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Base Hydrolysis of the $(+)_{589}$-*cis*-$[Co(en)_2X(glyO)]^+$ Ions ($X^- = Cl^-$, Br^-) and the Importance of Ion Pairs

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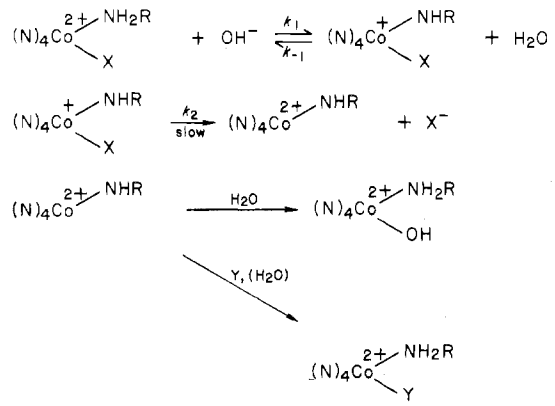
Base hydrolysis of Λ-$(+)_{589}$-*cis*-$[Co(en)_2X(glyO)]^+$ ions ($X^- = Cl^-$, Br^-; glyO = glycinate anion) gives 40.8% $[Co(en)_2(glyO)]^{2+}$ (32.1% Λ, 8.7% Δ), 49.3% *cis*-$[Co(en)_2OH(glyO)]^+$ (35.8% Λ, 13.5% Δ), and 9.9% *trans*-$[Co(en)_2OH(glyO)]^+$ in 1.0 mol dm^{-3} NaOH and 46.1% $[Co(en)_2(glyO)]^{2+}$ (36.2% Λ, 9.9% Δ), 45.1% *cis*-$[Co(en)_2OH(glyO)]^+$ (32.8% Λ, 12.3% Δ), and 8.8% *trans*-$[Co(en)_2OH(glyO)]^+$ in the pH range 10.0–13.0. Addition of NaN_3 results in Λ-*cis*, Δ-*cis*-, and *trans*-$[Co(en)_2N_3(glyO)]^+$ products in addition to $[Co(en)_2(glyO)]^{2+}$ and Λ-*cis*, Δ-*cis*-, and *trans*-$[Co(en)_2OH(glyO)]^+$, but the $[Co(en)_2(glyO)]^{2+}$ yield is affected more than the latter. The rates of base hydrolysis of the ions *cis*-$[Co(en)_2Br(amine)]^{2+,+}$ at 25.0 °C and $\mu \simeq 0$ (amine, k_{OH} (mol^{-1} dm^3 s^{-1}): glycylglycine isopropyl ester, 730; glycylglycinate anion, 470; glycinamide, 628; glycinate anion, 82) are reduced in $NaClO_4$, KCl, and Na_2SO_4 solutions, but the effect on *cis*-$[Co(en)_2Br(glyO)]^+$ is less than the others. The results are interpreted in terms of internal ion pairing by the glycinate carboxylate anion with competition by N_3^-, ClO_4^-, Cl^-, and SO_4^{2-} for the internal ion pair. The mechanism of base hydrolysis and the question of intermediates are discussed.

It has been generally accepted that base hydrolysis of cobalt(III) acido–amine complexes occurs via a limiting dissociative S_N1cB mechanism.[1-4] Rate-determining loss of the acido group from the conjugate base of the cobalt(III) complex forms an intermediate of reduced coordination number which competes for species in solution (see Scheme I).

The most convincing evidence for the existence of intermediates of reduced coordination number comes from the results of competitive reactions for these species.[5-9] For the *trans*- and *cis*-$[Co(en)_2NH_3X]^{2+}$ ($X^- = Cl^-$, Br^-, NO_3^-, SCN^-)[9,10] complexes, the stereochemistries were shown to be independent of leaving group within each series, and in the presence of competitors ($Y^- = N_3^-$, NO_2^-, SCN^-) the stereochemistries (cis/trans) and optical retentions ($\Lambda/\Delta\Lambda$) of the hydroxo products were the same as in the absence of Y. The competition ratio $[CoY^{2+}]/[CoOH^{2+}][Y]$ and the stereochemistry and optical retention in the $[Co(en)_2NH_3Y]^{2+}$ products were also constant for differing X. Evidence of a different sort for the existence of an intermediate along the reaction pathway comes from studies on multidentate amine complexes. In the base hydrolysis of α,β-(*R*)-[Co(tetraen)Cl]$^{2+}$,[11] twice as much (*S*)-hydroxo product was formed as the *R* form, and it was shown that this mutarotation did not occur during deprotonation of the reactant or in the (*R*)-hydroxo product. A similar situation occurs with Δ-β_2-(*R*)-[Co(trien)Cl(glyO)]$^+$ where the Δ-β_2-$[Co(trien)(glyO)]^{2+}$ product has a *R*:*S* ratio of 3:7 compared to the equilibrium value of 9:1.[12] The two results require mutarotation of the secondary-nitrogen center to occur after Cl^- loss but before H_2O or carboxylate entry, and the simplest interpretation is that this occurs in the five-coordinate intermediate.

However recent experiments with some [Co(Metren)$NH_3X]^{2+,3+}$ complexes (X = Cl^-, Br^-, NH_3)[13] and with $[Co(NH_3)_5X]^{3+}$,[14] and $(+)_{589}$-*cis*-$[Co(en)_2NH_3X]^{3+}$ [15] (X = Me_2SO, TMP) show that the previous competition experiments have been rather restrictive. In the earlier experiments the leaving group was a monoanion (X^-), and it now appears that these species were not sufficiently dissimilar to show changes in the competition ratio or stereochemistry as X was varied. The 3+ complexes show small but detectable increases in competition for added nucleophiles,[13-15] and for the $(+)_{589}$-*cis*-$[Co(en)_2NH_3X]^{3+}$ ions (X = Me_2SO, TMP) both the cis hydroxo and cis azido products have decidedly different optical retentions than previously observed.[15] These results suggest that ion-pair formation between the 3+ reactant and a competitor Y^- increases the concentration of Y^- in the vicinity of the five-coordinate intermediate thereby altering its properties. Moreover, the *same* intermediate or intermediates cannot be produced in the absence and presence of the competitor if it competes for "species in the bulk solution".

Scheme I



In the present study we advance the examination of this problem. By use of complexes of the type $(+)_{589}$-*cis*-$[Co(en)_2X(L)]^{2+,+}$ where L contains an additional entering group besides that already coordinated to the metal, the possibility exists for intramolecular competition in addition to competition by the solvent and added Y^-. This has already been observed with $(+)_{589}$-*cis*-$[Co(en)_2Br(glyOR)]^{2+}$ where ~45% of the ester carbonyl group was captured in addition to H_2O and N_3^-,[16] and it is important that the internal competitor can compete for only the cis stereochemical sites and not for the trans. We describe here a study of the base hydrolysis of $(+)_{589}$-*cis*-$[Co(en)_2X(glyO)]^+$ ($X^- = Cl^-$, Br^-; glyO = glycinate anion) in the presence and absence of N_3^- and less detailed results on $(+)_{589}$-*cis*-$[Co(en)_2X(glyNH_2)]^{2+}$ and $(+)_{589}$-*cis*-$[Co(en)_2X(glyglyOC_3H_7)]^{2+}$ ($glyNH_2$ = glycinamide; $glyglyOC_3H_7$ = glycylglycine isopropyl ester). The internal glycinate nucleophile competes to about the same extent as H_2O, and this leads to a maximum sensitivity to changes in the competition ratio in the presence of added N_3^-.

Experimental Section

Preparation of Complexes. The complexes *cis*-$[Co(en)_2X(glyOCH_3)]X_2$ ($X^- = Cl^-$, Br^-) were prepared as described by Alexander and Busch.[16] For $X^- = Br^-$ the complex was resolved into its optical enantiomers as described previously.[17]

cis-**$[Co(en)_2Br(glyOH)]Br_2$** was prepared from *cis*-$[Co(en)_2Br(glyOCH_3)]Br_2$ as follows. The complex (20 g) was dissolved in 0.01 mol dm^{-3} HBr (350 cm^3) at 50 °C and filtered, and 48% aqueous

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HBr (300 cm^3) was added. The mixture was left to stand for 24 h at 30–35 °C during which time most of the product had precipitated. After the mixture was cooled in ice, the purple solid was collected, washed with ethanol, and air-dried. Recrystallization from hot water (pH 3) by addition of solid NaBr and cooling of the mixture gave the glycine acid complex (no methyl signal in the ^1H NMR spectrum characteristic of the starting complex). Anal. Calcd for $[Co(en)_2Br(glyOH)]Br_2$: C, 14.6; H, 4.3; N, 14.2; Br, 48.5. Found: C, 14.8; H, 4.4; N, 14.2; Br, 48.8.

$(+)_{589}$-*cis*-$[Co(en)_2Br(glyOH)]Br_2 \cdot H_2O$. $(+)_{589}$-*cis*-$[Co(en)_2Br(glyOCH_3)]$-(+)-$(BCS)_2$ (9.5 g)[17] was dissolved in warm water (700 cm^3, 40 °C) and sorbed on Dowex 50W-X2 cation-exchange resin (H^+ form; 7 × 11 cm). The complex cation was eluted with 1.0 and then 2.0 mol dm^{-3} HBr, and the eluate (1200 cm^3) was reduced to 300 cm^3 on a rotatory evaporator. After the eluate stood at room temperature for 16 h, the solvent was removed and the solid redissolved in warm water (100 cm^3, 50 °C). On addition of solid NaBr and cooling of the mixture in ice, $(+)_{589}$-*cis*-$[Co(en)_2Br(glyOH)]Br_2$ separated. This was collected, washed with ethanol, and air-dried (yield 2.9 g, 60%). A 0.1% aqueous solution gave $\alpha_{589} = 0.103°$, $\alpha_{432} = -0.245°$ from which $[\alpha]_{589}$ is found to be 103° and $[\alpha]_{432}$ to be −245°. Anal. Calcd for $[Co(en)_2Br(glyOH)]Br_2 \cdot H_2O$: C, 14.1; H, 4.5; N, 13.7. Found: C, 14.2; H, 4.6; N, 13.7.

cis-**$[Co(en)_2Cl(glyOH)]Cl_2$** was prepared as for the bromo complex by using HCl and NaCl in place of HBr and NaBr. Anal. Calcd for $[Co(en)_2Cl(glyOH)]Cl_2 \cdot H_2O$: C, 19.03; H, 6.12; N, 18.50; Cl, 28.09. Found: C, 18.9; H, 6.1; N, 18.3; Cl, 28.0.

Base Hydrolysis Reactions. A 0.1500–0.2000-g sample of racemic or $(+)_{589}$-$[Co(en)_2X(glyOH)]X_2$ ($X^- = Cl^-, Br^-$) was base hydrolyzed at three different hydroxide concentrations in the presence, and then in the absence, of added $NaClO_4$ or NaN_3.

(a) 1.0 mol dm^{-3} NaOH. An aqueous solution of the complex (10 cm^3, 25 °C) was rapidly mixed into 10 cm^3 of 2 mol dm^{-3} NaOH (25 °C). After 5 s the reaction was quenched by using one of the two methods described below.

(b) 0.1 mol dm^{-3} NaOH. The complex in 10 cm^3 of 1 mol dm^{-3} $NaClO_4$, 1 mol dm^{-3} NaN_3, or 2 mol dm^{-3} NaN_3 (5 cm^3 of water followed by 5 cm^3 of 2 mol dm^{-3} $NaClO_4$, 2 mol dm^{-3} NaN_3, or 4 mol dm^{-3} NaN_3) was added to 10 cm^3 of a solution 0.2 mol dm^{-3} in NaOH and 1 or 2 mol dm^{-3} in $NaClO_4$ or NaN_3. The reaction was quenched after 10 s as described below.

(c) pH 10 ($X^- = Br^-$) and pH 10.5 ($X^- = Cl^-$). A solution of the complex in 20 cm^3 of 1 mol dm^{-3} $NaClO_4$, 1 or 2 mol dm^{-3} NaN_3 (10 cm^3 of water + 10 cm^3 of 2 or 4 mol dm^{-3} NaN_3), or water was base hydrolyzed against 1 mol dm^{-3} NaOH for 12–15 min (1 mol dm^{-3} $NaClO_4$ or H_2O), or 16–22 min (1 or 2 mol dm^{-3} NaN_3), by using a pH stat assembly.

Product Analysis following Base Hydrolysis of *cis*-$[Co(en)_2X(glyO)]^+$ Ions ($X^- = Cl^-, Br^-$). All products were evaluated by atomic absorption spectroscopy (Varian AA4) and spectrophotometric methods (Cary 118C or 16K). The following ϵ values were used (nm, mol^{-1} dm^3 cm^{-1}):[21] $[Co(en)_2(glyO)]^{2+}$ 487, 97 and 348, 105; *cis*-$[Co(en)_2(OH)(glyO)]^+$ 500, 95 and 368, 86; *trans*-$[Co(en)_2(OH)(glyO)]^+$ 498, 74; *trans*-$[Co(en)_2(OH_2)(glyO)]^{2+}$ 496, 52; *cis*-$[Co(en)_2(N_3)(glyO)]^+$ 510, 310; *trans*-$[Co(en)_2(N_3)(glyO)]^+$ 520, 260. These complexes are abbreviated as glyO, *cis*-OH, *trans*-OH, *trans*-H_2O, *cis*-N_3, and *trans*-N_3, respectively, and *cis*-$[Co(en)_2(OH_2)(glyO)]^{2+}$ as *cis*-H_2O.

A. Reactions in the Absence of NaN_3. The products were worked up in two different ways.

(i) Water Quenched. The reaction was quenched by adding water (100–300 cm^3, depending on ionic strength and base concentration) and the products were sorbed on Dowex 50 W-X2 cation-exchange resin (Na^+ form; ca. 1.5 × 7-cm bed of fresh resin; pH previously adjusted to 9). Complete sorption took from 30 to 90 min. Elution with 2 mol dm^{-3} $NaClO_4$ at pH 9–10 gave a fast-moving 1+ cherry red band followed by an orange 2+ band (identified as $[Co(en)_2(glyO)]^{2+}$, ϵ_{487} 97).[17] This 1+ band was acidified to pH ~4 (10 mol dm^{-3} HOAc) and the solution allowed to stand for 10 min. Under these conditions *cis*-$[Co(en)_2(OH_2)(glyO)]^{2+}$ is rapidly converted to $[Co(en)_2(glyO)]^{2+}$.[18] The solution was then diluted and sorbed on a small column of Dowex resin. Elution with 2 mol dm^{-3} $NaClO_4$–0.2 mol dm^{-3} $HClO_4$ separated the 2+ band ($[Co(en)_2(glyO)]^{2+}$) and 3+ band (*trans*-$[Co(en)_2(OH_2)(glyOH)]^{3+}$). Following removal of the 2+ band, the column was washed with 0.2 mol dm^{-3} "Tris" buffer (pH 8.1) until the eluate was basic and the 1+ band (*trans*-$[Co(en)_2(OH)(glyO)]^+$) then eluted by using 1 mol dm^{-3} $NaClO_4$ (pH 8.1). After standing overnight,[18] this solution gave a spectrum identical to that of $[Co(en)_2(glyO)]^{2+}$.

(ii) Acid Quenched. The solution was quenched to pH ~4 with HOAc, whereupon *cis*-$[Co(en)_2(OH)(glyO)]^+$ rapidly converts to $[Co(en)_2(glyO)]^{2+}$.[18] After dilution with water (100–300 cm^3) and sorption onto Dowex resin, the 2+ band ($[Co(en)_2(glyO)]^{2+}$) and 3+ band (*trans*-$[Co(en)_2(OH_2)(glyOH)]^{3+}$) were separated and eluted with 2 mol dm^{-3} $NaClO_4$–0.2 mol dm^{-3} $HClO_4$. The cobalt concentrations were estimated, and the *trans*-H_2O product was allowed to convert to $[Co(en)_2(glyO)]^{2+}$ (as described above) and was also determined spectrophotometrically.

B. Azide Competition. The products of two identical base hydrolysis reactions were worked up as follows.

(i) Water Quenched. The procedure outlined in A(i) was followed with the exception that 0.5 mol dm^{-3} $NaClO_4$ (pH 9) was used as eluent. Four bands separated in the order *trans*-$[Co(en)_2(N_3)_2]^+$ (1), *trans*-$[Co(en)_2(N_3)glyO)]^+$ (2), *cis*- and *trans*-$[Co(en)_2(OH)(glyO)]^+$ plus *cis*-$[Co(en)_2(N_3)(glyO)]^+$ (3), and $[Co(en)_2(glyO)]^{2+}$ (4). The first two bands were collected by using the above eluent, the third by using 1.0 mol dm^{-3} $NaClO_4$ (pH 9), and the last by using 2 mol dm^{-3} $NaClO_4$–0.2 mol dm^{-3} $HClO_4$. Because of the time required to elute with 0.5 mol dm^{-3} $NaClO_4$, very little or no *trans*-$[Co(en)_2(OH)(glyO)]^+$ was detected in the subsequent workup of band 3. If, however, 1.0 mol dm^{-3} $NaClO_4$ (pH 9) was used initially, bands 2 and 3 failed to completely separate and were collected together; however, reasonable agreement with the acid-quenched separation method was then obtained for the *trans*-$[Co(en)_2(OH)(glyO)]^+$ species. The hydroxo and azido complexes were separated by adjusting the eluate containing bands 2 and 3 to pH ~4 (0.5 cm^3, 10 mol dm^{-3} HOAc), and then *cis*- and *trans*-$[Co(en)_2(OH)(glyO)]^+$ are converted to $[Co(en)_2(glyO)]^{2+}$ and *trans*-$[Co(en)_2(OH_2)(glyO)]^{2+}$, respectively.[18] Separation from the 1+ azido products was then achieved by sorption onto and elution from Dowex resin (Na^+ form) with 1 mol dm^{-3} $NaClO_4$ (pH 4). From the known amount of *trans*-N_3 product obtained in the separation using 0.5 mol dm^{-3} $NaClO_4$ (pH 9, see above), the *cis*-N_3 component was calculated. The remaining 2+ bands containing the hydroxo products were then isolated by washing the column with 0.2 mol dm^{-3} $HClO_4$ and by eluting the 3+ (*trans*-H_2O) and 2+ ($[Co(en)_2(glyO)]^{2+}$) bands from the *cis*-H_2O band with 2 mol dm^{-3} $NaClO_4$–0.2 mol dm^{-3}. The azido complexes were also separately evaluated by treating the acidified eluate (pH ~1) with a small amount of $NaNO_2$[19] whence the *cis*-$[Co(en)_2(N_3)(glyO)]^+$ and *trans*-$[Co(en)_2(N_3)(glyO)]^+$ ions are converted to $[Co(en)_2(glyO)]^{2+}$ and *trans*-$[Co(en)_2OH_2(glyOH)]^{3+}$, respectively. These complexes were then separated as above.

(ii) Acid Quenched. When the method for A(ii) was followed, four bands were developed on the column by using 0.5 or 1 mol dm^{-3} $NaClO_4$ (pH 4). The first, *trans*-$[Co(en)_2(N_3)_2]^+$, was produced in greater amounts for the $(+)_{589}$ than for the racemic material, but then <2% was formed in 2 mol dm^{-3} NaN_3 (pH 10 and 13). The second and third bands were *trans*- and *cis*-$[Co(en)_2(N_3)(glyO)]^+$, respectively. Their cobalt concentrations were determined and the complexes then converted to $[Co(en)_2(glyO)]^{2+}$ as described in B(i) above and reestimated. The last band was a mixture of $[Co(en)_2(glyO)]^{2+}$ and *trans*-$[Co(en)_2(OH_2)(glyO)]^{2+}$. They were separated by using 2 mol dm^{-3} $NaClO_4$–0.2 mol dm^{-3} $HClO_4$ and estimated.

Experiments on Optically Active Complexes. Base Hydrolysis and Competition with Azide. $(+)_{589}$-$[Co(en)_2Br(glyOH)]Br_2 \cdot H_2O$ was base hydrolyzed at pHs 13 and 10 in the presence and absence of NaN_3. The products were separated as given above and ORD and visible spectra obtained for each product. In all cases the *trans*-OH and *trans*-N_3 complexes were optically inactive both before and after conversion to $[Co(en)_2(glyO)]^{2+}$. The $(+)_{589}$-$[Co(en)_2(OH)(glyO)]^+$ and $(+)_{589}$-$[Co(en)_2(N_3)(glyO)]^+$ ions were converted to $(+)_{589}$-$[Co(en)_2(glyO)]^{2+}$ by the methods given above. For the hydroxo species, this involves intramolecular cyclization,[18] and for the azido complex, treatment with HNO_2 presumably gives initially the *cis*-H_2O ion; both processes are known to occur with full retention of configuration about the metal center.[19] The optical retentions in the $[Co(en)_2(glyO)]^{2+}$ products were compared with that for optically pure $(+)_{589}$-$[Co(en)_2(glyO)]^{2+}$.[20] Three or four different wavelengths were monitored and the average value was taken.

Optically Pure $(+)_{589}$-$[Co(en)_2(glyO)]^{2+}$. $(+)_{589}$-$[Co(en)_2Br(glyOH)]Br_2 \cdot H_2O$ (50 mg, $[\alpha]_{589}$ +103°) was dissolved in 0.1 mol dm^{-3} $HClO_4$ (10 cm^3), and 1 mol dm^{-3} Hg^{2+} in 0.1 mol dm^{-3} $HClO_4$ (2 mL) was added. After 30 min the orange solution was sorbed on

and eluted from a small column of Dowex 50W-X2 cation exchanger (2 mol dm^{-3} $NaClO_4$–0.2 mol dm^{-3} $HClO_4$), and the optical rotations were measured as $\alpha_{589} = 0.140$, $\alpha_{546} = 0.289$, $\alpha_{473} = -0.522$, and $\alpha_{432} = -0.338$ at [Co] = 8.825×10^{-4} mol dm^{-3} resulting in $[M]_{589} = 1580°$, $[M]_{546} = 3270°$, $[M]_{473} = -5915°$, and $[M]_{432} = -3830°$. These $[M]_\lambda$ values are consistent with optically pure $(+)_{589}$–$[Co(en)_2(glyO)]I_2$ prepared and resolved separately.[20]

Effect of Ionic Strength and Electrolyte on the Rate of Base Hydrolysis. A weighed quantity (0.15–0.2 mmol) of the complexes $Br(glyOH)]Br_2$ and *cis*-$[Co(en)_2Br(glyNHR)]Br_2$ (R = H, CH_2CO_2H, $CH_2CO_2C_3H_7$) was dissolved in 20 cm^3 of distilled water or in 20 cm^3 of electrolyte ($NaClO_4$, KCl, Na_2SO_4) of varying ionic strength. The solution was transferred to a thermostated reaction vessel (25.0 °C) and base hydrolyzed at constant pH (pH 9.0–10.0, pH stat) against 0.1 mol dm^{-3} NaOH. Plots of log $(V_\infty - V_t)$ vs. time were linear for at least 3 half-lives (V = volume of NaOH added).

Treatment of Experimental Data. The products from the base hydrolysis of the *cis*-$[Co(en)_2X(glyO)]^+$ (X^- = Cl^-, Br^-) ions, both in the presence and absence of added NaN_3, are listed in Table I (supplementary material). The experiments were done in duplicate, and the reproducibilities for the $[Co(en)_2(glyO)]^{2+}$ and *cis*- and *trans*-$[Co(en)_2(OH)(glyO)]^+$ products were ±2%, ±2%, and ±1%, respectively. For the *cis*- and *trans*-N_3 species, the reproducibility was ±1% for both. Overall recoveries were >95%. The results are distinguished depending on whether the solution on completion of hydrolysis was diluted with water (nonquenched) or treated with HOAc to pH ~4 (quenched). The two types of quenching were necessary because the *trans*-OH, *trans*-N_3, and to a lesser extent *cis*-N_3 complexes reacted further when the reaction mixture was simply diluted with water, but only in this way could the *cis*-OH species be determined. Subsequent reactions of the *cis*-N_3, *trans*-N_3, and *trans*-OH ions could be ignored at pH 4. From the nonquenched experiments, the amount of *cis*-$[Co(en)_2(OH)(glyO)]^+$ was obtained directly, since its reaction during hydrolysis and isolation was minimal (pH 10; $k = 1.8 \times 10^{-5}$ s^{-1}).[18] The amounts of the other products were also determined from the nonquenched experiments, and these were used for comparison with those obtained in the quenched experiment.

When the reaction mixture is quenched pH 4, the *cis*-OH species is rapidly converted to $[Co(en)_2(glyO)]^{2+}$,[18] and the combined *cis*-OH and $[Co(en)_2(glyO)]^{2+}$ products were recovered as $[Co(en)_2(glyO)]^{2+}$. Knowledge of the *cis*-OH result from the nonquenched experiment gives the amount of $[Co(en)_2(glyO)]^{2+}$ formed directly, and these results appear in Table II (supplementary material). Quenching of the mixture to pH 4 also converts the *trans*-OH product to the *trans*-H_2O ion which only very slowly reacts in acid solution ($t_{1/2} \simeq$ 3 days),[21] and this could be readily separated from the $[Co(en)_2(glyO)]^{2+}$ product. Similarly the *cis*- and *trans*-N_3 ions do not react under these conditions, and the nonquenched results have been corrected accordingly and appear in Table II. A further 15–20% correction was applied to the amount of *trans*-OH complex for reactions at pH 10 (Br^-) and pH 10.5 (Cl^-) during the time of base hydrolysis (t, s). These corrections were obtained from the expression

$$\% \text{ reacted} = 100\left[1 - \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right]$$

where k_1 and k_2 are the rate constants for the process

$$cis\text{-Br} \xrightarrow{k_1} trans\text{-OH} \xrightarrow{k_2} \text{glyO}$$

and have the following values[21] at pH 10: $k_1 = 1 \times 10^{-2}$ s^{-1} (1 mol dm^{-3} $NaClO_4$), 6.5×10^{-3} s^{-1} (1 mol dm^{-3} NaN_3), 5.4×10^{-3} s^{-1} (2 mol dm^{-3} NaN_3); $k_2 = 2.3 \times 10^{-4}$ s^{-1}. In 0.1 and 1 mol dm^{-3} NaOH (pH 13; $k_2 = 2.6 \times 10^{-4}$ s^{-1};[21] t = 10 s) no correction was necessary for this process. However, in 0.1 and 1 mol dm^{-3} NaOH some *cis*- and *trans*-N_3 complex is consumed. For the former ion this is only minor, ~0.4% (pH 13; $k_2 = 4.2 \times 10^{-4}$ s^{-1}; t = 10 s)[21] and ~3% (pH 14; $k_2 = 5.6 \times 10^{-3}$ s^{-1}; t = 5 s),[21] and no correction was made. For the latter, at pH 13 ~31% ($k_2 = 3.75 \times 10^{-2}$ s^{-1}) and at pH 14 ~71% ($k_2 = 0.5$ s^{-1}) had reacted. The entry in Table II for the *trans*-N_3 product under these conditions is thus an average value of those obtained at pH 10 and 0.1 mol dm^{-3} NaOH.

In the nonquenched experiments, further reaction of the *cis*- and *trans*-N_3 complexes occurs, but no corrections were applied due to the varying times for sorption on to the ion-exchange resin. These subsequent reactions of the azido ions did not interfere with the *cis*-OH result. The *trans*-N_3 ion also did not give *cis*-OH product under these conditions.

The observed stereochemical retention results and the corrected values are given in Tables III and IV (supplementary material), respectively. No corrections were necessary for the *cis*-OH and *cis*-N_3 products, but the $[Co(en)_2(glyO)]^{2+}$ product is derived both directly from base hydrolysis and indirectly from the *trans*-OH ion, the latter giving rise to racemic product. The entry in Table IV for $[Co(en)_2(glyO)]^{2+}$ is corrected for this and gives the retention in the chelated product produced directly.

Results

The corrected product distributions (see supplementary material, Tables I–IV) are collected in Table V. The following conclusions can be drawn. First, in the absence of N_3^-: (1) The amounts of *cis*-OH, *trans*-OH, and glyO chelate are independent of X (Cl^-, Br^-) and are independent of pH over the range 10–13, at constant ionic strength (1.0 mol dm^{-3} $NaClO_4$). (2) More *cis*-OH (4.2%) and *trans*-OH (1%), and less glycinate chelate (5.2%), are formed in 1.0 mol dm^{-3} NaOH than in the pH range 10–13, at constant ionic strength (1.0 mol dm^{-3}). (3) In the absence of supporting electrolyte less *cis*-OH (~5%) and more glyO chelate (~5%) are formed than in 1.0 mol dm^{-3} $NaClO_4$ (pH 10 data). Other results[21] showed that the product distribution did not change further in the range 1.0–4.0 mol dm^{-3} $NaClO_4$. (4) Stereochemical retention (Λ vs. ΛΔ) in the *cis*-OH (45% Λ) and glyO chelate (57% Λ) is constant over the pH range 10–14.

Second, in the presence of 1.0 and 2.0 mol dm^{-3} NaN_3 the following conclusions obtain: (5) The overall sterochemistry $cis_T/trans_T$ (T = total) is independent of pH from 10 to 14, and a similar result occurs for the individual *cis*-N_3 and *trans*-N_3 products over the same pH range. (6) The increased amounts of *cis*-OH and *trans*-OH formed in 1.0 mol dm^{-3} NaOH ((2) above) are maintained proportionately in 1.0 and 2.0 mol dm^{-3} NaN_3. (7) In the pH range 10–13 the glyO/(*cis*-OH + *trans*-OH) ratio decreases with increasing $[N_3^-]$: 0.85 ($[N_3^-]$ = 0 mol dm^{-3}); 0.73 (1.0); 0.66 (2.0). A similar result occurs in 1.0 mol dm^{-3} NaOH: 0.69 ($[N_3^-]$ = 0 mol dm^{-3}); 0.61 (1.0); 0.53 (2.0). Thus N_3^- competes about twice as effectively for carboxylate entry as it does for water entry. (8) N_3^- entry gives proportionately more trans than cis product than does H_2O entry. (9) The overall stereochemistry $cis_T/trans_T$ decreases with increasing $[N_3^-]$ (10.4 ($[N_3^-]$ = 0), 6.8 (1.0), 6.0 (2.0)). Thus at least some *trans*-N_3 arises from paths which previously gave rise to cis capture of carboxylate or water. This occurs even though 3 times as much *cis*-N_3 is formed as *trans*-N_3. (10) The stereochemical retention (Λ) in the *cis*-OH and *cis*-N_3 products is independent of pH (in the range 10–13) and of $[N_3^-]$ (*cis*-OH 73% Λ, 27% Δ; *cis*-N_3 60% Λ, 40% Δ).

Table VI lists the second-order rate constants (k_{OH}) for base hydrolysis of *cis*-$[Co(en)_2Br(glyglyOC_3H_7)]^{2+}$, *cis*-$[Co(en)_2Br(glyNH_2)]^{2+}$, *cis*-$[Co(en)_2Br(glyglyO)]^+$, and *cis*-$[Co(en)_2Br(glyO)]^+$ at various concentrations of the supporting electrolytes $NaClO_4$, KCl, and Na_2SO_4. It is obvious that the lower charged 1+ ions are less reactive than the 2+ ions and that ionic-strength effects are more important with the 2+ species.

Discussion

The mechanism of base hydrolysis of the *cis*-$[Co(en)_2X(glyO)]^+$ (X^- = Cl^-, Br^-) ions is likely to be similar to that for other cis Co(III) acido–amine complexes. Rate determining loss of X^- forms a five-coordinate intermediate or set of intermediates which compete for H_2O, $-COO^-$, and N_3^- to form *cis*- and *trans*-$[Co(en)_2(OH)(glyO)]^+$, $[Co(en)_2(glyO)]^{2+}$, and *cis*- and *trans*-$[Co(en)_2(N_3)(glyO)]^+$.

In the absence of N_3^- and at pH <13, the results can be interpreted by using the two intermediates proposed previously

Table V. Summary of Product Distributions (%) in the Base Hydrolysis of *cis*-$[Co(en)_2X(glyO)]^+$ ($X^- = Cl^-, Br^-$) in the Absence and Presence of NaN_3[a]

pH	$[N_3^-]$, mol dm^{-3}	Co–O, total (Λ, Δ)	cis CoOH, total (Λ, Δ)	trans CoOH	cis CoN_3, total (Λ, Δ)	trans CoN_3	totals: cis CoOH + trans CoOH	totals: cis CoN_3 + trans CoN_3
14.0	0	40.8 (32.1, 8.7)	49.3 (35.8, 13.5)	9.9	0	0	59.2	0
14.0	1.0	30.4	41.4	8.7	14	5.5	50.1	19.5
14.0	2.0	23.6	36.2	8.2	24	8	44.4	32
13.0	0	46.1 (36.2, 9.9)	45.1 (32.8, 12.3)	8.8	0	0	53.9	0
to	1.0	33.7 (27.1, 6.6)	38.6 (28.4, 10.2)	7.3	14.3 (8.6, 5.7)	5.4	45.9	19.7
10.0	2.0	26.5 (21.5, 5.0)	34.2 (25.0, 9.2)	6.2_5	23.8 (14.2, 9.6)	7.7_5	40.4_5	31.5_5

[a] 25.0 °C; 1.0 mol dm^{-3} $NaClO_4$ or NaN_3 or 2.0 mol dm^{-3} NaN_3.

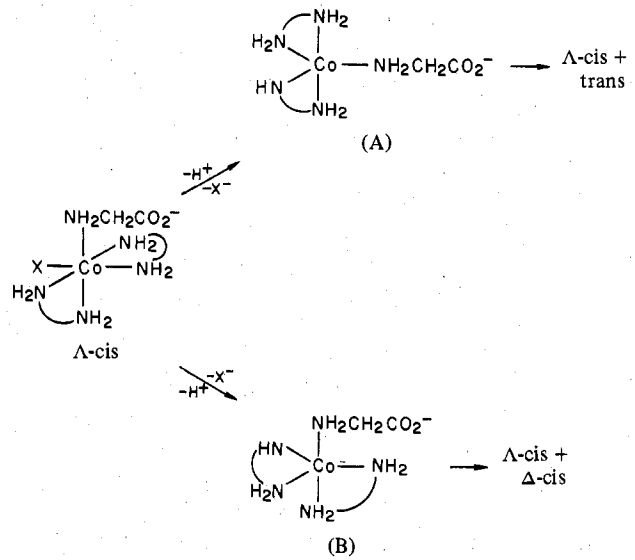
Table VI. Second-Order Rate Constants[a] (k_{OH}) for the Base Hydrolysis of *cis*-$[Co(en)_2Br(amine)]^{2+}$ Ions in Different Supporting Electrolytes

amine	k_{OH}, mol^{-1} dm^3 s^{-1}: H_2O $\mu \simeq 0$	$[NaClO_4]$, mol dm^{-3}: 0.1	0.5	1.0	[KCl], mol dm^{-3}: 0.1	0.5	1.0	$[Na_2SO_4]$, mol dm^{-3}: 0.1	0.25	1.0
glyglyOC$_3$H$_7$	730	422	230	200	250	154	130	40	17	5.3
glyglyO[b]	470	295	200	185	295	150	123	44	18	58
glyNH$_2$	628	380	212	170	250	150	110	27.5	18	5.2
glyO[b]	82	73	67	65	68	56	40	13.5	7.8	2.1

[a] Calculated by using pK_w (electrolyte) of 14.0 (H_2O), 13.78 (0.1 mol dm^{-3} $NaClO_4$), 13.74 (0.5 mol dm^{-3} $NaClO_4$), 13.80 (1.0 mol dm^{-3} $NaClO_4$), 13.78 (0.1 mol dm^{-3} KCl), 13.76 (0.5 mol dm^{-3} KCl), 13.80 (1.0 mol dm^{-3} KCl), 13.24 (0.1 mol dm^{-3} Na_2SO_4), 13.01 (0.25 mol dm^{-3} Na_2SO_4), and 12.78 (1.0 mol dm^{-3} Na_2SO_4) at 25.0 °C: Fisher, R.; Bye, J. *Bull. Soc. Chim. Fr.* **1964**, 2920. [b] Complex is a 1+ species.

for the base hydrolysis of *cis*-$[Co(en)_2(NH_3)X]^{2+}$ ($X^- = Cl^-$, Br^-, NO_3^-) ions.[22,9] These are shown in Scheme II. Of the two intermediates, (A) can lead to the trans and Λ-cis products, and if one assumes a statistical distribution of attack at the three faces of (A), then the product ratio will be 1:2 trans:Λ-cis. To fit the existing product distribution (i.e., 9% trans), (A) would be formed to an extent of 27% and (B) to 73%. For cis entry of the $-COO^-$ and H_2O groups into (A), it is assumed that they compete in the same 46/45 ratio as that of the final $[Co(en)_2(glyO)]^{2+}$/*cis*-$[Co(en)_2(OH)(glyO)]^+$ product ratio (Table V). A similar ratio is also assumed for (B). The observed stereochemical results then require the $-COO^-$ group to enter (B) with 73% retention of configuration and the H_2O group with 66%. This suggests that both cis entering groups, $-COO^-$ and H_2O, react with the five-coordinate intermediate (B) with a high degree of stereospecificity. If there is not a statistical entry of groups into (A), then two possibilities exist: (1) trans entry into (A) is favored over cis entry leading to a conclusion similar to that above or (2) cis entry is favored, resulting in an equal distribution of Λ- and Δ-cis products from (B). This situation is almost realized with the $(+)_{589}$-*cis*-$[Co(en)_2NH_3X]^{2+}$ ($X^- = Cl^-$, Br^-, NO_3^-) ions,[9] and the general question of reprotonation rates becomes important, since (B) is symmetric if reprotonation is fast compared to entry of the sixth ligand. Previously we argued that the deprotonated five-coordinate intermediate would preserve the amide group for its lifetime,[9] but the recent NMR relaxation study by Grunwald and Wong on $[Pt(NH_3)_5NH_2]^{3+}$,[23] suggests that this is unlikely. These authors showed that redistribution of the deprotonated amide site among the various amine centers via the solvent cage is a very fast process indeed, much faster than exchange of water (and presumably any ion-paired species) into or out of the bulk solution. This suggests that reprotonation of the conjugate base by an adjacent correctly positioned water molecule is likely to be very rapid, especially for sites of $K_a < K_w$ (i.e., for most Co(III) amine conjugates), and that the experimentally measured diffusion-controlled limit

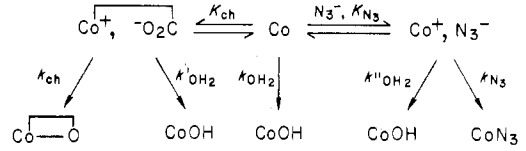
Scheme II



for exchange in such systems[24] could be slower as this is rather a measure of the time taken for redistribution to penetrate the bulk solution phase. It is therefore likely that both protonation of the amide center and entry of the sixth ligand into the five-coordinate intermediate would precede any diffusion process and that the solvation shell could remain trapped close to its original configuration. We will return to this aspect later.

If Scheme II, or ones similar to it,[25,26] were correct, however, the competition ratio $[[Co(en)_2(glyO)]^{2+}]/[[Co(en)_2(OH)(glyO)]^+]$ would be unaffected by the presence of N_3^- or ClO_4^-. This is required of any mechanism in which the intermediate or intermediates compete freely for species in solution. In this case, N_3^- should compete as effectively for carboxylate entry as for water, but this is clearly not so. Table V shows that N_3^- competes almost twice as effectively for $-CO_2^-$ capture

Scheme III



compared to H_2O. Also, Scheme II would predict that the increasing trans content would be accompanied by a corresponding reduction in the stereochemical retentive paths (A), and this is not observed. Retention in both the *cis*-OH and *cis*-N_3 products is independent of $[N_3^-]$, and the retention in $[Co(en)_2(glyO)]^{2+}$ possibly increases slightly. To accommodate these results, we observe that the relative amounts of A and B must be N_3^- dependent. Clearly N_3^- (and ClO_4^- to a lesser extent) affects the distribution or properties of the intermediate (or intermediates) in ways which have not been appreciated previously, and it is not possible to accommodate the new results by any mechanism involving intermediates which compete *independently* for species in solution.

The results, and those obtained previously,[9] can be better explained on the basis of ion pairs with the ion pair formed between $[Co(en)_2Br(glyO)]^+$ and N_3^- displacing the carboxylate moiety of an internal ion pair. Recently the importance of ion pairs in base hydrolysis[15] and anation[27] reactions has been recognized. Increased competition for N_3^- was observed in the base hydrolysis of $[Co(NH_3)_5Me_2SO]^{3+}$ (12–15%[14] vs. 9% for X^- = Cl^-, Br^-, NO_3^-, and $CF_3SO_3^-$[7]), and base hydrolysis of $[Co(NH_3)_5SCN]^{2+}$ and *trans*-$[Co(en)_2NH_3SCN]^{2+}$ leads to capture of NCS^- from within an internal ion pair as well as capture of H_2O.[6,28] Increased competition for N_3^- and a significant change in the optical retentions of the *cis*-OH and *cis*-N_3 products has also been found in the base hydrolysis of $(+)_{589}$-*cis*-$[Co(en)_2NH_3X]^{3+}$ (X = TMP, Me_2SO).[15] Ion pairs clearly exist in aqueous solutions of cationic complexes,[29] and a recent measurement of K_{ip} (ClO_4^-, Cl^-) for $[Rh(NH_3)_5H_2O]^{3+}$ gives a value (26.5 ± 0.8 mol^{-1} dm^3)[30] in good agreement with that predicted by the Fuoss equation.[31] The latter predicts K_{ip} values of 1–5 mol^{-1} dm^3 for 2+ ions with ClO_4^-, N_3^-, etc., which has 50–80% of the reactant in the ion-paired condition in 1.0 mol dm^{-3} electrolyte. Scheme III provides both for internal ion pairing with the glycinate carboxylic acid residue and for ion pairing with added N_3^- (or ClO_4^-, OH^-).

This scheme leads to the following product ratios

$$R_1 = \frac{[CoN_3]}{[CoOH][N_3^-]} = \frac{k_{N_3}K_{N_3}}{k_{OH_2} + k'_{OH_2}K_{ch} + k''_{OH_2}K_{N_3}[N_3^-]}$$

$$R_2 = \frac{[CoN_3]}{[\overline{C-O}][N_3^-]} = k_{N_3}K_{N_3}/k_{ch}K_{ch}$$

$$R_3 = \frac{[\overline{C-O}]}{[CoOH]} = \frac{k_{ch}K_{ch}}{k_{OH_2} + k'_{OH_2}K_{ch} + k''_{OH_2}K_{N_3}[N_3^-]}$$

and values for R_1, R_2, and R_3 listed in Table VII for the combined cis + trans CoN_3 and CoOH products show the expected trends. Both R_1 and R_3 decrease with increasing $[N_3^-]$, and the magnitude of the decrease indicates ~10% of the CoOH product comes from the Co^+,N_3^- ion pair. R_2 is almost N_3^- independent in agreement with $[Co(en)_2(glyO)]^{2+}$ being formed only from its own internal ion pair; i.e., a "combined" ion pair of the type $N_3^-,\overline{Co^+,^-O_2C}$ is unimportant. *R* values calculated for the cis products alone (Table VII) do not agree nearly as well (R_2 is now N_3^- dependent and R_1 is less so), and a similar result holds for the separate trans products. This implies that the cis and trans products are related and do not arise from separate paths or intermediates.

Table VII. Retention Ratios[a] for the CoN_3 and $\overline{Co-O}$ Products[b]

	trans + cis products			cis products only		
$[N_3^-]$, mol dm^{-3}	R_1	R_2	R_3	R_1	R_2	R_3
0 (μ = 0)			1.05			1.28
0 (1.0 mol dm^{-3} ClO_4^-)			0.85			1.02
0 (1.0 mol dm^{-3} OH^-)			0.69			0.83
1.0	0.43	0.58	0.73	0.37	0.42	0.87
2.0	0.39	0.59	0.66	0.35	0.45	0.77

[a] R_1, R_2, and R_3 are defined in the text; data from Table V. [b] See Scheme III.

Table VII also demonstrates that in the absence of any supporting electrolyte (μ = 0), the $\overline{Co^+,^-O_2C}$ internal ion pair is at its maximum concentration and that $K_{ip}(N_3^-)$ and $K_{ip}(OH^-)$ are probably similar but greater than $K_{ip}(ClO_4^-)$. Thus in 1.0 mol dm^{-3} OH^- the lower R_3 value suggests some direct entry of OH^- (to form CoOH) as well as competition for the $\overline{Co^+,^-O_2C}$ ion pair by Co^+,OH^-, whereas the somewhat higher R_3 value in 1.0 mol dm^{-3} N_3^- only results from the latter type of competition. The somewhat larger K_{ip} values for N_3^- and OH^- compared to ClO_4^- are in agreement with other results obtained in this laboratory.[15,32]

Scheme III allows only those anionic competitors directly involved in ion pairing to enter. Thus N_3^- does not enter from the carboxylate ion pair, or carboxylate from the N_3^- ion pair. This mutual exclusion is important and is strong evidence that only species adjacent to the complex can compete. This would seem to exclude solvent-separated ion pairs,[33,34] and more certainly ion triplets.[29]

Scheme III is quite general and does not specify the exact nature of the ion-paired species; these could be five-coordinate intermediates similar to those given in Scheme II, or they could be the ion-paired reactant ions containing the leaving group X. For the latter, any subsequently formed five-coordinate species would not be required to come to equilibrium with the bulk solution, and each could act independently. Thus the results give no information on the lifetimes, or even of the existence, of intermediates. However, the data given in Table VI do suggest that a similar degree of ion pairing affects the rate of loss of X as turns up in the products; that is, any ion-paired intermediates do not equilibrate before they react. The 1+ ions *cis*-$[Co(en)_2Br(glyO)]^+$ and *cis*-$[Co(en)_2Br(glyglyO)]^+$ hydrolyze at slower rates than the 2+ species *cis*-$[Co(en)_2Br(glyNH_2)]^{2+}$ and *cis*-$[Co(en)_2Br(glyglyOC_3H_7)]^{2+}$, and this is in accord with expectations.[35] However, the negatively charged carboxylic acid residue of the N-bound glycinate ligand is modified in the dipeptide acid complex presumably because it is further removed from the metal, and internal ion pairing with the amine groups is less effective. More interesting, however, is the relative effect of the added electrolytes; Figure 1 shows this for three of the complexes using plots of k_{OH}/k_{OH} (1 mol dm^{-3} $NaClO_4$) vs. $NaClO_4$ concentration. Similar curves occur for the KCl and Na_2SO_4 data (Table VI). For the *cis*-$[Co(en)_2Br(glyNH_2)]^{2+}$ ion, the effect of $NaClO_4$ is most pronounced with k_{OH} at μ ~ 0 (4×10^{-3} mol dm^{-3} complex), 3.7 times that in 1 mol dm^{-3} $NaClO_4$; similar rate ratios occur for the other 2+ ions $[Co(en)_2Br(glyglyOC_3H_7)]^{2+}$ (Table VI) and $[Co(en)_2BrNH_3]^{2+}$.[21] However, for *cis*-$[Co(en)_2Br(glyO)]^+$ a factor of only 1.26 is involved, and this suggests that for this complex internal ion pairing of the carboxylic acid function competes for the ion pair with ClO_4^-; *cis*-$[Co(en)_2Br(glyglyO)]^+$ adopts an intermediate position consistent with a weaker internal ion pair. $[Co(en)_2Br(glyO)]^+$ at μ ~ 0 behaves like the 2+ ions in 0.5 mol dm^{-3} $NaClO_4$, and with a K_{ip} value of 5 mol^{-1} dm^3, the complex behaves as if 70% of

Table VIII. Products of Base Hydrolysis of Λ-$(+)_{589}$-$[Co(en)_2Br(amine)]^{2+}$ Ions[a]

amine (monodentate)	ref	% $[Co(en)_2OH(amine)]^{2+}$ trans	% $[Co(en)_2OH(amine)]^{2+}$ $\Delta\Lambda$-cis	% $[Co(en)_2OH(amine)]^{2+}$ Λ-cis	% $[Co(en)_2(amine)]^{2+}$ $\Delta\Lambda$-cis	% $[Co(en)_2(amine)]^{2+}$ chelate	% $[Co(en)_2(amine)]^{2+}$ Λ-cis
$NH_2CH_2CO_2C_3H_7$	17		55			45	
$NH_2CH_2CONH_2$	38	6	20	34	20		20
$NH_2CH_2CONHCH_2CO_2C_3H_7$	38	7	19	44	10		20
$NH_2CH_2CONHCH_2CO_2^-$	38		70			30	
$NH_2CH_2CO_2^-$	this work	9	24.5	20.5	20		26
$NH_2CH_2CH_2OH$	39 (μ = 0.05)		35			65	
$NH_2CH_2CH_2NH_2$	40 (μ = 0.1)		~97			~3	
$NH_2CH_2CH_2NH_2$	41 (98% Me_2SO)		~50			~50	
$NH_2CH_2CH_2CO_2^-$	42	14	77			9	
$NH_2CH_2CH_2CO_2C_3H_7$	42	27	34	6	22		11

[a] 25.0 °C; μ = 1.0 mol dm^{-3} $NaClO_4$.

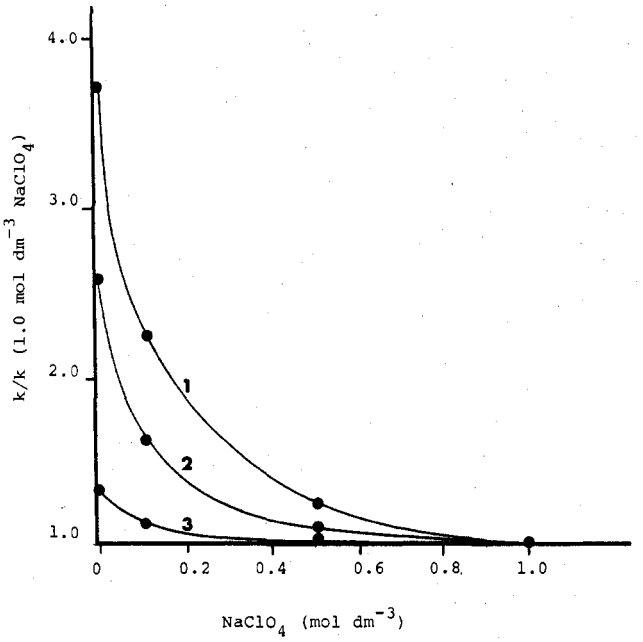


Figure 1. Relative rates, k/k (1.0 mol dm^{-3} $NaClO_4$), for base hydrolysis of *cis*-$[Co(en)_2Br(amine)]^{2+,+}$ ions vs. $NaClO_4$ concentration: amine = glycylglycine isopropyl ester, 1; glycylglycinate, 2; glycinate, 3.

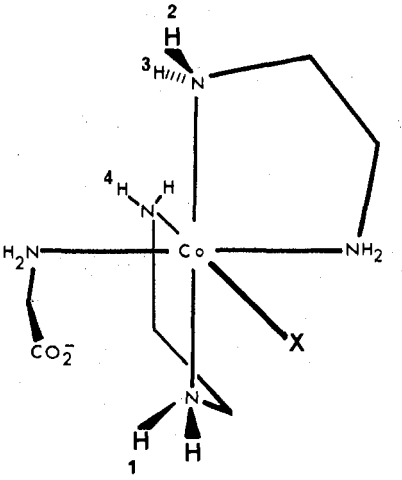
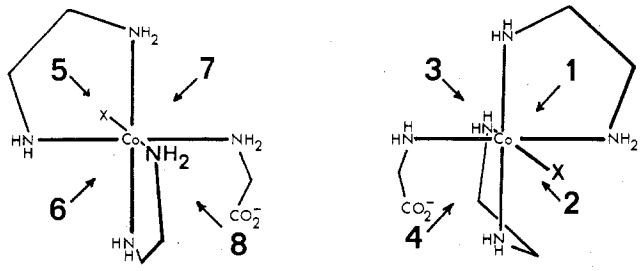


Figure 2. Λ-$[Co(en)_2X(glyO)]^+$ ion showing the four possible H-bonding sites (H(1)–H(4)) for internal ion pairing with the glycinate carboxalate anion.

it is in the ion paired condition and 30% is not. This is to be compared with 50% $[Co(en)_2(glyO)]^{2+}$ chelate formation at $\mu \sim 0$ (R_3, Table III). Similarly, $[Co(en)_2Br(glyglyO)]^+$ at $\mu \sim 0$ behaves like the 2+ ions in $\mu \simeq 0.08$ $NaClO_4$ which gives some 30% in the ion-paired condition. This is to be compared with 30% entry of the carbonyl function to form $[Co(en)_2(glyglyO)]^{2+}$ in the base hydrolysis reaction (Table VIII). These comparisons (Table VIII) suggest that there is a correspondence, perhaps a close correspondence, between the product compositions and the degree of ion pairing in the complexes and that if intermediates are involved, substantial changes in the ion pairs do not take place at this stage. This supports the earlier studies with the differently charged leaving groups where the increased entry of anionic competitors (N_3^-) with the more highly charged cationic species was accounted for in terms of increased ion pairing.[14,15,27] Even more definitively, the study with the three $[Co(Metren)NH_3X]^{2+,3+}$ isomers (X = Cl^-, Br^-, NH_3) seems to eliminate the existence of "chemically significant" five-coordinate intermediates altogether.[13]

This leaves the stereochemistry of the ion pairs and their relationship to the products to be commented on. Four sites exist for ion pairs between the dangling $-CO_2^-$ function and the N–H protons of the ethylenediamine chelates. These are indicated in Figure 2. Similar interactions have been found in the solid-state structures of the glutamic acid and aminomethylmalonic acid chelates Λ-$(+)_{495}$-$[Co(en)_2(R\text{-}gluO)](ClO_4)_2$[36] and Λ-$(-)_{436}$-β_2-$[Co(2,9\text{-}Me_2trien)(R\text{-}ala\text{-}(CO_2^-)](ClO_4)_2 \cdot H_2O$.[37] Sites H(1) and H(2) lie on the front face of the molecule (as defined by the four N atoms orthogonal to X), and ion pairing at these positions could lead to direct entry of the carboxyl function without configurational charge, i.e., to retention (Λ product). Hydrogen bonding to H(4) is unlikely to produce glycinate chelate as substantial reorganization of the structure would be required, but H(3) could lead to inversion (Δ) or retention (Λ) depending on whether the amino group of ethylenediamine or of glycinate moved to fill the coordination site vacated by X. Thus the ~20% Δ-$[Co(en)_2(glyO)]^{2+}$ would arise naturally from entry of the carboxyl function at this octahedral face (F(7), Figure 3a). The possible sites for ion pairing by N_3^-, and hence the position of entry, are not now restricted. Frontside ion pairing (adjacent to X) will be unfavorable for electrostatic reasons, and backside entry leads to increased amounts of trans and inverted Δ-cis products. The latter two may be related, with an increase in the Δ-cis CoN_3 (and CoOH) content accompanying a decrease in trans CoN_3. Thus for *cis*-$[Co(en)_2NH_3X]^{2+}$ (X^- = Cl^-, Br^-, NO_3^-) 30% of the CoN_3 product is trans while 20% is Δ-cis, whereas for the present complexes less trans CoN_3 (25%) and more Δ-cis CoN_3 (40%) occur. These products arise naturally from ion pairs formed with the N–H protons of faces F(5) and F(6) (Figure 3) and movement of the ethylenediamine chelate about one or the other of the two octahedral edges. The table accompanying Figure 3 lists the sites for ion pairs and entry of N_3^-, $-CO_2^-$, or H_2O in terms of the eight octahedral faces. Some trans CoN_3 is required to come from paths which previously gave rise to cis CoOH or $\overline{Co\text{–}O}$ products, and this must occur



(a) Backside Attack

	H_2O	N_3^-	$-CO_2^-$
5	trans(en)	trans(en)	O
	Δ(en)	Δ(en)	
6	trans(en)	trans(en)	O
7	Δ(en)	Δ(en)	Δ(en)
	Λ(NH_2R)	Λ(NH_2R)	Λ(NH_2R)
8	Λ(NH_2R)	Λ(NH_2R)	O

(b) Frontside Attack

	H_2O	N_3^-	$-CO_2^-$
1	Λ(O)	Λ(O)	O
2	Λ(O)	Λ(O)	O
3	Λ(O)	Λ(O)	Λ(O)
4	Λ(O)	Λ(O)	Λ(O)

Figure 3. (a) Backside (5–8) and (b) frontside (1–4) sites for entry of H_2O, N_3^-, and $-CO_2^-$ on the octahedral faces of Λ-[$Co(en)_2X(glyO)]^+$ and the stereochemistry of the products. Groups undergoing movement are indicated in parentheses.

through an increasing tendency for N_3^- to ion pair at F(5) or F(6). Clearly more stereochemical information is required to pinpoint precisely these sites although each complex can be expected to behave to some extent differently. However, further studies of this nature should clear up many of the issues raised.

Registry No. Λ-$(+)_{589}$-*cis*-$[Co(en)_2Cl(glyO)]^+$, 70050-71-4; Λ-$(+)_{589}$-*cis*-$[Co(en)_2Br(glyO)]^+$, 70051-54-6; Λ-*cis*-$[Co(en)_2(glyO)]^{2+}$, 19657-80-8; Δ-*cis*-$[Co(en)_2(glyO)]^{2+}$, 19657-79-5; Λ-*cis*-$[Co(en)_2OH(glyO)]^+$, 70050-72-5; Δ-*cis*-$[Co(en)_2OH(glyO)]^+$, 70050-73-6; *trans*-$[Co(en)_2OH(glyO)]^+$, 70050-74-7; Λ-*cis*-$[Co(en)_2N_3(glyO)]^+$, 69991-10-2; Δ-*cis*-$[Co(en)_2N_3(glyO)]^+$, 70050-75-8; *trans*-$[Co(en)_2N_3(glyO)]^+$, 70050-76-9; Λ-*cis*-$[Co(en)_2Br(glyglyOC_3H_7)]^{2+}$, 67843-77-0; Λ-*cis*-$[Co(en)_2Br(glyglyO)]^+$, 69991-11-3; Λ-*cis*-$[Co(en)_2Br(glyNH_2)]^{2+}$, 53346-43-3; (±)-*cis*-$[Co(en)_2Cl(glyO)]^+$, 39174-42-0; (±)-*cis*-$[Co(en)_2Br(glyO)]^+$, 70050-77-0.

Supplementary Material Available: Tables I–IV listing products following base hydrolysis of *cis*-$[Co(en)_2X(glyO)]^+$, corrected product distributions for base hydrolysis of *cis*-$[Co(en)_2X(glyO)]^+$ (X^- = Cl^-, Br^-), observed optical retentions, and corrected optical retentions, respectively (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reaction", 2nd ed.; Wiley: New York, 1967; p 182. (b) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon: Boston, MA, 1974; p 206.
(2) Tobe, M. L. *Acc. Chem. Res.* **1970**, *3*, 377.
(3) Poon, C. K. *Inorg. Chim. Acta, Rev.* **1970**, 123.
(4) Sargeson, A. M. *Pure Appl. Chem.* **1973**, *33*, 527.
(5) Green, M.; Taube, H. *Inorg. Chem.* **1963**, *2*, 948.
(6) Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655.
(7) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443.
(8) Panunzi, A.; Basolo, F. *Inorg. Chim. Acta* **1967**, *1*, 223.
(9) Buckingham, D. A.; Olsen, I. I; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6654.
(10) Buckingham, D. A; Creaser, I. I.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1972**, *11*, 2738.
(11) Buckingham, D. A; Foxman, B. M.; Marzilli, P. A.; Herlt, A. J.; Sargeson, A. M., unpublished results.
(12) Buckingham, D. A.; Marty, W.; Sargeson, A. M. *Helv. Chim. Acta* **1978**, *61*, 2223.
(13) Buckingham, D. A.; Edwards, J. D; Lewis, T. W.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 892.
(14) Marty, W.; Jackson, W. G., unpublished results. Reynolds, W. I.; Hafezi, S. *Inorg. Chem.* **1978**, *17*, 1819.
(15) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem. 1979*, **18**, 2046.
(16) Alexander, M. D.; Busch, D. H. *Inorg. Chem.* **1966**, *5*, 602.
(17) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 4102.
(18) Boreham, C. J.; Buckingham, D. A.; Francis, D. J; Sargeson, A. M., to be submitted for publication.
(19) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027. Loeliger, D. A.; Taube, H. *Ibid.* **1966**, *5*, 1376.
(20) Sargeson, A. M.; Reid, I. K., unpublished results (see also ref 17).
(21) Boreham, C. J. Ph.D. Thesis, The Australian National University, July 1978.
(22) Pearson, R. G.; Basolo, F. *J. Am. Chem. Soc.* **1956**, *78*, 4878; *Inorg. Chem.* **1965**, *4*, 1522.
(23) Grunwald, E.; Fong, D.-W. *J. Am. Chem. Soc.* **1972**, *94*, 7371.
(24) Eigen, M.; Kruse, W.; Maass, G.; De Maeyer, L. *Prog. React. Kinet.* **1963**, *2*, 308. Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.
(25) Nordmeyer, F. R. *Inorg. Chem.* **1969**, *8*, 2780.
(26) Green, M. *J. Chem. Soc. A* **1967**, 762.
(27) Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348.
(28) Buckingham, D. A.; Creaser, I. I.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1972**, *11*, 2738.
(29) Watts, D. W. *Rec. Chem. Prog.* **1968**, *29*, 131.
(30) Pavelich, M. J.; Maxey, S. M.; Pfaff, R. C. *Inorg. Chem.* **1978**, *17*, 564.
(31) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.
(32) Buckingham, D. A.; Clark, C. R.; Lewis, T. W., *Inorg. Chem.* **1979**, *18*, 1985.
(33) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *Chem. Ind. (London)* **1954**, 664. Winstein, S.; Clippinger, E.; Fainberg, A. H.; Heck, R.; Robinson, G. C. *J. Am. Chem. Soc.* **1956**, *78*, 328.
(34) Harris, J. M.; Clark, D. C.; Becker, A.; Fagan, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 4478. A general article on the importance of ion pairs in solvolytic reactions: Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348.
(35) Basolo, F.; Pearson, R. G. In "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1968; Table 3.21, p 181.
(36) Glusker, J. P.; Currell, H. L.; Job, R.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 5741.
(37) Gillard, R. D.; Payne, N. C.; Robertson, G. B. *J. Chem. Soc. A* **1970**, 2579.
(38) Boreham, C. J.; Buckingham, D. A.; Keene, F. R. *Inorg. Chem.* **1979**, *18*, 28.
(39) Buckingham, D. A.; Davis, C. E.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 6159.
(40) Hay, R. W.; Nolan, K. B. *J. Chem. Soc., Dalton Trans.* **1975**, 1622.
(41) Buckingham, D. A.; Edwards, J. D.; Lewis, T. W., unpublished results.
(42) Baraniak, E. Ph.D. Thesis, The Australian National University, March 1973.