

CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY,
AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA**Kinetics and Stereochemistry of the Aquation of Some [Co(trien)Cl₂]⁺ Isomers**

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The rate constants for the aquation of the D- α -, D- β -SS-, and *trans*-SS-[Co(trien)Cl₂]⁺ ions are reported and discussed in relation to the [Co(en)₂Cl₂]⁺ species. The *cis* isomers aquate with retention of *cis* configuration and optical activity, the *trans* isomer aquates stereospecifically to the β -[Co(trien)Cl(OH₂)]²⁺ ion, and evidence is produced for an S_N2 mechanism. The rate constants and rate laws for the subsequent aquation of the *cis*-chloroaquo isomers allow two significant pathways which are attributed to the chloroaquo and chlorohydroxo species. These aquations also take place with retention of configuration but some isomerization of the α -diaquo to the β -diaquo ion was observed (trien = triethylenetetramine).

Introduction

The stereochemistry of the [Co(trien)X₂]⁺ complexes has been discussed elsewhere¹⁻³ and therefore only the salient factors will be reiterated here. For the reactions of the dichloro ions we have only six forms (three racemate pairs) to consider at this time: D- and L-*cis*- α -, D- and L-*cis*- β -, and DL-*trans* (Figure 1). The sources of isomerism in these complexes are the skeletal arrangement of the ligand about the Co atom, which gives both geometrical and optical isomers, and the orientation of the protons on the *sec*-N atoms, which gives diastereoisomeric forms. Clearly there is another β isomer and a *meso* form of the *trans* complex which are possible from the latter source. It has been found, however, that these species are not detectable in the complexes whose reactions are described in this paper, although two forms of the β -[Co(trien)(H₂O)₂]³⁺ ion have now been identified in solution and are described elsewhere.³

Further geometric isomerism is possible in the β complexes when the substituents are different and the two β -[Co(trien)Cl(OH₂)]²⁺ isomers arising from this cause have been detected in solution by their different aquation rates.

These studies on multidentate aminocobalt(III) complexes were instituted with [Co(trien)X₂]⁺ and [Co(tetraen)X]²⁺ complexes to study possible rearrangements in the reactions of the molecular ions which would be stereospecific. For example, an edge displacement process like the following aquation (Figure 2) leads not only to inversion but also to a new geometrical form and therefore is more readily detected. We consider this to be a simplifying feature for the study of stereochemistry in relation to mechanism and we also consider that the trien systems are closely related to the [Co(en)₂X₂]⁺ systems with respect to the nature of the ligands and the correspondence between chemical and optical properties of the corresponding *cis* and *trans* isomers. They therefore have some bearing on the studies which have been carried out with these latter ions.

The reactions reported in this paper are the aquation

of the three dichloro isomers: D- α -, D- β -SS-, and *trans*-SS.³ The absolute configurations of the resolved complexes have been evaluated previously¹ and we can relate the structures of reactants and products with confidence. Also the configuration correlation¹ was confirmed by a recent study of the (+)₅₈₉-*trans*-dichloro-3,8-dimethyltriethylenetetraminecobalt(III) ion,⁴ which is formed stereospecifically and whose configuration coincides with that of (+)₅₈₉-*trans*-[Co(trien)Cl₂]⁺.⁵ The absolute configuration of (+)₅₈₉- β -[Co(trien)Cl(OH₂)]²⁺ is deduced from the fact that (+)₅₈₉-*trans*-[Co(trien)Cl₂]⁺ aquates stereospecifically to the optically pure β ion without change in configuration at the asymmetric *sec*-N centers.³

Experimental Section

The compounds used in this kinetic study were prepared optically and analytically pure by methods described previously.²

Kinetics.—The rates of chloride ion release were followed spectrophotometrically, conductometrically, and polarimetrically, using a Shimadzu QR-50 or RS-27 spectrophotometer, a Wayne-Kerr B221 conductivity bridge, and a Perkin-Elmer 141 photoelectric polarimeter coupled to a Zeiss 12 MM monochromator and a quartz iodine lamp, and in general they were reproducible to at least $\pm 5\%$. For some conductivity runs both bright and platinized electrodes were used, but no difference in rate was observed. For the aquation of the β -dichloro ion a precision conductance bridge (Leeds and Northrup, Jones Dyke) reading from 0 to 10,000 (± 0.001) ohms was used. In a typical run the total resistance change was from 3954.40 to 3699.37 ohms and the resistance measurements were accurate to better than 0.01 ohm. The temperature of the oil bath for the conductance measurements was controlled to $\pm 0.001^\circ$. Several cells with different cell constants (0.24, 1.87, 11.1, and 27.7 cm⁻¹) were employed with the different acid and complex concentrations to give the most convenient resistance change.

The reactions with Hg²⁺ ion were carried out in a stopped-flow reactor⁶ and followed spectrophotometrically. Adjustments to keep the ionic strength constant were made with NaClO₄ and, whenever possible, light was excluded.

Results

The rates of release of the Cl⁻ ion from the *trans*- and the α - and β -dichloro isomers were followed conductometrically, polarimetrically, and spectrophotometrically in aqueous acid solutions, and the results

(1) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).
 (2) A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).
 (3) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).

(4) S. Yoshikawa, T. Sekihara, and M. Goto, *ibid.*, **6**, 169 (1967).
 (5) D. A. Buckingham, P. A. Marzilli, A. M. Sargeson, S. F. Mason, and P. G. Beddoe, *Chem. Commun.*, 433 (1967).
 (6) Y. Inoue and D. D. Perrin, *J. Phys. Chem.*, **66**, 1689 (1962).

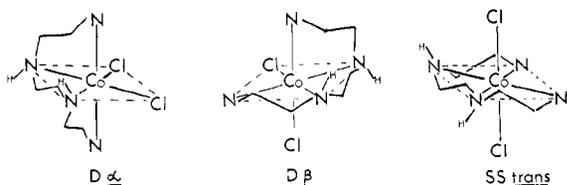


Figure 1.—Structure of the $[\text{Co}(\text{trien})\text{Cl}_2]^+$ isomers whose reactions are studied in this article.

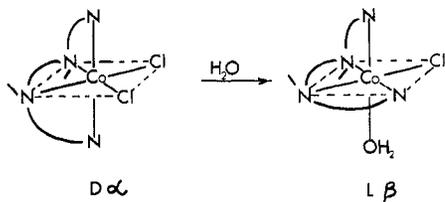


Figure 2.—A possible stereochance in the substitution of the $\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ ion.

are listed in Tables I-III. The rates were measured under various conditions of H^+ , ionic strength (μ), complex concentration ($[\text{Co}]$), and temperature.

TABLE I

RATE CONSTANTS FOR THE AQUATION OF $(+)\text{}_{589}\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ TO $(+)\text{}_{589}\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$					
$[\text{H}^+]$, M	Temp, $^\circ\text{C}$	$10^3[\text{Co}]$, M	μ	10^4k , sec^{-1}	Method ^a
0.0001	25	1.0	0.001	1.52	C (G)
0.001	25	1.0	0.002	1.45	C (G or E)
0.001	25	0.2	0.001	1.60	S (G or E)
0.01	25	1.0	0.01	1.43	C (E)
0.01	25	0.2	0.01	1.56	S (G)
0.01	25	1.0	0.01	1.70	S (G)
0.01	25	2.0	0.01	1.56	P
				1.71	P
0.10	25	0.2	0.1	1.58	S (E)
1.0	25	0.2	1.0	1.52	S (G or E)
0.01	15	1.0	0.01	0.433	C (E)
0.01	32	1.0	0.01	3.66	P
0.01	35	1.0	0.01	4.83	C (G)
0.01	35	1.0	0.01	5.28	S (E)
0.01	40	1.0	0.01	9.00	S (G)
0.01	40	1.5	0.01	8.66	P

^a C = conductivity; S = spectrophotometry; P = polarimetry. (G) = Guggenheim method used to plot the rate data: E. A. Guggenheim, *Phil. Mag.*, 2, 538 (1926). (E) = experimental infinity reading used.

$(+)\text{}_{589}\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$.—The rate of Cl^- release to give the $(+)\text{}_{589}\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ ion as measured conductometrically was the same as that followed spectrophotometrically (Figure 3) and polarimetrically⁷ and k_α was essentially independent of H^+ (for the range $1.0 > [\text{H}^+] > 10^{-4} M$), μ , and $[\text{Co}]$. The rate constant obtained for this isomer agreed with that reported previously.⁸ The aquation was shown to take place with full retention of configuration and activity by converting the chloroaquo product to the $(+)\text{}_{589}\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{CO}_3]^+$ ion whose optical purity was established by an independent resolution.¹

(7) The RD curves for the species discussed in this article are given in ref 1.
(8) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 59, 304 (1955).

TABLE II

RATE CONSTANTS FOR THE AQUATION OF $(+)\text{}_{589}\text{-}\beta\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ TO $(+)\text{}_{589}\text{-}\beta\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$					
$[\text{H}^+]$, M	Temp, $^\circ\text{C}$	$10^3[\text{Co}]$, M	μ	10^4k , sec^{-1}	Method
0.0001	25	1.0	0.001	1.13	C (G)
0.0001	25	0.3	0.0004	2.01	S (G)
0.001	25	1.0	0.002	1.10	C (G)
0.001	25	0.2	0.001	1.48	S (G or E)
0.001	25	2.0	0.092	1.68	S (E)
0.01	25	1.0	0.011	1.46	C (G)
0.01	25	2.0	0.012	1.42	C (G)
0.01	25	2.0	0.012	1.37	C (G) ^a
0.01	25	0.3	0.010	1.45	S (G or E)
0.01	25	2.0	0.092	1.43	S (E)
0.01	25	1.0	0.011	1.53	P (E)
0.1	25	0.2	0.10	1.48	S (E)
1.0	25	0.2	1.0	1.45	S (E)
0.01	5	1.0	0.011	0.100	C (G)
0.01	15	2.0	0.012	0.393	C (G)
0.01	30	0.4	0.010	2.46	S (G or E)
0.01	35	1.0	0.011	4.33	C (G)
0.01	35	2.0	0.012	3.83	C (G)

^a Bright Pt electrodes.

TABLE III

RATE CONSTANTS FOR THE AQUATION OF $\text{trans-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ TO $\beta\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$					
$[\text{H}^+]$, M	Temp, $^\circ\text{C}$	$10^3[\text{Co}]$, M	μ	10^4k , sec^{-1}	Method
0.01	5.4	1.0	0.01	1.62 (mean)	S (E) ^a
0.01	5	0.15	0.01	1.50	S (E)
0.01	10	0.15	0.01	3.25	S (E)
0.01	18	0.2	0.01	12.00	S (E)
0.0001	25	0.4	0.0005	39.7	S (E)
0.001	25	0.2	0.001	34.8	S (E)
0.01	25	1.0	0.01	35.5	S (E)
				35.3	
				34.7	
0.01	25	0.3	0.01	34.2	S (E)
0.01	25	1.0	0.01	35.0	C (G)
0.10	25	1.0	0.10	31.8 (mean)	S (E)
		0.1			
1.0	25	1.0	1.0	25.5 (mean)	S (E)
		0.2			

^a $\text{trans-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot\text{H}_2\text{O}$.

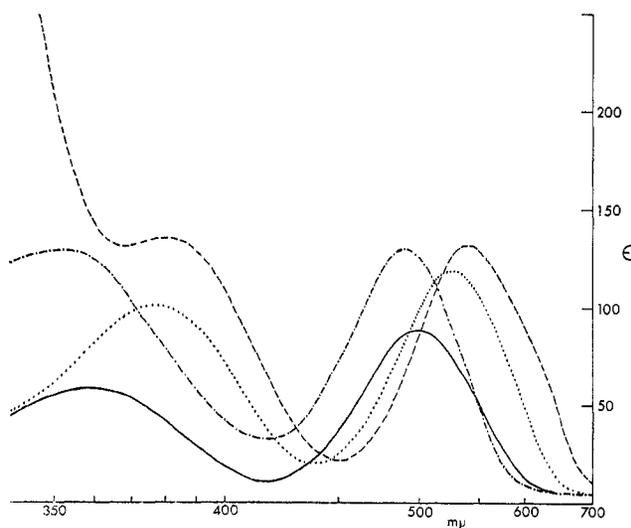


Figure 3.—Spectral changes for the aquation of $\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ (---), $\alpha\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ (·····), and $\alpha\text{-}[\text{Co}(\text{trien})(\text{OH}_2)_2]^{3+}$ (—) and equilibrium spectrum (- · - ·) ($10^{-2} M \text{HClO}_4$).

The α -dichloro ion has a twofold axis of symmetry (Figure 1) which makes both coordinated Cl^- ions equivalent and only one rate was observed for the subsequent aquation of the α - $[\text{Co}(\text{trien})\text{Cl}(\text{OH}_2)]^{2+}$ ion, Table IV. Linear plots of $\log(D - D_\infty)$, $\log(\alpha - \alpha_\infty)$, and $\log[1/R - 1/R_\infty]$ vs. time were obtained over at least 3 half-lives for the optical density (D), rotation (α), and conductance plots ($1/R$), respectively. Little or no interference occurred from the subsequent reaction of the chloroaquo ion for $[\text{H}^+] > 10^{-3} M$ and the aquation of the first Cl^- ion was $>98\%$ complete, under the conditions used. The observed activation energy was 21.5 ± 0.4 kcal/mole and the entropy of activation was -5.8 ± 1.4 eu.

[H ⁺], M	Temp, °C	10 ³ [Co], M	[NaClO ₄], M	μ	10 ³ k , sec ⁻¹	Method
0.0102	35	1.0		0.013	3.50	C (G or E)
0.0102	35	1.0	0.088	0.1	2.23	P
0.00102	35	1.0	0.097	0.1	4.62	P
1.02	40	1.0		1.0	4.18	P
0.102	40	1.0		0.1	3.83	P
0.0102	40	1.0	0.088	0.1	4.32	P
					4.65	S
0.0102	40	2.0		0.016	7.8	C (G)
0.0051	40	1.0	0.092	0.1	5.00	P
0.00204	40	1.0	0.092	0.1	6.47	P
0.00102	40	1.0	0.097	0.1	9.85	P
					9.10	S
0.0102	45	1.0	0.087	0.1	8.18	P
0.00102	45	1.0	0.096	0.1	21.0	P

(+) $_{\text{SS}}\alpha$ - $[\text{Co}(\text{trien})\text{Cl}(\text{OH}_2)]^{2+}$ Ion.—The aquation rate constants for the α -chloroaquo ion are listed in Table IV for a variety of conditions, and it can be seen that the rate constants are dependent on $[\text{H}^+]$, temperature, and ionic strength. Aquation was followed spectrophotometrically (Figure 3), polarimetrically, and conductometrically and agreement between all three methods was obtained. The α -chloroaquo ion aquated to the α -diaquo species substantially with retention of activity and configuration, but some subsequent isomerization of α -diaquo to β -diaquo was observed. The latter reaction interfered with the measurement of the α -diaquo \rightleftharpoons α -chloroaquo equilibrium constant and its value was not established conclusively. Moreover, the retention experiments for the aquation are tied to the isomerization and racemization of the diaquo ions and they will be discussed in detail along with the aquo species in a later publication.

The $[\text{H}^+]$ dependence for the aquation of the α -chloroaquo ion when $0.1 > [\text{H}^+] > 0.001 M$ allows a rate law of the form

$$k_{\text{obsd}} = k_{\text{H}_2\text{O}} + \frac{k_{\text{OH}}K_a}{[\text{H}^+]}$$

where the two paths are equated to hydrolysis of the chloroaquo ($k_{\text{H}_2\text{O}}$) and the chlorohydroxo ($K_a k_{\text{OH}}$) ions. At 40° and $\mu = 0.1$, $k_{\text{H}_2\text{O}} = 3.77 \times 10^{-6} \text{ sec}^{-1}$ and $K_a k_{\text{OH}} = 6.15 \times 10^{-9} M \text{ sec}^{-1}$, and it is evident that

in the $[\text{H}^+]$ region studied, the major reaction path is due to aquation of the aquo species except for the most dilute acid ($10^{-3} M$). The dissociation constant K_a could not be measured at 40° but was obtained at 10° ($\text{p}K_a = 7.46 \pm 0.02$) and 20° ($\text{p}K_a = 7.11 \pm 0.02$) at $\mu = 0.1$.⁹ A linear plot of $\text{p}K_a$ vs. $1/T$ was assumed which gave $\Delta H_a = 13.2$ kcal/mole and $\text{p}K_a = 6.48$. Linear plots of $\log k$ vs. $1/T$ were obtained for the separated rate constants of the two paths in the range 35 – 45° . The activation energies for the two reaction paths are $E_{\text{obsd}} = 24.1 \pm 0.3$ kcal/mole for the aquo path and $E_{\text{obsd}} = 32.6 \pm 0.3$ kcal/mole for the acid-dependent path. The latter reduces to 19.4 kcal/mole when allowance is made for the temperature dependence of K_a .

(+) $_{\text{SS}}\beta$ - $[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$.—The rate of hydrolysis of Cl^- was followed conductometrically, polarimetrically,¹ and spectrophotometrically (Figure 4), and linear

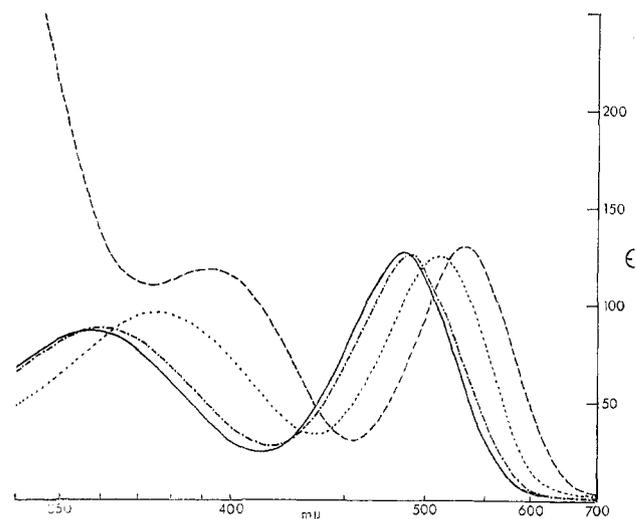


Figure 4.—Spectral changes for the aquation of β -SS- $[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ (---), β -SS- $[\text{Co}(\text{trien})\text{Cl}(\text{OH}_2)]^{2+}$ (····), and β -SS- $[\text{Co}(\text{trien})(\text{OH}_2)_2]^{3+}$ (—) and equilibrium spectrum (— · — ·) ($10^{-2} M \text{ HClO}_4$).

plots of $\log(D - D_\infty)$, $\log(\alpha - \alpha_\infty)$, and $\log[(1/R) - 1/R_\infty]$ vs. time were obtained over at least 2 half-lives for $1.0 > [\text{H}^+] > 10^{-3} M$. The rate constants are given in Table II and they agree within the order of accuracy for the different methods. The aquation to the chloroaquo species took place with full retention of geometrical configuration and activity¹ and was more than 98% complete under the conditions used. The degree of retention was established by allowing the chloroaquo species to react with HCO_3^- ion to give active β - $[\text{Co}(\text{trien})\text{CO}_3]^+$, a reaction which is known to occur with full retention of configuration.¹ The activation parameters for this ion were determined as $E_a = 21.1 \pm 0.4$ and $\Delta S^\ddagger = -2.7 \pm 1.4$ eu.

(+) $_{\text{SS}}\beta$ - $[\text{Co}(\text{trien})\text{Cl}(\text{OH}_2)]^{2+}$ Ions.—The two coordinated Cl^- ions are not equivalent in the β -dichloro complex and the rate constant measured is a composite one. The constants for each Cl^- ion were evaluated by

(9) C. J. Hawkins, A. M. Sargeson, and G. H. Searle, *Australian J. Chem.*, **17**, 598 (1964).

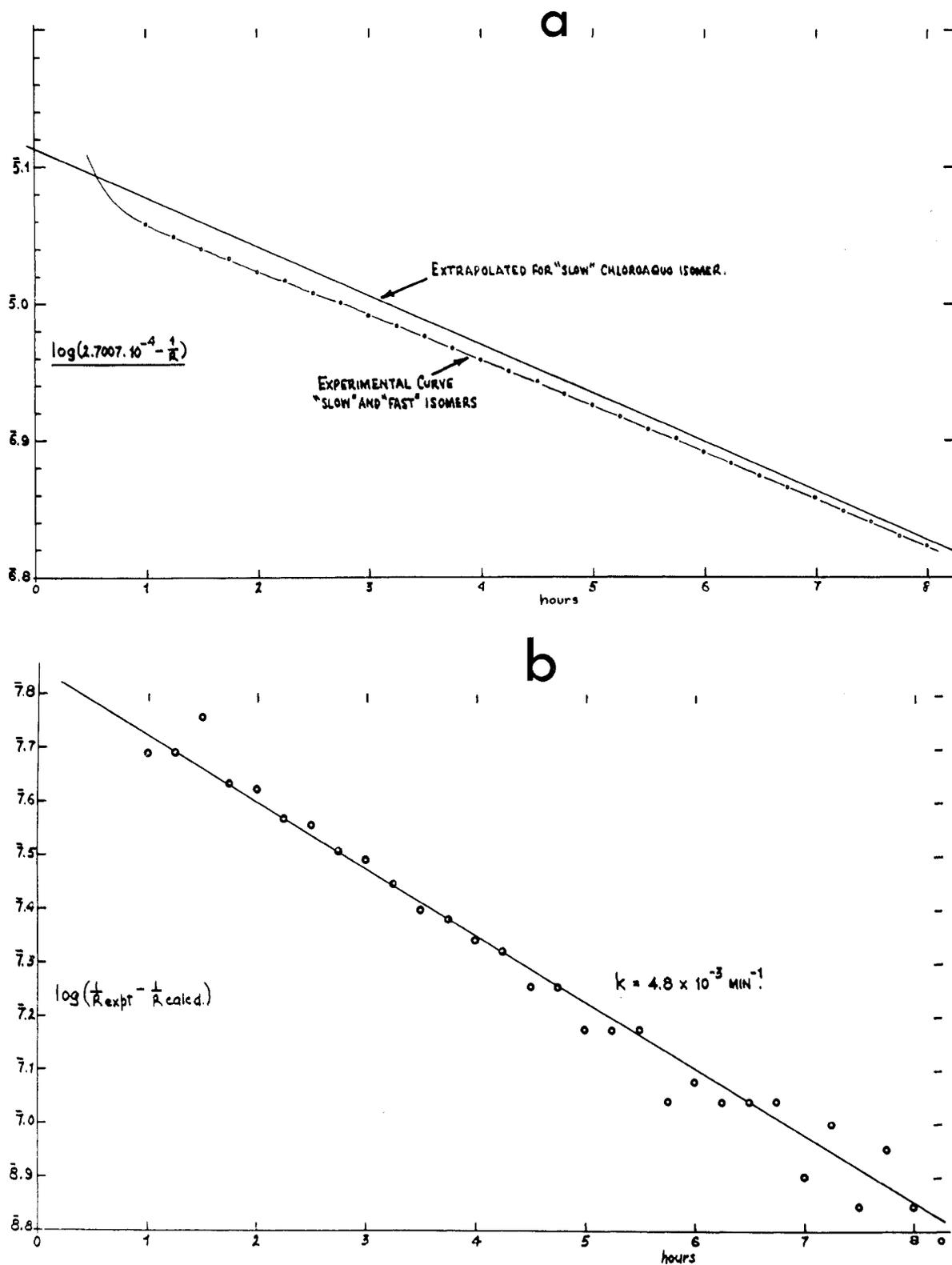


Figure 5.—(a) Expanded plot for the aquation of "slow" and "fast" β -chloroaquo isomers ($[\text{HClO}_4] = 10^{-2} M$, $[\text{Co}] = 2 \times 10^{-3} M$, $\mu = 0.01$, temperature 25°). (b) Guggenheim plot for the aquation of the "fast" β -chloroaquo isomer.

following the rates of release of Cl^- from the two β -chloroaquo species produced by the initial aquation. This was achieved with an accurate conductivity bridge and evidence for the presence of the two chloroaquo species was also obtained by following the rate spectrophotometrically. The conductivity method measured the rate of approach to the chloroaquo-diaquo

equilibrium and in all experiments the conductance reached a steady value. A typical plot of $\log [(1/R_\infty) - (1/R_t)]$ against t is given in Figure 5a. The initial steep slope of the aquation of the first Cl^- ion is not shown, but the extrapolated final linear plot for the aquation of the second Cl^- ion from the "slow" β - $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ isomer is given along with the experi-

mental curve. After the time required for essentially complete aqutation of the first Cl^- ion (~ 1 hr) the increase in conductance beyond that due to the aqutation of the "slow" chloroaquo species is due to the aqutation of a small amount of the "fast" chloroaquo species. The rate constant for the "fast" isomer was evaluated by determining the conductance change between the extrapolated line and the experimental conductance change. The results are plotted by the method due to Guggenheim¹⁰ in Figure 5b and clearly give a linear plot. This procedure was reproducible owing to extremely accurate resistance measurements ($10,000 \pm 0.001$ ohms).

The amount of "fast" isomer was estimated by taking the ratio of the maximum difference between the experimental and calculated chloroaquo conductance to the total conductance of $\beta\text{-[Co(trien)Cl(OH}_2\text{)]ClO}_4$. The proportion of "fast" isomer and rate constants for its aqutation under different conditions are given in Table Va. A similar but less accurate analysis of the amount of "fast" isomer produced was obtained from the spectrophotometric results. The optical density at the time of essentially complete aqutation of the first Cl^- ion ($7t_{1/2}$) is larger than the extrapolated value from the "slow" isomer aqutation. The amounts of "fast" isomer estimated at this stage are given in Table Vb, and they agree substantially with the results obtained conductometrically.

TABLE V

THE PROPORTION OF AND RATE CONSTANTS FOR THE AQUTATION OF THE "FAST" *cis*- $\beta\text{-[Co(trien)Cl(OH}_2\text{)]}^{2+}$ ISOMER FORMED DURING THE AQUTATION OF $\beta\text{-[Co(trien)Cl}_2\text{]ClO}_4^a$

(a) Conductometric Values			
[H ⁺], M	Temp, °C	10 ⁴ k, sec ⁻¹	% of "fast" isomer obsd
0.0102	15	0.37	1.1
0.0102	25	0.83	4.8
0.0102	25	0.80	2.8
0.0102	35	8.3 ^b	1.8
0.0102	35	10.0	0.9
(b) Spectrophotometric Values			
[H ⁺], M	Temp, °C	% of "fast" isomer obsd	
0.01	25	3.1	
0.05	40	1.7	
0.10	40	1.8	
1.0	40	1.7	

^a [Co] = 2×10^{-3} M; $\mu = 0.016$. ^b [Co] = 10^{-3} M; $\mu = 0.013$.

The aqutation rates showed a small dependence on ionic strength as μ was increased from 0.01 to 0.18 (Table VI) but there was negligible dependence on [Co]. Agreement between the conductometric, spectrophotometric, and polarimetric rate constants was observed, and there was no catalysis by the platinized electrodes.

The data in Table VI fit a rate law for the aqutation of the "slow" $\beta\text{-[Co(trien)Cl(OH}_2\text{)]}^{2+}$ isomer of the form

$$k_{\text{obsd}} = k_{\text{H}_2\text{O}} + \frac{k_{\text{OH}}K_a}{[\text{H}^+]}$$

The two paths are attributed to the aqutation of the "slow" β -chloroaquo ($k_{\text{H}_2\text{O}}$) and the chlorohydroxo ($K_a k_{\text{OH}}$) ions in the region $10^{-3} < [\text{H}^+] < 0.1$ M. At 40° and $\mu = 0.1$, $k_{\text{H}_2\text{O}} = 1.8 \times 10^{-5}$ sec⁻¹ and $k_{\text{OH}}K_a = 1.62 \times 10^{-6}$ M sec⁻¹, and it is apparent that at $[\text{H}^+] = 0.101$ M and $\mu = 0.1$ both paths contribute approximately equal amounts. However, at $[\text{H}^+] = 10^{-3}$ M and $\mu = 0.1$, the chlorohydroxo path is almost exclusively dominant. The paths at 35, 40, and 45° were separated and linear plots of $\log k$ vs. $1/T$ were obtained for both paths. The activation parameters for the two paths are $E_a(\text{H}_2\text{O})_{\text{obsd}} = 27.0 \pm 0.8$ kcal/mole and $E_a(\text{OH})_{\text{obsd}} = 30.4 \pm 0.4$ kcal/mole. As for the α isomer the K_a values for the coordinated water molecule were obtained at 10° ($\text{p}K_a = 6.2 \pm 0.1$) and 20° ($\text{p}K_a = 5.9 \pm 0.1$) at $\mu = 0.1$ ⁹ and were extrapolated to the higher temperatures assuming $\log K_a$ vs. $1/T$ was linear. The enthalpy change, $\Delta H = 11$ kcal/mole, calculated from these values is less accurate than but similar to that obtained for the α isomer and it leads to an activation energy for the chlorohydroxo path of 19 ± 4 kcal/mole. The uncertainty in this last value arises largely from the degree of error in the K_a measurements.

TABLE VI

RATE CONSTANTS FOR THE AQUTATION OF (+)₅₈₉- $\beta\text{-[Co(trien)Cl(OH}_2\text{)]}^{2+}$ "SLOW" OR MAJOR ISOMER TO (+)₅₈₉- $\beta\text{-[Co(trien)(OH}_2\text{)]}^{3+}$ ([Co] = 2×10^{-3} M)

[H ⁺], M	Temp, °C	μ	10 ⁴ k, sec ⁻¹	Method
0.0102	15	0.016	0.0305	C (G)
0.0102	25	0.09	0.168	S
0.0102	25	0.016	0.220	S
0.0102	25	0.016	0.240	C (E)
0.0102	25	0.016	0.228	C (E)
0.0102	25	0.013	0.215	P ^b
0.00102	25	0.09	1.19	S
0.00102	25	0.004	1.67	C (E) ^a
0.101	35	0.107	0.166	P
0.0505	35	0.101	0.227	P
0.0101	35	0.101	0.830	P
0.0102	35	0.09	0.863	S
0.0102	35	0.013	1.30	C (E) ^a
0.0102	35	0.016	1.17	C (E)
0.0051	40	0.09	3.40	S
0.00204	40	0.09	7.67	S
0.0102	40	0.09	13.6	S
0.0102	40	0.183	1.60	S
0.0102	40	0.089	1.83	S
0.0102	40	0.052	2.13	S
0.0102	40	0.033	2.28	S
0.0102	40	0.016	2.60	S
0.0102	40	0.09	1.95	S ^b
0.0101	40	0.101	1.78	P
0.051	40	0.10	0.505	S
0.0505	40	0.103	0.502	P
0.101	40	0.107	0.340	P
0.102	40	0.11	0.313	S
1.02	40	1.0	0.134	S
0.0101	45	0.100	3.88	P
0.0505	45	0.101	1.07	P
0.101	45	0.107	0.720	P
0.0102	50	0.09	9.05	S

^a [Co] = 10^{-3} M. ^b [Co] = 4×10^{-3} M.

(10) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

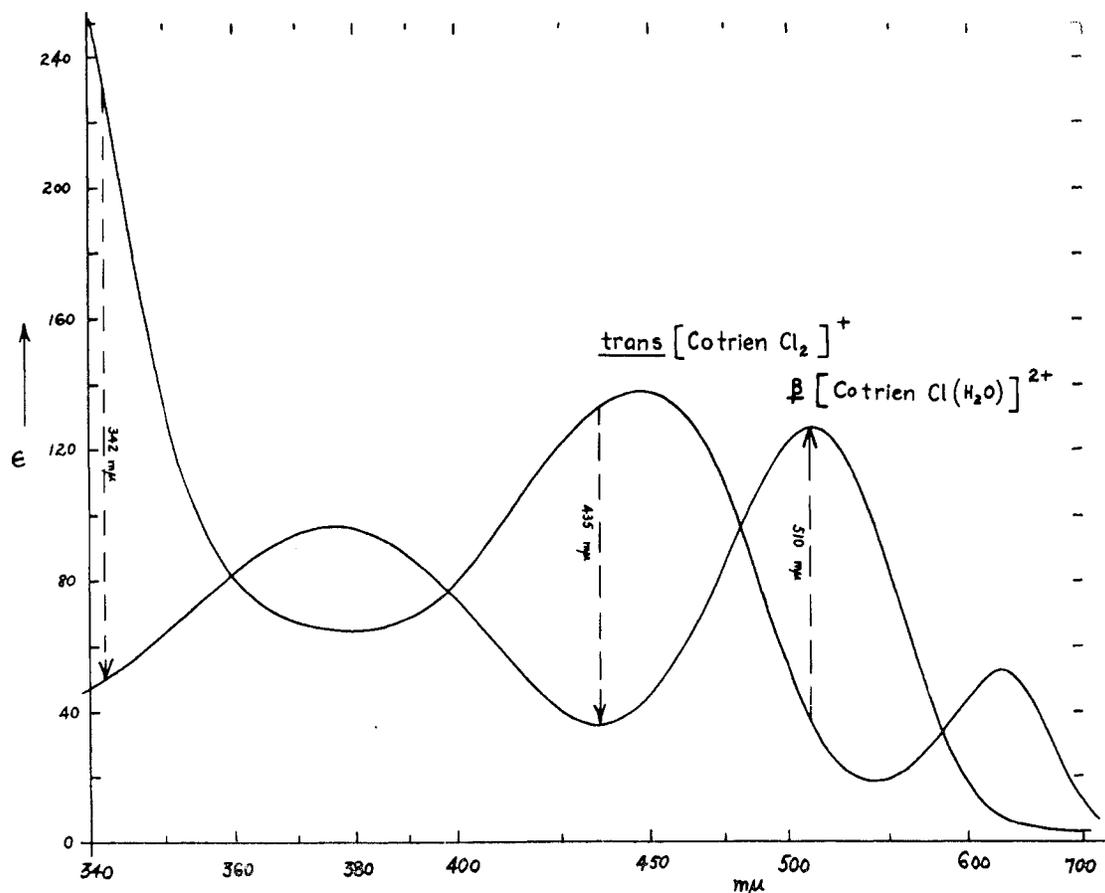


Figure 6.—Spectral change in the aquation of *trans*-SS- $[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ to β -SS- $[\text{Co}(\text{trien})\text{Cl}(\text{H}_2\text{O})]^{2+}$ ($10^{-2} M \text{HClO}_4$).

Isomerization and Equilibrium Measurements for the Chloroaquo Aquations.—During the aquation reactions some isomerization of the diaquo products occurred. The extent of these reactions during the aquation was measured by treating aliquots of the reaction mixture with NaHCO_3 at the beginning and end ($\sim 5t_{1/2}$) of each aquation run. From the absorption of the carbonato ions produced ($505 \text{ m}\mu$) and the molar absorptivities of the carbonato isomers ($\epsilon_\alpha 120 \pm 1$, $\epsilon_\beta 180 \pm 1$) the degree of isomerization was given by $\%(\alpha \rightarrow \beta) = (\epsilon_{\text{obsd}} - 120)/(180 - 120)$. The amounts were large for the α isomer but were undetected for the β isomer.

The equilibrium positions for the reaction



were evaluated spectrophotometrically at $520 \text{ m}\mu$ (Figure 3) where both diaquo isomers absorb equally ($\epsilon 77 \pm 2$). An estimate for the α system ($\epsilon_{520} 94 \pm 2$) gave $80 \pm 10\%$ diaquo and $20 \mp 10\%$ α -chloroaquo species.

Owing to the absence of isomerization, the β system was studied more successfully. The equilibrium spectrum (Figure 4) was independent of temperature (25 – 45°) and $[\text{H}^+]$ ($0.001 < [\text{H}^+] < 0.1 M$). The molar absorptivity for the equilibrium mixture at $\lambda_{\text{max}} 487 \text{ m}\mu$ was 118.8 ± 0.4 , and, using $\epsilon_{487} 98 \pm 1$ for β -chloroaquo and $\epsilon_{487} 122 \pm 1$ for β -diaquo, the equilibrium position was calculated as $85 \pm 5\%$ β -diaquo and $15 \mp$

5% β -chloroaquo. The same value was also obtained at other wavelengths.

(\pm) -*trans*- $[\text{Co}(\text{trien})\text{Cl}_2]^+$.—The rates of aquation of the racemic *trans* isomer were followed, conductometrically and spectrophotometrically, under a variety of conditions for H^+ , μ , temperature, and complex concentration. The results are given in Table III. The rate of loss of Cl^- followed conductometrically was the same as the rate of spectrophotometric change and the spectrum of the product was identical with that of the β -chloroaquo ion, obtained from the β -dichloro isomer. The subsequent aquation of Cl^- ion from the β -chloroaquo product gave a rate constant equal to that for the "slow" β -chloroaquo isomer, both conductometrically (Table VII) and polarimetrically.³ Also no evidence was found for the presence of the "fast" β -chloroaquo species. The spectral changes for these reactions are shown in Figure 6. The activation parameters were determined as $E_a = 26.0 \pm 0.2$ and $\Delta S^\ddagger = +15.5 \pm 0.7 \text{ eu}$.

Hg^{2+} Ion Catalyzed Reactions.—It has been shown elsewhere that the Hg^{2+} -catalyzed aquation of Cl^- for the α - and β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ ion occurs rapidly and substantially with retention of geometrical configuration and activity.¹¹

The mercuric ion induced aquation of the *trans* isomer was followed with a stopped-flow reactor at 15° in $0.1 M$

TABLE VII

RATE CONSTANTS FOR THE AQUATION OF THE CHLORO-AQUO PRODUCT (β , "SLOW" ISOMER) DERIVED FROM $trans\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ ($[\text{H}^+] = 1.02 \times 10^{-2} M$)				
Temp, °C	[Co], M	μ	$10^3 k$, sec $^{-1}$	Method
25	0.001	0.013	2.43	C (E)
25	0.002	0.016	2.33	C (E)
30	0.002	0.016	5.38	C (E)
35	0.002	0.016	12.1	C (E)

HClO_4 . After rapid mixing of the $trans\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ and $\text{Hg}(\text{ClO}_4)_2$ solutions, a continuous record of the optical density indicated that a fast initial reaction ($k = 24 M^{-1} \text{sec}^{-1}$) first order in Hg^{2+} preceded a slower reaction, $k = 1.7 \pm 0.1 \times 10^{-3} \text{sec}^{-1}$ independent of the Hg^{2+} concentration.¹² The spectral changes involved in these reactions are given in Figure 7 and it is clear that the initial induced aquation gives substantially $trans\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$, probably contaminated with some β -chloroaquo ion. The subsequent spectral change was due to isomerization of $trans \rightarrow \beta$ -chloroaquo ion complicated toward the end of the reaction by the Hg^{2+} -induced aquation of the second Cl^- ion. The rate constants for the isomerization of $trans\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ were evaluated using the β -chloroaquo spectrum, Figure 4, as the infinity spectrum.

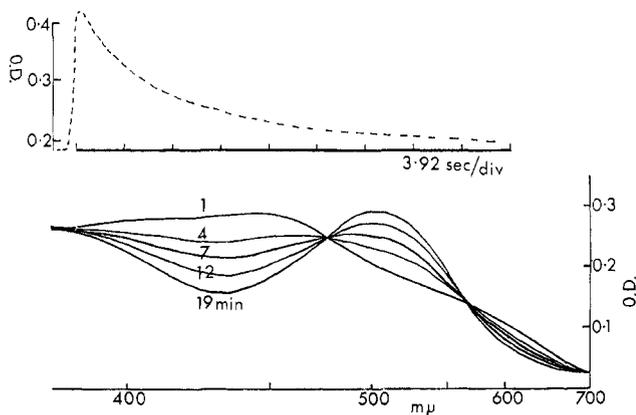


Figure 7.—Rate plot for the Hg^{2+} -induced aquation of $trans\text{-}SS\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{ClO}_4$ and the subsequent isomerization of $trans\text{-}SS\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ to $\beta\text{-}SS\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$.

Discussion

The rates were followed by the different methods to show the correspondence between the release of Cl^- (conductivity), the spectral change, and the mutarotation. These procedures permit an evaluation of the degree of isomerization and retention of activity in the products since the optical properties and purity of these species have been established.¹⁻³ All three methods measure the rate of approach to equilibrium, but for the aquation of the first Cl^- ion this is essentially the rate of the forward reaction. The forward and reverse rate constants for the second step have not been separated and this aspect of the results will be discussed in a subsequent communication.

The α -dichloro ion aquated to α -chloroaquo with

(12) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963).

full retention of configuration and activity within the accuracy of the measurements, Figure 8. Although this result precludes the possibility of an edge displacement as depicted in Figure 2, it does not exclude the possibility that the entering H_2O displaces Cl^- along an edge and eliminates the distant Cl^- from the coordination sphere. The same process is feasible in the $cis\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ ion which also aquates with full retention of activity and cis configuration.¹³ The C_2 symmetry of these ions does not allow this process to be detected, but experiments are in progress on less symmetrical complexes to determine if such shifts do take place.

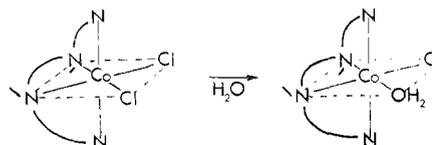


Figure 8.—Observed stereochemical course of the aquation of $D\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ to $D\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$.

The nonequivalent Cl^- ions in the β -dichloro complex give a composite rate for the first aquation step. However, the rates of aquation for the two sites were evaluated from this composite rate and the subsequent aquation rates of the chloroaquo isomers produced assuming that the two products do not arise from rearrangement in the course of the reaction. The aquation occurred with full retention of activity and $cis\text{-}\beta$ configuration, and the proposed reaction scheme is shown in Figure 9.

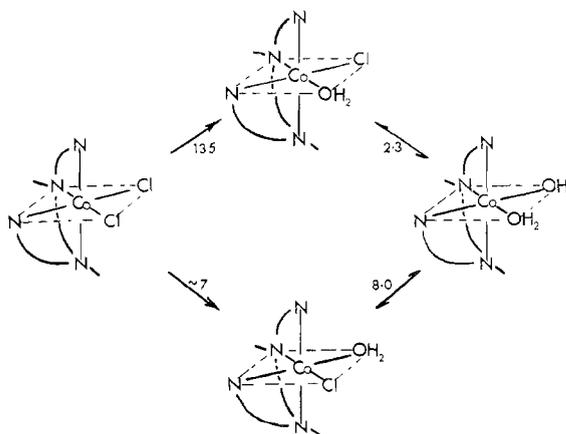


Figure 9.—Observed stereochemical course of the aquation of $D\text{-}\beta\text{-}SS\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ to the two $\beta\text{-}SS\text{-}[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ isomers (rate constants $\times 10^3 \text{sec}^{-1}$ at 25° , $[\text{HClO}_4] = 0.0102 M$, $[\text{Co}] = 2 \times 10^{-3} M$, $\mu = 0.012$).

There is one major path (96%) for the aquation of the first Cl^- ion and we have chosen the chloride ion cis to one $sec\text{-NH}$ and $trans$ to the other as the more labile of the two. This choice is not arbitrary but is related to the mode of aquation of $trans\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ which will be discussed shortly. The minor "fast" chloroaquo isomer produced then has the struc-

(13) J. P. Mathieu, *Bull. Soc. Chim. France*, [5] **4**, 687 (1937).

ture shown, Figure 9, where the chloride ion is *cis* to one *sec*-NH and *trans* to the other, while the "slow" chloro-aquo isomer has the Cl^- ion *cis* to both *sec*-NH groups. The difference in reactivity between the chloro-aquo species is approximately a factor of 3 and the concentration of the rapidly reacting isomer is always small (<5%).

The results for the α - and β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ ions are similar to those obtained for *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. They aquate with full retention of geometrical configuration and activity, with rate constants $k_{\text{Cl}_1} = 1.56 \times 10^{-4}$ and $1.45 \times 10^{-3} \text{ sec}^{-1}$ at 25° ($10^{-3} \leq [\text{H}^+] \leq 1.0 \text{ M}$) for the α and β ions, respectively, compared with $k_{\text{Cl}_1} = 2.5 \times 10^{-4} \text{ sec}^{-1}$ at 25° for *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. The activation energies for these species are 21.5 ± 0.4 , 21.1 ± 0.4 , and 22 kcal/mole , respectively, so that the difference in rates for the α and β isomers resides substantially in the entropy term: α , -5.8 ± 1.4 ; β , $-2.7 \pm 1.4 \text{ cal deg}^{-1} \text{ mole}^{-1}$. This might be ascribed to the degree of hydration in the transition state for the two ions; from an examination of the Dreiding or Leybold models of these species, it is conceivable that the α species might be more readily solvated than the β in the vicinity of the coordinated Cl^- ions. The full retention observed in these reactions is consistent either with some degree of bond making by water *cis* to the coordinated Cl^- ion or with the aquation of a five-coordinate square-pyramidal intermediate. For the NO^+ - and Hg^{2+} -induced aquation reactions of azido and halo $\text{Co}(\text{III})$ complexes in general there is evidence for intermediates of reduced coordination number,^{11,14-20} and in particular for $[\text{Co}(\text{en})_2\text{ClN}_3]^+$ and $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ there is evidence for the existence of a common intermediate, $[\text{Co}(\text{en})_2\text{Cl}]^{2+}$,^{11,19,20} which reacts to give substantial rearrangement. This is at variance with the full retention of configuration observed for the spontaneous aquation of *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$,¹³ although it is still possible that the last reaction could occur *via* a different intermediate. However, in those instances where evidence for intermediates exists, competition for the intermediate between H_2O and anions in the solvent water is observed.¹⁴⁻¹⁶ For the spontaneous aquations, aquation by another anion occurs *via* the aquated complex and not synchronously with the entry of water.^{21,22} Additional evidence for some involvement of water in the transition states for the aquation of $\text{Co}(\text{III})$ halo complexes might also be inferred from the linear free energy relationship found for the aquation of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ions ($\text{X} = \text{F}, \text{H}_2\text{PO}_4, \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$),²³ although it appears to be small.

(14) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

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

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

(17) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, **20**, 597 (1967).

(18) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **4**, 1032 (1965).

(19) D. A. Loeliger and H. Taube, *ibid.*, **5**, 1376 (1966).

(20) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **6**, 1807 (1967).

(21) F. Basolo, B. D. Stone, and R. G. Pearson, *J. Am. Chem. Soc.*, **76**, 3079 (1954).

(22) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

(23) C. H. Langford, *ibid.*, **4**, 265 (1965).

trans- $[\text{Co}(\text{trien})\text{Cl}_2]^+$ aquates at the same rate as the "slow" β - $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ product is formed. Moreover, it has been shown that the optically pure *trans* isomer gives the optically pure "slow" β -chloro-aquo ion.³ The last reaction decides the orientation of the *sec*-NH's in the β -chloro-aquo isomer as that depicted in Figure 10. We propose that the mechanism of the aquation requires some degree of bond making by H_2O at the face of the octahedron with concomitant edge displacement of the terminal NH_2 of the multidentate. For the configuration of the *trans* isomer in Figure 10 the bridge movement must take place in the direction shown, since assumption of the other β configuration requires racemization at the asymmetric *sec*-N. It has been shown moreover that the *sec*-N protons are preserved during the isomerization and that activity is fully retained.³

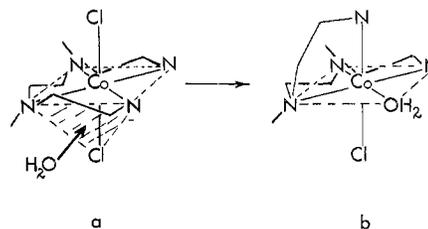


Figure 10.—Proposed $\text{S}_{\text{N}}2$ mechanism for the aquation of *trans*- SS - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ to β - SS - $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$.

Other possibilities which arise are the formation of a five-coordinate intermediate and the possible rapid rearrangement of *trans*- $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ which could be formed in the initial aquation step but is not observed. The latter possibility was eliminated by following the rearrangement of *trans*- $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ formed by treating *trans*- $[\text{Co}(\text{trien})\text{Cl}_2]^+$ with Hg^{2+} . The *trans*-chloro-aquo ion rearranges too slowly for the spontaneous aquation to occur by this pathway. A maximum of 20% *trans*-chloro-aquo ion would be formed under these circumstances, an amount which would be readily detected by the methods used. In addition, considerable evidence has now been collected to indicate that the Hg^{2+} -assisted aquations give rise to a five-coordinate intermediate,^{11,15,16,19,20} and in this instance the intermediate reacts to produce largely *trans*- $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ ion. It follows that the spontaneous aquation cannot occur through this five-coordinate intermediate and the possibility of other intermediates seems remote, since there was no competition by external NO_3^- or HSO_4^- ions during the spontaneous aquation. There appears then to be good evidence for some bond making by water in the manner described in Figure 10.

The position of Cl^- in the "slow" β - $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ isomer is crucial for this analysis of the results and an X-ray crystallographic analysis of β - $[\text{Co}(\text{trien})\text{ClOH}_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ shows that the structure is that depicted in Figure 10b ($R = 0.18$ unrefined).²⁴

The stereospecific aquation of *trans*- $[\text{Co}(\text{trien})\text{Cl}_2]^+$

(24) D. A. Buckingham, H. C. Freeman, I. A. Maxwell, and A. M. Sargeson, preliminary results.

differs from the steric course of aquation of $\text{trans-[Co(en)}_2\text{Cl}_2\text{)]}^+$ which gives 65% *trans*- and 35% *cis*- $[\text{Co(en)}_2\text{ClOH}_2]^{2+}$.²⁵ The respective activation energies for the two reactions are 26.0 and 26.7 kcal/mole²⁶ and the rate difference therefore resides substantially in the entropy term.

The relative rates of aquation of the α - and β -dichloro isomers might also be considered in conjunction with the rates for the series *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, *cis*- $[\text{Co(en)}(\text{NH}_3)_2\text{Cl}_2]^+$, *cis*- $[\text{Co(en)}_2\text{Cl}_2]^+$, and $[\text{Co}(\text{trien})\text{Cl}_2]^+$.⁸ For this series the rates decreased with increasing chelation and it was argued⁸ that the increase in size of the ion decreased the stability of the transition state because it became less efficiently solvated. Clearly the rate for the β isomer does not fit this pattern and it would seem that this explanation is not valid. Possibly the explanation offered earlier for the difference in reactivity of the α - and β -dichloro ions also applies for the rest of the series quoted, but there are not sufficient data available to check this proposition.

A similar pattern was observed for the aquations of

(25) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

(26) S. C. Chan, *Australian J. Chem.*, **20**, 595 (1967).

the α - and β - $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ ions by both the chloroaquo and the chlorohydroxo paths; both aquations occur largely with retention of configuration by the two paths. Of the two β -chloroaquo geometrical isomers, substantial data have been obtained only for the "slow" isomer. When this is compared with the results for the α -chloroaquo ion, it is apparent that the β isomer reacts about 5 times faster than the α form. For the chlorohydroxo paths however, the β isomer is more reactive than the α form by approximately a factor of 20.

The *trans*- $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ ion isomerized stereospecifically to the "slow" β - $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ ion and it has been shown elsewhere³ that (+)₅₈₉-*trans*- $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$ generated from optically pure (+)₅₈₉-*trans*- $[\text{Co}(\text{trien})\text{Cl}_2]^+$ isomerized to optically pure (+)₅₈₉- β - $[\text{Co}(\text{trien})\text{ClOH}_2]^{2+}$. This rearrangement has not been studied in detail yet, but it seems likely that the rearrangement is independent of $[\text{H}^+]$ like that for the *trans*- $[\text{Co(en)}_2\text{ClOH}_2]^{2+}$ ion, and there is some interest to see if it occurs with each act of water exchange. These factors along with the isomerization and racemization of the diaquo species and the degree of retention in the aquation of the chloroaquo ions will be considered in subsequent publications.

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Ligand Redox Studies. I. The Oxidation of Isothiocyanatopentaamminecobalt(III) Ion by Aqueous Hydrogen Peroxide¹

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The oxidation of isothiocyanatopentaamminecobalt(III) ion, $(\text{H}_3\text{N})_5\text{CoNCS}^{2+}$, by H_2O_2 in acidic solution yields Co^{3+} , $\text{Co}(\text{NH}_3)_6^{3+}$, HCN , CO_2 , and HSO_4^- with an acid-dependent stoichiometry for the cobalt, carbon, and nitrogen products. The rate law is of the form $d[(\text{H}_3\text{N})_5\text{CoNCS}^{2+}]/dt = k_2[\text{H}_2\text{O}_2][(\text{H}_3\text{N})_5\text{CoNCS}^{2+}]$ with k_2 dependent on acidity and on buffer concentration in bisulfate-sulfate buffers. The principal feature of the mechanism deduced from these results is the existence of a partially oxidized intermediate which can undergo either an *intramolecular* redox reaction with the Co(III) center or an acid-dependent hydrolysis. The oxidation rate is somewhat slower than for the free thiocyanate ion and the acid-dependent path relatively less important.

Introduction

Werner carried out oxidation reactions on many thiocyanate complexes of cobalt(III).³ His observation that the complex containing five ammonia and one thiocyanate ligands could be oxidized in acidic solution to hexaamminecobalt(III) ion by oxidants containing no nitrogen (*e.g.*, Cl_2 , H_2O_2) established the *isothiocyanate*

(N-bonded) nature of these complexes. All of Werner's observations, including some in which aquation (or other substitution reaction) occurred at the thiocyanate site, were qualitative in nature, and no subsequent quantitative studies have appeared on the oxidation of inert thiocyanate complexes.

In this paper we report the results of detailed kinetic and stoichiometric studies on the hydrolytic oxidation of isothiocyanatopentaamminecobalt(III) ion by hydrogen peroxide. Despite the complexities encountered, it has been possible to establish the main features of the mechanism which include the participation of Co(III) in an intramolecular redox step.

(1) (a) Based in part on a thesis submitted by M. D. G. in partial fulfillment of the requirements for the degree of Master of Science in chemistry, Jan 1966; (b) supported in part by National Science Foundation research participation grants and in part by NSF-GP2664; (c) preliminary results presented at the 7th International Conference on Coordination Chemistry, Stockholm, 1962.

(2) To whom inquiries should be addressed.

(3) A. Werner, *Z. Anorg. Chem.*, **22**, 91 (1900); *Chem. Ber.*, **44**, 876 (1911); *Ann. Chem.*, **386**, 1 (1919).