pared to ~9 Hz for $[Sn(SO_3F)_6]^{2-}$, indicative of rapid SO_3F-group exchange between solvent and solute as postulated in eq 6.

The ^{19}F NMR spectrum, shown in Figure 5, provides complementing evidence. A concentration-dependent broad single line is observed for solutions of $K[Sn(SO_3F)_5]$ in HSO_3F. For a 0.88 mol kg^{-1} solution of $K[Sn(SO_3F)_5$, this resonance is found at 41.42 ppm with a half line width of 24 Hz. Addition of solid KSO_3F to this solution causes a splitting of this broad resonance into two sharp components, one at 41.75 ppm attributed to $[Sn(SO_3F)_6]^{2-}$ and a second at 40.75 ppm due to the solution of excess KSO_3F in fluorosulfuric acid. It appears that the ^{19}F NMR experiment allows the monitoring of the acid–base titration, described by eq 8. The exchange broadening for $[Sn(SO_3F)_5]^-$ in HSO_3F indicates a coordinatively unsaturated species, with SO_3F^- addition producing now the $[Sn(SO_3F)_6]^{2-}$ ion.

Conclusions

In view of the scarcity of germanium(IV) oxyacid derivatives, some tentative comments on both the differences and similarities of the respective tin and germanium compounds may be made. Formation of $GeF_2(SO_3F)_2$ under conditions where $Sn(SO_3F)_4$ forms quantitatively indicates a greater tendency of the Ge–SO_3F group to undergo SO_3 elimination. The resulting $GeF_2(SO_3F)_2$ shows the same structural features as the tin compound; hexacoordination is achieved by bidentate SO_3F groups with a linear F–M–F evident from the Raman and infrared spectra. The similarities in thermal stabilities, solution behavior in HSO_3F, and the vibrational spectra of the $[M(SO_3F)_6]^{2-}$ complexes are rather striking.

The solution behavior of $[Sn(SO_3F)_5]^-$ and the detected acidity in HSO_3F suggest $H_2[Sn(SO_3F)_6]$ to be a rather strong dibasic acid. However, the intrinsic tendency toward hexacoordination necessary for superacid behavior is also the driving force behind the noted polymer formation.

Acknowledgment. Financial support by the Natural Sciences and Engineering Council of Canada is gratefully acknowledged. Professor J. R. Sams and L. Sallos are thanked for providing the ^{119}Sn Mössbauer spectra.

Registry No. $Sn(SO_3F)_4$, 88476-13-5; $Cs[Sn(SO_3F)_5]$, 88476-17-9; $K[Sn(SO_3F)_5]$, 88476-19-1; $Cs_2[Sn(SO_3F)_6]$, 37477-90-0; $K_2[Sn(SO_3F)_6]$, 37477-89-7; $GeF_2(SO_3F)_2$, 88476-15-7; $Cs_2[Ge(SO_3F)_6]$, 88476-20-4; $(ClO_2)_2[Ge(SO_3F)_6]$, 88476-22-6; Sn, 7440-31-5; $S_2O_6F_2$, 13709-32-5; Ge, 7440-56-4.

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Steric Course of Base Hydrolysis of *cis*- and *trans*-$[Co(en)_2(N_3)X]^{n+}$ and *cis*- and *trans*-$[Co(en)_2(NCS)X]^{n+}$ (X = Br^-, Cl^-, $OS(CH_3)_2$, $OCHN(CH_3)_2$, N_3^-, O_2CH^-)

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Received April 14, 1983

The steric course has been determined spectrophotometrically, by using two or three independent methods, for the base hydrolysis reactions of *cis*- and *trans*-$[Co(en)_2(NCS)X]^{n+}$ and *cis*- and *trans*-$[Co(en)_2(N_3)X]^{n+}$ (X = Cl^-, Br^-, N_3^-, HCO_2^-, $(CH_3)_2SO$, $(CH_3)_2NCHO$) at 25 °C. The following *cis*-/*trans*-$[Co(en)_2A(OH)]^+$ product distributions (±2%) were obtained. *cis*-$[Co(en)_2(N_3)X]^{n+}$: X = Cl^-, 48% cis; Br^-, 47.5%; $OS(CH_3)_2$, 39%. *trans*-$[Co(en)_2(N_3)X]^{n+}$: X = Cl^-, 24% cis; Br^-, 26%; O_2CH^-, 23%; N_3^-, 26%; $OS(CH_3)_2$, 30.5%; $OCHN(CH_3)_2$, 26%. *trans*-$[Co(en)_2(NCS)X]^{n+}$: X = Cl^-, 82% cis; Br^-, 75%; $OS(CH_3)_2$, 72%. *trans*-$[Co(en)_2(NCS)X]^{n+}$: X = Cl^-, 70% cis; Br^-, 75%; $OS(CH_3)_2$, 72%. The study includes earlier work, widened to improve the range of leaving groups and and reexamined to improve, in some cases, the accuracy and/or precision of the steric course data. The *trans*-$[Co(en)_2(N_3)(OCHN(CH_3)_2)]^{2+}$ ion reacts in part by OH^- attack at the ligand to give *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ and $(CH_3)_2NH$, and allowance has been made for this minor (3.3%) pathway. The results are internally consistent and reveal for the first time a small but definite influence of the leaving group X on the stereochemistry of base hydrolysis products, *cis*- and *trans*-$[Co(en)_2A(OH)]^+$. For varied A and reactant geometry, there is no obvious correlation between the product distribution on X. The "rules" for stereochemical change in these classic substitution processes are examined in light of the new data. The results are best explained in terms of the S_N1CB mechanism involving short-lived, common five-coordinate intermediates. Details of this and alternative mechanisms are considered. Experiments are described that preclude the possibility of preisomerization in the $[Co(en)_2(NCS)X]^{n+}$ reactions, where the unusual stereochemical outcome is a very similar product distribution for cis and trans reactants.

Introduction

The widely accepted[1] mechanism for the base hydrolysis of octahedral amine complexes of cobalt(III) is the dissociative conjugate base process (S_N1CB[2] or DCB[3]). An integral part of the mechanism (Scheme I) has been argued[1] to be the

Scheme I

$$A_4(RNH_2)CoX^{n+} + OH^- \overset{fast}{\rightleftharpoons} A_4(RNH)CoX^{(n-1)+} \xrightarrow{slow}$$

$$A_4(RNH)Co^{2+} + X^{(3-n)-} \xrightarrow[fast]{H_2O} A_4(RNH_2)CoOH_2^{3+}$$

formation of a reactive five-coordinate intermediate, and much evidence has been accumulated in support of their existence.[4,5] Among the earliest work on this problem was a paper[6] indicating that the steric course of base hydrolysis of the *cis*- and *trans*-$[Co(en)_2AX]^{n+}$ ions (A, X = Cl^-, Br^-, N_3^-, NCS^-, NO_2^-, and others) was independent of the leaving group, as the mechanism requires. The data that did not show this independence were of dubious accuracy or had large experimental errors. Since then, few precise results have been forthcoming, save from some careful work[7,8] on the Λ(+)-*cis*- and *trans*-

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$[\mathrm{Co(en)_2(NH_3)X}]^{n+}$ (X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NO_3^-}$, $\mathrm{SCN^-}$, $\mathrm{OP(OMe)_3}$, $\mathrm{OSMe_2}$) and Λ(+)-*cis*- and *trans*-$[\mathrm{Co(en)_2Cl_2}]^+$ and $[\mathrm{Co(en)_2(OH)(Cl)}]^+$ systems.[9,10] We have had other occasion[11] to prepare a range of *cis*- and *trans*-$[\mathrm{Co(en)_2(N_3)X}]^{n+}$ and $[\mathrm{Co(en)_2(NCS)X}]^{n+}$ complexes for other reasons, but ideally suited to improve this dearth of data and to comment on the following. The choice of complexes was prompted by reports that the steric course of base hydrolysis of the *trans*-$[\mathrm{Co(en)_2(N_3)X}]^+$ (X = $\mathrm{Br^-}$, 17% cis; X = $\mathrm{Cl^-}$, 8% cis)[12] and Λ(+)-*cis*-$[\mathrm{Co(en)_2(NH_3)X}]^{n+}$ (X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NO_3^-}$, 78% cis, 61% Λ(+)-cis; X = $\mathrm{OSMe_2}$, $\mathrm{OP(OMe)_3}$, 78% cis, 66% Λ-(+)-cis)[8] ions appear to depend on the nature of the leaving group. Furthermore, the *cis*-$[\mathrm{Co(en)_2(NCS)(Cl)}]^+$ and *trans*-$[\mathrm{Co(en)_2(NCS)(Br)}]^+$ ions are reported to hydrolyze to a common $[\mathrm{Co(en)_2(NCS)(OH)}]^+$ product distribution (81–82% cis).[13] This independence of the starting geometry is unusual, and the problem is examined here. Also, the role of the leaving group in base hydrolysis is given detailed consideration.

Experimental Section

A Cary 118C spectrophotometer was used to record the visible absorption spectra (ϵ_λ, $\mathrm{M^{-1}\,cm^{-1}}$) at 25 °C. ^{1}H NMR spectra were obtained with a Varian T60 instrument with use of $\mathrm{D_2O}$ (pD ~3, DCl) solvent and sodium (trimethylsilyl)propanesulfonate as the internal reference. For these measurements, $\mathrm{S_2O_6^{2-}}$ salts (~100 mg) were converted to the more soluble $\mathrm{Cl^-}$ salts by anion exchange using Dowex 1-X8 resin ($\mathrm{Cl^-}$ form, 200–400 mesh). Aqueous solutions so obtained were rotaevaporated (<35 °C) to dryness, and the residue was dissolved in $\mathrm{D_2O}$ (pD ~3). SP Sephadex C-25 ($\mathrm{Na^+}$ form) cation-exchange resin was used in all other chromatography experiments.

Synthesis and Characterization. The preparation and complete characterization of the isothiocyanato complexes are described elsewhere.[14] The following salts (air-dried) were used in this work (visible spectra in $\mathrm{H_2O}$): *cis*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{X}$ (X = $\mathrm{Cl^-}{\cdot}1.5\mathrm{H_2O}$, $\mathrm{NCS^-}$, $\mathrm{ClO_4^-}$) ($\epsilon_{501}{}^{\max}$ 170.5, $\epsilon_{434}{}^{\min}$ 64.0); *cis*-$[\mathrm{Co(en)_2(OSMe_2)(NCS)}]\mathrm{NO_3ClO_4}$ ($\epsilon_{496}{}^{\max}$ 208.5, $\epsilon_{427}{}^{\min}$ 66.0); *cis*-$[\mathrm{Co(en)_2(NCS)(Br)}]\mathrm{X}$ (X = $\mathrm{Br^-}{\cdot}\mathrm{H_2O}$, $\mathrm{ClO_4^-}$) ($\epsilon_{508}{}^{\max}$ 154.0, $\epsilon_{445}{}^{\min}$ 78.6); *cis*-$[\mathrm{Co(en)_2(OH_2)(NCS)}]\mathrm{X}$ (X = $\mathrm{S_2O_6^{2-}}{\cdot}4.5\mathrm{H_2O}$, $(\mathrm{NCS^-})_2$) ($\epsilon_{491}{}^{\max}$ 217.4); *trans*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{X}$ (X = $\mathrm{Br^-}{\cdot}2\mathrm{H_2O}$, $\mathrm{NCS^-}$, $\mathrm{ClO_4^-}$) ($\epsilon_{558}{}^{\max}$ 143.0, $\epsilon_{471}{}^{\min}$ 31.7); *trans*-$[\mathrm{Co(en)_2(NCS)(Br)}]\mathrm{X}$ (X = $\mathrm{Br^-}{\cdot}2\mathrm{H_2O}$, $\mathrm{NCS^-}$, $\mathrm{ClO_4^-}$) ($\epsilon_{575}{}^{\max}$ 154.5, $\epsilon_{484}{}^{\min}$ 27.1; *trans*-$[\mathrm{Co(en)_2(NCS)(OH)}]\mathrm{ClO_4^-}$) ($\epsilon_{575}{}^{\max}$ 154.5, $\epsilon_{484}{}^{\min}$ 27.1; *trans*-$[\mathrm{Co(en)_2(NCS)(OH)}]\mathrm{NCS{\cdot}H_2O}$, *trans*-$[\mathrm{Co(en)_2(NCS)(OH_2)}]$, *trans*-$[\mathrm{Co(en)_2(NCS)(OH)}](\mathrm{ClO_4})_3$, *trans*-$[\mathrm{Co(en)_2(NCS)(OH_2)}]\mathrm{S_2O_6}{\cdot}0.5\mathrm{H_2O}$, *trans*-$[\mathrm{Co(en)_2(NCS)(OH_2)}](\mathrm{NCS})_2{\cdot}\mathrm{H_2O}$ ($\epsilon_{538}{}^{\max}$ 184.6, $\epsilon_{456}{}^{\min}$ 51.5). The electronic spectra of the different salts of the same cation were identical, as were the spectra of the aqua, hydroxo, and *trans*-aqua/hydroxo (double) salts, measured in both acid (0.1 M $\mathrm{HClO_4}$) and base (0.01–0.1 M $\mathrm{OH^-}$, 0.01 M Tris or Dieth buffers). Other spectral data appear in the tables.

The majority of the azido complexes were from fresh batches fully characterized previously.[11,15] The new *cis*- and trans-$[\mathrm{Co(en)_2(N_3)(O_2CH)}]^+$ ions were obtained as follows. A solution of *cis*-$[\mathrm{Co(en)_2(OH_2)(N_3)}]\mathrm{S_2O_6{\cdot}H_2O}$[11] (4.0 g) in water (20 mL) was treated with an excess of a $\mathrm{HCO_2^-/HCO_2H}$ buffer (4.5 g of formic acid, half-neutralized with 2.1 g of $\mathrm{LiOH{\cdot}H_2O}$). The mixture was heated at 60 °C for 10 min, $\mathrm{Li_2S_2O_6}$ (5.0 g) was then added, and the solution was cooled in ice (~1 h). The crystals of essentially pure *cis*-$[\mathrm{Co(en)_2(N_3)(O_2CH)}](\mathrm{S_2O_6})_{1/2}{\cdot}\mathrm{H_2O}$ (0.9 g) that separated were collected, washed with methanol and ether, and air-dried. These were recrystallized from a minimum of hot water by addition of ethanol to afford shiny maroon plates of the pure cis form. The deep mauve filtrate from the initial crystallization step was treated with a large excess of acetone; when the resultant mixture was scratched and cooled in ice, mauve plates of the trans isomer separated (1.7 g). These were recrystallized twice from water (~20 °C) by the addition of excess acetone, after first filtering to remove traces of the much less soluble cis isomer. The air-dried trans isomer appeared also to be a monohydrate (visible spectrum); the lattice water was removed by vacuum drying over $\mathrm{P_2O_5}$. Anal. Calcd for $[\mathrm{Co(C_4H_{16}N_4)(N_3)(CHO_2)}](\mathrm{S_2O_6})_{1/2}$: C, 17.35; H, 4.95; N, 28.33; S, 9.26. Found (cis): C, 17.0; H, 5.0; N, 28.7; S, 9.3. Found (trans): C, 17.1; H, 5.1; N, 28.4; S, 8.8. Visible spectra ($\mathrm{H_2O}$): cis, $\epsilon_{515}{}^{\max}$ 268.5, $\epsilon_{442}{}^{\min}$ 71.6; trans, $\epsilon_{547}{}^{\max}$ 247.5, $\epsilon_{457}{}^{\min}$ 39.5. ^{1}H NMR spectra (10^{-3} M DCl): cis, δ 2.83 (br, m, 8 H, $\mathrm{CH_2}$), 3.7–6.0 (br, m, 8 H, $\mathrm{NH_2}$), 7.85 (s, 1 H, CHO); trans, δ 2.80 (m, 8 H, $\mathrm{CH_2}$), 4.97, 5.33 (br, 4 H, 4 H, $\mathrm{NH_2}$), 7.40 (s, 1 H, CHO). [Cf. free $\mathrm{HCO_2^-}$ at δ 8.30 (s, 1 H, CHO).]

Isomeric purity was established by the constancy of the visible spectra on recrystallization and from the ^{1}H NMR spectra (the $\mathrm{CoO_2CH}$ signals are isolated from other absorptions, sharp, and well separated ($\Delta\delta$ 0.45) for the cis and trans forms). It was confirmed by chromatography on Sephadex (vide infra).

The azido–formato complexes could be prepared also by using *cis*-$[\mathrm{Co(en)_2(N_3)(OSMe_2)}]\mathrm{NO_3ClO_4}$,[15] *cis*-$[\mathrm{Co(en)_2(N_3)X}]\mathrm{ClO_4}$ (X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$),[15] *trans*-$[\mathrm{Co(en)_2(OH_2)(N_3)}]\mathrm{S_2O_6}$,[15] or *trans*-$[\mathrm{Co(en)_2(N_3)X}]\mathrm{ClO_4}$ (X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$)[11] in place of *cis*-$[\mathrm{Co(en)_2(OH_2)(N_3)}]\mathrm{S_2O_6{\cdot}H_2O}$.[11,15] The product proportions were similar (~2:1 trans:cis) in each case. The *trans*- and *cis*-$[\mathrm{Co(en)_2(N_3)(O_2CH)}]^+$ ions separate easily on Sephadex cation-exchange resin (0.05–0.1 M $\mathrm{NaClO_4}$ eluent); the trans ion elutes first. Rotary evaporation (<35 °C) of the eluates to small volumes followed by addition of excess ethanol and cooling (5 °C, 3 h) produced well-formed crystalline perchlorate salts.

All the isomeric pairs *cis-/trans*-$[\mathrm{Co(en)_2(NCS)X}]^+$ (X = $\mathrm{Br^-}$, $\mathrm{Cl^-}$, $\mathrm{NCS^-}$, $\mathrm{N_3^-}$, $\mathrm{NO_2^-}$) are separated readily by chromatography (Sephadex, 0.05–0.1 M $\mathrm{NaClO_4}$ eluent), and in every case the trans form is eluted first. *cis*- and *trans*-$[\mathrm{Co(en)_2(NCS)(OH_2)}]^{2+}$ do not separate under the above conditions, but in basic solution (pH ~8, Tris) they come apart readily as their 1+ hydroxo forms. All the thiocyanato complexes used in this work were shown to be isomerically pure in this way. Moreover, $[\mathrm{Co(en)_2(NCS)X}]^{n+}$ were shown to be free of trace $[\mathrm{Co(en)_2X_2}]^{n+}$ and $[\mathrm{Co(en)_2(NCS)_2}]^+$ impurities either by direct chromatography (X = $\mathrm{OH_2}$, $\mathrm{OSMe_2}$, $\mathrm{OH^-}$) using an acidified eluant or by following selective base hydrolysis in 0.01 M $\mathrm{OH^-}$ (X = $\mathrm{Cl^-}$, $\mathrm{OSMe_2}$, $\mathrm{Br^-}$), as described elsewhere for $[\mathrm{Co(en)_2(N_3)X}]^{n+}$.[11] The *cis*- and *trans*-$[\mathrm{Co(en)_2(NCS)_2}]^+$ ions are inert to $\mathrm{OH^-}$ under the conditions (<30 min, 25 °C), while $[\mathrm{Co(en)_2X_2}]^+$ are hydrolyzed through to $[\mathrm{Co(en)_2(OH)_2}]^+$. Thus, acid-quenched solutions of $[\mathrm{Co(en)_2(NCS)X}]^{n+}$ in $\mathrm{OH^-}$ showed a single 2+ band on chromatography, $[\mathrm{Co(en)_2(NCS)(OH_2)}]^{2+}$; no 1+ ($[\mathrm{Co(en)_2(NCS)_2}]^+$) or 3+ ($[\mathrm{Co(en)_2(OH_2)_2}]^{3+}$) ions were detected (<0.5%).

Base Hydrolysis of $[\mathrm{Co(en)_2(NCS)X}]^{n+}$ and $[\mathrm{Co(en)_2(N_3)X}]^{n+}$. Accurately weighed samples of complex were dissolved directly in 0.010 M NaOH (25.00 mL, [Co] = 1–2 mM). The visible spectra were recorded immediately following complete hydrolysis (>$10t_{1/2}$: $\mathrm{NCS^-}$, cis-Cl, Br, $\mathrm{OSMe_2}$ (3.0 min); trans-Cl (20 min); trans-Br (3.0 min); $\mathrm{N_3^-}$, cis-Cl, Br, $\mathrm{OSMe_2}$, trans-Cl, Br, $\mathrm{OSMe_2}$ (2.0 min). In other experiments, 0.02 and 0.1 M $\mathrm{OH^-}$ were used and reaction times shortened accordingly. For the azido complexes in 0.1 M $\mathrm{OH^-}$, the product spectra were repetitively scanned and then extrapolated to zero time to correct for slow but significant base-catalyzed $\mathrm{N_3^-}$ loss from *trans*- and particularly *cis*-$[\mathrm{Co(en)_2(N_3)(OH)}]^+$. All the experiments above were repeated with ~15 mL rather than 25.00 mL of $\mathrm{OH^-}$, and after complete hydrolysis ($10t_{1/2}$) the reactions were quenched with excess 0.1 or 0.2 M $\mathrm{HClO_4}$ (~10–25.00 mL) to generate $[\mathrm{Co(en)_2(NCS)(OH_2)}]^{2+}$ or $[\mathrm{Co(en)_2N_3(OH_2)}]^{2+}$. For the latter, product spectra required extrapolation to zero time to accommodate a little subsequent cis $\rightleftarrows$ trans isomerization of $[\mathrm{Co(en)_2(N_3)(OH_2)}]^{2+}$.

Compared to their azido counterparts, $[\mathrm{Co(en)_2(NCS)(OH)}]^+$ and $[\mathrm{Co(en)_2(NCS)(OH_2)}]^{2+}$ are relatively unreactive, and hence the $\mathrm{NCS^-}$ product spectra were constant in the time scale of all the $[\mathrm{Co(en)_2(NCS)X}]^{n+}$ reactions. All experiments were performed at least twice.

The $\mathrm{HClO_4}$-quenched solutions for the base hydrolysis reactions of $[\mathrm{Co(en)_2(N_3)X}]^{n+}$ were kept at 25 °C for 48 h and their spectra

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Table I. Steric Course of Base Hydrolysis of $[Co(en)_2(NCS)X]^{n+}$ at 25 °C, Deduced from the $[Co(en)_2(NCS)(OH)]^+$ Product Spectra

reactant	$[OH^-]$, M	ϵ_λ(obsd) of products,[a] M^{-1} cm^{-1}		% cis product[b]
		$\lambda = 500$	$\lambda = 426$	
cis-$[Co(en)_2(NCS)(Cl)]^+$	0.01	159.7 (6)[c,d]	40.6 (6)[c,d]	81
	0.02	160.4 (2)[e]	40.5 (2)[e]	82
cis-$[Co(en)_2(NCS)(Br)]^+$	0.01	152.4 (2)[f]	38.5 (2)[f]	71.5
	0.02	154.2 (3)[d,h]	38.4 (3)[d,h]	74
cis-$[Co(en)_2(NCS)(OSMe_2)]^{2+}$	0.01	152.0 (3)	40.9 (3)	71
trans-$[Co(en)_2(NCS)(Cl)]^+$	0.01	150.9 (4)[d,g]	39.5 (4)[d,g]	69.5
	0.02	152.0 (2)[d,g]	39.3 (2)[d,g]	71
trans-$[Co(en)_2(NCS)(Br)]^+$	0.01	154.3 (6)[d,g]	39.7 (6)[d,g]	74
	0.02	154.0[e]	40.0 (2)[e]	73.5

[a] λ in nm; number in parentheses denotes determinations. [b] Calculated from ϵ_{500}(obsd) and the relation % cis = $10^2(\epsilon_{obsd} - \epsilon_{trans})/(\epsilon_{cis} - \epsilon_{trans})$; $\epsilon_{cis} = 174.5$ and $\epsilon_{trans} = 97.1$ for $[Co(en)_2(NCS)(OH)]^+$ at 500 nm. [c] $[Co(en)_2(NCS)(Cl)]Cl \cdot 1.5H_2O$ reactant. [d] $[Co(en)_2(NCS)X]ClO_4$. [e] $[Co(en)_2(NCS)X]NCS$. [f] $[Co(en)_2(NCS)(Br)]Br \cdot H_2O$. [g] $[Co(en)_2(NCS)X]Br \cdot 2H_2O$. [h] $[Co(en)_2(NCS)X]Br$.

Table II. Steric Course of Base Hydrolysis of $[Co(en)_2(NCS)X]^{n+}$ at 25 °C, Deduced from the $[Co(en)_2(NCS)(OH_2)]^{2+}$ Product Spectra

reactant	$[OH^-]$, M	ϵ_λ(obsd) of acid-quenched products,[a] M^{-1} cm^{-1}		% cis product[b]
		$\lambda = 496$	$\lambda = 428$	
cis-$[Co(en)_2(NCS)(Cl)]^+$	0.01	196.8 (4)[c]	73.5 (4)[c]	83
	0.02	196.7 (2)[c,d]	73.3 (2)[c,d]	83
cis-$[Co(en)_2(NCS)(Br)]^+$	0.01	189.8 (2)[e]	71.0 (2)[e]	76.5
	0.02	191.0 (3)[c,e]	71.2 (3)[c,e]	77.5
cis-$[Co(en)_2(NCS)(OSMe_2)]^{2+}$	0.01	186.7 (3)	73.2 (3)	73.5
trans-$[Co(en)_2(NCS)(Cl)]^+$	0.01	182.1 (4)[c,f]	71.8 (4)[c,f]	69.5
	0.02	185.0 (2)[c,d]	72.9 (2)[c,d]	72
trans-$[Co(en)_2(NCS)(Br)]^+$	0.01	189.5 (4)[c,f]	73.5 (4)[c,f]	76
	0.02	189.5 (2)[d]	74.3 (2)[d]	76

[a] λ in nm; number in parentheses denotes determinations. [b] Calculated from ϵ_{496}(obsd) and the relation % cis = $10^2(\epsilon_{obsd} - \epsilon_{trans})/(\epsilon_{cis} - \epsilon_{trans})$; $\epsilon_{cis} = 215.0$ and $\epsilon_{trans} = 107.5$ for $[Co(en)_2(NCS)(OH_2)]^{2+}$ at 496 nm. [c] $[Co(en)_2(NCS)X]ClO_4$ reactant. [d] $[Co(en)_2(NCS)X]NCS$. [e] $[Co(en)_2(NCS)(Br)] \cdot H_2O$. [f] $[Co(en)_2(NCS)X]Br \cdot 2H_2O$.

remeasured. Comparison with the accurately known $[Co(en)_2(N_3)(OH_2)]^{2+}$ equilibrium spectra[11,15] confirmed that there was no competitive loss of N_3^- in base hydrolysis. The cis/trans isosbestic point in the spectra of *cis*- and *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$ (ϵ_{537} 228.5) is also diagnostic (see Table IV), and the result was further substantiated chromatographically. *cis*- and *trans*-$[Co(en)_2(NCS)(OH_2)]^{2+}$ rearrange too slowly for this method to be a convenient check on competitive NCS^- loss from $[Co(en)_2(NCS)X]^{n+}$, but the chromatography establishes this fact.

The isosbestic points, which were sharp, were located for the slower base hydrolysis reactions by repetitive scanning (680–400 nm) for periods ranging from 0.5 to 2 half-lives. Dilute NaOH (5×10^{-4} M) or 2,2′-iminobis(ethanol)/$HClO_4$ buffer (0.01 M, pH ~9) were generally required to slow the reactions sufficiently. Stronger OH^- (up to 0.1 M) was used for the less reactive *trans*-$[Co(en)_2(N_3)_2]^+$ and *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ ions. The background aquation reactions, where hydrolysis leads to a different steric course, were negligible under all conditions (Table VI).

Base Hydrolysis of *trans*-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$. Accurately weighed samples (~0.25 g) of the *trans*-azido–DMF complex were dissolved rapidly in 0.01 M NaOH (100 mL, 25 °C). After 2.0 min, $HClO_4$ (25 mL, 0.1 M) was added to quench the reactions (to pH ~2). The diluted (H_2O, to ~400 mL) product solutions were sorbed on Sephadex, washed with water, and eluted with $NaClO_4$ (0.1 M, pH 3 ($HClO_4$)). A weak mauve band (trans 1+) was observed, followed by and well separated from a strong violet (2+) band. The latter was eluted more quickly with 0.2 M $NaClO_4$ (pH 3). The volumes and visible spectra of the eluates were recorded promptly, and the spectrum of the second band was recorded again after 48 h at ~25 °C. The first band was identified as *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ ($\epsilon_{547}{}^{max}$ 247.5, $\epsilon_{457}{}^{min}$ 39.5; cf. cis isomer: $\epsilon_{515}{}^{max}$ 268.5, $\epsilon_{442}{}^{min}$ 71.6), and the second as a *cis*-/*trans*-$[Co(en)_2(OH_2)(N_3)]^{2+}$ mixture ($\epsilon_{515}{}^{max}$ 249).[11] *cis*-$[Co(en)_2(N_3)(O_2CH)]^{2+}$, which elutes behind its trans isomer, was not observed. No attempt was made to separate the aqua–azido isomers, although the mauve trans ion elutes slightly in front of the cis (and they can be separated cleanly as their hydroxo forms—vide infra). The [Co] was determined by using ϵ_{537} 228.5, the isosbestic point between the two isomers. The same result (±0.5%) was obtained with $\epsilon_{515}{}^{max}$ 249, the maximum in the equilibrated (48 h, 25 °C) isomer mixture. In four experiments, we found 3.3 ± 0.2% of *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ and 96.7 ± 0.5% of $[Co(en)_2(OH_2)(N_3)]^{2+}$. The [Co] in the first band was determined by using $\epsilon_{547}{}^{max}$ 247.5, the value corresponding to the authentic *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ ion. The cobalt recovery from the columns was 98–101% in all cases. In a blank experiment on the *trans*-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$ complex (~0.5 g), allowed to aquate 48 h in 0.01 M $HClO_4$ at 25 °C, no formato complex was detected by chromatography (<0.2%).

Base-Catalyzed *cis*-/*trans*-$[Co(en)_2(NCS)(Cl)]^+$ Isomerization. A solution of *trans*-$[Co(en)_2(NCS)(Cl)]ClO_4$ (~0.1 g) in water (50 mL, 25 °C) was treated dropwise, while being well stirred, with dilute aqueous NaOH (50 mL, containing 0.5–0.75 equiv of OH^-, (1.5–2) $\times 10^{-3}$ M after mixing). After 10 min, the mixture was quenched to pH ~2 with 1 M $HClO_4$ and sorbed on and eluted from Sephadex (0.1 M $NaClO_4$ (pH 3) eluent). The two bands, residual (mauve) *trans*-$[Co(en)_2(NCS)(Cl)]^+$ and (red) $[Co(en)_2(NCS)(OH_2)]^{2+}$, were collected, and the eluate volumes and visible spectra recorded without delay. *cis*-$[Co(en)_2(NCS)(Cl)]^+$, which elutes behind the trans isomer but in front of $[Co(en)_2(NCS)(OH_2)]^{2+}$, was not observed. Similar experiments were performed on *cis*-$[Co(en)_2(NCS)(Cl)]^+$ partly hydrolyzed in dilute OH^- solution (0.5–0.75 equiv). Residual cis isomer and $[Co(en)_2(NCS)(OH_2)]^{2+}$ (but no *trans*-$[Co(en)_2(NCS)(Cl)]^+$) were found on chromatography. In both sets of experiments, the cobalt recovery was 99–101% for the two bands. The [Co] in the eluates was determined spectrophotometrically, by using the following values for the molar absorptivities: $[Co(en)_2(NCS)(Cl)]^+$ $\epsilon_{trans}{}^{658}$ 143.0, $\epsilon_{cis}{}^{501}$ 170.5; $[Co(en)_2(NCS)(OH_2)]^{2+}$ ϵ^{496} 183.5 when derived from the trans isomer, ϵ^{496} 196.5 when derived from the cis (see Table II).

Chromatographic Determination of the Steric Course of Base Hydrolysis. The products of the base hydrolysis of selected complexes (*cis*- and *trans*-$[Co(en)_2(NCS)(Cl)]^+$, *cis*-$[Co(en)_2(N_3)(Cl)]^+$), were determined by separating the *cis*- and *trans*-$[Co(en)_2A(OH)]^+$ (A = NCS^-, N_3^-) ions by ion-exchange chromatography on Sephadex (0.1 M $NaClO_4$ (pH ~8, Tris) eluent). The following values for the molar extinction coefficients were used to determine the [Co] in the eluates: $[Co(en)_2(NCS)(OH)]^+$ $\epsilon_{499}{}^{max}$(cis) 174.5, $\epsilon_{508}{}^{max}$(trans) 99.0; $[Co(en)_2(N_3)(OH)]^+$ $\epsilon_{521}{}^{max}$(cis) 221, $\epsilon_{540}{}^{max}$(trans) 166.

Results and Discussion

The steric course of base hydrolysis of five $[Co(en)_2(NCS)X]^{n+}$ and nine $[Co(en)_2(N_3)X]^{n+}$ complexes has been determined spectrophotometrically. Spectra have been re-

Table III. Steric Course of Base Hydrolysis of $[Co(en)_2(N_3)X]^{n+}$ at 25 °C, Deduced from the $[Co(en)_2(N_3)(OH)]^+$ Product Spectra

	ϵ_λ(obsd) of products,[a,b] M^{-1} cm^{-1}				
reactant	$\lambda = 480$	$\lambda = 500$	$\lambda = 510$	$\lambda = 520$	av % cis product[c]
cis-$[Co(en)_2(N_3)(Cl)]^+$	87.9 (2) [46.5]	140.2 (2) [47.5]	163.2 (2) [46.5]	179.3 (2) [46]	46.5
cis-$[Co(en)_2(N_3)(Br)]^+$	87.1 (2) [45.5]	139.1 (2) [46]	163.3 (2) [46.5]	181.2 (2) [48.5]	46.5
cis-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$	83.9 (6) [40]	131.9 (6) [38.5]	155.9 (6) [38.5]	173.3 (6) [38.5]	39
trans-$[Co(en)_2(N_3)(Cl)]^+$	73.1 (2) [23]	117.6 (2) [23]	142.0 (2) [23]	161.6 (2) [23]	23
trans-$[Co(en)_2(N_3)(Br)]^+$	73.9 (2) [24]	119.0 (2) [24.5]	142.9 (2) [24]	161.8 (2) [23.5]	24
trans-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$	76.6 (6) [28.5]	123.8 (6) [29.5]	148.6 (6) [30.5]	167.6 (6) [31.0]	30
trans-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$	74.3 (7) 75.0^d [26]	120.2 (7) 120.8^d [26.5]	143.8 (7) 143.8^d [25]	162.7 (7) 162.0^d [23.5]	25

[a] λ in nm; number in parentheses denotes determinations. All experiments performed for $[OH^-] = 0.01-0.02$ M. [b] Number in brackets denotes the % cis product obtained from ϵ_λ(obsd) (or ϵ_λ–see *d*) and the relation % cis = $(10^2(\epsilon_\lambda(\text{obsd}) - \epsilon_\lambda(\text{trans}))/(\epsilon_\lambda(\text{cis}) - \epsilon_\lambda(\text{trans}))$. The following values for the molar extinction coefficients of $[Co(en)_2(N_3)(OH)]^+$ were used: 480 nm, $\epsilon_{\text{cis}} = 121.2$, $\epsilon_{\text{trans}} = 58.8$; 500 nm, $\epsilon_{\text{cis}} = 188.8$, $\epsilon_{\text{trans}} = 96.4$; 510 nm, $\epsilon_{\text{cis}} = 211.9$, $\epsilon_{\text{trans}} = 121.0$; 520 nm, $\epsilon_{\text{cis}} = 220.4$, $\epsilon_{\text{trans}} = 144.0$. [c] The four values in brackets are equally weighted. [d] Corrected for the path that yields *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ (and Me_2NH) and does not involve substitution at the metal ion. The proportion (3.3%) was determined chromatographically (see text) and the correction to ϵ_λ(obsd) applied as follows: $\epsilon_\lambda = (\epsilon_\lambda(\text{obsd}) - 0.967\epsilon^F)/0.967$, where $\epsilon_\lambda{}^F$ is the known constant for *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$. $\epsilon_{480}{}^F = 55.2$, $\epsilon_{500}{}^F = 102.5$, $\epsilon_{510}{}^F = 142.5$, $\epsilon_{520}{}^F = 183.0$.

Table IV. Steric Course of Base Hydrolysis of $[Co(en)_2(N_3)X]^{n+}$ at 25 °C, Deduced from the $[Co(en)_2(N_3)(OH_2)]^{2+}$ Product Spectra

	ϵ_λ(obsd) of acid-quenched products,[a] M^{-1} cm^{-1}					
reactant	$\lambda = 502$	% cis[c]	$\lambda = 537^b$	$\lambda = 602$	% cis[c]	av % cis product[d]
cis-$[Co(en)_2(N_3)(Cl)]^+$	198.4 (2)	49.5	226.8 (2)	92.3 (2)	48.5	49
cis-$[Co(en)_2(N_3)(Br)]^+$	194.8 (2)	47.5	227.7 (2)	92.5 (2)	48.5	48
cis-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$	174.9 (2)	38	230.7 (2)	98.3 (2)	40	39
trans-$[Co(en)_2(N_3)(Cl)]^+$	145.4 (2)	24	231.1 (2)	107.9 (2)	26	25
trans-$[Co(en)_2(N_3)(Br)]^+$	152.1 (2)	27	231.0 (2)	105.8 (2)	29	28
trans-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$	160.7 (6)	31	231.5 (6)			31
trans-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$	154.0 (2) 155.5^e	28.5	228.0 (2) 227.7^e			28.5

[a] λ in nm; number in parentheses denotes determinations. All experiments refer to $[OH^-] = 0.01-0.02$ M. [b] Isobestic point between *cis*- and *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$ ($\epsilon_{537} = 228.5$). [c] Calculated from ϵ_λ(obsd) and the relation % cis = $10^2(\epsilon_\lambda(\text{obsd}) - \epsilon_\lambda(\text{trans}))/(\epsilon_\lambda(\text{cis}) - \epsilon_\lambda(\text{trans}))$ and with the following ϵ values for *cis*- and *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$: 502 nm, $\epsilon_{\text{cis}} = 303.4$, $\epsilon_{\text{trans}} = 95.8$; 602 nm, $\epsilon_{\text{cis}} = 56.8$, $\epsilon_{\text{trans}} = 125.9$. [d] Results for 502 and 602 nm weighted equally. [e] Corrected for the path leading to *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ and that does not involve substitution at the metal center (refer to *d*, Table III). The following ϵ values were used for *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$: $\epsilon_{502} = 109.4$, $\epsilon_{602} = 88.6$, $\epsilon_{537} = 239.5$.

Table V. Summary of Results: Steric Course of Base Hydrolysis of $[Co(en)_2(NCS)X]^{n+}$ and $[Co(en)_2(N_3)X]^{n+}$ at 25 °C

	% cis product[a]				
substrate	method 1[b]	method 2[c]	method 3[d]	weighted av[e]	lit. value [*T*, °C]
cis-$[Co(en)_2(NCS)(Cl)]^+$	81 (8)	83 (6)	83 (2)[j]	82	82 [0][f]
cis-$[Co(en)_2(NCS)(Br)]^+$	73 (5)	77 (5)	75 (2)	75	
cis-$[Co(en)_2(NCS)(OSMe_2)]^{2+}$	71 (3)	73.5 (3)		72	
trans-$[Co(en)_2(NCS)(Cl)]^+$	70 (6)	70.5 (6)	70 (2)	70	76 [0],[f] 72.5 [20][f]
trans-$[Co(en)_2(NCS)(Br)]^+$	74 (8)	76 (6)	73 (2)	75	81 [0][f]
cis-$[Co(en)_2(N_3)(Cl)]^+$	46.5 (2)	49 (2)	48 (2)[j]	48	50 [0],[g] 44 [0][h,i]
cis-$[Co(en)_2(N_3)(Br)]^+$	46.5 (2)	48 (2)		47.5	
cis-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$	39 (6)	39 (2)		39	
trans-$[Co(en)_2(N_3)(Cl)]^+$	23 (2)	25 (2)		24	8 [0],[g] 24 [0][h,i]
trans-$[Co(en)_2(N_3)(Br)]^+$	24 (2)	28 (2)		26	17 [0][g]
trans-$[Co(en)_2(N_3)(O_2CH)]^+$			23 (2)	23	
trans-$[Co(en)_2(N_3)_2]^+$			26 (2)	26	30,[h] 33[h,i]
trans-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$	30 (6)	31 (6)		30.5	
trans-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$	25 (7)	28.5 (2)		26	

[a] Number in parentheses denotes determinations. [b] Data from Tables I and III; $[Co(en)_2(NCS)(OH)]^+$ and $[Co(en)_2(N_3)(OH)]^+$ products analyzed. [c] Data from Tables II and IV; $[Co(en)_2(NCS)(OH_2)]^{2+}$ and $[Co(en)_2(N_3)(OH_2)]^{2+}$ products analyzed. [d] Data from Table VI; isosbestic point(s) method. [e] ±2%. [f] Ingold, C. K.; Nyholm, R. S.; Tobe, M. L. *J. Chem. Soc.* **1956,** 1591. [g] Ricevuto, V.; Tobe, M. L. *Inorg. Chem.* **1970,** *9,* 1785. [h] Stapes, P. J.; Tobe, M. L. *J. Chem. Soc.* **1960,** 4803. [i] Recalculated from the original data by using the correct molar extinction coefficients for *cis*- ($\epsilon^{502} = 303.4$) and *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$ ($\epsilon^{502} = 95.8$). [j] Ion-exchange separation and determination of *cis*- and *trans*-$[Co(en)_2A(OH)]^+$ products (see Experimental Section).

corded for the products in both basic (Tables I, III) and acidic (Tables II, IV) media, as an independent check on the stereochemistry. The *cis*- and *trans*-$[Co(en)_2(NCS)(OH_2)]^{2+}$ and $[Co(en)_2(NCS)(OH)]^+$ spectra differ significantly as do those of the analogous azido complexes, and the agreement between the two sets of results (Table V) strongly supports the analysis.

Table VI. Isosbestic Point Data for the Base Hydrolysis of $[Co(en)_2(NCS)X]^{n+}$ and $[Co(en)_2(N_3)X]^{n+}$ at 25 °C

		ϵ_λ of products, $M^{-1}\ cm^{-1}$ (λ, nm)[c]		
reactant	medium[a]	ϵ(obsd)	ϵ(calcd)	% cis product[b]
cis-$[Co(en)_2(NCS)(Br)]^+$	0.01 M dieth, pH 9	153.0 (503)	152.5 (503)	75
		98.2 (464)	98.3 (464)	75
trans-$[Co(en)_2(NCS)(Br)]^+$	0.01 M dieth, pH 9	102.0 (538)	102.5 (539)	73
		49.5 (440)	48.5 (439)	73
	5×10^{-4} M OH^-	102.5 (539)	102.5 (539)	73
		49.0 (439)	48.5 (439)	73
trans-$[Co(en)_2(NCS)(Cl)]^+$	0.01 M dieth, pH 9	113.0 (532)	111.5 (531)	70
		43.5 (432)	42.5 (433)	70
	10^{-3} M OH^-	114.0 (531)	111.5 (531)	70
		45.5 (433)	43.5 (433)	70
trans-$[Co(en)_2(N_3)_2]^+$	0.1 M OH^-	159.5 (517)	159.5 (517)	26
		51.0 (463)	50.0 (463)	26
trans-$[Co(en)_2(N_3)(O_2CH)]^+$	0.01 M OH^-	132.8 (508)	133.6 (507)	23
		41.8 (452)	41.5 (452)	23

[a] dieth = 2,2′-iminobis(ethanol) buffer; OH^- media, unbuffered. [b] Calculated from the relation $\epsilon(obsd) = (\% \ cis/10^2)\epsilon(cis) + (\% \ trans/10^2)\epsilon(trans)$. The % cis (column 5, (=100 − % trans)) has been chosen to best fit the results for the two isosbestic points observed for each substrate. The following molar extinction coefficient data for $[Co(en)_2A(OH)]^+$ were used. $[Co(en)_2(N_3)(OH)]^+$: $\epsilon_{517}(cis) = 219.8$, $\epsilon_{517}(trans) = 138.3$; $\epsilon_{463}(cis) = 70.6$, $\epsilon_{463}(trans) = 42.3$; $\epsilon_{507}(cis) = 204.0$, $\epsilon_{507}(trans) = 112.5$; $\epsilon_{452}(cis) = 51.1$, $\epsilon_{452}(trans) = 38.6$. $[Co(en)_2(NCS)(OH)]^+$: $\epsilon_{539}(cis) = 104.1$, $\epsilon_{539}(trans) = 98.0$; $\epsilon_{439}(cis) = 52.0$, $\epsilon_{439}(trans) = 39.3$; $\epsilon_{503}(cis) = 170.9$; $\epsilon_{503}(trans) = 97.2$; $\epsilon_{464}(cis) = 110.5$, $\epsilon_{464}(trans) = 61.8$; $\epsilon_{531}(cis) = 122.5$, $\epsilon_{531}(trans) = 85.5$; $\epsilon_{433}(cis) = 45.0$, $\epsilon_{433}(trans) = 36.4$. [c] All results are in duplicate.

Furthermore, the steric course is independent of $[OH^-]$, at least up to 0.1 M.

The product proportions indicated by the isosbestic point data (Table VI) are consistent, although generally this was a less sensitive method of analysis. For *trans*-$[Co(en)_2(N_3)_2]^+$ and $[Co(en)_2(N_3)(O_2CH)]^+$ this was the only method because the hydrolysis products rearrange significantly in the time required to completely base hydrolyze these relatively inert complexes. For their cis forms, also relatively inert, no isosbestic points were observed (680–380 nm). This was a predictable result since the absorption spectra of either of these substrates and a 50% *cis*-/50% *trans*-$[Co(en)_2(N_3)(OH)]^+$ product do not overlap in this region.

Table V summarizes the steric course results for the 14 base hydrolysis reactions studied. The present data are generally ≤±2% cis. The new data extend the range of leaving groups to include the neutral Me_2SO and $Me_2N{\cdot}CHO$ as well as anionic Cl^-, Br^-, N_3^-, and HCO_2^-.

The results for the $[Co(en)_2(NCS)X]^+$ systems (Table V) reveal a good agreement with the previous[13] and more limited results, especially when an apparent temperature dependence of the steric course is accommodated. All our data refer to 25 °C. Earlier results[13] for *trans*-$[Co(en)_2(NCS)(Cl)]^{2+}$ at 0 °C (76% cis product) and 20 °C (72.5% cis) suggest agreement with our 25 °C number (70% cis). Furthermore, the 0 °C results for *trans*-$[Co(en)_2(NCS)X]^+$ (X = Br^-, 81%; Cl^-, 76% cis) indicate more cis product (~5%) for the bromo complex, as we found at 25 °C (75 and 70% cis, respectively; Table V). The identity of the present (25 °C) and previous[13] (0 °C) results for *cis*-$[Co(en)_2(NCS)(Cl)]^+$ (82% cis) could be more apparent than real since the temperatures are different. An appreciable temperature dependence of the steric course of hydrolysis has been demonstrated previously.[16]

The new and previous results[12,17] for the $[Co(en)_2(N_3)X]^+$ systems reveal clear discrepancies. For example, *trans*-$[Co(en)_2(N_3)X]^+$ (X = Br^-, Cl^-) ions were recently reported[12] to give 17% and 8% cis product, respectively, at 0 °C. We find 26% and 24% cis product (25 °C), removing the apparent dependence on leaving group. These and other variations (Table V) cannot reasonably be ascribed to the temperature difference. Both *cis*- and *trans*-$[Co(en)_2(N_3)X]^+$ complexes were, at that time, difficult to obtain pure.[11,15] Furthermore, the spectra for the *cis*- and *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$ ions used in the previous product analyses[17] have been shown[11,15] to be in gross error, although when the earliest data[17] are corrected for this (Table V), the differences between the results are appreciably reduced. For *cis*-$[Co(en)_2(N_3)(Cl)]^+$, but not for *trans*-$[Co(en)_2(N_3)_2]^+$ (Table V), this difference could reside in the temperature.

It is appropriate to remark that in the synthesis of $[Co(en)_2(NCS)X]^+$ (and especially $[Co(en)_2(N_3)X]^+$), small but significant impurities comprising mixtures of $[Co(en)_2(NCS)_2]^+$ and $[Co(en)_2X_2]^+$ can easily result unless special precautions are taken. This is not readily detected by elemental analysis, but as described here (see Experimental Section) and elsewhere,[11,15] ion-exchange chromatography is profitably employed to detect as little as a 0.5% stoichiometric or isomeric impurity. Also, the constant (±0.5%) spectra of different salts of the same cation testify to the homogeneity of our samples; changing the counterion is expected to change the solubilities of impurities relative to the desired cation.

Finally in this section we note that the steric course of base hydrolysis was determined for some of the reactions by a direct chromatographic method. The *cis*- and *trans*-$[Co(en)_2A(OH)]^+$ hydrolysis products were separated and individually determined by spectrophotometry. These results (Table V) internally agree very well, and it is clear that the claimed accuracy (% cis, ±2%) is warranted. Although now the preferred tool in modern product analyses of this kind, the ion-exchange separation method offers no real advantages in accuracy except when the (two) product proportions differ greatly (>85:15), or as in anion competition studies,[7,8] there can be three or more light-absorbing species to accommodate if the products are not first separated.

Base Hydrolysis of *trans*-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$. This reaction warrants special comment. The amide complex can hydrolyze at the metal center as well as at the ligand.[18] The results (Tables III and IV) suggested normal base hydrolysis, but it was conceivable that C–N cleavage to produce *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ (and Me_2NH) first occurred, followed by normal base hydrolysis through to $[Co(en)_2(N_3)(OH)]^+$ (and HCO_2^-). It was important to distinguish the alternatives since, in the former case, the leaving group is neutral and in

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(18) Buckingham, D. A.; Harrowfield, J. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726.

the latter, anionic, and there was a particular interest in examining the effect on the steric course of a change in charge of the leaving group.

cis- and *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ were synthesized and their properties examined. An isomeric mixture (~2:1 trans:cis) was obtained in good yield by the HCO_2^- anation of *cis*- or *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$. The isomers were easily separated by fractional crystallization as their $S_2O_6^{2-}$ salts or by ion-exchange chromatography on Sephadex. The two isomers were characterized by elemental analysis, by visible and ^1H NMR spectroscopy, and by their elution behavior from Sephadex (characteristically, the less polar trans ion is eluted first). The visible spectra were found to closely resemble those[11,15] of the corresponding *cis*- and *trans*-$[Co(en)_2(N_3)(OH_2)]^{2+}$ ions. It follows that any formato complex produced in the base hydrolysis reaction of $[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$ would not be readily distinguished spectrophotometrically from $[Co(en)_2(N_3)(OH_2)]^{2+}$, even if it survived the treatment with OH^-. However, both *cis*- and *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ were shown to base hydrolyze very slowly; <5% reacts in the time allowed (~2 min) to completely base hydrolyze the *trans*-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$ complex in 0.01 M OH^- at 25 °C. Therefore *direct* evidence for a C–N cleavage path was sought. In four experiments in which the acid-quenched products of base hydrolysis of the DMF complex were exchanged on Sephadex, a weak mauve band (trans 1+ ion, 3.3 ± 0.3%) was eluted well in front of $[Co(en)_2(N_3)(OH_2)]^{2+}$ (97%). The visible spectrum of this minor component exactly matched that of authentic *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$. *cis*-$[Co(en)_2(N_3)(O_2CH)]^+$, which elutes behind the trans form, was not observed. No formato complex (<0.2%) was found in a blank experiment in which the DMF complex (1 g) was completely hydrolyzed in 0.01 M $HClO_4$, and the *trans*-azido–formato complex therefore arises as a direct result of base hydrolysis.

The $[Co(en)_2(N_3)(OH)]^+$ and $[Co(en)_2(N_3)(OH_2)]^{2+}$ product spectra (Tables III and IV) have been corrected for the presence of *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ (3.3%), and in passing the steric course of base hydrolysis of the *trans*-azido–formato ion has been determined (Tables V and VI). The major part of the base hydrolysis reaction of $[(NH_3)_5Co(OCHNMe_2)]^{3+}$ is ligand hydrolysis (88% of $[(NH_3)_5Co(O_2CH)]^{2+}$ and 12% of $[(NH_3)_5Co(OH)]^{2+}$ at 25 °C).[18] The result for the corresponding reaction of the *trans*-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$ complex is therefore surprising—only 3.3% C–N cleavage. This can be understood if the metal ion substitution path for this bis(ethylenediamine) complex is much faster than that for the pentaammine species, and this seems likely. For example, *trans*-$[Co(en)_2(N_3)X]^+$ ($X = Cl^-$, N_3^-) base hydrolyzes (by Co–X cleavage) from 20- to 30-fold faster than the corresponding $[(NH_3)_5CoX]^{2+}$ ions.[19] However, this factor alone is insufficient to accommodate the ~230-fold change in the $[CoOH^{n+}]/[Co(O_2CH)^{n+}]$ ratio, from 0.14 (12:88) to 32.3 (97:3) on going from $[(NH_3)_5Co(OCHNMe_2)]^{3+}$ to *trans*-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$. It follows that the latter complex is either unusually reactive in Co–O cleavage or that nucleophilic attack at the carbonyl center by OH^- is unusually slow (in fact, ~70-fold slower than for the pentaammine complex). The latter is not unreasonable since the bis(ethylenediamine) complex is a 2+ ion whereas the pentaammine species is 3+. Other explanations can be advanced—see for example the work on $[Co([15]aneN_5)(OCHNMe_2)]^{3+}$.[20] This complex hydrolyzes at the ligand ~30-fold slower than $[Co(NH_3)_5(OCHNMe_2)]^{3+}$, and yet these ions bear the same 3+ charge.

Table VII. Stereochemistry of Base Hydrolysis of Λ-*cis*-$[Co(en)_2(NH_3)X]^{n+}$ and *trans*-$[Co(en)_2(NH_3)X]^{n+}$ at 25 °C and $\mu = 1$ M

reactant	% cis product (±1%)	% Λ-cis product[i] (±2%)	% trans product (±1%)	ref
Λ-*cis*-$[Co(en)_2(NH_3)(Cl)]^{2+}$	78	61.5	22	*a, e*
	77.5	61	22.5	*b, e*
	77.5	55	22.5	*c, e*
	77.5	57.5	22.5	*a, g*
Λ-*cis*-$[Co(en)_2(NH_3)(Br)]^{2+}$	77	57	23	*a, e*
	77.5	57.5	22.5	*b, e*
	78.5	55.5	22.5	*b, g*
	78	56.5	22.5	*a, g*
Λ-*cis*-$[Co(en)_2(NH_3)(ONO_2)]^{2+}$	77	61	23	*a, e*
	77.0	61.5	23	*b, e*
	77.5	58	22.5	*c, e*
Λ-*cis*-$[Co(en)_2(NH_3)(OSMe_2)]^{3+}$	77	67	23	*a, g*
	77	67	23	*d, g*
Λ-*cis*-$[Co(en)_2(NH_3)(OP(OMe)_3)]^{3+}$	77.5	70	22.5	*a, g*
	77.5	70	22.5	*d, g*
trans-$[Co(en)_2(NH_3)(Cl)]^{2+}$	64		36	*a, e*
	64.5		35.5	*b, e*
	64		36	*c, e*
trans-$[Co(en)_2(NH_3)(ONO_2)]^{2+}$	63		37	*a, e*
	64		36	*b, e*
	64		36	*c, e*
trans-$[Co(en)_2(NH_3)(SCN)]^{2+}$	64		36	*h, f*
	66		34	*c, f*

[a] 1 M $NaClO_4$. [b] 1 M NaN_3; other products are $[Co(en)_2(NH_3)(N_3)]^{2+}$ (24–27% of total Co). [c] 1 M NaNCS; other products are $[Co(en)_2(NH_3)(SCN)]^{2+}$ and $[Co(en)_2(NH_3)(NCS)]^{2+}$ (~27% of total Co). [d] 1 M NaN_3; other products are $[Co(en)_2(NH_3)(N_3)]^{2+}$ (30–31% of total Co). [e] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968,** *90,* 6654. [f] Buckingham, D. A.; Creaser, I. I.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1972,** *11,* 2738. [g] Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Ibid.* **1979,** *18,* 1985. [h] $\mu = 0.1$ M (NaOH). [i] % Λ-cis = 10^2[Λ-cis]/[total cobalt].

Role of the Leaving Group. The question of the leaving group (X) dependence of the steric course of base hydrolysis of *cis*- and *trans*-$[Co(en)_2AX]^{n+}$ ions is an important one because it relates directly to mechanism. A cis/trans product ratio that is *approximately* independent of X implies a Co–X bond that is well stretched at the transition state, i.e., d activation (I_d mechanism). A product ratio that is *strictly* independent of X not only implies d activation but also implies that the Co–X bond has been completely severed to produce a five-coordinate intermediate and that X has departed, i.e., an $S_N1(lim)$[2] or a D mechanism.[3] In the past, precise measurements of the proportions of the isomeric hydrolysis products have been lacking (except for $[Co(en)_2(NH_3)X]^{n+}$) or of dubious accuracy, and a clear distinction between I_d and D mechanisms was not possible. We set out to more accurately define the steric of base hydrolysis for the $[Co(en)_2(N_3)X]^{n+}$ and $[Co(en)_2(NCS)X]^{n+}$ systems and to broaden the range of leaving groups (usually Cl^- or Br^-) to include additional anions and some neutral ligands. Of course a constant steric course, even when defined more accurately, does not guarantee a D mechanism, since coincidence could be argued. However, the greater the number of examples that conform, the stronger is the case militating against multiple coincidence. Furthermore, broadened conditions and improved accuracy more readily permit the identification of examples where X *does* measureably affect the stereochemical outcome.

Along with the new data for $[Co(en)_2(NCS)X]^{n+}$ and $[Co(en)_2(N_3)X]^{n+}$ (Table V), recent accurate results for the steric course of base hydrolysis of (+)-*cis*- and *trans*-$[Co(en)_2(NH_3)X]^{n+}$ are compiled in Table VII. These two tables contain sufficient reliable information to draw some definite

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(19) Data from a compilation by: Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.

(20) Hay, R. W.; Bembi, R. *Inorg. Chim. Acta* **1982**, *64*, L199.

conclusions about the detailed mechanism of base hydrolysis of $[Co(en)_2AX]^{n+}$.

First, it is clear that in the pentaamine systems cis and trans reactants give different product proportions (78% and 64% cis, respectively; Table VII). This is usual. Furthermore, the cis/trans product ratio can be seen to be *strictly* independent of the leaving group (cis reactants, five different X; trans reactants, three). This result holds for both the $[Co(en)_2(NH_3)OH]^{2+}$ and $[Co(en)_2(NH_3)Y]^{2+}$ competition products obtained in various media (1 M NaY; Y = ClO_4^-, N_3^-, ClO_4^-), although of course the isomer proportions differ for the water and Y^- capture paths.[7,8] The steric course is also independent of the concentration and nature of supporting electrolyte, and it is independent of the $[OH^-]$.

Second, a small but significant leaving group dependence of the Λ-/Δ-cis product ratio has been detected (Table VIII).[8] This small dependence was seen also in the $[Co(en)_2(NH_3)(N_3)]^{2+}$ product derived from N_3^- competition. Thus, as a result of the better definition of the product proportions than previously and because of the additional and more sensitive stereochemical probe (optical activity), a definite leaving-group-dependent product distribution for the base hydrolysis of $[Co(en)_2AX]^{n+}$ was established for the first time.

There are two additional points. The dependence of the steric course on X was found only for the active cis isomers, and then only when the leaving group was changed from an anion (Cl^-, Br^-, NO_3^-) to a neutral species (Me_2SO, $PO(OMe)_3$).[8] Also, and a related fact, the base hydrolysis of each of the three isomers derived from $[Co(Metren)(NH_3)X]^{n+}$ (X = Cl^-, Br^-, NH_3), a more sensitively stereochemically signposted system, yields isomeric product distributions that depend upon X, and this is particularly clear when X is changed from anionic Cl^- or Br^- to neutral NH_3.[21]

In light of these observations, it occasions little surprise that the refined data for the $[Co(en)_2(NCS)X]^{n+}$ and $[Co(en)_2(N_3)X]^{n+}$ reactions (Table V) also reveal a clear dependence of the stereochemical outcome on X. For anionic X (Cl^-, Br^-, N_3^-, HCO_2^-), a constant stereochemistry is observed for both *cis*-$[Co(en)_2(N_3)X]^+$ (48% cis product) and *trans*-$[Co(en)_2(N_3)X]^+$ (25% cis), but for the neutral leaving group Me_2SO, both the cis and trans reactants show significant variations. *cis*-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$ gives ca. 9% less cis product than for the other (two) cis azido ions, while *trans*-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$ yields ca. 5% more cis product than for the other (five) trans azido complexes. Surprisingly, the result for *trans*-$[Co(en)_2(N_3)(OCHNMe_2)]^{2+}$ does not depart from the norm (26% cis product).

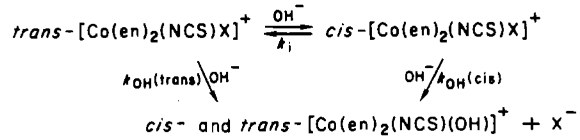
The $[Co(en)_2(NCS)X]^+$ results also reveal a small but real X dependence of the steric course. The *cis*-$[Co(en)_2(NCS)(OSMe_2)]^{2+}$ ion gives marginally less (72%) and the *cis*-$[Co(en)_2(NCS)(Cl)]^+$ ion significantly more cis product (82%) than does *cis*-$[Co(en)_2(NCS)(Br)]^+$ (75%). Thus, the result for Cl^- could be regarded as different. For *trans*-$[Co(en)_2(NCS)X]^+$ (X = Br^-, Cl^-), the bromo complex gives ca. 5% more cis product.

Clearly, the data show that the effect of the leaving group is not confined to charge alone.

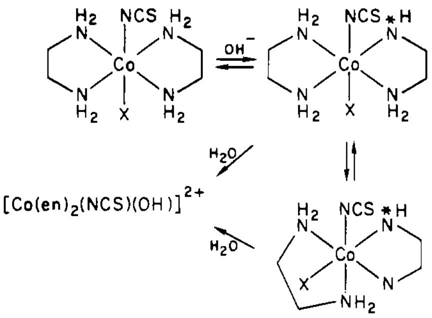
In summary, the collective steric course data (Tables V and VII) show small but definite dependences on X. This work represents the first time this has been seen for the cis/trans product distributions of the base hydrolysis reactions of $[Co(en)_2AX]^{n+}$ complexes.

There now seems little point in efforts to further improve the precision of the steric course measurements. There exist several (six) exceptions to a constant steric course result, and it seems likely that more accurate data would reveal several more. Indeed, *all* the steric course results could prove to be detectably dependent upon the leaving group.

Scheme II



Scheme III



There is no clear relationship in the leaving group dependence of the steric course. Most, but not all, of the "anomalies" involve the neutral leaving groups. The $[Co(en)_2(NCS)X]^{n+}$ data reveal differences even within the set of results for anionic leaving groups. And we can see no correlation with reactivity or donor type or bonding geometry of X. It is noted that the σ-donor pentaamine systems $[Co(en)_2(NH_3)X]^{n+}$ do not show a cis/trans product ratio that is detectably dependent upon X, whereas for the $[Co(en)_2AX]^{n+}$ systems where A is a potential π donor or acceptor (N_3^-, NCS^-) the results do reveal such a dependence. More data are required to comment further.

Mechanistic Implications. One result that has always been clear, namely that the steric course of base hydrolysis of $[Co(en)_2AX]^{n+}$ does not depend *greatly* on X, implies dissociative activation, and this is already widely accepted.[2,3,6] Nonetheless, the question as to why the result *does* depend on X, albeit slightly, must be addressed.

Several explanations may be advanced. First, base-catalyzed preisomerization could be competitive with base hydrolysis (Scheme II). This suggestion requires that intramolecular rearrangement of the conjugate base, the widely accepted reactive intermediate in the base hydrolysis reaction, to compete with hydrolysis of X (Scheme III). Measured rates of base hydrolysis and estimated pK_a values (~16) for the weakly acidic amine centers lead to first-order rate constants for the order of $\sim 10^4\ s^{-1}$ for hydrolysis of the conjugate base complex at 25 °C. This order of reactivity is not too dissimilar from that for the intramolecular rearrangement of fluxional (octahedral) labile metal–chelate complexes. Indeed, the enormous enhancement in substitution rates, afforded by the aminate ion, for the reactions of the normally kinetically inert cobalt(III) complexes has been attributed to a change in spin state,[22] from diamagnetic to a paramagnetic d^6 state; the rearrangements of the isoelectronic and paramagnetic d^6 Fe(II) complexes are usually very rapid. In at least one case, an exceptionally fast base-catalyzed internal rearrangement of a cobalt(III) complex has been demonstrated,[23] although admittedly examples are rare. Chiral tris(ethylenediamine)cobalt(III), for example, does not racemize rapidly in base.

In Scheme II, the relative rates of the direct (k_{OH}) and indirect (k_i) paths to hydroxo product must depend on X; hence, so also must the final stereochemistry. In the limit,

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(21) Buckingham, D. A.; Edwards, J. O.; Lewis, T. W.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 892.

(22) Archer, R. D. *Adv. Chem. Ser. No. 62*, **1967**, 452.

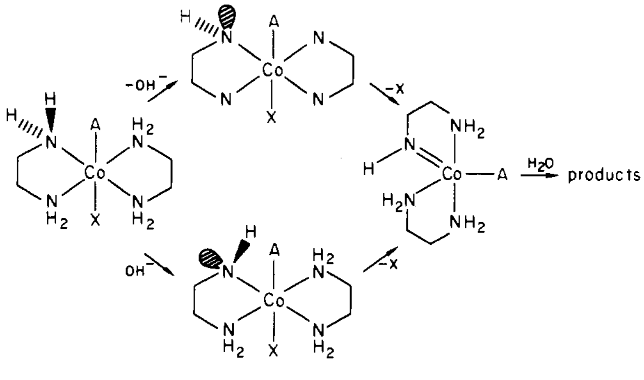
(23) Jackson, W. G.; Sargeson, A. M.; Watson, A. D. results to be submitted for publication.

$k_i >> k_{OH}$, the *same* stereochemistry must be observed starting with either *cis*- or *trans*-$[Co(en)_2AX]^{n+}$. For $[Co(en)_2(NCS)(Br)]^+$ this is the case (75% cis product, Table V), a fact that suggested the possibility of preisomerization. However, this limiting case ($k_i >> k_{OH}$) can be dispensed with immediately, since it requires *both* the observed stereochemistries and observed rates of base hydrolysis for the cis and trans isomers to be identical. No $[Co(en)_2AX]^{n+}$ system meets these requirements, not even $[Co(en)_2(NCS)(Cl)]^+$ (k_{OH}(cis) 1.40, k_{OH}(trans) = 0.34 M^{-1} s^{-1}, 0 °C).[13] Another difficulty with the mechanism is that, commencing with the more reactive isomer (cis), consecutive reactions should be observed, because the other isomer (trans) would accumulate and then decay to hydroxo product. Although the idea of preisomerization, in the context of base hydrolysis, does not seem to have been entertained before, the literature data provide no evidence of consecutive reactions in support of it. However, it remains a possibility that a preisomerization pathway could compete significantly with base hydrolysis when the substrate is the less reactive isomer. The preisomerized complex would not accumulate since it hydrolyzes faster than it forms, and biphasic kinetics would be difficult to detect under the usual conditions of base hydrolysis. We have checked this possibility by incompletely base hydrolyzing both *cis*- and *trans*-$[Co(en)_2(NCS)(Cl)]^+$, using a low concentration and less than a stoichiometric quantity of OH^-. The second-order rate constants for base hydrolysis of the cis and trans isomers differ by a factor of 4,[13] and it is readily shown that, under the conditions above, appreciable amounts of the other isomer would accumulate if preisomerization were significant. The acid-quenched products were ion exchanged on Sephadex, and recovered reactant was shown to be isomerically pure in each case (see Experimental Section). It is concluded that the leaving group dependence of the steric course of base hydrolysis, at least for the above complexes, does not arise through a competitive preisomerization pathway.

A second explanation for the dependence of the steric course on the leaving group arises if reaction occurs through two (or more) conjugate base complexes. The relative rates at which they are generated must depend upon X, and each will have different stereochemical outcomes. Proton-exchange studies indicate that, for complexes such as *cis*-$[Co(en)_2(NH_3)(Cl)]^{n+}$, which have several (at least five) inequivalent sites for deprotonation, one site is especially acidic (that trans to Cl^-).[7] It is clear that the conjugate base arising from trans-Cl deprotonation is 100-fold more abundant than any other. The difficulty in drawing a clear conclusion from this fact is that reaction could occur through a less abundant although more reactive conjugate base, and this vexing question, despite several elegant studies designed to answer it,[5] remains an outstanding problem in base hydrolysis studies.[5] Moreover, proton-exchange studies have not been performed for *cis*- or *trans*-$[Co(en)_2AX]^{n+}$ complexes other than those for which X = Cl^-, and results for the $[Co(NH_3)_5X]^{n+}$ systems indicate that the relative acidity of the potential sites for deprotonation are quire sensitive to X.[24]

The *trans*-$[Co(en)_2AX]^{n+}$ complexes have only two different sites for deprotonation, each cis to the leaving group X. Furthermore, if the aminato center becomes planar[2,3] or nearly so en route to products, the steric course of water entry should be the same via either conjugate base. This argument assumes that a reduced coordination number intermediate is involved (Scheme IV). Previously, only cis complexes have been unequivocally established to base hydrolyze with a stereochemistry depending upon X.[8] The present work has uncovered one or two trans ions that behave similarly (e.g. *trans*-$[Co(en)_2(N_3)(OSMe_2)]^{2+}$, Table V). The effect, while not large, is nonetheless real, and it is comparable to the variations seen for the cis complexes. One premise of the argument might be challenged, namely that the deprotonated amine center becomes essentially planar (through π bonding) en route, occupying an equatorial site of an essentially trigonal-bipyramidal transition state.[2,3] Although there is considerable evidence to support this case,[5,25] it is not unequivocal. In at least one instance ($\alpha\beta$-$[Co(tetraen)X]^{2+}$), the stereochemical results are difficult to rationalize without invoking a π-aminato, reduced coordination number intermediate.[5,26]

Scheme IV



It is concluded that the effect of the leaving group on the steric course is not satisfactorily accommodated by changes in the populations of two conjugate base complexes effective in base hydrolysis, at least for the trans complexes, unless planar π-bonded intermediates (*or* a reduced coordination number intermediate) are *not* involved. The question remains unresolved, because appreciable π bonding is possible without *exact* coplanarity, and this may be sufficient to accommodate a small difference in steric course between the two possible conjugate base forms of trans complexes.

A recent statement that the actual site of deprotonation may be irrelevant warrants comment. It has been suggested that the bound aminate ion, even if generated exclusively at one of several inequivalent sites, may be rapidly (intramolecularly) scrambled.[8] Contrary to earlier beliefs,[5,7] this possibility is not in conflict with the experimental fact that, within the same complex, different rates for proton exchange can be observed; proton abstraction by OH^- is rate determining. Nonetheless, it can be shown that the relative rates of proton exchange do still reflect the relative *abundances* of the various aminato (conjugate base) species, whether in rapid equilibrium or not. However, rapid aminate site exchange does imply that the measured rates of proton exchange do not relate to the relative acidities of the parent amine centers, a fact of wider mechanistic implications. It is not germane to the issues here and will be taken up elsewhere.

A third and obvious explanation for the small but real effect of the leaving group on the steric course of base hydrolysis arises if the reactions do not involve a common reduced coordination number intermediate. Thus, with a transition state containing X, the steric course of water entry must depend upon X. The key question is the degree of influence of bonded X. Recent arguments for and against this view have been presented.[1,8,27] Certainly it has always been recognized that, if common reduced coordination number intermediates are involved, they are very short lived.[4,7,28] Indeed it is certain that their lifetime is insufficient for the *complete* adjustment of metal–ligand bond angles[8,21] and pseudorotation[7] within the

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(24) Bramley, R.; Creaser, I. I.; Mackey, D. J.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 244.

(25) Henderson, R. A.; Tobe, M. L. *Inorg. Chem.* **1977**, *16*, 2576.

(26) Marzilli, P. A.; Sargeson, A. M., unpublished results.

(27) Reynolds, W. L.; Hafezi, S. *Inorg. Chem.* **1978**, *17*, 1819.

(28) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5129.

five-coordinate state. To illustrate, it is noted that *cis*- and *trans*-$[\mathrm{Co(en)_2AX}]^{n+}$ do not lead to a common stereochemical outcome for attack by H_2O or any other nucleophile (A = OH^-[9] and NCS^- expected), and N_3^- attack has been shown[7] to be faster than the intramolecular rearrangement (pseudorotation) of any intermediate. Despite these facts, steric change in base hydrolysis can be appreciable (up to 92% steric change),[2] and this can be argued as reflecting the preferred site of nucleophilic attack on an intermediate, rather than reflecting a stereochemistry for the intermediate that differs appreciably from its precursor. Indeed, results show conclusively that the intermediate inherits much of its stereochemical detail directly from its precursor. For example, a chiral cis complex *invariably* gives a cis product having a retained (>50%) absolute configuration, even when cis to trans rearrangement exceeds 50%. Other "rules" for stereochemical change in base hydrolysis,[2,3] first proposed in the early 1950s and based on a principle of minimal rearrangement in the (first) step leading to the intermediate, remain true. For example, a cis reactant always give more cis hydroxo product than a trans reactant, again reflecting a geometry for the intermediate inherited from the substrate. It should be stated that two versions of these "rules" exist, one based on OH^- deprotonation indiscriminantly trans or cis[2] and the other[29] on OH^- deprotonation exclusively cis to the leaving group, but the essence of these rationalizations, relevant to the above discussion, is the same.

In conclusion, the steric course data are accommodated by common reduced coordination number intermediates. As generally agreed, they must be extremely short-lived if they do exist, to the extent that they "remember" their parentage since the leaving group remains sufficiently close, once dissociated, to very *slightly* but detectably affect the steric course of water entry. This view is consistent with anion competition data for both $[\mathrm{Co(NH_3)_5X}]^{n+}$[1,27,30,31] and $[\mathrm{Co(en)_2(NH_3)X}]^{n+}$[7,8] systems, where the respective reduced coordination number intermediates do not survive long enough to equilibrate their inherited ion atmospheres with the bulk solution. To reject the view that reactive pentacoordinate intermediates are involved, the simpler and the seemingly more logical conclusion, is to ignore the *very slight* effect of the leaving group. For the alternative (single step) I_d process,[8,21,27] a weakly bonded leaving group, at the transition state, must be relatively close (say, ~300 pm) to the metal center, and its effect on the steric course of water entry might be expected to be more profound than is observed, particularly when its bulk, geometry, and charge are appreciably varied. Clearly the lifetime of the intermediate is a crucial issue, and further experiments pertinent to this will be described elsewhere.[32]

Registry No. *cis*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{Cl}$, 13820-99-0; *cis*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{NCS}$, 15304-77-5; *cis*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{ClO_4}$, 82704-34-5; *trans*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{Br}$, 15362-24-0; *trans*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{NCS}$, 16949-72-7; *trans*-$[\mathrm{Co(en)_2(NCS)(Cl)}]\mathrm{ClO_4}$, 13820-98-9; *cis*-$[\mathrm{Co(en)_2(NCS)(Br)}]\mathrm{Br}$, 88510-74-1; *cis*-$[\mathrm{Co(en)_2(NCS)(Br)}]\mathrm{ClO_4}$, 88510-76-3; *trans*-$[\mathrm{Co(en)_2(NCS)(Br)}]\mathrm{Br}$, 88510-75-2; *trans*-$[\mathrm{Co(en)_2(NCS)(Br)}]\mathrm{NCS}$, 51850-40-9; *trans*-$[\mathrm{Co(en)_2(NCS)(Br)}]\mathrm{ClO_4}$, 88510-77-4; *cis*-$[\mathrm{Co(en)_2(NCS)(OSMe_2)}]\mathrm{NO_3ClO_4}$, 88510-73-0; *trans*-$[\mathrm{Co(en)_2(NCS)(OSMe_2)}](\mathrm{ClO_4})_2$, 88586-02-1; *cis*-$[\mathrm{Co(en)_2(NCS)(OH_2)}]^{2+}$, 24913-07-3; *trans*-$[\mathrm{Co(en)_2(NCS)(OH_2)}]^{2+}$, 24913-06-2; *cis*-$[\mathrm{Co(en)_2(NCS)(OH)}]^{+}$, 88585-99-3; *trans*-$[\mathrm{Co(en)_2(NCS)(OH)}]^{+}$, 46139-39-3; *cis*-$[\mathrm{Co(en)_2(N_3)(Cl)}]\mathrm{ClO_4}$, 65760-54-5; *cis*-$[\mathrm{Co(en)_2(N_3)(Cl)}]^{+}$, 29544-71-6; *trans*-$[\mathrm{Co(en)_2(N_3)(Cl)}]\mathrm{ClO_4}$, 30051-75-3; *trans*-$[\mathrm{Co(en)_2(N_3)(Cl)}]^{+}$, 20487-55-2; *cis*-$[\mathrm{Co(en)_2(N_3)(Br)}]\mathrm{ClO_4}$, 65794-85-6; *cis*-$[\mathrm{Co(en)_2(N_3)(Br)}]^{+}$, 65794-31-2; *trans*-$[\mathrm{Co(en)_2(N_3)(Br)}]\mathrm{ClO_4}$, 82704-31-2; *trans*-$[\mathrm{Co(en)_2(N_3)(Br)}]^{+}$, 29770-06-7; $[\mathrm{Co(en)_2(N_3)_2}]^{+}$, 24996-36-9; *cis*-$[\mathrm{Co(en)_2(N_3)(O_2CH)}](\mathrm{S_2O_6})_{1/2}$, 88510-71-8; *trans*-$[\mathrm{Co(en)_2(N_3)(O_2CH)}](\mathrm{S_2O_6})_{1/2}$, 88585-98-2; *cis*-$[\mathrm{Co(en)_2(N_3)(OSMe_2)}]\mathrm{NO_3ClO_4}$, 59302-02-2; *cis*-$[\mathrm{Co(en)_2(N_3)(OSMe_2)}]^{2+}$, 59302-01-1; *trans*-$[\mathrm{Co(en)_2(N_3)(OSMe_2)}]^{2+}$, 82768-62-5; *trans*-$[\mathrm{Co(en)_2(N_3)(OCHNMe_2)}]^{2+}$, 82704-32-3; *cis*-$[\mathrm{Co(en)_2(OH_2)(N_3)}]\mathrm{S_2O_6}$, 65760-57-8; *cis*-$[\mathrm{Co(en)_2(N_3)(OH_2)}]^{2+}$, 29770-08-9; *trans*-$[\mathrm{Co(en)_2(N_3)(OH_2)}]\mathrm{S_2O_6}$, 65760-56-7; *trans*-$[\mathrm{Co(en)_2(N_3)(OH_2)}]^{2+}$, 29770-07-8; *cis*-$[\mathrm{Co(en)_2(N_3)(OH)}]^{+}$, 88586-00-9; *trans*-$[\mathrm{Co(en)_2(N_3)(OH)}]^{+}$, 65802-29-1; DMF, 68-12-2.

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(32) The *trans*-$[\mathrm{Co(en)_2(NCS)(OS(CH_3)_2)}](\mathrm{ClO_4})_2$ complex has now been synthesized and its stereochemistry of base hydrolysis determined. The result (72 ± 2% cis product) is identical with that for the corresponding cis reactant.