cyclic transition state with *t*-butyl alcohol. This conclusion is consistent with that derived from the H-isotope effects in the related aqueous medium.

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Cobalt(III)-Promoted Hydrolysis of Chelated Glycine Esters. Kinetics, Anion Competition, and O^{18}-Exchange Studies

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Abstract: Kinetic data for the hydrolysis of $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ in aqueous solution have been obtained, and the results confirm the proposal made by Alexander and Busch[1] that a chelated ester intermediate $[Co(en)_2(glyOR)]^{3+}$ is formed following the Hg^{2+}-induced removal of halide ion from $[Co(en)_2X(glyOR)]^{2+}$ (X = Cl, Br; R = CH_3, C_2H_5, C_3H_7). The same intermediate is generated following the HOCl oxidation of coordinated Br^-. Anion competition results indicate that the chelated ester intermediate is formed directly in the Hg^{2+}-assisted reaction but suggest that some $[Co(en)_2(H_2O)(glyOC_3H_7)]^{3+}$ is generated in the HOCl-promoted reaction. O^{18} studies establish that hydrolysis of $[Co(en)_2(glyOCH_3)]^{3+}$ proceeds without opening of the chelate ring and that the coordinated ester is bound to Co(III) through the carbonyl oxygen.

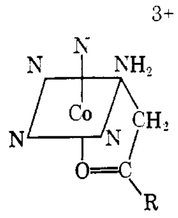
In a recent publication Alexander and Busch have discussed the cobalt(III)-promoted hydrolysis of coordinated glycine esters (reaction 1).[1] Similar, although less detailed information has been obtained for the hydrolysis of small and relatively simple peptide molecules (reaction 2).[2] Both reactions result in a final cobalt(III) product containing the chelated N-amino acid anion, and a marked enhancement in rate, compared to the uncatalyzed reactions, was found for hydrolysis of the ester and peptide bonds, respectively.

$$[Co(en)_2X(glyOR)]^{2+} + Hg^{2+} + H_2O \longrightarrow [Co(en)_2gly]^{2+} + HOR + H^+ + HgX^+ \quad (1)$$

$$X = Cl, Br; \; R = CH_3, C_2H_5, i\text{-}C_3H_7$$

$$[Co(trien)OH(H_2O)]^{2+} + NH_2CHRCONHCHR'\cdots CO_2R'' \longrightarrow [Co(trien)(NH_2CHRCO_2)]^{2+} + NH_2CHR'\cdots CO_2R'' + H_2O \quad (2)$$

Our interest in the above reactions has been stimulated following the isolation and characterization of chelated amino acid ester, amino acid amide, and dipeptide ester complexes of general structure I.[3] Coordination complexes of this structural type have been invoked in the metal ion catalyzed acceleration in the hydrolysis of such substrates,[4] but, with the exception of $[Co(trien)(glyglyOEt)]^{3+}$ which was isolated from reaction 2,[5] the reported evidence to support the formation of such intermediates either prior to or as a step in the hydrolysis reaction is largely of an indirect kind. For example, Alexander and Busch proposed a chelated ester intermediate $[Co(en)_2(glyOR)]^{3+}$ as the reactive intermediate (structure I) in the Hg^{2+}-promoted hydrolysis (reaction 1). The evidence for this species was obtained primarily from the change in the >C=O stretching frequency as the monodentate ester (1735 cm^{-1}) was first chelated (1610 cm^{-1}) and then hydrolyzed to $[Co(en)_2gly]^{2+}$ (1640 cm^{-1}).



I

R = OR, NRR′, NHRCHR′CO$_2$R″

As the $[Co(en)_2(glyOR)](ClO_4)_3$ compounds have now been isolated,[3] the hydrolysis rates can now be compared with those attributed to this intermediate by the previous authors. Other mechanistic aspects of this reaction which merit consideration are the following. (a) Does opening of the chelate ring precede hydrolysis? (b) Does removal of halide ion from the monodentate ester complex lead to initial incorporation of solvent at the vacated coordination site prior to chelation? (c) What properties does the monodentate ester aquo complex have? Some of these questions are potentially soluble using O^{18}-tracer techniques, and this paper presents some results obtained from such investigations.

Experimental Section

Analar reagents were used throughout without further purification.

O^{18}-Labeled glycine methyl ester hydrochloride was prepared as follows. Glycine hydrochloride was enriched by refluxing the salt for 24 hr at pH 0.5 (HCl) with 1.5 atom % O^{18}-enriched water.[6]

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

[2] D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *ibid.*, **89**, 1082 (1967).

[3] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 4539 (1967).

[4] (a) H. Kroll, *ibid.*, 74, 2036 (1952); (b) M. L. Bender and B. W. Turnquest, *ibid.*, 79, 1889 (1957); (c) an excellent review of this subject is given by M. L. Bender, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 19.

[5] J. P. Collman and E. Kimura, *J. Am. Chem. Soc.*, **89**, 6096 (1967).

The dry product (21 g) was methylated by refluxing until dissolved in methanol (200 ml) and thionyl chloride (12 ml). The methyl ester hydrochloride obtained on evaporation was redissolved in warm methanol and crystallized by cooling in an ice bath. *Anal.* Calcd for $C_3H_8O_2Cl$: C, 28.70; H, 6.42: N, 11.16. Found: C, 28.79; H, 6.26; N, 11.45. Glycine isopropyl ester was prepared in an analogous manner.

HOCl was prepared by freshly extracting a solution of chlorine(I) oxide in carbon tetrachloride into an equal volume of water (or dilute $HClO_4$).[7] The acid so prepared was consistently 1.8–2 *M* (estimated by iodometric titration).

Pmr spectra were recorded on a Perkin-Elmer R-10 spectrometer using sodium trimethylsilylpropanesulfonate (TPSNa) as an internal reference (D_2O) or tetramethylsilane (TMS) (acetone-d_6). Infrared spectra were taken on SP-200 Unicam or Perkin-Elmer 257 instruments. Hydrolysis of $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ was followed on the Perkin-Elmer 257 in 0.658 *N* DCl using a 0.025-mm lead spacer. Spectrophotometric rates were measured on a Cary 14 spectrophotometer. Bio-Rad analytical Dowex 50W × 2 (200–400 mesh) cation-exchange resin was used to analyze products from the competition experiments.

The O^{18} content in the CO_2 recovered from the labeled complexes were determined using an Atlas M-86 mass spectrometer.

Preparation of Complexes. *cis*-$[Co(en)_2Br(glyOCH_3)]Br_2$ and *cis*-$[Co(en)_2Br(glyOC_3H_7)]Br_2$ were prepared from *trans*-$[Co(en)_2Br_2]Br \cdot HBr$ and the appropriate glycine ester hydrochloride as described by Alexander and Busch.[8] These compounds were converted to their perchlorate salts by dissolving in hot 10^{-3} *M* $HClO_4$, followed by addition of excess $NaClO_4$ and cooling in an ice bath. The products were twice recrystallized from hot dilute $HClO_4$ by adding $NaClO_4$. They were washed with ethanol and dried in an evacuated desiccator. *Anal.* Calcd for $[Co(en)_2Br(glyOCH_3)](ClO_4)_2$: C, 15.38; H, 4.24; N, 12.80. Found: C, 15.28; H, 4.41; N, 12.93. Calcd for $[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$: C, 18.80; H, 4.73; N, 12.18. Found: C, 18.84; H, 4.99; N, 12.36. *cis*-$[Co(en)_2Cl(glyOC_3H_7)](ClO_4)_2$ was prepared in a similar manner from *trans*-$[Co(en)_2Cl_2]Cl$ and glycine isopropyl ester hydrochloride. *Anal.* Calcd for $[Co(en)_2Cl(glyOC_3H_7)](ClO_4)_2 \cdot H_2O$: C, 19.70; H, 5.33; N, 12.77. Found: C, 19.93; H, 5.33; N, 12.89.

Directions for preparing the chelated ester intermediates $[Co(en)_2(glyOCH_3)](ClO_4)_3$ and $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ will be described shortly in a paper describing peptide syntheses.[9]

Bromoglycinatobis(ethylenediamine)cobalt(III) Bromide. Powdered $[Co(en)_2Br(glyOCH_3)]Br_2$ (11 g) was added to 7.6 *N* HBr (100 ml) and the solution warmed at 50° for 15 min and then shaken at room temperature for 76 hr. The solution was cooled in an ice bath and the fine red precipitate was collected, washed with ethanol and acetone, and dried. This material was dissolved in the minimum volume of water at 80°, the solution was filtered, HBr was added (2 ml, 7.6 *N*), and the solution was allowed to stand overnight at 25°. The red crystals were collected and washed with dilute ice-cold HBr and methanol and air-dried (5.6 g). *Anal.* Calcd for $[Co(en)_2Br(glyOH)]Br_2$:[10] C, 14.59; H, 4.28; N, 14.18. Found: C, 14.37; H, 4.32; N, 14.48.

Preparation of O^{18}-Labeled Complexes. Carbonyl O^{18}-labeled *cis*-$[Co(en)_2Br(glyOCH_3)]Br_2$ was prepared from *trans*-$[Co(en)_2Br_2]Br \cdot HBr$ and O^{18}-labeled glycine methyl ester hydrochloride.[8] *Anal.* Calcd for $[Co(en)_2Br(glyOCH_3)]Br_2$: C, 16.55; H, 4.56; N, 13.79. Found: C, 16.35; H, 4.73; N, 13.70. This salt was converted to the perchlorate as described above. *Anal.* Calcd for $[Co(en)_2Br(glyOCH_3)](ClO_4)_2 \cdot H_2O$: C, 14.89; H, 4.46; N, 12.39. Found: C, 15.04; H, 4.44; N, 12.67.

Carbonyl-O^{18}-$[Co(en)_2(glyOCH_3)](ClO_4)_3$ was prepared from carbonyl-O^{18}-$[Co(en)_2Br(glyOCH_3)](ClO_4)_2$.[9]

Recovery of COO^{18}. O^{18}-Labeled glycine methyl ester hydrochloride was heated for not less than 2 hr at 400° in an evacuated sealed tube with an equimolar mixture of $HgCl_2$ and $Hg(CN)_2$,[11] and the CO_2 was distilled under vacuum, purified by passing through a gas chromatograph using He as the carrier, collected in a liquid nitrogen trap, and finally distilled into a Urey tube.[11b] The O^{18} content of the CO_2 was determined by the mass spectrometer. In a similar manner, glycine recovered from the complexes described below was decomposed with $HgCl_2$ and $Hg(CN)_2$ usually by heating overnight at 400°. The O^{18} content of the solvent was obtained by distilling the water (1 ml) on the vacuum line and equilibrating it with CO_2 (~0.1 mmole) overnight at 70°.[12]

O^{18}-Labeled *cis*-$[Co(en)_2Br(glyOMe)]Br_2$ was heated to 250° under 0.03 mm pressure, whereupon the free glycine methyl ester distilled over. The ester was collected in a liquid nitrogen cold trap and decomposed to CO_2 as described above.

Hg^{2+}-Induced Hydrolysis of O^{18}-Labeled *cis*-$[Co(en)_2Br(glyOMe)]^{2+}$. Carbonyl-$O^{18}$-labeled *cis*-$[Co(en)_2Br(glyOMe)](ClO_4)_2$ (0.5 g) was dissolved in 10 ml of 0.6 *M* Hg^{2+}–0.1 *M* $HClO_4$ solution. Hydrolysis of the purple bromo ester to the orange glycinato complex was complete within 30 sec at 20°. Excess NaI was added until all the initially precipitated HgI_2 had redissolved, and on cooling anhydrous $[Co(en)_2gly](HgI_4)$ precipitated. This was collected, washed with water and methanol, and dried in an evacuated desiccator for 2 hr. It was dried again in the vacuum line at 10^{-3} mm for 0.5 hr to remove all traces of solvents.

To recover the glycine, $[Co(en)_2gly](HgI_4)$ was heated slowly to 200° at 0.03 mm whereupon free glycine sublimed. This was collected on a cold-finger condenser, and the glycine decomposed to CO_2 with the $HgCl_2$–$Hg(CN)_2$ mixture.

Acid Hydrolysis of O^{18}-Labeled $[Co(en)_2(glyOMe)]^{3+}$. Carbonyl-O^{18}-$[Co(en)_2(glyOMe)](ClO_4)_3$ (0.9 g) was dissolved in 0.1 *M* $HClO_4$ (3 ml). After 5 min HgI_2, followed by excess NaI, was added. The $[Co(en)_2gly](HgI_4)$ product was collected and treated as above.

HOCl-Induced Hydrolysis of O^{18}-Labeled $[Co(en)_2Br(glyOMe)]^{2+}$. Carbonyl-$O^{18}$-*cis*-$[Co(en)_2Br(glyOMe)](ClO_4)_2$ (0.5 g) was treated with 5 ml of HOCl solution. (The solution was made by extracting a Cl_2O–carbon tetrachloride solution into an equal volume of 1.8 *M* $AgClO_4$–0.2 *M* $HClO_4$ solution and filtering to remove AgCl.) The reaction mixture turned orange within 30 sec at 20°. SO_2 was bubbled through the solution for 1 min to reduce unreacted HOCl, and excess NaI was added, whereupon the product precipitated as $[Co(en)_2gly](AgI_2)_2$. This was washed with water and methanol and dried in a vacuum desiccator overnight. The glycine was recovered in the same manner as for the $HgI_4{}^{2-}$ salt.

O^{18}-Labeled HOCl-Induced Hydrolysis of $[Co(en)_2Br(glyOCH_3)](ClO_4)_2$ The above procedure was repeated using O^{18}-labeled water,[13] and the complex was collected as the $HgI_4{}^{2-}$ salt.

Immediately after the addition of $HO^{18}Cl$ to the bromo ester, a sample of the solution was withdrawn and frozen in liquid nitrogen. The water from this sample was subsequently distilled under vacuum and equilibrated for 12 hr (70°) in a sealed tube with carbon dioxide.

Kinetic Measurements. The acid hydrolysis of $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ was followed spectrophotometrically at 487 mμ. A weighed quantity of $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ was dissolved in $HClO_4$ of known ionic strength at 25° and quickly transferred to a thermostated cell.

The HOCl-induced hydrolysis of $[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$ was followed at 480–490 mμ. A weighed quantity of *cis*-$[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$ in water at 25.0 ± 0.1° was rapidly mixed with an equal volume of HOCl and filtered into the thermostated cell. The HOCl was prepared immediately before use by extracting chlorine(I) oxide–carbon tetrachloride solution directly into an equal volume of either 1.12 *M* $NaClO_4$–0.2 *M* $HClO_4$ solution or 1.32 *M* $HClO_4$.

$[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ was also treated with 2,4,6-collidine buffer (0.05 *M*), pH 8.51 at 25.0°. From the visible spectrum of the solution (ϵ_{487} 98), it was concluded that hydrolysis to $[Co(en)_2gly]^{2+}$ was complete within the time of mixing ($t_{1/2} < 1$ min).

Measurement of O^{18} Exchange in Carbonyl- and Carboxyl-Labeled $[Co(en)_2gly]^{2+}$. Carbonyl-O^{18}-labeled $[Co(en_2)Br(glyOCH_3)](ClO_4)_2$ (3 g) was dissolved in 0.1 *M* $HClO_4$ (20 ml) containing $Hg(NO_3)_2$ (7 g), and the solution was filtered after 2 min. Excess NaI was added until the HgI_2 which initially precipitated had redissolved. $[Co(en)_2gly](HgI_4)$ precipitated on cooling. This was filtered off and washed with water and methanol, yield 6 g.

This material was shaken in water (20 ml) with excess AgCl for approximately 2 min. The precipitate of AgCl, AgI, and HgI_2 was filtered off, and the filtrate was made up to 50 ml, 0.1 *M* in

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(6) W. H. Mears, *J. Chem. Phys.*, 6, 295 (1938).

(7) G. H. Cady, *Inorg. Syn.*, 5, 158 (1957).

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

(9) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, to be submitted for publication.

(10) glyOH = monodentate $NH_2CH_2CO_2H$; glyO = monodentate $NH_2CH_2CO_2^-$; gly = chelated $NH_2CH_2CO_2^-$.

(11) (a) M. Anbar and S. Guttman, *J. Appl. Rad. Isotopes*, 5, 223 (1959); (b) A. Sargeson and H. Taube, *Inorg. Chem.*, 5, 1094 (1966).

(12) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, 79, 255 (1957).

(13) Under these conditions oxygen exchange between HOCl and H_2O is rapid: M. Anbar and H. Taube, *ibid.*, 80, 1073 (1958).

$HClO_4$ and 0.65 *M* in $NaClO_4$. The solution was thermostated to 25°, and 5-ml aliquots were periodically withdrawn. $[Co(en)_2gly](HgI_4)$ was recovered and the O^{18} content of the glycine was determined as described above.

The rate of O^{18} exchange in $[Co(en)_2gly]^{2+}$ labeled at the carbonyl oxygen was determined by following the above procedure using unlabeled $[Co(en)_2Br(glyOCH_3)](ClO_4)_2$, dissolved with $Hg(NO_3)_2$ in 0.1 *M* $HClO_4$ made from 1.5% O^{18}-enriched water.

Competition Experiments. Hydrolysis Promoted by Hg^{2+}. $[Co(en)_2Br(glyOH)]Br_2$, $[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$, and $[Co(en)_2gly]Br_2 \cdot H_2O$ (~0.1 mmole) were separately dissolved in solutions (10 ml) containing HNO_3 (0.1 *M*), $Hg(NO_3)_2$ (0.1 *M*), and $NaNO_3$ (5 *M*). After 30 min the visible spectra were recorded. The solutions from $[Co(en)_2Br(glyOH)]Br_2$ and $[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$ were sorbed on an ion-exchange column and eluted with 1 *M* KOAc, pH 5. The recovery of $[Co(en)_2gly]^{2+}$ was better than 99%, and no singly positively charged species were detected. For comparative purposes $[Co(en)_2NH_3Cl]Cl_2$ (1 mmole) was treated in the same manner and elution gave $[Co(en)_2NH_3NO_3]^{2+}$ (using 1 *M* KCl at pH 3) and $[Co(en)_2NH_3H_2O]^{3+}$ (using 3 *M* $HClO_4$). The concentrations were estimated spectrophotometrically, Table IV.

Hydrolysis Promoted by HOCl. $[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$ (0.1 mmole) in water (5 ml) was treated with an equal volume of HOCl (1.8 *M*) in 1.12 *M* $NaClO_4$–0.2 *M* $HClO_4$. After 10 min the visible spectrum was recorded from which the $[Co(en)_2gly]^{2+}$/$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ ratio was calculated, Table IV. The product distribution was confirmed using ion exchange with 1 *M* $NaClO_4$ as eluent, 99% recovery. A separate HOCl preparation gave a similar product distribution, and repeated washing of the HOCl solution with CCl_4 immediately prior to use (to remove Cl_2) also gave the same result, Table IV. When the above experiment was repeated following extraction of Cl_2O into 0.2 *M* $HClO_4$–1.8 *M* $AgClO_4$, no $[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ was detected either spectrophotometrically or by ion exchange, Table IV. Similarly, addition of NaCl to a 0.2 *M* $HClO_4$–1.8 *M* $AgClO_4$ solution of HOCl (10 ml) sufficient to make the final solution 1.5 *M* in chloride, followed by immediate addition at 5° of $[Co(en)_2Br(glyOC_3H_7)]^{2+}$ (1 mmole) in water (10 ml), gave ϵ_{500} 69 indicating 100% $[Co(en)_2Cl(glyOC_3H_7)]^{2-}$ formation, Table IV. $[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$ (0.1 mmole) was treated with HOCl (10 ml) made by extracting Cl_2O in CCl_4 (10 ml) into 3 *M* H_2SO_4 containing 2 *M* Li_2SO_4 at 5°. After 2 min the solution was diluted (100 ml) and eluted from a cation-exchange resin (2 *M* $NaClO_4$), pH 7). The $[Co(en)_2(SO_4)(glyOC_3H_7)]^+$, $[Co(en)_2gly]^{2+}$, and $[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ were estimated spectrophotometrically, Table IV. When first sorbed on the column, an orange band was observed above the purple $[Co(en)_2Cl(glyOC_3H_7)]^{2-}$ band, indicating the presence of a +3 ion, presumably $[Co(en)_2(glyOC_3H_7)]^{3+}$. This band rapidly faded forming $[Co(en)_2gly]^{2+}$ which moves faster than $[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ on elution. In a separate experiment using 3 *M* H_2SO_4 containing 2 *M* Li_2SO_4, no reaction was observed after 10 min and no +1 species were detected by ion exchange. Similar treatment of $[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$ (0.1 mmole in water, 5 ml) with HOCl (5 ml, 0.1 *M* $HClO_4$, 1.9 *M* $AgClO_4$, filtered) containing $NaNO_3$ (5 *M*) gave a red solution with ϵ_{490} 92, suggesting the presence of ~33% $[Co(en)_2NO_3(glyOC_3H_7)]^{2+}$, Table IV. However, this species could not be separated from $[Co(en)_2gly]^{2+}$ on the exchange resin.

Treatment of $[Co(en)_2Br(glyOC_3H_7)]^{2+}$ with Cl_2. $[Co(en_2)Br(glyOC_3H_7)](ClO_4)_2$ (0.1 g) in dilute $HClO_4$ (20 ml, pH 2) was treated with Cl_2 for 2 min. The visible spectrum of the resulting solution (ϵ_{525} 80; ϵ_{367} 85) indicates quantitative conversion to $[Co(en)_2Cl(glyOC_3H_7)]^{2+}$, Table IV. This was verified using the ion-exchange technique. In the presence of added SO_4^{2-} some 23–25% $[Co(en)_2SO_4(glyOC_3H_7)]^+$ is formed, Table IV.

Hydrolysis of $[Co(en)_2(glyOCH_3)](ClO_4)_3$ and $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ in the Presence of Added Anions. $[Co(en)_2(glyOCH_3)](ClO_4)_3$ (0.1 mmole) was hydrolyzed in 7.6 *N* HBr (10 ml) for 10 min. The visible spectrum (ϵ_{487} 99) and ion-exchange properties indicate quantitative conversion to $[Co(en)_2gly]^{2+}$. Similarly hydrolysis of $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ (0.1 mmole) in 0.1 *M* $HClO_4$ (10 ml) in the presence of added Cl^- (1 *M*), HSO_4^- (~2 *M*), and NO_3^- (5 *M*) results in no anion entry, Table IV.

Results

Kinetics. The first-order rate constants for the acid hydrolysis of $[Co(en)_2glyOC_3H_7]^{3+}$ are given in Table I. Also the same rate constants were obtained for the HOCl-promoted hydrolysis of $[Co(en)_2Br(glyOC_3H_7)]^{2+}$, Table II. The constants were obtained from linear plots of log ($D_\infty - D_t$) against time, and they are similar to the values obtained by Alexander and Busch for the Hg^{2+}-promoted reaction (also Table II) and are independent of pH in the range of 0.18–4.[1] The visible spectrum of $[Co(en)_2(glyOCH_3)](ClO_4)_3$ in 0.1 *M* $HClO_4$ was identical with that of $[Co(en)_2gly]^{2+}$ (ϵ_{346} 107, ϵ_{487} 97) in the time of mixing (2 min) and showed no change with time.

Table I. First-Order Rate Constants for the Hydrolysis of $[Co(en)_2(glyOC_3H_7)]^{3+}$ in Aqueous Solution[a]

μ, *M* ($NaClO_4$)	pH	[Complex], $M \times 10^3$	$k \times 10^3$ (±0.05), sec^{-1}
1.0	0	8.2	1.13
0.66	1.0	4.2	1.18
1.0	8.51[b]	9.2	>11.5

[a] 25.0 ± 0.1°, λ 487 mμ. [b] 2,4,6-Collidine buffer (0.05 *M*).

Table II. First-Order Rate Constants for the Hydrolysis of the Reaction Product from the Reaction of HOCl with *cis*-$[Co(en)_2Br(glyOC_3H_7)]^{2+}$ in Aqueous Solution[a]

pH	[Complex], $M \times 10^3$	$k \times 10^3$ (±0.05), sec^{-1}
1.0	9.0	1.02
1.0	8.9	1.18
0.18[b]	9.0	1.18
1.0[c]	9.0	1.13
4.0[d]	0.7	1.08

[a] 25.0 ± 0.1°, [HOCl] = 0.9 *M*, λ 480 mμ, μ = 0.66. [b] λ 490 mμ. [c] Reaction with 0.1 *M* Hg^{2+}. [d] Reference 1 (acetate buffer).

Pmr and Infrared Studies. Table III includes chemical shift data for $[Co(en)_2(glyOCH_3)](ClO_4)_3$ and $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ in acetone-d_6. Addition of water to the former results in an immediate shift of the glycine CH_2 triplet from 4.50 to 3.71 ppm and the appearance of a methanol CH_3 signal at 3.42 ppm. A similar but slower change was observed with $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$. The final spectra were identical with those of $[Co(en)_2gly]^{2+}$ and methanol or 2-propanol, respectively. In dimethyl sulfoxide-d_6 containing a trace of residual water, a slower hydrolysis rate for $[Co(en)_2(glyOCH_3)](ClO_4)_3$ was observed, Figure 1.

Table III. Chemical Shifts and Coupling Constants for Some Glycine Ester Complexes in Dilute DCl[a]

	Glycine ester absorptions, ppm	Coupling constants, cps
$[Co(en)_2Br(glyOCH_3)](ClO_4)_2$	3.87 (CH_3), 3.57 (CH_2)	8 (CH_2)
$[Co(en)_2Br(glyOC_3H_7)](ClO_4)_2$	1.31 (CH_3), 3.55 (CH_2), 5.3 (CH)	6 (CH_3)
$[Co(en)_2Cl(glyOCH_3)](ClO_4)_2$	3.87 (CH_3), ~3.55 (CH_2)	8 (CH_2)
$[Co(en)_2(glyOCH_3)](ClO_4)_3$[b]	4.25 (CH_3), 4.50 (CH_2)	6 (CH_2)
$[Co(en)_2(glyOC_3H_7)](ClO_4)_3$[b]	1.39 (CH_3), 4.48 (CH_2), ~5.5 (CH)	6 (CH_3)
$[Co(en)_2gly]^{2+}$ + CH_3OH	3.42 (*CH_3*OH), 3.71 (CH_2)	6 (CH_2)

[a] TPS Na reference. [b] Acetone-d_6 solvent (TMS reference).

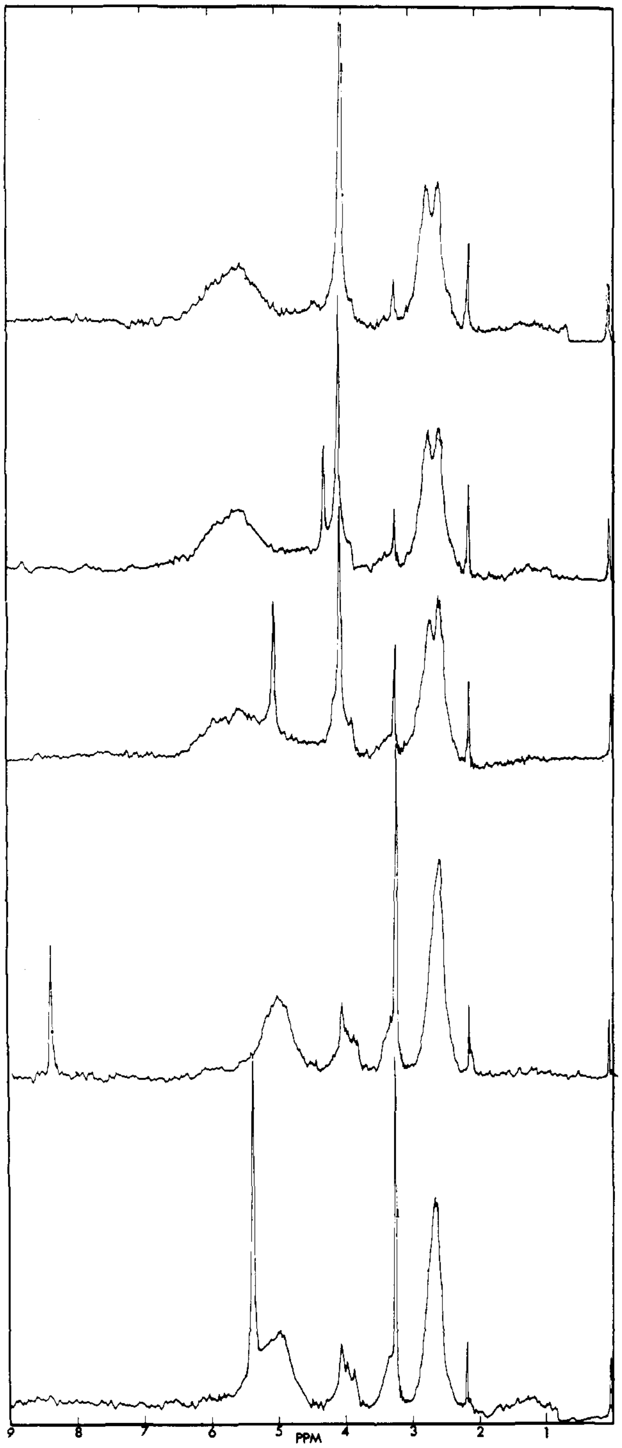

Figure 1. Pmr spectra of the hydrolysis products from $[Co(en)_2(glyOCH_3)](ClO_4)_3$ in dimethyl sulfoxide-d_6 containing a trace of residual water after 5 min, 35 min, 85 min, 8 hr, and 8 hr (water added), respectively (internal reference, tetramethylsilane).

The HOD signal slowly moves downfield as the solution becomes more acidic, and the CH_3 absorption at 4.03 ppm (chelated ester) concomitantly disappears as methanol is formed (3.25 ppm). No other signals of short duration appear during hydrolysis. The final spectrum was identical with that of $[Co(en)_2gly]^{2+}$ and methanol.

The infrared spectrum of $[Co(en)_2(glyOCH_3)](ClO_4)_3$ in anhydrous acetone, Figure 2, shows a sharp absorption at 1630 cm^{-1}, which is assigned to the ester carbonyl absorption, and another at 1310 cm^{-1}, which is assigned to the skeletal C–O stretching vibration. The low frequency of the former and the high frequency of the latter relative to the uncoordinated ester are consistent with $>C{=}O$ coordination.[5] The infrared spectrum of $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ has strong absorptions at similar frequencies. Acid hydrolysis of $[Co(en)_2(glyOC_3H_7)](ClO_4)_3$ in 0.66 *N* DCl was accompanied by a marked broadening in the $>C{=}O$ stretching frequency at 1620 cm^{-1} and a slight shift to a higher frequency. The shift was not as clearly defined as that given by Figure 6 of ref 1, although qualitative agreement was found.

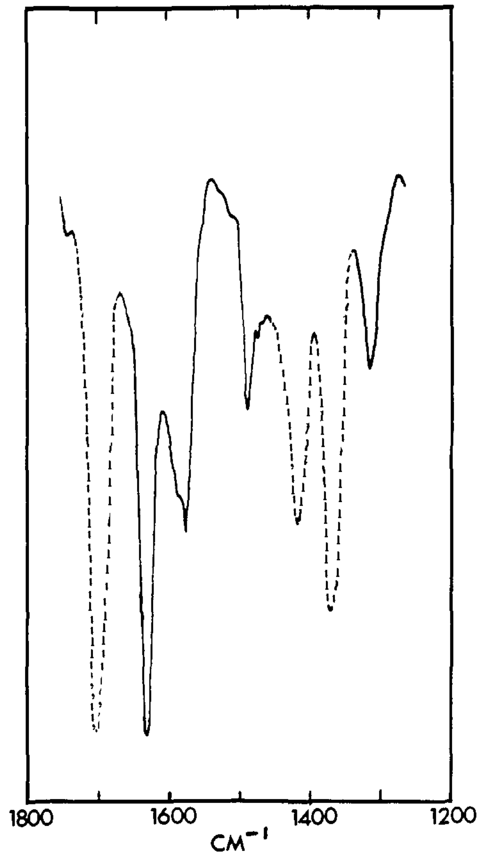

Figure 2. Infrared spectrum of $[Co(en)_2(glyOCH_3)](ClO_4)_3$ in anhydrous acetone (broken lines represent acetone absorptions).

Competition Studies. The results of competition studies for the Hg^{2+}- and HOCl-assisted hydrolysis of $[Co(en)_2Br(glyOC_3H_7)]^{2+}$ and $[Co(en)_2Br(glyOH)]^{2+}$ in the presence of added NO_3^-, HSO_4^-, and Cl^- (HOCl only), and for the reaction of Cl_2 on $[Co(en)_2Br(glyOC_3H_7)]^{2+}$ and acid hydrolysis of $[Co(en)_2(glyOR)]^{3+}$ ($R = C_3H_7$, CH_3) in the presence of HSO_4^- and Cl^-, Br^-, HSO_4^-, and NO_3^-, respectively, are given in Table IV. These reactions were carried out in a similar manner to the nitrosation and Hg^{2+}-assisted reactions of the ions $[Co(NH_3)_5X]^{2+}$ ($X^- = N_3^-$, $OCONH_2^-$; Cl^-, Br^-, I^-).[14] The competition products were analyzed spectrophotometrically both before and after separation on an ion-exchange column. At least 98% recovery of products was obtained from the ion-exchange experiments except in experiments 16 and 17 when 95 and 93% recoveries, respectively, were achieved.

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

Table IV. Spectrophotometric and Ion-Exchange Identification of the Co(III) Products Formed in the Reactions of $[Co(en)_2Br(glyOC_3H_7)]^{2+}$, $[Co(en)_2Br(glyOH)]^{2+}$, and $[Co(en)_2(glyOR)]^{3+}$ (R = CH_3, C_3H_7) with Hg^{2+}, HOCl, and Cl_2 in Acid Solution, in the Presence of Added Anions[a]

							Spectrophotometric data				
Expt	Complex[b]	Wt of complex, g	Reactant	$[H^+]$,[d] ml (*M*)	Added anion	Ion-exchange eluent	λ_{max}	$\epsilon_{\lambda obsd}$	$\epsilon_{\lambda calcd}$[c]	%	Product distribution[e]
1	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0510	0.1 *M* Hg^{2+}	10 (0.1)			488	98	98	100	$[Co(en)_2gly]^{2+}$
2	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0452	0.1 *M* Hg^{2+} [f]	10 (0.1[g])	5 *M* NO_3^-		487	97	98	100	$[Co(en)_2gly]^{2+}$
3	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.245	0.1 *M* Hg^{2+} [f]	10 (2.0[m])	HSO_4^-	1 *M* $NaClO_4$	490	98	98	100	$[Co(en)_2gly]^{2+}$
4	$[Co(en)_2Br(glyOH)]^{2+}$ [i]	0.0428	0.1 *M* Hg^{2+} [f]	10 (0.1[g])	5 *M* NO_3^-		487	100	98	100	$[Co(en)_2gly]^{2+}$
5	$[Co(en)_2gly]^{2+}$	0.0510	0.1 *M* Hg^{2+} [f]	10 (0.1[g])	5 *M* NO_3^-		487	98	98[h]	100	No reaction
6	$[Co(en)_2NH_3Cl]^{2+}$ [v]	0.319	0.1 *M* Hg^{2+}	10 (0.1[g])	5 *M* NO_3^-	1 *M* KCl	493		80[s]	47	$[Co(en)_2NO_3NH_3]^{2+}$
							485		65.5[s]	53	$[Co(en)_2H_2ONH_3]^{3+}$
7	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0500	0.9 *M* HOCl[j]	10 (0.1)		1 *M* $NaClO_4$	487		98.5	98	$[Co(en)_2gly]^{2+}$
8	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0359	0.9 *M* HOCl[j]	20 (0.1)	1.5 *M* Cl^-		500[k]	69	69	100	$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$
9	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0500	0.9 *M* HOCl	10 (0.1)	1.12 *M* ClO_4	1 *M* $NaClO_4$	487		98.5	60	$[Co(en)_2gly]^{2+}$
							525		82	40	$[Co(en)_2Cl(glyOC_3H_7)[^{2+}$
10	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0402	0.9 *M* HOCl[l]	10 (0.1)	1.12 *M* ClO_4		500	85	92	70	$[Co(en)_2gly]^{2+}$
									69	30	$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$
11	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0448	0.9 *M* HOCl	10 (3.0)[m]	2 *M* SO_4^{2-} [n]	2 *M* $NaClO_4$	505		61[o]	20	$[Co(en)_2SO_4(glyOC_3H_7)]^+$
									98.5		$[Co(en)_2gly]^{2+}$
									82	80[u]	$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$
12	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.0495	0.95 *M* HOCl[p]	10 (0.05)	5 *M* NO_3^-		490	92	98	67	$[Co(en)_2gly]^{2+}$
									80[t]	33	$[Co(en)_2NO_3(glyOC_3H_7)]^{2+}$
13	$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$	0.112	0.9 *M* HOCl[j]	10 (0.1)			522	75	77[h]		No reaction
14	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.1008	Cl_2, bubbling	20 (0.01)			525	80	77	100	$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$
15	$[Co(en)_2Br(glyOH)]^{2+}$ [i]	0.1052	Cl_2, bubbling	25 (0.01)		2 *M* $NaClO_4$	367	85	82	100	$[Co(en)_2Cl(glyOH)]^{2+}$
16	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.1062	Cl_2, bubbling	20 (0.1)	2 *M* SO_4^{2-} [n]	1 + 2 *M* $NaClO_4$	510 (355)		61[o]	25	$[Co(en)_2SO_4(glyOC_3H_7)]^+$
							490 (346)		98	21[q]	$[Co(en)_2gly]^{2+}$
							528 (369)		77	54	$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$
17	$[Co(en)_2Br(glyOC_3H_7)]^{2+}$	0.1072	Cl_2, bubbling	20 (3.0[m])	2 *M* SO_4^{2-} [n]	1 + 2 *M* $NaClO_4$	509 (355)		61[o]	23	$[Co(en)_2SO_4(glyOC_3H_7)]^+$
							488 (346)		98	13[q]	$[Co(en)_2gly]^{2+}$
							528 (368)		77	64	$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$
18	$[Co(en)_2(glyOCH_3)]^{3+}$	0.0781	H_2O	10 (7.6[r])	Br^-	1 + 2 *M* $NaClO_4$	487	97	98	100	$[Co(en)_2gly]^{2+}$
19	$[Co(en)_2(glyOC_3H_7)]^{3+}$	0.0568	H_2O	10 (0.10)	1 *M* Cl^-	1 *M* $NaClO_4$	490	98	98	100	$[Co(en)_2gly]^{2+}$
20	$[Co(en)_2(glyOC_3H_7)]^{3+}$	0.1071	H_2O	10 (2.0[m])	HSO_4^-		487	98	98.5	100	$[Co(en)_2gly]^{2+}$
21	$[Co(en)_2(glyOC_3H_7)]^{3+}$	0.1179	H_2O	10 (0.10)	5 *M* NO_3^-		490	100	98.5	~100	$[Co(en)_2gly]^{2+}$

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[a] The Hg^{2+} and HOCl reactions were complete within 2 min of mixing; the Cl_2 reactions were allowed 2 min at room temperature. [b] ClO_4^- salts unless stated otherwise. [c] Calculated absorptivities for the complex ions given in the last column. [d] $HClO_4$ unless stated otherwise. [e] When ion-exchange separation was used, the products are those separated on the column and are listed in the order of recovery; otherwise the products are those deduced from the spectrophotometric data of the resulting solution. [f] $Hg(NO_3)_2$. [g] HNO_3. [h] Calculated for no reaction. [i] Bromide salt. [j] 1.8 *M* $AgClO_4$ added (to remove Cl^-). [k] λ_{max} for solution was at 522 mμ. [l] Washed repeatedly with CCl_4 immediately before use. [m] H_2SO_4. [n] Li_2SO_4. [o] Calculated using ε 61 at λ_{max} 510 mμ as found in $[Co(NH_3)_5SO_4]^+$: R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388 (1938). [p] 0.9 *M* in $AgClO_4$. [q] This value was calculated assuming 100% recovery. [r] 7.6 *N* HBr. [s] I. Olsen, unpublished data. [t] Calculated using ε 80 at 493 mμ as for $[Co(en)_2NH_3NO_3]^{2+}$. [u] The major $[Co(en)_2Cl(glyOPr)]^{2+}$ and minor $[Co(en)_2gly]^{2+}$ bands did not separate sufficiently to allow separate analysis. [v] Chloride salt.

Experiments 18–21 establish that no Cl^-, Br^-, NO_3^-, and SO_4^{2-} competition occurs during the acid hydrolysis of $[Co(en)_2(glyOC_3H_7)]^{3+}$ and $[Co(en)_2(glyOCH_3)]^{3+}$. Other results (Table IV) show that, if competition did occur, the expected products $[Co(en)_2X(glyOR)]^{2+,+}$ or $[Co(en)_2X(glyOH)]^{2+,+}$ (X = Cl, Br, SO_4) are stable under the experimental conditions and are readily detectable by the ion-exchange technique.

No competition by SO_4^{2-} or NO_3^- for the intermediate generated by the Hg^{2+}-assisted removal of Br^- in $[Co(en)_2Br(glyOC_3H_7)]^{2+}$ and $[Co(en)_2Br(glyOH)]^{2+}$ was observed (experiments 2–4, Table IV). This is contrary to the established competitive properties of NO_3^- and SO_4^{2-} in the reactions of Hg^{2+} with $[Co(NH_3)_5X]^{2+}$ (X = Cl, Br, I)[14] and with experiment 6 (Table IV) where 47% $[Co(en)_2NO_3NH_3]^{2+}$ was formed from $[Co(en)_2ClNH_3]^{2+}$ in the presence of 5 *M* $NaNO_3$.

Oxidation of $[Co(en)_2Br(glyOC_3H_7)]^{2+}$ and $[Co(en)_2Br(glyOH)]^{2+}$ with HOCl in 0.1 *M* $HClO_4$ gave $[Co(en)_2gly]^{2+}$ quantitatively (experiment 7, Table IV). No $[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ or $[Co(en)_2Cl(glyOH)]^{2+}$ was formed during or subsequent to the removal of Br^-. These species do not react with HOCl over similar periods of time (experiment 13). Also, the quantitative formation of $[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ on treating $[Co(en)_2Br(glyOC_3H_7)]^{2+}$ with Cl_2 (experiment 14) is in general agreement with the similar results obtained with $[Co(NH_3)_5Br]^{2+}$ [15] and $[Co(en)_2NH_3Br]^{2+}$.[16] The presence of Cl^- in the HOCl oxidation results in appreciable amounts of $[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ being formed (experiments 8–10). This could arise either from Cl_2 oxidation (produced by HOCl oxidation of Cl^-) or by a mechanism involving more direct Cl^- participation. That added anions do compete in the HOCl reaction is shown by entries 11 and 12 in Table IV. Although a quantitative estimate of the amount of $[Co(en)_2NO_3(glyOC_3H_7)]^{2+}$ formed was not possible since it could be separated from $[Co(en)_2gly]^{2+}$ by the ion-exchange technique, the low molar absorptivity of the resulting solution (ϵ_{487} 92) suggests ~33% of $[Co(en)_2NO_3(glyOC_3H_7)]^{2+}$.[17] A more conclusive result was obtained with added SO_4^{2-} (5 *M*, experiment 11), where $[Co(en)_2SO_4(glyOC_3H_7)]^+$ was separated from $[Co(en)_2gly]^{2+}$ by ion exchange at pH 7. A 99% recovery was obtained and 20% $[Co(en)_2SO_4(glyOC_3H_7)]^+$ was formed assuming ϵ_{505} 61 as found for $[Co(NH_3)_5SO_4]^+$.[19] This result establishes that SO_4^{2-} and HSO_4^- compete favorably with the carbonyl grouping in the HOCl-assisted removal of Br^-.

O^{18}-Tracer Experiments. Results obtained for the O^{18}-labeling experiments are given in Table V. The first entry represents the O^{18} content of the *carbonyl*-labeled glycine methyl ester used for the complex preparations. Recovery of the ester by pyrolysis (250°) of $[Co(en)_2Br(glyOCH_3)]Br_2$ was only partly successful and was not reproducible (*E* = 0.269, 0.445). This may have resulted from contamination of the distilled ester with unlabeled methanol or water. However, the enrichment of the uncomplexed glycine ester is consistent with the enrichments found for glycine isolated from the products of the hydrolysis reactions.

Table V. O^{18} Enrichment of Reactants and Products for the Hydrolysis of Carbonyl-O^{18}-Labeled *cis*-$[Co(en)_2Br(glyOCH_3)](ClO_4)_2$

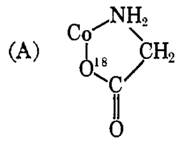
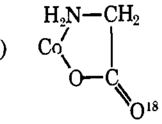
	Reaction	E^a Solvent	E^a Product^d	r^b
1	glyOMe		0.633 0.622	
2	H_2O–$[Co(en)_2(glyOCH_3)]^{3+}$		0.580	93
3	Hg^{2+}–$[Co(en)_2Br(glyOCH_3)]^{2+}$		0.595	95
4	HOCl–$[Co(en)_2Br(glyOCH_3)]^{2+}$		0.596	95
5^c	HOCl–$[Co(en)_2Br(glyOCH_3)]^{2+}$	1.393	0.707	102

[a] Represents the O^{18} enrichment in atom % of the species, less the atom % O^{18} in CO_2 of normal isotopic composition. [b] Represents the O^{18} retention of the product species as a percentage of O^{18} enrichment in the initial complex (taken as 0.627 atom %) or solvent. [c] Labeled HOCl, unlabeled complex. [d] $[Co(en)_2gly](HgI_4)$ in experiments 3–5.

Entries 2–4 establish that $[Co(en)_2gly]^{2+}$ recovered after acid hydrolysis of *carbonyl-O^{18}-labeled* $[Co(en)_2(glyOCH_3)](ClO_4)_3$ and Hg^{2+} and HOCl treatment of *carbonyl-O^{18}-labeled* $[Co(en)_2Br(glyOMe)]Br_2$, respectively, retains almost complete enrichment. In experiment 5, unlabeled complex was treated with O^{18}-labeled HOCl, and the result shows that only one oxygen atom from the solvent is incorporated.

Kinetics of Oxygen Exchange in the $[Co(en)_2gly]^{2+}$ Ion. The results of oxygen exchange between H_2O and $[Co(en)_2gly]^{2+}$ in 0.1 *M* $HClO_4$ at μ = 1 and 25° are given in Table VI. The two sets of results were

Table VI. Kinetic Data for Oxygen Exchange between Water and the Carboxyl (A) and Carbonyl (B) Oxygen of $[Co(en)_2gly]^{2+}$ ^{a}

Days	R^b	Atom % O^{18} ^{d}
	(A) 	
0	0.014928	0.540
1	0.014731	0.530
3	0.014301	0.509
4	0.014308	0.509
9	0.014054	0.497
12	0.014330	0.510
16	0.013899	0.489
	(B) 	
0^c	0.014937	0.540
1	0.015326	0.559
2	0.014545	0.521
5	0.012725	0,431
9	0.009631	0.278
14	0.007727	0.184
17	0.007055	0.151
21	0.005993	0.098

[a] $[H^+]$ = 0.1 *M*, μ = 1.0, 25°, $[Co(en)_2gly^{2+}]$ ~ 0.1 *M*. [b] $R = [46]/([44] + [45])$. [c] The H_2O^{18} solvent used to prepare this complex contained 1.122 atom % O^{18}. [d] Represents the O^{18} enrichment in atom % less the atom % O^{18} in CO_2 of normal isotopic composition (0.201). Atom % O^{18} = $100R/(2 + R)$.

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(15) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 3108 (1963).

(16) J. F. Remar, D. E. Pennington, and A. Haim, *Inorg. Chem.*, **4**, 1832 (1965).

(17) This estimate is based assuming similar absorptivities for $[Co(en)_2NO_3(glyOC_3H_7)]^{2+}$ and *cis*-$[Co(en)_2NO_3NH_3]^{2+}$ at 485 mμ. This assumption is thought to be a reasonable one since the two systems $[Co(en)_2X(glyOC_3H_7)]^{2+}$ and $[Co(en)_2XNH_3]^{2+}$ (X = Cl, Br) have similar absorptivities for the first visible absorption band.[18]

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

(19) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388 (1938).

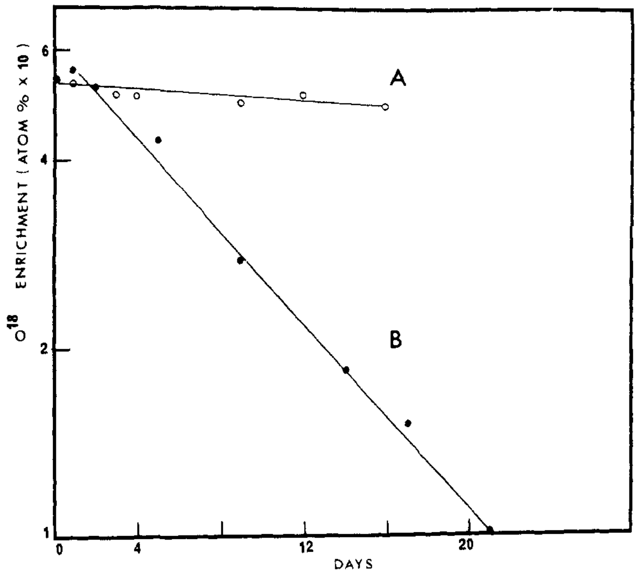


Figure 3. O^{18} exchange in (A) $[Co(en)_2gly]^{2+}$ prepared from carbonyl-O^{18}-$[Co(en)_2Br(glyOCH_3)]^{2+}$ and normal water; (B) $[Co(en)_2gly]^{2+}$ prepared from unlabeled $[Co(en)_2Br(glyOCH)_3]^{2+}$ with H_2O^{18} (0.1 *M* $HClO_4$, μ = 1.0, 25.0°).

obtained from $[Co(en)_2gly]^{2+}$ prepared by treating *carbonyl-O*^{18}-$[Co(en)_2Br(glyOCH_3)](ClO_4)_2$ with Hg^{2+} in water of normal enrichment, or by similar treatment of the unlabeled complex with H_2O.[18] A plot of log (O^{18} complex) against time was linear (Figure 3) for the complex obtained from the labeled solvent, giving a first-order rate constant of 1.0×10^{-6} sec^{-1} at 25°. The complex obtained *via* the labeled ester showed little exchange in 16 days under the same conditions. It is apparent from the results that there is little or no mixed label in the two instances and that the two oxygen sites in the glycinato chelate can be distinguished.

Discussion

Each of the reactions

$$[Co(en)_2Br(glyOR)]^{2+} + Hg^{2-} + H_2O \longrightarrow [Co(en)_2gly]^{2+} + HgBr^{+} + HOR \quad (3)$$

$$[Co(en)_2Br(glyOR)]^{2+} + HOCl \longrightarrow [Co(en)_2gly]^{2+} + BrCl + ROH \quad (4)$$

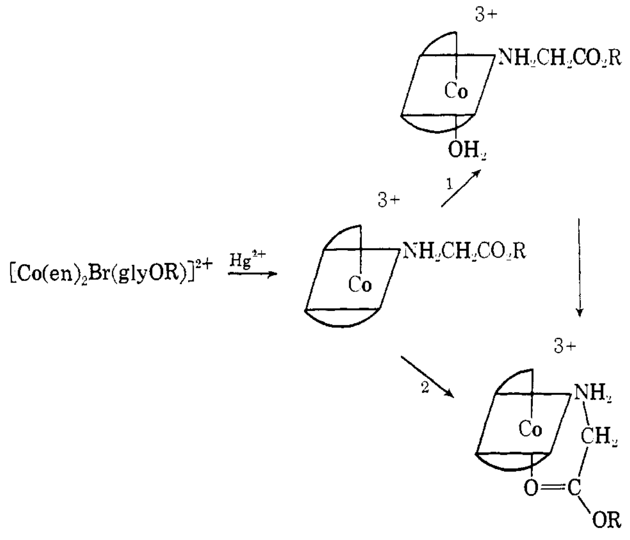
$$[Co(en)_2(glyOR)]^{3+} + H_2O \longrightarrow [Co(en)_2gly]^{2+} + ROH + H^{+} \quad (5)$$

results in the formation of $[Co(en)_2gly]^{2+}$ as the only cobalt-containing product. This was established spectrophotometrically for (3) by Alexander and Busch and verified for all three reactions by ourselves using the ion-exchange technique. If the aquo glycinato ion had been formed, it would have been detected by the ion-exchange experiments. $[Co(en)_2(OH)(glyO)]^{+}$ is eluted more rapidly than $[Co(en)_2gly]^{2+}$ using 1 *M* $NaClO_4$ at pH 9.[20] Since each of the above reactions differs at least in principle, it is desirable to discuss some aspects of each reaction separately.

Acid Hydrolysis of $[Co(en)_2(glyOC_3H_7)]^{3+}$. The agreement between the rate data for this reaction (Table I) and that for the Hg^{2+}- and HOCl-promoted reactions (Table II) indicate that $[Co(en)_2(glyOC_3H_7)]^{3+}$ is formed as an intermediate in the latter two reactions and is therefore a necessary precursor to hydrolysis. This is consistent with the proposals made by Alexander and Busch for the Hg^{2+}-promoted reaction on the basis of infrared evidence (*vide infra*).[1] In addition, the lack of competition by Br^-, Cl^-, and NO_3^- in the acid hydrolysis of $[Co(en)_2(glyOCH_3)]^{3+}$ and $[Co(en)_2(glyOC_3H_7)]^{3+}$ suggests that either the chelate ring remains intact before, during, and after hydrolysis or that the carbonyl group is a much better competitor than the anions or solvent.

Hg^{2+}-Assisted Reaction. Hydrolysis of the ester function cannot precede removal of Br^- since $[Co(en)_2Br(glyOR)]^{2+}$ hydrolyzes very slowly in acid solution in the absence of Hg^{2+},[1] nor can it occur in the resulting short-lived intermediate of reduced coordination number since the ester function is still intact in the subsequent $[Co(en)_2(glyOR)]^{3+}$ complex. There is ample evidence to conclude that the fast Hg^{2+}-promoted removal of Br^- leads to the formation of a five-coordinate intermediate.[21-23] Also, it has been established in the similar reactions with *cis*-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, Br)[16,24] and *trans*-$[Co(NH_3)_4(ND_3)X]^{2+}$ (X = Cl, Br, I)[25] that both the stereochemistry and optical properties are preserved in this type of intermediate. Applying these considerations to the present reaction eliminates the symmetrical trigonal bipyramid as a possible intermediate but does not further define its nature. We have chosen to represent it as a square pyramid. This species may then react with the solvent to give $[Co(en)_2(OH_2)(glyOR)]^{3+}$, with the carbonyl grouping to give direct formation of the chelate ester $[Co(en)_2(glyOR)]^{3+}$, or by a combination of these two paths (Scheme I). In the event of $[Co(en)_2(H_2O)(glyOR)]^{3+}$ being formed, the kinetic data require that this species lose water in a fast reaction to form $[Co(en)_2(glyOR)]^{3+}$. If this aquo product were formed, it would also be expected that added anions would compete favorably for the five-

Scheme I



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[20] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, unpublished results.

[21] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, 79, 255 (1957).

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

[23] D. A. Loeliger and H. Taube, *ibid.*, 5, 1376 (1966).

[24] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, press.

[25] Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, 20, 597 (1967).

coordinate intermediate generated on loss of Br^-. Evidence to support this argument is the demonstration that SO_4^{2-} and NO_3^- are better competitors than H_2O on a molar basis for the $[Co(NH_3)_5]^{3+}$ [22] and $[Co(en)_2NH_3]^{3+}$ intermediates[24] (also Table IV, entry 6) generated in the same way. In the absence of other considerations, there is no reason to expect the five-coordinate ion $[Co(en)_2(glyOR)]^{3+}$ to behave differently. The $[Co(en)_2NO_3(glyOR)]^{2+}$ and $[Co(en)_2SO_4(glyOR)]^+$ products expected from such anion competition reactions are stable under the experimental conditions. Thus, the absence of SO_4^{2-} and NO_3^- competition[26] suggests that H_2O is not involved, and that the ester grouping, due to its proximity, is a much better competitor than any other species in solution.[26a]

Oxidation by Cl_2 and HOCl. The reaction, *cis*-$[Co(en)_2Br(glyOC_3H_7)]^{2+}$ + Cl_2, is striking in that *cis*-$[Co(en)_2Cl(glyOC_3H_7)]^{2+}$ is quantitatively formed (Table IV, entry 14). This result may be compared with the quantitative formation of $[Co(NH_3)_5Cl]^{2+}$ from $[Co(NH_3)_5Br]^{2+}$ + Cl_2[15] and with *cis*-$[Co(en)_2ClNH_3]^{2+}$ formed from *cis*-$[Co(en)_2BrNH_3]^{2+}$.[16] The remarkable feature of the Cl_2 reaction is the complete lack of competition provided by the ester carbonyl group. Thus the intermediate involved cannot be the same as that proposed for the Hg^{2+}-assisted reaction, and it is likely that it is not one of reduced coordination number. This supports Haim and Taube's proposal[15] that the product is produced by interchange within the ion pair

$$Co^{3+}—Br^- --- Cl^+ \longrightarrow Co^{3+}—Cl^- --- Br^+$$

A similar mechanism was proposed for the HOCl and H_2O_2 oxidation of coordinated Br^- and I^-, namely

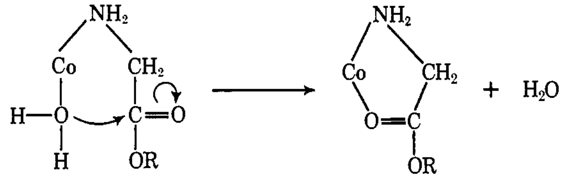
$$Co^{3+}—Br^- --- HO^+ --- Y^- \longrightarrow Co^{3+}—OH^- --- Br^+ --- Y^-$$
$$(Y = Cl, OH)$$

and in acid solution $[Co(NH_3)_5(OH_2)]^{3+}$ is quantitatively formed.[15] In the case of the $[Co(NH_3)_5I]^{2+}$ + H_2O_2 reaction, oxygen-tracer experiments established that at least 62% of the aquo product formed by this path derived its oxygen from the oxidizing agent. A similar tracer experiment was not possible for the HOCl oxidation due to rapid oxygen exchange with the solvent, but Haim and Taube clearly demonstrated the similarities between all three oxidants, Cl_2, HOCl, and H_2O_2. It appeared then that the HOCl oxidation was an ideal method of generating the aquo complexes $[Co(en)_2(OH_2)(glyOR)]^{3+}$ from the corresponding bromo derivative.

The results of the reactions given in Table II clearly demonstrate that the chelated ester $[Co(en)_2(glyOR)]^{3+}$ is the species observed in the HOCl reaction. Such a result may be accommodated by a mechanism whereby the coordinated water molecule in *cis*-$[Co(en)_2(OH_2)(glyOR)]^{3+}$ is rapidly displaced by the adjacent >C=O group in a concerted manner. An alternative to this is that the carbonyl group is involved in the ion-pair interchange without intervention of $[Co(en)_2(OH_2)glyOR]^{3+}$. This latter possibility seems unlikely. The analogous reaction with Cl_2 shows that the carbonyl group does not compete in the ion-pair interchange process, although anions such as SO_4^{2-} do. Also SO_4^{2-} and NO_3^- do compete in the HOCl reaction, and the competitive properties of these anions are similar to those found in the Cl_2 reaction. If these results are now compared to the analogous $[Co(NH_3)_5I]^{2+}$ system, similar competition values for the incorporation of sulfate are observed.[15] Also for the HOCl reaction with $[Co(en)_2NH_3Br]^{2+}$ both acido and aquo products are observed.[16] This implies that a similar pattern of events occurs with $[Co(en)_2Br(glyOR)]^{2+}$ and that some aquo glycinato ester complex is formed.

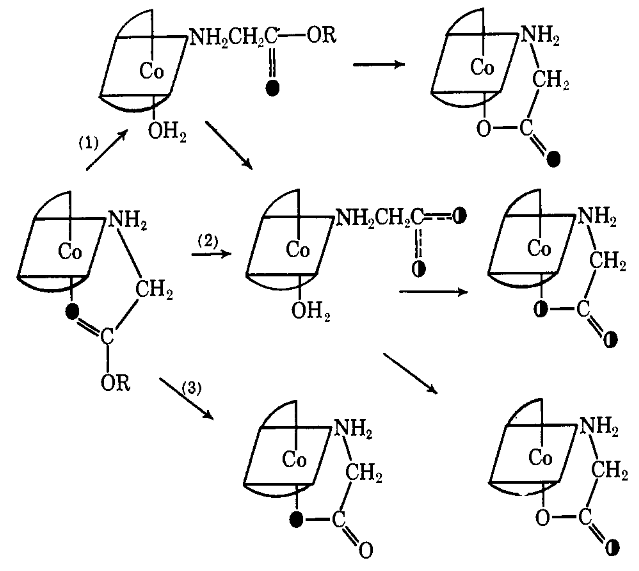
Tracer Studies. The O^{18} tracer results (Table V) show that in all cases examined one oxygen is enriched in the glycinato product. The O^{18} exchange rate in 0.1 *M* $HClO_4$ (Table VI) shows that the product formed *via* labeled solvent exchanges considerably faster than the product formed *via* labeled ester, and this property is ascribed to the two sites for the glycinato oxygen atoms. The O^{18} oxygen from the enriched ester is bound to cobalt and the O^{18} from the solvent is in the carbonyl position of the chelated glycine.

These results establish both the nature of the chelated ester intermediate and the main features concerning its subsequent hydrolysis. The position of incorporation of one solvent oxygen atom clearly eliminates the ester intermediate in which the ether oxygen rather than the >C=O oxygen is involved in chelation. Also, it is evident that formation of the chelated ester in the HOCl reaction must involve rapid $Co-OH_2$ bond rupture in the aquo ester precursor and that a mechanism such as



does not obtain. This is required by the full retention of the isotope label in the glycinate product (Table V). In view of the relatively fast rate of water exchange required here ($t_{1/2} < 30$ sec), compared to that found for the analogous $[Co(NH_3)_5(H_2O)]^{3+}$ ion ($t_{1/2} \sim 35$ hr,

Scheme II



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(26) The added anion concentration was *ca.* five times that used in ref 24.

(26a) NOTE ADDED IN PROOF. (−)D-$[Co(en)_2Br(glyOCH_3)]Br_2$, $[\alpha]_D$ −115°, gave (−)D-$[Co(en)_2gly]^{2+}$, $[\alpha]_D$ −306°, when treated with Hg^{2+} in 0.01 *M* $HClO_4$. The product is optically pure, indicating full retention of configuration during the reaction. This experiment will be reported in detail elsewhere.

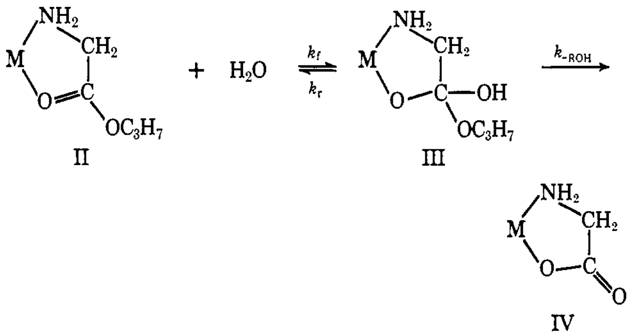
25°),[27] we suggest that the H_2O molecule is displaced in a concerted S$_N$2 process. The chelated ester intermediate may further react by aquation (path 1), by synchronous hydrolysis and aquation (path 2), or by direct hydrolysis without opening of the chelate ring (path 3), Scheme II. Path 1 leads either to a product containing the label entirely in the carbonyl position (attack by bound water at the ester carbon) or to a product containing a mixed label (following hydrolysis of the monodentate ester), while path 2 leads to a mixed labeled complex or to a product containing half the enrichment entirely in the carbonyl oxygen. Both these possibilities are eliminated by the results. Path 3, in which the chelate ring remains intact throughout hydrolysis, is the only path which satisfies the results. It allows incorporation of the labeled solvent solely in the carbonyl oxygen of the product with full retention of the labeled ester attached to cobalt.

Concluding Remarks

A summary of the conclusions for some aspects of this investigation is warranted. Clearly the isolated chelated ester intermediate hydrolyzes at the same rate as the species formed from the Hg^{2+}- and HOCl-assisted aquation of the bromo ester complexes. It appears that in each case the chelate skeleton remains intact before, during, and after hydrolysis. Also, the labeling experiments establish that C–OR bond cleavage occurs for the methyl ester. A similar result might be expected to hold for other alkyl groups, except perhaps *t*-butyl glycinate.

Activation for the rapid hydrolysis presumably arises from the effect of the Co(III) ion on the coordinated carbonyl group. The independence of the rate of hydrolysis on the H^+ concentration suggests that OH_2 is the nucleophile attacking the carbonyl carbon. The absence of a term first order in $[H^+]$, which is found in the free ester hydrolysis, can be accounted for by substitution of the cobalt(III) ion for H^+ in this mechanism. The considerable enhancement in rate which is observed in the present instance presumably arises from the fact that all the ester is present in the "protonated" form, whereas in the acid-catalyzed path for the uncoordinated ester only a small proportion is present as protonated ester. Preliminary results appear to indicate that at higher pH values a substantial increase in rate occurs. This path may coincide with the $[OH^-]$-dependent path observed in uncoordinated ester hydrolysis.

In both the acid- and base-dependent paths for hydrolysis of O^{18}-labeled alkyl benzoates, the equivalence of the two *enol* oxygen atoms in the intermediate R–$C(OH)_2OR$ has been established.[28] However, this situation is not possible for the Co(III) chelated ester, and our experiments do not lead to any conclusions about the presence of the intermediate III shown below.



Similar studies for the more labile Cu(II) ester complexes[29] indicate that the "enol" oxygens do become equivalent, possibly through one-ended dissociation of the chelate III. It seems probable therefore that III is formed for the cobalt (III) complex but is very labile toward dissociation.

Finally there is a similarity between the chelated ester intermediates and complexes involving carbonyl-oxygen chelated amino acid amides and peptide esters[30] (structure I). Accelerated hydrolysis of these species has been reported,[2] and it is tempting to suggest that the order of events established for the hydrolysis of the chelated esters applies to these related compounds. Some of these complexes are at present being investigated.

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[27] H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, 80, 2642 (1958).

[28] M. L. Bender, *ibid.*, 73, 1626 (1951).

[29] M. L. Bender and B. W. Turnquest, *ibid.*, 79, 1889 (1957).

[30] M. Fehlman, H. Freeman, I. Maxwell, P. A. Marzilli, P. A. Buckingham, and A. M. Sargeson, *Chem. Commun.*, 488 (1968).