the chelate (k_{ex} = 1.7 × 10^{-6} s^{-1} in 1.0 mol dm^{-3} NaOH).[1] Scheme II outlines this proposal. Previously[1], it was assumed that this occurred via hydroxide exchange in *cis*-$[Co(en)_2(OH)(glyO)]^+$ with hydrolysis and cyclization occurring via C–O rather than Co–O bond cleavage and formation (Scheme III). Clearly only a tracer study similar to that described here could resolve this uncertainty.

Registry No. $(-)_{589}$-$[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$, 101758-90-1; $[Co(en)_2(\beta\text{-alaO})]Cl_2$, 60866-21-9; OH^-, 14280-30-9.

Contribution from the Research School of Chemistry, The Australian National University, Canberra, ACT, Australia, and Department of Chemistry, University of Otago, Dunedin, New Zealand

Hg^{2+}- and OH^--Induced Reactions of *cis*-$[Co(en)_2X(\beta\text{-alaOR})]^{2+}$ and *cis*-$[Co(en)_2Br(\beta\text{-alaO})]^+$ (X = Cl, Br; R = H, Me, *i*-Pr)

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cis-$[Co(en)_2X(\beta\text{-alaOR})]X_2$ (X = Cl, Br; R = H, Me, *i*-Pr) complexes have been prepared and *cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]^{3+}$ has been resolved into its enantiomers. For R = H, pK_a values for the dangling carboxylic acid function are 3.85 ± 0.05 (X = Br) and 3.9 ± 0.1 (X = H_2O). Hg^{2+}-catalyzed removal of coordinated X (Cl, Br) occurs with retention of configuration about the metal, giving 80% *cis*-$[Co(en)_2(H_2O)(\beta\text{-alaOR})]^{3+}$ and 20% $[Co(en)_2(\beta\text{-alaOR})]^{3+}$ for R = H (k_{Hg} = 2.9 ± 0.1 mol^{-1} dm^3 s^{-1}, 25.0 °C, I = 1.0), and 90% and 10%, respectively, for R = Me and *i*-Pr (k_{Hg} = 2.4 mol^{-1} dm^3 s^{-1}). Alkaline hydrolysis occurs with ~60% racemization for R = *i*-Pr, X = Br^- and forms 90% *cis*-$[Co(en)_2(OH)(\beta\text{-alaO/R})]^{+/2+}$ and 10% $[Co(en)_2(\beta\text{-alaO})]^{2+}$ for R = carboxylate (k_{OH} = 46 ± 2 mol^{-1} dm^3 s^{-1}, 25.0 °C, I = 1.0) and 32% and 68%, respectively, for R = *i*-Pr (k_{OH} = 68 ± 2 mol^{-1} dm^3 s^{-1}). Competitive entry by N_3^- results in a greater decrease in the amount of chelated ester (R = *i*-Pr) compared to that of the hydroxo ester.

Introduction

The current work was undertaken to explore the consequences of expanding ring size on the capture of a competing intramolecular nucleophile (ester and carboxylate oxygen) by intermediates of reduced coordination number. This paper reports the preparation and resolution into enantiomers of *cis*-$[Co(en)_2X(\beta\text{-alaOR})]^{2+}$ (X = Cl, Br; R = H, Me, *i*-Pr) and the consequences of the Hg^{2+}- and OH^--induced removal of halide to form the six-membered β-alanine chelate in competition with entry by H_2O and N_3^-.

Previously it was shown that the related reaction of *cis*-$[Co(en)_2X(glyOR)]^{2+}$ with Hg^{2+} gives exclusive entry of ester oxygen to form the five-membered chelate $[Co(en)_2(glyOR)]^{3+}$.[1,2] This subsequently hydrolyzes rather rapidly to $[Co(en)_2(glyO)]^{2+}$ without ring opening. Alkaline hydrolysis of the same complex however results in substantial water entry for R = H (45–49% *cis*- and 7–10% *trans*-$[Co(en)_2(OH)(glyO)]^+$ are formed in addition to capture of carboxylate oxygen),[3] but for R = Me, Et, and *i*-Pr water entry could only be demonstrated by ^{18}O-tracer studies since the hydroxo ester rapidly cyclizes and hydrolyzes intramolecularly to $[Co(en)_2(glyO)]^{2+}$ under the reaction conditions.[4] In the present system the monodentate species $[Co(en)_2(OH_2)(\beta\text{-alaOR})]^{3+}$, $[Co(en)_2(OH)(\beta\text{-alaOR})]^{2+}$, and $[Co(en)_2(N_3)(\beta\text{-alaOR})]^{2+}$ can be directly identified as being distinct from the chelate $[Co(en)_2(\beta\text{-alaOR})]^{3+}$.

Experimental Section

Visible spectra were recorded on a Cary 14 spectrophotometer, and cobalt estimations were made by using a Techtron AA4 spectrophotometer.

A stock solution of Hg^{2+} in $HClO_4$ (I = 1.0 mol dm^{-3}) was prepared by dissolving HgO in $HClO_4$, diluting to $[Hg^{2+}]$ = 0.2 mol dm^{-3} and $[H^+]$ = 0.3 mol dm^{-3}, and adding $NaClO_4$. For reactions at pH ~4 $Hg(OAc)_2$ was dissolved in H_2O (0.025 mol dm^{-3}), and the ionic strength adjusted to 1.0 with $NaClO_4$.

Rate data were obtained by using a Cary 16K spectrophotometer and flow reactor assembly, or by pH stat titration with 1.0 mol dm^{-3} NaOH in a cell (3.2 cm) housed in the spectrophotometer. Optical rotations were measured at 25.0 °C with a Perkin-Elmer P22 spectropolarimeter (10-cm cell). Bio-Rad Analytical Dowex 50W-X2 (200–400 mesh, Na^+ form) and CM Sephadex C25 (Na^+–form) cation-exchange resins were used in separating reaction products.

Preparations. AnalaR reagents were used throughout.

$[Co(en)_2CO_3]Cl$ was prepared by the method of Springborg and Schaffer.[5] $[Co(en)_2CO_3]Br$ was crystallized from warm water with NaBr. *trans*-$[Co(en)_2X_2]X$ (X = Cl, Br) was prepared by dissolution of $[Co(en)_2CO_3]X$ in concentrated HX (50 g in 200 cm^3) at 70 °C followed by 1 h of cooling in an ice bath. The product was washed with ethanol and acetone until free of acid and dried at 100 °C for 3 h.

β-Alanine isopropyl ester hydrochloride was prepared by adding β-alanine (22.3 g) to cold 2-propanol (260 cm^3, 0 °C) to which had been slowly added thionyl chloride (20 cm^3). After 3 h of reflux (steam bath), the solution was evaporated to 50 cm^3 and cooled in ice and excess ether was added. The white opalescent crystals were washed with ether and recrystallized from 2-propanol by adding ether. Anal. Calcd for β-$alaOCH(CH_3)_2$·HCl: C, 42.99; H, 8.42; N, 8.35; Cl, 21.15. Found: C, 43.3; H, 8.3; N, 8.4; Cl, 21.1. β-Alanine methyl ester hydrochloride was prepared in a similar manner. Anal. Calcd for β-$alaOCH_3$·HCl: C, 34.40; H, 7.22; N, 10.04. Found: C, 33.9; H, 7.0; N, 9.5. β-Alaninamide hydrobromide was prepared via its dimedone derivative.[6,7] To β-alanine ethyl ester hydrochloride (0.2 mol) was added a solution of dimedone (0.2 mol) in chloroform (600 cm^3), and the suspension was neutralized with anhydrous triethylamine (0.2 mol). After 12 h at room temperature the filtrate was taken to dryness (steam bath), the residue dissolved in benzene, and NEt_3·HCl removed. The dimedone ethyl ester hydrochloride crystallized on cooling the filtrate overnight in a refrigerator. The amide was formed by adding concentrated ammonia and allowing the mixture to stand for 1 h. This was collected as a solid following removal of excess ammonia. An aqueous solution (400 cm^3, 70 °C) was treated dropwise with Br_2 until a yellow color remained and crystals of β-alaninamide hydrobromide deposited on cooling to 0 °C. These were washed with acetone and dried in an evacuated desiccator. Anal. Calcd for β-$alaNH_2$·HBr: C, 21.31; H, 5.36; N, 16.57. Found: C, 20.4; H, 5.1; N, 15.7.

***cis*-$[Co(en)_2X(\beta\text{-alaOR})]X_2$ (X = Br, Cl; R = Me, *i*-Pr).** These complexes were prepared by modifying a conventional method.[1] To a finely ground mixture of *trans*-$[Co(en)_2X_2]X$ (1.0 molar equiv), β-alanine ester hydrochloride (1.1 molar equiv), and a crystal of CoX_2·$6H_2O$ was added sufficient water to make a thick paste, and then diethylamine (1.0

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molar equiv) was added dropwise over 30 min with continuous mixing. Water was added from time to time to maintain the thick paste. The resulting mixture was cooled in ice and extracted and washed with ethanol followed by acetone. The purple product was recrystallized from hot, acidified (HX) water by cooling and adding excess HX or NaX. Anal. Calcd for $[Co(en)_2Br(\beta\text{-alaOMe})]Br_2$: C, 18.41; H, 4.83; N, 13.42. Found: C, 18.1; H, 4.6; N, 13.5. Calcd for $[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$: Co, 10.71; C, 21.09; H, 5.13; N, 12.30; Br, 43.58. Found: Co, 10.9; C, 21.1; H, 5.3; N, 12.3; Br, 43.2. Calcd for $[Co(en)_2Cl(\beta\text{-alaO-}i\text{-Pr})]Cl_2\cdot 0.5H_2O$: C, 28.22; H, 7.09; N, 16.46; Cl, 25.00. Found: C, 28.6; H, 7.1; N, 16.7; Cl, 25.0. Absorption maxima (nm) and molar absorptivities (mol^{-1} dm^3 cm^{-1}) in 0.1 M HCl and in 1 M $NaClO_4$ (25.0 °C) are as follows: *cis*-$[Co(en)_2Br(\beta\text{-alaOMe})]Br_2$, 540 ± 2 (ε = 81 ± 2); *cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$, 540 ± 2 (ε = 81 ± 2); *cis*-$[Co(en)_2Cl(\beta\text{-alaO-}i\text{-Pr})]Cl_2\cdot 0.5H_2O$, 527 ± 2 (ε = 78 ± 2), 367 ± 2 (ε = 86 ± 2).

cis-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})](ClO_4)_2$ was obtained by dissolution of the bromide salt (22 g) in a minimum volume of hot H_2O (80 °C) and adding slowly hot aqueous $AgClO_4$ (16.6 g). AgBr was removed and a large excess of $NaClO_4$ added. On cooling (0 °C), purple-red crystals separated. These were washed with cold aqueous ethanol and dried in an evacuated desiccator. Anal. Calcd for $[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})](ClO_4)_2$: C, 20.39; H, 4.96; N, 11.89; (ClO_4), 29.62. Found: C, 20.7; H, 5.1; N, 12.0; (ClO_4), 29.0.

Resolution of *cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$. The racemic bromide (7.75 g) in H_2O was converted to the acetate salt with silver acetate (5.00 g, 2 molar equiv) and AgBr removed. Addition of $(+)_{589}$-sodium bis(((+)-tartrato)diarsenate(III)) (3.9 g) and cooling in ice gave $[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})](As\text{-tart})_2$. Fractions were collected, and those of similar rotation were combined and recrystallized to constant rotation from warm H_2O. The pure diastereoisomer was converted back to the bromide salt by dissolution in a minimum volume of acidified H_2O (90 °C) and adding excess NaBr and cooling to 0 °C. $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ was collected and washed with ethanol and acetone and dried in an evacuated desiccator. A 0.1% aqueous solution gave $[\alpha]_{589}$ +64°, $[\alpha]_{546}$ −38°, (1-dm cell).

***cis*-$[Co(en)_2Br(\beta\text{-alaOH})]Br_2$.** *cis*-$[Co(en)_2Br(\beta\text{-alaOMe})]Br_2$ (7 g) was dissolved in 7.6 mol dm^{-3} HBr (70 cm^3) by warming to 50 °C, and over 15 min the solution was cooled to ~20 °C. After 70 h the volume was reduced to 30 cm^3 and ethanol added to the cooled (0 °C) solution. The purple-red crystals were twice recrystallized from hot H_2O by adding HBr and NaBr and cooling to 0 °C, and the product was collected and washed with ethanol and ether. Anal. Calcd for $[Co(en)_2Br(\beta\text{-alaOH})]Br_2$: Co, 11.60; C, 16.55; H, 4.56; N, 13.79; Br, 47.20. Found: Co, 11.9; C, 16.6; H, 4.7; N, 13.6; Br, 47.3. In 0.1 mol dm^{-3} HCl the absorption maximum occurs at 540 ± 2 nm (ε = 81 ± 2 mol^{-1} dm^3 cm^{-1}).

***cis*-$[Co(en)_2Br(\beta\text{-alaNH}_2)]Br_2$.** *trans*-$[Co(en)_2Br_2]Br$ (12.4 g) was ground with β-$alaNH_2\cdot HBr$ (5.0 g) to a paste in a minimum volume of H_2O, and triethylamine (3.0 g) in methanol (15 cm^3) was added over 1 h with good mixing. After a further 1 h the mixture had thickened to a deep purple color; small aliquots of H_2O were added to facilitate mixing. After 3 h methanol was added and the crude product collected and washed with methanol, ethanol, and acetone. It was recrystallized from a minimum volume of warm, acidified H_2O by adding NaBr and allowing the mixture to stand overnight in a refrigerator. The product was washed with methanol and ether and dried in an evacuated desiccator. Anal. Calcd for $[Co(en)_2Br(\beta\text{-alaNH}_2)]Br_2\cdot H_2O$: C, 16.01; H, 4.99; N, 16.00. Found: C, 16.1; H, 5.0; N, 16.1.

pK_a Determinations. An accurately weighed sample of *cis*-$[Co(en)_2Br(\beta\text{-alaOH})]Br_2$ (0.2–0.4 g) dissolved in 1.0 mol dm^{-3} $NaClO_4$ (10 cm^3) was titrated with standard aqueous NaOH (0.200 or 1.00 mol dm^{-3}) at 25.0 °C. The pH was then raised and maintained at 10.0 until coordinated bromide removal was complete. The solution was then back-titrated with standardized $HClO_4$ (0.500 mol dm^{-3}). The pK_a values for coordinated β-alaninate and coordinated water were obtained by standard procedures,[8] volume corrections being applied.

Kinetic Measurements. (a) Hg^{2+}-Catalyzed Reactions. A solution of *cis*-$[Co(en)_2Br(\beta\text{-alaOR})]Br_2$ (R = H, Me, *i*-Pr) in 1.0 mol dm^{-3} $NaClO_4$ (5×10^{-4} to 8×10^{-4} mol dm^{-3}) was mixed with an equal volume of Hg^{2+}/H^+ solution of known concentration, I = 1.0 ($NaClO_4$), 25.0 °C. Rates were obtained spectrophotometrically at several wavelengths in the range 600–300 nm.

(b) OH^--Induced Reactions. A solution of *cis*-$[Co(en)_2Br(\beta\text{-alaOR})]Br_2$ (R = H, Me, *i*-Pr) (~4×10^{-3} mol dm^{-3}) in 1.0 mol dm^{-3} $NaClO_4$ was mixed with an equal volume of glycine (0.2 mol dm^{-3}, I = 1.0, $NaClO_4$) or tris (1.0 mol dm^{-3}) buffer, and the absorbance change was followed at a fixed wavelength.

Rates were also obtained by measuring OH^- uptake by the pH stat method. The complex (0.2–0.4 g) dissolved in 1.0 mol dm^{-3} $NaClO_4$ (~10 cm^3) was titrated with standard NaOH (0.200 or 1.00 mol dm^{-3}) at I = 1.0, 25.0 °C. Hydrolysis of $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ was followed in an identical manner.

Product Analyses. (a) Hg^{2+}-Catalyzed Reactions. *cis*-$[Co(en)_2X(\beta\text{-alaOR})]X_2$ (~0.3 g) in H_2O (~2 cm^3) was treated with the Hg^{2+}/H^+ stock solution (15 cm^3; $[Hg^{2+}]$ = 0.02, 0.2 mol dm^{-3}; $[H^+]$ = 0.3 mol dm^{-3}; I = 1.0 ($NaClO_4$)), or the complex (X = Br; 0.05 g) dissolved in 0.025 mol dm^{-3} $Hg(CH_3COO)_2$ (50 cm^3) was adjusted to pH 4–5 by using 4 mol dm^{-3} NaOH. For X = Br, R = H the product solution was sorbed directly on to the H^+-form cation-exchange resin. The first orange $[Co(en)_2(\beta\text{-alaO})]^{2+}$ band was eluted with 1 mol dm^{-3} $NaClO_4$ at pH ~2 and the second $[Co(en)_2(H_2O)(\beta\text{-alaOH})]^{3+}$ band with either 2 mol dm^{-3} $NaClO_4$ (pH ~2) or 3 mol dm^{-3} HCl. For X = Cl and Br and R = Me and *i*-Pr the products were immediately titrated to pH 9, filtered, and then quenched to pH ~3 (1 mol dm^{-3} $HClO_4$) and sorbed on the H^+-form resin. The bands were eluted as above. Cobalt estimations were made by AA analysis, and the bands were characterized by comparison of elution rates and visible spectra with those of the authentic samples.

$(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ (0.1 g) was treated with 5 cm^3 of 0.2 mol dm^{-3} Hg^{2+}/0.3 mol dm^{-3} H^+ solution (I = 1.0 ($NaClO_4$), 25 °C). After 5 min an aliquot was withdrawn and diluted 20-fold ([Co] = 0.002 42 mol dm^{-3}), and its rotation was measured (10-cm cell). The remaining solution was sorbed on H^+-form resin and eluted with 2 mol dm^{-3} $NaClO_4$ (pH ~3). Rotations of eluted bands were measured, and [Co] was determined by AA. The rotation of the 3+ band was measured over several weeks, until no further change occurred. In a second experiment, $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ (0.1 g) was dissolved in 0.2 mol dm^{-3} Hg^{2+}/0.3 mol dm^{-3} H^+ (10 cm^3; I = 1.0, $NaClO_4$; 25.0 °C) and after 5 min titrated to pH 9.0 for ~30 s to hydrolyze the chelated ester product to the chelated acid. Following quenching to pH ~2 ($HClO_4$) the products were sorbed on to a H^+-form resin. The first $[Co(en)_2(\beta\text{-alaO})]^{2+}$ band was eluted with 2 mol dm^{-3} $NaClO_4$ (pH ~3) and the second $[Co(en)_2OH(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ band with 2 mol dm^{-3} $NaClO_4$ at pH ~9. Rotations were immediately measured (10 cm), and a sample was retained for Co estimation. The solution was then acidified ($HClO_4$) and a spectrum recorded and a rotation measured.

(b) OH^--Induced Reactions. On completion of bromide removal (pH stat) the solutions were adjusted to pH ~8 ($HClO_4$), diluted, and sorbed on Na^+-form cation-exchange resin. For reactions at pH >12 the solid complex (~0.3 g) was dissolved in H_2O (~2 cm^3) and mixed with a 10-fold excess of aqueous NaOH and the above procedure followed. Products were separated by using 0.5 mol dm^{-3} $NaClO_4$ (pH ~8) and were eluted with 2 mol dm^{-3} $NaClO_4$. For R = Me, and *i*-Pr the small 1+ band (~3%) was shown to be *cis*-$[Co(en)_2OH(\beta\text{-alaO})]^+$ by comparison with the authentic material prepared from *cis*-$[Co(en)_2Br(\beta\text{-alaOH})]Br_2$. Subsequent quenchings and elutions were carried out under acidic conditions (pH 4 and 2 (2 mol dm^{-3} $NaClO_4$), respectively), which allowed easy separation and recovery of the 3+ ($[Co(en)_2(H_2O)(\beta\text{-alaO-}i\text{-Pr})]^{3+}$) and 2+ ($[Co(en)_2(\beta\text{-alaO})]^{2+}$) products. These were analyzed spectrally and for Co as before. The 3+ product was also identified by its subsequent hydrolysis and chelation rate under alkaline conditions.

$(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ (0.2 g) dissolved in H_2O (5 cm^3) was treated with 10 cm^3 of 0.25 mol dm^{-3} NaOH containing 2.0 mol dm^{-3} NaN_3. After 5 s the solution was quenched to pH ~5.5 (HOAc), diluted (5 times), sorbed on Na^+-form resin (20-cm column), and eluted at pH 5.5 with 1 mol dm^{-3} (2+ bands) and 2 mol dm^{-3} (3+ band) $NaClO_4$.

Results

Preparations and Properties. The *cis*-$[Co(en)_2X(\beta\text{-alaOR})]X_2$ complexes (X = Cl, Br; R = H, Me, *i*-Pr) were prepared in a manner similar to that used for the glycine derivatives, starting from *trans*-$[Co(en)_2X_2]X$.[1] Visible absorption spectra were essentially identical for all R with maxima at 540 nm (ε = 81 mol^{-1} dm^3 cm^{-1}) for X = Br, and 527 nm (ε = 78 mol^{-1} dm^3 cm^{-1}) and 367 nm (ε = 86 mol^{-1} dm^3 cm^{-1}) for X = Cl. These agree closely with those found for the glycine complexes.[1] IR spectra showed sharp uncoordinated ester and acid absorptions at 1725 and 1700 cm^{-1} respectively, and ^1H NMR data are given in Table I. The methylene resonance for β-alanine is not distinguished from the ethylenediamine resonances at 100 MHz for X = Cl and Br, whereas it is for X = H_2O and for the chelated acid and ester.[9]

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Table I. ^{1}H NMR Absorptions[a] for *cis*-$[Co(en)_2Br(\beta\text{-alaOR})]Br_2$ in D_2O

chem shift			
R = H	R = Me	R = *i*-Pr	assignt
		1.73 (J = 6 Hz)	*gem*-CH_3
3.28[b]	3.28[b]	3.28[b]	CH_2 of en + β-ala
	4.25		CH_3
4.6[c]	4.6[c]	4.6[c]	NH_2 of β-ala
		5.6[d]	CH
5.8[c]	5.8[c]	5.8[c]	NH_2 of en

[a] In ppm downfield from Me_4Si (100 MHz). [b] Broad, multiplet. [c] Broad. [d] Multiplet.

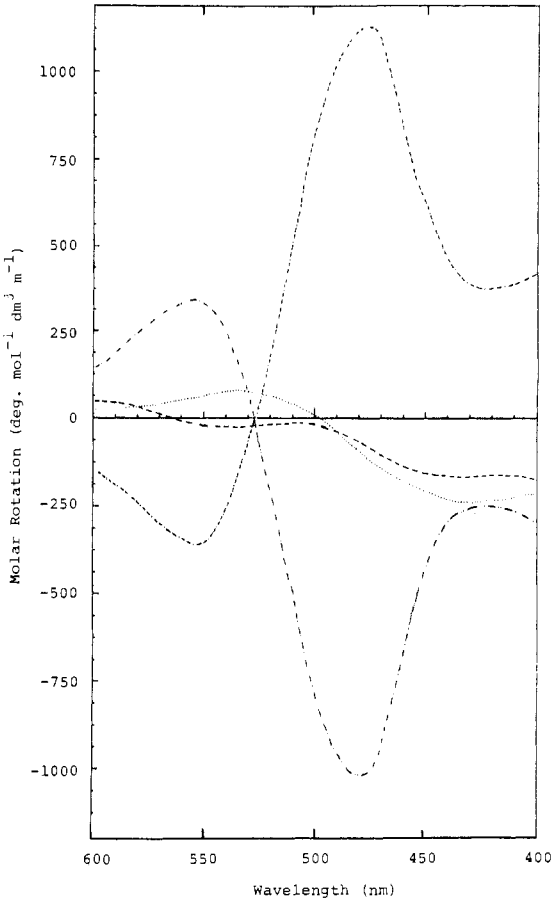

Figure 1. ORD spectrum of $(+)_{589}$-*cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ in 0.3 mol dm^{-3} $HClO_4$ (- -), following Hg^{2+}-induced removal of Br^- (···), and after allowing the $(+)_{589}$-*cis*-$[Co(en)_2(H_2O)(\beta\text{-alaO-}i\text{-Pr})]^{3+}$ so formed to cyclize and hydrolyze to $(+)_{589}$-$[Co(en)_2(\beta\text{-alaO})]^{2+}$ (-·-·-). The spectrum of optically pure $(-)_{589}$-$[Co(en)_2(\beta\text{-alaO})]^{2+}$ is given by (-----).

Resolution into enantiomers was achieved via the $(+)$-$[(As\text{-tart})_2]^{2-}$ diastereoisomer, and the ORD spectrum of $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ is given in Figure 1. $[M]_\lambda$ values are all low when compared to chelated derivatives, and this is consistent with previous experience.[10,11]

The pK_a of the dangling carboxylic acid function, eq 1 and 2, is 3.85 ± 0.05 for X = Br and 3.9 ± 0.1 for X = H_2O at I = 1.0 ($NaClO_4$) and 25.0 °C; this compares with a value of 3.55 for

cis-$[Co(en)_2Br(\beta\text{-alaOH})]^{2+} + H_2O \rightleftharpoons$
cis-$[Co(en)_2Br(\beta\text{-alaO})]^{+} + H_3O^+$ (1)

cis-$[Co(en)_2(H_2O)(\beta\text{-alaOH})]^{3+} + H_2O \rightleftharpoons$
cis-$[Co(en)_2(H_2O)(\beta\text{-alaO})]^{2+} + H_3O^+$ (2)

Table II. Spectrophotometric Rate Data for Hg^{2+}-Catalyzed Bromide Removal from *cis*-$[Co(en)_2Br(\beta\text{-alaOR})]Br_2$[a]

R	$[Hg^{2+}]$,[b] M	$[H^+]$,[b] M	$10^{-1}k_{obsd}$,[c] s^{-1}	k_{Hg},[d] M^{-1} s^{-1}
H	0.010	0.015	0.310	3.10
	0.010	0.148	0.294	2.94
	0.025	0.148	0.748	2.99
	0.050	0.148	1.51	3.02
	0.101	0.148	2.93	2.93
Me	0.010	0.015	0.239	2.39
	0.010	0.148	0.240	2.39
	0.050	0.148	1.20	2.40
	0.101	0.148	2.38	2.38
i-Pr	0.010	0.015	0.252	2.52
	0.010	0.148	0.241	2.41
	0.025	0.148	0.616	2.47
	0.045	0.134	1.07	2.37
	0.050	0.148	1.17	2.35
	0.101	0.148	2.48[e]	2.48

[a] [complex] ~ 5 × 10^{-4} to 8 × 10^{-4} M; λ = 322 nm; ΔOD > 0.4 units; I = 1.0, $NaClO_4$; 25.0 °C. [b] Perchlorate anion. [c] Values are averages of 3 runs. [d] $k_{Hg} = k_{obsd}/[Hg^{2+}]$. [e] Average of 5 runs, with differing λ (322, 350, 495 nm).

Table III. Product Analysis after Hg^{2+}-Catalyzed Halide Removal, in Acid, of *cis*-$[Co(en)_2X(\beta\text{-alaOR})]X_2$[a]

X	R	% $[Co(en)_2(\beta\text{-alaOR})]^{3+}$[b]	% $[Co(en)_2H_2O\text{-}(\beta\text{-alaOR})]^{3+}$
Br	H	18[c]	80
		20[d]	80
		19[e]	80
	Me	11[c]	87
		9[d]	90
	i-Pr	10[c]	88
		9[d]	88
		10[f]	90
Cl		10	90

[a] I = 1.0, $NaClO_4$; 25.0 °C. Values are averages of two experiments. [b] Estimated as the β-alanine chelate, after hydrolysis of the product solution at pH 9. [c] $[Hg^{2+}]$ = 0.1 M; $[H^+]$ = 0.15 M; ~0.3 g of complex used. [d] $[Hg^{2+}]$ = 0.01 M; $[H^+]$ = 0.15 M; ~0.06 g of complex used. [e] $[Hg^{2+}]$ = 0.025 M (acetate salt); pH ~4.5. [f] $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ reactant.

the diprotonated uncoordinated acid.[12] The overall charge on the complex ion apparently has little influence on this remote ionization, and the overall effect of the Co(III) moiety is somewhat smaller than that of H^+. This is also consistent with previous observations.[13,14]

Hg^{2+}-Catalyzed Reaction. Table II gives rate data for the Hg^{2+}-induced removal of bromide from *cis*-$[Co(en)_2Br(\beta\text{-alaOR})]^{2+}$, and a rate law of the form $k_{obsd} = k_{Hg}[Hg^{2+}]$ is evident. No acid dependence was observed, although, at pH >2 and when $Hg(OAc)_2$ was used, the data became difficult to interpret, particularly for R = H. This latter effect is, in part, due to ionization of the carboxylic acid residue, but other undetermined factors are also involved. For R = H, Me and *i*-Pr, k_{Hg} has values of 2.9 ± 0.1, 2.39 ± 0.03, and 2.44 ± 0.03 mol^{-1} dm^3 s^{-1}, re-

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Table IV. Rate Data for Base Hydrolysis of *cis*-$[Co(en)_2Br(\beta\text{-alaOH})]Br_2$ (I = 1.0, $NaClO_4$; 25.0 °C)

pH	λ, nm	10^2k_{obsd}, s^{-1}	k_{OH},[g] M^{-1} s^{-1}
	(I) Spectrophotometric Data[a]		
9.05	355[b]	0.081	43
9.17	361[c]	0.127	50
9.20	536[c]	0.119	44
9.39	355[b]	0.188	45
9.49	361[c]	0.248	47
9.52	536[c]	0.247	44
10.02	361[c]	0.837	47
10.05	536[c]	0.825	44
10.30	536[f]	1.63	48
10.44	361[c]	2.06	44
10.62	355[d]	3.07	43
11.24	355[d]	13.7	46
11.64	355[d]	33.5	45
	(II) pH Stat Data[f]		
8.40		0.020	48
8.75		0.043	45
9.00		0.075	44
9.12		0.109	48
9.23		0.146	50
9.38		0.175	46
9.61		0.330	47
9.65		0.316	42
10.30		1.60	48

[a] [complex] ~ 1×10^{-3} to 2×10^{-3} M; pH measurements were made at the conclusion of the reaction for buffer solutions. [b] 0.5 M Tris buffer. [c] 0.1 M glycine–NaOH buffer. [d] 0.25 M triethylamine buffer. [e] Solution titrated with NaOH to constant pH. [f] 0.2–0.4 g of complex, titrated with NaOH (0.2–1.0 M). [g] $k_{OH} = k_{obsd}/[OH^-]$.

spectively at 25.0 °C, I = 1.0 ($NaClO_4$).

Table III lists reaction products. They show no dependence on $[H^+]$, $[Hg^{2+}]$, or X (Cl, Br) but some dependence on R with more chelate being formed for R = H (20%) than for R = Me or *i*-Pr (10%) (eq 3). Figure 1 gives ORD data for treatment

$$cis\text{-}[Co(en)_2X(\beta\text{-alaOR})]^{2+} + Hg^{2+} \rightarrow cis\text{-}[Co(en)_2(H_2O)(\beta\text{-alaOR})]^{3+} + [Co(en)_2(\beta\text{-alaOR})]^{3+} + HgX^+ \quad (3)$$

of $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]^{2+}$. The immediate 90% aqua ester plus 10% chelated ester product (Table III) has a low rotation consistent with the large amount of monodentate ester. On standing, the rotation increased with time and after 36 h (pH ~9) had changed to that for optically pure $(+)_{589}$-$[Co(en)_2(\beta\text{-alaO})]^{2+}$ (Figure 1). The initial aqua ester and chelated ester produced in the Hg^{2+} reaction therefore have fully retained the configuration about the metal. Also the subsequent chelation and hydrolysis of the aqua ester must occur with retention of this configuration.[9] This analysis is reasonable provided complete inversion of configuration has not occurred. It can be argued by analogy with the chemistry of corresponding complexes[4,21-23] that the analysis is correct and moreover that the absolute configuration of $(+)_{589}$-$[Co(en)_2(\beta\text{-alaO})]^{2+}$ is Λ from the positive Cotton effect of its ORD curve. Similar conclusions can be made for the related complexes.

Alkaline Hydrolysis. Tables IV and V give rate data for the hydrolysis of *cis*-$[Co(en)_2Br(\beta\text{-alaO})]^+$ and *cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]^{2+}$, respectively. The agreement between the spectrophotometric and pH stat data shows that loss of Br^- is accompanied by uptake of OH^-. Both complexes follow the rate expression $k_{obsd} = k_{OH}[OH^-]$ with k_{OH} values of 46 ± 2 and 68 ± 2 mol dm^{-3} s^{-1} for the acid and ester complexes, respectively,

Table V. Rate Data for Base Hydrolysis of *cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ (I = 1.0, $NaClO_4$; 25.0 °C)

pH	λ, nm	10^2k_{obsd}, s^{-1}	k_{OH},[g] M^{-1} s^{-1}
	(I) Spectrophotometric Data[a]		
8.80	536[b]	0.076	69
8.86	361[c]	0.079	65
9.23	536[d]	0.199	69
9.25	361[d]	0.210	69
9.37	536[b]	0.257	72
9.38	355[c]	0.263	65
9.55	361[d]	0.418	69
10.06	361[d]	1.29	66
10.50	361[d]	3.52	66
10.58	355[e]	4.35	68
11.30	355[e]	23.5	70
	(II) pH Stat Data[f]		
8.98		0.104	66[h]
9.00		0.113	66[h]
9.08		0.140	72
9.37		0.246	72
9.91		0.880	65

[a] [complex] ~ 1×10^{-3} to 2×10^{-3} M; pH measurements were made at the conclusion of the reaction for buffer solutions. [b] Solution titrated to constant pH with NaOH. [c] 0.5 M Tris buffer. [d] 0.1 M glycine–NaOH buffer. [e] 0.25 M triethylamine buffer. [f] 0.2–0.4 g of complex, titrated with NaOH (0.2–1.0 M). [g] $k_{OH} = k_{obsd}/[OH^-]$. [h] Reaction carried out on the $(+)_{589}$ complex.

25.0 °C, I = 1.0 ($NaClO_4$). No buffer catalysis was observed with NEt_3, Tris, and glycine buffers, and the same rate was found for $(+)_{589}$-*cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]^{2+}$.

Table VI gives OH^- consumption data as well as the product distribution (eq 4). The latter information was obtained by

$$cis\text{-}[Co(en)_2X(\beta\text{-alaO/R})]^{+/2+} + OH^- \rightarrow [Co(en)_2(OH)(\beta\text{-alaOR})]^{2+} + [Co(en)_2(\beta\text{-alaOR})]^{3+} \xrightarrow{\text{fast, } OH^-} [Co(en)_2(\beta\text{-alaO})]^{2+} + OR^- \quad (4)$$

ion-exchange separation of the 2+ chelated acid from the 3+ monodentate ester with the latter being divided into *cis*- and *trans*-$[Co(en)_2(H_2O)(\beta\text{-alaOR})]^{3+}$ by comparing observed absorptivities with those of the authentic cis (ϵ = 72 mol^{-1} dm^3 cm^{-1}, 489 nm) and trans (ϵ = 55 mol^{-1} dm^3 cm^{-1}, 495 nm) complexes. Attempts to separate the cis and trans ions by using long columns were only partly successful since partial hydrolysis and chelation of *cis*-$[Co(en)_2(H_2O)(\beta\text{-alaO-}i\text{-Pr})]^{3+}$ occurred on the column. The data shows ~32% chelate is formed from the ester complex (X = Br, Cl) and ~10% for R = H (eq 4). Under these conditions the chelated ester is rapidly hydrolyzed to $[Co(en)_2(\beta\text{-alaO})]^{2+}$.[9] For the R = H reactant 1 molar equiv of OH^- is intially consumed in neutralizing the carboxylic acid, and no further OH^- is consumed for that part leading directly to $[Co(en)_2(\beta\text{-alaO})]^{2+}$; for R = *i*-Pr 1 molar equiv of OH^- is consumed in forming both products. The OH^- consumption data also shows little or no hydrolysis of the ester function in the $[Co(en)_2(OH)(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ product under the conditions although ~3% was detected by ion-exchange chromatography.

Table VII gives optical rotations for the products of hydrolysis of $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ in the absence (pH 9.02) and presence (0.17 mol dm^{-3} NaOH) of 1.3 mol dm^{-3} NaN_3. Ion-exchange-separated $[Co(en)_2(OH_2)(\beta\text{-alaO-}i\text{-Pr})]^{3+}$ was analyzed as the chelate, $[Co(en)_2(\beta\text{-alaO})]^{2+}$, following cyclization at pH 8 and in terms of 60% deriving from cis and 40% from the (inactive) trans species (Table VI). The low observed rotations ([Co] = 0.5–1.0 × 10^{-3} mol dm^{-3} for eluted bands) gives rise to considerable uncertainty in these values, but under both sets of conditions the directly formed chelate (eq 4) retains ~40% of the activity of optically pure $(+)_{589}$-$[Co(en)_2(\beta\text{-alaO})]^{2+}$ while *cis*-$[Co(en)_2(OH)(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ is ~40% active in the absence of N_3^- and ~30% active in its presence from the 436 nm data.

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Table VI. Base Consumption and Product Analysis in the Base Hydrolysis of *cis*-$[Co(en)_2X(\beta\text{-alaOR})]X_2$ (I = 1.0, $NaClO_4$; 25.0 °C)[a]

pH	equiv of base consumed[b]	X	$[Co(en)_2OH(\beta\text{-alaOR})]^{n+}$ % trans	% cis	total[d]	% $[Co(en)_2(\beta\text{-alaO})]^{2+}$
		(I) X = Br, R = H (n = 1 for pH >7)				
8.80			14	77	91	10
9.02	1.92				91	9
9.21			15	75	90	8
9.35	1.90		10	80	90	10
9.60					91	8
9.82			15	75	90	9
9.97	1.85				90	10
11.02	1.90				92	8
11.96					92	8
13.2[c]			16	76	92	8
13.3[c]					93	7
13.5			12	79	91	8
14.0			24	74	96	4[e]
		(II) R = *i*-Pr (n = 2)				
8.50	0.98	Br	27	38	65	35
9.20	1.0	Br	27	40	67	32
9.91	1.0	Br			68	32
13.0[c]		Br			68	31
10.40		Cl			67	32
13.0[c]		Cl			66	32
13.2		Br[f]			50	10

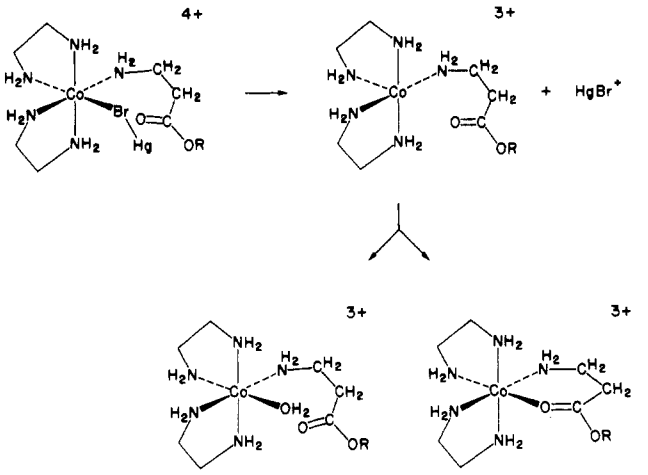
[a] When R = H, products eluted at pH >7; otherwise, they eluted at pH <4. Estimated error, ±2%. [b] Only for some experiments was this obtained. Otherwise, 1 M NaOH was added dropwise (without measurement) to give the required pH before the titrator was used. [c] Excess NaOH (>10 times; 0.2–1.0 M mixed with a solution of the complex (~0.2 g). [d] The cis and trans products, in some experiments, were collected together. [e] The complex (0.205 g) was left in 1.0 M NaOH (10 cm^3) for 3.5 h and then analyzed. [f] For the $(+)_{589}$ complex in the presence of 1.33 M NaN_3 22% *cis*-$[Co(en)_2N_3(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ and 14% *trans*-$[Co(en)_2N_3(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ are also formed.

The mauve *trans*- and *cis*-$[Co(en)_2N_3(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ species formed in the presence of N_3^- were rapidly separated and identified (ϵ_{518} = 220 mol^{-1} dm^3 cm^{-1} for trans; ϵ_{510} = 360 mol^{-1} dm^3 cm^{-1} for cis) with the latter being ~10% active on the basis of data for $(+)_{589}$-$[Co(en)_2N_3(NH_3)]^{2+}$.[15]

Discussion

Hg^{2+}-Induced Reaction. The new observation here is the formation of significant amounts of the aqua monodentate β-alaninate complex. For the corresponding reactions of *cis*-$[Co(en)_2X(glyOR)]^{2+}$ (R = H, *i*-Pr; X = Cl, Br) no detectable aqua monodentate glycinate occurs.[2,3] Furthermore the *cis*-$[Co(en)_2(H_2O)(\beta\text{-alaOR})]^{3+}$ reaction product is sufficiently stable toward subsequent hydrolysis or cyclization to permit its isolation and independent characterization. The corresponding aqua and hydroxo glycinate ions (R = H, *i*-Pr) cyclize via an intramolecular mechanism,[2,14] and only for R = H could this be identified and its subsequent reaction followed in isolation.[14] For R = Me, and *i*-Pr 90% *cis*-$[Co(en)_2(H_2O)(\beta\text{-alaOR})]^{3+}$ is formed, while for R = H the amount is less, 80%. The balance of the product is the chelated species $[Co(en)_2(\beta\text{-alaOR})]^{3+}$, and both are formed with

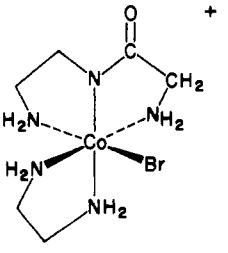
Scheme I



complete retention of the reactant configuration. This is in agreement with the analogous glycine ester and acid chemistry.[2,3]

It has been argued that removal of Br^- occurs via a limiting dissociative process[3,16] and the present results can be interpreted in terms of competitive entry of H_2O and ester carbonyl oxygen into a reactive five-coordinate intermediate (Scheme I). Apparently the more extended β-alaninate system allows access of a solvated H_2O molecule whereas the shorter glycinate moiety does not. Other studies have argued that the lifetime of such an intermediate is short and that it reacts immediately with its nearest neighbor or neighbors with diffusion from the bulk solution phase being impossible.[17,18] In such a circumstance orientation and H-bonding possibilities of the entering group assume major importance, and in this regard it is interesting to note that the two ester groupings (R = Me, *i*-Pr) give the same entry (10%) whereas R = H gives twice as much. This would suggest a closer location or a different specific interaction (possibly with the amine groups) in the precursor leading to the intermediate. The possibility of anchimeric assistance by R also cannot be ruled out, and it is interesting to note the somewhat faster rate for removal of $HgBr^+$ for R = H (2.9 mol^{-1} dm^3 s^{-1}) compared to R = Me, *i*-Pr (2.39 and 2.44 mol^{-1} dm^3 s^{-1}) in this context. Such assistance has been mooted previously in similar systems,[19,20] but direct confirmation of such processes is not yet possible.

Alkaline Hydrolysis. Loss of Br^- from *cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ is slower (k_{OH} = 68 mol^{-1} dm^3 s^{-1}) than for the similar glycine system *cis*-$[Co(en)_2Br(glyO\text{-}i\text{-Pr})]^{2+}$ (k_{OH} = 280 mol^{-1} dm^3 s^{-1}) even allowing for the 32% additional path leading to



in the latter study.[4] However, the lower charged *cis*-[Co-

Table VII. Molar Rotations[a] for the Products of the Alkaline Hydrolysis of $(+)_{589}$-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$

λ, nm	molar rotation, deg mol^{-1} dm^3 m^{-1} *cis*-$[Co(en)_2(OH_2)(\beta\text{-alaO-}i\text{-Pr})]^{3+}$[c]	$[Co(en)_2(\beta\text{-alaO})]^{2+}$ recovered	opt	pure	*cis*-$[Co(en)_2)N_3(\beta\text{-alaO-}i\text{-Pr})]^{2+}$	*trans*-$[Co(en)_2N_3(\beta\text{-alaO-}i\text{-Pr})]^{2+}$
589	50, 90[b]	350	350[b]	900	30[b]	0[b]
546	60, 150[b]	400	390[b]	1260	50[b]	0[b]
436	−500, −380[b]	−740	−500[b]	−1280	−140[b]	0[b]

[a] Errors are considerable for the cis monodentate product due to its low concentration (±30); the error for $[Co(en)_2(\beta\text{-alaO})]^{2+}$ is ±20° mol^{-1} dm^3 m^{-1}. [b] Experiment in the presence of 1.33 M N_3^-. [c] Analyzed as $[Co(en)_2(\beta\text{-alaO})]^{2+}$ following hydrolysis and chelation at pH ~8 with 60% deriving from *cis*-$[Co(en)_2(H_2O)(\beta\text{-alaO-}i\text{-Pr})]^{3+}$.

Table VIII. Properties of Glycine and β-Alanine Monodentate Complexes Following Alkaline Hydrolysis

	cis-$[Co(en)_2Br(amineCO_2)]^+$		*cis*-$[Co(en)_2Br(amineCO_2\text{-}i\text{-}Pr)]^{2+}$	
property	$NH_2CH_2CO_2^-$	$NH_2CH_2CH_2CO_2^-$	$NH_2CH_2CO_2$-*i*-Pr	$NH_2CH_2CH_2CO_2$-*i*-Pr
k_{OH}, mol^{-1} dm^3 s^{-1}	65	46	280	30
products	41% chelate (43% ΔΛ, 57% Λ) 49% monodentate cis (55% ΔΛ, 45% Λ)	10% chelate 90% monodentate (cis + trans)	68% chelate (50% ΔΛ, 50% Λ for R = Me): 45% of chelate derives from chelate ester, 55% from hydroxo ester 32% $[Co(en)_2(OH)(en\text{-}gly)]^+$	32% chelate (60% ΔΛ, 40% Λ) 41% monodentate cis (60% ΔΛ, 40% Λ) 27% monodentate trans
products (N_3^- present)	34% chelate (40% ΔΛ; 60% Λ) 39% monodentate cis (53% ΔΛ, 47% Λ) 7% monodentate trans 20% $[Co(en)_2N_3(glyO)]^+$ (14% cis, 5.4% trans)		14% chelate 59% *trans*-$[Co(en)_2N_3(glyO)]^+$ 17% *trans*-$[Co(en)_2(N_3)_2]^+$	10% chelate (60% ΔΛ, 40% Λ) 37% monodentate cis (70% ΔΛ, 30% Λ) 23% monodentate trans 36% $[Co(en)_2N_3(\beta\text{-}alaO\text{-}i\text{-}Pr)]^{2+}$ (22% cis (mostly ΔΛ), 14% trans)

$(en)_2Br(\beta\text{-}alaO)]^+$ ion hydrolyzes at a similar rate (k_{OH} = 46 mol^{-1} dm^3 s^{-1}) to the 2+ ester complex and to *cis*-$[Co(en)_2Br(glyO)]^+$ (k_{OH} = 65 mol^{-1} dm^3 s^{-1}). Such rate variations can easily be accounted for by compensatory changes in the acidities of amine functions of the substrate and loss of Br^- from the complex base conjugate (eq 5), and in the case of carboxylate, internal ion-

$$cis\text{-}[Co(en)_2Br(\beta\text{-}alaOR)]^{2+/+} + OH^- \underset{}{\overset{K_a/K_w}{\rightleftharpoons}}$$
$$cis\text{-}[Co(en)(en\text{-}H)Br(\beta\text{-}alaOR)]^{+/0} + H_2O \xrightarrow{k_{Br}} \text{products} \quad (5)$$

pairing appears to be involved in a significant manner for the glycinate reactant at least.[3] In the absence of measured K_a and K_{ip} values no detailed analysis of the rate data is possible.

Loss of Br^- from the deprotonated reactant (eq 5) is considered to lead to a reactive five-coordinate intermediate, which competes for adjacent nucleophiles.[3] The identical product distributions for X = Br and Cl agree with this, and entry of H_2O and N_3^- in competition with the ester and acid functions supports a reactive intermediate that coordinates only adjacent nucleophiles. However, the intermediate formed in the alkaline hydrolysis reaction is different from that formed in the Hg^{2+}-induced reaction since it leads to trans as well as cis entry of H_2O and to some inversion in the cis products; such features are absent in the Hg^{2+}-induced reaction. However these observations are not new, and no additional advances on this aspect of the mechanism are forthcoming from this investigation.

A comparison of the products formed in the β-alanine and glycine systems is more rewarding (Table VIII). In the absence of N_3^- (but in the presence of ClO_4^-, which may also compete successfully to give a product that is rapidly hydrolyzed under these conditions) the shorter glycinate ligand results in more, but not exclusive (cf. Hg^{2+}-induced reaction), carbonyl oxygen entry. For anionic carboxylate ~41% entry occurs for glycinate vs. ~10% for β-alaninate, but for the ester the two systems give more similar entries (~45% for glycinate vs. ~32% for β-alaninate). The former value is not a direct result, being derived from ^{18}O-tracer results on the rapidly formed $[Co(en)_2(glyO)]^{2+}$ ion.[2] The larger difference for the anionic competitor is probably related to specific H bonding to amine groups in the vicinity of the vacant coordination site. Such factors have already been discussed for the glycinate system.[3]

The presence of N_3^- introduces an additional competitor and it is interesting to note that the 36% *cis*- + *trans*-$[Co(en)_2N_3(\beta\text{-}alaO\text{-}i\text{-}Pr)]^{2+}$ (Table VIII) arises largely at the expense of $[Co(en)_2(\beta\text{-}alaO\text{-}i\text{-}Pr)]^{3+}$, which decreases from 32% to 10%. Such an effect can be interpreted as adjacent N_3^- in an N_3^- ion-paired intermediate obstructing entry of the ester oxygen to a greater extent than entry of solvate water when compared to the intermediate not containing N_3^-. Clearly capture of entering groups from at least two differently solvated or ion-paired intermediates is required by the results, but nothing concerning their lifetimes can be inferred; i.e. they could be in equilibrium with the bulk solution phase. However it is tempting to suggest that they are preformed before loss of X^-. Such effects have been noted previously in the hydrolysis of *cis*-$[Co(en)_2X(glyO)]^+$ where the results were analyzed in some detail.[3] No such analysis is warranted here with the limited data available, but the same gross effect is evident.

Registry No. $[Co(en)_2Br(\beta\text{-}alaO\text{-}i\text{-}Pr)]Br_2$, 101695-40-3; $(+)_{589}$-$[Co(en)_2Br(\beta\text{-}alaOCH(CH_3)_2)]Br_2$, 101914-10-7; $[Co(en)_2Br(\beta\text{-}alaOMe)]Br_2$, 101695-41-4; $[Co(en)_2Cl(\beta\text{-}alaO\text{-}i\text{-}Pr)]Cl_2$, 101695-42-5; *cis*-$[Co(en)_2Br(\beta\text{-}alaO\text{-}i\text{-}Pr)](ClO_4)_2$, 101695-44-7; $[Co(en)_2Br(\beta\text{-}alaOH)]Br_2$, 101695-45-8; *cis*-$[Co(en)_2Br(\beta\text{-}alaNH_2)]Br_2$, 62301-92-2; *trans*-$[Co(en)_2Br_2]Br$, 15005-14-8; *trans*-$[Co(en)_2Cl_2]Cl$, 14040-33-6; Hg, 7439-97-6; OH^-, 14280-30-9; β-alanine isopropyl ester hydrochloride, 51871-17-1; β-alanine methyl ester hydrochloride, 3196-73-4; β-alaninamide hydrobromide, 101695-46-9.