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Transition Metal Complexes of Tetraethylenepentamine. III. Kinetics of Hydrolysis of α- and β-Chlorotetraethylenepentaminecobalt(III) Cations[1]

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The kinetics of hydrolysis of α- and β-Co(tetren)Cl^{2+} have been investigated in aqueous $HClO_4$ in the dark, spectrophotometrically and by Cl^- release. Over the range 0.01–1 M H^+, with $C_0 \approx 1$ mF and $\mu = 1.0$ M, the hydrolysis follows the rate law: $-d(\mathrm{Co(tetren)Cl^{2+}})/dt = k(\mathrm{Co(tetren)Cl^{2+}})$, where $k = k_{aq} + k_b(\mathrm{OH^-})$, for the α isomer at 50, 65, and 70° and for the β isomer at 70°. For the α and β isomers, respectively, at 70°, $10^5k_{aq} = 2.2 \pm 0.3$ and 1.3 ± 0.1 sec^{-1}, $10^{-6}k_b = 5.7 \pm 0.7$ and 1.7 ± 0.2 M^{-1} sec^{-1}; $E_a = 27 \pm 2$ kcal mole^{-1} and log $PZ = 13 \pm 1$ sec^{-1} for aquation and 24 ± 2 kcal mole^{-1} and 22 ± 2 M^{-1} sec^{-1} for base hydrolysis of α-Co(tetren)Cl^{2+}. Values of k for both isomers were also obtained under other conditions; k increases with decreasing ionic strength at constant hydrogen ion concentration. The reaction product is Co(tetren)OH_2^{3+}, apparently the α isomer, for both α- and β-Co(tetren)Cl^{2+} hydrolysis. Under the conditions studied, isomerization between these chloro isomers is negligibly slow relative to the hydrolysis.

Introduction

In the first paper[2] of this series we have described the preparation, properties, and geometric configuration of α-[Cr(tetren)Cl]$ZnCl_4$ and of α- and β-[Co(tetren)Cl]$ZnCl_4$, containing the straight-chain pentadentate ligand tetraethylenepentamine,[3] and presented evidence suggesting that the α and β isomers probably have structures I and II, respectively (Figure 1). The second paper[4] described the isolation of additional salts of the above complex cations and the synthesis and properties of other acidotetraethylenepentamine complexes of cobalt(III) and chromium(III).

In the present paper we report the results of an investigation of the acid hydrolysis (aquation) and base hydrolysis of the α and β isomers of the chlorotetraethylenepentaminecobalt(III) cation, Co(tetren)Cl^{2+}, undertaken in part to provide further insight into the effect of chelation on hydrolysis rates of related cobalt(III) complexes.

Experimental Section

α- and β-Chlorotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—These compounds were made and characterized as described earlier.[2] Method A[2] was used to generate the isomeric mixture, using a water bath at 25° or an ice bath for the H_2O_2 addition to favor formation of the α or β isomer, respectively. The α compound was then made from this mixture by method G,[2] and the β compound by method F.[2] Seven lots of the α compound and two of the β compound were synthesized; these gave C, H, N, Co, and Cl analyses in good agreement with the experimental values given earlier[2] and with those calculated for [Co(tetren)Cl]$ZnCl_4$; in several cases not all of these analyses were made, but in all cases the visible absorption spectrum was taken to confirm the isomeric purity.

α-Aquotetraethylenepentaminecobalt(III) Perchlorate.—This substance was prepared in solution for visible absorption spectrum purposes by dissolving a weighed sample of α-[Co(tetren)OH](ClO_4)$_2$, synthesized and characterized by House as described earlier,[4] in a known volume of 0.1 F $HClO_4$, or of a solution 0.1 F in $HClO_4$ and 0.9 F in $NaClO_4$, in which the hydroxo complex is converted essentially quantitatively to the α-aquo complex. The molar absorbancy indices at the absorption peaks differed not more than 2% in these two media.

Sodium Perchlorate.—Commercial CP $NaClO_4$ has occasionally been found contaminated with a colored impurity, so $NaClO_4$ was made by neutralizing CP Na_2CO_3 with concentrated $HClO_4$ (J. T. Baker Analyzed) and recrystallizing from distilled water.

Other Chemicals.—All other chemicals were CP or reagent grade. The water was doubly distilled, then passed through a mixed-bed, cation–anion-exchange resin and monitored for purity by electrical conductivity.

Chemical Analyses.—Analyses of solids and certain solutions for Co, Cl, C, H, and N were made as described earlier.[2] Most of the C, H, and N analyses were made by Miss Heather King.

Chromatography of Hydrolyzed Solutions.—Solutions of α- and β-Co(tetren)Cl^{2+} in 0.1 F $HClO_4$ which had been allowed to react in the dark at 70° for several reaction times were adsorbed on 8-cm × 1-cm diameter columns of H^+ Dowex AG50W-X4 cation-exchange resin (200–400 mesh) and subjected to elution at

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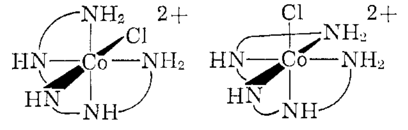
[1] (a) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the university. This paper constitutes Report No. UCLA-34P12-57 to the AEC. (b) Based upon research to be included in a thesis to be submitted in 1967 by T.-L. Ni in partial fulfillment of the requirements for the M.S. degree.

[2] D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966).

[3] $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; abbreviation tetren. Other abbreviations used: en = ethylenediamine, $H_2N(CH_2)_2NH_2$; dien = diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$; trien = triethylenetetramine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.

[4] D. A. House and C. S. Garner, *Inorg. Chem.*, **6**, 272 (1967).



I (α?) II (β?)

Figure 1.—Assignment of the geometric configuration of α and β isomers of $Co(tetren)Cl^{2+}$.

20–25° with four successive 50-ml portions of 1 F $HClO_4$, then three successive 50-ml portions of 2 F $HClO_4$.

Kinetic Runs.—Weighed samples of α- or β-$[Co(tetren)Cl]ZnCl_4$ were dissolved in known volumes of the reaction medium and sealed with a torch in Pyrex ampoules, which were then wrapped in Al foil to exclude light (the effect of light on the reaction rate was not tested, but some related complexes are photosensitive) and placed in baths thermostated at 49.88 ± 0.14, 64.78 ± 0.17, or 70.00 ± 0.11°. Zero reaction time was taken *ca.* 10 min after the ampoules had been put in the bath. Ampoules were removed at known times, quenched in ice, and in the runs at 50° kept for times up to several days at 5° prior to spectrophotometric examination (such storage was shown to result in negligible change of the solutions). The visible absorption spectrum of each reaction solution was then scanned in 10.00-cm silica cells (*vs.* a matching 10.00-cm silica cell filled with an identical solution except without the complex) over the range 700–340 mμ with a Cary Model 11 or Model 15 recording spectrophotometer at 20–25° to search for isosbestic points and provide absorbancy data for kinetic analysis.

In certain runs, the reaction was followed both spectrophotometrically and by titration of released Cl^-. For such runs, the α- or β-$[Co(tetren)Cl]ZnCl_4$ was dissolved in 0.001 F $HClO_4$ at 20–25° and immediately run through a 24-cm × 1-cm diameter column of NO_3^- Dowex AG1-X8 anion-exchange resin (50–100 mesh) under gravity flow, which effectively removed over 99% of the free Cl^- formed by dissociation of the $ZnCl_4^{2-}$ anion, thus permitting greatly improved accuracy in following the reaction rate by Cl^- titration. The effluent was made up to the desired $HClO_4$ and $NaClO_4$ concentrations by volumetric addition of $HClO_4$ and addition of a weighed amount of $NaClO_4$. These solutions were then sealed in Pyrex ampoules and processed as indicated earlier. Free Cl^- in those reaction samples was removed from the complexes by adsorbing aliquots on 8-cm × 1-cm diameter columns of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh), prefilled with 0.001 F $HClO_4$, at 20–25°, washing out the free Cl^- with three 10-ml portions of 0.001 F $HClO_4$, collecting in 50-ml volumetric flasks, making up to volume with 0.001 F $HClO_4$, and potentiometrically titrating with standard $AgNO_3$ 20-ml aliquots added to 80-ml portions of acetone–detergent mixture at 0°.[5] Chloride blanks were determined on control solutions containing everything except the complex and subtracted from the reaction sample titration volumes.

Table I

Pseudo-First-Order Rate Constants for Hydrolysis of α-$Co(tetren)Cl^{2+}$ in the Dark

Method[a]	Temp, °C	$(HClO_4)$, F	C_0, mF	μ, M[b]	10^6k, sec^{-1} [c]
Spectro	70.00	1.0	0.963	1.0	22.5 ± 0.5
Spectro	70.00	1.0	0.703	1.0	21.5 ± 0.5
Spectro	70.00	0.10	0.886	1.0	29.2 ± 0.5
Spectro	70.00	0.020	1.39	1.0	51.7 ± 2.6
Cl^-	70.00	0.020	1.39	1.0	52.1 ± 2.8
Spectro	70.00	0.010	0.846	1.0	79.4 ± 2.3
Spectro	70.00	0.10	1.20	0.35	34.1 ± 1.0
Spectro	70.00	0.10	0.867	0.10	41.1 ± 0.6
Spectro	70.00	0.10	0.779	0.10	45.7 ± 0.8
Spectro	70.00	0.10	0.845	0.10	44.7 ± 1.1
Spectro	70.00	0.10	0.834	0.10	41.9 ± 2.0
Cl^-	70.00	0.10	0.867	0.10	38.8 ± 1.0
Cl^-	70.00	0.10	0.845	0.10	44.2 ± 1.2
Spectro	70.00	0.010	1.17	0.10	141 ± 8
Spectro	70.00	0.010	0.685	0.10	139 ± 8
Spectro	70.00	0.010	0.868	0.010	190 ± 9
Spectro	64.78	1.0	0.552	1.0	12.8 ± 3.0
Spectro	64.78	1.0	0.775	1.0	12.9 ± 0.8
Spectro	64.78	0.020	0.870	1.0	27.0 ± 1.3
Spectro	64.78	0.010	0.604	1.0	42.3 ± 2.5
Spectro	64.78	0.10	0.788	0.10	20.3 ± 0.9
Spectro	64.78	0.10	0.867	0.10	20.9 ± 0.6
Cl^-	64.78	0.10	0.788	0.10	20.2 ± 0.8
Cl^-	64.78	0.10	0.867	0.10	20.4 ± 0.7
Spectro	49.88	1.0	0.575	1.0	1.91 ± 0.19
Spectro	49.88	0.020	0.690	1.0	3.50 ± 0.15
Spectro	49.88	0.010	1.06	1.0	5.18 ± 0.28
Spectro	49.88	0.10	0.825	0.10	3.23 ± 0.16
Spectro	49.88	0.10	0.784	0.10	3.20 ± 0.15
Cl^-	49.88	0.10	0.825	0.10	3.19 ± 0.07
Cl^-	49.88	0.10	0.784	0.10	3.22 ± 0.05
Spectro	49.88	0.010	0.919	0.10	9.57 ± 0.10
Spectro	49.88	0.0010	0.810	0.10	48 ± 27

[a] Spectro = weighted average of spectrophotometric values at 525 and 365 mμ; Cl^- = titration of released Cl^-. [b] Ionic strength, controlled with $NaClO_4$. [c] Errors are standard errors obtained from least-squares treatment.

Results

Table I presents the pseudo-first-order rate constants k defined by the equation

$$-d(\alpha\text{-Co(tetren)Cl}^{2+})/dt = k(\alpha\text{-Co(tetren)Cl}^{2+}) \qquad (1)$$

for the disappearance of α-$Co(tetren)Cl^{2+}$ in $HClO_4$ solutions of various acidities and ionic strengths at 70, 65, and 50°. In the spectrophotometric method k was evaluated for each kinetic run by the relation

$$2.303 \log [(A_0 - A_\infty)/(A - A_\infty)] = kt \qquad (2)$$

where A_0, A, and A_∞ are the optical absorbancies (at a given wavelength) at reaction time zero, at time t, and at 100% hydrolysis of the chloro ligand, respectively. With A_∞ calculated assuming hydrolysis to 100% α-$Co(tetren)OH_2^{3+}$, plots of this logarithmic function of the absorbancies at 525 and 365 mμ generally gave good straight lines up to at least 45% reaction, except for a single run in 0.01 F $HClO_4$ where curvature was evident after *ca.* 25% reaction. In the Cl^- release method k was determined with the relation

$$2.303 \log [(V_\infty - V_0)/(V_\infty - V)] = kt \qquad (3)$$

where V_0, V, and V_∞ are the volumes of $AgNO_3$ titrant for a standard aliquot (see Experimental Section) at reaction time zero, time t, and for complete Cl^- release, respectively. Plots of eq 3 were linear to *ca.* 50% reaction.

Table II presents rate data for the disappearance of β-$Co(tetren)Cl^{2+}$, evaluated by the same methods, taking A_∞ in the spectral method assuming hydrolysis to 100% α-$Co(tetren)OH_2^{3+}$ (see Discussion). Plots of eq 2 at 360 mμ and either 540 or 560 mμ and of eq 3 generally were linear for the first 50% of reaction.

Values of k given in Tables I and II were obtained from least-squares treatment of the data and were in

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(5) D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR HYDROLYSIS OF β-Co(tetren)Cl^{2+} IN THE DARK

Method[a]	Temp, °C	($HClO_4$), *F*	C_0, m*F*	μ, *M*[b]	10^6k, sec^{-1} [c]
Spectro	70.00	1.0	0.765	1.0	13.0 ± 0.4[d]
Spectro	70.00	0.10	0.791	1.0	31.8 ± 0.9
Spectro	70.00	0.010	0.582	1.0	180 ± 7
Spectro	70.00	0.10	0.737	0.35	48.2 ± 0.8
Spectro	70.00	0.10	0.839	0.10	64.7 ± 1.2
Cl^-	70.00	0.10	0.839	0.10	61.0 ± 2.9
Spectro	64.78	0.10	0.682	0.10	38.6 ± 2.0
Cl^-	64.78	0.10	0.682	0.10	38.6 ± 0.6
Spectro	49.88	0.10	0.775	0.10	4.43 ± 0.26

[a] Spectro = spectrophotometric analysis, weighted average of values at 360 mμ and either 540 or 560 mμ; Cl^- = titration of released Cl^-. [b] Ionic strength, controlled with $NaClO_4$. [c] Errors are standard errors obtained from least-squares treatment. [d] Spectro value at 540 mμ only.

good agreement with *k* values obtained from the slopes of the visually drawn rate plots.

In the spectrophotometric runs three good isosbestic points were observed over the range 340–700 mμ in the hydrolysis of each isomer. Typical sets of scans for each isomer are displayed in Figures 2 and 3.

Discussion

Figure 4 shows the near-ultraviolet and visible absorption spectra of α- and β-Co(tetren)Cl^{2+} and of the only isomer of the aquo ion, α-Co(tetren)OH_2^{3+}, known experimentally to us. From this figure we see that spectral scans made between 340 and 660 mμ during the hydrolysis of α- and β-Co(tetren)Cl^{2+} in acid solutions should give three isosbestic points, at 349 ± 2 mμ (a_M = 85 ± 2 M^{-1} cm^{-1}), 415 ± 3 mμ (a_M = 36 ± 2 M^{-1} cm^{-1}), and 500 ± 1 mμ (a_M = 105 ± 2 M^{-1} cm^{-1}) for the conversion of α-Co(tetren)Cl^{2+} to α-Co(tetren)OH_2^{3+}, and at 343 ± 2 mμ (a_M = 83 ± 2 M^{-1} cm^{-1}), 415 ± 3 mμ (a_M = 36 ± 2 M^{-1} cm^{-1}), and 508 ± 2 mμ (a_M = 96 ± 2 M^{-1} cm^{-1}) for conversion of β-Co(tetren)Cl^{2+} to α-Co(tetren)OH_2^{3+}. In the hydrolysis of α-Co(tetren)Cl^{2+} we find experimentally three good isosbestic points over at least 1–2 half-lives at 348 ±2 mμ (a_M = 83 ± 2 M^{-1} cm^{-1}), 415 ± 2 mμ (a_M = 37 ± 1 M^{-1} cm^{-1}), and 500 ±2 mμ (a_M = 105 ± 2 M^{-1} cm^{-1}) (see Figure 2 for typical run); these isosbestic points are in excellent agreement with the theoretically expected values for conversion to α-Co(tetren)OH_2^{3+}. In the hydrolysis of β-Co(tetren)Cl^{2+} three good experimental isosbestic points (see Figure 3 for typical run) exist for at least 1–2 half-lives at 344 ± 2 mμ (a_M = 83 ± 2 M^{-1} cm^{-1}), 414 ± 2 mμ (a_M = 36 ± 1 M^{-1} cm^{-1}), and 508 ± 1 mμ (a_M = 97 ± 1 M^{-1} cm^{-1}), in very good accord with the theoretical values for conversion of this complex to α-Co(tetren)OH_2^{3+}. Thus, α-Co(tetren)OH_2^{3+} appears to be the product of hydrolysis of both α- and β-Co(tetren)Cl^{2+}. This hypothesis is further supported by the good first-order rate behavior based upon A_∞ values calculated on this assumption (see Results) and the reasonably good agreement between the spectrophotometric and Cl^- release *k* values (Tables I and II). However, in the absence of a knowledge of the visible absorption spectra of the other three theoretically possible geometric isomers[2] of the aquo ion, we cannot exclude the possibility that the products of hydrolysis of α- and β-Co(tetren)Cl^{2+} are different isomers or even mixtures of isomers. Indeed, the spectrophotometric *k* values for α-Co(tetren)Cl^{2+} hydrolysis analyzed at 365 mμ are nearly always greater than the *k* values based upon 525 mμ and Cl^- release by *ca.* 10%; this may well

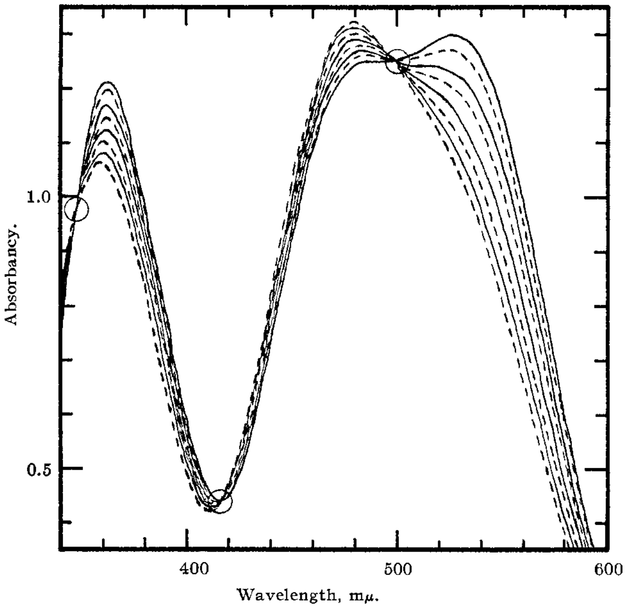

Figure 2.—Change in absorption spectrum of α-Co(tetren)Cl^{2+} (C_0 = 1.20 m*F*) in 0.1 *F* $HClO_4$ (μ = 0.35 *M*) with time at 70.00°: reading downward at 540 mμ, reaction time is 0, 31, 72, 110, 170, 230, 294, and 360 min, respectively. Actual recorded scans show sharpness and location of isosbestic points much more clearly than this figure does.

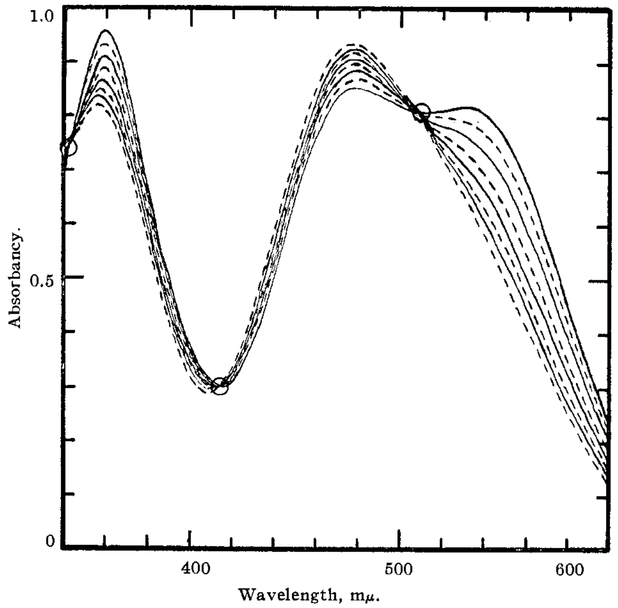

Figure 3.—Change in absorption spectrum of β-Co(tetren)Cl^{2+} (C_0 = 0.839 m*F*) in 0.10 *F* $HClO_4$ (μ = 0.10 *M*) with time at 70.00°: reading downward at 540 mμ, reaction time is 0, 25, 55, 85, 115, 150, 180, and 210 min, respectively. Actual recorded scans show sharpness and location of isosbestic points much more clearly than this figure shows.

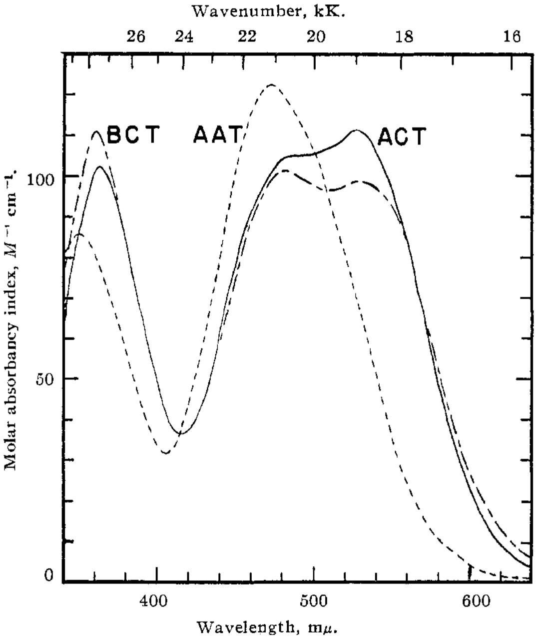

Figure 4.—Visible absorption spectra of chloro- and aquotetraethylenepentamine complexes of cobalt(III) in 0.1 *F* $HClO_4$ at 20–25°: AAT, α-Co(tetren)OH_2^{3+}; ACT, α-Co(tetren)Cl^{2+}; BCT, β-Co(tetren)Cl^{2+}; the molar absorbancy index a_M (extinction coefficient ϵ) is defined by the relation $\log(I_0/I) = A = a_M cd$, where *c* is the molarity of the absorbing complex and *d* is the optical path in centimeters.

mean that the hydrolysis product of α-Co(tetren)Cl^{2+} is not actually α-Co(tetren)OH_2^{3+}, but rather either an isomeric mixture or one of the other isomers should it have a visible absorption spectrum very similar to that of the α-aquo isomer. Inasmuch as extensive rearrangement of the complex would be required to form an aquo isomer other than the α- or β-aquo, we believe on theoretical grounds alone that α- and β-Co(tetren)-Cl^{2+} would hydrolyze to form either α- or β-Co(tetren)-OH_2^{3+}, or mixtures of these two isomers. Since α- and β-Co(tetren)Cl^{2+} have easily distinguished visible absorption spectra (see Figure 4), we infer that α- and β-Co(tetren)OH_2^{3+} would have different spectra also, which leads us back to the conclusion that the reaction product is very probably α-Co(tetren)OH_2^{3+} in each case.

Because the hydrolysis rates of α- and β-Co(tetren)-Cl^{2+} under the conditions studied differ by no more than one order of magnitude and essentially the same *k* values are obtained in each case spectrophotometrically and by Cl^- release, we may conclude that isomerization between these two chloro isomers plays no significant role in their hydrolysis. If either isomer isomerized at a rate very much greater than the experimentally found hydrolysis rates, the apparent hydrolysis rates of the two chloro isomers would be identical; if the isomerization rates were comparable to the hydrolysis rates, the good isosbestic points found experimentally would not be expected.

Of course, the observations do not exclude the possibility of the directly formed product of either α- or β-chloro hydrolysis being an aquo isomer (or hydroxo isomer which rapidly protonates in the acidic medium) which rapidly isomerizes on the time scale involved to the α-aquo ion. In such an event, we would think the directly formed product might well have the same geometric configuration as its parent complex, with the β-aquo ion then isomerizing to the observing α-aquo isomer.

A further point bearing on the hydrolysis product is worth noting. Cation-exchange chromatography (see Experimental Section) of 0.1 *F* $HClO_4$ solutions of α- and β-Co(tetren)Cl^{2+} which had been aged separately at 70° for 0.75 and 4.5 half-lives (α isomer) or for 1.2 half-lives (β isomer) gave only two bands, which upon elution gave effluents the visible absorption spectra of which corresponded essentially to the spectra of the parent complex and of α-Co(tetren)OH_2^{3+}. No color was left on the resin column after elution of the apparent α-aquo ion. Although the elution behavior of the other three theoretically possible isomers of the aquo complex is unknown to us and presumably similar, we would have thought from experience with isomers of related complexes that successive effluent fractions of the same eluent would have revealed some spectral differences if the product were an isomeric mixture. At the least there is no evidence of more than the one product isomer here. This chromatographic result also indicates that secondary hydrolysis, *i.e.*, hydrolysis of the aquo ion, is unimportant in the times involved, because the secondary hydrolysis product would be expected to remain on the column since this product should have a charge of 4+, assuming uptake of a proton by the tetraethylenepentamine N atom which has broken its N–Co bond.

Examination of Tables I and II shows that there is both an H^+ effect and an ionic strength effect on the hydrolysis rates.

In Figure 5 we give plots of *k vs.* $1/(H^+)$ at constant ionic strength and constant temperature, where (H^+) is taken as the formality of $HClO_4$ in the reaction solution. As Figure 5 shows, the data at ionic strength 1.0 *M* and 50, 65, and 70° for α-Co(tetren)Cl^{2+} hydrolysis are fit satisfactorily over the range 0.010–1.0 *M* H^+ by the rate law (1), with

$$k = k_{aq} + k_b K_w/(H^+) = k_{aq} + k_b(OH^-) \tag{4}$$

At 70° over the same range an analogous rate law holds for hydrolysis of the β isomer. This rate law has been cast in a form implying that the hydrolysis occurs concurrently *via* an aquation path

$$\alpha\text{- or }\beta\text{-Co(tetren)Cl}^{2+} + H_2O \xrightarrow{k_{aq}} \alpha\text{-Co(tetren)OH}_2^{3+} + Cl^- \tag{5}$$

and a base hydrolysis path

$$\alpha\text{- or }\beta\text{-Co(tetren)Cl}^{2+} + OH^- \xrightarrow{k_b} \alpha\text{-Co(tetren)OH}^{2+} + Cl^- \tag{6}$$

with the hydroxo product of reaction 6 rapidly protonating in the acidic medium to the observed α-aquo product.

Least-squares analysis of the data of Figure 5 (in good agreement with visual intercept and slope values)

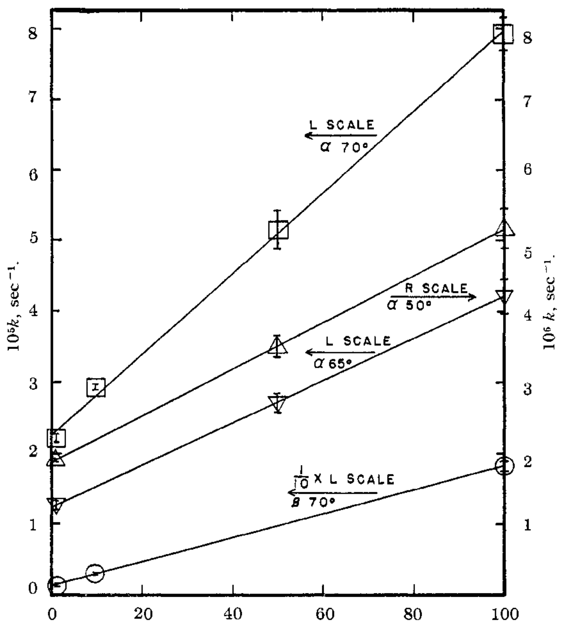

Figure 5.—Hydrogen ion dependence of hydrolysis rate of α- and β-Co(tetren)Cl^{2+} at μ = 1.0 *M*.

then leads to the k_{aq} and k_b values shown in Table III, where values of K_w, the ion-product constant for water, at the reaction temperature were simply taken as K_w in pure water read off a graph given by Butler,[6] and k_b was taken as the least-squares slope divided by K_w.

TABLE III

RATE CONSTANTS FOR THE AQUATION AND BASE HYDROLYSIS OF α- AND β-Co(tetren)Cl^{2+} AT μ = 1.0 *M* IN THE DARK[a]

Isomer	Temp, °C	10^5k_{aq}, sec^{-1}	$10^{-6}k_b$, M^{-1} sec^{-1}
α	49.88	0.19 ± 0.01	0.63 ± 0.03
α	64.78	1.2 ± 0.2	3.6 ± 0.5
α	70.00	2.2 ± 0.3	5.7 ± 0.7
β	70.00	1.3 ± 0.1	1.7 ± 0.2

[a] Errors are least-squares standard errors.

Decrease in ionic strength at constant acidity would be expected to affect k_{aq} little, but the Brønsted–Bjerrum theory predicts for this system an increase in k_b with decreasing μ, at least at sufficiently low values of μ. Plots of log *k* *vs.* $\sqrt{\mu}/(1 + \sqrt{\mu})$ for the hydrolysis of α- and β-Co(tetren)Cl^{2+} at 70° and constant acidity are shown in Figure 6; these plots are approximately linear and represent the dependence of the k_b part of *k* on μ, which is in the expected direction for ionic reactants of opposite charge sign. Least-squares values of *k* at 70.00° linearly extrapolated to μ = 0 from μ = 1.0–0.010 and 1.0–0.1 *M*, respectively, are $(2.3 \pm 0.3) \times 10^{-4}$ sec^{-1} for the α isomer (0.01 *F* HClO$_4$ data) and $(1.3 \pm 0.1) \times 10^{-4}$ sec^{-1} for the β isomer (0.1 *F* HClO$_4$ data). If we assume k_{aq} is independent of μ (it contributes little here anyhow) we may estimate $k_{b_0} = 2 \times 10^7$ M^{-1} sec^{-1} for the α isomer at 70° and zero ionic strength; this value of k_{b_0} has limited significance since the extrapolation is uncertain.

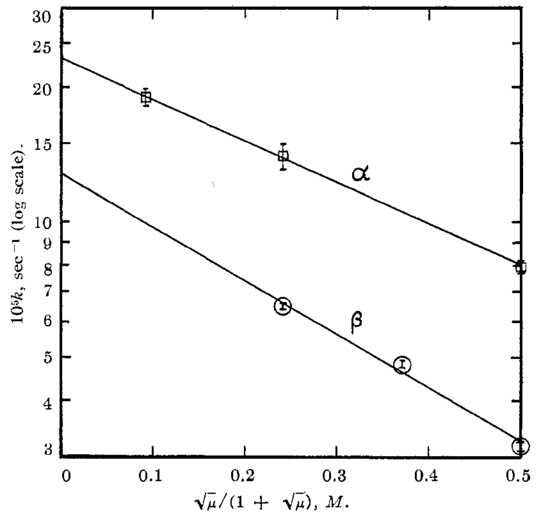

Figure 6.—Ionic strength dependence of hydrolysis rate of α-Co(tetren)Cl^{2+} in 0.010 *F* HClO$_4$ and β-Co(tetren)Cl^{2+} in 0.10 *F* HClO$_4$ at 70°.

The values of k_{aq} and k_b (Table III) for α-Co(tetren)Cl^{2+} hydrolysis in 1.0 *F* HClO$_4$ give linear Arrhenius plots from which E_a, log *PZ*, and ΔS^*_{298} were found by least-squares analysis to be, respectively, 27 ± 2 kcal mole^{-1}, 13 ± 1 sec^{-1}, and −5 ± 1 cal deg^{-1} mole^{-1} for aquation (reaction 5) and 24 ± 2 kcal mole^{-1}, 22 ± 2 M^{-1} sec^{-1}, and +41 ± 8 cal deg^{-1} mole^{-1} for base hydrolysis (reaction 6).

The data do not allow obtaining activation parameters for the aquation and base hydrolysis of β-Co(tetren)Cl^{2+}, but the pseudo-first-order *k* values for this complex in 0.1 *F* HClO$_4$ give a reasonably good Arrhenius plot, from which E_a = 29 ± 1 kcal mole^{-1}, log *PZ* = 14 ± 1 sec^{-1}, and ΔS^*_{298} = +5 ± 2 cal deg^{-1} mole^{-1}. When *k* for the α isomer in 0.1 *F* HClO$_4$ is similarly treated, the apparent activation parameters are E_a = 27 kcal mole^{-1}, log *PZ* = 13 sec^{-1}, and ΔS^*_{298} = −4 cal deg^{-1} mole^{-1}; except for ΔS^* (where the errors are large), the similarity between the parameters for the two isomers is sufficient to suggest that the activation parameters for the aquation and base hydrolysis of the β isomer are not greatly different from those for the α isomer.

In part I of this series,[2] a rough preliminary value of 1–2 for the ratio of *k* for the β isomer to *k* for the α isomer in 0.1 *F* HClO$_4$ at 35° was reported and used as additional support for assignment of the α and β isomers to configurations I and II (Figure 1). From the activation parameters we now calculate a ratio of *ca.* 1.3. At 70° and μ = 1 *M*, the α isomer aquates 1.7 times and base hydrolyzes 3.4 times as fast as the β isomer; these are small rate differences, as we would expect for these isomers assuming they do indeed have configurations I and II, in which the chloro ligand is *trans* to an unstrained coordinated secondary amine in both. Comments made in part I[2] regarding two earlier kinetic measurements made on poorly characterized mixtures

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[6] J. N. Butler, "Ionic Equilibrium," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1964, p 53. Values used for −log K_w: 70°, 13.00 (extrapolated); 65°, 13.08 (extrapolated); 50°, 13.28. For purposes of our approximate calculations we ignore the effect of ionic strength on these values.

of complexes considered possibly to be Co(tetren)Cl^{2+} isomers are still applicable.

Pearson, Boston, and Basolo[7] have discussed at some length the effect of increasing chelation on aquation rate constants of a series of chloropentaminecobalt(III) cations of charge 2+ at pH 1 and at 35°; their series included $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(en)_2(NH_3)Cl^{2+}$, *cis*-Co(trien)$(NH_3)Cl^{2+}$, and Co(dien)(en)Cl^{2+}. We have combined their aquation rate data with additional rate parameters, including those for α-Co(tetren)Cl^{2+}, and have added the available rate information on the base hydrolysis of these complexes. The results are given in Table IV, where the effect of increasing chelation is a reduction in aquation rate and an increase in the apparent base hydrolysis rate constants.

The reduction of aquation rate with increasing chelation is probably a solvent effect,[7,8] in which the organic ligands tend to break up the solvation shell of the reactant complex, but the latter makes greater demands on solvation on going to the transition state with separating charges. It seems to us that if the activation mechanism were an associative one,[8] the reduction in aquation rate for α-Co(tetren)Cl^{2+} with its highly sterically hindering pentadentate ligand should be much greater than is observed relative to Co(dien)(en)Cl^{2+} and the less chelated congeners. Consequently, we regard the observed aquation rate trend of Table IV as one more argument in favor of a dissociative activation process for Co(III) complexes of this kind.

The observed increase in base hydrolysis rate with increasing chelation (Table IV) may well be the result of increasing acidity of the N–H bonds with increasing chelation. If, as we consider probable, the mechanism involves removal of a proton from an amino group by the attacking OH^- ion in a rapid preequilibrium lying far toward the parent complex, followed by a rate-controlling aquation of the conjugate base of the complex, then the apparent base hydrolysis rate constant k (defined by eq 4) is the product of the unknown rate constant for aquation of the complex conjugate base and the unknown equilibrium constant K for the preequilibrium; K itself is K_a/K_w, where K_a is the acid dissociation equilibrium constant of the parent complex. Thus, if increasing chelation increases K_a, it should increase k_b proportionately. There is some evidence[9] for such increased acidity in related complexes. The rather large k_b for α-Co(tetren)Cl^{2+} (Table IV) may be associated with the presence of two secondary amino groups, which probably have enhanced acidity. The large absolute magnitudes of k_b for the complexes of Table IV seem to be related to abnormally large rate constants in the aquation step of the conjugate base mechanism, apparently from the presence of the amido group in the conjugate base complex.[8] It would be interesting to have base hydrolysis rate information on Co(dien)(en)Cl^{2+} and deuterium–hydrogen-exchange rates on the complexes of Table IV.

TABLE IV

RATES OF AQUATION AT 35° AND BASE HYDROLYSIS AT 25° OF CHLOROPENTAMINECOBALT(III) COMPLEXES[a]

	Aquation			Base hydrolysis		
Complex	10^7k_{aq}, sec^{-1}	E_a, kcal $mole^{-1}$	ΔS^*, cal deg^{-1} $mole^{-1}$	k_b, M^{-1} sec^{-1}	E_a, kcal $mole^{-1}$	ΔS^*, cal deg^{-1} $mole^{-1}$
$Co(NH_3)_5Cl^{2+}$	67^b	23^b	-9^b	0.86^b	29^b	$+37^b$
cis-$Co(en)_2(NH_3)Cl^{2+}$	14^c	...	...	54^d	30^d	$+48^d$
cis-Co(trien)$(NH_3)Cl^{2+}$	6.7^c	...	...	160^d	...	...
ω-Co(dien)(en)Cl^{2+}	$5.2^{c,e}$	24^e	-9^e	...	...	...
ϵ-Co(dien)(en)Cl^{2+}	1^e	25^e	-5^e	...	...	...
α-Co(tetren)Cl^{2+}	4^f	27^f	-7^f	$35{,}000^f$	24^f	$+41^f$

[a] Quantitative comparison of rates is not possible since ionic strength is not the same for each system; k_{aq} is for pH 1, except for the dien complexes (pH 2) and the tetren complex (pH 0). [b] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955). [c] Reference 7. [d] D. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 2, Table IX. [e] B. Bosnich and F. P. Dwyer, *Australian J. Chem.*, **19**, 2051 (1966), have recently reported a rate constant of 5.6 × 10^{-7} sec^{-1} (extrapolated to 35° from 65°) for ω-Co(dien)(en)Cl^{2+} hydrolysis in 0.01 *F* $HClO_4$ at 35°, in acceptable agreement with the Pearson, Boston, and Basolo value[7] in 0.1 *F* $HClO_4$, which suggests that this complex undergoes much slower base hydrolysis under these conditions than α- and β-Co(tetren)Cl^{2+} and that the value reported by Bosnich and Dwyer probably is valid for aquation. Bosnich and Dwyer also reported rates for hydrolysis of their ϵ isomer, for which the rate constant given in the table is an extrapolation from 65° to 35°. [f] This research; k values extrapolated.

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[7] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

[8] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, p 67.

[9] See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 131.