Cobalt(III)-Promoted Lysis at Saturated Carbon. Examples of Internal Nucleophilic Displacement

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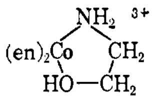
Abstract: Treatment of *cis*-$[Co(en)_2(NH_2CH_2CH_2Br)Br]^{2+}$ with OH^- in the pH range 8–14 results in the hydrolysis of coordinated Br^- followed by lysis of bromide in the coordinated amine. The first process has a rate law $k_{obsd} = k_{Br}[OH^-]$, with $k_{Br} = 180\ M^{-1}\ sec^{-1}$ at 25°, $\mu = 1.0$; the product is at least 86% *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+}$. The second process has a rate law $k_{obsd} = k_E + k_{Az}[OH^-]$, with $k_E = 3.3 \pm 0.2 \times 10^{-3}\ sec^{-1}$ and $k_{Az} = 1.1 \pm 0.2 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°, $\mu = 1.0$; the two paths result in $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ (containing chelated ethanolamine) and *cis*-$[Co(en)_2(OH)Az]^{2+}$ (Az = coordinated ethylenimine), respectively. Tracer studies (^{18}O) show that $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ is formed by intramolecular attack of coordinated hydroxide to eliminate Br^- and the rate of loss of Br^- is enormously faster than for reactions of uncoordinated alkyl bromides with OH^-. An analysis of equilibria and rate constants also indicates that lysis of Br^- by the coordinated amido group is 10^2–10^3 times faster than by the coordinated OH^-. A similar reaction path and rates obtain for β_2-$[Co(trien)(OH)(NH_2CH_2CH_2Br)]^{2+}$, while for *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2Cl)]^{2+}$ $k_E = 1.1 \pm 0.1 \times 10^{-4}\ sec^{-1}$ at 25°, $\mu = 1.0$. Preliminary results for the stereochemical course of the reaction are also given.

The efficacy of coordinated amide and hydroxo groups as nucleophiles has recently been demonstrated for Co(III) complexes containing amino acid esters.[1-3] Compared to the bimolecular reaction of solvent OH^- on the uncoordinated substrate, the results required the intramolecular path to involve a rate enhancement of at least 10^7.

Bearing in mind the sequential addition–elimination mechanism proposed for nucleophilic displacements at acyl carbon,[4] it was pertinent to examine whether acceleration *via* an intramolecular path could also be demonstrated at a saturated carbon center where a change in mechanism is likely, and to compare this rate with those for related uncoordinated organic molecules.

For this study we chose to look at the base hydrolysis of coordinated 2-bromo- and 2-chloroethylamine, and 3-bromopropylamine in the *cis*-$[Co(en)_2Br(NH_2R)]^{2+}$ ions. In a report[5,6] on the preparation and some properties of these ions, the acid hydrolysis of *cis*-$[Co(en)_2(H_2O)(NH_2CH_2CH_2X)]^{3+}$ (X = Cl, Br) at 70–80° was proposed to result in the formation of the chelated alcoholamine complex ion



Base hydrolysis of the halo complexes under changing pH conditions was held to give the corresponding coordinated hydroxy ethylenimine $[Co(en)_2(OH)Az]^{2+}$ according to the rate law $k_{obsd} = k_1 + k_2[OH^-]$. The results given in this paper show that in base the reaction is considerably more complex than described previously, and that the rate law above is not reproduced for the formation of the iminoalkane complex.

Experimental Section

Analytical reagents were used for kinetic measurements without further purification. 2-Bromoethylamine hydrobromide and 3-bromopropylamine hydrobromide were obtained from Aldrich Chemical Co. Ethanolamine was supplied by Ajax Chemical Co. and ethylenimine by Fluka. Oxygen-18-enriched water (1.5 atom %) was obtained from Bio-Rad Laboratories.

Spectrophotometric rate data and visible spectra were collected using a Cary 14 recording spectrophotometer. Rates of base consumption at constant pH and temperature were made using the following radiometer apparatus: TTA_3 electrode assembly, ABU_1 autoburet, TTT titrator, and SBR_2 titrigraph. Solutions of the complexes were continuously stirred as 0.2 *M* NaOH was added under a nitrogen atmosphere. The pmr spectra were recorded using a Varian HA-100 spectrometer. Bio-Rad analytical Dowex 50W-X2 (200–400 mesh) ion-exchange resin was used in all cation-exchange experiments. Cobalt estimations were made with a Techtron AA4 atomic absorption spectrometer. Optical rotations were measured with a Perkin-Elmer P22 spectropolarimeter (±0.002°) in a 1-dm tube.

The ^{18}O content of CO_2 recovered from labeled compounds was obtained using a GD-150 mass spectrometer. The ^{18}O enrichment in chelated ethanolamine was also determined with an AEI-MS-902 spectrometer.

Kinetic Measurements. (A) pH-stat Titrations. Hydrolysis was followed in a thermostated vessel by pH-stat titration with 0.2 *M* NaOH using the radiometer apparatus described above. A weighed quantity of complex (0.1–0.3 mmol) was dissolved in 0.1 *M* KNO_3 to give an ionic strength of 0.1 *M* when diluted to 20 ml. Solvent blanks were run at every pH and the volumes to reach pH subtracted from the base consumption with complex present to determine the consumption due to hydrolysis.

(B) Spectrophotometric Rates. The base hydrolysis of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)](NO_3)_2$ and *cis*-$[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3$ was followed spectrophotometrically at 570 nm for coordinated bromide removal and at 360 nm for the subsequent reaction at the coordinated amine. A solution of complex (5 m*M*) and buffer or NaOH was rapidly mixed at 25.0° using a stop-flow reactor[7] attached to a 1-cm cell. The reference beam contained a solution of the reaction products at the same pH. The pH's of the triethylamine buffers were checked against the effluent solutions from the stop-flow reactor and were found to be the same (±0.02).

Preparation of *cis*-$[Co(en)_2Br(NH_2R)]Br_2$ Complexes. The complexes [R = $-(CH_2)_2OH$, $-(CH_2)_2Br$, $-(CH_2)_3Br$, and ethylenimine

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[1] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **91**, 4102 (1969).

[2] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *ibid.*, **91**, 3451 (1969).

[3] D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **9**, 11 (1970).

[4] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

[5] S. C. Chan and F. Leh, *J. Chem. Soc. A*, 760 (1966).

[6] S. C. Chan and F. Leh, *ibid.*, *A*, 908 (1967).

[7] Y. Inoue and D. D. Perrin, *J. Phys. Chem.*, **66**, 1689 (1962).

(Az)] were prepared by conventional methods.[8] Equimolar quantities of *trans*-$[Co(en)_2Br_2]Br$ and the amine or amine hydrobromide were triturated in enough methanol or water to give a paste. When the hydrobromides were used an equimolar amount of NaOH or diethylamine was added dropwise. The addition of 5% by weight of $CoBr_2 \cdot 6H_2O$ to the *trans*-$[Co(en)_2Br_2]Br$ was found to greatly improve the yield. In the preparation of the ethanolamine complex the pH of the free amine solution was adjusted to 9–10 with 7.6 *M* HBr before addition to the dibromo complex.

Where desired, the bromides were converted to the more soluble perchlorate salts by dissolution in hot 0.01 *M* $HClO_4$ followed by the addition of excess $NaClO_4$ and cooling. Two or three such treatments were necessary to remove all the ionic bromide. Similarly, the nitrates were obtained by dissolution of the bromides in water at 60° followed by the addition of an equal volume of concentrated HNO_3. The process was twice repeated to remove all ionic bromide. All samples were washed with ethanol or methanol and dried in an evacuated desiccator.

Anal. Calcd for $[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$: C, 13.28; H, 4.09; N, 12.90; Br, 58.88. Found: C, 13.25; H, 4.13; N, 12.58; Br, 58.86. Calcd for $[Co(en)_2Br(NH_2CH_2CH_2Br)](ClO_4)_2$: C, 12.8; H, 3.81; N, 12.02. Found: C, 12.39; H, 3.91; N, 12.2. Calcd for $[Co(en)_2Br(NH_2CH_2CH_2Br)](NO_3)_2$: C, 14.24; H, 4.37; N, 19.35. Found: C, 14.17; H, 4.52; N, 19.79. Calcd for $[Co(en)_2Br(NH_2CH_2CH_2Cl)]Br_2$: C, 14.45; H, 4.42; N, 13.5. Found: C, 14.26; H, 4.65; N, 14.05. Calcd for $[Co(en)_2Br(NH_2(CH_2)_3Br)]Br_2$: C, 15.10; H, 4.31; N, 12.58. Found: C, 15.04; H, 4.31; N, 12.28. Calcd for $[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$: C, 15.02; H, 4.84; N, 14.59. Found: C, 14.85; H, 4.99; N, 14.59. Calcd for $[Co(en)_2Br(NH_2CH_2CH_2OH)](ClO_4)_2$: C, 12.8; H, 3.81; N, 12.02. Found: C, 12.39; H, 3.91; N, 12.17. Calcd for $[Co(en)_2Br(C_2H_4NH)]Br_2$: C, 15.60; H, 4.58; N, 15.18. Found: C, 15.43; H, 4.72; N, 14.98.

Preparation of $[Co(en)_2(NH_2CH_2CH_2OH)]Br_3 \cdot H_2O$. To a solution of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ (10 g in 1000 ml of H_2O) was added 1 *M* LiOH (36 ml) at pH 9.5 (pH-stat) and 25°. After 2 hr the solution was adjusted to pH 1–2 with 7M HBr and reduced to dryness on a vacuum evaporator. The orange residue was dissolved in the minimum volume of water, filtered, and fractionally crystallized by adding methanol and ethanol. The product was recrystallized from the minimum volume of warm dilute HBr by cooling in an ice bath. More product was obtained by addition of methanol to the filtrate (yield 7–8 g). *Anal.* Calcd for $[Co(en)_2(NH_2CH_2CH_2OH)]Br_3 \cdot H_2O$: C, 14.43; H, 5.06; N, 14.04; Br, 48.1. Found: C, 14.19; H, 4.97; N, 13.98; Br, 47.8 (ϵ_{492} 84; ϵ_{347} 93 in H_2O).

The chelated ethanolamine complex was also prepared in a similar manner at pH 9.5 from $[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$ (70–75% yield). *Anal.* Found: C, 14.89; H, 4.69; N, 14.16; Br, 48.7.

Resolution of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$. Silver acetate (4.02 g) was added to a solution of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ (6.52 g) in 160 ml of water acidified with acetic acid (10 drops, glacial). The suspension was shaken in a stopped flask until all the complex had dissolved. AgBr was filtered off and ammonium (+)-α-bromo-π-camphorsulfonate ($NH_4(+)BCS$) (7.88 g) was added to the combined filtrate and washings. The solution was reduced to 80 ml in a vacuum evaporator and the diastereoisomer crystallized at 40°. Several fractions (0.2–0.4 g) were collected, and those of similar activity were combined. The $(-)_{589}$ diastereoisomer was the least soluble. The combined levo fractions were recrystallized from dilute HBr to constant rotation. A 0.2% solution of $(-)_{589}$-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br(BCS)$ gave α_{589} −0.034° and α_{546} +0.154°, whence $[\alpha]_{589}$ −17°, $[\alpha]_{546}$ +77°. *Anal.* Calcd for $CoC_{16}H_{36}N_5O_4SBr_4$: C, 24.75; H, 4.68; N, 9.07. Found: C, 24.89; H, 4.97; N, 9.13. The fractions containing the (+) isomer were also recrystallized to constant rotation.

The $(-)_{589}$ diastereoisomer was dissolved in the minimum volume of water (50°) and excess 7.6 *M* HBr added. The bromide salt was fractionally collected following evaporation of the filtrate. Recrystallization showed no increase in rotation. A 0.1% solution of $(-)_{589}$-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ gave α_{589} −0.080° and α_{546} +0.059°, whence $[\alpha]_{589}$ −80° and $[\alpha]_{546}$ 59°. *Anal.* Calcd for $CoC_6H_{22}N_5Br_4$: C, 13.28; H, 4.09; N, 12.90. Found: C, 13.56; H, 4.25; N, 12.90.

Resolution of $[Co(en)_2(NH_2CH_2CH_2OH)]Br_3 \cdot H_2O$. Silver (+)-tartrate (3.9 g) was added to a solution of complex (7 g) in water (20 ml). The suspension was vigorously shaken in a stopped flask for 5 min and the AgBr filtered off. The filtrate and washings were reduced to ∼10 ml by vacuum evaporation; on cooling and addition of a few drops of methanol, the $(+)_{589}$ diastereoisomer crystallized. Two other active fractions were obtained by adding methanol to the filtrate at ∼35° and cooling. Subsequent addition of methanol produced inactive material. The $(+)_{589}$ diastereoisomer was recrystallized as above with no improvement in rotation. A 0.05% solution gave α_{589} +0.215° and α_{546} +0.072°, whence $[\alpha]_{589}$ +430° and $[\alpha]_{546}$ +144°. *Anal.* Calcd for $CoC_{10}H_{27}N_5O_7Br$: C, 25.55; H, 6.22; N, 14.88. Found: C, 25.05; H, 5.94; N, 14.96. The diastereoisomer was converted to the bromide salt using a Dowex 1 × 2 anion-exchange resin in the bromide form. The solution was reduced to 5–10 ml and several drops of 7 *M* HBr were added, followed by an excess of methanol and absolute ethanol. The solution was cooled and scratching induced crystallization. The product was collected, washed with methanol, and dried under vacuum. A 0.05% solution in water gave α_{589} +0.169° and α_{546} +0.245°, whence $[\alpha]_{589}$ 338° and $[\alpha]_{546}$ 490°. In 4 *M* HBr α_{589} +0.211° and α_{546} +0.296° (0.1% solution). In 0.2 *M* tris buffer and 0.05 *M* KNO_3 at pH 10.74, α_{589} +0.396° and α_{546} +0.024° (0.1% solution) (in water, ϵ_{492} 80; ϵ_{376} 88). *Anal.* Calcd for $[Co(en)_2(NH_2CH_2CH_2OH)]Br_3 \cdot H_2O$: C, 14.43; H, 5.06; N, 14.04. Found: C, 14.51; H, 4.81; N, 13.81.

$(+)_{589}$-$[Co(en)_2(NH_2CH_2CH_2OH)]Br_3$ retained 99.4% of its activity after 8 hr at 25° in 3 *M* HBr, and 99% after 24 hr in triethylamine buffer (0.05 *M* KNO_3) at pH 10.74

Resolution of *cis*-$[Co(en)_2Br(Az)]Br_2$. To the complex (5.5 g) in 160 ml of water at pH 4 (HOAc) was added silver acetate (7 g), and the suspension was shaken vigorously for several minutes. AgBr was removed and $NH_4(+)BCS$ (7.9 g) was added to the filtrate plus washings. The volume was reduced to ∼120 ml in a rotary evaporator and the diastereoisomer was allowed to crystallize at room temperature. Two fractions were collected, 1.5 and 2.8 g. The combined fractions were recrystallized from warm water to constant rotation (2.9 g). A 0.1% solution gave α_{589} +0.049° and α_{546} 0, whence $[\alpha]_{589}$ 49°. *Anal.* Calcd for $CoC_{26}H_{49}N_5O_8S_2Br_3$: C, 33.85; H, 5.36; N, 7.57. Found: C, 33.13; H, 5.37; N, 7.56. Evaporation of the filtrate to 8–10 ml gave no further crystalline diastereoisomer, and several drops of 7.6 *M* HBr were added to this solution followed by absolute ethanol. The resulting bromide salt was filtered off, washed with absolute ethanol and acetone, and air-dried (2 g). Fractional crystallization from dilute HBr gave no improvement in activity. A 0.1% solution gave rotations of α_{589} +0.018° and α_{546} +0.148°, whence $[\alpha]_{589}$ +18°, $[\alpha]_{546}$ +148°. *Anal.* Calcd for $[Co(en)_2BrAz)]Br_2$: C, 15.60; H, 4.58; N, 15.16. Found: C, 15.89; H, 4.68; N, 15.16. Similarly the least soluble (+)BCS salt (2.9 g) was converted to the bromide (1.1 g) with HBr. The observed rotations for 0.1% solution were α_{589} −0.016° and α_{546} −0.143°, whence $[\alpha]_{589}$ −16° and $[\alpha]_{546}$ −143°.

Preparation of ^{18}O-Labeled Complexes. $[Co(en)_2(NH_2CH_2CH_2Br)^{18}OH_2](NO_3)_3$. *cis*-$[Co(en_2)Br(NH_2CH_2CH_2Br)]Br_2$ (5.43 g) was suspended in 25 ml of 1.5 atom % enriched $H_2{}^{18}O$. To the suspension, a solution of HgO (6.50 g) dissolved in 5.2 ml of 70% $HClO_4$ was added. The mixture was vigorously shaken until all the complex dissolved. It was cooled in an ice bath, and the precipitated $HgBr_2$ removed. To the orange filtrate excess $LiNO_3 \cdot xH_2O$ was added, followed by a two- to threefold volume of methanol and ethanol until turbidity first appeared. On scratching and cooling in an ice bath *cis*-$[Co(en)_2(H_2{}^{18}O)(NH_2CH_2CH_2Br)](NO_3)_3$ crystallized. This was collected and washed with methanol, ethanol, and acetone and air-dried (yield 3.50 g).

The unlabeled compound was prepared in an identical fashion. It was recrystallized from a small volume of water by adding methanol. Scratching induced crystallization, and cooling in an ice bath and adding ethanol improved the yield. The product was collected, washed with acetone, and dried in a vacuum desiccator (yield ∼3–4 g). *Anal.* Calcd for $[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3$: C, 14.21; H, 4.77; N, 22.1. Found: C, 14.45; H, 4.55; N, 21.95.

$[Co(en)_2(NH_2CH_2CH_2{}^{18}OH)]Br_3 \cdot H_2O$. *cis*-$[Co(en)_2(H_2{}^{18}O)(NH_2CH_2CH_2Br)](NO_3)_3$ (3 g) was dissolved in deionized water (25 ml) and 1 *M* LiOH (11.6 ml) was titrated into the solution at pH 10.0 and 25° (pH-stat). After base consumption had ceased (40 min) the solution was adjusted with acetic acid to pH 3–4 and evaporated to dryness in a vacuum evaporator at ∼20°. To the orange product in ∼10 ml of H_2O was added LiBr followed by methanol and ethanol to the cloud point. On cooling and scratching the com-

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(8) J. C. Bailar, Jr., and L. B. Clapp, *J. Amer. Chem. Soc.*, 67, 171 (1945); M. D. Alexander and D. H. Busch, *Inorg. Chem.*, 5, 602 (1966), and references therein.

plex crystallized. This was collected, washed with methanol, ethanol, and acetone, and dried in an evacuated desiccator (yield 2.25 g).

The unlabeled compound was prepared and purified in the same manner. *Anal.* Calcd for [Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]Br$_3$·H$_2$O: C, 14.43; H, 5.06; N, 14.04; Br, 48.20. Found: C, 14.48; H, 5.09; N, 13.87; Br, 47.7.

Analytical Procedures. Oxygen-18 Estimations. Coordinated water in *cis*-[Co(en)$_2$(H$_2{}^{18}$O)(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_3$ (1 g) was removed by vacuum distillation at 70° and collected in a Urey tube cooled in Dry Ice-acetone. The enriched water sample was equilibrated with normal CO$_2$ ($\sim$0.01 mmol) overnight at 70° and the ^{18}O content in the CO$_2$ determined by the mass spectrometer. The ^{18}O content of the water containing the reaction products was determined using methods referenced previously.[9]

The ^{18}O enrichment in the coordinated ethanolamine was determined by two methods. An 0.2-g sample of [Co(en)$_2$(NH$_2$CH$_2$CH$_2{}^{18}$OH)]Br$_3$·H$_2$O prepared by base hydrolysis of *cis*-[Co(en)$_2$(H$_2{}^{18}$O)(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_3$ in unlabeled water was heated in a Urey tube under vacuum at 70° for about 1 hr to remove the H$_2$O of crystallization. The temperature was then increased to 200° and the ethanolamine vacuum distilled into a break-seal tube containing an equimolar mixture of HgCl$_2$ and Hg(CN)$_2$. The tube was then heated at 400° overnight and the ^{18}O content of the CO$_2$ formed on pyrolysis determined as previously.[9] The second procedure consisted of using a direct insertion probe of a AEI-MS 902 mass spectrometer. Pyrolysis of the complex at the source temperature (250–300°) resulted in the immediate ionization of coordinated ethanolamine as shown by mass spectrum (Figure 1). The ratio [63]/[61] was compared with that obtained from the unlabeled complex, and the figure shows that the [63] ethanolamine signal could be distinguished from the similar background signal.

Analysis of Products Formed on Base Hydrolysis of *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ and *cis*-[Co(en)$_2$(OH$_2$)(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_3$. (A) General Method. The aquo or bromo complexes (0.1–0.2 g) were dissolved in water to give 5–10 m*M* solutions. The complex was then hydrolyzed at constant pH by pH-stat titration, rapid mixing in a buffer, or addition of a 50–100-fold excess of NaOH. The reaction mixture was quenched with HBr after five–six half-lives or after 1 or 2 equiv of base was consumed. The solution was sorbed on an H$^+$ resin (20 × 1 cm) and eluted with 1 *M* HBr followed by 2 *M* HBr and finally 3 *M* HBr to remove the single orange 3+ band The eluent fractions were taken to dryness using a vacuum evaporator with a water bath at 80°. This procedure was used to separate the supporting electrolyte, buffer, or excess Na$^+$ from the complexes formed on hydrolysis. If only small amounts of extraneous ions were present, the complex was acidified with excess HBr and evaporated to dryness. The residue from evaporation in HBr was dissolved in water and sorbed on a H$^+$-form cation-exchange resin (12 × 30 mm fully swollen resin size). The violet bands of the bromo complexes were separated from the 3+ complexes using 1 *M* HBr followed by 2 *M* HBr. The orange 3+ ion was eluted with 3 or 4 *M* HBr. Cobalt estimations on each fraction were carried out by atomic absorption spectroscopy and spectrophotometrically.

Using the above separation technique a 97% recovery of *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ was obtained from an analytical sample of *cis*-[Co(en)$_2$(H$_2$O)(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_3$. By comparison [Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]Br$_3$ remained unchanged on the above treatment and a 98% recovery was obtained. In other experiments (+)$_{589}$-[Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]Br$_3$ was dissolved in 1 *M* NaOH and tris buffer (pH 9.12, 0.05 *M* KNO$_3$), respectively, and allowed to stand for 40 min at 25°. Reacidification followed by the above treatment gave full retention of optical activity (±1%) in the recovered [Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]$^{3+}$ ion.

(B) Reactions in Strong Base. Accurately weighed amounts (0.1–0.2 g) of *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ or *cis*-[Co(en)$_2$(H$_2$O)(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_3$ were added to 20 ml of 1, 0.5, and 0.25 *M* and 50 ml of 0.10 and 0.05 *M* NaOH with rapid stirring. After 30 min the solutions were adjusted to pH $\sim$2 with HBr and treated as described above. For the bromo complex three bands were obtained on elution with 1 *M* HBr; two violet 2+ ions and one orange 3+ ion (Table V). Band 1 was assigned to [Co(en)$_2$Br(H$_2$O)]$^{2+}$ since it formed *trans*-[Co(en)$_2$Br$_2$]Br on evaporation from concentrated HBr, and a pmr spectrum showed ethanolamine, 2-bromoethylamine, or ethylenimine to be absent. Band 2 (ϵ_{545} 68) was identified as *cis*-[Co(en)$_2$Br(Az)]Br$_2$, and band 3 (ϵ_{492} 73, ϵ_{340}, 115) was identified as [Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]Br$_3$, by pmr spectroscopy. For the aquo complex two products separated on elution with 1 *M* HBr. Band 1 was isolated and shown to be *cis*-[Co(en)$_2$Br(Az)]Br$_2$·H$_2$O. *Anal.* Calcd: C, 15.02; H, 4.83; N, 14.59. Found: C, 15.00; H, 4.69; N, 14.41, ϵ_{545} 69, pmr spectrum. Orange band 2 (3 *M* HBr) was identified as [Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]Br$_3$ by pmr and visible spectroscopy.

Base hydrolysis of (−)$_{589}$-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ (0.1086 g, $[\alpha]_{589}$ −79°) in 1 *M* NaOH (100 ml), followed by the above isolation procedure, gave two products: band 1 (ϵ_{545} 68, α_{546} −0.021°) represented 69% of the total Co and 31% retention based on (−)$_{546}$-[Co(en)$_2$Br(Az)]Br$_2$ ($[\alpha]_{546}$ −143°); band 2 (ϵ_{492} 73, ϵ_{340} 115; α_{546} −0.048°) represented 31% of total Co and 55% retention of activity based on (+)$_{546}$-[Co(en)$_2$NH$_2$CH$_2$CH$_2$OH)]Br$_3$ ($[\alpha]_{546}$ 296° (4 *M* HBr)).

A solution of *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ (2 g) in 200 ml of H$_2$O was rapidly added to 200 ml of 2 *M* NaOH. After 10 min the solution was acidified (HBr), diluted, and sorbed on and eluted from a cation-exchange resin using 2 *M* HBr. The eluent was taken to dryness in a vacuum evaporator at 80°. The residue was dissolved in dilute HBr and cooled, and the *cis*-[Co(en)$_2$Br(Az)]Br$_2$ collected (0.65 g). The complex was twice recrystallized from hot water and HBr (0.5 g, ϵ_{545} 81). *Anal.* Calcd for [Co(en)$_2$Br(Az)]Br$_2$·H$_2$O: C, 15.02; H, 4.83; N, 14.59; Br, 49.95. Found: C, 15.01; H, 4.79; N, 14.51; Br, 49.83. The pmr spectrum was identical with that for *cis*-[Co(en)$_2$Br(Az)]Br$_2$ prepared using ethylenimine.

trans-[Co(en)$_2$Br$_2$]Br (2.04 g) was hydrolyzed in 1 *M* NaOH (100 ml), and 1 *M* NaClO$_4$ and ethylenimine (0.17 g) in water (100 ml) were added subsequently. After 30 min at 25°, the solution was acidified with concentrated HBr and evaporated to dryness at 80°. The green residue was sorbed on and then eluted from the cation-exchange resin with 1 *M* HBr. No violet band corresponding to [Co(en)$_2$Br(Az)]$^{2+}$ was detected.

(C) Hydrolysis of *cis*-[Co(en)$_2$(H$_2$O)(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_3$ and *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ at pH <11. The following experiments were carried out and the products treated as above. (1) A 0.2 *M* solution of *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ was hydrolyzed at pH 9.5 for 2 hr at 25°, using the pH-stat. Four bands separated on elution with 1 *M* HBr: band 1, 3.4% (ϵ_{540} 71); band 2, 8.8% (ϵ_{554} 70); band 3, 1.3%; band 4, 86.4% (ϵ_{492} 81, ϵ_{342} 108). (2) (−)$_{589}$-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ (0.1086 g in 50 ml of H$_2$O) was hydrolyzed at pH 10.0 (0.1 *M* KNO$_3$) using the pH-stat. Three bands separated after treatment with HBr: band 1, 5.2% (inactive); band 2, 7.8% (ϵ_{550} 53, inactive); band 3, 87% (ϵ_{490} 74, ϵ_{340} 126, 3 *M* HBr) gave α_{546} −0.178°, representing 66% retention of optical activity when compared with (+)$_{546}$-[Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]Br$_3$ ($[\alpha]_{546}$ = 296°, 4 *M* HBr). (3) (−)-$_{589}$-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ (0.0543 g) was hydrolyzed in 50 ml of 0.2 *M* triethylamine buffer (0.05 *M* KNO$_3$), pH 10.74, 25°, 24 hr. The change in rotation against time was followed polarimetrically from 650 to 320 nm. The final solution gave α_{440} −0.104°, representing a 43% retention based on a 86% yield of [Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]$^{3+}$. (4) The above experiment was repeated except that the reaction was quenched with 70% HClO$_4$ (9.2 ml) after 30 sec, pH 10.74, 25°. The resulting solution (0.1 *M* H$^+$) gave α_{589} −0.016°, representing a 45% retention of activity based on (−)$_{589}$-[Co(en)$_2$(OH$_2$)(NH$_2$CH$_2$CH$_2$Br)]$^{3+}$ produced by Hg^{2+}-induced acid hydrolysis of (−)-$_{589}$-[Co(en)$_2$(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ (see below). (5) In a similar experiment [Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_2$ (0.51 g) was hydrolyzed in 0.2 *M* triethylamine buffer (400 ml, 0.05 *M* KNO$_3$), pH 10.74, 25°, for 30 min and then neutralized with concentrated HBr. Following elution from the ion-exchange resin (4 *M* HBr) the eluate was reduced to dryness and the orange residue recovered (0.45 g). This material was twice recrystallized from dilute HBr (pH 1–2) by addition of LiBr and methanol and cooling. The final product was collected and washed with methanol and ethanol and dried in an evacuated desiccator. *Anal.* Calcd for [Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)]Br$_3$·2H$_2$O: C, 13.97; H, 5.28; N, 13.57. Found: C, 13.87; H, 4.49; N, 13.14. (6) A solution of [Co(en)$_2$(H$_2$O)(NH$_2$CH$_2$CH$_2$Br)](NO$_3$)$_3$ ($\sim$0.1 g) in 0.1 *M* KNO$_3$ (100 ml) was hydrolyzed at pH 9.5 by pH-stat titration. After 30 min the solution was acidified and treated as before. Only one band (ϵ_{492} 73, ϵ_{340} 145) was observed on the ion-exchange column and represented a 97% recovery of Co.

Isolation of *cis*-[Co(en)$_2$(H$_2$O)(NH$_2$CH$_2$CH$_2$Br)]$^{3+}$ Following the Base Hydrolysis of *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br]Br$_2$. To a solution of *cis*-[Co(en)$_2$Br(NH$_2$CH$_2$CH$_2$Br)]Br$_2$ (2.72 g) in 274 ml of water was added 5 ml of 1 *M* LiOH by pH-stat titration at pH 10

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[9] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **90**, 6032 (1968).

(3 min). The solution was immediately neutralized with glacial acetic acid to pH ~3 and the volume reduced by vacuum evaporation at ~20° to ~30 ml. Excess $LiNO_3$ was added, followed by methanol and ethanol. On cooling in an ice bath an orange product crystallized. This was collected, washed with methanol and acetone, and air-dried (0.66 g) The crude product was recrystallized from an aqueous methanol–ethanol mixture. *Anal.* Calcd for $[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3$: C, 14.21; H, 4.77; N, 22.1; Br, 15.60. Found: C, 14.29; H, 4.66; N, 21.88; Br, 15.5 (ϵ_{492} 69, ϵ_{350} 80). The bromide salt was prepared similarly except that LiBr and HBr were used. *Anal.* Calcd for $[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)]Br_3$: C, 12.85; H, 4.31; N, 12.49. Found: C, 12.53; H, 4.52; N, 12.79 (ϵ_{490} 72, ϵ_{345} 96).

Base Hydrolysis of *cis*-$[Co(en_2)Br(NH_2CH_2CH_2Cl)]Br_2$. The complex (0.1 mmol) was hydrolyzed for 2 hr (25°) at pH 10 (μ = 0.1 *M* KNO_3) by pH-stat titration of NaOH. The resulting solution was acidified with 7 *M* HBr and sorbed on and eluted from a cation-exchange resin. The complex ions were eluted with 3 *M* HBr and treated as before. Two bands were observed, one violet (22%) and one orange (78%) (ϵ_{492} 78, 3 *M* HBr).

Base Hydrolysis of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$. A solution of the complex (0.096 g in 10 ml of water) was hydrolyzed at pH 9.5 by pH-stat titration of 0.2 *M* NaOH. After base consumption had ceased (10 min) the solution was acidified (7 *M* HBr) and treated as before. Cation-exchange chromatography revealed three bands, two violet 2+ ions and one orange 3+ ion: band 1 (violet), 34% (ϵ_{530} 72); band 2 (violet), 2% (ϵ_{520} 72); band 3 (orange), 62% (ϵ_{492} 81, ϵ_{342} 124). Band 2 was identified as $[Co(en)_2Br(H_2O)]^{2+}$ since in duplicate experiments it was eluted first as green *trans*-$[Co(en)_2Br_2]Br$. Pmr spectra of band 1 and band 3 showed ethanolamine to be present.

Base Hydrolysis of $(+)_{589}$-$[Co(en)_2Br(Az)]Br_2$. A 2 m*M* solution of $(+)_{589}$-$[Co(en)_2Br(Az)]Br_2$ (50 ml) was treated with 0.2 *M* NaOH at pH 9.5 and 10.4 by means of a pH-stat titration. When base consumption had ceased the solutions were acidified with 7 *M* HBr and treated as above. Only one violet band was observed on the ion-exchange column and a 97% recovery was obtained in both experiments. The solution gave α_{440} 0.218°, representing a retention of optical activity of 80% (ϵ_{542} 77 in 1 *M* HBr) when compared to a separate experiment in which the complex was not hydrolyzed in base but otherwise treated similarly (α_{440} −0.275°).

Isolation of Product from *cis*-$[Co(en)_2Br(NH_2(CH_2)_3Br)]Br_2$ in 1 *M* NaOH. *cis*-$[Co(en)_2Br(NH_2(CH_2)_3Br)]Br_2$ (1 g) was dissolved in 100 ml of H_2O and 2 *M* NaOH (100 ml) was added rapidly. The solution was kept for 3 hr at 25° and then acidified with HBr and sorbed on and eluted from (2 *M* HBr) a cation-exchange resin. After evaporation under reduced pressure the residue was taken up in the minimum volume of warm water, several drops of 7 *M* HBr were added, the solution was cooled in an ice bath, and the violet fibrous crystals were collected (0.6 g). The product was recrystallized from dilute HBr (0.4 g). *Anal.* Calcd for $[Co(en)_2Br(NH_2(CH_2)_3Br)]Br_2 \cdot H_2O$: C, 14.67; H, 4.57; N, 12.12. Found: C, 14.72; H, 4.58; N, 12.20.

Base Hydrolysis in the Presence of N_3^- Ion. A 2 m*M* solution of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$ was rapidly added to an equal volume of 0.2 *M* tris buffer (pH 8.62), 2 *M* in NaN_3. The mixture was kept for 30 min at 25°, diluted with water, and then sorbed on a cation-exchange resin (Na^+ form). On elution with 1 and 2 *M* NH_4NO_3, pH 6, two bands separated. The violet azido complex (ϵ_{514} 211) contained 32% of the cobalt, and the orange chelated ethanolamine plus aquoethanolamine band (in 3 *M* HBr, ϵ_{490} 72, ϵ_{342} 107) contained 67% Co.

HOCl Treatment of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)](ClO_4)_2$. To *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)](ClO_4)_2$ (0.098 g) was added 5 ml of freshly prepared HOCl.[10] After 5 min, nitrogen was bubbled through the solution to remove Br_2. The complex was sorbed on a cation-exchange resin, washed with water, and eluted with 3 *M* HBr. The HBr solution was reduced to dryness in a vacuum evaporator at 80°. The residue was sorbed on an ion-exchange resin and eluted successively with 1, 2, and 3 *M* HBr. A violet and an orange band separated. The orange fraction (ϵ_{492} 80, ϵ_{342} 115) contained 66% of the Co.

Hg^{2+}-Induced Acid Hydrolysis of $(-)_{589}$-$[Co(en)_2Br(NH_2CH_2CH_2Br]Br_2$. To a solution of $(-)_{589}$-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ (0.0543 g, $[\alpha]_{589}$ −79°) in 0.1 *M* $HClO_4$ (25 ml) was added 25 ml of 0.6 *M* $Hg(ClO_4)_2$ in 0.1 *M* $HClO_4$. After 20 min α_{589} −0.035°; whence $[\alpha]_{589}$ −32° for the resulting $(-)_{589}$-$[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)]^{3+}$ ion. The slow subsequent reaction to form $(-)_{589}$-$[Co(en)_2(NH_2CH_2CH_2OH)]^{3+}$ was followed polarimetrically over 7 days. A plot of log $(\alpha_\infty - \alpha_t)_{589}$ *vs.* time was linear for three half-lives, giving k_{obsd} = 3.8 × 10^{-6} sec^{-1} at 25°, 0.1 *M* H^+. The final solution gave α_{589} −0.272°, α_{546} −0.438°, which represents a 74% retention of configuration when compared to $(+)_{589}$-$[Co(en)_2(NH_2CH_2CH_2OH)]Br_3$ ($[\alpha]_{589}$ 337° in 0.1 *M* $HClO_4$, 0.3 *M* $Hg(ClO_4)_2$).

In another experiment *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ (0.1984 g) was treated with 5 ml of 0.3 *M* Hg^{2+} in 0.05 *M* $HClO_4$. After 5 min at 25°, a large excess of NaBr was added to the orange solution and the solution warmed for 20 min at ~75°. The violet residue was sorbed on and eluted from an ion-exchange resin (1 *M* HBr). A 95% recovery of $[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ was obtained, and the pmr spectrum was identical with that of the starting complex.

Hg^{2+}-Induced Acid Hydrolysis of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$. The complex (0.1849 g) was treated with 0.3 *M* Hg^{2+} in 0.05 *M* $HClO_4$ (5 ml) for 5 min at 25°. NaBr (~3 g) was added to the resulting orange solution, which was warmed for 60 min at ~75°. The diluted solution was sorbed on and then eluted from an ion-exchange column (1, 3 *M* HBr), and the two bands were collected and estimated for Co. The violet 2+ band represented 21% of the total Co and the orange 3+ band 77%. The former was reduced to dryness on a vacuum evaporator and had a pmr spectrum similar to that of the starting complex.

In a similar experiment in 3 *M* $HClO_4$ only orange $[Co(en)_2(NH_2CH_2CH_2OH)]^{3+}$ was observed on the ion-exchange resin, and a 100% recovery was obtained (ϵ_{492} 80, ϵ_{340} 115).

Results

Kinetics of Base Hydrolysis. Over the pH range 8–12 *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ showed two consecutive hydrolysis reactions (Tables Ia and IIa). For the first reaction, spectrophotometric data obtained at 570 nm, Table Ia, gave linear plots of log $(D_t - D_\infty)$ *vs.* time for three half-lives, and the data fit the rate law $k_{obsd} = k_{Br}[OH^-]$. During the reaction the absorption spectrum changed from that of the initial bromo complex, λ_{max} 545 nm, to that with λ_{max} ~490 nm. This change is characteristic of removal of coordinated bromide from bromo complexes of this type. The second-order rate constant k_{Br} was dependent on the buffer used (110 ± 20 M^{-1} sec^{-1} in 0.2 *M* triethylamine, 180 ± 20 M^{-1} sec^{-1} in 0.2 *M* trishydroxyaminomethane (tris) at μ = 1.0 *M*, 25°), and increased by a factor of ~4 on lowering the ionic strength to 0.15 *M*. However, the same rate law was observed in each system.

Spectrophotometric data obtained at 360 nm for the slower reaction following hydrolysis of coordinated bromide gave linear plots of log $(D_t - D_\infty)$ *vs.* time, for at least three half-lives. The observed rate constants, Table IIa, were independent of $[OH^-]$ over the pH range 10.5–12, giving k_E = 3.3 ± 0.2 × 10^{-3} sec^{-1}, μ = 1.0 *M*, 25°. In more acidic solutions, (pH <10.5), complications arose from the overlap of this rate with that for the removal of coordinated bromide. Since the data given in Table IIa are internally consistent at higher pH, and since bromide removal becomes rate determining for the second reaction at pH <9.3, data obtained in the pH range 9.3–10.5 were not analyzed further. However, in the pH range 12–14 the observed data were dependent on $[OH^-]$. The data fit the rate law $k_{obsd} = k_E + k_{Az}[OH^-]$, with k_{Az} = 1.1 ± 0.2 × 10^{-2} M^{-1} sec^{-1} and k_E = 3.3 ± 0.2 × 10^{-3} sec^{-1}. The base-independent term, k_E, is smaller in 0.15 *M* KNO_3 (k_E = 1.9 × 10^{-3} sec^{-1},) and the polarimetric (μ = 0.05) and spectrophotometric (μ = 0.15) data differ only slightly. The change in the rotatory dispersion curve

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[10] A. Haim and H. Taube, *J. Amer. Chem. Soc.*, 85, 3108 (1963).

Table I. Base Hydrolysis of Coordinated Bromide, (25°)

pH	$10^3\ k_{obsd}$, sec^{-1}	$10^{-2}k_{Br}$, M^{-1} sec$^{-1\ a}$
(a) $[Co(en)_2(NH_2CH_2CH_2Br)Br](NO_3)_2$[b]		
11.58[a]	380	1.0
11.07[d]	110	0.94
10.70[d]	54	1.1
10.55[d]	41	1.2
9.32[e]	3.7	1.8
8.97[g]	1.4	1.5
8.72[e]	0.94	1.8
8.35[e]	0.40	1.8
9.12[f]	6.9	5.2
8.52[f]	1.54	4.7
8.15[f]	0.58	4.1
(b) $[Co(en)_2(NH_2CH_2CH_2OH)Br]Br_2$[c]		
10.0	14.4	1.4
9.5	5.4	1.7
9.0	2.2	2.2
8.45	0.58	2.3
8.0	0.21	2.1
(c) $[Co(en)_2(Az)Br]Br_2$[c]		
10.0	19.2	1.9
9.5	4.8	1.5
8.95	1.8	2.0
8.0	0.19	1.9
(d) $[Co(en)_2(NH_2CH_2CH_2CH_2Br)Br]Br_2$		
9.87	11.6	1.6
9.0	1.6	1.6
8.0	0.2	2.0
pH	**10^3[amine]**	**10^4k_{obsd}, sec^{-1}**
(e) $NH_2CH_2CH_2Br$[c]		
11.6	5	6.3
11.0	10	6.8
11.0	20	6.6
10.5	5	6.3

[a] $k_{Br} = k_{obsd}/[OH^-]$. [b] Spectrophotometric rates followed at 570 nm, [Co] = 2.5×10^{-3} *M*. [c] pH-stat data, [Co] = 1.8×10^{-2} *M*, $\mu = 0.1$ (KNO_3). [d] $\mu = 0.9$ (0.2 *M* NEt_3 buffer, 0.8 *M* KNO_3). [e] $\mu = 0.9$ (0.2 *M* tris buffer, 0.8 *M* KNO_3). [f] $\mu = 0.15$ (0.2 *M* tris buffer, 0.05 *M* KNO_3). [g] $\mu = 0.95$ (0.1 *M* tris buffer, 1.0 *M* KNO_3).

Table II. Base Hydrolysis of $[Co(en)_2(NH_2CH_2CH_3X)OH]^{2+}$ Ions (X = Br, Cl; μ = 1.0, 25°)

pH	10^3k_{obsd}, sec^{-1}	$10^2k_{Az.obsd}$, sec^{-1}	10^2k_{Az}, M^{-1} sec^{-1}
(a) Produced Following Hydrolysis of $[Co(en)_2(NH_2CH_2CH_2Br)Br](NO_3)_2$[a]			
14.0[f]	15	1.2	1.2
13.7[f]	9.8	0.65	1.3
13.4[f]	5.7	0.24	1.0
12.07	3.3		
12.07	3.5		
11.55	3.7		
11.23	3.1		
10.95[b]	3.1		
10.70	3.3		
10.54	3.2		
10.74[b]	2.3		
10.58[g]	2.2		
11.7[g]	2.2		
11.1[g]	1.8		
10.6[g]	1.8		
10.1[g]	1.8		
10.72[d]	2.3		
(b) $[Co(en)_2(NH_2CH_2CH_2Br)(H_2O)](NO_3)_3$[b]			
14.0[f]	16.9	1.3	1.3
13.7[f]	10.8	0.73	1.5
11.55	4.1		
11.23	3.3		
10.95	3.5		
10.73	3.3		
10.85	3.6		
10.98[g]	2.4		
10.74[g]	2.4		
9.5[c]	2.0		
9.0[c]	2.1		
8.5[e]	2.1		
8.0[e]	2.5		
(c) Produced Following Hydrolysis of $[Co(en)_2(NH_2CH_2CH_2Cl)Br]Br_2$			
12.07[a]	0.12		
10.5[c]	0.11		

[a] Spectrophotometric data (λ 360 nm), 0.2 *M* NEt_3 buffer; [Co] = 2.5×10^{-3} *M*, $\mu = 0.9$ (KNO_3). [b] As in *a*, [Co] = 5×10^{-3} *M*. [c] pH-stat data, [Co] = 5×10^{-3} *M*, $\mu = 0.1$ (KNO_3). [d] Polarimetric rate (0.2 *M* NEt_3 buffer, 0.05 M KNO_3). [e] As in *c*, [Co] = 1.8×10^{-3} *M*. [f] As in *a*, pH adjusted with NaOH. [g] As in *a*, 0.2 *M* NEt_3 buffer, 0.05 *M* KNO_3 (μ = 0.15).

vs. time (Figure 2) shows that this second slower reaction is accompanied by an increase in optical activity between 450 and 550 nm.

The *cis* complexes $[Co(en)_2(NH_2CH_2CH_2OH)Br]Br_2$, $[Co(en)_2(Az)Br]Br_2$, and $[Co(en)_2(NH_2CH_2CH_2CH_2Br)Br]Br_2$ all showed the same rate law, $k_{obsd} = k_{Br} \cdot [OH^-]$, and similar rates in 0.1 *M* KNO_3, 25°, for hydrolysis of coordinated bromide (Table Ib–d). These data were obtained by measuring the rate of base consumption at constant pH (pH-stat), and linear plots of log $(V_\infty - V_t)$ *vs.* time were obtained for at least four half-lives. For these complexes no subsequent slower reaction was observed either spectrophotometrically (360 nm) or by pH-stat titration.

Hydrolysis of *cis*-$[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3$ was followed spectrophotometrically at 360 nm over the pH range 8–14, and linear plots of log $(D_\infty - D_t)$ *vs.* time were obtained for at least three half-lives. The observed data, Table IIb, fit the rate expression $k_{obsd} = k_E + k_{Az}[OH^-]$, with $k_E = 3.3 \pm 0.3 \times 10^{-3}$ sec^{-1} and $k_{Az} = 1.4 \pm 0.1 \times 10^{-2}$ M^{-1} sec^{-1} at μ = 1.0, 25°. At the lower ionic strength, μ = 0.1, pH-stat data give $k_E = 2.2 \pm 0.3 \times 10^{-3}$ sec^{-1} and spectrophotometric data at μ = 0.15 show an appreciably slower rate at the lower ionic strength. The rate law and rate constants obtained for this compound agree closely with those given above for the slower reaction of the $[Co(en)_2Br(NH_2CH_2CH_2Br)]^{2+}$ ion under the same conditions. Spectrophotometric (350 nm) and pH-stat data for hydrolysis of the *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2Cl)]^{2+}$ ion, Table IIc, were base independent over the pH range 10–12, with $k_E = 1.1 \pm 0.1 \times 10^{-4}$ sec^{-1}.

The β_2-Co(trien)$(NH_2CH_2CH_2Br)(OH)]^{2+}$ ion produced by hydrolysis of β_2-$[Co(trien)(NH_2CH_2CH_2Br)Br]Br_2$ also undergoes further hydrolysis, Table III, following the rate law $k_{obsd} = k_E + k_{Az}[OH^-]$, with $k_E = 3.4 \times 10^{-3}$ sec^{-1} and $k_{Az} = 1.9 \times 10^{-2}$ M^{-1} sec^{-1}, μ = 1.0, 25°.

Base hydrolysis of $NH_2CH_2CH_2Br$ was followed by pH-stat titration over the pH range 10.5–11.6, Table Id. Linear plots of log $(V_\infty - V_t)$ *vs.* time were obtained for at least four half-lives, and the data fit the rate law $\nu = k_{Az}[NH_2CH_2CH_2Br]$, with $k_{Az} = 6.5 \pm 0.2 \times 10^{-4}$ sec^{-1}, μ = 0.1, 25°. A 10^{-3} *M* solution of the quaternary ammonium salt $((CH_3)_3NCH_2CH_2Br)Cl$ failed to consume any base over 24 hr at 25°, pH 10, μ = 0.1 (KNO_3).

Base Consumption. pH-stat titration data showed close to 2 equiv of base was consumed in the hydrolysis

Table III. Base Hydrolysis of the β_2-$\mathrm{[Co(trien)(NH_2CH_2CH_2Br)(OH)]^{2+}}$ Ion[a] (μ = 1.0, 25°)

pH	10^3k_{obsd}, $\mathrm{sec^{-1}}$	$10^2k_{\mathrm{Az,obsd}}$, $\mathrm{sec^{-1}}$	$10^2k_{\mathrm{Az}} = k_{\mathrm{Az,obsd}}/[\mathrm{OH^-}]$, M^{-1} $\mathrm{sec^{-1}}$
14.0	23.4	2.0	2.0
13.7	13.6	1.0	2.0
13.4	8.0	0.46	1.8
11.55[b]	3.6		
11.07[b]	3.3		
10.98[c]	2.6		
9.4[d]	1.8		

[a] Produced following base hydrolysis of β_2-$\mathrm{[Co(trien)Br(NH_2CH_2CH_2Br)]Br_2}$. [b] μ = 1 (0.2 *M* $\mathrm{Et_3N}$, 0.8 *M* $\mathrm{KNO_3}$). [c] μ = 0.15 (0.2 *M* $\mathrm{Et_3N}$, 0.05 *M* $\mathrm{KNO_3}$). [d] pH-stat data, 0.1 *M* $\mathrm{KNO_3}$.

of *cis*-$\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2}$, *cis*-$\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Cl)]Br_2}$, and *cis*-$\mathrm{[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3}$, Table IV. For the *cis*-$\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]^{2+}}$ ion, this occurred in two stages, each requiring 1 equiv of base. This was demonstrated in the pH range 10.1–11.7 by extrapolation of the slower rate plot (log ($V_\infty - V_t$) *vs.* t) to zero time. The consumption for the faster rate was then obtained by subtraction. This procedure was not applicable below pH 10, where the two first-order rates approached each other, but the close agreement obtained for the total base consumption throughout the pH range 7.5–11.7 together with the observed separate values at high pH support the analysis. A similar result was found for the *cis*-$\mathrm{[Coen_2Br(NH_2CH_2CH_2Cl)]^{2+}}$ ion, Table IVb. For *cis*-$\mathrm{[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3}$, Table IVc, 1 equiv of base was consumed immediately to form the $\mathrm{[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+}}$ ion, and the remainder at a rate the same as that obtained for the slower reaction of the $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]^{2+}}$ ion. For $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2}$, $\mathrm{[Co(en)_2Br(Az)]Br_2}$, and $\mathrm{[Co(en)_2(NH_2(CH_2)_3Br)Br]Br_2}$, only 1.00 ± 0.05 equiv of $\mathrm{OH^-}$ was required for hydrolysis over the entire pH range (Table I).

Table IV. Base Consumption Data (Mol of $\mathrm{OH^-}$/Mol of Co), μ = 0.1 ($\mathrm{KNO_3}$), 25°

pH	k_1 path	k_2 path	Total
	(a) $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2}$		
11.7	1.19	1.05	2.24
11.1	1.10	1.05	2.15
10.6	1.06	0.82	1.88
10.1	0.98	0.80	1.78
9.45			2.01
8.95			1.95
8.5			2.02
8.0			1.91
7.5			1.91
	(b) $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Cl)]Br_2}$		
11.5	0.95	1.01	1.96
	(c) $\mathrm{[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3}$[a]		
9.5		1.00	2.08
9.0		1.00	1.96
8.5		0.98	2.00
8.0		0.96	1.95

[a] ($\mathrm{OH^-}_{\mathrm{total}} - \mathrm{OH^-}_{k_2\mathrm{path}}$) was consumed rapidly to neutralize the aquo complex.

Product Analysis. At pH <12 the major final products of base hydrolysis of $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2}$, $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2}$, and $\mathrm{[Co(en)_2(OH_2)(NH_2CH_2CH_2Br)](NO_3)_3}$ were the same. Hydrolysis of $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2}$ at pH 9.5 (pH-stat) for 2 hr resulted in 86% of an orange 3+ ion with the composition $\mathrm{[Co(en)_2(NH_2CH_2CH_2OH)]Br_3 \cdot H_2O}$. The same complex was isolated analytically pure after hydrolysis of $\mathrm{[Co(en)_2(NH_2CH_2CH_2Br)Br]^{2+}}$ in 0.2 *M* triethylamine buffer (pH 10.74) and was also formed in 62 and 97% yields after similar treatment of *cis*-$\mathrm{[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2}$ and *cis*-$\mathrm{[Co(en)_2(OH_2)(NH_2CH_2CH_2Br)](NO_3)_3}$, respectively. Analytical data and pmr and visible spectra of the isolated complex bromides were either identical with or closely similar to those of the complex formed from $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2}$. The complex was recovered unchanged from dilute solutions of $\mathrm{[Co(en)_2(NH_2CH_2CH_2OH)]Br_3}$ in 3–4 *M* HBr or 2 *M* NaBr (pH 1) after heating for 1 hr at 80°.

Hydrolysis of $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_3}$ and $\mathrm{[Co(en)_2(OH_2)(NH_2CH_2CH_2Br)](NO_3)_3}$ in 1 *M* NaOH followed by treatment with HBr resulted in two major products; a violet 2+ ion and an orange 3+ ion (separated by ion-exchange chromatography). The violet 2+ ion (~77%) was isolated as the bromide salt and characterized as *cis*-$\mathrm{[Co(en)_2(Az)Br]Br_2}$ (elemental analysis, pmr, infrared, and visible spectra) by comparison with an authentic sample prepared from *trans*-$\mathrm{[Co(en)_2Br_2]Br}$ and ethylenimine. The orange 3+ ion (23%) was characterized as $\mathrm{[Co(en)_2(NH_2CH_2CH_2OH)]Br_3}$ (visible spectra, pmr) by comparison with the complex isolated following hydrolysis of $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_3}$ at pH 9.5. The proportions of these two products varied with the base concentration used, Table V, and it is clear from these results that the ethanolamine complex results from the term in the rate law independent of base and the ethylenimine complex from that term first order in hydroxide ion.

Table V. Ion-Exchange Product Analysis of $\mathrm{[Co(en)_2(NH_2CH_2CH_2O)]^{2+}}$ and $\mathrm{[Co(en)_2(OH)(Az)]^{2+}}$ Formed in Strong Base (μ = 1.0, 25°)

	% found[b]		% calcd[a]
$[\mathrm{OH^-}]$, *M*	$\mathrm{[Co(en)_2(N\text{–}O)]^{2+}}$	$\mathrm{[Co(en)_2(OH)(Az)]^{2+}}$	$\mathrm{[Co(en)_2(OH)(Az)]^{2+}}$
	(a) $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2}$		
1.0	23	77	77
0.5	30	70	62
0.25	49	51	46
0.2	60	40	40
0.05	79	21	14
	(b) $\mathrm{[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)](NO_3)_3}$		
1.0	19	74	77
0.5	29	67	62
0.2	50	42	40
0.05	74	22	14

[a] Calculated from the rate law $k_{\mathrm{obsd}} = k_{\mathrm{E}} + k_{\mathrm{Az}}[\mathrm{OH^-}]$, with $k_{\mathrm{E}} = 3.3 \times 10^{-3}\ \mathrm{sec^{-1}}$ and $k_{\mathrm{Az}} = 1.1 \times 10^{-2}\ M^{-1}\ \mathrm{sec^{-1}}$. [b] Normalized to 100% for $\mathrm{[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2}$.

Treatment of *cis*-$\mathrm{[Co(en)_2(Az)Br]Br_2}$ with 0.2 *M* $[\mathrm{OH^-}]$ (five half-lives for hydrolysis) followed by treatment with 4 *M* HBr gave a 97% recovery of the reactant bromo complex (visible and pmr spectra). Coordi-

Table VI. ^{18}O Tracer Results

Substrate		Product		% ^{18}O
Reaction	Enrichment[a]	Complex	Enrichment[a]	retention[b]
$[Co(en)_2(NH_2CH_2CH_2Br)Br]Br_2 + {}^{18}OH^-$	1.36[c]	$[Co(en)_2(NH_2CH_2CH_2\text{-}(Br)(H_2{}^{18}O)](NO_3)_3$	1.04	76
$[Co(en)_2(NH_2CH_2CH_2Br)(H_2{}^{18}O)](NO_3)_3 + OH^-$	1.04	$[Co(en)_2(NH_2CH_2CH_2{}^{18}OH)]Br_3$	1.02 0.93 ± 0.04[d]	75 68 ± 3

[a] Represents (^{18}O enrichment in atom %) − (atom % ^{18}O in CO_2 of normal isotopic abundance) (0.201); % ^{18}O = $100R/(2 + R)$, where $R = [46]/[44] + [45]$. [b] Expressed as a per cent of the solution enrichment. [c] Solution enrichment. [d] Obtained from direct analysis of complexed ethanolamine in MS9; represents 100[63]/[61](enriched sample) − 100[63]/[61](unenriched sample); average of four runs.

nated ethylenimine shows distinctive pmr absorptions for the methylene region, Figure 1. No orange 3+ band was observed in this experiment. The pmr spectrum of *cis*-$[Co(en)_2(Az)Br]Br_2$ in 7.6 *M* HBr remained unchanged for 3 days at ~20°. This experiment implies that ring opening does not occur with coordinated ethylenimine in acid solution. Also, treatment of $[Co(en)_2(OH)_2]^+$ with equimolar ethylenimine in 1 *M* NaOH (five half-lives for base hydrolysis of *cis*-$[Co(en_2)Br(Az)]Br_2$) gave no ethylenimine complex. Hydrolysis of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2CH_2Br)]Br_2$ with 1 *M* NaOH for 3 hr followed by treatment with 2 *M* HBr at 80° gave only one violet 2+ ion. Analytical data and visible and pmr spectra of the recovered material identified it as the reactant complex.

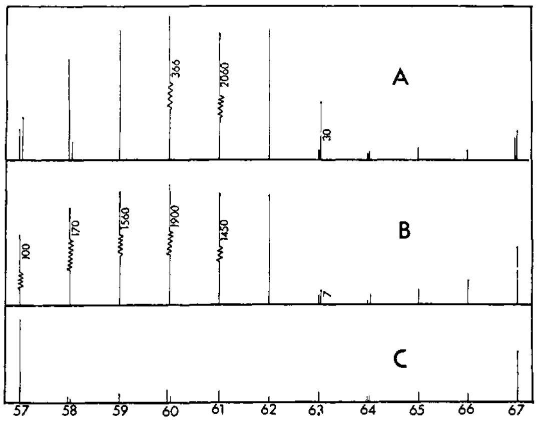


Figure 1. Mass spectrum of (A) ^{18}O-labeled and (B) unenriched ethanolamine in $[Co(en)_2(NH_2CH_2CH_2OH)]Br_3$; (C) background spectrum (AEIMX 902 spectrometer, complexes directly inserted into analyzer, 250°).

cis-$[Co(en)_2(H_2O)(NH_2CH_2CH_2Br)]^{3+}$ was isolated as the nitrate or bromide salt from the reaction mixture after hydrolysis of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ at pH 10 (five half-lives). The nitrate salt was also isolated following treatment of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ with Hg^{2+} in 2 *M* $HClO_4$. The aquobromoamine complex was distinguished from the chelated ethanolamine compound, $[Co(en)_2(NH_2CH_2CH_2OH)]Br_3$, by its analytical composition and its reconversion (95%) to *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ on treatment with 3 *N* HBr or saturated NaBr at ~80°. The visible spectra for the two complexes are similar to those of the chelated ethanolamine complex, having a slightly higher absorptivity in the visible region. However, the rotatory dispersion curves for the *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+}$ and $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ ions differ considerably, Figure 2.

Base hydrolysis (pH 9.5) of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$ (for five half-lives) followed by treatment with 3 *N* HBr resulted in 34% *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]^{2+}$ and 62% $[Co(en)_2(NH_2CH_2CH_2OH)]^{3+}$. Both ions were isolated as their bromide salts and characterized by pmr and visible spectra. Several attempts to isolate the *cis*-$[Co(en)_2(H_2O)(NH_2CH_2CH_2OH)]^{3+}$ ion from the products formed on hydrolysis of *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$ in base failed, but the above experiment requires that it was formed and reanated to the reactant on treatment with HBr. *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]^{2+}$ (21%) was also isolated after the Hg^{2+}-catalyzed acid hydrolysis of the bromo complex followed by treatment with excess NaBr at 80°. This experiment requires the formation of *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2OH)]^{3+}$ in acid conditions, some or all of which undergoes subsequent reanation. In this way, *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2OH)]^{3+}$ differs from the chelated ethanolamine ion, $[Co(en)_2(NH_2CH_2CH_2OH)]^{3+}$, which does not anate even under more vigorous conditions (100°, 7 *M* HBr).

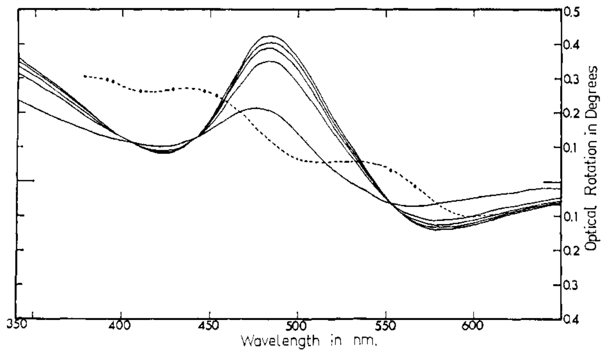


Figure 2. Change in rotatory dispersion at pH 10.72 for $(-)_{589}$-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$: initial complex in water (pH 4), ------; after loss of coordinated Br^- (2.5 min); after 9.5 min, 14.5 min, 19.5 min, and 67 min, complete formation of $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$, —— ($2 \times 10^{-3}$ *M* [Co] in 0.2 *M* NEt_3 buffer, 0.05 *M* KNO_3, 25°).

Oxygen Tracer Studies. The results of the ^{18}O-labeling experiments are given in Table VI. Labeled *cis*-$[Co(en)_2(NH_2CH_2CH_2Br)(H_2{}^{18}O)](NO_3)_3$ was prepared by the Hg^{2+}-catalyzed acid hydrolysis of *cis*-$[Co(en)_2(NH_2CH_2CH_2Br)Br]Br_2$ in $H_2{}^{18}O$, and crystallized by adding $LiNO_3$. The bound water was recovered and showed 76% retention of label compared to the solution value. The loss may be due to some exchange with NO_3^- and/or H_2O (from $LiNO_3 \cdot xH_2O$) under the conditions of the water recovery. This complex was hydrolyzed at pH 10 in normal water until base consumption ceased, and the product was recovered

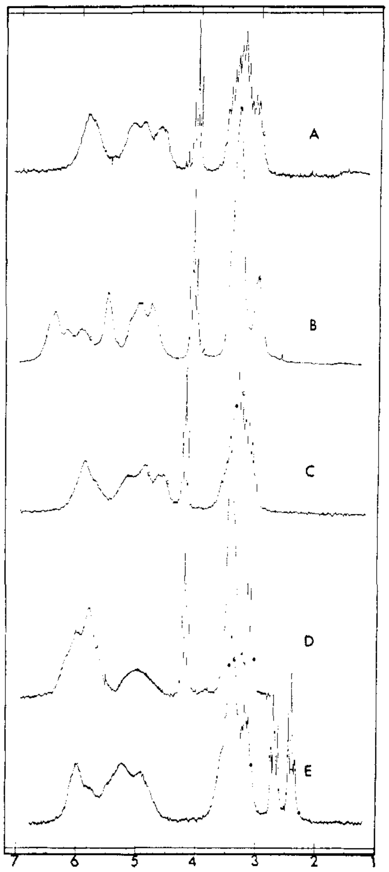


Figure 3. Pmr spectra (100 MHz) for (A) *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]Br_2$ in 10^{-3} *M* D_2SO_4, (B) *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2Br)](NO_3)_3$ in dilute DCl, (C) *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]Br_2$ in 10^{-3} *M* DCl, (D) $[Co(en)_2(NH_2CH_2CH_2OH])Br_3 \cdot H_2O$ in D_2O, and (E) *cis*-$[Co(en)_2Br(Az)]Br_2$ in 10^{-3} *M* DCl.

and recrystallized as $[Co(en)_2(NH_2CH_2CH_2OH)]Br_3 \cdot H_2O$. Following removal of the lattice water the remaining oxygen was converted to CO_2 to give a 98% retention of label when compared to that for the starting complex, or a 75% retention when compared to the initial solution value. The retention of label in the ethanolamine complex was also evaluated from data obtained on pyrolysis of the complex in the ionization chamber of the MS902 mass spectrometer at 250°. The ratio of mass numbers 63/61 for liberated ethanolamine gave the $^{18}O/^{16}O$ ratio, Table VI. Compared with the enrichment in the aquo complex, almost full retention of label was observed. Analysis of $H_2{}^{18}O$ in the aquo ethanolamine complex by the same method was impractical because of the relatively high H_2O background in the instrument.

Stereochemical Course of Hydrolysis. *cis*-$[Co(en)_2(NH_2CH_2CH_2OH)Br_3 \cdot H_2O$ was resolved in its enantiomers as the bromo tartrate salt, giving $(+)_{589}$-$[Co(en)_2(NH_2CH_2CH_2OH)]Br_3 \cdot H_2O$, $[\alpha]_{589}$ 211° in 4 *M* HBr. The cation was optically stable in 3 *M* HBr and triethylamine buffer (pH 10.74) over at least 72 hr at 25°. The *cis*-$[Co(en)_2(NH_2CH_2CH_2Br)Br]Br_2$ and *cis*-$[Co(en)_2(Az)Br]Br_2$ complexes were resolved using (+)-bromo-π-camphorsulfonate, to give $[\alpha]_{589}$ −80 and 18°, respectively, for the optically pure bromide salts in dilute acetic acid (pH 4). Hydrolysis of the ethylenimine compound at pH 9.5 followed by reanation using HBr at ~80° gave 80 ± 3% of $(+)_{589}$-$[Co(en)_2(Az)Br]Br_2$, (after 5 and 100 half-lives for base hydrolysis with a 97% recovery). These results show that both the $(-)_{589}$-$[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ and $(+)_{589}$-$[Co(en)_2(Az)OH]^{2+}$ ions are optically stable under the conditions of hydrolysis.

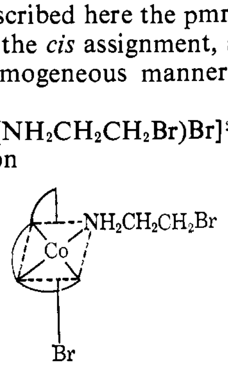
Hydrolysis of $(-)_{589}$-$[Co(en)_2(NH_2CH_2CH_2Br)Br]Br_2$ in triethylamine buffer (pH 10.74 for five half-lives) gave 45% retention of configuration in the $(-)_{589}$-$[Co(en)_2(NH_2CH_2CH_2Br)(OH)]^{2+}$ formed. Subsequent hydrolysis (five half-lives for the cyclization reaction) resulted in >95% retention, as shown by the formation of 43% $(-)_{589}$-$[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$. The latter process gave a large increase in specific rotation in the vicinity of 500 nm (Figure 2), consistent with the formation of chelated ethanolamine. The retention figure appeared to vary according to the experimental conditions (43%, pH 10.74, and 55%, pH 14). This aspect is being examined more carefully in a stereochemical study of these compounds.

The 31% retention for $[Co(en)_2(Az)OH)]^{2+}$ (1 *M* NaOH) compared to 55% retention for $(-)_{589}$-$[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ implies that either additional racemization accompanies the formation of the ethylenimine ring in $(-)_{589}$-$[Co(en)_2(NH_2CH_2CH_2Br)\ (OH)]^{2+}$, or it is also formed from *trans*-$[Co(en)_2(NH_2CH_2CH_2Br)(OH)]^{2+}$ ion. The final product, however, appears to be *cis*-$[Co(en)_2(Az)OH]^{2+}$, since the bromo product formed from it by treatment with HBr is identical (pmr, infrared) with *cis*-$[Co(en)_2(Az)Br]Br_2$. The $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ ion (43% $(-)_{589}$, 43% $(\pm)_{589}$, pH 10.74) probably results only from the *cis*-$[Co(en)_2(NH_2CH_2CH_2Br)OH]^{2+}$ ion, since only one rate of cyclization was observed. The 86% recovery may be compared with the 77% of *cis* products formed in the base hydrolysis of $(+)_{589}$-$[Co(en)_2(NH_3)Br]Br_2$.[11]

Discussion

Stereochemistry. All the complexes of the form $[Co(en)_2(NHR)_2X]^{n+}$ (n = 2, 3; X = Br, OH, OH_2, Cl) described in this study are assigned the *cis* configuration. Several of the bromo complexes were resolved into catoptric forms which confirmed the *cis* assignment. For the other bromo species, the evidence for the assignment comes primarily from the method of preparation,[8] which has only given the *cis* form in the past, and from pmr spectra (Figure 3). In one instance where both *cis* and *trans* forms have been studied, $[Co(en)_2NH_3Cl]^{2+}$,[11] the pmr spectra were widely different, particularly in the N–H region, and the two isomers were separated readily by ion-exchange chromatography. For the *bromo* isomers described here the pmr in the NH region is consistent with the *cis* assignment, and all the species behaved in a homogeneous manner chromatographically.

The $[Co(trien)(NH_2CH_2CH_2Br)Br]^{2+}$ ion is assigned the β_2 configuration



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[11] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 90, 6654 (1968).

from spectral and kinetic similarities between this ion and analogous β-amino acid ester and ammonia complexes.[12]

In those instances where $[Co(en)_2amineOH]^{2+}$ or aquo complexes are produced, the reconversion to the bromo ion using HBr is assumed to occur with full retention of configuration. The evidence to support this assumption arises from anation studies with related pentaamine type complexes such as *cis*- and *trans*-$[Co(en)_2NH_3OH_2]^{3+}$[11] and *trans*-$[Co(NH_3)_4(ND_3)(OH_2)]^{3+}$.[13]

The composition of the products formed on base hydrolysis can therefore be determined by identification of the recovered bromo complexes along with the other products.

Stoichiometry. At pH >11, hydrolysis of *cis*-$[Co(en)_2(NH_2CH_2CH_2Br)Br]^{2+}$ gave two major products, chelated $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ (86%) and $[Co(en_2)[OH)_2]^+$ (~10%), together with traces of two other ions (~4%) which were not identified. At pH >11 an ethylenimine complex *cis*-$[Co(en)_2(Az)OH]^{2+}$ was also formed along with the other products which occurred at lower pH values. For the purposes of this article only the paths leading to the production of chelated ethanolamine and the hydroxoethylenimine complexes are relevant. The traces of other species produced may be *trans*-$[Co(en)_2(NH_2CH_2CH_2Br)OH]^{2+}$ and *trans*-$[Co(en)_2(Az)(OH)]^{2+}$, but they have not yet been characterized.

Mechanism. The products formed from *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]^{2+}$ arise by two sequential reactions. The first consists of base hydrolysis of Br^- to give *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+}$ and the second is the reaction of this intermediate in two different ways to give the chelated ethanolamine complex $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$ and *cis*$[Co(en)_2(OH)Az]^{2+}$.

The rate law for Br^- removal (1), $k_{obsd} = k_{Br}[OH^-]$,

$$cis\text{-}[Co(en)_2Br(NH_2CH_2CH_2Br)]^{2+} + OH^- \longrightarrow cis[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+} + Br^- \quad (1)$$

and the second-order rate constant, k_{Br}, are similar to those found for related *cis*-$[Co(en)_2Br(NH_2R)]^{2+}$ ions, Table VII, and it is likely that this reaction occurs by the S_N1CB mechanism proposed[14] for base hydrolysis of cobalt(III)-acido complexes.

Table VII. Second-Order Rate Constants for Base Hydrolysis of Coordinated Bromide in $[Co(en)_2Br(amine)]^{2+}$ Ions (25°)

Amine	k_{Br}, M^{-1} sec^{-1}	Ionic strength	Ref
NH_3	66	0.1	*a*
$NH_2CH_2CH(CH_3)OH$	94	0.1	*a*
$\overline{NHCH_2CH_2}$	160	0.1	*a*
$NH_2CH_2CH{=}CH_2$	180	0.1	*a*
$NH_2CH_2CH_2OH$	190	0.1	*a*
$NH_2CH_2CH_2Br$	180	0.1	*a*
$NH_2CH_2CONH_2$	260	1.0	*b*
$NH_2CH_2CON(CH_3)_2$	247	1.0	*b*
$NH_2CH_2CONHCH_3$	280	1.0	*b*
$NH_2CH_2COOCH(CH_3)_2$	280	1.0	*c*

[a] This work. [b] D. A. Buckingham, D. M. Foster, C. E. Davis, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **92**, 6151 (1970). [c] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *ibid.*, **91**, 4102 (1969).

The second reaction (2) leading to the ethanolamine and ethylenimine complexes consists of alternate paths

$$\begin{tikzcd} & cis\text{-}[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+} + OH^- \arrow[dl, "k_E"'] \arrow[dr, "k_{Az}"] & \\ {[Co(en)_2(NH_2CH_2CH_2O)]^{2+} + Br^- + H_2O} & & cis\text{-}[Co(en)_2(OH)(Az)]^{2+} + Br^- + H_2O \end{tikzcd} \quad (2)$$

for intramolecular lysis of bromide in coordinated 2-bromoethylamine. The rate law for this process is

$$k_{obsd} = k_E + k_{Az}[OH^-]$$

and below pH 11 the product is essentially the ethanolamine complex, while at pH 14 the product is largely the ethylenimine–hydroxo ion (77%). Both paths consume OH^- ion, but only the rate of ethylenimine formation is dependent on OH^-; this requires base consumption to occur prior to or during the rate-determining step for ethylenimine formation, but subsequent to it for the ethanolamine complex.

The consumption of 1 mol of OH^- requires the ethanolamine complex to be in the form $[Co(en)_2(NH_2CH_2CH_2O)]^{2+}$. This ion was distinguished from *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2OH)]^{2+}$ by its inertness toward substitution by Br^- in acid solution, by its relatively large optical activity in the visible region, and by the acidity of its conjugate acid, $pK_a = 3.59 \pm 0.05$ (25°). *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2OH)]^{3+}$ readily forms *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]^{2+}$ on treatment with HBr, and the similar $[Co(en)_2(OH_2)(NH_2CH_2CH_2Br)]^{3+}$ ion has a pK_a of 6.2 (25°) and a considerably less intense ORD curve, Figure 2. The latter two observations are consistent with the properties of other aquopentaamine complexes of this type. Furthermore, if $[Co(en)_2(OH)(NH_2CH_2CH_2OH)]^{2+}$ were the product formed from $[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+}$, the rate law for its formation might be expected to be $[OH^-]$ dependent.

The tracer results, Table VI, establish that the coordinated hydroxo group in *cis*-$[Co(en)_2(^{18}OH)(NH_2CH_2CH_2Br)]^{2+}$ is incorporated into the chelated ethanolamine product. Based on the enrichment in the hydroxo complex, quantitative retention of label obtains. Moreover, the results given in Table V demonstrate that the ethylenimine complex arises entirely from *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+}$, and does not form during hydrolysis of coordinated Br^- in *cis*-$[Co(en)_2Br(NH_2CH_2CH_2Br)]^{2+}$. This result is also implied by the rate constants for the two processes if it is assumed that the amide ion is similarly reactive in the two complexes; $k_{Br} = 180\ M^{-1}\ sec^{-1}$, $k_{Az} = 1.1 \times 10^{-2}\ M^{-1}\ sec^{-1}$. For N to act as a nucleophile, a proton is required to be lost from the coordinated 2-bromoethylamine, and the pH dependence for this path agrees with this requirement. Mechanisms consistent with the above considerations are given in Scheme I.[15]

Both products are formed by attack of coordinated nucleophiles at the saturated C-2 atom (S_Ni); one by the coordinated hydroxide ion and the other by

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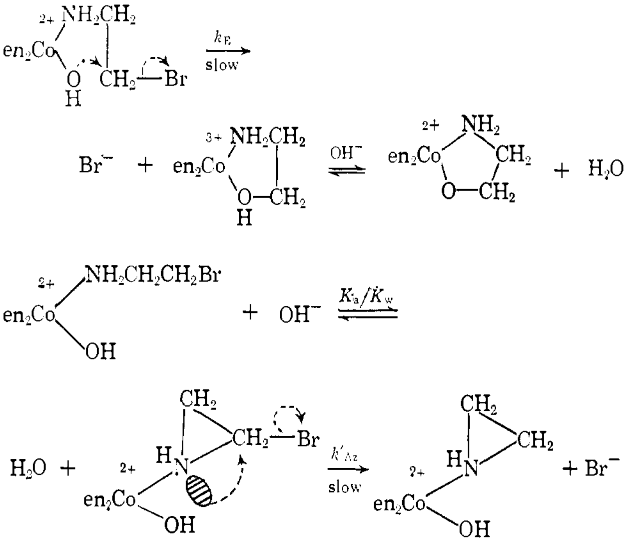
[12] D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 9, 11 (1970); M. Dwyer, unpublished work.

[13] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, 20, 597 (1967).

[14] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 261.

[15] Localized charges have been omitted in Scheme I since their residence is uncertain. The overall charge on the complex ion is placed on the Co(III) atom for convenience only.

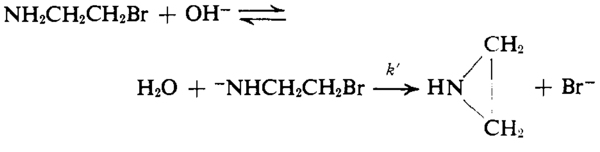
Scheme I. Mechanism for Base Hydrolysis of the *cis*-$[Co(en)_2(OH)(NH_2CH_2CH_2Br)]^{2+}$ Ion



coordinated amide ion. The two reactions are competitive, and it is striking that amide ion competes with OH^- when its concentration is considerably smaller. In the mechanism of Scheme I, k_{Az}, the derived second-order rate constant, is a composite $k_{Az}'K_a/K_w$. In the absence of an experimental value for K_A, the first-order rate constant for the amido complex cannot be calculated, but it may be estimated at ~1 sec^{-1} assuming $pK_a = 16$. By comparison, for internal attack of OH^-, $k_E = 3 \times 10^{-3}$ sec^{-1}. This implies that the amide ion is 10^2–10^3 more reactive than coordinated hydroxide.

The rate of ring closure to give ethanolamine from β_2-$[Co(trien)(NH_2CH_2CH_2Br)OH]^{2+}$ is similar to that for the bis(en) complex, but the loss of Cl^- from *cis*-$[Co(en)_2(NH_2CH_2CH_2Cl)OH]^{2+}$ is decreased by a factor of 30 relative to loss of Br^-. Both observations are consistent with an SNi mechanism. Changes in the reacting moieties markedly affect the rate, whereas changes in the amine ligands remote from the reaction centers do not. The last result is in marked contrast to substitutions at Co(III) centers for bis(en) and trien complexes which vary widely.[14]

It is of some interest to compare the present reactions with those found for the similar reactions of the organic molecules, Table VIII. Solomon and Freundlich and coworkers[16] studied the cyclization of compounds of the type $NH_2(CH_2)_nBr$, where $n = 2$–6, and established that the rates were hydroxide independent and varied appreciably with changing n, Table IX. This rate variation has been attributed to opposing effects of separation of the reactive centers and strain in the cyclic imine in the transition state.[17] Comparison of the rate for $HNHCH_2CH_2Br$ with that for $CoNHCH_2CH_2Br$ demonstrates that substitution of a proton by cobalt(III) results in a ~2000-fold increase in rate. This factor is much smaller than a comparison of proton basicities would suggest; $pK_b(HNHCH_2CH_2Br) = 5.5$, $pK_b(CoNHCH_2CH_2Br) \sim -2$. The smaller rate difference found in the displacement reaction may reflect steric crowding in the transition state by the $Co(en)_2$ moiety, or simply that proton basicity of nitrogen is not a gauge for nucleophilicity toward carbon in these systems.[18] Chan and Leh[19] observed that in strong base a base-dependent term is significant in the hydrolysis of $NH_2CH_2CH_2Br$. They ascribed this path to cyclization in the amide ion



$$NH_2CH_2CH_2Br + OH^- \rightleftharpoons H_2O + {}^-NHCH_2CH_2Br \xrightarrow{k'} HN(CH_2)_2 + Br^- \quad (3)$$

From the observed rate constant, 6.2×10^{-5} M^{-1} sec^{-1} at 0°,[19] a value of $\sim 10^{-3}$ M^{-1} sec^{-1} at 25° may be calculated. If $K_b \simeq 10^{21}$,[20] then $k' = kK_b = 10^{19}$ sec^{-1}. This large value implies that the attack of amide ion is controlled by the frequency of encounter of the two centers, which should be no faster than a C–N vibration, ~10^{13} sec^{-1}. This is enormously faster than cyclization in the parent amine ($k = 10^{-3}$ sec^{-1}) or cobaltamine (*ca.* 1 sec^{-1}).

Table VIII. Neighboring Group Effects in Halide Lysis at Saturated Carbon

Reactive substrate	k, sec^{-1}	Ref
$^-NHCH_2CH_2Br$	$\sim 10^{13}$	*a*
$HNHCH_2CH_2Br$	6×10^{-4}	*f*
$CoNHCH_2CH_2Br$	~1	*b*
$^-OCH_2CH_2Cl$	~10	*c*
$HOCH_2CH_2Cl$	$\sim 6 \times 10^{-13}$	*d*
$HOCoNH_2CH_2CH_2Cl$	1×10^{-4}	*b*
$HOCoNH_2CH_2CH_2Br$	3×10^{-3}	*b*
$HOCH_2CH_2CH_2Cl$	2×10^{-6}	*e*

[a] Estimated in this work. [b] This work. [c] Calculated from a second-order rate constant of 10^{-2} M^{-1} sec^{-1} [C. L. McCabe and J. C. Warner, *J. Amer. Chem. Soc.*, **70**, 4031 (1948)] and $pK_a = 16.9$ [S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948)]. [d] From A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1963, pp 300–302. [e] Reference 21 and this work. [f] See Table IX.

Table IX. First-Order Rates for Cyclization of Some Bromoamines, $NH_2(CH_2)_nBr$, in Water at 25°[a]

n	10^4k, sec^{-1}
2	6
3	0.08
4	5000
5	80
6	0.1

[a] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 181.

The data given in Table VIII suggest that the rate of cyclization of coordinated $NH_2(CH_2)_3Br$ should be slower than that for the formation of the ethylenimine complex, and indeed *cis*-$[Co(en)_2Br(NH_2(CH_2)_3Br)]^{2+}$ was recovered unchanged after 3 hr in 1 M NaOH and treatment with HBr. This result also implies that attack by coordinated hydroxide to form the six-membered propanolamine chelate ring is a much slower process than forming the five-membered ring,

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(16) G. Solomon, *Helv. Chim. Acta*, **16**, 1361 (1933); **17**, 851 (1934); F. Freundlich, *Z. Phys. Chem.*, **166**, 161 (1933); **122**, 39 (1926), and previous papers in this series.

(17) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 181.

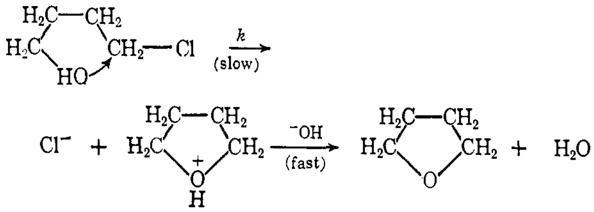
(18) J. Hine and R. D. Weimar, *J. Amer. Chem. Soc.*, **87**, 3387 (1965).

(19) S. C. Chan and F. Leh, *Aust. J. Chem.*, **19**, 2271 (1966).

(20) R. P. Bell in "The Proton in Chemistry," Methuen, London, 1959, p 88.

and that hydrolysis by solvent OH^- is also a slow process. The table predicts that a marked rate increase might be anticipated for the butylamine complex, with the product being exclusively the cobalt–pyrrolidine ion, since competition by the coordinated hydroxo group should be effectively excluded by the increase in ring size required.

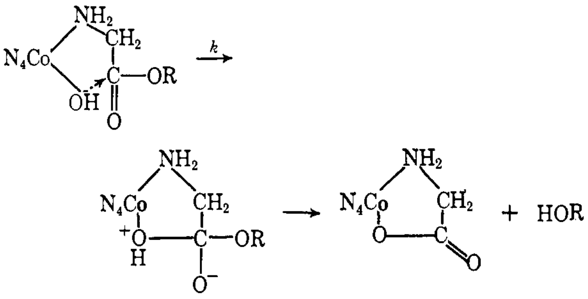
A similar comparison is possible for neighboring-group participation by the hydroxyl function. Heine and coworkers[21] have shown that ring closure in tetramethylenechlorohydrin in water yields tetrahydrofuran, and from the observed data a rate constant of 2×10^{-6} sec^{-1} at 25° may be calculated. The authors suggest a mechanism identical with the one proposed here, the major chemical distinction being the replacement of one methylene group by Co. A comparison of the rate constants shows that the Co system is faster by a factor of ~50, a considerably smaller factor than that suggested by the proton basicities; pK_b(Co-OH) ≃ 7.5, p$K_b(C_2H_5O^-)$ ≃ 16. Proton basicity evidently is a poor measure of the nucleophilic character of OH toward C in the two instances. It is of interest to note that, whereas the Co atom is part of the ring system in the transition state in this reaction, it is *exo* to it in the imine case.



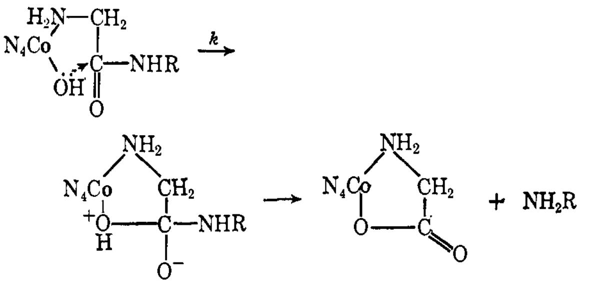
(4)

It is also pertinent to compare these rates with the corresponding bimolecular attack of hydroxide ion. The reaction $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$ has a rate constant of 2.5×10^{-3} M^{-1} sec^{-1} at 50° in water,[22] giving a value of 1.25×10^{-4} M^{-1} sec^{-1} at 25° assuming an activation energy of 23 kcal/mol. At pH 10 such a reaction would have a half-life of 5.5×10^7 sec, and this may be compared with a half-life of 2.1×10^2 sec for the $BrCH_2CH_2NH_2$-Co-OH reaction under the same conditions. A closer comparison, and one which more than compensates for any polarization of the carbon center by the cobalt atom, is that obtained using the quaternary ammonium ion, $N^+(C_2H_5)_3CH_2CH_2Br$. At pH 10 and 25° this ion failed to consume hydroxide over a period of 24 hr. Assuming that a 1% uptake of base would have been observed this gives a lower limit for $t_{1/2}$ of 6×10^6 sec. The large increase in rate for the cobalt system is therefore a classic example of neighboring-group assistance by an adjacent nucleophile.

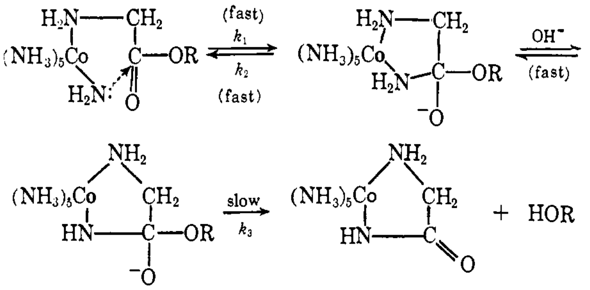
The reactions reported here fall into the small class of established cases of metal-ion assisted hydrolysis reactions; they enjoy the added distinction of containing both reacting groups attached to a common metal center. Other examples of assistance by neighboring groups attached to Co(III) involve the lysis of ester or amide functions by coordinated OH or NH_2.[1-3,23,24] In the former cases (N_4 = (en)$_2$, trien), reaction 5, the rate of intramolecular attack was not observed under the experimental conditions, but since neither $[Co(trien)(NH_2CH_2CO_2C_2H_5)OH]^{2+}$,[3] nor $[Co(en)_2(NH_2CH_2CO_2C_2H_5)OH]^{2+}$,[1] were detected at pH 8 and 11, respectively, a lower limit of $k \sim 0.2$ sec^{-1} may be calculated for unimolecular hydrolysis in these ions. For the amidolysis reaction (7), the attack of the amide ion is not rate determining, but from the third-order rate constant, $k_{\text{Im}} = 6.6 \times 10^6$ M^{-2} sec^{-1}, it can be estimated to have a value of $<6 \times 10^{10}$ sec^{-1}.[25] Since halide is a better leaving group than alkoxide in nucleophilic displacement at carbonyl carbon, it is apparent that loss of halide in the unsaturated system is a considerably faster process than at saturated carbon; a result in keeping with neighboring-group effects observed with organic esters, halohydrins, and haloamines.[26,27]



(5)



(6)



(7)

Base Hydrolysis. Although this study is primarily concerned with reactions of coordinated ligands, it has something to contribute in a preliminary way to our knowledge of base hydrolysis of cobalt(III) complexes. The rate laws for the reactions

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(21) H. W. Heine, A. D. Miller, W. H. Barton, and R. W. Greiner, *J. Amer. Chem. Soc.*, 75, 4778 (1953).

(22) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 302.

(23) D. A. Buckingham, submitted for publication.

(24) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 92, 6151 (1970).

(25) This value was obtained from the expression $k_{\text{Im}} = k_3k_1K_{a_1}K_{a_2}/k_2K_w^2 = 6.6 \times 10^6$ M^{-2} sec^{-1}, assuming $K_{a_1} = 10^{-16}$ and $K_{a_2} = 10^{-18}$, giving $k_1k_3/k_2 \sim 6.6 \times 10^{10}$ sec^{-1}. Since k_2 involves breaking the chelate ring, it is likely that k_3 greatly exceeds k_2, giving $k_1 < 6.6 \times 10^{10}$ sec^{-1}. It is noted here that in ref 2, p 3455, the base dissociation constants pK_1 and pK_2 are incorrectly given as >2; these should read <−2.

(26) T. C. Bruce and S. J. Benkovic, "Bioorganic Mechanisms," Vol. 1, W. A. Benjamin, New York, N. Y., 1966, p 125, and references therein.

(27) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 70, 828 (1948).

$$cis\text{-}[Co(en)_2(NHR_2)Br]^{2+} + OH^- \longrightarrow [Co(en)_2(NHR_2)OH]^{2+} + Br^-$$

(where NHR_2 = $NH_2CH_2CH_2Br$, $NH_2CH_2CH_2OH$, or C_2H_4NH) are the same, $k_{obsd} = k_{Br}[OH^-]$, and the second-order rate constants (k_{Br}) are similar, Table VII. Both sets of results are consistent with the SN1CB mechanism proposed for basic hydrolysis of acido cobalt(III) complexes.[14] Also, hydrolysis of the bromo monodentate ethanolamine complex in the presence of N_3^- ion leads to chelated ethanolamine, hydroxoethanolamine, and azidoethanolamine products, presumably by competition for the five-coordinate deprotonated intermediate by the coordinated nucleophile, water, and N_3^-. While similar competitive characteristics are shown during the hydrolysis of related complexes,[11] a novel feature in the present instance is the intervention of the coordinated nucleophile; this aspect of the study may lead to some interesting synthetic possibilities and to a more sensitive way of looking at competition during the base hydrolysis of cobalt(III) complexes.

All three *cis*-bromo complexes gave largely *cis*-hydroxo or tris-chelate products in somewhat larger amounts (~86%) then for the *cis*-$[Co(en)_2NH_3Br]^{2+}$ analog under the same conditions (77%). Also partial retention (~50%) of optical activity was observed, which agrees with previous observations.[11] However, these aspects need to be examined more closely under carefully controlled conditions, and the experiments will be repeated in detail in connection with other studies relating to the mechanism of the base hydrolysis reaction.

Concluding Remarks. The advantages of coordinated nucleophiles to effect organic reactions appear to be several. They seem to be extraordinarily efficient even though their basicity is reduced by a factor of at least 10^6–10^8 on coordination to Co(III). In this way substitution rates are enhanced over the intermolecular process by at least a factor of 10^4, and possibly by as much as 10^{12}.[24] Also the metal may function as a protecting group for sensitive areas in the coordinated molecule, and since the complex moiety is asymmetric it may direct the organic synthesis to give a stereospecific product. Recovery of the organic species is readily achieved through reduction of Co(III) to the labile Co(II) complex in acid solution. Coordinated OH^- could also be useful for hydrolysis of ligands sensitive to base in regions other than the reacting site, since the rate of the intramolecular reaction is likely to be independent of hydroxide ion at a pH >6. Finally, the reactions discussed in this paper offer interesting possibilities for the synthesis of chelate complexes. For example, using a sufficiently acidic *cis*-amine group, coordinated 2-bromoethylamine might be expected to chelate rather than cyclize internally to ethylenimine. In this way stereoisomers of multidentate ligands might by stereospecifically synthesized. Similarly, nucleophiles other than N and O should also be effective.

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Equilibria and Rates in the Formation of $[Ru(NH_3)_5N_2]^{2+}$ and $[(Ru(NH_3)_5)_2N_2]^{4+}$

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Abstract: The equilibrium constant K_1 for the reaction $Ru(NH_3)_5OH_2{}^{2+} + N_2(aq) = Ru(NH_3)_5N_2{}^{2+} + H_2O(liq)$ has been measured both by a static and a kinetic method. K_1 at 25° is 3.3×10^4, and $\Delta H_1{}^\circ$ and $\Delta S_1{}^\circ$ by the static and kinetic methods, respectively, are -10.1 ± 1.4, -9.4 ± 0.9 kcal/mol and -13 ± 5, -10 ± 3 eu. The equilibrium constant K_2 for the reaction $Ru(NH_3)_5OH_2{}^{2+} + Ru(NH_3)_5N_2{}^{2+} = [Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+} + H_2O(liq)$ has been measured by a static method. At 25° and $\mu = 0.10$, $K_2 = 7.3 \times 10^3$, $\Delta H_2{}^\circ = -11.2 \pm 1.4$ kcal/mol, and $\Delta S_2{}^\circ = -20 \pm 5$ eu. The rate constant k_1 for the formation of $Ru(NH_3)_5N_2{}^{2+}$ is $7.3 \times 10^{-2}\ M^{-1}\ sec^{-1}$, in good agreement with published measurements, $\Delta H_1{}^\ddagger = 18.3 \pm 0.3$ kcal/mol and $\Delta S_1{}^\ddagger = -2 \pm 1$ eu. For the aquation of $Ru(NH_3)_3N_2{}^{2+}$, $k_{-1} = 2.03 \times 10^{-6}\ sec^{-1}$ at 25.0°, $\Delta H_{-1}{}^\ddagger = 27.7 \pm 0.8$ kcal/mol, and $\Delta S_{-1}{}^\ddagger = 8 \pm 3$ eu.

Earlier experiments[1,2] showed $Ru(NH_3)_5N_2{}^{2+}$[3,4] and $[(Ru(NH_3)_5)_2N_2]^{4+}$ to be stable with respect to $Ru(NH_3)_5OH_2{}^{2+}$ and N_2 or $[Ru(NH_3)_5N_2]^{2+}$. Data on the rates of formation of the two complexes have been published,[5] and a recent communication[6] describes the results obtained in a calorimetric determination of ΔH° for the process

$$2Ru(NH_3)_5OH_2{}^{2+} + N_2(aq) = [(Ru(NH_3)_5)_2N_2]^{4+} + 2H_2O(liq)$$

It has also been reported[7] that over a period of 6 hr

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* To whom correspondence should be addressed.

[1] D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 5706 (1967).

[2] D. E. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

[3] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

[4] J. Chatt and J. E. Fergusson, *ibid.*, 126 (1968).

[5] I. J. Itzkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968).

[6] E. L. Farquhar, L. Rusnock, and S. J. Gill, *J. Amer. Chem. Soc.*, **92**, 416 (1970).

[7] J. N. Armor and H. Taube, *ibid.*, **92**, 2560 (1970).