generate an extensive interfacial region.[2a]

Since Kelex 100 has a large alkyl substituent at the 7-position, its anion is likely to have surface activity. If this is the case, the interfacial mechanism postulated previously[2a] (Scheme I) should be considered to apply to the 1:1 chelate formation reaction of the Kelex 100 anion.

According to Scheme I, the overall rate constant for the reaction of L, k_L', becomes

$$k_L' = \frac{K_a}{K_{DR}}\left(k_L + k_L^i K_M' K_L' \frac{Ad}{\bar{V}}\right) \qquad (9)$$

where k_L k_L^i are rate constants in the aqueous phase and the interfacial region, K_M' and K_L' are the distribution constants of nickel ion and anionic Kelex 100, L^-, between the interface and bulk aqueous phase, A is the total interfacial area in the extraction system, d is the thickness of the interfacial layer, and $\bar{V}$ refers to the volume of the aqueous phase.

Distribution of Kelex 100 at High-Speed Stirring and Intefacial Rate Constant. The apparent distribution ratio of Kelex 100 under conditions of high-speed stirring, D' (see eq 2), was studied as a function of pH, to clarify the interfacial mechanism referred to above. A significant decrease of D' with increasing pH was observed in the range of pH 11.7–12.4. The linear relation obtained between log D' and pH having a slope of −0.81 (correlation coefficient 0.990) yielded a $pH_{1/2}$ value of 14.1 ± 0.1, which is 1.8 pH units smaller than that obtained by conventional means.[8] This observation indicates that the interfacial region participated in a major way to the distribution of Kelex 100 under high-speed stirring conditions.

According to the previous paper,[2a] the following equation can be derived for the pH region much higher than the pK_a, where D is the distribution ratio obtained ordinarily, i.e. in the absence of stirring:

$$\log\left(\frac{D}{D'} - 1\right) = \log\left(10^{\Delta pH_{1/2}} - 1\right) = \log K_L' \frac{Ad}{\bar{V}} \qquad (10)$$

From eq 10, the $K'Ad/\bar{V}$ value for the present system was calculated to be (6.2 ± 1.6) × 10.

Although the perfect resolution of k_L into k_L and k_L^i terms is impossible, we can estimate the k_L^i value from eq 9 by assuming that the rate constant of 1:1 chelate formation of Kelex 100 anion with nickel ion in the aqueous phase is the same as that of its parent compound, 8-quinolinol, i.e., $k_L = 5.4 \times 10^5$ M^{-1} s^{-1},[2a] and the k_M' value is unity as assumed previously.[2a] The value of k_L' is obtained from Figure 2, and then k_L^i is calculated to be (8.3 ± 2.9) × 10^6 M^{-1} s^{-1}. It is interesting that the ratio of $k_L^i/k_L = 15 \pm 5$ for the present system is quite close to that obtained for alkylated dithizonates ($k_L^i/k_L = 10^{1.3}$).[2a]

It can be noted that this study not only clarifies the mechanism of extraction of nickel with Kelex 100 but also confirms the hypothesis that, in a highly hydrophobic chelating extractant system, the ligand anion can exhibit surface activity while the neutral ligand does not. Hence, the 1:1 chelate formation reaction of the anionic form of the extractant occurs mainly in an interfacial region under high-speed stirring because of its surface activity, while that with the neutral ligand occurs in the bulk aqueous phase. We further demonstrate that extraction systems with surface-active components can be quantitatively explained using our automated extraction apparatus.[6]

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On the Bailar Inversion Reaction of $\Lambda(+)$-$[Co(en)_2Cl_2]^+$

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The steric course for the base hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ has been precisely determined (25 °C, 23.5% cis (16% Λ, 7.5% Δ), 76.5% trans; 0 °C, 18.5% cis (13.5% Λ, 5.0% Δ), 81.5% trans). This result differs significantly from an earlier value (0 °C, 37% cis (21% Λ, 16% Δ)). More importantly it is shown to be independent of $[OH^-]$, again contrary to previous reports. The steric course for the base hydrolysis of Λ-$[Co(en)_2(OH)Cl]^+$, where there are similar discrepancies, is recorded also (25 °C, 94.5% cis (92.5% Λ, 2.0% Δ), 5.5% trans; 0 °C, 95% cis (93.5% Λ, 1.5% Δ), 5% trans). By careful control of the conditions, a unique base-catalyzed pathway is established, a route by which Λ-$[Co(en)_2Cl_2]^+$ hydrolyzes with the simultaneous loss of both Cl^- ions. This remarkable reaction path leads to a substantiant net inversion for the *cis*-$[Co(en)_2(OH)_2]^+$ product (0 °C, 82% cis (12% Λ, 70% Δ), 18% trans), and the steric course for this route is shown to be independent of $[OH^-]$ also. The complete rate law for the base hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ is deduced: $-d[CoCl_2^+]/dt = k_1[OH^-] + k_2[OH^-]^n$ where $n \lesssim 2$; the first term corresponds to the normal S_N1CB base hydrolysis pathway (loss of the first Cl^- ion), and the second term, to the path in which both Cl^- ions are lost together. The mechanistic implications of the present results are discussed, and the conflicting results of the several previous reports on these reactions are evaluated.

Introduction

The base hydrolysis of resolved *cis*-$[Co(en)_2AX]^+$ invariably leads to rearrangement.[1,2] *cis*- and *trans*-$[Co(en)_2A(OH)]^+$ result, and the cis product is partly racemized. Furthermore, in every case studied save one, there is net retention (Λ > Δ) for the cis product. The apparent exception, $\Lambda(+)$-*cis*-$[Co(en)_2Cl_2]^+$, has been studied by different groups[3-6] with different results. Tobe and Chan[3] claimed net retention (21% Λ, 16% Δ) for the *cis*-$[Co(en)_2(OH)Cl]^+$ product of the first base hydrolysis step and net retention (61% Λ, 36% Δ) for the hydrolysis of this ion through to $[Co(en)_2(OH)_2]^+$. Thus overall there was retention, albeit ~99% of the original activity

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was lost. However Bailar et al.[4] reported a change in stereochemistry with $[OH^-]$, retention at low concentrations and inversion at high concentrations. They suggested that this arose in the first base hydrolysis step since they found Λ-$[Co(en)_2(OH)Cl]^+$ to hydrolyze with net retention at all hydroxide ion concentrations. Subsequently Archer and Dittmar[5] presented data that indicated that the cis product of the first step was very largely (~97%) the retained configuration at low $[OH^-]$ but essentially racemic at higher concentrations, and they confirmed the retention for the second step at both low and high $[OH^-]$. In addition to the normal hydrolysis route, stepwise Cl^- loss, they claimed a path in which $[Co(en)_2(OH)_2]^+$ was produced *directly* from Λ-$[Co(en)_2Cl_2]^+$ at high $[OH^-]$ and that this gave rise to the net inversion reaction. However, Tobe and Farrago[7] have discredited some important aspects of this work, although in a later article Archer and Kwak[6] presented results that supported some of their other original claims. The facts are now unclear and, moreover, key questions remain unanswered. Since these remarkable results have rather alarming implications for the generally accepted mechanism of the base hydrolysis reaction, this paper presents new data on the base hydrolysis reactions of Λ-$[Co(en)_2Cl_2]^+$ and Λ-$[Co(en)_2(OH)Cl]^+$ and examines the validity of the earlier work.

Experimental Section

Visible spectra were recorded in matched 1-cm or 1-dm silica cells on a Cary 118C instrument at 25 °C. A Perkin-Elmer Model 241 automatic digital spectropolarimeter was used to record optical rotations (±0.001°) in 1-cm or 1-dm cells at 25 °C. Rotations were measured at the sodium (589 nm) and all mercury lines (578, 546, 478, and 365 nm); in no case did the absorbance exceed 1.5 at these wavelengths.

$(\pm)$-*cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$ was synthesized by a literature procedure,[8] recrystallized twice from $H_2O/HCl/Me_2CO$, and then resolved with use of ammonium α-bromocamphor-*trans*-π-sulfonate.[9] Λ-$[Co(en)_2Cl_2]Cl\cdot H_2O$ obtained from the less soluble diastereoisomer was recrystallized to isomeric and optical purity from $H_2O/HCl/Me_2CO$. The perchlorate salts were obtained by metathesis from cold water using $HClO_4$. The optical properties of the resolved complexes were identical with those of samples resolved with $(+)$-$[Co(en)(Ox)_2]^-$.[10] Anal. Calcd for $[Co(en)_2Cl_2]Cl\cdot H_2O$: C, 15.83; H, 5.98; N, 18.46; Cl, 35.04. Found (±): C, 15.92; H, 6.03; N, 18.57; Cl, 35.13. Found ($\Lambda(+)$): C, 16.07; H, 5.96; N, 18.45; Cl, 35.04. Calcd for $[Co(en)_2Cl_2]ClO_4$: C, 13.75; H, 4.61; N, 16.03; Cl, 30.43. Found(±): C, 13.86; H, 4.66; N, 15.84; Cl, 30.68. Found ($\Lambda(+)$): C, 13.89; H, 4.36; N, 16.02; Cl, 30.47. Molar rotations: $\Lambda(+)$, Cl^- salt (H_2O), $[M]_{589}$ +2196, $[M]_{578}$ +2604, $[M]_{546}$ +1537, $[M]_{436}$ −554, $[M]_{365}$ −1676; $\Lambda(+)$, Cl^- salt (DMF, 10^{-2} M), +2520, +2712, +836, −1015, −1904 at the same wavelengths respectively; ClO_4^- salt (H_2O) +2200, +2592, +1538, −565, −1666; ClO_4^- salt (DMF, 10^{-2} M), +2670, +2952, +1444, −277, −1071. The rotations were recorded in DMF because the results are easier to reproduce in this more solvolytically inert system. It is apparent that the data for the Cl^- and ClO_4^- salts show excellent agreement in H_2O but not in DMF. Also, they are concentration dependent for the Cl^- but not the ClO_4^- salt in DMF. This we attribute to ion association, known to be large in this solvent.[11] The visible spectra are less affected (Cl^- salt, ϵ_{537}^{max} 108.3, 10^{-2} M; ClO_4^- salt, ϵ_{540}^{max} 106.9, 10^{-4}–10^{-2} M).

$(\pm)$-*cis*-$[Co(en)_2(OH_2)Cl]\cdot H_2O$ was resolved with ammonium α-bromocamphor-*trans*-π-sulfonate.[12] Λ-$[Co(en)_2(OH_2)Cl]Br_2\cdot H_2O$ was obtained from the less soluble diastereoisomer and the Δ isomer from the filtrates of the initial resolution step with use of HBr (48%). The enantiomers were recrystallized from H_2O/HBr (twice) to constant and equal but opposite rotations. $(\pm)$-*cis*-$[Co(en)_2(OH_2)Cl]S_2O_6\cdot H_2O$ was from a batch previously characterized.[13] The racemates and optical antipodes gave satisfactory analyses, and all showed ϵ_{517}^{max} 87.5 (lit.[8,13] ϵ_{516}^{max} 87.9, 87.4). The optical purity was established by conversion to active $[Co(en)_2CO_3]^+$ with use of H^+/HCO_3^- as described elsewhere.[14] Found (for $\Lambda(+)$): $[M]_{589}$ +4575, $[M]_{578}$ +5467, $[M]_{546}$ +3768, $[M]_{436}$ −5701, $[M]_{365}$ −6271; ϵ_{510}^{max} 132.5. These numbers agree to better than ±1% with accepted values.[14]

Base Hydrolysis of $\Lambda(+)$-*cis*-$[Co(en)_2(OH)Cl]^+$. Aliquots (10–60 mL) of aqueous NaOH (0.1, 0.5, or 1.0 M) at 25 or 0 °C were added in one lot with rapid stirring to solid samples of $\Lambda(+)$-*cis*-$[Co(en)_2(OH_2)Cl]Br_2\cdot H_2O$. Hydroxide was always in large excess ([Co] = 10^{-3}–10^{-2} M); 1 equiv was instantaneously consumed in the retentive conversion of the aqua to the hydroxo complex. After $>10t_{1/2}$ of the base hydrolysis reaction (0.1 M ($[OH^-]$), 5 min; 1.0 M, 30 s (0 °C); 0.1 M, 60 s; 0.5 M, 12 s (25 °C)), excess $HClO_4$ (3 M) was added to pH ~1 followed by excess solid $NaHCO_3$ (~1.0 g). The solutions were made up to standard volume and the rotations and visible spectra recorded after 5–10 min. A similar set of experiments were performed on the racemate *cis*-$[Co(en)_2(OH_2)Cl]S_2O_6\cdot H_2O$. In some reactions the HCO_3^- quenching step was omitted.

Base Hydrolysis of Λ-$[Co(en)_2Cl_2]Cl\cdot H_2O$. The techniques were similar to those described above. Hydroxide ion concentrations in the range (5.0×10^{-3})–1.0 M were employed and were always greater than [Co]. The exact conditions are recorded in Tables II and III.

Ion-Exchange Chromatography. Aliquots (30 mL) of 1.0 M NaOH at 0 °C were added in one lot to solid samples (0.25–0.30 g) of racemic *cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$ while well magnetically stirred. After ~3 s, essentially all the complex had dissolved and the reactions were quenched immediately with $HClO_4$ (10 mL, 5 M, 0 °C). The solutions were diluted to 250 mL with ice/H_2O and promptly sorbed on an ice-jacketed column of Dowex 50W-X2 (H^+ form, 200–400 mesh) cation-exchange resin. Elution with 1.0 M NaCl/0.1 M HCl removed violet (cis) $[Co(en)_2Cl_2]^+$ followed by olive-green (largely trans) $[Co(en)_2(OH_2)Cl]^{2+}$ and then red (largely cis) $[Co(en)_2(OH_2)_2]^{3+}$. The last two bands were separately eluted from the column with 3.0 M NaCl/0.1 M HCl. No attempt was made to separate each band into its cis and trans components. The 2+ and 3+ eluates were each treated with excess solid $NaHCO_3$ (to pH ~7), and their volumes (~500 mL) and visible spectra were recorded without delay. The total cobalt concentration in each band was also determined spectrophotometrically by converting a sample of each band to $[Co(en)_2CO_3]^+$ (ϵ_{510}^{max} 133.5) by heating (30–60 min) sealed solutions on a steam bath. Excess $NaHCO_3$ (20 g) was added to the *cis*-$[Co(en)_2Cl_2]^+$ solution to effect this reaction. In separate experiments on authentic samples of *cis*-$[Co(en)_2Cl_2]^+$, *cis*- and *trans*-$[Co(en)_2(OH_2)Cl]^{2+}$, and *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$ it was shown that each gave $[Co(en)_2CO_3]^+$ quantitatively under the conditions. Elsewhere it is reported[14] that *trans*-$[Co(en)_2(OCO_2)Cl]$ and *trans*-$[Co(en)_2(OCO_2)_2]^-$ isomerize only slowly to $[Co(en)_2CO_3]^+$; the reactions proceed rapidly on heating.

A similar set of experiments was performed on Λ-$[Co(en)_2Cl_2]Cl\cdot H_2O$ in 0.333 and 1.0 M OH^- at 0 °C with use of marginally shorter reaction times (~2–3 s); it dissolved more quickly than the racemate. The optical rotations and visible spectra of the eluates were recorded in 1-dm cells.

Results and Discussion

Base Hydrolysis of Λ-$[Co(en)_2(OH)Cl]^+$. The results of the analysis of the visible spectra and optical rotations of the products of the reaction

$$\Lambda\text{-}[Co(en)_2(OH)Cl]^+ \xrightarrow{OH^-} \Lambda\text{-}cis\text{-} + \Delta\text{-}cis\text{-} + trans\text{-}[Co(en)_2(OH)_2]^+ + Cl^-$$

are recorded in Table I. The stereochemistries calculated from the spectra of the aqua and carbonato species agree well (94.5 ± 1.0% cis, 25 °C). The *cis*-hydroxochloro ion loses only 9.5 ± 0.5% of its activity in base hydrolysis, most (5.5%) as the *trans*-dihydroxo complex and the remainder (4.0%) as the racemic cis species. The cis product is thus 96.5% active, i.e., 98% has the retained (Λ) configuration. This result is at sharp

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Table I. Stereochemistry of Base Hydrolysis of Λ-$[Co(en)_2(OH)Cl]^+$ [a]

reactants			products					
T, °C	$[OH^-]$, M [b]	[Co], mM	ϵ_{510}, M^{-1} cm^{-1} [c]	% cis	% activity [d]	% Λ(+) [e]	% Δ(−) [e]	% trans
25	0.1	11.7	129.7	94.5	90.5	92.5	2.0	5.5
	0.1	13.9	129.7	94.5	90.7	92.5	2.0	5.5
25	0.5	9.38	129.3	94.0	90.7	92.4	1.7	6.0
	0.5	13.4	130.2	95.2	90.7	93.0	2.3	4.8
25	0.1	1.56 [g]	75.8 [f]	94.0				6.0
	0.1	2.22 [g]	75.7 [f]	94.0				6.0
25	0.1	1.94 [g]	128.0	92.0				8.0
	0.1	2.06 [g]	128.4	92.5				7.5
0	0.1	9.47	129.5	94.2	92.1	93.2	1.1	5.8
	0.1	9.05	130.2	95.2	92.0	93.6	1.6	4.8
0	1.0	9.33	130.7	95.9	92.8	94.4	1.6	4.1
0	1.0	9.49	130.4	95.5	92.7	94.1	1.4	4.5

[a] Starting material Λ-$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$. [b] Actual $[OH^-]$ is equal to the listed value less [Co], since 1 equiv is consumed in the conversion of the aqua to the hydroxo complex. [c] The reaction was quenched with H^+/HCO_3^-; the percent of cis product was calculated by using $\epsilon_{510} = 133.5$ for $[Co(en)_2CO_3]^+$ and $\epsilon_{510} = 65.1$ for *trans*-$[Co(en)_2(OCO_2)_2]^-$. [d] Measured as active $[Co(en)_2CO_3]^+$; average of the activities calculated from data collected at five wavelengths (see Experimental Section). [e] % Λ(+) = (% cis + % activity)/2; % Λ(−) = % cis − % Λ(+). [f] ϵ_{492}; reaction quenched with H^+. The percent of cis product was calculated by using $\epsilon_{492} = 79.3$ for *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ and $\epsilon_{492} = 17.8$ for *trans*-$[Co(en)_2(OH_2)_2]^{3+}$. [g] Reactant was the racemate, *cis*-$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$.

variance with that of Chan and Tobe,[3] who recorded 97 ± 2% cis product but a marked loss of activity (75%; cf. our 9.5%) in base hydrolysis (3% as trans, 72% as racemic cis; i.e., 61% Λ, 36% Δ, 3% trans). Archer and Dittmar[5] reported a 98 ± 4% cis (94–104% Λ) and 4–8% trans product distribution, which agrees more closely. Later Archer and Kwak[6] recorded >98% activity for the cis product, again close to the present result. Since the steric course is close to full retention, significant differences due to temperature would not be expected and indeed are not apparent (0 °C, 95.0 ± 0.5% cis, 92.5 ± 0.5% activity; Table I).

It is clear that the stereochemistry is independent of $[OH^-]$, at least in the range 0.1–1.0 M. The rate data[3] follow the rate law $k_0 = k_s + k_{OH}[OH^-]$, and under the present conditions, above 0.1 M OH^-, >99% of the reaction proceeds via the base-catalyzed (k_{OH}) pathway. We have reported[14] the steric course of the spontaneous aquation (k_s) of Λ(+)-$[Co(en)_2(OH)Cl]^+$, i.e., 84.5 ± 1.5% Λ-cis, 0% Δ-cis, and 15.5 ± 1.5% trans, a revision of an earlier result (~100% cis), and it is interesting to note that base hydrolysis gives *less* steric change than the spontaneous aquation reaction. This cobalt complex is unique in this respect, and it is noteworthy on two further counts. First, the cis product of base hydrolysis is essentially fully active, and second, both *cis*- and *trans*-$[Co(en)_2(OH)Cl]^+$ give a common product distribution (94% cis). It is unusual for cis and trans reactants to give different cis/trans product distributions in base hydrolysis and for the cis substrate to give more cis product. Furthermore, it is usually significantly racemized.[1,2]

Traditionally more than one reduced coordination number intermediate is invoked for the cis and trans reactions to accommodate the stereochemical results,[1,15] although one for each suffices.[2] The present results for $[Co(en)_2(OH)Cl]^+$ suggest a single intermediate, and the retained activity is consistent with the short-lived nature of such a species. It is worth remarking that there are now several examples of common product distributions arising in the base hydrolysis of isomeric substrates (e.g., $[Co(2,3,2\text{-tet})Cl_2]^+$ [16] and $[Co(en)_2(NCS)Br]^+$ [17,18]).

Base Hydrolysis of Λ-$[Co(en)_2Cl_2]^+$. 1. Steric Course for the First Hydrolysis Step. The published[3] rate data indicate that the first step is considerably faster than the second (~ 40-fold, 0 °C), and by using a stoichiometric amount of OH^-, it should be possible to determine the $[Co(en)_2(OH_2)Cl]^{2+}$ hydrolysis products. However, a parallel reaction path exists at high $[OH^-]$ (discussed ahead) which necessitates the use of low [Co] and $[OH^-]$ (<0.01 M). But under these conditions, subsequent hydrolysis of $[Co(en)_2(OH)Cl]^+$ via the $[OH^-]$-independent pathway (spontaneous aquation) becomes significant in the time required to completely hydrolyze Λ-$[Co(en)_2Cl_2]^+$. Therefore we used between 2 and 3 equiv of OH^- at levels of ~5 × 10^{-3} M to effect a fast and complete first step without interference from a secondary reaction. The H^+/HCO_3^--quenched product solutions were analyzed spectrophotometrically and polarimetrically, and the results are presented in Table II. Since both Λ-$[Co(en)_2(OH_2)Cl]^{2+}$ and Λ-$[Co(en)_2(OH_2)_2]^{3+}$ are rapidly and quantitatively converted to Λ-$[Co(en)_2CO_3]^+$ by HCO_3^- quenching,[14] and since Λ-$[Co(en)_2(OH)Cl]^+$ does not rearrange appreciably on further hydrolysis (6% trans, 9.5% racemization), the small amount (~10%) of secondary hydrolysis that occurs prior to quenching has no measurable effect on the result. The much less reactive (and major) product, *trans*-$[Co(en)_2(OH)Cl]^+$, undergoes no significant change on the time scale involved.[3,5,7]

For fast stepwise hydrolysis reactions of $[Co(en)_2X_2]^+$ the steric course for the first step can usually be evaluated by observations on the products after the loss of both X^- groups.[14,19] However, the method fails for the base hydrolysis of Λ-$[Co(en)_2Cl_2]^+$. A final ~95% cis, 5% trans $[Co(en)_2(OH)_2]^+$ distribution is obtained irrespective of the steric course of the first step since *cis*- and *trans*-$[Co(en)_2(OH)Cl]^+$ hydrolyze to a common product mixture. However, the trans isomer gives a racemic product and the cis gives an active product. The activity for the first step can therefore be obtained in this way. Two experiments in which all the cis species had hydrolyzed through to $[Co(en)_2(OH)_2]^+$ yielded 8.3% retention at 25 °C (Table II). This corrects to 8.3/0.905 = 9.2 (±0.4)% retention for the first step, which agrees with the directly measured result (8.5 ± 0.35%). (The same calculation for the 0 °C data shows a similar agreement, 8.2/0.925 = 8.9%; cf. 8.7% directly observed.)

For experiments on the racemate, both the H^+/HCO_3^--quenched products ($[Co(en)_2CO_3]^+$ and *trans*-$[Co(en)_2Cl(OCO_2)]$) and acid-quenched products (*cis*- and *trans*-$[Co(en)_2(OH_2)Cl]^{2+}$) were determined. The results agree very well (Table II), which indicate we are observing just the

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Table II. Stereochemistry for the First Step of the Base Hydrolysis Reaction of Λ-$[Co(en)_2Cl_2]^{+}$ [a]

T, °C	[Co], mM	$[OH^-]$, mM	$[OH^-]$/[Co]	reacn time, s	ϵ_{510},[b] $M^{-1}\ s^{-1}$	% cis	% activity[c]	% $\Lambda(+)$[d]	% $\Delta(-)$[d]	% trans
25	1.86	5.0	2.69	15	47.4	23.5	8.5	16.0	7.5	76.5
	1.61	3.0	1.86	15	46.3	22.5	8.5	15.5	7.0	77.5
25	2.54[e]	5.0	1.97	15	47.5	23.5				76.5
	1.97[e]	5.0	2.54	15	47.3	23.5				76.5
25	1.79[e]	5.0	2.79	15	24.1[f]	19.0				81.0
	1.95[e]	5.0	2.56	15	24.4[f]	19.0				81.0
25	1.61	5.0	3.11	120[g]			8.0[h]			
	1.71	5.0	2.92	120[g]			8.8[h]			
	1.68	5.0	2.98	180[g]			8.2[h]			
	1.78	5.0	2.81	180[g]			8.1[h]			
0	1.53	5.0	3.27	480	42.4	18.9	8.6	13.7	5.2	81.1
	2.06	5.0	2.43	480	41.8	18.3	8.8	13.5	4.8	81.7

[a] Complex supplied as $\Lambda(+)$-$[Co(en)_2Cl_2]Cl\cdot H_2O$. [b] Reaction quenched with H^+/HCO_3^-. The percent of cis product was calculated by using $\epsilon_{510} = 133.5$ for $[Co(en)_2CO_3]^+$ and $\epsilon_{510} = 21.2$ for *trans*-$[Co(en)_2Cl(OCO_2)]$. [c] Measured as active $[Co(en)_2CO_3]^+$; average (±0.3%) of the activities calculated from rotations at five wavelengths (see Experimental Section. [d] % $\Lambda(+)$ = (% cis + % activity)/2; % $\Delta(-)$ = % cis − % $\Lambda(+)$. [e] Reactant was the racemate, *cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$. [f] Reaction quenched with H^+. The percent of cis product was calculated using $\epsilon_{510} = 87.0$ for *cis*-$[Co(en)_2(OH_2)Cl]^{2+}$ and $\epsilon_{510} = 9.5$ for *trans*-$[Co(en)_2(OH_2)Cl]^{2+}$. The product mixture contains some $[Co(en)_2(OH_2)_2]^{3+}$ (see text). [g] Sufficient time for all the *cis*-$[Co(en)_2(OH)Cl]^+$ to have hydrolyzed to $[Co(en)_2(OH)_2]^+$. [h] The mean is 8.3 ± 0.4, and it corrects to 8.3/0.905 = 9.2 ± 0.4% activity for the $[Co(en)_2(OH)Cl]^+$ product at 25 °C (cf. 8.5 ± 0.3%, first two table entries).

products of the first hydrolysis step. They are also independent of $[OH^-]$ and $[OH^-]/[Co]$ at these low concentrations (2-fold variation).

Our results may be compared with those of Chan and Tobe,[3] who recorded a much higher percent of cis product (37%; cf. 18.5%) and lower activity (5%; cf. 8.7%) at 0 °C. Their result (21% Λ, 16% Δ, 63% trans) compared to ours (13.5% Λ, 5.0% Δ, 81.5% trans) suggests that they used an $[OH^-]$ where the inversion pathway, discussed ahead, contributes to the reaction. This path gives rise to more cis product and lower activity. Archer and Dittmar[5] recorded 23% cis product for low $[OH^-]$ at 0 °C, closer to our result, but claimed that it was 94% active (cf. our 46%). But more alarming are their data[5] that indicate that the Λ-/Δ-$[Co(en)_2(OH)Cl]^+$ product ratio is dependent on $[OH^-]$: 97/3 at 0.03 M, ~83/17 at 0.1 M, and close to 50/50 (racemic) at 0.3 M OH^-. Also, the *cis*-/*trans*-$[Co(en)_2(OH)Cl]^+$ ratio was reported to be $[OH^-]$ dependent. This remarkable result is in conflict with the widely accepted S_N1cB mechanism for base hydrolysis,[1,2] which predicts an $[OH^-]$ *in*dependent steric course, and it must be challenged. First, we obtain quite different results. Our low $[OH^-]$ steric course (Table II) is the same as that measured for 0.33 and 1 M OH^- (refer to the next section). Second, the method of analysis described by Archer and Dittmar[5] is of dubious accuracy. They used computer-assisted multicomponent spectral analysis for up to five light-absorbing species and three optically rotating species (but more usually four and two, respectively). Our analysis is based on just two absorbing components, only one of which is active (Λ-$[Co(en)_2CO_3]^+$). Moreover, this ion exhibits rotations ~5 times larger than either the Λ-$[Co(en)_2(OH)Cl]^+$ or Λ-$[Co(en)_2(OH)_2]^+$ ions and obviously such measurements are expected to be more sensitive by a similar margin. While the fallibility of the earlier application of the multicomponent spectral analysis method has been exposed by this and earlier work,[7] it is potentially a useful method, and comments on its intrinsic reliability would seem to be required. The evidence given[5] in support of its accuracy consisted of comparisons between known complex concentrations (synthetically constructed) and those obtained by computer analysis of a single spectrum of the mixture. The agreement for several three- and even some four-component mixtures was excellent. This certainly testifies to the potential of the method, but it is important to note that a similar agreement could be expected for synthetically constructed mixtures of *any* samples, provided they were homogeneous and these reference samples had different visible spectra; i.e., the agreement is independent of sample purity. It would appear that the spurious results lie with this critical item rather than with the suggested[7] overrefinement of the data.

Table III. Hydroxide Ion Concentration Dependence of the Overall Steric Course for the Base Hydrolysis[a] of Λ-$[Co(en)_2Cl_2]^+$

[Co], mM	$[OH^-]$, M	% net activity[b] (±0.3%)	[Co], mM	$[OH^-]$, M	% net activity[b] (±0.3%)
		25 °C			
37.8	1.0	−14.4	51.4	0.1[c]	+4.5
47.3	1.0	−15.2	42.1	0.1[c]	+4.8
28.7	0.75	−12.7	6.12	0.05	+5.0
47.7	0.75	−12.2	2.65	0.05	+4.3
61.7	0.5	−8.6	3.58	0.01	+6.7
53.8	0.5	−6.7[d]	6.57	0.01	+8.0
35.8	0.25	−1.7	1.61	0.005	+7.9
26.9	0.25	−1.2	1.71	0.005	+8.8
			1.68	0.005	+8.2
3.11	0.10	$+0.7_1$	1.78	0.005	+8.1
3.80	0.10	$+0.5_6$			
		0 °C			
14.1	1.0	−20.0	1.53	0.005	+8.6
13.2	1.0	−20.1	2.06	0.005	+8.8
1.64	1.0	−20.9			
13.8	1.0	−17.2[d]			

[a] The reaction time was sufficient to convert all *cis*-$[Co(en)_2Cl_2]^+$ and *cis*-$[Co(en)_2(OH)Cl]^+$ to $[Co(en)_2(OH)_2]^+$ ($>10t_{1/2}$ for slower second step). [b] The recorded percent activity refers to the activity of $[Co(en)_2CO_3]^+$ obtained by H^+/HCO_3^- quenching of the $[Co(en)_2(OH)_2]^+$ product; a plus sign denotes $\Lambda(+)$ as the dominant enantiomer, while a minus sign indicates $\Delta(-) > \Lambda(+)$. [c] $[OH^-] >> [Co]$ in all experiments except those where the relative amounts are almost stoichiometric. [d] Slow addition of aqueous OH^- to Λ-$[Co(en)_2Cl_2]Cl\cdot H_2O$; fast addition in all other cases.

Finally, we note that the activity results for 0 and 25 °C are essentially identical. This is coincidental since there is less cis product at 0 °C (18.5%; cf. 23%) but compensated by a greater retention in activity (46%; cf. 37%) at the lower temperature.

2. Steric Course for the Overall Reaction. Given that the hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ proceeds by the normal route of stepwise Cl^- loss

$$\Lambda\text{-}[Co(en)_2Cl_2]^+ \xrightarrow{OH^-} [Co(en)_2(OH)Cl]^+ \xrightarrow{OH^-} [Co(en)_2(OH)_2]^+$$

then on the basis of the results of the previous sections we predict the stereochemistry of the final $[Co(en)_2(OH)_2]^+$

products to be 95% cis and 5% trans, with $8.5 \times 0.905 = 7.7\%$ retention of activity (25 °C). But the results (Table III) are in accord with prediction only at the low end of the $[OH^-]$ range studied; there is a marked departure at higher $[OH^-]$. In these experiments, all the Λ-$[Co(en)_2Cl_2]^+$ has hydrolyzed to $[Co(en)_2(OH)_2]^+$; some *trans*-$[Co(en)_2(OH)Cl]^+$ remains unhydrolyzed, but this cannot affect the final optical rotations (see the Experimental Section). Clearly the overall result is $[OH^-]$ dependent, but equally remarkable is the fact that above ~0.1 M $[OH^-]$, there is a net inversion (Table III). Bailer et al.,[4] in a similar set of experiments,[20] recorded rotations for active $[Co(en)_2CO_3]^+$ that was fractionally crystallized from the product reaction mixture, but these are not necessarily those appropriate to the bulk solution. Furthermore, they used CO_3^{2-} rather than HCO_3^- to convert the cis product to $[Co(en)_2CO_3]^+$, and this reaction does not proceed with optical retention. Nonetheless there is a qualitative agreement with our results: their data[4] suggested a net inversion above ~0.2 M $[OH^-]$.[20]

There was a special practical problem with these experiments and those described ahead, and it necessitated attention. The rate of base hydrolysis of *cis*-$[Co(en)_2Cl_2]^+$ is especially fast ($t_{1/2} \approx 1$ μs, 1 M OH^-, 25 °C[3]). Therefore it was anticipated that mixing the complex and aqueous OH^- in a time short compared to the reaction time would be difficult since *cis*-$[Co(en)_2Cl_2]^+$ consumes OH^- and reduces the effective local $[OH^-]$. Archer et al.[5,6] mixed aqueous solutions of complex and OH^-, and it is uncertain whether mixing is sufficiently fast. We (and others[4]) have rapidly dissolved the solid complex directly in aqueous OH^- to minimize the problem. Inversion is observed at high $[OH^-]$ under both sets of conditions, which at least removes the possibility that the inversion arises from a heterogeneous reaction between aqueous OH^- and the surface of the solid complex. However, to be certain of the accuracy of the results, it needed to be established that the observed activity was independent of mixing time and [Co] under conditions where $[OH^-] >> [Co]$. The entries for 1 M OH^- at 0 °C in Table III indicate a constant result (−20.3 ± 0.4% activity) over a 10-fold variation in [Co], under conditions of rapid mixing, while slow mixing as expected gave a lower numerical result (−17.2%). The difference between results for 0.1 M OH^- where $[Co] \simeq 0.05$ or 0.003 M (Table III) are not associated with inadequate mixing, but rather there is less inversion at higher [Co] because the *effective* $[OH^-]$ is lower. The $[OH^-]$ commences at 0.1 M but drops to about 0.05 M before all the Λ-$[Co(en)_2Cl_2]^+$ is consumed. Therefore, closer agreement with the results for 0.05 M $[OH^-]$ (where $[OH^-] >> [Co]$) is expected, and indeed it is observed.

Since the steric course for Λ-$[Co(en)_2(OH)Cl]^+$ is net retention ($\Lambda > \Delta$) and it is independent of $[OH^-]$, it follows from the results (Table III) that either (i) the steric course for the first hydrolysis step of Λ-$[Co(en)_2Cl_2]^+$ is $[OH^-]$ dependent, and at higher $[OH^-]$ the reaction occurs with net inversion, or (ii) another path exists in which Λ-$[Co(en)_2Cl_2]^+$ loses both Cl^- ions simultaneously with net inversion. The first explanation was advanced by Bailar et al.[4] and the second by Archer and Dittmar,[5] but only the experiments of Archer et al.[5,6] allowed a decision, at least in principle, since they examined the stereochemistry of the individual chlorohydroxo and dihydroxo products. From observations on partly reacted Λ-$[Co(en)_2Cl_2]^+$ in OH^-, they claimed[5] $\Lambda > \Delta$ for *cis*-$[Co(en)_2(OH)Cl]^+$ but $\Delta > \Lambda$ for the *cis*-$[Co(en)_2(OH)_2]^+$ product formed in the same experiment under all conditions studied, 0.03–0.3 M $[OH^-]$. Therefore, the dihydroxo complex appeared to be formed directly from the dichloro complex, at least in part, and it increased with $[OH^-]$ relative to the amount formed by the normal route of stepwise Cl^- loss. However, the amounts of Λ-*cis*- and Δ-*cis*-dihydroxo complex were not large or did not differ greatly (0.03 M $[OH^-]$, 3% Δ and 1% Λ; 0.3 M $[OH^-]$, 20% Δ and 16% Λ). Moreover, the results were computed by multicomponent spectral analysis of dubious accuracy and are therefore unconvincing. Subsequently Archer and Kwak[6] analyzed the $[Co(en)_2(OH)Cl]^+$ and $[Co(en)_2(OH)_2]^+$ products separately after an (incomplete) separation by ion-exchange chromatography and confirmed these assertions. Since the proposition of the simultaneous loss of both Cl^- ions (hereon dubbed "double Cl^-") from Λ-$[Co(en)_2Cl_2]^+$ is unlikely on statistical ground alone, has never been observed in other systems, and has profound mechanistic implications, it was important to verify this result. Furthermore, while it is clear from the earlier[4,6] and present results that an overall inversion does occur at high $[OH^-]$, the relative contribution of the two paths (stepwise Cl^- and double Cl^-) to active $[Co(en)_2(OH)_2]^+$ is not established nor is the steric course and its $[OH^-]$ dependence for each path. Another important question is the $[OH^-]$ dependence of the rate of the double Cl^- loss pathway. The following experiments were designed to answer these questions.

Our strategy was to base hydrolyze Λ-$[Co(en)_2Cl_2]^+$ under conditions that minimize the contribution to *cis*-$[Co(en)_2(OH)_2]^+$ from the second step of the normal hydrolysis route (i.e., hydrolysis of $[Co(en)_2(OH)Cl]^+$) but that maximize the contribution from the double Cl^- loss route. The latter is best achieved by working at high $[OH^-]$ but using a reaction time sufficiently short to stop the stepwise Cl^- loss path (i.e., at the $[Co(en)_2(OH)Cl]^+$ stage) to meet the first condition. Fortunately the first step ($k_{OH} = 15\ M^{-1}\ s^{-1}$) is much faster than the second ($k_{OH} = 0.37\ M^{-1}\ s^{-1}$, 0 °C) at all $[OH^-]$,[3] and it is possible, in principle, to have all Λ-$[Co(en)_2Cl_2]^+$ reacted but a negligible amount of the $[Co(en)_2(OH)Cl]^+$. The practical limitation is the rate of dissolution of Λ-$[Co(en)_2Cl_2]Cl \cdot H_2O$, which at high $[OH^-]$ is comparable to its rate of base hydrolysis. Nonetheless several experiments were conducted at 1 M $[OH^-]$ and 0 °C with essentially the desired result, with use of reaction times of 2–3 s. The analyses of the products, which were clenaly separated by ion-exchange chromatography, are recorded in Table IV. Results for the racemate under slightly different conditions are included. It is noted that some (~10%) *cis*-$[Co(en)_2Cl_2]^+$ survives the base hydrolysis reaction whereas the known[3] rate data would suggest complete reaction ($t_{1/2} \approx 0.05$ s). However, this is expected if the time of dissolution is comparable to the total reaction time employed, and a little may not have dissolved at all. This possibility in no way impinges on the analysis below. The results (Table IV) show clearly that the hydroxochloro product retains the configuration of the $[Co(en)_2Cl_2]^+$ complex (Λ) whereas the *cis*-dihydroxo product is inverted (Δ). Since Λ-$[Co(en)_2(OH)Cl]^+$ reacts with OH^- to give $[Co(en)_2(OH)_2]^+$ with $\Lambda >> \Delta$ (Table I), we can confirm the assertion of Archer et al.[5,6] that at least some (if not all) of the *cis*-$[Co(en)_2(OH)_2]^+$ product arises directly from the Λ-$[Co(en)_2Cl_2]^+$ complex. The magnitude of our rotations (>0.1°, ±0.001°) makes this conclusion certain. It is also clear from the amounts of $[Co(en)_2(OH)_2]^+$ complex formed (band 3, Table IV). *trans*-$[Co(en)_2(OH)Cl]^+$, the major component (~80%) of band 2, is quite stable[3,7] to further hydrolysis in the 2–3-s reaction time, yet band 3 constitutes approximately 50% of the total cobalt.

The data were treated as follows to obtain the steric course for each reaction pathway. The observed activity for the $[Co(en)_2(OH_2)Cl]^{2+}$ product (band 2) was 4.4% in the first experiment (entry 3, Table IV) and 6.2% in the second (entry

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[20] In the experiments of Bailar et al.,[4] high concentrations (0.05–1.0 M) of both complex and OH^- were used, such that $[Co] \simeq [OH^-]$, whereas for most of our experiments $[OH^-] >> [Co]$.

Table IV. Stereochemical Analysis of the Products of the Incomplete[a] Base Hydrolysis Reaction of [Co(en)$_2$Cl$_2$]$^+$ at 0 °C

		obsd[b]						cor[h]						
band	complex[j]	amt of Co, mmol[c]	% of Co total	ϵ_{510},[d] M^{-1} s^{-1}	% cis[e]	% activity[f]	% cis activity[g]	amt of Co, mmol	% of Co total	% cis	% Δ(−)	% Λ(+)	% activity	% cis activity
	1. 1.00 M OH$^-$													
1	(±)Cl$_2$$^+$	0.108	11.1		100									
2	(OH$_2$)Cl^{2+}	0.422	43.3	47.8	23.7									
3	(OH$_2$)$_2$$^{3+}$	0.444	45.6	120.0	80.0									
	ΣCo(obsd)	0.974												
	ΣCo(calcd)[i]	0.976												
	% Co recovery	100.2												
	2. 1.00 M OH$^-$													
1	(±)Cl$_2$$^+$	0.080	8.1		100									
2	(OH$_2$)Cl^{2+}	0.498	50.5	50.4	26.0									
3	(OH$_2$)$_2$$^{3+}$	0.408	41.4	124.0	86.1									
	ΣCo(obsd)	0.986												
	ΣCo(calcd)[i]	0.976												
	% Co recovery	101.0												
	3. 1.00 M OH$^-$													
1	Λ-Cl$_2$$^+$	0.030	3.4		100	100	100	0.030	3.4					
2	(OH)$_2$Cl^{2+}	0.445$_5$	50.4	36.9	14.0	+4.4	+31.4	0.495$_5$	56.0	22.7			(8.7)[h]	+38.3
3	(OH$_2$)$_2$$^{3+}$	0.409	46.2	121.7	82.5	−45.2	−55.0	0.359	40.6	80.8	69.2	11.6	−57.6	−71.3
	ΣCo(obsd)	0.884$_5$						0.884$_5$						
	ΣCo(calcd)[i]	0.875												
	% Co recovery	101.0												
	4. 1.00 M OH$^-$													
1	Λ-Cl$_2$$^+$	0.057	4.8		100	100	100	0.057	4.8					
2	(OH$_2$)Cl^{2+}	0.635$_5$	53.5	39.0	16.0	+6.2	+38.8	0.677	57.0	21.1			(8.7)[h]	+41.2
3	(OH$_2$)$_2$$^{3+}$	0.495	41.7	123.0	84.5	−49.3	−58.0	0.454	38.2	83.5	70.8	12.7	−58.1	−69.6
	ΣCo(obsd)	1.188						1.188						
	ΣCo(calcd)[i]	1.170												
	% Co recovery	101.8												
	5. 0.333 M OH$^-$													
1	Λ-Cl$_2$$^+$	0.172$_5$	17.3		100	100	100	0.172$_5$	17.3					
2	(OH$_2$)Cl^{2+}	0.537	53.9	38.6	15.5	+5.4	+34.8	0.583	58.5	22.2			(8.7)[h]	+39.2
3	(OH$_2$)$_2$$^{3+}$	0.286$_5$	28.8	124.0	86.1	−37.8	−43.9	0.240$_5$	24.2	84.4	68.9	15.5	−53.4	−63.3
	ΣCo(obsd)	0.996						0.996						
	ΣCo(calcd)[i]	0.986												
	% Co recovery	101.0												
	6. 0.333 M OH$^-$													
1	Λ-Cl$_2$$^+$	0.343	31.3		100	100	100	0.343	31.3					
2	(OH$_2$)Cl^{2+}	0.506	46.2	39.0	16.0	+6.1	+38.1	0.540	49.3	21.4			(8.7)[h]	+40.7
3	(OH$_2$)$_2$$^{3+}$	0.247	22.5	125.0	87.5	−43.8	−50.1	0.213	19.4	86.3	72.0	14.3	−57.7	−66.9
	ΣCo(obsd)	1.096						1.096						
	ΣCo(calcd)[i]	1.088												
	% Co recovery	100.7												

[a] Reaction time ~2-3 s; quenched with excess HClO$_4$ at 0 °C. [b] Products and reactant separated by ion-exchange chromatography at ~5 °C. [c] Obtained by converting a sample of each band quantitatively to [Co(en)$_2$CO$_3$]$^+$; ϵ_{510} = 133.5. [d] Measured on H$^+$/HCO$_3$$^-$-quenched band. [e] ±(0.5-1.5)%; obtained from ϵ_{510} with use of the following data: [Co(en)$_2$CO$_3$]$^+$, ϵ_{510} = 133.5; *trans*-[Co(en)$_2$Cl(OCO$_2$)], ϵ_{510} = 21.2; *trans*-[Co(en)$_2$(OCO$_2$)$_2$]$^-$, ϵ_{510} = 65.1. [f] Mean value (±0.2%) from rotations recorded at five wavelengths. The plus sign denotes net Λ(+), and the minus sign denotes net Δ(−). [g] 10^2 (% activity/% cis). [h] Corrected for some conversion of *cis*[(OH)Cl]$^+$ to [(OH)$_2$]$^+$ during the base hydrolysis reaction. The correction is based on 8.7% activity for band 2 for no secondary reaction and uses the measured steric course 93.7% Λ[(OH)$_2$]$^+$, 1.3% Δ[(OH)$_2$]$^+$, and 5% *trans*[(OH)$_2$]$^+$ for the conversion of the pure isomer. [i] Preliminary experiments on the racemate; chromatography at ~5-10 °C. [j] Entries show the stereochemistry and/or the ligands, other than the en ligands, and the overall charge on the complex.

Table V. Hydroxide Ion Dependence of the Relative Contributions of the Two[a] Base Hydrolysis Pathways for Λ-$[Co(en)_2Cl_2]^+$ at 25 °C

$[OH^-]$, M	% activity[b]	% path 2[c]	% path 2/ % path 1	$[OH^-]$, M	% activity[b]	% path 2[c]	% path 2/ % path 1
1.0	−14.8	35	0.54	0.1	+0.6	11.5	0.13
0.75	−12.5	31.5	0.46	0.05	+4.7	5.5	0.06
0.5	−7.7	24	0.32	0.01	+7.4	1.5	0.02
0.25	−1.5	15	0.18	0.005	+8.3	0	0

[a] Path 1 = normal stepwise Cl^- loss; path 2 = double Cl^- loss. [b] Average values (~±0.4%) from Table III; a plus sign denotes net retention (Λ > Δ), and a minus sign denotes net inversion. [c] Calculated with use of +8.3% activity for path 1 and −58% activity (0 °C value) for path 2.

4).[21] These values are, respectively, ~50% and ~70% of the activity expected (8.7%). However, up to half of the *cis*-$[Co(en)_2(OH)Cl]^+$ formed initially is expected to hydrolyze to $[Co(en)_2(OH)_2]^+$ at 1 M $[OH^-]$ (0 °C) in the ~2–3-s reaction time ($k_{OH} = 0.37$, $t_{1/2} = 1.9$ s) and the results are therefore fully in accord with the formation of *cis*-$[Co(en)_2(OH)Cl]^+$ of the same activity found at low $[OH^-]$. A quantitative check on the results is provided by the fact that secondary hydrolysis depletes both the percent of activity and the percent of cis complex for band 2 to the same degree, i.e., the percent of cis activity should be unchanged. This follows from the fact that the trans isomer is relatively unreactive, while Λ-*cis*- and Δ-*cis*-$[Co(en)_2(OH)Cl]^+$ must react at identical rates. The results, after correction for secondary hydrolysis, show 23 and 21% cis product for band 2 in the two experiments, corresponding to 38 and 41% activity, respectively. The agreement with the expected 18.5% cis product (8.7/0.185 = 47% activity) is good, especially since we are dealing with quite a low percent of cis product. Moreover, the magnitude and sense of the discrepancy (~+3% cis, −8% activity) are consistent with a trace of *trans*-$[Co(en)_2(OH_2)Cl]^{2+}$ isomerization during the chromatography (~1 h, ~5 °C). This is clear from the experiments on the racemate (Table IV), where the chromatography took longer and was conducted at a slightly (~5 °C) higher temperature. The isomerization increases the apparent percent of cis product but not the activity since cis product by this route must be racemic.

It is concluded that the base hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ at 1 M $[OH^-]$ and 0 °C yields $[Co(en)_2(OH)Cl]^+$ of the same isomeric composition found at 5×10^{-3} M $[OH^-]$ (Table II). This is in sharp contrast to the results of Archer et al.,[5] which indicated a change from fully active to racemic cis product on going from low to high concentrations of OH^-.

The products derived from *cis*-$[Co(en)_2(OH)Cl]^+$ through secondary hydrolysis were deducted from the observed $[Co(en)_2(OH)_2]^+$ concentration (band 3, Table IV) to give the contribution from the direct double Cl^- hydrolysis path. This was done by using the observed activity rather than the percent of cis product for band 2 as the more reliable measurement of secondary hydrolysis since the polarimetric data are intrinsically more accurate and are unaffected by isomerization of $[Co(en)_2(OH_2)Cl]^{2+}$ under the conditions of the chromatography. It is easily shown that the number of moles of *cis*-$[Co(en)_2(OH)Cl]^+$ lost is equal to [(0.185/0.815)(8.7 − % activity)/8.7][moles of band 2 observed], and the results of the calculations are presented in the right-hand column of Table IV. Allowance has been made for the formation of 93.7% Λ; 1.3% Δ; and 5% *trans*-$[Co(en)_2(OH)_2]^+$ (Table I) on further hydrolysis of the first-formed *cis*-$[Co(en)_2(OH)Cl]^+$ and for the fact that the *cis*-$[Co(en)_2(OH)Cl]^+$ lost to band 3 is only 47% active (73.5% Λ, 26.5% Δ). The corrected isomer distributions for band 3 agree well for the two experiments, and the result (70% Δ, 12% Λ, 18% trans) represents the steric course for the double Cl^- loss path at 0 °C.

From the data we calculate a 41% contribution to the overall reaction (1 M $[OH^-]$, 0 °C) from the double Cl^- loss pathway. Using the values for the active product arising from both routes (+8.7%, stepwise Cl^- path; −60%, double Cl^- path), we deduce 0.59(8.7) + 0.41(−60) = −19.5 (±1)% activity for the complete hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ in 1.00 M $[OH^-]$ at 0 °C (the minus sign denotes a net Δ(−) isomer). This agrees very well with that observed directly (−20.3 ± 0.4%, Table III) and lends strong support to our analyses.

It remained to examine the $[OH^-]$ dependence of the steric course for the double Cl^- loss path. We performed two experiments at 0.333 M $[OH^-]$ at 0 °C similar to those described for 1.0 M $[OH^-]$, and the analyses of the products separated by ion-exchange chromatography are included in Table IV. As expected, the amounts of dihydroxo complex by the direct route were lower (28, 29% via the double Cl^- loss path) than at 1 M $[OH^-]$, and consequently the corrections for secondary hydrolysis of *cis*-$[Co(en)_2(OH)Cl]^+$ were more severe. Nonetheless, despite the anticipated reduced accuracy of the steric course data, it is celar that the $[Co(en)_2(OH)Cl]^+$ stereochemistry is the same (18.5% cis, 8.7% activity). More significantly, the values for the steric course for the double Cl^- loss path (70.5% Δ, 15% Λ, 15.5% trans) agree very well with the 1 M $[OH^-]$ data (70% Δ, 12% Λ, 18% trans). This result further supports the analysis and establishes that the $[OH^-]$ dependence of the observed activity for the overall reaction (Table III) results entirely from changes in the relative contributions of the two reaction pathways, stepwise and double Cl^- loss.

Finally we should note that the results (Table III) are deceptive insofar as they indicate that net inversion is significant at quite low $[OH^-]$. However, the normal stepwise Cl^- loss route gives a low percent activity (+8%) while the double Cl^- loss path gives a high percent of opposite sign (−60%), and therefore the overall result is especially sensitive to the contribution from the latter. We note also that the activity is ~25% lower at 25 °C than at 0 °C. This result is accommodated by either a higher activation energy for the stepwise Cl^- loss path or a temperature dependence of the steric course for the double Cl^- loss path (−49% activity is required for 25 °C; cf. −60% at 0 °C), or both.

Rate Law. At low $[OH^-]$ the hydrolysis of Λ-$[Co(en)_2Cl_2]^+$ follows the usual rate equation for the first base hydrolysis step[3]

$$-d[CoCl_2^+]/dt = k_{OH}[CoCl_2^+][OH^-]$$

This cannot be true at higher $[OH^-]$, where the double Cl^- loss path becomes prominent. Clearly this path has a dependence of $[OH^-]$ that is greater than first order. This dependence could not be directly determined by rate measurements because the reaction was too fast to measure in the higher $[OH^-]$ region with the equipment available ($t_{1/2} \approx 0.05$ s, 0 °C, 1 M OH^-). However, the form of the rate law can be deduced from the dependence of the overall steric course on $[OH^-]$ (Table III). The percent of the reaction occurring via each pathway was calculated for each $[OH^-]$ from the observed activity, with use of the values +8.3% and −58% activity for the stepwise and double Cl^- loss routes, respectively.

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(21) Note that it is not necessary for the results to agree in this respect. The reaction time (2–3 s) and rate of dissolution of Λ-$[Co(en)_2Cl_2]Cl\cdot H_2O$ are obviously critical.

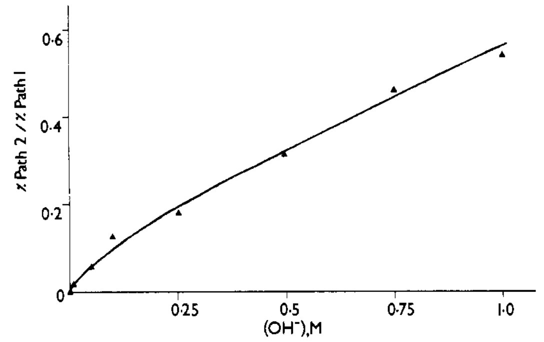

Figure 1. Plot of the $[OH^-]$ dependence of the relative importance of double Cl^- (path 2) and stepwise Cl^- (path 1) loss paths for the base hydrolysis of *cis*-$[Co(en)_2Cl_2]^+$ at 25 °C.

The results are given in Table V.

We will assume that the stepwise Cl^- loss path remains first order in $[OH^-]$ up to 1 M. With few exceptions,[22] all kinetic studies of Co(III) complexes bearing just one readily substituted ligand support this assumption. It follows that we are considering the double Cl^- loss path to be an additional reaction pathway. The complete rate law can be written in the form

$$-d[CoCl_2^+]/dt = k_1[OH^-] + k_2[OH^-]^n$$

and it is easily seen that

$$\frac{\%\text{ path }2}{\%\text{ path }1} = \frac{k_2[OH^-]^{n-1}}{k_1}$$

Thus a plot of the left-hand side (Table V) of the above equation against $[OH^-]$ should indicate the magnitude of n. The result (Figure 1) suggests $1 < n \lesssim 2$, but further quantification is not possible since k_2 is unknown and the data do not refer to constant ionic strength. Note that the plot for $n = 2$ should be linear and that, since increasing ionic strength diminishes k_{OH} values, it seems likely $n = 2$. Also we note that a rate law of the form

$$\frac{-d[CoCl_2^+]}{dt} = k_1[OH^-] + \frac{k_2[OH^-]^2}{1 + K[OH^-]}$$

where $K < 1$, equally well accommodates the data.

Mechanism. The *cis*- and *trans*-$[Co(en)_2AX]^{n+}$ ions commonly base hydrolyze with rearrangement.[1,2,15] The relative amounts of *cis*- and *trans*-$[Co(en)_2A(OH)]^{n+}$ products can be more than or less than the equilibrium distribution. By a similar process, it could be anticipated that the Λ and Δ components of the cis product derived from Λ-cis or Δ-cis reactant could be more or less than the equilibrium value (50/50). Perplexing is the fact that this is not so—in every case there is net retention ($\Lambda > \Delta$). One prominent exception, Λ-$[Co(en)_2Cl_2]^+$, now dissolves since we have shown that the inversion does not proceed by the normal S_N1cB route, not even in part. The spectrum of the steric course behavior for "normal" base hydrolysis can thus be accommodated still by very short-lived pentacoordinate intermediates that remember the parental chirality and that more readily permit cis to trans than Λ to Δ rearrangement.[1,2,15]

We must now ask how net inversion occurs by the path involving loss of both Cl^- ions. In light of the comments above, it is not so much the inversion that is surprising but rather the loss of two Cl^- ions in a single observable step. A number of mechanisms have been advanced[4-6,23] to account for the inversion reactions of Λ-$[Co(en)_2Cl_2]^+$ at high $[OH^-]$. The essence of the proposals is that the conjugate base derived from Λ-$[Co(en)_2Cl_2]^+$ ion associates with OH^- and the location of the OH^- in the ion pair influences the stereochemical outcome. The free ion gives predominantly trans product and some cis complex, with largely retention, while the ion pair gives predominantly the cis species, with largely inversion. The rate law clearly implicates the ion-paired conjugate base as the species responsible for the double Cl^- loss since the rate approaches second order in $[OH^-]$. It seems unlikely that both Cl^- ions would be lost in a single step, but to overcome this difficulty it has been proposed that the reduced coordination number intermediate derived from the conjugate base ion pair undergoes a transient change in spin.[5] Thus it can subsequently lose or substitute the remaining Cl^- ion before adding H_2O to return to a low-spin hexacoordinate product. If this explanation is accepted, it would seem that the free ion conjugate base does not lead to a similar spin change since only one Cl^- ion is lost by this route (the normal base hydrolysis path). The puzzling feature is that the existence of this unusual reaction pathway seems to be contingent upon the loss of the second ligand, since there is no clear reason why complexes with only one replaceable ligand such as Λ-$[Co(en)_2(NH_3)Cl]^{2+}$ should not also react by this ion-pair mechanism and thereby give a different steric course in strong $[OH^-]$.

This account is not especially compelling, but we cannot advance a more chemically reasonable explanation at this time. In particular the concept of an ion-paired conjugate base complex (which is electrically neutral) is disturbing; it implies a reactivity orders of magnitude greater than that of the free ion. However, if this leads to (labile) paramagnetic Co(III), it may not be unreasonable. It is at least clear that the mechanism for two hydrolysis pathways are substantially different, reflected in both the rate laws and stereochemical outcomes.

Although to date it is the only clear example of this behavior (in homogeneous solution), it is difficult to believe that Λ-$[Co(en)_2Cl_2]^+$ is unique. No doubt resolved cis complexes bearing two readily substituted ligands, e.g., Λ-$[Co(en)_2Br_2]^+$, Λ-$[Co(en)_2Cl(OSMe_2)]^{2+}$, and Λ-$[Co(en)_2(OSMe_2)_2]^{3+}$, will be shown to behave similarly. These will be especially revealing studies to test the ion-pair mechanism since the formal charge is increased. Also it would not be surprising if trans complexes such as *trans*-$[Co(en)_2Cl_2]^+$ were shown to base hydrolyze by a double Cl^- loss path, albeit the *cis*-$[Co(en)_2(OH)_2]^+$ product must be racemic. Other interesting questions are the nature of and extent of anion competition by the double Cl^- loss route. Can *two* anions be captured, and is inversion observed? These prospects are under active pursuit.

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Registry No. $\Lambda(+)$-*cis*-$[Co(en)_2Cl_2]^+$, 18660-62-3; $\Lambda(+)$-*cis*-$[Co(en)_2(OH)Cl]^+$, 19428-61-6.

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