

8-, 9-, and 10-methyl spectral regions show an interesting pattern. The three 10-methyl peaks in the  $\beta$  ( $\Delta$ -trans) isomer are centered close to the position of the 10-methyl peak in the  $\gamma$  ( $\Delta$ -cis) isomer which is shifted more than 0.1 ppm upfield from the position of the 10-methyl peak in the  $\delta$  ( $\Delta$ -cis) isomer. In fact, overall, the spectra of the  $\beta$  and  $\gamma$  isomers resemble one another in these regions as do the spectra of the  $\alpha$  and  $\delta$  isomers. Thus, if the two  $\beta$  peaks at  $-0.93$  (doubly degenerate) and  $-0.86$  ppm are given the same assignments as the  $\gamma$  peak at  $-0.90$  ppm and if the three  $\beta$  peaks centered at  $-0.70$  ppm are given the same assignments as the  $\gamma$  peak at  $-0.70$  ppm, then the effect on the spectrum of going from  $\gamma$  ( $\Delta$ -cis) to  $\beta$  ( $\Delta$ -trans) is quite small. The lowering of the symmetry from  $C_3$  to  $C_1$  barely serves to remove the degeneracy of the transitions. Likewise, if the appropriate relative assignments are made, the change from  $\delta$  ( $\Delta$ -cis) to  $\alpha$  ( $\Delta$ -trans) is so small that none of the spectral degeneracy is removed. The biggest differences in the spectra occur in the  $\Delta$  to  $\Lambda$  configurational inversion. Since most peaks are shifted upfield in going from  $\Delta$  to  $\Lambda$ , it would seem that the  $\Lambda$  isomers are more strongly solvated. The small changes upon conversion from trans to cis could be due to intramolecular electronic effects on the chemical shifts.

Benzene is known preferentially to solvate the positive end of molecular electric dipoles<sup>43</sup> and Linck and Sievers have shown that this is observed for neutral tris( $\beta$ -keto enolate) complexes.<sup>44</sup> In the cis isomers, the dipole moment lies along the  $C_3$  axis, but which end

(44) R. G. Linck and R. E. Sievers, *Inorg. Chem.*, **5**, 806 (1966).

of this axis would be more positive in these complexes is not known with certainty. Around one end are arrayed the acetyl methyl groups whose degenerate resonance position is not much affected by the change from  $\Delta$  to  $\Lambda$  although the  $\Lambda$  peak ( $\gamma$ ) is shifted slightly upfield. About the other end, are clustered the 8- and 10-methyl groups in the  $\Delta$  isomer. In the  $\Lambda$  molecule the 8-methyl groups become well shielded from the trigonal face at the end of the  $C_3$  axis by the 10-methyl groups which are still arrayed about it. The fact that the 10-methyl resonance, as mentioned before, shifts significantly upfield upon conversion from  $\Delta$  to  $\Lambda$  is consistent with increased solvation occurring at this face. The lesser number of methyl groups about this face in the  $\Lambda$  isomer might be the driving force for this increased solvation. It is interesting that the highest field methyl peak which (as also mentioned before) might be assigned to the 8-methyl group is hardly shifted at all upon conversion from  $\Delta$  to  $\Lambda$ .

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## Substitution Reactions of Metallic Complexes of $\beta, \beta', \beta''$ -Triaminotriethylamine. VI. Kinetics of Aquation of *cis*-Chloroaquo( $\beta, \beta', \beta''$ -triaminotriethylamine)cobalt(III) Ion

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The kinetics of the acid hydrolysis of *cis*-Co(tren)H<sub>2</sub>OCl<sup>2+</sup> (tren =  $\beta, \beta', \beta''$ -triaminotriethylamine) have been investigated between 25 and 70°. The pseudo-first-order rate constant for the reaction at 65.0° was found to be  $2.69 \times 10^{-4} \text{ sec}^{-1}$  and was ionic strength independent in 1 M HClO<sub>4</sub>. The acid hydrolysis reaction proved to be acid inhibited in the range of pH 1–2.3, presumably through an acid dissociation of the chloroaquo species to form the faster reacting chlorohydroxo species. The activation enthalpy for the reaction in 1 M HClO<sub>4</sub> was 21.6 kcal mol<sup>-1</sup>, and the entropy of activation was found to be  $-11.0 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . A second isomer of the chloroaquo ion is believed to be present in solution during the initial stages of the reaction.

### Introduction

Recently the kinetics of the acid hydrolysis of Co(tren)H<sub>2</sub>OBr<sup>2+</sup> (tren =  $\beta, \beta', \beta''$ -triaminotriethylamine) have been reported<sup>2</sup> and compared with those of the

reaction of Co(tren)Br<sub>2</sub><sup>3a</sup> and *cis*-Cr(en)<sub>2</sub>H<sub>2</sub>OBr<sup>2+</sup><sup>3b</sup> (en = ethylenediamine).

It was found that while the acid hydrolysis rate of Co(tren)Br<sub>2</sub><sup>3a</sup> is unaffected by pH changes in acid solution, the reaction of Co(tren)H<sub>2</sub>OBr<sup>2+</sup> is acid inhibited. This difference has been attributed to an acid–base equilibrium in the bromoaquo system, which results in

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(2) W. V. Miller and S. K. Madan, *Inorg. Chem.*, **9**, 2362 (1970).

(3) (a) S. K. Madan and J. Peone, Jr., *ibid.*, **6**, 463 (1967); (b) L. P. Quinn and C. S. Garner, *ibid.*, **3**, 1348 (1964).

the formation of a small amount of the bromohydroxo species. It was further observed that the hydrolysis of  $\text{Co}(\text{tren})\text{Br}_2^+$  at  $25^\circ$  is much faster than that of  $\text{Cr}(\text{en})_2\text{Br}_2^+$ , while the order for the hydrolysis rates of the corresponding bromoaquo species is reversed. The larger rate of reaction of  $\text{Co}(\text{tren})\text{Br}_2^+$  has been attributed to a distortion of the complex by the tren ligand, which exposes the bromide groups to solvent attack more than in an undistorted complex. The kinetic data for the acid hydrolysis of the corresponding bromoaquo species, however, indicate that the distortion in the tren complex may be greatly reduced after the loss of the first bromide group.

Since kinetic data for the acid hydrolysis of *cis*- $\text{Co}(\text{en})_2\text{Cl}_2^+$ ,<sup>4</sup> *cis*- $\text{Co}(\text{en})_2\text{H}_2\text{OCl}^{2+}$ ,<sup>5</sup> and *cis*- $\text{Co}(\text{tren})\text{Cl}_2^+$ <sup>6</sup> are available, a comparison of the acid hydrolysis rates for these complexes with that of the  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  would be useful in determining whether a similar reduction in the degree of distortion occurs after the loss of the first chloride group. Further, a study of the effects of temperature, ionic strength, and acid concentration on the hydrolysis rates of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  would be of interest since no such data are available for any other cobalt(III)-haloaquo systems.

With this purpose in mind, the kinetics of aquation of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  have been investigated under various conditions of temperature, ionic strength, and acid concentration, and the data are compared with those of similar systems.

### Experimental Section

**Preparation of Compounds.** (1)  $\beta, \beta', \beta''$ -Triaminotriethylamine Hydrochloride.—This compound was prepared by the method of Paoletti, Ciampolini, and Sacconi.<sup>7</sup>

(2) Carbonatotetraamminecobalt(III) Nitrate Hemihydrate.—This compound was synthesized by the method described by Schlessinger.<sup>8</sup>

(3) Dichloro(triaminotriethylamine)cobalt(III) Chloride Hemihydrate.—This complex was prepared from carbonatotetraamminecobalt(III) nitrate hemihydrate by the method of Liu.<sup>9</sup> To a solution of 12.8 g of triaminotriethylamine hydrochloride in 100 ml of water was added 6.3 g of lithium hydroxide monohydrate. This solution was added to a solution of 12.9 g of  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$  in 300 ml of water. A small amount of charcoal was added as catalyst, and the mixture was refluxed on the steam bath for 24 hr. At the end of this time no more ammonia gas could be detected. The mixture was filtered and the solution was evaporated to a small volume on the steam bath. While the mixture was still being heated on the steam bath, 50 ml of concentrated hydrochloric acid was added in small portions. The resulting solution was evaporated to dryness. The residue was extracted with 150 ml of absolute alcohol five or six times to remove lithium chloride. The residue consisted of violet crystals. The product weighed 12.0 g, which corresponds to a 73.0% yield. The product was recrystallized either from dilute (1:1) hydrochloric acid or from a dilute hydrochloric acid-alcohol mixture. *Anal.* Calcd for  $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{Cl} \cdot 0.5\text{H}_2\text{O}$ : C, 22.40; H, 5.92; N, 17.45. Found: C, 22.30; H, 5.70; N, 17.20.

(4) Dichloro(triaminotriethylamine)cobalt(III) Perchlorate.—One gram of dichloro(triaminotriethylamine)cobalt(III) chloride hemihydrate was dissolved in a minimum amount of water at  $25^\circ$ . The addition of 2.0 g of sodium perchlorate followed by immediate cooling to  $0^\circ$  resulted in the formation of deep blue crystals. The compound was filtered, washed with absolute ethanol, and dried *in vacuo*. The yield was 36.0%. *Anal.*

Calcd for  $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{ClO}_4$ : C, 19.25; H, 4.80; N, 14.94;  $\text{ClO}_4$ , 26.50. Found: C, 19.64; H, 5.08; N, 14.59;  $\text{ClO}_4$ , 26.25.

(5) Chloroaquo(triaminotriethylamine)cobalt(III) Sulfate.—One gram of dichloro(triaminotriethylamine)cobalt(III) perchlorate was dissolved in 20 ml of  $\text{H}_2\text{O}$  and was allowed to undergo the primary acid hydrolysis step at  $35.0^\circ$ . An excess of ammonium sulfate was added to the red solution, and cooling to  $0^\circ$  resulted in the formation of a red-violet precipitate. The compound was filtered, washed with ethanol, and dried *in vacuo*. The yield was 69%. *Anal.* Calcd for  $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{H}_2\text{OCl}]\text{SO}_4$ : C, 20.34; H, 5.69; N, 15.80;  $\text{SO}_4$ , 27.09. Found: C, 19.88; H, 5.90; N, 16.11;  $\text{SO}_4$ , 26.89.

**Physical Measurements. Electronic Absorption Spectra.**—All visible spectra reported here were obtained with a Cary Model 14M recording spectrophotometer using matched cells with 1-cm path length.

**Kinetic Measurements.**—The chloroaquo species used in this study was prepared *in situ* by allowing  $[\text{Co}(\text{tren})\text{Cl}_2]\text{ClO}_4$  to undergo the primary acid hydrolysis step at room temperature (1 hr). Since the secondary hydrolysis step is very slow at  $25^\circ$ , no appreciable secondary reaction occurred during this period. After the primary acid hydrolysis step, a series of scans of the visible spectrum during the secondary hydrolysis reaction at  $55.0^\circ$  showed that the initial spectrum was identical with that of  $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]\text{SO}_4$ , and the final spectrum was identical with that of  $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{3+}$ .<sup>3a</sup> These scans are reproduced in Figure 1. Two isosbestic points were observed in the spectra during

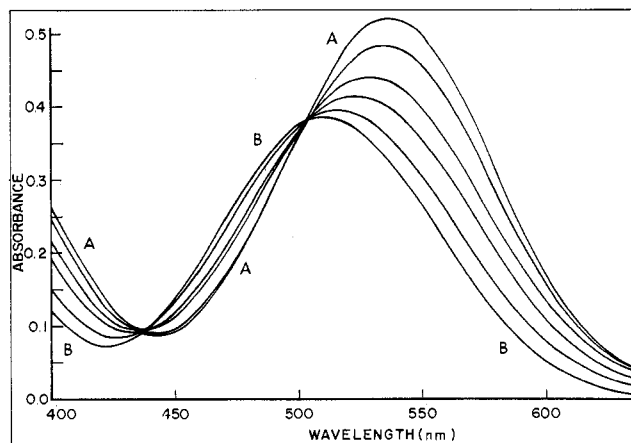


Figure 1.—Spectral changes during the acid hydrolysis of chloroaquo(triaminotriethylamine)cobalt(III) ion: (A) initial trace,  $3.63 \times 10^{-3} M \text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$ ; (B) final trace,  $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{3+}$ .

the entire course of the reaction, one at 508 and the other at 432 nm, although a slight shift in the isosbestic points was observed during the initial part of the reaction. The wavelength chosen for this kinetic study was 550 nm where the maximum difference in absorbance occurs between the reactant and the product.

All kinetic measurements were made spectrophotometrically, after withdrawing samples from a temperature bath controlled to within  $0.50^\circ$  using a Cary Model 16 spectrophotometer with matched cells of 1-cm path length. The pseudo-first-order rate constants were obtained from the slope of a plot of  $\ln(A_t - A_\infty)$  vs.  $t$  where  $A_\infty$  is the final absorbance reading and  $A_t$  is the absorbance at time  $t$ . The plots all gave straight lines for at least 3 half-lives after the first 10% of the reaction; however, a slight curvature was noted during the initial part of the reaction. Consecutive runs always agreed to within 3%.

### Results and Discussion

In order to establish that the acid hydrolysis of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  involves no side reactions, the reaction rate was determined at  $65.0^\circ$  and pH 0 at three different wavelengths. The observed values for the rate constant for aquation, at 565, 550, and 385 nm, are  $2.77 \times 10^{-4}$ ,  $2.69 \times 10^{-4}$ , and  $2.73 \times 10^{-4} \text{sec}^{-1}$ , respec-

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(7) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

(8) G. Schlessinger, *Inorg. Syn.*, **6**, 173 (1960).

(9) C. F. Liu, Doctoral Dissertation, University of Illinois, 1957.

tively. These values are all in good agreement with the average value of  $2.83 \times 10^{-4} \text{ sec}^{-1}$  obtained for the acid hydrolysis of  $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]\text{SO}_4$ .

In general, the kinetics of the acid hydrolysis of the chloroaquo species are similar to those of the bromoaquo complex described previously.<sup>2</sup> The rate constants for the hydrolysis of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  were obtained in 1 M  $\text{HClO}_4$  under various conditions of temperature and ionic strength, and the data are summarized in Table I. The Arrhenius plot for the data in

TABLE I  
RATES OF ACID HYDROLYSIS OF  
CHLORO-AQUO(TRIAMINOTRIETHYLAMINE)COBALT(III)  
ION IN 1 M  $\text{HClO}_4$  UNDER VARIOUS CONDITIONS

Temp, °C	Added electrolyte	Ionic strength	$k_2$ , $\text{sec}^{-1}$
25.0	None	1.00	$2.38 \times 10^{-6}$
50.0	None	1.00	$6.10 \times 10^{-6}$
55.0	None	1.00	$1.04 \times 10^{-4}$
60.0	None	1.00	$1.82 \times 10^{-4}$
65.0	None	1.00	$2.69 \times 10^{-4}$
70.0	None	1.00	$4.70 \times 10^{-4}$
65.0	1.50 M $\text{NaClO}_4$	2.50	$2.32 \times 10^{-4}$
65.0	1.00 M $\text{NaClO}_4$	2.00	$2.51 \times 10^{-4}$
65.0	0.50 M $\text{NaClO}_4$	1.50	$2.66 \times 10^{-4}$
65.0	0.005 M $\text{NaCl}$	1.01	$2.73 \times 10^{-4}$
65.0	0.10 M $\text{Na}_2\text{SO}_4$	1.30	$3.59 \times 10^{-4}$
65.0	0.05 M $\text{Na}_2\text{SO}_4$	1.15	$3.15 \times 10^{-4}$

Table I in the range of 50–70° gives a straight line with a standard deviation of 2.7%, from which an activation enthalpy,  $\Delta H^\ddagger$ , of 21.6 kcal mol<sup>-1</sup> is obtained. The free energy of activation,  $\Delta G^\ddagger$ , and the entropy of activation,  $\Delta S^\ddagger$ , were calculated to be 25.3 kcal mol<sup>-1</sup> and -11.0 cal mol<sup>-1</sup> deg<sup>-1</sup>, respectively, at 65°. It is interesting that the activation enthalpy for the primary acid hydrolysis of  $\text{Co}(\text{tren})\text{Cl}_2^+$  is higher than that for the corresponding reaction of the dibromo salt,<sup>3a</sup> while in the secondary hydrolysis reactions, the order is reversed. Further, in the hydrolysis reactions of the halopentaamminecobalt(III) and *cis*-dihalobis(ethylenediamine)cobalt(III) complexes, the value of  $\Delta H^\ddagger$  is also higher for the reactions of the bromo species. The higher value of  $\Delta H^\ddagger$  is most likely a result of the larger size of the bromide ion relative to that of the chloride ion, which makes it more difficult for a water molecule to enter the coordination sphere in a *cis* attack by an  $\text{S}_\text{N}2$  mechanism. That the opposite is true for the primary acid hydrolysis step of the tren complexes is most likely a result of the high degree of distortion in the dibromo complex, which facilitates a *cis* attack by incoming water molecules.

The value of  $\Delta S^\ddagger$  for the acid hydrolysis of the chloroaquo complex (-11.0 cal mol<sup>-1</sup> deg<sup>-1</sup>) is nearly identical with that for the hydrolysis of the dichloro complex (-10.4 cal mol<sup>-1</sup> deg<sup>-1</sup>). The reaction of the chloroaquo ion, unlike that of the bromoaquo species, does not seem to show an increase in  $\text{S}_\text{N}1$  character relative to the reaction of the dichloro species. This is reasonable since the smaller radius and higher nucleophilicity of the chloride ion would tend to diminish the tendency toward a dissociative type of mechanism with a highly charged cation.

The data in Table I at 65.0° and pH 0 also show that the addition of large concentrations of  $\text{NaClO}_4$  has only a small effect on the value of  $k_2$ . The slight decrease in the value of  $k_2$  with increasing ionic strength

was also observed in the kinetics of the acid hydrolysis of *trans*- $\text{CrNH}_3(\text{H}_2\text{O})_3\text{Cl}_2^{+10}$  but does not seem to be present in the kinetics of the reaction of any of the bromide compounds. At the high ionic strengths used, it is probably misleading to attribute the small ionic strength dependence of the reaction to any single cause, although a lowering of the water activity by large concentrations of  $\text{NaClO}_4$  could be at least partially responsible.

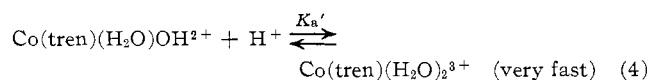
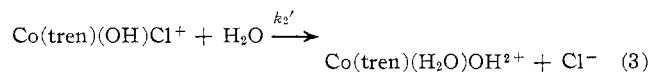
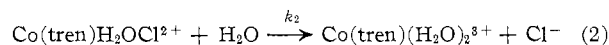
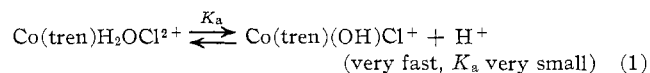
The addition of a fivefold excess of chloride ions did not affect the reaction rate as seen from the data in Table I. Large excesses of chloride ions were found to result in an incomplete reaction, however, with a large amount of the chloroaquo species remaining at equilibrium. The addition of an excess of  $\text{Na}_2\text{SO}_4$  was found to accelerate the reaction, just as in the aquation of  $\text{Co}(\text{tren})\text{H}_2\text{OBr}^{2+}$ .<sup>2</sup>

A study of the dependence of the acid hydrolysis rate of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  on acid concentration revealed that the kinetics are very similar to those of the bromoaquo species and showed that the hydrolysis reaction is acid inhibited. The data obtained for the acid hydrolysis of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  at 65.0° and at ionic strengths 1.00 and 0.10 M are summarized in Table II.

TABLE II  
RATES OF ACID HYDROLYSIS OF  
CHLORO-AQUO(TRIAMINOTRIETHYLAMINE)COBALT(III)  
ION FOR pH 1.0 AND 2.3 WITH ADDED  $\text{NaClO}_4$  AT 65.0°

$[\text{H}^+]$ , mM	Ionic strength	$10^4 k_{\text{obsd}}$ , $\text{sec}^{-1}$	$[\text{H}^+]$ , mM	Ionic strength	$10^4 k_{\text{obsd}}$ , $\text{sec}^{-1}$
7.50	0.10	5.12	5.00	1.00	4.54
10.00	0.10	4.75	6.67	1.00	4.23
13.30	0.10	4.22	10.00	1.00	3.74
20.00	0.10	3.94	20.00	1.00	3.11
50.00	0.10	3.49	50.00	1.00	2.99
100.0	0.10	3.29	100.0	1.00	2.87

The acid inhibition in aquo complexes of this type has been attributed to an equilibrium between the haloaquo complex and the more rapidly reacting halo-hydroxo complex. For  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$ , this equilibrium would lead to the reaction scheme



It is then proposed that the observed rate of acid hydrolysis is simply a combination of the rates for reactions 2 and 3, and the observed rate constant for the overall reaction,  $k_{\text{obsd}}$ , is given by

$$k_{\text{obsd}} = k_2 + k_2'K_a/[\text{H}^+] \quad (5)$$

A plot of  $k_{\text{obsd}}$  vs.  $1/[\text{H}^+]$  would then give a straight line with a slope equal to the product of  $k_2'K_a$  and an intercept equal to  $k_2$ . At  $\mu = 1.0$  a plot of  $k_{\text{obsd}}$  vs.  $1/[\text{H}^+]$  for the data in Table II gave a straight line. From the slope and intercept the expression

$$k_{\text{obsd}} = 2.8 \times 10^{-4} \text{ sec}^{-1} + 9.3 \times 10^{-7} \text{ M sec}^{-1}/[\text{H}^+] \quad (6)$$

was obtained. At ionic strength 0.10 *M* the expression was found to be

$$k_{\text{obsd}} = 3.2 \times 10^{-4} \text{ sec}^{-1} + 1.5 \times 10^{-6} M \text{ sec}^{-1}/[\text{H}^+] \quad (7)$$

Since no kinetic data are available for the aquation of  $\text{Co}(\text{tren})(\text{OH})\text{Cl}^+$ , the  $k_2/K_a$  product could not be separated into its components. However, the ionic strength dependence of the second term in eq 6 and 7 is similar to that which has been discussed in the kinetics of the bromoaquo system<sup>2</sup> and is due to changes in the activity coefficients of the charged species involved.

In comparing the kinetics of the bromoaquo and chloroaquo systems, it becomes apparent that the only major difference between the two occurs in the initial stages of their reactions. While the plot of  $\ln(A_t - A_\infty)$  vs.  $t$  is linear throughout the acid hydrolysis reaction of  $\text{Co}(\text{tren})\text{H}_2\text{OBr}^{2+}$ , a noticeable curvature is present in the similar plots for the reactions of the chloroaquo species. A typical plot of  $\ln(A_t - A_\infty)$  vs.  $t$  for the hydrolysis of  $[\text{Co}(\text{tren})\text{H}_2\text{OCl}]\text{SO}_4$  at pH 0 and 55.0° is illustrated in Figure 2.

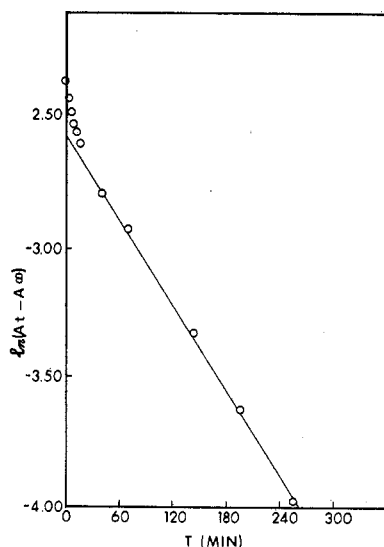
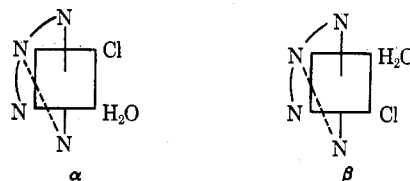


Figure 2.—Plot of  $\ln(A_t - A_\infty)$  vs.  $t$  for the acid hydrolysis of chloroaquo(triaminotriethylamine)cobalt(III) ion at 55.0°, in 1 *M*  $\text{HClO}_4$ .

A similar first-order plot has been observed in the acid hydrolysis of diethyl-*tert*-butylcarbinyl chloride<sup>11</sup> and also in the acid hydrolysis of chloro(tetramethylenepentamine)cobalt(III) ion.<sup>4</sup> In both cases the nonlinearity of the plot is believed to be a result of the presence of two isomers reacting at different rates. Since the more rapidly reacting isomer is used up more quickly than the other one, the hydrolysis rate during the initial part of the reaction is a sum of the rates of reaction of both isomers until the former has all reacted. During the later part of the reaction, the measured rate of hydrolysis is simply that of the less reactive isomer. By extrapolating the linear portion of the plot to  $t = 0$ , and plotting the difference between a point on this line and a point on the curve at time  $t$  vs.  $t$ , the rate constant for the first reaction can be obtained.

Since two isomers are possible for  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$ , it seems reasonable that the kinetics of the acid hydrolysis of the chloroaquo species may involve a similar

parallel reaction of two isomers to form the common diaquo product. The two possible isomers of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$  are represented below. The  $\alpha$  isomer



contains the chloride group cis to the tertiary nitrogen, while the  $\beta$  isomer contains the chloride group trans to the tertiary nitrogen atom. Although these isomers have never been isolated, evidence for the existence of isomers in other tren complexes has been found. In a study of the reaction of  $\text{Co}(\text{tren})(\text{H}_2\text{O})\text{OH}^{2+}$  with glycine ethyl ester it was found that two isomers of the chelated glycine complex could be obtained, one with the glycine oxygen cis and the other with it trans to the tertiary nitrogen atom.<sup>12</sup>

With the above information in mind, an attempt was made to determine the reaction rate for the more rapidly reacting isomer by using the method of Brown and Fletcher.<sup>11</sup> In determining the value of  $k_2$  for the more rapidly reacting isomer, consecutive runs usually agreed to within 10%, and the plots of  $\ln[(A_t - A_\infty)_{\text{exptl}} - (A_t - A_\infty)_{\text{ext}}]$  vs.  $t$  gave straight lines with typical standard deviations of 6%. However, because the absorbance change during the first reaction is only a small fraction of the total absorbance change (<15%), the error in calculating  $k_2$  for the more rapidly reacting isomer is much larger than for the other isomer. A further investigation of the reaction of the former isomer is in progress and will be reported in a future communication, along with studies of other isomers in mixed complexes of the types  $\text{Co}(\text{tren})\text{XY}^+$  and  $\text{Co}(\text{tren})\text{XY}^{2+}$ .

The activation parameters for the first reaction were obtained from the rate constants at 60.0, 55.0, 50.0, and 45.0°, which had values of  $2.95 \times 10^{-3}$ ,  $1.55 \times 10^{-3}$ ,  $8.90 \times 10^{-4}$ , and  $4.40 \times 10^{-4} \text{ sec}^{-1}$ , respectively. From these values, an Arrhenius plot was made which gave a straight line over the entire temperature range, with a standard deviation of 3%. From the plot values for the activation parameters,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ , and  $\Delta S^\ddagger$ , were calculated to be 25.4 kcal mol<sup>-1</sup>, 23.4 kcal mol<sup>-1</sup>, and 6.7 cal mol deg<sup>-1</sup>, respectively, at 55.0°. These activation parameters are quite different from those discussed earlier for the acid hydrolysis of the other isomer of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$ . The value of  $\Delta H^\ddagger$  for the hydrolysis of the more reactive isomer is a little higher than the value for the reaction of the other isomer, and the positive entropy of activation is quite different from the value of -11.0 cal mol<sup>-1</sup> deg<sup>-1</sup> reported earlier in this paper for the reaction of the major isomer of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}^{2+}$ . It is interesting, however, that the value of  $\Delta H^\ddagger$  for the isomerization of  $\text{Co}(\text{en})_2\text{H}_2\text{OCl}^{2+}$  reported in a previous study<sup>13</sup> is 26.6 kcal mol<sup>-1</sup> and is somewhat higher than that for the acid hydrolysis step. Further, the values of  $\Delta S^\ddagger$  for the isomerization of *cis*- $\text{Co}(\text{en})_2\text{H}_2\text{OCl}^{2+}$ <sup>13</sup> and *cis*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ <sup>14</sup> are 6.4 and 4.0 cal mol<sup>-1</sup> deg<sup>-1</sup>, respectively. These data compare favorably with the activation pa-

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rameters for the reaction of the more rapidly reacting isomer and seem to suggest that the first reaction may involve a change from one isomer to the other in the transition state. From the limited data for this reaction, determination of the exact nature of the reaction is not feasible, although the straight-line plots seem to indicate a parallel, rather than a series, first-order reaction.

A comparison of the rate of acid hydrolysis of  $\text{Co}(\text{tren})\text{H}_2\text{OCl}_2^{2+}$  with that of the corresponding ethylenediamine complex shows that, at  $25.0^\circ$ , the tren complex reacts about 75% faster.<sup>5</sup> On the other hand, the acid hydrolysis of  $\text{Co}(\text{tren})\text{Cl}_2^+$  proceeds at a rate nearly 1200% larger than that of *cis*- $\text{Co}(\text{en})_2\text{Cl}_2^+$  under similar conditions.<sup>6</sup>

These results are in good agreement with those already discussed in the study of the bromoaquo system and support the hypothesis that the labilization of the second halide group in dihalo(triaminotriethylamine)-cobalt(III) complexes is considerably less than that of the first. The observation that the first bromo group appears to be more labilized by the distortion of the complex than the first chloro group may account for the presence of only one isomer in the bromoaquo system.

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## A Stereochemical and Aquation Study of Phosphatoamminebis(ethylenediamine)cobalt(III)

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The preparations, pmr spectra, visible absorption spectra, and acid dissociation constants of *cis*- $\text{Co}(\text{en})_2\text{NH}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$  and *trans*- $\text{Co}(\text{en})_2\text{NH}_3\text{PO}_4 \cdot 5\text{H}_2\text{O}$  are reported. The aquations of the triprotonated species, *cis*- and *trans*- $\text{Co}(\text{en})_2\text{NH}_3\text{PO}_4\text{H}_3^{3+}$ , proceed with cobalt-oxygen bond fission and with full retention of configuration. The aquation rate parameters are  $k(70^\circ) = 17.0 \times 10^{-5} \text{ sec}^{-1}$ ,  $\Delta H^\ddagger = 27.1 \pm 0.8 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = -2.8 \pm 2.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$  for *cis*- $\text{Co}(\text{en})_2\text{NH}_3\text{PO}_4\text{H}_3^{3+}$  and  $k(70^\circ) = 16.5 \times 10^{-5} \text{ sec}^{-1}$ ,  $\Delta H^\ddagger = 27.0 \pm 0.3 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = -2.6 \pm 0.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$  for *trans*- $\text{Co}(\text{en})_2\text{NH}_3\text{PO}_4\text{H}_3^{3+}$  in 3.698 *M* perchloric acid.

### Introduction

A number of phosphatoamminecobalt(III) complexes, in which phosphate functions as a monodentate ligand, have been reported, and their aquation has been studied.<sup>2-5</sup> Where the possibility of geometric isomerism arose, only *cis* isomers were detected,<sup>4</sup> and stereochemical aquation studies of these species were precluded by the relatively rapid isomerization rates of the possible aquo products.

The object of this study was to prepare *cis*- and *trans*-phosphatoamminebis(ethylenediamine)cobalt(III) and to investigate the stereochemical pathways of their aquations. Comparison with the stereochemical aquation characteristics reported<sup>6,7</sup> for other  $\text{Co}(\text{en})_2\text{-XY}$  complexes should provide further insight into the phosphato aquation mechanism.

### Experimental Section

**Materials.**—*cis*- $[\text{Co}(\text{en})_2\text{NH}_3\text{H}_2\text{O}]\text{Br}_2 \cdot \text{H}_2\text{O}$  and *trans*- $[\text{Co}(\text{en})_2\text{NH}_3\text{H}_2\text{O}](\text{NO}_3)_2$  were prepared as described in the literature.<sup>8</sup> Other chemicals were either analytical grade or recrystallized reagent grade. Carrier-free phosphorus-32-labeled orthophosphate in dilute hydrochloric acid was obtained from AAEC, Lucas Heights, N.S.W., Australia.

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***cis*-Phosphatoamminebis(ethylenediamine)cobalt(III).**—A solution of 40 g of *cis*- $[\text{Co}(\text{en})_2\text{NH}_3\text{H}_2\text{O}]\text{Br}_2 \cdot \text{H}_2\text{O}$ , 120 g of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , and 32 ml of concentrated  $\text{H}_3\text{PO}_4$  in 200 ml of water was heated at  $70^\circ$  for 1 hr. This solution was then cooled to  $25^\circ$  and the cationic species were adsorbed onto a  $\sim 40 \text{ cm} \times 8 \text{ cm}$  diameter column of Zeokarb 225 cation-exchange resin in the acid form. The column was washed with 3 l. of water and the phosphato complex was then eluted from it with 0.1 *M* NaOH at  $25^\circ$ . The most concentrated fraction of the effluent (*ca.* 4 l.) was cooled to  $5^\circ$  and was added slowly with stirring to 8 l. of acetone at  $5^\circ$ . After 24 hr in a refrigerator the pink flocculent precipitate was filtered off, washed with acetone, and air dried. This product was recrystallized by dissolution in the minimum amount of water at  $50^\circ$ , cooling to  $0^\circ$ , and reprecipitating by dropwise addition of concentrated  $\text{NH}_4\text{OH}$  solution. The resultant amorphous precipitate was filtered off, washed with ethanol, and air dried; yield 6 g (20.5%). *Anal.* Calcd for *cis*- $\text{Co}(\text{en})_2\text{NH}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ : Co, 17.08; C, 13.92; N, 20.28; P, 8.97. Found: Co, 16.87; C, 14.01; N, 20.10; P, 8.90.

When *cis*- $[\text{Co}(\text{en})_2\text{NH}_3\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$  was used as the starting complex, a similar yield of *cis*- $\text{Co}(\text{en})_2\text{NH}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$  was obtained.

***trans*-Phosphatoamminebis(ethylenediamine)cobalt(III).**—A solution of 34 g of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , 75 ml of concentrated  $\text{H}_3\text{PO}_4$ , and 10 ml of water was heated to  $70^\circ$ . Solid *trans*- $[\text{Co}(\text{en})_2\text{NH}_3\text{H}_2\text{O}](\text{NO}_3)_2$  (12 g) was added slowly with stirring and the resultant solution was maintained at  $70^\circ$  for 1 hr. This solution was then cooled to  $25^\circ$  and diluted with 200 ml of water, and the cationic species were adsorbed onto a  $\sim 20 \text{ cm} \times 8 \text{ cm}$  diameter column of Zeokarb 225 in the acid form. The phosphato complex was eluted from the column and precipitated from solution in the same manner as the *cis* isomer. The precipitate was recrystallized by dissolution in the minimum amount of water at  $50^\circ$  and reprecipitating by cooling in a refrigerator overnight. The deep red crystals were washed with a small