DISUBSTITUTED COBALT(III) TRIETHYLENETETRAMINE COMPLEXES -
THEIR STEREOCHEMISTRY AND KINETICS OF AQUATION

A THESIS
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The work described in this thesis has been carried out by the candidate himself in the Biological Inorganic Chemistry Unit of the John Curtin School of Medical Research, under the supervision of Dr. A. M. Sargeson.

Signed,

[Signature]
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NOTATION FOR REPRESENTING OPTICAL ISOMERS

(+) and (-) refer to the signs of rotations in the Na\textsubscript{D} line. If the sign of rotation is given at another wavelength, then the wavelength appears as a subscript, i.e. (\(+\)\textsubscript{546}). Absolute configurations, represented by D or L, are made relative to the D(\(+\))[Co en\textsubscript{3}\textsuperscript{3+}] ion. Racemes are denoted by (\(+\)), dl or DL.

ABBREVIATIONS USED FOR LIGANDS

\begin{itemize}
  \item en = H\textsubscript{2}N-CH\textsubscript{2}-CH\textsubscript{2}-NH\textsubscript{2}, ethylenediamine C\textsubscript{2}H\textsubscript{8}N\textsubscript{2}, also represented by N-\(\equiv\)N.
  \item en-H = H\textsubscript{2}N-CH\textsubscript{2}-CH\textsubscript{2}-NH-
  \item pn = H\textsubscript{2}N-CH(CH\textsubscript{3})-CH\textsubscript{2}-NH\textsubscript{2}, propylenediamine
  \item dl-bn = H\textsubscript{2}N-CH(CH\textsubscript{3})-CH(CH\textsubscript{3})-NH\textsubscript{2}, dl-2,3-diaminobutane
  \item m-bn = "" , meso-2,3-diaminobutane
  \item i-bn = H\textsubscript{2}N-C(CH\textsubscript{3})\textsubscript{2}-CH\textsubscript{2}-NH\textsubscript{2}, 1,2-diaminobutane or isobutylenediamine
  \item dien = H\textsubscript{2}N-CH\textsubscript{2}-CH\textsubscript{2}-NH-CH\textsubscript{2}-CH\textsubscript{2}-NH\textsubscript{2}, diethylenetriamine
  \item trien = (H\textsubscript{2}N-CH\textsubscript{2}-CH\textsubscript{2}-NH-CH\textsubscript{2}-)\textsubscript{2}, triethylenetetramine C\textsubscript{6}H\textsubscript{16}N\textsubscript{4}, also represented by N-\(\equiv\)N-\(\equiv\)N-\(\equiv\)N
  \item tetraen = (H\textsubscript{2}N-CH\textsubscript{2}-CH\textsubscript{2}-NH-CH\textsubscript{2}-CH\textsubscript{2}-)\textsubscript{2}NH, tetraethylenepentamine
  \item tn = H\textsubscript{2}N-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}-NH\textsubscript{2}, trimethylenediamine
  \item dan = H\textsubscript{2}N-CH\textsubscript{2}-C(CH\textsubscript{3})\textsubscript{2}-CH\textsubscript{2}-NH\textsubscript{2}, 1,3-diamino-2,2-dimethylpropane
  \item cym = 1a,3a,5a-triaminocyclohexane
\end{itemize}
ox = "OOC-COO"\(^{-}\), oxalato C\(_{2}O_{4}\)\(^{2-}\)

mal = "OOC-C\(_{2}\)H\(_{2}\)COO"\(^{-}\), malonato C\(_{3}H_{2}O_{4}\)\(^{2-}\)

OTHER ABBREVIATIONS AND SYMBOLS

SbO-tart = antimonyl tartrate, SbO.C\(_{4}H_{4}O_{6}\)\(^{-}\)

HOAc = acetic acid, CH\(_{3}\)COOH

OAc = acetate, CH\(_{3}\)COO"\(^{-}\)

[H\(^{+}\)] = acid concentration (molar)

[Co] = concentration of cobalt complex species

[Co-H] = concentration of conjugate base derived from a cobalt complex species (usually an aquo complex).

Other symbols are explained in the text.
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THE STEREOCHEMISTRY OF TRIETHYLENETETRAMINE COMPLEXES

Whereas some work has been done on triethylenetetramine (trien) complexes by relating magnetism\(^1,2,3,10\) and spectra\(^4,5,6,7\) to stereochemistry in the solid state, little is known about the precise configurations of the few compounds isolated. Even less structural information on complexes obtained only in solution has been provided by studies of complex formation by various methods\(^1,2,11,21,23,26\) and measurements of formation constants\(^20,21,22,24\).

A comparison of the heats, free energies and entropies of formation of the 1:1 complexes \([M \text{ trien}]^{2+}\) and the analogous \([M \text{ en}_2]^{2+}\), indicated that the structures in solution were similar in the two series, and it was suggested that the complexes where \(M = \text{Mn, Fe, Co, Ni and Cu}\) were in fact diaquo octahedral ions\(^{27}\). However, these studies give no information about the disposition of the trien ligand around the metal ions.

It is clear from some of these studies (which are listed in detail in appendix A) that the ligand can coordinate to more than one metal ion, but these polynuclear complexes are beyond the scope of this thesis. In the mononuclear complexes, Leybold molecular scale-models show that the ligand may coordinate in several possible ways without undue strain. These configurations are tetrahedral, square planar and octahedral, and are shown in figure 1.

The tetrahedral structure has been suggested for the \([\text{Ag trien}]^{+}\)\(^{11}\) and \([\text{Zn trien}]^{2+}\)\(^{27}\) ions, but in no instance has this structure been
**Figure 1.** Possible configurations of trien in mononuclear complexes.
The planar structure is highly probable for the yellow ions 
[Ni trien]^{2+} \text{ (2,10)}, [Pd trien]^{2+} \text{ and [Pt trien]}^{2+} \text{ (3)} since their isolated compounds are diamagnetic, and it is also likely in the blue compounds [Cu trien]SO\textsubscript{4} \text{ (9)} and [Cu trien][ZnCl\textsubscript{4}] \text{ (10)}. However, there is some strain in this arrangement, and the preference for a non-planar ligand disposition is perhaps shown by the hydrolysis of [Cu trien]\text{aq}^{2+} \text{ in solutions of high pH to a species [Cu trien OH]}^{+} \text{ (28)}. One amine nitrogen might then be coordinated out of plane, or become free (figure 2).

\[ \begin{array}{c}
\text{Cu}^+ / \\
\text{N} \quad \text{OH}
\end{array} \]

**Figure 2.**

A similar one-ended dissociation of the ligand has also been proposed in the compound [Rh(trienH\textsubscript{2})Cl\textsubscript{4}]Cl \text{ (7)}, and in the [Ag trien]^{+} \text{ ion in solution where the hydrolysis and conductance behaviour were best interpreted} \text{ (11)} on the basis of a tetrahedral structure (figure 3).

\[ \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array} \overset{\text{slowly hydrolyses}}{\longrightarrow} \begin{array}{c}
\text{H}_2\text{O} \\
\text{OH}_2
\end{array} \]

**Figure 3.**

form isolated from alcohol
The three possible configurations of the ligand in octahedral complexes are denoted cis α, cis β, and trans (figure 1), so that when the two substituents are the same, as in [Co trien X₂]^{n+}, three geometric isomers are possible. However, when the substituents in the β complexes are different, [Co trien XY]^{n+}, two geometric isomers arise (denoted β' and β") because of the non-equivalence of the two substituent positions in relation to the ligand. The possible geometric isomers for [Co trien XY]^{n+} are shown in figure 4. The cis α and β complexes are dissymmetric and hence should be resolvable. This allows a total of seven isomers for a compound such as [Co trien Cl(H₂O)]^{2+}, whereas for [Co trien Cl₂]^{+} there are five.

The similarity between trien and two en groups has already been pointed out in the preface. It is clear from figure 5(a) that a process which involves a change from the α to the β configuration is essentially an inversion step. This is evident when the central ethylene bridge is removed (figure 5b) and the bis(en) complexes so produced are related as D and L.
Figure 4. Geometric isomers of \([\text{Co trien X}_2]^{n+}\) and \([\text{Co trien XY}]^{n+}\).
This aspect is relevant to the assignment of the relative and absolute configurations of the cobalt compounds prepared in this work, and to the kinetic studies, and is treated more fully in later chapters.

In 1948, cobalt(III) octahedral complexes of this ligand were studied by Basolo(4), who isolated the following disubstituted mononuclear compounds.

\[
\begin{align*}
&\text{[Co trien Cl}_2]\text{Cl} \\
&\text{[Co trien(NH}_3)\text{_2]Cl}_3} \\
&\text{[Co trien(NO}_2)\text{_2]Cl}_3\text{H}_2\text{O}} \\
&\text{[Co trien CO}_3] \text{(+camphor-π-sulphonate}} \\
&\text{[Co trien ox]Cl} \\
&\text{[Co trien en]Cl}_3 \\
&\text{[Co trien(NH}_3)\text{Cl](ClO}_4)\text{_2}} \quad (15) \\
&\text{[Co trien(NH}_3)\text{NO}_2]^{2+} \quad (16)
\end{align*}
\]
A cis configuration was assigned to [Co trien Cl₂]Cl on the basis of its purple colour and ultraviolet spectrum. The purple colour is characteristic of cis-dihalo tetramino complexes of cobalt(III) and chromium(III). The compound could not be resolved⁴,¹⁴, but a partial resolution was later achieved indirectly by Das Sarma and Bailar¹⁴ using a method of induced asymmetric synthesis, thus confirming unequivocally the cis assignment. Recently the analogous compounds [Cr trien Cl₂]Cl.H₂O (6) and [Rh trien Cl₂]Cl.H₂O (7) were prepared and assigned cis configurations from their spectra. Basolo⁴ also assigned [Co trien(NO₂)₂]Cl.H₂O as cis, by comparing its absorption spectrum with those of cis and trans [Co en₂(NO₂)₂]Cl, but resolution was not effected⁴,²⁹.

It was not determined whether the diammino, chloroammino and nitroammino compounds in the above series were cis or trans or mixtures, but they were presumed to have cis configurations¹⁵. Various attempts to prepare the trans isomers of [Co trien Cl₂]⁺ (4,¹⁴) and [Co trien(NO₂)₂]⁺ (4,²⁹) were unsuccessful, but Selbin and Bailar⁵ have since isolated the green trans isomer of [Co trien Br₂]Br as well as a violet cis isomer. These were distinguished and characterised by their different absorption spectra (ultraviolet, visible and infrared), and different solubilities and rates of aquation. Bailar and Das Sarma had previously noted that the cis[Co trien Cl₂]Cl (Basolo⁴) changed in methanol solution from purple to a grey-violet colour. By analogy with cis[Co en₂ Cl₂]Cl, which isomerises completely to the green trans isomer in this medium, they estimated spectrophotometrically that at equilibrium
\( \approx 40\% \) of the \textit{trans} form was present\(^{14}\).

If the \( \alpha \) configuration is assumed the most stable, the isolation of planar and \textit{trans}-octahedral trien complexes indicates that all configurations should be capable of existence. In the \textit{cis} \( \alpha \) configuration both secondary amine nitrogens of the ligand retain their normal tetrahedral angles (figure 4) while in the \textit{cis} \( \beta \) configuration one secondary nitrogen is tetrahedral and at the other the N-H and two N-C bonds lie in a disposition between tetrahedral and planar. Again, in the \textit{trans} configuration all bonds from the secondary nitrogens are considerably flattened, and the strain thus induced by this ligand arrangement is easily seen from molecular scale-models. The \textit{cis} \( \alpha \) configuration is relatively strain-free, and the \textit{cis} \( \beta \) is intermediate between \( \alpha \) and \textit{trans}, and on the basis of this angle-strain effect it has been tentatively suggested\(^{4,15,30}\) that the \textit{cis}-disubstituted compounds prepared of cobalt and chromium are more likely to have the \( \alpha \) configuration. In no instance, however, has any experimental evidence been obtained to enable a definite assignment of \( \alpha \) or \( \beta \) configuration to any of these \textit{cis} complexes. \textit{Cis} and \textit{trans} isomers may often be distinguished spectrally and by resolution of the \textit{cis}, but the \( \alpha \) and \( \beta \) forms are likely to have similar properties.

While the nitrogen bond-angle strain is expected to be the major factor in determining the relative stabilities of the isomers \( \alpha > \beta > \text{trans} \), other factors will contribute, and could combine to modify this order in particular compounds. Repulsion between the two negative acido ligands in \textit{cis} structures has been invoked to explain the higher
stability of \textit{trans}[Co trien Br_2]Br over the \textit{cis} isomer\(^{(5)}\). Conformational effects in the form of repulsions between non-bonded atoms, and hydration and lattice energies might also be important. In methanol the solvation energies of \textit{cis} and \textit{trans} dihalo cobalt complexes are quite different from those in water, and in these circumstances the \textit{trans} isomer may be energetically favoured as with \([\text{Co en}_2 \text{Cl}_2]\)\(^{31}\), and this seems to be the case with \([\text{Co trien Cl}_2]\)\(^{14}\).

Two other systems with similar isomeric complexity are perhaps relevant. Bailar and Peppard\(^{(32)}\) prepared three different geometric isomers of the \([\text{Co en(NH}_3)_2\text{Cl}_2]^{+}\) ion (figure 6) and this system may be considered intermediate between the \([\text{Co trien Cl}_2]^{+}\) and \([\text{Co en}_2 \text{Cl}_2]^{+}\) systems.

![Diagram](image)

\textit{cis} dichloro-\textit{trans} diammine \quad \textit{trans} dichloro-\textit{cis} diammine \quad \textit{cis} dichloro-\textit{cis} diammine

\textit{cis} \(\alpha\)-dichloro \quad \text{\textit{trans}-dichloro} \quad \textit{cis} \(\beta\)-dichloro

\textbf{Figure 6.} Isomers of \([\text{Co en(NH}_3)_2\text{Cl}_2]^{+}\).

The three isomers correspond to the possible trien configurations, with the important difference that only one of the \textit{cis} dichloro isomers (\(\beta\)) is optically active, the other possessing planes of symmetry. Although the
cis-dichloro-cis diammino-ethylenediamine cobaltic ion could not be resolved, the corresponding carbonate ion was partially resolved, and this enabled the configuration of the dichloro ions to be settled with reasonable certainty.

The complex diammino-(ethylenediamino-bis-acetylacetone) cobaltic ion (in which the ligand is represented by $\text{O} \text{N} \text{N} \text{O}$) has been suggested to exist in the same stereoisomeric forms as trien complexes. Morgan and Main-Smith\(^{(33)}\) claimed to have isolated all five isomers by careful fractional crystallisation of the (+)camphor-$\pi$-sulphonates. However they were unable to repeat the result, and for this reason the isolation of any active form is dubious. Such Schiff's base quadridentates normally demand planar configurations and are usually quite inflexible.

The stereochemical factors and problems which have been broadly outlined are discussed in the following chapters in more detail. In chapter 2 the syntheses, relative stabilities, and resolutions of $\alpha$, $\beta$, and trans isomers of a number of compounds of the type $[\text{Co trien XY}]^{2+}$ are described. The $\alpha$ and $\beta$ forms were resolved and were distinguished in various ways - by optical rotations, spectra, paper chromatography, powder photography, and reaction rates. However, the mere success of resolution of both forms was not sufficient to assign configurations, and this was done in two stages. The generic configurations of the $\alpha$ and $\beta$ isomers were established by a series of transformation reactions which are described in chapter 3. Active $\alpha$ or $\beta$ $[\text{Co trien Cl}_2]^+$ was transformed through the chloroaquo, carbonato, and diaquo compounds, and finally to
active α or β [Co trien(NO₂)₂]⁺, and all reactions occurred with full retention of configuration and activity. The α and β configurations were determined from the results of a study of the kinetics and stereochemical course of aquation of the three dichloro isomers. The two isomers arising from the β configuration, β' and β'' [Co trien Cl(H₂O)]²⁺ (figure 4) were detected by their different rates of aquation. Absolute configurations could then be assigned by relating the rotatory dispersion curves of all cis compounds to that of the D(+) [Co en₃]³⁺ ion.
CHAPTER TWO

THE PREPARATIONS, RESOLUTIONS, AND STEREOCHEMISTRY

OF \[\text{Co trien XY}^{n+}\] COMPLEXES

Basolo suggested that the disubstituted trien complexes of cobalt(III) that he prepared (p. 4) were all cis\(^{(4,15)}\), and later Kling and Schläfer suggested that the analogous cis[Cr trien Cl\(_2\)]Cl was only one geometric isomer, cis \(\alpha\), on the basis of "steric considerations"\(^{(6)}\). However, the isolation of a compound can be misleading with respect to the stability, since Ettle and Johnson\(^{(34)}\) have clearly shown that either cis or trans \([\text{Co en}_{2} \text{Cl}_{2}]^{+}\) can be isolated depending upon which anion is used to precipitate the complex. The configurations of the isolated trien compounds might then be determined by solubility rather than by stabilities in the expected order \(\alpha \succ \beta \succ \text{trans}\). The present work has shown that all configurations do exist, and that the compounds cis[Co trien Cl\(_2\)]Cl and cis[Co trien(NO\(_2\))\(_2\)]Cl.\(\text{H}_{2}\)O prepared by Basolo did in fact have cis configurations.

It is difficult to determine the stabilities of the dichloro compounds because of the complexity of the system in aqueous solution. However in methanol no appreciable solvation occurs, and there is good reason for believing that the \(\alpha\) and trans isomers are appreciably stable in this solvent (p. 15-17). In this medium then, it is clear that the bond-angle strain is not a major factor in determining the stabilities.
The relative stabilities of the α and β dinitro and diaquo isomers have been determined approximately, and it will be shown that the stability is more a function of the substituents than of the amine ligand.

Basolo's preparations all used α[Co trien Cl₂]Cl (synthesised directly) as the starting point, but it has now been found that α[Co trien(NO₂)₂]Cl can be obtained more efficiently by aerial oxidation of a mixture of CoCl₂, (trienH)Cl₂, and NaNO₂. This can be transformed quantitatively to cis[Co trien Cl₂]Cl (mostly α) from which all the other compounds and isomers can be obtained. The synthetic reactions are summarised diagrammatically in figure 7, which includes preparative methods used by previous workers. It will be noted that most of the substitution reactions yield products with the same configurations as the reactant complexes, but a significant exception is isomerisation of crude α[Co trien Cl₂]Cl in alkaline solution to β[Co trien CO₃]⁺, which is the starting material for the preparation of the other β complexes. Also, reaction of β[Co trien CO₃]⁺ with concentrated hydrochloric acid yields a mixture of the β and trans dichloro isomers.

The α and β dichloro-, α and β dinitro-, and β carbonato-compounds were resolved by diastereoisomer formation, and α[Co trien CO₃]ClO₄ and the α and β diaquo compounds were obtained optically active by transformations from other optically pure compounds. They were all obtained optically pure, since for most of the compounds fractional crystallisation or precipitation could not increase the rotations, and the transformation reactions considered in the following chapter provide unequivocal evidence for complete resolution.
FIGURE 7. PREPARATIONS OF $[\text{Co trien XY}]^{n+}$ ISOMERS

$\text{CoCl}_2 + \text{trien} + \text{O}_2 \overset{+ \text{HCl} + \text{heat}}{\rightarrow} \text{cis or trans}[\text{Co(NH}_3)_4\text{(NO}_2)_2\text{]}\text{Cl} \overset{+ \text{trien in alcohol, heat}}{\rightarrow} \text{Basolo}$

$\text{Na}_3[\text{Co(NO}_2)_6] + \text{trien} \overset{\text{heat}}{\rightarrow} \text{Basolo}$

\[ \begin{align*}
\text{heat HCl} \\
\text{heat NaNO}_2 \text{ (Basolo)}
\end{align*} \]

\[ \begin{align*}
\text{a}[\text{CotrienCl}_2]^+ \overset{\text{aquation in } H^+}{\rightarrow} g[\text{CotrienCl(H}_2\text{O})_2]^{2+} \overset{\text{NaHCO}_3}{\rightarrow} g[\text{CotrienCO}_3]^+ \\
\text{not isolated}
\end{align*} \]

\[ \begin{align*}
\text{HClO}_4 \overset{\text{NaNO}_2}{\rightarrow} g[\text{Cotrien(NO}_2)_2]^{3+} \\
\text{CoCl}_2 + \text{trien, HCl} + \text{NaNO}_2 + \text{O}_2 \overset{\text{some } \beta \text{ dinitro}}{\rightarrow}
\end{align*} \]

CIS $\alpha$ SERIES
Various methods including colour, visible ultraviolet and infrared spectra, rotatory dispersion, circular dichroism, reaction rates, paper chromatography, and solubility served to characterise and identify the α, β, and trans isomers. These are discussed in the following sections dealing with each compound.

[Co trien Cl₂]Cl ISOMERS

Deep purple crude cis α[Co trien Cl₂]Cl was prepared in quantitative yield by evaporating a mixture of α[Co trien(NO₂)₂]Cl and excess hydrochloric acid. (Basolo's method by direct synthesis (4) gave crude α in 80% yield). The crude cis β dichloro isomer was prepared by stirring a suspension of β[Co trien CO₃]Cl·1.5 H₂O in ethanol saturated with hydrogen chloride, and was obtained as a reddish-violet powder with yields approaching 90%. Rearrangement during this reaction was minimised by the use of alcohol as medium (35). Both preparations gave a mixture of α and β isomers, but predominantly the desired form. The α isomer was the less soluble and could thus be purified by recrystallisation, and the β was freed from most α in this way before it was resolved.

That the crude products from these reactions were isomeric mixtures was shown by paper chromatography of the mixtures of [Co trien(NO₂)₂]⁺ isomers obtained by transformation reactions (p. 38, 62), when two spots (α and β dinitro) were always obtained. The visible spectra of the α and β carbonato isomers are sufficiently different (figure 10) to be used for
estimating the approximate composition of \( \alpha \) and \( \beta \) isomeric mixtures, and
the dichloro isomers each may be transformed quantitatively to the
corresponding carbonato isomers by the reactions:

\[
[CotrienCl_{2}]^+ + 0.01M \text{HClO}_4 \rightarrow [CotrienCl(H_2O)]^{2+} + \text{NaHCO}_3 \rightarrow [CotrienCO_3]^+.
\]

The dichloro compounds were allowed to aquate at room temperature in acid
solution until aquation to \( \alpha[\text{Co trienCl(H}_2\text{O})]^{2+} \) was complete (10 hours)
and the carbonato solution was then formed with complete retention of
configuration from each isomer by excess NaHCO\(_3\) (chapter 3). By measure-
ment of the absorption at the visible peak, compositions of dichloro
preparations were roughly assessed and are given in table 1.

**TABLE 1. APPROXIMATE COMPOSITIONS OF cis[Co trien Cl\(_2\)]Cl PREPARATIONS**

<table>
<thead>
<tr>
<th>Sample of cis[Co trien Cl(_2)]Cl</th>
<th>% of other cis isomer present</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) prepared from ( \alpha[\text{Co trien(NO}_2\text{)}_2]\text{Cl.H}_2\text{O} ):</td>
<td></td>
</tr>
<tr>
<td>crude</td>
<td>up to 40% ( \beta )</td>
</tr>
<tr>
<td>recrystallised</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>methanol extracted</td>
<td>30</td>
</tr>
<tr>
<td>( \alpha ) prepared by synthesis, reference (4):</td>
<td></td>
</tr>
<tr>
<td>crude</td>
<td>15</td>
</tr>
<tr>
<td>recrystallised</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>( \beta ) prepared from ( \beta[\text{Co trien CO}_3]\text{Cl. 1.5 H}_2\text{O} ) by ethanol/hydrogen chloride:</td>
<td></td>
</tr>
<tr>
<td>crude</td>
<td>10 - 15% ( \alpha )</td>
</tr>
<tr>
<td>recrystallised</td>
<td>15</td>
</tr>
</tbody>
</table>
Basolo's product was also identified as the α isomer by its rate of aquation (p. 32) and by resolution.

Both cis dichloro isomers were resolved with Na(+)[Co en ox₂]·H₂O in dilute acetic acid solution to reduce hydrolysis, and the diastereoisomers (−) α or β [Co trien Cl₂](+) [Co en ox₂]·H₂O crystallised in good yields, with high optical purity. Because of low solubility, and because aquation takes place in solution, the diastereoisomers themselves could not be recrystallised. The dichloro compounds were recovered from the filtrates and from the diastereoisomers with NaI or NaClO₄. The dichloro iodide was then converted to the acetate or chloride and fractionally precipitated with NaI or NaClO₄. For both cis isomers, the optical isomers were less soluble than the racemates, and were fractionated to maximum optical rotations. In this way optically pure dichloro iodides and perchlorates were obtained, and their rotations are listed in table 2. Optical purity was substantiated by the transformation reactions in chapter 3. The work was carried out at low temperatures where possible, to minimise aquation. Because of the rapid aquation and the low rotation of β[Co trien Cl₂]⁺ the activity was more easily measured in terms of the β[Co trien CO₃]⁺, which was obtained with full retention of activity from the dichloro complex by the transformation reactions described above.
TABLE 2. OPTICAL ROTATIONS OF $\alpha$ AND $\beta$ [Co trien Cl$_2$]$^+$

<table>
<thead>
<tr>
<th>Formula</th>
<th>$[\alpha]_D$</th>
<th>$[\beta]_D$</th>
<th>$[\gamma]_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$[Co trien Cl$_2$]Cl $\cdot$ 0.5 H$_2$O</td>
<td>+ 2100°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$[Co trien Cl$_2$]ClO$_4$</td>
<td>+ 2330°</td>
<td>+ 4350°</td>
<td></td>
</tr>
<tr>
<td>$\beta$[Co trien Cl$_2$]ClO$_4$</td>
<td>- 230° *</td>
<td>- 3100°</td>
<td></td>
</tr>
</tbody>
</table>

* measured at low temperature

These rotations may be compared with that reported by Das Sarma and Bailar(14) for one of these isomers, $[\alpha]_D = -100^\circ$ for [Co trien Cl$_2$]Cl. This was probably the $\alpha$ isomer since they started with Basolo's $\alpha$ dichloro isomer. The rotatory dispersion and circular dichroism curves measured for the optically pure $\alpha$ and $\beta$ [Co trien Cl$_2$]ClO$_4$ differed greatly (figures 28 and 34) and further distinguished these isomers.

Previous attempts(4,14) to prepare trans[Co trien Cl$_2$]Cl have not been successful, probably because of the relatively low kinetic stability of this isomer. However the trans complex has been identified in solution by boiling a methanol solution of the cis forms. At equilibrium $\sim 40\%$ of the trans, and $50\%$ of both cis forms, was estimated(14). Under these same conditions the cis[Co en$_2$ Cl$_2$]$^+$ ion converts to the trans isomer quantitatively, but slow crystallisation of the grey-green solution of [Co trien Cl$_2$]Cl in dry methanol by a Soxhlet procedure gave largely the $\alpha$ isomer. Further, it seemed that the pure $\alpha$ isomer did not give any
trans even in boiling methanol, and when the Soxhlet extraction was repeated with LiClO₄ present, again only a[Co trien Cl₂]ClO₄ was obtained. Also, evaporation of the crude a[Co trien Cl₂]Cl in excess HCl, and evaporation of a[Co trien Cl₂]NO₃ (prepared from the chloride with one mole of AgNO₃) only gave the cis dichloro products in the solid state. These methods produce the trans[Co en₂ Cl₂]⁺ isomer from the cis(31,34). Nor could trans[Co trien Cl₂]⁺ be precipitated when solutions of the cis isomers were poured into ethanol solutions of NH₄NO₃ or (NH₄)₂SO₄(34).

However, when β[Co trien CO₃]Cl was treated with ice-cold concentrated HCl and allowed to stand, violet β[Co trien Cl₂]Cl contaminated with the green trans isomer crystallised slowly over several days. One small fraction was entirely trans[Co trien Cl₂]Cl.HCl.H₂O (trans-dihalo-tetramino cobalt(III) complexes frequently crystallise as hydrohalides(5,36) and the lattice water was confirmed by water bands in the infrared spectrum). The dichloro mixture on extraction with boiling methanol gave a green solution from which trans[Co trien Cl₂]ClO₄ was crystallised with LiClO₄. A second extraction gave more trans product, but no more was obtained on subsequent extraction and the purple residue was probably largely the a isomer (see above). Samples of β[Co trien Cl₂]Cl which contained no green crystals also gave the trans product by the above method.

More precise experiments were not carried out, but it would appear from the foregoing properties that β[Co trien Cl₂]⁺ isomerises to trans[Co trien Cl₂]⁺ in methanol, but a[Co trien Cl₂]⁺ does not isomerise (easily) under the same conditions. If the cis β configuration isomerises
to trans by the movement of the terminal ethylene bridge at the tetrahedral nitrogen atom (figure 8a), it is likely that the other terminal ethylene bridge, at the planar nitrogen, is also displaced to produce the cis α configuration (figure 8b).

\[ \text{Cis } \alpha \quad \text{Trans} \]

\[ \text{Cis } \beta \]

This would explain the large amount of cis material left after two extractions of $\beta$[Co trien Cl₂]Cl, and since the change $\alpha \rightarrow \beta \rightarrow \text{trans}$ was not observed, the probable order of thermodynamic stabilities is established as $\alpha > \text{trans} > \beta$ in methanol. The equilibrium mixture in methanol could not be isolated because the equilibrium alters and precipitates the least soluble form on concentration.

That trans[Co trien Cl₂]⁺ was obtained from $\beta$[Co trien Cl₂]Cl in methanol and not from the α isomer suggests that the β structure is intermediate between the α and trans structures (figure 8). This was supported by the reaction of (+)$\beta$[Co trien CO₃]ClO₄·H₂O (0.15 g.) with cold concentrated HCl (0.5 ml.). From the resulting scarlet diaquo solution, dichloro product began to crystallise after a few hours. Microscopic examination showed that the fine violet crystals of the β isomer
contained appreciable amounts of green crystals of trans[Co trien Cl₂]ClO₄ (but no a from spectral analysis). In the same reaction with (+)a[Co trien CO₃]ClO₄·H₂O, the solution soon became purple and the product, crystallising slowly over several days, consisted of large deep-purple crystals of a[Co trien Cl₂]ClO₄ (estimated to contain ~10% b), but no green trans isomer was present. The anation reactions diaquo → dichloro therefore take place largely with retention of the isomeric form, and the fact that only one of the carbonato isomers yields any trans[Co trien Cl₂]⁺ is further evidence for the configurations assigned. Similar observations have been made with the two carbonato isomers of [Co en(NH₃)₂CO₃]⁺ (32) and used to assign the configurations of the corresponding cis dichloro isomers.

The equilibration of the α, β and trans dichloro isomers in aqueous solution is complicated by aquation so the relative thermodynamic stabilities may never be determined precisely. However, from the intense purple colour of the solution in the direct synthesis preparation(4) it is likely that the α isomer is the most stable as it is in methanol. Further, a concentrated solution of β[Co trien Cl₂]Cl in concentrated HCl, which is initially red-violet, slowly changes to the purple colour of the α form.

The α and β isomers have similar visible and U.V. absorption spectra (figure 28), but the α absorbs at a slightly higher wavelength than the β isomer (λₘₐₓ α = 539 mµ, λₘₐₓ β = 531 mµ), and the absorption of α is markedly greater at long wavelengths (ε α = 40, ε β = 9 at 650 mµ) thus accounting for the reddish tinge in the β compound. Qualitatively the
absorptions of the dichloro compounds of the bis(en) and trien series are similar, but the trien absorptions are generally higher (37, 38), and a broad band at 380–385 μ in trans[Co en₂ Cl₂]⁺ and trans[Co pn₂ Cl₂]⁺ (39) is not apparent in trans[Co trien Cl₂]⁺. Absorption data are given in table 3.

The infrared spectra of the three [Co trien Cl₂]ClO₄ isomers are given in figure 9. For comparison, frequencies of the stronger bands of Basolo's α[Co trien Cl₂]Cl (4), measured by Bailar (5) are 1626, 1587, 1353, 1309, 1248, 1181, 1071, 994, 833 cm⁻¹, although the correspondence is not exact since the anions are different. Cis β[Co trien Cl₂]ClO₄ has the most complex spectrum with characteristics of both the α and trans spectra as might be expected from its intermediate structure. The greatest differences in the three structures expected to be reflected in the IR. spectra is the environments of the secondary amine N-H bonds. Whereas the α has two equivalent NH₂ groups, and two equivalent N-H bonds, the secondary amines in cis β (one) and trans (two) will have some sp² character. For these reasons it would be expected that the N-H region should be more complex in β and trans than in α. This is in fact observed, but the individual frequencies are not fully resolved. (α at 3280 cm⁻¹; β at 3270, 3210 cm⁻¹; trans at 3270, 3220 cm⁻¹). The consistent differences between cis and trans isomers noted in [Co en₂ X₂]⁺, [Co(NH₃)₄ Cl₂]⁺ (40) and [Co trien Br₂ Br]⁺ at the 1600 and 830 cm⁻¹ bands are difficult to observe here, but the single NH₂ asymmetric deformation band in trans[Co trien Cl₂]⁺ (1583 cm⁻¹) is split in β[Co trien Cl₂]⁺ (1590, 1577 cm⁻¹) as observed with the [Co en₂ Cl₂]⁺ isomers (41).
<table>
<thead>
<tr>
<th>Compound</th>
<th>Configuration</th>
<th>Solvent</th>
<th>$\lambda (\mu\text{m})$</th>
<th>$\varepsilon$</th>
<th>$\lambda$</th>
<th>$\varepsilon$</th>
<th>$\lambda$</th>
<th>$\varepsilon$</th>
<th>$\lambda$</th>
<th>$\varepsilon$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co trien (\text{Cl}_2)](\text{ClO}_4)</td>
<td>cis  (\alpha)</td>
<td>0.01 M (\text{HClO}_4)</td>
<td>(\lambda \leq 235) * 20 (\times 10^3)</td>
<td>381 * 135</td>
<td>539 132</td>
<td>(\lambda \approx 600) (shoulder)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>figs. 28, 66</td>
</tr>
<tr>
<td>&quot;</td>
<td>cis  (\beta)</td>
<td>&quot;</td>
<td>(\lambda \leq 235) 16 (\times 10^3)</td>
<td>392 * 118</td>
<td>531 131</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>figs. 28, 67</td>
</tr>
<tr>
<td>&quot;</td>
<td>trans</td>
<td>&quot;</td>
<td>not measured</td>
<td>446 138</td>
<td>621 53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>fig. 66</td>
</tr>
<tr>
<td>[Co trien (\text{Cl}_2)](\text{Cl}_2)(\text{HCl.H}_2\text{O})</td>
<td>trans</td>
<td>&quot;</td>
<td>not measured</td>
<td>445 136</td>
<td>620 53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co en(\text{L}_2) (\text{Cl})]</td>
<td>cis</td>
<td>MeOH-(\text{H}_2\text{O})</td>
<td>240 * 19 (\times 10^3)</td>
<td>390 * 78</td>
<td>530 76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(39)</td>
</tr>
<tr>
<td>&quot;</td>
<td>trans</td>
<td>&quot;</td>
<td>252 20 (\times 10^3)</td>
<td>385 44</td>
<td>450 25</td>
<td>625 35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(39)</td>
</tr>
</tbody>
</table>

* broad and diffuse bands
Figure 9. Infra-red spectra of [(CoIItrienCl₂)ClO₄] isomers.
(KBr disc method—air reference)
In [Co trien Cl₂]⁺, the chlorine atoms are in different environments in the three isomers and should theoretically show different shifts in the nuclear magnetic resonance spectra. However, these would probably be masked by line broadening, and the nitrogen atoms in [Co trien(NO₂)₂]⁺ would also give broad resonance lines.

Trans[Co trien Br₂]Br was prepared by Selbin and Bailar from cis[Co trien Cl₂]Cl, and by direct synthesis. On evaporation of a[Co trien Cl₂]Cl with excess HBr, the mixture slowly became olive-green, indicating that trans[Co trien Br₂]⁺ is the thermodynamically stable isomer. The product crystallised as the hydrochloride (λ ~ 170), and there was also the possibility of a mixed halo complex, [Co trien Br Cl]Br. A better preparation was by evaporating a[Co trien(NO₂)₂]Br·H₂O and excess HBr to dryness, when trans[Co trien Br₂]Br was obtained in good yield (λ = 112).

[Co trien Cl(H₂O)]²⁺ ISOMERS

The aquation of cis[Co en₂ Cl₂]⁺ in dilute acid solution to cis[Co en₂ Cl(H₂O)]²⁺ occurs with full retention of configuration, and the subsequent stereo change is due to isomerisation of the chloroaquo ion. Haloaquo complexes have usually been prepared from the corresponding dihalo complexes using such aquation reactions.

In the trien system, the cis dichloro compounds aquate in acid solution to the chloroaquo compounds with full retention of configuration and activity. These subsequently aquate at much slower rates to the diaquo compounds, largely with full retention. These reactions have been studied
stereochemically (chapter 3) and kinetically (chapter 5) and no isomerisation of the chloroaquo compounds has been detected. By aquating the cis dichloro compounds, the concentration of each chloroaquo isomer rose to a maximum (∨ 98% of total complex concentration for α, ∨ 94% for β.).

The complexes were extremely soluble and could not be isolated as the sulphates as was cis[Co en₂ Cl(H₂O)]SO₄ (44). Solid products were obtained with the anions [B(C₆H₅)₄]⁻, [PtCl₆]²⁻, [Cr(NH₃)₂(NCS)₄]⁻ and [C₂O₄]²⁻ but were not analytically pure. One coordinated chlorine in the α dichloro isomer was rapidly removed by Ag⁺ in the reactions:

α[CotrienCl₂]Cl + 2AgNO₃ + H₂O → α[CotrienCl(H₂O)](NO₃)₂ + 2AgCl

α[CotrienCl₂]Cl + Ag₂SO₄ + H₂O → α[CotrienCl(H₂O)]SO₄ + 2AgCl.

However only glasses and oils were obtained on evaporating these solutions, or precipitating the products with alcohol.

The chloroaquo ions were therefore prepared in acid solution, pH 1-2, by aquating the dichloro isomers for specified times (p. 79, 86). The racemic solutions could not be resolved, and the active isomers were prepared from active [Co trien Cl₂]ClO₄. In the preparation from β[Co trien Cl₂]⁺, the β⁺ and β⁻ chloroaquo isomers are both formed (figure 4), but one of these is present to the extent of only ∨ 3% (p. 135).

Absorption spectra of the cis[Co trien Cl(H₂O)]²⁺ complexes are given in figure 29, and table 4 compares the trien and bis(en) chloroaquo absorptions. The three cis spectra are similar, although α[Co trien Cl(H₂O)]²⁺ absorbs more than the β isomer in the red region,
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co trien Cl(H₂O)]²⁺</td>
<td>0.01 M HClO₄</td>
<td>cis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>trans</td>
</tr>
<tr>
<td>[Co en₂ Cl(H₂O)]²⁺</td>
<td></td>
<td>cis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>trans</td>
</tr>
</tbody>
</table>

| TABLE 4. ABSORPTION MAXIMA OF CHLOROACETO-TERTRAAMINO-COBALT (III) ISOMERS |
|---------------------------------|------------------|
| **Table 4. Absorption Maxima of Chloroaceto-Tetraamino-Cobalt (III) Isomers** |
| **Configuration**               | **Solvent**      |
| **Compound**                    | **0.01 M HClO₄** |
| [Co trien Cl(H₂O)]²⁺            | cis              |
| [Co en₂ Cl(H₂O)]²⁺              | cis              |

<table>
<thead>
<tr>
<th><strong>λ (nm)</strong></th>
<th><strong>E</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co trien Cl(H₂O)]²⁺</td>
<td></td>
</tr>
<tr>
<td>376</td>
<td>1.5 x 10⁻³</td>
</tr>
<tr>
<td>235</td>
<td>1.5 x 10⁻³</td>
</tr>
<tr>
<td>235</td>
<td>1.5 x 10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>λ (nm)</strong></th>
<th><strong>E</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co en₂ Cl(H₂O)]²⁺</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>1.8 x 10⁻³</td>
</tr>
<tr>
<td>235</td>
<td>1.8 x 10⁻³</td>
</tr>
<tr>
<td>235</td>
<td>1.8 x 10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>λ (nm)</strong></th>
<th><strong>E</strong></th>
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<th><strong>λ (nm)</strong></th>
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<tr>
<td>[Co en₂ Cl(H₂O)]²⁺</td>
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<td>1.8 x 10⁻³</td>
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</tr>
<tr>
<td>235</td>
<td>1.8 x 10⁻³</td>
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<tr>
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accounting for the more reddish colour of the latter isomer.

\textit{Trans}[Co trien Cl\textsubscript{2}]\textsuperscript{+} aquates stereospecifically to 
\textit{\beta}[Co trien Cl(H\textsubscript{2}O)]\textsuperscript{2+} in acid solution. However, in the presence of Hg\textsuperscript{2+}
one chlorine is removed rapidly and the product is largely
\textit{trans}[Co trien Cl(H\textsubscript{2}O)]\textsuperscript{2+}. This then isomerises rapidly to the \textit{\beta} isomer,
so that isolation was not possible (p./\textsuperscript{34}).

\textit{[Co trien CO\textsubscript{3}]}\textsuperscript{+} ISOMERS

On heating an aqueous solution of crude \textit{\alpha}[Co trien Cl\textsubscript{2}]Cl with 
Li\textsubscript{2}CO\textsubscript{3}, red \textit{\beta}[Co trien CO\textsubscript{3}]Cl. 1.5 H\textsubscript{2}O was obtained from the solution with
alcohol. It will be shown later (chapter 6) that the \textit{\beta} diaquo compound is
the more stable (\textit{\beta}/\textit{\alpha} \thicksim \textsuperscript{35}/\textsuperscript{15} at equilibrium). This suggests that both
chlorine atoms in \textit{\alpha}[Co trien Cl\textsubscript{2}]\textsuperscript{+} hydrolyse in the faintly alkaline
solution, and the hydroxoaqueo ion isomerises to the \textit{\beta} configuration very
rapidly, as occurs with the bis(en) complexes\textsuperscript{(46)}. The carbonate
subsequently adds to give the \textit{\beta} carbonato complex\textsuperscript{(47)}. The crude
\textit{\beta}[Co trien CO\textsubscript{3}]Cl contained some of the \textit{\alpha} form (\thicksim 20\%). It is
alternatively possible that the carbonate ion adds to the chlorohydroxo ion,
and isomerisation takes place in the subsequent hydrolysis of the chloride
ion. Further work is necessary to determine the exact course of these
reactions. \textit{\beta}[Co trien CO\textsubscript{3}]Br. 0.5 H\textsubscript{2}O. 0.5 C\textsubscript{2}H\textsubscript{5}OH was prepared by
reacting \textit{trans}[Co trien Br\textsubscript{2}]Br with Li\textsubscript{2}CO\textsubscript{3}. These \textit{\beta} carbonato compounds
were used to prepare the \textit{\beta} dichloro, diaquo and dinitro compounds by
transformation reactions which occur with retention of configuration.

Attempts were made to prepare the β carbonato complex from CoCl₂ by oxidation with PbO₂ (44) (this oxidises the trien also), and also by treating the [Co(CO₃)₃]³⁻ ion with trien and HCl (53). Neither method gave good results.

Resolution was best effected by treating β[Co trien CO₃]Br with Ag(+)[Co en mal₂]. (+)β[Co trien CO₃](+) [Co en mal₂].4H₂O was obtained as the less soluble diastereoisomer by precipitation from the solution with alcohol. The (+) and (-) optical forms were easily recovered as perchlorates by treating the diastereoisomer and filtrate with NaClO₄. α[Co trien CO₃]⁺ was prepared as the perchlorate by aquating α[Co trien Cl₂]ClO₄ to the chloroaquo complex in HClO₄, and adding NaHCO₃. The racemate could not be resolved, but the active α carbonato was easily obtained by the above transformation reactions from active α[Co trien Cl₂]ClO₄.

On recrystallising the α and β carbonato perchlorates to maximum rotations, the following activities were obtained:

\[ [\alpha]_D^\alpha = \dagger 1230^\circ, \quad [\alpha]_D^\beta = \dagger 780^\circ \]
\[ [\beta]_D^\alpha = \dagger 4740^\circ, \quad [\beta]_D^\beta = \dagger 2980^\circ \]

Optical purities were confirmed, and the configurations assigned, by transformation through the diaquo to the corresponding active dinitro compounds (chapter 3). Rotatory dispersion and circular dichroism curves are given later. (figures 30 and 36).
Both the α and β carbonato complexes were optically stable and had large rotations, so that these compounds were very useful reference compounds for assessing the amount of retention of activity during the aquation of the [Co trien Cl(H$_2$O)]$^{2+}$ isomers. Their maximum absorptions occur at the same wavelengths (figure 10) but the intensities differ ($\varepsilon_\alpha = 120, \varepsilon_\beta = 178$ at 505 m$\mu$). Thus these compounds were also useful for measuring the $\alpha \rightarrow \beta$ isomerisation which occurred during the kinetic studies (chapters 5 and 6), as chloroaquo and diaquo compounds convert to the carbonato compounds with full retention of configuration and activity (chapter 3). The $\alpha/\beta$ compositions of dichloro compounds were measured in a similar manner (p. 13).

An X-ray structural analysis of (2)$\beta$[Co trien CO$_3$]ClO$_4$·H$_2$O is being undertaken\(^{150}\). The molecular weight has been measured crystallographically, to an accuracy of better than 2%, and found to be 387 (calculated 382.7), confirming the mononuclear structures assigned to these compounds.

\[
\text{[Co trien(H}_2\text{O)}_2]\text{(ClO}_4\text{)}_3 \text{ ISOMERS}
\]

\[
\text{Cis[Co en}_2\text{(H}_2\text{O)}_2]^{3+} \text{ has been isolated by various methods}\(^{46,49a,50,51}\). However the simplest preparation was that of Linhard and Stirn from [Co en$_2$CO$_3$]ClO$_4$\(^{52}\). Optically active α and β [Co trien(H$_2$O)$_2$](ClO$_4$)$_3$ were obtained by treating the corresponding optically pure carbonato perchlorates with perchloric acid in slight excess. On evaporation the products crystallised. Their optical purities were confirmed by transformations to the corresponding active carbonato and dinitro compounds.
FIGURE 10. SPECTRA OF CARBONATO-TETRAMINO-COBALT (III) ISOMERS.
**Figure 11.** Spectra of cis [Co tren(H$_2$O)$_2$](ClO$_4$)$_3$ Isomers (in 0.1 M HClO$_4$)

- **cis** $\epsilon_{487} = 122$
- **cis** $\epsilon_{357} = 85$
- **trans** $\epsilon_{500} = 87$
- **trans** $\epsilon_{359} = 57$

**Figure 12.** Spectra of cis [Co en$_2$(H$_2$O)$_2$]$_3^{3+}$ and trans [Co en$_2$(H$_2$O)$_2$]$_3^{3+}$ Isomers (in 1 M NaNO$_3$)

- Cis [Co en$_2$(H$_2$O)$_2$]$_3^{3+}$
- Trans [Co en$_2$(H$_2$O)$_2$]$_3^{3+}$
The different colours of the two **cis** isomers (α scarlet-carmine, β light orange) were reflected in the spectral differences at the first bands (figure 11). No evidence was found in the subsequent kinetic studies on the diaquo system (chapter 6) for the presence of the **trans** isomer. The spectrum of the **trans** compound should be greatly different from those of the **cis** by comparison with the \([\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\) spectra (figure 12), and its presence in reasonable quantities (> 5%) should be detectable by this method. Further, the **trans**[Co trien Cl]⁺ ion aquates fully to \([\text{Co trien Cl(}\text{H}_2\text{O})]^{2+}\) which in turn aquates to the β diaquo species, so that it is most unlikely that any **trans** isomer is produced.

\[\text{Co trien(NO}_2)_2\]⁺ ISOMERS

**Cis** α[Co trien(NO₂)₂]⁺ was easily prepared by aerial oxidation of a mixture of CoX₂, trien·HX, and NaNO₂. The product precipitated as α[Co trien(NO₂)₂]X where X = Cl, Br, NO₃, OAc, (yields 60-80%) and always contained a little of the β isomer. With the chloride, the β isomer concentrated in the most soluble fractions but could not be obtained pure by this method. However β[Co trien CO₃]Cl on treatment with HNO₃ and NaNO₂ gave pure β[Co trien(NO₂)₂]NO₃, which was then converted to the chloride through the iodide.

The two dinitro isomers were separated and characterised in several ways. Paper chromatography of the chlorides or acetates using the solvent mixtures n-butanol : pyridine : water : acetic acid (4 : 3 : 2 : 1) or n-butanol : water : acetic acid (7 : 2 : 1) separated the α and β isomers.
Fractional recrystallisation of the chloride product from direct synthesis, and chromatography of the fractions established the proportions as $\alpha/\beta \sim 10/1$. Quantitative chromatography of a solution of acetates under equilibrium conditions (prepared by synthesis in the presence of Co$^{2+}$ ion) gave the $\alpha/\beta$ ratio as $2.7/1$, which established $\alpha$ as the thermodynamically stable isomer.

The $\alpha$ isomer gave a diastereoisomer with Na(-)[Co en ox$_2$]*H$_2$O, whereas the $\beta$ would precipitate only with sodium (+)antimonyl tartrate, and less readily with sodium(+)arsenyl tartrate. This property was also used to identify the isomers.

From resolution of the $\alpha$ isomer with Na(-)[Co en ox$_2$]*H$_2$O the diastereoisomer (+)$\alpha$[Co trien(NO$_2$)$_2$](-)[Co en ox$_2$]*H$_2$O was obtained. From this and the filtrate the optical isomers were recovered as iodides.

Resolution of the $\beta$ isomers with Na(+)SbO$_4$ tart gave the diastereoisomer (+)$\beta$[Co trien(NO$_2$)$_2$](+)[SbO$_4$ tart] and again both optical forms were obtained as iodides. An attempt to prepare (+)$\beta$[Co trien(NO$_2$)$_2$](+)[SbO$_4$ tart] by a second-order asymmetric synthesis from the labile cobalt(II) salt (acetate solution) was not successful.

Fractional recrystallisation or fractional precipitation of the active $\alpha$ and $\beta$ iodides, bromides or perchlorates gave the maximum rotations:

$$[\alpha]_{546}^M = 200-240^\circ, \quad [\beta]_{546}^M = 1080-1110^\circ.$$  

Optical purities were confirmed by transforming the optically pure $\alpha$ and $\beta$ carbonato compounds to the dinitro isomers having these rotations, and by resolving Na(+)[Co en ox$_2$]*H$_2$O with active $\alpha$[Co trien(NO$_2$)$_2$]DAc.
(Na[Co en ox₂₂]H₂O was obtained having [α]₆⁺ = +460° (54)).

By comparison with other dinitro(tetramino)cobalt(III) systems, trans[Co trien(NO₂)₂]⁺ should be distinguishable from the cis isomers by chromatography, powder-photography, its reaction with concentrated HCl (55), and by differences in ultraviolet (p. 28) and infrared spectra (40, 41).

Careful fractionation of the dinitro salts from the syntheses gave no fractions which could not be resolved. Basolo's products from the reactions (4)

\[
\text{cis or trans } [\text{Co(NH₃)}₄(\text{NO₂})₂]\text{Cl + trien } \rightarrow \quad \text{[Co trien Cl₂]Cl + 2NaNO₂} \rightarrow
\]

were shown to be largely the a dinitro isomer. Methods which gave trans[Co en₂(NO₂)₂]⁺ were not successful in preparing the trans trien isomer. Reaction of Na₃[Co(NO₂)₆] with trien (one mole) gave only the a isomer (precipitated as iodide, perchlorate, or nitrite in 60% yield). On refluxing a[Co trien(NO₂)₂]⁺ in water no isomerisation was detected, although cis[Co en₂(NO₂)₂]⁺ isomerises on prolonged boiling or evaporation to the trans, which can then be precipitated as the less soluble nitrate or nitrite (56). Selbin also tried to prepare the trans[Cotrien(NO₂)₂]⁺ (29) but there is no evidence that the trans isomer has ever been obtained.

On reacting the a and β dinitro isomers with concentrated HCl, the solutions slowly became deep purple and red-violet respectively, typical of the colours of the a and β dichloro compounds. This indicates that these reactions take place largely with retention of configuration.

The absorption spectra of dinitro(tetramino)cobalt(III) complexes have been studied thoroughly and it is now accepted that cis and trans isomers
are distinguishable by small but significant differences. In the ultra-
violet region the third band is always broader and at lower wavelengths
for the cis isomer\(^{(39, 57)}\). The spectra of the \(\alpha\) and \(\beta\) trien isomers
differ slightly in \(\lambda\) and \(\varepsilon\) at the first and second bands (figure 13),
and the spectral data in table 5 confirm that Basolo\(^{(4)}\) and Selbin\(^{(58)}\)
prepared the \(\alpha\) isomers.

To obtain supporting evidence for the configurations assigned,
infrared spectra were taken of the optically active \(\alpha\) and \(\beta\)
\([\text{Co trien(NO}_2)_2\text{]ClO}_4\) (figure 14). Of special interest were the N-H
absorptions (3200 cm\(^{-1}\)), and to isolate these from the neighbouring C-H
stretching (2800-3000 cm\(^{-1}\)) and water bands (3600 cm\(^{-1}\)), the samples were
deuterated at these labile N-H bonds. The resulting N-D bands were then
observed at lower frequencies (2400-2500 cm\(^{-1}\)), and their fine structures
were measured on a high resolution single-beam instrument (figure 15).

The two N-D groups in the \(\beta\) isomer have different environments, as do
the two ND\(_2\) groups. For this reason a more complex spectrum would be
expected in the N-D stretching region than for the \(\alpha\) isomer (3 absorptions
for \(\alpha\), at least 4 and possibly 6 for \(\beta\)). This is in fact observed, figure
15(c), in accord with the assigned structures. Although the splittings
represent N-D stretches of the ND\(_2\) and ND groups, it is impossible to
assign the frequencies, as there can be up to 100 cm\(^{-1}\) difference between
the symmetric and antisymmetric NH\(_2\) stretches.

X-ray powder photographs of the \(\alpha\) and \(\beta\) dinitro isomers measured in
Cu K\(_{\alpha}\) radiation were different (figure 16).
FIGURE 13.

SPECTRA OF
CIS $\left[\text{Coen}_2(\text{NO}_2)_2\right]$ $\text{ClO}_4$ ISOMERS
(ABOVE) IN WATER

SPECTRA OF
$\left[\text{Coen}_2(\text{NO}_2)_2\right]$ $\text{NO}_3$ ISOMERS
(LEFT) IN METHANOL-WATER
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<tr>
<th>Compound</th>
<th>Isomer</th>
<th>Solvent</th>
<th>$\lambda$(μ)</th>
<th>$\varepsilon$</th>
<th>$\lambda$</th>
<th>$\varepsilon \times 10^{-3}$</th>
<th>$\lambda$</th>
<th>$\varepsilon \times 10^{-3}$</th>
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<tr>
<td>[Co(NH$_3$)$_4$(NO$_2$)$_2$]$^+$</td>
<td>cis</td>
<td>MeOH/H$_2$O</td>
<td>448</td>
<td>174</td>
<td>327</td>
<td>4.3</td>
<td>238</td>
<td>15</td>
<td>(39)</td>
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<tr>
<td></td>
<td>trans</td>
<td>&quot;</td>
<td>440</td>
<td>251</td>
<td>356</td>
<td>5.2</td>
<td>255</td>
<td>15</td>
<td>(39)</td>
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<tr>
<td>[Co en$_2$(NO$_2$)$_2$]$^+$</td>
<td>cis</td>
<td>&quot;</td>
<td>438</td>
<td>220</td>
<td>325</td>
<td>5.0</td>
<td>240</td>
<td>17</td>
<td>(39)</td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>&quot;</td>
<td>433</td>
<td>220</td>
<td>347</td>
<td>4.2</td>
<td>250</td>
<td>12</td>
<td>(39)</td>
</tr>
<tr>
<td>[Co trien(NO$_2$)$_2$]ClO$_4$</td>
<td>cis $\alpha$</td>
<td>H$_2$O</td>
<td>434</td>
<td>212</td>
<td>323</td>
<td>4.6</td>
<td>244</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cis $\beta$</td>
<td>&quot;</td>
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<td>241</td>
<td>319</td>
<td>4.1</td>
<td>244</td>
<td>25</td>
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<td>4.6</td>
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<td>(58)</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>242</td>
<td>23</td>
<td>(4)</td>
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FIGURE 14. INFRA-RED SPECTRA OF $\alpha$ AND $\beta$ [Co(phen)$_2$ClO$_4$].
Figure 15. Infra-red Spectra of α and β [CoH₃NO₂]ClO₄, Deuterated.
It has already been shown that the cis \( \beta \) isomer is the thermodynamically less stable, but it is also the more labile. This was investigated by observing changes in optical rotations and visible spectra of the two isomers. Rotations of \((+)\alpha[\text{Co trien(NO}_2)_2]\text{ClO}_4\) (in water) showed no measurable change after 30 hours at 50\(^\circ\) (\(\alpha_{500} = 0.44^\circ\)). \(\alpha_{546}\) for \((-)\beta[\text{Co trien(NO}_2)_2]\text{ClO}_4\) decreased gradually at the following rates:

\[
\begin{align*}
t_{0.5} & \sim 40 \text{ minutes at 99}\(^\circ\) \\
 t_{0.1} & \sim 5 \text{ hours at 50}\(^\circ\) \\
 t_{0.25} & \sim 50 \text{ hours at 20}\(^\circ\)
\end{align*}
\]

\(\text{NO}_2^-\) ion had no significant effect on these rates, but more alkaline conditions (\(\text{NaOAc}\) solution) caused a more rapid decrease in rotations.

The visible spectrum of \(\alpha\) in water was constant over one day at 20\(^\circ\) but thereafter the 323 \(\mu\) band began to increase slowly, although the absorption at the 434 \(\mu\) band was unaffected (60 days). The 437 \(\mu\) band of
the cis $\beta$ spectrum gradually decreased and the 319 $\mu\lambda$ band increased, but there was little net change in the absorption maximum around 437 $\mu\lambda$ ($\approx 3\%$ over 4 days). These changes were slower in the presence of NaNO$_2$. However, NaOAc had a greater effect (maximum absorption of $\beta$ remained constant over 11 days, absorption of $\alpha$ began to increase after one day).

The most likely interpretation of these observations is that the $\alpha$ isomer is quite stable, and may be satisfactorily studied in solution. The $\beta$ isomer on standing reacts with water or decomposes, rather than isomerising to $\alpha$, and for this reason the compound was isolated from solution as soon as possible in transformation reactions (p. 63).

STABILITIES OF GEOMETRIC ISOMERS

Assuming no trans isomer was present in the dinitro equilibrium mixture the cis $\alpha$ structure is thermodynamically favoured (over $\beta$) by about 0.6 kcal/mole (p. 26). However, the $\beta$ is favoured over the $\alpha$ isomer for the diaquo compounds by 1.0 kcal/mole (p. 73). It is also probable that (in acid) $\alpha[Co\ trien\ Cl_2]^+$ is the most stable of the three isomers (p. 8). Examination of molecular models established that, if angle strain at the secondary amine nitrogen was the most important factor, the order of stabilities would be cis $\alpha >$ cis $\beta >$ trans (p. 6). However, the stability of $\beta[Co\ trien(H_2O)_2]^+$ indicates that other factors must be important.

Of the various conformations possible for the two cis structures,
those that are considered to involve the least number of non-bonded H-H interactions are shown in figure 17 (a) and (b). In figure 17(a) all the C-H and N-H bonds are completely staggered. Br, Cl, H$_2$O or NO$_2$ groups can be accommodated at both positions A and B (which have equivalent environments), and it might be expected that for cis $\alpha$[Co trien(NO$_2$)$_2$]$^+$, the nitro groups would both be inclined (in the same sense) to the N-N-A-B plane (figure 17 c).

In any conformational model of the cis $\beta$ configuration some H-H interaction cannot be avoided (figure 17 b). Substituents such as Br, Cl, H$_2$O, and NO$_2$ groups can be accommodated without serious interactions at position A. However some non-bonded interaction will occur between a substituent at B and hydrogen atoms 1 and 2 (figure 17 b), and this will largely be a function of the size of the group. From this effect alone the $\alpha$ compound should be more stable than the $\beta$.

However it is conceivable that the water molecules in the $\alpha$ and $\beta$ diaquo ions can hydrogen-bond with one another. The suggested structures are shown in figure 18 (a) and (b), and it can be seen that the $\beta$ condition is more favourable in terms of the non-bonded interactions between the hydrogens on the carbons and the hydrogens on the oxygens. It would seem that in this instance the interaction between the stable trien conformation and the substituent is larger than the conformational effect when the substituent is too small to contribute. The energy difference between $\alpha$ and $\beta$ diaquo is only 1 kcal/mole, and this is small enough to be accounted for by these small interactions.
Figure 17(a). Most stable conformation of cis $\text{Co} \text{trien AB}$.$^+^-$

Figure 17(b). Most stable conformation of cis $\text{Co} \text{trien AB}$.$^+^-$

Figure 17(c). Expected structure of cis $\text{Co} \text{trien(NO$_2$)$_2$}$.$^+_1$ion.
Figure 18(a). Leybold model of suggested structure of 
\[ \text{cis } \left[ \text{Co trien(H}_2\text{O})_2 \right]^{3+} \text{ isomer.} \]

The two aquo groups are uppermost, and the suggested hydrogen-bonding between them is indicated by - - - - . Some H-H interaction such as X X (between OH\text{2} and CH\text{2}) cannot be avoided.
Figure 16(b). Leybold model of suggested structure of 

cis $\mathcal{P}[[\text{Co trien}(H_2O)_2]]^{3+}$ isomer.

The two aquo groups are uppermost, and the suggested hydrogen-bonding between them is indicated by \ldots \ldots \ldots \ldots \ldots \ldots \ldots . The H-H interaction in the trien conformation (CH$_2$,CH$_2$) is denoted by H H. (These are the atoms marked 1 and 2 in figure 17b.)
**Figure 19. Conformation of trans $[\text{CotrienAB}]^{n^+}$.
The chelate rings in the model of the trans structure can not be joined without appreciable nitrogen angle-strain. This strain is probably the largest contribution to the instability of this configuration, since the conformations in figure 19 are reasonably staggered.

No conclusions could be reached about solvation effects.

An important factor to be considered in accounting for the stabilities of the cis and trans structures is the interaction between the two substituents A and B. It is clear that the size and charge of these substituents will be significant, and that for two substituents which are negatively charged the most stable arrangement electronically will be the trans, where the central positive ion is interposed between the two negative charges. The size of the ligands may also be a major factor, and this is probably demonstrated by the stability of trans[Co trien Br₂]⁺ over the cis isomer⁵. Other cis dibromo cobalt(III) compounds are also difficult to prepare⁶.

**EXPERIMENTAL**

Triethylenetetramine (from Carbide and Carbon Chemicals Company, N.Y.) was used without further purification.

**Microanalyses**

Microanalyses of carbon and hydrogen were by the standard combustion method. Nitrogen was determined by the Kjeldahl method, except for the dinitro compounds where the Dumas method was employed. For these latter compounds rather drastic Dumas combustion conditions were necessary to
liberate all the nitrogen.

**Ultraviolet and Visible Spectra**

Spectra were measured on a Shimadzu recording spectrophotometer RS-27 in 1 cm. cells, against water as reference. Dichloro compounds were dissolved in ice-cold 0.01 N HClO₄ solution, and the spectra recorded as soon as possible (2-3 minutes). Chloroaquo spectra were measured after the above solutions had equilibrated for the appropriate times. Diaquo compounds were measured in 0.01 N HClO₄, or obtained by dissolving the corresponding carbonato isomers in 0.1 N HClO₄. Carbonato and dinitro spectra were measured in water.

**Infrared Spectra**

These were obtained over the NaCl region using a Unicam SP200 double-beam infrared spectrometer. The KBr disc method was employed for all spectral runs (1 mg. of sample in 200 mg. KBr) with either air or a KBr disc in the reference beam.

Samples of the optically active isomers of [Co trien(NO₂)₂]ClO₄ were deuterated by recrystallisation from D₂O (99.7%). The fine structures of the N-D absorptions (∼ 2400 cm⁻¹) were measured on a Perkin Elmer 112 single-beam spectrophotometer fitted with a LiF prism and calibrated with HBr gas.

**Optical Rotations**

Rotations were measured visually with a Bellingham and Stanley polarimeter, in a 1 dm. tube unless otherwise stated.
α-dinitro(triethylentetramine)cobalt(III) chloride 1-hydrate

Ice cold solutions of trien.HCl (75 ml. in 44 ml. of 11.6 N HCl) and CoCl₂·6H₂O (119 g. in 100 ml. water) were mixed and added quickly to solid NaNO₂ (72.5 g.). The mixture was aerated vigorously and the yellow cis dinitro salt commenced to separate (2 minutes). Aeration was continued for 1.5 hours at 0°C. The product was filtered, washed with ice-cold hydrochloric acid (1 N), alcohol, acetone, and air dried. (Yield 100 g., 57%).

Additional dinitro product was obtained as iodide 1-hydrate by adding excess sodium iodide to the solution. (Yield 30 g., 13%).

When the chloride was fractionally recrystallised from hot water (90°C), the least soluble material (86 g.) was shown to be the α isomer. The next fractions (8.3 g.), obtained by evaporation of the mother liquor in a stream of air over a steam bath, contained appreciable amounts of the β isomer (p. 25).

The corresponding α dinitro bromide, nitrate, and acetate may be prepared in a similar manner by using the respective cobaltous salts and acids. Varying the order of mixing the three constituents, the presence of charcoal, longer aeration times, the presence of a large excess of the respective anion (i.e. NaBr in the preparation of the bromide), or the use of trien.HOAc and excess LiCl to replace trien.HCl in the preparation of the chloride, gave no significant improvements in yield.

The analogous preparation of [Co trien(NO₂)₂]ClO₄ from Co(ClO₄)₂ solution (11.9 g. CoCO₃ in 206 ml. 1.0 N HClO₄ blown down to 50 ml. over a
steam bath), trien.HClO₄ (15 ml. in 50 ml. water and 33 ml. 3.1 N HClO₄) and NaNO₂ (14.6 g.) also gave a mixture of α and β isomers (yield 31 g., 77%). Here the order of solubilities was reversed; on fractional recrystallisation the least soluble material (2.4 g.) was largely the β isomer. (The perchlorate was converted to the triiodide with excess NaI, one drop glacial acetic acid, and hydrogen peroxide added dropwise. A suspension of the triiodide in ethanol was reduced to the iodide by bubbling through SO₂. The iodide was converted to the dinitro chloride solution by grinding with AgCl in a little water).

**Anal. Calcd.** for \(\left(\frac{1}{2}\right)\alpha[Co(C₆H₁₈N₄)(NO₂)₂]·Cl·H₂O:

<table>
<thead>
<tr>
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<th>Calcd.</th>
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<td>N</td>
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**Calcd. for \(\left(\frac{1}{2}\right)\alpha[Co(C₆H₁₈N₄)(NO₂)₂]·I·H₂O:

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**Calcd. for \(\left(\frac{1}{2}\right)\alpha[Co(C₆H₁₈N₄)(NO₂)₂]·Br·H₂O:

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**Calcd. for \(\left(\frac{1}{2}\right)\alpha[Co(C₆H₁₈N₄)(NO₂)₂]·NO₃:

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<td>N</td>
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**Calcd. for \(\left(\frac{1}{2}\right)\alpha[Co(C₆H₁₈N₄)(NO₂)₂]·ClO₄:

<table>
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<th>Calcd.</th>
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<td>H</td>
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<tr>
<td>N</td>
<td>21.19</td>
<td>20.90</td>
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</table>
Resolution of α-dinitro(triethylenetetramine)cobalt(III) chloride

To an aqueous solution of $\text{g}[\text{Co trien(NO}_2)_2]\text{Cl}_2\text{H}_2\text{O}$ (2.0 g. in 30 ml.) at 35°, Na(-)[Co en ox$_2$].H$_2$O (1.0 g.) (54) was added gradually, and red-brown $\text{g}[\text{Co trien(NO}_2)_2]$(-)[Co en ox$_2$].H$_2$O commenced to separate immediately. This was filtered after 5 minutes, washed with a small volume of iced water, alcohol and acetone, and air dried. (Yield 1.3 g., 75%)

Anal. Calcd. for $\text{g}[\text{Co(C}_6\text{H}_{18}\text{N}_4]\text{(NO}_2)_2](-)[\text{Co en ox}_2]\text{H}_2\text{O}$: C, 23.61; H, 4.62; N, 18.36. Found: C, 23.76; H, 4.54; N, 18.36.

The diastereoisomer was ground with excess NaI (added gradually) in sufficient water to give a slurry. Yellow $\text{g}[\text{Co trien(NO}_2)_2]\text{I}_2\text{H}_2\text{O}$ separated and was filtered, washed with ice-cold NaI solution, alcohol and acetone, and air dried. An 0.32% aqueous solution gave $\alpha_{546} = +0.15°$ whence $[\alpha]_{546} = +47°$.

Anal. Calcd. for $\text{g}[\text{Co(C}_6\text{H}_{18}\text{N}_4]\text{(NO}_2)_2]\text{I}_2\text{H}_2\text{O}$: C, 16.30; H, 4.56; N, 19.01. Found: C, 16.40; H, 4.86; N, 18.78.

The laevo isomer was fractionally precipitated from the filtrate as iodide or bromide by gradually adding NaI or NaBr respectively. The least soluble fractions were optically pure, for the iodide $[\alpha]_{546} = -50°$, for the bromide $[\alpha]_{546} = -55°$. 
Anal. Calcd. for (-) \text{[Co(C}_6\text{H}_{18}\text{N}_4\text{)(NO}_2\text{)}_2\text{]}I_2\text{H}_2\text{O}:

C, 16.30; H, 4.56; N, 19.01

Found: C, 16.24; H, 4.97; N, 18.85.

Calcd. for (-) \text{[Co(C}_6\text{H}_{18}\text{N}_4\text{)(NO}_2\text{)}_2\text{]}Br\text{H}_2\text{O}:

C, 18.24; H, 5.10; N, 21.27

Found: C, 18.40; H, 5.01; N, 21.04.

Racemic \text{[Co trien(NO}_2\text{)}_2\text{]} nitrate and acetate were resolved in the same manner as the chloride. The iodide and bromide were too insoluble to be resolved directly and were first converted to the acetate by shaking with a slight deficiency of silver acetate (0.95 molar ratio).

Optical isomers (+) and (-) \text{[Co trien(NO}_2\text{)}_2\text{]} iodide or bromide were fractionally recrystallised from hot water (90°) without racemisation. The least soluble fractions were optically pure, e.g.

(1) \([\alpha]_{546} = -55°

(2) \(-49°

(3) \(0

The perchlorates of the optical isomers were obtained as fine yellow needles by fractional precipitation with NaClO\text{₄} from a solution of active chloride ([\alpha]_{546} = +50°).

Anal. Calcd. for (+) \text{[Co(C}_6\text{H}_{18}\text{N}_4\text{)(NO}_2\text{)}_2\text{]}ClO\text{₄}:

Chromatographic separation of α and β dinitro isomers

Solutions of the dinitro chlorides or acetates were applied to the paper as spots, and eluted with the solvent mixtures:

- n-butanol : pyridine : water : glacial acetic acid (4 : 3 : 2 : 1) or
- n-butanol : water : acetic acid (7 : 2 : 1). Relative R.F. values for the two isomers were $\frac{\beta}{\alpha} \approx 1.7/1$. The presence of extraneous ions (NaNO₂, NaOAc, NaBr) caused some streaking so it was better to isolate the dinitro compounds before chromatographing.

In determining the $\frac{\alpha}{\beta}$ equilibrium ratio, the solution from the acetate preparation was applied to a wide sheet of chromatography paper (Whatman 3MM) in a horizontal band immediately after aerating the solution for 4 hours. After separation (8 hours), the two horizontal bands were cut apart and the isomer eluted from each band with water. Relative concentrations were determined spectrophotometrically at 435 nm (figure 13) to be $\frac{\alpha}{\beta} = 2.7$. This ratio increased with the time the acetate solution was left stand before chromatographing, probably due to decomposition of the β isomer (p. 30). $\frac{\alpha}{\beta} = 3.5$ after two days. Both isomers showed little change in rotations or spectra after standing in the chromatography solvent over the time taken for separation.

α-dichloro(triethylenetetramine)cobalt(III) chloride

A mixture of α[Co trien(NO₂)₂]Cl.H₂O (97.5 g. in 100 ml. water) and excess HCl (70 ml. of 11.6 N) was evaporated on a steam bath to dryness (overnight). The purple product was ground in ethanol, filtered, washed with ethanol and acetone, and air dried. The yield of mixed α and β
[Co trien Cl₂]Cl was theoretical (86 g.). (table 1).

The method described by Basolo(4), aeration of a mixture of triethylenetetramine and excess CoCl₂, followed by addition of 10 N HCl and evaporation of the solution, gave a crude product which was blue rather than violet. The blue colour was probably due to the anion [CoCl₄]²⁻ and was difficult to remove by recrystallisation. In Basolo's method, as evaporation proceeded and successive crops of crystals were filtered, the mother liquor became dark olive-green. However, the addition of LiClO₄ did not precipitate trans[Co trien Cl₂]ClO₄ (p. 56).

The product was dissolved in the minimum volume of boiling 3N HCl, filtered through a sintered-glass filter, and stood overnight in a refrigerator. The crystals were filtered off, washed with ice-cold HCl (1N), alcohol and acetone, and air dried. Two recrystallisations gave the pure a isomer, (solubility approximately 2.6 g./100 ml.).


Found: C, 23.10; H, 5.81; N, 17.75.

Resolution of α-dichloro(triethylenetetramine) cobalt(III) chloride

The resolution was carried out in slightly acid solution to suppress fast hydrolysis reactions. The extent of aquation was minimised by working quickly. Small-scale preliminary trials established the solubility of this isomer, and hence the amount of preweighed resolving agent to be used in the large-scale resolution.

A saturated solution of twice recrystallised α[Co trien Cl₂]Cl (28 g.) was made by shaking it vigorously with 800 ml. acetic acid solution pH 3 at room temperature for two minutes. The undissolved material (8.1 g.) was
filtered off. Na⁺[Co en ox₂].H₂O (54) was then added (11.2 g.), and
the solution was stirred and the beaker was scratched with a glass rod.
The red-violet diastereoisomer (−)Co trien Cl₂(+)Co en ox₂].H₂O began
to separate immediately, and was filtered after 5 minutes, washed with
methanol and acetone, and air dried. It was quite insoluble and could not
be recrystallised. The yield was not improved by working at lower
temperatures nor by allowing the solution to stand for a longer time.
(Yield 15.3 g., 81%). The measured optical rotations were:
[α]₀ = −1050°, [α]₀ = −0.43° for 0.0408% solution in 0.01 N HClO₄,
[α]₅₇₈ = −1590° (at this wavelength the resolving agent has nearly zero
rotation).

Anal. Calcd. for (−)Co(C₆H₁₆N₄)Cl₂(+)Co(CₙHₙ₉N₉)₂Cl₂O₄]:
C, 24.44; H, 4.75; N, 14.25. Found: C, 24.57; H, 4.92;
N, 14.34.

(−)α-dichloro(triethylenetetramine)cobalt(III) iodide, 0.5-hydrate

The diastereoisomer was ground (twice) in an ice-cold mortar with
NaI (excess) and a little ice-cold water containing 1 drop of glacial
acetic acid. The slightly soluble (−)Co trien Cl₂]I was filtered off,
washed with a little ice-cold NaI solution, alcohol and acetone and air
dried. The grinding of the slurry was carried out as quickly as possible.

The (−)Co trien Cl₂]I was converted to the chloride by shaking it
vigorously with excess AgCl in water containing a drop of acetic acid.
AgI was filtered off and the α isomer was fractionally crystallised as the
iodide or perchlorate by adding NaI or NaClO₄. Both iodide and perchlorate
crystallised as deep-violet needles and the optical forms were less soluble
than the racemates.

Alternatively, the iodide was transformed to acetate by shaking it vigorously for three minutes with a slight deficiency of silver acetate in a small volume of ice-water containing one drop of acetic acid. AgI was filtered off and the iodide or perchlorate fractionally crystallised as before.

The maximum rotations measured were: iodide, $[\alpha]_D = +2100^\circ$, $-2130^\circ$ ($\alpha_D = -1.06^\circ$ for 0.05% solution in acetic acid), $[\alpha]_{578} = +2320^\circ$, $-2340^\circ$; perchlorate, $[\alpha]_D = +2330^\circ$, $-2250^\circ$ ($\alpha_D = +0.93^\circ$ for 0.04% solution in acetic acid).

Anal. Calcd. for $[\text{Co(C}_6\text{H}_{18}\text{N}_4\text{)}\text{Cl}_2]\text{I}_0.5\text{H}_2\text{O}$:

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<th>Found (for dextro isomer)</th>
<th>Found (for laevo isomer)</th>
</tr>
</thead>
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<td>17.59</td>
</tr>
<tr>
<td>H</td>
<td>4.61</td>
<td>4.59</td>
<td>4.59</td>
</tr>
<tr>
<td>N</td>
<td>13.59</td>
<td>13.28</td>
<td>13.59</td>
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</table>

Calcd. for $[\text{Co(C}_6\text{H}_{18}\text{N}_4\text{)}\text{Cl}_2]\text{ClO}_4$:

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
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<td>19.38</td>
</tr>
<tr>
<td>H</td>
<td>4.82</td>
<td>4.75</td>
<td>4.81</td>
</tr>
<tr>
<td>N</td>
<td>14.91</td>
<td>14.55</td>
<td>14.80</td>
</tr>
</tbody>
</table>

Active $[\text{Co trien Cl}_2]\text{I}$ was converted to perchlorate by grinding twice in an ice-cold mortar with a little water containing one drop of acetic acid and excess NaClO$_4$.

In another resolution the diastereoisomer (15.3 g.) was ground twice in an ice-cold mortar with a little water containing one drop of 5N HClO$_4$, and excess NaClO$_4$ (added in small portions). The (-)$[\text{Co trien Cl}_2]\text{ClO}_4$
which crystallised was filtered, washed with ice-cold NaClO₄ solution, methanol and ether, and air dried. (Yield 10.3 g.). The following rotations were observed: $[\alpha]_D = -1780^\circ$ ($\alpha_D = -0.73^\circ$ for a 0.411% solution in 0.01 N HClO₄), $[\alpha]_{578} = -2030^\circ$ (76% optically pure).

(+) $\alpha$-dichloro(triethylenetetramine)cobalt(III) perchlorate

From the filtrate from the separation of the diastereoisomer, the opposite optical isomer (+)$\alpha$[Co trien Cl₂]Cl and remaining resolving agent were totally precipitated by adding a large excess of acetone (10 litres), and filtered after 10 minutes.

This product was ground with HClO₄ and NaClO₄ as described for the diastereoisomer, and the (+)$\alpha$[Co trien Cl₂]ClO₄ was filtered off. (Yield 10.3 g., 86%). It was 77% optically pure, $[\alpha]_D = +1790^\circ$, $[\alpha]_{578} = +2090^\circ$.

The dextro isomer could not be precipitated from the filtrate by ClO₄⁻ or I⁻ ions.

Samples of (+) and (-) perchlorates could not be purified.

The resolving agent was recovered from the filtrates by precipitating it with excess ethanol.

(-) $\alpha$-carbonato(triethylenetetramine)cobalt(III) perchlorate 1-hydrate

Twice recrystallised $\alpha$[Co trien Cl₂]Cl (20.7 g.) was added to HClO₄ solution (150 ml. of 0.013 M), and the solution was stirred for a time sufficient for the dichloro chloride to dissolve, and aquate completely to the chloro-aquo stage (30 hours). Excess NaHCO₃ (12.6 g.) was added, followed by NaClO₄ (14 g.). The mixture was then evaporated in a current of air at room temperature and (-)$\alpha$[Co trien CO₃]ClO₄ soon began to
crystallise. It was filtered off, and recrystallised fractionally from hot water (80°) by cooling and adding NaClO₄. The fractions were filtered off, washed with methanol containing a little water, ethanol and acetone, and dried at 50°. By their visible spectra, the first two fractions (yield 8.7 g., 34%) were shown to be pure [Co trien CO₃ClO₄·H₂O].

A resolution of the compound was attempted by adding K(+)[Co en mal₂]·2H₂O (1 mole) to a solution of [+]g[Co trien CO₃ClO₄·H₂O] (1 mole) at 50°. On evaporation at room temperature (+)g[Co trien CO₃ClO₄] separated as the least soluble component. This contrasts with [Co trien CO₃ClO₄], which may be resolved in this way since KClO₄ first separates, and then the diastereoisomer may be crystallised.

(+) α-carbonato(triethylenetetramine)cobalt(III) perchlorate, 1-hydrate.

This was prepared in a similar manner to the racemic perchlorate by transforming the active cis α dichloro perchlorate with full retention of configuration (chapter 3). (+)g[Co trien Cl₂]ClO₄ (11.5 g., [α]D = +1600°, 77% optically pure) was aquated in 0.01 M HClO₄ (200 ml) for 15 hours. NaHCO₃ (5.7 g.) was added, and after 15 minutes NaClO₄ (8.4 g.) was added. Orange-red crystals of (+)g[Co trien CO₃]ClO₄·H₂O began to crystallise in a few minutes, and were filtered off after one hour. They were washed with methanol/water, ethanol and acetone, and dried at 50°. (Yield 5.4 g., 46%). This fraction gave [α]D = +1200° (αD = +1.24° for 0.103% aqueous solution), [α]578 = +1450°. Anal. Calcd. for (+)g[Co(C₆H₁₆N₄)CO₃]ClO₄·H₂O: C, 21.97; H, 5.27; N, 14.64. Found: C, 21.99; H, 5.21; N, 14.71.
A further fraction (4.1 g.), obtained by reducing the volume to 50 ml. in a rotary evaporator, gave \([\alpha]_D = +1050^\circ\) and \([\alpha]_{578} = +1300^\circ\).

On recrystallisation from warm water (50°) as described for the racemic isomer, the measured rotation could not be increased above \([\alpha]_D = +1200^\circ\), and the optical isomers were less soluble than the racemate. The (+)\([\text{Co trien CO}_3]\text{ClO}_4\cdot\text{H}_2\text{O}\) crystallised as plates or prisms; the corresponding \(\beta\) isomer was obtained only as needles.

\((+)_546\alpha\text{-diaquo(triethylenetetramine)cobalt(III) perchlorate}\)

To (+)\([\text{Co trien CO}_3]\text{ClO}_4\cdot\text{H}_2\text{O}\) (2.59 g., \([\alpha]_D = +1200^\circ\)) 10% excess HC\(\text{ClO}_4\) (3.0 ml. of 5M) was added dropwise with stirring at 0°C. After effervescence was complete, the solution in a beaker was placed in a vacuum desiccator. When the solution had evaporated nearly to dryness (1 week) the well-formed deep reddish-carmine crystals of (+)_546\alpha[\text{Co trien(H}_2\text{O})_2]\text{ClO}_4\cdot3 were filtered off in a sintered-glass filter, washed twice with ether, and quickly placed in the vacuum desiccator. They were analysed after 3 days. (Yield 3.13 g., 86%).

Anal. Calcd. for (+)_546\alpha[\text{Co(C}_6\text{H}_{16}N_4)(\text{H}_2\text{O})_2]\text{ClO}_4\cdot3: C, 13.35; H, 4.11; N, 10.39. Found: C, 13.29; H, 4.02; N, 10.22.

The measured rotation was \([\alpha]_D = -168^\circ\) \(q_D = -0.19^\circ\) for 0.0566% solution in 0.01 M HC\(\text{ClO}_4\) in a 2 dm. tube.

The (+)\([\text{Co trien(H}_2\text{O})_2]\text{ClO}_4\cdot3 was slightly hygroscopic. A sample on an enclosed balance increased in weight by about 1% in 15 minutes. Therefore, the compound was weighed out quickly for kinetic runs in the
normal manner. The sample used was re-analysed after the kinetics had been completed and was found to be still analytically pure. However, the complex decomposed when left under vacuum for an extended period, (p. 50).

Trans-dibromo(triethylenetetramine)cobalt(III) bromide

This was prepared in a similar manner to that described for $\text{g}[\text{Co trien } \text{Cl}_2] \text{Cl} \cdot \text{g}[\text{Co trien}(\text{NO}_2)_2] \text{Br} \cdot \text{H}_2\text{O}$ (79.0 g. in 100 ml. water) was treated with excess HBr (77 ml. of 5.8 N) and after evaporation to dryness, the olive-green product was ground in ethanol, filtered, washed with ethanol and ether, and dried at 50°. (Yield 85 g., 95%). The product contained a little unreacted $\text{g}[\text{Co trien}(\text{NO}_2)_2] \text{Br} \cdot \text{H}_2\text{O}$, but recrystallisation was not possible (5).

$\beta$-Carbonato(triethylenetetramine)cobalt(III) chloride 1.5-hydrate

A mixture of $\text{g}[\text{Co trien } \text{Cl}_2] \text{Cl}$ (85 g. of crude) and Li$_2$CO$_3$ (25 g.) in water (170 ml.) was heated on a steam bath with occasional stirring. The violet colour soon changed to red, and after the solution had become alkaline (60 minutes) the excess Li$_2$CO$_3$ was filtered from the hot solution. After cooling, CaCl$_2$ (4 g.) was added to eliminate carbonate ion and the solution was filtered again. From the filtrate, $\beta[\text{Co trien } \text{CO}_3] \text{Cl} \cdot 1.5\text{H}_2\text{O}$ was crystallised by carefully adding ethanol. After standing, the crystals were filtered, washed with ethanol and acetone, and air dried. (Yield 79 g., 89%). The visible spectrum of this crude product showed that it contained about 80% of the $\beta$ isomer. The product was recrystallised from a small volume of warm water by carefully adding ethanol.
Anal. Calcd. for $\beta[\text{Co(C}_6\text{H}_{18}\text{N}_4\text{)}\text{CO}_3]\text{Cl}$. 1.5 H$_2$O: C, 25.65; H, 6.41; N, 17.10. Found: C, 25.52; H, 6.33; N, 17.19.

The $\beta$ carbonato perchlorate was obtained as well-formed red needles by adding NaClO$_4$ to a solution of $\beta[\text{Co trien CO}_3]\text{Cl}$. It was recrystallised slowly from hot water (50°C) by leaving the solution to stand (5 days). The large crystals which first separated had a visible spectrum identical to that of optically pure $(-)\beta[\text{Co trien CO}_3]\text{ClO}_4\cdot\text{H}_2\text{O}$.

$\beta[\text{Co trien CO}_3]\text{Br}$. 0.5 H$_2$O. 0.5 C$_2$H$_5$OH was prepared from trans [Co trien Br$_2$]Br (89 g. in 180 ml. water) and Li$_2$CO$_3$ (20 g.) in a similar manner to that above. After removing excess Li$_2$CO$_3$, the solution was cooled in an ice bath for one hour. The impurity $\alpha[\text{Co trien(NO)}\text{Br}]\text{Br}\cdot\text{H}_2\text{O}$ which separated (p. 45) was filtered. Ethanol was added to the filtrate and the deep-red product crystallised on standing. (Yield 57 g., 83%). It was recrystallised from water by the addition of ethanol.

Anal. Calcd. for $\beta[\text{Co(C}_6\text{H}_{18}\text{N}_4\text{)}\text{CO}_3]\text{Br}$. 0.5 H$_2$O. 0.5 C$_2$H$_5$OH: C, 25.48; H, 5.89; N, 14.86. Found: C, 25.49; H, 5.71; N, 15.18.

The same sample was also recrystallised from water by methanol.

Anal. Calcd. for $\beta[\text{Co(C}_6\text{H}_{18}\text{N}_4\text{)}\text{CO}_3]\text{Br}$. 0.5 H$_2$O. 0.5 CH$_3$OH: C, 24.33; H, 5.72; N, 15.14. Found: C, 24.45; H, 5.48; N, 15.21.

The difficulties experienced by previous workers (4, 14) in crystallising trien carbonato compounds were ascribed to high solubilities, but it was likely that mixtures of the carbonato and diaquo isomers were present. Once crystallised, all $\alpha$ and $\beta$ carbonato derivatives could be
Silver (++) bis(malonato)ethylenediamine cobalt(III) 2-Hydrate

To an aqueous solution of K[Co en mal\(_2\)] \(\cdot\) \(2\)H\(_2\)O (54) (38.8 g. in 70 ml.), a warm solution containing a slight excess of AgNO\(_3\) (17.4 g. in 25 ml.) was added. On cooling, Ag[Co en mal\(_2\)] \(\cdot\) 2H\(_2\)O precipitated. It was filtered off, washed with a small volume of iced water, methanol and acetone, and air dried. From the filtrate more product was precipitated by adding ethanol. The second fraction was recrystallised from hot water (60\(^\circ\)) by the addition of ethanol, and added to the main crop. (Yield 43.1 g., 94%). The product had the following rotations:

\[ [\alpha]_D = +1430^\circ \quad (\alpha_D = +0.73^\circ \text{ for an } 0.0511\% \text{ aqueous solution}), \]

\[ [\alpha]_{576} = +2080^\circ, \quad [\alpha]_{546} = +1060^\circ. \]

Anal. Calcd. for Ag[Co(C\(_2\)H\(_6\)N\(_2\))(C\(_5\)H\(_2\)O\(_4\))] \(\cdot\) 2H\(_2\)O: C, 20.57; H, 3.45; N, 6.00. Found: C, 20.76; H, 3.56; N, 5.96.

Resolution of \(\beta\)-carbonato(triethylenetetramine)cobalt(III) Bromide

Ag[Co en mal\(_2\)] \(\cdot\) 2H\(_2\)O (43.1 g.) was shaken with a slight excess of \(\beta\)[Co trien CO\(_3\)]Br \(\cdot\) 0.5 H\(_2\)O, 0.5 C\(_2\)H\(_5\)OH (32.6 g. in 100 ml. water) for 5 minutes in a stoppered flask. The silver bromide was filtered off and washed with water, and the filtrate and washings (which were free of Ag\(^+\) ion) were evaporated in a rotary evaporator to 100 ml. Methanol and ethanol were added, and on standing overnight the diastereoisomer (+)\(\beta\)[Co trien CO\(_3\])\(\cdot\)\(\beta\)[Co en mal\(_2\)] \(\cdot\) 4H\(_2\)O crystallised as fine silvery-pink
plates. It was filtered off, washed with methanol and acetone, and air-dried. (Yield 23.7 g., 78%). The product gave the following rotations:

\[ \alpha_D = +1500^\circ \]
\[ \alpha_D = +0.66^\circ \text{ for an 0.044% aqueous solution}, \]
\[ \alpha_{578} = +2230^\circ. \]

On evaporating the filtrate further, to 60 ml., and repeating the precipitation with methanol/ethanol, very little more diastereoisomer was obtained (0.3 g. having \[ \alpha_D = +1440^\circ \]).

The diastereoisomer was recrystallised from the minimum volume of water by adding methanol (or dimethylformamide) to incipient crystallisation and allowing the solution to stand. The maximum rotation obtained (least soluble fraction) was \[ \alpha_D = +1540^\circ \], so that the diastereoisomer obtained in the above resolution was almost optically pure.

**Anal. Calcd. for (+)β-[Co(\(C_6H_{18}N_4\))CO_3](+)[Co(\(C_2H_6N_2\))(\(C_3H_4O_2\))_2]·4H_2O:**

\[ \text{C, 27.27%; H, 5.76%; N, 12.73. Found: C, 27.35; H, 5.88; N, 12.50.} \]

(+) β-carbonato(triethylenetetramine)cobalt(III) perchlorate 1-hydrate

The diastereoisomer (22.5 g., \[ \alpha_D = +1540^\circ \]) was dissolved in the minimum volume of water (50 ml.), and when excess NaClO_4 was added, orange-red (+)β[Co trien CO_3]ClO_4·H_2O began to crystallise immediately. It was filtered after 5 minutes, washed with methanol containing a little water, methanol and acetone, and air-dried. (Yield 12.0 g., 88%). The product was recrystallised from warm water (50°) by adding ethanol to incipient crystallisation. (+)β[Co trien CO_3]ClO_4·H_2O crystallised as orange-red needles and was filtered fractionally, washed with ice-cold NaClO_4 solution, methanol and acetone, and dried at 50°. The optical isomers were less
soluble than the racemate. The yield of pure isomer, $[\alpha]_D = +770^\circ$ ($\alpha = 0.73^\circ$ for 0.0957% aqueous solution), was 11.3 g.

Anal. Calcd. for $[\pm]_D^2 [\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4\text{CO})_3\text{ClO}_4\cdot\text{H}_2\text{O}]$: C, 21.97; H, 5.27; N, 14.64. Found: C, 21.91; H, 5.37; N, 14.55.

The diastereoisomer was also converted to the carbonato iodide (through the triiodide and reduction with Na$_2$S$_2$O$_3$), and to the tetraphenylborate derivative, which was acetone soluble.

Anal. Calcd. for $[\pm]_D^2 [\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4\text{CO})_3\text{B}(\text{C}_6\text{H}_5)_4] \cdot 1.5 \text{H}_2\text{O}$: C, 60.91; H, 6.55. Found: C, 60.63; H, 6.62.

$(-)\beta$-carbonato(triethylenetetramine)cobalt(III) perchlorate 1-hydrate

The filtrate from the separation of diastereoisomer was reduced in volume on a rotary evaporator to 50 ml. On addition of excess NaClO$_4$; $(-)\beta$[Co trien CO$_3$]ClO$_4$·H$_2$O crystallised immediately and this was recrystallised as described above. The pure product had the following rotations: $[\alpha]_D = -780^\circ$, $[\alpha]_{576} = -930^\circ$. (Yield 9.5 g, 54%).

Anal. Calcd. for $(-)\beta[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4\text{CO})_3\text{ClO}_4\cdot\text{H}_2\text{O}]$: C, 21.97; H, 5.27; N, 14.64. Found: C, 22.08; H, 5.31; N, 14.64.

The resolving agent Na(+)[Co en mal$_2$]·2H$_2$O was precipitated from the filtrates with ethanol.

$(-)\beta$-diaquo(triethylenetetramine)cobalt(III) perchlorate

This was prepared in a similar manner to that described for the corresponding cis $\alpha$ isomer (p. 44). $(-)\beta[\text{Co trien CO}_3\text{ClO}_4\cdot\text{H}_2\text{O}$ (1.3 g).
[α]D = -730° was carefully treated with excess HClO₄ (2.0 ml. of 5N), and the solution placed in a vacuum desiccator. The orange-red product slowly crystallised and after 4 hours was filtered off on a sintered-glass filter, washed with ether, and dried in a vacuum desiccator (3 days). It was very soluble in water, soluble in the alcohols and acetone, but insoluble in ether.


An 0.205 M solution in 0.01 M HClO₄ gave αD = -0.38° whence [α]D = -186°, [α]₅₇₈ = -200°. It was shown to be optically pure by transforming the above solution to optically pure (-)$_{5468}$Co trien CO₃⁺ with excess NaHCO₃. The carbonato solution had αD = -1.12°, whence [M]D = -2970°.

A sample of (-)$_{5468}$Co trien(H₂O)₂(ClO₄)₃ on an enclosed balance increased in weight by 6% in 13 minutes. Samples for kinetics were weighed in the normal manner as quickly as possible.

Decomposition of cis-diaquo(triethylenetetramine)cobalt(III) Perchlorates

When samples of both the α and β isomers were kept in a desiccator (over calcium chloride) for a long period (3 months) both isomers darkened in colour (the α changed from reddish-carmine to violet-red, the β changed from reddish-orange to brownish-orange), were much less hygroscopic than the original samples, and both contained some dark brown or dark green-brown material, insoluble in water. However the samples were completely soluble in ethanol and acetone. The dry, freshly prepared samples were
merely stored in stoppered bottles, and under these conditions they were quite stable.

*3-dinitro(triethylenetetramine)cobalt(III) nitrate*

A slight excess of HNO₃ (101 ml. of 2N) was slowly added to [Co trien CO₃]Cl. 1.5 H₂O (32.7 g.). After 30 minutes, NaN₃ (15.0 g.) was added to the diaquo solution and yellow-orange crystals of [Co trien(NO₂)₂]NO₃ slowly separated (1 hour). The product was filtered off after one day, washed quickly with ice-cold HNO₃ (1 N), alcohol and acetone, and air-dried. (Yield 28 g., 80%). It was recrystallised from hot water (90°).


*3-dinitro(triethylenetetramine)cobalt(III) iodide*

NaI was added to a hot solution of [Co trien(NO₂)₂]NO₃ (4.4 g. in 90 ml. water at 80°) and the corresponding iodide crystallised out. It was filtered off, washed with ice-cold NaI solution, alcohol and acetone, and air-dried. (Yield 4.8 g., 90%). The complex was recrystallised quickly from hot water, 90°.

Anal. Calcd. for [Co(C₆H₁₈N₄)(NO₂)₂]I: C, 16.99; H, 4.28; N, 19.82. Found: C, 17.06; H, 4.27; N, 19.84.

Resolution of 3-dinitro(triethylenetetramine)cobalt(III) iodide

[Co trien(NO₂)₂]I (10.0 g. in 80 ml. water containing one drop of glacial acetic acid) was transformed to the acetate, by shaking the
solution with a slight deficiency of silver acetate (3.9 g.). The AgI was filtered off and sodium(+)antimonyl tartrate (3.6 g.) was added slowly to the solution. On scratching the sides of the vessel, the yellow diastereoisomer \((+)_546[\text{Co trien(NO}_2)_2] (+)[\text{SbO-tart}]\) commenced to separate immediately. (Yield 6.4 g.) The diastereoisomer was recrystallised fractionally from hot water (70°). The least soluble fractions were the most active, and the highest rotations measured were: \([\alpha]_D = +138°\) \((\alpha_D = +0.41° \text{ for } 0.30\% \text{ aqueous solution}), [\alpha]_{578} = +142°, [\alpha]_{546} = +198°.\)

Anal. Calcd. for \((+)_546[\text{Co(C}_6\text{H}_{18}\text{N}_4)(\text{NO}_2)_2] (+)[\text{SbO(C}_4\text{H}_4\text{O}_6}]\): C, 20.60; H, 3.80; N, 14.42. Found: C, 20.63; H, 3.89; N, 14.25.

The diastereoisomer was shaken in solution with excess NaI, and \((+)_546[\text{Co trien(NO}_2)_2] \)I precipitated.

The laevo isomer was precipitated as the iodide, by addition of NaI to the filtrate after the removal of the diastereoisomer.

Active dinitro iodides were purified by rapid fractional recrystallisation from hot water (95°). The fractions were filtered, washed with ice-cold NaI solution, ethanol and acetone, and air dried. The optical isomers were less soluble than the racemate, and the maximum rotations measured were: \([\alpha]_D = +149°, -156°; [\alpha]_{578} = +160°, -167°; [\alpha]_{546} = +255°, -255°.\)

Anal. Calcd. for \([\text{Co(C}_6\text{H}_{18}\text{N}_4)(\text{NO}_2)_2] \)I:

C, 16.99; H, 4.28; N, 19.62

Found (dextro isomer): C, 17.03; H, 4.24; N, 19.70

(laevo isomer): C, 17.01; H, 4.26; N, 19.53.
Active β dinitro perchlorates were prepared by shaking the corresponding active iodides with excess AgCl in water. The silver halides were filtered off and the perchlorates were fractionally precipitated as yellow plates by adding NaClO₄ solution slowly. The active isomers which were less soluble than the racemate, were filtered, washed with ice-cold NaClO₄ solution, ethanol and acetone, and air dried. The optically pure laevo perchlorate gave the following rotations:

\[[\alpha]_D = -156^\circ \text{ (} [\alpha]_D = -0.31^\circ \text{ for an 0.198% aqueous solution)}\], \[[\alpha]_{578} = -181^\circ\], \[[\alpha]_{546} = -282^\circ\].

Anal. Calcd. for \((-\)₅₄₆\[\text{Co(C}_6\text{H}_₁₈\text{N}_₄\text{)}(\text{NO}_₂)_₂\]ClO₄; C, 18.17; H, 4.56; N, 21.19. Found: C, 18.30; H, 4.71; N, 21.20.

Although not quite as stable optically as the α isomer, the β dinitro perchlorate and iodide were recrystallised from boiling water by cooling and adding NaClO₄ or NaI without appreciable change in rotations.

β-dichloro(triethylenetetramine)cobalt(III) chloride 0.5-hydrate

β[Co trien Cl₂]Cl. 1.5 H₂O (16.1 g.) was suspended in ethanol (500 ml.) saturated with dry hydrogen chloride, and stirred. There was a slow effervescence, and in the early stage more HCl was bubbled through the solution periodically. After standing overnight, β[Co trien Cl₂]Cl was filtered off as a fine reddish-violet powder, washed with ethanol and acetone, and air-dried. (Yield 12.5 g., 82%).

This product was resolved without purification, but for analysis a saturated solution was made up quickly in dilute acetic acid (pH 3) at room temperature, and the compound recrystallised by cooling quickly in an
ice-bath and adding hydrochloric acid (12 N).

Anal. Calcd. for $\beta[\text{Co(C}_{6}\text{H}_{18}\text{N}_{4})\text{Cl}_{2}]\text{Cl} \cdot 0.5 \text{H}_{2}\text{O}$: C, 22.46; H, 5.93; N, 17.47. Found: C, 22.16; H, 5.83; N, 17.38.

Resolution of $\beta$-dichloro(triethylenetetramine)cobalt(III) chloride

This isomer aquated rapidly ($\frac{1}{2}$ in acid solution $\approx$ 8 minutes at $25^\circ$) and the resolution was therefore carried out quickly, and where possible at low temperatures. A saturated solution of the dichloro isomer, prepared by shaking the solid with dilute acetic acid solution (pH 3) at $20^\circ$C for 2 minutes, was filtered quickly into a flask cooled in an ice bath. (The residue was enriched in the less soluble $\alpha$ isomer). A solution thus prepared (8.2 g. in 300 ml.) was immediately treated with Na(+)$[\text{Co en ox}_2]\cdot\text{H}_2\text{O}$ (5.0 g.) (54). The diastereoisomer $(-)\beta[\text{Co trien Cl}_2](+)[\text{Co en ox}_2]\cdot\text{H}_2\text{O}$ separated immediately and was filtered off after 4 minutes. It was washed with a little iced water, alcohol and acetone, and air dried. (Yield 5.0 g., 65%). An 0.066% solution in cold 0.01 N HClO$_4$ gave $\sigma_D = +0.09^\circ$, $\sigma_{578} = -0.09 \pm 0.02^\circ$, whence $[\mathcal{M}]_D \approx +800^\circ$, $[\mathcal{M}]_{578} \approx -800^\circ$. The optical purity of the complex was determined more accurately by converting the above solution, after it had aquated to the chloroaquo ion (1 hour at $25^\circ$) to the carbonato complex with excess NaHCO$_3$ (p. 70). The rotation measured was $\sigma_{578} = -0.35^\circ$, whence $[\mathcal{M}]_{578} = -3100^\circ$. At this wavelength the $(+) [\text{Co en ox}_2]^{-}$ ion has nearly zero rotation, and the resolved $\beta$ carbonato compound has $[\mathcal{M}]_{578} = -3700^\circ$. No diastereoisomer separated when the resolution was carried out at room temperature.
Anal. Calcd. for \((-\)\beta[Co(C_6H_{16}N_4)Cl_2](+)\alpha[Co(C_2H_8N_2)(C_2O_4)_2].H_2O: \text{C, 24.44; H, 4.75; N, 14.25. Found: C, 24.25; H, 4.86; N, 14.04.}

\((-\)\beta[Co trien Cl_2])I was recovered from the diastereoisomer by a procedure identical to that described for the \(\alpha\) isomer, (p. 40). The grinding with NaI was carried out quickly at 0°C. The isomer was purified by shaking the iodide (3 g.) in an ice-cold dilute acetic acid solution (60 ml.) with an excess of AgCl. The silver halides were filtered off (2 minutes) and NaClO_4 was added in small portions to the filtrate to fractionally precipitate \((-\)\beta[Co trien Cl_2]ClO_4 as violet plates. These were washed with ice-cold NaClO_4 solution, ethanol and acetone, and air dried. The optical isomer was less soluble than the racemate, and the rotation measured for the least soluble fraction was \(\alpha_D = -0.12^\circ\) for a 0.051% solution, whence \([\alpha]_D = -230^\circ\). The solution was transformed to \(\beta[Co trien CO_3]^+\) and \(\alpha_D = -0.42^\circ\) whence \([\Delta]_D = -3100^\circ\).


After removal of the diastereoisomer, \((+)\beta[Co trien Cl_2]ClO_4 was precipitated fractionally from the filtrate by adding NaClO_4. (Total yield 3.9 g., 80%). An 0.057% solution of the least soluble fraction (1 g.) gave \(\alpha_D = +0.15^\circ\) whence \([\alpha]_D = +240^\circ\). The solution was converted to the \(\beta[Co trien CO_3]^+\) ion which gave \([\Delta]_D = +2650^\circ\). Fractions 2 (1.4 g.) and 3 (1.5 g.) gave \([\Delta]_D = +1600^\circ\) and +450° respectively for the carbonato complex.
The combined filtrates were reduced to a small volume and the resolving agent recovered by adding ethanol.

**Trans-dichloro(triethylenetetramine)cobalt(III) chloride and perchlorate**

$\beta[\text{Co trien CO}_3]\text{Cl. }1.5\text{H}_2\text{O} (20\text{ g.})$ was treated with excess ice-cold HCl (50 ml. of 12 N.). The solution was placed in the refrigerator and as the product crystallised, it was filtered fractionally in a sintered-glass filter, washed with acetone, and air-dried. The first two fractions (7.0 g.), which separated after one day, were red-violet. The next fraction obtained (0.2 g., after 2 days) was all green trans$[\text{Co trien Cl}_2]\text{Cl. HCl. H}_2\text{O}$.

Anal. Calcd. for trans$[\text{Co(C}_6\text{H}_{15}\text{N}_4)\text{Cl}_2]\text{Cl.HCl.H}_2\text{O}$: C, 19.69; H, 5.78; N, 15.31. Found: C, 19.51; H, 6.07; N, 15.25.

More violet product was filtered off over the next 7 days, and this was shown to be largely the $\beta$ isomer (p. 13). A microscopic examination showed that all fractions contained some green crystals of the trans isomer.

The violet product (about 10 g.) was refluxed in methanol (300 ml.) for one hour. The residue was filtered off and excess dry LiClO$_4$ was then added to the green solution. On cooling in an ice bath and scratching the vessel walls with a glass rod, green crystals of trans$[\text{Co trien Cl}_2]\text{ClO}_4$ were obtained. These were filtered off after 10 minutes to avoid contamination with the cis isomers, washed with ethanol and ether, and air dried. The residue was extracted again and more of the trans isomer obtained. (Total yield 1.5 g.).
Anal. Calcd. for \text{trans}[\text{Co(C}_6\text{H}_{16}\text{N}_4\text{Cl}_2]\text{ClO}_4: \text{C}, 19.16; \text{H}, 4.82; \text{N}, 14.91. \text{Found: } \text{C}, 19.23; \text{H}, 4.72; \text{N}, 14.82.
INTRODUCTION TO TRANSFORMATION REACTIONS

Many substitution reactions of geometrical isomers of cobalt(III) complexes yield a mixture of cis and trans products, and rearrangements to form the other geometrical isomer are quite common. However, some reactions always seem to occur predominantly with retention of geometrical (and optical) configuration, and a few proceed with complete retention of geometric structure and optical activity \((35,70)\).

To determine the relative geometric configurations \((\alpha\) or \(\beta\)) of the prepared cis diacido-triethylenetetramine-cobalt(III) compounds, it was necessary to utilise reactions which are known to occur without any rearrangement or racemisation in similar systems, in particular the bis(en) series. In fact this consideration dictated the preparations described in chapter 2, and the isomers were incorporated in the following scheme of reactions:

\[
\begin{align*}
\text{cis[CotrienCl_2]^+} & \xrightarrow{H_2O} \text{cis[CotrienCl(H_2O)]}^2+ \xrightarrow{2\text{HCO}_3^-} \text{[CotrienCO_3]^+} \\
& \xrightarrow{2\text{H}^+} \text{cis[Cotrien(H_2O)_2]^3+} \xrightarrow{2\text{NO}_2^-} \text{cis[Cotrien(NO_2)_2]^+}
\end{align*}
\]

It is convenient to review the stereochemical, kinetic and mechanistic
evidence that each of these separate steps occurs with retention in similar systems.

The stereochemical course of aquation reactions is reviewed in chapter 4, and in particular it has been found that all cis compounds of the type [Co en₂ ACl]ⁿ⁺ aquate stereospecifically in acid solution to give cis[Co en₂ A(H₂O)](n⁺+1)⁺ as the first aquation product. In all instances where active compounds have been used, no loss of activity was found to occur during the aquation reactions. Sometimes however, the aquation product may racemise, or isomerise to the trans isomer as occurs with cis[Co en₂ Cl(H₂O)]²⁺. If the rates of these subsequent reactions are comparable with the aquation rate, then some activity will be lost before the aquation is complete.

Optically pure (+)[Co en₂ Cl(H₂O)]²⁺ is converted to optically pure (+)[Co en₂ CO₃]⁺ with sodium bicarbonate, and the rotation of the isolated product agrees with that obtained by resolution of (⁵)[Co en₂ CO₃]⁺ ion, so the configuration is retained⁴⁴. There has been little work on the detailed mechanism of this reaction, but oxygen-18 studies of Hunt et al.⁶⁰ and Posey and Taube⁶¹ on the reverse reaction of acid on carbonato complexes (see below) suggest that the bicarbonate ion or CO₂ adds to the coordinated water without cleavage of this Co-O bond. The chloride ion then dissociates from either species (a) or (b) (figure 20) and the carbonato group subsequently coordinates intramolecularly⁶². This mechanism is consistent with the retention of configuration.
The reaction of $^{(+)\text{[Co }\text{en}_2\text{CO}_3\text{]}}^+$ with acid to form the diaquo ion $^{(+)\text{[Co }\text{en}_2(\text{H}_2\text{O})_2\text{]}}^{3+}$ also proceeds with full retention of activity, and this was demonstrated by reconversion to the carbonato ion when the original rotation was regained$^{(44)}$. The exchanges of $\text{H}_2\text{O}^{18}$ with $[\text{Co(NH}_3)_4\text{CO}_3]^+$ $^{(61)}$ and $[\text{Co(NH}_3)_5\text{CO}_3]^+$ $^{(60)}$ in acid solution have shown that the proposed mechanism (figure 21) is consistent with retention of activity in the bis(en) complex. Only one of the water molecules in the tetrammine product was enriched with $\text{O}^{18}$ (fraction of coordinated water enriched found $= 0.493$) and the released $\text{CO}_2$ was of normal abundance (enrichment found $\sim 1\%$). In the postulated mechanism (figure 21), the $\text{CO}_2$ is subsequently eliminated by a decarboxylation reaction involving C-O bond cleavage and one Co-O bond is thus not broken.
Nitrite ion added to active \( \text{[Co en}_2(\text{H}_2\text{O})_2]^{3+} \) gives the cis-dinitro complex with the same rotation as that obtained by resolution of the \( (+)^{+}[\text{Co en}_2(\text{N}O_2)_2]^{+} \) ion (44). The mechanism of this two-stage reaction (for each water molecule replaced) has been investigated in recent years by kinetic (63,64,65,66) and isotope (67) studies in a number of cobalt(III) compounds, and is depicted in figure 22 for \( \text{[Co en}_2(\text{NH}_3)(\text{H}_2\text{O})]^+ \).
compound cis[Co en$_2$(H$_2$O)$_2$]$^{3+}$ the second water molecule will be replaced by NO$_2^-$ ion in a similar manner. Initially the Co-O bonds are not broken, and the O$^{18}$ studies showed that neither of the oxygen atoms (of OND) exchanged with the solvent or added NO$_2^-$ ion. 97.5% retention of the Co-O bond was found in the product from cis[Co en$_2$(H$_2$O)$_2$]$^{3+}$ (67). The intramolecular rearrangement occurs also in the solid state, but at a slower rate (64, 67, 68).

Thus it has been shown, by comparing optical rotations of products obtained in these transformation reactions of bisethylenediamine compounds with those of the corresponding resolved compounds, that there is no loss of optical activity. Coupled with the mechanistic evidence outlined above, this establishes that full retention of configuration occurs in these reactions (i.e. inversions are excluded). Independent rotatory dispersion evidence also indicated full retention, and by relating R.D. curves to that of the D(+) [Co en$_3$]$^{3+}$ ion, the absolute configurations of the products in the bis(en) series were assigned (62). These two approaches are used in the following sections to first relate the configurations of all the α and β trien complexes, and then to assign their absolute configurations.

**TRANSFORMATIONS OF TRIETHYLENETETRAMINE COMPLEXES**

Optically pure cis α and β [Co trien Cl$_2$]ClO$_4$ were each transformed through the chloroaquo, carbonato and diaquo compounds to the corresponding α or β dinitro complexes, according to the scheme previously outlined (p. 58). The rotations and R.D. curves measured for the carbonato and
dinitro compounds, both in solution and after isolation as the perchlorates, could then be compared with the rotations obtained by resolving the racemic compounds.

The aquations of the dichloro compounds were carried out in acid solution at room temperature. From a knowledge of these rates (chapter 5) and the rates of subsequent aquations to the diaquo compounds (chapter 6) the times when the concentrations of the chloroaquo compounds rose to the maxima were calculated using the equation in appendix D. Measurements of rotation and R.D. were made at these times. In the $\beta$ aquation a mixture of two chloroaquo isomers ($\beta'$ and $\beta''$, figure 4) was produced, but one of these is present to the extent of only $\sim 3\%$ (p. 119). No isomerisation of the chloroaquo compounds occurred.

The solutions of the aquated complexes were transformed to the carbonato solutions with excess NaHCO$_3$, and these compounds were subsequently converted to the diaquo solutions with excess concentrated HClO$_4$.

Finally, treatment of solutions of the diaquo compounds with NaNO$_2$ gave the dinitro compounds. The reaction in the $\beta$ system was more rapid than in the $\alpha$. When the $\beta$ product was retained in solution, the activity and spectral observations paralleled those of Pearson et al. (63) and Murmann (65) on the analogous bis(en) system, so that the dinitro complex was first formed. This subsequently underwent isomerisation and mutarotation to the dinitro compound, which then tended to decompose.
If the products are isolated as perchlorates, isomerisation to the dinitro compounds is completed in the solid state, and decomposition is avoided.

Tables 6 and 7 give the rotations measured for the products in the α and β reaction series.

On comparing the rotations of the carbonato and dinitro products in each series with those of the corresponding resolved compounds (or α carbonato recrystallised to maximum rotation) it is evident that optical activity is totally preserved to better than 95\% throughout each series. With incomplete recovery of the dinitro compounds, retention may be stated to be better than \(\sim 90\%\), but it is noted also that these latter rotations are much smaller and solutions are more highly absorbing, so that these rotations are less accurate. Rotations of the isolated diaquo isomers (chapter 2) are the same as were measured in solution during the transformations, and optical purity was confirmed by transforming the isolated compounds to the corresponding active dinitro and carbonato compounds. The diaquo \(\rightarrow\) carbonato transformation occurs with full retention, as in the bis(en) series\(^{(44)}\). The results also confirm that complete resolution of both isomers of the dichloro, carbonato, and dinitro compounds has been attained.

The tables show that for the dichloro, chloroaquo, carbonato and diaquo compounds, the α isomer has the larger rotation at all wavelengths (except α diaquo at 578 \&\mu\). However, the β dinitro compound has larger
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<td>-910</td>
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**Note:** The table lists molecular rotations in (+) CIS A TRANSFORMATION SERIES.
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>DICHLOORO</th>
<th>CHIORAQUO</th>
<th>CARBONATO [Co trien CO₃]⁺</th>
<th>DIAQUO [Co trien(H₂O)₂]³⁺</th>
<th>DINITRO [Co trien(NO₂)₂]⁺</th>
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<td><strong>By transformn. in solution</strong></td>
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<td><strong>By transformn. in solution</strong></td>
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<tr>
<td>[M]₅₄₆</td>
<td>+ 500</td>
<td>+ 50</td>
<td>- 4200</td>
<td>- 4300</td>
<td>- 1050</td>
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rotations than the \( \alpha \) isomer. This reversal of the relative magnitudes of rotations on going from \( \beta \) carbonato (with the lower rotations) to \( \beta \) dinitro (with the higher rotations) was fortunate and significant, for it (i) eliminates the possibility that \( \beta\text{[Co trien Cl}_2\text{]}^+ \) and \( \beta\text{[Co trien CO}_3\text{]}^+ \), with the lower rotations, might have been incompletely resolved \( \alpha \) isomers, and also (ii) indicates that isomerisation \( \beta \rightarrow \alpha \) does not occur in these two transformation steps. If isomerisation did take place, the measured dinitro rotation would be lower than that of resolved \( \beta\text{[Co trien(NO}_2\text{)_2]}^+ \).

From measurements of rotations, it was found that the transformation reactions

\[
\begin{align*}
\alpha\text{[Co trien (NO}_2\text{)_2]}^+ & \xrightarrow{H^+} \text{cis[Co trien(H}_2\text{O)_2]}^3+ \\
\alpha \text{ or } \beta\text{[Co trien Cl(H}_2\text{O)_2]}^2+ & \xrightarrow{\text{excess NO}_2^-} \text{cis[Co trien(NO}_2\text{)_2]}^+ 
\end{align*}
\]

also proceed largely with retention of configuration. (p. 85 and 90). It will be appreciated that the second of these reactions is not as simple as the corresponding transformation from diaquo complexes, for the first-formed product will be \( \text{cis[Co trien Cl(NO}_2\text{)]}^+ \). Subsequent hydrolysis of the \( \text{Cl}^- \) ion in the neutral solution might not be stereospecific.

ROTATORY DISPERSION CURVES AND ASSIGNMENT OF ABSOLUTE CONFIGURATIONS FROM COTTON EFFECTS

Plane polarised light may be considered to be composed of left- and right-circularly polarised components (denoted \( l \) and \( r \) ) superimposed, and
optical rotation ($\alpha$) results from a difference in the refractive indices ($n$) for the left and right components when the active medium is irradiated with plane polarised light. Also, in the vicinity of an optically active electronic transition there is a difference in absorption ($\epsilon$) for the left- and right-components by the sample, causing the emergent light beam to be elliptically polarised to an extent measured by the ellipticity, $\Theta$, such that $\Theta \propto (\epsilon_1 - \epsilon_r)_\lambda$. This elliptic polarisation is called "circular dichroism". Thus the optical rotation, $\alpha$, is measured by the angle between the plane of polarisation of the incident light and the major axis of the emergent elliptically polarised light, and $\alpha \propto (n_1 - n_r)_\lambda$.

The variation of rotation, hereafter expressed in terms of molecular rotation $[M]$, with wavelength is called "rotatory dispersion".

Both of these effects, optical rotation and C.D. arise from an optically active transition, and in the vicinity of an isolated transition the R.D. and C.D. curves have the characteristics shown in figure 23 (a) or (b). Whereas the C.D. is either positive or negative, the rotation is both positive and negative and goes through zero in the middle of the band where the ellipticity is greatest. The R.D. curve which is positive on the long wavelength side of the corresponding absorption band, and has a positive slope of $\alpha/\lambda$ is associated with a positive C.D. as in figure 23(a). The quantitative relationships between the R.D. and C.D. have been summarised by Mason and it is noted that the amplitude $[A]$ of the "anomaly" in the R.D. curve is related to the maximum C.D. by:

$$[A] = [M]_{\text{max}} - [M]_{\text{min}} = 4028 (\epsilon_1 - \epsilon_r)_{\text{max}}.$$
**Figure 23.** The relationship between optical rotation ($\eta_L - \eta_R$) and circular dichroism ($\epsilon_L - \epsilon_R$) for an isolated absorption band ($\epsilon$).
This is useful in correlating the two effects, since a large C.D. is associated with a large R.D. effect. They are thus complementary, both being due to unequal interactions of a dissymmetric molecule with the two circularly polarised components of plane polarised light in an active transition region, and are together referred to as the "Cotton effect". A positive Cotton effect then refers to a transition giving a positive C.D. band, and an R.D. curve of positive slope. Just as the optical isomers are mirror images, so are the R.D. and C.D. curves (compare a and b of figure 23). Thus the shape of each R.D. curve and the sign of each C.D. band may be used as criteria for the configuration of the asymmetric centre. However, it is not possible to assign the configuration empirically from these curves, and reference must be made to some absolute structure. An absolute standard has been provided for cobalt and related complexes by the absolute X-ray analysis of the D(+) [Co en$_3$]$_3^+$ ion$^{(72)}$, and if the configurations of complexes can be related to this ion through their R.D. and C.D. effects, their absolute configurations are thus determined. However, it follows from the origin of optical rotatory power that such correlations of configuration will only be valid when the Cotton effects for the different complexes are compared at the corresponding electronic transitions.

These measurements were first successfully applied by Mathieu$^{(73)}$ to relate the configurations of a number of analogous complexes of the type (+)[Co en$_2$ XY]$^{n+}$, where XY = CO$_3^-$, ox$^-$ or X, Y = Cl$^-$, Br$^-$, SCN$^-$, NH$_3$, NO$_2^-$, H$_2$O. Most of these complexes showed two active transitions in the visible absorption band (called band I) so that the measured R.D. was
a composite of at least two separate R.D. curves, and in the cases where both transitions contributed significantly to the rotation they were resolved by the C.D. These latter curves showed two bands, and for some complexes these had opposite signs. In all instances most of the activity arose from the transition which was observed as the maximum absorption, and which Mathieu called the "principal" absorption. The less important transition, the "accessory" band, was sometimes observed as a shoulder on band I. From the sign of the Cotton effect for the "principal" absorption in each complex the configurations were related, complexes with the same sign having the same configuration.

This procedure has been used in a number of instances since\(^{(74-79)}\), configurations being related from the signs of the Cotton effect determined from the slope of the R.D. curves at the "principal" bands. This approach was rather empirical however, in the sense that it could not be certain that the same electronic transition was involved where the comparisons were made, and as late as 1958 it was claimed that the method alone could not be taken as proof of relative configuration\(^{(70)}\). However it has been justified by the agreement of the R.D. results with those from Werner's least soluble diastereoisomer method, Delépine's active racemate method, and kinetic and mechanistic evidence in a variety of complexes of Co(III), Rh(III), Ir(III) and Cr(III)\(^{(62)}\).

In many cobalt(III) complexes, the "principal" absorption bands are sufficiently isolated to interpret the corresponding R.D. curves clearly in terms of the Cotton effect (from the slope of the R.D. curve). However
when the R.D. curve is complicated by a number of overlapping active absorption bands, the C.D. must be measured to determine the sign of the Cotton effect for each transition. Also in these complicated instances, C.D. measurements may characterise in more detail than do simple absorption measurements the electronic transitions responsible for the absorption and rotatory power, since the individual C.D. peaks are usually well separated and fairly narrow for each transition. One can thus expect a greater use of C.D. in the future both to assign spectroscopic transitions\(^{(87)}\) and to aid in correlating configurations\(^{(71)}\).

An approach which largely eliminated the uncertainty that different transitions were responsible for the R.D. comparisons was to consider a series of cis cobalt(III) bis(en) complexes in which the substituents were varied systematically\(^{(62)}\). For the \(+[\text{Co en}_2(\text{NH}_3)X]^{n+}\) compounds where \(X = \text{Cl}^-, \text{H}_2\text{O}, \text{NH}_3, \text{NO}_2^-\), the R.D. curves all had essentially the same maximum rotatory power on the long wavelength side of the visible absorption band and a positive Cotton effect which shifted towards the violet as the substituents followed the order in the spectrochemical series \(\text{Cl}^- \rightarrow \text{H}_2\text{O} \rightarrow \text{NH}_3 \rightarrow \text{NO}_2^-\) \(^{(85)}\). Similarly the ions \(+[\text{Co en}_2 XY]^{n+}\), where \(XY = \text{Cl}_2, \text{Cl}(<\text{H}_2\text{O}), \text{CO}_3^-, (\text{H}_2\text{O})_2^-, (\text{NH}_3)_2^-, (\text{NO}_2)_2^-, \) showed essentially the same spectrochemical gradation (figure 26). However the maximum rotatory powers were not expected to correspond exactly since the symmetries of the individual complexes varied more widely than in the former series, but approached essentially "cubic" symmetry in \([\text{Co en}_2(\text{NH}_3)_2]^{3+}\) (in the crystal field sense). The regularities were taken to indicate that the same active transition was involved in all the
complexes of both series. The common configuration of each of the above complexes was then related to that of the D(+)\([\text{Co en}_3]^{3+}\) ion, since this ion and \([\text{Co en}_2(\text{NH}_3)_2]^{3+}\) have essentially the same "cubic" symmetry, and the spectra and R.D. curves were practically identical (figures 24 and 25).

Until recently the electronic transitions responsible for the absorption of radiation and the rotatory power of metal complexes were not understood in any detail. However, at the present time rapid progress is being made in the interpretation and understanding of the spectra, especially of d^3 and strong-field d^6 complexes, and configurations may now be related confidently by comparing R.D. and C.D. curves.

Transition metal complexes usually have three main absorption bands. Band I is located in the visible region, band II is usually in the near U.V., and band III is a charge-transfer band located in the U.V., and the disposition of these broad bands is shown for the complex [\text{Co en}_3]^{3+} in figure 24. These bands arise from a number of electronic transitions involving the metal ion, and all or some of these transitions will be optically active if the complex is dissymmetric.

Mason\(^{(71)}\) has shown that complexes of octahedral symmetry, O_h, e.g. [\text{Co(NH}_3)_6]^{3+} have one d \(\rightarrow\) d transition, \(^1A_1 \rightarrow ^1T_1\) within band I. In dihedral complexes of D_3 symmetry, e.g. [\text{Co en}_3]^{3+}, \(^1T_1\) splits into two active transitions \(^1A_2\) and \(^1E\) (denoted \(E_a\)) and these are necessarily opposed in their sign of C.D. The solution and crystal spectra and C.D. of the (+)[\text{Co en}_3]^{3+} ion of known absolute configuration (denoted D\(^{(72)}\))
Figure 24. Absorption, C.D. and R.D. of D(+) [Coen₃] (ClO₄)₃.

Absorption

log ε

C.D.

εₑ₁ - εₑᵣ

Transitions

hₒ → E₀

h₂ → E₂

h₄ → E₄

(Weak absorptions)
FIGURE 25. ABSORPTION, C.D.\(^{(83)}\) AND R.D.\(^{(62)}\) OF D(+)CIS[Coen\(_2\)(NH\(_3\)_2](ClO\(_4\))\(_5\).
have been extensively studied\(^{(71,82,84)}\), and the \(^1A_2\) and \(^1E\) transitions have been definitely assigned as shown in figure 24. In all the dihedral complexes so far studied, the \(^1E\) transition gives a considerably larger C.D. than the neighbouring transitions and is thus readily identified. It has been proposed that all dihedral \(^d^3\) and \(^d^6\) complexes where the intense C.D. band for the E transition is positive should have the absolute D configuration (figure 24)\(^{(82,84)}\).

When the symmetry is lowered further to \(C_2\), as in the cis complexes [Co en\(_2\) X\(_2\)]\(^n^+\), \(^1E\) splits into two components of A and B symmetries, and \(^1A_2\) becomes a transition with B symmetry. These complexes with the absolute configuration D of (+)[Co en\(_3\)]\(^3^+\) should give an A transition (from \(^1E_2\)) with a positive C.D. band\(^{(71)}\). The similarity between the absorption, R.D. and C.D. of (+)[Co en\(_3\)]\(^3^+\) and (+)[Co en\(_2\)(NH\(_3\))\(_2\)]\(^3^+\) will be evident from figures 24 and 25 and the common absolute configuration D of these ions is thus established. It is clear then that the large positive C.D. band in D(+)[Co en\(_2\)(NH\(_3\))\(_2\)] has A symmetry. This fact will be used to relate the configurations of the trien complexes to the bis(en), and thence to the absolute configuration of D(+)[Co en\(_3\)]\(^3^+\).

The electronic transitions responsible for the rotatory power have not been characterised experimentally in any detail in complexes with a symmetry lower than \(D_3\) (dihedral). It seems probable however from Mason’s studies that the transitions giving rise to most of the rotatory power in the cis[Co en\(_2\) XY]\(^n^+\) complexes previously mentioned were A transitions, and these coincided with the "principal" absorptions. Gillard\(^{(86)}\) has also
assigned (from C.D.) the transition at 462 µm in (+)[Co en₂(NO₂)₂]⁺ as that with A symmetry, and the R.D. inflexion is observed at this wavelength (figure 26). The situation has also been rationalised by Brushmiller et al. (61) by assuming that the cis[Co en₂ XY]ⁿ⁺ complexes approximated to D₃ symmetry. The "principal" absorptions were then assigned as the ¹E transitions giving rise to most of the R.D., and the "accessory" bands observed in the absorption and C.D. were assigned to the ¹A₂ transitions. It was noted in Brushmiller's studies that, depending on the relative crystal field strengths of the X and Y ligands, the two observed C.D. bands had the same sign (X and Y different field strengths as in the chloroammino complex) or different signs (X and Y similar strengths as in the dichloro complex). The relative energies of the ¹A₂ and ¹E transitions also depended on the relative strengths of X and Y, and when these were similar, as in all the trien and bis(en) complexes considered below, the ¹A₂ "accessory" transition was located on the long wavelength side of band I.

ASSIGNMENT OF CONFIGURATIONS TO THE TRIEN COMPLEXES

Since the trien ligand may be considered as two ethylenediamine molecules bridged, and in view of the great similarity of the absorption spectra (tables 3-5, figures 10-13) and R.D. curves (figures 26, 27 and 33) for the cis[Co en₂ XY]ⁿ⁺ and α and β [Co trien XY]ⁿ⁺ ions, the above considerations should be valid for the trien compounds. The trien complexes have C₂ symmetry or approximate to C₂ symmetry, and the R.D. arises mainly from the one transition of A symmetry.
Figure 26. R.D. Curves of the D(+)\([\text{Coen}_2\text{XY}]^{n+}\) ions\(^{62}\)

- \([\text{Coen}_2\text{Cl}_2]^+\)
- \([\text{Coen}_2\text{Cl}(\text{H}_2\text{O})^2+\)
- \([\text{Coen}_2\text{CO}_3]^+\)
- \([\text{Coen}_2(\text{H}_2\text{O})_2]^3+\)
- \([\text{Coen}_2(\text{NO}_2)_2]^+\)
- \([\text{Coen}_2(\text{NH}_3)_2]^3+\)
R.D. curves of the cations studied in the (+) cis a transformation series are shown in figure 27. It will be noted that in the vicinity of the first absorption band (band I, "principal" absorption) each compound exhibits a positive Cotton effect. These absorption bands and the R.D. inflexion points shift towards the violet as the substituents essentially follow the order in the spectrochemical series, \( \text{Cl}^- \rightarrow \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} \rightarrow \text{NO}_2^- \). The displacements of the inflexion points, and the relative magnitudes of \([M]\) at the long wavelength maximum exactly parallel those previously found in the \((+)[\text{Co en}_2 XY]^{n+}\) series (62) (figure 26) so that the A transition is involved in all these complexes.

The individual contributions to the R.D. curves are made clear by the C.D. measurements on the (+) a trien complexes, given with the R.D. curves in figures 28 to 32. For the dichloro, chloroaquo, diaquo and dinitro compounds where the acido substituents have identical or similar crystal field strengths, the two main active transitions in band I are clearly resolved by the C.D. curves. By comparison with the analogous bis(en) compounds, it is the A transitions which give rise to most of the rotation (this follows from the relation between C.D. and rotation given earlier) and coincide with the "principal" absorptions. B transitions will lie at shorter and longer wavelengths but in each of these compounds only one B is observed, the "accessory" band, and this is probably the B transition derived from \( ^1A_2 \) (81). This has much less rotatory power than the A transition and is opposed in sign, and for the dichloro, chloroaquo, and diaquo ions lies on the long wavelength side of band I appearing as a shoulder in figures 28 and 31. In the dinitro compound it can not be
**Figure 27. R.D. Curves in D Cis = \([\text{CotrienXY}]^{n+}\)**

**Transformation Series.**

- \([\text{Cotrien} \text{Cl}_2]^+\) 0.002 M in 0.01 M HClO₄
- \([\text{Cotrien} \text{ClH}_2\text{O}]^{2+}\)
- \([\text{Cotrien} \text{CO}_3]^+\) 0.005 M in NaHCO₃ solution (double scale)
- \([\text{Cotrien}(\text{H}_2\text{O})_2]^{3+}\) HClO₄
- \([\text{Cotrien}(\text{NO}_2)_2]^+\) 0.005 M in water (double scale)
**Figure 28.** R.D. AND C.D. OF D(+) ≈ [Co trien Cl₂] ClO₄.
**Figure 29.** R.D. and C.D. of D(+) $\equiv [\text{Cotrien Cl(H}_2\text{O)}]^{2+}$. 

- **R.D.**
- **[M]**

- **C.D.**
- $\epsilon_i - \epsilon_f$

- **Absorption**
- $\log \epsilon$

---

 wavelengths: 200 to 700 nm

absorbance values: -10 to +10

calibration: $10^3$
Figure 30. R.D. and C.D. of \( D(x) \approx [\text{CoTrienCO}_3]\text{ClO}_4\cdot\text{H}_2\text{O} \).
Figure 31. R.D. and C.D. of D(+)_{54G} = [Co^3+n(e)(H_2O)_2](ClO_4)_3.

R.D.

C.D.

\[ \epsilon_1 - \epsilon_r \]

Absorption

log \( \epsilon \)
Figure 32. R.D. and C.D. of D(+)546 vs [Catrien(NO2)2]ClO4.

R.D. [M]

C.D. $\epsilon_l - \epsilon_r$

Absorption

$\log \epsilon$

$\lambda \rightarrow \mu m$
certain which B transition is responsible for the weak C.D. peak at 400 m\(\mu\), but it is clearly opposed in sign to the A (figure 32). The carbonato compound is of higher symmetry, the bis(en) carbonato being treated as octahedral by Brushmiller\textsuperscript{(81)}, and only one strong C.D. band is observed, although this probably arises from two transitions of similar energies. The C.D. data for the dichloro compound suggests that the discrepancies between the calculated and measured R.D. curves for \((+)[\text{Co en}_2 \text{Cl}_2]^+\)\textsuperscript{(81)} are due to the band II transitions rather than charge-transfer transitions as was suggested\textsuperscript{(81)}. Thus since the C.D. is positive for the A transitions throughout the series of (+) cis \(\alpha\) complexes, the common configuration is established. Also since the R.D. curves exactly parallel those of the analogous (+)[Co en\(_2\) XY]\textsuperscript{N+} ions, the common configuration of the following ions is established as absolute D.

\[
\begin{align*}
(+)[\text{Co trien Cl}_2]^+ & \quad (+)[\text{Co en}_2 \text{Cl}_2]^+ \\
(+)[\text{Co trien Cl}(\text{H}_2\text{O})]^2+ & \quad (+)[\text{Co en}_2 \text{Cl}(\text{H}_2\text{O})]^2+ \\
(+)[\text{Co trien CO}_3]^+ & \quad (+)[\text{Co en}_2 \text{CO}_3]^+ \\
(+)[\text{Co trien (H}_2\text{O})_2]^3+ & \quad (+)[\text{Co en}_2 (\text{H}_2\text{O})_2]^3+ \\
(+)[\text{Co trien (NO}_2)_2]^+ & \quad (+)[\text{Co en}_2 (\text{NO}_2)_2]^+ \\
(+)[\text{Co trien (HgO)}]^2+ & \quad (+)[\text{Co en}_2 (\text{HgO})]^2+ \\
(+)[\text{Co trien (NH}_3)_2]^3+ & \quad (+)[\text{Co en}_2 (\text{NH}_3)_2]^3+ \\
\end{align*}
\]

and D(+)\[\text{Co en}_3\text{]}^{3+}

The R.D. curves for the complexes in the (-) cis \(\beta\) trien transformation series are given in figure 33, and all have negative Cotton effects for the principal transition. Although the C.D. curves for the (-) \(\beta\) trien complexes (figures 34 to 38) are not as well resolved as for
Figure 33. R.D. CURVES IN L CIS & [CotrienXY]n+
TRANSFORMATION SERIES.

- [Cotrien Cl₂]⁺ 0.002 M in 0.01 M HClO₄
- [Cotrien Cl H₂O]²⁺ =
- [Cotrien CO₃]⁺ = NaHCO₃ Solution
- [Cotrien(H₂O)₂]³⁺ = HClO₄
- [Cotrien(NO₂)₂]⁺ 0.005 M in water
Figure 34. R.D. and C.D. of L(-)β [Co trien Cl₂] ClO₄.
**Figure 35.** R.D. and C.D. of L(-)β [Cotrien Cl (H₂O)]²⁺.
Figure 36. R.D. and C.D. of L(-)β [Cotrien CO₃]ClO₄·H₂O.

Note: double scale of α isomer, fig. 30.
Figure 37. R.D. and C.D. of \( \text{L}(\text{L})_{546} \alpha [\text{Co tren}(\text{H}_2\text{O})]_2(\text{ClO}_4)_3 \).

R.D.

\[ [M] \]

Note: double scale of \( \alpha \) isomer, fig. 31.

C.D.

\[ \epsilon_l - \epsilon_r \]

Absorption

\[ \log \varepsilon \]

\[ \lambda \rightarrow \text{m} \]
Figure 38. R.D. and C.D. of L(-)$_{546} \beta$[cotrien(NO$_2$)$_2$]ClO$_4$.

R.D. Note: half scale of $g_5$ isomer, fig. 32.

C.D. $\epsilon_l - \epsilon_r$

Absorption

$\log \epsilon$

$\lambda \rightarrow \mu$
the $\alpha$ compounds, the signs of the $A$ transitions are clearly negative, and the $B$ transitions are very weak. Moreover, it appears from figures 34, 35 and 37 that for the $\beta$ configurations the $A$ and $B$ transitions have the same sign. The negative Cotton effects for the $A$ transition ("principal" absorption) over the series of $(-)[\text{Co trien } XY]^{n+}$ compounds indicates that these complexes all have the same configurations as $(-)[\text{Co en}_2 XY]^{n+}$ and $(-)[\text{Co en}_3]^{3+}$, which is absolute $L$. Thus the $\beta$ transformation reactions all occurred with retention of configuration.

It has been mentioned previously (p. 3) that if the centre ethylene bridges were removed in the cis $\alpha$ and cis $\beta$ triethylenetetramine structures $[\text{Co trien } XY]^{n+}$, the two configurations would be related as $D$ to $L$ $[\text{Co en}_2 XY]^{n+}$. In this sense the trien and bis(en) complexes have identical symmetry properties. This means that if an isomerisation $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ occurred in any step in the $\alpha$ and $\beta$ transformation series respectively, by the movement of a terminal ethylene bridge, this would be in effect the same as an inversion of configuration $D$ to $L$ in the bis(ethylenediamine) compounds. Isomerisation should be reflected therefore in a change in sign of Cotton effect. Since this does not occur, it must be concluded that the compounds within each series transform without change of configuration, and this is in agreement with the observed retentions of activity for the reactions and the mechanistic evidence presented earlier.

The absolute optical configurations of the trien and bis(en) complexes are summarised in figure 39. The figure shows that in the cis $\beta$ trien
Figure 39. ABSOLUTE CONFIGURATIONS OF COBALT (III) TRIEN AND BIS (en) COMPLEXES.

\[ \text{Cis}[\text{Co} \text{en}_2]_{\text{X}}^{\text{Y}} \]

\[ \text{Cis}[\text{Co} \text{en}_3]^{\text{3+}} \]

\[ \text{cis} \]
compounds the optical configuration is fixed by the ligand, and not by the relative positions of the substituents \( X \) and \( Y \). Thus the two geometric isomers \( \beta' \) and \( \beta'' \) should have qualitatively similar R.D. and C.D. characteristics. However, the different ligand field strengths of the Cl and \( \text{H}_2\text{O} \) groups might be expected to alter the magnitude of the C.D. for the two transitions observed in band I, when their positions are interchanged.

The magnitudes of the circular dichroism curves are also consistent with the \( \alpha \) and \( \beta \) structural assignments. Models of the two \textit{cis} isomers indicate that the tetramine ligand forms an extended helix in the \( \alpha \) complexes (left-handed for the \( \text{D} \) configuration, figure 39), whereas the ligand in the \( \beta \) isomers is only about \( 1/2 \) to \( 2/3 \) helical, the rest being a quasi-linear zig-zag chain. Because of these stereochemical arrangements of the ligand, Mason\(^{(83)}\) has suggested that the \( \alpha \) isomers should have a larger C.D. than the \( \beta \) isomers (in absolute magnitude), particularly in the charge-transfer regions where ligand electrons are more intimately involved. This is observed (figures 28 and 34, 30 and 36, 31 and 37, 32 and 38) and additionally, the C.D. in the visible region is larger for the \( \alpha \) isomers also, as might be expected if the ligand charge-transfer and the metal ion transitions mix together to some degree. Unfortunately the aquation product from \( (-)\beta[\text{Co trien Cl}_2]^+ \) gives a small and fairly featureless dichroism, so that it is not possible to deduce which of the two \( (-)\beta \) chloroaquo isomers (figure 39) is formed predominantly\(^{(83)}\).

The assignments of relative optical configurations of the \( \alpha \) and \( \beta \) trien- and bis(en)-compounds by Cotton effects agree with Werner's
solubility criterion. Werner\(^{(86)}\) proposed that the least soluble
diastereoisomers of similar complexes with the same resolving agent had
the same configuration, and the method has been found to apply
generally\(^{(62)}\). The least soluble diastereoisomers of the trien and bis(en)
complexes with Na\((+)[Co \text{ en ox}_2]\).H\(_2\)O are as follows (chapter 2):

\[
\begin{align*}
(+) & & \text{[Co trien Cl}_2\text{]}(-)[\text{Co en ox}_2]\cdot\text{H}_2\text{O} \\
(+546) & & \text{[Co trien(NO}_2\text{)}_2\text{]}(-)[\text{Co en ox}_2]\cdot\text{H}_2\text{O} \\
(+546) & & \text{[Co en}_2\text{ Cl}_2\text{]}(-)[\text{Co en ox}_2]\cdot\text{H}_2\text{O} \\
(+546) & & \text{[Co en}_2\text{(NO}_2\text{)}_2\text{]}(-)[\text{Co en ox}_2]\end{align*}
\]

Hence the above cations should have the same optical configuration, in
agreement with the R.D. and C.D. considerations (figure 39).

**EXPERIMENTAL.**

**Measurement of optical rotation and optical**

**rotatory dispersion curves**

Rotations at 589 m\(\mu\) (sodium D line), 578 m\(\mu\) (mercury yellow line) and
546 m\(\mu\) (mercury green line) were measured visually on a Bellingham and
Stanley polarimeter.

R.D. curves in the visible range (400 to 700 m\(\mu\)) were obtained with a
polarimeter attached to the Shimadzu photoelectric Spectrophotometer QR-50.
Rotations were generally measured at room temperature, at intervals of 20
m\(\mu\), using a 1 dm. or 2 dm. polarimeter tube. Slits corresponding to band
widths of less than 10 μm were used, except in regions of high absorption (in the vicinity of the "cross-over" point in the R.D. curve, and below 400 μm for these complexes). The accuracy was generally better than +0.03° except in regions of high absorption, where specific rotations were very sensitive to slit-width and concentration. Rotations were not measured for the dinitro compounds below 460 μm, because of high absorption.

Rotations are expressed in molecular rotations [M], which are related to other quantities by the expressions:

\[ [\alpha]_\lambda = \frac{100 \alpha}{cd} \]

\[ [M]_\lambda = \frac{M [\alpha]_\lambda}{100} = \frac{M\alpha}{cd} = \frac{10\alpha}{md} \]

where
- \( \alpha \) = actual rotation at wavelength \( \lambda \) μm
- \([\alpha]_\lambda \) = specific rotation at wavelength \( \lambda \) μm
- \( c \) = % concentration of solution
- \( m \) = molar concentration of solution
- \( M \) = molecular weight of solute
- \( d \) = path length of cell in decimetres.

All rotations were measured in a 1 dm, tube unless otherwise stated.

Circular dichroism curves

C.D. curves over the visible and ultraviolet range were kindly measured by Dr. S. F. Mason, University of Exeter, England.
Measurement of R.D. of (-)β[Co trien Cl₂]ClO₄

The half-life time (t 1/2) for aquation to the chloro-aquo stage is about 12 minutes at room temperature. To reduce this rate, 20 ml. of ice-cold 0.01 N HClO₄ was pipetted into a flask containing the weighed optically pure sample ([M]₀ of transformed β carbonato = -2950°) (0.0150 g.) to give 0.00200 M solution of complex. The flask was stoppered, shaken vigorously to dissolve the sample and the solution was quickly transferred to a dry polarimeter tube thermostated at 10°C. When thermal equilibrium was established (2-3 minutes after the acid was added) rotations were measured. Several separate solutions had to be prepared to record the complete R.D. curve, given in figure 34. Fogging of cell windows was prevented by blowing air into the cell compartment of the spectrophotometer.

Transformation of (-)β[Co trien Cl₂]ClO₄ to
(-)β[Co trien Cl(H₂O)]²⁺

The 0.00200 M solution of (-)β[Co trien Cl₂]ClO₄ in 0.01 N HClO₄ was allowed to warm to room temperature, and stand for 70-80 minutes, when the initial red-violet colour changed to carmine. This corresponds to about 6 half-lives for aquation at this temperature, when the concentration of the β chloroaquo is a maximum (approximately 93%). The R.D. curve then measured (figure 35) has small contributions from traces of the dichloro and diaquo compounds.

Rotations did not vary after aquation times between about 40 and 90 minutes, but solutions aquating for longer times gave rotations tending to those of (-)β[Co trien(H₂O)₂]³⁺.
Transformation of \((-\beta[Co trien Cl(H_2O)]^{2+})\) to \((-\beta[Co trien CO_3]^+)\)

After aquation to \(\beta[Co trien Cl(H_2O)]^{2+}\) was complete, (90 minutes) the solution containing aquated species of total concentration 0.002 M was converted quantitatively to \(\beta[Co trien CO_3]^+\) by adding excess NaHCO_3 (0.05 g, about 2 \times excess) over the quantity required to neutralise the HClO_4 and 2 moles to react with complex.

\[
[Co(trien)Cl(H_2O)]^{2+} + 2 \text{NaHCO}_3 \rightarrow [Co(trien)CO_3]^+ + \text{CO}_2 + \text{H}_2\text{O} + 2\text{Na}^+ + \text{Cl}^-
\]

On shaking, the solution changed to carmine-scarlet and the high absorption carbonato peak (507 m\(\mu\)) developed almost immediately, but on standing the absorption then decreased slightly (2-3\%) which was probably associated with a two-stage reaction (page 59). The R.D. curve (figure 36) was measured after the solution had stood for about 30 minutes. The spectrum and rotations of \(\beta[Co trien CO_3]^+\) were unaffected by excess NaHCO_3.

NaHCO_3 was a more convenient reagent than Na_2CO_3, for this reaction is much faster at low pH (69) and moreover, competition from OH\(^{-}\) ion is avoided.

The conversion to carbonato after aquation times between about 50 minutes and 3 hours gave the same optical rotation. The time before transforming aquated solutions to the carbonato was thus not critical, for racemisation of \(\beta[Co trien(H_2O)]^{3+}\) is comparatively slow at pH 2. At considerably longer aquation times however, some loss of activity occurred.
The (-)\(\beta\)[Co trien CO\(_3\)]\(^+\) ion was optically stable in aqueous solution. The rotation of a solution at 50° decreased 7% after 14 hours.

**Transformation of (-) \(\beta\)[Co trien CO\(_3\)]\(^+\) to (-)\(546\beta\)[Co trien(H\(_2\)O)\(_2\)]\(^{3+}\)**

\(\text{HClO}_4\) (11.6 N) was added drop by drop to the 0.00200 M solution of (-)\(\beta\)[Co trien CO\(_3\)]\(^+\) until the solution had pH \(\nless than\) 2. On shaking in a stoppered flask, the colour changed almost immediately to light scarlet-orange of the \(\beta\) diaquo compound. As only a few drops of concentrated acid were required, the concentration of complex changed negligibly compared to the precision with which rotations could be measured on the Shimadzu instrument. The R.D. curve (figure 37) was measured after 15 minutes when spectral measurements showed the formation of the diaquo compound was complete.

Starting with fully resolved (-)\(\beta\)[Co trien CO\(_3\)]ClO\(_4\)·H\(_2\)O ([\(\alpha\)]\(D\) = -770°), this was dissolved in 0.1 N HClO\(_4\) to give 0.00204 M (-)\(546\beta\)[Co trien(H\(_2\)O)\(_2\)]\(^{3+}\) solution, whose R.D. curve was measured after one hour and found identical to the above.

Optically pure (-)\(546\beta\)[Co trien(H\(_2\)O)\(_2\)](ClO\(_4\))\(_3\) ([\(\alpha\)]\(D\) = -166°, [\(\mathbb{M}\)]\(D\) = -900°) was isolated by treating (-)\(\beta\)[Co trien CO\(_3\)]ClO\(_4\)·H\(_2\)O with concentrated HClO\(_4\). This was described previously (p. 49).

That the reverse transformation, from diaquo to carbonato, also occurs with full retention of configuration was shown by treating a 0.00378 M solution of (-)\(546\beta\)[Co trien(H\(_2\)O)\(_2\)](ClO\(_4\))\(_3\) in 0.01 M HClO\(_4\).
\((\alpha_D = -0.34^\circ, \ [M]_D = -900^\circ)\) with NaHCO\(_3\) until the solution was alkaline. The measured rotation \((\alpha_D = -1.12^\circ, \ [M]_D = -2970^\circ)\) corresponded to optically pure \((-) \beta[\text{Co trien CO}_3]^+\), and on transforming back to diaquo with HClO\(_4\), the original rotation \((\alpha_D = -0.34^\circ)\) was restored.

**Transformation of \((-)_{546} \beta[\text{Co trien(H}_2\text{O)}_2]^3+ to \((-)_{546} \beta[\text{Co trien(NO})_2_2]^+**

This transformation was studied, starting with the resolved \(\beta\) carbonato or \(\beta\) diaquo perchlorates.

To a 0.00378 M solution of optically pure \((-)_{546} \beta[\text{Co trien(H}_2\text{O)}_2]\text{CO}_3\) in 0.01 M HClO\(_4\) \([\ [M]_D = -900^\circ]\), excess NaNO\(_2\) was added. The colour changed to the yellow of the dinitro compound in about 10 minutes, and the following rotations were measured:

<table>
<thead>
<tr>
<th>Time from adding NaNO(_2)</th>
<th>1/4 hour</th>
<th>1/2 hour</th>
<th>15 hours</th>
<th>([M]) at 15 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_D)</td>
<td>-0.35^\circ</td>
<td>-0.34^\circ</td>
<td>-0.27^\circ</td>
<td>-720^\circ</td>
</tr>
<tr>
<td>(\alpha_{578})</td>
<td>-0.39</td>
<td>-0.33</td>
<td>-0.29</td>
<td>-770^\circ</td>
</tr>
<tr>
<td>(\alpha_{546})</td>
<td>-0.58</td>
<td>-0.56</td>
<td>-0.40</td>
<td>-1060^\circ</td>
</tr>
<tr>
<td>([M]_{546})</td>
<td>-1540^\circ</td>
<td>-1480^\circ</td>
<td>-1060^\circ</td>
<td></td>
</tr>
</tbody>
</table>

The rotations measured at 15 hours correspond with those of resolved \((-)_{546} \beta[\text{Co trien(NO}_2_2)]\text{CO}_3\) \([\ [M]_{546} = -1120^\circ]\).

\((-) \beta[\text{Co trien CO}_3]\text{C}10_4\cdot\text{H}_2\text{O},\) essentially optically pure, 
\([\ [M]_D = -2890^\circ]\) (0.3827 g.) was dissolved in 5 ml. of water, and HClO\(_4\) was
added (2.1 ml. of 1.0 N) so that the resulting diaquo solution was 0.01 M in HClO₄. After 20 minutes excess NaN₃ was added (0.35 g., 2 x excess) to neutralise the acid and form the dinitro complex. The yellow product \((-\)₅₄₆\[^{\beta}][\text{Co trien(NO}_₂)_₂]\text{ClO}_₄\) began to crystallise from the yellow-orange solution (pH ≈ 4) in 10 minutes, and was filtered off after 1.5 days, washed with 70% methanol, methanol and acetone, and air dried. The orange filtrate was acidified with one drop of acetic acid, and NaClO₄ (0.065 g.) was added. On evaporation in a rotary evaporator to 3 ml. and cooling in an ice-bath, a further small yield of product was obtained. Total yield was 0.359 g., 91%. Rotations measured were

\[
\begin{align*}
[M]_D &= -610^\circ \\
[M]_{578} &= -710^\circ \\
[M]_{546} &= -1080^\circ & (\alpha_{546} = -0.53^\circ \text{ for } 0.195\text{% aqueous solution})
\end{align*}
\]

which correspond with those of fully resolved \((-\)₅₄₆\[^{\beta}][\text{Cotrien(NO}_₂)_₂]\text{ClO}_₄\) \([M] = -620^\circ, -720^\circ, -1120^\circ \text{ for D, 578 and 546 }\mu \text{ respectively}\).

Measurement of the visible absorption gave for the maximum \(\varepsilon_{439} = 240 \text{ in } 0.00262 \text{ M aqueous solution}\). The same rotations \([M]_{546} = -1070^\circ\) and absorption maximum \(\varepsilon_{438} = 241\) were obtained after the solid product had been left at 30° for 5 days to ensure that nitrito-nitro isomerisation was complete, and rotations and spectrum were constant as the solution stood for 2 hours.

Anal. Calcd. for \((-\)₅₄₆\[^{\beta}][\text{Co(C}_6\text{H}_1₈\text{N}_₄)(\text{NO}_₂)_₂]\text{ClO}_₄\): C, 18.17; H, 4.56; N, 21.19. Found: C, 18.33; H, 4.70; N, 21.32.
The same transformation from $(-)\beta[\text{Co trien CO}_3]\text{ClO}_4\cdot\text{H}_2\text{O}$ was carried out in more dilute solution (0.00500 M) so that the dinitro product remained in solution. In dilute solutions, the colour changed to yellow soon after addition of NaNO$_2$, and measurements of rotations (0.00500 M solution) and visible absorption (0.00200 M solution) gave the following results:

<table>
<thead>
<tr>
<th>Time after addition of NaNO$_2$</th>
<th>$[M]_D$</th>
<th>$[M]_{578}$</th>
<th>$[M]_{546}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 hours</td>
<td></td>
<td></td>
<td></td>
<td>449 m$m\mu$</td>
<td>184</td>
</tr>
<tr>
<td>5 &quot;</td>
<td>-680$^\circ$</td>
<td>-800$^\circ$</td>
<td>-1360$^\circ$</td>
<td>444</td>
<td>206</td>
</tr>
<tr>
<td>9 &quot;</td>
<td>-580</td>
<td>-700</td>
<td>-1040</td>
<td>443</td>
<td>216</td>
</tr>
<tr>
<td>19 &quot;</td>
<td>-520</td>
<td>-620</td>
<td>-900</td>
<td>442</td>
<td>250</td>
</tr>
<tr>
<td>26 &quot;</td>
<td>-500</td>
<td>-580</td>
<td>-880</td>
<td>441</td>
<td>215</td>
</tr>
<tr>
<td>32 &quot;</td>
<td></td>
<td></td>
<td></td>
<td>440</td>
<td>215</td>
</tr>
<tr>
<td>44 &quot;</td>
<td></td>
<td></td>
<td></td>
<td>440</td>
<td>207</td>
</tr>
</tbody>
</table>

On standing, the spectrum slowly changed, with $\lambda_{\text{max}}$ decreasing and becoming constant at about 440 m$m\mu$, while $\varepsilon_{\text{max}}$ increased to a maximum then slowly began to decrease. Initial rotations were higher than those of $(-)\beta[\text{Co trien(NO}_2)_2]^+$, but slowly decreased and corresponded to those of resolved $(-)\beta[\text{Co trien(NO}_2)_2]\text{ClO}_4$ at about the time $\varepsilon$ was a maximum (about 15 hours). Although precise experiments were not carried out, these observations are interpreted, by comparison with the $\text{cis}[\text{Co en}_2(\text{NO}_2)_2]^+$ system, as isomerisation and mutarotation of
$\beta[\text{Co trien(ONO)}_2]^+ \text{ to } \beta[\text{Co trien(ONO)(NO}_2)]^+$, thence to $\beta[\text{Co trien(NO}_2)_2]^+$. The $\beta$ dinitro product may then decompose since the absorption and rotations decrease simultaneously (p. 30).

Transformation of $(-) \beta[\text{Co trien Cl(H}_2O)]^{2+}$ to $(-)_{546}\beta[\text{Co trien(NO}_2)_2]^+$

$(-)\beta[\text{Co trien Cl}_2]ClO_4$ (0.0413 g.) was equated in 0.01 M HC1O_4 (20 ml.) for one hour. The resulting 0.0055 M chloroaquo solution (shown to be optically pure by transformation to carbonato having $[M]_D = -2950^\circ$) was transformed directly to the dinitro with excess NaNO_2. After 2 hours the solution had turned yellow and measurement of rotation gave:

$$\alpha_{578} = -0.29^\circ \text{ whence } [M]_{578} = -530^\circ$$

$$\alpha_{546} = -0.45^\circ \quad [M]_{546} = -820^\circ$$

(dispersion ratio $\alpha_{546}/\alpha_{578} = +1.55$)

On standing at room temperature, these rotations slowly decreased, and after 2.5 days,

$$\alpha_{578} = -0.24^\circ, \quad \alpha_{546} = -0.37 \text{ (dispersion ratio } = +1.54).$$

These rotations are compared with the corresponding values for resolved $(-)_{546}\beta[\text{Co trien(NO}_2)_2]ClO_4$,

$$[M]_{578} = -720^\circ, \quad [M]_{546} = -1120^\circ \text{ (dispersion ratio } = +1.55).$$
Measurement of R.D. curve of (+) $\text{a[Co trien Cl}_2\text{]}\text{ClO}_4$

Aquation of this isomer to the chloroaquo stage has $t_{1/2}$ about 80 minutes at 25° in 0.01 N HClO$_4$, so the R.D. curve (figure 28) was measured quickly at room temperature, in 0.00200 M solution. The sample used was optically pure, $[\alpha]_D = +2330^\circ$.

Transformation of (+) $\text{a[Co trien Cl}_2\text{]}\text{ClO}_4$ to
(+) $\text{a[Co trien Cl(H}_2\text{O)}\text{]}^{2+}$

The solution of 0.00200 M (+) $\text{a[Co trien Cl}_2\text{]}\text{ClO}_4$ in 0.01 M HClO$_4$ was allowed to stand until the first stage of aquation was complete (10 hours, 98% (+) $\text{a[Co trien Cl(H}_2\text{O)}\text{]}^{2+}$) and the colour had changed from deep blue-violet to deep carmine. Rotations were constant up to at least 40 hours, so the R.D. curve (figure 29) was measured between these limits.

Transformation of (+) $\text{a[Co trien Cl(H}_2\text{O)}\text{]}^{2+}$ to
(+) $\text{a[Co trien CO}_3\text{]}^+$

This transformation was carried out exactly as described for the $\beta$ isomer (p. 80).

Three separate experiments, in which solutions of (+) $\text{a[Co trien Cl}_2\text{]}\text{ClO}_4$ were aquated for 5.5, 16 and 43 hours gave identical rotations on transformation to carbonato solution. The 0.00200 M solution of (+) $\text{a[Co trien CO}_3\text{]}^+$ was very stable optically; no change in rotation occurred in 24 hours at room temperature. The R.D. curve is given in figure 30.

Addition of NaHCO$_3$ before aquation to the chloroaquo ion was complete
(that is, in less than 4.5 hours) gave a lower rotation for the carbonato product, due to isomerisation to the β hydroxoaquo isomer in alkaline conditions.

The carbonato product of this transformation was isolated as the perchlorate and tetraphenylborate derivatives. Optically pure (+)₉[Co trien Cl₂]ClO₄, [α]₉ = + 2330° (0.100 g.) was aquated in 0.01 M HClO₄ (10 ml) for 15 hours, and excess NaHCO₃ (0.055 g.) and NaClO₄ (0.044 g.) were then added. The solution was evaporated in a current of air (room temperature) to deposit red plates of (+)₉[Co trien CO₃]ClO₄·H₂O which were filtered off, washed with methanol and acetone, and air dried. The rotations were [α]₉ = + 0.96°, [α]₅₇₈ = + 1.18°, [α]₅₄₆ = + 1.25° for 0.0792% solution in water, whence [M]₉ = + 4650°, [M]₅₇₈ = + 5700°, [M]₅₄₆ = + 6030°. A second smaller fraction of pink crystals (95% optically pure) was precipitated on addition of alcohol. Total yield was 0.0924 g., 91%.

Anal. Calcd. for (+)₉[Co(C₆H₁₆N₄)CO₃]ClO₄·H₂O: C, 21.97; H, 5.27; N, 14.64. Found: C, 21.82; H, 5.29; N, 14.68.

On fractional recrystallisation from water, the maximum rotation which could be obtained was [M]₉ = + 4730°, [M]₅₇₈ = + 5920°, [M]₅₄₆ = + 6170° ([α]₉ = + 0.95° for 0.0765% solution, [α]₉ = + 1240°) so that the above isolated product was optically pure.

In a similar manner, addition of a concentrated aqueous Na[B(C₆H₅)₄] solution to the carbonato solution precipitated (+)₉[Co trien CO₃]
(\(\alpha_D = +0.40^\circ\), \(\alpha_{578} = +0.46^\circ\), \(\alpha_{546} = +0.49^\circ\) for 0.0524% solution in acetone/water). (Yield 1.13 g. from 1.00 g. of (+)\([\text{Co trien} \text{Cl}_2]\text{ClO}_4\), 69%). This was insoluble in water, but soluble in acetone/water.

Anal. Calcd. for (+)\([\text{Co(C}_6\text{H}_{18}\text{N}_4\text{)}\text{CO}_3]\) \([\text{B(C}_6\text{H}_5\text{)}_4]\) \(\text{2H}_2\text{O}\): C, 60.05; H, 6.83; N, 9.04. Found: C, 60.83; H, 6.65; N, 8.86.

Transformation of (+)\([\text{Co trien} \text{CO}_3]^{+}\) to

\(+\)\([\text{Co trien(H}_2\text{O)}_2]^{3+}\)

0.00200 M solution of optically pure (+)\([\text{Co trien} \text{CO}_3]^{+}\) prepared as described in the previous sections, was converted to the \(\alpha\) diaquo with \(\text{HClO}_4\) as described for the corresponding \(\beta\) transformation (p. 8/). The \(\alpha\) diaquo solution was carmine coloured, and had the following rotations:

\([M]_D = -950^\circ\) (\(\alpha_D = -0.19^\circ\))

\([M]_{578} = -300^\circ\)

\([M]_{546} = +4700^\circ\)

The R.D. curve is given in figure 31.

Optically pure (+)\([\text{Co trien} \text{CO}_3]\)\(\text{ClO}_4\)\(\text{H}_2\text{O}\), \([\alpha]_D = +1200^\circ\), (0.00322 g. in 10 ml. water) was also transformed to the diaquo by adding one drop of concentrated \(\text{HClO}_4\) to the 0.00215 M solution, and the following rotations were measured after 20 minutes:

\([M]_D = -930^\circ\) (\(\alpha_D = -0.20^\circ\))

\([M]_{578} = -190^\circ\)

\([M]_{546} = +4750^\circ\)
(+)_546 \text{g}[\text{Co trien(H}_2\text{O)}_2](\text{ClO}_4)_3 ([M]_D = -910^0, [M]_578 = -190^0, [M]_546 = +4260^0), almost optically pure, was isolated from the reaction of (+)\text{g}[\text{Co trien CO}_3]\text{ClO}_4\cdot\text{H}_2\text{O} as described previously (p.44).

Transformation of (+)_546 \text{g}[\text{Co trien(H}_2\text{O)}_2]^{3+}
to (+)_546 \text{g}[\text{Co trien(NO}_2)_2]^+$

(+)_546 \text{g}[\text{Co trien Cl}_2]\text{ClO}_4 (1.00 g. having } [\alpha]_D = +2250^0) was aquated in 0.0012 M HC\text{ClO}_4 (50 ml.) for 12 hours, then excess NaHCO\text{3} (0.46 g.) was added, followed by excess HC\text{ClO}_4 (7.8 ml. of 1.0 M) after 30 minutes. To the resulting diaquo solution excess NaNO\text{2} (1.8 g.) was added after a further 50 minutes. (+)_546 \text{g}[\text{Co trien(NO}_2)_2]\text{ClO}_4 formed slowly and precipitated as yellow-brown needles. These were filtered off in three fractions, washed with ice-cold NaClO\text{4} solution, alcohol and ether, and air-dried, and the R.D. curve (figure 32) was measured after two days. Each fraction had the same rotations, \([M]_{546} = +220^0 ([\alpha]_{546} = +0.11^0), [M]_D = +20^0, [M]_{578} = +40^0. \) (Yield 0.95 g., 90%). The yellow-brown filtrate from which no more clean product could be obtained on evaporation was inactive.

Anal. Calcd. for (+)_546 \text{g}[\text{Co(C}_6\text{H}_18\text{N}_4)(\text{NO}_2)_2]\text{ClO}_4: C, 18.17; H, 4.56; N, 21.3. Found: C, 18.06; H, 4.59; N, 20.5.

This series of transformations was repeated, starting with (+)\text{g}[\text{Co trien Cl}_2]\text{ClO}_4, \([\alpha]_D = +2160^0 (0.100 g.)). The dinitro product was not isolated but the final volume was adjusted to 50 ml. with water, and the R.D. curve of this solution (0.0053 M) was measured after 2 days, and found similar to that obtained above. \([M]_{546} = +190^0.\)
On treating the $\alpha$ diaquo solution with excess NaNO$_2$, the yellow colour of the dinitro developed slowly (over 12 hours). This contrasted with the more rapid formation of the corresponding $\beta$ dinitro product.

Transformation of $(+)\alpha[\text{Co trien Cl(H$_2$O)}]^2+$

to $(+)\delta_{546}\alpha[\text{Co trien(NO$_2$)$_2$}]^+$

A solution of $(+)\alpha[\text{Co trien Cl(H$_2$O)}]^2+$, prepared by aquating $(+)\alpha[\text{Co trien Cl$_2$}]\text{ClO$_4$}$ in 0.01 M HClO$_4$, was transformed directly to dinitro solution by addition of excess NaNO$_2$. The solution was diluted (to 0.0086 M) and the R.D. curve was measured when the yellow colour had completely developed (two days). $[M]_{546} = +180^\circ$, $[M]_D = 0^\circ$. Comparison with the values for resolved $(+)\alpha[\text{Co trien(NO$_2$)$_2$}]^+$ ($[M]_{546} = +220^\circ$) shows that most of the activity was retained.

Transformation of $(+)\delta_{546}\alpha[\text{Co trien(NO$_2$)$_2$}]^+$

to $(+)\delta_{546}\alpha[\text{Co trien(H$_2$O)$_2$}]^3+$

A 0.0020 M solution of $(+)\delta_{546}\alpha[\text{Co trien(NO$_2$)$_2$}]\text{ClO$_4$}$ in 0.1 M HClO$_4$ changed slowly to the scarlet diaquo solution. After a long period (2.5 months) rotations were

$[M]_D = -950^\circ$ (a$_D = -0.19^\circ$)

$[M]_{578} = -350^\circ$

$[M]_{546} = +3200^\circ$.

Comparison with the rotations of $(+)\delta_{546}\alpha[\text{Co trien(H$_2$O)$_2$}](\text{ClO$_4$})_3$

$([M] = -950^\circ, -300^\circ, +4700^\circ$ for D, 578, and 546 m$\mu$ respectively)
indicates that the transformation occurred largely with retention of configuration and activity (at least 70%), racemisation of the diaquo solution being negligible in this time.
Inorganic substitution reactions include the replacement of one ligand \((X)\) by another \((Y)\) in a complex, or one metal ion \((M)\) by another \((M')\). These two broad classes of reactions are called nucleophilic \((S_N)\) and electrophilic \((S_E)\) substitution reactions, and are represented schematically as follows:

\[
Y^- + M - X \rightarrow M - Y + X^- \quad (S_N)
\]

\[
M' + M - X \rightarrow M' - X + M \quad (S_E)
\]

\(S_E\) reactions, for example the reaction of \(\text{Hg}^{2+}\) with \([\text{Co(NH}_3)_5\text{Cl}]^{2+}\), are less commonly studied than \(S_N\) reactions, and most of the reactions discussed in this and the following chapters are of the latter type.

Two distinctly different reaction paths are visualised for nucleophilic substitutions. These are the \(S_N1\) (dissociative) and \(S_N2\) (displacement) mechanisms, and modifications of these, such as conjugate-base mechanisms, are also likely in certain instances.

An \(S_N1\) mechanism implies that the \(M - X\) bond dissociates (in an octahedral complex) to give a 5-coordinated intermediate, while in an \(S_N2\)
mechanism the incoming reagent $Y$ bonds to give a transition state of increased coordination number. In these instances the mechanisms are described as "pure" or "limiting" and are denoted as $S^1_N (\text{lim})$ and $S^2_N (\text{lim})$. In aquation reactions, to which this thesis will be confined, the incoming reagent $Y$ is water, and the dissociative mechanism is commonly pictured as a prior lengthening of the $M - X$ bond to a critical distance, followed by the bonding of a water molecule and the expulsion of $X$. Water then plays a significant part in this aquation mechanism, and such a process has been described as "solvent-assisted $S^1_N$", figure 40.

![Figure 40. Solvent-assisted $S^1_N$ mechanism.](image)

However, in an $S^2_N$ mechanism the bonding of water leads the liberation of $X$. These considerations show that the differences between these two mechanisms depend on the relative importance of the bond-breaking and bond-making steps, so that there may be a continuous range of mechanism from $S^1_N (\text{lim})$ to $S^2_N (\text{lim})$. The greater part of the effort expended in studying substitution reactions of complexes has been concerned with the identification of the $S^1_N$ or $S^2_N$ mechanisms. Frequently the differences between the two is subtle and unequivocal evidence for one or
the other is difficult to obtain.

Two major approaches to the subject have been used, the kinetics of isotopic water exchange in labile aquo complexes\(^{(91,92)}\), and kinetic and stereochemical investigations of more inert compounds. Although the vast excess of solvent water reduces all the reactions to pseudo first-order, considerable information may be obtained from the relative rates and the kinetic parameters for similar complexes.

Since a wide range of cobalt(III) and chromium(III) complexes have been prepared, and these are relatively inert, they are the logical systems for mechanistic studies, and most of the work has been done on these complexes. The rates of substitution reactions depend very much on ligand field stabilisation energies (L.F.S.E.), and for ions with d\(^3\) and low-spin d\(^6\) configurations the octahedral structure is favoured in terms of these energies. In going from the octahedral to any other structure in the activated state, a considerable loss in L.F.S.E. occurs so that these complexes are generally measurably slow in their reactions. The inertness of cobalt(III) complexes is also a consequence of the high charge and small size of the central atom. These same factors enter into the reactions of the analogous d\(^6\) ions Rh\(^{3+}\) and Ir\(^{3+}\), but in these higher transition series ions the higher effective charges and larger ligand field effects cause their reactions to be slower still, and to have higher activation energies. Stereochemical and kinetic studies on octahedral complexes other than those of Co(III) and Cr(III) have been limited, but they are gradually being extended to the less labile complexes of Rh(III)\(^{(91,93,118)}\), Ir(III)\(^{(118)}\) and Pt(IV)\(^{(91)}\).
**Figure 41. Possible intermediates and transition states from [MA₅ₓ]ⁿ⁺ for Sₙ₂ (a) to (d) and Sₙ₁ mechanisms (e) and (f).**
For each of the limiting mechanisms $S_N^1$ and $S_N^2$ several intermediates are considered possible, and these are shown, as derived from an octahedral complex $[MA_5X]^{n+}$, in figure 41. Basolo, Stone and Pearson originally assumed that the seven-coordinate transition state for an $S_N^2$ reaction would be a pentagonal bipyramid (figure 41a or b) formed by attack of Y at an octahedral edge. It is now considered more likely that a nucleophilic reagent would enter into an open space between the ligands, that is at an octahedral face. This would be a position of minimum electron density with respect to the orientation of the d-orbitals, as well as being the least sterically congested. In addition, Ingold has pointed out that the pentagonal bipyramid structure would involve excessive bond rearrangement which could be alleviated by face attack, and two different structures have to be invoked depending on whether Y attacks at a face adjacent to the departing ligand X or trans to X (figure 41 c and d). In the structure shown in figure 41(d), one of the inert ligands A has moved along an octahedral edge, and as Y enters and X is expelled, this ligand A gradually assumes the position occupied by X in the original octahedron. This process has been described as "edge-displacement" by Brown, Ingold and Nyholm. For the $S_N^1$ mechanism, the two plausible intermediates are the tetragonal pyramid and the trigonal bipyramid (figure 41 e and f).

The ligand field theory has enabled many aspects of transition metal chemistry to be understood in terms of the splittings of the metal d-orbitals. For example, in octahedral $d^3$ and $d^6$ complexes where all the d-electron density (filled $t_{2g}$ orbitals) is concentrated between
the ligands, the addition of a seventh ligand is hindered by the large energy rearrangement necessary to promote a \( t_{2g} \) electron to an \( e_g \) orbital before the bond can form\(^{(95)} \). However the ligand field calculations show that some transition states are quite feasible. In table 8 these calculations are given for the various possible intermediates and transition states arising from \( d^3 \) (Cr(III)) and \( d^6 \) (Co(III), Rh(III), Ir(III)) octahedral complexes, and the calculations have been made taking all the ligands (five or seven) as equivalent. Values for the octahedron, square pyramid, trigonal bipyramid and pentagonal bipyramid are taken from Basolo and Pearson\(^{(30)} \). Hush's calculations\(^{(100)} \) for the trigonal bipyramid where the incoming and outgoing groups occupy adjacent faces on the octahedron were for two models, where the angle \( \Theta \) in figure 41(c) had values of \( 109.28^\circ \) and \( 90^\circ \). The calculations showed that the \( 109^\circ \) model was the more realistic as it gave the smaller \( \Delta E_a \) for all configurations \( d^n \).

The difference between the stabilisation energy for a given intermediate and the original octahedron is considered as a contribution \( \Delta E_a \) to the total activation energy of the reaction, so that a large \( \Delta E_a \) value implies a slow reaction by that particular path. (A negative \( \Delta E_a \) value is essentially a zero value, so that high-spin \( d^6 \) complexes will be labile\(^{(30)} \).) These calculations assume that the spin does not change in going from an octahedral ground state to the respective transition state, i.e. the electrons remain in the same orbitals. Inspection of table 8 leads to the following predictions concerning the rival mechanisms, on ligand field considerations only.
<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>( d^3 )</th>
<th>( d^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIGAND FIELD</td>
<td>strong and weak fields, no spin pairing.</td>
<td>strong field, low-spin complexes</td>
</tr>
<tr>
<td>COMPLEXES</td>
<td>e.g. Cr(III) amine complexes</td>
<td>e.g. Co(III), Rh(III), Ir(III), Pt(IV) amine complexes</td>
</tr>
</tbody>
</table>

**LIGAND FIELD STABILISATION ENERGIES OF VARIOUS GEOMETRIES IN UNITS OF Dq.**

<table>
<thead>
<tr>
<th>Geometry</th>
<th>( d^3 )</th>
<th>( d^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedron</td>
<td>12 Dq</td>
<td>24 Dq</td>
</tr>
<tr>
<td>Square pyramid</td>
<td>10.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Trigonal bipyramid</td>
<td>12.5</td>
<td>15.48</td>
</tr>
<tr>
<td>Pentagonal bipyramid</td>
<td>7.74</td>
<td>10.42</td>
</tr>
<tr>
<td>Trigonal bipyramid (( \Theta = 109^\circ 28' ))</td>
<td>7.74</td>
<td>10.42</td>
</tr>
</tbody>
</table>

**LIGAND FIELD ACTIVATION ENERGIES FOR S_N1 AND S_N2 MECHANISMS, \( \Delta E_a \).**

<table>
<thead>
<tr>
<th>Transformation</th>
<th>( \Delta E_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedron → square pyramid</td>
<td>2.00 Dq</td>
</tr>
<tr>
<td>Octahedron → trigonal bipyramid</td>
<td>11.5</td>
</tr>
<tr>
<td>Octahedron → pentagonal bipyramid</td>
<td>4.26</td>
</tr>
<tr>
<td>Octahedron → trigonal bipyramid, ( \Theta = 109^\circ 28' )</td>
<td>1.58</td>
</tr>
</tbody>
</table>
$\Delta E_a$ is smaller for the trigonal biprism transition complex (with all bond lengths equal) than for a symmetrical pentagonal bipyramid (for all $d^n$ systems\(^{(100)}\)). Calculations have not been made for Ingold's edge-displacement model (figure 41 d) but it must have a similar energy to the trigonal biprism (figure 41 c) since edge-displacement and non-edge-displacement can be observed in similar molecules\(^{(92)}\).

For an $S_{11}$ mechanism a trigonal bipyramid is less favoured than a square pyramid as far as ligand field effects are concerned\(^{(100)}\). However it should be noted that strong $p_{\pi} - d_{\pi}$ bonding from an electron-donating ligand could stabilise the trigonal bipyramid intermediate\(^{(101,30)}\), and there is also less steric repulsion between the ligands in this structure. These factors are not taken into account in the above calculations.

The L.F.S.E.'s of the trigonal biprism and tetragonal pyramid structures are so similar that ligand field effects would not be expected to predispose a system to undergo reaction by an $S_{11}$ mechanism, rather than $S_{22}$, as has previously been thought to be the case\(^{(30)}\). One must consider that these two configurations are equally plausible, and it is later shown that both these paths should lead to retention of configuration. Since this is not always observed, some or all of the other structures must be involved.

That ligand field effects are very large is shown by the good qualitative agreement between predictions based on ligand field calculations and experimentally observed reaction rates for systems with various numbers of $d$ electrons. These calculations emphasize that the inertness of Co(III) and Cr(III) complexes is due to high L.F.S.E.'s.
However, the predictions in regard to stability and geometries of metal complexes may be modified by electrostatic, covalent and steric factors, but when these factors vary uniformly over a series of metal ions the theory can account for the observed differences.$^{30,96}$

**GENERAL ASPECTS OF AQUATION**

The most important and widely occurring reactions of complexes are hydrolysis reactions. Both OH$^-\,$ ion and the water molecule may be considered as nucleophilic reagents, and in cobalt(III) complexes a factor of approximately $10^6$ is observed between the rate constants for these two reactions.$^{30}$ Whereas attack by water is referred to as "aquation" or "acid hydrolysis", attack by OH$^-\,$ is called "base hydrolysis". Both processes overlap, but in acid solution below pH 3, aquation is usually independent of hydrogen ion concentration and base hydrolysis is eliminated, unless the complex is also an acid, e.g. $[\text{Co en}_2 \text{Cl(H}_2\text{O})]^{2+}$.

With the possible exception of OH$^-\,$ ion, there is no evidence for the direct reaction of a nucleophilic reagent, Y, at the cobalt atom in cobalt(III) complexes in aqueous solution. In acid solution water usurps the function of substituting agent in the presence of other nucleophilic agents such as Cl$^-\,$, NO$_2^-\,$, etc., so that the reaction mechanism for the substitution of X by Y proceeds through the intermediate formation of an aquo complex.

$$[\text{Co(NH}_3)_5 X]^{2+} + H_2O \rightarrow [\text{Co(NH}_3)_5(H_2O)]^{3+} + X^-$$

$$[\text{Co(NH}_3)_5(H_2O)]^{3+} + Y^- \rightarrow [\text{Co(NH}_3)_5 Y]^{2+} + H_2O.$$
Thus the investigation of substitution reactions generally, relies on a complete understanding of aquation.

Aquation was the first reaction of complexes to be studied kinetically when Lamb and Marden\(^{102}\) in 1911 measured the rates and equilibria of the reactions:

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons [\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]\text{Cl}_3
\]

A number of important early studies on cobalt(III) ammine and amine systems, and particularly the acidopentammine, diacidotetrammine and diacidobisethylenediamine series, were made by Lamb\(^{102-105}\), Brönsted\(^{106,107}\), Mathieu\(^{49,108}\) and Garrick\(^{109}\), but most of the systematic data has been accumulated in the last decade. Despite considerable effort an unambiguous and universally acceptable mechanism for aquation in cobalt(III) complexes has yet to be agreed on, although at present it seems likely that both S\(_N^1\) and S\(_N^2\) mechanisms occur.

In recent years two main views as to the mechanism of aquation have arisen and several reviews\(^{30,96,110-115,89,91,99,92}\) have given the evidence which the authors consider to support one or other of the probable mechanisms. Whereas Basolo and Pearson\(^{30}\) have placed more weight on the S\(_N^1\) mechanism, Ingold, Nyholm and Tobe\(^{112}\), drawing on organic chemical experience hold that a greater range of S\(_N^1\) and S\(_N^2\) mechanisms occur. Certainly the weight of evidence seems to support bond-breaking being more important than bond-making for the aquation of many halo complexes of cobalt(III).

It has already been pointed out that the problem in octahedral
aquation arises from the fact that kinetics in aqueous solution give no direct information as to molecularity of the reactions or the role played by the solvent. There are few solvents of low complexing power in which charged metal complexes are soluble, so that almost all aquation studies have so far been made in water. However the kinetic study of reactions between complex ions and water in non-aqueous systems, for example tetrahydrothiophen dioxide, has begun\(^{(114)}\), but the importance of the back anation reaction and ion-pair effects has so far excluded any deduction as to the molecularity of the aquation reactions. Other substitution reactions however, have been studied in solvents such as methanol\(^{(115)}\) and dimethylsulphoxide\(^{(116)}\) where the aquation reactions can be avoided, although it has been pointed out\(^{(117)}\) that there is no assurance that in such situations one type of solvolytic process has not merely been replaced by another.

Since a number of factors undoubtedly contribute to the rate and mechanism for any particular complex, a complete kinetic study on any one compound may reveal only limited details of mechanism as the various factors can not be separated\(^{(30,89)}\). Some of these factors are discussed later. An approach which has been commonly used is to study a series of compounds where some of these contributing effects are expected to remain essentially constant. By correlating the observations with the remaining factors, some information as to mechanism can sometimes be inferred.

**REACTION INTERMEDIATES AND OVERLAP OF MECHANISMS**

If the existence of intermediates of reduced or increased coordination
number can be inferred from the experimental data pertaining to an aquation reaction, the $S^1_1$ or $S^2_2$ mechanisms are thus demonstrated. Posey and Taube\(^{(80)}\) made a search for a five-coordinate intermediate with a finite lifetime by studying the aquation of \([\text{Co(NH}_3)_5X]^2^+\) ions, where $X = \text{Cl, Br, I}$, in the presence of $\text{Hg}^{2+}$, $\text{Ag}^+$ and $\text{Tl}^{3+}$ ions. The reactions were carried out in $\text{H}_2^0^{16}$-enriched acid solutions, and the $0^{18}$ enrichment ratio in the \([\text{Co(NH}_3)_5(\text{H}_2^0)]^{3+}\) product from each of the three complexes was measured. The results showed that an intermediate of common properties was not formed when the reactions were catalysed by $\text{Ag}^+$ or $\text{Tl}^{3+}$, but the same isotopic ratio was found for the three halogen complexes when $\text{Hg}^{2+}$ was used. This implied that the rapid removal of $X$ by $\text{Hg}^{2+}$ gave the same intermediate, \([\text{Co(NH}_3)_5]^{3+}\), and this is probably the strongest evidence for the $S^1$ mechanism in an aquation reaction. Pearson, Schmidt\(^{(116)}\) and Basolo\(^{(116)}\) have recently demonstrated the existence of a five-coordinated intermediate \([\text{Co en(en-H)}(\text{NO}_2^\text{Cl})]^0\) in the reaction of \([\text{Co en}_2(\text{NO}_2^\text{Cl})]^+\) with nucleophilic reagents ($\text{NO}_2^-$, $\text{SCN}^-$, $\text{N}_3^-$) in dimethylsulphoxide and with catalytic amounts of bases present. In this case the intermediate is the conjugate base, formed by dissociation of a hydrogen ion, and the observed kinetics could not be explained in terms of a bimolecular mechanism.

It is rare however, that such definite conclusions have been reached for substitution reactions, but these results regarding the intermediates do not necessarily apply in aqueous acid solution and in the absence of metal ions. In fact Posey and Taube's observations suggested that the aquation of \([\text{Co(NH}_3)_5X]^2^+\) in the absence of $\text{Hg}^{2+}$ to facilitate $\text{Co-X}$ bond
rupture involved some $S_{2}^2$ character, and this agrees with the $S_{N}^2$ mechanism assigned to the aquation of $[\text{Co en}_2(\text{NH}_3)\text{Cl}]^{2+}$ which is discussed later.

Also, such observations need not extend to similar compounds. For example, while the tetragonal pyramid structure would be expected for the above $[\text{Co}(\text{NH}_3)_5]^{3+}$ intermediate on a ligand field basis(99), the five-coordinated intermediate which would result from $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ by dissociation of $\text{Cl}^-$ is more likely to be a trigonal bipyramid because of $\pi$-bonding stabilisation. Preliminary experiments on the $\text{Hg}^{2+}$-catalysed aquations of cis$[\text{Co en}_2\text{Cl}_2]^+$ and $\alpha$ and $\beta$ $[\text{Co trien Cl}_2]^+$ appear to support this latter structure.

A square pyramidal intermediate would have a very limited lifetime, so that most reactions proceeding through this intermediate may be solvent-assisted $S_{N1}$ (p. 93). A similar idea has been expressed by Adamson(117) who measured the rate of solvolytic replacement of the first SCN$^-$ group from $[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]^-$ in a number of solvents. The rate constants in water and in a series of alcohols were not greatly dependent on these solvents, but decreased by a factor of two when measured in $D_2O$, and were negligibly small in non-hydroxylic solvents such as nitromethane. The kinetic importance of the solvent, and the inability of strong nucleophiles ($\text{CN}^-$, $\text{N}_3^-$, $\text{I}^-$) to accelerate the rate suggested that $S_{N1} (\text{lim})$ and $S_{N2} (\text{lim})$ mechanisms could be eliminated. In the mechanism proposed, described as $S_{N2}$ $FS$ (front-side), the role of the solvent OH group was paramount, the solvent being hydrogen-bonded to the ligands in the transition state (figure 42).
Adamson thus considers that most substitution reactions of octahedral complexes in ROH type solvents can take place via the $S_{N}^{2}$ FS process, where the intermediate $M$-ROH-X may be present in only catalytic quantities. $S_{N}^{2}$ IP ("ion-pair") and $S_{N}^{2}$ CB ("conjugate base") mechanisms account for other situations, and it is claimed that much of the evidence cited for $S_{N}^{1}$ aquation mechanisms could also be explained by $S_{N}^{2}$ FS$^{(117)}$, although clearly the latter mechanism can not apply when extensive rearrangement occurs.

The above considerations draw attention again to the continuous range of mechanism between $S_{N}^{1}$ (lim) and $S_{N}^{2}$ (lim) that may be expected. In the next section it is shown that it is very difficult to distinguish between the $S_{N}^{1}$ tetragonal pyramid and $S_{N}^{2}$ cis-attack mechanisms since they both lead to retention of configuration, but stereochemical changes can sometimes give valuable evidence as to mechanism. These situations are discussed in the following section.
STEREOCHEMISTRY

Most of the data accumulated so far on aquation refer to pentammine or bis(en) compounds. In the first instance, only one configuration exists so studies on this system give no information on the stereochemical course of a reaction. Bis(en) compounds can exist in trans and D and L cis isomeric forms, so that observations of stereochemical changes can give a good deal of information. Before considering the stereochemical results which have been obtained, it is convenient to review the possible products which may result from each reaction intermediate, for the stereochemical changes occurring during reaction are expected to depend somewhat on the mechanism involved. The mechanisms are discussed in terms of the cis and trans bis (diamine) compounds of the type \([\text{Co(AA)}_2 \text{BX}]^{n+}\) where X is the ligand replaced and B is a non-participating reference ligand, following Basolo and Pearson's account. AA represents a diamine molecule such as ethylenediamine.

The stereochemical consequences of $S_N^1$ reactions of the D-cis and trans isomers, involving the two alternative intermediates, are shown in figure 43. In these discussions it is assumed that the incoming group Y (a water molecule in aquation), should enter the activated complex at the most accessible positions, which are indicated by arrows. In the tetragonal pyramid it is thus assumed that Y will enter the position vacated by X, while for the trigonal bipyramid intermediate the addition of Y is assumed to take place in the trigonal plane. The ratios of the isomeric products

TRANS + Y → TRANS

TETRAHEDRAL PYRAMID

TRIGONAL BIPYRAMID I

D-CIS

TRIGONAL BIPYRAMID II

Figure 43. Stereochemical Changes Accompanying SN₁ Reaction of [Coen₂BX]^n+ with Y.
shown are statistical, assuming attack of Y is equally likely at all the possible positions. From these considerations it is evident that only a trigonal bipyramid will permit rearrangement, and that loss of activity from the cis can occur only through trigonal bipyramid II or by isomerisation to trans through trigonal bipyramid I (figure 43).

The concept of "edge-displacement" for bimolecular mechanisms was referred to earlier. This was able to account for any observed stereo change cis $\leftrightarrow$ trans or D $\leftrightarrow$ L in terms of a singular type of change depicted in figure 44.

![Figure 44. Edge-displacement](image)

This is because the labels attached to complexes D, L, or cis and trans merely depend on the position of some unaffected group A, which may be at any of the four remaining positions. Trans $\leftrightarrow$ trans substitutions however can not occur by such a representation, and cis $\leftrightarrow$ cis and D $\leftrightarrow$ D substitutions need not, so that substitution can occur with or without edge-displacement. In the instance where edge-displacement is not possible, i.e. trans $\leftrightarrow$ trans, the trigonal biprism (which always leads
to retention of configuration) is considered to be involved\(^{(97)}\), and this can also explain a change \(D \leftrightarrow D\), so that this last observed change cannot be interpreted unambiguously on the bis(en) model. The third structure considered, but the least likely (p. 95'), is the pentagonal bipyramid, and bimolecular attack by \(Y\) might then occur at an octahedral edge cis or trans to the displaced ligand \(X\). Edge-displacement is then essentially equivalent to trans-attack, and the trigonal bipyramid to cis-attack, so that the stereochemical changes are drawn for clarity in terms of the pentagonal bipyramid, (figure 45). The correlation with the other models is given in the figure.

Figures 43 and 45 show that all possible stereochemical changes can be observed with both the \(S_N^1\) and \(S_N^2\) mechanisms, so that the stereochemistry of the reaction product is often not in itself diagnostic of the mechanism. There is one instance however, where a stereospecific reaction can be assigned a mechanism with a high degree of certainty. If a trans isomer yields exclusively a cis product, then this would be good evidence in support of a trans-displacement mechanism. If a seven-coordinate intermediate can be excluded, then this rearrangement could occur only through a trigonal bipyramid (I in figure 43), but it would be unlikely to be completely stereospecific since statistically the cis product is favoured. Inversion is less specific, as the figures show that it can result from a trigonal bipyramid (II in figure 43), or by trans-attack (edge-displacement) at one edge of the octahedron (figure 45). Inversion will occur from a trigonal bipyramid however, only if the two chelate groups AA are different so that II is not symmetrical and attack at position (1)
Figure 45. Stereochemical changes accompanying $S_{n2}$ reaction of $[\text{Co}(\text{AA})_2\text{BX}]^{n+}$ with $Y$. 
is preferred (figure 43). Thus if the two diamine groups AA are identical (as in bis(en) complexes) an inversion must result from an $S_N^2$ mechanism by preferential attack at position (2) (figure 45). Such specificity could only result from a unique combination of inductive and steric effects of the groups attached to the metal, making the positions of attack non-equivalent.

No instances of inversion are known in aquation reactions, but what is believed to be the first instance of a stereospecific trans $\rightarrow$ cis change is presented later in this thesis.

Some of the stereochemical evidence on aquation mechanisms will now be outlined.

**Stefeeochemical results of aquation**

Until recently, the stereochemical aspects and products of aquation have been relatively neglected, and frequently kinetic measurements of aquation have not been accompanied by stereo studies. Sometimes this has been due to the difficulty in isolating the pure aquo products for spectral comparison, but often because of the rapid rates of subsequent reaction or isomerisation of the aquation products. However Tobe and his colleagues are now undertaking refined kinetic studies of aquation reactions and correcting for subsequent isomerisations, so that the ratio of isomeric products as a direct consequence of reaction can be determined.

Tables 9 and 10 list the reported observations on the steric course of aquation which are considered reliable, and most of these have been made only in the last few years.
TABLE 9. ISOMER RATIOS OF FIRST-FORMED PRODUCTS IN AQUATION

\[ [\text{Co en}_2 A X]^+ + H_2O \rightarrow [\text{Co en}_2 A(H_2O)]^{2+} + X^- \]

<table>
<thead>
<tr>
<th>X</th>
<th>A</th>
<th>Conditions</th>
<th>% Cis*</th>
<th>% Trans*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Cl</td>
<td>OH</td>
<td>H$_2$O</td>
<td>100</td>
<td>0</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>N$_3$</td>
<td>HClO$_4$</td>
<td>100</td>
<td>0</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>HNO$_3$</td>
<td>100</td>
<td>0</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>NCS</td>
<td>HClO$_4$</td>
<td>100</td>
<td>0</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>NH$_3$</td>
<td>HClO$_4$/AgClO$_4$</td>
<td>75</td>
<td>25 ?</td>
<td>94</td>
</tr>
<tr>
<td>cis-Br</td>
<td>NCS</td>
<td>&quot;</td>
<td>100</td>
<td>0</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>NH$_3$</td>
<td>&quot;</td>
<td>100</td>
<td>0</td>
<td>112,122</td>
</tr>
<tr>
<td>cis-NO$_3$</td>
<td>NH$_3$</td>
<td>&quot;</td>
<td>100</td>
<td>0</td>
<td>112</td>
</tr>
<tr>
<td>cis-F</td>
<td>F</td>
<td>HNO$_3$</td>
<td>+</td>
<td>-</td>
<td>123</td>
</tr>
<tr>
<td>trans-Cl</td>
<td>OH</td>
<td>H$_2$O</td>
<td>75</td>
<td>25</td>
<td>119</td>
</tr>
<tr>
<td></td>
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<td>HClO$_4$</td>
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<tr>
<td></td>
<td>Cl</td>
<td>HNO$_3$</td>
<td>35</td>
<td>65</td>
<td>119</td>
</tr>
<tr>
<td>trans-[Co(AA)$_2$Cl$_2$]$^+$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
<td>+</td>
<td>124</td>
</tr>
</tbody>
</table>

essentially retention of configuration claimed but not proved, where

AA = N- and C-substituted en, tn, pn, bn, dan.

<table>
<thead>
<tr>
<th></th>
<th>NCS</th>
<th>HClO$_4$</th>
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<th>50-30</th>
<th>121</th>
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<tbody>
<tr>
<td>NH$_3$</td>
<td>&quot;</td>
<td>0</td>
<td>100</td>
<td>125</td>
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<tr>
<td>NO$_2$</td>
<td>&quot;</td>
<td>0</td>
<td>100</td>
<td>94,97</td>
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<tr>
<td>CN</td>
<td>H$_2$O or H$^+$/Hg$^{2+}$</td>
<td>$\sim$ 0</td>
<td>$\sim$100</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>trans-Br</td>
<td>NCS</td>
<td>HClO$_4$</td>
<td>43</td>
<td>57</td>
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<td>H$_2$O</td>
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<td>100</td>
<td>114</td>
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<tr>
<td>trans-NO$_3$</td>
<td>NH$_3$</td>
<td>HClO$_4$</td>
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<td>100</td>
<td>125</td>
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</tbody>
</table>

* (Notation of + signifies chief isomeric product)
<table>
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<tr>
<th>Compound</th>
<th>Conditions</th>
<th>% Cis</th>
<th>% Trans</th>
<th>Reference</th>
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<tr>
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<td>HCl</td>
<td>$\sim 100$</td>
<td>$\sim 0$</td>
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<tr>
<td>cis[Cr en$_2$(H$_2$O)Cl]$_2^+$</td>
<td>HNO$_3$</td>
<td>$\sim 100$</td>
<td>$\sim 0$</td>
<td>129</td>
</tr>
<tr>
<td>cis[Cr en$_2$ F$_2$]$^+$</td>
<td>&quot;</td>
<td>+</td>
<td>-</td>
<td>130</td>
</tr>
<tr>
<td>trans[Cr en$_2$ Cl$_2$]$^+$</td>
<td>HNO$_3$ or HClO$_4$</td>
<td>some</td>
<td>most</td>
<td>128, 131</td>
</tr>
<tr>
<td>trans[Cr en$_2$(H$_2$O)Cl]$_2^+$</td>
<td>HNO$_3$</td>
<td>some</td>
<td>some</td>
<td>129</td>
</tr>
<tr>
<td>cis[Rh py$_2$ Cl$_4$]$^-$</td>
<td>H$_2$O</td>
<td>+</td>
<td>-</td>
<td>132</td>
</tr>
<tr>
<td>cis[Ir py$_2$ Cl$_4$]$^-$</td>
<td>&quot;</td>
<td>+</td>
<td>-</td>
<td>132</td>
</tr>
<tr>
<td>trans[Rh py$_2$ Cl$_4$]$^-$</td>
<td>&quot;</td>
<td>-</td>
<td>+</td>
<td>132</td>
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<tr>
<td>trans[Ir py$_2$ Cl$_4$]$^-$</td>
<td>&quot;</td>
<td>-</td>
<td>+</td>
<td>132</td>
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<tr>
<td>cis[Rh en$_2$ Cl$_2$]$^+$</td>
<td>KOH or HNO$_3$</td>
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<td>$\sim 0$</td>
<td>93</td>
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<tr>
<td>trans[Rh en$_2$ Cl$_2$]$^+$</td>
<td>&quot;</td>
<td>$\sim 0$</td>
<td>$\sim 100$</td>
<td>93</td>
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<tr>
<td>and other dichloro tetramino Rh(III) ions</td>
<td>full retention</td>
<td>93</td>
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Up to a few years ago the available data suggested that all reactions of geometric isomers of the type

\[ [\text{Co}(\text{AA})_2\text{BX}]^{n+} + \text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{AA})_2\text{B}(<\text{H}_2\text{O})]^{(n+1)} + \text{X}^- \]

(both forward aquation and reverse anation reactions) proceeded largely without stereochemical change, and this in turn suggested that substitution proceeded by an S\textsubscript{N}1 mechanism through a tetragonal pyramid, or by S\textsubscript{N}2 with cis-attack (without edge-displacement). More detailed studies indicated that while retention of configuration was predominant, rearrangement did occur in some instances and this, together with kinetic data led Ingold and Aßperger in 1956\textsuperscript{97} to propose that the two mechanisms operate in different complexes of the type cis and trans \[ [\text{Co en}_2\text{BX}]^+ \], where for a constant replaced ligand X, the S\textsubscript{N}1 or S\textsubscript{N}2 (cis-attack) mechanism is decided by the orienting ligand B. The correlation of rates and stereo change with the polar effects of B is indeed very convincing, for it is just those ligands B which can exhibit a \( \pm \)E (electromeric) effect (OH, N\textsubscript{3}, Cl, NCS) which always cause stereo-change from trans factors by a proposed S\textsubscript{N}1 mechanism. In the other instances of trans factors, and always with cis factors, the retention is complete (also borne out by the limited data on Cr(III), table 10) and the following stereochemical rule has been proposed\textsuperscript{(112)}: "In octahedral aquations which replace X in filled-sub-shell complexes MR\textsubscript{4}AX of a transition metal M, configuration will be totally preserved, unless A and X are trans, and A but not R has unshared electrons adjoining M." The predominating tendency for complete retention is explained by one water molecule in a tightly bound and well-ordered
inner solvation shell being in such close juxtaposition to the replaced group that it will merely substitute at the same position, whether loosening ($S^l_N$) or binding ($S^2_N$) is in the lead. Tobe has suggested that hydrogen-bonding between the incoming water and outgoing Cl$^-$ ion in the transition states in both $S^l_N$ and $S^2_N$ aquations might predetermine the orientation of substitution before the Cl$^-$ has completely passed the transition state separation. The operation of the $\pm E$ effect to cause stereo change only in trans factors by the $S^l_N$ mechanism is postulated to arise from the requirement of non-orthogonality for the effect to be manifested. The orienting group might then cause sufficient prior loosening of a normally less easily loosened cis-group (i.e. amino group) to allow some edge-displacement involving dissociation of the labile trans group. The extent of rearrangement should then be in the order Cl $>$ Br $>$ NO$_3$ for replaced groups X, correlating with the binding energies of the Co-X bond, although the available data is not sufficient to test this.

A similar suggestion to account for the observed rearrangements has been made by Basolo and Pearson in that electron-donating ligands such as Cl$^-$, OH$^-$ and NH$_2^-$ (in the predicted order Cl$^-$ $<$ OH$^-$ $<$ NH$_2^-$) which are cis to the removed ligand might $\pi$-bond to a cobalt 4p orbital, whose energy would be lowered by dissociation of the negative ligand. The cis position is thereby labilised more than the trans, which accounts for the greater rates for the cis isomers (see later). On the other hand if a group dissociates completely leaving an intermediate of coordination number...
five, $p_\pi - d_\pi$ bonding to the vacated d-orbital could favour rearrangement to a trigonal bipyramid. The energy of this d-orbital would be lowered and strong $\pi$-bonding could take place in the trigonal plane. $\pi$-bonding might thus over-ride ligand field factors, and reference to figure 43 shows that stereochange should result, especially from a trans factor. The difference between these postulates and those of the former authors arises in that Ingold suggests dissociation might accompany rather than precede the edge-displacement in the case of the trans isomer, while the cis isomer will always aquate more rapidly through a tetragonal pyramid intermediate. Basolo and Pearson's postulates should lead to some rearrangement and racemisation from a cis factor through a trigonal bipyramid, but this has never been observed (table 9).

It is of interest to mention Mathieu's application of polarimetric methods to study the stereochemical course of aquation of some complexes, since these methods have been used in the present work. By measurements of the R.D. curves Mathieu\(^{108}\) showed that the aquations of 

\[ (+)[Co\,en_2\,A\,Cl]^+ \text{ or } 2^+ \quad \text{where } A = Cl, \ H_2O, \ NO_2, \ NCS, \ NH_3 \]

took place essentially with retention of generic configuration. These conclusions were also supported by the solubility criterion and by circular dichroism, but the measurements were not quantitative. Further evidence that 

\[ (+)[Co\,en_2\,Cl_2]^+ \] 

aquates with retention was furnished by measuring the rate of mutarotation to \[ (+)[Co\,en_2\,Cl(H_2O)]^{2+} \]. This rate was found equal to the rate of loss of Cl\(^-\) determined conductimetrically\(^{49}\) so that the change in optical activity was a direct result of the replacement of Cl\(^-\).
ion by water, and the amount of racemisation and isomerisation was not extensive. More recent work by Pearson, Meeker and Basolo\(^{(133)}\) showed that the products resulting from aquation of \(\text{cis}[\text{Co en}_2 \text{Cl}_2]^+\) at pH 3 and 25\(^\circ\) were \([\text{Co en}_2 \text{Cl}(\text{H}_2\text{O})]^2+\) in the isomeric ratio 79\% cis, 21\% trans. This agreed with the isomeric ratio of chloroaquo products calculated from Mathieu's determination of the subsequent loss of activity, if this was assumed to be due to isomerisation of cis to trans \([\text{Co en}_2 \text{Cl}(\text{H}_2\text{O})]^2+\). The ratio quoted above was that found at the end of the aquation, but it has since been determined\(^{(119)}\) that the actual aquation of \(\text{cis}[\text{Co en}_2 \text{Cl}_2]^+\) does occur with 100\% retention to \(\text{cis}[\text{Co en}_2 \text{Cl}(\text{H}_2\text{O})]^2+\). This then isomerises to an equilibrium mixture of 73\% cis, 27\% trans (in 0.01 M HNO\(_3\)) with the forward rate identical to the rate of loss of activity\(^{(45,119)}\). These results are represented by the following reaction scheme:

\[
\begin{align*}
\text{cis}[\text{Co en}_2 \text{Cl}_2]^+ & \rightarrow \text{cis}[\text{Co en}_2 \text{Cl}(\text{H}_2\text{O})]^2+ & \rightarrow \text{cis}[\text{Co en}_2 (\text{H}_2\text{O})_2]^3+ + \text{Cl}^- \\
+ \text{H}_2\text{O} & \quad & + \text{Cl}^- \\
\quad & \quad & \quad \quad \text{73\% cis} \\
\quad & \quad & \quad \quad 27\% \text{ trans} \\
\text{trans}[\text{Co en}_2 \text{Cl}_2]^+ & \rightarrow \text{trans}[\text{Co en}_2 \text{Cl}(\text{H}_2\text{O})]^2+ & \rightarrow \text{trans}[\text{Co en}_2 (\text{H}_2\text{O})_2]^3+ + \text{Cl}^- \\
+ \text{H}_2\text{O} & \quad & + \text{Cl}^-
\end{align*}
\]

Under the kinetically controlled conditions quoted above the rates for the initial aquation and chloroaquo isomerisation are much greater than those for aquation of the second chloro group. The isomerisation could
occur by water exchange through a five-coordinate intermediate, or by an intramolecular mechanism, but water exchange rates have yet to be measured.

The aquations of chloroaquo tetramino compounds, as represented by the equilibria on the right of the above scheme, have received more limited attention, probably because of the complexity of the system in that the rates of approach to cis-trans chloroaquo equilibrium are greater than the rates of subsequent aquation to diaquo isomers. Brönsted was the first to make reliable kinetic measurements on these systems. In acid solutions of pH < 3 the rates of aquation of \( \text{cis}[\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})\text{NO}_3]^{2+} \) and \( \text{cis}[\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})\text{Cl}]^{2+} \) showed a linear dependence on \( \frac{1}{[H^+]} \) and could be expressed by the equation

\[
 k_{\text{obs}} = k_0 + \frac{k'}{[H^+]} 
\]

The \( k_0 \) term was ascribed to aquation of the aquo species \( [\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})X]^{2+} \) while \( k' \) (slightly dependent on total concentration) was due to aquation of the conjugate base \( [\text{Co(NH}_3\text{)}_4(\text{OH})X]^+ \) so that the aquation reaction went through two paths. The reaction scheme postulated was:

\[
 \begin{align*}
 [\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})\text{Cl}]^{2+} + \text{H}_2\text{O} & \overset{k_1}{\rightleftharpoons} [\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})_2]^{3+} + \text{Cl}^- \\
 [\text{Co(NH}_3\text{)}_4(\text{OH})\text{Cl}]^+ + \text{H}_2\text{O} & \overset{k_2}{\rightleftharpoons} [\text{Co(NH}_3\text{)}_4(\text{OH})(\text{H}_2\text{O})]^{2+} + \text{Cl}^- 
\end{align*}
\]
which yields the rate expression

\[ k_{\text{obs}} = k_1 + \frac{k_2 K_a}{[H^+]} \]

At \(20^\circ\)

\[ k_{\text{obs}} = 1.3 \times 10^{-4} + 1.6 \times 10^{-6} \frac{1}{[H^+]} \]

and if \(K_a\) (the acid dissociation constant of the aquo ion) \(\leq 10^{-6}\)
then \(k_2\) is about \(10^4 \times k_1\). This greater reactivity of the hydroxochloro as compared to the aquochloro complex was accounted for by its smaller positive charge, but it can also be attributed to \(\pi\)-bonding (p.121).

Brönsted failed to account for cis-trans isomerisation in the chloroaquo and diaquo compounds since he used the conductivity method, so the constants determined refer to the overall aquation rate, but the above reaction course is accepted as being correct. Complexes such as

\([\text{Co(NH}_3)_5\text{Cl}]^{2+}\) and \([\text{Co(NH}_3)_5\text{NO}_3]^{2+}\) without such acidic protons aquate much more slowly, and with rates independent of \([H^+]\) at low \(pH(106,107,109)\).

The corresponding bis(ethylenediamine) system was first studied by Mathieu(49) using potentiometric titration, glass electrode, and conductivity methods, so that again isomerisation was neglected. It was shown however that the equilibrium

\[ \text{cis}[\text{Co en}_2 \text{Cl(H}_2\text{O})]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Co en}_2(\text{H}_2\text{O})_2]^{3+} + \text{Cl}^- \]

was sensitive to the conditions, being displaced to the right by decreasing concentration of complex or chloride ions, decreasing
temperature, or decreasing \([H^+]\). In a later paper\(^{108}\), active diaquo solution was obtained by the above aquation so that essentially little isomerisation was claimed to occur. In these studies the rates were not separated into the chloroaquo and chlorohydroxo paths, but Tobe and co-workers\(^{119}\) recently made a refined kinetic study of the aquation and isomerisation in water of cis and trans \([Co\,en\,\,Cl(OH)]^+\). Aquation and isomerisation rates were comparable but they could be separated and the precise steric course determined. The rates of aquation of the chlorohydroxo isomers had previously been determined by Pearson, Meeker and Basolo\(^{153}\). The stereochemical results are shown in the following scheme:

\[
\begin{align*}
\text{cis}[Coen_2(H_2O)Cl]^2+ - H^+ & \rightarrow [Coen_2(OH)Cl]^+ , \\
\text{cis}[Coen_2(OH)(H_2O)]^{2+} & + H_2O \rightarrow \text{cis}[Coen_2(OH)(H_2O)]^{2+} , \\
\text{in 0.01 M H}^+ & \rightarrow \text{trans}[Coen_2(OH)(H_2O)]^{2+} , \\
\text{in water} & \rightarrow \text{in water} , \\
\end{align*}
\]

The foregoing remarks summarise almost all of the relevant data on the steric course of aquation of cobalt(III) compounds where only two geometric isomers are possible. Very little kinetic work has been recorded on systems with greater isomeric complexity, and even less work has been done on the stereochemical aspects. Aquation rates have been
measured for the compounds \([\text{Co en dien Cl}]^{2+}\), \([\text{Co tetraen Cl}]^{2+}\), \([\text{Co trien(NH}_2\text{Cl}]^{2+}\) and \([\text{Co trien Cl}_2]^+\), but each exists in several isomeric forms (figures 46 and 4) and the stereochemistry was not elucidated\(^{15}\). The kinetics showed that the \([\text{Co tetraen Cl}]^{2+}\) was a mixture of isomers, but it could not be decided whether these were different arrangements of the penta-coordinated ligand around the metal, or whether they were due to isomerisation in the ligand itself. The kinetics of the other compounds indicated that only one isomer was present in each instance. The \([\text{Co en dien Cl}]^{2+}\) system was recently studied in more detail, and the three isomers (figure 46) may have been separated by their different solubilities in water, methanol and ethanol,
but the dissymmetric isomers could not be resolved. Similarly, the kinetics have been measured for [Co i-bn cytam Cl]^2+ (figure 46), but this also was not resolved. The rates of aquation of the trans dichloro and one of the cis dichloro isomers of [Co en(NH3)2Cl2]^+ (figure 6) were found to be very similar, and this behaviour is intermediate to that in the systems [Co en2 Cl2]^+ and [Co trien Cl2]^+ (chapter 5). It would thus be interesting to determine the stereochemical course of aquation of trans-dichloro [Co en(NH3)2Cl2]^+.

The study of aquation will inevitably expand in the direction of more complex systems such as the above, but many preparative difficulties have to be overcome.

KINETICS

The following are the factors contributing to the rates of aquation of octahedral complexes, and many of the experimental approaches which have been used in an attempt to separate these factors are also indicated.

Environmental Effects

(A) External pressure

Application of this tool has so far been very limited, and has not allowed very definite deductions to be made. The volume change and ΔS‡ for the reaction

\[ [\text{Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^3+ + \text{H}_2\text{O}^{16} \rightleftharpoons [\text{Co(NH}_3\text{)}_5(\text{H}_2\text{O}^{18})]^3+ + \text{H}_2\text{O} \]

did eliminate a compact S_N^2 mechanism, so that some S_N^1 character was
involved\(^{(135)}\).

(B) The effect of added ions

Aquation rates are for the most part independent of ionic strength \(\mu\), especially at low \(\mu\), in accord with the Debye-Huckel theory on the primary salt effect. Some specific catalytic effects at higher \(\mu\) with \(\text{SO}_4^{2-}\) and \(\text{NO}_3^-\) ions have been attributed to ion-pair formation\(^{(109,80)}\). An ionic strength dependence can be expected for reactions of weak acids, such as aquo complexes, by a "secondary salt effect", and this is discussed later in connection with the aquation of \([\text{Co trien Cl(H}_2\text{O)}]\)^{2+} ions.

Aquations which proceed to equilibrium, e.g.

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^3+ + \text{Cl}^-
\]

are dependent on \([\text{Cl}^-]\) because of the mass-action effect. The replacements of the first chlorine atoms in dichloro complexes are essentially complete, but the positions of equilibria in the subsequent aquations are dependent on \([\text{Cl}^-]\) as above\(^{(106)}\), and the reverse anations show second-order kinetics.

Cations like \(\text{Hg}^{2+}\), \(\text{Ag}^+\) and \(\text{Tl}^{3+}\) catalyse aquation of halo-complexes, the rates being first order both in complex ion and cation concentrations. The \(S_N\), \(\text{Hg}^{2+}\) - catalysed aquation of \([\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}\) was mentioned earlier, and the \(S_N\) designation of mechanism refers to the reaction with water. These reactions are essentially \(S_E\) reactions however, in that the initial and rate determining step is the rapid
removal of the Cl⁻ ion by Hg²⁺. It has recently been shown for the [Co en₂ Cl₂]⁺ isomers that the subsequent aquation then takes place largely with retention of configuration, and in this way trans[Co en₂ Cl(H₂O)]²⁺ was isolated for the first time (44).

(c) Hydrogen ion concentration

Monoacido complexes usually aquate at a rate independent of [H⁺] below pH 4, but aquo-acido complexes, being weak acids, show a dependence on [H⁺] as discussed previously.

Aquations of complexes containing strongly basic ligands, such as [Co(NH₃)₅CO₃]⁺, or those containing ligands with a high tendency to hydrogen bonding are acid catalysed at low pH, where protonated species must be formed. In the latter category is the aquation of trans[Co en₂ F₂]⁺ and cis[Cr en₂ F₂]⁺ where hydrogen bonding is held to weaken the Co-F bond in the reactive species en₂F-Co-F-H⁺. No such catalysis has yet been observed with other halo complexes (123, 130).

(d) Solvent

The little data available on this factor has been referred to previously.

Structural Effects

(E) The Central Metal Atom

From the limited data on complexes of metals other than cobalt(III) good correlations have been found between measured values of rates and
activation energies, and those predicted by the ligand field and effective ionic charge theories. For example, the slower reactions of rhodium(III) complexes have \( E_a \) about 2 kcal/mole higher than corresponding cobalt(III) reactions, but from the insensitivity of hydrolysis rates of rhodium complexes to charge, \( S_N^2 \) (trigonal bipyramid) mechanisms are extremely likely here\(^{(93)}\).

(F) The displaced ligand

In the series \([\text{Co(NH}_3\text{)}_5\text{X}]^{2+} \) or \( 3^+ \), the rates varied markedly with the nature of \( X \), and decreased in the order \( \text{HCO}_3^- > \text{NO}_3^- > \text{I}^- > \text{Br}^- > \text{H}_2\text{O} > \text{Cl}^- > \text{SO}_4^{2-} > \text{OAc}^- > \text{SCN}^- > \text{NO}_2^- \). This same order has been observed in other series, and generally correlates with the order of ligand field strengths. It has been suggested from the wide variation of rates with the displaced group that bond-breaking is important\(^{(30)}\), but the above order does not correlate with the reported activation energies.

The rates of aquation of carbon-substituted acetato complexes \([\text{Co(NH}_3\text{)}_5(\text{CR}_3\text{COO})]^{2+} \) (\( R = \text{H, halogen, alkyl, OH} \)) followed the trend of basicities of the acetato groups, and steric factors appeared to have little effect. This was evidence against an \( S_N^2\text{cis-attack mechanism} \), but was in agreement with either \( S_N^1 \) or \( S_N^2\text{trans-attack mechanism} \)(136). Although in this series the basicities of the acetate ions differed by a factor of \( 10^4 \), the rates differed only by a factor of 12, tending to support the bimolecular mechanism\(^{(113)}\).
Tobe (125) has also investigated the effect of the displaced ligand in the series \( \text{trans}[\text{Co en}_2(\text{NH}_3)X]^{2+} \) where \( X = \text{Cl}^-, \text{Br}^-, \text{NO}_3^- \). These aquation mechanisms have been assigned as \( S_N^2 \) (cis-attack), in accord with a previous bimolecular assignment for the \([\text{Co(NH}_3)_5X]^{2+}\) ion. The rates increase along the series \( \text{Cl} < \text{Br} < \text{NO}_3 \) but the activation energies also increase, so that the rates are determined largely by the entropies with the solvation greatest in the chloro compound. The difference between the chloro and nitrato complexes was attributed to the greater hydrogen-bonding of Cl with the entering water than of NO\(_3\), as the latter group may be already intramolecularly hydrogen-bonded through the amine groups (figure 47).

![Figure 47](image)

(G) The net charge on the complex

Many aquations involve displacement of a negative ligand from a positively charged complex. For a dissociation mechanism, the effect of increased positive charge would be to decrease the rate and increase the activation energy, although for an \( S_N^2 \) mechanism there is not necessarily
any correlation. In all cases of chloro complexes investigated, singly positively charged complexes aquate much more rapidly than doubly positively charged cations. For example,

\[ \frac{k_{\text{cis}}[\text{Coen}_2\text{Cl}_2]^+}{k_{\text{cis}}[\text{Coen}_2(\text{NH}_3)\text{Cl}]^{2+}} = 550 \]

\[ \frac{k_{\text{trans}}[\text{Co( NH}_3)_4\text{Cl}_2]^+}{k[\text{Co( NH}_3)_5\text{Cl}]^{2+}} = 800 \]

and these ratios\(^{101}\) are in accord with that calculated on the basis of an electrostatic treatment of a dissociation mechanism\(^{89}\). Similarly,

\[ \frac{k[\text{dichloro complex}]^+}{k[\text{corresponding chloroaquo complex}]^{2+}} \cong 100 \] \(^{30}\) .

The greater reactivity of a dichloro complex (e.g. \([\text{Co( NH}_3)_4\text{Cl}_2]^+\)) compared to a monochloro complex (\([\text{Co( NH}_3)_5\text{Cl}]^{2+}\)) may also be attributed to \(\pi\)-bonding from the remaining chlorine to the metal in the tetramino complexes. This would tend to stabilise the transition state and favour a trigonal bipyramid, and the same consideration applies to the relative rates of dichloro and chloroaquo complexes, and the chlorohydroxo and chloroaquo complexes, since the OH group will \(\pi\)-bond more effectively than chlorine\(^{101}\). It is perhaps more significant if the activation energies as well as the rates can be correlated with these factors.

There is some evidence that in chloro complexes containing polyamines a correlation exists between rate and the number of N-H bonds, and it has been suggested that when the increased positive charge in the transition state can be dispersed to the peripheral atoms more effectively, \(E_a\) should be lowered and the rate increased. This is as observed (section \(H\) below)
and would be especially so for dissociation\(^{(15)}\). With an increasing number of N-H bonds the solvation should also be increased (lower \(\Delta S^f\)) and this should also help to disperse the charge and aid reaction.

(H) **Chelation**

Pearson, Boston and Basolo\(^{(15)}\) investigated this effect in the three series of complexes below, where the rates of aquation of the first chlorine atoms \(\times 10^{-4}\) \(\text{min}^{-1}\) are given for 25°C and pH 1.

\[
\begin{align*}
\text{cis}[\text{Co (NH}_3\text{)}_4 \text{Cl}_2]^+ & \quad \text{very fast} & \quad \text{trans}[\text{Co (NH}_3\text{)}_4 \text{Cl}_2]^+ & \quad 1100 \\
\text{cis}[\text{Coen(NH}_3\text{)}_2 \text{Cl}_2]^+ & \quad 140 & \quad \text{trans}[\text{Coen(NH}_3\text{)}_2 \text{Cl}_2]^+ & \quad 130 \\
\text{cis}[\text{Co en}_2 \text{Cl}_2]^+ & \quad 150 & \quad \text{trans}[\text{Co en}_2 \text{Cl}_2]^+ & \quad 19 \\
\text{g}[\text{Co trien Cl}_2]^+ & \quad 90
\end{align*}
\]

\[
\begin{align*}
\text{[Co (NH}_3\text{)}_5 \text{Cl }]^{2+} & \quad 4.0 & \text{ cis [Co en}_2(\text{NH}_3) \text{Cl}]^{2+} & \quad 0.85 \\
\text{ cis [Coen(NH}_3\text{)} \text{Cl}]^{2+} & \quad 0.40 \quad \text{(probably cis g)} & \text{[Co en dien Cl]}^{2+} & \quad 0.31 \\
\text{[Co tetraen Cl]}^{2+} & \quad 0.15 & * & \text{ isomer unknown}
\end{align*}
\]

In each series increasing chelation caused a decrease in rate. However in such series the inductive effects of the coordinated nitrogen, the number of N-H hydrogens (see above) and the molecular size (hence solvation energies) varied also, so that an unequivocal choice between mechanisms was difficult. The trend of basicities of the amines could not
be correlated with the observed rate order so that the other effects were important. It was claimed that the highly chelated ions were virtually shielded from $S_N^2$ trans-attack, and the observations were more consistent with an $S_N^1$ (section G above) than with an $S_N^2$ cis-attack mechanism.

(I) **The size of neutral ligands**

The aquation rates of $\text{trans}[\text{Co(AA)}_2\text{Cl}_2]^+$ complexes where $\text{AA} = \text{NH}_2-\text{CR}_2-\text{CR}_2-\text{NH}_2$ and $R = \text{H}$ and/or $\text{CH}_3$ increase with increasing methylation, and this was considered strong support for a dissociation mechanism. Rearrangement of the remaining five groups could then occur to relieve the steric crowding.$^{(124)}$ This type of approach has been criticised by Tobev$^{(113)}$ on the grounds that not only is the steric effect altered over the series, but the solvation shell may be considerably disturbed also, thereby considerably changing the rates as "water-repelling" hydrocarbon groups are added to the complex.

(J) **Isomerism of neutral ligands**

Rates for $\text{trans}[\text{Co(AA)}_2\text{Cl}_2]^+$, where $\text{AA} =$ the three isomeric butylenediamines, differ significantly$^{(124)}$ and reflect the relative non-bonded interactions of the methyl groups. This will be discussed further in chapter 7.

(K) **The electrical character of neutral ligands**

The evidence from the foregoing effects led Basolo and Pearson to suggest that aquation of most types of cobalt(III) complexes takes place by the $S_N^1$ mechanism, and probably through a square pyramid intermediate.
Their observations on rates of a series of substituted pyridine complexes [Co en₂(X-py)Cl]²⁺, where X was varied such that the relative inductive effects could be observed while maintaining steric factors approximately constant, were consistent with a dissociative mechanism. Increase in base strength of X-py increased the rate but the effect was found to be small (20-fold increase in base strength gave only 40% rate increase)\(^{(137)}\).

Ingold, Nyholm and Tobe\(^{(112)}\) have systematically studied the two series of complexes, cis and trans [Co en₂ A Cl]⁺, in which the polar effects of A were varied over almost the extreme range by changing this ligand. Electron-donating ligands A will increase the chance of an S\(_{\text{N1}}\) process, while electron-attracting substituents such as NO\(_2^-\) will favour an S\(_{\text{N2}}\) process. When the ligands A are arranged in order of decreasing electron supply to, or increasing electron withdrawal from the metal, the rate of aquation at first falls sharply, and then rises sharply along the series. The experimental results have been plotted in figure 48. For each series, the graph consists of two intersecting curves and is similar to that found for carbon substitutions, where the intersection represented a change from S\(_{\text{N1}}\) to S\(_{\text{N2}}\) mechanism. Thus the above diagrams also suggest a change of mechanism, the two presumed mechanisms having opposite polar requirements. Along the falling S\(_{\text{N1}}\) curve the expelled Cl⁻ ion carries out electrons, and no compensating import of electrons by the entering water occurs in the rate controlling step by this mechanism. The increasing rate along the S\(_{\text{N2}}\) curve is attributed to the increasing binding of water using a 4d cobalt orbital; the strongly electronegative
Figure 48. Effect of neutral ligands, A, on the rate of aquation of cis and trans [Coₐn₂ACL]⁺. (After Ingold).
water can contract and concentrate this orbital, a process which
liberates a large amount of energy, so the number of cobalt orbitals
increases from 6 towards 7 in the transition state.

In deducing the order in which to arrange the ligands A in the above
schematic diagram, Ingold has considered the various types of polar
properties that each should possess. These are three-fold:
inductive + I effects, electromeric conjugation +E, and the conjugative
-T effect. The order based only on + I effects was modified slightly
where it was considered, based on organic chemical experience, that the
other effects might predominate. It is the +I and -T effects which
should mainly contribute to the rates, whereas the +E effect is postulated
to facilitate only S_N1 aquations and will be the only effect determining
the steric course which was discussed previously. The order of polar
effects on rates was thus established to be

\[
\text{OH} > \text{N}_3 > \text{Cl} > \text{NCS} > \text{NH}_3 > \text{OH}_2 > \text{NO}_2
\]

(If the groups NH_3, OH_2 are written as NH_3 and OH_2, then relatively the
groups OH^-, N_3^-, etc. may be written as neutral entities). With more
complete quantitative data on rearrangement in the aquations of trans-
factors (table 9), the order of +E effect has been suggested to be
OH > NCS > Cl > N_3, but there appears to be no correlation between the
labilising effect of the orienting group and steric change^{119}. The more
fragmentary data available on other series (e.g. Br replacing Cl, and
(NH_3)_4 replacing en_2 ) also seem to conform to these predictions.
However it is not yet known whether these observations are in fact general, or whether they are peculiar to the cobalt(III) bis(en) series (113).

Adamson (117) suggests that $S_N^2$ aquation might be aided by hydrogen-bonding between ligands and water ($S_N^2$ FS mechanism) as in ciss[Co en$_2$(NO$_2$)Cl]$^+$ (figure 49).

![Figure 49. $S_N^2$ FS Mechanism](image)

This effect would be greatest with the NO$_2$ as orienting group, and this special type of mechanism can also be accommodated in Ingold's scheme.

There are some deficiencies in the above approach which only further experiment can clarify. The activation energies vary widely, so the order of orienting ligands in labilising power will depend on the temperature chosen for the comparison, and the order considered above refers to $25^\circ$. For an $S_N^1$ mechanism $E_a$ should decrease with greater $S_N^1$ character, but Tobe has pointed out that the lack of correlation between rates and $E_a$ can be ascribed to differences in solvation about the orienting ligand A (119). Moreover, the charges of the complexes differ.
within the series, so that the relative importance of bond-breaking and bond-making might also differ, as the charge effect would be large for an \( S_N^1 \), but not necessarily for an \( S_N \) mechanism (section G).

(I) Geometrical Isomerism

There is only one known instance in cobalt(III) complexes where a trans isomer aquates faster than the corresponding cis isomer. In \([\text{Co en}_2(\text{NO}_2)\text{Cl}]+\) this has been ascribed\(^{(112)}\) to the -T effect of the \( \text{NO}_2 \) group acting more strongly at trans positions, a so-called "trans effect", as observed in Pt(II) complexes\(^{(138)}\). The other polar effects +I and +E will combine to operate more strongly at positions cis to the polar group, facilitating \( S_N^1 \) aquations.

KINETIC METHODS

Since reactions of coordination compounds are often complicated by consecutive reactions and isomerisations, it has become customary to employ several methods in order to uniquely define the particular reaction being studied. Conductivity has been widely used to measure rates of aquation because of the high sensitivity possible, but since in a reaction it is the proportional change in total conductance which determines the sensitivity the method is difficult to use in solutions having \( \text{pH} < 2 \) or ionic strength \( \mu > 0.01 \). The method is inapplicable to consecutive reactions which do not differ greatly in rates. Spectrophotometry (generally limited to the visible region for complexes) has the advantage that a single reaction may be isolated by a judicious choice of wavelength,
and also measurements at different wavelengths may give the rates of aquation and simultaneous isomerisation. Aquation as well as racemisation may be measured polarimetrically, and again wavelengths may be chosen so that each of these reactions may be measured simultaneously, and isolated from isomerisation. Of the other methods which have been employed in aquation measurements, many involve Ag$^+$ or Hg$^{2+}$ ions (e.g. titration of Cl$^-$, E.M.F. measurements in a Cl$^-$ concentration cell, polarography). Since aquations of cobalt(III) halo complexes are usually catalysed by these ions, the methods found useful for the present work were limited to conductivity, spectrophotometry, and polarimetry. The less sensitive Hg(NO$_3$)$_2$ titration of Cl$^-$ was tried for some very slow reactions. Both this and conductance measure the rate of release of Cl$^-$ ion from a complex, so take no account of the steric course. It is likely that high-frequency conductance or capacitance methods will be used for aquation measurements in the future, since these eliminate all electrode effects.

**SCOPE OF KINETIC AND STEREOCHEMICAL STUDIES**

The special feature of the trien complexes which makes them potentially useful for a study of reaction mechanisms is that the centre ethylene bridge is in effect an additional point of reference in the molecule. Thus any single terminal ethylene bridge movement, denoted by arrows in figure 50, which occurs during a reaction will result in isomerisation between the geometrical isomers, either D cis $\alpha$↔L cis $\beta$.
Figure 50. Relationships between [Co$_{tri}$en$_{XY}$]$^{n+}$ and [Co$_{en_2}$en$_{XY}$]$^{n+}$ isomers.
or L cis $\beta \leftrightarrow$ trans. The corresponding bridge movements, or edge-displacements, in a bis(en) compound will give only D $\leftrightarrow$ L or D $\leftrightarrow$ trans, and the stereochemical relationships between the trien and bis(en) compounds are shown by the vertical comparisons in figure 50. All the possibilities of single bridge movements are outlined in the figure, but movements which would involve the two bridges at a secondary nitrogen atom are considered improbable (chapter 7). Moreover, edge-displacement of a substituent X by Y could be made apparent by the observable isomeric change from D cis $\beta'$ $\leftrightarrow$ D cis $\beta''$ (due to the non-equivalence of the substituent positions) but would not be detectable in the cis[Co en$_2$ XY]$^{n+}$ or cis $\alpha$ trien compounds. The trien compounds thus offer possibilities of stereo change exceeding those in bis(en) compounds.

Figure 51 summarises the stereo course of the aquation of each of the three dichloro trien isomers. The system was studied in the following stages:

1. Aquation of the $\alpha$, $\beta$ and trans dichloro isomers and
2. Aquation of the $\alpha$ and $\beta$ chloroaquo isomers, chapter 5.
3. Racemisation and isomerisation of the $\alpha$ and $\beta$ diaquo isomers, chapter 6.

In the final chapter the results of (3) are correlated with those from (2), and the mechanisms of these reactions are discussed.
\[
\begin{align*}
D \alpha[\text{CotrienCl}_2]^+ & \quad \rightarrow \quad D \alpha[\text{CotrienCl(H}_2\text{O})]^2+ & \quad \leftrightarrow & \quad D \alpha[\text{Cotrien(H}_2\text{O})_2]^3+ & \quad \leftrightarrow & \quad L \beta[\text{Cotrien(H}_2\text{O})_2]^3+ \\
(\hat{\text{r}}) \alpha[\text{CotrienCl(H}_2\text{O})]^2+ & \quad \leftrightarrow & \quad (\hat{\text{r}}) \alpha[\text{Cotrien(H}_2\text{O})_2]^3+ & \quad \leftrightarrow & \quad (\hat{\text{r}}) \beta[\text{Cotrien(H}_2\text{O})_2]^3+
\end{align*}
\]

\[
\begin{align*}
L \beta[\text{CotrienCl}_2]^+ & \quad \leftrightarrow & \quad L \beta[\text{CotrienCl(H}_2\text{O})]^2+ & \quad \sim 97\% & \quad \leftrightarrow & \quad L \beta[\text{Cotrien(H}_2\text{O})_2]^3+ & \quad \leftrightarrow & \quad D \alpha[\text{Cotrien(H}_2\text{O})_2]^3+ \\
L \beta^1[\text{CotrienCl(H}_2\text{O})]^2+ & \quad \sim 3\% & \quad \leftrightarrow & \quad L \beta[\text{Cotrien(H}_2\text{O})_2]^3+ & \quad \leftrightarrow & \quad D \alpha[\text{Cotrien(H}_2\text{O})_2]^3+ \\
\text{trans}[\text{CotrienCl}_2]^+ & \quad \rightarrow & \quad (\hat{\text{r}}) \beta[\text{CotrienCl(H}_2\text{O})]^2+ & \quad \leftrightarrow & \quad (\hat{\text{r}}) \beta[\text{Cotrien(H}_2\text{O})_2]^3+ & \quad \leftrightarrow & \quad (\hat{\text{r}}) \alpha[\text{Cotrien(H}_2\text{O})_2]^3+
\end{align*}
\]
CHAPTER 5

KINETICS OF AQUATION OF THE DICHLOORO AND CHLOROAUQUO
TRIETHYLENETETRAMINE COBALT(III) ISOMERS

THE DICHLOORO ISOMERS

Introduction

The active $\alpha$ and $\beta$ dichloro isomers have been shown to undergo aquation to the chloroaquo compounds with full retention of configuration and activity (chapter 3). In acid solution, $\text{trans}[\text{Co trien Cl}_2]^+$ changed from green to red in a few minutes ($20^\circ$), and since $\text{trans}[\text{Co en}_2\text{Cl(H}_2\text{O)}]^2+$ is green, this indicated that isomerisation accompanied aquation. Furthermore, on aquation the spectrum became identical with that of $\beta[\text{Co trien Cl(H}_2\text{O)}]^2+$, and confirmation that $\text{trans}[\text{Co trien Cl}_2]^+$ aquated to cis $\beta[\text{Co trien Cl(H}_2\text{O)}]^2+$ was obtained from the rates of aquation of the second chlorine atom.

The rates were measured conductimetrically, spectrophotometrically and polarimetrically. The conductance method gave the rate of loss of Cl$^-$ ion, and polarimetry measured the rates of mutarotation of the cis isomers. In the case of the $\text{trans}$ isomer, the spectrophotometric method gave the rate of isomerisation $\text{trans} \rightarrow \text{cis} \beta$ which accompanied aquation.

The rates were measured under various conditions of $[\text{H}^+]$, ionic strength $\mu$ (adjusted with NaClO$_4$), initial dichloro complex concentration
Results and Discussion

Rates of aquation of the α, β and trans dichloro isomers are given in tables 11 to 13.

The rate data are plotted as log k vs. \( \frac{1}{T} \) for the three isomers in figures 52 to 54. Activation energies \( E_a \) were obtained by first calculating the mean slopes of these plots by regressing log k (from all runs) as a linear function of \( \frac{1}{T} \). Then \( E_a = -2.303 R \times \text{mean slope} \), which follows from the equation:

\[
\log \frac{k_1}{k_2} = -\frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

The error was calculated as the standard deviation of the mean ( = standard error, S.E.). Standard errors in mean rates were calculated using

\[
\text{S.E.} = \left( \frac{\sum d^2}{n(n-1)} \right)^{1/2}
\]

From \( E_a \), and the mean of the measured rate constants at 25°, entropies of activation \( \Delta S^f \) were calculated using the transition state theory equation:

\[
k_T = \left( \frac{kT}{h} \right) e^{\frac{\Delta S^f}{R}} e^{\frac{-(E_a - RT)}{R}}
\]

where \( k_T \) is in sec\(^{-1}\), and \( E_a \) is in calories mole\(^{-1}\). The aquation of \( \text{trans}[\text{Co trien Cl}_2]^+ \) showed a small dependence on \([H^+]\) or \( \mu \), so \( E_a \) was calculated from data at \([H^+] = 0.01 \text{ M}\) only. The rate data at 25° are given in table 14 for the three isomers, and the data for \([\text{Co en}_2 \text{Cl}_2]^+\)
TABLE 11: RATES OF AQUATION OF (+) cis a [Co (trien) Cl₂]⁺

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[H⁺] M</th>
<th>[Co] M</th>
<th>k x 10⁵ min⁻¹</th>
<th>method*</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.0001</td>
<td>25</td>
<td>9.1</td>
<td>C (G)</td>
</tr>
<tr>
<td>2</td>
<td>0.0002</td>
<td>25</td>
<td>8.7</td>
<td>C (G or E)</td>
</tr>
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<td>3</td>
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<td>25</td>
<td>9.6</td>
<td>C (E)</td>
</tr>
<tr>
<td>4</td>
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<td>25</td>
<td>2.6</td>
<td>S (G or E)</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>15</td>
<td>8.6</td>
<td>C (E)</td>
</tr>
<tr>
<td>6</td>
<td>0.02</td>
<td>15</td>
<td>9.4</td>
<td>S (G)</td>
</tr>
<tr>
<td>7</td>
<td>0.01</td>
<td>15</td>
<td>10.2</td>
<td>P</td>
</tr>
<tr>
<td>8</td>
<td>0.01</td>
<td>10</td>
<td>9.4</td>
<td>2.2</td>
</tr>
<tr>
<td>9</td>
<td>0.01</td>
<td>29</td>
<td>10.3</td>
<td>5.2</td>
</tr>
<tr>
<td>10</td>
<td>0.01</td>
<td>54</td>
<td>9.5</td>
<td>5.8</td>
</tr>
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<td>11</td>
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<td>589</td>
<td>9.1</td>
<td>5.9</td>
</tr>
<tr>
<td>12</td>
<td>0.01</td>
<td>589</td>
<td>9.1</td>
<td>5.9</td>
</tr>
<tr>
<td>13</td>
<td>0.01</td>
<td>589</td>
<td>9.1</td>
<td>5.9</td>
</tr>
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<td>14</td>
<td>0.01</td>
<td>589</td>
<td>9.1</td>
<td>5.9</td>
</tr>
<tr>
<td>15</td>
<td>0.01</td>
<td>589</td>
<td>9.1</td>
<td>5.9</td>
</tr>
</tbody>
</table>

* C = conductivity; S = spectrophotometry; P = polarimetry.

(6) = Guggenheim method used to plot the rate data.

(E) = Experimental infinity reading used.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>[H+]</th>
<th>t °C</th>
<th>[Co]</th>
<th>([\text{NaClO}_4])</th>
<th>(\mu)</th>
<th>(k \times 10^2)</th>
<th>method</th>
<th>(\lambda_{\text{mu}})</th>
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<td>17</td>
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<td>&quot;</td>
<td>0.0003</td>
<td>0.0004</td>
<td>12.1</td>
<td>S (G)</td>
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<td>&quot;</td>
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<td>0.001</td>
<td>8.9</td>
<td>S (G or E)</td>
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<td></td>
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<td>&quot;</td>
<td>0.002</td>
<td>0.084</td>
<td>0.09</td>
<td>10.1</td>
<td>S (E)</td>
<td>430</td>
</tr>
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<td>5</td>
<td>0.001</td>
<td>0.01</td>
<td>0.60</td>
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<td>0.01</td>
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<td>C (G)</td>
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<td>&quot;</td>
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<td>C (G) (bright Pt electrodes)</td>
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<td>&quot;</td>
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<td>S (G or E)</td>
<td>320</td>
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<td>28</td>
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<td>P (E)</td>
<td>580</td>
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<td>$[Co]$</td>
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<td>method</td>
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<td>S (E)</td>
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<td>0.97 (mean)</td>
<td>S (E)</td>
<td>calculated at 342,435,510; trans[CotrienCl$_2$]Cl$_2$HCl$_2$O used.</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>0.0003</td>
<td>0.01</td>
<td>20.5</td>
<td>S (E)</td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.001</td>
<td>0.01</td>
<td>21</td>
<td>C (G)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>0.10</td>
<td>25</td>
<td>0.001</td>
<td>0.10</td>
<td>19.1 (mean)</td>
<td>S (E)</td>
<td>calculated at 342,435,510,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>1.0</td>
<td>25</td>
<td>0.001</td>
<td>1.0</td>
<td>15.3 (mean)</td>
<td>S (E)</td>
<td>calculated at 342,435,510,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>Isomer</td>
<td>$k_{25^\circ}$</td>
<td>$E_a$</td>
<td>$\Delta S^#$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>---------------------------------</td>
<td>------------------------</td>
<td>----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis $\alpha$</td>
<td>$(9.3 \pm 0.3) \times 10^{-3}$ min$^{-1}$</td>
<td>$21.5 \pm 0.4$ kcal./mole</td>
<td>$- 5.8 \pm 1.4$ e.u.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basolo (15)</td>
<td>$9.0 \times 10^{-3}$ min$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis $\beta$</td>
<td>$(8.7 \pm 0.1) \times 10^{-2}$ min$^{-1}$ (total rate)</td>
<td>$21.1 \pm 0.4$</td>
<td>$- 2.7 \pm 1.4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sim 0.3 \times 10^{-2}$ min$^{-1}$ (to &quot;fast&quot; $\beta$ chloroaquo isomer only)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans</td>
<td>$(20.9 \pm 0.2) \times 10^{-2}$ min$^{-1}$</td>
<td>$26.0 \pm 0.2$</td>
<td>$+ 15.5 \pm 0.7$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| cis[Coen$_2$Cl$_2$]$^+$ | $1.48 \times 10^{-2}$ min$^{-1}$ (119,139) | $22.2$ (49b) | $- 2$ |
| trans[Coen$_2$Cl$_2$]$^+$ | $1.92 \times 10^{-3}$ min$^{-1}$ (119,139) | $24.2$ (49b) | $0$ |
FIGURE 52. RATE OF AQUATION OF (+)=[Co trenCl₂]ClO₄,
TEMPERATURE DEPENDENCE.

$log k$

$E_a = 21.5$ kcal.mole$^{-1}$
FIGURE 53. RATE OF AQUATION OF (-){\text{P}}\text{[CotrienCl}_{2}]\text{ClO}_{4},
TEMPERATURE DEPENDENCE.

\[ E_a = 21.1 \text{ kcal.mole}^{-1} \]
Figure 54. Rate of Aquation of Trans \([\text{CotrienCl}_2\text{ClO}_4]\), Temperature Dependence (\([H^+] = 0.01\text{M}\)).

\[ E_a = 26.0 \text{ kcal.mole}^{-1} \]
are included for comparison.

For aquations of $\alpha$ and $\beta$ [Co trien $\text{Cl}_2]^+$, $k$ was independent of $[\text{H}^+]$, $\mu$ and [Co], at $[\text{H}^+] > 0.0001 \text{ M}$. Conductivity rates were the least reliable at pH 4, because here the rates of the subsequent aquations (of the chloroaquo compounds) were of the same orders of magnitude as the dichloro aquation rates. Otherwise, the rates obtained by the three methods (C, S and P) agreed within the errors of the methods.

Cis $\beta$[Co trien $\text{Cl}_2]^+$ aquated to produce the two cis $\beta$ chloroaquo isomers by concurrent reactions, but although these gave a linear first-order plot the rate constant observed was actually composite. Data from the aquation of the second $\text{Cl}^-$ ion enabled the proportions in which the two $\beta$ chloroaquo isomers were formed, to be estimated as about 97% and 3% ($p^*_{135}$). The rate of formation of the minor isomer was therefore taken as 3% of the observed total rate. The rate of formation of the major isomer would be only slightly lower than the observed total rate, but this difference would be within the experimental error in the measured rate constant.

Basolo measured the rate of aquation of one of the cis-dichloro isomers, and the excellent agreement with the rate of aquation of the $\alpha$ isomer (table 14) thus identifies his product.

For the trans isomer, the conductimetric and spectrophotometric methods gave the same rates. These rates showed a small variation ($\sim 40\%$) with $[\text{H}^+]$ and/or $\mu$ in the range $1 < \text{pH} < 4$; $k$ decreased as $[\text{H}^+]$ increased. The identical rates by the two methods showed that trans[Co trien $\text{Cl}_2]^+$ isomerised to the cis $\beta$ configuration at the same
rate as $\text{Cl}^{-}$ ion was expelled. No measurable amounts of $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^{2+}$ were formed during the aquation as evidenced by:

(i) the identical spectrophotometric rates at four wavelengths

(ii) the strictly linear plots obtained (up to two half-lives)

(iii) the constancy of the isobestic points (when a series of complete visible spectra were recorded).

That no $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^{2+}$ was observed did not preclude its formation as an intermediate however, so that the rate data is consistent with either of two possible mechanisms. In the first, isomerisation is synchronous with aquation and the first-formed product is $\text{cis}[\text{Co trien Cl(H}_2\text{O)}]^{2+}$ (the "slow" isomer). Alternatively, $\text{trans}[\text{Co trien Cl}_2]^+$ aquates with retention of configuration to $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^{2+}$ which subsequently isomerises rapidly to the $\beta$ isomer. It will be recalled (chapter 4) that the aquation of $\text{trans}[\text{Co en}_2 \text{Cl}_2]^+$ is not stereospecific and the aquation product is largely $\text{trans}[\text{Co en}_2 \text{Cl(H}_2\text{O)}]^{2+}$ (65%). This then isomerises largely to the cis isomer (73% cis at equilibrium). On this basis, both of the above mechanisms for the aquation of $\text{trans}[\text{Co trien Cl}_2]^+$ are plausible.

The mechanism involving formation and subsequent isomerisation of $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^{2+}$ was eliminated after studying the aquation of $\text{trans}[\text{Co trien Cl}_2]\text{ClO}_4$ in 0.1 M $\text{HClO}_4$ in the presence of $\text{Hg}^{2+}$ ion. After rapid mixing of the $\text{trans}[\text{Co trien Cl}_2]^+$ and $\text{Hg}^{2+}$ solutions, a continuous record of optical density indicated that a very fast initial reaction was followed by a slower reaction. Repetition of the reaction with the
complete spectrum being recorded at successive times showed that the spectrum at the end of the initial fast reaction was different to those of $\text{trans}[\text{Co trien Cl}_2]^+$ and $\beta[\text{Co trien Cl(H}_2\text{O)}]^2+$, but subsequently became identical with the spectrum of $\beta[\text{Co trien Cl(H}_2\text{O)}]^2+$ (figure 55). The spectrum of the intermediate product was consistent with its being largely $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^2+$, formed by the rapid removal of one Cl$^-$ from the dichloro complex by Hg$^{2+}$ ion, and the two reactions involved were then:

$$\text{trans}[\text{Co trien Cl}_2]^+ \xrightarrow{k_{aq}} \text{trans}[\text{Co trien Cl(H}_2\text{O)}]^2+ \xrightarrow{k_1} \beta[\text{Co trien Cl(H}_2\text{O)}]^2+$$

The rate constants at 15° are given in table 15. The direct aquation of $\text{trans}[\text{Co en}_2 \text{Cl}_2]^+$ to $\text{trans}[\text{Co en}_2 \text{Cl(H}_2\text{O)}]^2+$ is known to be dependent on [Hg$^{2+}$], and $k_{aq}$ should therefore be [Hg$^{2+}$] dependent. However it is evident from table 15 that the isomerisation $k_1$ was not dependent on [Hg$^{2+}$], and this was also found for $\text{trans}[\text{Co en}_2 \text{Cl(H}_2\text{O)}]^2+$ (table 16). The rate of isomerisation of $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^2+$ ($k_1 = 1.0 \times 10^{-1} \text{ min}^{-1}$) is seen to be only 2.2 times greater than the observed rate of aquation of $\text{trans}[\text{Co trien Cl}_2]^+$ in the absence of Hg$^{2+}$ ($k = 4.5 \times 10^{-2} \text{ min}^{-1}$, taken from figure 54). If the aquation in the absence of Hg$^{2+}$ ion did occur by this path, the above values for the rates $k_{aq}$ and $k_1$ would require a maximum concentration of the $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^2+$ intermediate of about 20% which would have been detected.

The isomerisation of $\text{trans}[\text{Co trien Cl(H}_2\text{O)}]^2+$ and the aquation of $\text{trans}[\text{Co trien Cl}_2]^+$ in the absence of Hg$^{2+}$ are thus established as independent processes, and the latter aquation reaction proceeds with 100%
1. TRANS \([\text{Co}^{II} \text{en} \text{Cl}_2]^+ \) \(4 \times 10^{-3}\text{M}\) IN \(\text{HClO}_4\) (1 CM CELL).
2. TRANS \([\text{Co}^{II} \text{en} \text{Cl}_2]^+ + \text{Hg}^2+\) : AFTER 2 MINUTES AT \(-5^\circ\) = TRANS \([\text{Co}^{II} \text{en} \text{Cl} \text{(H}_2\text{O})]^2+\)
3. \(10 = -10^\circ\)
4. \(15 = \) AND \(\beta [\text{Co}^{II} \text{en} \text{Cl} \text{(H}_2\text{O})]^2+\)
5. \(40 = \) AND \(\beta [\text{Co}^{II} \text{en} \text{Cl} \text{(H}_2\text{O})]^2+\)

**Figure 55.** Spectral changes in aquation of \(\text{TRANS} [\text{Co}^{II} \text{en} \text{Cl}_2]\text{ClO}_4\) in the presence of \(\text{Hg}^2+_+\).
### TABLE 15. RATES OF AQUATION OF trans[Co trien Cl₂]⁺ AND ISOMERISATION OF trans[Co trien Cl(H₂O)]²⁺ IN THE PRESENCE OF Hg²⁺

Spectrophotometric rates; \([H^+] = 0.1 \text{ M HClO}_4\), temperature = 15°C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>trans[Co trien Cl₂]ClO₄</th>
<th>[Hg(ClO₄)₂]</th>
<th>(k_{aq})</th>
<th>(k_i)</th>
<th>(\lambda_{mu})</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>0.0005 M</td>
<td>0.005 M</td>
<td>7.2 min⁻¹</td>
<td>(1.2 \times 10^{-1}) min⁻¹</td>
<td>(320)</td>
</tr>
<tr>
<td></td>
<td>(20-fold excess for one Cl)</td>
<td></td>
<td></td>
<td>(0.9 \times 10^{-1}) min⁻¹</td>
<td>(340) or (433)</td>
</tr>
<tr>
<td>46</td>
<td>0.0005</td>
<td>0.00025</td>
<td>1.0 \times 10⁻¹</td>
<td></td>
<td>(320)</td>
</tr>
<tr>
<td></td>
<td>(equivalent for one Cl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 16. ISOMERISATION OF trans[Co en₂ Cl(H₂O)]²⁺

in HClO₄, temperature = 15°C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>trans[Co en₂ Cl(H₂O)]SO₄</th>
<th>[Hg(ClO₄)₂]</th>
<th>(k_i) (to equilibrium)</th>
<th>(\lambda_{mu})</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>0.001 M</td>
<td>0.005 M</td>
<td>(1.15 \times 10^{-3}) min⁻¹ ((H^+ = 0.1 \text{ M}))</td>
<td>(510)</td>
</tr>
<tr>
<td></td>
<td>(10-fold excess for one Cl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47α</td>
<td>0</td>
<td>0</td>
<td>(1.12 \times 10^{-3}) min⁻¹ ((H^+ = 0.1))</td>
<td>(510)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>(1.0 \times 10^{-3}) min⁻¹ ((H^+ = 0.012))</td>
<td>reference 45</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>(1.3 \times 10^{-3}) min⁻¹ ((H^+ = 0.012))</td>
<td>reference 119</td>
</tr>
</tbody>
</table>
isomerisation to the β configuration. It is also evident that the rapidity of the isomerisation of \( \text{trans}[\text{Co trien Cl(H}_2\text{O)}]^2^+ \) may prevent its isolation.

The two cis dichloro isomers aquate at widely differing rates, but the kinetic behaviour and full retention of configuration parallel the observations on aquation of cis[Co en\(_2\) Cl\(_2\)]^+.

**THE CHLOROAQUO ISOMERS**

**Introduction**

Because of its lower symmetry, the cis β configuration allows of two chloroaquo isomers, whereas there is only one cis α[Co trien Cl(H\(_2\)O)]\(^{2+}\) isomer. These β isomers would be expected to have different rate constants for aquation to diaquo compounds. Since the chloroaquo salts could not be isolated, these aquations had to be studied starting with the optically active α and β dichloro isomers.

β[Co trien Cl\(_2\)]^+ was found to aquate to a mixture of the two β[Co trien Cl(H\(_2\)O)]\(^{2+}\) isomers with one (the minor isomer) present to the extent of only about 3%. Since this is the more labile of the β chloroaquo isomers with respect to aquation, this will be referred to as the "fast" isomer. It was only by using sensitive conductance measurements, and only in 0.01 M HCIO\(_4\), that the proportion and rate of aquation of this isomer could be assessed. Polaritymetry and titration of Cl\(^-\) ion were not sufficiently sensitive for its detection, but spectrophotometry also gave evidence for this isomer.
α and β [Co trien Cl(H₂O)]²⁺ aquate with full retention of configuration, but measurements of the rates of aquation and retentions of activity were complicated by isomerisation of each of the diaquo products to an equilibrium mixture, and also by the reverse anation reactions. The thermodynamic chloroaquo-diaquo equilibria are never fully established due to the subsequent isomerisations. Nevertheless, the kinetics and stereochemistry have been elucidated, aided by separate studies of the racemisation and isomerisation of the pure diaquo compounds (chapter 6).

Both diaquo isomers should have similar conductivities, so that the conductivity method should measure the rate of approach to chloroaquo-diaquo equilibrium and be independent of subsequent isomerisation. In all runs the conductivity did reach a steady value and readings were plotted as log \( \frac{1}{R_{\text{equil}} - \frac{1}{R_t}} \) vs. t. Except with β[Co trien Cl₂]⁺ at 0.01 M HClO₄, the resulting graphs (figures 85b, 92b, appendix E) showed an initial steep curve, representing the aquation of the first Cl⁻ ion, followed by a linear plot which thus corresponded to the aquations of α[Co trien Cl(H₂O)]²⁺ or β[Co trien Cl(H₂O)]²⁺ ("slow" or "major" isomer). Plots from β[Co trien Cl₂]⁺ at 0.01 M HClO₄ showed an inflexion between these two regions. The inflexion was evident after the time for completion of the dichloro aquation (figure 63 in experimental section), thus corresponding to the aquation of the "fast" β[Co trien Cl(H₂O)]²⁺ isomer. The proportion and rate of aquation of this isomer could thus be evaluated, and the method of calculation (experimental section) was justified by an analytical treatment (appendix B) of conductance changes.
expected for the system:

\[
\begin{align*}
\beta^1[\text{CotrienCl(H}_2\text{O)}]^{2+} & \xrightarrow{k_1\text{ fast}} \beta^1[\text{CotrienCl}_2]^+ \\
& \xrightarrow{k_2\text{ slow}} \beta^1[\text{CotrienCl(H}_2\text{O)}]^{2+}
\end{align*}
\]

"slow" or major isomer

\[
\begin{align*}
\beta^1[\text{CotrienCl(H}_2\text{O)}]^{2+} & \rightarrow \beta^1[\text{Cotrien(H}_2\text{O)}]^{3+} \\
& \xrightarrow{(\text{s(k)n})} \beta^1[\text{CotrienCl(H}_2\text{O)}]^{2+}
\end{align*}
\]

"fast" or minor isomer

Aquation of the α chloroaquo isomer was measured spectrophotometrically at 540 m\(\mu\) where the α and β diaquo isomers have similar absorptions, so that the rates obtained are for the approach to the α chloroaquo-α diaquo equilibrium. The optical densities became almost constant after 5 half-lives, but decreased further at considerably longer times due to contributions from β chloroaquo and β diaquo compounds.

Aquation of β[Co trien Cl(H\(_2\)O)]\(^{2+}\) was followed spectrophotometrically at 560 m\(\mu\), and again this method measured the approach to β chloroaquo-β diaquo equilibrium. Here the subsequent isomerisation was less important since the α ←→ β diaquo equilibrium position lies largely towards the β isomer (\(β\) diaquo/α diaquo ~ \(80/20\), chapter 6), and the rate of isomerisation \(β \rightarrow \text{equilibrium}\) (table 27) is very much less than the aquation rate.

The rates of mutarotation of the cis chloroaquo isomers to the respective diaquo isomers were also measured polarimetrically. Wavelengths were chosen for each isomer where the diaquo product had essentially zero rotation, and the data were usually plotted as log α vs. t. However the
aquations do not proceed to completion (approximately 15% chloroaquo, 85% diaquo are present at equilibrium) and if loss of activity of the diaquo compounds did not occur the rotations would not fall to zero. It is proposed that the mutarotation to zero rotation (at the wavelength chosen) measures the forward rate only, since the anation should occur largely with loss of activity. The racemisation of the $\alpha$ and $\beta$ diaquo compounds is thought to occur with each act of water exchange by analogy with the $\text{cis[Co en}_2(H_2O)_2]^{3+}$ ion (chapter 6), and in the anation Cl$^-\text{would compete with water in the exchange process. The } \alpha \text{ system is represented as follows:}

$$
\text{D } \text{aq[CotrienCl(H}_2\text{O})_2]^{2+} + H_2\text{O} \xrightleftharpoons[k_1]{k_{-1}} \text{D } \text{aq[Cotrien(H}_2\text{O})_2]^{3+} + Cl^- \text{ (Zero rotation at } \lambda \text{ used)}
$$

The rate of racemisation (isomerisation) $k_2$ of the $\alpha$ diaquo compound (table 27) is comparable with the anation rate $k_{-1}$, so that the amount of active $\alpha$ diaquo is decreasing and retention of activity in the anation reaction would be diminished further by this process. Similar considerations apply to the polarimetric measurements on the $\beta$ system, where again the racemisation rate (table 28) is comparable with the rate of anation. Irrespective of these arguments, an "initial rate" plot of $\log \alpha$ vs. $t$ should give the forward rate ($k_1$) and in fact all the rate plots were linear up to 2 half-lives (figure 93, appendix E).
In each run, aliquots of the reacting solution were transformed to carbonato compounds (with excess NaHCO₃) at the beginning of the chloroaquo aquation (chloroaquo concentrations approximately maximum) and at the end of the reaction (usually about 5 half-lives). Measurements of the rotations and spectra then allowed the loss of optical activity and isomerisation ($\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$) which took place during the aquation reaction to be estimated, and it will be shown later (chapter 7) that these changes were due to subsequent racemisation and isomerisation in the diaquo product.

A few runs were also measured by titration of the total ionic Cl⁻ with Hg(NO₃)₂. This method gives the rate of approach to the chloroaquo-diaquo equilibrium and is independent of the subsequent isomerisation and racemisation of the diaquo product.

Conditions of [H⁺], $\mu$, [Co] and temperature were varied, and the aquation rates of the chloroaquo isomers were sensitive to these changes.

Results and Discussion

Rates of aquation of the $\alpha$ and $\beta$ ("slow" isomer) chloroaquo compounds are listed in tables 17 and 18. The rates for the chloroaquo product resulting from trans[Co trien Cl₂]⁺ are given in table 19. These latter rates were identical with the rates of $\beta$[Co trien Cl(H₂O)]²⁺, ("slow" isomer) thus identifying the stereochemical course of the trans[Co trien Cl₂]⁺ aquation (compare runs 80 and 24, runs 82 and 31). The absence of any suggestion of a third rate in the trans conductivity plots (figure 92, appendix E) showed that little or no $\alpha$[Co trien Cl(H₂O)]²⁺ was formed.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>[H(^+)]</th>
<th>t°C</th>
<th>[Co]</th>
<th>[NaClO(_4)]</th>
<th>μ</th>
<th>(k \times 10^4)</th>
<th>min(^{-1})</th>
<th>method*</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>1.02 M</td>
<td>40</td>
<td>0.001 M</td>
<td>0</td>
<td>1.0</td>
<td>2.51</td>
<td></td>
<td>P at 578 m(\mu) (forward rate only)</td>
</tr>
<tr>
<td>49</td>
<td>0.102</td>
<td>40</td>
<td>0.001</td>
<td>0</td>
<td>0.1</td>
<td>2.30</td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>50</td>
<td>0.0102</td>
<td>35</td>
<td>0.001</td>
<td>0.088</td>
<td>0.1</td>
<td>1.34</td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>51</td>
<td>&quot;</td>
<td>40</td>
<td>0.001</td>
<td>0.088</td>
<td>0.1</td>
<td>2.59</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>52</td>
<td>&quot;</td>
<td>45</td>
<td>0.001</td>
<td>0.087</td>
<td>0.1</td>
<td>2.79</td>
<td></td>
<td>S at 540 m(\mu) (forward and reverse rates)</td>
</tr>
<tr>
<td>53</td>
<td>0.0051</td>
<td>40</td>
<td>0.001</td>
<td>0.092</td>
<td>0.1</td>
<td>3.00</td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>54</td>
<td>0.00204</td>
<td>40</td>
<td>0.001</td>
<td>0.092</td>
<td>0.1</td>
<td>3.88</td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>55</td>
<td>0.00102</td>
<td>35</td>
<td>0.001</td>
<td>0.097</td>
<td>0.1</td>
<td>5.46</td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>56</td>
<td>&quot;</td>
<td>40</td>
<td>0.001</td>
<td>0.097</td>
<td>0.1</td>
<td>5.91</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>57</td>
<td>&quot;</td>
<td>45</td>
<td>0.001</td>
<td>0.096</td>
<td>0.1</td>
<td>12.6</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>58</td>
<td>0.00102</td>
<td>40</td>
<td>0.005</td>
<td>0</td>
<td>0.016</td>
<td>8.2</td>
<td></td>
<td>T (E) (forward and reverse rates)</td>
</tr>
<tr>
<td>59</td>
<td>0.0102</td>
<td>35</td>
<td>0.001</td>
<td>0</td>
<td>0.013</td>
<td>2.1</td>
<td></td>
<td>C (G or E) &quot;</td>
</tr>
<tr>
<td>60</td>
<td>&quot;</td>
<td>40</td>
<td>0.002</td>
<td>0</td>
<td>0.016</td>
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<td></td>
<td>C (G) &quot;</td>
</tr>
<tr>
<td>61</td>
<td>0.102</td>
<td>40</td>
<td>0.005</td>
<td>0</td>
<td>0.12</td>
<td>2.8</td>
<td></td>
<td>T (E) &quot;</td>
</tr>
</tbody>
</table>

* C = conductance; S = spectrophotometric; P = polarimetric;
(G) = Guggenheim method of plotting (E) = experimental infinity reading used in plotting rate data.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>[H⁺]</th>
<th>t°C</th>
<th>[Co]</th>
<th>[NaClO₄]</th>
<th>μ</th>
<th>$k \times 10^3$</th>
<th>method</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>1.02 M</td>
<td>40</td>
<td>0.002 M</td>
<td>-</td>
<td>1.0</td>
<td>0.802</td>
<td>S at 560 mp</td>
</tr>
<tr>
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<td>40</td>
<td>&quot;</td>
<td>-</td>
<td>0.11</td>
<td>1.88</td>
<td>(forward and reverse rates)</td>
</tr>
<tr>
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<td>0.051</td>
<td>40</td>
<td>&quot;</td>
<td>0.038 M</td>
<td>0.10</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.0102</td>
<td>25</td>
<td>&quot;</td>
<td>0.073</td>
<td>0.09</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>&quot;</td>
<td>40</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.02</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>&quot;</td>
<td>35</td>
<td>&quot;</td>
<td>0.073</td>
<td>0.09</td>
<td>5.18</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>&quot;</td>
<td>40</td>
<td>&quot;</td>
<td>0.167</td>
<td>0.183</td>
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</tr>
<tr>
<td>69</td>
<td>&quot;</td>
<td>40</td>
<td>&quot;</td>
<td>0.073</td>
<td>0.089</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.073</td>
<td>0.089</td>
<td>11.0</td>
<td></td>
</tr>
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<td>&quot;</td>
<td>&quot;</td>
<td>0.017</td>
<td>0.033</td>
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<td>72</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.016</td>
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<tr>
<td>73</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.034</td>
<td>0.067</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>&quot;</td>
<td>50</td>
<td>0.002</td>
<td>&quot;</td>
<td>0.073</td>
<td>0.09</td>
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</tr>
<tr>
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<td>0.09</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>0.00204</td>
<td>40</td>
<td>&quot;</td>
<td>0.083</td>
<td>0.09</td>
<td>46.0</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>0.00102</td>
<td>25</td>
<td>&quot;</td>
<td>0.084</td>
<td>0.09</td>
<td>7.14</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>&quot;</td>
<td>40</td>
<td>&quot;</td>
<td>0.084</td>
<td>0.09</td>
<td>81.5</td>
<td></td>
</tr>
</tbody>
</table>

Contd...
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<th>No.</th>
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<th>O₂</th>
<th>O₂</th>
<th>C</th>
<th>O₂</th>
<th>C</th>
<th>O₂</th>
<th>O₂</th>
<th>C</th>
<th>O₂</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.0102</td>
<td>15</td>
<td>0.002</td>
<td>-</td>
<td>0.016</td>
<td>0.183</td>
<td>C (G) (forward and reverse rates)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>&quot;</td>
<td>25</td>
<td>0.002</td>
<td>-</td>
<td>0.016</td>
<td>1.44</td>
<td>C (E) &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.002</td>
<td>-</td>
<td>0.016</td>
<td>1.37</td>
<td>C (E) (bright Pt. electrodes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.001</td>
<td>-</td>
<td>0.013</td>
<td>1.29</td>
<td>P at 480 μ (forward rate only)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.009</td>
<td>-</td>
<td>0.04</td>
<td>1.3</td>
<td>T (E) (forward and reverse rates)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>&quot;</td>
<td>35</td>
<td>0.001</td>
<td>-</td>
<td>0.013</td>
<td>7.8</td>
<td>C (E) &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.002</td>
<td>-</td>
<td>0.016</td>
<td>7.0</td>
<td>C (E) &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>0.00102</td>
<td>25</td>
<td>0.001</td>
<td>-</td>
<td>0.004</td>
<td>10.0</td>
<td>C (E) &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run No.</td>
<td>[H+]</td>
<td>t°C</td>
<td>[Co]</td>
<td>μ</td>
<td>k x 10^3</td>
<td>min⁻¹</td>
<td>Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>----------</td>
<td>-----</td>
<td>----------</td>
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<td>----------------------</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>42</td>
<td>0.0102 M</td>
<td>25</td>
<td>0.001 M</td>
<td>0.013</td>
<td>1.46</td>
<td></td>
<td>C (E) (forward and reverse rates)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
<td>0.002</td>
<td>0.016</td>
<td>1.40</td>
<td></td>
<td>C (E)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81</td>
<td></td>
<td>30</td>
<td>0.002</td>
<td>0.016</td>
<td>3.23</td>
<td></td>
<td>C (E)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>82</td>
<td></td>
<td>35</td>
<td>0.002</td>
<td>0.016</td>
<td>7.24</td>
<td></td>
<td>C (E)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The spectrophotometric and polarimetric methods gave similar rates for \( \text{Co trien Cl(H}_2\text{O)}^2+ \) (runs 51 and 56). However, the spectrophotometric rates (forward and reverse rates) should be somewhat greater than the polarimetric rates (which were assumed to be the forward rates only) but closer correspondence than in run 56 might not be expected, and the spectrophotometric rates are the less accurate. The thermodynamic equilibrium position has been roughly assessed spectrophotometrically (p. 52). The general agreement between the four methods (C, P, S and T) indicates that racemisation or isomerisation of \( \text{Co trien Cl(H}_2\text{O)}^2+ \) was not important compared to the rate of aquation. Furthermore, there was no evidence from rates or the equilibrium spectra that any \( \text{trans}[\text{Co trien(H}_2\text{O)}^2+ \) was formed. However, these isomerisations do occur in the bis(ethylenediamine) chloroaquo and diaquo compounds (45, 46).

From the rates for (-) \( \beta[\text{Co trien Cl(H}_2\text{O)}]^2+ \) (table 18) it is seen that there was a small ionic strength dependence (runs 68 to 72) such that the rates decreased as \( \mu \) was increased from 0.01 to 0.18 (figure 56), but there was negligible dependence on [Co] (compare runs 69 and 73, 30 and 31). Agreement of conductimetric and spectrophotometric rates was good (compare runs 24 and 66, 31 and 67, 18 and 77, allowing for \( \mu \) differences) and the one titrimetric rate (run 79) also agreed with the other methods. Runs 24 and 25 indicate there was no catalysis by platinised electrodes, although such catalysis of aquation has been noted in other cobalt(III) systems (106, 105, 121). Polarimetry gave a rate similar to the other methods (runs 28, 25 and 66) but would be expected to give a lower rate since it measured the forward reaction only. Since the plot was linear (figure 69,
FIGURE 56. AQUATION OF CIS β [CotrienCl(H₂O)]²⁺ (MAJOR ISOMER) "SLOW"

µ DEPENDENCE AT [H⁺] = 0.01 M, 40°.
appendix E), no significant contribution from the "fast" isomer was indicated. Furthermore no evidence was found for an isomerisation of "slow" to "fast" $\text{Co trien Cl(H}_2\text{O)}^2\text{+}$ isomers.

The conductivity results for the "fast" $\text{Co trien Cl(H}_2\text{O)}^2\text{+}$ isomer are given in table 20, and this isomer was present to the extent of about 3%. The rates ($10^3 \text{ min}^{-1}$) given in figure 57 for the complete $\beta$ system were calculated from run 25 at pH 2. The method of obtaining the two rates for the first aquation stage is given in appendix C.

![Diagram of isomers](image)

Figure 57. Aquation of $\text{Co trien Cl}_2^+$ in 0.0102 M H$^+$ at 25°C.

It is seen that the "fast" chloroaquo isomer aquates about 4 times faster than the "slow" isomer. At pH's 3 and 4, the rates for the chloroaquo
<table>
<thead>
<tr>
<th>Run No.</th>
<th>[H+]</th>
<th>t°C</th>
<th>[Co]</th>
<th>[Cl(H2O)4]²⁺</th>
<th>k x 10^5</th>
<th>% of &quot;fast&quot; isomer observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.002 M</td>
<td>15</td>
<td>0.016</td>
<td>0.016</td>
<td>2.2</td>
<td>1.1</td>
</tr>
<tr>
<td>24</td>
<td>0.002 M</td>
<td>25</td>
<td>0.016</td>
<td>0.016</td>
<td>5.0</td>
<td>4.8</td>
</tr>
<tr>
<td>25</td>
<td>0.002 M</td>
<td>25</td>
<td>0.016</td>
<td>0.016</td>
<td>8.0</td>
<td>2.8</td>
</tr>
<tr>
<td>30</td>
<td>0.001 M</td>
<td>35</td>
<td>0.013</td>
<td>0.013</td>
<td>50</td>
<td>1.8</td>
</tr>
<tr>
<td>31</td>
<td>0.002 M</td>
<td>35</td>
<td>0.016</td>
<td>0.016</td>
<td>60</td>
<td>0.9</td>
</tr>
</tbody>
</table>
aquations are higher relative to the dichloroaquation and this precludes the detection of the "fast" isomer; the conductivity plots showed no inflexions. Like the aquation of the "slow" isomer, the "fast" isomer aquation rate was almost certainly acid dependent.

Some of the spectrophotometric runs at \([H^+] \geq 0.01 \text{ M}\) showed a small initial curvature at times when the "fast" isomer was known (from conductivity) to be aquating (figure 58). These small initial deviations were thus ascribed to the "fast" isomer and the proportions of this isomer were assessed as follows.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>([H^+])</th>
<th>(t^\circ)C</th>
<th>% of &quot;fast&quot; isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>0.01 M</td>
<td>25</td>
<td>3.1</td>
</tr>
<tr>
<td>64</td>
<td>0.05</td>
<td>40</td>
<td>1.7</td>
</tr>
<tr>
<td>63</td>
<td>0.1</td>
<td>40</td>
<td>1.8</td>
</tr>
<tr>
<td>62</td>
<td>1.0</td>
<td>40</td>
<td>1.7</td>
</tr>
</tbody>
</table>

These proportions substantially agree with those calculated from the conductivity runs.

Table 21. Proportions of "fast" \(\beta[\text{CotrienCl}(\text{H}_2\text{O})]^2+\) isomer observed in spectrophotometric runs of aquation of \(\beta[\text{Co trien Cl}_2]^+\)
FIGURE 58. "FAST" [Cu(cryptolH2O)]2+ ISOMER IN SPECTROPHOTOMETRIC PLOT OF AQUATION. (0.01 M HClO4, 0.02 M, 25°C; RUN 66.)
EVIDENCE FOR THE ASSIGNMENT OF α AND β CONFIGURATIONS

(1) The detection of the two chloroaquo isomers formed by aquation of β[Co trien Cl₂]⁺ is definite evidence for the geometrical configurations which have been assigned. It was shown earlier that only the less symmetrical dichloro structure can give rise to two chloroaquo isomers, and rate plots for the cis α system gave no such evidence. All the other evidence supporting this assignment is summarised below.

(2) Trans[Co trien Cl₂]⁺ aquates stereospecifically in acid solution to give β[Co trien Cl(H₂O)]²⁺, and this associates the trans structure more closely with the cis β structure, since the isomerisation would be expected to take place with one terminal ethylene bridge movement rather than two.

(3) Trans[Co trien Cl₂]⁺ was obtained by the reaction of β[Co trien CO₃]⁺ with concentrated hydrochloric acid, and by isomerisation of β[Co trien Cl₂]Cl in methanol (chapter 2). Trans[Co trien Cl₂]⁺ could not be obtained from the corresponding α compounds, and this also associates the trans structure more closely with the β.

(4) The relative magnitudes of the C.D. curves were also consistent with the assignments (chapter 3).

(5) The complexity of the infrared spectra of the β dichloro and β dinitro compounds relative to the spectra of the α isomers was consistent with the β structure being the less symmetrical (chapter 2).
REACTION PATHS AND TEMPERATURE PARAMETERS

FOR $\alpha[\text{Co trien Cl(H}_2\text{O)}]^2+$ AQUATION

Figure 59 shows the $[H^+]$ dependence of the forward rates at $40^\circ C$. The rate is relatively insensitive to $[H^+]$ and increases by a factor of only 4 for a 1000-fold decrease in $[H^+]$. The data is consistent with three reaction paths and the rate can thus be expressed by the empirical equations:

$$\text{Rate} = k_H[\text{Co}][\text{H}_2\text{O}][H^+] + k_{\text{H}_2\text{O}}[\text{Co}][\text{H}_2\text{O}] + k_{\text{OH}}[\text{Co-H}][\text{H}_2\text{O}]$$

or

$$k_{\text{obs}} = k_H[H^+] + k_{\text{H}_2\text{O}} + k_{\text{OH}}K_a \frac{1}{[H^+]} \quad (1)$$

[Co] represents the chloroaquo concentration, and [Co-H] represents the chlorohydroxo conjugate base. The first term in equation (1) refers to an acid-catalysed path, the second to aquation of $[\text{Co trien Cl(H}_2\text{O)}]^2+$, and the last term refers to aquation of $[\text{Co trien Cl(OH)}]^+$, $K_a$ being the acid dissociation constant of the aquo ion. A contribution from base hydrolysis can be excluded, since the $[\text{OH}^-]$ concentration at pH 3 (the maximum concerned here) is $10^{-11}$ M, and the base hydrolysis rate constant would have to be of the order of $10^7 \text{M}^{-1}\text{min}^{-1}$ to give rates comparable with the observed aquation rates ($10^{-4} \text{min}^{-1}$). The rate constant for base hydrolysis of cis$[\text{Co en}_2\text{Cl(OH)}]^+$ is $22 \text{M}^{-1}\text{min}^{-1}$ at $0^\circ$ (140). For a similar reason aquation or base hydrolysis of the conjugate base formed by acid dissociation of the amino ligand need not be considered since the concentration of this species must be extremely small ($pK_a > 14$).
Figure 59. AQUATION OF CIS ≈ [Co₃(C₄H₄O₆)][Cl(H₂O)]²⁺

$[H⁺]$ Dependence of forward rates (polarimetric)

At 40°C, $\mu = 0.1$. 

$log k$ vs. $-log [H⁺]$
Contributions from these latter two reactions were neglected in measurements of aquation rates of \([\text{Co en}_2 \text{Cl(OH)}]^+\) in neutral solution\(^{(133,119)}\). The experimental rates at \([H^+] = 0.001, 0.01\) and 0.1 M at 40° (runs 56, 51 and 49) were substituted in equation (1) and solution of the three simultaneous equations gave:

\[
\begin{align*}
  k_H &= 4.712 \times \frac{1}{0.00102} \times 10^{-8} \text{ M}^{-1} \text{ min}^{-1} \\
  k_{H_2O} &= 2.216 \times 10^{-4} \text{ min}^{-1} \\
  k_{OH^+a} &= 3.694 \times 0.00102 \times 10^{-4} \text{ M} \text{ min}^{-1}
\end{align*}
\]

Equation (1) then becomes:

\[
k_{\text{obs}} \times 10^4 = \frac{0.4712}{1.02} [H^+] + 2.216 + 3.6936 \times 1.02 \times 10^{-3} \times \frac{1}{[H^+]}
\tag{2}
\]

This equation gives good agreement with \(k_{\text{obs}}\) at other \([H^+]\) values (runs 54, 53 and 48. The maximum discrepancy was with run 48, and here the ionic strengths were not comparable). The rate vs. \([H^+]\) plot (figure 59) is thus represented closely by equation (2), at 40°, \(\mu = 0.1\). The contribution of each path to the total rate constant may therefore be calculated at any \([H^+]\), and at 0.00102, 0.0102, 0.102 M \([H^+]\) these are (all \(x 10^4 \text{ min}^{-1}\)):

<table>
<thead>
<tr>
<th>([H^+])</th>
<th>(k_H[H^+])</th>
<th>(k_{H_2O})</th>
<th>(k_{OH^+a} \times \frac{1}{[H^+]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00102</td>
<td>0.000</td>
<td>2.216</td>
<td>3.694</td>
</tr>
<tr>
<td>0.0102</td>
<td>0.005</td>
<td>2.216</td>
<td>0.369</td>
</tr>
<tr>
<td>0.102</td>
<td>0.471</td>
<td>2.216</td>
<td>0.037</td>
</tr>
</tbody>
</table>
It is evident that the major reaction path is direct aquation $k_{H2O}$, and the acid-catalysed path $k_{H}[H^+]$ becomes significant only at $[H^+] \geq 0.1 \text{ M}$. The chlorohydroxo path is also a minor one except at $[H^+] \leq 0.002 \text{ M}$. With the available data $k_{H}$ can not be calculated more accurately than $k_{H} = (0.5 \pm 0.3) \times 10^{-4} \text{ M}^{-1} \text{min}^{-1}$.

The temperature dependence of the observed rates is given in figure 60. The plot at 0.001 M $[H^+]$ is not linear, and this is due to the different activation energies for the two major paths which contribute to about the same extent at this pH. The activation energy for each path was obtained by first separating the observed rates at 35° and 45°, as was done above for 40°. Since the acid-catalysis is negligible at $[H^+] \leq 0.01$, the temperature dependence at only two $[H^+]$ values was necessary to obtain $k_{H2O}$ and $k_{OH}K_a$. Solution of the equation,

$$k_{obs} = k_{H2O} + \frac{k_{OH}K_a}{[H^+]} \quad (3)$$

at 35° (runs 50 and 55) and 45° (runs 52 and 57) gave:

$$
\begin{align*}
    k_{H2O} &= 1.181 \times 10^{-4} \\
    k_{OH}K_a &= 1.589 \times 1.02 \times 10^{-7} \\
    k_{H2O} &= 4.056 \times 10^{-4} \\
    k_{OH}K_a &= 8.544 \times 1.02 \times 10^{-7}
\end{align*}
$$

To obtain the absolute rate constant $k_{OH}$ for the chlorohydroxo path it is necessary to measure the acid dissociation constant $K_a$ of the
FIGURE 60. AQUATION OF CIS $\Rightarrow$ [CatrianCl(H$_2$O)]$^{2+}$

TEMPERATURE DEPENDENCE OF FORWARD RATES (POLARIMETRIC)

AT [H$^+] = 0.001, 0.01, \mu = 0.1.$
chloroaquo species. This could not be done at 35° and 45° but $pK_a$ was measured at 10° and 20° ($pK_a = 7.46$ at 10°, 7.11 at 20°, both $\pm 0.02$, at $\mu = 0.1$ with NaClO₄; chapter 6). The values at the higher temperatures were obtained by extrapolation from the assumed linear plot of $pK_a$ vs. $1/T$. The absolute rates were then calculated (table 22).

**TABLE 22. RATE CONSTANTS FOR THE TWO MAJOR AQUATION PATHS**

OF $\text{g}[\text{Co trien Cl(H}_2\text{O)}]^2^+$ (in min⁻¹)

<table>
<thead>
<tr>
<th>t°C</th>
<th>$k_{H_2O}$</th>
<th>$k_{OH}K_a$ (extrapolated)</th>
<th>$pK_a$</th>
<th>$k_a$</th>
<th>$k_{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>$1.181 \times 10^{-4}$</td>
<td>$1.589 \times 1.02 \times 10^{-7}$</td>
<td>6.63 $\pm$ 0.05</td>
<td>$2.34 \times 10^{-7}$</td>
<td>0.70</td>
</tr>
<tr>
<td>40</td>
<td>2.216</td>
<td>3.694</td>
<td>6.48</td>
<td>3.31</td>
<td>1.14</td>
</tr>
<tr>
<td>45</td>
<td>4.056</td>
<td>8.544</td>
<td>6.33</td>
<td>4.68</td>
<td>1.86</td>
</tr>
</tbody>
</table>

From the above rate data, the following activation energies and entropies were calculated.

For the chloroaquo path, $E_{aH_2O} = 24.1 ^\pm 0.1$ kcal·mole⁻¹. Using this value of $E_{aH_2O}$, and the rate constant at 40° ($k_{H_2O} = 2.216 \times 10^{-4}$ min⁻¹), $\Delta S_{H_2O}^\#$ was calculated as $\Delta S_{H_2O}^\# = -8.5 \pm 0.5$ e.u.

For the chlorohydroxo path, $E_{aOH} = 19.0 ^\pm 0.3$ kcal·mole⁻¹, and from this and $k_{OH} = 1.14$ M·min⁻¹ at 40°, $\Delta S_{OH}^\# = -7.8 \pm 1.1$ eu. It may also be calculated (from the $k_{OH}K_a$ values in table 22) that the observed activation energy for this path is $E_{aOH}^{obs} = 32.7 ^\pm 0.3$ kcal·mole⁻¹, and the difference between this and $E_{aOH}$ (calculated from the absolute rates $k_{OH}$) shows that
the temperature dependence of $K_a$ is important in calculating $\Delta S'$, and $K_a$ cannot be assumed to be temperature independent. This may also be allowed for by using the equation derived for the diaquo compounds (chapter 6):

$$E_{a_{OH}} = E_{a_{obs}} + \frac{\Delta (pk_a) \times 4.576}{\Delta (1/T)}$$

On substituting the measured $pK_a$ values (7.46 at 10°, 7.11 at 20°, both ±0.02) $E_{a_{OH}}$ is calculated as 19.4 kcal.mole$^{-1}$. This eliminates the extrapolation of $pK_a$'s to higher temperatures.

**REACTION PATHS AND TEMPERATURE PARAMETERS FOR $\beta$[Co trien Cl(H$_2$O)$_2$]$^{2+}$ AQUATION**

The $[H^+]$ dependence of this reaction (at 40° C, $\mu=0.1$) is shown in figure 61. The linearity of the plot at $[H^+] \leq 0.01 \text{ M}$, corresponding to the equation

$$k_{obs} = 2.53 \times 10^{-4} [H^+]^{-0.89}$$

suggests that the main reaction path here is through the chlorohydroxo, and the positive deviations from this line at $[H^+] > 0.01$ suggest that the chloroaquo path contributes in this region. The observed rates can be expressed by the empirical equation:

$$k_{obs} = k_{H_2O} + \frac{k_{OH^+} K_a}{[H^+]}$$
FIGURE 61. AQUATION OF $\beta$ [CoTrenCl(H$_2$O)]$^{2+}$ ('SLOW' ISOMER)

$[H^+]$ DEPENDENCE OF SPECTROPHOTOMETRIC RATES

AT 40°C, $\mu = 0.1$
It is probable however that the overall patterns for the $\alpha$ and $\beta$ cis isomers are similar, and that an acid-catalysed path would become evident at $[H^+] \gg 1$, but this was not studied. This is consistent with the $\beta$ chloroaquo isomer being a stronger acid than the $\alpha$ ($pK_{a1}$ at $40^\circ$: $\alpha$, 6.48; $\beta$, 5.35), so that proportionately more of the $\beta$ compound would exist as the chlorohydroxo conjugate base at any particular pH. This would in effect shift the plot of log $k$ vs. pH to lower pH values in the $\beta$ instance compared to the $\alpha$ isomer.

Equation (5) was solved using $k_{\text{obs}}$ at $40^\circ$ (runs 76 and 63) to give

$$k_{\text{obs}} \times 10^3 = 0.980 + 0.09004 \times 1.02 \times \frac{1}{[H^+]}$$  \hspace{1cm} (6)

The rate constant could then be calculated at any $[H^+]$, and the agreement between the calculated and observed rates was $\pm$ 10% (runs 78, 75, 69, 64). The poorer agreement compared to the $\alpha$ system could be associated with the lower accuracy of the spectrophotometric method employed here and possibly (although less likely) with a contribution from base hydrolysis. The above rates are the combined rates of the forward and reverse reactions but the treatment was justified because the position of equilibrium

$$\beta[\text{Co trien Cl(H}_2\text{O)}]^{2+} \rightleftharpoons \beta[\text{Co trien(H}_2\text{O)}]_2^{3+}$$

was found to be independent of $[H^+]$ (p.452). However the empirical equation (5) should strictly include terms in $[\text{Cl}^-]$ for the reverse anation reactions, but the accuracy of the data does not warrant using a more refined expression.
From (6) the contributions of the two aquation paths are calculated at the various acid concentrations at 40° to be (all \( \times 10^3 \) min\(^{-1} \)):

\[
\begin{array}{c|c|c}
[H^+] & k_{H_2O} & \frac{k_{OH}K_a}{[H^+]} \\
0.00102 M & 0.98 & 90.04 \\
0.0102 & 0.98 & 9.00 \\
0.102 & 0.98 & 0.90 \\
\end{array}
\]

It is evident that the chlorohydroxo path predominates at \([H^+] \leq 0.01\) M, but the chloroaquo path is the major one at \([H^+] = 1.0\) M. That the one path is predominant is confirmed by the identical slopes of the \(\log k_{obs} \) vs. \(1/T\) plots for 0.01 and 0.001 M \([H^+]\) (figure 62).

As was done for the \(\alpha\) system, the rates at 25° and 40° for \([H^+] = 0.01\) and 0.001 M were resolved into the component rates. These are given in table 23 with the \(pK_a\) values (extrapolated from \(pK_a = 6.2\) at 10°, 5.9 at 20°, both \( \mp 0.1\), in \(\mu = 0.1\) with \(NaClO_4\); chapter 6).

**TABLE 23. RATE CONSTANTS FOR AQUATION PATHS OF**

\(\beta[\text{CotrienCl(H}_2\text{O)}^2]^+\), "SLOW ISOMER" (in min\(^{-1}\))

<table>
<thead>
<tr>
<th>(t^\circ C)</th>
<th>(k_{H_2O})</th>
<th>(k_{OH}K_a)</th>
<th>(\frac{pK_a}{K_a})</th>
<th>(K_a)</th>
<th>(k_{OH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.33 x 10(^{-3})</td>
<td>6.81 x 1.02 x 10(^{-3})</td>
<td>5.75 (\mp) 1</td>
<td>1.8 x 10(^{-6})</td>
<td>3.9 x 10(^3)</td>
</tr>
<tr>
<td>40</td>
<td>0.98</td>
<td>90.04</td>
<td>5.35 (\mp) 2</td>
<td>4.5</td>
<td>20</td>
</tr>
</tbody>
</table>
FIGURE 62. AQUATION OF CIS & [Co(trien)Cl(H2O)]^{2+} ("SLOW" ISOMER).

TEMPERATURE DEPENDENCE AT [H^+] = 0.01 M, \( \mu = 0.1 \)
From these values the activation parameters are calculated to be:

\[
\begin{align*}
E_{H_2O}^a &= 13.4 \text{ kcal mole}^{-1}, \quad \Delta S_{H_2O}^f = -40 \text{ e.u.} \\
E_{OH}^a &= 20 \text{ kcal mole}^{-1}, \quad \Delta S_{OH}^f = +16 \text{ e.u.}
\end{align*}
\]

Great reliance can not be placed on these parameters, due mainly to the inaccuracy in the pK\textsubscript{a} measurements.

**ISOMERISATION AND EQUILIBRIUM POSITION IN CHLOROAQUO AQUATIONS**

During the aquations some isomerisation of the diaquo products occurs. The \( \alpha \) diaquo isomerises to 85% \( \beta \) at equilibrium (chapter 6) whereas the isomerisation of \( \beta \) to \( \alpha \) is necessarily much less. The extent of these isomerisations during the aquations was measured by converting aliquots of the mixed chloroaquo and diaquo solutions to the carbonato complexes with NaHCO\textsubscript{3} at the beginning and end (\( \approx 5 \) half-lives) of each aquation run. From the equilibrium absorption at the carbonato peak (505 m\( \mu \)) and the absorptions of the pure carbonato isomers (\( \varepsilon_{\alpha} = 120 \pm 1 \), \( \varepsilon_{\beta} = 179 \pm 1 \)), the isomerisation which occurred during the aquation of \( \alpha[\text{Co trien Cl(H}_2\text{O)}]^{2+} \) was given by:

\[
\% \text{ isomerisation } \alpha \text{ to } \beta = \frac{\varepsilon_{\text{equilib carbonato}} - 120}{179 - 120}
\]

This was quite extensive. In the \( \beta \) aquation however, little isomerisation
of the β diaquo complex was detected (the optical densities of the carbonato solutions at the beginning and end of the aquation did not differ outside the experimental error).

Similarly, measurements of the optical activities of the carbonato solutions gave the observed retention of activity in each run. As the α diaquo product isomerised it simultaneously lost activity (chapter 6), so that after each α or β run, the remaining activity was due to the carbonato isomer of the same configuration as the chloroaquo complex. These isomerisations and retentions of activity were correlated with the expected isomerisations and racemisations of the diaquo compounds, and the results are discussed in chapter 7.

The thermodynamic equilibrium

$$\text{α}[\text{Co trien Cl(H}_2\text{O)}]^{2+} \rightleftharpoons \text{α}[\text{Co trien(H}_2\text{O)}]^{3+}$$

was assessed approximately as (80 ± 10)% towards the diaquo side, from the equilibrium extinction coefficient ($\varepsilon = 94 ± 2$) at the wavelength where the two diaquo isomers absorb equally ($\varepsilon_{520 \text{ m}_{\mu}} = 77 ± 2$).

Because isomerisation was negligible, the equilibrium

$$\beta[\text{Co trien Cl(H}_2\text{O)}]^{2+} \rightleftharpoons \beta[\text{Co trien(H}_2\text{O)}]^{3+}$$

could be more satisfactorily studied, and this was done in two ways. First, the constancy of the equilibrium spectra from all runs (runs 62 to 78) showed that the equilibrium position was independent of [H+] and temperature. The extinction coefficient at the wavelength maximum of $\beta[\text{Co trien(H}_2\text{O)}]^{3+}$ was $\varepsilon_{487 \text{ m}_{\mu}} = 116.8 ± 0.4$ (S.E.). Second, using the extinction coefficients of β chloroaquo and β diaquo at 487 mμ as 98 ± 1
and 122 + 1 respectively, the equilibrium position was assessed as about 
(85 ± 5)\% towards the diaquo side. (This value was also obtained at 
other wavelengths). When \( [\text{Co trien Cl(H_2O)}]^2+ \) hydrolysed in NaOH 
solution (one mole) the equilibrium solution after acidification had the 
same absorption as above (\( E_{487} = 118 \)).

**SUMMARY**

It has been shown in this chapter that the \( \beta \) compounds have the 
configuration assigned in the introduction, since the two chloroaquo 
isomers produced by aquation of \( [\text{Co trien Cl}_2]^+ \) were detected by their 
differing aquation rates. The "fast" isomer however was produced in 
amounts not exceeding about 4\% of the total, and although the rate of 
aquation of this isomer to \( [\text{Co trien(H_2O)}_2]^3+ \) was measured at 0.01 M [H\(^+\)], 
insufficient data could be obtained to study the details of its reaction 
paths.

The \( \alpha \) and \( \beta \) chloroaquo isomers aquate to the diaquo compounds at 
least largely with retention of configuration and activity (chapter 7) but 
these products subsequently isomerise and racemise (chapter 6) so that the 
final equilibrium solutions must contain five species (\( \alpha, \beta' \) and \( \beta'' \) 
chloroaquo, and \( \alpha \) and \( \beta \) diaquo compounds). The thermodynamic equilibrium 
position between the **cis** chloroaquo and the corresponding diaquo compound 
was assessed approximately however, as about 85\% towards the diaquo for 
each isomer.

It was shown that the **cis** chloroaquo isomers aquate through three
paths. The acid-catalysed path was not observed in the $\beta$ compound and was not of great importance in the $\alpha$ system, in the pH region studied. In the $\beta$ system the chlorohydroxo path accounted for most of the reaction, but this and the chloroaquo path were both important for the $\alpha$ compound. In both instances the chlorohydroxo path had the greater absolute rate, and the activation parameters were calculated.

**EXPERIMENTAL**

Application of conductivity to aquation of dichloro and chloroaquo compounds.

Rates for the aquation of a dichloro isomer and the subsequent aquation of the chloroaquo isomer were usually measured in the same run. Because the two stages of aquation involve similar changes of conductivity, the rate of the first stage was usually calculated by Guggenheim's method but the time interval chosen ($\Delta$) had to be relatively short ($\sim t_{1/2}$ or less). Data were plotted as $\log \left( \frac{1}{R_t} + \Delta - \frac{1}{R_t} \right)$ vs. $t$. Under conditions where the consecutive rates differed by a large factor ($>30$), an almost constant value of $R_\infty$ was obtained after about $8 \times t_{1/2}$ for the first reaction. Data were then plotted as $\log \left( \frac{1}{R_\infty} - \frac{1}{R_t} \right)$ vs. $t$, where $R_t$ = resistance at time $t$. From both these plots, the rate constant $k = -2.303 \times$ slope of the line of best fit through the experimental points.

Conductivity was not a very reliable method for measuring the very slow rate of aquation of $\alpha[\text{Co trien Cl(H}_2\text{O)}]^{2+}$, because over the long
periods involved the conductance was subject to errors possibly arising from electrode catalysis or from slow desorption of ions from electrodes. However when the rate of \( \alpha[\text{Co trien Cl(H}_2\text{O)}]^{2+} \) was measured by this method, and the data plotted as \( \log \left( \frac{1}{R_{\infty}} - \frac{1}{R_t} \right) \) vs. t, the resulting graphs consisted of two parts (figure 85, appendix E). The initial steep curve was due to the aquation of \( \alpha[\text{Co trien Cl}_2]^+ \). The linear plot was due to the aquation of \( \alpha[\text{Co trien Cl(H}_2\text{O)}]^{2+} \) and the rate constant was calculated from the slope of this line. Similar plots were obtained for \( \beta[\text{Co trien Cl(H}_2\text{O)}]^{2+} \) at \([H^+] \leq 0.001\), where the "fast" isomer was obscured.

Separation of rates in the \( \beta[\text{Co trien Cl(H}_2\text{O)}]^{2+} \) system from conductivity data.

In 0.01 M \text{HClO}_4, the plots of \( \log \left( \frac{1}{R_{\text{equilib}}} - \frac{1}{R_t} \right) \) vs. t showed two distinct regions separated by an inflexion region as shown in figure 63. \( R_{\text{equilib}} \) is the steady resistance attained when the equilibrium

\[
\beta' \text{ and } \beta'' \quad [\text{Co trien Cl(H}_2\text{O)}]^{2+} \xleftrightarrow{} \beta[\text{Co trien(H}_2\text{O)}_2]^{3+}
\]

was established. The inflexion was due to the faster aquation rate of the \( \beta' \) chloroaquo isomer, compared with that for the "slow" \( \beta'' \) isomer. The latter rate was calculated from the slope of the final linear portion of the graph.

The rate of aquation of the "fast" isomer was evaluated by extrapolating the final linear portion of the above plot back over the inflexion region, and the differences between this extrapolation and the
experimental curve were obtained in terms of the conductances. The plot of the inflexion region in figure 63 is shown on a magnified scale in figure 64.

The conductance due to the "slow" isomer in the inflexion region, $\frac{1}{R_t^{\text{calc}}}$, at time $t$ was calculated from the equation of the extrapolated line. At the same time $t$, $\frac{1}{R_t^{\text{expt}}}$ was obtained from the experimental curve. These values were plotted as $\log \left( \frac{1}{R_t^{\text{expt}}} - \frac{1}{R_t^{\text{calc}}} \right)$ vs. $t$, and this plot is given in figure 65. From the slope of this plot, $k_{\text{isomer}} = -2.303 \times \text{slope}$. This method of calculation was justified by an analytical treatment of the conductance changes expected for a system involving two concurrent consecutive reactions (appendix B). A Guggenheim plot of the above data,

$$
\log \left[ \left( \frac{1}{R_t^{\text{expt}}} - \frac{1}{R_t^{\text{calc}}} \right) - \left( \frac{1}{R_{t+\Delta}^{\text{expt}}} - \frac{1}{R_{t+\Delta}^{\text{calc}}} \right) \right] \text{ vs. } t
$$
gave the same order of rate.

The proportion of "fast" isomer was estimated by taking the ratio of the maximum difference in conductivities (experimental and calculated) to the total conductivity due to $\beta[\text{Co trien Cl(HgO)}]^{2+}$ at the same time, i.e.

$$
\% \text{ of "fast" isomer} = \left( \frac{1}{R^{\text{expt}}} - \frac{1}{R^{\text{calc}}} \right)_{\text{maximum}}
$$

$\frac{1}{R_{H^+}}$ was the conductivity of the acid only, measured before the kinetic run.
Figure 63. Conductivity plot of aquration of $\text{P}[\text{catrienCl}_2]\text{ClO}_4$.

Second chlorine. (0.01 HClO$_4$, 25°C, run 25.)

$\log (2.7007 \times 10^{-4} - R)$

$k_{\text{slow isomer}} = 1.37 \times 10^{-3} \text{ min}^{-1}$
FIGURE 64. CONDUCTIVITY PLOT OF AQUATION OF $\text{Pb}[\text{CotrienCl}_2]\text{ClO}_4$, SECOND CHLORINE. (0.01 M $\text{H}^+$, 25°C, RUN 25).

MAGNIFIED PLOT OF INFLEXION REGION IN FIGURE 63.

Extrapolated for "slow" chloroaquo isomer.

$\log \left( \frac{1}{t_{\text{calc}}} - \frac{1}{t_{\text{calc}}} \right)$

Experimental curve "slow" and "fast" isomers

$\log (t_{\text{calc}} - t_{\text{exp}})$

Time: 0, 1, 2, 3, 4, 5, 6, 7, 8
Figure 65. Rate plot (conductivity) of aquation of "fast"
\[ \beta [\text{CotrienCl(H}_2\text{O)}]^{2+}/\text{ISOMER (0.01 M H}^+, 25^\circ, \text{RUN 25.}} \]

\[ \log (\frac{k_{\text{expt}}}{k_{\text{calc.}}}) \]

\[ k = 4.8 \times 10^{-3} \text{ MIN}^{-1} \]

TIME (hours) ➔
Details of conductance runs.

Usually cells with platinised electrodes were used. Four different cells (with cell constants 0.24, 1.87, 11.1, 27.7) were used, so that for a particular run a cell constant could be chosen to make the resistance change convenient with respect to the bridge. A cell with bright platinum electrodes (constant 17.8) was used in some runs to show that electrode catalysis was not important.

All runs were initiated by dissolving a weighed amount of a dichloro complex in a measured volume of the appropriate acid solution equilibrated at the temperature of the run. With the time taken to fill the cell and for temperature equilibrium to be re-attained it was at least 4 minutes after commencement of a reaction before rate readings could be obtained, but this was important only with the trans isomer, and with the β isomer at higher temperatures.

Solution resistances were balanced against standard resistances in an A.C. Wheatstone bridge, operated from an oscillator at 1000 c.p.s. and at an output of 1 volt. Null-points were detected with an oscilloscope. For many runs a decade resistance box, reading from 0 to 10,000 ohms in 1 ohm steps, was used. In a typical run (β dichloro in 0.01 M[H+] run 31) the total resistance change for both aquation stages was from 5755 to 5433 ohms. The more accurate runs, where the "fast" β chloroaquo isomer was assessed, were measured using a Leeds and Northrup A.C. bridge reading to 10,000 ohms in steps of 0.002 ohm. In a typical run (β dichloro in 0.01 M[H+], run 25) the total resistance change was from 3954.30 to 3699.37.
ohms, and the accuracy of each reading was better than 0.01 ohm, so that the conductivity differences could be measured to 1 part in 25,000.

A precise knowledge of cell constant was necessary only to compute molecular conductivity values. Those for the dichloro compounds were obtained from the rate plots for aquation of the first chloride ion by extrapolation to zero time; for the chloroaquo compounds, values were obtained by extrapolating the rate plots for the second aquation stage to the time of commencement of this reaction. Conductivities of the final equilibrium solutions were computed from the experimental values of $R_\infty$.

These molecular conductivities were of the orders expected for 1:1, 2:1, and 3:1 electrolytes respectively (table 24).

<table>
<thead>
<tr>
<th></th>
<th>[CotrienCl$_2$]ClO$_4$</th>
<th><a href="ClO$_4$">CotrienCl(H$_2$O)</a>$_2$</th>
<th>Equilibrium Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis $\alpha$</td>
<td>80 - 90</td>
<td>190 - 220</td>
<td>250 - 280</td>
</tr>
<tr>
<td>cis $\beta$</td>
<td>65 - 80</td>
<td>160 - 210</td>
<td>270 - 340</td>
</tr>
<tr>
<td>trans</td>
<td>$\sim$ 50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Application of spectrophotometry to aquation of dichloro compounds.

Figures 66 to 68 give the visible spectra of the three dichloro isomers and their chloroaquo aquation products. It is seen that the greatest absorption differences occur at low wavelengths, and rates were usually measured at 320 m$\mu$ where there was very little absorption change.
during the second stage of aquation. Some of the runs of trans[Co trien Cl₂]⁺ were followed by measuring the complete visible spectrum at successive times on a recording spectrophotometer, and the rates were then calculated at 342, 435 and 510 mµ. Aquation of β[Co trien Cl₂]⁺ was followed also at 430 mµ in several runs. Data were plotted as log (Dₜ - Dₜ⁺) vs. t or log (Dₜ⁺ - Dₜ) vs. t, where D = optical density, and the rate constants were calculated from the slopes of these plots.

The aquation of trans[Co trien Cl₁]ClO₄ in 0.1 M HClO₄ in the presence of Hg²⁺ ion was studied after rapid mixing of the trans (in HClO₄) and Hg(ClO₄)₂ solutions in a stopped-flow reactor coupled to a 1 cm. cell (141). A continuous record of optical density at 320 mµ was made from the instant of mixing on a recording spectrophotometer run at a fast speed.

Application of spectrophotometry to aquation of chloroaquo compounds.

Figures 69 and 70 give the spectral changes on aquation of the α and β chloroaquo isomers to equilibrium, and also the spectra of the corresponding pure diaquo isomers.

Aquation of α[Co trien Cl(H₂O)]²⁺ was measured at 540 mµ (where the α and β diaquo isomers have similar absorptions) and the densities became almost constant after 5 half-lives. β[Co trien Cl(H₂O)]²⁺ was followed at 560 mµ. The solutions were thermostated in 5 cm. jacketed cells.
FIGURE 66. SPECTRAL CHANGES IN AQUATION OF $\text{[CmH}[\text{en}]\text{Cl}_2]\text{ClO}_4$. 

- Dichloro, $\varepsilon_{539} = 132$
- Chloroaquo, $\varepsilon_{524} = 118$

$\lambda$ (nm) vs. $\varepsilon$ (molar absorbance coefficient)
FIGURE 67. SPECTRAL CHANGES IN AQUATION OF \(
\beta [\text{CotrienCl}_2]\text{ClO}_4.\)

\(\beta\) dichloro \(\epsilon_{539} = 132\)

\(\beta\) chloroaquo \(\epsilon_{511} = 126\)
Figure 68. Spectral changes in aquation of $\text{trans}[\text{CotrienCl}_2]\text{ClO}_4$. 

$\text{trans}[\text{CotrienCl}_2]^+$

$\mu\left[\text{CotrienCl(H}_2\text{O)}\right]^{2+}$
FIGURE 69. SPECTRAL CHANGES IN AQUATION OF $\alpha\left[\text{CotrienCl(H}_2\text{O)}\right]^{2+}$
Figure 70. Spectral changes in aquation of $[\text{Cotrien Cl} \, (\text{H}_2\text{O})]^2+$. 

$[\text{Cotrien Cl} \, (\text{H}_2\text{O})]^2+$

"equilibrium" $(1 \times t_{1/2})$

$[\text{Cotrien} \, (\text{H}_2\text{O})_2]^3+$
Spectrophotometers and details of kinetic runs.

The two spectrophotometers employed throughout this work were a Shimadzu QR-50 manual and a recording Shimadzu type RS-27. Fast reactions (β and trans [Co trien Cl₂]⁺) were followed on the recording machine, either at a fixed wavelength or by recording a series of complete spectra with solutions contained in a jacketed 5 cm. cell. The slower rates were measured manually, in a 5 cm. water-jacketed cell, or in a 1 cm. stoppered cell held in a thermistor-controlled electrically-heated metal block. All reference cells contained distilled water, and light was excluded whenever possible.

Application of polarimetry to aquation of dichloro compounds.

Reference to the R.D. curves of the ½ dichloro and chloroaqau isomers (figures 28 and 29) shows that wavelengths 589 and 578 mµ give sufficient changes to follow the aquation of (+)½[Co trien Cl₂]⁺. These rates were measured either visually on a Bellingham and Stanley polarimeter or on a polarimeter attached to a Shimadzu QR-50 spectrophotometer (accuracy + 0.01°) in 1 dm. or 2 dm. jacketed cells.

Aquation of (-)½[Co trien Cl₂]⁺ is not so amenable to polarimetric measurement (R.D. curves figures 34 and 35), but one run was followed at 580 mµ on a Perkin-Elmer 141 automatic polarimeter (accuracy + 0.002°), with the solution in a 1 dm. jacketed cell. Data were plotted as log (αₜ - α∞) vs. t, where αₜ = measured rotation at time t.
Application of polarimetry to aquation of chloroaquo isomers.

The rate of aquation of (+)Co[trien Cl(H2O)]2+ (α578 = + 0.40° for 0.001 M solution) was followed polarimetrically at 578 mμ where (+)Co[trien(H2O)2]3+ had nearly zero rotation (α578 = −0.019° for 0.001 M solution). At [H+] ≥ 0.002 M the data were plotted as log (α578 + 0.019) vs. t. At [H+] = 0.001 M, where the a diaquo product lost activity faster than the rate of its formation by aquation, the data were plotted as log α578 vs. t. The rate constants obtained from these plots measured the forward rate of aquation only,

[Co trien Cl(H2O)]2+ → [Co trien(H2O)2]3+

and were independent of subsequent isomerisation of the a diaquo product. Solutions were transformed to carbonato compounds at the end of the aquation reactions to assess the extent of isomerisation and retention of activity.

The only suitable wavelength for measuring aquation of β[Co trien Cl(H2O)]2+ was 480 mμ where β[Co trien(H2O)2]3+ had zero rotation, so that data were plotted as log α480 vs. t. Only one run was measured this way (by recording the complete R.D. curve at successive times) and only the rate calculated at 480 mμ could be unambiguously interpreted.

Both α and β rates were determined using a Perkin-Elmer 141 automatic polarimeter, with solutions contained in a 1 dm. jacketed cell. For wavelengths other than the sodium or mercury lines, the instrument was used in conjunction with a Zeiss monochromator.
The titrimetric method for aquation rates.

This consisted of titrating the total ionic Cl\(^-\) in aliquots drawn from a thermostated aquating solution with standard 0.01 M Hg(NO\(_3\))\(_2\) solution to the turbidity end-point with sodium nitroprusside indicator\(^{63a,124}\). The reliability of this method was questionable because of the usual catalysing effect of Hg\(^{2+}\) ion, and it lacked precision because the end-point was difficult to detect in the coloured solutions. It also required large amounts of compound for each run.

In \([\text{Co trien Cl(H}_2\text{O)}]\)\(^{2+}\) aquations, only about 50\% of the Cl\(^-\) was titrated after \(7 \times t^{1/2}\), and the rates did not agree well with the other more reliable methods. The agreement was better but still not good for \([\text{Co trien Cl(H}_2\text{O)}]\)\(^{2+}\) aquation, so the method was not useful in these studies.

Constant temperature baths and thermostats.

Kinetic runs followed by spectrophotometry or polarimetry were carried out in cells jacketed to the desired temperature by water from thermostated baths controlled to \(\pm 0.05^\circ\text{C}\) by a Braun Thermomix immersion heater.

Conductance cells were immersed in baths of Shell Fusus oil, controlled either by a Jumo mercury thermostat \((\pm 0.01^\circ\text{C})\), or in the most accurate runs (for \([\text{Co trien Cl}_2]\)\(^+\)) by a toluene-mercury thermostat to better than \(\pm 0.005^\circ\text{C}\).

Conditions for kinetic runs.

Rates were measured under various conditions of HClO\(_4\) concentration
[H\(^+\)], ionic strength \(\mu\), complex concentration \([\text{Co}]\), and temperature.

Ionic strength was maintained constant by adding NaClO\(_4\) as an inert electrolyte. The dichloro complexes were used as the perchlorates (except one run on the trans isomer where the chloride was used).

**Sodium perchlorate.**

The sample used for adjusting ionic strengths in kinetic runs was analysed for NaClO\(_4\) by ignition with NH\(_4\)Cl and H\(_2\)PtCl\(_6\) and titrating the Cl\(^-\) ion\(^{(142)}\). The mean percent of NaClO\(_4\) corresponded to a molecular weight of about 150, which was used in computing \(\mu\).
CHAPTER 6

KINETICS OF RACEMISATION AND ISOMERISATION
OF THE CIS DIAQUO COMPLEXES

INTRODUCTION.

It has long been known that cis and trans isomers of aquo complexes isomerise in aqueous solution to equilibrium mixtures, but the detailed study of these reactions has received attention only in recent years. Again, most of the work has been concentrated on cobalt(III) complexes, and the following discussion is limited to these systems.

Aquo complexes are weak acids, so that in solution equilibria of the following type occur:

\[
[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+} \rightleftharpoons [\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]^{2+} + \text{H}^+ \rightleftharpoons [\text{Co en}_2(\text{OH})_2]^+ + 2\text{H}^+
\]

Each complex species then isomerises at its particular rate, so that the overall rate is a function of these acid-base equilibria. Isomerisation studies have thus to be combined with measurements of acid dissociation constants to completely define the reacting system.

Racemisation of aquo complexes has been studied only for monoaquo complexes of the type cis[Co en$_2$ X(H$_2$O)$_2$]$^{2+}$ (where X = Cl, F, NO$_2$, NCS, NH$_3$), and again acid-base equilibria may be involved. Acid dissociation constants are not easily determined in these systems since the hydroxo complexes (formed on titration with NaOH) are extremely labile and isomerise
readily. The detailed mechanisms of racemisation are as yet unknown but it seems likely that racemisation and isomerisation may occur by similar mechanisms. Sufficient data has now become available to enable racemisation and isomerisation rates to be compared with those of water exchange (using $\text{H}_2\text{O}^{18}$) for a few complexes. In all instances, isomerisation reactions have been measured spectrophotometrically and acid-base equilibria have been measured with a glass electrode. Work relevant to the present study will be reviewed under the headings of diaquo and monoaquo complexes.
Diaquo Complexes

Bjerrum and Rasmussen in 1952\(^{46}\) made a complete study of all the acid-base and cis-trans equilibria which were established spontaneously in solutions of \([\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\) ions. The complete system was represented by the following scheme:

\[
\begin{align*}
\text{cis}[\text{Coen}_2(\text{H}_2\text{O})_2]^{3+} & \rightleftharpoons \text{cis} \quad \text{Ka}_1 \quad \text{cis}[\text{Coen}_2\text{H}_2\text{O}(\text{OH})]^{2+} \rightleftharpoons \text{cis} \quad \text{Ka}_2 \quad \text{cis}[\text{Coen}_2(\text{OH})_2]^{2+} \\
\text{trans}[\text{Coen}_2(\text{H}_2\text{O})_2]^{3+} & \rightleftharpoons \text{trans} \quad \text{Ka}_1 \quad \text{trans}[\text{Coen}_2\text{H}_2\text{O}(\text{OH})]^{2+} \rightleftharpoons \text{trans} \quad \text{Ka}_2 \quad \text{trans}[\text{Coen}_2(\text{OH})_2]^{2+}
\end{align*}
\]

\[
\begin{align*}
\text{cis} \quad \text{Ka}_1 & = 10^{-6.06} & \text{cis} \quad \text{Ka}_2 & = 10^{-8.19} \\
\text{trans} \quad \text{Ka}_1 & = 10^{-4.45} & \text{trans} \quad \text{Ka}_2 & = 10^{-7.94}
\end{align*}
\]

The following values were obtained for these seven equilibrium constants in 1 M \(\text{NaNO}_3\) solution at 25°:

\[
\begin{align*}
\text{cis} \quad \text{Ka}_1 & = 58 & \text{hydroxo} \quad \text{K} & = 1.42 & \text{dihydroxo} \quad \text{K} & = 0.80 \\
\text{cis} \quad \text{Ka}_2 & = 10^{-8.19}
\end{align*}
\]

isomerisation rate, \(t_{1/2}\) minutes. (forward and reverse reactions)

\[
\begin{align*}
\text{conditions} & \quad \text{diagoon} \quad \text{hydroxo} \quad \text{dihydroxo} \\
\text{0.1 N HNO}_3 & \quad 1020 \quad 637 \quad \text{fast} \quad 1500 \\
\text{0.5 N NaOH} & \quad 1 \text{ M NaNO}_3 \\
\text{1 M NaNO}_3 & \quad 1 \text{ M NaNO}_3
\end{align*}
\]
These show that the trans-diaquo ion is a significantly stronger acid than the cis-diaquo ion. The isomerisation equilibrium constants show that in acid solution trans-diaquo isomerises almost completely to cis, while neutral and alkaline solutions contain about equal amounts of the cis and trans complexes in equilibrium. These equilibria showed little dependence on temperature. In determining these equilibrium constants spectrophotometrically, the authors also measured the rates of approach to equilibrium in the diaquo and dihydroxo species and these rates are indicated above. In acid solution, the rate of trans to cis isomerisation showed a small dependence on $[H^+]$ (10% decrease in rate in the range 0.05 to 0.10 M HNO₃) and a dependence on $\mu$ (rate increased about 30% on changing $\mu$ from 0.06 to 1.0). The rate was increased greatly by the addition of charcoal. The rate of isomerisation of the $[\text{Co en}_2(H_2O)(OH)]^{2+}$ ions was much higher (39) and was not measured quantitatively.

Tong and Yankwich (50) made further rate measurements on this system, but under different conditions of $[H^+]$ (1.0 M HClO₄) to those used by the above authors (0.1 M HNO₃). The half-life for isomerisation of the diaquo ions was found to be 1670 minutes at 24.8°, and was independent of complex concentration. The rate for the dihydroxo species was also independent of $[\text{Co}]$ and independent of $[\text{OH}^-]$ in the range 1.0 to 0.01 M NaOH; $t_{1/2} = 270$ minutes at 35°.

These first-order kinetics give no information as to molecularity but recently Kruse and Taube (51) have remeasured these isomerisation rates and also the water exchange rates in $H_2O^{18}$, for the diaquo, hydroxoao and
dihydroxo ions. The significant results are extracted in table 25. As far as conditions were comparable, agreement was found with rates measured by the previous authors \(^{(46,50)}\). The different rates for the isomerisations of \(\text{trans}[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\) were due to the fact that Bjerrum and Rasmussen used weaker acid solutions and thus measured a greater contribution from the labile hydroxo-aquo species. The rates in the above table show that the isomerisation has an ionic strength dependence and a very marked \([\text{H}^+]\) dependence, with the rate being greatly accelerated at very high \([\text{H}^+]\). Some type of acid-catalysis was indicated and chelate ring opening was suggested. The rates of exchange for cis and trans diaquo and dihydroxo complexes are independent of \([\text{H}^+]\) or \([\text{OH}^-]\) (respectively) at moderate levels, and in this reaction also, the hydroxo-aquo complexes are the most labile. Table 25 also reveals that the exchange and isomerisation kinetics are not related, so that the molecular processes do not bear a 1:1 relationship. However the roughly comparable rates of exchange and isomerisation for \(\text{trans}[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\) and the hydroxo-aquo and dihydroxo species indicated that isomerisation might occur by water exchange. Experiments were then carried out to determine the isotopic enrichment in the product during isomerisation of \(\text{trans}[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}, \text{trans}[\text{Co en}_2(\text{H}_2\text{O})(\text{OH})]^{2+}\) and \(\text{cis}[\text{Co en}_2(\text{OH})_2]^+\). These showed that in the isomerisation of the diaquo and hydroxo-aquo ions the extent of exchange corresponded closely to one of the two water molecules reaching isotopic equilibrium with the solvent. Thus \([\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\) could exchange by a relatively slow aquation-type reaction, but the exchange and isomerisation could still be explained by an
TABLE 25. EXCHANGE AND ISOMERISATION RATES FOR $[\text{Co en}_2 X_2]^{n+}$

at $25^\circ$, $X = \text{H}_2\text{O}$, $\text{OH}^-$. (Reference 51).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Medium</th>
<th>$k \times 10^4$</th>
<th>$\Delta H^\ddagger$</th>
<th>$\Delta S^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EXCHANGE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis$[\text{Co en}_2 (\text{H}_2\text{O})_2]^{3+}$</td>
<td>0.8 M HClO$_4$</td>
<td>4.5</td>
<td>28.3</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>or ${0.3$ M HClO$_4$, 0.5 M NaClO$_4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans$[\text{Co en}_2 (\text{H}_2\text{O})_2]^{3+}$</td>
<td>&quot;</td>
<td>6.8</td>
<td>30.5</td>
<td>21</td>
</tr>
<tr>
<td>cis$[\text{Co en}_2 (\text{H}_2\text{O})(\text{OH})]^2+$</td>
<td>water</td>
<td>$\sim$ 280</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans$[\text{Co en}_2 (\text{H}_2\text{O})(\text{OH})]^2+$</td>
<td>&quot;</td>
<td>$\sim$ 150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis$[\text{Co en}_2 (\text{OH})_2]^+$</td>
<td>0.8 M NaOH</td>
<td>18</td>
<td>27.4</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>or ${0.3$ M NaOH, 0.5 M NaClO$_4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans$[\text{Co en}_2 (\text{OH})_2]^+$</td>
<td>&quot;</td>
<td>1.4</td>
<td>30.4</td>
<td>20</td>
</tr>
<tr>
<td><strong>ISOMERISATION</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans$[\text{Co en}_2 (\text{H}_2\text{O})_2]^{3+}$</td>
<td>10 M HClO$_4$</td>
<td>700*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 M HClO$_4$</td>
<td></td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>${1$ M HClO$_4$, 4 M NaClO$_4}$</td>
<td></td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M HClO$_4$</td>
<td>4.1</td>
<td>25.6</td>
<td>4</td>
</tr>
<tr>
<td>trans$[\text{Co en}_2 (\text{H}_2\text{O})(\text{OH})]^2+$</td>
<td>water</td>
<td>$\sim$ 500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans$[\text{Co en}_2 (\text{OH})_2]^+$</td>
<td>1 M NaOH</td>
<td>1.9</td>
<td>28-31</td>
<td></td>
</tr>
<tr>
<td>cis$[\text{Co en}_2 (\text{OH})_2]^+$</td>
<td>&quot;</td>
<td>2.2</td>
<td>28-31</td>
<td></td>
</tr>
</tbody>
</table>

* forward rates of isomerisation only
intermediate with either a reduced or expanded coordination number. The lability of \([\text{Co en}_2(H_2O)(OH)]^{2+}\) might be due to a trigonal bipyramidal intermediate being stabilised by \(\pi\)-bonding so that this mechanism might be favoured, but the acts of exchange led essentially to retention of configuration. In the isomerisation of \([\text{Co en}_2(OH)_2]^+\) only a fraction of one \(H_2O^{18}\) molecule per ion exchanged for each act of isomerisation, and this together with the fact that \(\Delta H^+\) varied with temperature indicated that more than one mechanism occurred. Certainly exchange was not greatly involved in the isomerisation, and the other path could be Co-NH\(_2\) bond breaking.

The authors were unable to account for all the isomerisation and exchange rates for the diaquo ions on the basis of a single intermediate, but proposed a mechanism involving two intermediates. However these could not be clearly defined, except to suggest that one might be a tetragonal pyramid and the other a trigonal bipyramid if the mechanism were \(S_N\)1. Rough data on the racemisation of \(\text{cis}[\text{Co en}_2(H_2O)_2]^{3+}\) taken from Mathieu\(^{(108)}\) was correlated with the rate of isomerisation of \(\text{cis}[\text{Co en}_2(H_2O)_2]^{3+}\), and this suggested that the cis-trans equilibrium might account for the loss of activity.

A brief study has been made on the corresponding tetrammine diaquo system. Yalman and Kuwana\(^{(66)}\) found that this equilibrium favoured the trans isomer \((\text{trans/cis} = 6.0)\) but undoubtedly hydroxoaquo ions participated greatly at the \([H^+]\) concentration used \((0.001 \text{ M HClO}_4)\).
Monoaquo Complexes

Racemisation and isomerisation studies on cis[Co en\textsubscript{2} Cl(H\textsubscript{2}O)]\textsuperscript{2+} have been mentioned previously (chapter 5), and the rates of these reactions are equal and independent of [H\textsuperscript{+}] over a considerable range. Racemisation therefore occurs by isomerisation of cis to trans, and the most likely mechanism is water exchange.

Rates and equilibria which have been measured for other complexes of this type [Co en\textsubscript{2}(H\textsubscript{2}O) X]\textsuperscript{n+} are summarised in table 26. Clearly these depend on the nature of the orienting ligand X. The only complete set of studies has been made on the isomers of [Co en\textsubscript{2}(NH\textsubscript{3})(H\textsubscript{2}O)]\textsuperscript{3+} by Martin and Tobe\textsuperscript{144}, who found that the isomerisation rates obeyed the formula:

\[
\frac{k_1}{k_{obs}} + \frac{k_2 K_a}{[H^+]} \]

Racemisation rates conformed to a similar expression, and these observations were consistent with two paths for these reactions:

\[
\begin{align*}
\text{trans[Co en}_2(\text{NH}_3)(\text{H}_2\text{O})]\textsuperscript{3+} & \xrightleftharpoons[K_a]{k_1} \text{trans[Co en}_2(\text{NH}_3)(\text{OH})]\textsuperscript{2+} + \text{H}^+ \\
\text{cis[Co en}_2(\text{NH}_3)(\text{H}_2\text{O})]\textsuperscript{3+} & \xrightleftharpoons{k_2} \text{cis[Co en}_2(\text{NH}_3)(\text{OH})]\textsuperscript{2+} + \text{H}^+
\end{align*}
\]

Rates of isomerisation, racemisation and exchange have been separated into
<table>
<thead>
<tr>
<th>Complex</th>
<th>Conditions</th>
<th>Cis/trans at equilibrium</th>
<th>Rate racemisation</th>
<th>Rate isomerisation</th>
<th>Rate $H_2O^{18}$ exchange</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co}en_2(H_2O)Cl]^{2+}$</td>
<td>0.01-0.1 M HClO$_4$, 30°</td>
<td>2.7</td>
<td>$k = 2.6 \times 10^{-3}$</td>
<td>$k_0 = 2.7 \times 10^{-3}$</td>
<td>$k_0$</td>
<td>(45)</td>
</tr>
<tr>
<td>$[\text{Co}en_2(H_2O)F]^{2+}$</td>
<td>0.1 M HNO$_3$, 25°</td>
<td></td>
<td>$k = 3.9 \times 10^{-4}$</td>
<td></td>
<td></td>
<td>(123)</td>
</tr>
<tr>
<td>$[\text{Co}en_2(H_2O)NO_2]^{2+}$</td>
<td>$H_2O$, 90°</td>
<td>0.45</td>
<td>$k \triangleleft 4 \times 10^{-5}$</td>
<td></td>
<td></td>
<td>(97)</td>
</tr>
<tr>
<td></td>
<td>0.01 M HNO$_3$, 30°</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(108)</td>
</tr>
<tr>
<td>$[\text{Co}en_2(H_2O)NCS]^{2+}$</td>
<td>0.007-0.5 M HClO$_4$, 63°</td>
<td>4.6</td>
<td></td>
<td>$k_0 + k_t = 9.8 \times 10^{-3}$</td>
<td>(127)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01 M HNO$_3$, 30°</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(108)</td>
</tr>
<tr>
<td>$[\text{Co}en_2(H_2O)NH_3]^{3+}$</td>
<td>aquo, trans (hydroxo)</td>
<td>100% cis</td>
<td>$k_1 = 3 \times 10^{-6}$</td>
<td>$k_1 = 2.7 \times 10^{-4}$</td>
<td></td>
<td>(144)</td>
</tr>
<tr>
<td></td>
<td>cis aquo in HClO$_4$, 25°</td>
<td></td>
<td>$k_1 = 1.8 \times 10^{-6}$</td>
<td></td>
<td>$k_1 = 6.6 \times 10^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>
the contributions from the aquo \((k_1)\) and hydroxo species \((k_2)\) in table 26. All the exchange observations, including those of Kruse and Taube, on aquo compounds \([\text{Co en}_2\text{H}_2\text{O}^X]^n^+\) where \(X = \text{NH}_3, \text{H}_2\text{O},\) or \(\text{OH}^-\), can be reconciled if water exchange is visualised as an aquation process in which the replaced ligand is also water. Then when \(X = \text{H}_2\text{O}\) or \(\text{OH}^-\), most exchange acts must result in steric change (isomerisation), whereas when \(X = \text{NH}_3\), exchange occurs with about 99\% retention (exchange rates are about 100 times faster than isomerisation or racemisation rates). It is likely that aquation of the aquo complexes (exchange) is mechanistically very similar to aquation of the corresponding chloro complexes \([\text{Co en}_2\text{Cl}^X]^n^+\).

Martin and Tobe prefer a bimolecular mechanism to explain all the data for \([\text{Co en}_2\text{H}_2\text{O}(\text{NH}_3)]^3^+\), with largely cis-attack to explain the high degree of retention of configuration in exchange. Some trans-attack however would account for the isomerisation and racemisation. However they could not rigorously exclude an \(S_N^1\) mechanism, with a square pyramid intermediate partly rearranging to a trigonal bipyramid. Basolo and Pearson have pointed out \((101,145)\) that the involvement of the latter intermediate is likely due to \(\pi\)-bonding, in racemisation and isomerisation of \(\text{cis}[\text{Co en}_2\text{H}_2\text{O}\text{Cl}]^{2^+}\), and this was also the explanation used by Kruse and Taube for the hydroxo compound \([\text{Co en}_2\text{H}_2\text{O}(\text{OH})]^2^+\).

Water exchange is not involved in the isomerisation of \([\text{Co en}_2(\text{NH}_3)(\text{OH})]^2^+\), (table 26) and the authors suggested an intramolecular mechanism where one end of an ethylenediamine group dissociates. This parallels the situation found in \([\text{Co en}_2(\text{OH})_2]^+\), and an intramolecular mechanism was suggested as one of the mechanisms in this isomerisation also \((51)\).
The incompleteness of much of the data on these aquo complexes suggests many useful experiments. Often rates have been determined only over a limited pH range, sometimes only at one pH, but it is clear from the discussion on aquation of the \([\text{Co trien Cl(H}_2\text{O)}]^2^+\) complexes (chapter 5) that in general the observed rates should obey an equation of the form

\[
k_{\text{obs}} = k_H[H^+] + \frac{k_{OH}K_a}{[H^+]} + k_{H_2O}
\]

where the three terms refer to independent reaction paths. From much of the reported data, the relative magnitudes of the three paths are not clear, but it appears likely that for isomerisation of \([\text{Co en}_2 \text{Cl(H}_2\text{O)}]^2^+\) and \([\text{Co en}_2 \text{NCS(H}_2\text{O)}]^2^+\) only \(k_{H_2O}\) is important. In other instances, such as \([\text{Co en}_2 (\text{NH}_3)(\text{H}_2\text{O)}]^3^+\), the \(k_{OH}\) term is most significant. In most of the systems acid catalysis has not been investigated. It can also be expected that water exchange experiments will play an increasingly important part in these mechanistic studies.

In the trien diaquo system, the kinetics of isomerisation and racemisation have been studied over the pH range 0 to 3, and the observed rate constants have been separated into the components.

THE DIAQUO TRIEN COMPLEXES: RESULTS AND DISCUSSION

Both cis isomers isomerise and lose activity and as the rates are slow, elevated temperatures were used. The rates were determined under various conditions of complex concentration \([\text{Co}], [\text{HClO}_4]\) and temperature,
and the ionic strength \( \mu \) was usually maintained constant at 0.1 by adding NaClO₄.

The compounds isomerise to an equilibrium mixture of the \( \alpha \) and \( \beta \) diaquo isomers, so that the rates of isomerisation measured spectrophotometrically are the sum of the forward and reverse reactions \( (k_\alpha + k_\beta) \). The position of the \( \beta/\alpha \) diaquo equilibrium was assessed from the spectrum of the equilibrium diaquo solution, or after this was converted to a solution of the mixed carbonato isomers.

Rate data are given in tables 27 and 28, where all rate constants are in units of min⁻¹, and the notation \( k_\alpha \) refers to the rate of isomerisation of the \( \alpha \) to \( \beta \) diaquo isomer. The acid dissociation constants of the cis diaquo compounds measured at 10° and 20° are given in table 29.

The cis \( \alpha \) diaquo system

The equilibrium solutions containing the two diaquo isomers from all the runs had the same absorption (after at least eight half-lives) of \( \epsilon_{487} = 112.7 \pm 1.6 \) (S.E.). The absorptions of the pure diaquo isomers under the same conditions were \( \epsilon_\beta = 122 \), \( \epsilon_\alpha = 82 \), from which it was calculated that the equilibrium position, independent of temperature and \( [H^+] \), was 77% of the \( \beta \) isomer, 23% \( \alpha \). (Similar calculations using absorptions measured on the manual spectrophotometer gave 75 \( \pm \) 7% \( \beta \)). The equilibrium absorption of the transformed carbonato solutions from all runs was \( \epsilon_{\text{max at 506 m}} = 169.3 \pm 0.5 \) (S.E.), and using \( \epsilon_\beta = 178 \), \( \epsilon_\alpha = 120 \), the equilibrium was calculated as 85 \( \pm \) 5% of the \( \beta \) diaquo isomer. Since there was no preference for either method, (80 \( \pm \) 5)% \( \beta \) was taken as the
<table>
<thead>
<tr>
<th>Run No.</th>
<th>[H⁺] (M)</th>
<th>t°C</th>
<th>[Co]</th>
<th>[NaClO₄]</th>
<th>μ</th>
<th>$k_{rac} \times 10^4$</th>
<th>$(k_α + k_β) \times 10^4$</th>
<th>$k_α \times 10^4$</th>
<th>$k_β \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>83</td>
<td>1.02</td>
<td>60</td>
<td>0.001</td>
<td>-</td>
<td>1.0</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>84</td>
<td>0.102</td>
<td>60</td>
<td>&quot;</td>
<td>-</td>
<td>0.10</td>
<td>1.87</td>
<td>2.6</td>
<td>2.1</td>
<td>0.5</td>
</tr>
<tr>
<td>85</td>
<td>0.051</td>
<td>60</td>
<td>&quot;</td>
<td>0.049</td>
<td>0.10</td>
<td>3.63</td>
<td>4.70</td>
<td>3.7</td>
<td>1.0</td>
</tr>
<tr>
<td>86</td>
<td>0.0102</td>
<td>40</td>
<td>&quot;</td>
<td>0.065</td>
<td>0.10</td>
<td>0.363</td>
<td>&lt; 0.33</td>
<td>&lt; 0.29</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>87</td>
<td>&quot;</td>
<td>60</td>
<td>&quot;</td>
<td>0.035</td>
<td>0.05</td>
<td>21.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>88</td>
<td>&quot;</td>
<td>60</td>
<td>&quot;</td>
<td>0.065</td>
<td>0.10</td>
<td>17.2</td>
<td>24</td>
<td>19</td>
<td>5</td>
</tr>
<tr>
<td>89</td>
<td>&quot;</td>
<td>60</td>
<td>0.003</td>
<td>0.072</td>
<td>0.10</td>
<td>18.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>65</td>
<td>0.001</td>
<td>0.064</td>
<td>0.10</td>
<td>42.1</td>
<td>64</td>
<td>51</td>
<td>13</td>
</tr>
<tr>
<td>91</td>
<td>&quot;</td>
<td>70</td>
<td>&quot;</td>
<td>0.064</td>
<td>0.10</td>
<td>101</td>
<td>155</td>
<td>124</td>
<td>31</td>
</tr>
<tr>
<td>92</td>
<td>0.0051</td>
<td>60</td>
<td>&quot;</td>
<td>0.069</td>
<td>0.10</td>
<td>34.3</td>
<td>45</td>
<td>36</td>
<td>9</td>
</tr>
<tr>
<td>93</td>
<td>0.00204</td>
<td>60</td>
<td>&quot;</td>
<td>0.092</td>
<td>0.10</td>
<td>89</td>
<td>122</td>
<td>97</td>
<td>25</td>
</tr>
<tr>
<td>94</td>
<td>0.00102</td>
<td>40</td>
<td>&quot;</td>
<td>0.095</td>
<td>0.10</td>
<td>3.90</td>
<td>4.67</td>
<td>3.7</td>
<td>1.0</td>
</tr>
<tr>
<td>95</td>
<td>&quot;</td>
<td>60</td>
<td>&quot;</td>
<td>0.097</td>
<td>0.10</td>
<td>173</td>
<td>214</td>
<td>171</td>
<td>43</td>
</tr>
<tr>
<td>96</td>
<td>&quot;</td>
<td>70</td>
<td>&quot;</td>
<td>0.099</td>
<td>0.10</td>
<td>670</td>
<td>&lt; 900</td>
<td>&lt; 700</td>
<td>&lt; 200</td>
</tr>
<tr>
<td>97</td>
<td>0.0002</td>
<td>60</td>
<td>&quot;</td>
<td>0.092</td>
<td>0.10</td>
<td>560</td>
<td>730</td>
<td>580</td>
<td>150</td>
</tr>
<tr>
<td>Run No.</td>
<td>$[H^+]$</td>
<td>$t^\circ C$</td>
<td>$[\text{Co}]$</td>
<td>$[\text{NaClO}_4]$</td>
<td>$\mu$</td>
<td>$k_{\text{rac}} \times 10^3$</td>
<td>$\mu$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>-------------</td>
<td>-------------</td>
<td>----------------</td>
<td>--------</td>
<td>------------------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>1.02 M</td>
<td>40</td>
<td>0.0013</td>
<td>-</td>
<td>1.02</td>
<td>0.083</td>
<td>440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99</td>
<td>0.102</td>
<td>40</td>
<td>&quot;</td>
<td>-</td>
<td>0.110</td>
<td>0.16</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.0102</td>
<td>25</td>
<td>&quot;</td>
<td>0.077</td>
<td>0.095</td>
<td>0.109</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>&quot;</td>
<td>35</td>
<td>&quot;</td>
<td>0.077</td>
<td>0.095</td>
<td>0.62</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>&quot;</td>
<td>40</td>
<td>0.0026</td>
<td>0.069</td>
<td>0.096</td>
<td>1.29</td>
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<td></td>
</tr>
<tr>
<td>103</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.0013</td>
<td>0.077</td>
<td>0.095</td>
<td>1.68</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.058</td>
<td>0.076</td>
<td>1.61</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.041</td>
<td>0.059</td>
<td>1.57</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.021</td>
<td>0.039</td>
<td>1.68</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.007</td>
<td>0.024</td>
<td>2.17</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>108</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
<td>0.018</td>
<td>2.90</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>109</td>
<td>&quot;</td>
<td>50</td>
<td>&quot;</td>
<td>0.077</td>
<td>0.095</td>
<td>7.84</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>0.0051</td>
<td>40</td>
<td>&quot;</td>
<td>0.082</td>
<td>0.095</td>
<td>3.28</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>0.00204</td>
<td>40</td>
<td>&quot;</td>
<td>0.085</td>
<td>0.095</td>
<td>8.24</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>0.00102</td>
<td>40</td>
<td>&quot;</td>
<td>0.085</td>
<td>0.094</td>
<td>16.4</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>113</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.0024</td>
<td>-</td>
<td>0.016</td>
<td>31</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.0030</td>
<td>-</td>
<td>0.019</td>
<td>30</td>
<td>578 (visually)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>0.0002</td>
<td>40</td>
<td>0.0013</td>
<td>0.086</td>
<td>0.094</td>
<td>56</td>
<td>440</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 29. ACID DISSOCIATION CONSTANTS OF TRIEN DIAQUO COMPLEXES*

<table>
<thead>
<tr>
<th>Isomer</th>
<th>(+)<a href="ClO%E2%82%84">Cotrien(H₂O)₂</a>₃</th>
<th>(-)<a href="ClO%E2%82%84">Cotrien(H₂O)₂</a>₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(++)</td>
<td>(-)</td>
</tr>
<tr>
<td>pKₐ₁ (at 10°)</td>
<td>5.8 ± 0.05</td>
<td>5.6 ± 0.05</td>
</tr>
<tr>
<td>pKₐ₁ (at 20°)</td>
<td>5.4 ± 0.05</td>
<td>5.3 ± 0.05</td>
</tr>
</tbody>
</table>

| pKₐ₂ (at 10°)   | 7.6 ± 0.1                 | 7.9 ± 0.1                 |
| pKₐ₂ (at 20°)   | 7.3 ± 0.1                 | 7.8 ± 0.1                 |

* Concentration pKₐ's at 0.1 μ (NaClO₄).

Mean + maximum deviation from three titrations.
equilibrium position in the diaquo system.

In the preparation of $[\text{Co trien CO}_3]^+$ from $[\text{Co trien Cl}_2]\text{Cl}$ and $\text{Li}_2\text{CO}_3$ in approximately neutral solution, the isomerisation probably takes place largely through the cis hydroxoaquo isomers (p. 22). Thus it seems likely from this preparation that this equilibrium favours the $[\text{Co trien(OH)(H}_2\text{O)}]^{2+}$ isomer and this agrees with the above observation, that the diaquo equilibrium is independent of pH.

Now the observed isomerisation rates are due to the forward and reverse reactions, and using the above equilibrium position the observed rates have been separated into the individual components by taking

$$k_\alpha = 80\% \text{ of } (k_\alpha + k_\beta),$$

in table 27. The rates $k_\alpha$ are then seen to closely parallel the rates $k_{\text{rac}}$ over the complete range of temperature and $[H^+]$ studied, so that the loss of activity of $[\text{Co trien(H}_2\text{O)}]^{3+}$ is due to its isomerisation to the $[\beta$] isomer, and $k_{\text{rac}} \approx k_\alpha$.

The rates show no dependence on $[\text{Co}]$ (runs 88 and 89) but decrease as $\mu$ increases (runs 87 and 88). The $\mu$ dependence of the rates is due to the variation of $pK_a$ with $\mu$; $pK_{a1}$ was found to increase as $\mu$ increased, so that there was less contribution from the labile hydroxoaquo species at high $\mu$. (This variation of rate with $\mu$ is opposite to the trend noted for the isomerisation of $\text{trans[Co en}_2\text{(H}_2\text{O)}]^{3+}$, p.67). All the other runs were carried out at constant ionic strength, $\mu = 0.1$.

When the $[H^+]$ dependence of the rates at 60° and $\mu = 0.1$ is plotted as $\log k_{\text{rac}}$ vs. $\log [H^+]$ (figure 71), all the experimental points in the range $0.1 > [H^+] > 0.001 \text{ M}$ are seen to lie on a straight line (slope 0.985). However the point at $[H^+] = 1.0 \text{ M}$ lies slightly above this line, so that
Figure 71. Isomerisation of $\text{CIS} \approx [\text{CoTien} (\text{H}_2\text{O})_2]^{3+}$

[$\text{H}^+]$ dependence of $k_{\text{rac}}$ at $60^\circ\text{C}, \mu=0.10$. 
the data can be represented by the equation

\[ k_{\text{obs}} = k_1 + \frac{k_2}{[H^+]} \]

When this is solved using the data at \([H^+] = 0.00102 \text{ M} \) (run 95) and \(0.102 \text{ M} \) (run 84),

\[ k_{\text{obs}} \times 10^4 = 0.141 + \frac{0.1729 \times 1.02}{[H^+]} \text{ min}^{-1} \]

The contributions from the two paths, and the total rate constant \((x 10^4 \text{ min}^{-1})\) can then be calculated at any \([H^+]\), as below.

<table>
<thead>
<tr>
<th>([H^+])</th>
<th>(k_1)</th>
<th>(k_2/[H^+])</th>
<th>(k_{\text{calc}})</th>
<th>(k_{\text{obs}})</th>
<th>run no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00102 M</td>
<td>0.14</td>
<td>172.86</td>
<td>173.00</td>
<td>173 (=(k_{\text{calc}}))</td>
<td>95</td>
</tr>
<tr>
<td>0.0102</td>
<td>0.14</td>
<td>17.29</td>
<td>17.43</td>
<td>17.6</td>
<td>88</td>
</tr>
<tr>
<td>0.102</td>
<td>0.14</td>
<td>1.73</td>
<td>1.87</td>
<td>1.87 (=(k_{\text{calc}}))</td>
<td>84</td>
</tr>
<tr>
<td>1.02</td>
<td>0.14</td>
<td>0.17</td>
<td>0.31</td>
<td>0.23</td>
<td>83</td>
</tr>
</tbody>
</table>

At \([H^+] \leq 0.1 \text{ M}\) the agreement between \(k_{\text{calc}}\) and \(k_{\text{obs}}\) is better than 3\% (runs 85, 88, 92, 93), but the values at \([H^+] = 1.0 \text{ M} \) (run 83) are not comparable because \(k_{\text{obs}}\) refers to \(\mu = 1.0\). Thus the constant term \(k_1 = 0.14 \times 10^{-4}\) can be attributed to isomerisation of the aquo species, while \(k_2 = 0.176 \times 10^{-4} = k_{\text{OH}} K_a \) represents the major contribution to the overall rate through the hydroxoaquo species. This accords with the relative rates for the corresponding paths in \(\text{trans}[\text{Co en}_2(\text{NH}_3)\text{H}_2\text{O}]^{3+}\) isomerisation (table 26). The aquo reaction path makes negligible
contribution over the range $0.1 > [H^+] > 0.001 \text{ M}$, and the equality of the measured activation energies $E_{a_{\text{obs}}}$ at $[H^+] = 0.01$ and $0.001 \text{ M}$ (see below) agrees with this. The reaction scheme is thus defined as follows:

$$
(+)[Co \text{ trien}(H_2O)_2]^{3+} \xrightleftharpoons{K_a} (+)[Co \text{ trien}(H_2O)(OH)]^{2+} + H^+
$$

$$
(+)[Co \text{ trien}(H_2O)(OH)]^{2+} + H^+ \xrightarrow{k_2^*} \text{Co trien}(H_2O) + H_2O^-
$$

That the trans diaquo isomer was not present to measurable extents in these equilibria is seen from the following evidence: (1) the equilibrium spectra are intermediate between those of the $a$ and $\beta$ isomers. The trans isomer would have a minimum in the region of the cis maxima (figure 12); (2) the amount of isomerisation of cis $a \rightarrow$ cis $\beta$ is sufficient to account completely for the racemisation; (3) trans[Co trien Cl(H_2O)]^{2+} is unstable, and isomerises rapidly and completely to the cis $\beta$ configuration. However the trans isomer is not thereby excluded from participating in the mechanism and this is discussed later.

$E_{a_{\text{obs}}}$ at $[H^+] = 0.01 \text{ M}$, $\mu = 0.1$, was calculated from the data of runs 86, 88, 90, 91 (figure 72) by regression to give $E_{a_{\text{obs}}} = 40.0 \pm 0.1 \text{ kcal mole}^{-1}$ (S.E.) (From runs 94 and 95, $E_{a_{\text{obs}}} = 39.3$ at $[H^+] = 0.001 \text{ M}$).
FIGURE 72. ISOMERISATION OF CIS = [Cotrien(H₂O)₂]³⁺

TEMPERATURE DEPENDENCE OF $k_{rac}$ AT $[H^+] = 0.01$, $\mu = 0.1$. 
It has already been shown that at 0.01 M HClO₄ almost all of the reaction occurs by the hydroxo aquo path, so $E_a^{\text{obs}}$ is due to this path only. However $E_a^{\text{obs}}$ includes the temperature variation of $K_a$, and this can be allowed for by using the following relationships which hold at $[H^+] = 0.01 \text{ M}$. 1 and 2 denote two temperatures $T_1$ and $T_2$.

$$
\frac{k_{\text{obs}}}{k_{\text{obs}}} = \frac{k_{\text{OH}} \cdot K_a}{[H^+]}
$$

$$
\frac{k_{\text{obs}}}{k_{\text{obs}}} \frac{1}{2} = \frac{k_{\text{OH}} \cdot k_{\text{a}}}{k_{\text{OH}} \cdot k_{\text{a}}}
$$

Now

$$
\log \left( \frac{k_{\text{obs}}}{k_{\text{obs}}} \right) = - \frac{E_a^{\text{obs}}}{4.576} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
$$

and

$$
\log \left( \frac{k_{\text{OH}}}{k_{\text{OH}}} \right) = - \frac{E_a^{\text{OH}}}{4.576} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
$$

$$
E_a^{\text{OH}} = E_a^{\text{obs}} - \frac{(pK_1^1 - pK_2^2) 4.576}{\frac{1}{T_1} - \frac{1}{T_2}}
$$

Substituting the values $E_a^{\text{obs}} = 40.0$, and the $pK$ values measured at 10° and 20° (table 29),

$$
\frac{E}{a_{\text{OH}}} = \frac{(248 + 4)}{\text{kcal mole}^{-1}}
$$
To calculate $\Delta S^\ddagger$, the following values were used at 40°:

$$k_{OH}K_a = 0.363 \times 10^{-4} \text{ M.min}^{-1} \text{ (run 86), } pK_a = 4.7 \pm 0.1 \text{ (by extrapolation), }$$

whence $k_{OH} = 1.78 \text{ M.min}^{-1}$, $E_a_{OH} = 24.8 \text{ kcal.mole}^{-1}$. Substitution in the transition state equation gives

$$\Delta S_{OH}^\ddagger = + 12 \text{ e.u. (} \pm 13\text{)}$$

The errors in these calculations arise mainly from the errors in the $pK_a$ values, and the resulting error in $E_a_{OH}$ translates to a larger uncertainty in $\Delta S_{OH}^\ddagger$. However it appears that the activation entropy is positive.

The cis $\beta$ diaquo system

The rates of racemisation of $\beta[\text{Co trien(H$_2$O)$_2$}(\text{ClO}_4)_3$ (table 28) show a significant dependence on concentration (runs 102, 103) and also a dependence on $\mu$ at low values. However saturation appears to be reached as $\mu$ increases to about 0.04 as above this value the rates are constant (runs 103 to 108).

The log - log plot of rate vs. $[H^+]$ is linear in the range $0.1 > [H^+] > 0.001 \text{ M}$, with slope 1.00 (figure 73). However the point at $[H^+] = 1.0 \text{ M}$ shows that another reaction path is important here, and this could be either through the diaquo species or a protonated species, so the complete equation to express the data would be

$$k_{obs} = k_H[H^+] + k_{H_2O} + \frac{k_{OH}K_a}{[H^+]}$$
FIGURE 73. RACEMISATION OF CIS\(\beta\) [\(\text{Co}\text{t}r\text{ien}(\text{H}_2\text{O})_2\)]\(^{3+}\)

\([\text{H}^+]\) Dependence at 40°, \(\mu = 0.1\)
However the available data is not sufficient to solve for $k_H$ and $k_{H_2O}$. Although the relative importance of these paths can not be accurately determined, it seems likely from comparison with the a diaquo system and with the chloroaquo aquations (chapter 5) that acid-catalysis is more important in the $\beta$ diaquo system. To a first approximation therefore $k_{H_2O}$ will be neglected, and the data will be fitted to the equation

$$k_{\text{obs}} = k_H [H^+] + \frac{k_{OH} K_a}{[H^+]}.$$

Solution of this equation from the points $[H^+] = 1.02, 0.00102$ M (runs 98, 112) gives:

$$k_{\text{obs}} \times 10^4 = \frac{0.67}{1.02} [H^+] + \frac{0.164 \times 1.02}{[H^+]} \text{ min}^{-1} \text{ at } 40^\circ.$$

The contributions at various conditions of $[H^+]$ are then ($x 10^4$ min$^{-1}$):

<table>
<thead>
<tr>
<th>$[H^+]$</th>
<th>$k_H [H^+]$</th>
<th>$\frac{k_{OH} K_a}{[H^+]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00102 M</td>
<td>0.00</td>
<td>164</td>
</tr>
<tr>
<td>0.0102</td>
<td>0.01</td>
<td>16.40</td>
</tr>
<tr>
<td>0.102</td>
<td>0.07</td>
<td>1.64</td>
</tr>
<tr>
<td>1.02</td>
<td>0.67</td>
<td>0.16</td>
</tr>
</tbody>
</table>

and the agreement between $k_{\text{calc}}$ and $k_{\text{obs}}$ is within 6.5% (runs 99,103,110; 111). Extrapolation of a $k_{\text{obs}}$ vs. $\frac{1}{[H^+]}$ plot to $\frac{1}{[H^+]} = 0$ puts an upper limit on $k_{H_2O}$ for the acid independent path (through the diaquo) of $0.5 \times 10^{-4}$ min$^{-1}$ at $40^\circ$, so that the contribution from this path may be important only at 1.0 M $[H^+]$. 
In the range of $[H^+]$ up to 0.1 M, essentially all the racemisation
proceeds therefore through the labile hydroxo aquo species. For this
reaction path the rates from runs 100, 101, 103, 109 were used to compute
$E_{a_{obs}} = 32.9 \pm 0.7$ kcal mole$^{-1}$ (S.E.) (figure 74). Substituting in the
equation

$$E_{a_{OH}} = E_{a_{obs}} - \frac{\Delta(pK_a) 4.576}{\Delta \left(\frac{1}{T}\right)}$$

using the $pK_a$ data in table 29,

$$E_{a_{OH}} = 21.5 \pm 4.5$$

$\Delta S_{OH}^{\neq}$ was calculated as described for the $a$ isomer to be

$$\Delta S_{OH}^{\neq} = + 9 \text{ e.u.} (\pm 15)$$

($k_{rac} = 1.68 \times 10^{-3}$ at 40°C, $pK_a = 4.7 \pm 0.1$ (by extrapolation) whence

$k_{OH} = 62.1 \text{ M.min}^{-1}$ at 40°C, $E_{a_{OH}} = 21.5$). Again, it appears that $\Delta S^{\neq}$ is
probably positive.

It will be noted that for both $a$ and $\beta$ isomers the hydroxo aquo has a
much higher absolute rate than the diaquo reaction. Insufficient data is
available to calculate the parameters for the diaquo and acid-catalysed
paths for isomerisation and racemisation, and these would have to be
obtained from measurements at acid concentrations higher than used in the
present work.
FIGURE 74. RACEMISATION OF CIS & [Cotrien(H$_2$O)$_2$]$^{3+}$, TEMPERATURE DEPENDENCE AT [H$^+$] = 0.01, $\mu = 0.1$
MECHANISM

The rate parameters for the reactions of the two hydroxo aquo isomers are summarised below.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_{OH}$ M min$^{-1}$ at 40°</th>
<th>$E_a$</th>
<th>$\Delta S^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerisation of $\alpha$[Cotrien(H$_2$O)(OH)]$^{2+}$</td>
<td>1.78</td>
<td>24.8</td>
<td>+12</td>
</tr>
<tr>
<td>Racemisation of $\beta$[Cotrien(H$_2$O)(OH)]$^{2+}$</td>
<td>82.1</td>
<td>21.5</td>
<td>+9</td>
</tr>
</tbody>
</table>

It seems that the difference in rates of these reactions, if they occur by similar mechanisms, may be due largely to the difference in activation energies, although the $\Delta S^f$ values are somewhat uncertain. However $\Delta S^f$ is positive in each instance and is also of the same order as those for the exchange and isomerisation of $[\text{Co} \text{en}_2(H_2O)_2]^{3+}$ isomers (table 25). Unfortunately the activation parameters have not been measured for the bis(en) hydroxo aquo isomers (table 25). In considering possible mechanisms, the displacement of secondary nitrogen atoms has been excluded from discussion because this would involve the extensive rearrangement of at least two interdependent chelate rings. An intramolecular mechanism of the type suggested by Ray and Dutt$^{(145)}$ has also been excluded as this also would be considered to involve excessive bond rearrangement. A common mechanism might be expected for the isomerisation and racemisation reactions of the two cis hydroxo aquo isomers and for these reactions in the bis(ethylenediamine) system, so that any postulated mechanism should be consistent with all the observations on these systems. Possible mechanisms for racemisation of $\beta$[Cotrien(H$_2$O)(OH)]$^{2+}$ are the following, and are
illustrated in figure 75.

(a) $\mathrm{S}\_1$ dissociation of water, to give a trigonal bipyramidal intermediate which would be stabilised by $\pi$-bonding from the OH group (figure 75 a) seems the most plausible mechanism. The three other 5-coordinated intermediates from water dissociation are excluded either on stereochemical grounds, or by the fact that they would lead to the $\alpha$ isomer which was not observed (exclusively $\alpha$ from one intermediate, $\alpha$ and $\beta$ from another).

Further it has been shown that the rates of racemisation of $\beta$ are very much greater than the rate of isomerisation of $\alpha \rightarrow \beta$. The water molecule could re-enter at the three positions indicated (figure 75 a) to give a mixture of the original active cis $\beta$ compound, and the corresponding trans isomer. This latter is likely to exchange water rapidly (by comparison with $\text{trans[Co trien Cl(H\textsubscript{2}O)]}^{2+}$ and $\text{trans[Co en\textsubscript{2} Cl(H\textsubscript{2}O)]}^{2+}$ isomerisations, and water exchange in $\text{trans[Co en\textsubscript{2} (OH)(H\textsubscript{2}O)]}^{3+}$) to give racemic $\beta[\text{Co trien(H\textsubscript{2}O)(OH)}]^{2+}$. This postulated mechanism would invoke that water exchange of $\beta[\text{Co trien(H\textsubscript{2}O)(OH)}]^{2+}$ and isomerisation of $\text{trans[Co trien(H\textsubscript{2}O)(OH)]}^{2+}$ are both more rapid than the observed racemisation rate. Because of the high rate of water exchange in $[\text{Co en\textsubscript{2}(H\textsubscript{2}O)}\textsubscript{2}]^{3+}$, it seems likely that the water will exchange most of the time with retention but some exchange acts will give the trans as a labile intermediate by the water re-entering at position C (figure 75 a). This mechanism is favoured for the bis(en) system, and the difference in rates between the bis(en) and trien racemisations may be due to the restriction in ease of rearrangement of the trien intermediate (figure 75 a) by the additional steric factor in the
Figure 75. Possible mechanisms for racemisation of $\beta[\text{Cotrien(H}_2\text{O)}(\text{OH})]^{2+}$. 
central ethylene bridge.

(b) $S_{N1}$ dissociation of a Co-N bond. The OH group could weaken all bonds by a reduction of charge from that of the diaquo ion. After Co-N dissociation $\pi$-bonding could again stabilise the intermediate (figure 75 b). Reassociation at the three indicated positions would give a mixture of D cis $\beta$, L cis $\beta$ and trans isomers.

(c) Intramolecular racemisation, in which the octahedron is viewed as a trigonal antiprism and the indicated trigonal face rotates, could lead directly to racemisation $^{(145)}$ (figure 75 c).

(d) $S_{N2}$ trans attack of water would have to be stereospecific at the face indicated (figure 75 d) and for this reason is the least favoured of these possibilities. Attack at other faces would lead to the $\alpha$ structure.

Although the diaquo path contributes its rate is small, and this corresponds to the relative diaquo and hydroxo aquo rates in the bis(en) system. No choice can be made from the above four mechanisms for this reaction, although Kruse and Taube favoured water exchange in the bis(en) diaquo complexes.

The acid-catalysed path involves a protonated intermediate. It is conceivable that the rate of water exchange increases at high $[H^+]$, since protonation of an aquo group would create a large repulsion factor in $[\text{Co trien(H}_2\text{O)}(\text{H}_3\text{O}^+)]^{3+}$ and facilitate water dissociation. It was noted
in the bis(en) system that the isomerisation rates increase rapidly at high \([H^+]\), but the corresponding water exchange rates were not measured at these high \(H^+\) concentrations. It is also possible that the intermediate where the Co-N bond dissociates (figure 75 b) could account for the increased rates of racemisation, since the dissociated amino group could protonate and not re-form easily before the water had reassociated. This mechanism need not require rapid water exchange whereas the water dissociation mechanism would, so \(H_2O^{18}\) studies might define the system more clearly. The intramolecular mechanism would not be expected to be acid-catalysed.

The same four mechanisms are able to account for all observations on the cis \(\alpha\) system, and all lead to the \(\beta\) isomer having the opposite absolute configuration to that of the reactant. The mechanisms are outlined in figure 76. Since the rate of racemisation of \(\beta\) is much greater than the rate of isomerisation of \(\alpha \rightarrow \beta\) the inversion is not observed, and only racemic \(\beta\) is obtained. The higher \(E_a\) and slower rate of this reaction is in accord with the greater steric strain in the intermediates formed by \(S_N^1\) dissociation, compared to the \(\beta\) system. By analogy with the bis(en) system it would seem that the first intermediate is the most likely, with most of the water exchange taking place with retention at position A and some with isomerisation at B (figure 76). Again the rates are much slower than in the bis(en) system.
Figure 76. Mechanisms for \( \alpha \rightarrow \beta \) isomerisation of \([\text{CoTrient}(\text{H}_2\text{O})(\text{OH})]^2+\).
EXPERIMENTAL

Isomerisation and loss of activity of the α diaquo isomer

Isomerisation of the α to β diaquo ions was measured spectrophotometrically at 467 mÙ where the maximum difference in absorptions was observed (εβ = 122, εα = 83). This was the wavelength of maximum absorption of the β isomer, figure 11. Since the isomerisation proceeded to an equilibrium mixture (about 80% β, 20% α) the observed density changes were not great (D changed from 0.41 to 0.55), so that high accuracy could not be expected.

The positions of equilibrium were assessed directly by comparing the equilibrium absorptions with those of the pure cis diaquo isomers, but were calculated more accurately by transforming the equilibrium solutions to the mixtures of carbonato isomers with excess NaHCO₃, and comparing the measured absorptions (at 505 mÙ) with those of the pure carbonato isomers. Beer's law was rigidly obeyed by β[Co trien(H₂O)₂]³⁺ over the concentration range used.

The loss of activity of α[Co trien(H₂O)₂](ClO₄)₃ was conveniently followed at 546 mÙ (figure 31) and since the rate of racemisation of the β isomer is much greater than the rate of loss of activity of cis α, zero was used as the infinity rotation, and the data were plotted as log α₅₄₆ vs. t.

Solutions were made up by adding appropriate volumes of HClO₄ solutions to weighed amounts of the diaquo complexes, and sufficient NaClO₄.
was added to give ionic strengths ≈ 0.1. Solutions were sealed into pyrex tubes and placed in an oil bath controlled to ± 0.1°C. For each reading the tube was removed, cooled in ice, and broken and the solution transferred to a spectrophotometer or polarimeter cell jacketed at 25°C. Isomerisation and racemisation rates were measured concurrently using a Shimadzu QR-50 spectrophotometer and a Perkin-Elmer 141 polarimeter. The spectra of the equilibrium solutions of diaquo isomers were measured both on the manual (QR-50) and recording (RS-27) spectrophotometers, and the absorptions after transforming the solutions to carbonato isomers were measured on the recording spectrophotometer.

Racemisation of the β diaquo isomer

Racemisation rates of $\beta[\text{Co trien(H}_2\text{O})_2](\text{ClO}_4)_3$ were higher than those of the α isomer, and were usually measured at 40°C. The wavelength 440 μm was used (figure 37) and some measurements were made at 578 or 589 μm. The absorption was high at 440 μm, but the large rotational change made this wavelength the most suitable.

The rates were measured with the solutions in a cell (usually 2 dm) jacketed at the desired temperature to ± 0.1°C. Rotations were measured on a polarimeter attached to the Shimadzu QR-50 spectrophotometer (at 440 μm), and the runs at 578 and 589 were measured visually on a Bellingham and Stanley polarimeter. In slower runs aliquots were taken from solutions maintained in thermostated flasks.

Rates of isomerisation of the β diaquo to the equilibrium mixture of cis isomers were very much slower than the racemisation rates, and the
spectra of the diaquo (or transformed carbonato) solutions barely changed in the time for complete racemisation. In no case was more than 4% isomerisation measured during the racemisation runs but the loss of activity could be due to isomerisation through the trans isomer.

**Acid Dissociation constants of aquo complexes**

The method used to determine concentration $pK_a$'s was titration of HClO$_4$ solutions of the aquo complexes (as perchlorates) with NaOH to partial neutralisation, the pH changes being followed with a glass electrode. The chloroaquo trien complexes were obtained by allowing the corresponding cis dichloro complexes (as perchlorates) to aquate in HClO$_4$ until the chloroaquo concentrations reached the maxima.

Since these $pK_a$'s were determined in collaboration with others, the details for the diaquo trien, and chloroaquo trien and bis(en) cobalt(III) complexes will be published independently of this thesis.

**DISCUSSION OF ACIDITIES OF AQUO COMPLEXES**

A number of $pK_a$ measurements on cobalt(III) aquo complexes has been reported ($146, 46, 63a, 139, 113$), but different conditions and methods have been used by different workers. For example Brønsted ($146$) used indirect methods of solubility and rate measurements, but now the titration method is considered the most reliable. $pK_a$ determinations are complicated by the often fast cis-trans isomerisations which occur in hydroxoaquo species, as the cis and trans isomers usually have different $pK_a$ values.
Measurements on monoaquo complexes \([\text{Co en}_2 \text{X}(\text{H}_2\text{O})]^n+\) are further complicated by rapid base hydrolysis of the group X. These complications are minimised by the rapidity of the titration method.

Isomerisation in the trien complexes was minimised by titrating the chloroaquo and diaquo complexes in \(\text{HClO}_4\) solution with a measured amount of \(\text{NaOH}\) and following the \(\text{pH}\) change on a recorder. This method was considered to be more reliable than titration of alkaline solutions of the aquo complexes with acid (139), where there is a greater chance of each of hydrolysis and isomerisation. With the chloroaquo compounds, the \(\text{pH}\) decreased after reaching the maximum, and this was probably due to base hydrolysis of the chloro group. The \(\text{pH}\) remained at the maximum for about 30 seconds for \(\text{a}[\text{Co trien Cl}(\text{H}_2\text{O})]^2+\), but only for a few seconds for the \(\beta\) isomer \((20^\circ)\). For the diaquo compounds however, the \(\text{pH}\) remained steady, so that isomerisation was not significant, and this was also shown by the spectrum of the diaquo isomer being reproduced (on acidification) after the titration had been completed.

\(\text{pK}_a\) values are dependent on temperature and ionic strength but almost no quantitative work has been reported on the relationships. The temperature dependence has already been noted for the trien chloroaquo and diaquo complexes, \(\text{pK}_a\) decreasing by 0.3 from \(10^\circ\) to \(20^\circ\). This same factor, which represents a 2-fold increase in the dissociation for the \(10^\circ\) temperature rise, was also found for the \text{cis and trans}[\text{Co en}_2 \text{Cl}(\text{H}_2\text{O})]^2+\) complexes. The ionic strength dependence was examined for the \(\alpha\) and \(\beta\) trien diaquo complexes, and \(\text{pK}_a\) was found to increase by 0.2 for the
change of \( \mu \) from 0.03 to 0.09. This salt effect is consistent with the equation Brönsted\(^{(146)} \) gave for \([\text{Co(NH}_3\text{)}_{6-x}\text{(H}_2\text{O})_x]^{3+}\) complexes,

\[
pK_o = pK_a - 2\sqrt{\mu} + \mu
\]

The \( \beta[\text{Co trien(H}_2\text{O})_2]^{3+} \) isomer is the stronger acid with respect to dissociation of both the first and second aquo groups, and similarly \( \beta[\text{Co trien Cl}(\text{H}_2\text{O})]^2+ \) is a stronger acid than the \( \alpha \) isomer. These must be correlated with the different effects of the trien ligand in the \( \alpha \) and \( \beta \) configurations. In a series of diaquo complexes, those with the greater chelation were found to be more acidic, though the differences were rather small\(^{(139)} \). Just as decreasing rates of aquation of dichloro complexes with increased chelation could not be correlated with inductive effects (base strengths) of the ligands\(^{(15)} \), nor can the \( pK_{\alpha_1} \) values of diaquo complexes be satisfactorily correlated in this way.
This reaction takes place with negligible isomerisation and with a high degree of observed retention of activity in the product mixture, as shown in table 30. The reaction scheme is therefore proposed as follows:

\[
(-)_B[\text{Co trien Cl(H}_2\text{O})]^2+ \xrightarrow{k_1} \xleftarrow{k_{-1}} \rightarrow (-)_548\beta[\text{Co trien(H}_2\text{O})_2]^3+ \xrightarrow{k_3} \xleftarrow{k_{-3}} \rightarrow \alpha[\text{Co trien(H}_2\text{O})_2]^3+
\]

The rates of racemisation \(k_2\) are about 5-10 times slower than the aquation rates \(k_1\) (tables 18 and 28) and the isomerisation rates \(k_3\) are about 1000 times slower (table 27). If the aquation takes place with full retention of activity, then the observed activity loss should be accounted for only by the rates \(k_2\). On this basis the retention of activity in each aquation run was calculated using \(k_1\), \(k_2\) and the time \(t\) when the retention was measured. The results are given in table 30 and the method of calculation is explained in appendix D. Values of \(k_2\) used were estimated from table 28.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>$[H^+]$</th>
<th>$t^0$</th>
<th>$k_1$ ($= 85% \text{ of } k_{1+k_1}$)</th>
<th>$k_2$</th>
<th>$\sqrt[4]{4 \times t_{1/2}}k_1$</th>
<th>Calculated retention</th>
<th>Observed retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>1.02 M</td>
<td>40</td>
<td>$0.68 \times 10^{-3} \text{ min}^{-1}$</td>
<td>$0.075 \times 10^{-3}$</td>
<td>4950 mins.</td>
<td>77 %</td>
<td>56 %</td>
</tr>
<tr>
<td>63</td>
<td>0.10</td>
<td>40</td>
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<td>0.14</td>
<td>1350</td>
<td>89</td>
<td>64</td>
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<tr>
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<tr>
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<td>0.096</td>
<td>1860</td>
<td>89</td>
<td>73</td>
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<tr>
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<td></td>
<td>25</td>
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<td>0.17</td>
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<td>63</td>
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<tr>
<td>68</td>
<td></td>
<td>40</td>
<td>8.2</td>
<td>1.5</td>
<td>400</td>
<td>66</td>
<td>56</td>
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<td></td>
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<td>1.5</td>
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<td>76</td>
<td>59</td>
</tr>
<tr>
<td>71</td>
<td></td>
<td>40</td>
<td>12</td>
<td>2.5</td>
<td>250</td>
<td>66</td>
<td>59</td>
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<tr>
<td>72</td>
<td></td>
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<td>13</td>
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<td>240</td>
<td>65</td>
<td>54</td>
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<tr>
<td>73</td>
<td></td>
<td>40</td>
<td>10</td>
<td>1.2</td>
<td>280</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>74</td>
<td></td>
<td>50</td>
<td>46</td>
<td>6</td>
<td>200 ($13 \times t_{1/2}$)</td>
<td>35</td>
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<tr>
<td>75</td>
<td>0.005</td>
<td>40</td>
<td>17</td>
<td>2.9</td>
<td>270</td>
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</tr>
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<td></td>
<td>40</td>
<td>69</td>
<td>15</td>
<td>65</td>
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<td>56</td>
</tr>
</tbody>
</table>
The observed retentions were generally of the same order as those calculated, especially at low \([H^+]\). However the values of \(k_2\) used in the calculations correspond to diaquo concentrations of \(< 0.002 \text{ M}\), and these racemisation rates are dependent on \([\text{Co}]\). Yet as the diaquo product is formed its concentration is always much less than 0.002 M. The actual rate of racemisation therefore will be greater than for 0.002 M, so the calculated retentions are likely to be too high. Further, the activity effects of \([\text{Co trien Cl(H}_2\text{O)}])^2+\) and \(\text{Cl}^-\) ions are unknown, so that a close correlation between calculated and observed retentions might not be expected. Certainly aquation through both the chloroaquo and chlorohydroxo paths must occur largely with retention of optical activity.

**ISOMERISATION AND RETENTION OF ACTIVITY IN AQUATION OF α[Co trien Cl(H}_2\text{O)}])^2+**

During this aquation, there was extensive isomerisation of the \(α\) to \(β\) diaquo product. The loss of activity therefore had to be correlated with the amount of isomerisation, since \(β[\text{Co trien(H}_2\text{O)}]_2^3+\) racemised \(k_3\) about 40 times faster than it was formed \((k_2)\) (tables 27 and 28).

\[
(+)[\text{Co trien Cl(H}_2\text{O)}]^2+ \xrightarrow{k_1 \quad k_2 \quad k_3} (+)[\text{Co trien(H}_2\text{O)}]_2^3+ \xrightarrow{k_3} (\beta)[\text{Co trien(H}_2\text{O)}]_2^3+
\]
<table>
<thead>
<tr>
<th>Run No.</th>
<th>$[H^+]$</th>
<th>$t^o$</th>
<th>$k_1$ min$^{-1}$</th>
<th>$k_2$ min$^{-1}$</th>
<th>Time (minutes)</th>
<th>Calculated retention of (+) cis α configuration</th>
<th>Observed retention of cis α configuration</th>
<th>Observed retention of (+) cis α activity</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1</td>
<td>40</td>
<td>$2.3 \times 10^{-4}$</td>
<td>$0.039 \times 10^{-4}$</td>
<td>$1.46 \times 10^4$</td>
<td>94%</td>
<td>69%</td>
<td>72%</td>
</tr>
<tr>
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<td>0.127</td>
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<td>77</td>
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<td>3.9</td>
<td>0.85</td>
<td>9</td>
<td>26</td>
<td>9</td>
</tr>
</tbody>
</table>
The retentions of configuration were calculated from values of \( k_1 \), \( k_2 \) and time (appendix D), and are given in table 31. Values of \( k_2 \) were estimated from table 27, using \( \text{Ea}_{\text{obs}} = 40.0 \text{ kcal mole}^{-1} \), and they appear to be independent of \([\text{Co}]\).

The measured retentions of configuration (spectrophotometric) agree with the measured activity retentions except at 0.001 M \([\text{H}^+]\). The calculations show that the loss of activity in runs at low \([\text{H}^+]\) can be accounted for entirely by the isomerisation, and therefore aquation through the chlorohydroxo species takes place with full retention both of configuration and activity. At \([\text{H}^+] \leq 0.002 \text{ M}\) however, the reverse anation rates \( k_{-1} \) are greater than isomerisation rates \( k_2 \). As anations are not stereospecific the calculations in this \([\text{H}^+]\) range must lead to retention values that are too high, and this is borne out by the discrepancy between these and the measured retentions of configuration.

In the \( \alpha \) and \( \beta \) cis chloroaquo compounds therefore, aquations through the chlorohydroxo species take place with retention of activity, in accord with Ingold, Nyholm and Tobe's stereokinetic rule, that aquations of cis isomers occur with full retention of configuration and activity. Furthermore, no evidence has been found to show that aquations through the other reaction paths violate this rule.

**MECHANISM OF AQUATION**

One of the most important results from this work is that \( \text{trans}[\text{Co trien Cl}_2]^+ \) aquates synchronously with isomerisation to give one
of the isomers (the "slow" isomer) of $[\text{Co trien Cl(H}_2\text{O)}]^2+$. This complete stereospecificity is good evidence that the mechanism is $S_N^2$ with trans-attack (p. 106). This mechanism is preferred over the $S_N^1$ trigonal bipyramidal intermediates where several isomeric products should arise (the two different cis $\beta$ isomers and trans in one instance, and $\beta$ and $\alpha$ isomers in the other, figure 43). It is most likely that the entering water molecule causes edge-displacement of one terminal ethylene bridge as shown in figure 77, and this assigns the configuration of the "slow" $[\text{Co trien Cl(H}_2\text{O)}]^2+$ isomer as that where the water is trans to the planar nitrogen atom (figure 77).

As already discussed for the diaquo compounds (chapter 6), edge-displacement of a secondary amino group should involve too much bond rearrangement, and is not considered. Similarly a mechanism involving
two synchronous edge-displacements, of terminal NH$_2$ and Cl groups, would also be expected to involve excessive bond rearrangement (this would lead to the $\beta$ chloroaquo isomer of different configuration to that in figure 77). The mechanism involving aquation with retention of the trans configuration followed by a more rapid isomerisation of trans $\longrightarrow \beta$ chloroaquo was eliminated in chapter 5, because the isomerisation rate is too slow to account for the observed complete stereospecificity.

Whereas aquations of the cis isomers of [Co en$_2$ Cl$_2$]$^+$ and [Co trien Cl$_2$]$^+$ have similar activation energies ($E_a = 22.2$ for bis(en)$^{(49b)}$, 21.5 for $\alpha$ trien, 21.1 for $\beta$ trien), the trans isomers have higher $E_a$ values in both the bis(en) and trien systems. It may be significant that $E_a$ for the trans[Co trien Cl$_2$]$^+$ aquation (26.0 kcal$\cdot$mol$^{-1}$) is greater than for trans[Co en$_2$ Cl$_2$]$^+$ (24.2$^{(49b)}$), since the latter compound has been postulated to aquate by an $S^1$ mechanism (chapter 4). The more positive $\Delta S^\neq$ value for trans[Co trien Cl$_2$]$^+$ than for trans[Co en$_2$ Cl$_2$]$^+$ ($\Delta S^\neq = +15$, 0 e.u. respectively, table 14) is also consistent with a different mechanism.

In the rapid Hg$^{2+}$ - catalysed aquation of trans[Co trien Cl$_2$]$^+$ the mechanism is clearly different. This aquation probably proceeds through a five-coordinated intermediate as found by Posey and Taube$^{(80)}$ for the [Co(NH$_3$)$_5$Cl]$^{2+}$ - Hg$^{2+}$ aquation, and the subsequent addition of a water molecule occurs largely with retention of the trans configuration.

* $E_a = 28$ kcal$\cdot$mol$^{-1}$ has also been reported for this isomer$^{(124)}$ but the plot of log $k$ vs. $1/T$ was not linear.
Whereas the uncatalysed aquation proceeds with stereo change for each act of aquation ($S_N^2$), the catalysed reaction occurs largely with retention ($S_N^1$). Preliminary observations are consistent with an $S_N^1$ reaction for the $\left(\text{+}\right)\left[\text{Co en}_2 \text{Cl}_2\right]^+$ - $\text{Hg}^{2+}$ aquation also (p. 102).

The observations on aquation (full retention and relative rates) of all the cis compounds, $\alpha$ and $\beta$ dichloro and chloroaquo isomers, and $\alpha\left[\text{Co trien(NH}_3\text{) Cl}\right]^2+$ (15), parallel those of the corresponding cis compounds in the bis(en) and tetrammine series. Charge effects are of importance, for the doubly positively charged chloroaquo and amminochloro complexes aquate much less readily than the singly charged hydroxochloro and dichloro ions. The rates are summarised in table 32, and it is evident that the cis compounds could fit into a similar scheme to that proposed by Ingold, shown in figure 78. The full retentions and relative rates of the hydroxochloro and dichloro reactions are consistent with an $S_N^1$ mechanism, where the bond-breaking step leads bond-making as the ubiquitous water enters the coordination position being vacated. The high rates for the trien hydroxochloro compared to the dichloro compounds (all singly positively charged) are in accord with observations on other tetramino systems, and the ratio of rates $\frac{\text{Cl(OH)}}{\text{Cl}_2}$ is especially high in the $\beta$ instance. However it should be mentioned that the $\beta$ dichloro aquation is also consistent with an $S_N^2$ trans-attack mechanism where a chlorine atom undergoes edge-displacement, and this will be discussed further below. The rates of the amminochloro and chloroaquo reactions are consistent with $S_N^2$ cis-attack by water as proposed by Ingold in the bis(en) system.
### Table 32. Rates of Aquation of cis[Co trien A Cl]⁺

<table>
<thead>
<tr>
<th>Isomer</th>
<th>A</th>
<th>k min⁻¹ at 40°</th>
<th>Eₐ</th>
<th>ΔS°</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis α</td>
<td>OH</td>
<td>1.1</td>
<td>19 kcal.mole⁻¹</td>
<td>- 8 e.u.</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>5.3 x 10⁻²</td>
<td>21.5</td>
<td>- 6</td>
</tr>
<tr>
<td></td>
<td>NH₃⁺</td>
<td>1.0 x 10⁻⁴*</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>OH₂⁺</td>
<td>2.2 x 10⁻⁴</td>
<td>24</td>
<td>- 8</td>
</tr>
<tr>
<td>cis β</td>
<td>OH</td>
<td>2 x 10⁴</td>
<td>20</td>
<td>+ 16**</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>4.8 x 10⁻¹</td>
<td>21.1</td>
<td>- 3</td>
</tr>
<tr>
<td></td>
<td>OH₂⁺</td>
<td>1 x 10⁻³</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* calculated from k = 4.0 x 10⁻⁵ at 35° (15), assuming Eₐ = 25.
** inaccurate, p. 151.

Figure 78.
All the cis $\beta$ rates are greater than those for the corresponding cis $\alpha$ compounds, and this difference is due largely to entropy effects (table 32). However the activation parameters for $\alpha$ and $\beta$ 

$[\text{Co trien Cl(OH)}]^+$ are somewhat different to those reported\(^{(119)}\) for

$[\text{cis-Co en}_2\text{Cl(OH)}]^+$ ($E_a = 23$, $\Delta S^\neq = +8$). No activation parameters are available for aquation of chloroaquo compounds through the aquo path for comparison with the trien system.

In the series of complexes containing substituted ethylenediamines $\text{trans}[\text{Co} \,(\text{AA})_2\text{Cl}_2]^+$, the increase in rate of aquation with increase in steric crowding is valuable evidence supporting the $S_{N2}$ mechanism\(^{(124)}\) (chapter 4). The observed rates and parameters for the three trans compounds containing the isomeric butylenediamine ligands (racemic dl, iso and meso) can be rationalised on the basis of steric crowding. This is greatest in the $\text{trans}[\text{Co(m-bn)}_2\text{Cl}_2]^+$ isomer, from which Cl$^-$ ion should be more easily expelled (fastest rate and lowest $E_a$). The dl-bn compound (with the two methyl groups in equatorial positions on each amine ligand) is the least sterically crowded, and has the slowest rate and highest $E_a$\(^{(124)}\). Further, the dl compound would be expected to permit more solvation in the transition state and hence have the lowest $\Delta S^\neq$, as observed. Similar considerations to these may rationalise observations on the $\alpha$ and $\beta$ cis $[\text{Co trien Cl}_2]^+$ isomers; the $\beta$ isomer is more sterically crowded around one of the chlorine atoms, so that dissociation of this chlorine would be facilitated (higher rate, slightly lower $E_a$) relative to the chlorine atom in the $\alpha$ isomer. Solvation would
be expected to be greater in the more open structure in the transition state, to correspond to a more negative $\Delta S^\ddagger$ in this instance. Yet the structure of the "slow" $\beta[\text{Co trien Cl}(\text{H}_2\text{O})]^2^+$ isomer would be different on this basis to that assigned from the proposed mechanism of the $\text{trans}[\text{Co trien Cl}_2]^+$ aquation. However if $\beta[\text{Co trien Cl}_2]^+$ aquated by $S_N^2$ with edge-displacement of a chlorine atom (figure 79) the configuration of the "slow" $\beta$ chloroaquo isomer would be the same as already assigned, and the relative $\beta/\alpha$ rates would be rationalised.

Figure 79. Possible $S_N^2$ edge-displacement mechanism for $\beta[\text{Co trien Cl}_2]^+$ aquation.

Arguments of this nature must be regarded as tentative however, for they do not always correlate with observed results. For example, methyl substitution in the six-membered ring in the compound $\text{trans}[\text{Co (NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2 \text{Cl}_2]^+$ decreases rather than increases the rate.
Thus while it is likely that $\text{aq}[\text{Co trien Cl}_2]^+$ aquates by an $S_N^1$ mechanism, it is difficult to decide between the $S_N^1$ and chlorine-displacement mechanisms for the $\beta$ isomer and both mechanisms may occur.

Whereas it is generally agreed that both cis and trans $[\text{Co en}_2 \text{Cl}_2]^+$ aquate by $S_N^1$ (chapter 4), the higher rate for the trans dichloro trien isomer compared to the cis is consistent with the assigned $S_N^2$ mechanism. In this mechanism the inductive effect of the orienting chloro group should be dominant, as the electromeric (+E) effect can not labilise a trans position (112). Similarly trans$[\text{Co trien Br}_2]^+$ aquates more rapidly than the cis dibromo isomer (5).

Another important aspect is the acid-catalysed aquation paths for the cis chloroaquo isomers. This path was readily observed for the $\alpha$ isomer, but was not apparent for the $\beta$ isomer in $[\text{H}^+]$ up to 1.0 M. However, there seems no reason to doubt that the kinetic pattern would be similar for the $\alpha$ and $\beta$ chloroaquo isomers, and the absence of the catalytic reaction in the $\beta$ isomer up to 1.0 M $[\text{H}^+]$ could be due merely to the different acidities of the isomers. Since the ligand nitrogens are all coordinated, there are only two plausible sites for the protonation (figure 80).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure80.png}
\caption{Figure 80}
\end{figure}
Protonation at the chlorine atom could certainly facilitate dissociation of Cl⁻, and the activation energy should be considerably lower than for the chloroaquo path, but these Eₐ's were not determined. Protonation at the water site increases the positive charge on the complex making Co-Cl dissociation more difficult, yet hydrogen-bonding between the coordinated Cl⁻ and H₂O could conceivably weaken the Co-Cl bond. Although protonation at the Cl⁻ is the more attractive possibility, this mechanism is mitigated by the absence of acid-catalysis in the dichloro isomers. It seems less likely that the catalysis is due to dissociation of one end of the trien ligand, and that subsequent protonation prevents the recoordination of the nitrogen. If this mechanism occurred some overall decomposition might be expected, or at least some evidence of intermediate species. However only the chloroaquo and diaquo species could be detected. The kinetic data are insufficient to assign activation parameters to the acid-catalysed reactions, and clearly there is scope to examine these reactions further in the high acid region.

FURTHER WORK

In the course of this work, one isomer of [Co trien ox]⁺ was prepared and resolved (for the iodide-1-hydrate, [α]₀ D = -525°, [α]₀ 578 = -600°) using either (-)[Co en ox₂]⁻ or (-)[Co en mal₂]⁻. By its method of preparation, compared to that of the analogous carbonato compound, it probably had the β configuration.

It would be of interest to extend the studies described in this thesis to a wider range of substituted trien complexes and it is possible
that suitable choice of substituents could cause marked stereospecificity. Similarly, methylation of the trien ligand at the carbon or nitrogen atoms should change the relative stabilities of the three configurations.

Very few other cobalt(III) complexes with quadridentate ligands have been prepared, and there is considerable scope to extend the preparative and kinetic work to other ligands of this type. A range of these ligands has been described by Goodwin and Lions\(^{(147)}\), and MacDermott\(^{(148)}\) has prepared the following optically active sulphur-containing ligands:

\[
\begin{align*}
\text{CH}_3\text{CH}-\text{S}-\text{CH}_2\text{-CH}_2\text{-NH}_2 & \quad \text{CH}_3\text{CH}-\text{S}-\text{CH}_2\text{-CH}_2\text{-NH}_2 \\
\text{CH}_2\text{-S}-\text{CH}_2\text{-CH}_2\text{-NH}_2 & \quad \text{CH}_2\text{-S}-\text{CH}_2\text{-CH}_2\text{-NH}_2 \\
\text{CH}_3 & \\
\end{align*}
\]

Other useful kinetic studies on cobalt(III)- trien compounds could be suggested, but in particular it would be of interest to determine whether the same stereochemical course is followed in aquation of the \([\text{Co trien Br}_2]^+\) isomers as with the dichloro compounds.

As in the bis(en) system\(^{(44)}\), an inversion takes place on treating a solution of D\(\text{a}[\text{Co trien Cl}_2]^+\) with AgNO\(_3\) (2 moles), NaOH (2 moles) and HNO\(_3\) (2 moles). In the trien system, an inversion of the D to L optical configuration causes isomerisation also, from D\(\text{a}\) to L\(\text{b}\). About 20% of the optically pure L\(\text{b}\) dinitro isomer was separated chromatographically from the mixture after the diaquo solution was transformed to the dinitro compounds, and this was the proportion of inversion that occurs in the bis(en) system\(^{(44)}\). This reaction has yet to be studied quantitatively in more detail.
### APPENDIX A

#### ISOLATED TRIETHYLENETETRAMINE COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>Methods</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni$_2$trien$_3$]$^{4+}$ as chloride, nitrate, tetrachloroplatinate(II) sulphate</td>
<td>Paramagnetic, in accord with octahedral structures; Various configurations possible.</td>
<td>(1)</td>
</tr>
<tr>
<td>[Ni trien][AgBrI]$_2$</td>
<td>Conductivity.</td>
<td>(8)</td>
</tr>
<tr>
<td><a href="SCN">Ni trien</a>$_2$</td>
<td>Yellow; diamagnetic; planar.</td>
<td>(2)</td>
</tr>
<tr>
<td>[Ni trien]ZnCl$_4$.H$_2$O</td>
<td>Blue; paramagnetic; octahedral; water insoluble.</td>
<td>(2)</td>
</tr>
<tr>
<td>[Ni trien]ZnCl$_4$</td>
<td>Blue; paramagnetic; I.R. spectrum shows water is coordinated.</td>
<td>(10)</td>
</tr>
<tr>
<td>[Pd trien][PdCl$_4$] and [Pt trien][PtCl$_4$]</td>
<td>Orange; diamagnetic; formed from monohydrate at 110$^\circ$; reverts to monohydrate in water.</td>
<td>(10)</td>
</tr>
<tr>
<td>[Cu trien]SO$_4$</td>
<td>Conductimetric titrations of anions with Ag$^+$ verified these formulations; diamagnetism showed configurations were square-planar.</td>
<td>(3,9)</td>
</tr>
<tr>
<td>[Cu trien]ZnCl$_4$.H$_2$O</td>
<td>Blue.</td>
<td>(9)</td>
</tr>
<tr>
<td>[Cu trien]ZnCl$_4$</td>
<td>Violet-black; paramagnetic; I.R. shows water is coordinated.</td>
<td>(10)</td>
</tr>
<tr>
<td>[Cu trien]ZnCl$_4$</td>
<td>Deep-violet; formed from monohydrate at 110$^\circ$; reverts to monohydrate in water.</td>
<td>(10)</td>
</tr>
</tbody>
</table>

Contd./
<table>
<thead>
<tr>
<th>Complex</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag trien]NO₃</td>
<td>Isolated only from alcohol; has low solubility in water, but slowly hydrolyses to the 1:1 species formed in water; structure suggested tetrahedral. (11)</td>
</tr>
<tr>
<td>[Co²⁺ trien(H₂O)₂]Cl₂</td>
<td>Structure unknown; could be polymeric. (4,12)</td>
</tr>
<tr>
<td>Re⁹⁺ trien Cl₆</td>
<td>Spectra (visible and U.V.); cis, but configuration not assigned. (4)</td>
</tr>
<tr>
<td>[Co³⁺ trien Cl₂]Cl</td>
<td>Partial resolution by indirect method. (14)</td>
</tr>
<tr>
<td>[Co trien(NO₂)₂]Cl.H₂O</td>
<td>Partially isomerises to trans in methanol. (14)</td>
</tr>
<tr>
<td>[Co trien XY]ⁿ⁺</td>
<td>Spectra; cis (not assigned). (4)</td>
</tr>
<tr>
<td>[Co₂ trien]Cl₆</td>
<td>Various compounds, all presumed cis. (4,15,16)</td>
</tr>
<tr>
<td>[Co₂ en₄ trien]Cl₆</td>
<td>Conductivity. (4,17)</td>
</tr>
<tr>
<td>[Co trien Br₂]Br</td>
<td>I.R. spectra; cis (not assigned) and trans. (5)</td>
</tr>
<tr>
<td>[Co trien(CHO-C₆H₄-O)₂⁺</td>
<td>Configuration not assigned. (18)</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Co trien glycine</a>₂</td>
<td>and other aminoacid chelates; probably β. (19)</td>
</tr>
<tr>
<td>[Cr³⁺ trien Cl₂]Cl.H₂O</td>
<td>cis (not assigned). (6)</td>
</tr>
<tr>
<td>[Rh³⁺ trien Cl₂]Cl.H₂O</td>
<td>cis (not assigned). (7)</td>
</tr>
<tr>
<td>[Rh(trienH₂)Cl₄]Cl</td>
<td>cis; suggested free amine groups. (7)</td>
</tr>
</tbody>
</table>
## APPENDIX A

**TRIETHYLENETETRAMINE COMPLEXES STUDIED IN SOLUTION**

<table>
<thead>
<tr>
<th>Complex ion</th>
<th>Methods</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M trien]^{2+}</td>
<td>Measurements of formation constants, all form stable complexes.</td>
<td>(20, 21, 22)</td>
</tr>
<tr>
<td>M = Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pb.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Spectrophotometry; two 1:1 species, yellow and blue, present in equilibrium; yellow form favoured in strong salt solutions; blue form postulated as cis[Ni trien X₂⁺], X = water, alcohol, anions.</td>
<td>(21, 1, 2)</td>
</tr>
<tr>
<td>Cu</td>
<td>Kinetics of dissociation.</td>
<td>(59)</td>
</tr>
<tr>
<td>Cd</td>
<td>Spectrophotometry.</td>
<td>(21)</td>
</tr>
<tr>
<td>[M₂ trien₃]^{4+}</td>
<td>Formations constants.</td>
<td>(24)</td>
</tr>
<tr>
<td>M = Mn, Fe, Co, Ni, Cd.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Spectrophotometry.</td>
<td>(21, 1)</td>
</tr>
<tr>
<td>[Ag trien]⁺ and [Ag₂ trien]^{2+}</td>
<td>Formation constants. Light scattering demonstrated existence of 1:1 complex. Conductance showed both ions present in aqueous and alcoholic solutions.</td>
<td>(20, 11)</td>
</tr>
<tr>
<td>[Fe III trien]</td>
<td>Suggested in aqueous solution is dihydroxo octahedral, probably cis a.</td>
<td>(25)</td>
</tr>
<tr>
<td>[Co II trien(H₂O)(OH)]⁺</td>
<td>Conductometric, potentiometric and spectrophotometric titrations with OH⁻.</td>
<td>(26)</td>
</tr>
</tbody>
</table>
APPENDIX B

ANALYTICAL TREATMENT OF CONDUCTANCE CHANGES DURING AQUATION OF cis β[Co trien Cl₂]ClO₄

The system is represented as follows, with equilibria neglected.

\[
\begin{align*}
\beta'[\text{CotrienCl(H}_2\text{O})^2^+ + \text{Cl}^-] & \quad \text{B, "slow" isomer} \\
\beta'[\text{CotrienCl(H}_2\text{O})]^{3^+} & \quad \text{D} \\
\beta''[\text{CotrienCl(H}_2\text{O})]^{2^+} + \text{Cl}^- & \quad \text{C, "fast" isomer}
\end{align*}
\]

At any time, the measured conductance will be a composite quantity. There will be a constant background conductance from HC₁₀₄ and the ClO₄⁻ ion from the complex A. Superimposed on this will be contributions from the four complex ions A to D, and Cl⁻ ion, each of these changing as aquation proceeds. The background conductance will be included in the \( \frac{1}{R_{\infty}} \) value so need not be considered in the analysis. The following notation will be used.

k₁ to k₄ are the rate constants as above.

A to D represent concentrations of the complex ions in the above scheme in moles/c.c.

\( A_0 \) = initial concentration of A.
\[ D_{\infty} = \text{final concentration of } D. \]

When equilibria are neglected \( D_{\infty} = A_0. \)

\[ \Lambda_A = \text{molecular conductivity of ion } A. \]

\[ \Lambda_B = \text{molecular conductivity of ion } B \text{ and } Cl^- . \]

\[ \Lambda_D = \text{molecular conductivity of ion } D \text{ and } Cl^- . \]

Assume \( \Lambda_C = \Lambda_B. \)

\( \lambda \) = measured conductance (apart from background) at time \( t. \)

\( \lambda_0 \) = initial conductance.

\( \lambda_{\infty} \) = final conductance.

The kinetic equations for the first order reactions involved here are \((149)\):

\[ A = A_0 e^{-(k_1 + k_2)t} \]

\[ B = \frac{A_0 k_1}{k_1 + k_2 - k_3} \begin{pmatrix} -k_3 t & -(k_1 + k_2) t \\ e & -e \end{pmatrix} \]

\[ C = \frac{A_0 k_2}{k_1 + k_2 - k_4} \begin{pmatrix} -k_4 t & -(k_1 + k_2) t \\ e & -e \end{pmatrix} \]

Then \( D = A_0 - A - B - C \)

\[ = A_0 \left[ 1 - e^{-(k_1 + k_2)t} + \frac{k_1}{k_1 + k_2 - k_3} \begin{pmatrix} -(k_1 + k_2) t & -k_3 t \\ e & -e \end{pmatrix} + \frac{k_2}{k_1 + k_2 - k_4} \begin{pmatrix} -(k_1 + k_2) t & -k_4 t \\ e & -e \end{pmatrix} \right] \]
Expressions for conductances are:

\[ \lambda_0 = A_0 \wedge_A \cdot \frac{1}{a} \quad (a = \text{cell constant}) \]

\[ \lambda_\infty = D_\infty \wedge_D \cdot \frac{1}{a} = A_0 \wedge_D \cdot \frac{1}{a} \]

\[ \lambda_t = \frac{1}{a} \left[ A \wedge_A + (B + C) \wedge_B + D \wedge_D \right] \]

Substituting for concentrations from above:

\[ \frac{2}{A_0} (\lambda_\infty - \lambda_t) = -\wedge_A e^{-(k_1 + k_2)t} \]

\[ -\wedge_B \left[ \frac{k_1}{k_1+k_2-k_3} \left( e^{-k_3 t} - (k_1+k_2)t \right) + \frac{k_2}{k_1+k_2-k_4} \left( e^{-k_4 t} - (k_1+k_2)t \right) \right] \]

\[ -\wedge_D \left[ e^{-(k_1+k_2)t} \left( \frac{k_1}{k_1+k_2-k_3} \left( e^{-k_3 t} - k_3 t \right) + \frac{k_2}{k_1+k_2-k_4} \left( e^{-k_4 t} - k_4 t \right) \right) \right] \]

\[ e^{-(k_1+k_2)t} \left( \wedge_D - \wedge_A \right) + \frac{k_1}{k_1+k_2-k_3} \left( e^{-k_3 t} - (k_1+k_2)t \right) \left( \wedge_D - \wedge_B \right) \]

\[ + \frac{k_2}{k_1+k_2-k_4} \left( e^{-k_4 t} - (k_1+k_2)t \right) \left( \wedge_D - \wedge_B \right) \]

Because of the constants involved, this reduces to the form:

\[ (\lambda_\infty - \lambda_t) = P e^{-(k_1+k_2)t} + Q e^{-k_3 t} + R e^{-k_4 t} \]

If \((k_1+k_2) > k_4 > k_3\), the largest term on the R.H.S. is that in \(e^{-k_3 t}\).
After some time when $k_3$ becomes the only reaction,

$$\lambda_\infty - \lambda_t = Q e^{-k_3 t}$$

and the plot $\log(\lambda_\infty - \lambda_t)$ vs. $t$ has slope $-k_3/2.303$. The mathematical procedure corresponding to extrapolating this linear portion back consists of calculating contributions from D and the "slow" isomer B only. A may be neglected in the regions concerned, where the first aquation stage is completed, i.e. $\lambda_t^{\text{calc}} = \frac{1}{a} (\Lambda_B \cdot B + \Lambda_D \cdot D)$.

Then $\lambda_t^{\text{expt}} - \lambda_t^{\text{calc}} = \frac{1}{a} \Lambda_B \cdot C$

$$= \frac{A}{a} \Lambda_B \frac{k_2}{k_1+k_2-k_4} \left( e^{-k_4 t} - e^{-(k_1+k_2) t} \right)$$

$$= S \left( e^{-k_4 t} - e^{-(k_1+k_2) t} \right)$$

If $(k_1+k_2) > k_4$, then $e^{-(k_1+k_2) t}$ may be neglected so that

$$\log(\lambda_t^{\text{expt}} - \lambda_t^{\text{calc}})$$

vs. $t$ has slope $-k_4/2.303$. Thus for this plot to be linear and give a rate value for the "fast" isomer depends on there being sufficient difference only between the total rate of the first aquation stage $(k_1+k_2)$ and the faster rate of the second stage $(k_4)$, and this is in fact the case in this system.
Appendix C

Separation of the Rates of Aqueation of cis $\beta$[Co trien Cl$_2$]$^+$

Equations have already been given (appendix B) for the concentrations of each of the four complex species involved in this aqueation system. From these the following expression is obtained for the proportion of the "fast" isomer (C) in the mixture of chloroaquo isomers (B + C):

$$\frac{C}{B+C} = \frac{k_2}{k_1 + k_2 - k_4} \left( \frac{-k_4t - (k_1 + k_2)t}{(k_1 + k_2 - k_4)e^{-(k_1 + k_2)t} + \frac{k_2}{k_1 + k_2 - k_4}e^{-k_3t} - \frac{k_1}{k_1 + k_2 - k_4}e^{-k_4t}} \right)$$

From the most accurate conductance run (run 25) at 0.0102 M $[H^+]$ and 25$^\circ$, the following data were obtained:

$$k_1 + k_2 = 82 \times 10^{-3} \text{ min}^{-1} \quad \therefore k_1 = 82 \times 10^{-3} - k_2$$

$$k_3 = 1.4 \times 10^{-3}$$

$$k_4 = 4.8 \times 10^{-3}$$

$$\frac{C}{B+C} = 2.8\% \text{ at 90 minutes.}$$

When these values are substituted in the above expression, $k_2$ is obtained as $k_2 = 3 \times 10^{-3} \text{ min}^{-1}$; then $k_1 = 79 \times 10^{-3} \text{ min}^{-1}$. The complete data for this run are summarised in figure 57. It is to be noted that the
maximum proportion of C observed (2.8 %) is not necessarily the same as
the maximum proportion of C formed. The ratio in which C and B are
formed initially is given by $\frac{C}{B} = \frac{k_2}{k_1} \times \frac{1}{26}$, which is in fact the same
as the observed ratio within the experimental error.
RATE EQUATIONS FOR CONSECUTIVE REACTIONS, AND
CALCULATION OF RETENTION OF ACTIVITY

For the consecutive reactions,
\[ \begin{array}{c}
A & \xrightarrow{k_1} & B & \xrightarrow{k_2} & C \\
\text{active} & \text{active} & \text{racemic} \\
\text{chloroaquo} & \text{diaquo} & \text{diaquo}
\end{array} \]

expressions for the concentration of each species at time \( t \) are \(^{(149)}\)

\[
A = A_0 \cdot e^{-k_1 t} \\
B = A_0 \cdot \frac{k_1}{k_1 - k_2} \left( e^{-k_2 t} - e^{-k_1 t} \right) \\
C = A_0 \left[ 1 + \frac{1}{k_1 - k_2} \left( k_2 e^{-k_1 t} - k_1 e^{-k_2 t} \right) \right]
\]

In measuring the retention of activity in aquation of
\((-)\beta[\text{Co trien Cl(H}_2\text{O)}]^2^+\) all the species \((A + B + C)\) were transformed to
\(\beta[\text{Co trien CO}_3]^+\). In the above scheme \(C\) then represents racemic
carbonato, so the retention of activity measured was

\[
\frac{A + B}{A + B + C} = \frac{A + B}{A_0} 
\]

This was then calculated (table 30) from the above
expressions as:

\[
\frac{A + B}{A_0} = e^{-k_1 t} + \frac{k_1}{k_1 - k_2} \left( e^{-k_2 t} - e^{-k_1 t} \right)
\]
In the \( \text{g[Co trien Cl(H\textsubscript{2}O)}]^{2+} \) aquation, \( k_2 \) corresponds to the isomerisation of the \( \text{g} \) to \( \text{\beta} \) diaquo product, so the degree of retention of the \( \text{g} \) configuration is again calculated as \( \frac{A + B}{A_0} \) (table 31).
APPENDIX E

SAMPLES OF RATE PLOTS

Figures 81 to 94 give sample rate plots of kinetic runs for the aquation, racemisation and isomerisation reactions by the various methods. They are listed here for reference.

AQUATIONS

Figure

81. $(\pm)\alpha[\text{Co trien \text{Cl}_2]\text{ClO}_4]$. Spectrophotometric at 320 m$\mu$, Guggenheim plot.
   
   $(0.01 \text{ M HClO}_4, 40^\circ; \text{run 12})$.

82. Spectrophotometric at 320 m$\mu$.
    
    $(0.01 \text{ M H}^+, 35^\circ; \text{run 11})$.

83. Polarimetric at 589 m$\mu$.
    
    $(0.01 \text{ M H}^+, 40^\circ; \text{run 13})$.

84. Conductimetric. $(0.001 \text{ M H}^+, 25^\circ; \text{run 2})$.

85. Conductimetric. $(0.01 \text{ M H}^+, 35^\circ; \text{run 10})$.

(a) Aquation of first chlorine, Guggenheim plot.
(b) Aquation of second chlorine.

86. Aquation of second chlorine.
    
    $(0.01 \text{ M H}^+, 40^\circ; \text{run 51})$.

Spectrophotometric at 540 m$\mu$.
Polarimetric at 578 m$\mu$. 
87. (−)β[Co trien Cl₂]ClO₄. Conductimetric, Guggenheim plot.
   (0.01 M H⁺, 25°; run 25).

88. " Spectrophotometric at 320 μm.
   (0.01 M H⁺, 25°; run 26).

89. " Polarimetric. (0.01 M H⁺, 25°; run 28).
   (a) First chlorine at 580 μm.
   (b) Second chlorine at 480 μm.

90. trans[Co trien Cl₂]ClO₄. Spectrophotometric at 320 μm.
   (0.01 M H⁺, 10°; run 38).

   (1.0 M H⁺, 25°; run 44).

92. " Conductimetric. (0.01 M H⁺, 25°; run 42).
   (a) Aquation of first chlorine, Guggenheim plot.
   (b) Aquation of second chlorine (β chloroaquo).

ISOMERISATION AND RACEMISATION

93. (+)₅₄₆α[Co trien(H₂O)₂](ClO₄)₃. (0.01 M H⁺, 60°; run 88).
   Isomerisation at 487 μm.
   Loss of activity at 546 μm.

94. (−)₅₄₆β[Co trien(H₂O)₂](ClO₄)₃. (0.01 M H⁺, 50°; run 109).
   Racemisation at 440 μm.
The following kinetic plots are given in chapter 5.

Figure 58. Aquation of $\beta[\text{Co trien Cl(H}_2\text{O)}]^{2+}$. Spectrophotometric plot showing "fast" isomer. (0.01 M H$^+$, 25°; run 66).

Figures 63 and 64. Aquation of $\beta[\text{Co trien Cl}_2]^\text{ClO}_4^-$. Conductivity plot of second chlorine showing inflexion due to "fast" chloroaquo isomer. (0.01 M H$^+$, 25°; run 25).

Figure 65. Aquation of $\beta[\text{Co trien Cl(H}_2\text{O)}]^{2+}$. Conductivity plot giving rate for "fast" isomer only. (0.01 M H$^+$, 25°; run 25).
Figure 81: AQUATION OF \( [\text{CotriencI}_2] \text{ClO}_4 \),
SPECTROPHOTOMETRIC, 320 nm, GUGGENHEIM PLOT.
(0.01 M HClO₄, 40°C; RUN 12)

\[
\log(D_{320} - D_{310})
\]

\[
k = 5.4 \times 10^{-2} \text{ min}^{-1}
\]
FIGURE 82. AQUATION OF $\equiv[\text{Cotencl}_2]\text{ClO}_4^-$.
SPECTROPHOTOMETRIC AT 320 M$\mu$.
($0.01 \text{ M } \text{KClO}_4, 35^\circ\text{C}; \text{RUN 11}$.)

$k = 3.17 \times 10^{-2} \text{ min}^{-1}$

$\log (D - 0.109) = \frac{D}{10 t_{1/2}}$
Figure 83. Aquation of (4) = [Co trenCl₂]ClO₄⁻

Polarimetric at 589 nm.

(0.01 M HClO₄, 40°; Run 13.)

\[ \log(\alpha - 0.50) \]

\[
\frac{\alpha}{t} \text{ after 5.4 } t_{1/2}
\]

\[ k = 5.2 \times 10^{-2} \text{ min}^{-1} \]
FIGURE 84. AQUATION OF $[\text{CPhenCl}_2\text{CO}_4]^{-}$

CONDUCTIMETRIC.

(0.001 M HClO$_4$, 25°; RUN 2.)

$K = 8.9 \times 10^{-3} \text{ min}^{-1}$

$R = \frac{t}{t_{1/2}}$

$\log(275.8 \times 10^{-3} - R)$

Time (mins)

0

100

150

200

250

300

450

600

750

900

1050

1200

1350

1500

Log

0

0.5

1
Aquation of $\text{CoC}_{3} \text{Cl}_{2} \text{ClO}_{4}$, conductivity, 0.01 M HClO$_{4}$, 35$^\circ$C, Run 10.

Figure 85(a). Aquation of first chlorine (Guggenheim plot).

$log\left(\frac{1}{R_{t+20}} - \frac{1}{R_{t}}\right)$

$k = 2.9 \times 10^{-2}$ min$^{-1}$
AQUATION OF $\approx [\text{Co}^\text{II}\text{ienCl}_2]\text{ClO}_4^{-}$

CONDUCTIVITY, 0.01 M HClO$_4$, 35°; RUN 10.

FIGURE 85(b). AQUATION OF SECOND CHLORINE.

$log \left( \frac{2.6080 \times 10^{-3} - \frac{1}{R}}{R} \right)$

$k = \frac{1}{5 t_{1/2}}$

$k = 2.1 \times 10^{-4}$ min$^{-1}$
FIGURE 86. AQUATION OF (4) = [CotrienCl₂]ClO₄, SECOND CHLORINE.

(0.01 M HClO₄, 40°; RUN 51)

SPECTROPHOTOMETRIC AT 540 mμ.
POLARIMETRIC AT 578 mμ.
Figure 87. Aqueation of $\text{B}[\text{CoetrynCl}_2]\text{ClO}_4^-$
Conductivity, Guggenheim plot.
(0.01 M HClO$_4$, 25°C; RUN 25.)

$$\log \left( \frac{1}{R_{t+10}} - \frac{1}{R_t} \right)$$

$k = 8.23 \times 10^{-2}$ min$^{-1}$
Figure 88. AQUATION OF $\beta$ [CotrienCl$_2$]ClO$_4$,
SPECTrophotometric AT 320 M$\mu$.

$(0.01$ M HClO$_4$, 25°; RUN 26.)

$\log(D - 0.136)$

$K = 8.72 \times 10^{-2}$ min$^{-1}$

$\tau_{1/2}$

Time (mins)
AQUATION OF $(-)_{\frac{1}{2}}[(\text{o-trien})\text{Cl}_2]\text{ClO}_4$.

$(0.01\text{ M }\text{HClO}_4, 25^\circ\text{C}; \text{RUN 28})$

**Figure 89(a). First chlorine, polarimetric at 580 m.$\mu$.**

$\log (0.136 - \alpha)$

$\alpha$ after $\frac{9}{10} t_{1/2}$

$k = 9.2 \times 10^{-2}$ min$^{-1}$

$\bar{t}_{1/2}$
AQUATION OF (-) B [Cotrien Cl₂] ClO₄
(0.01 M HClO₄, 25° C RUN 28)

FIGURE 89(b) SECOND CHLORINE, POLARIMETRIC AT 480 MÙ.

\[ \log \alpha \]

\[ k = 1.29 \times 10^{-3} \text{ min}^{-1} \]
FIGURE 90. AQUATION OF TRANS $[\text{Co} \text{trien} \text{Cl}_2] \text{ClO}_4$.

SPECTROPHOTOMETRIC AT 320 m\u21a6.

($0.01 \text{ M HClO}_4$, 10°; RUN 38.)

$\log (D - 0.084)$

$k = 1.95 \times 10^{-2} \text{ min}^{-1}$
Figure 9. Aqueation of Trans [Co(thenCl₂)]ClO₄⁻
Spectrophotometric at 342, 435, 510 mµ.
(1.0 M HClO₄, 25°, Run 44.)

\[ \log(D_{342} - 0.290) \]
\[ \log(D_{435} - 0.190) \]
\[ \log(0.713 - D_{510}) \]

\[ k = 1.53 \times 10^{-1} \text{ min}^{-1} \]
Figure 92(a) First chlorine: conductimetric.

AQUATION OF TRANS $[\text{CotrienCl}_2]\text{ClO}_4$.

$0.01 \text{ M HClO}_4$, $25^\circ \text{C}$, RUN 42.

$\log\left(\frac{1}{R_{t+4}} - \frac{1}{R_t}\right)$

$k = 2.1 \times 10^{-1} \text{ min}^{-1}$

$\frac{1}{R}$

$0 \rightarrow 15$
AQUATION OF \text{TRANS} \left( \text{Co}^{2+} \right) \text{ClO}_4^-(0.01 \text{ M HClO}_4, 25^\circ \text{C}, \text{RUN 42})

\text{FIGURE 92(b). SECOND CHLORINE (B[CoCl(H_2O)_6]^{2+}), CONDUCTIMETRIC.}

\log \left( 2.3266 \times 10^{-3} - \frac{1}{R} \right) \quad \text{\( t \) after \( \frac{t}{t_{1/2}} \)}

\text{\( t_{1/2} \)}

\text{\( R = 1.46 \times 10^{-3} \text{ min}^{-1} \)}

\text{Time \longrightarrow \text{ hours}}
FIGURE 93. ISOMERISATION AND LOSS OF ACTIVITY

OF $\mu_{546}$ as[Cotrien(H$_2$O)$_2$](ClO$_4$)$_3$.

(0.01 M HClO$_4$, 60°; RUN 88.)

ISOMERISATION AT 487 mμ.

LOSS OF ACTIVITY AT 546 mμ.

$$\log \alpha$$

$$\log (0.554 - D)$$

$$k = 1.72 \times 10^{-3} \text{ min}^{-1}$$

$$k = 2.4 \times 10^{-3}$$

$T_1/2$
FIGURE 94. RACEMISATION OF \( \alpha \)-[Co tren(4-H)\( \text{II} \)\( \text{II} \)]\( \text{ClO}_4 \text{}_3 \) 
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