rate of water exchange of $[Co(en)_2OH(H_2O)]^{2+}$ compared to β-$[Co(trien)OH(H_2O)]^{2+}$, or from a combination of these factors.

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The Induced Aquation Reactions of the Resolved Azidochlorobis(ethylenediamine)cobalt(III) Ion

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The induced aquation of Cl^- and N_3^- from $(+)_{589}$-$[Co(en)_2ClN_3]^+$ using Hg^{2+} and NO^+, respectively, has been examined. Both reactions give substantial rearrangement to both *cis* and *trans* products whereas the spontaneous aquation of Cl^- gave full retention of the *cis* configuration and activity. The results are compared with the NO^+-assisted aquation of $(+)_{589}$-$[Co(en)_2(N_3)_2]^+$ and the Hg^{2+}-assisted aquation of $(+)_{589}$-$[Co(en)_2Cl_2]^+$ where the same products are produced. A common result was obtained for the two sets of reactions which is interpreted to indicate a common intermediate.

Introduction

The steric courses of aquation of $[Co(en)_2XY]^{n+}$ complexes (where X and Y are a series of substituents such as Cl, Br, NCS, NH_3, OH_2, N_3, NO_2, etc.) have been well studied,[1] and it is still not clear if these reactions proceed by a bimolecular displacement reaction or through an intermediate of reduced coordination number. Attempts have been made to generate the possible five-coordinate intermediates involved,[2-4] to study their properties, and to see if the steric course of the reaction of the supposed intermediate coincides with that of the spontaneous aquation. The methods used have been derived from studies of induced aquations in substituted cobalt(III) pentaammine complexes, namely, the reactions of $[Co(NH_3)_5X]^{2+}$ ions (X = Cl, Br, I) with Hg^{2+}[5] and of $[Co(NH_3)_5N_3]^{2+}$ with NO^+.[6] Evidence has been collected[5-8] to support the existence of a common five-coordinate intermediate in the induced aquations and these reactions have also been used with *cis*- and *trans*-$[Co(en)_2Cl_2]^+$,[2] $[Co(en)_2(N_3)_2]^+$,[3] $[Co(en)_2OH_2N_3]^{2+}$,[3] $[Co(en)_2ClOH_2]^{2+}$,[4] $[Co(en)_2BrOH_2]^{2+}$,[4] $[Co(en)_2ClBr]^+$,[4] and *trans*-$[Co(en)_2ClN_3]^+$[4] ions, to show that the steric courses of the induced aquation and the spontaneous aquations differ. Loeliger and Taube have tabulated data[4] for the Hg^{2+}- and NO^+-induced aquations to show that for the same product a constant ratio of *cis* and *trans* isomers is obtained from different reactants. The authors suggest that the common result indicates the same intermediate is formed in the reactions.

The present work is related to this last study and involves primarily the steric course of the Hg^{2+}-assisted aquation of Cl^-, the NO^+-assisted aquation of N_3^-, and the spontaneous aquation of Cl^- in the (+)-$Co(en)_2ClN_3]^+$ ion.

Experimental Section

$(+)_{589}$-*cis*-$[Co(en)(N_3)_2]ClO_4$ was prepared as described.[9] *Anal.* Calcd: C, 13.25; H, 4.45; N, 38.63. Found: C, 13.38; H, 4.55; N, 38.98.

trans-$[Co(en)_2(N_3)_2]ClO_4$ was prepared by the same method as for *cis*-$[Co(en)_2(N_3)_2]ClO_4$ using $Co(ClO_4)_2$ and $HClO_4$ instead of $Co(NO_3)_2$ and HNO_3. A yield of 87% brown *trans*-$[Co(en)_2(N_3)_2]ClO_4$ was obtained. *Anal.* Calcd: C, 13.25; H, 4.45; N, 38.63. Found: C, 13.44; H, 4.50; N, 38.90.

trans-$[Co(en)_2N_3Cl]ClO_4$ was prepared from *trans*-$[Co(en)_2(N_3)_2]ClO_4$ as described.[10]

cis-$[Co(en)_2N_3Cl]Cl$ was prepared by treating *cis*-$[Co(en)_2(N_3)_2]NO_3$ (20 g) with HCl (10 *N*) saturated with LiCl (75 ml) at room temperature until the solution became bluish red (~6 min). The azidochloro complex was then precipitated by pouring the reaction mixture into a large amount of ethanol. It was recrystallized from water at pH 3–4 by adding ethanol until precipitation commenced. The solution was then cooled in an ice bath, yield 5 g.

$(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]ClO_4$.—To *cis*-$[Co(en)_2ClN_3]Cl$ (7.5 g) dissolved in water (80 ml) at pH 3–4 was added $(-)_{589}$-$Na[Co(en)(C_2O_4)_2]\cdot H_2O$ (4.1 g) with stirring. The diastereoisomer (4.4 g) precipitated rapidly and was collected and washed with ice-cold water and methanol. The isomer $(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]I$ (2.4 g) was obtained from the diastereoisomer by grinding an ice-cold suspension of the latter with solid NaI in a mortar. The precipitated iodide was collected and washed with a dilute aqueous solution of NaI and ethanol. The rotation of the iodide was measured, and, in order to ensure that optical purity was obtained, the complex was reresolved. The iodide was converted to the chloride by treating an aqueous suspension (pH 3) with AgCl. After filtration, solid $(-)_{589}$-$Na[Co(en)(C_2O_4)_2]$ (1.83 g) was added to the filtrate and the diastereoisomer collected was converted to the iodide as before. The final rotation of the iodide was the same as that obtained from the first diastereo-

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(1) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).
(2) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).
(3) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **4**, 1032 (1965).
(4) D. A. Loeliger and H. Taube, *ibid.*, **5**, 1376 (1966).
(5) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).
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(10) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).

isomer. (For a 0.025% solution in 10^{-3} *M* $HClO_4$ α is $-0.144°$ at 520 mμ and 20° in a 1-dm tube.) The complex iodide was then converted to the perchlorate by treating it with an aqueous suspension of AgCl followed by excess $NaClO_4$. Two fractions were obtained of which the first one contained a small amount of diazido complex. The pure perchlorate gave $[\alpha]^{20}_{520}$ $-608°$ (for a 0.025% solution in 10^{-3} *M* $HClO_4$ α is $-0.152°$ at 520 mμ and 20°) and $[\alpha]^{20}_{589}$ $+240°$. *Anal.* Calcd for $(+)_{589}$-$[Co(en)_2N_3Cl]ClO_4$: N, 27.54; C, 13.49; H, 4.52. Found: N, 27.67; C, 13.67; H, 4.45. The purity of the complex was also tested by thin layer chromatography on cellulose.[11] The components of a mixture of *cis*-$[Co(en)_2(N_3)_2]ClO_4$ and *cis*-$[Co(en)_2Cl_2]ClO_4$ readily separated by elution with a mixture of 1-butanol (H_2O saturated)–$HClO_4$ (100:3), and the azidochloro complex moved as a single band between the diazido and dichloro reference samples.

***cis*-$[Co(en)_2(H_2O)N_3]SO_4 \cdot H_2O$.**—*cis*-$[Co(en)_2N_3Cl]Cl$ (3 g) dissolved in 1 *M* H_2SO_4 (10 ml) was treated with an aqueous solution of mercuric acetate (3.2 g). After the reaction was complete, a large amount of ethanol was added to precipitate the products. The precipitate was extracted with water and the dark red residue was collected. This was dissolved in very dilute acetic acid and methanol was added to incipient precipitation. The compound was recrystallized by this method until a constant absorption spectrum was obtained (ϵ_{508} 300). *Anal.* Calcd: C, 13.60; H, 5.70; N, 27.76. Found: C, 13.84; H, 5.54; N, 27.86.

***trans*-$[Co(en)_2(H_2O)N_3]SO_4 \cdot 2H_2O$.**—A suspension of *trans*-$[Co(en)_2N_3Cl]ClO_4$ (2.1 g) in 1 *M* H_2SO_4 (6 ml) was treated with mercuric acetate (0.95 g) dissolved in water. When the violet complex had dissolved and had become bluish red, the solution was filtered and poured into ethanol where the aquoazido compound precipitated. It was recrystallized by dissolution in cold sulfuric acid (10^{-3} *N*) and by adding ethanol until precipitation started. *Anal.* Calcd: C, 12.94; H, 5.97; N, 26.42. Found: C, 13.59; H, 5.95; N, 26.14.

$(+)_{589}$-$[Co(en)_2Cl_2]ClO_4$.—$[Co(en)_2Cl_2]Cl$ was resolved as described previously,[2] except that the $(+)_{589}$-$[Co(en)_2Cl_2]I$ isolated was resolved twice more by the same procedure to guarantee its optical purity. *Anal.* Calcd for $(+)_{589}$-$[Co(en)_2Cl_2]ClO_4$: C, 13.74; H, 4.61; N, 16.03. Found: C, 13.82; H, 4.74; N, 15.99. The Hg^{2+}-induced aquation of $[Co(en)_2Cl_2]ClO_4$ was also carried out as described previously,[2] except that the optical density was measured more accurately with a Cary 14 spectrophotometer and the rotations were measured with a Perkin-Elmer 141 spectropolarimeter (±0.002°). Successive experiments gave optical densities of 0.364 and 0.362 at 518 mμ, compared with 0.34 ± 0.01 observed previously[2] using a Shimadzu RS27 spectrophotometer. The first values correspond to 76% *cis*- and 24% *trans*-chloroaquo product (±2%, obtained using the molar absorptivities recorded in ref 2). The corresponding rotations of the carbonato complex formed from these solutions were $\alpha^{20}{}_{D}$ $+1.780°$ and $+1.790°$ which correspond with $78 \pm 1\%$ D-*cis*-$[Co(en)_2ClOH]^{2+}$.

In order to ensure that no isomerization or racemization of $(-)_{589}$-$[Co(en)_2Cl_2]ClO_4$ took place catalyzed by Hg^{2+} ions, the complex (0.035 g) was dissolved in $HClO_4$ (10 ml, 0.1 *N*) at 20° and $Hg(ClO_4)_2$ (2.5 ml of 10^{-2} *M* HgO in 0.1 *N* $HClO_4$) was added. After 5 min, the solution was transferred to an ion-exchange column (Bio-Rad analytical resin Dowex (H^+) 50W-X2 200–400 mesh 15 × 120 mm) and the mixture was eluted at 0° with 1 *M* $NaClO_4$ (pH 3). An appropriate volume of eluent containing *cis*-$[Co(en)_2Cl_2]^+$ was collected and the absorption (D_{535} 0.430 in a 5-cm cell) and optical rotation (α_{589} $-0.174°$) were measured. The spectrum and rotation of optically pure $(-)_{589}$-$[Co(en)_2Cl_2]ClO_4$ in 1 *M* $NaClO_4$ (pH 3) gave $[M]^{20}{}_{D}$ $-1868°$ and ϵ_{535} 91.8, from which the molar rotation of the unreacted $(-)_{589}$-$[Co(en)_2Cl_2]^+$ ion was calculated as $[M]^{20}{}_{D}$ $-1858°$.

Kinetic Studies.—The rate data were obtained conductometrically, spectrophotometrically, and polarimetrically using a Wayne-Kerr B221 universal bridge, a Cary 14 spectrophotometer, and a Perkin-Elmer 141 spectropolarimeter, respectively.

The nitrous acid induced aquations were performed by dissolving the complex (0.01 g) in $HClO_4$ (40 ml, 0.1 *M*) at 20° and adding $NaNO_2$ immediately after dissolution. To form the $[Co(en)_2(H_2O)N_3]^{2+}$ products 1 equiv of $NaNO_2$ was added to *cis*-$[Co(en)_2(N_3)_2]ClO_4$; in the other nitrosations a 10% excess was used. After 5 min the rotatory dispersion and absorption spectra were recorded. Then an excess of solid $NaHCO_3$ was added to the reaction mixture and the solution was allowed to stand for 15 min before the optical activity of the formed carbonato complex was measured at the Na D line. In the mercuric ion assisted reactions *cis*-$[Co(en)_2N_3Cl]ClO_4$ (0.01 g) was dissolved in $HClO_4$ (20 ml, 0.1 *M*) and the Hg^{2+} solution (20 ml of 0.01 *M* HgO in 0.1 *M* $HClO_4$) was added. The visible absorption spectrum of the aquoazido complexes was measured after 5 min and followed by the addition of a 10% excess of $NaNO_2$. After a further 5 min the spectrum of the mixture of diaquo complexes was obtained and finally addition of $NaHCO_3$ in excess gave the $[Co(en)_2CO_3]^+$ ion. *cis*-$[Co(en)_2N_3OH_2]SO_4 \cdot H_2O$ (0.01 g in 40 ml of 0.1 *M* $HClO_4$) was treated with 20% excess of solid $NaNO_2$ at 20° and the visible spectrum was measured after 5 min (ϵ_{492} 80.7).

The spontaneous aquation of $(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]ClO_4$ was followed by dissolving the complex (0.01 g) in 0.1 and 0.01 *M* $HClO_4$ (40 ml) at 25° and allowing the solutions to stand for 3.75 and 4.5 hr, respectively. The reaction mixtures were then treated with 10% excess of solid $NaNO_2$. After 5 min, $NaHCO_3$ was added and the rotations of the formed carbonato complexes were measured at the Na D line. Isomerization of *cis*-$[Co(en)_2(H_2O)N_3]SO_4 \cdot H_2O$ (0.7×10^{-3} *M*) was followed spectrophotometrically at 25° in 0.01 *N* $HClO_4$.

Results

The visible absorption spectra of *cis*-$[Co(en)_2ClN_3]^+$ and *cis*- and *trans*-$[Co(en)_2N_3H_2O]^{2+}$ ions are given in Figure 1. The results differ somewhat from those described by Staples and Tobe[9] but agree substantially with those recorded by Taube and Loeliger.[3] Considerable effort was expended to test the isomeric purity of the samples, and some of the problems encountered are discussed below.

Unfortunately the molar absorptivity at the maximum for the first absorption band for *cis*-$[Co(en)_2N_3Cl]ClO_4$ (ϵ 215) is close to that at the same wavelength for an equimolar mixture of *cis*-$[Co(en)_2Cl_2]ClO_4$ (ϵ 85) and *cis*-$[Co(en)_2N_3)_2]ClO_4$ (ϵ 335). However, the isolated chloroazido complexes were chromatographed on thin layer cellulose with a C_4H_9OH–H_2O–$HClO_4$ mixture. This procedure separated all three possible *cis* species and showed that the (+)-$[Co(en)_2ClN_3]ClO_4$ samples used in this investigation contained no detectable amounts of dichloro or diazido complexes. Conductance measurements for the aquation of *cis*-$[Co(en)_2ClN_3]ClO_4$ (2×10^{-3} *M*) to the aquoazido complex in perchloric acid (10^{-3} *M*) at 25° gave a rate constant of 2.6×10^{-4} sec^{-1} which is close to the value reported by Staples and Tobe and also to that for the aquation of the *cis*-$[Co(en)_2Cl_2]^+$ ion ($k = 2.5 \times 10^{-4}$ sec)[12] under the same conditions. For *cis*-$[Co(en)_2(N_3)_2]ClO_4$ the rate constant for the aquation of the first azide ion is too slow to contribute.[13] Clearly the visible spectra and rate of aquation of Cl^-

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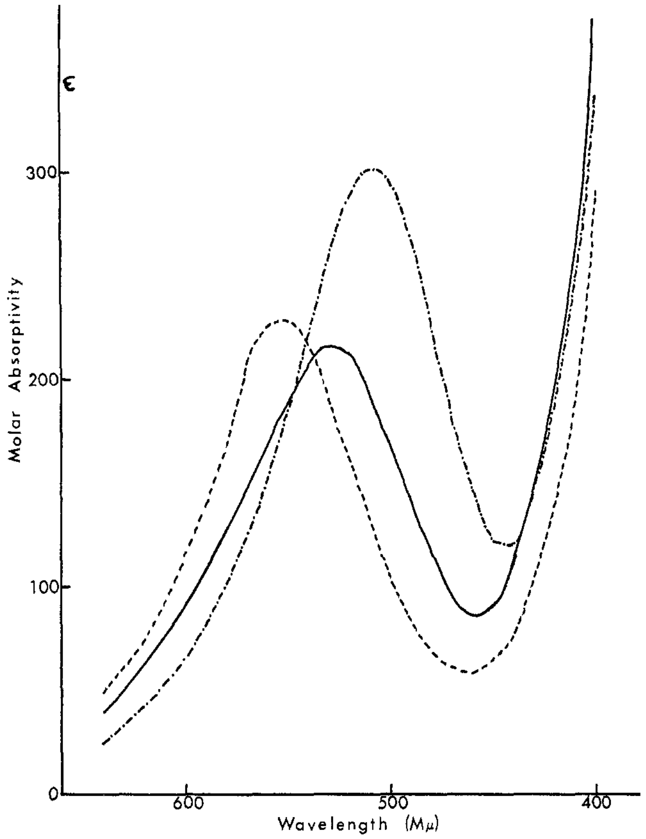

Figure 1.—Visible absorption spectra of: ———, $(+)_{589}$-*cis*-$[Co(en)_2N_3Cl](ClO_4)_2$; - - - -, *trans*-$[Co(en)_2N_3H_2O]SO_4 \cdot 2H_2O$; – · – ·, *cis*-$[Co(en)_2N_3H_2O]SO_4 \cdot H_2O$.

do not allow a characterization of the chloroazido species but the initial and final molar conductivities Λ compared with those for the reference ions *cis*-$[Co(en)_2(NO_2)_2]ClO_4$ (Λ = 86 ohm^{-1}) and $[Co(en)_2((-)val)]Cl_2$ (Λ = 194 ohm^{-1}) also showed that the chloroazido complex was free of the dichloro and diazido complexes. For *cis*-$[Co(en)_2N_3Cl]ClO_4$ Λ was found to be 85 ohm^{-1} and for the aquated product Λ was 198 ohm^{-1}, after correction for the conductance of the acid. It is clear that a mixture of the dichloro and diazido complexes would release less than one anion per molecular ion under the conditions used. In the infrared spectrum of *cis*-$[Co(en)_2(N_3)_2]ClO_4$ a doublet appeared for the azide N–N stretching mode at 2025 and 2100 cm^{-1} but only a singlet appeared at 2050 cm^{-1} for *cis*-$[Co(en)_2ClN_3]ClO_4$. This is also consistent with the conclusion that the complex is not a mixture.

The *cis*- and *trans*-$[Co(en)_2(H_2O)N_3]^{2+}$ complexes were isolated as the sulfates. At 500 mμ the molar absorptivities were found to be ε 293 for *cis*-$[Co(en)_2(H_2O)N_3]SO_4 \cdot H_2O$ and ε 103 for *trans*-$[Co(en)_2(H_2O)N_3]SO_4 \cdot 2H_2O$. These results agree with those of Loeliger and Taube[3] and confirm their conclusion that the separation of the two isomers prepared by Staples and Tobe was incomplete. Optically impure *cis*-$[Co(en)_2(H_2O)N_3]SO_4$ was prepared from the $(+)$-$[Co(en)_2ClN_3]^{2+}$ ion. Some racemization occurred during the preparation, and the solubility difference between the active and racemic isomers was too small to effect a sharp fractionation. However, the *cis*-aquoazido complex reacted with NO^+ to give 100% *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ in agreement with ref 3.

The composition of the product mixtures in the reactions described below was calculated from spectrophotometric data using the above molar absorptivities for *cis*- and *trans*-$[Co(en)_2ClN_3]^+$ and the following literature values for the other complex ions: *trans*-$[Co(en)_2(H_2O)_2](NO_3)_3$, ϵ_{492} 19.2; *cis*-$[Co(en)_2(H_2O)_2](NO_3)_3$, ϵ_{492} 80.0;[14] *cis*-$[Co(en)_2(H_2O)Cl]SO_4 \cdot 2H_2O$, ϵ_{515} 91; *trans*-$[Co(en)_2(H_2O)Cl]SO_4$, ϵ_{515} 11.2.[15] For the molar rotation of $(-)_{589}$-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$ $[M]_D$ is −4511° mole^{-1} cm^{-1}.[16]

Induced Aquations of $(+)_{520}$-$[Co(en)_2N_3Cl]ClO_4$.—The Hg^{2+} ion assisted aquation in dilute $HClO_4$ gave 84 ± 2% *cis*- and 16 ± 2% *trans*-$[Co(en)_2(H_2O)N_3]^{2+}$ complex (spectrophotometric values). This mixture when treated with HNO_2 gave 88% *cis*- and 12% *trans*-$[Co(en)_2(H_2O)_2]^{3+}$ (spectrophotometric values). The optical rotation of the carbonato complex formed by treating the diaquo mixture with $NaHCO_3$ showed that 81 ± 2% of the diaquo product was optically pure D$(+)_{589}$. It has been established elsewhere[16] that D-*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ reacts with HCO_3^- to give D-$[Co(en)_2CO_3]^+$ with full retention of activity and configuration. Loeliger and Taube[3] found that *cis*-$[Co(en)_2(H_2O)N_3]^{2+}$ reacted with nitrous acid without change in configuration and this conclusion is confirmed by the present work. The nitrous acid induced aquation of $(+)_{589}$-$[Co(en)_2N_3Cl](ClO_4)$ gave 79 ± 2% *cis*- and 21 ± 2% *trans*-$[Co(en)_2(H_2O)Cl]^{2+}$, and reaction of the chloroaquo products with $NaHCO_3$ gave 79 ± 2% D$(+)_{589}$-$[Co(en)_2CO_3]^+$.[16]

Induced Aquation of $(+)_{589}$-$[Co(en)_2Cl_2]^+$.—The Hg^{2+}-induced aquation of $(+)_{589}$-$[Co(en)_2Cl_2]^+$ described in an earlier article[2] has been repeated yielding slightly different results. The spectrophotometric values were 76% *cis*- and 24% *trans*-$[Co(en)_2Cl(OH_2)]^{2+}$ and the polarimetric value was 78% D-*cis*. The discrepancy between these values and those previously reported (70% *cis*, 30% *trans*, and 70% D-*cis*) is ascribed to the more accurate instruments used in this study. The differences however do not alter the conclusions reached in the previous article.

It should be noted that Hg^{2+} does not catalyze the isomerization *trans*- ⇌ *cis*-$[Co(en)_2ClOH_2]^{2+}$ [15] nor *cis* ⇌ *trans*-$[Co(en)_2Cl_2]^+$.

Induced Aquation of $(+)_{589}$-*cis*-$[Co(en)_2(N_3)_2]ClO_4$.—The reaction of $(+)_{589}$-*cis*-$[Co(en)_2(N_3)_2]ClO_4$ with nitrous acid was studied by Loeliger and Taube,[3] who found that the complex reacted to form 77 ∓ 3% *cis*- and 23 ± 3% *trans*-aquoazido complexes, that the *cis*-aquoazido complex reacts further to give *cis*-diaquo with retention of configuration, and that *trans*-$[Co(en)_2(H_2O)N_3]^{2+}$ reacts to give 40 ± 5% *cis*-diaquo complex. By repeating these reactions and using the molar absorptivities of the prepared *cis*- and *trans*-$[Co(en)_2(H_2O)N_3]^{2+}$ complexes, we found that in the

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(16) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Am. Chem. Soc.*, **85**, 1215 (1963).

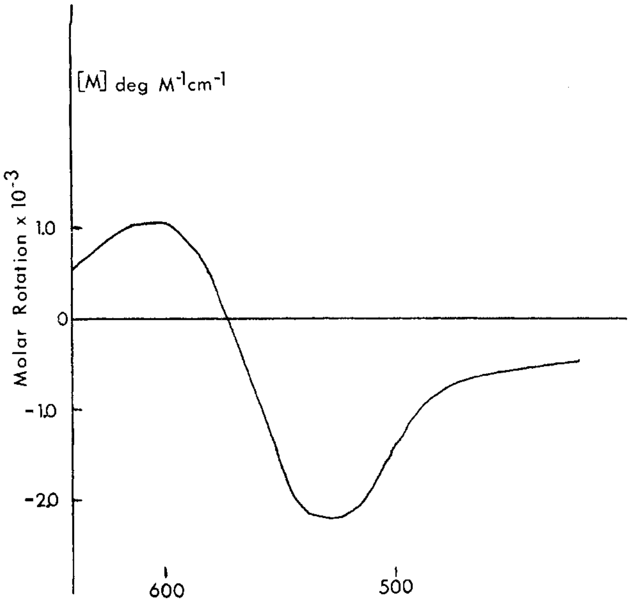

Figure 2.—Rotary dispersion curves for $(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]ClO_4$.

first step 84 ± 2% *cis*- and 16 ± 2% *trans*-aquoazido was formed and that this mixture reacted with another equivalent of nitrous acid to give 90 ± 2% *cis*-diaquo of which 82 ± 2% by conversion to the carbonato complex was shown to be optically active. The amounts of *trans*-aquoazido and *trans*-diaquo complexes formed were too small to allow a reliable estimation of the concentration of these complexes but qualitatively the results agree with those of Loeliger and Taube.[3]

Spontaneous Aquation of $(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]ClO_4$.—The release of the chloride ion from $(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]ClO_4$ was followed conductometrically in 10^{-3} *M* perchloric acid at 25°. A plot of log $(\lambda_\infty - \lambda_t)$ against time where λ_∞ and λ_t are the measured conductances at $t = \infty$ and t, respectively, gave a straight line. The first-order rate constant was calculated to be 2.6×10^{-4} sec^{-1} in reasonable agreement with Staples and Tobe's result[17] (2.4×10^{-4} sec^{-1} at 25°, 10^{-2} *M* $HClO_4$). In order to determine the steric course of the reaction, the rate of isomerization of *cis*-$[Co(en)_2(H_2O)N_3]^{2+}$ and the equilibrium composition were remeasured.[17] From the rotation of the carbonato complex formed after the nitrosation of the aquoazido aquation product, the amount of active *cis*-$[Co(en)_2(H_2O)N_3]^{2+}$ was calculated. The isomerization studies of the *cis*-aquoazido complex in 10^{-2} *M* perchloric acid at 25° showed that isomerization took place with a first-order rate constant $k_1 + k_{-1} = 1.4 \times 10^{-4}$ sec^{-1} and gave an equilibrium concentration of 58 ± 2% *cis*- and 42 ∓ 2% *trans*-$[Co(en)_2(H_2O)N_3]SO_4$. From these data and the rate constant for the aquation of *cis*-$[Co(en)_2N_3Cl]ClO_4$ (2.6×10^{-4} sec^{-1}), the spontaneous aquation of the optically active chloroazido complex was calculated to have occurred with 100 ± 2% retention of *cis* configuration and activity. These results show not only that there is full retention of the geometrical configuration which is consistent with the conclusion of Staples and Tobe, but also that there is full retention of the D(+) configuration. It is necessary to establish the latter fact since it is conceivable that a D-*cis* reactant could give both D- and L-*cis* products. The configurational relationship between $(+)_{589}$-$[Co(en)_2ClN_3]^+$, $(+)_{589}$-$[Co(en)_2(N_3)_2]^+$, and the reaction products was deduced from the circular dichroism,[18] the rotatory dispersion curves,[19] and previous structural[20] and chemical[19] studies.

The isomerization results for *cis*-$[Co(en)_2(H_2O)N_3]SO_4$ differ slightly from those of Staples and Tobe,[17] who found a rate constant $k_1 + k_{-1} = 1.0 \times 10^{-4}$ sec^{-1} and an equilibrium mixture of 73% *cis*- and 27% *trans*-$[Co(en)_2(H_2O)N_3](ClO_4)_2$. This ratio adjusts to 57% *cis* and 43% *trans* if the present values for the molar absorptivities of the aquoazido ions are used.

Spontaneous Aquation of $(+)_{589}$-$[Co(en)_2Cl_2]ClO_4$.—The course of aquation of $(+)_{589}$-$[Co(en)_2Cl_2]^+$ was established by allowing the dichloro ion to aquate to the chloroaquo species ($5t_{1/2}$) which was then converted with $NaHCO_3$ to the active carbonato complex. The degree of retention observed after allowance had been made for the subsequent isomerization of the *cis*-chloroaquo isomer showed that the dichloro aquated with retention (100 ± 2%) of the D-*cis* configuration. A similar result was obtained by extrapolating the plot of log α^0 *vs.* t for the racemization of the D-*cis*-chloroaquo ion obtained above to zero time whence the extrapolated rotation agreed with that for optically pure D-$[Co(en)_2ClOH_2]Br_2 \cdot 2H_2O$.

The catalyzed aquations in the presence of mercuric ions and nitrous acid are rapid by comparison with the subsequent isomerization and aquation reactions of the azidoaquo,[17] the chloroaquo,[15] and the diaquo[14] complexes. All measurements were performed immediately after completion of the reactions and it was possible in all cases to measure the composition of the product mixtures before further aquation or isomerization became significant, so that there was no doubt that the observed product distributions were due to the induced aquations and not complicated by further reactions. A summary of the steric course of the aquation reactions is presented in Scheme I.

Discussion

The induced aquations are rapid, are effected by reagents which lead to good leaving groups at the cobalt(III) center, and are therefore conducive to the production of intermediates of reduced coordination number. These considerations, coupled with isotope fractionation, competition studies, and stereochemical evidence from the induced aquations for the cobalt(III) pentaammine complexes,[5-8] suggest that five-coordinate intermediates are likely. With these factors in

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[17] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4803 (1960).

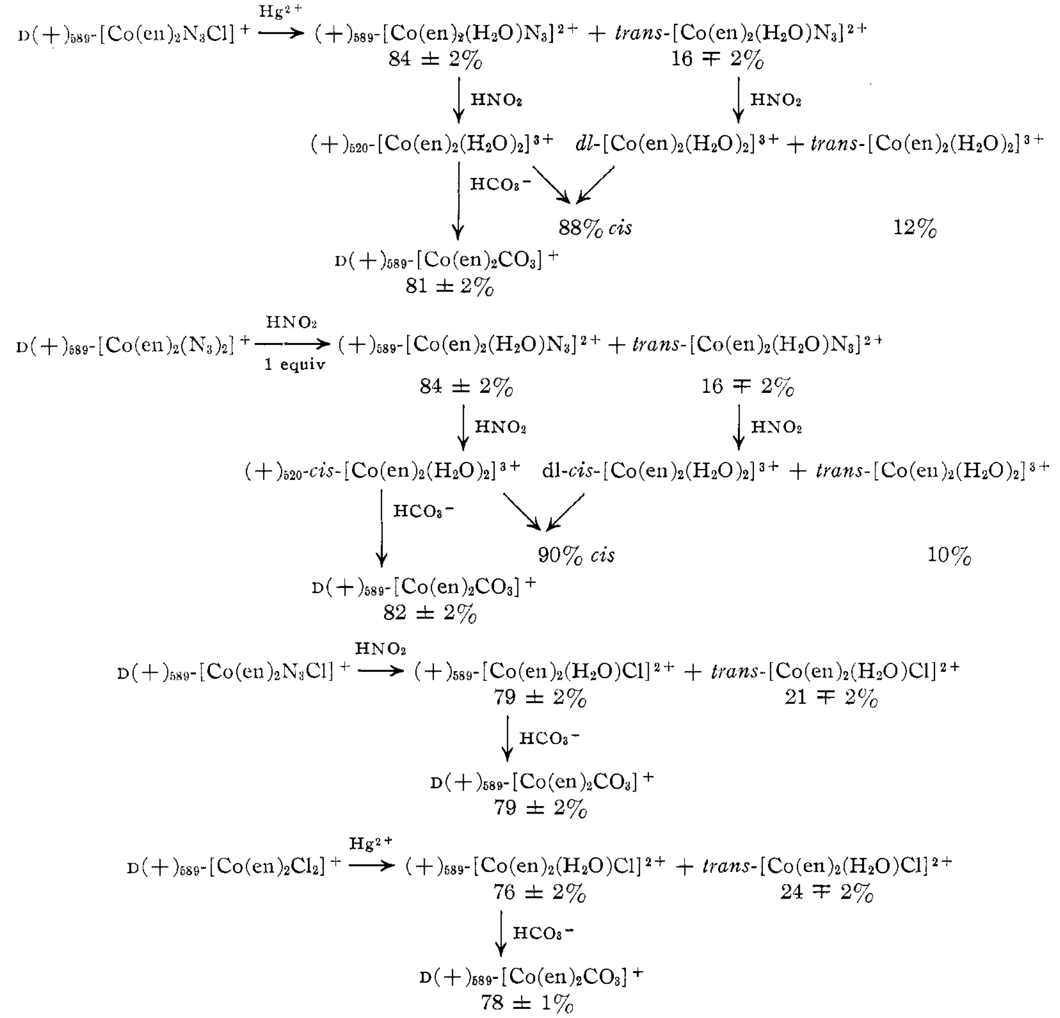
[18] A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 5094 (1965).

[19] T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

[20] G. A. Barclay, E. Goldschmeid, N. C. Stephenson, and A. M. Sargeson, *Chem. Commun.*, 540 (1966).

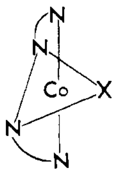
SCHEME I

STERIC COURSE OF THE INDUCED AQUATIONS



mind the results are arranged to show the amounts of *cis*- and *trans*-$[Co(en)_2ClOH_2]^{2+}$ or -$[Co(en)_2OH_2N_3]^{2+}$ derived from the different reactions. It is clear from the data in Scheme I that *cis*-$[Co(en)_2Cl_2]^+$ + Hg^{2+} and *cis*-$[Co(en)_2N_3Cl]^+$ + NO^+ give a common chloroaquo product and that *cis*-$[Co(en)_2(N_3)_2]^+$ + NO^+ and *cis*-$[Co(en)_2ClN_3]^+$ + Hg^{2+} give a common aquoazido product within the experimental error. These results fit the general pattern outlined by Taube and Loeliger in Table IV of ref 4 and are consistent with the production of a five-coordinate intermediate. The results are meaningful since appreciable amounts of both *cis* and *trans* isomers are produced from the *cis* reactants. When little rearrangement occurs, the distinction between 99% *cis* and 99.9% *cis* product is difficult to ascertain and no clear decision can be made about the steric course of the reaction.[4] The results are sufficiently accurate to allow conclusions to be drawn about the existence of the $[Co(en)_2Cl]^{2+}$ and $[Co(en)_2N_3]^{2+}$ intermediates, but they do not permit any conclusions concerning the existence of the possible $[Co(en)_2H_2O]^{3+}$ intermediate derived from the nitrosation of the *trans*-$[Co(en)_2N_3OH_2]^{2+}$ by-product. The amounts of *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$ formed from this source are not sufficiently different from the experimental error to warrant more than the statement that they agree qualitatively with the more precise results of Loeliger and Taube[3] for this reaction.

The steric course for the spontaneous aquation for D-$[Co(en)_2Cl_2]^+$ and D-$[Co(en)_2ClN_3]^+$ occurs with full retention (100 ± 2%) of the D-*cis* configuration. The azidoaquo and chloroaquo products subsequently isomerize. However, the steric courses of the induced aquations differ widely from those for the corresponding spontaneous aquations and are consistent with the production of a trigonal bipyramid of the form of I,



I

which reacts with the solvent in the trigonal plane and which shows some dependence for the product ratio on the nature of X, where X = Cl, N_3, or H_2O. The D-$[Co(en)_2OH_2]^{3+}$ intermediate reacts with full retention of the *cis*-D configuration[4] whereas $[Co(en)_2Cl]^{2+}$ and $[Co(en)_2N_3]^{2+}$ give both *cis* and *trans* isomers in similar amounts. Also it seems that there is some preference, over the statistical values, for reaction in the positions *cis* to the substituent and this may be associated with the ability of the incoming solvent molecule to hydrogen bond with the electronegative substituent. The *cis* product in each instance is optically pure (±2%) and this excludes any appreciable amount of the alternative form of the trigonal bipyramid.

The results may be contrasted with those obtained for the induced aquations of *trans*-$[Co(NH_3)_4(ND_3)N_3]^{2+}$ and *trans*-$[Co(NH_3)_4(ND_3)X]^{2+}$[8] (X = Cl, Br) where no rearrangement was observed. The difference between the two sets of data may result from the possible stabilization of the trigonal bipyramid in the $[Co(en)_2X]$ system by bonding the filled p orbitals of appropriate symmetry on the substituent to the vacated cobalt orbital as suggested by Basolo and Pearson.[21] This possibility does not arise when X = NH_3 so that to be consistent with this proposal full retention of configuration should be observed in the induced aquations of *cis*-$[Co(en)_2NH_3N_3]^{2+}$ and *cis*-$[Co(en)_2NH_3Cl]^{2+}$. These systems are at present being examined. Also initial studies show that full retention of configuration occurs in the analogous reactions of the [Co(tetraethylenepentamine)X]$^{2+}$ isomers (X = N_3, Cl, Br).[22]

It seems unlikely that these and previous results[2-8] can be explained by coincidences in the reactivity pattern for the reaction intermediates $RCoNNNO^{3+}$ and $RCoClHg^{4+}$ over a range of complexes and for several methods of detecting their behavior. It is more logical to argue that the common results obtained for the isotopic fractionation factor, the competition studies, and the stereochemistry of the products for the sets of complexes are explained by a common cause, rather than by multiple coincidences.

Acknowledgment.—The authors thank the Microanalytical Unit of the John Curtin School of Medical Research for the C, H, and N microanalyses.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Synthesis, Nuclear Resonance, and Electronic Spectra of Tris(2-hydroxypropiophenimine)cobalt(III)

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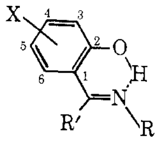
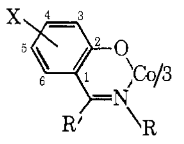
Several tris(N-alkyl-2-hydroxypropiophenimine)cobalt(III) compounds have been synthesized by a nonaqueous chelation reaction. Tris(N-methyl-2-hydroxypropiophenimine)cobalt(III) exists as a 1:1 dichloromethane adduct in which dichloromethane is held very strongly in the crystal lattice. The chelates exist exclusively in the *trans* form. The aromatic region of the nuclear resonance spectra of the chelates is discussed in some detail, and it is shown that definite assignments can be made for several signals. The crystal field spectra of the chelates are compatible with an essentially octahedral field having a rhombic component. This component clearly splits the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in some cases. A shoulder around 24,000 cm^{-1} presumably represents the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition.

Introduction

As part of our general program[1,2] on the studies of transition metal complexes derived from ligands of type **1**, we recently reported the nuclear resonance and crystal field spectra of 2-hydroxyacetophenimine chelates of trivalent cobalt[1] (**3**, R = alkyl, X = H). These complexes belong to the class Co(A–B)$_3$ where A–B is an unsymmetrical bidentate ligand. The *trans* geometry of **2** and **3** was demonstrated unequivocally by proton resonance spectra.[1,3] In the present paper we report the synthesis, nuclear resonance, and electronic spectra of the corresponding 2-hydroxypropiophenimine chelates **4** (R = alkyl, X = H or 5-CH_3). Synthesis of **3** required a nonaqueous chelation reaction in most cases. The same is found to be true for **4**, as one might intuitively expect. The salicylaldimines, **2**, can, on the other hand, be made in general by aqueous chelation.[3,4]



1



2, R′ = H
3, R′ = CH_3
4, R′ = C_2H_5

The nuclear resonance spectra of **4** both in alkyl and aromatic regions are compatible only with the expected *trans* structure. To facilitate analysis of the spectrum in the aromatic region in detail, complex **3** (R = CH_3, X = 4,5-$(CH_3)_2$) was synthesized.

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(1) A. Chakravorty and K. C. Kalia, *Inorg. Chem.*, **6**, 690 (1967).

(2) A. Chakravorty, T. S. Kannan, and S. Gupta, copper and nickel complexes of **1** (R′ = CH_3), to be published.

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