though the spectra sharpened on cooling to −190°, only one Cotton effect was still observed, probably due to the relatively small energy differences between the three components.

From the above discussion it is apparent that the observed CD spectra can be rationalized in terms of a vicinal effect from the L-amino acids imposing Cotton effects of opposite sign onto the two components of the E_g band, with the positive Cotton effect at lower energy. Unfortunately, the tetragonal splitting of the first cubic absorption band is not sufficiently large to enable the sign of the Cotton effect of the $A_{1g} \rightarrow A_{2g}$ (D_{4h}) transition to be assigned unambiguously. Nevertheless, the general shape of the observed CD bands and, for some spectra, the position of the high-energy negative Cotton effect suggest that this transition has a negative Cotton effect. This is supported by a study[2] of complexes of the type *trans*-$Co(en)_2(L\text{-}amH)_2^{3+}$, which also have a tetragonal chromophore with the E_g transition at the lower energy. For these complexes, the tetragonal splitting is twice that for the monocarboxylato complexes, and the E_g and A_{2g} components are visibly separated in the absorption spectra. For L-alanine and L-proline, two negative bands are clearly observable under the T_{1g} band, with one directly under the A_{2g} absorption band.

In theory, the signs of the Cotton effects of the d–d transitions of these pentaamminecobalt(III) complexes could be used to assign an absolute configuration to a new α-amino acid. However, in practice, this method is handicapped by the large variation in the observed Cotton effects. This type of system has previously been proposed for the determination of the absolute configuration of α-substituted carboxylates.[10] However, Dunlop and Gillard's proposal that the sign of the dominant Cotton effect for the T_{1g} band is indicative of the absolute configuration would seem to have no foundation.

Acknowledgment.—The authors gratefully acknowledge financial support from the Australian Research Grants Committee and record their appreciation for the assistance given by Mr. C. L. Wong.

(10) J. H. Dunlop and R. D. Gillard, *Tetrahedron*, **23**, 349 (1967).

CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY,
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Cobalt(III)-Promoted Hydrolysis of Glycine Ethyl Ester. Hg^{2+}-Induced Acid Hydrolysis and Base Hydrolysis of the β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ Ion

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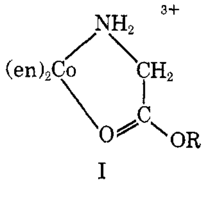
Received July 8, 1969

Hg^{2+}-induced acid hydrolysis of β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ follows the rate law $k_{obsd} = k[Hg^{2+}]$, with $k = 1.0 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°, $\mu = 1.0$. Full retention of configuration is observed, and ^{18}O-tracer studies enable the two positions for oxygen in the β_2-$Co(trien)gly^{2+}$ product to be distinguished. Base hydrolysis of β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ follows the rate law $k_{obsd} = k[OH^-]$, with $k = 2.2 \times 10^5\ M^{-1}\ sec^{-1}$ at 25°, $\mu = 1.0$. Full retention of configuration about the metal is observed. Base hydrolysis in ^{18}O-labeled solvent shows that 84% of the β_2-$Co(trien)gly^{2+}$ product arises from coordination of the ester carbonyl oxygen, while the remainder is produced by intervention of a solvent oxygen atom in the bridging position. The latter path is interpreted as an internal nucleophilic displacement of the ester moiety by bound OH^- ion. Visible, CD, and ORD spectra are presented for D(+)$_{589}$-(*SS*)-β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2 \cdot 0.5H_2O$.

Introduction

In a recent publication it was demonstrated that the Hg^{2+}- and HOCl-induced removal of bromide from $Co(en)_2Br(glyOR)^{2+}$ ($R = CH_3$, $CH(CH_3)_2$) leads to the formation of the chelated ester intermediate $Co(en)_2(glyOR)^{3+}$ (I) in which the oxygen atom bound to cobalt is derived from the carbonyl oxygen atom of the monodentate ester. Tracer experiments were used to distinguish between the two oxygen atoms of the chelated glycinate anion of $Co(en)_2gly^{2+}$ formed on acid hydrolysis of I, and the results demonstrated that ester hydrolysis proceeded without opening of the chelate ring.[1]



I

In a separate investigation it was proposed that $Co(en)_2gly^{2+}$ formed by base hydrolysis of $Co(en)_2Br(glyOCH(CH_3)_2)^{2+}$ arose from two paths. About half was produced by incorpation of the ester carbonyl oxygen to form the intermediate given by structure I, while the second path was attributed to coordination of hydroxide ion to form $Co(en)_2OH(glyOCH(CH_3)_2)^{2+}$, followed by internal attack by the bound hydroxide at the carbonyl center.[2]

(1) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6032 (1968).

(2) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *ibid.*, **91**, 4102 (1969).

These studies raised several questions pertinent to the understanding of mechanisms of hydrolysis of amino acid esters at a cobalt(III) center. For example, in the base hydrolysis of $(-)_{589}$-$[Co(en)_2Br(glyOCH_3)]^{2+}$ equal amounts of $(-)_{589}$- and *rac*-$Co(en)_2gly^{2+}$ were formed, and the question arose as to whether these products were related by the two paths for hydrolysis.[2] Also, are intermediates similar to I formed in the Hg^{2+}-induced reaction and base hydrolysis of other $CoN_4X(glyOR)^{2+}$ complexes, and do such intermediates have similar properties to the analogous bis-ethylenediamine compounds? Does base hydrolysis result in the formation of any *cis*-$CoN_4(OH)(glyOR)^{2+}$ ion, and does this ion subsequently hydrolyze by internal attack of bound hydroxide? It was reasoned that these and related questions might be answered by studying the hydrolysis of other suitable cobalt(III) systems.

During base hydrolysis β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ ion loses Cl^- ion $\sim 10^3$ times more rapidly than the similar bis-ethylenediamine complex. Also, unlike the latter complex, the triethylenetetramine compound has the advantage that only chelated glycinato products are formed.[3] In this paper we report the results of kinetic, stereochemical, and ^{18}O-tracer studies of the two reactions

$$\beta_2\text{-Co(trien)Cl(glyOC}_2\text{H}_5)^{2+} + \text{Hg}^{2+} + \text{H}_2\text{O} \longrightarrow \beta_2\text{-Co(trien)gly}^{2+} + \text{C}_2\text{H}_5\text{OH} + \text{HgCl}^+ + \text{H}^+ \quad (1)$$

$$\beta_2\text{-Co(trien)Cl(glyOC}_2\text{H}_5)^{2+} + \text{OH}^- \longrightarrow \beta_2\text{-Co(trien)gly}^{2+} + \text{Cl}^- + \text{C}_2\text{H}_5\text{OH} \quad (2)$$

Experimental Section

Visible spectra were recorded on a Cary Model 14 spectrophotometer and rotatory dispersion (RD) curves were recorded on a PE 141 polarimeter fitted with a Zeiss monochromator and quartz–iodine lamp or on a Cary 60 spectropolarimeter. The CD spectrum was measured on a Jouan Dichrographe. Oxygen-18 analysis of the CO_2 samples recovered from the complexes was carried out with Atlas M86 or Atlas GD150 mass spectrometers. Dowex 50WX2, 200–400 mesh, cation-exchange resin was used in chromatographic separations.

Preparation and Resolution of β_2-$[Co(trien)Cl(glyOC_2H_5)]Cl_2$.—An improved method of preparing this compound[3] is the following. A mixture of β_2-$[Co(trien)Cl_2]Cl\cdot H_2O$ (6.3 g) and glycine ethyl ester hydrochloride (2.8 g) was ground to a fine powder and water (2 ml) was added. N-Methylethylenediamine (1.2 g) in water (1 ml) was added dropwise over 1 hr with continuous stirring of the thick paste. In the latter stages, a few drops of water were added to facilitate mixing. The paste eventually became red-brown and hardened. It was ground with ethanol and acetone and then collected. The crude product was dissolved in a minimum volume of hot dilute 0.1 *N* HCl and the resulting solution was filtered and cooled in an ice bath. The red crystals were washed with cold 0.1 *N* HCl, ethanol, and ether and then air dried. A further crop was obtained by adding LiCl. One further recrystallization was necessary to give a pure product. *Anal.* Calcd for $[Co(trien)Cl(glyOC_2H_5)]Cl_2$: C, 28.96; H, 6.56; N, 16.89. Found: C, 29.01; H, 6.68; N, 17.00. The perchlorate salt was obtained by recrystallizing the chloride salt three times from hot 0.01 *M* $HClO_4$ and adding excess $NaClO_4$. *Anal.* Calcd for $[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2$: C, 22.13; H, 5.02; N, 12.91. Found: C, 22.34; H, 4.97; N, 12.66.

A mixture of β_2-$[Co(trien)Cl(glyOC_2H_5)]Cl_2$ (15 g) and Ag(+)-BCS·H_2O (28.6 g) was shaken for 10 min with warm water (170 ml) and HCl (2 drops, 11.6 *N*) was added. The solution was filtered and the AgCl was washed with warm water (40 ml). On standing at room temperature the *l*-(+)BCS salt separated from the combined filtrate and washings and this was collected (4.5 g, α_{589} −0.125° for a 0.1% solution). The filtrate was then cooled overnight at 10° and the *d*-(+)BCS salt separated (6.3 g, α_{589} +0.210° for a 0.1% solution). Several further fractions of both diastereoisomers were obtained which were combined and recrystallized to constant rotation. The final products were $(-)_{589}$- and $(+)_{589}$-β_2-$[Co(trien)Cl(glyOC_2H_5)]((+)BCS)_2$, 3.1 g, $[\alpha]_{589}$ −121°, and 1.9 g $[\alpha]_{589}$ +244°, respectively. *Anal.* Calcd for $[Co(trien)Cl(glyOC_2H_5)](C_{20}H_{30}O_9S_2Br_2)_2$: C, 37.37; H, 5.75; N, 7.27. Found for the $(-)_{589}$ isomer: C, 37.15; H, 5.68; N, 7.48. Found for the $(+)_{589}$ isomer: C, 37.27; H, 5.88; N, 7.19. These diastereoisomers were ground in a mortar with excess $NaClO_4$ and methanol and the resulting perchlorate salts were recrystallized several times from hot water (pH ~4) by adding $NaClO_4$. *Anal.* Calcd for β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2\cdot 0.5H_2O$: C, 21.77; H, 5.12; N, 12.70. Found for the $(-)_{589}$ isomer: C, 21.91; H, 5.17; N, 12.58. Found for the $(+)_{589}$ isomer: C, 21.59; H, 4.97; N, 12.65. A 0.1% solution of $(-)_{589}$-β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2\cdot 0.5H_2O$ gave α_{589} −0.332°; hence $[\alpha]_{589}$ is −332°. For the $(+)_{589}$ isomer α_{589} is 0.336°; hence $[\alpha]_{589}$ is 336°.

Carbonyl-^{18}O-labeled β_2-$[Co(trien)Cl(glyOC_2H_5)]Cl_2$ was prepared as described above from β-$[Co(trien)Cl_2]Cl$ (6.2 g), carbonyl-^{18}O-labeled glycine ethyl ester hydrochloride[1] (2.8 g), H_2O (2 ml), and N-methylethylenediamine (1.2 g). *Anal.* Calcd for $[Co(trien)Cl(glyOC_2H_5)]Cl_2$: C, 28.16; H, 6.56; N, 16.89. Found: C, 28.86; H, 6.63; N, 16.97. This salt was converted to the perchlorate by recrystallizatiom from hot 0.1 *M* $HClO_4$ using $NaClO_4$.

Competition Experiments in the Hg^{2+} Reaction.—β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2$ (*ca.* 0.1 mol) was dissolved in a solution (10 ml) containing HNO_3 (0.1 *M*), $Hg(NO_3)_2$ (0.1 *M*), and $NaNO_3$ (1 *M*). A similar experiment used H_2SO_4 (0.1 *M*), $Hg(NO_3)_2$ (0.1 *M*), and Li_2SO_4 (0.9 *M*). After 1 hr at ~25° the visible spectra were recorded. The diluted solutions were then sorbed on an ion-exchange resin and eluted with 1 *M* $NaClO_4$.

Base Hydrolysis.—$(+)_{589}$-β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2\cdot 0.5H_2O$ (0.0329 g, $[\alpha]_{589}$ 336°) was treated with "Tris" buffer (50 ml), pH 8.15, for 1 min at 25° and then neutralized to pH ~4 and sorbed on a cation-exchange resin. Elution with 1 *M* NH_4Cl resulted in the separation of two glycinato bands. These were collected and estimated by spectrophotometry, by polarimetry, and by atomic absorption spectroscopy for cobalt. Band 1, $(+)_{589}$-(*SR*)-β_2-$Co(trien)gly^{2+}$: 100 ml, 1.88×10^{-4} *M* (32% of reactant), ϵ_{486} 142, α_{589} 0.034° giving $[\alpha]_{589}$ 157°. Band 2, $(+)_{589}$-(*SS*)-β_2-$Co(trien)gly^{2+}$: 100 ml, 3.77×10^{-4} *M* (63%), ϵ_{478} 134, α_{589} 0.042° giving $[\alpha]_{589}$ 202°.

Base Hydrolysis in the Presence of Azide Ion.—A solution of $(+)_{589}$-β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2$ (0.0714 g, $[\alpha]_{589}$ +336°) was hydrolyzed in 1 *M* NaN_3 buffered with acetic acid (10 ml, pH 7) for 20 min, adjusted to pH 4 with acetic acid, diluted, sorbed on an ion-exchange resin (Dowex 50W, 200–400 mesh, Na^+ form), and eluted with 1 *M* NH_4Cl. Four bands separated, corresponding to two orange glycinato and two red azido products. These were analyzed by spectrophotometry, by atomic absorption spectroscopy for Co, and from their rotatory dispersion curves. Band 1, $(+)_{589}$-(*SR*)-β_2-$Co(trien)gly^{2+}$: 115 ml, 3.60×10^{-4} *M* (32% of reactant), ϵ_{486} 143, α_{589} +0.032° giving $[\alpha]_{589}$ +161°. Band 2, $(+)_{589}$-(*SS*)-β_2-$Co(trien)gly^{2+}$: 108 ml, 6.695×10^{-4} *M* (56%), ϵ_{478} 134, α_{589} +0.076° ($[\alpha]_{589}$ +206°). Band 3, $(+)_{589}$-(*SR*)-β_2-$Co(trien)N_3(glyOC_2H_5)^{2+}$: 75 ml, 4.877×10^{-5} *M* (3%), ϵ_{510} ~350, α_{589} +0.004°. Band 4, $(+)_{589}$-(*SS*)-β_2-$Co(trien)N_3(glyOC_2H_5)^{2+}$: 175 ml, 3.02×10^{-5} *M* (5%), ϵ_{510} ~340, α_{589} +0.005°. The azido products were then treated with HNO_2 at pH 1 and their visible and RD spectra were remeasured. Band 3 gave λ_{max} 485 mμ with an RD curve crossing zero at 587 mμ. Band 4 gave λ_{max} 480 mμ with an RD curve crossing zero at 492 mμ. Band 1 was equilibrated at pH

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[3] L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967).

~8.5 for 30 days and then neutralized to pH 4 (ϵ_{479} 133), diluted, and sorbed on an ion-exchange resin. Elution with 1 *M* NH_4Cl gave two bands corresponding to the two β_2 glycine isomers.

Kinetics.—Spectrophotometric rates were followed on a Cary 14 spectrophotometer using 1- or 5-cm cells. Polarimetric rates were followed on a Perkin-Elmer 141 polarimeter using a thermostated 1-dm cell. To weighed amounts of β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ was added 25 ml of the appropriate Hg^{2+} or buffer solution at 25°, and the solution was quickly transferred to the thermostated cell.

Oxygen-Exchange Experiments. (a) Carbonyl-O^{18}-labeled [Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ (4 g) was dissolved with Hg(NO$_3$)$_2$ (7 g) in 0.1 *M* HClO$_4$ (20 ml) and the solution was stirred and left for 15 min. After filtration, excess NaI was added to the filtrate and the precipitate of [Co(trien)gly]I$_2$, [Co(trien)gly]HgI$_4$, and HgI$_2$ was collected, washed with methanol, and air dried. The product was shaken with excess AgCl in 20 ml of 0.1 *M* HClO$_4$ and filtered, and the filtrate was made up to 50 ml, 0.1 *M* in HClO$_4$, μ = 1.0 (NaClO$_4$). Aliquots (10 ml) were sampled at appropriate intervals by precipitating the complex as the HgI_4^{2-} salt and converting the oxygen to CO$_2$.[1]

(b) The above procedure was repeated for unlabeled [Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ (4 g) in $H_2{}^{18}O$ (~2 atom %, 20 ml) using 3 drops of 70% HClO$_4$ and Hg(NO$_3$)$_2$ (7 g).

(c) Unlabeled [Co(trien)Cl(glyOC$_2$H$_5$)]Cl$_2$ (6.5 g) was hydrolyzed in water (70 ml, *ca.* 2 atom % ^{18}O) for 30 min, by pH-stat titration at pH 8.6 using 0.5 *M* NaOH. The neutralized solution (pH ~4) was reduced to 30 ml on a rotary evaporator, and excess NaI was added. On cooling, [Co(trien)gly]I$_2$ precipitated. This was washed with methanol and ether and dried in an evacuated desiccator (5.3 g). The product was converted to the chloride using excess AgCl, and the filtrate (20 ml) was made up to 50 ml, 0.1 *M* in HClO$_4$, μ = 1.0 (NaClO$_4$). This solution was kept at 25°, 5-ml aliquots were periodically withdrawn, and their ^{18}O enrichment was determined as in (a) above.

A duplicate run employed 30 ml of ^{18}O-labeled water and 4 g of complex. A representative sample of the recovered β_2-[Co(trien)gly](HgI$_4$) was converted to the chloride salt and sorbed to and eluted from an H$^+$ form resin. Only the (*SS* + *RR*) isomers were found. However, the duration of base hydrolysis (30 min, pH 8.6) was sufficient for this sample to be representative of all of the glycine isomers formed.[4]

(d) Carbonyl-^{18}O-labeled [Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ (6.5 g) was hydrolyzed in unlabeled water (100 ml, 30 min) at pH 8.5 and treated as in (c) above. The isolated Co(trien)gly^{2+} product showed the following enrichments on exchange in 0.1 *M* HClO$_4$ (μ = 1.0, NaClO$_4$): 0.560, 0.483, 0.564, 0.497, 0.487, and 0.462 atom % ^{18}O after 5, 9, 15, 20, 30, and 40 days, respectively. The enrichments of the parent ester complex and hydrolyzed product were not determined initially, but it is apparent from the rate of label exchange that very little if any of the label can be present in the oxygen not bound to cobalt.

Results

Preparation and Resolution.—β_2-[Co(trien)Cl(glyOC$_2$H$_5$)]Cl$_2$ was obtained in good yield by triturating a moist mixture of β-[Co(trien)Cl$_2$]Cl and glycine ethyl ester hydrochloride with almost 2 equiv of N-methylethylenediamine. Lower yields were obtained using triethylamine and diethylamine as the base to initiate the reaction.[5,6] Treatment of β_2-[Co(trien)Cl(glyOC$_2$H$_5$)]Cl$_2$ with silver (+)bromocamphor-π-sulfonate (Ag(+)BCS) gave (−)$_{589}$-(*RR*)-β_2-[Co(trien)Cl(glyOC$_2$H$_5$)]((+)BCS)$_2$ as the least soluble diastereoisomer from which (−)$_{589}$-(*RR*)-β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ ([α]$_{589}$ −332°) was obtained by trituration with LiClO$_4$.[7] The (+)$_{589}$-(*SS*)-β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ isomer ([α]$_{589}$ 336°) was obtained from the more soluble diastereoisomer fractions. The visible–uv spectrum and rotatory dispersion (RD) and CD curves of (+)$_{589}$-(*SS*)-β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ are given in Figure 1.

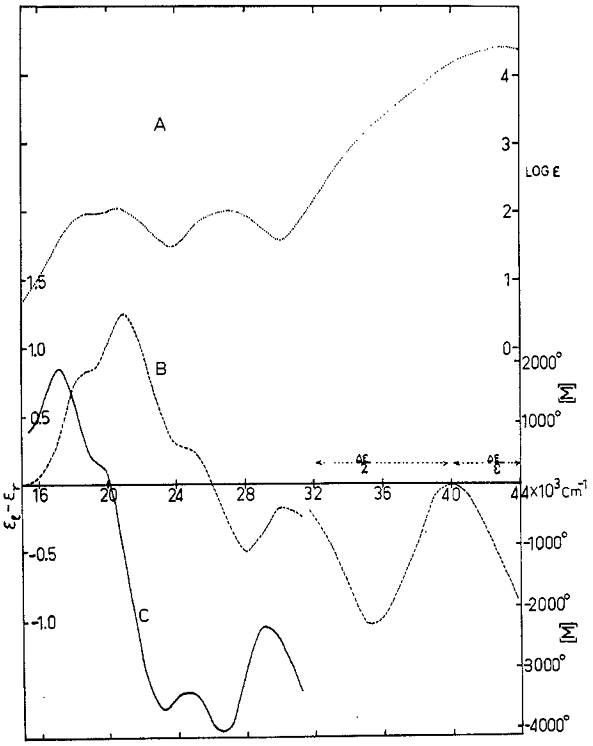

Figure 1.—(A) Visible spectrum (· · · · · ·), (B) CD curve (-----), and (C) RD curve (———) for (+)$_{589}$-(*SS*)-β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ in 0.01 *M* HClO$_4$.

Hg^{2+}-Induced Reaction.—Table I gives spectrophotometric and polarimetric rate data for reaction 1.

TABLE I

RATE DATA FOR THE Hg^{2+}-ASSISTED HYDROLYSIS OF β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ AT 25°, μ = 1.0 (NaClO$_4$)

[Hg^{2+}], *M*	[H$^+$], *M*	10^3k_{obsd}, sec^{-1}	10^2k_{Hg}, *M*$^{-1}$ sec^{-1}	Method[a]
0.1	0.05	0.90	0.90	S
0.1	1.0	1.00	1.00	P
0.2	1.0	2.10	1.05	P
0.2	1.0	1.99	1.00	S

[a] S = spectrophotometric; P = polarimetric.

Plots of log ($D_t - D_\infty$) at 350 mμ or log ($\alpha_t - \alpha_\infty$) at 540 mμ *vs.* time were linear for more than 3 half-lives, and isosbestic points occurred at 520, 420, and 367 mμ in the spectrophotometric runs. The data fit the rate law $R = k_{Hg}$[complex][Hg^{2+}], and there is no appreciable dependence on H$^+$ concentration.

From optically pure (+)$_{589}$-(*SS*)-β_2-Co(trien)Cl(glyOC$_2$H$_5$)$^{2+}$ ([α]$_{589}$ 336°) optically pure (+)$_{589}$-(*SS*)-β_2-Co(trien)gly^{2+} was obtained, [α]$_{589}$ 206°. The visible

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(4) D. A. Buckingham, L. G. Marzilli, K. R. Turnbull, and A. M. Sargeson, unpublished results.

(5) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 602 (1966).

(6) J. Meisenheimer and K. Kiderlen, *Ann.*, **438**, 212 (1924); J. C. Bailar and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945); A. Ablov, *Bull. Soc. Chim. France*, [5] **4**, 1783 (1937).

(7) *R* or *S* designates the absolute configuration about the two secondary N atoms joining ethylenediamine residues in different or the same coordination planes, in that order.

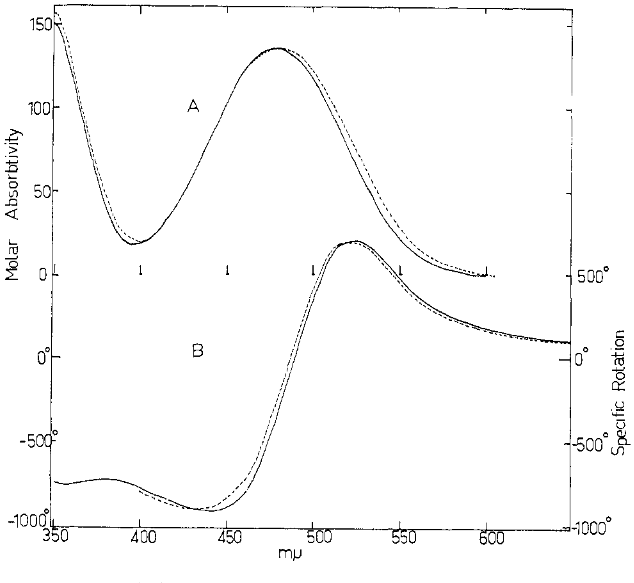

Figure 2.—(A) Visible spectra and (B) RD curves for $(+)_{589}$-(SS)-β_2-Co(trien)gly^{2+} prepared by treating $(+)_{589}$-(SS)-β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ in 1 M HClO$_4$ with 0.2 M Hg(ClO$_4$)$_2$ (———) and $(+)_{589}$-β_2-Co(trien)gly^{2+} formed by base hydrolysis of $(+)_{589}$-(SS)-β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ in 0.01 M NaOH (-----).

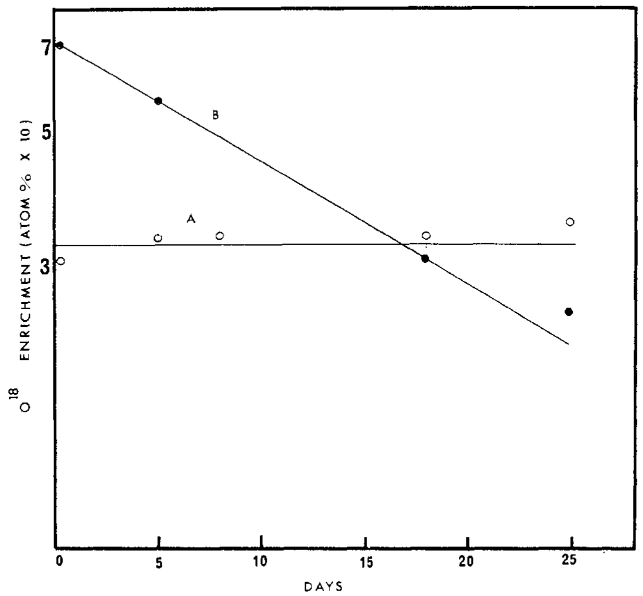

Figure 3.—Oxygen-18 exchange in (A) β_2-Co(trien)gly^{2+} prepared from carbonyl-^{18}O-labeled β_2-[Co(trien)Cl(glyOC$_2$H$_5$)]-(ClO$_4$)$_2$ in normal water and in (B) β_2-Co(trien)gly^{2+} prepared from unlabeled β_2[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ in H$_2{}^{18}$O (0.1 M HClO$_4$, μ = 1.0, 25°).

spectrum and RD curve for this product, Figure 2, were identical with those of $(+)_{589}$-(SS)-β_2-[Co(trien)-gly]I$_2$ prepared and resolved previously.[3] The product was homogeneous on the ion-exchange column using NaClO$_4$ or NH$_4$Cl eluents, and its RD curve and visible spectrum remained unchanged on elution. The Hg^{2+}-induced removal of Br from $(-)_{589}$-[Co(en)$_2$-Br(glyOCH$_3$)]Br$_2$ ($[\alpha]_{589}$ −115°) resulted in $(-)_{589}$-Co(en)$_2$gly^{2+}, $[\alpha]_{589}$ −305°. This rotation may be compared with that for optically pure $(+)_{589}$-[Co(en)$_2$-gly]I$_2$, $[\alpha]_{589}$ +308° in water.[8]

The anions SO$_4{}^{2-}$, HSO$_4{}^-$, and NO$_3{}^-$ do not effectively compete (<1%) for the intermediate generated on the Hg^{2+}-promoted removal of Cl$^-$ since Co(trien)-(SO$_4$)(glyOC$_2$H$_5$)$^+$ and Co(trien)(NO$_3$)(glyOC$_2$H$_5$)$^{2+}$ were not detected spectrophotometrically or by ion-exchange chromatography in the products following hydrolysis in 0.1 M H$_2$SO$_4$ (0.9 M Li$_2$SO$_4$) and 1 M NaNO$_3$, respectively. The properties of the possible acido competition products have not yet been established, but the analogous Co(en)$_2$NH$_3$X$^{+,2+}$,[9] Co(en)$_2$X-(glyOCH(CH$_3$)$_2$)$^{+,2+}$,[1] and Co(NH$_3$)$_5$X$^{+,2+}$[10] (X = SO$_4$, NO$_3$) ions are stable to substitution under these conditions and it is likely that the analogous trien–nitrato and –sulfato complexes will behave similarly and would be observed if formed.

The results of the ^{18}O-labeling experiments are given in Table II. It can be seen from Figure 3 that β_2-Co(trien)gly^{2+} derived from carbonyl-^{18}O-labeled Co(trien)Cl(glyOC$_2$H$_5$)$^{2+}$ retained its label in 0.1 M H$^+$ over 25 days at 25° (Table IIA), whereas the product derived from unlabeled complex in H$_2{}^{18}$O showed 35% enrichment by the solvent, which was slowly lost in 0.1 M H$^+$ at 25° (Table IIB). This exchange process gave a first-order rate constant of 0.54 × 10^{-6} sec^{-1}, at 25°, Figure 3, and the results allow a distinction to be made between the two types of glycine oxygens.

No value was obtained for the enrichment of the ester used to prepare the labeled complex in Table IIA. However, in a separate experiment β_2-[Co(trien)-gly](HgI$_4$) of enrichment 0.536 atom % (R = 0.014849) was obtained by Hg^{2+}-induced acid hydrolysis of carbonyl-^{18}O-labeled β_2-[Co(trien)Cl(glyOC$_2$H$_5$)](ClO$_4$)$_2$ prepared from glycine ethyl ester hydrochloride of enrichment 0.608 atom % (R = 0.016320). This represents an 88% retention of enrichment. The product enrichment from hydrolysis in labeled solvent

Table II

Kinetic Data for Oxygen Exchange in β_2-Co(trien)gly^{2+} Produced *via* Hg^{2+}-Assisted Acid Hydrolysis ([H$^+$] = 0.1 M, μ = 1.0 (NaClO$_4$), [Complex] ≃ 0.1 M, 25°)

Days	Enrichment, atom % ^{18}O^b	Days	Enrichment, atom % ^{18}O^b
(A) $\mathrm{Co(trien)Cl}$-$(\mathrm{NH_2CH_2}\overset{\overset{\bullet}{\|}}{\mathrm{C}}\mathrm{OC_2H_5})^{2+}$ + H_2O		(B) $\mathrm{Co(trien)Cl}$-$(\mathrm{NH_2CH_2}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{OC_2H_5})^{2+}$ + $H_2{\bullet}^a$	
0	0.308	0	0.708
5	0.337	5	0.571
8	0.332	18	0.308
18	0.339	25	0.252
25	0.353		

^{a} The H$_2{}^{18}$O solvent used to prepare this complex was enriched by 2 atom % ^{18}O. ^{b} Represents the ^{18}O content in atom per cent minus the atom per cent of ^{18}O in CO$_2$ of normal isotopic composition (0.201). Atom % ^{18}O = 100R/(2 + R), where R = [46]/{[44] + [45]}.

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[8] I K. Reid and A. M. Sargeson, unpublished results.

[9] D A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6654 (1968).

[10] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).

(35%) is somewhat less than the 50% expected for incorporation of one solvent oxygen, but this may be attributed to loss of label during isolation and purification of the product (see below).

Base Hydrolysis.—Table III gives spectrophotometric and polarimetric rate data for reaction 2. Plots of log $(D_t - D_\infty)$ (480 and 350 mμ) and log $(\alpha_t - \alpha_\infty)$ (520 mμ) against time were linear for at least 3 half-lives. Isosbestic points occurred at 526, 415, and 368 mμ in the spectrophotometric runs. The data fit the usual rate law for base hydrolysis of Co(III)–halo complexes, $R = k_{OH}[\text{complex}][OH^-]$, with a second-order rate constant $k_{OH} = (2.2 \pm 0.2) \times 10^5\ M^{-1}\ \text{sec}^{-1}$. It can be seen from Table III that similar rates occurred in pyridine and phthalate buffers and that they are largely independent of the buffer concentration and the ionic strength medium.

Base hydrolysis of $(+)_{589}$-(*SS*)-β_2-[Co(trien)Cl(glyOC_2H_5)]$(ClO_4)_2$ over the pH range 5.6–14 resulted in full retention of configuration about the Co(III) center, Figure 2, but with some inversion about the "planar" secondary N atom of triethylenetetramine. Both the $(+)_{589}$-(*SR*) and $(+)_{589}$-(*SS*) isomers were separated by ion-exchange chromatography. After hydrolysis at pH 8.15 for 1 min, 32% $(+)_{589}$-(*SR*)-β_2-Co(trien)gly^{2+} ($[\alpha]_{589}$ 162°) and 63% $(+)_{589}$-(*SS*)-β_2-Co(trien)gly^{2+} ($[\alpha]_{589}$ 202°) were obtained. The result for the β_2-(*SS*) isomer establishes that no racemization has occurred in forming this product, and the result in 0.1 *M* NaOH is consistent with full retention occurring in the D-(*SR*)-β_2 product.[4] This latter result was substantiated by mutarotation at pH ~13 of the D-(*SR*)-β_2 isomer formed by hydrolysis at pH 8.15 and separation of the D(*SS*)-β_2 product from the ion-exchange column. This product gave $[\alpha]_{584}$ 204° (calculated using ϵ_{478} 134). The identification of the two β_2 products formed on hydrolysis as internal diastereoisomers, as well as other experiments concerning the stereochemistry of the Co(trien)gly^{2+} isomers, will be described in a subsequent publication.[4]

TABLE III

RATE DATA FOR BASE HYDROLYSIS OF β_2-[Co(trien)Cl(glyOC_2H_5)]$(ClO_4)_2$ AT 25°, $\mu = 1.0$

pH[a]	10^4k_{obsd}, sec^{-1}	$10^{-5}k_{OH}$, $M^{-1}\ \text{sec}^{-1}$	Method[b]
(a) Pyridine–HCl Buffer (0.05 *M*), $\mu = 1.0$ (KCl)			
5.07	2.57	2.2	S
5.58	8.89	2.3	P
5.93	19.2	2.3	P
(b) Potassium Acid Phthalate–NaOH Buffer (0.05 *M*), $\mu = 1.0$ (KNO_3)			
5.10	2.57	2.0	S
5.65	8.89	2.0	S
4.79[c]	1.47	2.4	S
5.69[d]	0.94	0.19	S

[a] Solution pH at conclusion of each run. [b] S = spectrophotometric; P = polarimetric. [c] [Buffer] = 0.1 *M*. [d] β_2-[Co(trien)NH_3Cl]Cl_2.

Base hydrolysis of $(+)_{589}$-(*SS*)-β_2-[Co(trien)Cl(glyOC_2H_5)]$(ClO_4)_2$ at pH ~7.5 for 2 min in the presence of 1 *M* NaN_3 followed by elution from the cation-exchange resin resulted in the separation of two orange Co(trien)gly^{2+} products and two red Co(trien)N_3(glyOC_2H_5)$^{2+}$ products. The former were characterized by spectrophotometry, by rotatory dispersion (RD), and by atomic absorption analysis for cobalt, as $(+)_{589}$-(*SS*)-β_2-Co(trien)gly^{2+} (56%) and $(+)_{589}$-(*SR*)-β_2-Co(trien)gly^{2+} (32%), and the latter complexes were identified in a similar manner as the corresponding β_2 isomers of Co(trien)N_3(glyOC_2H_5)$^{2+}$ (5 and 3%) by conversion to the glycinate isomers using HNO_2. Base hydrolysis at pH 9.25 ("Tris" buffer) in 1 *M* NaN_3 for 5 min resulted in no azido products being detected on the ion-exchange column. However, when the isolated azido complexes were treated with buffer at pH 9.25, base hydrolysis was rapid and the glycinato complexes ensued.

The results of the ^{18}O-labeling experiments are given in Table IV and Figure 4. The initial enrichments demonstrate that the β_2-Co(trien)gly^{2+} products incorporate close to one oxygen atom from the solvent, and Figure 4 shows that these products subsequently show two rates for oxygen exchange. These two rates correspond closely to those given in Figure 3. Extrapolation of the duplicate slower rate gives an intercept at zero time of ~0.16 atom % ^{18}O, or 16% of the original enrichment taken as half the solution enrichment.

TABLE IV

KINETIC DATA (DUPLICATE RUNS) FOR OXYGEN EXCHANGE BETWEEN WATER AND THE OXYGEN OF β_2-Co(trien)gly^{2+} PREPARED BY BASE HYDROLYSIS OF β_2-Co(trien)Cl(glyOC_2H_5)$^{2+}$ IN LABELED SOLVENT AT pH 8.6, 25° ($[H^+] = 0.1\ M$, $\mu = 1.0$ ($NaClO_4$), [COMPLEX] $\simeq 0.1\ M$)

Days		Atom % ^{18}O[c]	
0[a]		0.804	
	0[b]		0.923
5		0.575	
9		0.428	
	14		0.473
15		0.337	
20		0.243	
	25		0.239
	42		0.191
50		0.163	
	51		0.175
	64		0.173
70		0.152	
134			0.147

[a] $H_2{}^{18}O$ solution enriched by 2.013 atom % ^{18}O. [b] $H_2{}^{18}O$ solution enrichment 2.084 atom % ^{18}O. [c] Represents the ^{18}O content in atom per cent minus the atom per cent in CO_2 of normal isotopic composition (0.201). Atom % $^{18}O = 100R/(2 + R)$, where $R = [46]/\{[44] + [45]\}$.

The discrepancy between the observed solvent incorporation in the complex at zero time and half the solution enrichment can be attributed to loss of carbonyl label during the isolation and purification procedure. In the duplicate experiments in $H_2{}^{18}O$ (Table IV) the initial enrichments are 45% (one recrystallization from hot water) and 40% (two recrys-

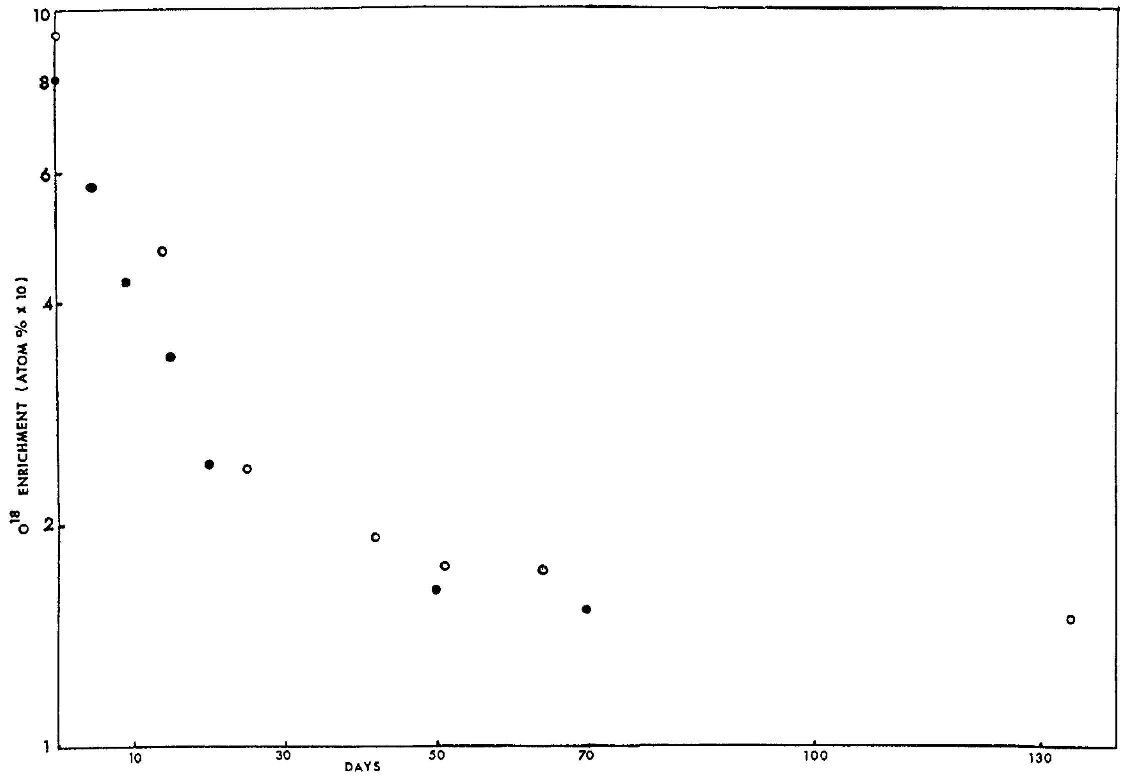
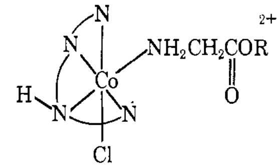


Figure 4.—Oxygen-18 exchange in β_2-Co(trien)gly^{2+} prepared by base hydrolysis of β_2-[Co(trien)Cl(glyOC$_2$H$_5$)]Cl$_2$ in H$_2$^{18}O for 30 min at pH 8.6 (0.1 *M* HClO$_4$, μ = 1.0, 25°). Duplicate runs.

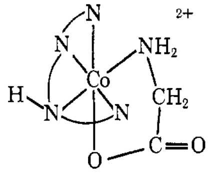
tallizations from hot water) of the solvent figure; the enrichments after complete exchange of the carbonyl label are both 8%. A similar loss of carbonyl label occurred on isolating and recrystallizing [Co(en)$_2$gly]I$_2$ formed by base hydrolysis of [Co(en)$_2$Br(glyOCH(CH$_3$)$_2$)](ClO$_4$)$_2$.[2]

Discussion

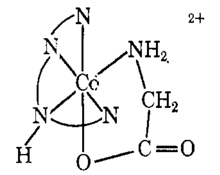
The structures of the chloro ester and glycinato products in these reactions are



L-(*RR*)-β_2-Co(trien)Cl(glyOC$_2$H$_5$)$^{2+}$



L-(*RR*)-β_2-Co(trien)gly^{2+}

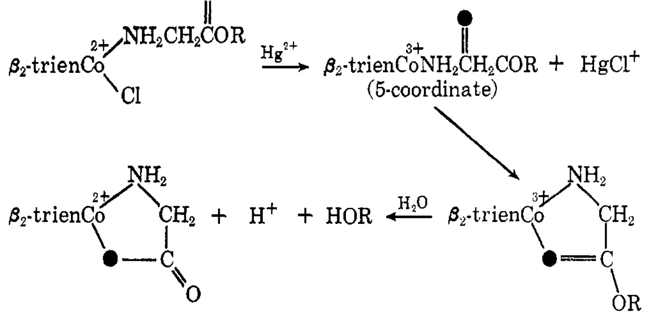


L-(*RS*)-β_2-Co(trien)gly^{2+}

The structural assignments will be defended in detail in a subsequent publication.[4] The presence of the two glycinato diastereoisomers does not affect the conclusions reached about the mechanism of hydrolysis of the ester group. For this reason the significance of their occurence in these reactions will not be discussed but will be reserved for a later paper concerning the inorganic aspects of the reaction.[4]

Hg^{2+}-Catalyzed Reaction.—Some of the results bear a close resemblance to those obtained with the Co(en)$_2$X(glyOR)$^{2+}$ ions.[1,11] Both β_2-Co(trien)Cl(glyOC$_2$H$_5$)$^{2+}$ and *cis*-Co(en)$_2$Cl(glyOR)$^{2+}$ (R = CH$_3$, CH(CH$_3$)$_2$) show (1) the same rate law and similar rates of reaction, (2) the glycinato product as the sole product of the reaction, (3) full retention of optical activity in the product, (4) no competition by added anions (SO$_4$$^{2-}$, NO$_3$$^-$), and (5) the same source for the oxygen atoms in the product; the Co–O oxygen is derived from the carbonyl oxygen of the ester, and the >C═O oxygen is derived from the solvent.

The last result requires that during the reaction the oxygens never become equivalent and this can be realized by formation of the chelated ester intermediate β_2-Co(trien)(glyOC$_2$H$_5$)$^{3+}$ prior to ester hydrolysis. A similar intermediate is formed with *cis*-Co(en)$_2$X(glyOR)$^{2+}$ ions (X = Cl, Br),[1,11] and the above comparison implies that the same pattern of events occurs here.[1] The lack of NO$_3$$^-$ and HSO$_4$$^-$



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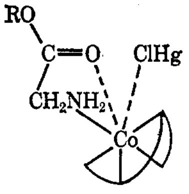
[11] M. D. Alexander and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 1130 (1966).

competition suggests that $Co(trien)(H_2O)(glyOC_2H_5)^{3+}$ is not formed prior to the chelated ester intermediate. Such anions have been shown to be better competitors on a molar basis than H_2O for the five-coordinate intermediates generated on loss of $HgCl^+$ from $Co(NH_3)_5Cl^{2+}$ [10] and $Co(en)_2NH_3Cl^{2+}$.[9] The results then require the ester group to compete exclusively for a five-coordinate intermediate formed on loss of $HgCl^+$.

An alternative mechanism in the light of the lack of anion competition is one of the SN2 type, where the ester carbonyl is partly bound in the transition state. Such a proposal has been made for the formation of $Co(EDTA)^-$ from $CoCl(EDTA)^{2-} + Hg^{2+}$ on the basis of the slower reactivity of the conjugate acid $CoCl(HEDTA)^-$ and on the grounds that $Co(H_2O)(EDTA)^-$ is not formed at an intermediate stage.[12] In the present instance such a mechanism would allow the lack of anion and solvent competition and would support full retention of optical activity in the product. However, the similarity in rate constants, $k_{Hg^{2+}}$, Table V, for the chloro esters and other chloro–amine complexes of the same charge which do not contain the entering >C=O group militates against a synergic process involving binding of the ester group in the transition state. However, the possibility of entry of >C=O synchronously with loss of $HgCl^+$ but without influencing the rate cannot be excluded.



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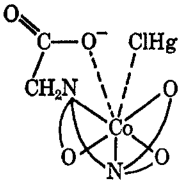

III

TABLE V

COMPARISON OF SECOND-ORDER RATE CONSTANTS FOR THE Hg^{2+}-INDUCED REMOVAL OF CHLORIDE IN SOME COBALT COMPLEXES, $\mu = 1.0$, 25°

Complex	$k_{Hg^{2+}}$, M^{-1} sec^{-1}
cis-$Co(en)_2Cl(NH_3)^{2+}$ [a]	1.4×10^{-2}
cis-$Co(en)_2Cl(glyOC_2H_5)^{2+}$ [b]	1.7×10^{-2}
cis-$Co(en)_2Cl(H_2O)^{2+}$ [a]	4.1×10^{-2}
cis-$Co(en)_2Cl(py)^{2+}$ [a]	1.5×10^{-2}
β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$	1.0×10^{-2}
$Co(NH_3)_5Cl^{2+}$ [a]	1.2×10^{-1}

[a] C. Bifano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968). [b] M. D. Alexander and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 1130 (1966).

Base Hydrolysis.—Unlike the Hg^{2+}-induced reaction, base hydrolysis of β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2$ differs in some respects from that for $[Co(en)_2Cl(glyOR)](ClO_4)_2$.[2] The following comparisons can be made. (1) Although both ions obey the same rate law $R = k_{OH}[\text{complex}][OH^-]$, the second-order rate constants differ by a factor of ~3000 (Table VI). (2) Whereas β_2-$Co(trien)gly^{2+}$ is the sole product in the present instance, only ~40% $Co(en)_2gly^{2+}$ is formed on base hydrolysis of $[Co(en)_2Cl(glyOC_2H_5)](ClO_4)_2$. (3) Full retention of optical activity obtains in the base hydrolysis of the trien complex, whereas 50% of $Co(en)_2gly^{2+}$ from $[Co(en)_2Br(glyOCH_3)]Br_2$ is racemic. (4) N_3^- competition is observed for both complexes. (5) Base hydrolysis of β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ results in the incorporation of ~84% of the ester carbonyl oxygen and ~16% of solvent oxygen into the Co–O position of the product. The same experiment using $Co(en)_2Br(glyOCH(CH_3)_2)^{2+}$ showed about equal amounts of ester and solvent oxygen incorporation into the similar position in $Co(en)_2gly^{2+}$.[2]

TABLE VI

COMPARISON OF SECOND-ORDER RATE CONSTANTS FOR BASE HYDROLYSIS OF SOME $[CoN_5Cl]^{2+}$ COMPLEX IONS AT 25°, $\mu = 1.0$

Complex ion	k_{OH}, M^{-1} sec^{-1}
$Co(NH_3)_5Cl^{2+}$	0.85
$Co(en)_2NH_3Cl^{2+}$	3.3
$Co(en)_2(glyOR)Cl^{2+}$	70 [a]
β_2-$Co(trien)NH_3Cl^{2+}$	2.1×10^4
β_2-$Co(trien)(glyOC_2H_5)Cl^{2+}$	2.2×10^5
$Co(NH_3)_5Br^{2+}$	6.1
$Co(en)_2NH_3Br^{2+}$	43
$Co(en)_2(glyOR)Br^{2+}$	360

[a] Estimated from a value of 200 M^{-1} sec^{-1} at $\mu = 0.03$.[2]

Base hydrolysis of $Co(en)_2Cl(glyOR)^{2+}$ has been shown to involve only minor contributions *via* the initial hydrolysis of the ester group of the monodentate amino acid. The rate constants for Cl removal in these compounds, k_{OH} ~70 M^{-1} sec^{-1}, are ~$^1/_{3000}$th as large as those for β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$. Also, the rate constant for formation of $Co(NH_3)_5(glyO)^{2+}$ in the base hydrolysis of the monodentate ester in $Co(NH_3)_5(glyOC_2H_5)^{3+}$, $k_{OH} = 30$ M^{-1} sec^{-1}, is also considerably less than that for the present reaction. These factors strongly support ester hydrolysis occurring subsequent to Cl removal in the triethylenetetramine complex and in a manner substantially different from the bimolecular attack of hydroxide on the monodentate ester.

The ^{18}O-tracer results may then be interpreted in a manner similar to that discussed in detail for base hydrolysis of *cis*-$Co(en)_2Br(glyOCH(CH_3)_2)^{2+}$.[2] It is proposed that the five-coordinate intermediate $Co(trien\text{-}H)glyOC_2H_5^{2+}$ partitions between water and carbonyl entry. However, the final product ratio of 84:16 does not necessarily reflect the competition for the five-coordinate intermediate by >C=O and water, since other results demonstrate rapid anation of β_2-$Co(trien)(OH)NH_3^{2+}$ by N_3^- at pH 6–7. Thus some of the chelated ester intermediate could result *via* the hydroxo ester. This possibility is excluded in the bis-ethylenediamine system, where *cis*-$Co(en)_2(OH)(glyO)^+$, containing a carboxyl group of nucleophilicity at least comparable to that of the ester carbonyl group, is known to chelate only slowly.[14] Intramolecular hydrolysis of the ester by bound hydroxide follows,

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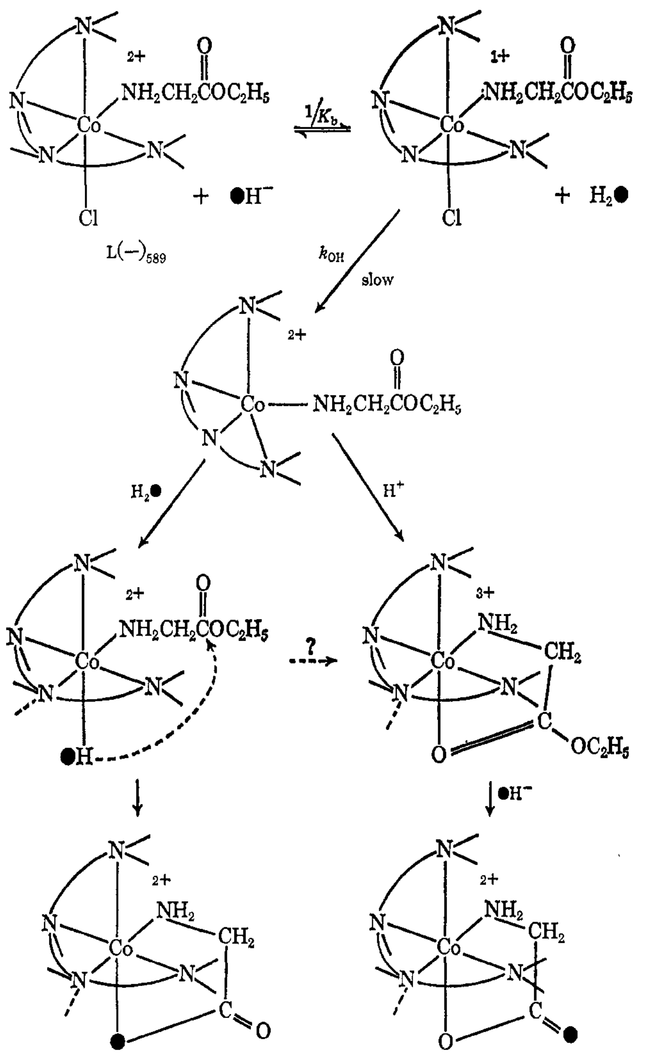
(12) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 2788 (1963).

(13) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **91**, 3451 (1969).

(14) D. M. Foster and L. G. Warner, unpublished work.

SCHEME I



along with intermolecular hydrolysis of the chelated ester by external OH$^-$ ion, Scheme I. Both reactions lead directly to the β_2-Co(trien)gly^{2+} products of the observed composition. Competition by azide ion is consistent with the presence of the five-coordinate intermediate and with the competition by a water molecule. For the chelated ester and for the glycinato product no oxygen scrambling is expected (pH 8.6) since none occurs in the related bis-ethylenediamine complex.[2] It follows therefore that entry of labeled solvent in the bridging position cannot occur *via* the chelated ester and it also supports the proposal for the five-coordinate intermediate reacting partly with solvent.

It is clear that the chelated ester and hydroxo ester complexes are labile intermediates relative to the rate of base hydrolysis, since neither is observed. This is consistent with the rapid rate for OH$^-$ attack at the carbonyl center for the analogous chelated ester Co(en)$_2$(glyOCH(CH$_3$)$_2$)$^{3+}$,[15] $k_{OH} = (1.5 \pm 0.5) \times 10^6$ M^{-1} sec^{-1} at 25°, $\mu = 1.0$. Also, in a related study with Co(en)$_2$Br(glyNR$_2$)$^{2+}$ complexes there is unequivocal evidence for rapid hydrolysis by the bound OH$^-$ path relative to the hydrolysis of the chelated amide by external OH$^-$ [14] at pH 9.0.

The similarity between the amide and ester reactions implies that the same correlation should occur for the present intermediates. Hydrolysis by bound OH$^-$ is fast relative to base hydrolysis of the chelated ester.

The full retention of the D-β_2 configuration about the metal ion on base hydrolysis contradicts our previous view[2] that there may be a correlation between rearrangement about the metal ion and ^{18}O incorporation. The present result requires that both paths for hydrolysis (Scheme I) incur no racemization about the metal ion.

Acknowledgments.—The authors wish to thank Professor S. F. Mason of the University of East Anglia for the CD spectra and Dr. F. J. Bergerson and Mr. G. Turner of the CSIRO Division of Plant Industry for determining some of the isotopic enrichments.

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(15) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, submitted for publication.