.7	2.17	2.13	1.3
20.4	8.23	1.08	1.8	3.03	2.97	1.6
23.6	8.16	1.38	2.0	4.36	4.26	2.1

[a] Measured at 290 nm. [b] [Complex] = 4×10^{-4} M, [unprotonated amine] = 0.050 M, $\mu = 0.043$. [c] Calculated from data in ref 9 and 10. [d] Corrected for the background aquation using data from ref 11.

ratio k_{-1}/k_2 by inserting the experimental value for k_B and k_1 in the above expression. Taking k_1 as $3 \times 10^6\ M^{-1}\ s^{-1}$ (the average value for the two most labile protons, one of which is involved in generating the active conjugate base) and k_B as $1.7 \times 10^4\ M^{-1}\ s^{-1}$ it seems that $k_{-1}/k_2 = (3 \times 10^6)/(1.7 \times 10^4) = 180$. This ratio is probably underestimated by a factor of approximately 2 because k_1 refers to the removal of deuterium while k_B relates to the normal complex (isotope effects are between 1.5 and 1.7 for the two trans isomers[4]) and the proton exchange was studied at a somewhat higher ionic strength than the base hydrolysis. This must be compared with the value for $k_{-1}/k_2 < 0.05$ estimated for the *trans*-dichloro-*R*,*R*(*S*,*S*) isomer.[3] This dramatic, more than 8000-fold, change in the ratio on going from the β-cis to the trans isomer cannot be ascribed to a change in k_2 alone. Since the two conjugate bases dissociate to give a common five-coordinate intermediate,[3] the two transition states are likely to be fairly similar. It is less easy to estimate the relative stabilities of the conjugate bases themselves but the deprotonation is unlikely to exert a major effect upon the relative stabilities of the original amine complexes. The β-cis complex is actually more labile than the trans complex [k_{aq}(β-cis, 25.0 °C) = $1.1 \times 10^{-3}\ s^{-1}$; k_{aq}(trans-*R*,*R*(*S*,*S*), 25.0 °C) = $2.9 \times 10^{-4}\ s^{-1}$],[11] but this is not necessarily a measure of the relative stabilities since there is no common intermediate. It might therefore be concluded that a major part of the increase in the ratio k_{-1}/k_2 on going from the trans isomer to the β-cis form is due to an increase in k_{-1}. This leads to the extremely important conclusion that, for these complexes at least, proton-exchange lability is not necessarily a measure of the acidity of the amino group. A linear free energy relationship can only be ensured when the reprotonation is diffusion controlled and this is certainly not so in the case of the trans isomer. With this in mind one should reexamine the argument put forward by Sargeson[6] in support of the claim that the dissociatively active conjugate base in the base hydrolysis of *sym*-[Co(trenen)Cl]$^{2+}$ (trenen = 1,8-diamino-3-(aminoethyl)-3,6-diazaoctane) is formed by the deprotonation of the unique secondary nitrogen trans to chlorine. This claim is the crux of the reasoning that the labilizing effect of the amido group was not due to π donation to cobalt in the five-coordinate intermediate because the nitrogen in question was shown to retain its configuration during the act of base hydrolysis. It was assumed that the 10^5-fold difference in the exchange labilities of the protons on nitrogens cis and trans to the leaving chlorine was a measure of their acidity, i.e., that k_{-1} was the same for all of the amido groups and so, if the substitutionally labile conjugate base was one with the amido group cis to the leaving chlorine, it would be necessary for its k_2 to be 10^6 times greater than that of the more readily formed trans amido species. It was thought that a cis-specific labilizing effect of this magnitude was unreasonable and indeed Endicott[12] has shown that *trans*-$(NH_3)_2$([14]tetraeneN$_4$)Co^{III} cations undergo base hydrolysis with relatively large second-order rate constants even though there are no protons on nitrogens cis to the leaving group ([14]tetraeneN$_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene). However, we have now shown that the ratio k_{-1}/k_2 can change by as much as 10^4 when we go from the *trans*- to the *β-cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl$_2$]$^+$ cations even though the active amido group can be cis to the leaving group in both cases. If, as we claim, this is mainly due to the change in the reprotonation rate constant, k_{-1}, on going from an amido group trans to nitrogen to one trans to chlorine, then a much smaller change in k_2 need be invoked if the same applied to the *sym*-[Co(trenen)Cl]$^{2+}$ complex and the cis amine group were implicated as the site of deprotonation in the active conjugate base. Taking account of the statistical factor of 6, the ratio of k_2(cis)/k_2(trans) need not be outside the range 10–100. Such a ratio is not out of line with the directly observed ratio for the cis and trans isomers of [Co(en)$_2$OH(Cl)]$^+$ (k(cis)/k(trans) = 8 at 25 °C)[13] where the labilizing power of hydroxide is attributed, in part at least, to the π-donor ability that it possesses.

(d) Proton Exchange in the Reaction Products. The data in Table II show quite clearly that the deuteriums that were not exchanged in the unreacted *β-cis*-dichloro complex are slowly replaced by protons in the *R*,*S* trans reaction product. While the method adopted does not allow a precise evaluation of the rate constants for proton exchange, it does permit a semiquantitative treatment of sufficient accuracy to allow comparison with data evaluated for the trans-*R*,*S* product of the base hydrolysis of the *trans*-(*R*,*S*)- and *trans*-(*R*,*R*(*S*,*S*))-dichloro species at lower pH.[3] It is possible to estimate a value for the ratio, $\alpha = k_D/k'_B$, where k_D and k'_B are the first- (or pseudo-first-) order rate constants for proton exchange in the product and for base hydrolysis of the *β-cis*-dichloro species, respectively, using the curve-fitting procedure described in ref 3. Indeed, in the case of the primary amine protons, the ratio is small enough for k_D to be determined by a simple first-order analysis of the increasing area under the peak at τ 4.60, assigned to the primary amine protons, in the recovered product. Thus, for the secondary amine proton, $\alpha = 0.5 \pm 0.1$ at 20.0 °C and pH 8.32, and, at 20.0 °C and pH 8.23, $k'_B = 3.03 \times 10^{-2}\ s^{-1}$ (the value estimated for pH 8.32 is therefore $3.3 \times 10^{-2}\ s^{-1}$). It follows, therefore, that $k_D = 1.6 \times 10^{-2}\ s^{-1}$ at 20.0 °C and pH 8.32. A direct calculation gives k_D for the primary amine proton as $6 \times 10^{-3}\ s^{-1}$ at 20°C and pH 8.32. Similar analyses of the exchange data for the same species generated from *trans*-(*R*,*S*)- and *trans*-(*R*,*R*(*S*,*S*))-dichloro species at pH 6.19 and 6.40 give $k_D = (1.2 \pm 0.4) \times 10^{-2}\ s^{-1}$ (25 °C) for the secondary amine proton and $k_D = 1.5 \times 10^{-3}$ and $(1.0 \pm 0.2) \times 10^{-3}\ s^{-1}$ for the primary amine protons in the products of the base hydrolysis of the *trans*-(*R*,*S*)- and *trans*-(*R*,*R*(*S*,*S*))-dichloro species, respectively. In spite of the crudeness of these experiments it is clear that the rate of exchange of the secondary amine protons is independent of pH in the range 6.19–8.32 while the rate of exchange of the primary amine protons increases significantly but by nowhere near the factor of 10^2 required for a first-order dependence on [OH$^-$]. The first-order rate constant for the exchange of the secondary amine proton is of a similar magnitude to that for the aquation of *trans*-[Co(*R*,*S*-2,3,2-tet)OH(Cl)]$^+$ ($k_{aq} = 3.0 \times 10^{-2}\ s^{-1}$ at 13.5 °C) and may well indicate that exchange takes place rapidly in the hydroxoaquo (or dihydroxo) product, the aquation becoming the rate-determining, preliminary step. Alternatively, this may be evidence for an internal conjugate-base mechanism in which transfer of a proton from the secondary amine nitrogen to the coordinated hydroxide is a necessary preliminary to the act of aquation. A proper, quantitative kinetic study of the exchange is required in order to distinguish between these mechanisms and this is now under way. The exchange of the primary amine protons is far too slow to occur in the *trans*-aquochloro species and must be taking place in the hydroxoaquo or dihydroxo species. Since the pK_a of the *trans*-$[Co(R,S\text{-}2,3,2\text{-tet})OH(H_2O)]^{2+}$ cation is 7.5 at 25 °C,[1] the data span the range of pH where the dominant species changes from the hydroxoaquo to the dihydroxo form and, again, a much more detailed study of the pH dependence of the rate of exchange is required.

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Registry No. *β-cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]Cl, 60409-16-7; *β-cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)CO_3]ClO_4, 52500-16-0; *β-cis*-[Co-[*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-$^2H_6$]-(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]Cl, 60384-65-8; *β-cis*-[Co[*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-$^2H_6$]-(*R*,*R*(*S*,*S*)-2,3,2-tet)CO_3]ClO_4, 52500-19-3; *β-cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]$^+$, 60409-17-8; *β-cis*-[Co[*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-$^2H_6$]-(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]$^+$, 60384-66-9; *trans*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]$^+$, 46239-27-4.

References and Notes

(1) R. Niththyananthan, Ph.D. Thesis, London, 1970.
(2) G. Marangoni, M. Panayotou, and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1989 (1973).
(3) E. Ahmed and M. L. Tobe, *Inorg. Chem.*, **13**, 2956 (1974).
(4) E. Ahmed, M. L. Tobe, and M. L. Tucker, *Inorg. Chem.*, **14**, 1 (1975).
(5) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).
(6) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).
(7) D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, **14**, 1485 (1975).
(8) E. A. Guggenheim, *Philos. Mag.*, **2**, 538 (1926).
(9) L. Hepler and E. M. Wooley, *Water: Compr. Treatise*, **3**, 146 (1972).
(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions", Reinhold, New York, N.Y., 1958, p 752.
(11) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).
(12) D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **95**, 6987 (1973).
(13) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

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Effect of Pressure on the Isomerization Rate of the Diaquobis(ethylenediamine)cobalt(III) Ion

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In a 0.05 M perchloric acid medium, the isomerization of *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ exhibits a pressure-dependent volume of activation, with $\Delta V_0{}^{\ddagger} = 14.3 \pm 0.2$ cm^3 mol^{-1} and $\Delta\beta^{\ddagger} = 0.010 \pm 0.002$ cm^3 mol^{-1} MPa^{-1}, together with $\Delta H^{\ddagger} = 131.4 \pm 1.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = +103 \pm 5$ J K^{-1} mol^{-1}. A D mechanism with aquo ligand release to bulk solvent is proposed. In 1.0 M perchlorate media, the pressure dependence of the volume of activation is even more marked, with $\Delta V_0{}^{\ddagger} = 13.2 \pm 0.7$ cm^3 mol^{-1} and $\Delta\beta^{\ddagger} = 0.10 \pm 0.03$ cm^3 mol^{-1} MPa^{-1}, together with $\Delta H^{\ddagger} = 121.7 \pm 1.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = +64 \pm 4$ J K^{-1} mol^{-1}. Dissociative aquo ligand release with extensive desolvation from secondary hydration zones around associated ions is proposed as the mechanism in high electrolyte concentrations. Two distinct dissociated transition states for isomerization and exchange[2] are revealed by the pressure studies.

Introduction

We have selected the diaquobis(ethylenediamine)cobalt(III) cation $Co(en)_2(OH_2)_2{}^{3+}$ as an appropriate substrate for the systematic evaluation of volumes of activation for anation reactions proceeding by ion-pair interchange mechanisms. As a basis for these studies, we report in this paper the volumes of activation and other activation parameters for the isomerization of *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ to *cis*-$Co(en)_2(OH_2)_2{}^{3+}$. The succeeding paper by Tong, Krouse, and Swaddle[2] reports the volume of activation for the exchange of $H_2{}^{18}O$ with *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ and in a third paper we report[3] volumes of activation for reactions of oxalate with *cis*-$Co(en)_2(OH_2)_2{}^{3+}$.

Kruse and Taube[4] have shown that whereas the stereoretentive exchange of an aquo ligand in *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ is only 1.68 times faster, at 298 K, than the rate of the trans → cis interconversion, the rate of aquo ligand exchange in *cis*-$Co(en)_2(OH_2)_2{}^{3+}$ is 250 times faster than the rate of the cis → trans interconversion. These observations require the postulation of two distinct transition states (and probably two intermediates) for the exchange and isomerization reactions. However, on the basis of the data available, Kruse and Taube were unable to decide unambiguously on whether the presumed intermediates were generated by a dissociative mechanism or by an associative edge-displacement mechanism. We believe that the volumes of activation now reported for the exchange and isomerization reactions provide good evidence for two intermediates generated by dissociative release of an aquo ligand with extensive desolvation as one intermediate rearranges to the other intermediate.

Experimental Section

Materials. *trans*-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$ was prepared in 50% yield by the method of Kruse and Taube[4] and the product purified by recrystallization from dilute sodium perchlorate. Dissolution of this solid salt in perchloric acid yielded *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ whose extinction coefficient (19.2 M^{-1} cm^{-1} at 492 nm) was in excellent agreement with published values.[5]

Perchloric acid of the desired molarity was prepared from concentrated Analar perchloric acid by dilution with doubly distilled water and was standardized against AR mercuric oxide and potassium iodide.

Sodium perchlorate (G. F. Smith Co.) was recrystallized twice from water and dried overnight at 120 °C.

High-Pressure Procedures. Two types of high-pressure vessels were employed: one from which samples could be withdrawn periodically for individual spectrophotometric analysis (the "sampling vessel") and the other (the "optical vessel") in which the pressurized reactant was monitored continuously in the beam of a Unicam SP800 spectrophotometer equipped with scale expansion facilities. The temperatures of the sampling vessel and the optical vessel were continuously regulated to within ±0.01 and ±0.05 K, respectively. Hydraulic pressures[6] in the range 10–200 MPa were maintained to within ±0.5 MPa. The reactant in the sampling vessel was contained within a Perspex (Lucite) cylinder provided with a floating Teflon