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Stereochemistry of Spontaneous and Induced Aquation of Some Resolved *cis*-Bis(ethylenediamine)cobalt(III) Complexes—Nonretentive Spontaneous Aquation

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The stereochemistry of spontaneous aquation of (+)-*cis*-$Co(en)_2Br_2^+$, (+)-*cis*-$Co(en)_2Cl_2^+$, (+)-*cis*-$Co(en)_2(OH)X^+$ (X = Br, Cl), and (+)-*cis*-$Co(en)_2N_3X^{n+}$ (X = Br, Cl, Me_2SO) has been examined or reexamined spectrophotometrically and polarimetrically at 25 °C in dilute $HClO_4$. *All* ions were found to aquate with significant stereochemical change (15–30%) but the cis product was always optically pure. This general result is contrary to the widely accepted view that cis ions aquate with retention. The kinetics of hydrolysis (k_a) and rates of subsequent isomerization (k_i) and racemization (k_r) of the product $Co(en)_2(OH_2)X^{2+}$ species are reported. The new or revised results for spontaneous aquation are as follows: (+)-$Co(en)_2Br_2^+$, 72 ± 2% (+)-cis; (+)-$Co(en)_2Cl_2^+$, 76 ± 2% (+)-cis; (+)-$Co(en)_2(OH)Br^+$, 85 ± 1% (+)-cis; (+)-$Co(en)_2(OH)Cl^+$, 84.5 ± 1.5% (+)-cis; (+)-$Co(en)_2N_3Br^+$, $k_a = (11.6 \pm 0.3) \times 10^{-4}\ s^{-1}$, 85 ± 2% (+)-cis; (+)-$Co(en)_2N_3Cl^+$, $k_a = (2.4 \pm 0.1) \times 10^{-4}\ s^{-1}$, 84 ± 3% (+)-cis; (+)-$Co(en)_2N_3(Me_2SO)^{2+}$, $k_a = (2.1 \pm 0.1) \times 10^{-4}\ s^{-1}$, 85 ± 3% (+)-cis. The isomerization and racemization results for (+)-*cis*- and *trans*-$Co(en)_2(OH_2)X^{2+}$ in 0.1 M $HClO_4$ at 25 °C are as follows: X = Br, $k_r = (4.6 \pm 0.2) \times 10^{-5}\ s^{-1}$; X = N_3, $k_i = (1.63 \pm 0.05) \times 10^{-4}\ s^{-1}$, $k_r = (4.3 \pm 0.2) \times 10^{-5}\ s^{-1}$, 68 ± 1% (±)-cis at equilibrium. The data establish that racemization occurs exclusively by isomerization to the inactive trans form. Because of gross discrepancies between the present work and that previously documented, the methods for treating and evaluating all these data are reviewed. The Hg^{2+}-induced aquation stereochemistries are reported for (+)-*cis*-$Co(en)_2Br_2^+$ and (+)-*cis*-$Co(en)_2Cl_2^+$, and both Hg^{2+}- and NO^+-induced aquation results are reported for (+)-*cis*-$Co(en)_2N_3X^{n+}$ (X = Br, Cl, Me_2SO). Details of the Cl_2-induced hydrolysis[36] of bound Me_2SO in (+)-*cis*-$Co(en)_2X(Me_2SO)^{2+}$ (X = Cl, Br) are also given. The evidence for reduced coordination number intermediates in both spontaneous and induced aquation is reconsidered in the light of the present results which demonstrate that at least for (+)-*cis*-$Co(en)_2AX^{n+}$, the steric courses of spontaneous and induced aquations are the same and are independent of the nature of the leaving group.

Introduction

trans-Diacido(tetraamine)cobalt(III) complexes aquate often with stereochemical change while *cis*-diacido ions are reported to aquate with retention. Several rationales have been suggested for these characteristics of octahedral cobalt(III) ions.[1,2] By contrast, induced aquation of the *cis*-diacido complexes occurs with substantial stereochemical change.[3,4] However, recent and more accurate studies have revealed two apparent exceptions to the cis retention "rule" for spontaneous aquation, namely, *cis*-$Co(en)_2Br_2^+ \rightarrow$ 72% *cis*-$Co(en)_2(OH_2)Br^{2+}$ at 25 °C[5] and *cis*-$Co(en)_2(N_3)Cl^+ \rightarrow$ 85% *cis*-$Co(en)_2(OH_2)N_3^{2+}$ at 0 °C.[6] These two results have raised some questions about the validity of the earlier data. Also, few studies have been made with chiral cis complexes, and advances in spectrophotometry and polarimetry now allow a more accurate and expanded determination of the steric course of both spontaneous and induced aquation.

This paper therefore reexamines much of the earlier work as well as some new systems using the resolved cis ions. The validity of the current evidence[7] for intermediates of reduced coordination number in both spontaneous and induced aquation is reconsidered in the light of new results.

Experimental Section

Complexes. (−)-*cis*-$[Co(en)_2Cl_2]ClO_4$ (ϵ^{535} 85.3, $[\alpha]^{25}{}_D$ −575°; 10^{-2} M $HClO_4$) was prepared and resolved with Na[(+)-$[Co(en)(ox)_2]$] as described.[8] $[Co(en)_2CO_3]ClO_4$ (ϵ^{510} 133.0; H_2O) was prepared and resolved similarly,[8] giving (−)-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$ (ϵ^{510} 133.5, $[\alpha]^{25}{}_D$ −1331°; H_2O). *cis*-$[Co(en)_2(OH_2)Cl]SO_4 \cdot 2H_2O$ and *cis*-$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ (ϵ^{516} 91.8, 0.1 M $HClO_4$) were obtained from *trans*-$[Co(en)_2Cl_2]Cl$[9] and/or $[Co(en)_2CO_3]Cl$.[10] *cis*-$[Co(en)_2(OH_2)Cl]BrNO_3$ was crystallized from the bromide in water by addition of $LiNO_3$ and ethanol, added slowly at 0 °C. Anal. Calcd for $[Co(en)_2(OH_2)Cl]BrNO_3$: C, 12.8; H, 4.9; N, 18.7; Br, 21.4; Cl, 9.5. Found: C, 13.1; H, 5.0; N, 19.0; Br, 21.4; Cl, 9.5. (+)-*cis*-$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ (ϵ^{516} 91.3, 0.1 M $HClO_4$; $[\alpha]^{20}{}_{578}$ +310°, 10^{-3} M $HClO_4$) was resolved through the α-bromo-D-(+)-camphor-*trans*-π-sulfonate salt.[8,11] (−)-*cis*-$[Co(en)_2(OH_2)Br]Br_2 \cdot H_2O$ (ϵ^{530} 91.5, 0.1 M $HClO_4$; $[\alpha]^{25}{}_{460}$ +464°, 10^{-2} M $HClO_4$) was prepared directly from (−)-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$, as described for the racemate[10] (ϵ^{530} 91.8, 0.1 M $HClO_4$). Anal. Calcd for $[Co(en)_2(OH_2)Br]Br_2 \cdot H_2O$: C, 10.6; H, 4.4; N, 12.3; Br, 52.7. Found ((−) form): C, 10.8; H, 4.5; N, 12.2; Br, 53.0. *trans*-$[Co(en)_2(OH_2)Cl]SO_4 \cdot 0.5H_2O$ was obtained[8] from *trans*-$[Co(en)_2Cl_2]Cl$[8] and recrystallized from 10^{-3} M H_2SO_4/C_2H_5OH (20 °C) as green plates of the previously uncharacterized hemihydrate (ϵ^{510} 10.0, ϵ^{584} 30.8; 0.1 M $HClO_4$). Anal. Calcd for $[Co(en)_2(OH_2)Cl]SO_4 \cdot 0.5H_2O$: C, 14.2; H, 5.7; N, 16.6; S, 9.5; Cl, 10.5. Found: C, 14.2; H, 5.8; N, 16.3; S, 9.5; Cl, 10.4. $[Co(en)_2CO_3]ClO_4$ treated with 1 M $HClO_4$ and flushed with N_2 expelled CO_2. Neutralization with NaOH (1 M) to pH 7 finally afforded *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ (ϵ^{492} 17.2, ϵ^{553} 31.7; 0.1 M $HClO_4$). *trans*-$[Co(en)_2(OH_2)_2]SO_4 \cdot HSO_4$ was crystallized from *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ in cold 1 M H_2SO_4/C_2H_5OH and *trans*-$[Co(en)_2(OH_2)_2](ClO_4)_3$ from a concentrated solution in $HClO_4$. Anal. Calcd for $[Co(en)_2(OH_2)_2]SO_4 \cdot HSO_4$: Co, 14.4; C, 11.8; H, 5.2; N, 13.7; S, 15.7. Found: Co, 14.8; C, 11.8; H, 5.1; N, 13.6; S, 15.3. Calcd for $[Co(en)_2(OH_2)_2](ClO_4)_3 \cdot 1.5H_2O$: C, 8.9; H, 4.3; N, 10.4; Cl, 19.7. Found: C, 9.0; H, 4.3; N, 10.3; Cl, 19.8. *cis*-$[Co(en)_2Br_2]Br \cdot H_2O$ and $[Co(en)_2Br_2]ClO_4$ (ϵ^{552} 110, 10^{-2} M $HClO_4$) were obtained from both $[Co(en)_2CO_3]Br$[10] and *cis*-$[Co(en)_2(N_3)_2]NO_3$.[5] Excess NO^+ removed residual azido impurity in material more conveniently prepared from the latter source. *cis*-$[Co(en)_2(N_3)_2]NO_3$[12] and *trans*-$[Co(en)_2(N_3)_2]ClO_4$[3] were prepared as reported and recrystallized twice from hot water to remove traces of Co(II) salts. *trans*-$[Co(en)_2(N_3)_2]ClO_4$ treated with $N(C_2H_5)_4Cl$ in dimethylformamide (DMF) deposited the chloride as blue plates which transformed to brown needles on standing. These were recrystallized from water/acetone. *trans*-$[Co(en)_2N_3Cl]ClO_4$ was prepared as described.[3] If the *trans*-$[Co(en)_2(N_3)_2]Cl$ reactant contained appreciable Co(II), the product[6] was largely *cis*-$[Co(en)_2Cl_2]Cl$. Residual *trans*-$[Co(en)_2Cl_2]ClO_4$ impurity in crude *trans*-$[Co(en)_2N_3Cl]ClO_4$ was conveniently removed by selective base hydrolysis at pH 10 at 0 °C using a $Na_2CO_3/NaHCO_3$ buffer (5 min) and a concentrated solution of crude *trans*-$[Co(en)_2N_3Cl]Cl$. (The latter was prepared from the perchlorate in DMF by the addition of $N(C_2H_5)_4Cl$.) Careful acidification (0 °C, $HClO_4$) yielded pure *trans*-$[Co(en)_2N_3Cl]ClO_4$. *cis*-$[Co(en)_2(N_3)_2]NO_3$ was resolved with sodium antimonyl-(+)-tartrate.[12] (+)-*cis*-$[Co(en)_2(N_3)_2]_2[Sb_2((+)\text{-tart})_2]$, converted to the iodide (concentrated aqueous NaI, 0 °C), and (−)-*cis*-$[Co(en)_2(N_3)_2]I$, from the resolution filtrate (NaI), were recrystallized from DMF/aqueous NaI, converted to the perchlorates ($AgCH_3CO_2$; $NaClO_4$), and finally recrystallized twice from warm water ($(+)_D$ isomer: $[\alpha]^{20}{}_{531}$ −1077°; $(-)_D$ isomer: $[\alpha]^{20}{}_{531}$ +1072°; ϵ^{518} 343; H_2O). *cis*-$[Co(en)_2(OH_2)N_3]SO_4$[3] was prepared from *cis*-$[Co(en)_2N_3Cl]Cl$[3] or *cis*-$[Co(en)_2N_3Br]ClO_4$ and $Hg(CH_3CO_2)_2$ (1.0 equiv) in 1 M H_2SO_4 at 0 °C. Material recrystallized from water (pH 3) at 0 °C by the slow addition of ethanol afforded red-violet plates of the previously

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uncharacterized anhydrous material (air-dried; ϵ^{505} 303, 10^{-2} M $HClO_4$). Anal. Calcd for $[Co(en)_2(OH_2)N_3]SO_4$: Co, 17.6; C, 14.3; H, 5.4; N, 29.3; S, 9.6. Found: Co, 17.6; C, 14.2; H, 5.5; N, 29.7; S, 9.6. The dithionate obtained from the sulfate and $Li_2S_2O_6$ in water/methanol was recrystallized as plates (20 °C, rapidly) or needles (0 °C, slowly) containing varying amounts of loosely held methanol and water of crystallization (CH_3OH was confirmed by the ^1H NMR spectrum). Anal. Calcd for $[Co(en)_2(OH_2)N_3]S_2O_6\cdot 0.25CH_3OH\cdot 0.5H_2O$: Co, 14.2; C, 12.3; H, 4.8; N, 23.6; S, 15.4. Found (needles): Co, 14.2; C, 12.0; H, 4.7; N, 23.7; S, 15.2. Prolonged vacuum drying (10 mm, P_2O_5) yielded desolvated salt. Anal. Calcd for $[Co(en)_2(OH_2)N_3]S_2O_6$: Co, 14.8; C, 12.0; H, 4.5; N, 24.6; S, 16.1. Found: Co, 14.4; C, 12.0; H, 4.7; N, 23.7; S, 16.1 (ϵ^{505} 306, 10^{-2} M $HClO_4$). *trans*-$[Co(en)_2(OH_2)N_3]SO_4\cdot 2H_2O$[3] was prepared from purified *trans*-$[Co(en)_2N_3Cl]ClO_4$ and $Hg(CH_3CO_2)_2$ (1.0 equiv) in 1 M H_2SO_4. The $[Co(en)_2N_3Cl]ClO_4$ needs to be pure since *trans*-$[Co(en)_2(N_3)_2]_2SO_4$ and *trans*-$[Co(en)_2(OH_2)Cl]SO_4$ are difficult to remove from the *trans*-aquaazido salt. A better route to this complex follows. *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ (33.0 g) was shaken with water (450 mL) containing NaN_3 (5.2 g) and the mixture warmed to ~40 °C to complete dissolution. The clear deep mauve-violet solution was left undisturbed at 0 °C for 4–6 h whence mauve plates of *trans*-$[Co(en)_2(OH)N_3]ClO_4\cdot 2NaClO_4\cdot H_2O$ (6.0 g) deposited. Further fractions contained increasing amounts of the cis isomer and *trans*-$[Co(en)_2(N_3)_2]ClO_4$. The complex was recrystallized twice from water by addition of $NaClO_4$ and cooling and was finally recrystallized from $HClO_4$ solution (0 °C) and filtered to remove any trace of *trans*-$[Co(en)_2(N_3)_2]ClO_4$. The pH was then adjusted to 9 with Tris to give the aqua–hydroxo double salt. This method cleanly removes any of the more soluble cis isomer. Anal. Calcd for $[Co(en)_2(OH_2)N_3][Co(en)_2(OH)N_3](ClO_4)_3$: Co, 15.2; C, 12.4; H, 4.6; N, 25.3; Cl, 13.7. Found: Co, 15.2; C, 12.4; H, 4.5; N, 25.5; Cl, 13.6. This material (ϵ^{551} 260.4, ϵ^{500} 95.1; 10^{-2} M $HClO_4$) in 10^{-2} M $HClO_4$ when treated with $Li_2S_2O_6$ in water/ethanol deposited glistening mauve plates of the dithionate (ϵ^{551} 253.4, ϵ^{500} 95.6; 10^{-2} M $HClO_4$). Anal. Calcd for $[Co(en)_2(OH_2)N_3]S_2O_6$: Co, 14.8; C, 12.0; H, 4.5; N, 24.6; S, 16.1. Found: Co, 14.9; C, 12.0; H, 4.6; N, 24.4; S, 16.1. The sulfate was obtained in a similar way from cold 1 M H_2SO_4/CH_3OH (ϵ^{551} 256.5, ϵ^{500} 95.0; 10^{-2} M $HClO_4$) as blue-lilac plates. Anal. Calcd for $[Co(en)_2(OH_2)N_3]SO_4\cdot 2H_2O$: Co, 15.9; C, 12.9; H, 6.0; N, 26.4. Found: Co, 15.8; C, 12.6; H, 5.1; N, 25.8. *cis*-$[Co(en)_2(Me_2SO)_2](ClO_4)_3$ (ϵ^{510} 112.0, H_2O) was synthesized from *cis*- or *trans*-$[Co(en)_2X_2]ClO_4$ (X = Cl, Br) and $AgClO_4$ (2.1 equiv) in Me_2SO (60 °C, 20 min). It was recrystallized as both the triperchlorate ($NaClO_4$) and nitrate diperchlorate ($LiNO_3$, $LiClO_4$) from water. Anal. Calcd for $[Co(en)_2(Me_2SO)_2](ClO_4)_2NO_3$: C, 16.1; H, 4.7; N, 11.8; S, 10.8; Cl, 11.9. Found: C, 15.8; H, 4.8; N, 12.0; S, 11.0; Cl, 11.8. *cis*-$[Co(en)_2(Me_2SO)Br](ClO_4)_2$ and $[Co(en)_2(Me_2SO)Br]NO_3ClO_4$ (ϵ^{529} 102.8, H_2O) were prepared from *cis*- or *trans*-$[Co(en)_2Br_2]ClO_4$ in Me_2SO containing $AgClO_4$ (1.01 equiv; 60 °C, 5 min).[14] Anal. Calcd for $[Co(en)_2(Me_2SO)Br]NO_3ClO_4$: C, 14.5; H, 4.5; N, 14.1; S, 6.4; Br, 16.2; Cl, 7.2. $[Co(en)_2CO_3]Br$ rather than $[Co(en)_2CO_3]Cl$ and HBr were used to prepare the reactant dibromo complex to avoid chloro complex impurities. *cis*-$Co(en)_2(OH_2)_2^{3+}$ was generated from $[Co(en)_2CO_3]ClO_4$ and $HClO_4$[4] and (+)-$Co(en)_2(OH_2)_2^{3+}$ from (−)-$[Co(en)_2CO_3]ClO_4\cdot 0.5H_2O$ (ϵ^{492} 80.0, 0.1 M $HClO_4$; 80.9, 1.0 M $HClO_4$; $[M]^{25}_{520}$ −1779°, 0.1 M $HClO_4$). (N.B.—The units of $[M]^t_\lambda$ are properly deg M^{-1} m^{-1}. However, throughout this paper the symbol ° will be used.)

***cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$.** *cis*-$[Co(en)_2(Me_2SO)_2](ClO_4)_3$ (63.3 g) in Me_2SO (500 mL, 20 °C) was treated with a fine suspension of NaN_3 (6.5 g, 1.0 equiv) in Me_2SO while being well stirred. After 1.5–2 h, the deep wine red product was obtained as an oil by pouring into a tenfold volume of ether/ethanol (10:1) and caused to solidify by prolonged trituration with ethanol and ether. The diperchlorate in saturated aqueous solution (20 °C, pH 3) deposited the less soluble nitrate perchlorate (30 g) on addition of saturated aqueous $LiNO_3$ followed by $LiClO_4\cdot 3H_2O$. Further fractions were contaminated with the more soluble *cis*-$[Co(en)_2(Me_2SO)_2](ClO_4)_2NO_3$. Two further recrystallizations from water afforded brown needles which after 12 h at 0 °C were collected, washed with CH_3OH and ether, and air-dried (yield 19 g, 41%; ϵ^{506} 326, H_2O). Anal. Calcd for $[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$: Co, 12.8; C, 15.6; H, 4.8; N, 24.3; S, 7.0; Cl, 7.7. Found: Co, 12.6; C, 15.4; H, 4.8; N, 24.5; S, 7.0; Cl, 7.9. Preparations using the more readily available *cis*-$[Co(en)_2Me_2SO](ClO_4)_2NO_3$ reactant led to the isolation of lustrous brown-violet plates or needles similar to the above but which proved to be a constant-crystallizing mixture of *cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$ (ca. two parts) and *cis*-$[Co(en)_2(Me_2SO)Cl]NO_3ClO_4$ (ca. one part). The latter component was obtained pure by converting the azido complex to the more soluble aqua derivative with NO^+, and the recovered material was recrystallized and identified by comparison with an authentic sample[13] (^1H NMR, visible spectrum, analysis). Anal. Calcd for $[Co(en)_2(Me_2SO)Cl]NO_3ClO_4$: C, 15.9; H, 4.9; N, 15.4; S, 7.1; Cl, 15.6. Found: C, 15.9; H, 5.2; N, 15.2; S, 7.0; Cl, 15.5. Its occurrence in significant yield under the mild conditions (20 °C) suggests ClO_4^- was reduced to Cl^- in the $Me_2SO/NO_3^-/ClO_4^-/N_3^-$ mixture and Cl^- was incorporated during base (N_3^-) catalyzed elimination of Me_2SO.

***cis*-$[Co(en)_2N_3Cl]ClO_4$.** *cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$ (20 g) in *N,N*-dimethylacetamide (DMA) (100 mL, 60 °C) was treated with LiCl (10 g, ~5 equiv). Following the wine red to deep violet color change (~10 min, 60 °C), crude *cis*-$[Co(en)_2N_3Cl]Cl$ was precipitated quantitatively with excess ether/ethanol (10:1). The product was recrystallized from water as the perchlorate (yield 11.5 g, 75%; ϵ^{528} 216, 10^{-3} M $HClO_4$) and the iodide. Anal. Calcd for $[Co(en)_2N_3Cl]ClO_4$: C, 13.5; H, 4.5; N, 27.5; Cl, 19.9. Found: C, 13.5; H, 4.8; N, 27.7; Cl, 20.0. Calcd for $[Co(en)_2N_3Cl]I$: C, 12.5; H, 5.0; N, 24.6; Cl, 9.2; I, 33.1. Found: C, 12.5; H, 4.8; N, 25.1; Cl, 9.1; I, 33.1.

***cis*-$[Co(en)_2N_3Br]ClO_4$.** The bromo species was prepared analogously using LiBr in place of LiCl. It was recrystallized from cold water/HBr (48% w/v). Anal. Calcd for $[Co(en)_2BrN_3]Br\cdot H_2O$: C, 12.0; H, 4.6; N, 24.6; Br, 40.1. Found: C, 12.0; H, 4.5; N, 24.6; Br, 40.1. Violet-brown needles of the perchlorate (yield 12 g, 70%; ϵ^{529} 212, 10^{-3} M $HClO_4$) were obtained rapidly from water (0 °C, pH 3). Anal. Calcd for $[Co(en)_2N_3Br]ClO_4$: C, 12.0; H, 4.0; N, 24.5; Br, 20.0; Cl, 8.9. Found: C, 12.1; H, 4.1; N, 24.3; Br, 20.0; Cl, 9.0. In larger scale (>20 g) *cis*-$Co(en)_2N_3X^+$ preparations, the products were more conveniently recovered from DMF solution by dilution with aqueous (0 °C) $NaClO_4$ or NaI. *trans*-$[Co(en)_2N_3X]ClO_4$ salts were conveniently prepared from the cis isomers by refluxing them in saturated methanol solutions (X = Br, ~30 min; X = Cl, ~3 h). Isomerization was complete but prolonged refluxing led to some disproportionation. The products were purified as detailed earlier.

(−)-*cis*-$[Co(en)_2(Me_2SO)Br]NO_3ClO_4$. (+)-*cis*-$[Co(en)_2Br_2]ClO_4$ (1.0 g; see later) in Me_2SO (20 mL, 20 °C) was treated dropwise with $AgClO_4$ (0.48 g, 1.02 equiv) in Me_2SO (5 mL). After 30 min, when the initially green-violet solution had become mauve, AgBr was removed and the complex precipitated as an oil by addition of the mixture to excess ethanol/ether (1:10). The complex was crystallized from water ($LiNO_3$, $LiClO_4$), and crude (+)-*cis*-$[Co(en)_2(Me_2SO)Br]NO_3ClO_4$ (0.90 g) so obtained was fractionated from water (F1, plates, racemate, 0.3 g; F2, needles, 0.4 g, $[\alpha]^{20}_{576}$ +323°, $[\alpha]^{20}_{490}$ −344°; ϵ^{529} 101.5; H_2O). Two recrystallizations raised the rotations of F2 to constant values ($[\alpha]^{20}_{576}$ +433°, $[\alpha]^{20}_{490}$ −458°). Anal. Calcd for $[Co(en)_2(Me_2SO)Br]NO_3ClO_4$: C, 14.5; H, 4.5; N, 14.1; S, 6.4; Br, 16.0; Cl, 7.1. Found: C, 14.7; H, 4.6; N, 14.0; S, 6.3; Br, 15.9; Cl, 7.0.

(−)-*cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$. The complex was prepared from (−)-*cis*-$[Co(en)_2N_3Br]ClO_4$ and $AgClO_4$ in Me_2SO, similar to the above synthesis or from (−)-*cis*-$[Co(en)_2(N_3)_2]ClO_4$ and $NOCF_3SO_3$ in Me_2SO. (−)-*cis*-$[Co(en)_2N_3Cl]ClO_4$ reacts with $AgClO_4$ (1 equiv or excess) in Me_2SO but more slowly than (−)-*cis*-$[Co(en)_2N_3Br]ClO_4$ or even (−)-*cis*-$[Co(en)_2Cl_2]ClO_4$ under the same conditions. Also some racemization detracts from this method of synthesis. (−)-*cis*-$[Co(en)_2(N_3)_2]ClO_4$ (3.6 g) in Me_2SO (25 mL) was treated dropwise (over 3 min) at 20 °C with a fresh solution of $NOCF_3SO_3$ (5.4 g, ≲3 equiv) in Me_2SO (25 mL) (*caution*!). After 15 min, an oil was produced with excess ether addition. Prolonged ether trituration yielded a sticky solid which on dissolution in water (100 mL) containing $NaNO_3$ and $NaClO_4$ yielded crystals (20 °C, 5 min; 0.6 g, (−)-*cis*-$[Co(en)_2(N_3)_2]ClO_4$ and (±)-*cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$). The second fraction was collected after 2 h at 0 °C (1.2 g, (−)-*cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$). Fraction 2, recrystallized from water (15 mL) after filtration to remove (−)-*cis*-$[Co(en)_2(N_3)_2]ClO_4$, afforded brown needles, the rotations of which increased from $[\alpha]^{20}_{550}$ −766° to a constant $[\alpha]^{20}_{550}$ −823° on two further recrystallizations from water (0.2 g; ϵ^{505} 324; $[\alpha]^{20}_{467}$ +1312°; H_2O). Anal. Calcd for $[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$: Co, 12.8; C, 15.6; H, 4.8; N, 24.3; S, 7.0; Cl, 7.7. Found: Co, 12.5; C, 15.6; H, 4.8; N, 24.2; S, 7.1; Cl, 7.9. $Na[(+)\text{-}[Co(en)(ox)_2]]\cdot$

$3.5H_2O$ was prepared and resolved as described and recrystallized from water/ethanol[15,16] (ϵ^{537} 126.3, ϵ^{380} 197.4; $[\alpha]^{20}_{546}$ −1339°, $[\alpha]^{20}_{615}$ +1130°). Anal. Calcd for $Na[Co(en)(C_2O_4)_2]\cdot 3.5H_2O$: Co, 15.5; C, 18.9; H, 4.0; N, 7.4. Found: Co, 15.4; C, 18.8; H, 3.9; N, 7.1.

(+)- and (−)-*cis*-$[Co(en)_2N_3Cl]ClO_4$. The resolution followed earlier lines[3] using crude *cis*-$[Co(en)_2N_3Cl]Cl$ obtained as above or the iodide treated with $AgCH_3CO_2$ (1.0 equiv, pH 3) and 0.7 rather than 0.5 equiv of $Na[(+)\text{-}[Co(en)(ox)_2]]\cdot 3.5H_2O$. The less soluble diastereoisomer was converted to (−)-*cis*-$[Co(en)_2N_3Cl]I$ (aqueous NaI, 0 °C) and (+)-*cis*-$[Co(en)_2N_3Cl]I$ obtained quickly from the filtrate with NaI (0 °C). Recrystallization of the enantiomers from DMF/aqueous NaI did not increase their rotations significantly ($[\alpha]^{25}_{520}$ ±558°; 10^{-2} M $HClO_4$). Treatment with AgCl followed by $NaClO_4$ after filtration yielded the perchlorates ((−) form, $[M]^{25}_{520}$ +2140°, $[M]^{25}_{460}$ −2810°, $[M]^{25}_{550}$ +3687°; (+) form, $[M]^{25}_{520}$ −2140°, $[M]^{25}_{460}$ +2820°, $[M]^{25}_{550}$ −3690°; DMF; ϵ^{532} 250, DMF; ϵ^{528} 216, H_2O). Specific rotations were unchanged by recrystallization and, in the case of (−)-*cis*-$[Co(en)_2N_3Cl]ClO_4$, reresolution. Anal. Calcd for $[Co(en)_2N_3Cl]ClO_4$: C, 13.5; H, 4.5; N, 27.5; Cl, 19.9. Found ((−) form): C, 13.8; H, 4.7; N, 27.5; Cl, 19.8. Found ((+) form): C, 13.5; H, 4.6; N, 27.8; Cl, 19.9.

(+)- and (−)-*cis*-$[Co(en)_2N_3Br]ClO_4$. The resolution followed that described for the chloro analogue above. Crude *cis*-$[Co(en)_2N_3Br]Br$ was used as it dissolves readily to give concentrated and supersaturated aqueous solutions (0 °C). Rapid treatment is required to avoid losses through aquation which leads to an excessive resolving agent:complex ratio and hampers an otherwise clean resolution. Twice recrystallized (water) (−)-*cis*-$[Co(en)_2BrN_3]ClO_4$ from the less soluble diastereoisomer showed ϵ^{531} 256, $[M]^{25}_{470}$ −4988°, and $[M]^{25}_{560}$ +2966° (DMF), while the (+)-cis diastereosiomer gave ϵ 255, $[M]^{25}_{470}$ +4940°, and $[M]^{25}_{560}$ −2985°. Rotations were unaltered by further recrystallization. Anal. Calcd for $[Co(en)_2N_3Br]ClO_4$: C, 12.0; H, 4.0; N, 24.5; Br, 20.0; Cl, 8.9. Found ((−) form): C, 12.0; H, 4.2; N, 24.6; Br, 19.9; Cl, 8.8. Found ((+) form): C, 12.2; H, 4.2; N, 24.2; Br, 19.6; Cl, 8.9.

(+)- and (−)-*cis*-$[Co(en)_2Br_2]ClO_4$. Method 1. Bailar's procedure[17] was modified as follows. *cis*-$[Co(en)_2Br_2]Br\cdot H_2O$ (20 g) suspended in water (0 °C, pH 3; 400 mL) was shaken vigorously with excess fresh AgCl (6.9 g, 1.05 equiv) and on dissolution filtered quickly onto excess ammonium α-bromo-D-(+)-camphor-*trans*-π-sulfonate ($NH_4[(+)\text{-BCS}]$, 40 g, ~2.7 equiv). The dull green-gray diastereoisomer (+)-*cis*-$[Co(en)_2Br_2][(+)\text{-BCS}]$ was collected in two fractions (F1, 2.0 g; F2, 2.4 g) over 1 h at 0 °C. Each was converted to the iodide (NaI), recrystallized from DMF/aqueous NaI, and then converted to the perchlorate, as above. Recrystallization of each from water raised the rotation of only F2 (from $[M]^{25}_{D}$ +1200° to $[M]^{25}_{D}$ +1560°; F1, $[M]^{25}_{D}$ +1590; ϵ^{552} 119, DMF). Anal. Calcd for $[Co(en)_2Br_2]ClO_4$: C, 11.0; H, 3.7; N, 12.8; Br, 36.5; Cl, 8.1. Found: C, 11.1; H, 4.1; N, 12.3; Br, 36.3; Cl, 8.1.

Method 2. The above procedure was followed using $Na[(+)\text{-}[Co(en)(ox)_2]]\cdot 3.5H_2O$ (0.5 equiv) in place of $NH_4[(+)\text{-BCS}]$. The (−)-*cis*-$[Co(en)_2Br_2]\text{-}(+)\text{-}[Co(en)(ox)_2]\cdot H_2O$ diastereoisomer crystallized readily. After 0.5 h at 0 °C, the violet crystals (7.8 g) were collected and washed with methanol/water (0 °C, 1:2), methanol, and ether. After a further 0.5 h, the filtrate was refiltered and crude (+)-*cis*-$[Co(en)_2Br_2]I$ obtained with excess NaI. The diasteroisomer was converted to the iodide (aqueous NaI, 0 °C), and the enantiomers recrystallized once from DMF/aqueous NaI showed ϵ^{552} 118.2, $[M]^{25}_{D}$ +1597° ((+) form) and ϵ^{552} 117.3, $[M]^{25}_{D}$ −1587 ((−) form). Anal. Calcd for $[Co(en)_2Br_2]I$: C, 10.3; H, 3.5; N, 12.0; Br, 34.3; I, 27.2. Found ((−) form): C, 10.7; H, 4.0; N, 11.9; Br, 34.0; I, 27.2. Conversion to the perchlorates and recrystallization from water as deep green-gray plates did not change their molar rotations. The active *cis*-$Co(en)_2Br_2^+$ salts, although distinctly green in the solid state (cf. racemate, violet-gray), are violet in aqueous solution and contain none of the yellow-green trans isomer. This was confirmed by cation-exchange chromatography. Synthetic cis/trans mixtures readily separated on Dowex 50WX2 (200–400 mesh, H^+ form) on elution with 0.5 HCl at 2 °C, whereas the active cis samples eluted as single violet (1+) bands. Anal. Calcd for $[Co(en)_2Br_2]ClO_4$: C, 11.0; H, 3.7; N, 12.8; Br, 36.5; Cl, 8.1. Found ((−) form): C, 11.2; H, 4.2; N, 12.6; Br, 36.4; Cl, 8.1. Found ((+) form): C, 11.0; H, 4.0; N, 12.5; Br, 36.6; Cl, 8.3.

Instruments. Electronic spectra were measured on a Cary 118C recording spectrophotometer and rotatory dispersion spectra on a recording Perkin-Elmer P22 spectropolarimeter (α ± 0.002°). Concentrations used to calculate $[\alpha]$ are % w/v (DMF, d^{25} 0.9441). Solvent expansion (DMF, $\gamma = 88.4 \times 10^{-5}\ \text{deg}^{-1}$) was allowed for where appropriate. ^1H NMR spectra were recorded on a Jeol Minimar 100-MHz instrument for D_2O solutions containing sodium trimethylsilylpropanesulfonate as standard.

Kinetics. Aquation of *cis*-$[Co(en)_2N_3Br]ClO_4$, *cis*-$[Co(en)_2N_3Cl]ClO_4$, and *cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$ and isomerization of *cis*- and *trans*-$[Co(en)_2(OH_2)N_3]S_2O_6$ in 0.01 M $HClO_4$ were each followed spectrophotometrically (at 600, 580, 500, or 480 nm) at 25.0 ± 0.05 °C. Mean complex concentrations were determined from initial (extrapolated) and final absorbances.

(−)-*cis*-$Co(en)_2(OH_2)X^{2+}$ ($X = Br, N_3$) racemizations were followed by a sampling technique (25.0 °C, 0.1 or 0.01 M $HClO_4$). Aliquots (~5 mL, X = Br) were quenched with $NaHCO_3$ (solid, excess) at ~1.5-h intervals over ~12 h, and the rotations (2 cm) recorded for (−)-$Co(en)_2CO_3^+$ after 10–15 min. Similarly, aliquots (5.00 mL, $X = N_3$) were withdrawn for solutions of (−)-*cis*-$[Co(en)_2N_3Br]ClO_4$ in $HClO_4$ (0.01 or 0.1 M) commencing at 1.5 h (>99% Br^- aquation) and treated with $HClO_4$ (5.00 mL, 1 M), aqueous $NaNO_2$ (1.00 mL, ca. 8.00×10^{-2} M), and, after 5 min, $NaHCO_3$ (solid, excess), and measurements were made as above at 570, 490, and 470 nm.

The aquation of *cis*-$Co(en)_2Br_2^+$ in 0.01 M $HClO_4$ at 25.0 °C was followed at 556 nm using the technique described previously.[5]

Reacting solutions of (−)-*cis*-$Co(en)_2N_3X^+$, (−)-*cis*-$Co(en)X_2^+$ (X = Cl, Br), (−)-*cis*-$Co(en)_2(Me_2SO)N_3^{2+}$, and *cis*- and *trans*-$Co(en)_2(OH_2)N_3^{2+}$ in 0.01 M $HClO_4$ at 25.0 °C were scanned (620–400 nm) over periods up to $3t_{1/2}$ to locate initial isosbestic and isorotatory points.

Computation. Rate data were handled by nonlinear least-squares fitting of functions specified later. We thank Dr. M. Bruce (ANU), who wrote the program (MGB002) and assisted in the processing of the data on a Univac 1108 computer. Some results were obtained using the least-squares exponential fitting program described elsewhere.[18]

Isomeric and Optical Purity. Chemical Correlations. (−)-*cis*-$[Co(en)_2Br_2]ClO_4$, (−)-*cis*-$[Co(en)_2N_3Br]ClO_4$, and (−)-*cis*-$[Co(en)_2N_3Cl]ClO_4$ each derive from their less soluble (+)-$Co(en)(ox)_2^-$ diastereoisomer. Both enantiomers were recovered in each resolution and showed equal and opposite activity after recrystallization to maximum rotation. (+)-*cis*-$[Co(en)_2Br_2]ClO_4$ obtained independently from (+)-BCS had properties identical with those from the (+)-$Co(en)(ox)_2^-$ resolution. Finally, reresolution of (−)-$Co(en)_2N_3X^+$ (X = Cl, Br) and (−)-$Co(en)_2Br_2^+$ with (+)-$Co(en)(ox)_2^-$ did not increase their activity. (−)-*cis*-$[Co(en)_2(Me_2SO)Br]NO_3ClO_4$, (−)-*cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$, and (−)-*cis*-$[Co(en)_2(OH_2)Br]Br_2\cdot H_2O$ were prepared directly from (−)-*cis*-$[Co(en)_2Br_2]ClO_4$, (−)-*cis*-$[Co(en)_2(N_3)_2]ClO_4$, and (−)-$[Co(en)_2CO_3]ClO_4\cdot 0.5H_2O$, respectively. These observations and those described below establish all the complexes to be isomerically and optically pure (±1%).

(−)-*cis*-$[Co(en)_2(OH_2)Br]Br_2\cdot H_2O$ dissolved in 0.01 M $HClO_4$ was treated immediately with excess $NaHCO_3$. After 10 min, ϵ^{510} was 134.7, $[M]^{20}_{470}$ was +7526°, and $[M]^{20}_{D}$ was −4637°, identical (100 ± 1%) with those values of optically pure (−)-$Co(en)_2CO_3^+$. (+)-*cis*-$[Co(en)_2(OH_2)Cl]Br_2\cdot H_2O$ treated similarly gave ϵ^{510} 133.2, $[M]^{20}_{490}$ −8580°, and $[M]^{20}_{570}$ +5938° (100 ± 1% activity) (Table I). Also (−)-*cis*-$[Co(en)_2(OH_2)Br]Br_2\cdot H_2O$ treated with Cl_2 (0.08 M) in HCl (0.5 M) gave ϵ^{516} 91.5 and $[M]^{20}_{D}$ −948°, i.e., 100 ± 2% conversion to (−)-*cis*-$Co(en)_2(OH_2)Cl^{2+}$ (ϵ^{516} 91.3, $[M]^{20}_{D}$ −903° in Cl_2/HCl). Subsequent $NaHCO_3$ quenching yielded ϵ^{510} 134.0, $[M]^{20}_{490}$ +8439°, and $[M]^{20}_{570}$ −5998°, confirming this. The optical purity of (+)- or (−)-*cis*-$Co(en)_2(OH)X^+$ (X = Cl, Br) generated in alkaline buffers from the aqua complexes follows.

(−)-$[Co(en)_2CO_3]ClO_4\cdot 0.5H_2O$ ($[M]^{20}_{570}$ −5921°, $[M]^{20}_{490}$ +8541°, ϵ^{510} 133.5) in 0.1 M $HClO_4$ gave 100 ± 1% (+)-*cis*-$Co(en)_2(OH_2)_2^{3+}$ (ϵ^{492} 80.0, $[M]^{20}_{520}$ −1779°), confirmed by $NaHCO_3$ quenching which after 10 min showed ϵ^{510} 133.0, $[M]^{20}_{490}$ +8500°, and $[M]^{20}_{570}$ −5950°, identical with the original results.

trans-$[Co(en)_2(OH_2)Cl]SO_4\cdot 0.5H_2O$ reacted rapidly with excess $NaHCO_3$ to give blue *trans*-$Co(en)_2Cl(OCO_2H)^+$ (ϵ^{586} 75.6, ϵ^{448} 27.6). Fresh solutions did not yield AgCl immediately (cf. *trans*-$Co(en)_2(OH)Cl^+$, which rapidly loses Cl^-), and addition of $HClO_4$ regenerated green *trans*-$Co(en)_2(OH_2)Cl^{2+}$ quantitatively (ϵ^{584} 30.8, ϵ^{510} 10.4). This *trans*-carbonato species converts only very slowly to $Co(en)_2CO_3^+$ (over hours, 20 °C) and hence *cis*-/*trans*-$Co(en)_2(OH_2)Cl^{2+}$ mixtures were conveniently analyzed for cis content in

Table I. Molar Extinction Coefficients and Molar Rotations Used in Product Analyses

Complex	Medium	ε (λ), M^{-1} cm^{-1} (nm)	$[M]^{20}$ (λ), deg M^{-1} m^{-1} (nm)
Λ-(+)-$Co(en)_2(OH_2)Cl^{2+}$	0.01–0.1 M $HClO_4$	91.2 (510)	+903 (589), +1272 (578)
trans-$Co(en)_2(OH_2)Cl^{2+}$	0.1 M $HClO_4$	10.0 (510), 30.0 (439)	
Λ-(+)-$Co(en)_2(OH_2)Br^{2+}$	0.01–0.1 M $HClO_4$	84.1 (556), 91.5 (530), 81.3 (507), 43.3 (476)	+1298 (570), +1376 (562), +1396 (560), −1399 (497), −2110 (460), −2067 (450)
trans-$Co(en)_2(OH_2)Br^{2+}$	0.01–0.1 M $HClO_4$	19.0 (556), 11.5 (530), 11.7 (507), 15.8 (492), 21.2 (476)	
Λ-(+)-$Co(en)_2(OH_2)N_3^{2+}$	0.01 M $HClO_4$	60.5 (600), 90.2 (580), 186 (545.5), 191.5 (544), 197 (542.5), 226 (535), 298 (500), 233 (480), 136 (455.5)	+1332 (603), −1020 (519), −1957 (509), −3837 (470)
trans-$Co(en)_2(OH_2)N_3^{2+}$	0.01 M $HClO_4$	130 (600), 197 (580), 255 (545.5), 252 (544), 250 (542.5), 229 (535), 95.5 (500), 58.4 (484), 58.0 (480), 52.0 (455.5)	
Λ-(−)-$Co(en)_2(OH_2)_2^{3+}$	0.01–0.1 M $HClO_4$	80.0 (492)	+1779 (520), −1387 (440)
	1.0 M Hg^{2+}/1.0 M $HClO_4$^{c}	81.1 (492)	+1922 (520), −1504 (440)
trans-$Co(en)_2(OH_2)_2^{3+}$	0.01–0.1 M $HClO_4$	17.4 (492)	
	1.0 M Hg^{2+}/1.0 M $HClO_4$^{c}	17.8 (492)	
trans-$Co(en)_2Cl(HCO_3)^+$	0.1–0.3 M $NaHCO_3$	21.2 (510)^a	
	0.08 M Cl_2/0.01–0.1 M $HClO_4$, 0.2–0.3 M $NaHCO_3$^{b}	21.2 (510)^a	
trans-$Co(en)_2(HCO_3)_2^+$	0.1–0.3 M $NaHCO_3$	65.1 (510)	
Λ-(+)-$Co(en)_2CO_3^+$	H_2O	133 (510)	+4627 (589), +5445 (578), +5921 (570), −8541 (490), −7384 (470), −6230 (450), −4994 (410)
	0.08 M Cl_2/0.01–0.1 M $HClO_4$, 0.2–0.3 M $NaHCO_3$^{b}	133.5 (510)	+4590 (589), +5431 (578), +5808 (570), −8540 (490), −7485 (470), −5047 (410)
cis-$Co(en)_2N_3Br^+$	0.01 M $HClO_4$	169 (500), 118 (600)	
cis-$Co(en)_2N_3Cl^+$	0.01 M $HClO_4$	168 (500), 96.0 (600)	
cis-$Co(en)_2N_3(Me_2SO)^{2+}$	0.01 M $HClO_4$	70.8 (600), 101 (580), 326.5 (500), 255 (480)	
cis-$Co(en)_2Br_2^+$	0.01 M $HClO_4$	110 (556)	

[a] ε agreement coincidental; spectrum is pH dependent. [b] Reagents added in this order consecutively. [c] Reagents added simultaneously.

terms of the carbonato ions (ϵ^{510}_{cis} 133.5, ϵ^{510}_{trans} 21.2). Similarly, *cis*-/*trans*-$Co(en)_2(OH_2)_2^{3+}$ mixtures quenched with HCO_3^- were analyzed (ϵ^{510}_{cis} 133.5, ϵ^{510}_{trans} 65.1). *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ in aqueous $NaHCO_3$ reacted rapidly (seconds) and with retention to give the deep pink *trans*-$Co(en)_2(OCO_2H)_2^+$ (ϵ^{538} 87.6, ϵ^{419} 23.2); addition of excess $HClO_4$ regenerated *trans*-$Co(en)_2(OH_2)_2^{3+}$ (ϵ^{492} 17.6). This carbonato species is very stable around pH 7 (cf. *trans*-$Co(en)_2(OH_2)OH^{2+}$, $t_{1/2} \approx 4$ min, 25 °C).

(−)-*cis*-$[Co(en)_2Br_2]ClO_4$ reacted with Cl_2 (0.08 M) in HCl (0.5 M) and showed ϵ^{533} 91.2 and $[M]^{25}_D$ −2104°. (−)-*cis*-$[Co(en)_2Cl_2]ClO_4$ in the same medium showed ϵ^{534} 91.8 and $[M]^{25}_D$ −2100°. This result established the identical optical purity of (−)-*cis*-$[Co(en)_2X_2]ClO_4$ (X = Cl, Br) and showed that both (−)-*cis*-$Co(en)_2Br_2^+$ and (−)-*cis*-$Co(en)_2BrCl^+$ chlorinate with 100 ± 2% retention of geometric and optical configuration. Further, since both the spontaneous and Hg^{2+}-induced aquations of (−)-*cis*-$Co(en)_2Br_2^+$ proceed with significant steric change,[4,5] as we show in this paper, the result strengthens Haim's conclusion[20] that these reactions occur with retention of configuration. (−)-*cis*-$Co(en)_2N_3Br^+$ could not be chemically correlated to (−)-*cis*-$Co(en)_2N_3Cl^+$ in Cl_2/HCl because of concurrent Cl_2 oxidation of bound azide.

Isomeric purity was confirmed in most instances using previously recorded criteria;[4,5] i.e., different salts of the same cation were recrystallized to constant spectra (ε, [M]) until agreement was achieved.

Absolute configurations deduced chemically as above and from aquation studies described herein were related to Λ-(+)-$Co(en)_2Cl_2^+$[21] and data appropriate to the arbitrarily chosen Λ forms are indicated in all tables. All reported rotations refer to aqueous solution except where stated, and it is noted that Λ-*cis*-$Co(en)_2N_3X^+$ (X = Cl, Br) which are of the $(+)_D$ form in water are $(-)_D$ in DMF.

Induced Aquations. The essential techniques have been described.[3,4] Specific conditions are given in Table II. In Hg^{2+}-induced aquations both $Hg(ClO_4)_2$ (HgO in $HClO_4$) and $Hg(CH_3CO_2)_2$ were used. The latter for stoichiometric experiments was added as a $HClO_4$ solution (pH ~0.5), dropwise with stirring, to fresh complex solution in sufficient $HClO_4$ (10^{-3} M) such that the final pH was ~1. This procedure prevented a local excess of reagent where at higher pH initial $CH_3CO_2^-$ incorporation occurs. For *cis*-$[Co(en)_2Br_2]Br\cdot H_2O$ and *cis*-$[Co(en)_2Br_2]ClO_4$, this technique also allowed a clean and direct observation of the first Br^--loss step (1.0 and 0.5 equiv of Hg^{2+} salt, respectively); [complex] in solution always exceeded $[Hg^{2+}] + [HgBr^+]$ and it transpired that residual undissolved complex went into solution and reacted significantly faster than $HgBr^+$-induced Br^- loss from *cis*- and *trans*-$Co(en)_2(OH_2)Br^{2+}$. The importance of avoiding local reagent excess is emphasized by the fact that *cis*-$Co(en)_2(OH_2)Br^{2+}$ itself reacts completely in <5 s with $HgBr^+$ (1 equiv, ~20 °C, ~10^{-2} M). Similar experiments using *cis*-$[Co(en)_2Br_2]ClO_4$ (1.0 equiv of Hg^{2+}) and *cis*-$[Co(en)_2Br_2]Br\cdot H_2O$ (3.0 equiv of Hg^{2+}) resulted in total consumption of *cis*-$Co(en)_2Br_2^+$ and the *cis*-$Co(en)_2(OH_2)Br^{2+}$ product, giving *cis*- and *trans*-$Co(en)_2(OH_2)_2^{3+}$ (95% cis) and leaving *trans*-$Co(en)_2(OH_2)Br^{2+}$ untouched. All Hg^{2+}-induced aquations were complete inside 1.0 min, except for *cis*-$Co(en)_2(OH_2)Cl^{2+}$ in 0.1 M Hg^{2+} (20 min) and 1.0 M Hg^{2+} (2.0 min), *trans*-$Co(en)_2(OH_2)Cl^{2+}$ (1.0 M Hg^{2+}, 15 min), and *cis*-$Co(en)_2N_3Cl^+$ (1.0 equiv Hg^{2+}, 3.0 min). HCO_3^--quenched solutions of $Co(en)_2(OH_2)_2^{3+}$ or $Co(en)_2(OH_2)Cl^{2+}$ were allowed 10–15 min for the quantitative formation[8] of $Co(en)_2CO_3^+$ and the *trans*-bicarbonato ions. Solutions containing Hg^{2+} (≥0.1 M) were not accurately analyzed in this way due to opalescence or precipitation (HgO); filtration or centrifugation resulted in some Co loss through adsorption. Cl_2 oxidations were performed by directly dissolving the complex in Cl_2-saturated (~0.08 M) $HClO_4$ (0.01–0.1 M) or HCl (0.1 M) and allowing 2–3-min reaction time. It proved impractical to perform all induced aquations in homogeneous solution because of solubility limitations, but test experiments on (+)-*cis*-$[Co(en)_2Br_2]ClO_4$ and Hg^{2+} and (+)-*cis*-$[Co(en)_2ClN_3]ClO_4$ and $NaNO_2/HClO_4$ yielded identical results for complex either fully or only partly dissolved prior to addition of inducing reagent. All nitrosations were performed using excess $NaNO_2$ (2–3 equiv) in 0.1 M $HClO_4$ and allowing a 3.0-min reaction time. The sequence of $NaNO_2$ (solid or aqueous solution) and $HClO_4$ additions proved immaterial provided a final pH of ≲1 was achieved inside 1 min. In all cases rotation and extinction coefficient measurements were made at time intervals immediately following induced aquation, extrapolated to zero time, and analyzed using the data given in Table I.

Table II. Molar Extinction Coefficients, Molar Rotations, and Calculated[a] Steric Course Data for the Products of the Rapid Cobalt(III) Aquations at 20 °C

Reactant	Conditions[b]	ϵ (λ), M^{-1} cm^{-1} (nm)	$[M]^{20}$ (λ), deg M^{-1} m^{-1} (nm)	% *cis*-$(OH_2)X^{2+}$ [c]	% Λ-(+)-$(OH_2)X^{2+}$ [d]	% *cis*-$(OH_2)_2{}^{3+}$	% Λ-(−)-$(OH_2)_2{}^{3+}$
cis-$Co(en)_2Br_2{}^+$	1.0 M Hg^{2+}, 0.1 M $HClO_4$ (1)	64.8 (492)		64.5		74.5	
	0.5 M Hg^{2+}, 0.5 M $HClO_4$ (1)	63.7 (492)		62		73	
	0.25 M Hg^{2+}, 0.25 M $HClO_4$ (1)	64.8 (492)		64.5		74.5	
	0.25 M Hg^{2+}, 0.25 M $HClO_4$ (2)	63.3 (492)		61*		72.5	
	0.5 equiv of Hg^{2+}, 0.01 M $HClO_4$ (1)	62.7 (530)		64			
	1.0 equiv of Hg^{2+}, 0.1 M $HClO_4$[e] (1)	52.5 (492)		62		59	
Λ-(+)-$Co(en)_2Br_2{}^+$	0.1 M Hg^{2+}, 0.1 M $HClO_4$ (1)	62.0 (492)	+981 (520), −787 (440)	59	59.5	71	56
	3.0 equiv of Hg^{2+}, 0.15 M $HClO_4$ (1)	64.0 (492)	+986 (520), −791 (440)	63	59.5	74	56
	0.5 equiv of Hg^{2+}, 0.15 M $HClO_4$ (1)	62.7 (530)		64			
	0.5 equiv of Hg^{2+}, 0.1 M $HClO_4$ (2)	60.8 (530)	+840 (560), −1247 (460)	61.5*	59.5		
	3.0 equiv of Hg^{2+}, 0.15 M $HClO_4$; excess $HCO_3{}^-$ (2)		+3425 (570), −4920 (490)		61		57
	0.5 equiv of Hg^{2+}, 0.15 M $HClO_4$; excess $HCO_3{}^-$ (2)		+3485 (570), −5215 (490)		60*		
	1.0 equiv of Hg^{2+}, 0.1 M $HClO_4$; excess $HCO_3{}^-$ (1)		+3490 (570), −5190 (490)		60		
cis-$Co(en)_2BrN_3{}^+$	3.0 equiv of $NaNO_2$, 0.1 M $HClO_4$ (1)	70.3 (530)		73.5			
	2.0 equiv of $NaNO_2$, 0.1 M $HClO_4$ (2)	70.5 (530)		73.5*			
Λ-(+)-$Co(en)_2BrN_3{}^+$	2.0 equiv of $NaNO_2$, 0.15 M $HClO_4$ (2)	69.5 (530)	+990 (560), −1481 (460)	72.5*	70.5		
	2.0 equiv of $NaNO_2$, 0.2 M $HClO_4$; 1.0 equiv of Hg^{2+} (1)	67.6 (492)		73		79.5	
	2.0 equiv of $NaNO_2$, 0.15 M $HClO_4$; excess $HCO_3{}^-$ (2)		+4040 (570), −5997 (490)		70.5*		
	2.0 equiv of $NaNO_2$, 0.15 M $HClO_4$; 2.0 equiv of Hg^{2+}, excess $HCO_3{}^-$ (1)		+3911 (570), −5627 (490)		70		66
cis-$Co(en)_2(Me_2SO)Br^{2+}$	0.08 M Cl_2, 0.1 M $HClO_4$ (2)	64.3 (510)		67			
	0.08 M Cl_2, 0.1 M $HClO_4$; excess $HCO_3{}^-$	99.9 (510)		70			
	0.8 M Cl_2, 0.1 M $HClO_4$ (1)	64.6 (510)		67			
	0.08 M Cl_2, 0.1 M HCl (1)	68.5 (510)		72			
	0.08 M Cl_2, 0.1 M HCl; excess $HCO_3{}^-$ (2)	101 (510)		71*			
Λ-(+)-$Co(en)_2(Me_2SO)Br^{2+}$	0.08 M Cl_2, 0.1 M HCl (1)	69.0 (510)		72.5			
	0.08 M Cl_2, 0.1 M $HClO_4$; excess $HCO_3{}^-$ (2)	98.2 (510)	+3210 (589), −6100 (490)	68.5	70.5*		
	0.08 M Cl_2, 0.1 M HCl; excess $HCO_3{}^-$ (1)	99.4 (510)	+3296 (589), −6126 (490)	69.5*	71.5		
Λ-(+)-$Co(en)_2Cl_2{}^+$	1.0 M Hg^{2+}, 0.5 M $HClO_4$ (1)	68.8 (492)	+1391 (520), −1074 (440)	76	76.5	81.0	72.0
cis-$Co(en)_2ClN_3{}^+$	2.0 equiv of $NaNO_2$, 0.2 M $HClO_4$ (1)	70.4 (510)		74.5			
Λ-(+)-$Co(en)_2ClN_3{}^+$	2.0 equiv of $NaNO_2$, 0.2 M $HClO_4$; excess $HCO_3{}^-$ (1)		+4512 (570), −6782 (490)		77.5		
	2.0 equiv of $NaNO_2$, 0.2 M $HClO_4$ (1)	70.6 (510)		75			

cis-Co(en)$_2$(OH$_2$)Br^{2+}	1.0 M Hg^{2+}, 1.0 M HClO$_4$ (2)	77.8* (492)				95*	
	0.1 M Hg^{2+}, 0.1 M HClO$_4$ (1)	76.4 (492)				94	
	3.0 equiv of Hg^{2+}, 0.1 M HClO$_4$ (1)	76.1 (492)				94	
Λ-(+)-Co(en)$_2$(OH$_2$)Br^{2+}	1.0 M Hg^{2+}, 1.0 M HClO$_4$ (2)	77.6 (492)	+1850 (520), −1386 (440)			95*	95
	0.1 M Hg^{2+}, 0.1 M HClO$_4$ (1)		+1679 (520)				94.5
	3.0 equiv of Hg^{2+}, 0.1 M HClO$_4$ (1)	76.3 (492)	+1644 (520), −1255 (440)			94	91
	3.0 equiv of Hg^{2+}, 0.1 M HClO$_4$; excess HCO$_3^-$ (1)		+5955 (570), −8196 (490)				94*
cis-Co(en)$_2$(OH$_2$)Cl^{2+}	1.0 M Hg^{2+}, 1.0 M HClO$_4$ (2)	77.5 (492)				95	
Λ-(+)-Co(en)$_2$(OH$_2$)Cl^{2+}	1.0 M Hg^{2+}, 1.0 M HClO$_4$ (2)	78.7 (492)	+1816 (520), −1381 (440)			96*	93*
	0.1 M Hg^{2+}, 0.1 M HClO$_4$ (1)	74.1 (492)	+1626 (520), −1239 (440)			90	90
trans-Co(en)$_2$(OH$_2$)Cl^{2+}	1.0 M Hg^{2+}, 1.0 M HClO$_4$ (1)	39.3 (492)				34.5	
	1.0 M Hg^{2+}, 0.1 M HClO$_4$ (1)	39.6 (492)				34.5	
cis-Co(en)$_2$N$_3$Br$^+$	0.5 M Hg^{2+}, 0.1 M HClO$_4$ (1)	259 (500)		81.5			
Λ-(+)-Co(en)$_2$N$_3$Br$^+$	1.0 equiv of Hg^{2+}, 0.15 M HClO$_4$ (2)	261 (500)	+1078 (603), −3172 (470)	82.5*			
	1.0 equiv of Hg^{2+}, 0.15 M HClO$_4$; 2.0 equiv of NaNO$_2$ (1)	71.1 (492)	+1418 (520), −1132 (440)	83.5	85.5	85.5	80.5
	1.0 equiv of Hg^{2+}, 0.15 M HClO$_4$; 2.0 equiv of NaNO$_2$; excess HCO$_3^-$ (1)		+4654 (570), −6725 (490)		83.5*		78.5
cis-Co(en)$_2$N$_3$Cl$^+$	0.5 M Hg^{2+}, 0.1 M HClO$_4$ (1)	260 (500)		82			
Λ-(+)-Co(en)$_2$N$_3$Cl$^+$	0.5 M Hg^{2+}, 0.1 M HClO$_4$ (2)		+1128 (603), −3220 (470)				
	1.0 equiv of Hg^{2+}, 0.15 M HClO$_4$; 2.0 equiv of NaNO$_2$ (1)	70.5 (492)		83*		85	
	1.0 M Hg^{2+}, 0.1 M HClO$_4$ (1)	261.0 (500)		82.5			
	1.0 equiv of Hg^{2+}, 0.15 M HClO$_4$; 2.0 equiv of NaNO$_2$; excess HCO$_3^-$ (1)		+4652 (570), −6690 (490)		83.5*		78.5
Λ-(+)^f-Co(en)$_2$(OH)Br$^+$	pH 9.42, diet,^{g} 0.06 M, 2.5 min; 0.1 M HClO$_4$ (1)	71.8 (492)				86*	
	Excess HCO$_3^-$ (1)	126 (510)	+4973 (570), −7351 (490)			89	85
	pH 9.39, diet, 0.06 M, 3.5 min; 0.1 M HClO$_4$ (1)	70.9 (492)				84.5*	
	Excess HCO$_3^-$ (1)	126 (510)	+4941 (570), −7365 (490)			88.5	85
	pH 8.31, Tris,^{h} 0.05 M, 3.0 min; 0.1 M HClO$_4$ (1)	66.5 (492)				78*	
	Excess HCO$_3^-$ (1)	122 (510)	+4143 (570), −6334 (490)			82.5	72
Λ-(+)^f-Co(en)$_2$(OH)Cl$^+$	pH 9.22, diet, 0.06 M, 10.0 min; 0.1 M HClO$_4$ (1)	71.4 (492)				85*	
	Excess HCO$_3^-$ (1)	123 (510)	+5003 (570), −7313 (490)			85	85
	pH 9.27, diet, 0.06 M, 12.0 min; 0.1 M HClO$_4$ (1)	70.0 (492)				83*	
	Excess HCO$_3^-$ (1)	123 (510)	+4950 (570), −7239 (490)			84	84
	pH 8.99, Tris, 0.05 M, 11.5 min; 0.1 M HClO$_4$ (1)	67.5 (492)				79.5*	
	Excess HCO$_3^-$ (1)	121 (510)	+4451 (570), −6558 (490)			82	76

[a] Using data given in Table I. Numbers judged the most accurate are indexed with an asterisk (method dependent—see text). [b] M Hg^{2+} from Hg(ClO$_4$)$_2$, equiv of Hg^{2+} from Hg(CH$_3$CO$_2$)$_2$. Reagents used together are separated by a comma. A semicolon indicates a time lag (given in text) before addition of the next listed reagent. [Co] ≈ 5 × 10^{-3} to 2 × 10^{-2} M. Number of determinations is indicated in parentheses. [c] X = Cl, Br, or N$_3$. Either directly measured or calculated from % *cis*-(OH$_2$)$_2$$^{3+}$ assuming *cis*-(OH$_2$)X^{2+} gives 95% *cis*- and 5% *trans*-(OH$_2$)$_2$$^{3+}$ and *trans*-(OH$_2$)X^{2+} gives 37% *cis*- and 63% *trans*-(OH$_2$)$_2$$^{3+}$ in the second step of induced aquation. [d] Either directly measured or calculated from % Λ-(−)-(OH$_2$)$_2$$^{3+}$ assuming Λ-(+)-(OH$_2$)X^{2+} gives 94% Λ-(−)-(OH$_2$)$_2$$^{3+}$ in the second step of induced aquation. [e] % *cis*-(OH$_2$)X^{2+} and % *cis*-(OH$_2$)$_2$$^{3+}$ obtained by analyzing the product spectrum for Co(en)$_2$(OH$_2$)$_2$$^{3+}$ (assuming 95% cis and 5% trans) and *trans*-Co(en)$_2$(OH$_2$)Br^{2+}. [f] Sign of rotation not checked; refers to (+) rotation of parent aqua complex. [g] diet = diethanolamine. Hydroxo complex generated in situ quantitatively from aqua complex (pK_a ≈ 7[22]) and buffer. Resultant pH was calculated using pK_a = 8.9 (25.0 °C) for diet.[23] [h] Tris = tris(hydroxymethyl)methylamine, pK_a = 8.08 (25.0 °C).[23]

Table III. S-CH_3 Resonances in ^1H NMR Spectra of *cis*-$Co(en)_2(Me_2SO)X^{2+}$

Complex	τ^a (S-CH_3)
cis-$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$	7.18, 7.19
cis-$[Co(en)_2(Me_2SO)Br](ClO_4)_2$	7.21, 7.22
cis-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$	7.20, 7.22
cis-$[Co(en)_2(Me_2SO)(OH_2)](NO_3)_2ClO_4$	7.08, 7.10
cis-$[Co(en)_2(Me_2SO)_2](ClO_4)_3$	7.02, 7.05
Me_2SO^b	7.31

[a] D_2O or 10^{-3} M DCl. τ values field independent (60 and 100 MHz). NaTPS internal reference (τ 10.00). [b] In D_2O.

Spontaneous Aquations. Weighed samples of salts of (+)-*cis*-$Co(en)_2BrN_3^+$, $Co(en)_2ClN_3^+$, $Co(en)_2(Me_2SO)N_3^{2+}$, $Co(en)_2Br_2^+$, and $Co(en)_2Cl_2^+$ in 0.1, 0.01, or 0.001 M $HClO_4$ ($[Co] \approx 10^{-2}$ M) were each allowed to aquate $\gtrsim 10t_{1/2}$ at 25.0 °C and then quenched with excess $NaHCO_3$. The azido complexes were first treated with excess $NaNO_2$ (2–3 equiv), after adjusting the pH to 1 with $HClO_4$ and allowing 3.0 min for quantitative nitrosation, before the addition of $NaHCO_3$ and making up the solutions to known volume with water. After 10–15 min, rotations and absorbances were measured. The aquations of (+)-*cis*-$Co(en)_2(OH)X^+$ (X = Cl, Br) were studied in both diethanolamine (diet, 0.05 M) and tris(hydroxymethyl)methylamine (Tris, 0.06 M) buffers at 25.0 °C. The hydroxo complexes were quantitatively generated from the corresponding aqua species ($pK_a \approx 7^{22}$) by dissolution of weighed samples in a known volume of excess buffer, and aquation was allowed to proceed (7–10)$t_{1/2}$ before quenching with 0.1 M $HClO_4$ (to pH ~2) to generate (−)-*cis*- and *trans*-$Co(en)_2(OH_2)_2^{3+}$. Excess aqueous $NaHCO_3$ was added and measurements were made as above after adjustment to a known volume. The pH at which aquation occurred was calculated using pK_a = 8.9 (dietH^+) and 8.08 (TrisH^+) at 25.0 °C.[23] All the above experiments were performed at least twice, and different quench times were used for the hydroxo aquations (see Results and Discussion).

Results

Synthesis. The resolution of the $[Co(en)_2N_3Br]^+$ and $[Co(en)_2(Me_2SO)X]^{2+}$ (X = Cl, Br, N_3) ions is certain evidence for the cis configuration. The *trans*-$[Co(en)_2(Me_2SO)X]^{2+}$ ions have not been characterized. The ^1H NMR spectra (Table III) for the Me_2SO complexes in addition to confirming the cis assignment also indicate their isomeric purity. In each case a single sharp doublet (SCH_3) was observed. The diastereotopic splittings (1–3 Hz, 60 and 100 MHz) also diagnose the cis geometry.

cis-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$ was prepared from *cis*-$[Co(en)_2(Me_2SO)_2](ClO_4)_3$ and NaN_3 (1 equiv) in Me_2SO. NMR and chromatography indicated the absence of the trans isomer and potential $Co(en)_2(N_3)_2^+$ and $Co(en)_2(Me_2SO)_2^{3+}$ impurities. It eluted from Dowex 50WX2 (H^+ form, 200–400 mesh) cation-exchange resin as a single (2+) band with 1.0 M $NaClO_4$, conditions which were shown to readily separate diazido and bis(dimethyl sulfoxide) ions. *cis*-$[Co(en)_2N_3X]^+$ ions were readily obtained pure from *cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$ and LiX in Me_2SO, DMF, or DMA. Since bound azide is inert to X^- substitution, this two-step strategy ensured the absence of *cis*-$Co(en)_2(N_3)_2^+$ and *cis*-$Co(en)_2X_2^+$, contaminants difficult[3] to fractionate from *cis*-$Co(en)_2N_3X^+$. Moreover, a characterization problem is avoided since, unlike *cis*-$Co(en)_2(Me_2SO)N_3^{2+}$, most properties of $Co(en)_2N_3X^+$ are similar to those of 1:1 $Co(en)_2X_2^+$/$Co(en)_2(N_3)_2^+$ mixtures. The properties of *cis*-$[Co(en)_2N_3Cl]ClO_4$ prepared previously[3] agree with those prepared by this more rigorous and fruitful synthesis.

Table IV. Spontaneous Aquation of Λ-(+)-$Co(en)_2AX^{n+}$

Observed Isosbestic Points (25 °C)

Reactant	ϵ (λ), M^{-1} cm^{-1} (nm)	% cis	Av % cis
cis-$Co(en)_2N_3Br^+$	202 (544)	83	85 ± 2
	126 (455)	86.5	
cis-$Co(en)_2N_3Cl^+$	200 (545)	82.5	83
	122 (434)	$(88)^a$	
cis-$Co(en)_2N_3(Me_2SO)^{2+}$	206 (542)	82	82
	402 (394)	*a*	
cis-$Co(en)_2Br_2^+$	37 (476)	74	72.5 ± 1.5
	61.0 (507)	71	
cis-$Co(en)_2Cl_2^+$	72.4 (510)	77	77
	20.1 (439)	$(86)^a$	

Observed Isorotatory Points (25 °C)

	$[M]^{20}$ (λ), deg M^{-1} m^{-1} (nm)	% Λ	Av % Λ
Λ-(+)-$Co(en)_2N_3Cl^+$	+1124 (603)	85^b	85 ± 0.5
	−1672 (509)	85.5^b	
Λ-(+)-$Co(en)_2N_3Br^+$	−890 (519)	87^b	87
Λ-(+)-$Co(en)_2Br_2^+$	+990 (562)	72	71.5 ± 0.5
	−996 (497)	71	

[a] Not sufficiently sensitive to isomer proportions. [b] Calculated using $[M]^{20}{}_\lambda$ data for Λ-(+)-$Co(en)_2(OH_2)N_3^{2+}$ generated from Λ-(+)-$Co(en)_2N_3X^+$ (X = Cl, Br) and Hg^{2+} (83.5% Λ)–Table I.

Although we[24] have observed that *trans*-$Co(en)_2N_3X^+$ ions readily isomerize to their cis forms in Me_2SO, these are not useful cis preparations since the reactant trans isomers (particularly X = Br) are difficult to obtain in good yield and free from *trans*-$Co(en)_2X_2^+$. In passing, we have recorded a purification method for *trans*-$Co(en)_2N_3Cl^+$ based on the large difference[6,25] in base hydrolysis rates between *trans*-$Co(en)_2N_3Cl^+$ and *trans*-$Co(en)_2Cl_2^+$. Also convenient high-yield preparations of *trans*-$[Co(en)_2N_3X]ClO_4$ salts are described through isomerization of the accessible cis isomers in methanol, reactions which proceed quantitatively.

Finally, we note that the *trans*-$Co(en)_2(OH_2)N_3^{2+}$ spectrum reported here (ϵ^{551} 256, ϵ^{500} 95.5; 0.01 M $HClO_4$) differs substantially from those[3,4,6] given previously (ϵ^{550} 230, ϵ^{500} ~103), but the discrepancies do not seriously affect previous[3,4] calculations of steric course of aquation using ϵ^{500}. The present claim to pure *trans*-$Co(en)_2(OH_2)N_3^{2+}$ is substantiated by the isolation of both *trans*-$[Co(en)_2(OH_2)N_3]S_2O_6$ and *trans*-$[Co(en)_2(OH_2)N_3]SO_4{\cdot}2H_2O$ and the double salt *trans*-$[Co(en)_2(OH_2)N_3]$-*trans*-$[Co(en)_2(OH)N_3](ClO_4)_3$, all of which have identical spectra in 0.1 M $HClO_4$. The double salt is probably isomorphous with its known Cr(III) analogue.[26] We also note marked differences between the rotatory power of the present samples of resolved *cis*-$Co(en)_2Br_2^+$ and *cis*-$Co(en)_2(OH_2)Br^{2+}$, carefully checked for optical purity, and previous resolutions.[17]

Steric Course of Spontaneous Aquation. The stereochemical course of aquation was determined for the resolved cis ions using visible and rotatory dispersion spectra measured at optimum times. The present results differ significantly from earlier work and there is a need to describe the methods used and their limitations and accuracy in some detail. Extinction coefficients and molar rotations used in these analyses are given in Table I. In suitable cases, isosbestic and isorotatory points provided a check on the derived steric course and these data are summarized in Table IV.

The spontaneous aquations were all described by the reaction scheme 1, where B represents the initial and C the final

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{1}$$

cis-/*trans*-$Co(en)_2(OH_2)X^{2+}$ (X = N_3, Cl, Br) isomer distribution. For this consecutive reaction sequence it is readily shown that for spectrophotometric data

$$\epsilon - \epsilon_C = \left[(\epsilon_A - \epsilon_C) + \frac{k_1}{k_2 - k_1}(\epsilon_B - \epsilon_C)\right]e^{-k_1 t} - \left[\frac{k_1}{k_2 - k_1}(\epsilon_B - \epsilon_C)\right]e^{-k_2 t} \tag{2}$$

Table V. Isomerization Rates for $Co(en)_2(OH_2)N_3^{2+}$ in 0.01 M $HClO_4$ at 25.0 °C

$$\text{cis} \underset{k_{tc}}{\overset{k_{ct}}{\rightleftharpoons}} \text{trans}$$

Reactant	$10^3[Co]$, M	10^4k_i,[a] s^{-1}	λ,[b] nm
cis-$[Co(en)_2(OH_2)N_3]S_2O_6$	7.34–8.56	1.64 (2)	500
	8.34	1.64 (2)	580
	6.52	1.54 (2)	600
trans-$[Co(en)_2(OH_2)N_3]S_2O_6$	12.1	1.70 (2)	500
	9.10	1.62 (2)	580
	Av	1.63 ± 0.05	

[a] The number of determinations is given in parentheses and the average and standard deviation below. [b] Wavelength used.

where k_1 is the aquation rate constant for A (k_a) and k_2 is the isomerization rate constant (k_i), and the other symbols have their usual meaning. A similar expression (eq 3) holds for

$$[M] = \left[[M]_A + \frac{k_1}{k_2 - k_1}[M]_B\right]e^{-k_1t} - \left[\frac{k_1}{k_2 - k_1}[M]_B\right]e^{-k_2t} \qquad (3)$$

polarimetric data; $k_1 = k_a$, and k_2 is the racemization rate constant (k_r) as defined in eq 4 and 5.

$$\begin{tikzcd}
(+)\text{-}cis\text{-}Co(en)_2(OH_2)X^{2+} \arrow[r, shift left, "k_{inv}"] \arrow[dr, shift left, "k_{ct}"] & (-)\text{-}cis\text{-}Co(en)_2(OH_2)X^{2+} \arrow[l, shift left, "k_{inv}"] \arrow[d, shift left] \\
& trans\text{-}Co(en)_2(OH_2)X^{2+} \arrow[ul, shift left, "k_{tc}"] \arrow[u, shift left]
\end{tikzcd}$$

$$k_i = k_{ct} + k_{tc} \qquad (4)$$

$$k_r = k_{ct} + 2k_{inv} \qquad (5)$$

The problem was to obtain $[M]_B$ and ϵ_B from which the steric course was then readily calculated from the relations

$$\%\,\text{cis} = 100\frac{\epsilon_B - \epsilon_{trans}}{\epsilon_{cis} - \epsilon_{trans}} \qquad (6)$$

$$\%\,(+)\text{-cis} = 100\frac{[M]_B}{[M]_{(+)\text{-cis}}} \qquad (7)$$

where

$$\%\,(+)\text{-cis} = 10^2\left[\frac{[(+)\text{-cis}] - [(-)\text{-cis}]}{[(+)\text{-cis}] + [(-)\text{-cis}]}\right]$$

Since the condition $k_1 >> k_2$ never existed, $[M]_B$ and ϵ_B could not be directly measured following aquation, and corrections were required to allow for subsequent isomerization or racemization. Therefore the exact expressions (2) and (3) were used together with independently measured k_i and k_r, ϵ_A, $[M]_A$, ϵ_B, $[M]_B$, and ϵ_C. Different approaches were followed depending upon the significance of the correction terms in eq 2 and 3. The steric course was obtained from results at several wavelengths, the choice of which not only depends on the relative magnitudes of ϵ_B and ϵ_C but also depends critically upon k_a/k_i. Some of the rate constants k_a, k_i, and k_r needed for the calculations have been measured previously.[3,5,6,27] The others were measured or remeasured where necessary.

The isomerization *cis*-$Co(en)_2(OH_2)N_3^{2+} \rightleftharpoons$ *trans*-$Co(en)_2(OH_2)N_3^{2+}$ has been reexamined and our rate and equilibrium data differ significantly from previous work.[3,6] The equilibrium was approached from either side using *cis*-$[Co(en)_2(OH_2)N_3]S_2O_6$ and *trans*-$[Co(en)_2(OH_2)N_3]S_2O_6$ in 0.01 M $HClO_4$ at 25.0 °C.

Linear first-order rate plots of log $|\epsilon - \epsilon_\infty|$ against time ($>4t_{1/2}$) were obtained and yielded the rate constant and equilibrium data of Tables V and VI. Cis and trans reactants gave identical results ($k_i = (1.63 \pm 0.06) \times 10^{-4}\ s^{-1}$ at 25.0 °C, 68 ± 1% cis at equilibrium). Previous values were $k_i = 1.0 \times 10^{-4}$,[6,12] $1.4 \times 10^{-4}\ s^{-1}$,[3] and 58 ± 2% cis[3,6] at equilibrium.

The purity of the complexes of the Staples and Tobe study[12] has been questioned,[3,28] while SO_4^{2-} salts of the *cis*- and *trans*-$Co(en)_2(OH_2)N_3^{2+}$ isomers were used in a reexamination.[3] In yet another, more recent work, the cis SO_4^{2-} complex was again used while the trans ion was obtained indirectly by base hydrolysis of *trans*-$Co(en)_2N_3Cl^+$ and subsequent acidification.[6] The discrepancies between the previous and present work would seem to lie largely in the use of SO_4^{2-} media and difficulties in obtaining pure *trans*-$Co(en)_2(OH_2)N_3^{2+}$, conclusions supported by the following. *cis*- and *trans*-$Co(en)_2(OH_2)N_3^{2+}$ have spectra which are anion independent (SO_4^{2-}, $S_2O_6^{2-}$, ClO_4^-), but after equilibration in 0.01 M $HClO_4$, the SO_4^{2-} salt spectra differ significantly with those derived from the other salts (Table VI). In each case, cis and trans reactants with the same anion gave identical final spectra, which is expected if equilibrium is attained and will be true irrespective of final composition. However, equilibrium in the presence of SO_4^{2+} (Table VI) contains species additional to *cis*- and *trans*-$Co(en)_2(OH_2)N_3^{2+}$. They are likely to be sulfato complexes having spectra similar to those of their aqua counterparts. The results in SO_4^{2-} ($[Co] = 3.2 \times 10^{-3}$ M, $[HClO_4] = 0.01$ M) media (500 nm) correspond to the apparent composition 56% cis, in agreement with previous results.[3,6]

The calculated amounts at other wavelengths are similar (Table VI). However, a [complex] and pH (1–4) dependence of the equilibrium spectra for SO_4^{2-} but not ClO_4^- or $S_2O_6^{2-}$ media was noted, as anticipated for a component involving a

Table VI. Equilibrium Data for *cis*- ⇄ *trans*-$Co(en)_2(OH_2)N_3^{2+}$ in 0.01–0.1 M $HClO_4$ at 25.0 °C

Reactant[a]	ϵ_∞,[b] $M^{-1}\ cm^{-1}$ 600 nm	580 nm	500 nm	480 nm	% cis_∞^{500} [f]	Av % cis_∞ [g]
cis-$Co(en)_2(OH_2)N_3^{2+}$	81.5	123.3	231.0	177.0	67.0	65.5
cis-$Co(en)_2(OH_2)N_3^{2+}$ [c]	90.6	138.6	208.6	159.3	(56)[d]	(55)[e]
trans-$Co(en)_2(OH_2)N_3^{2+}$	83.8	126.7	234.7	179.0	68.5	67.5
trans-$Co(en)_2(OH_2)N_3^{2+}$ [c]	93.0	140.1	195.4	147.0	(49.5)[d]	(50.5)[e]
cis-$Co(en)_2N_3Cl^+$	85.3	130.0	230.5	175.1	66.5	68.0
cis-$Co(en)_2N_3Br^+$	84.7		234.0	179.1	68.5	68.5
cis-$Co(en)_2(Me_2SO)N_3^{2+}$	83.1	126.7	235.2	179.3	69.0	67.5
Average	83.7	126.7	233.1	177.9	68.0 ± 1.0[h]	67.5 ± 1.0[h]

[a] Results are averages of ⩾5 determinations on all salts, racemic and active. [b] $[Co] = 2 \times 10^{-4}$ to 10^{-2} M. [c] SO_4^{2-} salts: $[Co]^{cis} \approx 3.2 \times 10^{-3}$ M, $[HClO_4] = 0.01$ M; $[Co]^{trans} = 5.9 \times 10^{-3}$ M, $[HClO_4] = 0.1$ M. [d] Apparent composition; calculated assuming only *cis*- and *trans*-$Co(en)_2(OH_2)N_3^{2+}$ present and ignoring sulfato species. [e] As *d*, using e^{480}. [f] e^{500} provides the most accurate result. [g] Average for all wavelengths (three and four) given equal weights. [h] Mean and standard deviation.

Table VII. Isomerization and Racemization of Λ-(+)-*cis*-$Co(en)_2(OH_2)X^{2+}$ ($X = Cl, Br, N_3$) at 25.0 °C

$$\text{cis} \underset{k_{tc}}{\overset{k_{ct}}{\rightleftarrows}} \text{trans}; \quad \Lambda\text{-}(+)\text{-cis} \xrightarrow{k_r} \Lambda,\Delta\text{-}(\pm)\text{-cis} + \text{trans}$$

System	% cis_∞ [b]	$\Delta H^\ddagger$, kcal mol^{-1}	$10^5 k_{25}$, s^{-1}			
			k_i [a]	k_{tc}	k_{ct} [j]	k_r [j]
$Co(en)_2(OH_2)Br^{2+}$	75[c]	27.6	20.4	15.3	5.1 ± 0.4	4.65 ± 0.2[i]
	76[d]	27.6	21.4	16.3	5.1 ± 0.4	
$Co(en)_2(OH_2)N_3^{2+}$ [i]	68		16.3	11.1	5.2 ± 0.4	4.30 ± 0.2[i]
	(58)[e,k]	(32.0)	(10.0)	(5.8)	(4.2)	
	(58)[f]		(14.0)	(8.1)	(5.9)	
$Co(en)_2(OH_2)Cl^{2+}$	(73)[g]	(27.8)	(9.6)	(7.0)	(2.6 ± 0.4)	
	(73.5)[h]	(27.8)	(7.4)	(5.4)	(2.0 ± 0.4)	(2.0 ± 0.1)

[a] $k_i = k_{tc} + k_{ct}$. [b] % $cis_\infty = k_{tc}/k_{ct}$. [c] C. G. Barraclough, R. W. Boschen, W. W. Fee, W. G. Jackson, and P. T. McTigue, *Inorg. Chem.*, **10**, 1994 (1971); 0.2 M $HClO_4$. [d] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963); 0.01 M HNO_3. [e] V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, 9, 1785 (1970); 0.01 M $HClO_4$. P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4803 (1960); 0.01 M $HClO_4$. [f] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, 6, 1807 (1967); 0.01 M $HClO_4$. [g] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961); 0.01 M HNO_3. [h] A. M. Sargeson, *Aust. J. Chem.*, **16**, 352 (1963); 0.01 M $HClO_4$. [i] This work; 0.1 M $HClO_4$. [j] Errors calculated assuming k_i, k_r ±5% and % cis_∞ ± 1.5%. [k] Parentheses indicate use of SO_4^{2-} salts.

HSO_4^- anation–aquation equilibrium. Also, the equilibria in non-SO_4^{2-} media are accurately reproduced (±1%) commencing with *cis*-(±)- or *cis*-(+)-$[Co(en)_2N_3X]ClO_4$ (X = Cl, Br), *cis*- or *trans*-$Co(en)_2(OH_2)N_3^{2+}$ salts, or *cis*-$[Co(en)_2(Me_2SO)N_3]NO_3ClO_4$, all of widely different synthetic origin and spectra. The latter observation supports the claim that all these compounds are at least stoichiometrically pure, that X aquation (Cl, Br, Me_2SO) goes to completion (≥99%), that equilibrium has been attained, and that only *cis*- and *trans*-$Co(en)_2(OH_2)N_3^{2+}$ are detectable. The agreement between the calculated percent cis values at different wavelengths confirms the last aspect.

A single sharp isosbestic point at 535 nm was observed for both *cis*- (ϵ 226.0) and *trans*-$[Co(en)_2(OH_2)N_3]S_2O_6$ (ϵ 229) in 0.01 M $HClO_4$, in accordance with prediction (ϵ^{535} 227.5). Neither *cis*- nor *trans*-$[Co(en)_2(OH_2)N_3]SO_4$ ([Co] = 5.9 × 10^{-3} M, 0.1 M $HClO_4$) gave a sharp isosbestic point ($\lambda \sim 525$ nm, $\epsilon \sim 203$), consistent with SO_4^{2-} incorporation during isomerization. Accordingly, the previous rate data[3,6,12] do not correspond to "clean" isomerization, and in any event the equilibrium discrepancies render the application of a simple B ⇌ C procedure to the rate constant calculation invalid, despite linear plots of ln $|\epsilon - \epsilon_\infty|$ vs. *t*.

The rate and equilibrium data for two independent investigations[5,27,29,31] of each of the two other *cis*-/*trans*-$Co(en)_2(OH_2)X^{2+}$ isomerizations (X = Cl, Br) substantially agree despite the use of SO_4^{2-} in one case[27] and were not reexamined; the data are summarized in Table VII.

Racemization. The loss of activity (k_r) from (+)-*cis*-$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ in 0.01 M $HClO_4$ has been reported.[27] New data for (+)-*cis*-$Co(en)_2(OH_2)Br^{2+}$ and (+)-*cis*-$Co(en)_2(OH_2)N_3^{2+}$ are given in Table VIII. Values of k_r obtained from linear plots ($\geq 4t_{1/2}$) of ln $|\alpha|$ vs. *t* at each of three wavelengths are in good agreement. Comparison of k_r with k_{ct} (Table VII) reveals that in each case (X = Cl, Br, N_3) racemization ($k_r = k_{ct} + 2k_{inv}$) proceeds exclusively by isomerization to the inactive trans form, within experimental error (i.e., $k_r = k_{ct}$; $k_{inv} << k_{ct}$). This conclusion is emphasized by the fact that in principle k_r must be greater than or equal to k_{ct} yet $k_{ct} \geq k_r$ is observed. Clearly k_r equals k_{ct} within the experimental error.

(+)-*cis*-$Co(en)_2N_3Br^+$ Spontaneous Aquation. The aquation rate constant k_a (0.01 M $HClO_4$, 25.0 °C) was extracted from absorbance vs. time traces at 500 and 600 nm, characterized by a rapid initial rise (500 nm) or fall (600 nm) followed by a slower decay and indicative of two clear steps. Note that these observations alone do not permit the conclusion that the first step (aquation) is the faster.[30] However, it transpired that the smaller rate constant derived for each of the *cis*-Co$(en)_2N_3X^{n+}$ (X = Br, Cl, Me_2SO) ions was the same and this common result is interpreted as the cis-/*trans*-$Co(en)_2(OH_2)N_3^{2+}$ isomerization rate.

Table VIII. Racemization Rates for Λ-(+)-$Co(en)_2(OH_2)X^{2+}$ (X = Cl, Br) in 0.1 and 0.01 M $HClO_4$ at 25.0 °C

$$\Lambda\text{-}(+)\text{-cis} \xrightarrow{k_r} \text{trans} + \Lambda,\Delta\text{-}(\pm)\text{-cis}$$

X	10^3[Co], M	[$HClO_4$], M		$10^5 k_r$,[a] s^{-1}	λ,[b] nm
Br[c]	8.44	0.01		4.37 (2)	490
				4.44 (2)	470
				4.36 (2)	570
			Av	4.39 ± 0.03	
Br	7.04	0.10		4.73 (2)	490
				4.67 (2)	470
				4.53 (2)	570
			Av	4.65 ± 0.07	
N_3[c]	12.0	0.01		4.03 (1)	490
				4.22 (1)	470
				3.98 (1)	570
			Av	4.08 ± 0.09	
N_3	4.20	0.10		4.29 (2)	490
				4.29 (2)	470
				4.33 (2)	570
			Av	4.30 ± 0.02	

[a] Number of determinations given in parentheses; average and standard deviation given below. [b] Wavelength used. [c] Racemization studies following Λ-(+)-$[Co(en)_2N_3Br]ClO_4$ aquation.

The general methods for extracting values for k_a, k_i, and ϵ_B from the data are now detailed. Different strategies have different accuracies in the various circumstances and all of them were used and evaluated.

A. Equation 2 reduces to eq 8 provided $k_a > k_i$ and *t* is

$$\epsilon - \epsilon_B = (\epsilon_A - \epsilon_B)e^{-k_a t} \tag{8}$$

sufficiently small. Using ϵ_B and k_a as parameters and fitting ϵ, *t* data to eq 8 for the faster first step yielded the results given in Table IX (k_a, ϵ_B; see footnote *c*). Conventional plots of ln $|\epsilon - \epsilon_B|$ vs. *t* using the ϵ_B value(s) so obtained were linear over $(3–4)t_{1/2}$ indicating that at least up to this point subsequent isomerization was insignificant. ϵ_B corresponds to 86 ± 2% cis product at 500 nm and 82 ± 2% cis at 600 nm (using eq 6). Also k_a values obtained at each wavelength agree closely (Table IX).

B. The same ϵ, *t* data were fitted to the exact expression (eq 2), using only k_a and ϵ_B as parameters but allowing a correction for subsequent isomerization ($k_i = 1.63 \times 10^{-4}$ s^{-1}; fixed value). The results (Table IX; see footnote *g*) justify

Table IX. Kinetic and Stereochemical Data for Spontaneous Aquation of Λ-(+)-Co(en)$_2$N$_3$Br$^+$ in 0.01 M HClO$_4$ at 25.0 °C

10^3[Co], M	$10^4 k_a$, s^{-1}	$10^4 k_i$, s^{-1}	λ, nm^a	ϵ_B, M^{-1} cm^{-1}	% cis^b
5.38–6.88	11.6 ± 0.3		500 (3)^c	268 ± 4	85.5 ± 2
	11.6 ± 0.3	1.53 ± 0.09	500 (3)^d	270 ± 5	86 ± 2.5
	10.0 ± 1.0	1.55 ± 0.10	500 (3)^e	286 ± 10	91 ± 5
8.85–9.18	11.6 ± 0.2		600 (2)^c	74 ± 1	81.5 ± 1.5
	11.6 ± 0.2	1.55 ± 0.10	600 (2)^d	72 ± 2	83.5 ± 3
	10.5 ± 1.0	1.58 ± 0.10	600 (2)^e	71 ± 3	85 ± 4
	11.6 ± 0.2	1.63 ± 0.05	500 (3)^f	275 ± 6^h	89 ± 3
	11.6 ± 0.2	1.63 ± 0.05	600 (2)^f	71.5 ± 2^h	84 ± 3
	10.4 ± 0.4		500 (3)^g	278 ± 4	90 ± 2
	10.9 ± 0.4		600 (2)^g	71 ± 1	85 ± 1.5

[a] Number of determinations is given in parentheses; 10^3[Co] = 5.38–9.18 M. [b] Calculated from ϵ_B and the extinction coefficients recorded in Table I. [c] Determined using early-time ϵ, t data ($\sim 3t_{1/2}$) and ignoring subsequent isomerization (method A—see text). [d] Determined using later-time ϵ, t data, following ($\gtrsim 7t_{1/2}$) complete aquation. [e] Determined using ϵ, t data for entire reaction (method D). [f] Best values for k_a and k_i; k_i independently measured (see Table V). [g] Determined using early-time ϵ, t data ($\sim 4t_{1/2}$) and correcting for subsequent isomerization (method B). [h] Determined from ϵ at $B_{\max}$, $t_{B_{\max}}$ and best values for k_a, k_i (method E).

Table X. Polarimetric Steric Course Data for Λ-(+)-Co(en)$_2$N$_3$X^{n+}(X = Br, Cl, Me$_2$SO) Spontaneous Aquation at 25.0 °C in Dilute HClO$_4$

			[M]^{20}, deg M^{-1} m^{-1}				
Reactant	Quench time, s	λ, nm	[M]^d	[M]$_{\text{cor}}$^{e}	[M]$_B$^{f}	% Λ^g	
Λ-(+)-Co(en)$_2$N$_3$Br$^+$	4 500 (1)^c	570	+4131	+4395	+5171	87.3	87.8 ± 0.5
		490	−6029	−6414	−7546	88.3	
	4 365 (1)^b	570	+3919	+4169	+4882	82.5	83.6 ± 1.3
		490	−5811	−6182	−7239	84.8	
						Av 85.5 ± 2.0 (2)	
	4 500 (2)^a	490	−7056	−7506	−7231	84.7	84.2 ± 0.8
		470	−6097	−6486	−6249	84.6	
		570	+4821	+5129	+4941	83.4	
	4 365 (2)^b	490	−7121	−7576	−7299	85.5	86.4 ± 2.5
		470	−6416	−6825	−6575	89.0	
		570	+4888	+5200	+5010	84.6	
						Av 85.5 ± 2 (2)	
Λ-(+)-Co(en)$_2$N$_3$Cl$^+$	18 749 (1)^a	570	+2362	+2513	+4737	80.0	82.8 ± 2.8
		490	−3645	−3878	−7310	85.6	
	21 300 (2)^b	570	+2219	+2361	+4760	80.4	81.2 ± 0.8
		470	−2822	−3002	−6052	82.0	
						Av 81.5 ± 3	
Λ-(+)-Co(en)$_2$N$_3$(Me$_2$SO)$^{2+}$	21 285 (1)^b	578	+2193	+2333	+4618	84.8	84.6 ± 0.2
		470	−2964	−3153	−6241	84.5	
	21 345 (1)^b	578	+2202	+2343	+4650	85.4	85.8 ± 0.4
		470	−3015	−3208	−6366	86.2	
						Av 85.0 ± 3	

[a] 0.1 M HClO$_4$. [b] 0.01 M HClO$_4$. [c] 0.001 M HClO$_4$. [d] Observed molar rotation following NO$^+$ and HCO$_3^-$ quenching. [e] Corrected (×1.064) for activity loss on nitrosation of Λ-(+)-Co(en)$_2$(OH$_2$)N$_3$$^{2+}$. [f] Calculated from eq 10 using $10^4 k_a$ = 11.6 (Br), 2.4 (Cl), 2.1 (Me$_2$SO) and $10^5 k_r$ = 4.1 (0.01 M HClO$_4$), 4.3 (0.1 M HClO$_4$) s^{-1}; 25.0 °C. [g] Calculated from eq 7 using $[M]_B^{20}$ and $[M]^{20}$ data for Λ-(+)-Co(en)$_2$CO$_3^+$ recorded in Table I.

the use of the simpler approach A above.

C. Equation 2 reduces to eq 9 at large t provided $k_a > k_i$.

$$\epsilon - \epsilon_C = (\epsilon_B - \epsilon_C)\frac{k_a}{k_i - k_a} e^{-k_i t} \tag{9}$$

Thus plots of ln $|\epsilon - \epsilon_C|$ vs. t gave k_i. Results obtained at 500 and 600 nm (Table IX; see footnote *d*) agree well and compare favorably with independently measured k_i (Table V). These plots extrapolated to $t = 0$ gave an intercept $(k_a/(k_i - k_a))(\epsilon_B - \epsilon_C)$ from which ϵ_B was obtained (using $k_a = 11.6 \times 10^{-4}$ s^{-1}). The ϵ_B results (Table IX) agree with those obtained by treating the first step separately (A and B).

D. Fitting the entire ϵ, t data to eq 2 yielded values for k_a, k_i, and ϵ_B simultaneously (Table IX; see footnote *e*). The k_i results are in good agreement with those determined for the two separate steps but k_a values at 500 nm are somewhat lower. This is an artifact arising from least-squares fitting of eq 2 where the ϵ, t input data are for constant time intervals.[18,19] Under these conditions, the second term in eq 2 is dominant for most of the data, particularly at 500 nm, which leads to greater standard deviations in the larger rate constant. The rate difference is ~7:1 and thus k_a and ϵ_B values so obtained are not expected to be as precise as those derived from treating the first step separately.

E. Finally, ϵ_B was also calculated directly from eq 2 using the best values $k_a = 1.16 \times 10^{-3}$ s^{-1}, $k_i = 1.63 \times 10^{-4}$ s^{-1}, and ϵ measured at optimum time for $[B]_{\max}$ ($t_{B_{\max}} = (1/(k_i - k_a))\ln(k_i/k_a) = 1969$ s, $\sim 3.3t_{1/2}$ of aquation). When $k_a >> k_i$ (~7:1) the accuracy of ϵ_B so obtained does not depend critically on accumulated errors in k_a, k_i, ϵ_A, and ϵ_C but the results are sensitive only to the accuracy of $\epsilon_{t_{\max}}$. This is seen in ϵ_B values so calculated (Table IX; see footnote *f*) and it is emphasized by calculating the product distribution from the observed product spectrum uncorrected for subsequent isomerization. Molar absorptivities at 500 nm, $\epsilon_{\max}$ 263 ± 2 (3), and at 600 nm, $\epsilon_{\min}$ 75.8 ± 0.7 (3), correspond to $\sim 5t_{1/2}$ and $6t_{1/2}$ for aquation, respectively. These numbers are not greatly different from those calculated above, indicating that the correction terms in eq 2 are small (i.e., $\epsilon_{\max}$ or $\epsilon_{\min} \approx \epsilon_B$).

Methods similar to C and E were used for the polarimetric data. Thus (+)-*cis*-Co(en)$_2$N$_3$Br$^+$ aquations (0.01 M HClO$_4$ at 25.0 °C) quenched at t = 4500 and 4365 s ($\sim 7t_{1/2}$) yielded the $[M]^{20}_{\lambda}$ values given in Table X. Using $k_a = 1.16 \times 10^{-3}$

Table XI. Rate Constants and Steric Course for Spontaneous *cis*-$Co(en)_2N_3X^{n+}$ (X = Cl, Me_2SO) Aquation in 0.01 M $HClO_4$ at 25.0 °C

Reactant	10^3[Co], M	10^4k_a, s^{-1}	10^4k_i, s^{-1}	λ,[b] nm	ϵ_B, M^{-1} cm^{-1}	% cis[e]
cis-$Co(en)_2N_3Cl^+$	7.62-11.2	2.30 ± 0.1		600 (2)[a]	68 ± 4	89 ± 5
	5.36-5.97	2.55 ± 0.1		500 (4)[a]	275 ± 6	89 ± 3
		2.38 ± 0.1	1.45 ± 0.05	600 (2)[c]	71 ± 5	85 ± 6
		2.30 ± 0.1	1.46 ± 0.05	500 (2)[c]	278 ± 6	90 ± 3
cis-$Co(en)_2N_3(Me_2SO)^{2+}$	8.82-10.1	1.68 ± 0.05	1.68 ± 0.05	580 (2)[d]	102 ± 4	88.5 ± 5
	6.09-7.90	1.69 ± 0.01	1.69 ± 0.01	500 (3)[d]	278 ± 6	90 ± 3
	4.83	1.67 ± 0.05	1.67 ± 0.05	480 (1)[d]	214 ± 6	89 ± 3
		1.61 ± 0.05		580 (2)[a]		
		1.59 ± 0.1		500 (3)[a]		
		1.65 ± 0.1		480 (1)[a]		
		2.2 ± 0.1	1.45 ± 0.05	580 (2)[c]	102 ± 3	88.5 ± 4
		2.1 ± 0.1	1.40 ± 0.05	500 (2)[c]	276 ± 7	89.5 ± 4
		2.05 ± 0.1	1.38 ± 0.05	480 (1)[c]	210 ± 4	87 ± 3

[a] Calculated from early-time ϵ, t data ($\sim 4t_{1/2}$) correcting for subsequent isomerization (method B–see text). [b] Number of determinations is given in parentheses. [c] Calculated from ϵ, t data for the entire reaction (method D). [d] Calculated from ϵ, t data for the entire reaction with the restriction $k_a = k_i$. [e] Calculated from ϵ_B using eq 6 and the extinction coefficients recorded in Table I.

and $k_r = 4.30 \times 10^{-5}$ s^{-1}, $[M]_B$ was calculated from eq 10. For these HCO_3^--quenched solutions, $[M]_B >> [M]_A$ and since $k_a > k_r$ (~30:1), it can be shown that the first term in eq 3 contributes <0.5% at $t \approx 4000$ s and hence eq 3 simplifies to

$$[M] = \frac{k_a}{k_r - k_a} [M]_B \left(e^{-k_a t} - e^{-k_r t}\right) \tag{10}$$

The error in $[M]_B$ so calculated rests largely in [M] since the correction for subsequent racemization is small (~15%) and therefore is not especially sensitive to the accuracy of k_r.

$[M]_B$ was also calculated from plots of ln |[M]| vs. t. Equation 3 reduces to eq 11 at large t provided $k_a > k_r$ and

$$(k_a/(k_r - k_a))[M] = \frac{k_a}{k_r - k_a} [M]_B e^{-k_r t} \tag{11}$$

thus the later time linear portion of the curves extrapolated to $t = 0$ gave $(k_a/(k_r - k_a))[M]_B$ from which $[M]_B$ was readily obtained. Again, since $k_a >> k_r$, the error in $[M]_B$ does not depend significantly on the accuracy of k_r. The results are included in Table X; the percent (+)-cis product has been calculated from $[M]_B$ using eq 7.

The agreement between the results obtained at different wavelengths using the different strategies and the correspondence between the % cis (85 ± 2) and % (+)-cis (85 ± 2) product leads to the conclusion that spontaneous aquation of (+)-*cis*-$Co(en)_2N_3Br^+$ proceeds with significant stereochemical change to trans and chiral cis products without significant racemization. Although less precise, the isosbestic- and isorotatory-point methods also afford quantitative agreement (Table IV). The points were well-defined over at least $2t_{1/2}$ for the rotatory dispersion and $3t_{1/2}$ for the visible spectra, and the product distributions were calculated from eq 6 and 7; it is readily shown that $\epsilon = \epsilon_B$ and $[M] = [M]_B$ at each of the iso points.

(+)-*cis*-$Co(en)_2N_3Cl^+$ Spontaneous Aquation. Here $k_a \gtrsim k_i$ and it was not possible to treat each rate step separately (methods A and C) without serious restrictions on the absorbance changes appropriate to each. Two approaches were made. First, early-time ϵ, t data ($\leq 3t_{1/2}$) were fitted to eq 2, whence the first term makes the larger contribution; since k_i is known (1.63×10^{-4} s^{-1}, 25.0 °C, 0.01 M $HClO_4$), it became essentially a two-parameter problem (k_a, ϵ_B; method B). The results at two wavelengths are given in Table XI (footnote *a*).

The second and less accurate procedure involved fitting eq 2 to the entire ϵ, t data set using k_a, ϵ_B as well as k_i as parameters (method D). The results are indicated in Table XI (footnote *c*) and the increased parameterization, despite more ϵ, t data, resulted in larger standard deviations in k_a, k_i, and ϵ_B. The % cis product calculated from ϵ_B values at two wavelengths are in reasonable agreement (85–90%) as are the rate constants (Table XI). The % (+)-cis product was evaluated by quenching (+)-*cis*-$Co(en)_2N_3Cl^+$ aquation at $\sim 7t_{1/2}$, converting this to active-carbonato complex, and finally measuring [M], as described for (+)-*cis*-$Co(en)_2N_3Br^+$: $k_a = 2.4 \times 10^{-4}$ and $k_r = 4.1 \times 10^{-5}$ s^{-1} values were used for the calculation. The results are given in Table X.

Again, the isosbestic and isorotary point data provide quantitative agreement (Table IV). Clearly the spontaneous aquation is not retentive, as first reported[3] and recently disputed (0 °C, 85% cis),[6] and the activity experiments now confirm this and establish full retention for the cis product.

The problem with the earlier polarimetric result (100 ± 2% (+)-cis)[3] can be traced to the inaccuracy of the equilibrium constant (K_e) arising from sulfato impurities. Racemization k_r (assumed equal to k_{ct}) was calculated from $k_{ct} = k_iK_e/(1 + K_e)$ as 5.9×10^{-5} s^{-1} compared with 4.1×10^{-5} s^{-1} measured directly (Table VIII). The original result[3] corrects to 87% (+)-*cis*-aquoazido product if the present values for k_a and k_r are used, i.e., in closer agreement with the value reported now, 82 ± 3%.

(+)-*cis*-$Co(en)_2(Me_2SO)N_3^{2+}$ Spontaneous Aquation. Preliminary graphical solutions to eq 2 indicated approximate equality for k_a and k_i. After k_i was set equal to 1.63×10^{-4} s^{-1}, attempts were made to obtain k_a and ϵ_B by fitting the primary aquation ϵ, t data to eq 2 (method B). Convergence in least-squares fitting was slow or failed as a result of the insensitivity of ϵ to ϵ_B. The output revealed shallow least-squares minima in the region of quite marked variation in ϵ_B. However, the determination of k_a was not sensitive to ϵ_B and the results are given in Table XI (footnote *a*). Equation 2 was fitted in the form of eq 12 where the parameter N is a function

$$\epsilon = \epsilon_C + (\epsilon_A - \epsilon_C + N)e^{-k_a t} - Ne^{-k_i t} \tag{12}$$

of ϵ_B, the other parameter k_a, and the constant k_i. Thus as $k_a \rightarrow k_i$, eq 12 approximates eq 13 whence N and hence ϵ_B

$$\epsilon = \epsilon_c + (\epsilon_A - \epsilon_C)e^{-kt} \tag{13}$$

are undefined. Although ϵ_{obsd} and ϵ_{calcd} agreed and k_a was well-defined with small standard deviations (±3%), ϵ_B values so obtained were meaningless. The ϵ, t data were refitted to eq 14, the correct relation[30] for the limit $k_a = k_i$, and equally

$$\epsilon = \epsilon_C + [(\epsilon_A - \epsilon_C) + kt(\epsilon_B - \epsilon_C)]\, e^{-kt} \tag{14}$$

good fits obtained. The k_a result (Table XI) was close to the independently measured k_i and suggested that the fortuitous circumstance $k_a = k_i$ was operative.

We need note that this conclusion is not correct but that the analysis is very dependent upon the time interval chosen. To illustrate, the two sets of constants $k_a = 2.2 \times 10^{-4}$, $k_i = 1.45 \times 10^{-4}$ s^{-1} and $k_a = 1.80 \times 10^{-4}$, $k_i = 1.63 \times 10^{-4}$ s^{-1}, for given ϵ_A and ϵ_C values, generated two sets of ϵ, t data, over

Table XII. Polarimetric Steric Course Data for Λ-(+)-$Co(en)_2X_2^+$ (X = Br, Cl) Spontaneous Aquation at 25.0 °C in 0.01 M $HClO_4$

Reactant	Quench, time, s	λ, nm	$[M]^{20}$, deg M^{-1} m^{-1}		% $Λ^c$
			$[M]^a$	$[M]_B{}^b$	
Λ-(+)-$Co(en)_2Br_2^+$	5 385 (2)	578	+3076	+3749	68.9 ± 1
		490	−4892	−5963	69.8 ± 1
					Av 69.4 ± 1.5
Λ-(+)-$Co(en)_2Cl_2^+$	20 670 (1)	570	+3117	+4373	73.9
		490	+4585	−6433	75.3
	20 505 (1)	570	+3148	+4403	74.4
		490	−4682	−6548	76.7
					Av 75.0 ± 1.5

[a] Observed molar rotations following (~15 min) HCO_3^- quenching; [Co] ≈ 5 × 10^{-3} M. [b] Calculated using eq 3 and the following rate constants: X = Br, $k_a = 9.95 \times 10^{-4}$, $k_r = 4.4 \times 10^{-5}$ s^{-1}; X = Cl, $k_a = 2.50 \times 10^{-4}$, $k_r = 2.0 \times 10^{-5}$ s^{-1}; 0.01 M $HClO_4$, 25.0 °C. [c] Calculated from eq 7 using $[M]^{20}{}_B$ and $[M]^{20}$ data for Λ-(+)-$Co(en)_2CO_3^+$ given in Table I.

as much as $4t_{1/2}$ aquation, which differed by less than ±0.1% in ϵ at any time. Clearly, present instrumentation cannot provide data of sufficient accuracy to define k_i and more particularly k_a in these circumstances. A variation in k_a is compensated by a corresponding variation in k_i, and the additional parameter ϵ_B provides sufficient flexibility such that experimental definition is not possible. Much the same problem was encountered at other wavelengths as will always be so when $k_a \approx k_i$ and the data do not cover almost the entire reaction period.

The problem was solved by using ϵ, t data up to $10t_{1/2}$ primary aquation, where in least-squares fitting to eq 2 conversion was rapid and all three parameters k_a, k_i, and ϵ_B had sufficiently small standard deviations. The results are given in Table XI (footnote *c*).

The polarimetric results for Λ-(+)-*cis*-$Co(en)_2(Me_2SO)N_3^{2+}$ aquation are given in Table X. Nonretentive aquation was observed (89 ± 4% (cis)) with chiral (cis) product (Λ—84 ± 3%). The results are also supported by the product ratio determined from the isosbestic point as 82 ± 4% (Table IV).

Spontaneous (+)-*cis*-$Co(en)_2Br_2^+$ Aquation. Recently[5] the steric course of aquation has been carefully studied spectrophotometrically. The stereochemistry was deduced by two independent methods—from the positions (ϵ_B, λ) of the isosbestic points and from spectral analysis for the concentrations and hence proportions of the three component ions. The *cis-/trans*-$Co(en)_2(OH_2)Br^{2+}$ ratio obtained by the latter approach was found for $t = 0$ by an extrapolation procedure which is accurate provided the isomer ratio does not change rapidly with time, i.e., provided $k_i \leq k_a$ and the kinetic and equilibrium distributions do not differ markedly. In this system one or both conditions are met in the range 15–40 °C; $k_i/k_a \approx {}^1/_7$ at 15 °C and increases with temperature to $\sim{}^1/_3$ at 40 °C while the kinetic product distributions are 77% (15 °C) and 65% (40 °C); the thermodynamic distribution, 75% cis, is temperature independent. Both methods agreed[5] for the steric course.

We now confirm the results for 25 °C using polarimetry and a third independent spectrophotometric method, A.

A plot of ln $|\epsilon - \epsilon_B|$ vs. t is predicted to be linear for almost the entire primary aquation at all visible wavelengths, the slope representing k_a. At 556 nm (ϵ_{cis^+} 111; $\epsilon_{cis^{2+}}$ 84; $\epsilon_{trans^{2+}}$ 19) these plots were linear over at least $4t_{1/2}$, giving $10^3k_a = 9.95 \pm 0.08$ (2) s^{-1} and ϵ_B 67.0 ± 0.7 (2), corresponding to 74 ± 2% cis product. Moreover, the previous study[5] indicated almost identical kinetic (72%) and equilibrium (74.5%) distributions at 25.0 °C, consistent with the present observation that ϵ rose barely significantly from 67 ($\sim\epsilon_B$) to 68 (ϵ_c 75% cis) following aquation. Thus our results closely duplicate the previous[5] numbers (25.0 °C, $k_a = 9.9 \times 10^{-4}$ s^{-1}, 0.01 M $HClO_4$ or HNO_3; 72% cis initial, 75% cis final). Also, the remeasured isosbestic points, each definitive of the steric course (Table IV), confirm those of the earlier study[5] for 25 °C.

(+)-$Co(en)_2Br_2^+$ aquation quenched with HCO_3^- at $\sim 7t_{1/2}$ gave the results of Table XII, using eq 3, $k_a = 9.95 \times 10^{-4}$ and $k_r = 4.4 \times 10^{-5}$ s^{-1}. The spectrophotometric (74 ± 2% cis) and polarimetric (70 ± 2% (+)-cis) results agree.

(+)-*cis*-$Co(en)_2Cl_2^+$ Spontaneous Aquation. The polarimetric result, 75 ± 2% (+)-cis (Table XII, using eq 3, $k_a = 2.5 \times 10^{-4}$, and $k_r = 2.0 \times 10^{-5}$ s^{-1}), does not agree with that reported[3] (100 ± 2% (+)-cis) previously. However, the original result has been miscalculated and the recalculated result from the original data ($[M]_{589}$ = 830 ± 10 (2)°, HCO_3^--quenched solution of aquated (+)-$Co(en)_2Cl_2^+$ at t = 240 min ($\sim 5t_{1/2}$) in 0.01 M $HClO_4$ at 25.0 °C) using eq 3 gave 79.5% (+)-cis, in closer accord with the present work.

These findings prompted a spectrophotometric reexamination also, and the results were obtained as described for *cis*-$Co(en)_2Br_2^+$ above (0.01 M $HClO_4$, 25.0 °C): $k_a = (2.50 \pm 0.06) \times 10^{-4}$ s^{-1}, $\epsilon_B{}^{510}$ 71.7 ± 0.8 (2), and $\epsilon_C{}^{510}$ 69.3 ± 0.3 (2). The latter numbers correspond to 76 ± 2% and 73 ± 1% *cis*-chloroaqua product for the kinetic and equilibrium distributions, respectively; the rate constant and equilibrium % cis data agree with earlier determinations,[27,29] and the isosbestic point data (Table IV) confirm the revised kinetic distribution. Clearly, both previous steric course results[3,29] are in error, and (+)-*cis*-$Co(en)_2Cl_2^+$ aquation is now seen to follow the pattern of (+)-*cis*-$Co(en)_2Br_2^+$ and (+)-*cis*-$Co(en)_2N_3X^{n+}$ (X = Br, Cl, Me_2SO).

Spontaneous (+)-*cis*-$Co(en)_2(OH)X^+$ (X = Cl, Br) Aquations. The rates of base-independent (k_a) and base-catalyzed (k_b) hydrolysis of *cis*-$Co(en)_2(OH)X^+$ (X = Cl, Br) have been measured:[25,29,31] at 25.0 °C, $k_a = 1.2 \times 10^{-2}$ s^{-1}, $k_b = 11.9$ M^{-1} s^{-1}, X = Cl; $k_a = 6.3 \times 10^{-2}$ s^{-1}, $k_b = 86$ M^{-1} s^{-1}, X = Br. Thus, at pH ~9.4, $k_a/k_b[OH^-] \simeq 40$ for Cl and $k_a/k_b \simeq 28$ for Br. Thus aquation represents ≥97% of reaction. At higher pH, base hydrolysis becomes more significant, while at lower pH, subsequent isomerization and racemization of the labile (+)-*cis*-$Co(en)_2(OH_2)OH^{2+}$ product become important ($pK_a \approx 8.2$;[22] $k_i \simeq 5 \times 10^{-3}$; $k_{ct} \simeq 2 \times 10^{-3}$; $k_r \simeq 3 \times 10^{-3}$ s^{-1}, 25 °C).[29,32,33] Therefore, measurements of product spectra were made after quenching for diethylamine buffers at pH ~9.4 where aquation is complete ($\geq 7t_{1/2}$ or ≥98%, ≥7 min (X = Cl), ≥1.5 min (X = Br)) but before significant (>2%) subsequent rearrangement of *cis*- and *trans*-$Co(en)_2(OH)_2^+$ ($k_i = 6.5 \times 10^{-6}$, $k_{ct} = 3.6 \times 10^{-6}$, $k_{tc} = 2.9 \times 10^{-6}$, $k_r = 9.4 \times 10^{-6}$ s^{-1}, 25 °C)[34,35] and (+)-*cis*-$Co(en)_2(OH_2)OH^{2+}$, which at this pH represents <5% of the products. The results (Table II), analyzed as both the diaqua and carbonato ions, are the same and are also independent of leaving group (X = Br, 87 ± 2% cis, 85 ± 1% (+)-cis; X = Cl, 84.5 ± 2% cis, 84.5 ± 1% (+)-cis). The lack of interfering subsequent rearrangement at pH ~9.4 is suggested by the concordance of the results for different reaction times ($5t_{1/2}$ and $10t_{1/2}$). Also we noted a small but significant drop in % cis and particularly % (+)-cis product at the lower pH (8.3

Table XIII. Steric Course of Λ-$Co(en)_2AX^{n+}$ Aquation at 25 °C

Aquation	Method	Products (cis + trans)	% cis	% Λ
Λ-$Co(en)_2Br_2^+$	Spont	$Co(en)_2(OH_2)Br^{2+}$	73.5 ± 1.5	70 ± 2
Λ-$Co(en)_2BrN_3^+$	NO^+ induc		72.5 ± 1.5	70.5 ± 1
Λ-$Co(en)_2Br(Me_2SO)^{2+}$	Cl_2 induc		70.5 ± 1.5	70.5 ± 1
Λ-$Co(en)_2Br_2^+$	Hg^{2+} induc		61.5 ± 1.5	60 ± 1
Λ-$Co(en)_2Cl_2^+$	Spont	$Co(en)_2(OH_2)Cl^{2+}$	75 ± 1.5	75 ± 1.5
Λ-$Co(en)_2Cl_2^+$	Hg^{2+} induc		76 ± 1.5	76.5 ± 1
Λ-$Co(en)_2ClN_3^+$	NO^+ induc		75 ± 1.5	77.5 ± 1
Λ-$Co(en)_2N_3Br^+$	Spont	$Co(en)_2(OH_2)N_3^{2+}$	85 ± 2	85.5 ± 2
Λ-$Co(en)_2N_3Cl^+$	Spont		86 ± 4	82 ± 3
Λ-$Co(en)_2N_3(Me_2SO)^{2+}$	Spont		86 ± 4	84 ± 3
Λ-$Co(en)_2N_3Br^+$	Hg^{2+} induc		82 ± 1.5	83.5 ± 1
Λ-$Co(en)_2N_3Cl^+$	Hg^{2+} induc		83 ± 1.5	83.5 ± 1
Λ-$Co(en)_2(OH_2)Cl^{2+}$	Hg^{2+} induc	$Co(en)_2(OH_2)_2^{3+}$	95.5 ± 1	93 ± 1
Λ-$Co(en)_2(OH_2)N_3^{2+}$	NO^+ induc		95	95
Λ-$Co(en)_2(OH_2)Br^{2+}$	Hg^{2+} induc		95 ± 1.5	94 ± 1
Λ-$Co(en)_2(OH)Cl^+$	Spont	$Co(en)_2(OH_2)OH^{2+}$	84 ± 1	84.5 ± 1
Λ-$Co(en)_2(OH)Br^+$	Spont		85 ± 1	85 ± 1

and 9.0). The latter data for Tris buffers are readily explained in terms of the subsequent rearrangement of (+)-*cis*-$Co(en)_2(OH_2)OH^{2+}$ which is ~10 times more abundant at pH 8.3 than at pH 9.4. Since the drop in % cis product is only 5% (and ~9% in (+)-cis) for a tenfold decrease in $[OH^-]$, the results may be interpreted to confirm that subsequent rearrangement at pH 9.4 is insignificant. The data are also consistent with (+)-*cis*-$Co(en)_2(OH_2)OH^{2+}$ losing activity by way of both inversion and isomerization as indicated previously.[33] Clearly the stereochemical result (85% (+)-cis) is a kinetic distribution since the cis product is fully active and these figures are well removed from the equilibrium distributions.

Induced Aquations. The conditions, primary data, and results are summarized in Table II. Reactions not previously examined are (+)-*cis*-$Co(en)_2N_3Br^+$ + Hg^{2+} and/or +NO^+, (+)-*cis*-$Co(en)_2Br_2^+$ + Hg^{2+}, (+)-*cis*-$Co(en)_2(Me_2SO)Br^{2+}$ + Cl_2, and (+)-*cis*-$Co(en)_2(OH_2)X^{2+}$ (X = Br, N_3) + Hg^{2+} or NO^+. Others, e.g., (+)-*cis*-$Co(en)_2N_3Cl^+$ + Hg^{2+} and/or +NO^+,[3] have been reexamined because of the earlier uncertainty in the $Co(en)_2(OH_2)N_3^{2+}$ spectra[3,4,6,12,28] and because of the fact that the activity loss (5%)[4] in the second step (+)-*cis*-$Co(en)_2(OH_2)X^{2+}$ → (+)-*cis*-$Co(en)_2(OH_2)_2^{3+}$ + *trans*-$Co(en)_2(OH_2)_2^{3+}$ was not accommodated.

In most cases, both the first and second induced aquation steps were examined. For aquations driven through to $Co(en)_2(OH_2)_2^{3+}$, the first-step stereochemistry was calculated using the known rearrangements for the intermediate (+)-*cis*-$Co(en)_2(OH_2)X^{2+}$ and *trans*-$Co(en)_2(OH_2)X^{2+}$ species ($cis^{2+} \rightarrow$ 95% cis, (+)-$cis^{2+} \rightarrow$ 94 ± 1% (+)-cis^{3+}, $trans^{2+} \rightarrow$ 63% $trans^{3+}$). The most accurate numbers are marked with an asterisk in Table II and derive usually from analysis for the initial ($(OH_2)X$) products; the most accurate polarimetric data come from HCO_3^--quenched solutions because of the large molar rotations (coupled with low absorption) of (+)-$Co(en)_2CO_3^+$. The other data may be taken as confirmation of these results.

It is noted that the repeated work does not give numbers appreciably different from those published earlier,[3] suggesting some compensatory sources of error. The new data for (+)-*cis*-$Co(en)_2(OH_2)X^{2+}$ (X = Cl, Br) + Hg^{2+} (94% (+)-cis; 95% cis) support the results of previous spectrophotometric investigations (95% cis).[4] The reaction (+)-*cis*-$Co(en)_2(OH_2)N_3^{2+}$ + NO^+ was not examined directly, but comparison of the observed % cis and corresponding activities in the two steps of, e.g., (+)-*cis*-$Co(en)_2XN_3^+$ (X = Cl, Br) + Hg^{2+} then +NO^+, indicates that (+)-*cis*-$Co(en)_2(OH_2)N_3^{2+}$ + NO^+ involves a loss in activity of ~5%. The nitrosation of *cis*-$Co(en)_2(OH_2)N_3^{2+}$ was reported recently[4] as giving 95% cis^{3+} product, and the present results support this. The attempted characterization of the supposed (+)-$Co(en)_2Br^{2+}$ intermediate from (+)-*cis*-$Co(en)_2Br_2^+$ + Hg^{2+}, (+)-*cis*-$Co(en)_2BrN_3^+$ + NO^+, and (+)-*cis*-$Co(en)_2(Me_2SO)Br^{2+}$ + Cl_2 provided the only anomalous induced aquation result. If the coincidence of the steric course of induced aquation of (+)-*cis*-$Co(en)_2BrN_3^+$ + NO^+ and (+)-*cis*-$Co(en)_2(Me_2SO)Br^{2+}$ + Cl_2 and spontaneous (+)-*cis*-$Co(en)_2Br_2^+$ aquation (all 72% (+)-cis, Table II and XIII) is not regarded as fortuitous, then the result (62% (+)-cis) for (+)-*cis*-$Co(en)_2Br_2^+$ + Hg^{2+} is anomalous and to date provides the only example of an induced aquation giving a clear leaving-group-dependent result. Considerable effort was expended to quantitatively substantiate the figure of 62% (+)-cis which is well outside experimental error of the other induced aquation results (72 ± 2% cis). The polarimetric and spectrophotometric data agree for the calculation based on products derived from the directly observed first step (0.5 equiv of Hg^{2+}), from completely aquated solutions (excess Hg^{2+}), and even from partly aquated solutions (1.0 equiv of Hg^{2+}) (Table II). Independent analyses were made for (+)-$Co(en)_2(OH_2)Br^{2+}$, (−)-$Co(en)_2(OH_2)_2^{3+}$, and (+)-$Co(en)_2CO_3^+$ products, and there can be little doubt that the concordant result is substantially correct. A previous spectrophotometric result (58% cis)[4] based on $Co(en)_2(OH_2)_2^{3+}$ product analysis for completely aquated *cis*-$Co(en)_2Br_2^+$ closely agrees, and it is clear the excess-reagent method is valid (see (+)-*cis*-$Co(en)_2Cl_2^+$ + excess Hg^{2+}, Table II).

Discussion

In view of the errors discovered in the early work on the steric course of aquation, several methods of evaluating the data have been explored. General concordance was found, although the results differ by up to 5% with the different analytical methods. Some effort has been directed to gauging the more reliable values. The results are summarized in Table XIII and the following points emerge.

(1) Each of the spontaneous aquations for the cis isomers proceeds with significant stereochemical change. All except for the new systems (*cis*-$Co(en)_2N_3X^{n+}$: X = Br, Me_2SO; *n* = 2, 3) were recorded previously[3,29] as retentive. It now seems certain that *cis*-$Co(en)_2BrCl^+$ will be found to aquate with rearrangement.[29] The rearrangements reported for the aquation of *cis*-$Co(en)_2Br_2^+$[5] and *cis*-$Co(en)_2N_3Cl^+$[6] were also confirmed.

(2) The steric course is the same for each ion by the spontaneous and the induced path, with the exception of *cis*-$Co(en)_2Br_2^+$ in the presence and absence of Hg^{2+} ion. Here a special effect is argued and this is discussed in detail later.

(3) For the groups of complex ions which aquate to common products, the steric course is leaving-group independent except

for the special instance in point 2.

(4) The cis component of the products in both spontaneous and induced aquation had not racemized detectably.

The case for the presence of five-coordinate intermediates in induced aquation of Co(en)$_2$AX^{n+} and Co(NH$_3$)$_5$X^{n+} ions (X = N$_3^-$, $^-$OCONH$_2$, Cl$^-$, Br$^-$, I$^-$, OS(CH$_3$)$_2$, and others) has rested on demonstrating the independence of the results from the nature of the leaving group. Product distributions for the oxygen isotopes of water,[46] anions or neutral nucleophiles competing with water,[3,47,48] and the stereochemistry of the products[3,4,28,37] have all served to define this independence.[7,36] Until recently, the course of spontaneous aquation of Co(en)$_2$AX^{n+} ions supposedly differed from the course of induced aquation,[37] although the sets of *cis*-[Co(en)$_2$NH$_3$X]$^{n+}$ and [Co(NH$_3$)$_5$X]$^{n+}$ ions aquated with retention of configuration within the error of the experiment.[44]

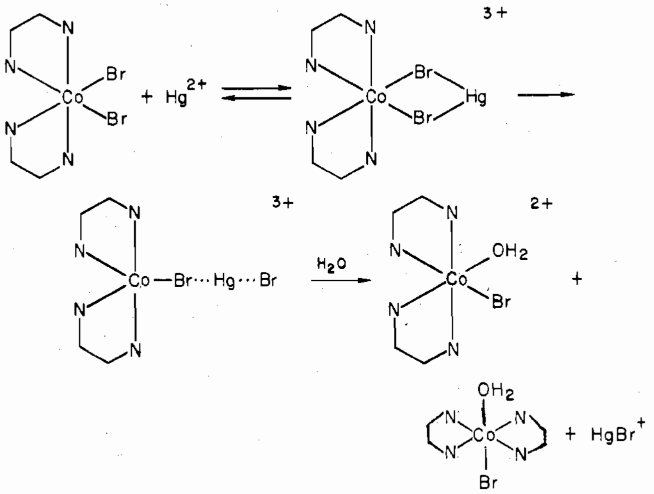
For the pentaamines, however, anion competition was substantial for the induced path relative to water[3,47,48] and negligible or small[49] by the spontaneous path. It was argued, therefore, either that the intermediates were different in the two instances or that the induced path required a five-coordinate intermediate and that some bond making by the entering water molecule was required for the spontaneous reaction.

At this point, one of the major experimental differences vanishes, namely, the difference in steric course between spontaneous and induced aquation. The discrimination now rests substantially with the anion-competition differences which have been carried out with only the Co(NH$_3$)$_5$X^{n+} and Co(en)$_2$NH$_3$X^{n+} systems. The literature also indicates a difference between the spontaneous and induced aquation for the *trans*-Co(en)$_2$AX^{n+} isomers.[4] However, in the light of the present agreement for the cis ions, the steric course of those spontaneous aquations warrants a reexamination.

One obvious question which now arises but which remains unanswered is whether both spontaneous and induced aquations of the *cis*-Co(en)$_2$AX^{n+} ions considered here occur via the same intermediate or whether the stereochemical agreement is fortuitous. Unfortunately, the competition experiments with anions are not revealing since aquation of the competition products and anation of the aqua ions are competitive with the time for chromatographic separation of the reaction products.[50] Also it is difficult to devise the crucial competition experiments which allow a direct comparison between the corresponding spontaneous and induced processes, but experiments are now under way to settle this problem.

Some comment is warranted on some of the individual stereochemical results. The steric course of the Hg^{2+}-induced aquation of (+)-Co(en)$_2$Br$_2^+$ is not consistent with the other data (Table XIII). No dependence of the steric course on the [Hg^{2+}] or [HgBr$^+$] concentration was found (Table II). The anomaly may arise through Hg^{2+} attachment to both Br$^-$ ions as shown in Scheme I.

Scheme I



The proposal is consistent with the known high affinity of Hg^{2+} for Br$^-$ ion. Binuclear adducts have been isolated or observed with cobalt(III) ions containing N$_3^-$,[37] Cl$^-$, and NCS$^-$. There is a requirement, however, that HgBr$^+$ remain attached for the lifetime of the five-coordinate intermediate and not equilibrate with free Hg^{2+} in solution. The requirement seems reasonable when the evidence[7] suggests that the intermediate's lifetime is governed by the rate of loss of the entering nucleophile from the water structure and probably does not survive more than a few encounters. The group directing entry of H$_2$O is now different for this instance relative to the other bromo intermediates and common agreement is no longer required. However, at present there does not seem to be any reasonable correlation between the properties of the directing group and the degree of rearrangement. The inference in this argument of course is that Hg^{2+} is largely attached to only one atom in the ions *cis*-Co(en)$_2$N$_3$Cl$^+$, *cis*-Co(en)$_2$Cl$_2^+$, and *cis*-Co(en)$_2$BrN$_3^+$. This is reasonable if the relatively lower affinity of Hg^{2+} for the free ligand and the more demanding geometry for chelation are borne in mind.

Chlorine oxidation of coordinated Me$_2$SO is a relatively new method for generating a good leaving group even though it is not yet clear whether the chlorosulfoxonium ion or the sulfone is the actual leaving group.[36,41] However, for (+)-Co(en)$_2$(Me$_2$SO)Br^{2+} bound Br$^-$ is also oxidized but Cl$^-$ substitutes in the course of the reaction with retention of configuration, in agreement with previous observations.[20] Excess HCl suppressed the further complication of concurrent oxidation by HOCl,[20] (cf. results for HCl and HClO$_4$ media, Table II). It was not possible to establish unequivocally whether the observed stereochemistry of aquation (72 ± 2% (+)-cis) reflected the properties of the (+)-Co(en)$_2$Br^{2+} or the (+)-Co(en)$_2$Cl^{2+} intermediate exclusively since the expected values were 72 or 77% (+)-cis, respectively. The present results confirm the earlier measurements on racemic *cis*-Co(en)$_2$(Me$_2$SO)Br^{2+}.

The competition experiments conducted with this type of reaction are complicated by a path which directly injects the anion associated with the Cl$^+$ oxidant into the coordination sphere.[36,41] However, this work indicates that in the low concentration of the extraneous anion used for the stereochemical studies, this path would be negligible and the common stereochemical data support the proposal[36] for a common intermediate of reduced coordination number.

The experiments associated with aquation of (+)-Co(en)$_2$(OH)X$^+$ (X = Cl, Br) ions, formed from the relevant aqua ions, stemmed from a suggestion[4] that *trans*-Co(en)$_2$(OH)X$^+$ aquation and *trans*-Co(en)$_2$(OH)(OH$_2$)$^{2+}$ water exchange are equivalent to base hydrolysis of the relevant Co(en)$_2$(OH$_2$)X^{n+} ion, where deprotonation is effectively at amine nitrogen rather than at oxygen. The suggestion therefore implied a steric course independent of the leaving group, as observed for the trans ions, substantial steric change, and some racemization in the cis product. All are features essentially characteristic of the conjugate-base mechanism for hydrolysis.[43,44] The observed full retention of configuration in the cis product is in contrast with the expected racemization for the base-hydrolysis path and it implies the reactions are conventional aquation processes.

Summary and Conclusions

Both *cis*- and *trans*-Co(en)$_2$AX^{n+} isomers can aquate spontaneously with steric change. In this respect they are no longer fundamentally different.[1,2] Aqua product distributions are independent of the nature of the leaving group. This we have shown to be true for the cis substrates with anionic and neutral leaving groups alike and there are indications that it is true also for the trans ions.[4,51] The invariance of the stereochemistry of aquation now covers a wide range of leaving groups, from the poor to the especially good, generated through induced aquation, and this result indicates no fundamental distinction between the spontaneous and induced processes. The absence of leaving-group effects on the stereochemistry implies that X dissociation in Co(en)$_2$AX^{n+} is well advanced toward pentacoordination in the transition state. Whether this implies a discrete intermediate or not is uncertain. It has always been clear and is emphasized by this work that the aqua product distributions largely reflect the stereochemistry of the reactants. Cis gives largely cis where the cis product retains the chirality while trans gives more trans than cis usually.[1,2,7] Furthermore, cis and trans reactants do not give common products. These memory effects indicate that the "intermediate" inherits its geometry and environment rather than acquiring them by independent equilibration. Also they imply a short lifetime for any intermediate of reduced coordination number.

Competition experiments also indicate that the lifetime of the intermediate, if it exists, is very short. Apparently, it samples its immediate atmosphere and the nucleophiles in solution do not have an opportunity to exert their nucleophilic capacities.[7] Current competition studies show promise as more sensitive probes on the lifetime and history of the intermediates. We observe a marked dependence of the competition ratios on the charge of the complex and the type of leaving group for the spontaneous aquation. However, the competition ratios for a particular competitor are constant for the induced aquations.[7] This evidence still discriminates between the two types of processes at the moment and it still supports the proposal for a presumed common intermediate Co(NH$_3$)$_5$$^{3+}$.

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Registry No. *cis*-[Co(en)$_2$(OH$_2$)Cl]BrNO$_3$, 38833-28-2; (−)-*cis*-[Co(en)$_2$(OH$_2$)Br]Br$_2$, 15744-50-0; *trans*-[Co(en)$_2$(OH$_2$)Cl]SO$_4$, 15083-99-5; *trans*-[Co(en)$_2$(OH$_2$)$_2$]SO$_4$·HSO$_4$, 65760-59-0; *cis*-[Co(en)$_2$(OH$_2$)N$_3$]SO$_4$, 65760-58-9; *cis*-[Co(en)$_2$(OH$_2$)N$_3$]S$_2$O$_6$, 65760-57-8; *trans*-[Co(en)$_2$(OH$_2$)N$_3$]-*trans*-[Co(en)$_2$(OH)N$_3$](ClO$_4$)$_3$, 65802-30-4; *trans*-[Co(en)$_2$(OH$_2$)N$_3$]S$_2$O$_6$, 65760-56-7; *trans*-[Co(en)$_2$(OH$_2$)N$_3$]SO$_4$, 65760-55-6; *cis*-[Co(en)$_2$(Me$_2$SO)$_2$](ClO$_4$)$_2$NO$_3$, 59302-00-0; *cis*-[Co(en)$_2$(Me$_2$SO)$_2$](ClO$_4$)$_3$, 14781-36-3; *cis*-[Co(en)$_2$(Me$_2$SO)N$_3$]NO$_3$ClO$_4$, 59302-02-2; *cis*-[Co(en)$_2$(Me$_2$SO)Cl]NO$_3$ClO$_4$, 59366-40-4; *cis*-[Co(en)$_2$N$_3$Cl]ClO$_4$, 65760-54-5; *cis*-[Co(en)$_2$BrN$_3$]Br, 65794-86-7; *cis*-[Co(en)$_2$N$_3$Br]ClO$_4$, 65794-85-6; (+)-*cis*-[Co(en)$_2$Br$_2$]ClO$_4$, 65760-53-4; (−)-*cis*-[Co(en)$_2$(Me$_2$SO)Br]NO$_3$ClO$_4$, 65878-19-5; (−)-*cis*-[Co(en)$_2$(Me$_2$SO)N$_3$]NO$_3$ClO$_4$, 65794-84-5; (−)-*cis*-[Co(en)$_2$(N$_3$)$_2$]ClO$_4$, 61542-81-2; (+)-*cis*-[Co(en)$_2$N$_3$Cl]ClO$_4$, 65830-06-0; (−)-*cis*-[Co(en)$_2$N$_3$Cl]ClO$_4$, 65794-83-4; (−)-*cis*-[Co(en)$_2$N$_3$Br]ClO$_4$, 65794-82-3; (+)-*cis*-[Co(en)$_2$N$_3$Br]ClO$_4$, 65830-05-9; *trans*-[Co(en)$_2$(OH$_2$)(OH)](ClO$_4$)$_2$, 14099-22-0; *cis*-[Co(en)$_2$Br$_2$]Br, 14911-27-4; (−)-*cis*-[Co(en)$_2$Br$_2$]I, 65794-81-2; (−)-*cis*-[Co(en)$_2$Br$_2$]ClO$_4$, 65794-80-1; cobalt, 7440-48-4; (−)-*cis*-Co(en)$_2$(OH$_2$)Br^{2+}, 45836-37-1; (−)-*cis*-Co(en)$_2$(OH$_2$)N$_3$$^{2+}$, 65794-39-0; (−)-*cis*-Co(en)$_2$N$_3$Cl$^+$, 65794-38-9; (−)-*cis*-Co(en)$_2$N$_3$Br$^+$, 65794-37-8; (−)-*cis*-Co(en)$_2$Cl$_3$$^+$, 45837-15-8; (−)-*cis*-Co(en)$_2$Br$_2$$^+$, 65794-36-7; (−)-*cis*-Co(en)$_2$(Me$_2$SO)N$_3$$^{2+}$, 65794-35-6; *cis*-Co(en)$_2$(OH$_2$)N$_3$$^{2+}$, 29770-08-9; *trans*-Co(en)$_2$(OH$_2$)N$_3$$^{2+}$, 29770-07-8; (+)-Co(en)(ox)$_2$$^-$, 20673-37-4; (−)-[Co(en)$_2$CO$_3$]ClO$_4$, 38673-77-7; (+)-*cis*-[Co(en)$_2$(OH$_2$)Cl]$^{2+}$, 45837-52-3; HCO$_3$$^-$, 71-52-3; *trans*-Co(en)$_2$Cl(OCO$_2$H)$^+$, 65749-28-2; *trans*-Co(en)$_2$(OCO$_2$H)$_2$$^+$, 65749-27-1; *cis*-[Co(en)$_2$(Me$_2$SO)Br]NO$_3$ClO$_4$, 65749-26-0; Λ-(+)-Co(en)$_2$Br$_2$$^+$, 52881-86-4; Λ-(+)-Co(en)$_2$Cl$_2$$^+$, 18660-62-3; (+)-*cis*-Co(en)$_2$(OH)Br$^+$, 65794-34-5; (+)-*cis*-Co(en)$_2$(OH)Cl$^+$, 19428-61-6; Λ-(+)-Co(en)$_2$N$_3$Br$^+$, 65794-33-4; Λ-(+)-Co(en)$_2$N$_3$Cl$^+$, 18195-24-9; (+)-*cis*-Co(en)$_2$N$_3$(Me$_2$SO)$^{2+}$, 65794-32-3; Hg^{2+}, 14302-87-5; NO$^+$, 14452-93-8; *cis*-Co(en)$_2$N$_3$Cl$^+$, 29544-71-6; *cis*-Co(en)$_2$N$_3$Br$^+$, 65794-31-2; *cis*-Co(en)$_2$(Me$_2$SO)N$_3$$^{2+}$, 59302-01-1; Λ-(+)-Co(en)$_2$(OH$_2$)N$_3$$^{2+}$, 56846-53-8; Λ-(+)-Co(en)$_2$(OH$_2$)Br^{2+}, 65749-24-8; *cis*-Co(en)$_2$Br$_2$$^+$, 18904-84-2; *cis*-Co(en)$_2$Br(Me$_2$SO)$^{2+}$, 15696-69-2; *cis*-[Co(en)$_2$(OH$_2$)Cl]$^{2+}$, 23443-93-8; *cis*-Co(en)$_2$(OH$_2$)Br^{2+}, 24947-15-7; *trans*-Co(en)$_2$(OH$_2$)Cl^{2+}, 14403-92-0; *trans*-Co(en)$_2$(OH$_2$)Br^{2+}, 24913-01-7; Λ-(+)-Co(en)$_2$(OH$_2$)$_2$$^{3+}$, 18485-08-0; *trans*-Co(en)$_2$(OH$_2$)$_2$$^{3+}$, 19314-32-0; Λ-(+)-Co(en)$_2$CO$_3$$^+$, 46140-38-9; Λ-(+)-Co(en)$_2$(Me$_2$SO)Br^{2+}, 65794-30-1; *cis*-Co(en)$_2$(Me$_2$SO)$_2$$^{3+}$, 16073-02-2; *cis*-[Co(en)$_2$(Me$_2$SO)(OH$_2$)]NO$_3$ClO$_4$, 59301-99-4; (−)-*cis*-Co(en)$_2$(OH$_2$)Cl^{2+}, 45837-48-7.

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