

Cobalt(III)-Promoted Hydrolysis of Glycine Esters. Kinetics, Product Analysis, and Oxygen-18 Exchange Studies of the Base Hydrolysis of $[\text{Co}(\text{en})_2\text{X}(\text{glyOR})]^{2+}$ Ions

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Abstract: The base hydrolysis of the complexes of the type $\text{cis-}[\text{Co}(\text{en})_2\text{X}(\text{NH}_2\text{CH}_2\text{COOR})]^{2+}$ (where $\text{X} = \text{Cl}$ and Br ; $\text{R} = \text{CH}_3$, C_2H_5 , $\text{CH}(\text{CH}_3)_2$, $(\text{CH}_2)_3\text{CH}_3$, $\text{C}(\text{CH}_3)_3$, and $\text{CH}_2(\text{C}_6\text{H}_5)$) leads to $[\text{Co}(\text{en})_2\text{glycinato}]^{2+}$ primarily, along with numerous side products some of which are not yet characterized. Substantially, $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ arises rapidly after loss of X^- and coincides with loss of the ester group. ^{18}O tracer experiments with $\text{cis-}[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]^{2+}$ show $\sim 50\%$ $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ arises from coordination of the ester carbonyl oxygen while the remainder is produced by the 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. Base hydrolysis of $(-)\text{-}_{889}\text{-}[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}_3)]^{2+}$ leads to 50% racemization in the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ product, and this factor may be related to the O^{18} distribution.

In a previous study,¹ the Hg^{2+} - and HOCl -induced removal of bromide ion from $[\text{Co}(\text{en})_2\text{Br}(\text{glyOR})]^{2+}$ ($\text{R} = \text{CH}_3$ and $\text{CH}(\text{CH}_3)_2$) to form $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ($\text{gly} =$ chelated $\text{NH}_2\text{CH}_2\text{CO}_2^-$; $\text{glyOH} =$ monodentate $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$; $\text{glyO} =$ monodentate $\text{NH}_2\text{CH}_2\text{CO}_2^-$; $\text{glyOR} =$ monodentate (or chelated) $\text{NH}_2\text{CH}_2\text{CO}_2\text{R}$) was shown to proceed *via* the chelated ester intermediate $[\text{Co}(\text{en})_2(\text{glyOR})]^{3+}$, as had been previously proposed.² Incorporation of solvent water was inferred in the case of the HOCl -induced reaction, with rapid concerted displacement of the bound water by the ester carbonyl group. By contrast, the Hg^{2+} -induced reaction was believed to involve exclusive incorporation of the carbonyl group in the vacant coordination site of the five-coordinate intermediate.

These systems have the merit that the coordinated amino acid derivative remains bound in solution and the order of events in the reaction can be examined in more detail than for labile systems such as Ni^{2+} and Cu^{2+} complexes. Moreover, the compounds may possibly be considered as models for metal-ion activated esterases. Whatever the propriety of this claim, it would seem worthwhile to possess an account of the processes involved in the $\text{Co}(\text{III})$ -promoted hydrolysis of glycine esters under conditions more closely approaching physiological conditions than those in the induced acid hydrolyses. In general, base hydrolyses of complexes of the type $[\text{CoN}_5\text{X}]^{2+}$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{N} =$ amine) are held to occur *via* five-coordinate intermediates³⁻⁷ which are different from those formed in the Hg^{2+} -induced reactions. For the ester complexes the possibility arises of the ester carbonyl group and solvent water competing for the vacated site. The latter path leads to the hydroxo ester complexes and the possibility of subsequent internal nucleophilic displacement of

the ester group by the bound OH^- . Certainly, in a related study of the base hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{CH}_2\text{COOR}]^{3+}$, the importance of the role of the internal nucleophile was established.⁸

During the course of the work, a communication appeared⁹ which discussed the base hydrolysis of $[\text{Co}(\text{en})_2\text{Cl}(\text{glyOC}_2\text{H}_5)]\text{Cl}_2$ in terms of preliminary hydrolysis of the monodentate ester moiety, followed by hydrolysis of chloride. The variance between this interpretation and our own observations on $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)](\text{ClO}_4)_2$, together with the over-all complexity of the reactions, caused us to extend this study to cover several other complexes of the type $[\text{Co}(\text{en})_2\text{X}(\text{glyOR})]\text{X}_2$.

Experimental Section

Analar reagents were used throughout without further purification.

O^{18} -Labeled glycine isopropyl ester hydrochloride was prepared by refluxing O^{18} -enriched glycine hydrochloride (prepared as described previously¹) in isopropyl alcohol with thionyl chloride. Unlabeled methyl, ethyl, isopropyl, *n*-butyl, and benzyl esters of glycine were prepared similarly from the appropriate alcohols. Glycine *t*-butyl ester hydrochloride (Puriss) was obtained from Fluka.

Infrared spectra were recorded on a Perkin-Elmer 457 instrument. Spectrophotometric rate data were collected on both Cary 14 and Shimadzu RS 27 recording spectrophotometers; the Cary 14 instrument was used in the characterization of eluate fractions from ion exchange of reaction mixtures. Bio-Rad analytical Dowex 50W \times 2 (200-400 mesh) cation-exchange resin was used in the ion-exchange separation experiments. pH determinations were made on a Cambridge bench instrument. Some cobalt estimations were made using a Techtron AA4 atomic absorption spectrophotometer.

The O^{18} content of CO_2 recovered from the labeled compounds was determined using Atlas M-86 and GD-150 mass spectrometers. α_{889} values for optically active complexes were measured with a Perkin-Elmer 141 spectropolarimeter using a 1-dm cell. Concentrations of isopropyl alcohol liberated during base hydrolysis of the corresponding ester complex were determined using a Varian Aerograph 600D gas chromatograph.

Rates of base uptake were determined at constant pH and temperature by pH-Stat titration with the following Radiometer apparatus: TTA₃ electrode assembly, ABU₁ autoburet, TTT₁ titrator,

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

(2) M. D. Alexander and D. H. Busch, *ibid.*, **88**, 1130 (1966).

(3) R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

(4) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

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(6) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 597 (1967).

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

(8) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *ibid.*, **91**, 3451 (1969).

(9) R. W. Hay, M. L. Jansen, and P. I. Cropp, *Chem. Commun.*, 621 (1967).

and SBR₂ titrator. The thermostated reaction vessel was continuously stirred as the titrant (NaOH of appropriate concentration) was added under a nitrogen atmosphere.

Preparation of Complexes. Complexes of the type *cis*-[Co(en)₂X(glyOR)]X₂ (where X = Cl and Br; R = CH₃, C₂H₅, CH(CH₃)₂, (CH₂)₃CH₃, CH₂C₆H₅, and C(CH₃)₃) were prepared from *trans*-[Co(en)₂Br₂]Br·HBr or *trans*-[Co(en)₂Cl₂]Cl with the appropriate glycine ester hydrochloride (glycine ester *p*-toluenesulfonate in the case of the benzyl ester), in the manner described by Alexander and Busch.¹⁰

Where desired, these complexes were converted to their perchlorate salts by dissolution in hot 10⁻³ M HClO₄, followed by addition of excess NaClO₄ and cooling in an ice bath. The products were twice recrystallized from hot, dilute HClO₄ by adding NaClO₄. They were washed with ethanol and dried in an evacuated desiccator. *Anal.* Calcd for [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂: C, 15.38; H, 4.24; N, 12.80. Found: C, 15.28; H, 4.41; N, 12.93. Calcd for [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂: C, 18.80; H, 4.73; N, 12.18. Found: C, 18.84; H, 4.99; N, 12.36. Calcd for [Co(en)₂Br(glyOCH₂C₆H₅)]Br₂: C, 26.73; H, 4.66; N, 11.99. Found: C, 26.83; H, 4.76; N, 11.78. Calcd for [Co(en)₂Br(glyO(CH₂)₂CH₃)]Br₂: C, 21.84; H, 5.32; N, 12.74. Found: C, 22.73; H, 5.93; N, 13.07. Calcd for [Co(en)₂Br(glyO(CH₂)₃CH₃)]Br₂: C, 21.84; H, 5.32; N, 12.74. Found: C, 21.84; H, 5.19; N, 12.92. Calcd for [Co(en)₂Cl(glyOCH(CH₃))](ClO₄)₂·H₂O: C, 19.70; H, 5.33; N, 12.77. Found: C, 19.93; H, 5.33; N, 12.89. Calcd for [Co(en)₂Cl(glyOCH₂C₆H₅)](ClO₄)₂·H₂O: C, 17.97; H, 5.09; N, 13.10. Found: C, 17.85; H, 5.00; N, 12.89. Calcd for [Co(en)₂Cl(glyOCH₂)]Cl₂·0.5H₂O: C, 21.91; H, 5.78; N, 18.26. Found: C, 22.06; H, 6.03; N, 18.45.

Carbonyl O¹⁸-labeled *cis*-[Co(en)₂Br(glyOCH(CH₃))]₂Br₂ was prepared from *trans*-[Co(en)₂Br₂]Br·HBr and O¹⁸-labeled glycine isopropyl ester hydrochloride. *Anal.* Calcd for [Co(en)₂Br(glyOCH(CH₃))]₂Br₂·H₂O: C, 19.51; H, 5.28; N, 12.64. Found: C, 18.78; H, 5.42; N, 12.87. *cis*-[Co(en)₂NH₃Br]₂Br₂ was prepared as described by Werner.¹¹ *Anal.* Calcd for [Co(en)₂NH₃Br]₂Br₂: C, 11.02; H, 4.39; N, 16.07. Found: C, 10.8; H, 4.3; N, 15.8.

Measurement of Oxygen Exchange in O¹⁸-Labeled [Co(en)₂gly]²⁺ Produced via Base Hydrolysis of [Co(en)₂Br(glyOCH(CH₃))]²⁺. I. Labeled Complex. Carbonyl O¹⁸-labeled *cis*-[Co(en)₂Br(glyOCH(CH₃))]₂Br₂ (10 g) in water (1000 ml) was hydrolyzed at pH 8.6 and 25° for 90 min, by pH-Stat titration against 30% NaOH. The solution was then taken to pH 6 and reduced to ca. 200 ml on a rotary evaporator. On addition of excess NaI and methanol, [Co(en)₂gly]I₂ precipitated. This was collected, washed with cold NaI solution, methanol, and ether, and recrystallized from hot water by addition of NaI. The final product (3.7 g) was washed as before and dried in an evacuated desiccator. The purity of the product was confirmed by comparison of its ir spectrum with that of [Co(en)₂gly]I₂. The dried material was shaken with excess AgCl in water (20 ml) for 2 min and the precipitate of AgCl and AgI removed. The filtrate was made up to 50 ml, 0.1 M in HClO₄ and 0.60 M in NaClO₄. This solution was thermostated at 25° and 5-ml aliquots were periodically withdrawn. From these, [Co(en)₂gly](HgI₄) was recovered and the O¹⁸ content of the glycine determined as previously described¹ (Table VIA).

II. Labeled Solvent. The above procedure was followed using unlabeled [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂ in enriched water (1.5–2 atom % O¹⁸). A solvent sample was taken immediately after initiation of hydrolysis and its O¹⁸ enrichment determined as described previously.¹

In one instance (B, Table VI) *cis*-[Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂ (6 g) in H₂O¹⁸ (30 ml) was hydrolyzed at pH 8.6 for 60 min, after which time [Co(en)₂gly]I₂ was precipitated from the solution with NaI and twice recrystallized as in section I above, yield 1.6 g. This was converted to the chloride salt in solution and made up to 25-ml volume, pH 1.0, μ = 1.0 (NaClO₄).

In another instance (C, Table VI), [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂ (7.5 g) in H₂O¹⁸ (60 ml) was hydrolyzed at pH 8.6 for 90 min, neutralized, and then sorbed directly on to an H⁺-form resin and the [Co(en)₂gly]²⁺ band was eluted with 1 M NaClO₄, pH 7–8. The eluate band was reduced almost to dryness by rotary evaporation and filtered to remove NaClO₄; [Co(en)₂gly](HgI₄) precipitated from the filtrate by addition of HgI₂ then NaI. The product was washed with water and methanol and dried in an evacuated desic-

cator. After conversion to the chloride, it was made up to 50 ml as before, 0.1 M in HClO₄, and μ = 1.0.

Supplementary Labeling Experiments. To determine the rate of exchange between coordinated glycine and solvent under basic conditions, [Co(en)₂gly]I₂ (0.5 g) was dissolved in H₂O¹⁸ (10 ml) at pH 9.0. After 60 min the product was reprecipitated as the iodide salt by addition of excess NaI and cooling. This was recrystallized from warm water at pH 4, precipitated as the HgI₄²⁻ salt, washed with water and acetone, dried in an evacuated desiccator, and analyzed for O¹⁸ (Table VID).

To determine whether coordinated glycine was subject to intramolecular oxygen scrambling under basic conditions, carbonyl O¹⁸-labeled [Co(en)₂gly]²⁺ was prepared from carbonyl O¹⁸-labeled [Co(en)₂Br(glyOCH(CH₃))]₂Br₂ by dissolving 2 g in 0.1 M HClO₄ (20 ml) with Hg(NO₃)₂ (7 g), filtering after 2 min, and precipitating [Co(en)₂gly](HgI₄) by addition of excess NaI to the filtrate.¹ The product was washed with water and methanol and dried. It was then shaken with excess AgCl in water (100 ml), and after filtration, the filtrate was kept at pH 8.7 for 90 min and then neutralized (pH 6) and [Co(en)₂gly](HgI₄) precipitated from solution. After the usual washing and drying procedures, a sample was retained, while the remainder was converted to the chloride by shaking with AgCl and made up to 10 ml, 0.1 M in HClO₄. Two 5-ml aliquots were sampled (Table VIE).

To determine whether the chelated glycine esters were subject to intramolecular oxygen scrambling during base hydrolysis, carbonyl O¹⁸-labeled [Co(en)₂glyOCH(CH₃)](ClO₄)₂ (3 g) was prepared from carbonyl O¹⁸-labeled [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂¹⁶ and hydrolyzed in water (50 ml) at pH 8.6 using the Radiometer. After 5 min all base uptake had ceased. The solution was then filtered, and reduced in volume on a rotary evaporator and [Co(en)₂gly]I₂ precipitated by addition of NaI and cooling. The product was washed with water and methanol and dried in an evacuated desiccator (1 g), then converted to the chloride by shaking with AgCl and made up to 10 ml, 0.1 M in HClO₄, μ = 1.0 (NaClO₄). Two 5-ml aliquots were sampled (Table VIF).

To test the enrichment of the recovered starting material [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂ (1.5 g) was dissolved in H₂O (1.5 atom % O¹⁸) and hydrolyzed at pH 8.6 for 10 min, 25°. The solution was returned to pH 5–6 with HClO₄, and excess NaClO₄ added. On cooling, [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂ precipitated. This was recrystallized from unlabeled water and air-dried (0.1 g). The identity of the material was confirmed by ir. It was dissolved in 0.01 M HClO₄ (5 ml saturated in Hg(NO₃)₂) and allowed to stand for 1 hr. Excess NaI was added and the [Co(en)₂gly](HgI₄) obtained examined for O¹⁸ (Table VIG).

Resolution of *cis*-[Co(en)₂Br(glyOCH₃)](ClO₄)₂ and the Measurement of Optical Retention in the Hydrolyzed Product. *cis*-[Co(en)₂Br(glyOCH₃)](ClO₄)₂ (5.5 g) was dissolved in hot dilute acetic acid (100 ml, pH 4), and ammonium *d*-bromocamphorsulfonate (NH₄(+)-BCS, 3.28 g) added. On standing at room temperature (–)₃₈₉[Co(en)₂Br(glyOCH₃)](–)(+)-BCS₂ slowly crystallized. Successive fractions were removed, washed with ice water and acetone, and dried. The first three fractions were combined (1.9 g) and once recrystallized from hot dilute acetic acid. The diastereoisomer ([α]₃₈₉ 11.6°) was then converted to the bromide salt by trituration with NaBr at pH 4, and the resulting (–)₃₈₉[Co(en)₂Br(glyOCH₃)]Br₂ recrystallized to constant rotation from hot, dilute acetic acid by adding excess NaBr and cooling. A 0.1% solution in 0.01 M HClO₄ gave α₃₈₉ –0.115°, whence [α]₃₈₉ –115°. *Anal.* Calcd for (–)₃₈₉[Co(en)₂Br(glyOCH₃)]Br₂: C, 16.55; H, 4.56; N, 13.79. Found: C, 16.81; H, 4.78; N, 13.85.

(–)₃₈₉[Co(en)₂Br(glyOCH₃)]Br₂ (0.1006 g) was hydrolyzed by pH-Stat titration at pH 8.6 and 25° for 90 min using 0.2 M NaOH. The solution was then adjusted to pH 6 and sorbed onto an H⁺-form resin. After washing, the [Co(en)₂gly]²⁺ band was collected (100 ml), estimated spectrophotometrically (75.4%), and its rotation measured (α₅₈₉ –0.117°, whence [α]₅₈₉ –154°). (+)₃₈₉[Co(en)₂gly]I₂ (0.1033 g, [α]₃₈₉ 300°) treated in an identical manner showed no change in rotatory power.

Kinetic Measurements. The base hydrolysis of [Co(en)₂Br(glyOCH(CH₃))](ClO₄)₂ and [Co(en)₂Br(glyOCH₃)](ClO₄)₂ was followed spectrophotometrically after rapid dissolution of a weighted quantity of complex in tris(hydroxymethyl)aminomethane (Tris) or glycine buffer at μ = 1.0 (NaClO₄) and 25°. Some rate measurements were obtained by running the spectrum from 600 to 300 mμ to spaced time intervals, while others were obtained from runs at a set wavelength.

Base hydrolysis of all complexes was also followed by pH-Stat

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

(11) A. Werner and W. E. Boes, *Ann.*, **386**, 55, 178 (1912).

titration of 0.2 M NaOH using the Radiometer apparatus. A weighed quantity of complex (~0.2 g) was dissolved either in water or in a solution of KNO₃ of known ionic strength (20 ml) and transferred to the thermostated reaction vessel.

To measure the rate of alcohol production in the base hydrolysis of [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂, the complex (0.009 g) was dissolved in 2,4,6-collidine buffer (10 ml, pH 8.55, μ = 1.0) at 25°, and 2-ml aliquots were periodically withdrawn, quenched with HClO₄ (1 drop 70%), and then immediately frozen in methanol-Dry Ice. The frozen solvent was distilled under vacuum and analyzed chromatographically for isopropyl alcohol.

Product Analysis by Ion-Exchange Chromatography. A. Separation of the Products of Base Hydrolysis. The complex (ca. 1 mmole) was hydrolyzed at known pH within the range 8–9, either by dissolution into buffer or by pH-Stat titration. A specified period of time, or a period of time sufficient to account for a selected base consumption, was allowed, and the reaction then quenched with acid. The solution was diluted and sorbed on a H⁺-form resin (ca. 1.5 × 25 mm when fully swollen), and eluted with NaClO₄, 1–2 M. The pH of elution was normally 5–6. The cobalt concentrations in the eluate fractions were determined spectrophotometrically and/or by atomic absorption spectroscopy.

B. Azide Competition. *cis*-[Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂ (0.53 g) was dissolved in Tris buffer, pH 9.2, 0.9 M in NaN₃ (25 ml). After ca. 20 min, the solution was diluted to 100 ml and sorbed on a H⁺-form resin. Elution was with 1 M NaClO₄, pH 6–7. *cis*-[Co(en)₂Br(glyOCH(CH₃)₂)]Br₂ (0.10 g) was dissolved in the same buffer, 0.9 M in NaN₃ (10 ml), and after 17 min the solution was diluted and sorbed on a Na⁺-form resin. Elution was with 1 M NH₄Cl (pH 6–7). All eluate bands were examined spectrophotometrically.

Results

A. Kinetics. Two rates were observed for base hydrolysis of the [Co(en)₂X(glyOR)]²⁺ ions. Table IA

Table I. Data for Base Hydrolysis of [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂

pH ^a	10 ³ [complex], M	10 ⁴ k ₁ ^c , sec ⁻¹	10 ⁵ k ₂ ^c , sec ⁻¹	10 ⁻² k ₁ ^f , M ⁻¹ sec ⁻¹	10 ⁻¹ k ₂ ^f , M ⁻¹ sec ⁻¹
A. Spectrophotometric Data in 0.1 M Tris Buffer (μ = 1.0 (NaClO ₄), 25.0°)					
8.00	1.39	2.8	5.1	2.8	5.1
8.54	1.5	8.2	12.1	2.4	3.5
8.48 ^b	8.5	9.0	10.8	3.0	3.6
8.52	3.35	9.6	8.0	2.9	2.4
9.14	1.66	36.2	52.5	2.6	3.8
9.13	1.75	38.5	48.2	2.8	3.6
8.55 ^c	1.49	8.9	12.3	2.5	3.5
9.58 ^d	1.60	96	137	2.9	3.6
B. Radiometer Data (μ = 0.05, 25.0°)					
8.0	14.8	6.6	8.5	6.6	8.5
8.5	14.8	16.7	35.0	5.3	11.1
8.5	14.8	18.5	30.8	5.9	9.8
8.5 ^e	4.5	18.3	33.0	5.8	10.4
9.1	14.8	72.1	85.5	5.7	6.8

^a pH at conclusion of hydrolysis. ^b 0.05 M Tris buffer. ^c [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂. ^d 0.1 M glycine buffer. ^e Spectrophotometric data, 0.1 M Tris buffer, μ = 0.063. ^f k = k'/[OH⁻].

presents data for [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂ obtained spectrophotometrically at 480 mμ and in some instances at 340 mμ. Plots of log (D_∞ - D_t) vs. time were initially curved, but at longer times became linear for at least two half-lives of the second reaction. The extrapolated optical density (D_{ext}) attributed to the slower rate was subtracted from the observed data at shorter times to give in all cases a linear plot of log (D_{ext} - D_t) vs. time over at least two half-lives. Both rates fit the rate law

$$R = k[\text{complex}][\text{OH}^-]$$

and the second-order constants k₁ and k₂ are given in Table IA.

The penultimate entry in Table IA refers to rates obtained for the methyl ester, [Co(en)₂Br(glyOCH₃)](ClO₄)₂. The agreement between these rates and those cited for the isopropyl ester suggests that hydrolysis of the ester moiety is not rate determining for either path. The reactions are not subject to general base catalysis, insofar as changing the buffer concentration does not effect the rates, and changing the buffer has no effect.

Table IB gives rate constants obtained from the rate of base uptake by [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂ at constant pH in the absence of buffer. The experimental data were treated in a similar manner to that for the spectrophotometric data. The ionic strength is lower than in Table IA, and the quoted second-order rates are consequently faster, but the pattern is consistent with the spectrophotometric data in Table IA. This is supported by the inclusion in Table IB of a spectrophotometric run performed at a similarly low ionic strength. The results establish that the same series of reactions are being followed both spectrophotometrically and by pH-Stat titration, that Tris buffer is not exerting an inhibitory effect upon the system,¹² and that both rates involve the consumption of hydroxide ion.

Table II gives rate data obtained by pH-Stat titration for the series of complexes [Co(en)₂X(glyOR)]X₂ (where X = Cl and Br; R = CH₃, CH₂CH₃, CH(CH₃)₂, CH₂C₆H₅, (CH₂)₃CH₃, and C(CH₃)₃). The second-order rate constants k₁ show a sensitivity toward X, but not toward a change in R for constant X.

Table II. Base Hydrolysis of [Co(en)₂X(glyOR)]X₂^a

X	Complex R	M ⁻¹ sec ⁻¹		% [Co(en) ₂ gly] ²⁺ pH 8.6 pH 9.0 ^c	
		10 ⁻² k ₁	10 ⁻¹ k ₂		
Br	C(CH ₃) ₃	8.2	7.9	76	73
Br	CH ₂ CH ₂ CH ₂ CH ₃	8.2	14.6	68	
Br	CH(CH ₃) ₂ ^b	8.9	11.2	68	69
Br	CH ₃	8.2	15.0	68	59
Br	(-)-39-CH ₃	7.5	14.3	75	
Br	CH ₂ C ₆ H ₅	9.5	9.5	59	54
Cl	CH(CH ₃) ₂ ^b	1.9	6.1	51	40
Cl	C ₂ H ₅ ^b	2.0	5.4	45	40
Cl	CH ₃	2.1	7.0	45	35

^a pH 8.6, 25.0°, μ ~ 0.03. ^b Perchlorate salt. ^c μ ~ 0.1.

Table III gives the rate dependence upon ionic strength for loss of bromide ion in [Co(en)₂BrNH₃]Br₂ and [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂ at 25°. Observed rates were obtained from base consumption at

Table III. Rate Dependence of Base Hydrolysis upon Ionic Strength^a

Complex	10 ⁴ k _{obs} , sec ⁻¹				
	μ = 0.04	μ = 0.1	μ = 0.2	μ = 0.5	μ = 1.0
[Co(en) ₂ Br(NH ₃)]Br ₂	9.8	7.9	6.3	4.6	4.3
[Co(en) ₂ Br(glyOCH(CH ₃) ₂)](ClO ₄) ₂	72	72		46	36

^a pH 9.0, 25.0°, [complex] ≈ 10⁻³ M.

(12) D. E. Allen, D. J. Baker, and R. D. Gillard, *Nature*, **214**, 906 (1967).

Table IV. Ion-Exchange Separation of Products on Base Hydrolysis of $[\text{Co}(\text{en})_2\text{Cl}(\text{glyOCH}_3)]\text{Cl}_2^a$

Band	Color	Probable charge	λ_{max} , m μ	Abundance	Assignment
1	Blue-red	+1	545, 350	Trace	<i>trans</i> - $[\text{Co}(\text{en})_2\text{OH}(\text{glyO})]^+$
2	Red	+1	513, 355	Trace	<i>cis</i> - $[\text{Co}(\text{en})_2\text{OH}(\text{glyO})]^+$
3	Red	+1	520, 364	5%	$[\text{Co}(\text{en})_2\text{Cl}(\text{glyO})]^+$
4	Red-brown	+2	525, 465, 358	Major product	$[\text{Co}(\text{en})_2(\text{OH})_2(\text{gly en-H})]^{2+}$ (?)
5	Orange	+2	487, 347	28%	$[\text{Co}(\text{en})_2\text{gly}]^{2+}$
6	Red	+2	520, 365	17%	$[\text{Co}(\text{en})_2\text{Cl}(\text{glyOCH}_3)]^{2+}$
7	Red	+3	498, 360	Minor product	condensation products (?)
8, 9	Brown	+3 or higher	...	Minor products	

^a 7.7 min, pH 9.0, 25°, $\mu = 0.15$; eluent, 1–3 M NaClO₄.

constant pH, using KNO₃ as the supporting electrolyte. It can be seen that in both instances an increase from $\mu = 0.04$ to 1.0 results in about a twofold decrease in rate, and that the $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]^{2+}$ ion hydrolyzes about 10 times faster than the $[\text{Co}(\text{en})_2\text{Br-NH}_3]^{2+}$ ion. A similar factor is observed between the β_2 - $[\text{Co}(\text{trien})\text{Cl}(\text{glyOC}_2\text{H}_5)]^{2+}$ and β_2 - $[\text{Co}(\text{trien})\text{ClNH}_3]^{2+}$ ions,¹³ even though these ions base hydrolyze some 3000 times faster than the corresponding ethylenediamine complexes.

Figure 1 gives the rate of isopropyl alcohol production in the base hydrolysis of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)](\text{ClO}_4)_2$ at pH 8.55, $\mu = 1.0$ (NaClO₄), and 25°. Log $(C_\infty - C_t)$, where C represents the concentration of liberated isopropyl alcohol measured from peak areas, was plotted against time. The observed rate constant $k_{\text{obsd}} = 7 \times 10^{-4} \text{ sec}^{-1}$ may be compared with k_1 of the second entry in Table IA obtained spectrophotometrically under the same conditions of pH and ionic strength. After 200 min, 93% of the theoretical amount of isopropyl alcohol in the ester complex was recovered on the gas chromatograph.

B. Reactant and Product Analysis. Included in Table II is a result for optically pure $(-)_589$ - $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}_3)]\text{Br}_2$. The consistency of the rate data obtained for this complex with those for the unresolved material and the other ester complexes in general suggests that in all cases only *cis* complexes have been studied. Further evidence in support of this claim was found by elution of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]^{2+}$ from a 80-cm ion-exchange column (H⁺-form resin) using 1 M NaClO₄ at pH 2. Only a single band resulted. Under these conditions the *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{-NH}_3\text{Cl}]^{2+}$ ions can be separated.⁷ These results agree with those of Alexander and Busch,¹⁰ Meisenheimer,¹⁴ and Bailar and Clapp;¹⁵ the latter authors studied the reaction of several amines with *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{-Cl}_2]\text{Cl}$. Only *cis* products arose from these experiments.

Table IV gives a product analysis for $[\text{Co}(\text{en})_2\text{Cl}(\text{glyOCH}_3)]\text{Cl}_2$, obtained following ion-exchange elution of the hydrolyzed solution. The first six bands were well separated on elution with 1 M NaClO₄. Bands 7–9 were immobile until 3 M NaClO₄ was used. Probable charge assignments were made on the basis of

elution speed in 1 M NaClO₄ for a Dowex 50W \times 2 (200–400 mesh) resin.

Bands 1 and 2 were rapidly displaced by 1 M NaClO₄ and are tentatively assigned to *trans*- and *cis*- $[\text{Co}(\text{en})_2\text{-OH}(\text{glyO})]^+$ species, respectively; they were also

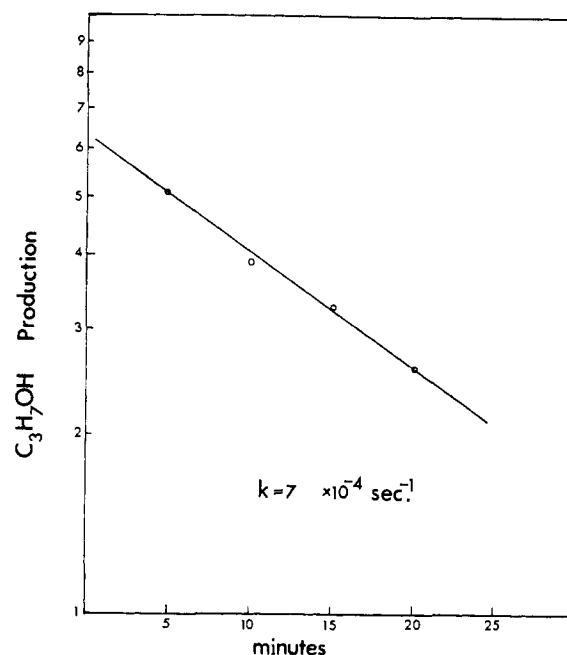
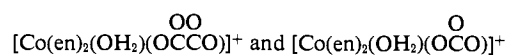


Figure 1. Rate of isopropyl alcohol production in the hydrolysis of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)](\text{ClO}_4)_2$ (pH 8.55, $\mu = 1.0$, 25°). Isopropyl alcohol concentration in arbitrary units.

observed in higher yields as hydrolysis products from $[\text{Co}(\text{en})_2\text{Br}(\text{glyOH})]\text{Br}_2$.¹⁶ The peak at 545 m μ in the *trans* isomer shifts to shorter wavelengths on standing at pH 5, while the *cis* isomer reacts rapidly to give the absorption spectrum for $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ on acidification.

The former observation suggests a slow isomerization to the *cis* species, and the latter resembles in many respects the rapid chelation of monodentate oxalate and bicarbonate in the



ions, respectively.^{17,18} This aspect of the study is being

(13) D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, in press.

(14) J. Meisenheimer and K. Kiderlen, *Ann.*, **438**, 238 (1924).

(15) J. C. Bailar and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945).

(16) D. A. Buckingham, D. M. Foster, A. M. Sargeson, and L. G. Warner, unpublished results.

(17) P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).

(18) H. Scheidegger and G. Schwarzenbach, *Chimia*, **19**, 166 (1965).

Table V. Comparison of Observed and Calculated Base Consumption^a

Complex	Equiv/mole of complex		Mole/mole of complex			
	Obsd	Calcd	k_2 path Obsd	[Co(en) ₂ gly] ²⁺ production	k_1 path Calcd	k_1 path ^c Calcd - obsd
[Co(en) ₂ Br(glyOC(CH ₃) ₃)] ²⁺	1.15	1.27	0.60	0.73	0.70	-0.03
[Co(en) ₂ Br(glyOCH(CH ₃) ₂)] ²⁺ ^b	1.31	1.31	0.32	0.69	0.84	0.15
[Co(en) ₂ Br(glyOCH ₃)] ²⁺	1.55	1.41	0.35	0.59	0.82	0.23
[Co(en) ₂ Br(glyOCH ₂ C ₆ H ₅)] ²⁺ ^b	1.37	1.46	0.14	0.54	0.93	0.39
[Co(en) ₂ Cl(glyOCH(CH ₃) ₂)] ²⁺	1.60	1.60	0.47	0.40	0.77	0.37
[Co(en) ₂ Cl(glyOC ₂ H ₅)] ²⁺	1.72	1.61	0.48	0.39	0.76	0.37
[Co(en) ₂ Cl(glyOCH ₃)] ²⁺	1.73	1.68	0.51	0.32	0.75	0.43

^a pH 9.0, 25.0°, $\mu = 0.1$. ^b pH 9.1. ^c Consumption of base by species other than [Co(en)₂gly]²⁺ via the k_1 path (column 5 - column 4).

investigated further. Band 3 was identified as [Co(en)₂-Cl(glyO)]⁺ by ion exchange and a spectral comparison with an authentic sample prepared by acid hydrolysis of [Co(en)₂Cl(glyOCH₃)]Cl₂.¹⁹ Band 4 was a major product of the reaction of unknown constitution. It was homogeneous by ion exchange and did not contain chloride ion. The absorption band at 465 m μ increased in intensity with a concomitant decrease in the 525-m μ band on standing at pH 5. Its elution rate relative to [Co(en)₂Cl(glyO)]⁺ and [Co(en)₂gly]²⁺ supports its designation as a 2+ ion. Bands 5 and 6 were identified by spectrophotometric comparison with the authentic complexes, as [Co(en)₂gly]²⁺ and unreacted starting material, respectively. Small amounts of more firmly sorbed ions were retained on the column (bands 7-9) and were eluted only at higher ionic strengths (3 M); all together they represented a substantial portion of the reaction products.

The complexity of the product distribution observed for [Co(en)₂Cl(glyOCH₃)]Cl₂ was also qualitatively found with [Co(en)₂Cl(glyOC₂H₅)](ClO₄)₂ and [Co(en)₂-Cl(glyOCH(CH₃)₂)](ClO₄)₂, but a detailed separation of the products (apart from [Co(en)₂gly]²⁺) was not attempted. In general, the bromo esters, with the exception of [Co(en)₂Br(glyOCH₂C₆H₅)]Br₂, gave only trace quantities of colored eluate before [Co(en)₂gly]²⁺. [Co(en)₂Br(glyOCH₂C₆H₅)]Br₂, alone of the bromo esters, produced significant quantities of bands 1, 2, and 4 after hydrolysis at pH 9.0 and $\mu = 0.1$. However, less of band 4 was observed at pH 8.7; this was also true for [Co(en)₂Cl(glyOCH₃)]Cl₂ treated under both sets of conditions. In general, [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂ and [Co(en)₂Br(glyOC(CH₃)₃)]Br₂ gave predominantly [Co(en)₂gly]²⁺, with only small amounts of other products.

C. [Co(en)₂gly]²⁺ Production. Included in Table II is the percentage of [Co(en)₂gly]²⁺ formed from each substrate, a value obtained by ion-exchange separation (at pH 6) of the products of reaction after base consumption had ceased. The table shows that [Co(en)₂gly]²⁺ is in all cases the major product of hydrolysis (except for [Co(en)₂Cl(glyOCH₃)]²⁺ at pH 9), and the extent of its formation depends upon X and to a lesser degree upon R, pH, and ionic strength. In all instances less [Co(en)₂gly]²⁺ is formed when X = Cl than when X = Br and the amount increases with increasing stability of the ester group toward base hydrolysis. For instance, for the bromo complexes 54 and 73% [Co(en)₂gly]²⁺ are formed in the case of the benzyl and *t*-butyl esters, respectively, at pH 9.0. This gradation is less marked, but still apparent, at pH 8.6. Also, at

(19) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 1590 (1966).

higher pH's, and at higher complex concentrations, less [Co(en)₂gly]²⁺ is formed.

Table V shows the observed and calculated base consumption at constant pH for a variety of ester complexes. The first column gives the observed base consumption during hydrolysis, as found from base uptake on the pH-Stat. At least a portion of the product is [Co(en)₂gly]²⁺, and 1 equiv of base is required for its production. The fourth column of values gives the observed figure for base consumption due to production of [Co(en)₂gly]²⁺ (isolated on the ion-exchange column, Table V). If it is then assumed that all other products consume 2 equiv of base, the figure calculated for the total base consumption is that cited in column 2. In all cases, the calculated base consumption is greater than 1 equiv and agrees with the observed value.

Table V, column 3, gives values for base consumed by the k_2 path. This value was obtained from the rate plots by extrapolating the k_2 path to zero time and expressing this value as a percentage of the total observed base consumption. To determine the maximum amount of [Co(en)₂gly]²⁺ (column 5) which can arise by the k_1 path, half the extrapolated value (column 3) is subtracted from unity. The fact that the observed [Co(en)₂gly]²⁺ production (column 4) is either equal to or less than the calculated figure (column 5), but within experimental error never exceeds it (column 6), is in agreement with the proposal that all the [Co(en)₂gly]²⁺ is formed rapidly following release of halide. Direct confirmation of this conclusion in the case of the [Co(en)₂Cl(glyOCH₃)]²⁺ ion is provided by the following experiment. [Co(en)₂Cl(glyOCH₃)]Cl₂ was allowed to base hydrolyze at pH 9.0, $\mu = 0.15$, 25°, for 7.7 min ($\sim 2t_{1/2}$ for k_1 rate), and rapidly adjusted to pH 3. It was then eluted from the ion-exchange column using 1 M NaClO₄; 28% [Co(en)₂gly]²⁺ was recovered compared to 35% recovery from an identical experiment left for 82 min.

D. Competition with Added Azide. The products from the base hydrolysis of [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂ at pH 9.0 in 0.9 M NaN₃, $\mu = 1.0$, were, in order of elution from a H⁺-form resin, *trans*-[Co(en)₂(N₃)₂]⁺ ($\sim 17\%$, ϵ_{560} 335),²⁰ [Co(en)₂N₃(glyO)]⁺ ($\sim 59\%$), [Co(en)₂gly]²⁺ (14%), and unreacted [Co(en)₂Br(glyOCH(CH₃)₂)](ClO₄)₂ ($\sim 4\%$). No *cis*-[Co(en)₂(N₃)₂]⁺ was detected.²⁰ The [Co(en)₂N₃(glyO)]⁺ formed was assigned the *trans* configuration on the basis of its absorption maximum at 530 m μ . *cis*-[Co(en)₂N₃(glyO)]⁺, which was observed as a product in the base hydrolysis of the halo acids [Co(en)₂X(glyO)]⁺ in the presence of N₃⁻ ion,¹⁶ has an absorption maximum at

(20) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4803 (1960).

Table VI. Kinetic Data for Oxygen Exchange between Water and the Oxygen of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ Recovered from Basic Solution^a

Days	Atom % O ¹⁸ ^b	Days	Atom % O ¹⁸
A. H₂O +			
$[\text{Co}(\text{en})_2\text{BrNH}_2\text{CH}_2\text{C}(=\bullet)\text{OCH}(\text{CH}_3)_2]^{2+}$			
0	0.605	B. H₂● +	
0	0.597	$[\text{Co}(\text{en})_2\text{BrNH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}(\text{CH}_3)_2]^{2+}$	
5	0.496	Solvent	1.416
10	0.359	0	0.626
15	0.309	5	0.503
25	0.288	10	0.470
40	0.282	21	0.412
46	0.249	98	0.355
57	0.280		
66	0.249		
C. H₂● +			
$[\text{Co}(\text{en})_2\text{BrNH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}(\text{CH}_3)_2]^{2+}$			
Solvent	1.491	D.^c H₂● +	
0	0.534	$[\text{Co}(\text{en})_2\text{NH}_2\text{CH}_2\text{C}(=\text{O})\text{O}]^{2+}$	
7	0.434	60 min	0.01
8	0.363		
10	0.345		
26	0.325		
40	0.332		
E.^d H₂O +			
$[\text{Co}(\text{en})_2\text{NH}_2\text{CH}_2\text{C}(=\bullet)\text{O}]^{2+}$			
0	0.683	F.^e H₂O +	
5	0.613	$[\text{Co}(\text{en})_2\text{NH}_2\text{CH}_2\text{C}(=\bullet)\text{OCH}(\text{CH}_3)_2]^{2+}$	
10	0.607	0	0.699
G.^f H₂● +			
$[\text{Co}(\text{en})_2\text{BrNH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}(\text{CH}_3)_2]^{2+}$			
10 min	0.05	15	0.711

^a $[\text{H}^+] = 1.0$, $\mu = 1.0$ (NaClO_4), 25° $[\text{Co}(\text{en})_2\text{gly}]^{2+} \sim 0.1 M$.
^b Represents the O¹⁸ enrichment in atom %, less the atom % O¹⁸ in CO₂ of normal isotopic composition (0.201). Atom % O¹⁸ = $100R/(2 + R)$, where $R = [46]/([45] + [44])$.
^c Enrichment of initially unlabeled $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ recovered after 60 min in H₂O (*ca.* 1.5 atom % O¹⁸) at pH 8.6.
^d $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ prepared by Hg²⁺-induced acid hydrolysis of labeled $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]\text{Br}_2$, and recovered after 90 min at pH 8.7; labeled in the carboxyl position.
^e $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ prepared by base hydrolysis at pH 8.6 of carbonyl O¹⁸-labeled $[\text{Co}(\text{en})_2\text{glyOCH}(\text{CH}_3)_2](\text{ClO}_4)_3$.
^f $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ prepared by Hg²⁺-induced acid hydrolysis of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)](\text{ClO}_4)_2$ recovered after 10 min in H₂O (*ca.* 1.5 atom % O¹⁸) at pH 8.6.

510 μm . *trans*- $[\text{Co}(\text{en})_2\text{N}_3(\text{glyO})]^+$ was estimated either by atomic absorption spectroscopy or spectrophotometrically, $\epsilon_{330} 230$. By using the Na⁺ form of the resin and neutral eluent, it was possible to isolate the azido ester complex in the base hydrolysis of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOC}(\text{CH}_3)_3)]\text{Br}_2$. The products of hydrolysis were in order of elution, *trans*- $[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$ (~21%), $[\text{Co}(\text{en})_2\text{N}_3\text{glyO}]^+$ (~14%), $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ (47%), and *cis*- $[\text{Co}(\text{en})_2\text{N}_3(\text{glyOC}(\text{CH}_3)_3)]^{2+}$ (~9%, $\lambda_{\text{max}} 510 \mu\text{m}$). Treatment of the *cis*- $[\text{Co}(\text{en})_2\text{N}_3(\text{glyOC}(\text{CH}_3)_3)]^{2+}$ solution with HNO₂ gave $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ ($\lambda_{\text{max}} 485 \mu\text{m}$, $\epsilon 98$). $[\text{Co}(\text{en})_2\text{Br}(\text{glyOC}(\text{CH}_3)_3)]\text{Br}_2$ was stable toward HNO₂. The azide in the azido ester complex was partly displaced under the conditions of elution (~6% $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ was formed from the azido ester band during elution), and the failure to detect the corresponding azido isopropyl ester from the H⁺ form of the column was ascribed to this behavior.

E. O¹⁸-Tracer Experiments. Table VIA-C presents data obtained for the kinetics of oxygen exchange in $[\text{Co}(\text{en})_2\text{gly}]^{2+}$, isolated from base hydrolysis of

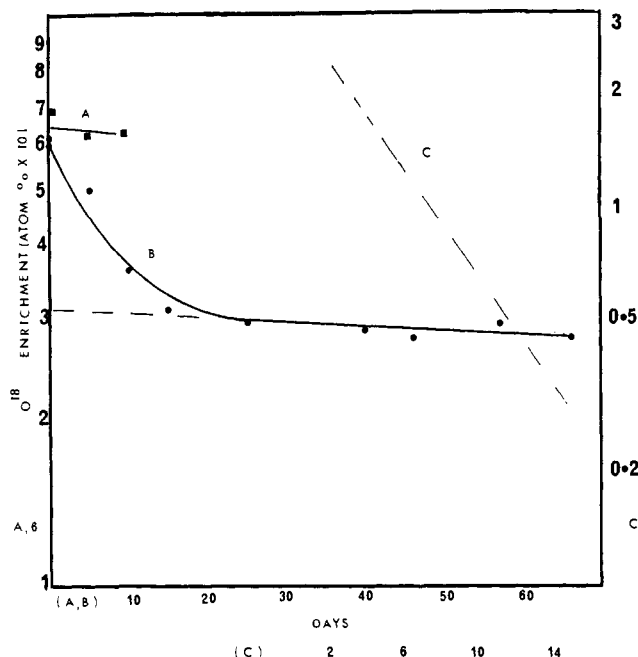


Figure 2. O¹⁸ exchange in (A) $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ prepared by Hg²⁺-induced acid hydrolysis of O¹⁸-carbonyl-labeled $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]\text{Br}_2$ and recovered after 90 min at pH 8.7; and (B) $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ prepared by base hydrolysis of O¹⁸-carbonyl-labeled $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]\text{Br}_2$ for 90 min at pH 8.7. (C) represents the rate obtained by subtracting from (B) the extrapolated value for its slower rate of exchange (0.1 M HClO₄, $\mu = 1.0$, 25°).

$[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]^{2+}$ at pH 8.6. The labeling and isolation procedures corresponding to the entries in Table VIA-G are listed in the Experimental Section. Table VIA presents results following the hydrolysis of carbonyl-O¹⁸-labeled $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)](\text{ClO}_4)_2$ in unlabeled water. The $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ formed in the reaction was isolated and recrystallized as $[\text{Co}(\text{en})_2\text{gly}]_2$. Since a direct measure of the enrichment in the parent bromo ester complex has been shown to be impracticable,¹ it was necessary to determine indirectly the enrichment using the Hg²⁺-induced hydrolysis reaction which gives virtually full retention of the carbonyl-O¹⁸ label.¹ This resulted in a figure of 0.683 atom % (Table VIE). The first entry in Table VIA then represents 88% retention of the label in the base hydrolysis experiment. The discrepancy from 100% was accounted for by loss of label during the isolation and recrystallization procedure. Subsequent enrichments are given in Table VIA, and these are plotted against time using a logarithmic ordinate in Figure 2, curve B. Two rates of oxygen exchange are apparent and extrapolation of the slower rate to zero time gives an intercept of 0.31 atom %, or 45% of the original enrichment. Subtraction of this rate from the observed curve gave a linear plot, Figure 2C, for the faster exchange with a rate constant of $2 \times 10^{-6} \text{ sec}^{-1}$. These two rates of oxygen exchange are similar to those previously attributed¹ to labeling in the carboxyl and carbonyl oxygens, respectively.

Table VIB presents results for exchange in $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ obtained from hydrolysis of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)](\text{ClO}_4)_2$ in O¹⁸-labeled water. The first entry represents the solvent enrichment, and the second entry is for $[\text{Co}(\text{en})_2\text{gly}]_2$ at zero time. This latter figure is 44% of the solvent value, indicating the incorporation of

almost one oxygen atom from the solvent in the product. The discrepancy from 50% was attributed to slight exchange occurring during recovery and recrystallization of the $[\text{Co}(\text{en})_2\text{gly}]_2$. Table VIC gives results of a similar experiment, except that $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ was isolated and purified by a more lengthy procedure including elution from an H^+ -form ion-exchange column. In this case the enrichment is only 36% of the solvent figure, indicating more extensive oxygen exchange during isolation. In both B and C two rates for oxygen exchange in 0.1 M H^+ are apparent, and extrapolation of the slower rate to zero time in a similar manner to that depicted by Figure 2 gives for B an ordinate intercept of 0.34 atom % O^{18} (46% of half the solvent figure) and for C, 0.41 atom % O^{18} (58% of half the solvent figure).

Table VID-G gives the results of some supplementary O^{18} -labeling experiments. D records the observation that unlabeled $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ placed in 1.5 atom % H_2O^{18} remains unlabeled under conditions used in the base hydrolysis of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]^{2+}$. E gives the kinetic results obtained when exclusively carboxyl O^{18} -labeled $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ was permitted to exchange under acid conditions after being exposed to the experimental conditions of base hydrolysis. The results of E are also shown in Figure 2 (curve A). There is effectively little exchange, indicating that the oxygen label has remained intact in the Co-O position. Similar results for the O^{18} -labeled chelated ester intermediate $[\text{Co}(\text{en})_2(\text{glyOCH}(\text{CH}_3)_2)]^{3+}$ are given in Table VIF. Again the method of preparation ensures that the labeled oxygen is initially exclusively in the Co-O position¹⁶ and base hydrolysis does not result in any scrambling of the oxygen label, as seen from the lack of exchange in the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ product.

In another experiment, Table VIG, the bromo complexes were recovered after base hydrolysis for one half-life in labeled solvent, pH 8.6, 25°. The ir spectrum of this material was identical with that of the original $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)](\text{ClO}_4)_2$. Moreover, elution of species sorbed on the ion-exchange resin from the filtrate failed to reveal any bromide-containing species, indicating that the above isolation was essentially quantitative. Entry G indicates little or no label incorporation in this material. This eliminates exchange in the monodentate ester prior to bromide removal and also eliminates the formation of a stable ester hydrate which, if formed, would have incorporated one-half of the solvent enrichment.

F. Base Hydrolysis of $(-)\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}_3)\text{Br}_2$. When $(-)\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}_3)\text{Br}_2$ ($[\alpha]_{589} -115^\circ$) was hydrolyzed for 90 min under conditions identical with those used in the O^{18} -tracer experiments the resulting $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ isolated by ion exchange gave $[\alpha]_{589} -154^\circ$. This may be compared with optically pure $(-)\text{Co}(\text{en})_2\text{glyI}_2$, $[\alpha]_{589} -305^\circ$.²¹ $(-)\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}_3)\text{Br}_2$ was shown to be optically pure by treatment with Hg^{2+} , when $(-)\text{Co}(\text{en})_2\text{glyI}_2$, $[\alpha]_{589} -305^\circ$, was formed. In another experiment, a solution of $(+)\text{Co}(\text{en})_2\text{glyI}_2$, $[\alpha]_{589} 300^\circ$, was left standing for the same time and under the same conditions as for base hydrolysis of $(-)\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}_3)\text{Br}_2$. It was then sorbed on and eluted from the ion-exchange resin. The $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ in the eluate showed full retention of optical

activity, $[\alpha]_{589} 300^\circ$. The results require base hydrolysis of $(-)\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}_3)\text{Br}_2$ to occur with 50% racemization.

Discussion

The following discussion is primarily concerned with the path leading to the formation of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$. The sections are concerned with the order of events relating to loss of halide, ester function, and the intervention of solvent in the course of the reaction. The amount of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ product varies between 35 and 76% for the different substrates, and numerous by-products occur, some of which are not yet identified. The final section is devoted to a discussion of some of these species and their origin, but in general they are considered only in regard to their role in the production of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$.

Kinetics and Competition Studies. The $[\text{Co}(\text{en})_2\text{X}(\text{glyOR})]^{2+}$ ions show the common property of two consecutive pseudo-first-order reactions on base hydrolysis at pH 8.6, Table II. For $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]^{2+}$ these two reactions have the rate law $R = k[\text{complex}][\text{OH}^-]$ (Tables IA and IB), and it seems justified by the data in Table II to assume that this is a general result. The faster reaction (k_1) is insensitive to variation of the ester grouping but exhibits a fourfold rate increase between $\text{X} = \text{Cl}$ and $\text{X} = \text{Br}$. The former observation suggests little or no ester involvement, since if this occurred a substantial variation in rate with changing R group might be anticipated. For example, benzyl acetate base hydrolyzes at a faster rate than methyl acetate which in turn is a factor of 100 times faster than *t*-butyl acetate.²² A similar large variation in rate is found in both the uncoordinated²³ and chelated² amino acid esters.

Also, the spectral change (545–490 m μ) for the k_1 path with $[\text{Co}(\text{en})_2\text{Br}(\text{glyOR})]^{2+}$ ions indicates loss of Br^- . A similar result obtains for the chloro ester complexes. The fourfold rate difference between $\text{X} = \text{Br}$ and $\text{X} = \text{Cl}$ correlates with base hydrolysis of other pentaamminecobalt(III)-halo complexes, e.g., the $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ and $[\text{Co}(\text{en})_2\text{NH}_3\text{X}]^{2+}$ ions.^{24,25} Also, in the presence of N_3^- as a competing anion, base hydrolysis of $[\text{Co}(\text{en})_2\text{Br}(\text{glyOC}(\text{CH}_3)_3)]\text{Br}_2$ gave 9% $[\text{Co}(\text{en})_2\text{N}_3(\text{glyOC}(\text{CH}_3)_3)]^{2+}$ which requires that loss of Br^- does, at least in part, precede ester hydrolysis for this complex. A more significant experiment in this regard is the following (Table IV). After $\sim 2t_{1/2}$ for the initial hydrolysis (k_1) of $[\text{Co}(\text{en})_2\text{Cl}(\text{glyOCH}_3)]^{2+}$, only 5% $[\text{Co}(\text{en})_2\text{Cl}(\text{glyO})]^+$ was detected on ion exchange, whereas 28% of the expected 36% $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ was formed. This represents close to the maximum quantity of $[\text{Co}(\text{en})_2\text{Cl}(\text{glyO})]^+$ formed in the reaction, since this ion is known to base hydrolyze about five times slower than $[\text{Co}(\text{en})_2\text{Cl}(\text{glyOCH}_3)]^{2+}$ under the same conditions.¹⁶ The final product is in the latter case exclusively $[\text{Co}(\text{en})_2\text{gly}]^{2+}$. Thus, no more than 10% of $[\text{Co}(\text{en})_2\text{Cl}(\text{glyO})]^+$ is possible from the hydrolysis of $[\text{Co}(\text{en})_2\text{Cl}(\text{glyOCH}_3)]^{2+}$, which allows less than 30% of the observed $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ to come *via* this route. Moreover, the latter value will represent a maximum

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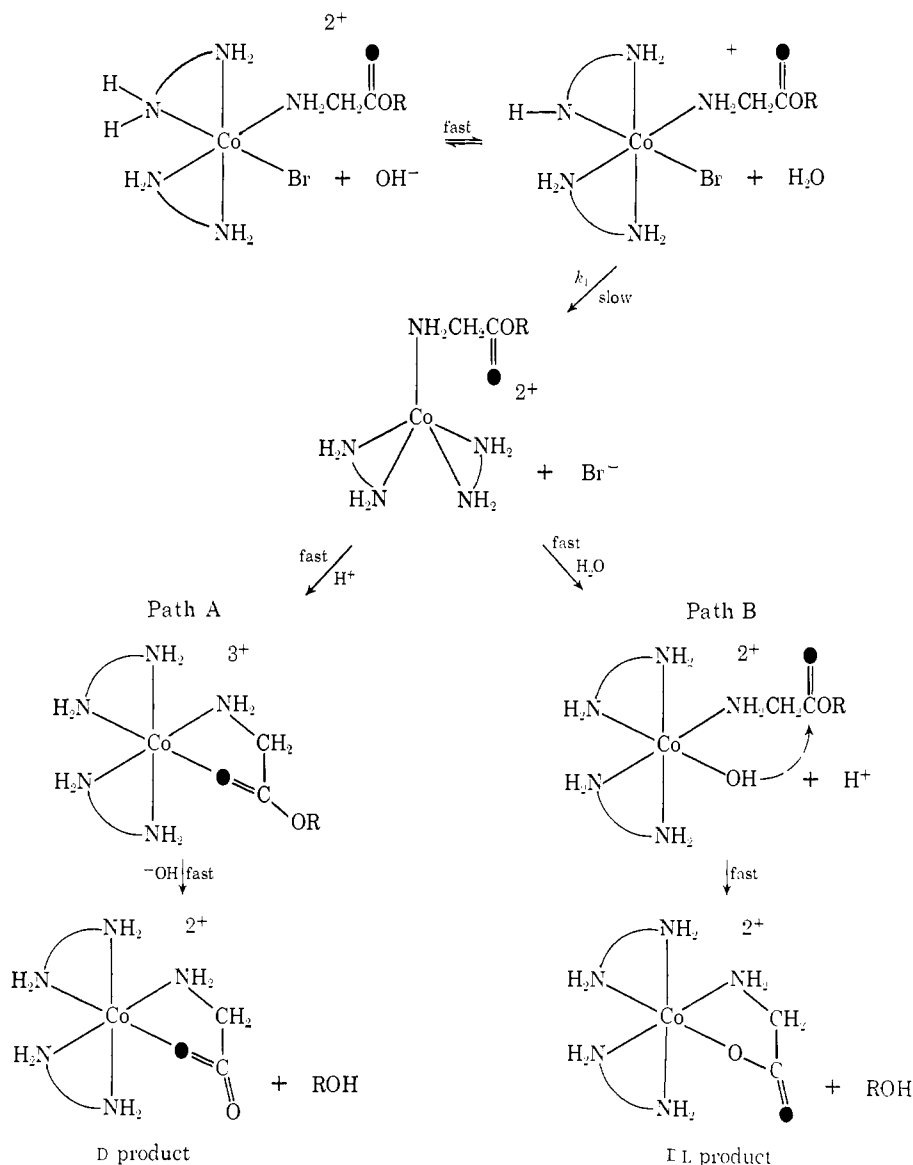


Figure 3. Proposed paths for production of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$.

limit for the ester complexes in general, since the chloromethyl ester represents the most favorable opportunity for monodentate ester hydrolysis. For the bromo esters, this pathway may be eliminated entirely since no $[\text{Co}(\text{en})_2\text{Br}(\text{glyO})]^+$ was found by the ion-exchange method after quenching the reaction at times most favorable for its appearance. The bromoglycinato, like the chloroglycinato, complex base hydrolyzes about five times slower than the corresponding halo ester.¹⁶

The data for the chloro ester complexes contradict the proposals of Hay and coworkers⁹ that ester hydrolysis precedes halide hydrolysis for the $[\text{Co}(\text{en})_2\text{Cl}(\text{glyOC}_2\text{H}_5)]^{2+}$ ion, and that the $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ product arises largely from the intermediate $[\text{Co}(\text{en})_2(\text{OH})(\text{glyO})]^+$ ion.

Hydrolysis of the ester moiety therefore does not precede or effectively compete with loss of halide in the $[\text{Co}(\text{en})_2\text{Br}(\text{glyOR})]^{2+}$ ions. However, release of isopropyl alcohol ($\text{R} = \text{CH}(\text{CH}_3)_2$) occurs at a rate close to that of bromide release (Figure 1), and certainly much faster than the subsequent slower base hydrolysis

reaction (k_2). This result requires that ester hydrolysis proceed rapidly following bromide removal. It is unlikely that this occurs in the five-coordinate intermediate since such species are likely to have approximately diffusion-controlled lifetimes. Also from the Results, section C, it is evident that $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ arises from the k_1 path. This requires that $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ be produced rapidly, but not necessarily directly, following release of alcohol.

Moreover, the formation of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ from *cis*- and *trans*- $[\text{Co}(\text{en})_2(\text{glyO})(\text{OH})]^+$ is slow, so that these ions cannot provide a route for the rapid production of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ from the bromo or chloro esters. In fact, the isomers of $[\text{Co}(\text{en})_2(\text{glyO})(\text{OH})]^+$ arise from the base hydrolysis of *cis*- $[\text{Co}(\text{en})_2(\text{glyO})\text{Cl}]^+$ rather than from *cis*- and *trans*- $[\text{Co}(\text{en})_2(\text{OH})(\text{glyOR})]^{2+}$.¹⁶

The rate law is consistent with base hydrolysis of cobalt(III) pentaammine-type complexes, and the cumulative data support an SN1CB mechanism for these processes.^{4,5,26,27} The evidence for the existence of

(26) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Re-

deprotonated five-coordinate intermediates is substantial and allows H₂O or the carbonyl oxygen to be a competitor for the vacated coordination position.

O¹⁸-Tracer Studies and Mechanism. After halide removal, there are at least two ways in which the monodentate ester complex can react to facilitate ester hydrolysis. One possibility is that the ester carbonyl oxygen occupies the vacated site in the five-coordinate deprotonated intermediate to form the chelated ester [Co(en)₂(glyOR)]³⁺. This species is known to hydrolyze very rapidly in base to form [Co(en)₂gly]²⁺ + HOR (*k*_{OH} = 1.5 × 10⁶ M⁻¹ sec⁻¹ for R = CH(CH₃)₂).¹⁶ The other possibility is that water competes favorably for the intermediate to form *cis*-[Co(en)₂(OH)(glyOR)]²⁺, and that the bound hydroxide then attacks the carbonyl center in a concerted manner. These possibilities are given in Figure 3 as paths A and B. *trans*-[Co(en)₂(OH)glyOR]²⁺ was not considered as a route to [Co(en)₂gly]²⁺ since studies on the related complex *trans*-[Co(en)₂NH₃(OH)]²⁺ indicate isomerization to the *cis* ion would be a slow process.²⁵

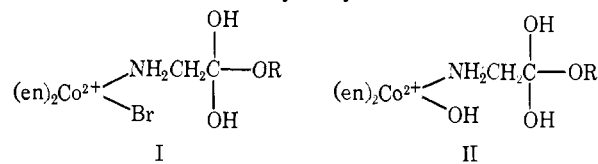
As indicated in Figure 3, one method of distinguishing between paths A and B is by using an O¹⁸ label; the chelated ester giving rise to Co-O¹⁸, and intramolecular attack of bound OH resulting in C=O¹⁸, in the [Co(en)₂gly]²⁺ product. A previous study has shown that these two products may be distinguished; the Co-O oxygen exchanges slowly with the solvent in 0.1 M H⁺ while the C=O exchanges readily.¹

The results of the O¹⁸ experiments (Table VI; Figure 2) show that close to one oxygen atom of the solvent is incorporated. This eliminates from further consideration entry of the ether oxygen in the intermediate, followed by alkyl-oxygen bond fission. It is clear that when *carbonyl*-O¹⁸-[Co(en)₂Br(glyOCH(CH₃)₂)]²⁺ is hydrolyzed in normal water, or unlabeled complex in H₂O¹⁸, enrichment occurs in both the carbonyl and carboxyl oxygens of [Co(en)₂gly]²⁺. The former result gives 45% retention of the O¹⁸ label in the carboxyl position, while the latter experiments in H₂O¹⁸ give 54 and 42% incorporation of the monodentate ester carbonyl into the Co-O position. The ~50% distribution of label requires that paths A and B of Figure 3 contribute about equally to the production of [Co(en)₂gly]²⁺. The result cannot be explained by intramolecular interchange between the carbonyl and carboxyl oxygens in [Co(en)₂gly]²⁺ during hydrolysis (Table VI). Nor can it be accommodated by a scrambling mechanism during hydrolysis of the chelated ester intermediate, since *carbonyl*-O¹⁸-[Co(en)₂(glyOCH(CH₃)₂)]³⁺ shows no oxygen interchange on base hydrolysis (Table VIF).

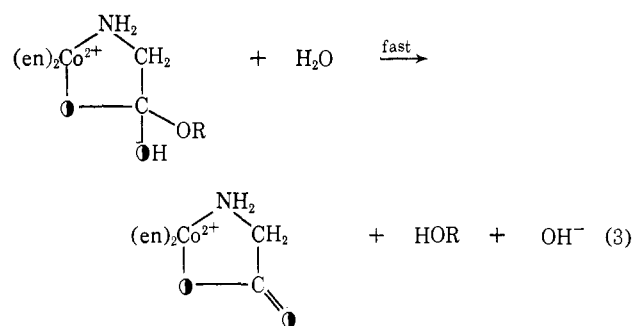
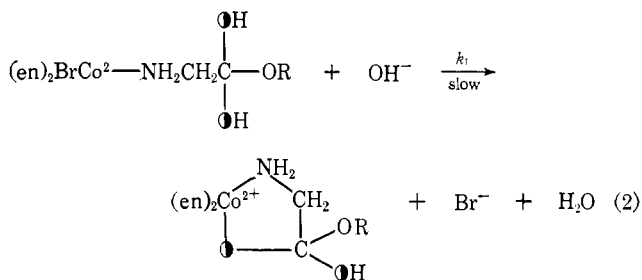
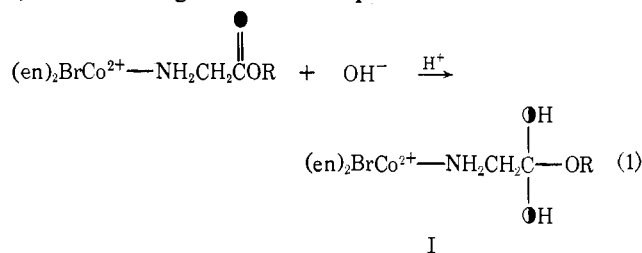
The 50% incorporation of label (R = CH(CH₃)₂) compares with the 50% racemization (R = CH₃) in the [Co(en)₂gly]²⁺ product. Additional work using the [Co(trien)Cl(glyOC₂H₅)]²⁺ species¹³ suggests that this is not a coincidence and that (+)₅₈₉-[Co(en)₂gly]²⁺ may arise solely from path A. This aspect of the problem is being tested by hydrolyzing (-)₅₈₉-[Co(en)₂Br(glyOCH₃)]²⁺ in labeled solvent, separating the active

and racemic [Co(en)₂gly]²⁺, and examining each half for the position of the O¹⁸ label.

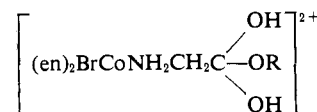
Another mechanistic possibility is that I and II, which could be formed in the hydrolysis of the monodentate



ester, react here exclusively by expelling coordinated Br⁻ or OH⁻, respectively. For example, in the case of I, the following mechanism equates the rate of alcohol



production, Br⁻ release, and base consumption, and supports the observed insensitivity of *k*₁ to the nature of the ester. The experimental results merely require that the ester hydrate intermediate not be in equilibrium with the reactants since loss of oxygen label is not observed. The rate of Co-Br bond cleavage must also exceed that for C-OR, since no [Co(en)₂Br(glyO)]⁺ is formed. Reaction 1 cannot be rate determining, since this would predict a reaction rate which was sensitive to the ester grouping and insensitive to the nature of the coordinated halide. However, the bromo-containing species collected after one half-life were shown to be identical with the starting material and incorporated no solvent oxygen. This result requires that solvent participation in hydrolysis occur subsequent to Br⁻ release, and the the ester hydrate

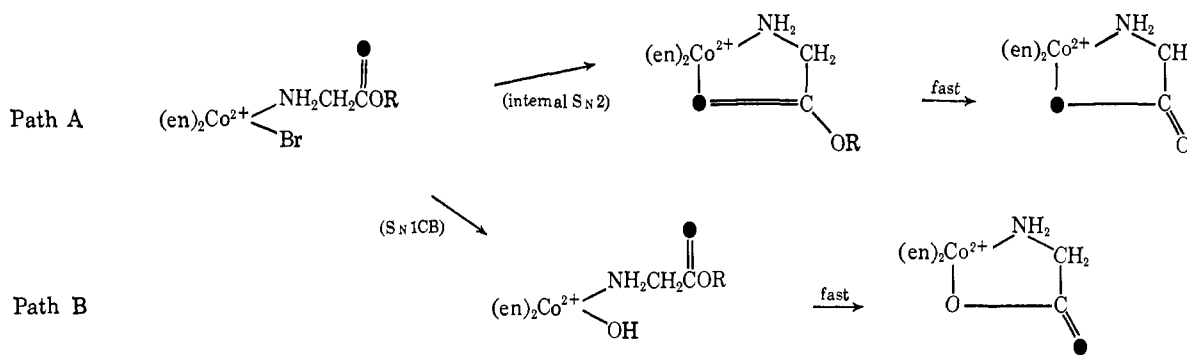
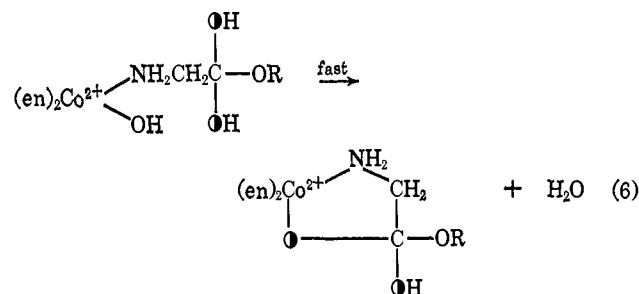
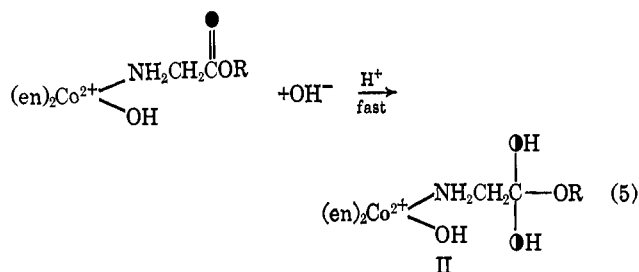
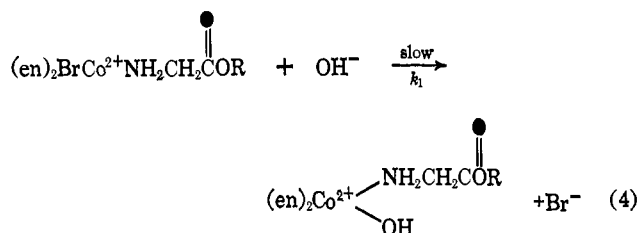


is not involved.

actions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 124 ff.

(27) (a) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **88**, 5443 (1966); (b) *ibid.*, **90**, 6654 (1968).

(28) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).



The alternative possibility, proceeding *via* eq 4–6, is also consistent with the experimental data and requires that II not be in equilibrium with its precursor. This mechanism requires that II be formed from $[\text{Co}(\text{en})_2(\text{OH})\text{glyOR}]^{2+}$ but not from $[\text{Co}(\text{en})_2\text{Br}(\text{glyOR})]^{2+}$ and that the rapid displacement of coordinated OH^- by the ester hydrate function occur exclusively. Further, $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ is formed only slowly from $\text{cis}[\text{Co}(\text{en})_2(\text{OH})(\text{glyO})]^+$ which contains a carboxylate function of at least comparable nucleophilicity to the ester hydrate of II. These limitations suggest to us that this mechanism is unlikely.

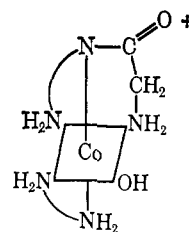
A further possibility which cannot be eliminated by the results is that of duality of mechanism. It is possible that the incorporation of O^{18} label into the two positions results from two different paths: one involving internal synergic displacement of Br^- by the carbonyl group to form the chelated ester directly (path A), and the other proceeding *via* the normal $\text{S}_{\text{N}}1\text{CB}$ mechanism (path B). The oxygen label has been shown to remain fixed in the subsequent hydrolysis of the chelated ester intermediate (path A), while

the intermediate hydroxo ester in path B is required to hydrolyze by attack of bound hydroxide. Such a mechanism differs from that given by Figure 3 by the absence of a common intermediate for the two paths. It is in principle possible to distinguish between the two mechanisms by making use of this difference, but a distinction has not yet been attempted.

An analogous example of intramolecular attack by a coordinated nucleophile is found in the reaction of $[\text{Co}(\text{NH}_3)_5(\text{glyOC}_2\text{H}_5)]^{3+}$ with base.³ The observed rate law, $k_{\text{obsd}} = k_1[\text{OH}] + k_2[\text{OH}]^2$, equates k_1 to hydrolysis by external hydroxide to form $[\text{Co}(\text{NH}_3)_5(\text{glyO})]^{2+}$, and k_2 to internal attack by deprotonated ammonia to form $[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_2\text{CONH})]^{2+}$ in which glycine imide is chelated to the metal through both nitrogens. The small concentration of the coordinated amido group ($\text{p}K_{\text{a}} > 16$) competes effectively with external hydroxide ion for lysis of the ester group at pH 9. It is not surprising then that bound OH^- ($\text{p}K_{\text{a}} \sim 6$) in the hydroxo complex also competes efficiently with external OH^- for the same site. The enormous difference in concentration between coordinated NH_2^- and OH^- compensates for any difference in nucleophilic character of the two species.

Reaction By-Products. The identification of some of the other products of hydrolysis (Table IV) is uncertain, but in view of the preceding discussion we suggest that the ion separated as band 4, Table IV, could be the

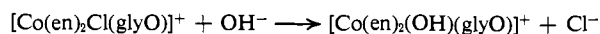
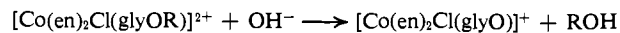
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This ion fulfills the requirement of consuming 2 equiv of base in its formation, contains no halide, and elutes as a 2+ ion at pH 5–6. It represents the product expected from attack by a deprotonated ethylenediamine amido group at the carbonyl center. This species occurs as a major product for the chloro esters, and this suggests that the imide forms prior to loss of halide. Attempts to isolate the compound from the eluate were unsuccessful.

Table II shows that the amount of $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ produced is a function of both halide and to a lesser extent ester moiety. The analysis of base consumed

during hydrolysis (Table V) shows that all products other than $[\text{Co}(\text{en})_2\text{gly}]^{2+}$ have consumed 2 equiv of OH^- , and columns 3 and 6 of Table V show that base consumption can occur before, during, and after the k_1 path. For example small amounts of *cis*- and *trans*- $[\text{Co}(\text{en})_2(\text{OH})(\text{glyO})]^+$ were formed from the chloro



esters. Also, it is evident from the agreement between columns 5 and 6, for $[\text{Co}(\text{en})_2\text{Br}(\text{glyOCH}(\text{CH}_3)_2)]^{2+}$ (Table V), that the $\sim 27\%$ of other products results

from reactions occurring after loss of Br^- (k_1). For the other halo esters the side products form both before and after loss of halide.

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The Crystal Structure of β, β', β'' -Triaminotriethylamineisothiocyanatozinc(II) Thiocyanate¹

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Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. Received February 13, 1969

Abstract: The crystal structure of β, β', β'' -triaminotriethylamineisothiocyanatozinc(II) thiocyanate, $[\text{Zn}(\text{tren})(\text{NCS})](\text{SCN})$, has been determined by Fourier methods and refined by full-matrix least squares using three-dimensional X-ray data consisting of 2561 independent reflections measured with Mo $K\alpha$ radiation on a four-circle diffractometer by the ω - 2θ scan technique. The final values of R and R_w are 0.054 and 0.038, respectively. The crystals have space group $Pbca$ and a cell of dimensions $a = 12.888$, $b = 16.466$, $c = 13.633$ Å containing eight molecules. Calculated and measured densities are 1.504 and 1.49 g cm^{-3} , respectively. The crystal structure consists of trigonal-bipyramidal $[(\text{tren})(\text{SCN})\text{Zn}]^+$ cations and SCN^- anions, connected by a network of $\text{NH} \cdots \text{N}$ and $\text{NH} \cdots \text{S}$ hydrogen bonds.

The structures of the complexes of the polyamine ligand, β, β', β'' -triaminotriethylamine ($\text{N}(\text{CH}_2\text{CH}_2\text{-NH}_2)_3 \equiv \text{tren}$) with bivalent metal ions are of considerable interest. X-Ray crystallographic studies of the solids have shown that $\text{Ni}(\text{tren})(\text{NCS})_2$ ⁴ has a six-coordinate *cis*-octahedral structure, while the copper(II)⁵ and zinc(II)¹ compounds have a five-coordinate trigonal-bipyramidal structure. Thermodynamic, conductometric, and spectral studies of solutions suggest⁶ that the manganese(II) and iron(II) compounds are probably six-coordinate and the cobalt(II) compound is five-coordinate.

A study of the complexes of tris(2-dimethylaminoethyl)amine with the bivalent metal bromides of Mn, Fe, Co, Ni, Cu, and Zn has shown the six compounds to be isomorphous and to consist of trigonal-bipyramidal MLBr^+ cations and bromide anions.⁷⁻⁹

(1) A short communication has been published: P. C. Jain, E. C. Lingafelter, and P. Paoletti, *J. Am. Chem. Soc.*, **90**, 519 (1968).

(2) Istituto di Chimica Fisica, Università di Parma, 43100 Parma, Italy.

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(8) M. Di Vaira and P. L. Orioli, *Acta Cryst.*, **B24**, 595 (1968).

(9) M. Ciampolini, M. Di Vaira, and P. L. Orioli, personal com-

We report here the details of the X-ray crystallographic study of the zinc compound, $[\text{Zn}(\text{tren})(\text{NCS})](\text{SCN})$.

Experimental Section

$[\text{Zn}(\text{tren})(\text{NCS})](\text{SCN})$ was prepared from aqueous solution by the method of Barclay and Barnard¹⁰ and recrystallized from water.

A colorless crystal of dimensions $0.28 \times 0.16 \times 0.16$ mm was selected for study. Oscillation and equinclination Weissenberg photographs showed the crystal to be orthorhombic. Systematic absence of $0kl$ for $k \neq 2n$, $h0l$ for $l \neq 2n$, and $hk0$ for $h \neq 2n$ indicate the space group $Pbca$. The lattice parameters were determined using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) from the least-squares fit to measurements of 22 θ values in the range 13 – 21° (determined by the $+2\theta$, -2θ technique), taken on a Picker single-crystal diffractometer at 24° .

Crystal Data. The lattice parameters are $a = 12.888 \pm 0.002$, $b = 16.466 \pm 0.003$, $c = 13.633 \pm 0.002$ Å; cell volume 2893.1 Å³. The density measured by the flotation method, 1.49 g cm^{-3} , agrees satisfactorily with that calculated, 1.504 g cm^{-3} , for eight formula units per cell. $F(000) = 1360$. The linear absorption coefficient for Mo $K\alpha$ radiation is 20.1 cm^{-1} .

The crystal was mounted with the a axis parallel to the ϕ axis of a Picker automated single-crystal diffractometer equipped with a pulse-height analyzer. Intensity data were collected using Mo $K\alpha$ radiation. Diffractometer settings for each possible reflection with all indices positive for the ω - 2θ scan method were calculated using

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