205. On the Mechanism of the Hg^{2+} and Base Induced Hydrolysis Reactions of the β_2-(*RR, SS*)-Co(trien)(glyOR)Cl^{2+} Ions (R = H, C_2H_5), Evidence for the Site of Deprotonation in the Reactive Conjugate Base

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Summary

Acid hydrolysis of the ester function in Δ-$(-)_{589}$-β_2-(*RR*)-[Co(trien)(glyOEt)Cl]$^{2+}$ ((−)-**1**) produces optically pure Δ-$(-)_{589}$-β_2-(*RR*)-[Co(trien)(glyOH)Cl]$^{2+}$ ((−)-**4**). Hg^{2+} induced removal of chloride in (−)-**4** follows the rate law $k_{obs} = k_{Hg}[Hg^{2+}]$ with $k_{Hg} = (1.36 \pm 0.03) \times 10^{-2}\,M^{-1}s^{-1}$, 25°, $\mu = 1.0$, and produces optically pure Δ-$(-)_{589}$-β_2-(*RR*)-[Co(trien)(glyO)]$^{2+}$ ((−)-**2**). Competition by NO_3^- occurs in this reaction ($[NO_3^-] = 1\,M$, 3%) indicating a path whereby external nucleophiles ($Y = NO_3^-$, H_2O) compete with the intramolecular carboxylate function for an intermediate of reduced coordination number. Rapid ring closure to **2** must ensue for $Y = H_2O$. Base hydrolysis of chloride in (±)-**1** produces (±)-**2** together with its diastereoisomer β_2-(*RS, SR*)-[Co(trien)(glyO)]$^{2+}$, ((±)-**3**), in which one secondary amine function has an inverted configuration. **2** and **3** incoporate ^{18}O-labelled solvent into the Co-O position of the coordinated carboxylate moiety (**2**: 9.0%; **3**: 12.3%) indicating that at least part of the product arises *via* intramolecular hydrolysis in β_2-hydroxo ethylglycinate intermediates *(Fig. 4)*. Base hydrolysis of (−)-**4** follows the rate law $k_{obs} = k_{OH}[OH^-]$ with $k_{OH} = (6.3 \pm 0.6) \times 10^{-4}\,M^{-1}s^{-1}$, 25°, $\mu = 1.0$ producing (−)-**2** (37–45%) and (−)-**3** (63–55%), the ratio being somewhat medium dependent. Competition by added N_3^- (1 M) occurs using (±)-**4** forming β_2-(*RR, SS*)-[Co(trien)(glyO)N_3]$^+$ (~2%) and β_2-(*RS, SR*)-[Co(trien)(glyO)N_3]$^+$ (~13%). Mutarotation at the secondary nitrogen centre is shown to occur after the rate determining loss of Cl^- in **1** and **4** and before the formation of **2** and **3**. It is concluded that this secondary nitrogen is the site of deprotonation in the reactive conjugate bases of **1** and **4**, and possible mechanisms for the mutarotation process are considered.

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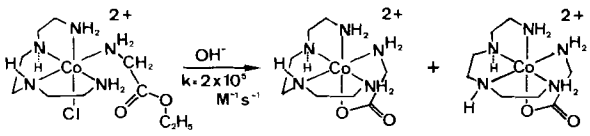
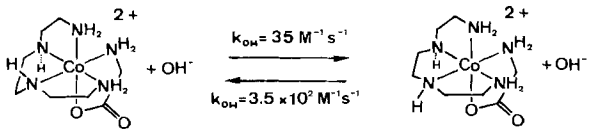
Introduction. - *Buckingham et al.* [1] have previously studied hydrolysis of the ester function in **1** during an investigation of the Hg^{2+} and OH^- assisted removal of Cl^-. In the latter reaction two diastereomeric chelated glycinate complexes, viz. **2** and **3** are formed. These are similar except for their configuration about one of the secondary amine functions *(Fig. 1)*.



1 **2** **3**

Fig. 1. *Base hydrolysis of* Δ-(RR)-β_2-*[Co(trien)(glyOEt)Cl]*$^{2+}$ (**1**)

Recently the results of X-ray structure determinations, structural energy minimization calculations, and the kinetic and thermodynamic parameters for the base-catalysed interconversion reactions *(Fig. 2)* for **2** and **3** were reported [2].



2 **3**

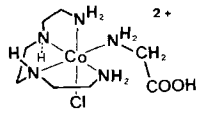
Fig. 2. *Mutarotation of* Δ-(RR)-β_2*[Co(trien)(glyO)]*$^{2+}$ (**2**) *and* Δ-(RS)-β_2-*[Co(trien)(glyO)]*$^{2+}$ (**3**)

These data [1] [2] demonstrate that although both mutarotation in **2** and **3** and base hydrolysis of chloride in **1** are catalysed by OH^- ions the former is a much slower process than the latter. This raises the following interesting questions:

(1) is the observed non-equilibrium distribution of isomers in base hydrolysis affected by substitutents at the carboxylate function, and by other species in solution;

(2) at what stage in the reaction does inversion at nitrogen occur, and

(3) can the proton leading to base hydrolysis be clearly distinguished.



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In this paper we report some results on the Hg^{2+}, and base induced, reactions of the chloro monodentate glycinate complex **4** (R = H), and on the order of events in the latter reaction: loss of Cl^-, mutarotation, and entry of carboxylate or water to give **2** and **3**. Also, using an ^{18}O label in the hydrolysis of **1** the incoming nucleophile (ester carbonyl or water) has been identified for each of **2** and **3**.

Preparation and Properties of 4. – (±)-**4** was obtained by hydrolysis of the ester function in (±)-**1** using concentrated hydrochloric acid. (+)-**4** was similarly obtained using the 3-bromo-(+)-10-camphor sulfonate salt of (+)-**1** ($[M]_{589}^{25} = 1843°$). In the ^{1}H-NMR. spectrum of **4**, the peaks of the ethoxycarbonyl group of the parent material ($\delta = 4.30$ ppm, *qa*, CH_2; $\delta = 1.27$ ppm, *t*, CH_3, rel. to ext. TMS) were absent, the other features being very similar. The IR. spectrum was similar to that of the starting material but showed an additional weak absorption at ~2500 cm^{-1} and the ν (C=O) stretching frequency had shifted from 1745 cm^{-1} to 1730 cm^{-1}. The UV./VIS. spectrum of (±) **4** in 1M HCl ($\varepsilon_{535} = 88$ $M^{-1}cm^{-1}$ (shoulder), $\varepsilon_{486.5} = 100$ $M^{-1}cm^{-1}$, $\varepsilon_{370} = 104$ $M^{-1}cm^{-1}$) was similar to that of (±)-**1** ($\varepsilon_{535} = 83$ $M^{-1}cm^{-1}$, $\varepsilon_{486.5} = 104$ $M^{-1}cm^{-1}$ and $\varepsilon_{369} = 111$ $M^{-1}cm^{-1}$). In an acidimetric titration **4** behaves as a monoprotonic acid with $pK_a \simeq 2.3$. This value could not be determined precisely as base hydrolysis of chloride interfered at pH > 4.

The Hg^{2+}-Induced Reaction. – The reaction

$$\beta_2(RR,SS)\text{-}[Co(trien)(glyOH)Cl]^{2+} + Hg^{2+} \longrightarrow \beta_2\text{-}(RR,SS)\text{-}[Co(trien)(glyO)]^{2+} + H^+ + HgCl^+$$

was followed spectrophotometrically, or using resolved material, polarimetrically *(Tab. 1)*. First-order runs at excess $[Hg^{2+}]$ gave linear plots of $\log(D_t - D_\infty)$ or $\log(\alpha_t - \alpha_\infty)$ *vs.* time for at least three half-lives. Isosbestic points occurred at 525, 416 and 321 nm in repetitive spectral scans. The experimental rate law

$$v = k_{Hg}[\text{complex}][Hg^{2+}]$$

holds. (+)-**4** ($[M]_{589}^{25} = 1843°$) gave (+)-**2** ($[M]_{589}^{25} = 1117°$). The VIS. spectrum and optical rotations of the latter were identical with that for (+)-**2** prepared and resolved separately [1] [2], and this establishes that the (+)-**4** is optically pure. Some 3% competition [3] for NO_3^- was found when (±)-**4** was hydrolysed with $Hg(NO_3)_2 \cdot \frac{1}{2} H_2O$ in 1M NO_3^-. From its elution behaviour on an ion-exchange column at pH 0 the competition product clearly has a 2+ charge. This species, Λ,Λ-β_2-(*RR*, *SS*)-[Co(trien)(glyOH)NO_3]$^{2+}$, is characterized by its VIS. absorption

Table 1. *Rate Data for the Hg^{2+}-induced Hydrolysis of β_2-(RR,SS)-[Co(trien)(glyOH)Cl](ClO$_4$)$_2$* (25°, $\mu = 1.0$, (ClO_4^-), $[Co]_t = (1 \pm 0.2) \times 10^{-3}$M)

$[Hg^{2+}]$ M	$[H^+]$ M	$10^4 k_{obs}$, s^{-1}	$10^2 k_{Hg^{2+}}$, $M^{-1}s^{-1}$
0.025	0.45	3.41	1.36[a]
0.025	0.45	3.42	1.37[a]
0.025	0.45	3.52	1.40[b]
0.05	0.45	6.60	1.32[a]
0.05	0.45	6.60	1.32[a]
0.05	0.45	6.85	1.37[b]
		mean value	
		$k_{Hg} = (1.36 \pm 0.03) \times 10^{-2} M^{-1}s^{-1}$	

[a] Spectrophotometric data at 550 nm.

[b] Polarimetric data at 550 nm, using Λ-(+)$_{589}$-β_2-(*SS*)-[Co(trien)(glyOH)Cl]Cl$_2 \cdot 1.5\ H_2O$.

($\varepsilon_{489} = 142$, maximum and $\varepsilon_{337} \approx 1000$, shoulder) and the spectrum remains unchanged over several hours in the presence of excess Hg^{2+}. These results eliminate possible contamination by unreacted starting material, or by β_2-[Co(trien)$(OH_2)_2$]$^{3+}$ ($\varepsilon_{487} = 122$, $\varepsilon_{357} = 85$), [4].

Base Hydrolysis. – *Table 2* lists kinetic data for the reaction

$$\Delta,\Lambda\text{-}\beta_2\text{-}(RR,SS)\text{-}[Co(trien)(glyOH)Cl]^{2+} + OH^- \longrightarrow \Delta,\Lambda\text{-}\beta_2\text{-}(RR,SS)\text{-}[Co(trien)(glyO)]^{2+} + \Delta,\Lambda\text{-}\beta_2\text{-}(RS,SR)\text{-}[Co(trien)(glyO)]^{2+} + Cl^- + H_2O$$

Plots of $\log(D_t - D_\infty)$, or for resolved starting material of $\log(\alpha_t - \alpha_\infty)$, *vs.* time were linear for three half-lives or more. Isosbestic points were observed at 526, 415.5, 367 and 322 nm in repetitive spectral scans. The kinetic data show a minor dependence on the nature of the buffer but are consistent with the usual rate law for such reactions:

$$v = k_{OH}[complex][OH^-]$$

with $k_{OH} = (5.6 \pm 0.1) \times 10^4\ M^{-1}s^{-1}$ in phosphate buffers, $k_{OH} = (6.8 \pm 0.2) \times 10^4\ M^{-1}s^{-1}$ in collidine buffers at 25°, $\mu = 1.0$ ($NaClO_4$).

Table 3 gives the product distributions under different conditions and it is clear that extensive inversion occurs about the N-centre joining the two chelate rings of trien in the same plane ('planar' sec. N). However, the β_2-(*RR, SS*)/β_2-(*RS, SR*) ratio also appears to vary with buffer concentration, and with pH. Hydrolysis of

Table 2. *Rate Data for the Base Hydrolysis of* β_2-(RR,SS)-*[Co(trien)(glyOH)Cl](ClO$_4$)$_2$* (25°, $\mu = 1.0$ ($NaClO_4$), $[Co]_t = (2 \pm 0.2) \times 10^{-3}$ M)

pH[a])	$10^4\ k_{obs}$, s^{-1}	$10^{-4}\ k_{OH}$[b]) [$M^{-1}s^{-1}$]
(a) Phosphate/$HClO_4$ buffer (0.1 M)		
5.66	4.20	5.42[c])
5.70	4.81	5.66[c])
6.20[e])	16.3	6.06[c])
6.21	14.7	5.33[c])
6.67	45.6	5.72[c])
(b) Collidine/$HClO_4$ buffer (0.1 M)		
6.93	100.8	6.98[d])
6.93	101.0	6.99[d])
6.97[e])	110	6.92[c])
7.01	119	6.87[c])
7.01	118	6.79[c])
7.26	199	6.52[d])
7.26	197	6.45[d])
7.29	217	6.56[c])
7.29	224	6.77[c])

[a]) pH of reaction mixture measured at the end of each run.
[b]) Calculated using pK_w (25°, $\mu = 1$ ($NaClO_4$)) = 13.77.
[c]) Spectrophotometric data at 550 nm.
[d]) Polarimetric data at 515 nm, using Λ-(+)$_{589}$-β_2-(*SS*)-[Co(trien)(glyOH)Cl]$Cl_2 \cdot 1.5\ H_2O$.
[e]) [Buffer] = 0.05 M.

Table 3. *Product Distributions for Base Hydrolysis of* β_2-(RR,SS)-*[Co(trien)(glyOH)Cl]*$^{2+}$ *in different media at* ~ 25°, 1.0M $NaClO_4$

pH	Buffer/conc. [M]	Time [s]	% Product β_2(RR,SS)	β_2(RS,SR)
7.23[a])	Tris, 0.5	286	37	63
7.23[a])	Tris, 0.5	280	36	64
7.23	Tris, 0.25	286	36	64
7.23	Tris, 0.1	286	47	53
5.50[b])	pH stat.	1740	45	55
7.23[c])	Tris, 0.1	250	32 (2, N_3)[d])	53 (13, N_3)[d])

[a]) *Λ*-(+)$_{589}$-β_2-(*SS*)-resolved complex; cf. Experimental Part.
[b]) pH-stat. titration with 0.1M NaOH.
[c]) 1M NaN_3, 0.5M $NaClO_4$.
[d]) Azido-glycinate complex arising in 1M N_3^-.

(+)-**4** at pH 7.23 gave 37% (+)-**2** ($[M]_{589} = +1140°$) and 63% (+)-**3** ($[M]_{589} = +857°$) and this corresponds to full retention of configuration about the metal centre for both diastereoisomers [1] [2]. In the presence of 1.0M N_3^- under the same conditions 2% *Λ*-(*SS*)- and 13% *Λ*-(*SR*)-β_2[Co(trien)(glyOH)N_3]$^{2+}$ were formed as well as 32% (+)-**2** and 53% (+)-**3**. Under the experimental conditions (pH 7.23, 4.1 min.) no significant base hydrolysis of either azido product was found to occur. Treatment of the *Λ*-(*SS*)-azido species with HNO_2 [5] [6] gave optically pure (+)-**2** and a corresponding result was found for the *Λ*-(*SR*)-azido ion, so that the azido products are formed with full retention of configuration. Thus no racemization about the Co-centre occurs in either the glycinate or azido competition products.

Partial Base Hydrolysis Experiments. – Hydrolysis of (−)-**1** for about one half-life at pH 5.67 and ion-exchange separation of the products resulted in the complete separation of optically pure (−)-**3** (20%), but in the incomplete separation of unreacted starting material and (−)-**2**. However subsequent treatment of the latter band with Hg^{2+} followed by ion-exchange produced <0.7% (−)-**3** with the remainder being optically pure (−)-**2** (79%). A similar experiment using racemic reactant and high pressure chromatography resulted in more rapid ion-exchange separation of the two bands, but again no (±)-**3** was detected (<0.1%) in the fraction containing the starting material. Thus inversion at the planar secondary N-centre in (±)-**1** does not occur prior to loss of chloride.

A similar result was found using the chloro-acid, (±)-**4**. In this case it was found essential to use the high pressure ion-exchange technique to separate (±)-**3** (32%) from the other two components. Subsequent treatment of the latter band with Hg^{2+} gave only (±)-**2** (68%) and no (±)-**3** (<0.1%).

^{18}O-Tracer Study of Base Hydrolysis of 1. – The incorporation of label in the base hydrolysis (±)-**1** in ^{18}O-labelled water has been determined previously [1], but the enrichment was not determined for the separate products, (±)-**2** and (±)-**3**.

This has now been done by separating the (*RR, SS*)- and (*RS, SR*)-β_2-[Co(trien)(glyO)]$^{2+}$ diastereoisomers using ion-exchange chromatography following base hydrolysis in H_2 ^{18}O. Subsequent complete exchange of the non-coordinated

carboxylate oxygen label in 0.1 M $HClO_4$ of normal isotopic composition (3 months, 20–25°) resulted in ^{18}O enrichments of 0.064% (*RR, SS*)-isomer, and 0.089% (*RS, SR*)-isomer, compared to a solvent figure of 1.47%. In a second separate experiment values of 0.040% (*RR, SS*), 0.056% (*RS, SR*) and 0.89% (solvent) were found. Relative to the solvent figure these duplicate experiments represent 4.4, 4.5% (*RR, SS*) and 6.0, 6.3% (*RR, SR*) enrichments in the coordinated glycinate moiety, and when account is taken for the fact that only the coordinated oxygen atom is enriched under the conditions this represents 8.8, 9.0% (*RR, SS*) and 12.0, 12.6% (*RS, SR*) incorporation of solvent label in this position. Clearly the results differ for the two diastereoisomers, although the combined result of ~11% ($8.85 \times 0.45 + 12.3 \times 0.55$) falls short of that found previously (16%) [1]. This discrepancy may reside in the different conditions used for the two experiments (pH 6.0 *vs.* 8.6 [1]).

Discussion. – This work parallels and extends that previously reported for **1** [1] with the configuration of Λ-$(-)_{589}$-β_2-(*RR*)-[Co(trien)(glyOH)Cl]$^{2+}$ being related to that of the corresponding glycine ethyl ester complex. The configurations of both the Λ-$(-)_{589}$-β_2-(*RR*)- and Λ-$(-)_{589}$-β_2-(*RS*)-[Co(trien)(glyO)]$^{2+}$ ions have been described in some detail previously [2].

Hg^{2+}-Induced Hydrolysis. The Hg^{2+}-induced removal of chloride from **4** resembles that for **1** in two respects; (1) it obeys the same rate law, $k_{obs} = k_{Hg}[Hg^{2+}]$ and occurs at a similar rate ($k_{Hg} = 1.35 \times 10^{-2}$ M^{-1} s^{-1} (**4**) *vs.* 1.0×10^{-2} M^{-1} s^{-1} (**1**)); (2) full retention of configuration about both the Co- and N-centres occurs. Both aspects are common to other Co(III)-amine systems [6] [7], and are fully consistent with the generally accepted S_N1_{lim} (or D) mechanism, involving the formation of a 5-coordinate intermediate of square pyramidal geometry which reacts with other species in solution [7]. However, the Hg^{2+}-induced reaction of the chloro-acid **4** differs from that found for **1** [1], or for the corresponding *cis*-[Co(en)$_2$(glyOEt)X]$^{2+}$

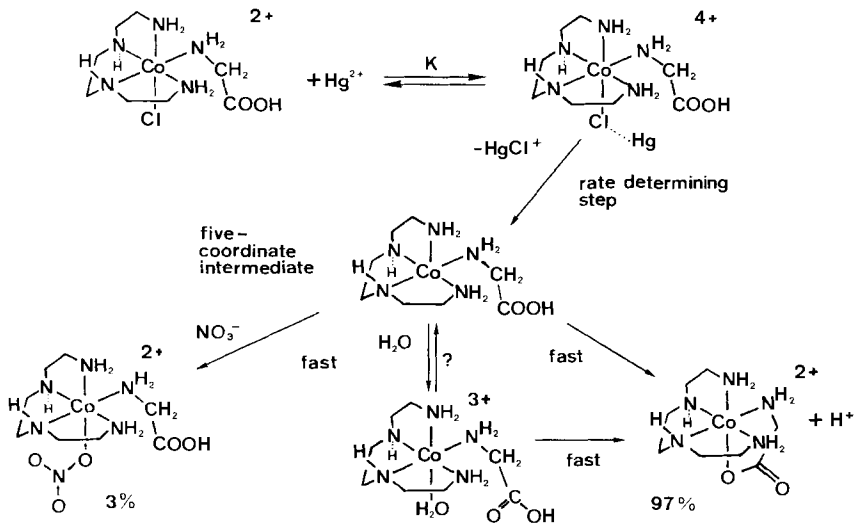

Fig. 3. *Proposed Mechanism for Hg^{2+}-Induced Hydrolysis of Λ-(RR)-β_2-[Co(trien)(glyOH)Cl]$^{2+}$* (**4**)

ions (X = Cl, Br) [8] [9], in that some β_2-(*RR, SS*)-$[Co(trien)(glyOH)(NO_3)]^{2+}$ is formed when the reaction is carried out in 1M NO_3^-. Thus 3% nitrato glycinate was recovered by ion-exchange chromatography and, in a less quantitative experiment, a similar amount of β_2-$[Co(trien)(glyOH)(SO_4)]^+$ was detected following hydrolysis in 1M H_2SO_4/0.1M Hg^{2+}. No competition by NO_3^- or HSO_4^- was observed in the similar reactions of **1** [1] or in the bis(ethylenediamine) system [8]. This implies that the 5-coordinate intermediate captures NO_3^- and HSO_4^- as well as the dangling carboxylate function and in this respect the latter appears to be a somewhat poorer nucleophile towards the cobalt centre than is the ester. Also, it has previously been shown that although anions such as NO_3^- and HSO_4^- are on a molar basis more effective than H_2O, at 1.0M Y^- the aqua product predominates [3] [6] [8]. Thus it might be expected that H_2O will compete in the present situation and that some β_2-(*RR, SS*)-$[Co(trien)(glyOH)OH_2)]^{3+}$ will be formed along with the glycinate chelate. Under the conditions used in the present experiments it is unlikely that this species would be detected, and certainly no 3+ ion was obtained by ion-exchange chromatography, and no secondary reaction was observed spectrophotometrically or polarimetrically following the removal of chloride. The similar *cis*-$[Co(en)_2(glyOH)(OH_2)]^{3+}$ ion has been prepared in a related study [10]; it cyclizes to $[Co(en)_2(glyO)]^{2+}$ *via* the intramolecular addition of the coordinated water molecule. This process is relatively rapid, $k_{obs} = 1.73 \times 10^{-2}\,s^{-1}$, and is pH independent (if pH < 4.5). It is clear that if a similar rate occurred following Hg^{2+}-induced hydrolysis of **4** it would remain unobserved. Alternatively, rapid water exchange in the β_2-(*RR, SS*)-$[Co(trien)(glyOH)(OH_2)]^{3+}$ ion would lead to the formation of β_2-(*RR, SS*)-$[Co(trien)(glyO)]^{2+}$ without incorporation of the bound water molecule, and this process would essentially reverse the competitive entry of solvent into the 5-coordinate intermediate. Certainly water exchange in the β-$[Co(trien)(H_2O)_2]^{3+}$ ion is a fast process (complete in 5 min [11]) and the anation of the related β_2-$[Co(trien)(NH_3)(OH_2)]^{3+}$ ion is also fast compared to that found for other pentaamine complexes [12].

Irrespective of the fate of the aqua-glycine complex it appears that the Hg^{2+}-induced reaction of **4** differs from that of **1** in degree at least (the latter argument can be used for **1** as well), and certainly the reaction differs from that for *cis*-$[Co(en)_2(glyOEt)Br]^{2+}$ where the properties of the aqua-ester complex prohibit its formation [13] in the Hg^{2+}-catalysed reaction.

Base Hydrolysis. The base hydrolysis of **1** and **4** also follow similar paths. The usual rate law obtains, $k_{obs} = k_{OH}[OH^-]$, consistent with the S_N1(CB) process [14–16]. The difference in k_{OH} values ($\sim 6 \times 10^4$ $M^{-1}s^{-1}$ (**4**) *vs.* $\sim 2 \times 10^5$ (**1**)) probably reflects the lower 1+ charge of **4** under the experimental conditions ($pK_a \simeq 2.3$ for the glycinate carboxyl proton in **4**). **1** shows little buffer dependence on the rate [1], but in **4** a minor specific buffer catalysis effect becomes apparent [$k_{OH} = (5.6 \pm 0.1) \times 10^4$ $M^{-1}s^{-1}$ (phosphate buffers); $k_{OH} = (6.8 \pm 0.2) \times 10^4$ $M^{-1}s^{-1}$ (collidine buffers)]. **1** and **4** both form the glycinato complexes **2** and **3** quantitatively but in different proportions. While the ester complex **1** forms 35% of the product inverted at the planar sec. N-centre [1], the acid complex **4** produces *(Tab. 3)* almost twice as much (55–64%). The extent of inversion in the products

of **4** is also rather sensitive to the concentration of buffer, with the higher buffer strengths giving rise to more inverted product. The reason for this product-determining effect is not clear at the present time but it may relate to the observed buffer catalysis of the rate. The presence of the buffer species at or near the N-centre during loss of chloride could influence the subsequent reprotonation and mutarotation processes, or alternatively the buffer base could prolong the lifetime of the intermediate and influence the mutarotation in this manner. Full retention of stereochemistry about the Co(III) centre obtains in both the (*RR, SS*) and (*RS, SR*) products of **4** (as well as **1** [1]). This property differs from that found for the *cis*-$[Co(en)_2(glyOR)X]^{2+}$ and *cis*-$[Co(en)_2(glyO)X]^+$ ions where some racemic $[Co(en)_2(glyO)]^{2+}$ is formed along with the stereoretentive product [16] [10].

Both **1** and **4** compete for added azide ion (1M) to give azido glycine ester [1] and azido glycinate complexes of both (*RR, SS*)- and (*RS, SR*)-configuration at the planar nitrogen. The glycine acid complex **4** seems to compete more effectively than **1**, with the observed distribution of (*RR, SS*)/(*RS, SR*)-azido products of 2:12 representing the largest discrimination in favour of the least thermodynamically stable (*RS, SR*)-configuration yet found. It also appears that the azido product arises largely at the expense of (*RR, SS*)-$[Co(trien)(glyO)]^{2+}$ and this represents a change in the (*RR, SS*)/(*RS, SR*)-ratio for the chelated glycinato complexes from 0.9 to 0.6 in 1M NaN_3 under otherwise the same conditions (0.1M Tris, *Tab. 3*). Medium effects obviously have a strong influence, revealing a more complex situation than uninhibited competition for the deprotonated intermediate(s). A similar observation has recently been made for H_2O, N_3^-, and $-CH_2COO^-$ competition for the intermediate(s) generated in the base hydrolysis of *cis*-$[Co(en)_2(glyO)X]^+$ ($X = Cl^-, Br^-$). Further discussion of the implications of these results will be taken up in a subsequent publication [17].

These features are interpreted in terms of the mechanistic schemes for **1** *(Fig. 4)* and **4** *(Fig. 5)*. They incorporate the generally accepted amine deprotonation preequilibrium [a], and rate determining loss of halide to give a reactive deprotonated intermediate of reduced coordination number [b] capable of competing for entering nucleophiles. In both cases mutarotation in the deprotonated reactant is ruled out [c] by the partial base hydrolysis experiments, but only in the case of **1** have the ^{18}O-tracer experiments been done to quantify intramolecular hydrolysis of the ester function *(Fig. 4)*. Thus 9% of the (*RR, SS*)-$[Co(trien)(glyO)]^{2+}$ is formed by this path and 12% of the (*RS, SR*)-diastereoisomer. These reactions will be somewhat faster than the base-catalysed removal of chloride, as estimates based on the related glycinamide and β-alanine ester complexes [18] [19] suggest rate constants of 7×10^{-1} s^{-1} and 5×10^{-3} s^{-1} for the aqua and hydroxo (at pH 7) glycine ethyl ester complexes, respectively. This is in agreement with the process not being observed. Also, it is possible that the above amounts do not accurately represent the incorporation of water into the 5-coordinate intermediate, since it is known that hydroxide exchange in the analogous β_2-$[Co(trien)(NH_3)(OH)]^{2+}$ ion is reasonably rapid [12] and for the hydroxo glycine ester species a similar process would lead directly, or indirectly *(Fig. 4 [d])*, back to the chelated ester. However, it is unlikely that the latter process is as fast as the intramolecular ester hydrolysis reaction at pH 7; certainly the results require it not to be appreciably faster.

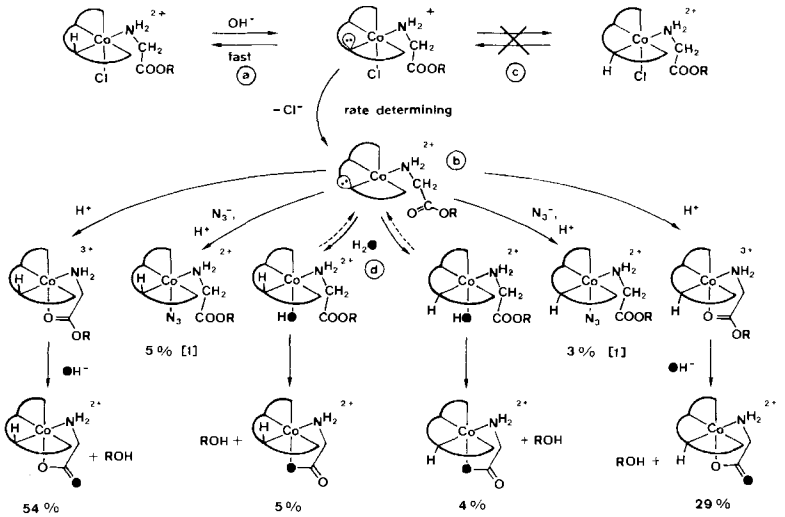

Fig. 4. *Proposed Mechanism for Base Hydrolysis of* Δ-(RR)-β_2-*[Co(trien)(glyOR)Cl]*$^{2+}$ (R = C_2H_5) (**1**) *in the presence of* 1M N_3^- (for symbols a–d see text)

For **4** it is unlikely that the (*RR, SS*)- and (*RS, SR*)-hydroxo glycinate ions *(Fig. 5)* result in direct formation of the glycinato chelate *via* an intramolecular process as for the ester. The corresponding intramolecular reaction for *cis*-$[Co(en)_2(glyO)(OH)]^+$ is very slow in slightly alkaline solution ($k_{obs} \simeq 10^{-4}$ s^{-1}, pH 7.4, [10]) and there is no reason to expect the rate for the trien complex to be especially different. No secondary reaction was observed spectrophotometrically, or polarimetrically, following hydrolysis of β_2-(*RR, SS*)-[Co(trien)(glyO)Cl]$^+$ at

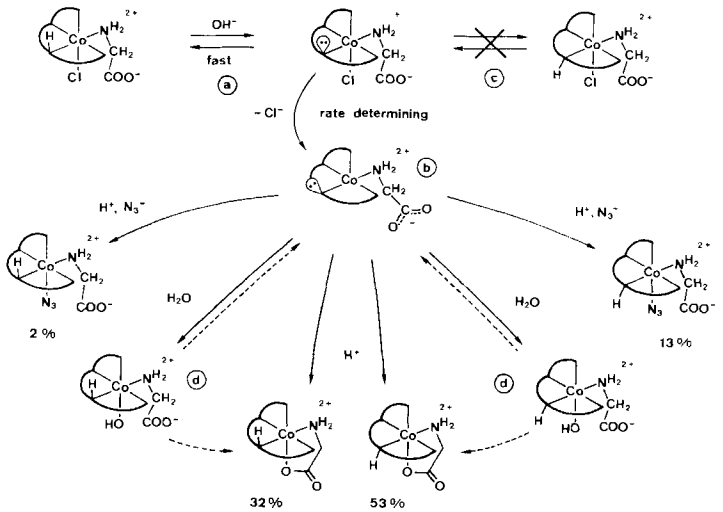

Fig. 5. *Proposed Mechanism for Base Hydrolysis of* Δ-(RR)-β_2-*[Co(trien)(glyOH)Cl]*$^{2+}$ (**4**) *in the presence of* 1M N_3^- (for symbols a–d see text)

pH 7.29 ($k_{obs} = 2{,}2 \times 10^{-2}$ s^{-1}) so that chelation in the hydroxo-glycinate complex undoubtedly formed must be appreciably faster than this. For this ion more rapid exchange of hydroxide is likely to occur [12], with return of the hydroxo glycinate to the five-coordinate intermediate *(Fig. 5 [d])*, or possibly synergic incorporation of the carboxylate moiety without the formation of the intermediate. This would predict the absence of solvent label in the Co-O position in the β_2-(*RR, SS*)- or β_2-(*RS, SR*)-[Co(trien)(glyO)]$^{2+}$ products and obviously an ^{18}O-tracer experiment is called for.

In summary, the present experiments and their comparison to observations in related systems indicate that the amounts of products formed from **4**, and possibly from **1**, do not provide information on the relative competition values for H_2O, $-CH_2COO^-$ and N_3^- for the five-coordinate intermediate(s) formed in the base hydrolysis reaction.

Two intriguing questions remain; the site of deprotonation leading to loss of chloride, and the lifetime of the five-coordinate intermediate. Some observations are worth making on these points. The first order in [OH^-]-dependence of the rate requires loss of only one proton as a necessary prerequisite for rapid loss of chloride, and the absence of mutarotation in **1** and **4** prior to this act, and the absence of mutarotation in the products **2** and **3** under the experimental conditions, requires inversion at the planar sec. N-centre to occur after the leaving group has gone beyond the transition state for bond breaking and before the glycinato chelate is formed in its ground state configuration. The possibility that in the partial base hydrolysis experiments any (*RS, SR*)-chloro ester, or (*RS, SR*)-chloro acid, inverts rapidly and quantitatively back to the (*RR, SS*)-species is most improbable as these species are isolated in acidic media where inversion at N has never been observed. Also, if the current valency rules for trivalent tetracoordinate nitrogen are maintained in these compounds inversion at the planar N-centre demands that it be deprotonated before this can occur. This coincidence requires either the deprotonated 5-coordinate intermediate to invert before it reacts, or a subsequent product such as the hydroxo-acid or -ester or chelated ester to mutarotate towards the observed value at a rate faster than, or at least commensurate with, its lifetime. The first possibility is unlikely for a normal Co(III) species since the rates of inversion at similarly charged 6-coordinate complexes have been estimated at 10^3–10^4 s^{-1}, and reprotonation rates are at least at the diffusion controlled limit, 10^9–10^{10} s^{-1} [20]. If the five-coordinate intermediate behaves similarly it will certainly reprotonate before it inverts, and possibly before it reacts with the entering group provided the reprotonation is largely an encounter process. Subsequent deprotonation of this reprotonated 3+ charged five-coordinate intermediate is unlikely to occur any more rapidly than for a similar six-coordinate 3+ ion ($k_H \simeq 10^7$–10^8 M^{-1}s^{-1}) so that equilibration between the (*RR, SS*)- and (*RS, SR*)-five-coordinate species seems unlikely on these grounds. Alternatively, inversion at N could be much faster than 10^3–10^4 s^{-1}, and this possibility arises if the five-coordinate intermediate has very different properties. A change in spin-state, or electron transfer in the deprotonated R_2N^-–Co(III) moiety to form $R_2\dot{N}$–Co(II), are especially attractive. The latter would undoubtedly mutarotate rapidly, and the results require that this compete for the reprotonation process.

Alternatively inversion at nitrogen and entry of the nucleophile could be concerted processes especially if the deprotonated N-centre is distorted towards the planar condition. For H_2O entry this is particularly attractive since intramolecular H-transfer, or H-transfer *via* intermediacy of the solvent, would occur on the side which leads to inversion. Certainly the water molecule will become increasingly acidic as the $Co-OH_2$ bond is made which would assist rapid H-transfer. However this latter mechanism cannot account for the extensive inversion in the azido products ($\sim 13\%$ (*RS, SR*) *vs.* $\sim 2\%$ (*RR, SS*)). Neither of these undergo significant base hydrolysis under the experimental conditions, but neither their mutarotation rates nor the rates of anation of the hydroxo intermediates by N_3^- have been measured. Clearly anation experiments, using β_2-(*RR, SS*)- and β_2-(*RS, SR*)-$[Co(trien)(NH_3)OH]^{2+}$ as models, will give some appreciation of whether or not the azido products derive directly from the five-coordinate intermediate, and kinetic measurements will determine whether or not mutarotation occurs in the azido glycinate products under the conditions used in the base hydrolysis experiments. These latter experiments may also give some appreciation of the rates of mutarotation in the hydroxo glycinate intermediates and the results of these and the experiments mentioned above will be reported in a subsequent publication.

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Experimental Part

Physical measurements and analytical procedures. UV./VIS. spectra, and the kinetic data, were obtained using *Cary* 14 or *Cary* 16K instruments fitted with high-intensity tungsten lamps. For the kinetic measurements a stopped-flow mixing device [16] attached to a 1 cm quartz cell was used. ^{1}H-NMR. spectra were run on *Jeol* Minimar 100 MHz or *HA* 100 instruments at 35° in D_2O/DCl. Optical rotations and polarimetric rate data were obtained on a *Perkin Elmer* 22 Spectropolarimeter using a 10 cm quartz cell. This was connected to a stopped flow mixing device [19] for the kinetic measurements. IR. spectra were recorded on a *Perkin Elmer* 257 instrument. Ion-exchange separations were carried out on Dowex 50WX2, 200–400 mesh cation exchange resin (35 × 1 cm, H^+ form). The volumes of the eluate fractions were determined by weighing against known volumes of the eluents. Cobalt was determined by atomic absorption spectrophotometry (AAS) using a Techtron AA4 instrument fitted with a high-intensity Co lamp.
Abbreviations: RT. = room temperature.

Preparation of (±)-β_2-(RR,SS)-*[Co(trien)(glyOH)Cl]*$Cl_2 \cdot 1.5\ H_2O$. (±)-β_2-(*RR, SS*)-$[Co(trien)(glyOC_2H_5)Cl]Cl_2$ [1] (6.9 g) was suspended in aqueous HCl-solution (37%, 25 ml) and allowed to stand at RT. in a stoppered flask. The starting material gradually dissolved to give a red solution. After eight days, 1-propanol was added to incipient crystallization. After a few minutes, the crystals were filtered off. More 1-propanol was added in portions to precipitate further fractions. Each of these was washed with chloroform and diethyl ether (total yield 5.6 g). The absence of unreacted ester complex was checked by ^{1}H-NMR. spectroscopy. The last few fractions were usually contaminated with some unreacted ester complex and were once more treated as above.

$C_8H_{23}Cl_3CoN_5O_2 \cdot 1.5\ H_2O$	Calc.	C 23.23	H 6.34	N 16.92%
(413.59)	Found	,, 23.20	,, 6.56	,, 16.70%

From this, the diperchlorate salt was obtained by repeated precipitation of the dichloride using 0.1M $HClO_4/NaClO_4$.

Preparation of Λ-(+)$_{589}$-β_2-(SS)-*[Co(trien)(glyOH)Cl]Cl$_2$* · 1.5 H_2O. Λ-(+)$_{589}$-β_2-(*SS*)-[Co(trien)(glyOC$_2$H$_5$)Cl](3-bromo-(+)-10-camphor sulfonate)$_2$ [1] (3 g, $[\alpha]_{589}^{25} = +244°$) was treated with aqueous HCl-solution (37%, 7 ml). A precipate formed which dissolved within a few hours. After seven days at RT., only a little residue remained which was dissolved by adding more aqueous HCl-solution (37%, 5 ml). After 24 h, 1-propanol (5 ml) was added portionwise. Crystals of the chloride salt (0.65 g, $[\alpha]_D^{25} = 450°$) separated which were collected and washed with ethanol and ether. Further addition of 1-propanol (20 ml) to the filtrate gave another fraction (0.27 g). The two fractions were recrystallized separately and gave $[\alpha]_{589}^{25} = 456°$ and 455°, respectively. The ^{1}H-NMR. spectrum showed no resonances of ethoxycarbonyl protons. The VIS. spectrum agreed with that of the racemate and the optical purity was established from the result of the Hg^{2+}-induced reaction (see below).

$C_8H_{23}Cl_3CoN_5O_2 \cdot 1.5\ H_2O$	Calc.	C 23.23	H 6.34	N 16.92%
(413.59)	Found	„ 23.23	„ 6.26	„ 16.46%

pK_a *determination on* (±)-β_2-(RR,SS)-*[Co(trien)(glyOH)Cl]*$^{2+}$. The chloride salt of this cation (100.47 mg, 0.243 mmol) was dissolved in aqueous $NaClO_4$-solution (1M, 20 ml). The solution was degassed with purified dinitrogen and titrated with carbonate free 0.5M NaOH using a combined glass electrode connected to a Radiometer TTT_1 titrator. For higher ratios $[OH]_{added}/[acid]_t$ no stable potentials were observed and the base consumption was higher than one equivalent due to incipient hydrolysis.

Product analysis in the Hg^{2+}*-induced reaction.* Λ-(±)$_{589}$-(*SS*)-β_2-[Co(trien)(glyOH)]Cl$_2$ · 1.5 H_2O (39.53 mg, 9.56×10^{-5} mol, $[\alpha]_{589}^{25} = 456°$ was treated (20 min) with a solution of $Hg(ClO_4)_2$ (10 ml, $[Hg^{2+}] = 0.5$, $[H^+] = 0.5$). The diluted reaction mixture (150 ml) was sorbed on a column and eluted with 1M HCl until tests for Hg^{2+} were negative. Elution with 1M NH_4Cl gave only one band (113.2 ml) with $\varepsilon_{478} = 132$, $\varepsilon_{347} = 149$, $\alpha_{589}^{25} = 0.095°$, $\alpha_{546}^{25} = 0.223°$ (whence $[M]_{589}^{25} = 1117°$, $[M]_{546}^{25} = 2636°$) based on AAS for Co (8.21×10^{-4}M).

Pure Λ-(+)$_{589}$-β_2(*SS*)-[Co(trien)(glyO)]$^{2+}$ has $\varepsilon_{478} = 130$, $\varepsilon_{347} = 146$, $[M]_{589}^{25} = 1130°$ and $[M]_{546}^{25} = 2611°$ [1] [2].

Competition for NO_3^- *in* Hg^{2+}*-induced reaction.* (±)-β_2-(*RR, SS*)-[Co(trien)(glyOH)Cl]Cl$_2$ · 1.5 H_2O (41.48 mg, 1.00×10^{-4} mol) was reacted (20 min) with a solution of Hg^{2+}/NO_3^- (10 ml, $[Hg^{2+}] = 0.05$, $[H^+] = 0.1$, $[NO_3^-] = 1.0$ Na^+ salt). The solution was diluted, sorbed on a column and eluted with 1M HCl to remove Hg^{2+}. 1M NH_4Cl (pH 3) eluted the first of two fractions ((±)-β_2-(*RR, SS*)-[Co(trien)(glyO)]$^{2+}$, 173.7 ml, $\varepsilon_{476} = 130$, $\varepsilon_{347} = 145$, $[Co] = 5.27 \times 10^{-4}$M (AAS), 92% of reactant). The second fraction was eluted with 2M H_2SO_4 (supposed β_2-(*RR, SS*)-[Co(trien)(glyOH)NO$_3$]$^{2+}$, 44.2 ml, $\varepsilon_{489} \simeq 136$, $\varepsilon_{340} \simeq 1000$ (shoulder); $[Co] = 6.51 \times 10^{-4}$M, 3% of reactant). The second fraction remained spectrally unchanged for 2 h upon addition of Hg^{2+}.

Product analysis in base hydrolysis. Λ-(+)$_{589}$-β_2-(*SS*)-[Co(trien)(glyOH)Cl]Cl$_2$ · 1.5 H_2O (37.42 mg, 9.06×10^{-5} mol, $[\alpha]_D^{25} = 456°$) was reacted (286 sec., $8 \times t_{1/2}$) in 'Tris' buffer (40 ml, 0.5M, pH 7.23, $\mu = 1$ (ClO_4^-)). The solution was acidified with 10M $HClO_4$ to pH 2, diluted (150 ml) and sorbed on a column. On elution with 1M NH_4Cl two bands separated which were analyzed by spectrophotometry, AAS (Co), by their ORD. curves or optical rotations at selected wavelengths. Band 1: Λ-(+)$_{589}$-β_2(*SR*)-[Co(trien)(glyO)]$^{2+}$, 57.7 ml, 9.69×10^{-4}M (62% of reactant, $\varepsilon_{484} = 148$, $\alpha_{589}^{25} = 0.084°$, whence $[M]_{589}^{25} = 857°$. Band 2: Λ-(+)$_{589}$-β_2(*SS*)-[Co(trien)(glyO)]$^{2+}$, 58.5 ml, 5.61×10^{-4}M (36% of reactant) $\varepsilon_{478} = 136$, $\alpha_{589}^{25} = 0.062°$, whence $[M]_{589}^{25} = 1140°$). Further experiments were carried out by the same procedure on racemic starting material using different buffers and media *(Tab. 3)*.

Base hydrolysis in the presence of 1M N_3^-*; product analysis.* Λ-(+)$_{589}$-β_2(*SS*)-[Co(trien)(glyOH)Cl]-Cl$_2$ · 1.5 H_2O (40.41 mg, 9.76×10^{-5} mol, $[\alpha]_D^{25} = 456°$) was dissolved in aqueous 2M NaN_3 (10 ml) and 'Tris' buffer (0.1M, pH 7.23, 10 ml, $\mu = 1$ (ClO_4^-)) and reacted for 250 sec. The solution was then adjusted to pH 4 (CH_3COOH, 100%). Elution from a column (1M, NH_4Cl, pH 2) separated four bands which were analyzed as above. Band 1: Λ-(+)$_{589}$-β_2-(*SR*)-[Co(trien)(glyO)]$^{2+}$, 77.5 ml, 6.42×10^{-4}M (51% of reactant), $\varepsilon_{485} = 151$; $\alpha_{589}^{25} = 0.057$, corresponding to $[M]_{589}^{25} = 860°$. Band 2: Λ-(+)$_{589}$-β_2-[Co(trien)(glyO)]$^{2+}$, 82.62 ml, 3.58×10^{-4}M (30% of reactant), $\varepsilon_{478} = 139$; $\alpha_{589}^{25} = 0.042°$, whence $[M]_{589}^{25} = 1094°$. Band 3: 101.8 ml, Λ-(+)$_{589}$-β_2-(*SR*)-[Co(trien)(glyO)N$_3$]$^{2+}$, 1.20×10^{-4}M (12% of

reactant, $\varepsilon_{513} \simeq 250$; $\alpha_{589}^{25} = 0.009°$, whence $[M]_{589}^{25} \simeq 750°$. Band 4: Λ-(+)$_{589}$-β_2-(*SS*)-[Co(trien)-(glyO)N_3]$^{2+}$, 158.72 ml, 1.39×10^{-5}M (2% of reactant), $\varepsilon_{512} \simeq 220$; $\alpha_{589}^{25} = 0.001°$ whence $[M]_{589}^{25} \simeq 720°$. The solutions containing the azido species were treated (20 min) with solid $NaNO_2$ (~ 50 mg) and $HClO_4$ (0.1 ml, 70%). N_2 was then passed through the solutions and their VIS. and ORD. spectra were run subsequently. Band 3: λ_{max} at 483 nm, ORD. zero crossing point at 486 nm. Band 4: λ_{max} at 478 nm, ORD. zero crossing point at 492 nm.

Partial base hydrolysis of Λ-(−)$_{589}$-β_2-(RR)-*[Co(trien)(glyOC$_2$H$_5$)-Cl](ClO$_4$)$_2$* · 0.5 *H$_2$O*. The complex (107.91 mg, 1.95×10^{-4} mol, $[\alpha]_D^{25} = -335°$) [1] was treated (25°, 450 sec., $1 \times t_{1/2}$) with sodium hydrogen phosphate buffer (50 ml, pH = 5.67, 0.2M, $\mu = 1$ (ClO_4^-)), acidified (pH 2.5 with hydrochloric acid), diluted (900 ml) and sorbed on a column, on elution (1M $HClO_4$), three bands appeared. The first orange band was completely separated from the following red and orange bands which overlapped. Band 1: Λ-(−)$_{589}$-β_2-(*RS*)-[Co(trien)(glyO)]$^{2+}$, 130.3 ml, 2.92×10^{-4}M (19.7% of reactant), $\varepsilon_{484} = 148$, $\alpha_{589}^{25} = 0.026°$, $[M]_{589}^{25} = -883°$. Bands 2 and 3 were eluted together (4M $HClO_4$) and the eluate was treated with excess acidic $Hg(ClO_4)_2$ solution (30 min), diluted and sorbed on another column (10 × 2 cm). After removal of Hg^{2+} (1M HCl), the material was completely eluted (3M HCl). The diluted eluate was sorbed again on the first column[3]). On elution (1M HCl) only one appeared. However, the eluate was collected before the band had reached the bottom of the column. Two fractions of the eluent were collected and analyzed for Co:

Fraction 1: (112 ml) $[Co] \leqslant 4.8 \times 10^{-6}$M; Fraction 2: (19.4 ml) $[Co] = 4.1 \times 10^{-5}$M. Together, they constituted < 0.7% of the reactant. The following fraction contained Λ-(−)$_{589}$-β_2-(*RR*)-[Co(trien)-(glyO)]$^{2+}$, 307 ml, 5.34×10^{-4} (78.9% of the reactant), $\varepsilon_{478} = 133$; $\alpha_{589}^{25} = -0.062$, $[M]_{589}^{25} = 1131°$. Some 36 h were required to complete this experiment. In a similar experiment racemic material (54.65 mg, 1.01×10^{-4}M) was treated as above (25°, 470 sec., $1 \times t_{1/2}$) and sorbed on a column (Aminex 50WX2, cation-exchange resin 200-250 mesh, 15 × 0.8 cm, H^+-form) of a Chromatronix high-pressure (30 atm) chromatography system. The (*RS,SR*)-isomer was eluted and the remaining components were, after treatment with Hg^{2+}, separated as before. Again only one band appeared ((*RR,SS*)-isomer), but in the eluent preceding this band, no cobalt was detected by AAS. This experiment required < 6 h to complete.

Partial base hydrolysis of (±)-β_2-(RR,SS)-*[Co(trien)(glyOH)Cl]Cl$_2$* · 1.5 *H$_2$O*. It was not possible to separate the unreacted starting material from β_2-(*RS,SR*)-[Co(trien)(glyOH)]$^{2+}$ using gravity chromatography. Thus, (±)-β_2-[Co(trien)(glyOH)Cl]Cl_2 · 1.5 H_2O (22.14 mg, 12×10^{-5} mol) was treated (35 sec., $0.8 \times t_{1/2}$) with buffer solutions (20 ml, Tris/$HClO_4$, 0.1M, pH 7.12, $\mu = 1.0$ ($NaClO_4$)), acidified (pH 3, 70% $HClO_4$), diluted and sorbed on the high-pressure chromatography column (see above) and eluted (1M $HClO_4$, 30 atm). Three bands were observed of which the last two were incompletely separated (see above). Band 1: (±)-β_2-(*RS,SR*)-[Co(trien)(glyO)]$^{2+}$, 17.06 ml, D_{484} (5 cm) = 0.637 (30.5% of reactant, based on $\varepsilon_{478} = 130$ $M^{-1}cm^{-1}$); Band 2 and 3: unreacted starting material and (±)-β_2-(*RR,SS*)-[Co(trien)(glyO)]$^{2+}$, 50.1 ml was treated (8 h) with solid hydrated $Hg(ClO_4)_2$ (250 mg, 5×10^{-4}M) to give (±)-β_2-(*RR,SS*)-[Co(trien)(glyO)]$^{2+}$ (D_{478} (10 cm) = 0.850, 64% of reactant, based on $\varepsilon = 130$ M^{-1} cm^{-1}). After removing Hg^{2+}, a subsequent separation procedure as above gave only one band and no Co was detected by AAS in the eluent preceding this band.

^{18}O-Tracer experiment. (+)-β_2-(*RR,SS*)-[Co(trien)(glyOC$_2$H$_5$)-Cl]Cl_2 (8.3 g, 0.02 mol) was hydrolyzed with alkali (Radiometer pH-stat, 1M NaOH, pH 6.0, 25 min 25°) in ^{18}O enriched water (100 ml). The solution was acidified (pH 3, 100% CH_3COOH) and the solvent was recovered by vacuum distillation (25°). The residue was dissolved in water (pH 3, $HClO_4$), sorbed on a column (1000 × 50 mm) and eluted (1M $HClO_4$). After 20 h, two bands had separated completely. Band 1: (±)-β_2-(*RS,SR*)-[Co(trien)(glyO)]$^{2+}$, had reached the bottom of the column. Band 2: (±)-β_2-(*RR,SS*)-[Co(trien)(glyO)]$^{2+}$. The moist resin was pushed out of the column and sections containing the bands were placed in a column and eluted with 1M HCl. The eluates were evaporated to dryness at room temperature. From the residue of band 1, the (*RS,SR*)-isomer crystallized as the chloride salt from methanol and it was recrystallized from water/methanol (1.09 g). From the other residue, the (*RR,SS*)-isomer crystallized as the diiodide (4.5 g) which was converted to the dichloride with excess AgCl.

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[3]) This procedure was necessary as removal of the Hg^{2+} caused spreading of the band(s) with possible loss of separation.

Solutions of the isomer (0.1M $HClO_4$) were then stored in the dark at RT. (94 days). From these, the isomers were recovered as the diiodides (950 mg (*RR,SS*); 2.1 g (*RS,SR*)). Glycine was recovered by heating the solids to 200–250° *in vacuo* for several hours. The resulting sublimate was extracted with absolute methanol/ether and dried in vacuo (24 h, 25°). The enrichment of the glycine was determined as described [8]. The values for $R_{CO_2} = I(m/e = 46)/I(m/e = 44)$ were 0.033461 for the solvent, 0.004753 for the (*RR,SS*)-isomer, 0.005247 for the (*RS,SR*)-isomer and 0.003460 for a sample of normal CO_2. In a second experiment, the separated (*RR,SS*)- and (*RS,SR*)-isomers were isolated as the diiodides and left in the dark for carbonyl oxygen exchange (0.1M HCl, RT., 153 and 158 days, respectively). Some poly-iodide crystallized under these conditions in the (*RR,SS*)-isomer. The ^{18}O-enrichments were determined as above. R_{CO_2} was 0.021980 for the solvent, 0.004683 for the (*RR,SS*)-isomer, 0.005011 for the (*RS,SR*)-isomer and 0.003879 for a sample of natural CO_2.

REFERENCES

[1] *D.A. Buckingham, D.M. Foster, L.G. Marzilli & A.M. Sargeson,* Inorg. Chemistry *9*, 11 (1970).
[2] *D.A. Buckingham, M. Dwyer, G.J. Gainsford, V. Janson Ho, L.G. Marzilli, W.T. Robinson, A.M. Sargeson & K.R. Turnbull,* Inorg. Chemistry *14*, 1739 (1975).
[3] *D.A. Buckingham, I.I. Olsen, A.M. Sargeson & H. Satrapa,* Inorg. Chemistry *6*, 1027 (1967).
[4] *A.M. Sargeson & G.H. Searle,* Inorg. Chemistry *6*, 787 (1967); *A.M. Sargeson & G.H. Searle,* Inorg. Chemistry *6*, 2172 (1967).
[5] *D.A. Buckingham, I.I. Olsen & A.M. Sargeson,* J. Amer. chem. Soc. *88*, 5443 (1966).
[6] *D.A. Buckingham, I.I. Olsen & A.M. Sargeson,* J. Amer. chem. Soc. *88*, 6654 (1968).
[7] *D.A. Buckingham, I.I. Olsen & A.M. Sargeson,* Austral. J. Chemistry *20*, 597 (1967).
[8] *D.A. Buckingham, D.M. Foster & A.M. Sargeson,* J. Amer. chem. Soc. *9*, 6032 (1968).
[9] *M.D. Alexander & D.H. Busch,* J. Amer. chem. Soc. *88*, 1130 (1966).
[10] *C. Boreham, D.A. Buckingham, D. Francis & A.M. Sargeson,* Manuscript in preparation.
[11] *D.A. Buckingham, K.R. Turnbull & A.M. Sargeson,* unpublished data.
[12] *D.A. Buckingham, M. Dwyer & A.M. Sargeson,* unpublished data.
[13] *D.A. Buckingham & M. Wein,* Inorg. Chemistry *13*, 3027 (1974).
[14] *M.L. Tobe,* Accounts chem. Res. *3*, 377 (1970).
[15] *A.M. Sargeson,* Pure appl. Chemistry *33*, 527 (1973).
[16] *D.A. Buckingham, D.M. Foster & A.M. Sargeson,* J. Amer. chem. Soc. *91*, 4102 (1969).
[17] *C. Boreham and D.A. Buckingham,* manuscript in preparation.
[18] *D.A. Buckingham, F.R. Keene & A.M. Sargeson,* J. Amer. chem. Soc. *96*, 4981 (1974).
[19] *E. Baraniak,* Ph. D. Thesis, Australian National University 1973.
[20] *B. Halpern, A.M. Sargeson & K.R. Turnbull,* J. Amer. chem. Soc. *88*, 4630 (1966); *D.A. Buckingham, L.G. Marzilli and A.M. Sargeson,* ibid. *89*, 825 (1967).