coupling of these protons with the phosphorus nuclei given in Table II. For example, J_{P-MnCH_3} is greater in *cis*-$CH_3Mn(CO)_4L$[2] than in 2,4-L_2-1-$CH_3Mn(CO)_3$ for the same L as the positive charge on phosphorus in the monoligated complex is greater than in the diligated complex. Also, those complexes with the greater positive charge on phosphorus should have the greater negative charge on manganese. The chemical shift (τ) of the CH_3Mn protons (Table II) reflect this fact as these protons are usually more shielded in the disubstituted complexes than in *cis*-$CH_3Mn(CO)_4L$.[2]

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Competition Studies and the Stereochemistry for the Base Hydrolysis and Induced Aquation of Some Acidoamminebis(ethylenediamine)cobalt(III) Ions

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Abstract: The stereochemistry of the *cis*- and *trans*-hydroxo products from the base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, Br, NO_3) and *trans*-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, NO_3) is independent of the nature of the leaving groups. In the presence of anions (Y^-) such as N_3^-, NCS^-, and NO_2^-, base hydrolysis leads to incorporation of the anion, and the competition ratio $[Co(en)_2NH_3Y]^{2+}/[Co(en)_2NH_3OH]^{2+}$ also is independent of the leaving group. Also, the stereochemistry of the $[Co(en)_2NH_3Y]^{2+}$ products is constant for each competing anion within each series of reactants. These results suggest the formation of a common intermediate or intermediates from a series of reactants.

In some recent studies[1-3] on the mechanism of base hydrolysis of acidopentaamminecobalt(III) complexes, results are reported which appear to support an SN1CB mechanism. The studies embrace competition experiments[1,2] and the stereochemistry of the products,[3] and the conclusion concerning the mechanism was drawn from the fact that all the results were independent of the nature of the leaving group. This suggested the formation of a common intermediate by the following path[4]

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2X]^+ + H_2O$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + X^-$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+}$$

Bimolecular attack of OH^- at the cobalt atom (SN2)[5]

$$[Co(NH_3)_5X]^{2+} OH^- \xrightarrow{k} [Co(NH_3)_5OH]^{2+} + X^-$$

does not permit the competition products observed and would be unlikely to give the same stereochemistry for the products with different substrates. The SN2CB mechanism[6]

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2X]^+ + H_2O$$

$$[Co(NH_3)_4NH_2X]^+ + H_2O \xrightarrow{k} [Co(NH_3)_5OH]^{2+} + X^-$$

or

$$[Co(NH_3)_4NH_2X]^+ + Y^- + H^+ \longrightarrow [Co(NH_3)_5Y]^{2+} + X^-$$

still contains X in the intermediate and would also be expected to give different competition values and stereochemistry of the products for different substrates. All of these mechanistic proposals conform to the observed rate law $R = k[\text{complex}][OH^-]$.

In one of these previous studies the stereochemistry of the products of base hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ ions (X = Cl, Br, NO_3) was examined using pmr spectroscopy.[3] Also the stereochemistry of the competition product $[Co(NH_3)_4(^{15}NH_3)N_3]^{2+}$, obtained by base hydrolysis in the presence of N_3^-, was examined by the same technique. Close to 50% *cis*- and 50% *trans*-aquo product was observed for all the substrates, whereas the azido product was described as totally *trans*. This aspect of the original study[3a] was in error and the correct result is 70% *cis* and 30% *trans* for the azido product.[3b] The results were rationalized tentatively in favor of a trigonal-bipyramidal intermediate. However, no firm conclusions were reached concerning the intermediate's structure and the possibility of the intermediate competing for the species in solution and rearranging before the competition was not excluded.

The ^{15}N isotope experiments were expensive and the isolation of the competition products for the pmr measurements was difficult. To look at the problems more

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closely with less expense and more revealing compounds in terms of stereochemical detail, we have turned our attention to the analogous *cis*- and *trans*-$[Co(en)_2NH_3X]^{2+}$ ions (where X = Cl, Br, NO_3). This paper records primarily the results of the base hydrolysis of some of these species in terms of the stereochemistry of the hydroxo products, the competition values for the anions N_3^-, NO_2^-, and NCS^-, and the stereochemistry of the azido products. The rates of base hydrolysis of $[Co(en)_2NH_3X]^{2+}$ ions (X = Cl, Br, NO_3) are much larger than those of the corresponding azido, isothiocyanato, and nitro complexes so that subsequent hydrolysis of the competition product is not significant. Similarly the rates of isomerization and/or racemization for the *cis*- and *trans*-hydroxo and -aquo complexes are too small[7,8] to affect the analysis of the results. No detectable rearrangement of any of the products takes place in the time required for the experiments.

Finally the stereochemical course of the Hg^{2+}-induced aquation of *cis*-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, Br) and *trans*-$[Co(en)_2NH_3Cl]^{2+}$ is reported along with that of the NO^+-induced aquation of *cis*-$[Co(en)_2NH_3N_3]^{2+}$.

Experimental Section

The salt $(+)_{589}$-*cis*-**$[Co(en)_2NH_3Cl]Br_2$** was prepared as described by Werner,[9] $[\alpha]^{25}{}_{589}$ +135°. *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3Cl]Br_2$: N, 17.89; H, 4.89; C, 12.27. Found: N, 17.6; H, 4.9; C, 12.1.

trans-**$[Co(en)_2NH_3Cl]ClClO_4$** was prepared as described by Werner.[10] *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3Cl]ClClO_4$: N, 19.11; H, 5.22; C, 13.10. Found: N, 19.15; H, 4.9; C, 12.8.

$(+)_{589}$-$[Co(en)_2NH_3Br]Br_2$ was prepared as described by Werner,[11] $[\alpha]^{25}{}_{589}$ +103°. *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3Br]Br_2$: N, 16.07; H, 4.39; C, 11.02. Found: N, 15.8; H, 4.3; C, 10.8.

$(+)_{589}$-$[Co(en)_2NH_3NO_3]S_2O_6$. $(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$ (2 g) was dissolved in water (15 ml at pH 3) and added to a solution of $Hg(NO_3)_2$ in 15 *M* HNO_3(50 ml of 1 *M* Hg^{2+}). When the reaction was completed (10 min), the solution was cooled in an ice bath and the product precipitated by adding ice-cold ethanol. After filtration the product was dissolved in water and crystallized by adding $Na_2S_2O_6$. Three fractions were collected, washed with ice-cold water, ethanol, and ether, and dried in a vacuum desiccator. The first two fractions had the same rotation. (For a 0.1% solution α +0.095° at 589 mμ and 25° in a 1-dm tube, whence $[\alpha]^{25}{}_{589}$ +95°). *Anal.* Calcd: N, 20.09; H, 4.58; C, 11.48. Found: N, 20.1; H, 4.6; C, 11.3.

trans-**$[Co(en)_2NH_3NO_3]S_2O_6$.** *trans*-$[Co(en)_2NH_3Cl]ClClO_6$ was treated with $Hg(NO_3)_2$ in concentrated HNO_3 in the same way as for the *cis*-chloro complex. *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3NO_3]S_2O_6$: N, 20.09; H, 4.58; C, 11.48. Found: N, 20.5; H, 4.5; C, 11.6.

$(+)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$. $(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$ (2 g) was dissolved in the minimum amount of water (pH 3–4) at room temperature. $Hg(ClO_4)_2$ (35 ml of 1 *M* Hg^{2+} in 0.1 *M* $HClO_4$) was added and the solution left for 20 min at room temperature. The volume was reduced in a vacuum evaporator and concentrated HBr was added until no more $HgBr_2$ precipitated. After filtration a mixture of concentrated HBr and Br_2 was added dropwise. The tribromide complex was collected and dissolved in aqueous HBr (10^{-4} *M*), and the aqueous solution was extracted with CCl_4 until the organic phase became colorless. The solution was reduced in volume and $(+)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ precipitated by adding a large excess of concentrated HBr with cooling. The bromide was recrystallized from a minimum volume of water by adding an equal volume of concentrated HBr and cooling the solution. Another fraction was obtained by adding a large volume of ethanol and cooling. The two fractions had the same rotation. The crystals were washed with ethanol and ether and dried in air at room temperature. It was shown also by mixing some optically active complex with racemate that a separation was readily achieved by recrystallization. The molar rotation curves of $(+)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ in 0.01 *M* $HClO_4$ and in 3 *M* HCl are given in Figure 1 (ϵ_{485} 67.9, 3 *M* HCl). *Anal.* Calcd for $[CoC_4H_{16}N_4OH_2NH_3]Br_3 \cdot H_2O$: N, 14.84; H, 4.90; C, 10.18. Found: N, 14.9; H, 4.8; C, 10.2.

trans-**$[Co(en)_2NH_3H_2O](NO_3)_3$** was prepared as described by Werner[10] (ϵ_{485} 45.5, 3 *M* HCl). *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3OH_2](NO_3)_3$: N, 28.00; H, 5.29; C, 12.00. Found: N, 28.0; H, 5.4; C, 11.8.

cis-**$[Co(en)_2NH_3N_3]Cl_2$.** *cis*-$[Co(en)_2N_3Cl]Cl$[12] was treated with liquid NH_3 containing a trace of NH_4Cl and the ammonia left to evaporate over 2 days. The product was extracted with dilute $NaClO_4$ solution and *cis*-$[Co(en)_2NH_3N_3]Cl_2$ was precipitated by adding a large excess of solid LiCl with cooling. The compound was recrystallized by dissolving it in a small volume of water at room temperature and adding solid LiCl until precipitation started. The solution was then cooled in an ice bath and the crystals were collected, washed with ice-cold water, ethanol, and ether, and dried in a vacuum desiccator.

$(-)_{589}$-$[Co(en))_2NH_3N_3]S_2O_6$. *cis*-$[Co(en)_2NH_3N_3]Cl_2$ (0.65 g) was dissolved in water (3 ml) at 44°. Solid (+)-ammonium α-bromocamphor-π-sulfonate (0.65 g) was added and the solution was left at 44° for 0.5 hr. The precipitated diastereoisomer was filtered off and recrystallized from water until constant rotation was obtained. The isomer $(-)_{589}$-$[Co(en)_2NH_3N_3)S_2O_6$ was obtained from the diastereoisomer by dissolving the latter in water and adding solid $Na_2S_2O_6$. The compound was collected, washed with ice-cold water, ethanol, and ether, and dried in a vacuum desiccator. The molar rotation curve of the complex in 1 *M* KCl is given in Figure 1 (ϵ_{508} 347, 1 *M* KCl). *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3N_3]S_2O_6$: N, 28.14; H, 4.81; C, 12.06. Found: N, 28.0; H, 4.7; C, 11.6.

trans-**$[Co(en)_2NH_3N_3]S_2O_6$.** *trans*-$[Co(en)_2N_3Cl]ClO_4$[13] was treated with liquid NH_3 containing a trace of NH_4Cl for 1 hr and taken down to dryness by blowing air over the solution. The product was extracted with water and $[Co(en)_2NH_3N_3]Cl_2$ was precipitated by adding solid LiCl to a cold solution. The chloride was dissolved in water and precipitated as the dithionate by adding $Na_2S_2O_6$. The crystals were washed and dried in the same way as for the *cis* complex. Three fractions were collected having the same molar absorptivity, ϵ_{512} 277 in 1 *M* KCl. The compound was tested for the presence of *cis* isomer by absorbing a solution containing the complex on an ion-exchange column (see later) and eluting with 1 *M* $NaClO_4$. Only one band was detected while a mixture of *cis* and *trans*-$[Co(en)_2NH_3N_3]^{2+}$ gave two clearly separated bands. *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3N_3]S_2O_6$: N, 28.14; H, 4.81; C, 12.06. Found: N, 28.5; H, 4.9; C, 12.1.

cis-**$[Co(en)_2NH_3NCS](SCN)_2$** was prepared as described by Werner[10] with molar absorptivities ϵ_{490} 220 and ϵ_{303} 1660 in 1 *M* KCl. *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3NCS](NCS)_2$: N, 30.35; H, 5.16; C, 22.67. Found: N, 30.3; H, 5.5; C, 22.7.

trans-**$[Co(en)_2NH_3NCS](SCN)_2$** was prepared as described by Werner[10] with molar absorptivities ϵ_{490} 168 and ϵ_{303} 1590 in 1 *M* KCl. *Anal.* Calcd for $[CoC_4H_{16}N_4NH_3NCS](NCS)_2$: N, 30.35; H, 5.16; C, 22.67. Found: N, 29.9; H, 5.4; C, 22.5.

Base Hydrolysis Reactions. $(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$, $(+)_{589}$-$[Co(en)_2NH_3Br]Br_2$, $(+)_{589}$-$[Co(en)_2NH_3NO_3]S_2O_6$, *trans*-$[Co(en)_2NH_3Cl]ClClO_4$, and *trans*-$[Co(en)_2NH_3NO_3]S_2O_6$ were hydrolyzed by dissolving the complex (0.1 mmole) in $NaClO_4$ solution (5 ml of 1 *M*) at 25° and then adding a solution of NaOH (5 ml of 0.4 *M* in 1 *M* $NaClO_4$) also at 25°. After 3 min the mixture was acidified with concentrated $HClO_4$ and the products were determined spectrophotometrically and polarimetrically. The rate constant for the base hydrolysis of *cis*-$[Co(en)_2NH_3Cl]^{2+}$ in 1 *M* $NaClO_4$ was found to be 3.3 M^{-1} sec^{-1} at 25°. Base hydrolysis for *cis*-$[Co(en)_2NH_3Br]^{2+}$, *cis*- and *trans*-$[Co(en)_2NH_3NO_3]^{2+}$, and *trans*-$[Co(en)_2NH_3Cl]^{2+}$ are known to be faster than for the *cis*-chloro complex.[7]

Competition Experiments. The competition experiments were performed by dissolving the complex (0.2 mmole) in a solution of the sodium or potassium salt of the competing anion (5 ml of 1 *M* Na(K)Y adjusted to pH 7 with $HClO_4$) at 25°. A solution of NaOH (5 ml of 0.4 *M*) in the sodium (potassium) salt of the anion (1 *M*) at 25° was added and the mixture left for 3 min at 25°. When

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Table I. The Stereochemistry of the Products from the Base Hydrolysis of $[Co(en)_2NH_3X]^{2+}$ Ions in 0.2 *M* NaOH and 1 *M* $NaClO_4$ at 25°

Complex	Products, $[Co(en)_2NH_3H_2O]^{3+}$, % *trans*	DL-*cis*	D-*cis*
$(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$	22	30	48
$(+)_{589}$-$[Co(en)_2NH_3Br]Br_2$	23	33	44
$(+)_{589}$-$[Co(en)_2NH_3NO_3]S_2O_6$	23	30	47
trans-$[Co(en)_2NH_3Cl]Cl\ ClO_4$	36	64	
trans-$[Co(en)_2NH_3NO_3]S_2O_6$	37	63	

Table II. Competition Values and the Stereochemistry of the Products from the Base Hydrolysis of $[Co(en)_2NH_3X]^{2+}$ Ions in 0.2 *M* NaOH and 1 *M* Anion Y^- at 25°

		Products					
		$[Co(en)_2NH_3H_2O]^{3+}$, %			$[Co(en)_2NH_3Y]^{2+}$, %		
Y^-	Complex	*trans*	DL-*cis*	D-*cis*	*trans*	DL-*cis*	D-*cis*
N^{3-} (0.5 *M*)	$(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$	19	27	40	4	4	6
(1 *M*)	$(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$	17	23	36	7	8	9
	$(+)_{589}$-$[Co(en)_2NH_3Br]Br_2$	17	25	34	7	9	8
	$(+)_{589}$-$[Co(en)_2NH_3NO_3]S_2O_6$	17	22	35	8	9	9
	trans-$[Co(en)_2NH_3Cl]ClClO_4$	27	49		8	16	
	trans-$[Co(en)_2NH_3NO_3]S_2O_6$	27	48		9	16	
SCN^- (1 *M*)	$(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$	20	31	38	4		
	$(+)_{589}$-$[Co(en)_2NH_3NO_3]S_2O_6$	20	29	40	4		7
	trans-$[Co(en)_2NH_3Cl]ClClO_4$	32	57		5	6	7
	trans-$[Co(en)_2NH_3NO_3]S_2O_6$	32	57		5	6	
NO_2^- (1 *M*)	*cis*-$[Co(en)_2NH_3Cl]Br_2$	89			11		
	cis-$[Co(en)_2NH_3Br]Br_2$	88			12		
	cis-$[Co(en)_2NH_3NO_3]S_2O_6$	88			12		

the competing anion was N_3^- or SCN^-, the solutions were neutralized with concentrated $HClO_4$, diluted with water, and adsorbed on an ion-exchange column (Bio-Rad analytical Resin Dowex (H^+) 50 W-X 2, 200–400 mesh, 10 × 70 mm). After the complexes were adsorbed, the column was washed with water to remove extraneous ions. When the competing anion was NO_2^-, the basic reaction mixture was adsorbed on the column in the Na form, then washed thoroughly with water, and finally acidified with dilute acetic acid. The $[Co(en)_2NH_3Y]^{2+}$ complexes were separated from the $[Co(en)_2NH_3H_2O]^{3+}$ complexes by eluting with 1 *M* $NaClO_4$ at pH 3–4. After the $[Co(en)_2NH_3Y]^{2+}$ complexes were eluted they were readsorbed directly on a long column (25–30 cm packed in 1 *M* $NaClO_4$). Once the $[Co(en)_2NH_3Y^{2+}$ complexes were removed from the small column the aquo complexes were eluted with 3 *M* HCl, and adsorption spectra and rotations of the solutions were measured immediately. The long column containing the $[Co(en)_2NH_3Y]^{2+}$ complexes was eluted with 1 *M* $NaClO_4$ until the *cis*- and *trans*-$[Co(en)_2NH_3Y]^{2+}$ ions were well separated. The column was then washed through with 1 *M* NaCl to remove ClO_4^- ions and the complexes were eluted from the column with 1 *M* KCl. Their absorption spectra and rotations were then recorded immediately. The total cobalt concentration of the mixtures of *cis*- and *trans*-aquo complexes was determined by atomic absorption spectroscopy using a Techtron atomic absorption spectrophotometer Model AA-4 with a high-intensity Co lamp. The absorption spectra were measured in a Cary 14 spectrophotometer and the rotations on a Perkin-Elmer P 22 spectropolarimeter. Each experiment except the competition experiments with SCN^- and NO_2^- was repeated at least five times. The recovery of the complexes from the ion-exchange column was quantitative (100 ± 1%). In one experiment $(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$ (0.36×10^{-3} mole) was dissolved in a solution of 0.5 *M* NaN_3 and 0.5 *M* $NaClO_4$ (10 ml) at 25°. A solution of 0.5 *M* NaN_3, 0.5 *M* $NaClO_4$, and 0.4 *M* NaOH (10 ml) was added and the mixture left for 3 min at 25°, neutralized, and adsorbed on an ion-exchange column. The aquo and azido complexes were then eluted from the column as before.

In order to ensure that no base hydrolysis took place with the *cis*- and *trans*-$[Co(en)_2NH_3N_3]^{2+}$, -$[Co(en)_2NH_3NCS]^{2+}$, and -$[Co(en)_2NH_3NO_2]^{2+}$ products during the competition experiments, the pure compounds were dissolved in a solution of 1 *M* $NaClO_4$ and 0.2 *M* NaOH for 3 min at 25° which was then neutralized and adsorbed on the ion-exchange column. No aquo complexes were detected on elution. To ensure that the Y^- ions do not replace the X^- ions directly, the $[Co(en)_2NH_3X]^{2+}$ complexes were treated with 1 *M* Na(K)Y at pH 5 for 3 min. The solutions were adsorbed on the ion-exchange column which was then washed thoroughly with water. The adsorbed complexes were hydrolyzed on the column with 0.2 *M* NaOH, acidified with acetic acid, and eluted with 1 *M* $NaClO_4$. No $[Co(en)_2NH_3Y]^{2+}$ complexes were detected. Also it was established that the formed aquo complexes do not exchange H_2O with Cl^- in 3 *M* HCl in the time required for eluting and measuring the absorption and rotation of the complexes. The hydroxo complex (1 mmole) was treated with NaN_3 (50 ml, 1 *M*) for 3 min and the solution adsorbed on the column. Elution with 1 *M* $NaClO_4$ did not show any azido product.

Hg^{2+}-Induced Aquation of $(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$, $(+)_{589}$-$[Co(en)_2NH_3Br]Br_2$, and *trans*-$[Co(en)_2NH_3Cl]ClClO_4$. The complex (0.02 g) was dissolved in water (10 ml, pH 3) at 25°. A solution of $Hg(ClO_4)_2$ [10 ml of 0.4 *M* Hg^{2+} in 0.2 *M* $HClO_4$) was added. Absorption spectra and rotations were measured after 15–20 min; for $[Co(en)_2NH_3H_2O]^{3+}$ from (+)-*cis*-chloro ϵ_{480} 66.0, $[M]^{25}{}_{420}$ $-1012°$; from (+)-*cis* bromo ϵ_{480} 66.6, $[M]^{25}{}_{420}$ $-1000°$; and from *trans*-chloro ϵ_{480} 45.0. The measured ϵ_{480} for the pure aquo complexes in 0.1 *M* $HClO_4$ was 65.5 for *cis* and 44.8 for *trans*. The molar rotation for the pure $(+)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ at 420 mμ was $-1016°$ in 0.1 *M* $HClO_4$.

NO^+-Induced Aquation of $(+)_{589}$-$[Co(en)_2NH_3N_3]S_2O_6$ and *trans*-$[Co(en)_2NH_3N_3]S_2O_6$. The complex (0.01 g) was dissolved in $HClO_4$ (10 ml of 0.1 *M*) at 25°. Solid $NaNO_2$ (10% excess) was added and absorption spectra and rotation were measured after 10 min; for $[Co(en)_2NH_3H_2O]^{3+}$ from (+)-*cis*-azido ϵ_{480} 67.7, $[M]^{25}{}_{420}$ $+1035°$; from *trans*-azido ϵ_{480} 44.0.

Results

The results from the base hydrolysis reactions of $(+)_{589}$-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, Br, NO_3) and *trans*-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, NO_3) in 1 *M* $NaClO_4$ are given in Table I. The results from base hydrolysis in the presence of added anions are given in Table II. The experimental error for each of the aquo products is ±2%; for the azido, isothiocyanato, and nitro products, ±1%. These results show, within the experimental error, the following.

1. The stereochemistry of the aquo products from the reactions where no competition takes place (in 1 *M* $NaClO_4$) is different for *cis* and *trans* reactants but is independent of the leaving group within each of these series of reactants.

2. When added anions Y^- ($Y^- = N_3^-, SCN^-, NO_2^-$) are present, competition takes place and the competition ratio $[Co(en)_2NH_3Y]^{2+}/[Co(en)_2NH_3OH]^{2+} \cdot [Y^-]$ is independent of the leaving group for both *cis* and *trans*

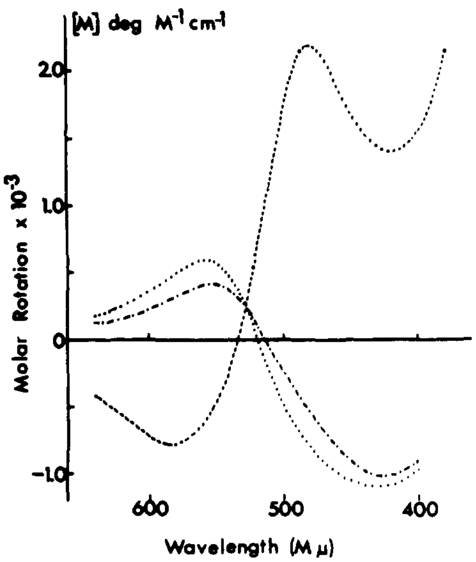

Figure 1. Molar rotation curves of $(+)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ in 0.01 *M* $HClO_4$ (-·-·-·), in 3 *M* HCl (........); $(-)_{589}$-$[Co(en)_2NH_3N_3]S_2O_6$ in 1 *M* KCl (- - - -).

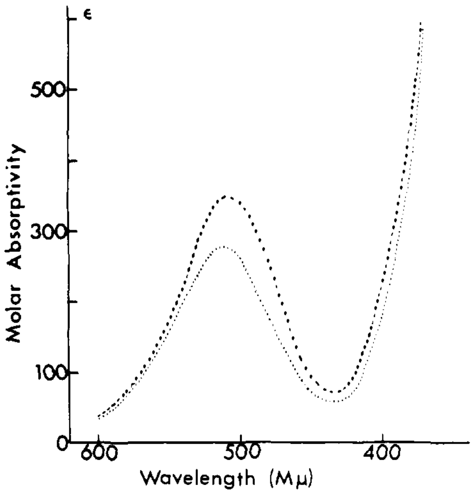

Figure 2. Visible absorption spectra of *cis*-$[Co(en)_2NH_3N_3]S_2O_6$ (- - - -) and *trans*-$[Co(en)_2NH_3N_3]S_2O_6$ (. . . .).

reactants for each competing anion. Moreover, the competition ratio is independent of the anion concentration as found for the $[Co(NH_3)_5X]^{2+}$ complexes.[2]

3. The stereochemistry of the aquo products from the competition experiments is constant for each added anion within each series of complexes, and the same relative distribution of product isomers is observed as from the reactions in 1 *M* $NaClO_4$.

4. The stereochemistry of the products containing the competing anion, $[Co(en)_2NH_3Y]^{2+}$, is constant for each competing anion within each series of reactants but is different from that of the aquo products.

5. Hydrolysis of the substrate followed by the addition of N_3^- ion did not give any azido complex. This result is in agreement with the known[8] slow rate of exchange of OH^- in the complex with solvent.

In 1 *M* azido ions 25 ± 1% azido products was formed from the *cis*-chloro, -bromo, and -nitrato complexes and 24 ± 1% from the *trans*-chloro and -nitrato complexes. When 1 *M* SCN^- was used as the competing anion 11 ± 1% of $[Co(en)_2NH_3NCS]^{2+}$ products was formed from the *trans* as well as the *cis* reactants. Because of experimental difficulties in determining the *trans*/*cis* ratio of the $[Co(en)_2NH_3NCS]^{2+}$ complexes, due to their lower molar absorptivities and the small amount formed, the results obtained are not as accurate as those for the azido products. Furthermore, it was not possible to measure accurately the rotation of the *cis* complex in the dilute solution collected from the column. Only the total amounts of *cis*-$[Co(en)_2NH_3NCS]^{2+}$ are given in the table. The experimental difficulties were even greater with the yellow nitro complexes, and, after observing that 11 ± 1% $[Co(en)_2NH_3NO_2]^{2+}$ complexes were formed from base hydrolysis of the *cis*-chloro, -bromo, and -nitrato complexes in the presence of 1 *M* NO_2^- ions, no further experiments were done with this anion.

The stereochemical course of the base hydrolysis reactions of the chloro, bromo, and nitrato complexes without added anions have been reported before[7] at other ionic strengths. They are repeated here in 1 *M* $NaClO_4$ in order to compare the results with those obtained in the competition experiments. Within the experimental error the relative distribution of aquo isomers was found to be the same in the two types of reactions. The molar absorptivities of the acidified reaction mixtures were approximately the same as those reported by Nyholm and Tobe,[7] but the distribution of isomers differed because the molar absorptivities of the *cis* and *trans* aquo complexes were found to be slightly different from the previous values. Also, optically pure $(-)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ was isolated, and this salt had a different $[M]^{25}{}_{589}$ from the value used by Staples and Tobe, namely that estimated by Mathieu.[14] The molar rotation curve of $(-)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ was found to be markedly dependent on the acidity of the solution (see Figure 1).

The interrelation between the configurations of $(+)_{589}$-$[Co(en)_2NH_3Cl]^{2+}$, $(+)_{589}$-$[Co(en)_2NH_3Br]^{2+}$, and $(+)_{589}$-$[Co(en)_2NH_3OH_2]^{3+}$ has been evaluated in different ways with common agreement.[15,16] Namely, the ions have the D configuration related to that of the D-$(+)_{589}$-$[Co(en)_3]^{3+}$ ion.[17] Similarly, the rotatory dispersion curve (Figure 1) and the aquation of $(-)_{589}$-$[Co(en)_2NH_3N_3]^{2+}$ to $(-)_{589}$-$[Co(en)_2NH_3OH_2]^{2+}$ with full retention of activity requires this ion to have the L configuration.

A method for the preparation of *cis*-$[Co(en)_2NH_3N_3]S_2O_6$, by treating *trans*-$[Co(en)_2N_3Cl]ClO_4$ with liquid NH_3, has been published.[18] However, we found that the *trans*-azido chloro complex reacted rapidly with liquid NH_3 + NH_4Cl to give essentially *trans*-$[Co(en)_2NH_3N_3]^{2+}$, while the *cis*-azidochloro complex reacted more slowly to give essentially *cis*-$[Co(en)_2NH_3N_3]^{2+}$. These isomers were checked for geometrical purity by eluting them on an ion-exchange column whence the *cis* and *trans* forms separate easily. The *trans* isomer was eluted first.

The absorption spectra of the *cis*- and *trans*-$[Co(en)_2NH_3Y]^{2+}$ complex ions were similar (Figure 2),

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[14] J. P. Mathieu, *Bull. Soc. Chim. France*, 3, 476 (1936).

[15] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

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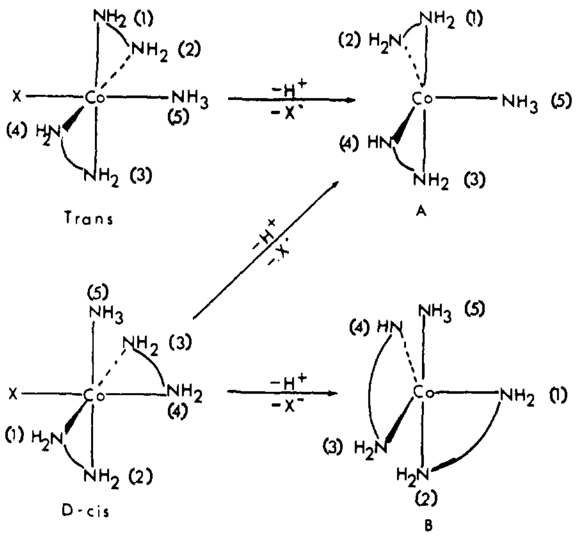

Figure 3. Possible trigonal-bipyramidal intermediates for the base hydrolysis of D-*cis*- and-*trans*-[Co(en)$_2$NH$_3$X]$^{2+}$ ions.[20]

so it was necessary to separate the isomers to obtain an accurate ratio. This was accomplished using a long ion-exchange column, and the best results were obtained with the intensely colored azido complexes (ϵ ~300). Some difficulty was experienced in detecting the separation of the *cis*- and *trans*-[Co(en)$_2$NH$_3$NCS]$^{2+}$ and [Co(en)$_2$NH$_3$NO$_2$]$^{2+}$ ions, and these experiments were not pursued to the same length as for the azido system. Similarly, an attempt to separate the *cis*- and *trans*-hydroxo amino ions was only partly successful. In two experiments 20 and 25% *trans*-hydroxo complex were obtained while the spectroscopic analysis of the mixture gave 22% *trans*. The lack of reproducibility for this ion-exchange experiment also arose from the poor separation of the *cis*- and *trans*-hydroxo ions on the column.

D-$(+)_{589}$-[Co(en)$_2$NH$_3$H$_2$O]Br$_3\cdot$H$_2$O, D-$(+)_{589}$-[Co(en)$_2$NH$_3$NO$_3$]S$_2$O$_6$, D-$(+)_{589}$-[Co(en)$_2$NH$_3$Cl]Br$_2$, D-$(+)_{589}$-[Co(en)$_2$NH$_3$Br]Br$_2$, and L-$(-)_{589}$-[Co(en)$_2$NH$_3$N$_3$]S$_2$O$_6$ were prepared optically pure by fractional crystallization of the least soluble diastereoisomers to constant rotation and/or fractional crystallization of the optical isomer to constant rotation. In some instances the complexes were interconverted. The *cis*- and *trans*-halo complexes when treated with Hg^{2+} ion gave the aquo complex with full retention of the optical and/or geometrical configuration. The catalyzed aquation of the *cis*- and *trans*-azido complexes with NO$^+$ also gave the same result. The conversion of the *cis* halo complexes and the azido complex to the aquo complex with the same rotatory power as the isolated aquo complex confirms the optical purity of these species. It seems highly improbable that all the independently resolved ions could have the same degree of optical impurity.

Discussion

The constant stereochemistry observed for the products from the base hydrolysis of D-*cis*-[Co(en)$_2$NH$_3$X]$^{2+}$ (X = Cl, Br, NO$_3$) and also of *trans*-[Co(en)$_2$NH$_3$X]$^{2+}$ (X = Cl, NO$_3$) ions (Table I) supports the conclusions of the previous studies on the analogous *trans*-(^{15}NH$_3$)-pentaammine ions.[3] The results are best rationalized in terms of an S$_N$1CB mechanism which requires a common intermediate or set of intermediates for the different substrates. In addition we find the same competition value with the different substrates for an anion in solution during base hydrolysis. For 1 *M* azide ion 25 ± 1% of the azido product was observed after hydrolysis of the *cis*-chloro, -bromo, and -nitrato complexes. Similar observations were also made for the *trans*-chloro and -nitrato ions hydrolyzed under the same conditions (24 and 25%) and for the *cis* and *trans* complexes hydrolyzed in the presence of 1 *M* NCS$^-$ (11%) and 1 *M* NO$_2^-$ (11%) ions. Both the competition and stereochemical results are consistent with the results found for the pentaamminecobalt(III) ions.[2,3]

There is now a separate source of detailed information concerning the common characteristics of the reactions of the different substrates, namely the stereochemistry of the competition products. These results are presented in Table II. Clearly the amounts of *trans* racemate, and D isomers are constant for the azido products from all three D-*cis* reactants within the experimental error. Also the *trans* substrates give a similar agreement along with the *cis*- and *trans*-isothiocyanato competition products.

In summation then, the data from this study, the constant stereochemistry of the aquo products, the constant competition values, and the constant stereochemistry of the competition products all support the presence of a common intermediate or of common intermediates in the reactions.

The nature of the intermediates or intermediate has given rise to some speculation.[19,20] An explanation of the results can be obtained by invoking two trigonal-bipyramidal intermediates for the *cis* and one for the *trans* substrate.[19,20] These are depicted in Figure 3. Intermediate A reacts to give D + *trans* and B reacts to give D + L, not necessarily in equal amounts. (In ref 20 the intermediate A is that which leads to the mirror image of the *cis* reactant; otherwise the figure is reproduced unaltered.) To fit the existing data A should be formed to the extent of 61% and B 39%. A then reacts to 36% *trans* and 64% *cis* products. In competition with azide ion A is seen to give the same total *cis* and *trans* distribution within the experimental error, 37% *trans* and 63% *cis* products. The amount of the intermediate A is computed for *cis* reactants from the *trans* product which can only arise from A. Then the optically active intermediate B must yield largely racemate (16% L, 20% D) to account for the product isomer distribution.

A problem which arises in this analysis of the data is the proton exchange rate relative to the lifetime of the intermediate. For example, B would be symmetrical if the former was fast relative to its reactivity. The studies on the *trans*-[(^{15}NH$_3$)(NH$_3$)$_4$CoX]$^{2+}$ species[3] suggested that proton exchange was slow for the intermediate relative to its reactivity since the ammonia groups did not become equivalent. We assume therefore that the deprotonated five-coordinate intermediate preserves the imide group for its lifetime. The concentrations of the deprotonated reactants are thereby determined by the relative acidities of the various types of NH groups. At the moment these have not been measured because they appear mostly to have pK_a's

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(19) R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, 78, 4878 (1956).

(20) R. G. Pearson and F. Basolo, *Inorg. Chem.*, 4, 1522 (1965).

> 14. However, some idea of the relative acidity can be gauged from their exchange rate. From preliminary studies,[21] it seems that the NH protons opposite the substituent in the *cis* isomer are the most reactive, followed by the NH_3 and the NH_2 group *trans* to each other, and then by the two NH_2 groups *trans* to each other. For the *trans* isomer the NH_3 group exchanges most rapidly, and the four equivalent NH_2 groups exchange at the same rate. There appears to be no distinction between the N protons *cis* to the substituent and those *cis* to the ammonia. This suggests that the intermediates A + B are those most likely to be generated from the deprotonated *cis* isomer of highest concentration, if the deprotonated forms have equivalent reactivities. However, the same argument applied to the *trans* complex would require the ammonia to be deprotonated in the progenitor for the intermediate. The implication is then that either this species is very slow to react relative to the progenitor of A or that intermediate A is not formed and a separate intermediate is required from the *trans* substrate. We are unaware of the relative reactivity of the various forms of deprotonated reactants, but it seems unlikely that the deprotonated NH_3 group in the *trans* complex is unreactive. This proposal is supported by the results for the pentaammine complexes[3] where it is argued that the group *trans* to the substituent loses a proton to give the reactive species. This argument requires an alternative intermediate derived from the *trans* complex where the ammonia group is deprotonated. These last considerations imply that only one of the deprotonated reactants leads to the five-coordinate species.

One possibility which should be discussed is that from the D-*cis* isomer the trigonal-bipyramidal intermediate A (Figure 3) is produced which then undergoes pseudorotation[22] and competes for the nucleophiles in solution. Pseudorotation leads to the inverted form of the same intermediate provided the process is restricted to the motion which always leaves the chelate rings spanning an apical atom and an atom in the trigonal plane. An intermediate where a chelate spans two atoms in the trigonal plane is considered less stable[23] on the grounds that the chelate now subtends ~120° at the metal center instead of the normal angle for the stable chelate, ~90°. Such an intermediate should be considerably strained and should be much less stable than the favored structure A.

This possibility of competitive pseudorotation to give racemic product can be eliminted by the experiments conducted in the presence of 0.5 and 1.0 M N_3^-. Since N_3^- is a better competitor than water (~20×) we should see a proportional increase in the amount of the D-*cis*-azido product in going from 0.5 to 1.0 M N_3^- relative to the *racemic* product. Clearly this is not observed.

If the argument is accepted concerning the lack of stability of the trigonal-bipyramidal intermediate where the chelate ring spans one edge of the trigonal plane, then intermediate B becomes less likely. In this context we also note that five-coordinate chelate complexes whose structures are known are either of the form Figure 3A or square pyramidal.[24]

An alternative to the intermediates in Figure 3 arises if the *cis* and *trans* isomers deprotonate at the position *trans* to the leaving group and give the square-pyramidal intermediates shown in Figure 4A and B, respectively. The intermediates can account for the observed results provided reaction can occur above and below the plane of the chelated atoms. It is also possible that both species may be stabilized by overlap of the filled p orbital on the deprotonated N center with the vacated orbital on cobalt. However, the degree of π stabilization of these species relative to that for the trigonal-bipyramidal species is not yet clear.

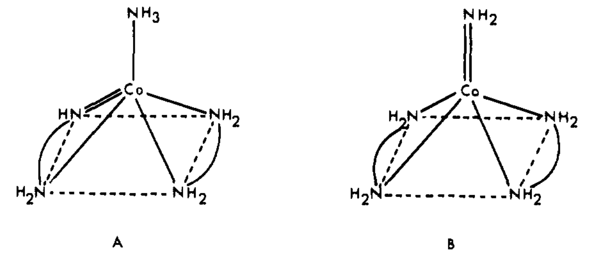

Figure 4. Possible five-coordinate intermediates for the base hydrolysis of (a) D-*cis*- and (b) -*trans*-$[Co(en)_2NH_3X]^{2+}$ ions.

In a previous article[25] on the stereochemical course of the induced aquations of halo and azido complexes, it was suggested that the $[Co(en)_2NH_3X]^{2+}$ ions would follow the same pattern as for the *trans*-$[Co(NH_3)_4ND_3X]^{2+}$ ions.[26] This has now been shown to be the case. The Hg^{2+}-catalyzed removal of Cl^- and Br from the *cis* and *trans* complexes occurred with full retention of the geometrical and optical configuration. A similar result was observed for the NO^+-assisted aquation of the *cis*- and *trans*-azido ions. However, the same stereochemical course was found for the spontaneous aquation of the halo complexes.[26,27] In this instance the agreement between the results for the induced and spontaneous aquation detracts somewhat from the use of the stereochemical course of the reaction to help diagnose the mechanism. However, the common result for the different substrates and types of reactions is still consistent with the formation of a five-coordinate intermediate for the induced aquation reactions. Also, competition by the intermediate was observed for anions in the course of the induced aquation in the same manner as found for the pentaammine complexes.[28] The stereochemistry of the competition product was the same as that for the reactant which also agrees with previous observations.[26]

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