square-planar arrangement is more suitable than an octahedral arrangement for π bonding, then the contrasting behavior of octahedral systems and square-planar systems can be understood. Evidence in the form of MO calculations,[11] spectroscopic studies,[11,12] and the results presented here support point (1) above; the second and third points are well established.[22] There does not seem to be a need for two theories (symbiosis and MO) to account for the contrasting behavior discussed above. It seems unlikely that any theory will adequately explain in detail every case of linkage isomerism since the energy differences found must be quite small (~1 kcal/mol) for isomers to coexist in detectable amounts.

Registry No. $K[Co(DH)_2(SCN)_2]$, 38625-16-0; $As(C_6H_5)_4[Co(DH)_2(SCN)_2]$, 39494-93-4; $As(C_6H_5)_4[Co(DH)_2(NCS)(SCN)]$, 39494-94-5; $As(C_6H_5)_4[Co(DH)_2(NCS)_2]$, 39494-95-6.

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Contribution from the Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Acidopentaaminecobalt(III) Complexes with Polyamine Ligands. VIII. Kinetics of Hydrolysis of π-, κ-, and ω-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) and α- and β-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Cations in Aqueous Acidic Solution

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The kinetics of hydrolysis of π-, κ-, and ω-$Co(en)(dien)Cl^{2+}$ and α- and β-$Co(en)(dpt)Cl^{2+}$ have been investigated in aqueous $HClO_4$, by spectrophotometry and by chloride release. Over the range 0.01–1.0 F H^+, with $C_0 \approx 1$ mF and $\mu = 1.0$, the hydrolysis of the π isomer follows the rate law: $-d[Co(en)(dien)Cl^{2+}]/dt = k[Co(en)(dien)Cl^{2+}]$ at 70°, independent of $[H^+]$. The hydrolysis of the other cations was investigated in 1.0 F $HClO_4$ only, over the 65–85° (π, κ, ω), 50–70° (α), or 35–55° (β) temperature ranges. For the π, κ, ω, α, and β cations respectively at 65.0°, 10^5k (sec^{-1}) = 5.22 ± 0.31, 2.58 ± 0.11, 2.22 ± 0.12, 26.07 ± 0.96, and 169.4 ± 2.5 (extrapolated); E_a (kcal mol^{-1}) = 27.0 ± 1.1, 26.2 ± 1.1, 26.7 ± 0.5, 25.2 ± 0.7, and 22.6 ± 0.4; $\Delta S^{\ddagger}{}_{298}$ (cal deg^{-1} mol^{-1}) = −0.4 ± 3.6, −4.2 ± 3.6, −2.8 ± 1.7, −2.5 ± 2.3, and −6.1 ± 1.0. Under the conditions studied, isomerization between these chloro isomers is negligibly slow relative to the hydrolysis, and only in the case of the κ isomer is any isomerization of the aquo product observed. The κ-$Co(en)(dien)(OH_2)^{3+} \rightarrow \pi$-$Co(en)(dien)(OH_2)^{3+}$ isomerization was followed spectrophotometrically over the 65–85° temperature range in 1.0 F $HClO_4$. At 65.0°, the first-order rate constant for this reaction is 10^5k (sec^{-1}) = 4.75 ± 0.19; E_a (kcal mol^{-1}) = 29.7 ± 1.1 and $\Delta S^{\ddagger}{}_{298}$ (cal deg^{-1} mol^{-1}) = +7.4 ± 3.6. The Hg^{2+}-catalyzed aquation of the π-, κ-, and ω-$[Co(en)(dien)Cl]ZnCl_4$ isomers has also been investigated spectrophotometrically. In the 15–35° temperature range at $\mu = 1.0$ ($HClO_4$) with $[Hg^{2+}] \approx 0.155$ F and $C_0 \approx 0.01$ F, the observed rate law is $-d[Co(en)(dien)Cl^{2+}]/dt = k_{obsd}[Co(en)(dien)Cl^{2+}]$ where $k_{obsd} = k[Hg^{2+}]$. At 25.0° ($\mu = 1.0$), for the π, κ, and ω isomers respectively, 10^3k (M^{-1} sec^{-1}) = 14.7 ± 0.5, 5.11 ± 0.09, and 4.86 ± 0.1; E_a (kcal mol^{-1}) = 13.9 ± 0.4, 19.5 ± 0.3, and 18.0 ± 0.3; $\Delta S^{\ddagger}{}_{298}$ (cal deg^{-1} mol^{-1}) = −22.3 ± 1.4, −5.6 ± 1.1, and −10.7 ± 1.1. Evidence is also presented for the $HgCl^+$-catalyzed hydrolysis of the π isomer.

Introduction

The effect of chelation on the rate of acid hydrolysis of Co(III) complexes has been investigated by several workers.[1-3] The classic paper of Pearson, Boston, and Basolo[1] gives data for several chloropentaaminecobalt(III) complexes with polyamine ligands but, in most cases, the configuration (or even the isomeric purity) of the particular chloropentaamine complex was not established. The $Co(en)(dien)Cl^{2+}$ system[4] was further investigated by Bosnich and Dwyer,[2] who separated two isomers (ω and ϵ) and measured their rates of acid hydrolysis, but, again, the geometric configurations were not known with certainty. Following the successful synthesis of the α- and β-$Co(tetren)Cl^{2+}$ isomers,[5,6] Ni and Garner[3] measured the rates of acid hydrolysis. At the time of the kinetic study, the geometric configurations were unknown, but later, single-crystal X-ray analysis showed that the α and β cations contained a similar polyamine skeleton and were related by alternate positions available to the secondary NH proton in the peripheral polyamine configuration (Figure 1).[7]

Three (π, κ, ω) $Co(en)(dien)Cl^{2+}$ and two (α, β) $Co(en)(dpt)Cl^{2+}$ isomers have recently been isolated[8-10] and their structures have been established by single-crystal X-ray analysis[11-14] (Figure 1). In this present paper we report

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(4) Abbreviations used: en, $NH_2(CH_2)_2NH_2$; tmd, $NH_2(CH_2)_3NH_2$; dien, $NH_2(CH_2)_2NH(CH_2)_2NH_2$; dpt, $NH_2(CH_2)_3NH(CH_2)_3NH_2$; trien, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; tren, $N[(CH_2)_2NH_2]_3$; tetren, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; trenen, $N[(CH_2)_2NH_2]_2[(CH_2)_2NH(CH_2)_2NH_2]$.

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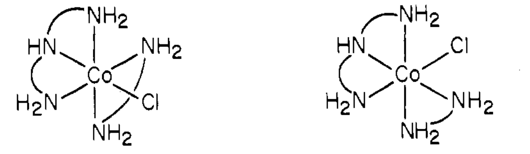
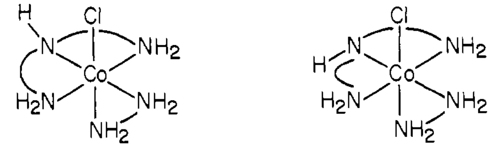
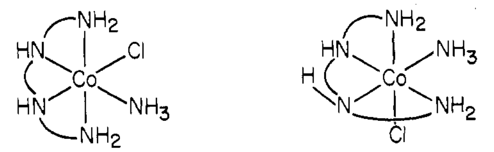
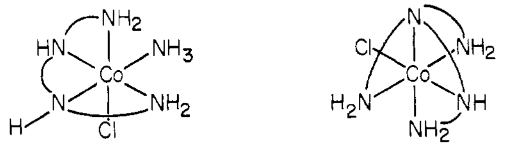
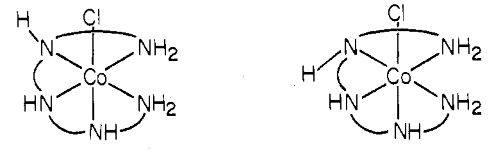

ω-Co(en)(dien)Cl^{2+} (a) π-Co(en)(dien)Cl^{2+} (b)


α-Co(en)(dpt)Cl^{2+} (c) β-Co(en)(dpt)Cl^{2+} (d)
κ-Co(en)(dien)Cl^{2+} (b)


α-Co(trien)(NH_3)Cl^{2+} (e) β_2-Co(trien)(NH_3)Cl^{2+} (f)


β_2'-Co(trien)(NH_3)Cl^{2+} (f) *sym*-Co(trenen)Cl^{2+} (g)


α-Co(tetren)Cl^{2+} (h) β-Co(tetren)Cl^{2+} (h)
(or $\alpha\beta$-(*R*)- (or $\alpha\beta$-(*S*)-

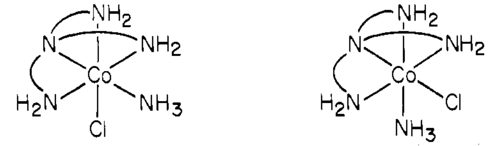

α-Co(tren)(NH_3)Cl^{2+} (i) β-Co(tren)(NH_3)Cl^{2+} (i)

Figure 1. Geometric configurations proposed or established for some chloropentaaminecobalt(III) complexes with polyamine ligands: (a) ref 14; (b) ref 13; (c) ref 12; (d) ref 11; (e) M. Dwyer and I. E. Maxwell, *Inorg. Chem.*, 9, 1459 (1970); (f) M. Dwyer, Ph.D. Thesis, Australian National University, Canberra, 1971; (g) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 8, 1595 (1969); (h) ref 7; (i) C-H. Yang and M. W. Grieb, *J. Chem. Soc., Chem. Commun.*, 656 (1972).

the results of an investigation of the acid hydrolysis (aquation) and Hg^{2+}-catalyzed hydrolysis (π, κ, ω only) of these cations, undertaken in part to provide further insight into the effects of chelation and ring size[15-17] on hydrolysis rates of Co(III) complexes and to try to establish structure-reactivity patterns in these systems.

Experimental Section

Syntheses. The compounds π-[Co(en)(dien)Cl]$ZnCl_4$ (racemic), κ-[Co(en)(dien)Cl]$ZnCl_4$, ω-[Co(en)(dien)Cl]$ZnCl_4$, α-[Co(en)(dpt)-Cl]$ZnCl_4$, and β-[Co(en)(dpt)Cl]$ZnCl_4$ were prepared and purified as described previously.[8,9,18] The aquo cations were generated in solution from the chloro isomers by addition of base (0.1 *F* NaOH) and acidification with 1.0 *F* $HClO_4$ after 5 min at room temperature. Spectral parameters used in this work are listed in Table I.

Other Chemicals. All other chemicals were CP or reagent grade. Perchloric acid solutions were prepared by dilution of 60% $HClO_4$ with distilled water and standardized by titration with carbonate-free NaOH solution. Solutions of Hg^{2+} were prepared from weighed quantities of $Hg(NO_3)_2 \cdot H_2O$ and standardized by titration with NaCl solution using diphenylcarbazone–Bromophenyl Blue indicator.[19]

Kinetic Runs. Weighed samples (*ca.* 120 mg) of the salts were dissolved in 250 ml of the appropriate $HClO_4$-$NaClO_4$ reaction medium and 30-ml aliquots were placed in tightly stoppered volumetric flasks (the use of sealed ampoules was shown to have a negligible change in the resulting rate data), which were then wrapped in Al foil to exclude light and placed in oil baths at 30.0–80.0°. Temperature control was better than ±0.05° in the 30.0–50.0° range and better than ±0.15° in the 55.0–80.0° range. Zero reaction time was taken 10–15 min after the flasks had been placed in the bath. Flasks were removed at known time intervals, quenched in ice, and kept at times up to several days at 0° prior to spectrophotometric estimation (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 glass cells (*vs.* a matching 10.00-cm cell filled with an identical solution except without the complex) over the 350–650-nm range with a Shimadzu MPS-50L recording spectrophotometer at 20–25° to search for isosbestic points and provide absorbancy data for kinetic analysis.

In certain runs, the reaction was followed by titration of released chloride ion. An aliquot (20 ml) of each cooled reaction solution was passed through an 8 cm × 1 cm Dowex 50W-X8 cation-exchange column in the H^+ form under gravity flow at room temperature. The column was washed with two bed volumes of distilled water and an equal volume of 2 *F* $HClO_4$ was added to the total effluent. The chloride ion concentration in the effluent was determined by the Volhard method.[20]

Isomerization of κ-Co(en)(dien)$OH_2{}^{3+}$. Weighed samples (*ca.* 120 mg) of κ-[Co(en)(dien)Cl]$ZnCl_4$ were dissolved in 50 ml of 0.2 *F* NaOH in 1.0 *F* $NaClO_4$. After 5 min at room temperature, 200 ml of 1.0 *F* $HClO_4$ was added to generate the aquo complex. Aliquots (30 ml) of this solution were heated in flasks at the appropriate temperature and the spectral changes (Table I) were measured on the cooled solutions at known time intervals, as for the chloro complexes.

Hg^{2+}-Catalyzed Reactions. These reactions were followed spectrophotometrically at constant wavelength (Table I). Temperature control to ±0.1° was achieved by means of constant-temperature water circulating around the cell compartment. The temperature was measured by means of a thermometer mounted in a 1.0-cm brass block placed in the cell position and was recorded at the beginning and end of each kinetic run. The initial complex concentration, C_0, was chosen such that the initial absorbance ranged from 0.6 to 0.8 for a 1.00-cm cell, and to obtain pseudo-first-order kinetics, the initial Hg^{2+} concentration, $[Hg^{2+}]_i$, was $>10C_0$. Stock solutions (25 ml, 18–25 m*F*) of π-, κ-, and ω-Co(en)(dien)Cl^{2+} were prepared from weighed amounts of the $ZnCl_4{}^{2-}$ salts in 1.0 *F* $HClO_4$, diluted with water to give an ionic strength of 1.0. These were stored at 0° and were discarded after 4 days. Stock solutions of Hg^{2+} (*ca.* 0.2 or 0.3 *F*) were prepared by dissolving the appropriate weight of $Hg(NO_3)_2 \cdot H_2O$ in 250 ml of 0.4 or 0.1 *F* $HClO_4$. In each case the $HClO_4$ concentration was calculated to give an ionic strength of 1.0. The separate solutions of Hg^{2+} and Co(en)(dien)-Cl^{2+} were brought to thermal equilibrium, 5 ml of each was added to a conical flask with a pipet, the contents were mixed and transferred to a 1.00-cm spectrophotometer cell, and the chart recorder was activated at time zero. For faster reactions at the higher temperatures, 5-ml syringes were used to deliver the reactants. The change in absorbance with time was monitored continuously for 30–50 min and 2–4 hr later an "infinity" reading was recorded.

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Throughout each run, the sample and the reference solution (1.0 F $HClO_4$) were left in the temperature-controlled cell compartment of the spectrophotometer.

Results

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

$$-d[\text{complex}]/dt = k[\text{complex}] \quad (1)$$

for the disappearance of π-, κ-, and ω-Co(en)(dien)Cl^{2+} and α- and β-Co(en)(dpt)Cl^{2+} in $HClO_4$ solutions (1.0 F except for π) and ionic strength of 1.0 at various temperatures.

In the spectrophotometric method, k was evaluated for each kinetic run by the relation

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

where A_0, A, and A_∞ are the optical absorbancies (at the wavelengths listed in Table I) at reaction time zero, at time t, and at 100% hydrolysis of the chloro ligand, respectively. With A_∞ calculated assuming hydrolysis to 100% of the isomerically pure $Co(N_5)(OH_2)^{3+}$, plots of this logarithmic function of the absorbancies generally gave good straight lines up to at least 75% reaction. Point-by-point calculations of k showed only random fluctuation over the same period and the mean k so obtained was in excellent agreement with that obtained graphically.

In the chloride release method, k was calculated using the relation

$$2.303 \log [(c_\infty - c_0)/(c_\infty - c_t)] = kt \quad (3)$$

where c_0, c_t, and c_∞ are the concentrations of free chloride ion at zero time, at time t, and at (assumed) 100% hydrolysis of the chloro ligand. Agreement within experimental error was obtained for k determined by these two methods under similar conditions (Table II).

In the Hg^{2+}-catalyzed aquations ($\mu = 1.0$) conditions were chosen such that $[Hg^{2+}]_i$ was greater than 10 times the initial complex ion concentration. In these situations, pseudo-first-order kinetics were observed, *i.e.*

$$-d[\text{complex}]/dt = k_{\text{obsd}}[\text{complex}] \quad (4)$$

where

$$k_{\text{obsd}} = k[Hg^{2+}]_i$$

The spectrophotometric data were evaluated using eq 2 and good straight lines were obtained up to 85% reaction. Table III lists the values of k_{obsd} and k obtained under the conditions investigated. For the slower reacting κ- and ω-Co(en)(dien)Cl^{2+} isomers, k was independent of $[Hg^{2+}]_i$, within experimental error in the 0.1-0.15 F Hg^{2+} range (Table III). For the faster reacting π isomer, however, a variation of k outside experimental error is observed with variation in $[Hg^{2+}]_i$ (Table III). We attribute this to $HgCl^+$ catalysis (see Discussion) and the rate data for the π isomer are expressed in terms of

$$k_{\text{obsd}} = k_2[Hg^{2+}] + k_2'[HgCl^+] \quad (6)$$

The calculated limiting values of k_2 and k_2' for the π isomer are listed in Table III.

The isomerization reaction

$$\kappa\text{-Co(en)(dien)}OH_2^{3+} \rightarrow \pi\text{-Co(en)(dien)}OH_2^{3+} \quad (7)$$

was also studied spectrophotometrically and the pseudo-first-order rate constants obtained in 0.76 F $HClO_4$ at $\mu = 1.0$ are presented in Table II.

Table I. Absorption Spectral Parameters for π-, κ-, and ω-Co(en)(dien)Cl^{2+} and α- and β-Co(en)(dpt)Cl^{2+} and Their Aquo Analogs in 1.0 F $HClO_4$ at 20–25°[a]

				Wavelength used in the kinetic analysis	
Isomer	Max	Min	Max	Acid hydrolysis	Hg^{2+} catalysis
π-Cl^{2+}	362 (68.5)	415 (15.1)	525 (66.5)	475	540
π-OH_2^{3+}		402 (18.5)	480 (75.8)		
κ-Cl^{2+}	367 (87.5)	415 (29.3)	517 (86.4)	517	540
κ-OH_2^{3+}		402 (24.6)	470 (95.3)	470	
ω-Cl^{2+}	364 (101.0)	419 (20.7)	531 (91.0)	540	550
ω-OH_2^{3+}		401 (15.8)	492 (71.6)		
α-Cl^{2+}	374 (86.9)	430 (15.8)	542 (73.5)	545	
α-OH_2^{3+}	358 (79.2)	417 (14.0)	498 (71.2)		
β-Cl^{2+}	379 (95.3)	437 (15.2)	553 (78.1)	565	
β-OH_2^{3+}	359 (71.6)	417 (9.1)	498 (67.6)		

[a] Numbers inside parentheses are the molar absorbancy indices, a_M (M^{-1} cm^{-1}). Wavelengths are in nanometers (±2 nm).

Table II. Pseudo-First-Order Rate Constants for the Hydrolysis of Some Co(en)(ABA)Cl^{2+} Isomers in Acid Solution at $\mu = 1.0$

Complex	$[HClO_4]$, F	Temp, °C	10^5k,[a] sec^{-1}	Method[b]
π-Co(en)(dien)Cl^{2+}	1.0	65.0	5.22 ± 0.31	S(3)
	1.0	70.0	8.75 ± 0.52	S(4)
	0.5	70.0	9.63 ± 0.57	S(1)
	0.1	70.0	9.19 ± 0.55	S(2)
	0.01	70.0	9.58 ± 0.56	S(1)
	0.00	70.0	21.32 ± 0.95	S(1)
	1.0	75.0	16.03 ± 0.96	S(4)
	1.0	80.0	25.24 ± 1.15	S(5)
	1.0	80.0	23.64 ± 1.41	H(2)
	1.0	85.0	51.01 ± 3.05	S(3)
κ-Co(en)(dien)Cl^{2+}	1.0	65.0	2.58 ± 0.11	S(2)
	1.0	70.0	4.27 ± 0.29	S(3)
	1.0	75.0	7.15 ± 0.31	S(4)
	1.0	80.0	12.51 ± 0.45	S(4)
	1.0	80.0	12.08 ± 0.54	H(1)
	1.0	85.0	22.99 ± 1.00	S(2)
ω-Co(en)(dien)Cl^{2+}	1.0	65.0	2.22 ± 0.12	S(4)
	1.0	70.0	3.68 ± 0.19	S(3)
	1.0	75.0	6.12 ± 0.32	S(3)
	1.0	80.0	11.22 ± 0.60	S(4)
	1.0	80.0	12.46 ± 0.66	H(2)
	1.0	85.0	20.58 ± 1.10	S(3)
α-Co(en)(dpt)Cl^{2+}	1.0	50.0	4.35 ± 0.16	S(3)
	1.0	55.0	7.97 ± 0.29	S(2)
	1.0	60.0	15.26 ± 0.56	S(2)
	1.0	65.0	26.07 ± 0.96	S(3)
	1.0	70.0	41.77 ± 1.53	S(2)
β-Co(en)(dpt)Cl^{2+}	1.0	35.0	7.09 ± 0.18	S(3)
	1.0	40.0	13.67 ± 0.35	S(2)
	1.0	45.0	23.84 ± 0.60	S(2)
	1.0	50.0	41.10 ± 1.05	S(2)
	1.0	55.0	67.77 ± 1.71	S(3)
Isomerization Reaction				
κ-Co(en)(dien)$(OH_2)^{3+}$ → π-Co(en)(dien)$(OH_2)^{3+}$	0.76	65.0	4.75 ± 0.19	S(2)
	0.76	70.0	8.71 ± 0.33	S(3)
	0.76	75.0	15.30 ± 0.62	S(3)
	0.76	80.0	29.71 ± 1.81	S(3)
	0.76	85.0	56.45 ± 2.20	S(2)

[a] Average values of k ± the standard deviation. [b] Method used to monitor the reaction: S, spectrophotometric; H, chloride release titration. Numbers in parentheses are the number of individual determinations used to obtain the mean value of k.

Table III. Spectrophotometrically Determined Rate Constants for the Hg^{2+}-Catalyzed Hydrolysis of Some $Co(en)(dien)Cl^{2+}$ Isomers in Acid Solution at $\mu = 1.0$

Complex[h]	$[HClO_4]$, F	C_0, mF	$[Hg^{2+}]_i$,[a] mF	$[Cl^-]_i$,[b] mF	Temp,[c] °C	$10^4 k_{obsd}$,[d] sec^{-1}	$10^3 k$,[d,e] M^{-1} sec^{-1}	$10^2 k_2$,[d,f] M^{-1} sec^{-1}	$10^2 k_2'$,[d,g] M^{-1} sec^{-1}
π-$Co(en)(dien)Cl^{2+}$	0.54	3.125	156	12.5	15.8 (2)	9.11 ± 0.28	5.84 ± 0.14	0.64 ± 0.03	7.30 ± 0.30
	0.50	12.5	156	50.0	15.8 (4)	10.82 ± 0.38	6.95 ± 0.23	1.02 ± 0.05	2.16 ± 0.10
	0.65	12.5	101	50.0	15.8 (1)	6.75 ± 0.23	6.69 ± 0.22	1.32 ± 0.06	1.35 ± 0.06
								0.58 ± 0.5[i]	0.81 ± 0.70[i]
	0.54	3.125	156	12.5	25.0 (2)	20.5 ± 0.7	13.25 ± 0.6	1.43 ± 0.06	16.4 ± 0.7
	0.69	3.125	101	12.5	25.0 (1)	13.5 ± 0.5	13.37 ± 0.5	1.53 ± 0.07	10.8 ± 0.5
	0.50	12.5	156	50.0	25.0 (3)	22.9 ± 0.7	14.70 ± 0.5	2.16 ± 0.09	4.58 ± 0.18
	0.65	12.5	102	50.0	25.0 (2)	15.85 ± 0.35	15.55 ± 0.4	3.05 ± 0.10	3.17 ± 0.10
								1.27 ± 0.6[i]	1.86 ± 0.9[i]
	0.50	12.5	156	50.0	30.0 (3)	34.3 ± 1.1	22.0 ± 0.7		
	0.50	12.5	155	50.0	35.0 (4)	48.9 ± 1.9	31.5 ± 1.2		
κ-$Co(en)(dien)Cl^{2+}$	0.51	10.0	156	40.0	15.9 (2)	2.89 ± 0.09	1.86 ± 0.06		
	0.66	10.0	102	40.0	25.0 (2)	5.23 ± 0.10	5.12 ± 0.10		
	0.51	10.0	155	40.0	25.0 (3)	7.90 ± 0.14	5.10 ± 0.09		
	0.51	10.0	156	40.0	30.0 (1)	13.8 ± 0.4	8.84 ± 0.27		
	0.66	10.0	101	40.0	35.0 (3)	15.5 ± 0.5	15.3 ± 0.5		
	0.51	10.0	155	40.0	35.0 (3)	23.7 ± 0.8	15.3 ± 0.5		
ω-$Co(en)(dien)Cl^{2+}$	0.67	9.0	102	36.0	15.5 (1)	1.87 ± 0.05	1.85 ± 0.05		
	0.52	9.0	155	36.0	15.5 (1)	2.88 ± 0.06	1.86 ± 0.04		
	0.67	9.0	102	36.0	25.0 (2)	4.97 ± 0.11	4.87 ± 0.11		
	0.52	9.0	155	36.0	25.0 (2)	7.54 ± 0.19	4.86 ± 0.12		
	0.67	9.0	101	36.0	35.0 (2)	13.5 ± 0.5	13.4 ± 0.5		
	0.52	9.0	155	36.0	35.0 (2)	21.0 ± 0.6	13.6 ± 0.4		

[a] Total $[Hg^{2+}]$ added. [b] Initial free $[Cl^-] = [HgCl^+]_i$; see footnote *h*. [c] Numbers in parentheses are the number of individual runs used to determine the mean values. [d] Mean rate constant ± the standard deviation. [e] $k_{obsd} = k[Hg^{2+}]_i$. [f] Calculated on the assumption that all the initial Cl^- ion combines to form $HgCl^+$, *i.e.*, $k_{obsd} = k_2([Hg^{2+}]_i - [Cl^-]_i) = k_2[Hg^{2+}]_{free}$. [g] $k_{obsd} = k_2'[HgCl^+]_i$. [h] $ZnCl_4^{2-}$ salts were used so that $[Cl^-]_i = 4C_0$. [i] From the slope and intercept of the relationships $k_{obsd}/[Hg^{2+}]_i = k_2'[HgCl^+]_i/[Hg^{2+}]_{free} + k_2$ and $k_{obsd}/[HgCl^+]_i = k_2' + k_2[Hg^{2+}]_{free}/[HgCl^+]_i$ (see footnote *f*).

Table IV. Kinetic Parameters for the Acid Hydrolysis of Some Chloropentaaminecobalt(III) Complexes with Polyamine Ligands at 35°

Complex	$[H^+]$, F	μ, F	$10^6 k$,[a] sec^{-1}	log PZ, sec^{-1}	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$, cal deg^{-1} mol^{-1}	Ref
$Co(NH_3)_5Cl^{2+}$	0.01	0.01	6.34		23.5	−6	*b, c*
cis-$Co(en)_2(NH_3)Cl^{2+}$	0.17	0.2	1.42		24		*d-f*
trans-$Co(en)_2(NH_3)Cl^{2+}$	0.17	0.2	1.6	10.9	23.6		*d, g*
?-$Co(trien)(NH_3)Cl^{2+}$	0.1	0.1	0.67		23.5–25.5		*e, h*
π-$Co(en)(dien)Cl^{2+}$	1.0	1.0	0.63	13.1	27.0 ± 1.1	−0.4 ± 3.6	This work
ϵ-$Co(en)(dien)Cl^{2+}$	0.01	0.01	1		25 ± 1	−5 ± 2	*i*
κ-$Co(en)(dien)Cl^{2+}$	1.0	1.0	0.5	12.3	26.2 ± 1.1	−4.2 ± 3.6	This work
ω-$Co(en)(dien)Cl^{2+}$	0.01	0.01	0.52		24 ± 1	−9 ± 2	*i*
ω-$Co(en)(dien)Cl^{2+}$	1.0	1.0	0.5	12.6	26.7 ± 0.5	−2.8 ± 1.7	This work
α-$Co(en)(dpt)Cl^{2+}$	1.0	1.0	6.3	12.7	25.2 ± 0.7	−2.5 ± 2.3	This work
β-$Co(en)(dpt)Cl^{2+}$	1.0	1.0	71	11.9	22.6 ± 0.4	−6.1 ± 1.0	This work
α-$Co(tetren)Cl^{2+}$	1.0	1.0	0.13	13	27 ± 2	−5 ± 1	*j*
β-$Co(tetren)Cl^{2+}$	0.1	0.1	0.25	14	29 ± 1	−5 ± 2	*j*
α-$Co(tren)(NH_3)Cl^{2+}$	0.1	0.1	1.23 (26°)				*k*
β-$Co(tren)(NH_3)Cl^{2+}$	0.1	0.1	2.5 (26°)				*k*

[a] Most of these 35° rate constants have been calculated using the log PZ and E_a data obtained at higher temperatures. [b] S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, 724 (1965). [c] R. K. Linck, *Inorg. Chem.*, **8**, 1016 (1969). [d] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956). [e] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 59, 304 (1955). [f] S. C. Chan and F. Leh, *J. Chem. Soc. A*, 136 (1968). [g] M. L. Tobe, *J. Chem. Soc.*, 3776 (1959). [h] S. C. Chan, *J. Chem. Soc. A*, 291 (1967). [i] B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, 19, 2051 (1966). From the method of synthesis, the ϵ isomer described in this work is probably our π isomer. [j] T-L. Ni and C. S. Garner, *Inorg. Chem.*, 6, 1071 (1967). [k] C-H. L. Yang and M. W. Grieb, *J. Chem. Soc., Chem. Commun.*, 656 (1972).

From the temperature dependence of k, activation parameters, E_a, log PZ, and $\Delta S^{\ddagger}_{298}$ (Table IV) have been calculated for the thermal acid hydrolysis reaction using the standard methods and equations;[21] $k(35°)$ values are also estimated (Table IV). Similarly, for the isomerization reaction 7, we calculate $E_a = 29.7 \pm 1.1$ kcal mol^{-1}, log $PZ = 14.8$ sec^{-1}, and $\Delta S^{\ddagger}_{298} = +7.4 \pm 3.6$ cal deg^{-1} mol^{-1}.

Because of the possibility of combined Hg^{2+} and $HgCl^+$ catalysis in the reaction between the $Co(en)(dien)Cl^{2+}$ isomers and Hg^{2+}, the kinetic parameters (Table V) are composites and refer only to the stated initial ionic strength and complex ion, chloride ion, and Hg^{2+} ion concentrations. Nevertheless, these data have been calculated to provide interisomeric comparisons.

Discussion

Acid Hydrolysis. With the exception of the hydrolysis of κ-$Co(en)(dien)Cl^{2+}$, generally good isosbestic points were observed in the spectrophotometric scans for each of the complexes in the 350–650-nm range and these were in good agreement with those predicted (Table VI).

Although $ZnCl_4^{2-}$ salts were used,[22] there was no evidence for the reverse reaction

$$Co(N_5)OH_2{}^{3+} + Cl^- \rightarrow Co(N_5)Cl^{2+} + H_2O \qquad (8)$$

and the spectrum of the product left for 10 half-lives agreed

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(21) A. J. Cunningham, D. A. House, and H. K. J. Powell, *J. Inorg. Nucl. Chem.*, 33, 572 (1971), eq 11 and 12.

(22) At the concentrations used, this ion is completely dissociated into Zn^{2+} and Cl^- ions. Thus the initial $[Cl^-] = 4C_0$, and the final $[Cl^-] = 5C_0$.

Table V. Kinetic Parameters for the Combined (Hg^{2+} + $HgCl^+$)-Catalyzed Aquation of Some $Co(en)(dien)Cl^{2+}$ Isomeric Cations at $\mu = 1.0$ in Aqueous Acidic Solution[a]

Isomer	Temp, °C	10^3k, M^{-1} sec^{-1}	10^3k(calcd),[b] M^{-1} sec^{-1}	E_a,[c] kcal mol^{-1}	Log PZ,[c] M^{-1} sec^{-1}	$\Delta S^{\ddagger}_{298}$,[d] cal deg^{-1} mol^{-1}
π	15.8	6.97 ± 0.23	7.01	13.9 ± 0.4	8.38	−22.3 ± 1.4
	25.0	14.70 ± 0.5	14.9			
	30.0	22.0 ± 0.7	22.6			
	35.0	31.5 ± 1.2	31.5			
κ	15.9	1.86 ± 0.06	1.84	19.5 ± 0.3	11.98	−5.6 ± 1.1
	25.0	5.11 ± 0.09	5.21			
	30.0	8.84 ± 0.27	8.44			
	35.0	15.3 ± 0.5	15.0			
ω	15.5	1.86 ± 0.05	1.82	18.0 ± 0.03	10.89	−10.7 ± 1.1
	25.0	4.86 ± 0.12	4.95			
	35.0	13.6 ± 0.4	13.2			

[a] Initial Hg^{2+} concentration of 0.155 F and C_0 concentrations of 12.5, 10.0, and 9.0 mF give initial $HgCl^+$:Hg^{2+} ratios of 0.476, 0.348, and 0.303, respectively, for the π, κ, and ω isomers. [b] Calculated using the E_a and log PZ data in columns 5 and 6. [c] Calculated using the least-squares slope and intercept of a plot of log k vs. 1000/T°K. [d] Calculated using eq 12 of ref 21.

Table VI. Isosbestic Points Observed and Predicted in the Acid Hydrolysis of $Co(N_5)Cl^{2+} \rightarrow Co(N_5)OH_2{}^{3+}$

N_5	λ[c]					
	Observed[a]			Predicted[b]		
π-(en)(dien)	353 (66.0)	405 (18.2)	508 (61.0)	353 (65.6)	403 (18.1)	511 (62.0)
κ-(en)(dien)		None		352 (73.6)	417 (30.3)	492 (83.9)
ω-(en)(dien)		411 (19.5)	505 (70.5)		416 (21.0)	498 (70.6)
α-(en)(dpt)	362 (72.6)	423 (13.3)	515 (63.5)	362 (71.0)	432 (15.9)	517 (63.0)
β-(en)(dpt)	364 (75.8)	426 (15.8)	522 (65.2)	363 (76.9)	426 (16.0)	517 (66.6)
κ-(en)(dien)[d]			523 (52.0)			517 (56.2)

[a] Observed during the acid hydrolysis reaction in 1.0 F $HClO_4$. [b] Predicted from the superposition of the $Co(N_5)Cl^{2+}$ and $Co(N_5)(OH_2)^{3+}$ spectra obtained in 1.0 F $HClO_4$. [c] Wavelengths in nm (±2 nm). Values in parentheses are the molar absorbancy indices, a_M, M^{-1} cm^{-1} (±2 M^{-1} cm^{-1}). [d] For the reaction κ-$Co(en)(dien)(OH_2)^{3+} \rightarrow \pi$-$Co(en)(dien)(OH_2)^{3+}$.

well with the spectrum of the corresponding isomeric aquo complex.

In the case of κ-$Co(en)(dien)Cl^{2+}$, acid hydrolysis leads to isomeric change and isosbestic points were not held in the spectral scans. Examination of the "infinite time" spectrum showed that the π-aquo was formed. By independently generating κ-$Co(en)(dien)OH_2{}^{3+}$ and allowing it to undergo reaction under similar kinetic conditions, it was found that the π-aquo was formed irreversibly and completely. The rate of this spontaneous isomerization is almost twice as fast as the rate of acid hydrolysis of κ-$Co(en)(dien)Cl^{2+}$, despite the relatively higher activation energy (29.7 vs. 26.2 kcal mol^{-1}). This rate difference is probably due to the difference in activation entropy (+7.4 eu for (7) vs. −4.2 eu for the acid hydrolysis) which offsets the less favorable activation energy.

Because the acid hydrolysis rates of the π-, κ-, and ω-$Co(en)(dien)Cl^{2+}$ cations differ by no more than 1 order of magnitude and essentially the same k values are obtained in each case by spectrophotometry and by chloride release, we may conclude that isomerization between these three chloro isomers plays no significant role in their hydrolysis. If any isomer isomerized at a rate very much greater than the experimentally found hydrolysis rates, the apparent hydrolysis rate of 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 observed. Similar remarks apply to the α- and β-$Co(en)(dpt)Cl^{2+}$ isomers.

In the case of the κ-chloro isomer, we believe the directly formed product to have the same geometric configuration as the parent complex, with the κ-aquo isomer then isomerizing to the observed π-aquo isomer. This is supported by our method of analysis of the change in spectra with time in the acid hydrolysis of κ-$Co(en)(dien)Cl^{2+}$ where the wavelength used to calculate k corresponds to the isosbestic point for reaction 7. The values of k thus calculated are in good agreement with those obtained by chloride release (Table II).

The rate of hydrolysis of the π-chloro isomer was found to be independent of $[H^+]$ in the 0.01–1.0 F H^+ range, but in neutral solution a twofold rate increase was observed (Table II). This lack of dependence of the rate on $[H^+]$ is in contrast to the α- and β-$Co(tetren)Cl^{2+}$ system but is not surprising when the relative rates of base hydrolysis are considered. In the hydrolysis of chloropentaamminecobalt(III) complexes, the observed increase in rate as the pH is increased is generally due to the onset of base hydrolysis (OH^- rather than H_2O as the nucleophile). If the rate of base hydrolysis is rapid, then this rate increase will manifest itself at a lower pH than if the rate of base hydrolysis is slow. For α-$Co(tetren)Cl^{2+}$ and π-$Co(en)(dien)Cl^{2+}$, the rates of base hydrolysis are 3.5×10^4 and 362 M^{-1} sec^{-1}, respectively, at 25° (Table VII). The 100-fold difference thus accounts for the relative insensitivity of the hydrolysis rate of the π-chloro to $[H^+]$ in the 0.01–1.0 F H^+ range. As we were primarily concerned with acid hydrolysis rates in this work, dependence of the rate constant on acidity was not investigated further on other isomers, except to ensure a hydrogen ion concentration high enough to prevent any contribution from base hydrolysis.

Increasing the size of the chelate rings from two fused five-membered rings in a peripheral configuration to two fused six-membered rings in a similar configuration, *i.e.*, κ-$Co(en)(dien)Cl^{2+}$ to β-$Co(en)(dpt)Cl^{2+}$ (Figure 1), causes the acid hydrolysis rate to increase by a factor of 65 (at 65°). This increase in rate on expansion of the chelate ring has previously been observed for Co(III) complexes[17,23,24] and has been attributed to "release of steric strain in forming a dissociated transition state" as the six-membered rings are "more crowded"[24] or to the formation of boat or twist-boat ring conformations in solution,

[23] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 3089 (1953).

[24] I. R. Jonassan, R. S. Murray, D. R. Stranks, and Y. K. Yandell, *Proc. Int. Conf. Coord. Chem.*, **12**, 32 (1969).

Table VII. Kinetic Parameters for the Base Hydrolysis at 25° of Some Chloropentaaminecobalt(III) Complexes with Polyamine Ligands

Complex	pH	μ	$k, M^{-1}\ sec^{-1}$	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$, cal deg^{-1} mol^{-1}	Ref
$Co(NH_3)_5Cl^{2+}$			0.86	29	37	*a, b*
cis-$Co(en)_2(NH_3)Cl^{2+}$			54	30	48	*c*
?-$Co(trien)(NH_3)Cl^{2+}$			160			*c*
α-$Co(trien)(NH_3)Cl^{2+}$	10.85	1.0	10.7			*d*
β_2-$Co(trien)(NH_3)Cl^{2+}$	8.13	1.0	4.8×10^4			*d*
β_2'-$Co(trien)(NH_3)Cl^{2+}$	5.49	1.0	2.3×10^5			*d*
π-$Co(en)(dien)Cl^{2+}$	6.60	0.1	3.6×10^2			*e*
κ-$Co(en)(dien)Cl^{2+}$	9.40	0.1	4.7×10^4			*e*
ω-$Co(en)(dien)Cl^{2+}$	9.6–10.2	0.1	7.26			*e*
α-$Co(en)(dpt)Cl^{2+}$	6.60	0.1	8.6×10^3			*e*
β-$Co(en)(dpt)Cl^{2+}$	6.60	0.1	2.2×10^3			*e*
α-$Co(tetren)Cl^{2+}$		1.0	3.5×10^4	24	41	*f*
β-$Co(tetren)Cl^{2+}$		1.0	8.3×10^3 [g]			*f*
sym-$Co(trenen)Cl^{2+}$	7.17–8.42	1.0	8.8×10^2			*h*

[a] G. C. Lalor and J. Lang, *J. Chem. Soc.*, 5620 (1963). [b] S. C. Chan, K. Y. Hui, J. Miller, and W. S. Tsang, *ibid.*, 3207 (1965). [c] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, 78, 709 (1956). [d] M. M. Dwyer, Ph.D. Thesis, Australian National University, 1971. [e] R. W. Hay, personal communication. [f] T-L. Ni and C. S. Garner, *Inorg. Chem.*, 6, 1071 (1967). [g] Calculated from 70° data using the E_a for the α isomer. [h] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 8, 1595 (1969).

which then interact sterically with the out-going chloride ion.[15–17]

The structure of β-$Co(en)(dpt)Cl^{2+}$ [11] (Figure 1) indicates that only one chair six-membered ring is in close proximity to the coordinated chloride and thus the κ-$Co(en)(dien)Cl^{2+}$-β-$Co(en)(dpt)Cl^{2+}$ system is best compared with the *trans*-$Co(en)_2Cl_2^+$-*trans*-$Co(en)(tmd)Cl_2^+$ [4] system where the acid hydrolysis rate increase is a factor of 12.6 (at 25°) rather than the *trans*-$Co(en)_2Cl_2^+$-*trans*-$Co(tmd)_2Cl_2^+$ system with a relative rate increase of 1660 (at 25°).[24]

The α-$Co(en)(dpt)Cl^{2+}$ isomer with the *sec*-NH(dpt) proton adjacent to the coordinated chloride (Figure 1) already has a twist-boat six-membered ring in close proximity to the leaving group.[12] Further distortions to a complete boat form, leading to more steric interaction, is difficult[12] because of the *sec*-NH(dpt) proton, and the smaller rate increase of about 10 (at 65°) relative to κ-$Co(en)(dien)Cl^{2+}$ is observed. Unfortunately, the theoretical dien analog of α-$Co(en)(dpt)Cl^{2+}$ with the *sec*-NH(dien) proton adjacent to the coordinated chloride (called here κ') has not yet been isolated. The rate increase of 6.5 (at 65°) for β-Co(en)(dpt)Cl^{2+} relative to the α isomer also reflects the difficulty of distorting the α form, and this rate increase is the largest observed in the acid hydrolysis of any isomeric chloropentaaminecobalt(III) pair yet investigated (Table IV).[25]

It is noteworthy that while κ-$Co(en)(dien)OH_2{}^{3+}$ isomerizes to the π isomer, the analogous β-$Co(en)(dpt)OH_2{}^{3+}$ is stable under the conditions investigated. To attain a π-type configuration (Figure 1), the tridentate dpt ligand would have to adopt a facial configuration. Such configurations have not yet been realized for this ligand.[26,27] However, in basic solution, *sec*-NH(dpt) proton inversion readily occurs and the α-$Co(en)(dpt)OH^{2+}$ ion is formed.[8]

The rearrangement of κ-$Co(en)(dien)OH_2{}^{3+}$ to the π-aquo isomer probably occurs as a result of water exchange. The positive $\Delta S^{\ddagger}_{298}$ (+7.4 eu) is consistent with a dissociative mechanism in which there is a loosening of the structure in the transition state, presumably *via* a trigonal-bipyramid intermediate. Figure 2 shows the reaction paths possible under these assumptions. Two possible bipyramidal intermediates can be postulated: one (sym-I) arising from movement of the NH_2 ends of the dien ligand into the trigonal plane caused by the leaving H_2O and the other (unsym-II) arising from movement of the *sec*-NH(dien) enNH_2 groups into this trigonal plane. These intermediates (sym-I and unsym-II) generate racemic π-aquo and κ'-aquo isomers, respectively. The stereospecificity observed (only the racemic π-aquo is formed) is apparently due to the difficulty of moving the *sec*-NH(dien) group into the trigonal plane.

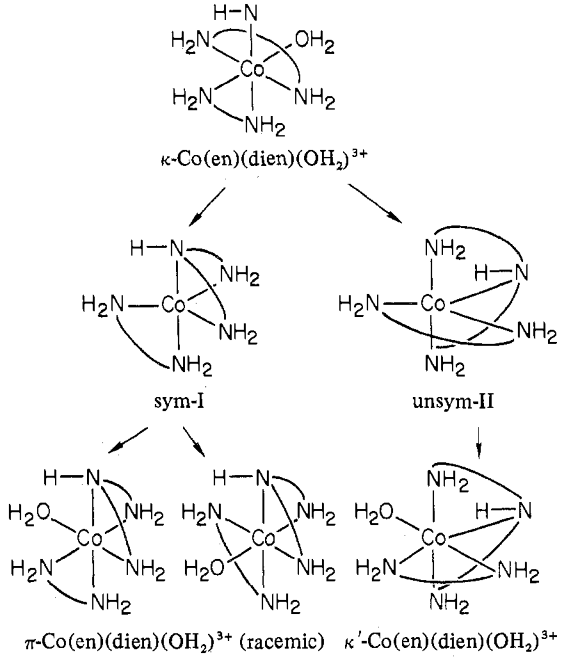

Figure 2. Possible intermediates and reaction products in the isomerization of κ-$Co(en)(dien)(OH_2)^{3+}$.

Hg^{2+}-Catalyzed Hydrolysis. Addition of Hg^{2+} to solutions of the $Co(en)(dien)Cl^{2+}$ isomers causes the rapid formation of aquo ions. No attempt was made to determine the steric course of these reactions but Bosnich and Dwyer[2] stated that, for the ω isomer at least, Hg^{2+} catalysis, Ag^+ catalysis, and base hydrolysis followed by acidification all yield the same aquo isomer.

In kinetic studies, Bronsted and Teeter[28] have established

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(25) The comparison of relative rates measured at different temperatures must be interpreted with caution, as the differing activation parameters for the different systems could cause reasonable changes in these numbers. Thus, while κ-$Co(en)(dien)Cl^{2+}$ aquates more rapidly than the ω isomer at 65°, the reverse is true at 0°.

(26) M. C. Couldwell and D. A. House, *J. Inorg. Nucl. Chem.*, 33, 2583 (1971).

(27) A. R. Gainsford and D. A. House, *J. Inorg. Nucl. Chem.*, 32, 688 (1970).

(28) J. N. Bronsted and C. E. Teeter, *J. Phys. Chem.*, 28, 579 (1924).

that Hg^{2+}-catalyzed hydrolysis reactions are sensitive to variation in ionic strength and this has been confirmed by later workers.[29,30] Apparently no studies have been made to determine the effect of acidity, although Cho and Morawetz[31] pointed out that considerable amounts of $HgOH^+$ could exist at pH 2-5. Apart from this uncertainty in the nature of the initial reactant, there is also the possibility of $HgCl^+$ catalysis, as the effective charge reduction, when compared with that of Hg^{2+}, would allow this product to overcome cation-cation electrostatic repulsion more easily. On the other hand, the stability constant for the formation of $HgCl^+$ is greater than that for the formation of $HgCl_2$. In the Hg^{2+}-catalyzed hydrolysis of $Co(NH_3)_5Cl^{2+}$, it was found that addition of chloride ions caused a rate increase of about 8% and this was attributed to $HgCl^+$ catalysis.[32] Similarly, an 11% increase was observed in the $Cr(NH_3)_5Cl^{2+}$ system.[33] Thus, the rate expression for these reactions should probably be written as

$$-d[\text{complex}]/dt = k_{aq}[\text{complex}] + \sum_{x=0}^{x=4} k_{HgCl_x{}^{2-x}}[HgCl_x{}^{2-x}][\text{complex}] \qquad (9)$$

where k_{aq} is the rate constant for the uncatalyzed reaction.[34]

In this work, the use of tetrachlorozincate(II) salts provides an initial chloride ion background of 4 times the complex concentration and it is assumed[32] that all this chloride is completely complexed with Hg^{2+} to give $HgCl^+$. For the κ and ω isomers, the calculated second-order rate constants, k (eq 5), are independent of the initial Hg^{2+}:Cl^- ratio (Table III) and the rate of $HgCl^+$ catalysis is probably not appreciably faster than the rate of Hg^{2+} catalysis. However, for the π isomer, the value of k is dependent on the initial Hg^{2+}:Cl^- ratio and this is interpreted as evidence for $HgCl^+$ catalysis. The limiting k_2 and k_2' values (eq 6) have been calculated from the data in Table III (see footnote i) to give $HgCl^+$ as a slightly more effective (the rate increases by a factor of 1.4) catalyst, in agreement with previous workers.[32-34]

Structure-Reactivity Relationships. The data in Table IV indicate that the rates of acid hydrolysis are rather insensitive to geometry within a group of isomers. At 65°, the rates of acid hydrolysis increase in the order $\omega < \kappa < \pi$ for the $Co(en)(dien)Cl^{2+}$ systems, $\alpha < \beta$ for $Co(en)(dpt)Cl^{2+}$, and $\beta < \alpha$ for $Co(tetren)Cl^{2+}$. In these last two systems, the individual isomers differ only in the position of the *sec*-NH proton (Figure 1), and perhaps little change in reactivity would be expected. For the ω- and κ-$Co(en)(dien)Cl^{2+}$ isomers, however, there is considerable change in geometry but almost similar acid hydrolysis rates.

Similar remarks apply to the Hg^{2+}-catalyzed acid hydrolysis rates, although here data are only available for the π-, κ-, and ω-$Co(en)(dien)Cl^{2+}$ isomers. These rates parallel the thermal acid hydrolysis and a plot of log $k_{aq}(65°)$ *vs.* log $k_{Hg}(25°)$ is linear with a slope of 0.7 (*cf.* 0.6 as found by Bifano and Linck[30] for an analogous plot for some $Co(en)_2XCl^+$ complexes).

Kinetic parameters for the acid hydrolysis reactions are also not particularly influenced by geometry. The negative $\Delta S^{\ddagger}{}_{298}$ values are consistent with a dissociative mechanism proceeding without extensive geometric rearrangement[35] and the activation energies are normal for this type of reaction.

Of more interest is the variation in the rate of base hydrolysis with geometry (Table VII). Here, rate constants vary by 10^4 within a particular isomeric series. One structure-reactivity pattern that emerges is that chloro complexes containing a $RNH(CH_2)_xNH(CH_2)_xNHR$ group (R = H or $(CH_2)_x$; x = 2 or 3) in a trans (peripheral) configuration are base hydrolyzed 10^2-10^4 times faster than chloro complexes where this group is in the cis (facial) configuration. Thus κ-$Co(en)(dien)Cl^{2+}$ and β_2 (or β_2')-$Co(trien)(NH_3)Cl^{2+}$ (Figure 1) are base hydrolyzed much more rapidly than the ω-$Co(en)(dien)Cl^{2+}$ or α-$Co(trien)(NH_3)Cl^{2+}$ forms. Within these fast reacting systems, those with the peripheral *sec*-NH proton adjacent to the leaving group, *e.g.*, α-$Co(en)(dpt)Cl^{2+}$ and α-$Co(tetren)Cl^{2+}$, react slightly (4-5 times) faster than isomeric complexes with the *sec*-NH proton remote from the coordinated chloride ion. One exception to these generalizations is *sym*-$Co(trenen)Cl^{2+}$ (Figure 1), which has a peripheral N-N-N system but a relatively small base hydrolysis rate constant.

Registry No. π-$[Co(en)(dien)Cl]ZnCl_4$, 24771-19-5; π-$[Co(en)(dien)H_2O]^{3+}$, 39678-75-6; κ-$[Co(en)(dien)Cl]ZnCl_4$, 24771-18-4; κ-$[Co(en)(dien)H_2O]^{3+}$, 39678-77-8; ω-$[Co(en)(dien)Cl]ZnCl_4$, 24797-79-3; ω-$[Co(en)(dien)H_2O]^{3+}$, 39678-79-0; α-$[Co(en)(dpt)Cl]ZnCl_4$, 36654-42-9; α-$[Co(en)(dpt)H_2O]^{3+}$, 39678-81-4; β-$[Co(en)(dpt)Cl]ZnCl_4$, 39678-82-5; β-$[Co(en)(dpt)H_2O]^{3+}$, 39678-83-6; mercury, 7439-97-6.

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