Table V. Infrared Spectrum of [Pt(dabp)$_2$]Cl$_2$

ν, cm^{-1}	Intensity	ν, cm^{-1}	Intensity	ν, cm^{-1}	Intensity
3390	m	1538	w	1164	w
3086	sh	1508	sh	1117	w
2315	w	1490	s	1085	w
1647	sh	1418	sh	840.3	w
1618	sh	1342	sh	814.3	w
1590	s	1239	m	768.6	s
1563	sh	1199	m	735.3	m

The compound gave almost the same infrared spectrum as the beige crystals, as shown in Table V.

All attempts to convert [Pt(dabp)$_2$][PtCl$_4$] to [Pt(dabp)$_2$]Cl$_2$ by reaction with diaminobiphenyl according to the equation

$$[\mathrm{Pt(dabp)_2}][\mathrm{PtCl_4}] + 2\ \mathrm{dabp} \longrightarrow 2[\mathrm{Pt(dabp)_2}]\mathrm{Cl_2}$$

were unsuccessful, probably because of the insolubility of [Pt(dabp)$_2$][PtCl$_4$]. The resolution of [Pt(dabp)$_2$]Cl$_2$ by means of tartrate was attempted, but the solution of [Pt(dabp)$_2$][tart] decomposed, giving a reddish brown color before any crystals separated.

A study of atomic models of the two complex ions, [Pt(en)(dabp)]$^{2+}$ and [Pt(dabp)$_2$]$^{2+}$, shows that there is a slight distortion in the model of [Pt(dabp)$_2$]$^{2+}$. Some of the hydrogen atoms which surround the platinum atom are so close together that they interfere with each other. This may explain why [Pt(dabp)$_2$]$^{2+}$ is not stable enough to be resolved. In the case of [Pt(en)(dabp)]$^{2+}$, there is no distortion. In any event, it is clear the diaminobiphenyl is the only seat of the optical activity. We hope, at a later time, to study the kinetics and mechanism of the racemization of [Pt(en)(dabp)]$^{2+}$.

Acknowledgment. We wish to express our thanks to Konishiroku Photo Industries, Ltd., for a leave of absence to T. Habu, and to the National Science Foundation for financial support through Grant No. GP-191.

Reactions of Coordinated Ligands. XIII. Cobalt(III)-Promoted Hydrolysis of Glycine Esters[1a]

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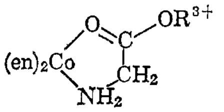
Abstract: Metal ion promoted hydrolysis of α-amino esters is a matter of significance. The investigation of cobalt(III) systems has provided insight into the nature of this accelerated hydrolysis. The glycine ester containing complexes, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)X]X$_2$, where en is ethylenediamine, R is CH$_3$, C$_2$H$_5$, or *i*-C$_3$H$_7$, and X is Cl or Br, are relatively inert with respect to hydrolysis in aqueous solution. However, in acid solution, mercury(II) ion reacts readily with each of the complexes, resulting in hydrolysis of the ester and formation of glycinatobis(ethylenediamine)cobalt(III) as the sole final product. Spectrophotometric studies reveal that the coordinated halide is removed by the mercury(II) in a first step, and that hydrolysis of the ester occurs in a subsequent step. Infrared spectral data strongly suggest that the intermediate is the chelated ester complex



The hydrolysis of the chelated ester is very much more rapid than the hydrolysis of the ester bound through the amino group alone. The rate of reaction of the intermediate is insensitive to hydrogen ion concentration below pH 4. However, a study of the reaction in a number of buffer systems has shown that the reaction is subject to general nucleophilic or general base catalysis.

Divalent transition metal ions are known to promote the hydrolysis of esters of α-amino acids.[2a] The nature of the hydrolytic process is of special interest because of its possible relationship to similar enzymatic processes occurring in biological systems. With this in mind Bender and Turnquest[2b] have studied in some detail the copper(II)-promoted hydrolysis of certain of these esters. On the basis of oxygen-18 exchange data and kinetic studies, they have proposed a mechanism for the promotion which involves formation of a complex in which the ester is chelated to the metal ion through the amino group and the carbonyl oxygen. The accelerated hydrolysis is then explained on the assumption that the polarization of the carbonyl group makes the carbon more susceptible to nucleophilic attack.

The earlier studies do not exclude the possibility of mechanisms other than that summarized above, for example, one involving attack of the dangling ester function by coordinated water or hydroxide ion. Resolution of such problems relating to the mechanism is extremely difficult using the systems previously studied because of the labile nature of the complexes involved. The present investigation utilizes relatively inert cobalt(III) complexes in order to permit preparation and characterization of intermediates and isolation of the steps in the complicated over-all rate process. The glycine ester containing complexes, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)Cl]Cl$_2$, where en is ethylenediamine and R is CH$_3$, C$_2$H$_5$, and *i*-C$_3$H$_7$, described elsewhere,[3] together with the corresponding bromo complexes, have proved useful in this connection.

In addition to the elucidation of the hydrolytic process, the studies involving these compounds have

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(1) (a) From the Ph.D. Thesis of M. D. A.; (b) Ethyl Corporation Fellow, 1962-1963; American Oil Company Fellow, 1963-1964.

(2) (a) H. Kroll, *J. Am. Chem. Soc.*, 74, 2036 (1952); (b) M. L. Bender and B. W. Turnquest, *ibid.*, 79, 1889 (1957).

(3) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, in press.

thrown additional light on the mercury(II) ion induced expulsion of coordinated halide from cobalt(III) complexes.[4–6]

Experimental Section

Preparation of Complexes. The chloro complexes, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)Cl]Cl$_2$, where R is CH$_3$, C$_2$H$_5$, and *i*-C$_3$H$_7$, were prepared as described in a previous paper.[3] The corresponding bromo complexes were prepared in an identical manner substituting *trans*-[Co(en)$_2$Br$_2$]Br for *trans*-[Co(en)$_2$Cl$_2$]Cl and the ester hydrobromide for the hydrochloride. Similar bromo(amine)bis(ethylenediamine)cobalt(III) complexes have been prepared in this way by Ablov.[7] These bromo ester compounds were characterized using visible and infrared spectral data. The *cis* configuration is assigned to the bromo complexes on the basis of the similarity of their infrared spectra to those of the corresponding chloro complexes and the similarity of their visible spectra to that of *cis*-[Co(en)$_2$NH$_3$Br]Br$_2$.

Materials. A mercury(II) perchlorate stock solution (0.19 *M* in Hg(ClO$_4$)$_2$, 0.10 *M* in HClO$_4$, ionic strength of 0.66) was prepared by treating 40.7 g (0.19 mole) of mercury(II) oxide (yellow, reagent) with the appropriate amount of standardized perchloric acid (60%, reagent) and diluting the resulting solution to 1 l. The solution was standardized by titrating potentiometrically with sodium hydroxide solution to determine the total hydrogen ion plus mercury(II) ion concentration. The hydrogen ion concentration was determined by titrating with sodium hydroxide in the presence of sodium bromide to complex with the mercury(II) ion. The mercury(II) ion concentration was determined by difference.

A sodium perchlorate stock solution (0.56 *M* in NaClO$_4$, 0.10 *M* in HClO$_4$, ionic strength of 0.66) was prepared by treating 47.4 g (0.564 mole) of sodium bicarbonate (reagent) with the appropriate amount of standardized perchloric acid (60%) followed by boiling the solution for a few minutes to drive off carbon dioxide and then diluting to a volume of 1 l. The solution was standardized by titrating with sodium hydroxide solution.

Chloroacetate and acetate buffer solutions were prepared from sodium hydroxide, acid and sodium perchlorate stock solutions. For all solutions a constant ratio of sodium hydroxide to acid was used; however, the solutions prepared had various concentrations of the anion derived from the buffer. Sodium perchlorate was employed to adjust the ionic strength of the solutions to 0.66.

Tris(hydroxymethyl)aminomethane, 2,6-lutidine, and quinoline buffer solutions were prepared from the bases and stock solutions of nitric acid and sodium nitrate. The purpose of the sodium nitrate was to adjust the ionic strength of the solutions to 0.66.

A mercury(II) perchlorate solution (0.19 *M* in Hg(ClO$_4$)$_2$, pH 1.7, ionic strength of 0.66), was prepared from the Hg(ClO$_4$)$_2$ stock solution, described above, by the dropwise addition of 10 *M* sodium hydroxide to 250 ml of the stock solution until a slight cloudiness persisted. The resulting solution was filtered.

For infrared measurements, a solution of mercury(II) perchlorate in deuterium oxide (0.2 *M* in Hg(ClO$_4$)$_2$) was prepared by mixing 0.44 g of mercury(II) oxide with 0.40 ml of perchloric acid (60%) in 9.6 ml of deuterium oxide. The pH of the resulting solution was approximately 1.

Visible Spectra of the Products of the Reaction of Mercury(II) Ion with *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)X]X$_2$. In 5.00 ± 0.02 ml of the NaClO$_4$ stock solution, 0.0200 ± 0.0003 g of the ester complex was dissolved, and to this was added 5.00 ml of the Hg(ClO$_4$)$_2$ stock solution. The reaction was allowed to proceed at room temperature for 2 hr (kinetic data indicate the reaction has reached completion by this time in each case), and the visible spectrum of the solution was obtained using a Cary Model 14 recording spectrophotometer and matched 1-cm quartz cells.

Kinetic Measurements. A Beckman Model DU spectrophotometer and a Cary Model 14 recording spectrophotometer, each equipped with thermostated cell compartments, were used for the kinetic measurements. Both 1-cm and 5-cm quartz cells were used. The procedure consisted of dissolving a weighed amount of complex in a certain volume of NaClO$_4$ stock solution and equilibrating the temperature of the solution to 25.0 ± 0.1° in a constant temperature bath. To initiate the reaction, the desired amount of Hg(ClO$_4$)$_2$ stock solution, also at 25.0°, was added. The resulting solution was rapidly mixed and transferred to the cell which was immediately placed in the cell compartment of the spectrophotometer for spectral measurements.

In order to determine the hydrogen ion dependence of the rate of reaction of the intermediate produced in the reaction of mercury(II) ion with *cis*-Co(en)$_2$(NH$_2$CH$_2$CO$_2$-*i*-C$_3$H$_7$)Br^{2+}, the following procedure was used. In 0.2 ml of water was dissolved 0.010 g of complex. The solution was mixed with 0.4 ml of Hg(ClO$_4$)$_2$ stock solution and 45 sec later this solution was mixed rapidly and thoroughly with 25 ml of buffer solution (acetate, chloroacetate, tris(hydroxymethyl)aminomethane), previously equilibrated at 25.0 ± 0.1°. The solution was immediately transferred to a 5-cm cell which was then placed in the cell compartment of the spectrophotometer. The pH of the solution was measured at the conclusion of reaction using a Beckman Model G pH meter.

For the reaction in the 2,6-lutidine buffer, the procedure was modified since mercury(II) ion reacts with 2,6-lutidine to yield a white precipitate. Forty-five seconds after initiation of the reaction, the solution was mixed thoroughly with a quinoline buffer; a dense white precipitate formed. This solution was immediately filtered and the filtrate was mixed with a 2,6-lutidine buffer. This solution was transfered to a cell for spectral measurements. The indication is that the quinoline removed the mercury(II) ion. By acidifying the solution after the quinoline precipitation and then measuring the rate of reaction of the intermediate, it has been shown that the quinoline does not react with the complex.

The reaction of mercury(II) with the ester complexes was observed in the carbonyl region of the infrared in the following manner. A weighed amount of complex was dissolved in a measured amount of D$_2$O, and this solution was mixed with a portion of the Hg(ClO$_4$)$_2$ solution in D$_2$O. The resulting solution was transferred to a calcium fluoride cell consisting of two calcium fluoride plates separated by an aluminum spacer (0.003-in. thickness) which was coated with stopcock grease to protect it from acid and mercury(II) ion. The cell was placed in the Perkin-Elmer Model 337 infrared spectrophotometer along with a reference cell containing D$_2$O, and the carbonyl region was scanned periodically during the course of reaction.

Results and Discussion

In the glycine ester containing complexes, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)X]X$_2$, the ester is bonded to the cobalt(III) solely through the amino group, and the ester function remains free. Each of these complexes can be maintained in aqueous solution, even at a low pH, for several hours without appreciable hydrolysis of the ester. This observation substantiates Bender and Turnquest's claim that two sites in the coordination sphere of the metal ion must be available to the ester in order to accelerate the hydrolysis. In these compounds the five other positions about the cobalt(III) are occupied by the halo group and the ethylenediamines.

Table I. Visible Spectra of *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)X]X$_2$ and of the Products of the Reaction of Mercury(II) Ion with *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)X]^2

	Complex			Product	
R	X	λ_{max} ± 2, mμ	ϵ_{max} ± 1	λ_{max} ± 2, mμ	ϵ_{max} ± 2
CH$_3$	Cl	525	77	487	95
		367	82	346	105
C$_2$H$_5$	Cl	525	77	487	99
		367	82	346	108
i-C$_3$H$_7$	Cl	525	77	487	97
		367	82	346	109
CH$_3$	Br	545	85	487	98
				346	108
C$_2$H$_5$	Br	545	82	487	97
				346	107
i-C$_3$H$_7$	Br	545	81	487	97
				346	107

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

(5) P. Duke and W. C. E. Higginson, *J. Chem. Soc.*, 1270 (1963).

(6) A. M. Sargeson, *Australian J. Chem.*, 17, 385 (1964).

(7) A. Ablov, *Bull. Soc. Chim.*, France, [5], **4**, 1783 (1937).

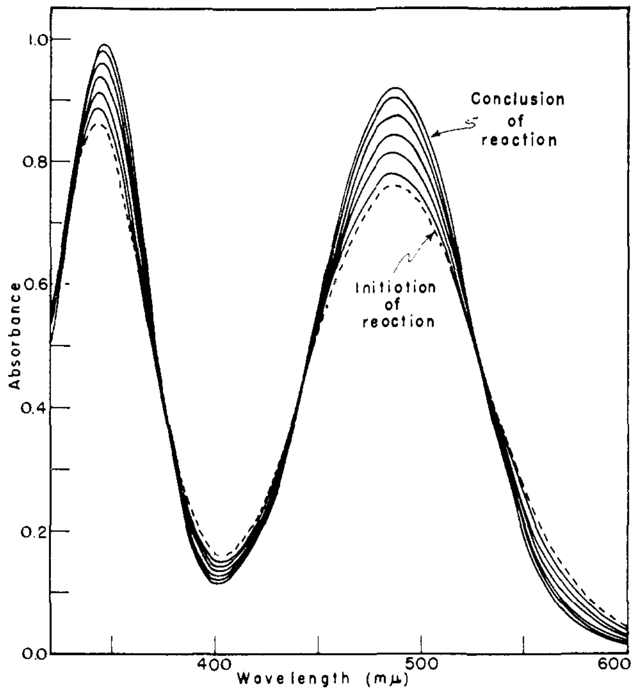
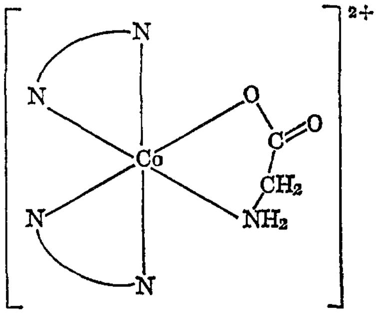


Figure 1. Visible spectra obtained during the course of reaction of mercury(II) ion and *cis*-$[Co(en)_2(NH_2CH_2CO_2\text{-}i\text{-}C_3H_7)Br]^{2+}$.

Mercury(II) ion greatly facilitates the expulsion of the coordinated halide from halopentaamminecobalt(III) ion.[4] Similarly, mercury(II) ion effects the removal of the coordinated halide ion from each of the ester complexes. In Table I the visible absorption spectrum of the product of the reaction with mercury(II) ion is compared to that of each of the halo ester complexes. The spectra of the three chloro complexes differ considerably from those of the bromo compounds. However, the spectra of all the products are identical within experimental error. Furthermore, the spectra of the products are indistinguishable from that of glycinatobis(ethylenediamine)cobalt(III) chloride (structure I),



I

prepared by other means. This suggests that the glycinato complex is formed as the final product in each case, a notion which is substantiated by two other observations. Firstly, the reactions have been run in deuterium oxide which has permitted the measurement of the infrared spectra, in the carbonyl stretching region, of the products in solution. In each case an intense band occurs at 1640 ± 5 cm^{-1}, the position of the carbonyl stretching band for the glycinato complex. Secondly, in the chloro ethyl ester case the product was isolated from solution and found to have an infrared spectrum identical with that of the glycinato complex. It should be emphasized that the formation of the glycinato complex must result from hydrolysis of the ester.

Since the visible spectrum of the glycinato complex is considerably different from those of the ester-containing complexes, spectrophotometric methods were employed to study the kinetics of the reactions. The conditions chosen for the kinetic experiments were as follows: strongly acid solution, $[H^+] = 0.10 \pm 0.005$ *M;* temperature, 25.0 ± 0.0°; constant ionic strength, 0.66; mercury(II) ion concentrations in large excess compared to that of complex; perchlorate used as the anion because of its poor coordinating ability.

It is intuitively obvious and can be readily proved that if one absorbing species reacts to yield another absorbing species without the buildup of any intermediates, then at any wavelength at which the two species have identical molar extinction coefficients there will be no change in absorbance of the reaction mixture during the course of reaction. For the three chloro ester complexes, a wavelength at which their spectra are identical with that of the glycinato complex is 514 mμ. For each of these complexes it was found that during the reaction with mercury(II) ion the absorbance of the reaction solution at this wavelength did not remain constant but first decreased, reached a minimum, and finally increased asymptotically approaching that for the pure product. Clearly the presence of long-lived intermediates is indicated.

The reactions of mercury(II) ion with the bromo complexes are very much faster than with the chloro compounds. In Figure 1 spectra are presented which were taken intermittently during the course of the reaction of the bromo isopropyl ester complex. It is important to note that by the time the first spectrum was obtained, the removal of the coordinated bromide was complete. Qualitatively, this was indicated by the very rapid color change from the red-violet of the bromo complex to an orange. Also, in the spectrum of each of the bromo complexes there is a very intense charge-transfer band in the ultraviolet which carried over into the visible, completely obscuring the high frequency d–d band in that part of the spectrum. In the spectra of Figure 1 there is no evidence of this charge-transfer band. The isosbestic points in Figure 1 suggest the presence of only two uniquely absorbing species. Thus the occurrence of a single long-lived intermediate is indicated. Plots of $\ln (D_\infty - D_t)$ *vs.* time were obtained from the spectra of Figure 1 at two different wavelengths (D_t and D_∞ are the absorbances at time t and at the conclusion of reaction, respectively). The plots are linear with identical slopes confirming the notion of a single observable intermediate. The reactions of mercury(II) ion with all three of the bromo complexes were studied at various mercury(II) ion concentrations. For all runs linear $\ln (D_\infty - D_t)$ *vs.* time plots were obtained (Figure 2). The plots for the three bromo complexes extrapolate to the same value at zero time, signifying that the spectra of the intermediates are identical. That the intermediates are the same for the three cases is denied, however, by the uniqueness of the slopes. Rate data are presented in Table II. It is seen that the reaction of the inter-

Table II. First-Order Rate Constants for the Reaction of *cis*-$Co(en)_2(NH_2CH_2CO_2R)Br^{2+}$ with Mercury(II) Ion ($[H^+]$ = 0.10 *M*, μ = 0.66, 25.0°)

R	[Complex], *M* × 10^3	$[Hg(ClO_4)_2]$, *M*	k_{obsd}, min^{-1}
CH_3	2.84	0.095	1.5 ± 0.2
C_2H_5	2.77	0.095	0.44 ± 0.05
i-C_3H_7	4.62	0.195	0.0651 ± 0.003
i-C_3H_7	5.82	0.095	0.0627 ± 0.003
i-C_3H_7	6.01	0.063	0.0657 ± 0.003

mediate is first order in complex and independent of the mercury(II) ion concentration.

Posey and Taube have shown that the mercury(II) ion promoted aquation of $Co(NH_3)_5X^{2+}$, where X is Cl, Br, or I, passes through a five-coordinate, highly reactive, and very short-lived species, the species being the same for the three halo complexes.[4] Their work suggests that the intermediates observed in the reactions of the chloro ester complexes are identical with those observed in the reactions of the corresponding bromo complexes. Several experiments were designed to test this expectation.

If a single long-lived intermediate is produced in the reaction of each of the chloro complexes, as is the case for the bromo compounds, then during the reaction there will be three absorbing species present: reactant, intermediate, and product, which we will designate A, B, and C, respectively. It can be easily shown that if a reaction proceeds through an observable intermediate, eq 1, which relates absorbance

$$\frac{D_t - D_\infty}{D_0 - D_\infty} = \frac{[A]_t}{[A]_0} \qquad (1)$$

of the solution, D_t, to the concentration of reactant, $[A]_t$, will apply if the wavelength of the measurements is one at which the intermediate and product have identical molar extinction coefficients. Such a wavelength for the bromo complexes is 530 mμ since an isosbestic point occurs at this wavelength in the spectra of Figure 1. Equation 1 is expected then to apply to the chloro case for measurements made at this wavelength.

The reactions of the three chloro complexes were observed at 530 mμ using a variety of mercury(II) ion concentrations. In each case linear ln $(D_t - D_\infty)$ *vs.* time plots were obtained. Rate data are presented in Table IV. The observed first-order rate constants, k_{obsd}, are seen to be proportional to the mercury(II) ion concentration. The second-order rate constants, $k_{obsd}/[Hg^{2+}]$, are the same for the three ester complexes and, furthermore, are identical with that for the mercury(II) ion assisted aquation of the similar *n*-butylamine complex, *cis*-$[Co(en)_2(NH_2\text{-}n\text{-}C_4H_9)Cl]Cl_2$. The linearity of the ln $(D_t - D_\infty)$ *vs.* time plots clearly indicates that the disappearance of the reactant is being followed at this wavelength, which is in accord with the expectation that the intermediate is the same for corresponding chloro and bromo complexes. Moreover, the identity of the second-order rate constants with that for the assisted aquation of *cis*-$[Co(en)_2(NH_2\text{-}C_4H_9)Cl]Cl_2$ implies that the rate-determining step in formation of the intermediate is the expulsion of the coordinated chloride ion.

Table III. Pseudo-First-Order Rate Constants, k_{obsd}, for the Reaction of Mercury(II) Ion with *cis*-$[Co(en)_2(NH_2CH_2CO_2R)Cl]Cl_2$ and *cis*-$[Co(en)_2(NH_2\text{-}n\text{-}C_4H_9)Cl]_2{}^+$ ($[H^+]$ = 0.10 *M*, μ = 0.66, 25.0°, Wavelength = 530 mμ)

R	[Complex], *M* × 10^3	$[Hg(ClO_4)_2]$, *M*	k_{obsd} ± 0.003, min^{-1}	$k_{obsd}/[Hg^{2+}]$, l. $mole^{-1}$ min^{-1}
CH_3	4.05	0.0764	0.081	1.06
CH_3	4.05	0.1145	0.121	1.06
C_2H_5	4.83	0.0372	0.039	1.05
C_2H_5	4.83	0.0372	0.042	1.13
C_2H_5	4.83	0.0744	0.077	1.04
C_2H_5	4.83	0.0764	0.078	1.02
C_2H_5	4.83	0.1116	0.118	1.05
C_2H_5	4.83	0.1488	0.148	1.00
C_2H_5	4.83	0.0764	0.077	1.01
i-C_3H_7	4.77	0.0764	0.080	1.04
i-C_3H_7	4.77	0.1145	0.125	1.09
Y[a]	4.4	0.076	0.083	1.09

[a] Y = *cis*-$[Co(en)_2(NH_2\text{-}n\text{-}C_4H_9)Cl]Cl_2$.

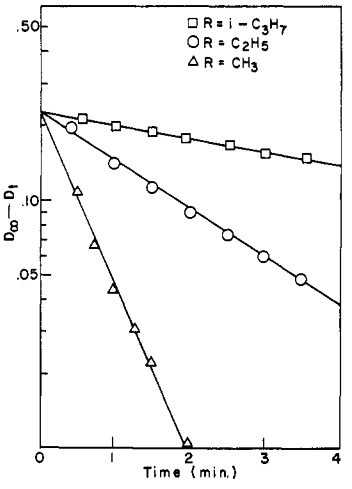


Figure 2. Plots of ln $(D_\infty - D_t)$ *vs.* time for reaction of mercury(II) ion and *cis*-$[Co(en)_2(NH_2CH_2CO_2R)Br]^{2+}$.

The data presented up to this point are consistent with the suggestion that the over-all reaction of the chloro ester complexes involves two consecutive first-order reactions (the first step is pseudo first order because of the large excess in mercury(II) ion). For any process involving two consecutive first-order steps with rate constants k_1 and k_2, eq 2[8] gives the con-

$$[b]_t = \frac{[a]_0 k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \qquad (2)$$

centration of intermediate, $[b]_t$, as a function of time, *t*; $[a]_0$ is the initial concentration of reactant. Using as k_1 the constants obtained from the measurements made at 530 mμ and as k_2 the constants obtained from the measurements made on the reactions of the bromo compounds, curves plotting $[b]_t$ *vs.* time were calculated.

Equation 3, which can be derived readily, is applicable to a reaction proceeding through a single long-lived intermediate. This equation relates the con-

$$(D_\infty - D_t) = (\epsilon_{A,C} - \epsilon_B)l[B]_t \qquad (3)$$

centration of the intermediate, $[B]_t$, to the absorbance of the reaction solution, D_t, at a wavelength at which the product and reactant have the same absorption;

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[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc. New York, N. Y., 1961.

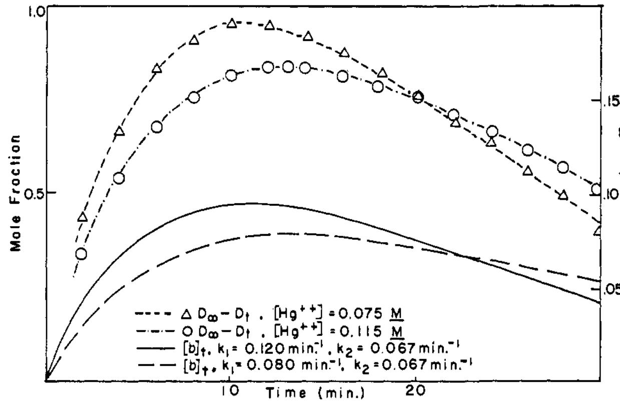

Figure 3. Plots of $[b]_t$ *vs.* time in comparison to plots of $D_\infty - D_t$ (514 mμ) *vs.* time for reaction of mercury(II) ion with *cis*-$[Co(en)_2(NH_2CH_2CO_2\text{-}i\text{-}C_3H_7)Cl]^{2+}$.

$\epsilon_{A,C}$ is the molar extinction of the reactant and product; ϵ_B is that of the intermediate; and l is the length of the cell. Note that the quantity $D_\infty - D_t$ is proportional to the concentration of the intermediate. Recall that the chloro complexes and the glycinato complex absorb the same at 514 mμ; hence, eq 3 is expected to apply to the reactions of the chloro complexes for measurements made at this wavelength. Representative plots of $D_\infty - D_t$, obtained at 514 mμ, and of $[b]_t$ (eq 2) *vs.* time for the reaction of the chloroisopropyl ester complex are presented in Figure 3. Corresponding curves are proportional, which signifies that a single intermediate is produced which reacts at the same rate as the intermediate observed in the reaction of the corresponding bromo complex. Moreover, the proportionality constant obtained from the plots of Figure 3 yields a value for the molar extinction coefficient of the intermediate at this wavelength which is identical with that of the intermediate for the bromo case.[9]

These observations clearly verify that the same intermediate is produced from corresponding bromo and chloro complexes. Similar affirmative results were obtained from the methyl and ethyl ester complexes.

Although the kinetics of the reactions of the ester complexes appear to be established at this point, another series of verificative experiments was performed. For a reaction involving a single observable intermediate, the relationship between the concentration of product, $[C_t]$, and the absorbance of the solution at a wavelength at which the reactant and intermediate absorb identically is given by

$$[C]_t = [A]_0\left(1 - \frac{D_\infty - D_t}{D_\infty - D_0}\right) \tag{4}$$

The spectrum of each of the chloro complexes and that of the intermediate observed in the bromo studies intersect at 507 mμ. The reactions of the chloro complexes were observed at this wavelength, and concentration of product, $[C]_t$, *vs.* time curves were calculated using eq 4. For any process involving two consecutive first-order reactions, the concentration of product, $[C]_t$, is given as a function of time by eq 5. The $[C]_t$ *vs.* time curves

$$[C]_t = [a]_0\left[1 + \frac{1}{k_1 - k_2}(k_2e^{-k_1t} - k_1e^{-k_2t})\right] \tag{5}$$

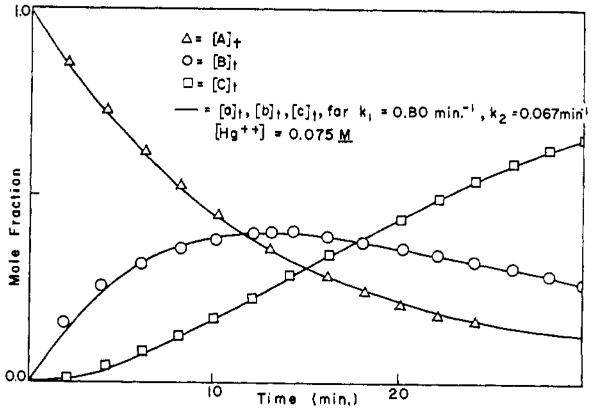

Figure 4. Concentration *vs.* time plots for reaction of mercury(II) ion with *cis*-$[Co(en)_2(NH_2CH_2CO_2\text{-}i\text{-}C_3H_7)Cl]Cl_2$; $[H^+] = 0.10$ *N*.

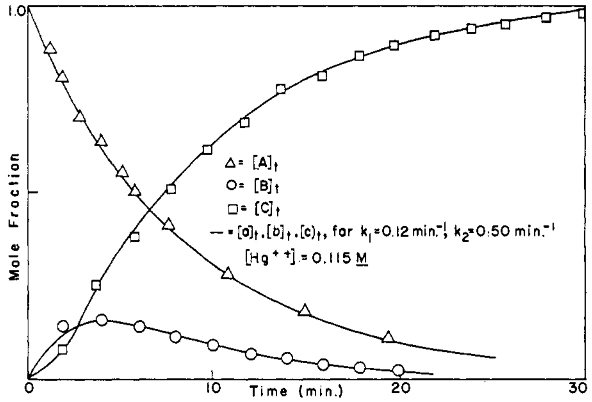

Figure 5. Concentration *vs.* time plots for reaction of mercury(II) ion with *cis*-$[Co(en)_2(NH_2CH_2CO_2C_2H_5)Cl]Cl_2$; $[H^+] = 0.10$ *N*.

obtained from the measurements made at 507 mμ using eq 4 were found to coincide with $[C]_t$ *vs.* time curves calculated using eq 5 with the rate of constants previously obtained; the coincidence of the curves lends support to the above-mentioned kinetic conclusions. These curves are illustrated in Figures 4 and 5 along with concentration *vs.* time curves for the respective intermediates and reactants; the self-consistency of the data is apparent.

The kinetic data for the reactions of the halo ester complexes with mercury(II) ion are condensed in Table IV. To recapitulate, the first step in the reaction

Table IV. Kinetic Data for the Reaction of Mercury(II) Ion with *cis*-$[Co(en)_2(NH_2CH_2CO_2R)X]^{2+}$ in Aqueous Solution ($[H^+] = 0.10 \pm 0.01$ *M*, $\mu = 0.66 \pm 0.01$, $25.0 \pm 0.1°$)

R	X	k_1,[a] l. mole^{-1} min^{-1}	k_2,[b] min^{-1}
CH_3	Cl	1.06 ± 0.05	
	Br	>50	1.6 ± 3
C_2H_5	Cl	1.04 ± 0.05	
	Br	>50	0.43 ± 0.05
i-C_3H_7	Cl	1.06 ± 0.05	
	Br	>50	0.067 ± 0.002

[a] Second-order rate constant for reaction of halo complex with mercury(II) ion. [b] First-order rate constant for reaction of intermediate to yield product.

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[9] The spectrum of the intermediate in the bromo case can be calculated very easily by extrapolation of the spectra in Figure 1 to zero time; the dashed spectrum in Figure 1 was so calculated.

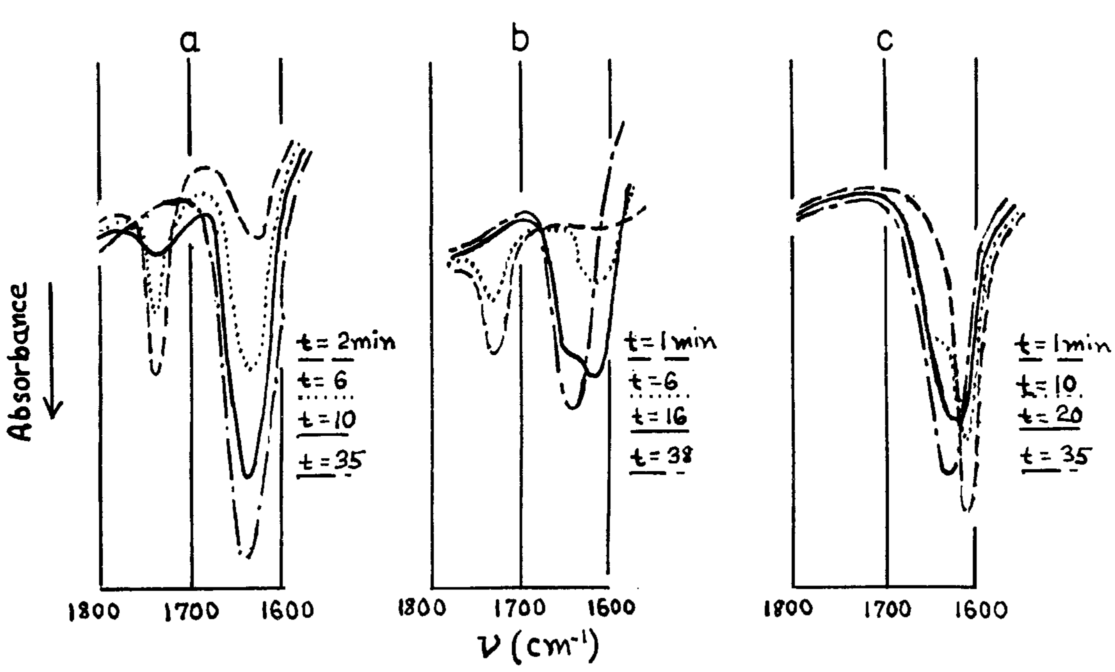
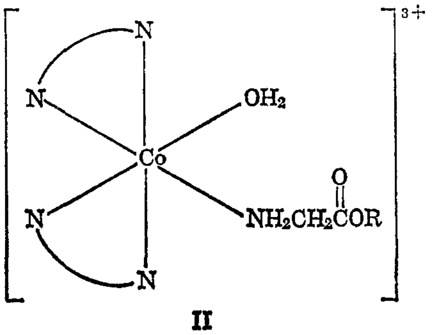


Figure 6. Reaction of mercury(II) ion with *cis*-$[Co(en)_2(NH_2CH_2CO_2R)X]^{2+}$ followed in the carbonyl region of the infrared spectrum; $[D^+] = 0.10$ *N*: (a) X = Cl, R = CH_3; (b) X = Cl, R = *i*-C_3H_7; (c) X = Br, R = *i*-C_3H_7.

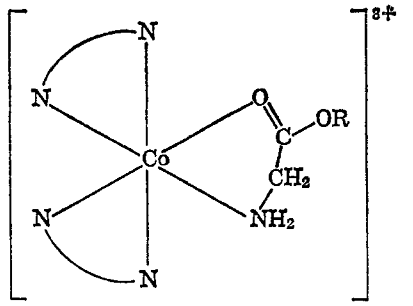
of each of the complexes, the removal of the coordinated halide, is first order in complex and first order in mercury(II) ion. The second step is first order in intermediate and independent of the mercury(II) ion concentration. A common intermediate is obtained for corresponding chloro and bromo complexes.

Up to this point very little has been said concerning the nature of the intermediates observed in the spectrophotometric studies. Referring to Table IV, it is seen that there is a marked dependence of the rate of the second step upon the nature of the ester group: $CH_3 > C_2H_5 > i\text{-}C_3H_7$. This indicates strongly that the intermediate retains the ester group.

The data suggest that the expulsion of the coordinated halide results in a five-coordinate species just as is the case for the reaction of mercury(II) ion with the complex, $Co(NH_3)_5X^{2+}$. It appears likely then that a solvent water molecule could take the sixth position about the cobalt(III), forming as the intermediate the aquo–ester complex (structure II). However, visible and infrared spectral data provide substantial evidence against formulation of the intermediate as the aquo ester complex.



II



III

The visible spectrum of the intermediate calculated from the spectra of Figure 1 has maxima at 487 and 344 mμ with molar extinction coefficients of 80 and 92, respectively. The positions of these bands are nearly the same as in the spectra of known *cis*-aquo(amine)bis(ethylenediamine)cobalt(III) complexes; however, considering relative intensities of the bands, for the intermediate the band at lower wavelength is the more intense of the two while the opposite is true for known aquo complexes (for *cis*-$Co(en)_2NH_3(H_2O)^{3+}$ the bands at 480 and 340 mμ have molar extinction coefficients of 64 and 60, respectively).

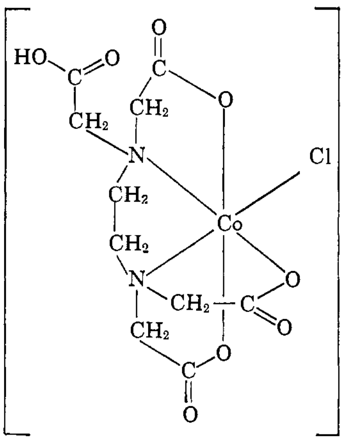
By using deuterium oxide as the solvent rather than water it is possible to observe the carbonyl stretching region in the infrared during the course of reaction. This was done for the reactions of the chloro methyl ester, the chloro isopropyl ester, and bromo isopropyl ester complexes. The results are shown in Figure 6. Bands are observed at three frequencies: 1740, 1640, and 1610 cm^{-1}. The bands at 1740 and 1640 cm^{-1} arise from carbonyl stretching modes of the halo ester complex and the glycinato complex, respectively. A comparison of the rate at which the band at 1610 cm^{-1} first appears and then disappears for the three cases to the kinetic data obtained spectrophotometrically confirms that the band is associated with the intermediate.

This band is 130 cm^{-1} lower in frequency than the ester carbonyl band in the halo ester complexes and, hence, is much lower than would be expected if the intermediate were the aquo ester complex. Hydrogen bonding of the carbonyl to a coordinated water molecule could account for a small downward shift in the frequency of the carbonyl band, <50 cm^{-1}, but not for a shift as great as 130 cm^{-1}.[10,11]

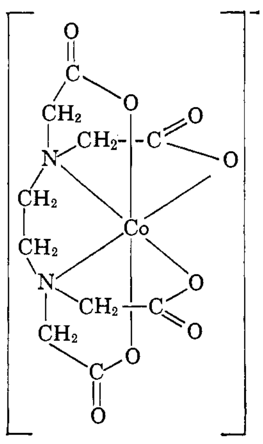
Another possible formulation for the intermediate is as the chelated ester complex (structure III). This complex would result from the carbonyl oxygen of the ester taking the vacated position about the cobalt(III) after expulsion of the coordinated halide; the process would appear to be statistically very favorable. Note that this complex is analogous to the transient intermediate proposed for the copper(II) system studied by Bender and Turnquest to account for the acceleration in hydrolysis of the ester.

Springer and Curran[12] have prepared a number of glycine and alanine ester complexes of copper(II), nickel(II), and cadmium(II) in which the esters are chelated to the metal ion just as in the proposed structure for the intermediate. They report that in the infrared spectrum of these compounds the carbonyl stretching frequency is as much as 90 cm^{-1} lower than in the spectra of the ester hydrochlorides; for the hydrochlorides the frequencies are approximately 1740 cm^{-1}. The magnitude of this difference increases in the order Cd < Ni < Cu, indicating that the greater the strength of the metal–oxygen bond the lower the frequency of the carbonyl stretching mode. Since a cobalt(III)–oxygen bond would be expected to be stronger than a copper(II)–oxygen bond, one would expect that the decrease of the carbonyl stretching frequency on coordination of an ester carbonyl to cobalt(III) would exceed 90 cm^{-1}. Consequently, it seems most probable that the band at 1610 cm^{-1}, associated with the intermediate, is the carbonyl stretching band of a coordinated ester carbonyl. Hence, the infrared data provide excellent evidence that the intermediate is the chelated ester complex. The indication is then that after the mercury(II) ion effects the removal of the coordinated halide to yield a five-coordinate species, the ester carbonyl oxygen competes so efficiently with solvent water for the sixth position in the coordination sphere of the cobalt(III) that, within experimental error, the chelated ester complex is formed exclusively.

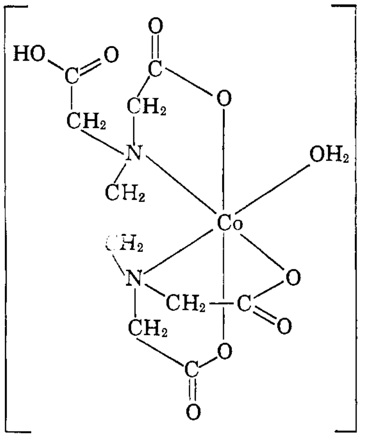
This conclusion is in accord with a mechanism postulated to occur in the reaction of mercury(II) ion with Co(HEDTA)Cl$^-$, structure IV, to yield Co(EDTA)$^-$, structure V.[5] Kinetic data indicate that the aquo complex, structure VI, is not formed as an intermediate, and it has been concluded, therefore, that on removal of the chloride the carbonyl oxygen of the dangling acid function takes the vacated position. This is followed rapidly by expulsion of a proton to yield the product.



IV

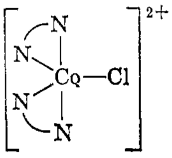


V

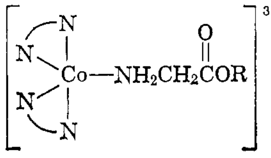


VI

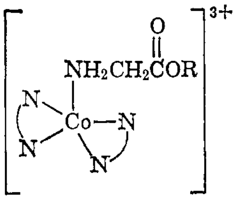
It is pertinent to consider the structure of the five-coordinate species formed after removal of the halide from a halo ester complex. Sargeson[6] has studied the mercury(II) ion assisted aquation of *cis*-Co(en)$_2$Cl$_2^+$ and has concluded that the short-lived five-coordinate species formed initially has a trigonal bipyramidal structure with two of the amino groups in axial positions (structure VII). In view of this conclusion, one might consider the possibility that the five-coordinate species in the ester case has a similar structure (VIII). If this is true, the reaction of mercury(II) ion with the ester complexes should yield the glycinato complex with retention of configuration. The optical antipode of chloro ethyl ester complex having a specific rotation of +75° at 623.4 mμ has been found to react with mercury(II) ion to yield the glycinato complex having a specific rotation of +235° at the same wavelength. At this wavelength optical isomers of the chloro ester complex and the glycinato complex having the same configuration are expected to have the same sign of rotation.[13] Consequently, it appears that reaction



VII



VIII



IX

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(10) G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co., San Francisco, Calif., 1960.

(11) D. Hadzi, "Hydrogen Bonding," Pergamon Press, New York, N. Y., 1959.

(12) M. P. Springer and C. Curran, *Inorg. Chem.*, **2**, 1270 (1963).

(13) T. E. McDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

proceeds with retention of configuration, an observation which is consistent with the trigonal bipyramidal structure. These data do not establish the trigonal bipyramidal structure, though, since they are also consistent with the tetragonal pyramidal structure. However, the symmetrical structure (IX) is excluded by the data.

In considering the reaction of the chelated ester intermediate to yield the glycinato complex, one would expect, on the basis of Bender and Turnquest's contention, that the carbonyl carbon undergoes nucleophilic attack by solvent water or hydroxide ion. Referring back to Table IV it is seen that the rate constants for the reaction of the intermediate are in the ratio $3:1:{}^1/_6$ for the methyl, ethyl, and isopropyl esters, respectively. For the base hydrolysis of the methyl, ethyl, and isopropyl acetates the ratio of the rate constants is $2:1:{}^1/_4$.[14] Note that the ratios for the two series are similar. In the latter case the reaction is known to involve nucleophilic attack at the carbonyl carbon, and it is widely accepted that steric considerations are the important factor in determining the relative rates.[14] It would appear that the similarity of relative rates for the two series is consistent with the notion that nucleophilic attack at the carbonyl carbon also occurs in the hydrolysis of the chelated ester complexes.

The question as to whether water or hydroxide ion is the nucleophile remains to be discussed. The hydrogen ion dependence of the rate of hydrolysis of the chelated isopropyl ester complex has been studied. The results are summarized in Table V. It is seen that the rate of reaction is insensitive to a several-fold change in hydrogen ion concentration, *i.e.*, in the pH range 1–4 (lines 1, 2, 7, 12). The indication is that attack by hydroxide ion is not important in this pH range.

Table V. Rate of Reaction of Intermediate (Isopropyl Case) to Yield Glycinatobis(ethylenediamine)cobalt(III) in Various Buffer Systems (25.0 ± 0.1°; [Complex] = 7.0×10^{-4} *M;* $\mu = 0.66$)

	Buffer system	[N][a]	pH	k_B, min^{-1} [b]
1	Perchloric acid	. . .	1.0	0.067 ± 0.001
2		. . .	1.7	0.064 ± 0.004
3	Chloroacetic acid	0.075	2.27	0.130 ± 0.005
4		0.050	2.25	0.115 ± 0.005
5		0.025	2.25	0.095 ± 0.005
6		0.0125	2.02	0.079 ± 0.005
7		0.000[c]	2	0.065 ± 0.005
8	Acetic acid	0.025	4.35	0.23 ± 0.02
9		0.0175	4.34	0.19 ± 0.01
10		0.0125	4.35	0.15 ± 0.01
11		0.005	3.90	0.099 ± 0.005
12		0.000[c]	4	0.065 ± 0.010
13	2,6-Lutidine	0.0125	6.8	C, 2 min[d]
14	Tris[e]	0.015	7.3	C, 2 min
15		0.065	8.0	C, 2 min

[a] Molar concentration of anion or free base derived from buffer. [b] Observed first-order rate constant. [c] Obtained by extrapolation to zero concentration of the graph of rate *vs.* anion concentration. [d] C designated reaction is complete in time specified. [e] Tris(hydroxymethyl)aminomethane.

If one examines the rate data for the chloroacetate and acetate buffer systems, one sees that at constant pH there is a marked dependence of the reaction rate upon the concentration of the anion of the buffer. This dependence is illustrated in Figure 7. The dependence is linear, within experimental error, and is greater in the acetate case than in the chloroacetate. This strongly suggests that the rate law for the conversion of intermediate to the glycinato complex should be written as

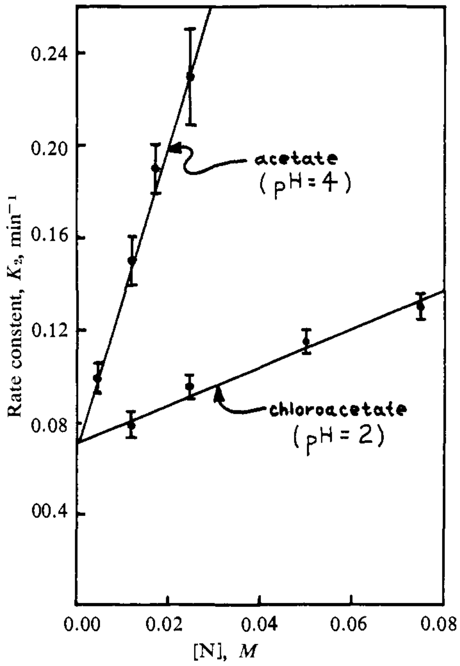

Figure 7. Dependence of rate of reaction of intermediate (isopropyl case) upon the concentration of anion derived from the chloroacetate and acetate buffer systems.

$$\frac{-\text{d[inter]}}{\text{d}t} = k_{\text{H}_2\text{O}} + \sum_i K_{\text{N}_i}[\text{N}_i] \tag{6}$$

where the N_i are the various nucleophiles (or bases) present in the system and $k_{\text{H}_2\text{O}}$ is the observed rate constant in the absence of nucleophilic and general base catalysis. Since both nucleophilic and base catalysis have been observed for ester hydrolysis,[15–18] the rate law is consistent with formulation of the intermediate as the chelated ester complex.

At higher pH values (7–8) the rate of reaction of the chelated ester complex is very rapid (Table IV). These fast rates may be due to nucleophilic or base catalysis or due to direct hydroxide attack. Steric considerations essentially eliminate the possibility that 2,6-lutidine is catalyzing the hydrolyses nucleophilically. Moreover, it has been shown that this species is relatively ineffective as a base catalyst in similar systems, even though steric requirements for base catalysis are considerably less than for nucleophilic attack.[18] Therefore, the possibility of direct hydroxide attack should be considered. Since no base hydrolysis was observed at pH 4, the rate of base hydrolysis must be approximately 10^2 faster than hydrolysis *via* attack by water, if in the 2,6-lutidine buffer the 2,6-lutidine is not itself catalyzing the hydrolysis. This is quite possible since the base hydrolysis of uncoordinated α-amino esters has been observed to be much faster than acid hydrolysis at a pH of

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[14] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

[15] M. L. Bender and B. W. Turnquest, *J. Am. Chem. Soc.*, **79**, 1652, 1656 (1957).

[16] M. L. Bender and B. W. Turnquest, *ibid.*, **80**, 5388 (1958).

[17] T. C. Bruice and R. Lapinski, *ibid.*, **80**, 2265 (1958).

[18] F. Covitz and F. H. Westheimer, *ibid.*, **85**, 1773 (1963).

7.[2b] Electrostatic considerations lend support to the notion that hydroxide attack is occurring. The base hydrolysis of $(CH_3)_3N^+CH_2CO_2C_2H_5$ is about 10^3 times faster than that of $(CH_3)_2NCH_2CO_2C_2H_5$, even though steric requirements for the former are greater. The effect of the positive charge on the nitrogen is apparent.[2] It follows, then, that in the case of the chelated ester complex the positive charge of +3 on the complex should greatly enhance attack by hydroxide.

At this point it is appropriate to summarize the conclusions reached pertaining to the reaction of the glycine ester containing complexes with mercury(II) ion. Mercury(II) ion reacts with *cis*-$Co(en)_2(NH_2CH_2CO_2R)X^{2+}$ in aqueous solution to yield a five-coordinate, highly reactive complex. The vacated position in the coordination sphere of the cobalt(III) is taken by the carbonyl oxygen of the ester to yield the chelated ester complex, $Co(en)_2(NH_2CH_2CO_2R)^{3+}$. In the absence of other nucleophiles, water attacks the positive center, the carbonyl carbon, resulting in hydrolysis of the ester and formation of $Co(en)_2(NH_2CH_2CO_2)^{2+}$. The rate of hydrolysis of the chelated ester is extremely rapid in comparison to that for the ester molecule coordinated through the amino group alone. The hydrolysis of the chelated ester is subject to general nucleophilic or general base catalysis.

These conclusions are in support of the mechanism proposed by Bender and Turnquest for the copper(II)-promoted hydrolysis of α-amino esters. These particular cobalt(III) systems cannot, of course, be taken as establishing the mechanism for the copper ion case. In fact, the demonstration of the path discussed here clearly does not preclude the existence of other mechanisms in other systems, even those containing cobalt(III).

Acknowledgment. The support of these investigations by the National Science Foundation is sincerely appreciated.

Concerning the Status of Bis(cyclopentadienyl)titanium

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Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712. *Received October 23, 1965*

Abstract: The status of earlier reports on the synthesis and properties of bis(cyclopentadienyl)titanium is reviewed and evaluated. A synthesis *via* reduction of $(C_5H_5)_2TiCl_2$ with $NaC_{10}H_8$ in tetrahydrofuran, and numerous properties of $(C_5H_5)_2Ti$, are reported and discussed.

In 1956, Fischer and Wilkinson[1] reported the synthesis of $(C_5H_5)_2Ti$ by the reaction

$$TiCl_2 + 2NaC_5H_5 \longrightarrow (C_5H_5)_2Ti + 2NaCl \qquad (1)$$

in tetrahydrofuran (THF). When failure to confirm (1) was reported from this laboratory,[2] we were unaware that the work of Fischer and Wilkinson was antedated by a patent application[3] filed in 1953, claiming synthesis of $(C_5H_5)_2Ti$ *via* reaction 1, but without evidence supporting the identity of the product. We also overlooked the reported synthesis of $(C_5H_5)_2Ti$ by reaction 2 in hexane[4]; the product was characterized only by an

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \longrightarrow (C_5H_5)_2Ti + 2CH_4 \qquad (2)$$

analysis for titanium.

Levy[5] has stated that $(C_5H_5)_2Ti$ has been prepared only by Fischer and Wilkinson and by Long, both *via* (1). In the latter instance, however, the analytical and other data obtained are not convincing although the identity of the product was assumed.[6] Another laboratory[7] has been unable to verify the results of Fischer and Wilkinson. Also with regard to prior work, Vol'pin, *et al.*,[8] have reported the synthesis of the stable adduct $(C_5H_5)_2Ti(C_6H_5C{\equiv}CC_6H_5)_2$ by addition of $TiCl_4$ and $C_6H_5C{\equiv}CC_6H_5$ to a THF solution of NaC_5H_5. Still more recently, Yokokawa and Azuma[9] reported that they had prepared $(C_5H_5)_2Ti$ by the reaction

$$(C_5H_5)_2TiCl_2 + 2NaHg \longrightarrow (C_5H_5)_2Ti + 2NaCl + Hg \qquad (3)$$

using 1% sodium amalgam in dry toluene; the product of (3), however, was neither isolated nor characterized.

In part because of widespread theoretical speculation[10-17] about the structure of compounds of this type and the obvious need to re-examine the unexpected diamagnetism of $(C_5H_5)_2Ti$, we have continued our work on this compound and report here a synthesis in high yield by the reaction

$$(C_5H_5)_2TiCl_2 + 2NaC_{10}H_8 \longrightarrow (C_5H_5)_2Ti + 2C_{10}H_8 + 2NaCl \qquad (4)$$

under an inert atmosphere in THF at 25°. The results given below show that the product initially crystallized

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[1] A. K. Fischer and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 149 (1956).

[2] G. W. Watt and L. J. Baye, *ibid.*, **26**, 2099 (1964).

[3] J. C. Brantley, U. S. Patent 2,983,741 (1961).

[4] K. Clauss and H. Bestian, *Ann.*, **654**, 8 (1962).

[5] D. A. Levy, Dissertation, Cambridge University, 1960, p 146.

[6] W. P. Long, private communication.

[7] E. O. Fischer, private communication.

[8] M. E. Vol'pin, V. A. Dubovitskër, O. V. Nogina, and D. N. Kurnasov, *Dokl. Akad. Nauk SSSR*, **151**, 623 (1963).

[9] K. Yokokawa and K. Azuma, *Bull. Chem. Soc. Japan*, **38**, 859 (1965).

[10] W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).

[11] J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

[12] M. Yamazaki, *ibid.*, **24**, 1260 (1956).

[13] E. Ruch, *Rec. Trav. Chim.*, **75**, 638 (1956).

[14] A. D. Liehr and C. J. Ballhausen, *Acta Chem. Scand.*, **11**, 207 (1957).

[15] F. A. Matsen, *J. Am. Chem. Soc.*, **81**, 2023 (1959).

[16] H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **64**, 70 (1960).

[17] R. S. Becker and D. R. Scott, *J. Chem. Phys.*, **35**, 516 (1961).