THE KINETICS AND MECHANISMS

OF SOME REACTIONS OF

COBALT(III) BIS(ETHYLENEDIAMINE)

COMPLEXES

A THESIS

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ABSTRACT.

A recent report on the base hydrolysis of $\underline{\text{trans}}[Co(en)_2(OH)Cl]^+$ has questioned the interpretation of earlier work and presented a new mechanism from which it may be predicted that exchange should occur between free chloride ions and the complex. A re-examination of this reaction using ^{36}Cl has shown that little or no exchange occurs even after considerable reaction time.

The isomerisation of the $[Co(en)_2(OH)_2]^+$ cation has been studied in highly basic media. The results are explained in terms of an intramolecular process, with the complex 'twisting' about four imaginary C_3 axes.

The isomerisation of $[Co(en)_2(OH_2)_2]^{3+}$ in dilute and concentrated acid appears to proceed through a trigonal bipyramidal intermediate. In concentrated acid the isomerisation rate is greatly increased compared with that found in dilute acid solution. This increase is discussed in terms of the greater attraction of the protons to the coordinated water ligands, weakening the cobalt-oxygen bond and increasing the rate of formation of the reactive intermediate. The activation enthalpies in dilute and concentrated acid reflect this lowering of the energy required to form the intermediate, being 28.0 and 25.5 kcal.mole^{-1} respectively.

The racemisation of the optically active $\underline{\text{cis}}[Co(en)_2(OH_2)_2]^{3+}$ in dilute acid, appears to proceed $\underline{\text{via}}$ the $\underline{\text{cis}}$ to $\underline{\text{trans}}$ isomerisation, since the rate is similar to the rate of isomerisation. The enthalpies of activation for the two reactions are almost identical being 29.4 kcal.mole^{-1} for isomerisation and 29.2 kcal.mole^{-1} for racemisation.

In the isomerisation of the $[Co(en)_2(OH_2)NCS]^{2+}$, the disproportionate

increases in the rate with increasing acid concentration are found at $\geqslant$ 6M $HClO_4$. This lower acid concentration value is thought to be due to the orientation of water molecules around the thiocyanato ligand.

Preliminary studies of the equilibria in the reactions between $\left[Co(en)_2SO_3(OH_2)\right]^+$ and Cl^-, Br^-, and NCS^- ions have shown that the equilibrium constants are approximately in the order predicted by the theory of hard and soft acids and bases.

C O N T E N T S.

Papers published during the course of this work are contained in the folder inside the back cover.

SECTION I.

Introduction.

Octahedral complexes containing cobalt(III) as the central metal ion have been extensively studied since Werner and Jorgenson detailed their methods of preparation in the late 19th and early 20th centuries. Since the majority of the complexes are relatively inert, they react at conveniently measurable rates. Kinetic studies on the cobalt(III) complexes, mainly the cobalt-ammino compounds[1] has led to the interpretations of the types of mechanisms operating in octahedral complex reactions.

Reactions at octahedral centres are usually substitution processes. In these one of the coordinated ligands is replaced by an incoming ligand. There are, however, exceptions to this process, where a reaction proceeds <u>via</u> an intramolecular rearrangement rather than by an intermolecular mechanism as out-lined above. The intramolecular process is relatively rare and will be discussed with reference to the isomerisation of $[Co(en)_2(OH)_2]^+$ later in this work (Section III p. 42).

The most commonly studied substitution reaction is aquation. This is the replacement of a coordinated ligand by a molecule of water. The reverse of aquation or acid hydrolysis is anation, in which a coordinated ligand is replaced by an attacking nucleophile. In base hydrolysis an hydroxyl ion replaces one of the coordinated ligands. It has been suggested that anation never takes place directly, but that it is a two-step process. The first step being acid hydrolysis of the complex, which is then followed by the displacement of the water molecule by the incoming ligand.[2]

Before discussing acid and base hydrolysis in greater detail it is appropriate to review the various theories of mechanisms in octahedral

Compounds.

The SN1 and SN2 mechanisms, as applied to octahedral systems.

The first attempt to classify inorganic reaction mechanisms was made
by Ingold and Hughes.[3] They separated the mechanisms operating in
inorganic reactions into two categories. These were reactions which
proceeded _via_ an associative path and reactions which occurred
through a dissociative mechanism. These two mechanisms were designated
SN1 (substitution, nucleophilic, unimolecular) and SN2 (substitution,
nucleophilic, bimolecular), respectively. Bond breaking was thought to be
the most important factor in the unimolecular mechanism, whereas bond
making was the determining factor in bimolecular reactions.

Basolo and Pearson[4] later expanded the Ingold and Hughes mechanisms
into four main categories _viz._SN1, SN1(limiting), SN2, and SN2(limiting).
The criterion for an SN1(limiting) reaction is that definite evidence
exists on the formation of an intermediate of reduced coordination number.
Similarly, when there is real evidence of an intermediate of increased
coordination number, then an SN2(limiting) mechanism is operating.
When the kinetics and steric course of a reaction indicate that
a dissociative process is occurring, the reaction is proceeding
through an SN1 mechanism. If, however, the steric and kinetic data
indicate that an associative process is taking place, the reaction is
occurring _via_ an SN2 mechanism. In SN1 and SN1(limiting) reactions, bond
breaking is a major factor in determining the rate of the reaction.[5]
For an SN2 process there is appreciable bond breaking and bond making in
the rate determining step. In an SN2(limiting) mechanism the rate of
reaction is determined by the rate of bond formation.[5]

As the above nomenclature has been employed in the present
work, the two main processes are discussed in greater detail below.

The SN1 mechanism.

An SN1 process involves the formation of an intermediate of reduced coordination number. A five coordinate structure may take the form of a trigonal bipyramid or a tetragonal pyramid. These two structures are the most likely as stable compounds possessing these forms are known, and because their generation from the octahedron requires the minimum amount of atomic motion[6]. From the figure below (Fig. i) it may be seen that a reaction proceeding _via_ a tetragonal pyramid results in a product of the same configuration as the original complex.
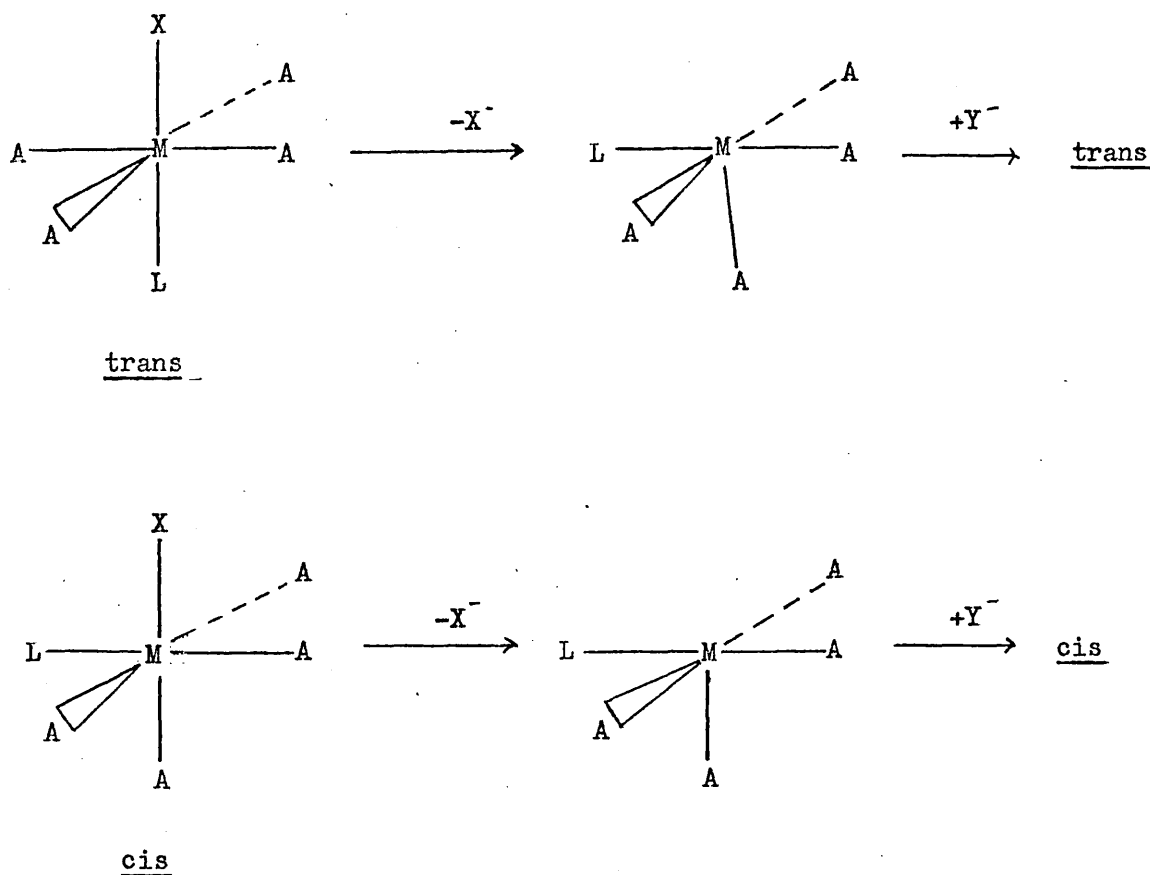
Fig. i.

The reaction of _cis_ and _trans_- MA$_4$LX with a nucleophile Y$^-$, _via_ a tetragonal pyramid.

Rearrangement may only take place if the reaction proceeds _via_ a

trigonal bipyramid, as shown in figures ii and iii.

Figure ii.

The reaction of _trans_ MA_4LX with a nucleophile Y^-, _via_ a trigonal bipyramidal

intermediate.

Figure iii.

The reaction of _cis-_ MA_4LX with a nucleophile Y^-, _via_ two different

trigonal bipyramidal intermediates.

In a tetragonal pyramid it is assumed that the incoming nucleophile will enter the same position as the outgoing ligand. Here the metal ion would be most easily accessible to the attacking group, and the generation of the octahedron would not require any additional atomic motion. The vacant d^2sp^3 hybrid orbital is projected outwards in this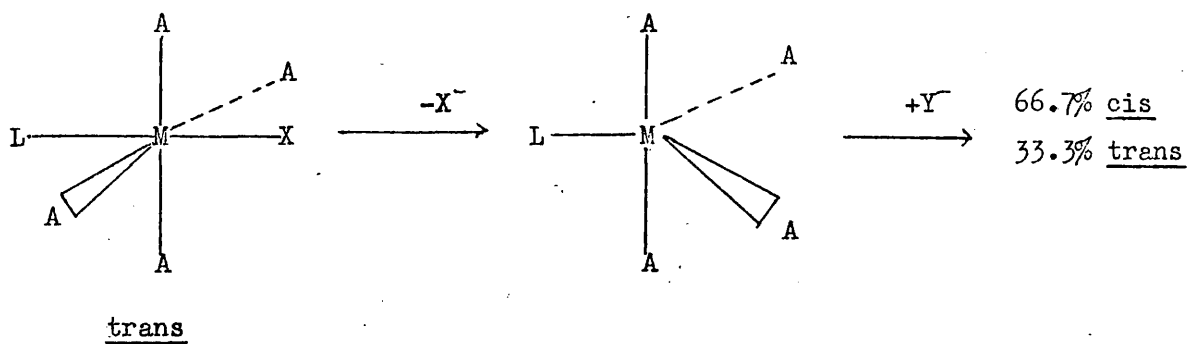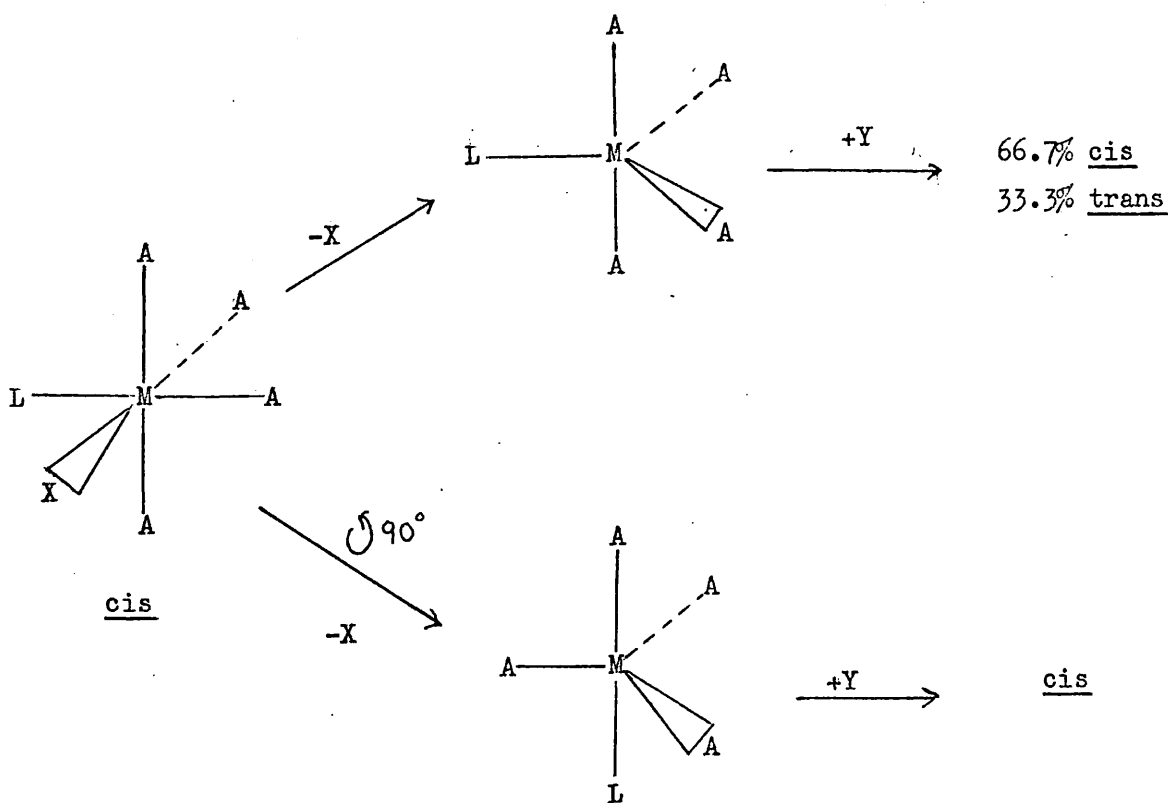 direction facilitating maximum overlap with the electrons of the entering nucleophile.[6] As has been demonstrated above (fig. ii and iii), a trigonal bipyramid permits rearrangement and statistically a trans compound reacting via such a mechanism would give 66.6% cis and 33.3% trans product. A cis reactant should produce 83.3% cis and 16.6% trans complex. These proportions are rarely acheived experimentally, as both steric and electronic factors can control the position of entry of the attacking nucleophile. However, it may be safely concluded that a dissociative mechanism proceeding through a tetragonal pyramidal inter- mediate will not allow rearrangement, whereas a reaction occurring via a trigonal bipyramidal intermediate does permit rearrangement.

Tobe[7] has suggested that in the aquation reactions of a group of complexes of the type cis- $\left[Co(en)_2 ACl \right]$ where $A = OH^-$, Br^-, Cl^- or a primary aliphatic amine, the higher activation entropies are diagnostic of the formation of a trigonal bipyramidal intermediate. The lower activation entropies were, it was thought, diagnostic of a tetragonal pyramidal intermediate.

The SN2 mechanism.

Substitution at an octahedral centre may also occur by an SN2 mechanism, which requires the formation of an intermediate of increased coordination number. Stable compounds in which the central metal ion is seven coordinate are known, and two different structures for these compounds have been established. ZrF_7^{3-}[8] and IF_6[9] both possess a pentagonal bipyramidal structure and NbF_7^{2-}[10] is trigonally prismatic, with one of the fluoride ions projected from one of the trigonal faces (fig. iv).

(a)   F   (b)
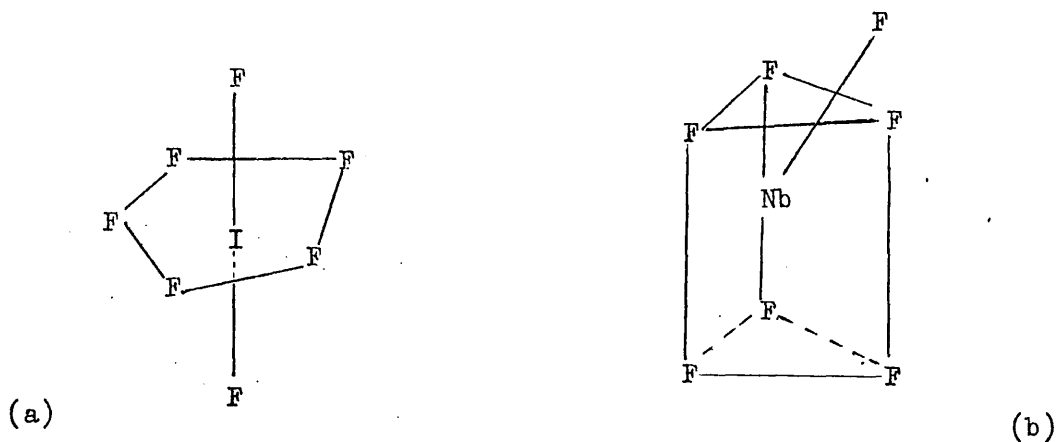
Figure iv.

The pentagonal bipyramidal structure of IF_7 (a) and the trigonal prismatic

structure of $NbF_7{}^{2-}$ (b)

The structure of the seven-coordinated intermediate in the SN2

mechanism has been assumed to be the pentagonal bipyramid, as this

may be easily obtained from the octahedron. The intermediate may be formed

by an attack adjacent to the leaving group i.e. cis attack, or the

nucleophile may attack opposite the departing ligand i.e. trans

attack[11] (Fig. v.).

Figure v.

Trans attack always results in a rearranged product, whether the

starting material possessed a trans configuration or a cis configuration.

Cis attack gives a product of the same configuration as the reactant

(Fig. vi.).

Figure vi.

Whether or not the product has undergone configurational change

provides only an indication to the type of mechanism which has occurred.

A cis compound may give only a cis product from both an SN1 mechanism

involving a tetragonal pyramidal intermediate and from an SN2

mechanism in which the nucleophile has attacked cis to the departing

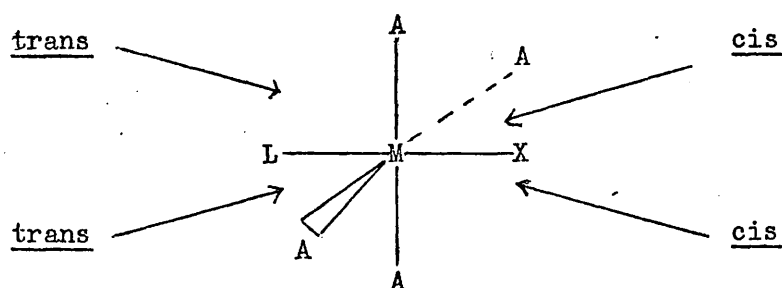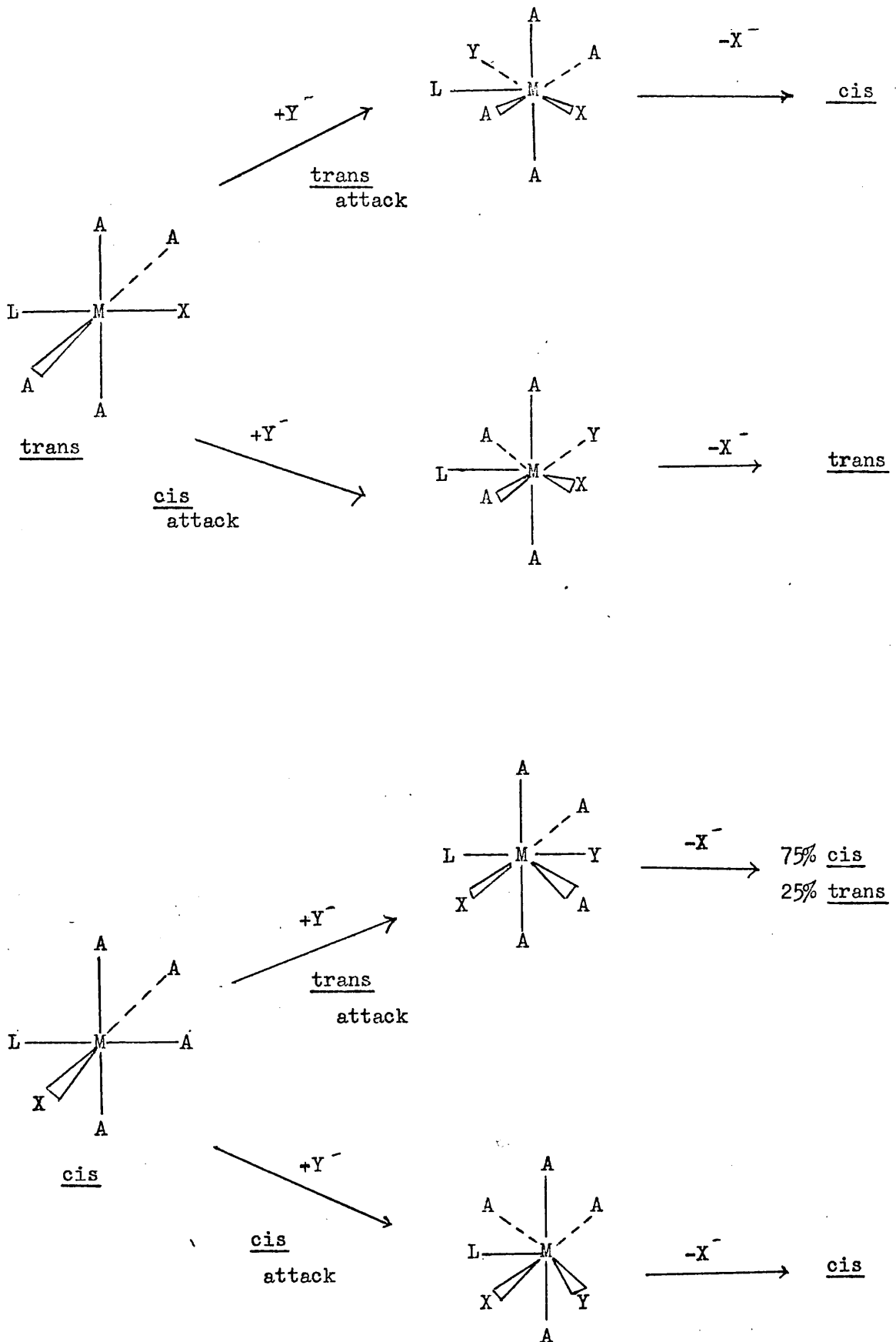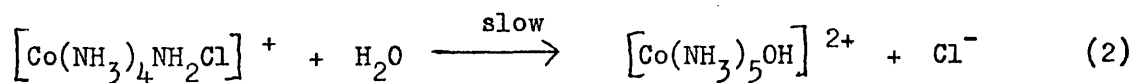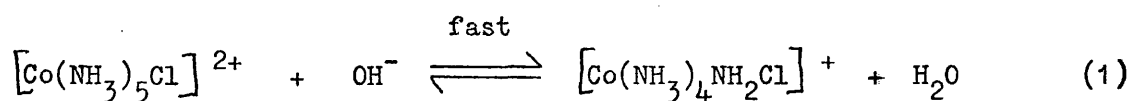ligand. Thus, to distinguish between these two possibilities the

molecularity of the reaction must be known.

The A, I_a, I_d, and D Mechanisms.[12]

The method of categorising substitution mechanisms employed by

Basolo and Pearson includes cases which appear to be second order in the

stoichiometric sense but on closer inspection have been stated to be

similar to unimolecular reactions. This occurs in the base hydrolysis

of the chloroamminocobalt(III)[13] complexes, where the reaction is said to

first order in both hydroxide and complex, but an SN1CB mechanism is

thought to be operating. In this mechanism (SN1CB) the hydroxyl

group rapidly abstracts a proton from the ammino group to form the

complex conjugate base. This then undergoes a slow rate determining

aquation reaction to give the hydroxo product (equations 1 and 2).

$$[Co(NH_3)_5Cl]^{2+} + OH^- \underset{\longleftarrow}{\overset{fast}{\rightleftharpoons}} [Co(NH_3)_4NH_2Cl]^+ + H_2O \qquad (1)$$

$$[Co(NH_3)_4NH_2Cl]^+ + H_2O \overset{slow}{\longrightarrow} [Co(NH_3)_5OH]^{2+} + Cl^- \qquad (2)$$
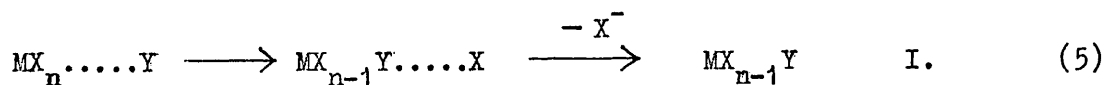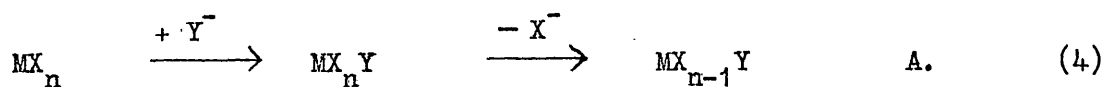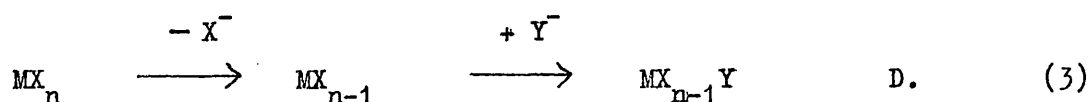
This mechanism requires an acidic proton which is readily removable to

form the conjugate base. It is substantiated by the fact that the rates

of base hydrolysis of compounds not containing such an acidic proton

do not have an hydroxide dependent term in their rate equation.[14] Also,

an acceleration of base hydrolysis is observed in complexes containing

such acidic protons.

In attempt to define 'intimate' mechanisms more clearly
Langford and Gray[12] proposed three main categories of reaction
mechanism, and they are as follows:-

1. D, a dissociative mechanism in which the ligand is lost in the
first step of the reaction and an intermediate of reduced coordination
number is definitely produced. This is similar to the SN1(limiting)
mechanism.

2. A, an associative mechanism in which the incoming ligand becomes
attached in the first step of the reaction to give a definite intermediate
of increased coordination number (similar to the SN2(limiting) mechanism).

3. I, an interchange reaction in which the attacking nucleophile moves
into the inner coordination sphere of the complex as the outgoing
ligand moves to the outer coordination sphere. This does not involve the
formation of an intermediate of a different coordination number to
the original complex. The type of intermediate visuallised is
that of an outer sphere complex similar to e.g. $\left[Co(NH_3)_6\right]^{3+}.....SO_4^{2-}$.
The above three mechanisms are illustrated in equations 3 - 5.

$$MX_n \xrightarrow{-X^-} MX_{n-1} \xrightarrow{+Y^-} MX_{n-1}Y \qquad D. \qquad (3)$$

$$MX_n \xrightarrow{+Y^-} MX_nY \xrightarrow{-X^-} MX_{n-1}Y \qquad A. \qquad (4)$$

$$MX_n.....Y \longrightarrow MX_{n-1}Y.....X \xrightarrow{-X^-} MX_{n-1}Y \qquad I. \qquad (5)$$

The interchange mechanism is further defined for cases in which the rate
is sensitive to the nature of the incoming nucleophile. These were
designated I_a mechanisms, and are similar to the SN2 mechanism of Basolo
and Pearson. A lack of dependence of the rate on the type of nucleophile
was said to give an I_d mechanism, which is similar to the SN1 mechanism.

In the I_a category are reactions where the activation energy is lowered due to the assistance of the attacking nucleophile, i.e. bond making is important in the rate determining step. Reactions proceeding through an I_d mechanism, the nature of the leaving group is more important, i.e. bond breaking is the major factor in the rate determining stage.

The trans Effect in Octahedral Complexes.

The trans effect has been defined as the 'effect of a coordinated group upon the rate of substitution reactions of ligands opposite to it in a metal complex.' [15]

Reports in the literature[16-19] show that certain ligands in the trans position to the leaving group, possess a labilising influence on the rate of departure of this ligand. It was found that in the hydrolysis reaction of $[Co(en)_2Cl(NO_2)]^+$, where Cl^- is the departing ligand, the trans isomer reacted at a considerably faster rate than the cis compound.[16] It has also been shown[17] that the sulphito group is more strongly activating when in the trans position.

In a study of the anation reactions of complexes of the type trans-$[Rh(en)_2L(OH_2)]^{2+}$ (L^- = Cl, Br, I) with Cl^-, Br^- or I^- ions, it was found[18,19] that the kinetic trans effect of L on the $Rh-OH_2$ bond was in the order $I > Br > Cl$. The effect of L on the metal-oxygen bond increases with increasing softness[20] or class (b) character.[21] Similarly, the labilising effect of ligand L in the reactions of trans-$[Rh(en)_2LX]^+$ (L^- = Cl, Br, I and X^- = Cl or Br) increases in the order $I > Br > Cl$. The high trans effect of the iodide ion was ascribed to the ease with which it may compensate for either an increase or a decrease in the electron density at the rhodium centre.[18]

All cases in which the trans effect has so far been observed, the activating ligand is either unsaturated and may form ligand to metal π bonds with the t_{2g} electrons on the metal; or possesses such soft character that considerable σ covalent bonding occurs.[22] In either case trans activation will be exhibited, facilitating the removal of the departing ligand, assisting the formation of the reactive intermediate and increasing the overall rate of reaction.

Acid Hydrolysis Reactions.

Studies on the rate of acid hydrolysis in dilute aqueous solutions have been found to give first order kinetics. Since the concentration of water, which is both a reactant and the solvent, does not alter during the reaction, the rate of hydrolysis is dependent only on the change in concentration of the complex and first or pseudo first order kinetics are observed. As the kinetics were first order a dissociative mechanism was proposed. This would involve the formation of a five - coordinated intermediate which is then attacked by water to form the octahedral product. Complete removal of the outgoing ligand in the transition state is not required, only that it is sufficiently far away to have no direct influence on the the remaining five ligands. That an SN1 mechanism operates has been substantiated by several reports on the acid hydrolysis reactions of the chloroammino complexes of cobalt(III). [23]

During acid hydrolysis of the compounds it was observed that increasing the chelation number of the ligands e.g. replacing ammonia by ethylenediamine or ethylenediamine by diethylenediamine, the rate of hydrolysis is gradually reduced. This progressive decrease may be explained by considering the stereochemistry at the octahedral centre. If an associative mechanism (SN2) were operating, attack _trans_ to the chloride ligand would be hindered and in the case of $[Co(en)(dien)Cl]^{2+}$ would be almost negligible. This complex, however, undergoes acid hydrolysis at only a slightly slower rate than $[Co(trien)NH_3Cl]^{2+}$, in which an SN2 _trans_ attack mechanism would not be sterically unfavourable. [24]

The effect of carbon or nitrogen substitution in the ethylenediamine cobalt(III) complexes has also been studied. [23] It was found that, generally, increasing substitution increased the rate of acid hydrolysis. This is in agreement with a dissociative mechanism, as greater crowding at the cobalt(III) centre would favour the formation

of an intermediate of reduced coordination number.

As a general rule, cis isomers tend to react without a change in configuration, whereas trans isomers tend to undergo acid hydrolysis with change in configuration. This must mean that the cis isomer reacts reacts via a tetragonal pyramidal intermediate, as this does not permit rearrangement. Trans isomers must react through a trigonal bipyramidal structure as this will allow rearrangement.[25]

Base Hydrolysis Reactions.

A detailed study of the kinetics and stereochemistry of base hydrolysis reactions of compounds of the type $\left[Co(en)_2LX\right]^{n+}$, has been undertaken by Tobe and his co-workers.[26] The reaction may be generalised as in equation 6.

$$\left[Co(en)_2LX\right]^{n+} + OH^- \longrightarrow \left[Co(en)_2LOH\right]^{n+} + X^- \qquad (6)$$
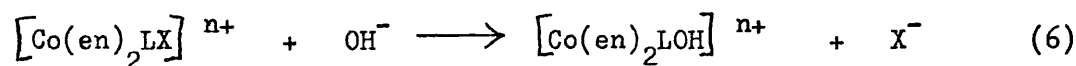
In this study it was shown that both cis and trans isomers react with considerable rearrangement during base hydrolysis. This is in direct contrast to the stereochemical course of acid hydrolysis, which for a cis isomer occurs with 100% retention of configuration.[23]

The hydroxide ion occupies a unique position amongst nucleophiles.[27] Even at low concentrations of hydroxide ions, increases in the rate of release of halide ions and other labile ligands from the ammino complexes of cobalt(III) are observed.[26] This is surprising as the rate of hydrolysis of $\left[Co(NH_3)_5Cl\right]^{2+}$ is relatively unaffected by the presence of large concentrations of negative ions such as NO_3^-, ClO_4^- and SO_4^{2-}.[28] Similarly, more strongly basic anions e.g. N_3^- and NO_2^- do not affect the rate of hydrolysis of $\left[Co(en)_2NO_2Cl\right]^+$.[29]

It has been suggested that most substitution reactions occur as outlined in equations 7 and 8 overleaf.[30]

$$\left[Co(en)_2LX\right]^{n+} + H_2O \longrightarrow \left[Co(en)_2L(OH_2)\right]^{(n-1)+} + X^- \qquad (7)$$

$$\left[Co(en)_2L(OH_2)\right]^{(n-1)+} + Y^- \longrightarrow \left[Co(en)_2LY\right]^{n+} + H_2O \qquad (8)$$
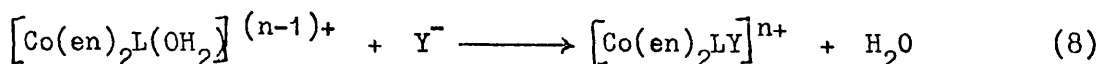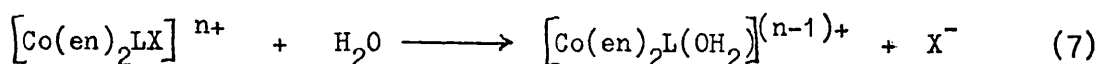
As the hydroxide ion may penetrate the second coordination shell

via the Grotthus chain mechanism, it need not displace a molecule of

water to give the hydroxo product. This could account for the observed

increases in the rates of base hydrolysis.[27]

A more generally accepted explanation for the mechanism of base

hydrolysis was proposed by Garrick.[13] He suggested the following reaction

scheme for the base hydrolysis of $\left[Co(NH_3)_5Cl\right]^{2+}$ (equations 9-11)

$$\left[Co(NH_3)_5Cl\right]^{2+} + OH^- \underset{}{\overset{fast}{\rightleftharpoons}} \left[Co(NH_3)_4NH_2Cl\right]^+ + H_2O \qquad (9)$$

$$\left[Co(NH_3)_4NH_2Cl\right]^+ \overset{slow}{\longrightarrow} \left[Co(NH_3)_4NH_2\right]^{2+} + Cl^- \qquad (10)$$

$$\left[Co(NH_3)_4NH_2\right]^{2+} + H_2O \overset{fast}{\longrightarrow} \left[Co(NH_3)_5OH\right]^{2+} \qquad (11)$$
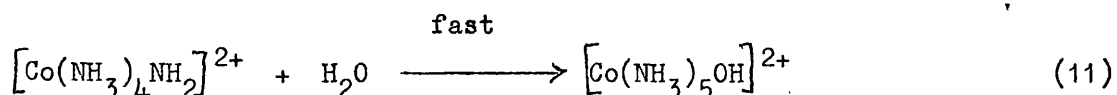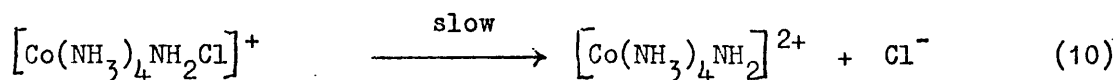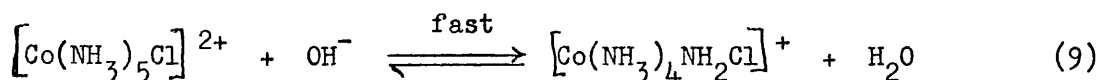
This involves the formation of a very fast pre-equilibrium in which

the conjugate base is formed by the hydroxyl ion abstracting an

ammino proton. The resulting amido complex dissociates to form the

five coordinated intermediate. This reaction (eqn. 10) is the rate

determining step. A condition for the mechanism is that the equilibrium

should be set up more rapidly than the overall rate of reaction. This

mechanism was termed SN1CB (substitution, nucleophilic, unimolecular,

conjugate base). For an SN1CB mechanism to occur the complex must contain

an acidic amine proton. The conjugate base mechanism is supported by

the data on the rates of hydrolysis of compounds lacking such an acidic proton. The base hydrolysis rates of <u>trans</u>-dinitrobis(2,2"-bipyridine)-cobalt(III)[31] and chloropentacyanocobalt(III)[32] are relatively unaffected by increases in the concentration of hydroxyl ions. The results obtained by Garrick[13] have also been explained in terms of an SN2 mechanism.[33]

A kinetic method for distinguishing between the SN2 and the SN1CB mechanisms was suggested which involved the use of hydrogen peroxide.[33] The anion of H_2O_2, HO_2^- is a better nucleophilic reagent than the hydroxyl ion, in reactions where an SN2 mechanism is considered to be operating. Hydrogen peroxide is a stronger acid than water having $pK_a = 11.8$ relative to $pK_a = 14$ for water, and the equilibrium constant for the reaction (eqn. 12) is large. When H_2O_2 is added to an aqueous solution

$$OH^- + H_2O_2 \rightleftharpoons H_2O + HO_2^- \qquad (12)$$

of hydroxyl ions and a substrate, a large increase in the rate should be observed if the reaction occurs <u>via</u> an SN2 mechanism. The HO_2^- ion is a better nucleophile than OH^- and as such should increase the reaction rate. Similarly, a decrease in the reaction rate would be expected if an SN1CB mechanism is operating. The addition of H_2O_2 to the reaction of benzyl bromide with OH^- ions in an acetone/water solvent (considered to be an SN2 mechanism) greatly increased the rate of bromide release. Addition of hydrogen peroxide to a solution of ethylenechlorohydrin and alkali, in water, reduced the base hydrolysis rate by a factor $\sim 10^2$. This reaction is a well authenticated example of an SN1CB mechanism and[34] is summarised in equations 13 and 14.

$$C_2H_4ClOH + OH^- \rightleftharpoons C_2H_4ClO^- + H_2O \qquad (13)$$

$$C_2H_4ClO^- \longrightarrow C_2H_4O + Cl^- \qquad (14)$$
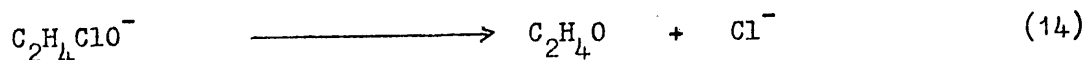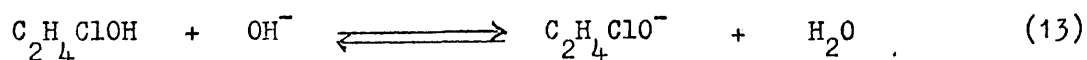
In the base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$, the addition of 2M H_2O_2 almost completely stopped the release of chloride ion from the complex cation.[33] This would seem to provide good evidence for an SN1CB mechanism operating in base hydrolysis reactions. These reactions occur with change in configuration and from this it may be concluded that the five coordinate intermediate possesses a trigonal bipyramidal structure. From a study of a large number of base hydrolysis reactions Basolo and Pearson concluded that a _cis_ reactant never gives less _cis_ product than the corresponding _trans_ isomer.[25] The steric course of base hydrolysis is illustrated in Fig. vii.
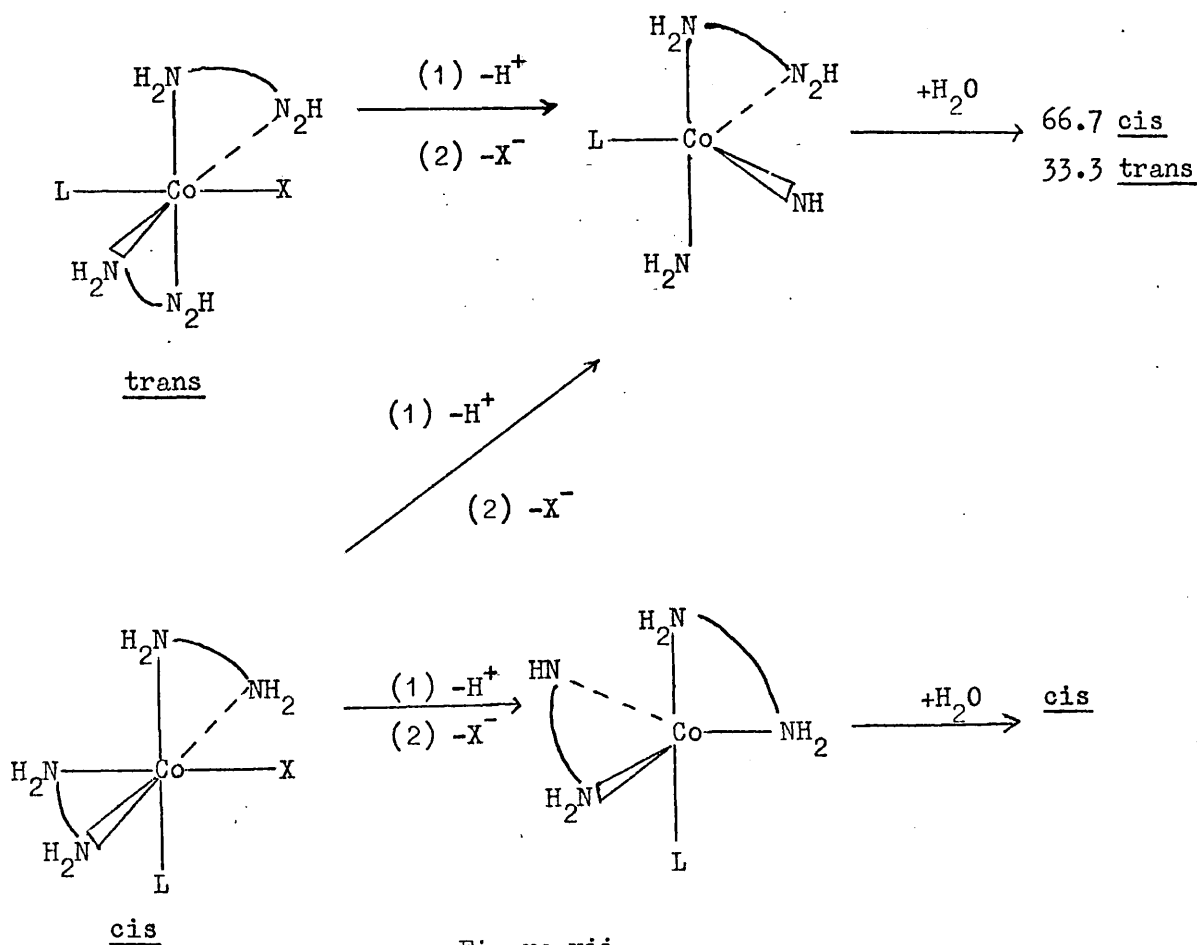

Figure vii.

The steric course of base hydrolysis of _cis_ and _trans_ $[Co(en)_2LX]$

The trans isomer can only readily form one intermediate, whereas two different intermediates may be readily generated from the cis isomer.

It is of interest to note that an investigation of the steric course[26] of base hydrolysis of compounds of the type $[Co(en)_2LX]^{n+}$ where $L = Cl^-$, $X = Cl^-$ or Br^-; $L = NCS^-$, $X = Cl^-$ or Br^-; $L = N_3^-$, $X = Cl^-$ or N_3^-, it was found that the nature of the ligand L influenced the isomeric distribution of the products. L is the ligand which remains attached to the central metal ion during the reaction. X is the leaving group. When $L = Cl^-$ the proportion of cis and trans-$[Co(en)_2ClOH]^+$ products was identical whether $X = Cl^-$ or Br^-. Hence, X can have no influence in determining the products, unlike the SN2 mechanism where X is present in the transition state and must affect the configuration of the final product. This would seem to point to the conclusion that base hydrolysis reactions of compounds containing acidic protons proceed via a five coordinate intermediate, which is the conjugate base $[Co(en)en-HL]$.[26]

Optical Activity in Octahedral Compounds.

When a cis compound may exist in two configurations, one of which is the mirror image of the other, the compound is said to exhibit optical activity.[35,36]

If monochromatic plane polarised light is passed through an optically active compound, the plane of polarisation is rotated. The magnitude and sign of rotation observed varies with the wavelength of the light used. This variation is termed optical rotatory dispersion.

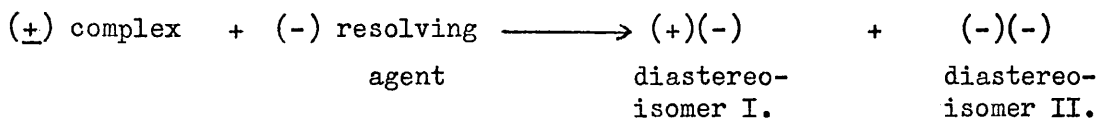The sign of optical rotation is said to be (+) or (-) at the Na_D line. D^* and L^* denote the absolute configuration of an enantiomer relative to a compound whose absolute configuration has been established by X-ray crystallography e.g. $D^*(+)-[Co(en)_3]^{3+}$. D and L are used to denote relative configurations for similar compounds, but whose absolute configuration has not been completely ascertained.[37]

It has been suggested that Λ and Δ[38] should be employed rather than D^* and L^* to depict the absolute configuration of a metal complex. When $M(AA)_3$ (where AA is a bidentate ligand) is viewed along the C_3 axis, the chelate rings appear to be helical.[38] A left-handed helix was designated Λ and a right-handed helix was given the symbol Δ. Thus $D^*(+)-[Co(en)_3]^{3+}$ becomes Λ $(+)[Co(en)_3]^{3+}$. However, if $\Lambda(+)-[Co(en)_3]^{3+}$ is viewed along the C_2 axis, the chelate rings appear to form a right-handed helix.[37] It was thus thought that the $C_2(D^*)$ nomenclature would have wider applications than the $C_3(\Lambda)$ system, since it could be applied to compounds not possessing a C_3 axis, e.g. all the compounds of the type $[Co(en)_2X_2]$.[37]

A very large number of compounds have been found to exhibit optical activity. Resolution of 6-coordinated complexes of metal ions e.g. Ni(II), Fe(II), Ru(III), Cr(III) and Co(III) has been widely reported.

The separation of optical isomers generally follows two main methods:-

1. For ionic compounds, the racemic mixture is converted into two diastereoisomers and these are separated by fractional crystallization.

$(\pm)$ complex + $(-)$ resolving $\longrightarrow$ $(+)(-)$ + $(-)(-)$

                         agent   diastereo-   diastereo-

                                      isomer I.   isomer II.

(a) Cationic species may be resolved using D-tartrate, antimonyl-D-tartrate, D-camphor-π-sulphonate etc.

(b) Anionic isomers may be obtained by their conversion to the salt of an optically active base, such as bruccine, quinine or strychnine. The resolving agent is then removed by precipitation or extraction and the optically active isomer obtained. Recently Dwyer et al.[39] have used optically active metal complexes to resolve

similar metal chelate compounds e.g. $D(+)$-<u>cis</u>-$[Co(en)_2(NO_2)_2]^+$

may be used to resolve $[Co(en)(ox)_2]^-$.

2. Non-ionic compounds have been resolved by one enantiomer being

preferentially adsorbed onto the surface of optically active solids

e.g. quartz[40] and lactose[41].

Optically active compounds may undergo intermolecular or intramolecular

reactions, in which the optical activity is either retained or lost.

The mechanisms operating in these reactions are discussed in detail

in Section III p.42 and Section IV p.60.

GENERAL DISCUSSION OF RESULTS.

The work described herein is significant in view of the insight which it provides into the reactivity of Co(III) complexes. The compounds of Co(III) are generally inert but the reaction conditions used in these studies have produced a marked lability. Thus, while the isomerisation reactions of such complexes as $[Co(en)_2(OH_2)_2]^{3+}$ in dilute acid and $[Co(en)_2(OH)_2]^{+}$ in dilute alkali, exhibit normal behaviour, the rates of isomerisation of $[Co(en)_2(OH_2)_2]^{3+}$ and $[Co(en)_2(OH_2)NCS]^{2+}$ in concentrated acid are very fast at ambient temperatures. Furthermore, the rates of the substitution reactions of the sulphito complexes of Co(III) are too fast to be measured using conventional techniques. The celerity of these reactions has been explained from a consideration of the kinetic data. A summary of this follows.

At high acid concentrations both $[Co(en)_2(OH_2)_2]^{3+}$ and $[Co(en)_2(OH_2)NCS]^{2+}$ undergo fast isomerisation reactions. The observed first order rate constant is not directly proportional to the acid concentration and an SN1 mechanism, similar to that in dilute acid, is thought to be operating in these systems. The rate of isomerisation of the diaquo complex in dilute acid is considerably slower than that in concentrated acid. In neutral solution the diaquo complex is deprotonated to form the extremely labile hydroxoaquo species. In basic media the dihydroxo complex is formed from the hydroxoaquo compound and the rate of isomerisation is again reduced. The lability

of the hydroxoaquo species may be understood on the basis of the exchange rates of these complexes <u>viz</u>. $[Co(en)_2(OH_2)_2]^{3+}$, $[Co(en)_2(OH)(OH_2)]^{2+}$, and $[Co(en)_2(OH)_2]^+$ with labelled solvent. In dilute acid the diaquo complex undergoes water exchange by a slow acid hydrolysis type of reaction, whereas the hydroxoaquo complex exchanges water by a faster base hydrolysis mechanism.

The very fast rates of isomerisation of the $[Co(en)_2(OH_2)_2]^{3+}$, in concentrated acid, are explained by the greater attraction of the acidic protons for the coordinated water molecules. In concentrated acid there is insufficient water present for the protons to be tetrahydrated. In the present work this lack of available water molecules for complete tetrahydration commences at $\sim 8M$ acid, which is in agreement with previous studies of reactions in highly acid media. The increased lability observed in the $[Co(en)_2(OH_2)NCS]^{2+}$ is first really noticeable at $\sim 6M$ acid. This increase in the rate of isomerisation, which occurs at a lower acid concentration than for the diaquo system, is explained by the fact that the thiocyanato group possesses a large dipole moment and hence, may also be able to orientate water molecules in its vicinity. This would further decrease the number available for proton hydration. The greater attraction of the acidic protons for the coordinated water molecules would lead to a weakening of the $Co - OH_2$ bond by withdrawing electrons from the cobalt ion. This would facilitate the formation of the reactive five coordinate intermediate and increase the rate of isomerisation.

The slow rate of isomerisation of the $[Co(en)_2(OH)_2]^+$

complex may be ascribed to the stability of the cobalt-oxygen

bond in this complex, relative to that of the cobalt-oxygen

bond in the diaquo complex. This would prevent rapid exchange

with the solvent and hence reduce the rate of isomerisation.

From this work it is thought that the factors conducive to

a twist mechanism are present in the dihydroxo complex in

basic solution.

It is concluded that the isomerisation reactions of the

$[Co(en)_2(OH_2)_2]^{3+}$ and $[Co(en)_2(OH_2)NCS]^{2+}$ complexes proceed

through a five coordinated trigonal bipyramidal intermediate.

This would permit the observed configurational changes, whereas

reactions proceeding via a tetragonal pyramidal intermediate

give a product of the same configuration as the original

compound.

Substitution reactions of the sulphito complexes of

Co(III) occur by an SN1(lim.) mechanism. The extreme lability

exhibited by these complexes was originally attributed to

the possibility of $d\pi$ - $d\pi$ bonding, between the cobalt atom

and the coordinated sulphur ligand. This high reactivity

is now considered to arise from the ligand to metal donation

of charge through the σ bond. The lability is further explained

by the extremely large trans effect shown by sulphur-bonded ligands.

In this, electrons are released to the outgoing ligand, particularly

when in the trans position, assisting its removal and greatly

increasing the rate of formation of the five coordinate intermediate.

Thus, the cause of lability in the reactions of the Co(III) complexes studied may be due to factors operating within the complex (as in the case of the sulphito compounds), or, to the external environment, as is found in the isomerisation reactions of the $[Co(en)_2(OH_2)_2]^{3+}$ and $[Co(en)_2(OH_2)NCS]^{2+}$ in concentrated acid solution.

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SECTION II.

The Base Hydrolysis of the trans-Chlorohydroxobis(ethylenediamine)-

cobalt(III) Cation.

Introduction.

In a study of the steric course of base hydrolysis of compounds

of the type $\left[Co(en)_2AX\right]^{n+}$ where A = hydroxo, chloro, bromo, or

nitrito and X = chloro or bromo, Chan and Tobe[1] concluded that trans-

$\left[Co(en)_2(OH)Cl\right]^+$ reacts to form 94% cis-$\left[Co(en)_2(OH)_2\right]^+$, thus

undergoing base hydrolysis and change of configuration simultaneously.

The kinetics of this reaction were second order and were consistent with

either a single-stage bimolecular attack of hydroxyl ions on the cobalt

atom (SN2), or the formation of a pre-equilibrium in which the

hydroxyl ion functions as a base, removing a proton from the amine

nitrogen, to form the amido conjugate base(SN1CB). This conjugate base

was assumed to rapidly expel the chloro ligand due to the labilising

influence of the amido group.[2] Both mechanisms require that the electron

displacing properties of ligand A do not affect the rate of the reaction.

It was concluded that the mechanism was bimolecular, but that the way

in which the complex and the hydroxyl ion came together was modified

due to the high reactivity of the hydroxyl ion. This reactivity has been

explained in terms of its mobility through the solvent shell of the

complex ion[3] via Grotthus proton transfer. A 'sticky' collision was

visuallised[1] in which the reactants were kept together longer than is

usual and thus had time to change their relative orientations. Such a

mechanism may well be indistinguishable from ion-pair formation.

In the case of the trans- $\left[Co(en)_2Cl_2\right]^+$ complex, where A and X

are identical and lie on a symmetry axis of the complex ion, attack

adjacent, rather than opposite the departing ligand is more favourable.

The interaction between the incoming group (OH⁻) and the out-going

chloro will assist replacement of the chloro ligand. There will thus be the least disturbance of the other five ligands and the surrounding solvent shell. The hydroxyl ion will attack in the position where there is least negative or most positive charge and again this is more likely adjacent to the outgoing negatively charged chloride ion. It was observed that the product contained 95% trans- $\left[Co(en)_2(OH)Cl \right]^+$.

In the series trans- $\left[Co(en)_2ACl \right]^{n+}$ where A = isothiocyanato or ammino, the probability of finding the hydroxyl ion in the vicinity of ligand A is much greater than it would be in the region of the chloro ligand as the residual positive charge on $-NH_3^{\delta+}$ or $-\overset{+}{N}\equiv\overset{-}{C}-\overset{-}{S}$ attracts the negatively charged hydroxyl ion. When A = hydroxo, the attraction of the hydroxyl ion to the hydroxo ligand is probably due to the presence of one or more water molecules strongly bonded to it forming part of the Grotthus chain, which also includes the coordinated hydroxo group(Fig. i).
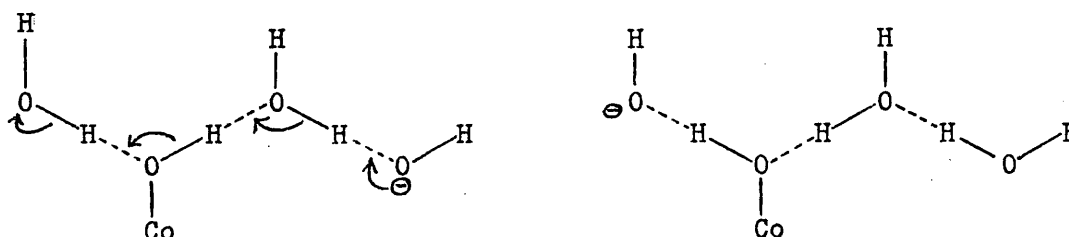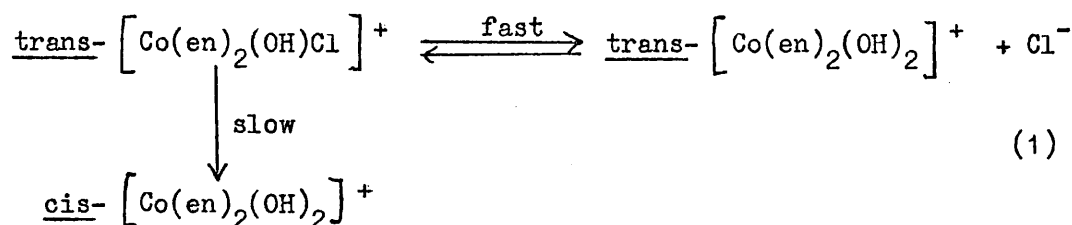

<u>Fig. i.</u>

Hydroxyl attack <u>via</u> the Grotthus chain mechanism.

The relatively slow rate of base hydrolysis when A = hydroxo was explained by considering the hydroxyl ion to be prevented from direct attack on the central cobalt atom.

A recent study[4] has re-examined the kinetics and steric course of the base hydrolysis of trans- $\left[Co(en)_2(OH)Cl \right]^+$. On the basis of

a computer analysis of UV and visible spectra of reaction solutions, it was concluded that a fast equilibrium was set up between trans-$\left[Co(en)_2(OH)Cl \right]^+$ and trans- $\left[Co(en)_2(OH)_2 \right]^+$, which was independent of the concentrations of hydroxide and chloride ions, under the conditions at which the reaction was studied. It was suggested that this equilibrium had not been observed in the preceding study[1] as the reaction was followed at a wavelength at which the extinction coefficients of the two trans compounds are almost identical. The following reaction scheme was proposed for the base hydrolysis of trans-$\left[Co(en)_2(OH)Cl \right]^+$:

$$\text{trans-} \left[Co(en)_2(OH)Cl \right]^+ \underset{\xrightarrow{\quad\text{fast}\quad}}{\rightleftharpoons} \text{trans-} \left[Co(en)_2(OH)_2 \right]^+ + Cl^-$$

$$\downarrow \text{slow}$$

$$\text{cis-} \left[Co(en)_2(OH)_2 \right]^+ \tag{1}$$

If the rapid interchange of ligands in the trans compounds were due to an ion-pairing mechanism a reduction of the effect should be noticeable in less concentrated solutions, but this was not observed. Approximately 9% trans-$\left[Co(en)_2(OH)_2 \right]^+$ was said to exist at equilibrium and this concentration decreased with the increase in concentration of the cis-$\left[Co(en)_2(OH)_2 \right]^+$ complex. A dissociative mechanism was proposed, involving a tetragonal pyramid, for the formation of the trans-$\left[Co(en)_2(OH)_2 \right]^+$, since it is thought that the trans hydroxo ligand promotes a unimolecular reaction by labilising the chloro ligand.[5] An ion-pairing mechanism was thought unlikely due to the low charge and the lack of evidence of ion-pairing in trans systems.[6] The rearrangement of the trans- $\left[Co(en)_2(OH)Cl \right]^+$ to the cis- $\left[Co(en)_2(OH)_2 \right]^+$ was very slow as would be expected due to the high energy barrier that strong field complexes must overcome to undergo isomerisation.[7]

The trans-dichloro complex undergoes base hydrolysis with very

little change in configuration[1] to give 95% trans- $\left[Co(en)_2(OH)Cl\right]^+$,
whereas considerable change in configuration is observed in the base
hydrolysis of the trans- $\left[Co(en)_2(OH)Cl\right]^+$ ion. This is surprising
since the hydroxyl group is a poorer π - electron donor than the
chloro ligand and would thus not be expected to facilitate the
formation of a trigonal bipyramid, if the attack proceeded via an
attack trans to the departing ligand by the hydroxyl ion on the trans-
$\left[Co(en)_2(OH)Cl\right]^+$ complex.

Dittmar and Archer[4] also thought that a conjugate base mechanism
could be operating, since the attraction between the acidic protons
on the nitrogen and the hydroxyl ion would disturb the electronic
structure of the complex ion. This would weaken the bonding and aid
the dissociation of the chloro ligand of the trans- $\left[Co(en)_2(OH)Cl\right]^+$
in the equilibrium process and assist the movement of the amines in
the isomerisation process.

If the reaction path proposed in equation (1) were correct i.e. that
there is a fast, reversible formation of 9% trans- $\left[Co(en)_2(OH)_2\right]^+$ on
the addition of alkali to the trans- $\left[Co(en)_2(OH)Cl\right]^+$, then it would
be expected that on the addition of chloride ions to trans- $\left[Co(en)_2(OH)_2\right]^+$
91% of the complex would be rapidly converted to trans- $\left[Co(en)_2(OH)Cl\right]^+$.
This should then change to 94% cis- $\left[Co(en)_2(OH)_2\right]^+$ at the rate
observed for the base hydrolysis of trans- $\left[Co(en)_2(OH)Cl\right]^+$. Thus
the isomerisation of the dihydroxobis(ethylenediamine)cobalt(III)
species, which is very slow, should exhibit chloride catalysis.

To test this mechanism the rate of isomerisation of the trans-
dihydroxo cation to the cis isomer was studied at various temperatures
in the presence and absence of added chloride ions.[11] The mechanism of
Dittmar and Archer also requires that trans- $\left[Co(en)_2(OH)Cl\right]^+$ will
exchange its chloro ligand with free chloride ions in solution if
the equilibrium represented in eqn. 1. is achieved. The reaction of

the trans-chlorohydroxo complex in alkali was carried out under the identical conditions to those employed above[4] except for the presence of $^{36}Cl^-$ ions. After terminating the reaction at various stages the unreacted trans- $\left[Co(en)_2(OH)Cl \right]^+$ was precipitated as the tetraphenyl borate and tested for radioactivity.[11]

Experimental.

Isomerisation

Two methods were used to study the rate of the trans to cis isomerisation of the $\left[Co(en)_2(OH)_2 \right]^+$ cation.

1. A known weight of trans- $\left[Co(en)_2(OH)(OH_2) \right](ClO_4)_2$ was dissolved in a solution of sodium hydroxide (10ml. of 0.07M), thermostatted at the required temperature. 3ml. of the solution were then placed in a 1cm. silica cell in a Unicam S.P.800 spectrophotometer. The cell holder was thermostatted at the same temperature as above. The change in absorbance with time was recorded

      a. at a fixed wavelength, using an S.P.850 scale expansion

         unit and an external slave recorder

      b. by scanning from 15,000 - 30,000cm.$^{-1}$(667 - 333nm.) at

         fixed time intervals.

The above experiment was repeated but with the addition of a known amount of sodium chloride to the sodium hydroxide. The observed rate constant was obtained by plotting $\log (A_\infty - A_t)$ v.time and from the equation

$$k_{obs.} = 2.303 \; \log \frac{(A_\infty - A_t)}{(A_\infty - A_o)} \Big/ t \quad sec.^{-1}$$

where A_∞ = absorbance at time $t = \infty$

    A_t = absorbance at time $t = t$

    A_o = absorbance at time $t = 0$

2.The reaction was initiated as above i.e. by the addition of solid trans- $\left[Co(en)_2(OH)(OH_2) \right] (ClO_4)_2$ to sodium hydroxide solution (both in the presence and absence of chloride ions), but at known time intervals aliquots were withdrawn and quenched in an excess of dilute perchloric acid. On the addition of acid to the chlorohydroxo complexes they are immediately converted to the corresponding aquo species[8] with complete retention of configuration. The isomerisation of the chloro-aquo cation is very much slower than that of the chlorohydroxo complex.

Tracer Studies.

Chlorine 36 was obtained from the Radiochemical Centre, Amersham, as a 4M solution of hydrochloric acid.

A solution of 0.04M $H^{36}Cl$ and 0.16M sodium hydroxide was thermostatted at 0° and a weighed amount of trans- $\left[Co(en)_2(OH)Cl \right] Cl.H_2O$ added. 5ml. aliquots of the reaction mixture were withdrawn at recorded time intervals and the reaction quenched by addition to 5ml. of 1.44M perchloric acid. This was then made up to 25ml. with distilled water and the UV and visible spectrum recorded, so that the extent of the reaction could be determined. The unreacted trans- $\left[Co(en)_2(OH)Cl \right]^+$ was then precipitated by the careful drop-wise addition of a concentrated solution of sodium tetraphenyl borate ($\sim$ 1 -2ml.). The precipitate was immediately filtered off and washed with water, until the washings contained no significant radioactivity, and dried in a dessicator. The precipitate was dissolved in 10ml. of AnalaR acetone and its UV and visible absorption spectrum recorded to obtain the concentration. The solution was then placed in a liquid counter and any radioactivity present was counted on a Dynatron Radio Ltd. S.C.200 scaling unit.

All spectra were recorded on a Unicam S.P.800 spectrophotometer using 1cm. silica cells.

Measurement of Temperature.

All temperatures were recorded using thermometers previously

standardised at the National Physical Laboratories.

The reaction temperature of the isomerisation mixture was recorded in

the thermostatted cell contained in the spectrophotometer.

Results.

No detectable change was observed in the spectrum of the trans-

$\left[Co(en)_2(OH)_2\right]^+$ at $0°$, and in the presence of chloride ions, over

a period of at least 25 minutes. Nor was there any change in the spectra

of the acidified aliquots under the same conditions. The spectra remained

identical to that of the trans- $\left[Co(en)_2(OH_2)_2\right]^{3+}$ cation, which is

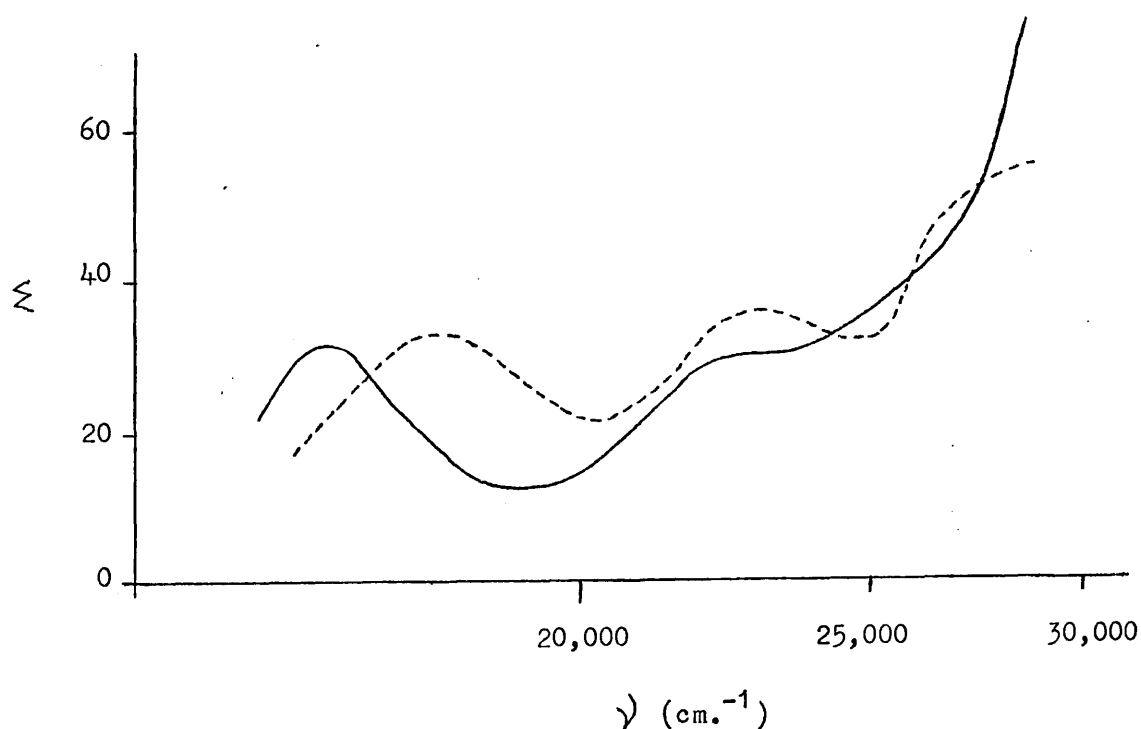quite distinct from that of the trans- chloroaquo cation, as may

be seen in Fig. ii.

Figure ii.

UV and visible spectra of trans-$\left[Co(en)_2(OH_2)_2\right]^{3+}$ (-----) and

trans-$\left[Co(en)_2Cl(OH_2)\right]^{2+}$ (———).

To observe any change in the spectrum of the trans-dihydroxo species during a reasonable length of time, it was necessary to raise the temperature. Good first-order plots were then obtained from the spectral changes, at higher temperatures and the results are given in Table 1. These show that the rate of isomerisation is independent of the concentrations of both the hydroxide and chloride ions.

Table 1.

Observed First-order Rate Constants Obtained in the Isomerisation

Reaction $\quad$ trans-$\left[Co(en)_2(OH)_2\right]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ cis-$\left[Co(en)_2(OH)_2\right]^+$

$$k_{obs.} = k_1 + k_{-1}$$

Temp. (°C)	[Complex] (mM.)	[OH⁻] (M.)	[Cl⁻] (M.)	$10^4 k_{obs.}$ (sec.⁻¹)	ν (cm.⁻¹)
59.1	9.22	.067	0	12.0 (a)	27,000
59.1	9.22	.067	0.35	13.0	27,000
59,1	9.22	.067	0.35	12.8	27,000
50.8	6.95	.067	0	4.41 (a)	27,000
50.8	6.95	.067	0.35	4.49	27,000
50.8	6.95	.067	0.35	4.34	27,000
50.8	6.95	.067	0.35	4.41	19,200
50.7	8.00	.050	0.40	4.40	20,000

(a) is average of five rate constants taken from Table I, Section III.

The results of the isotopic exchange experiments are shown in Table 2, and it is obvious that even after considerable reaction, there is no significant chloride exchange with the unreacted trans-$\left[Co(en)_2(OH)Cl\right]^+$ cation.

Table 2.

Uptake of ^{36}Cl in Unreacted trans-$[Co(en)_2(OH)Cl]^+$ at $0.^o$

Time (sec.)	% reaction	10^{-2} x specific activity of trans-$[Co(en)_2(OH_2)Cl] B(C_6H_5)_4$ 3 (counts/mmol min.)	% exchange
40	13	7.8	0.26
60	18	6.9	0.23
90	29	9.5	0.32
180	38	10.9	0.36

Initial $[complex]$ = 0.05M; $[NaCl]$ = 0.04M; initial $[OH^-]$ = 0.16M; specific activity of $^{36}Cl^-$ = 1.08 x 10^6 counts/mmol min.

Discussion.

An earlier study[10] of the rate of base hydrolysis of cis-$[Co(en)_2Cl_2]^+$, using equivalent concentrations of hydroxide and complex, showed that a considerable amount of the dihydroxo product, as well as both chlorohydroxo isomers, was obtained. This is surprising as the rate of reaction of the monochloro species with hydroxide ions was thought to be slower than that of the cis-dichloro species. This means that the trans-$[Co(en)_2(OH)Cl]^+$ ion competes, with considerable success, with the cis-$[Co(en)_2Cl_2]^+$ species for the hydroxyl ion. From the absence of the cis-dihydroxo complex it was inferred that the cis-chlorohydroxo compound reacts more slowly with hydroxyl ions.

It was pointed out that an equilibrium between the trans-dihydroxo and the trans-chlorohydroxo ions could explain these observations. The

following reaction scheme for the base hydrolysis of cis-$\left[Co(en)_2Cl_2\right]^+$ was proposed:-

$$cis\left[Co(en)_2Cl_2\right]^+ \xrightarrow{\text{OH}^-} trans-\left[Co(en)_2(OH)Cl\right]^+ \quad + \quad cis-\left[Co(en)_2(OH)Cl\right]^+$$

20OH$^-$ Cl$^-$ OH$^-$ OH$^-$

$$cis-\left[Co(en)_2(OH)_2\right]^+$$

$$trans-\left[Co(en)_2(OH)_2\right]^+ \quad + \quad cis-\left[Co(en)_2(OH)_2\right]^+$$
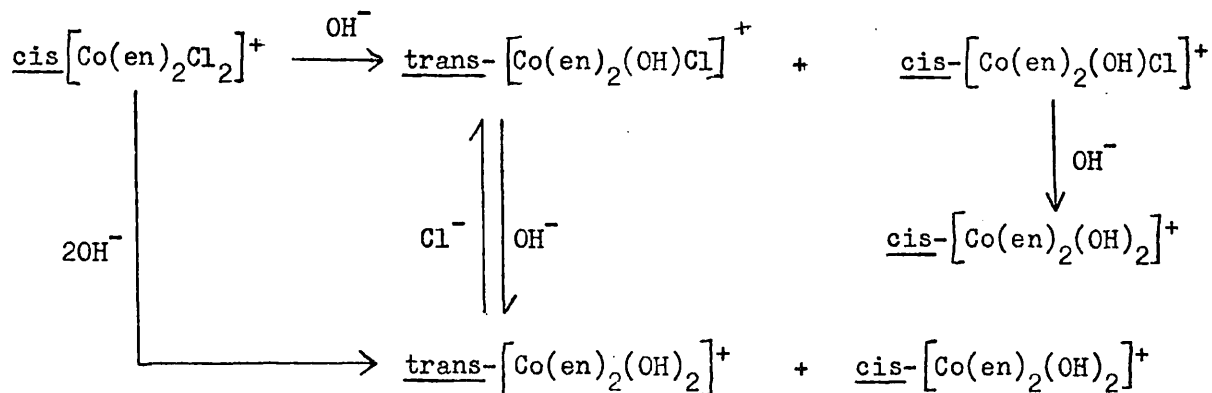
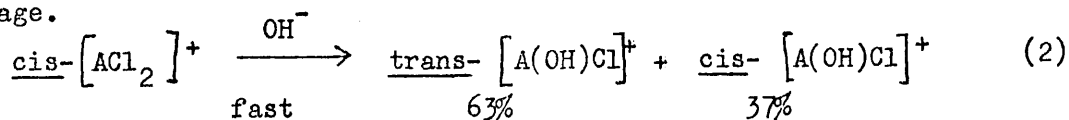Thus, the equilibrium between the trans-chlorohydroxo and the trans-dihydroxo cations must be established at a rate which is very similar to the rate of base hydrolysis of the cis-dichloro complex. It was concluded that the rate of base hydrolysis of trans-$\left[Co(en)_2(OH)Cl\right]^+$ given by Chan and Tobe[1] was in fact the rate of stereochemical conversion to the cis-dihydroxo complex, rather than the rate of base hydrolysis.

When alkali was added rapidly to the cis-dichloro complex, the formation of some dihydroxo product was observed[1] It was found that careful drop-wise addition of sodium hydroxide to well stirred solution of the cis-dichloro complex, at 0°, allowed separation of the first reaction from the second. The reaction scheme formulated by Chan and Tobe is given in equations 2 -4, where A = $Co(en)_2$

1st stage.

$$cis-\left[ACl_2\right]^+ \xrightarrow[\text{fast}]{\text{OH}^-} \underset{63\%}{trans-\left[A(OH)Cl\right]^+} + \underset{37\%}{cis-\left[A(OH)Cl\right]^+} \qquad (2)$$

2nd stage

$$trans-\left[A(OH)Cl\right]^+ \xrightarrow[\text{fast}]{\text{OH}^-} \underset{94\%}{cis-\left[A(OH)_2\right]^+} + \underset{6\%}{trans-\left[A(OH)_2\right]^+} \qquad (3).$$

$$cis-\left[A(OH)Cl\right]^+ \xrightarrow[\text{slow}]{\text{OH}^-} \underset{97\%}{cis-\left[A(OH)_2\right]^+} \qquad (4)$$
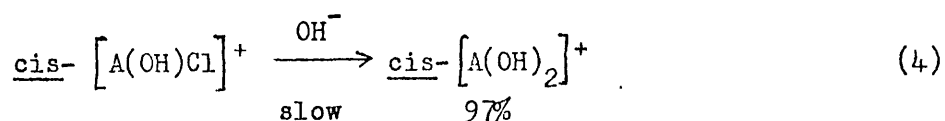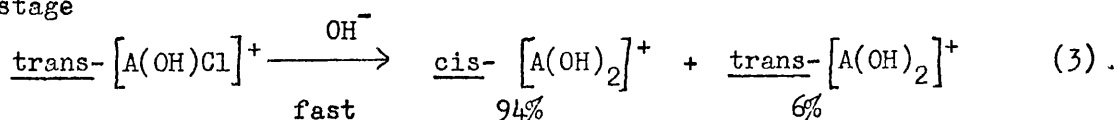
The results obtained in the present study of the trans to cis

isomerisation of the dihydroxo complex clearly show that the rate

of isomerisation is unaffected by the addition of chloride ions to

the reaction mixture. Whereas, if the reaction scheme in equation 1

were correct, chloride catalysis should have been observed.

It was also stated that the concentration of the trans-dihydroxo

cation decreased as the concentration of the cis-dihydroxo cation

increased. The equilibrium mixture of the cis- and trans-dihydroxo

isomers has frequently been reported [9] as comprising of 56% trans

isomer and 44% cis isomer, independent of the hydroxide concentration,

so that such a mechanism would not be possible.

The fact that there was no significant radioactivity found in the

isolated trans-$[Co(en)_2(OH)Cl]^+$, even after considerable base hydrolysis,

also indicates that the equilibrium in equation 1 is unlikely.

From the experiments herein it may be concluded that the mechanism

suggested by Dittmar and Archer does not occur and that their

conclusions result from an over-refinement of their data. There   would

thus seem to be no reason to doubt the original data on the rate

and steric course of the base hydrolysis of trans-$[Co(en)_2(OH)Cl]^+$.[1]

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9. (a) J.Bjerrum and S.E.Rasmussen, Acta Chem.Scand., 1952, 6, 1265.

   (b) J.Y.P.Tong and P.E.Yankwich, J.Amer.Chem.Soc., 1958, 80, 2664.

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SECTION III.

The Isomerisation Reactions of the Dihydroxobis(ethylenediamine)cobalt(III)

Cations in Basic Solution.

Introduction.

The literature contains several reports[1,2,3] on the isomerisation

of the cis- and trans-dihydroxobis(ethylenediamine)cobalt(III) cations.

Bjerrum and Rasmussen[1] investigated the rates of isomerisation

and the position of equilibrium at 25°. The overall observed rate for

the isomerisation was found to be $7.6 \times 10^{-6} sec.^{-1}$ and the

equilibrium constant was 0.80. The equilibrium mixture thus comprises

40% cis- and 60% trans- $\left[Co(en)_2(OH)_2 \right]^+$. Studies on the isomerisation

in varying concentrations of alkali have shown that the rate of

isomerisation is independent of alkali concentration up to ~1M. [2,3]

Isotopic exchange experiments[3] using coordinated $^{18}OH^-$ have

shown that only a very small fraction of solvent exchange occurred

for each act of isomerisation.

The activation energies for the trans to cis and for the cis to

trans isomerisations are not constant over the temperature range

14 - 37° and Kruse and Taube concluded[3] that this was due to the

isomerisation proceeding via two main paths. The isomerisation may

occur by cobalt-nitrogen bond fission or via cobalt-oxygen cleavage.

Since so little of the coordinated hydroxo group exchanges with the

solvent during isomerisation, the latter path cannot be of major

importance.

In the present work the isomerisation of the cis→trans and of the

trans→cis- $\left[Co(en)_2(OH)_2 \right]^+$ has been studied over an extended

temperature range and at high alkali concentration levels.[4] The results

are discussed in terms of the Bailar 'twist' mechanism, which,

as it will be demonstrated, permits both isomerisation and optical

inversion _via_ an intramolecular transformation.

Experimental.

Preparation of Reaction Solutions.

The _cis_- and _trans_-dihydroxobis(ethylenediamine)cobalt(III) cations

were generated, in solution, from $\left[Co(en)_2CO_3\right]$ (ClO_4) and

trans- $\left[Co(en)_2(OH)(OH_2)\right]$ $(ClO_4)_2$, respectively.

The _cis_- $\left[Co(en)_2(OH)_2\right]^+$ ion was obtained in 100% yield by the

addition of perchloric acid to the solid $\left[Co(en)_2CO_3\right]$ (ClO_4) and

the subsequent addition of sodium hydroxide.[21] When _trans_-

$\left[Co(en)_2(OH)(OH_2)\right]$ $(ClO_4)_2$ is dissolved in sodium hydroxide

solution the _trans_- $\left[Co(en)_2(OH)_2\right]^+$ cation is generated.

Kinetic Measurements.

1. A known weight of $\left[Co(en)_2CO_3\right]$ (ClO_4) was dissolved in a known

excess of standard perchloric acid. 0.5ml. of this solution were

transferred to a known volume of standard sodium hydroxide

contained in a 1cm. silica cell. The change in the absorbance of the

sample, with time, was followed at $27,000cm.^{-1}$ (~ 370 nm.) or $19,200cm.^{-1}$

(~ 520 nm.) on a Unicam S.P.800 spectrophotometer, fitted with a

scale expansion unit and an external slave recorder as in Section II,

p. 34 .

2. A known weight of _trans_- $\left[Co(en)_2(OH)(OH_2)\right]$ $(ClO_4)_2$ was dissolved

in a known excess of standard sodium hydroxide, thermostatted at the

required temperature. The solution was transferred to the

thermostatted cell compartment of the spectrophotometer and the change

in absorbance followed as above.

3. The reaction solution was prepared as in 1. and 5ml. samples were

placed in glass ampoules which were then sealed and placed in a

thermostatting bath.. At recorded time intervals the samples were removed and cooled rapidly on ice. The absorbance of the sample was measured at 19,200cm.$^{-1}$ ($\sim$520 nm.) using a Unicam SP 500 spectrophotometer.

Measurement of Temperatures.

In methods 1. and 2. temperatures were measured in the thermostatted cell compartment of the spectrophotometer, using thermometers standardised at the National Physical Laboratories. In method 3. the temperature of the thermostatting bath was taken as the reaction temperature.

Results.

The results of the kinetic measurements are given in Table 1. The kinetic runs gave straight line first-order plots when log $(A_\infty - A_t)$ was plotted against time (Fig. i). The observed overall rate of isomerisation was calculated from equation 1.

$$k_{obs.} = 2.303 \log (A_\infty - A_t) / t \qquad \text{sec.}^{-1} \qquad (1)$$

where A_∞ is the final absorbance

A_t is the absorbance at time = t

The specific rate constants k_1 (<u>trans</u> $\rightarrow$ <u>cis</u>) and k_{-1} (<u>cis</u> $\rightarrow$ <u>trans</u>) of the isomerisation

$$\underline{\text{trans-}} \left[Co(en)_2(OH)_2 \right]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underline{\text{cis-}} \left[Co(en)_2(OH)_2 \right]^+$$
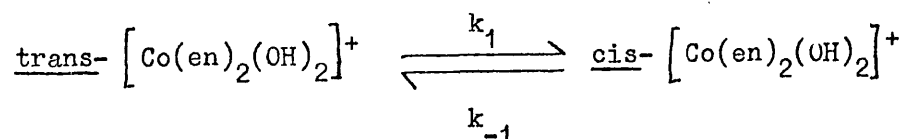
were calculated from equations 2 and 3.

Figure i.

A typical rate plot for the reaction <u>trans</u> $Co(en)_2(OH)_2^+$

$$\Updownarrow$$

<u>cis-</u> $Co(en)_2(OH)_2^+$

$$k_{obs.} = 1.27 \times 10^{-3} \text{ sec.}^{-1}$$

Time (sec.)
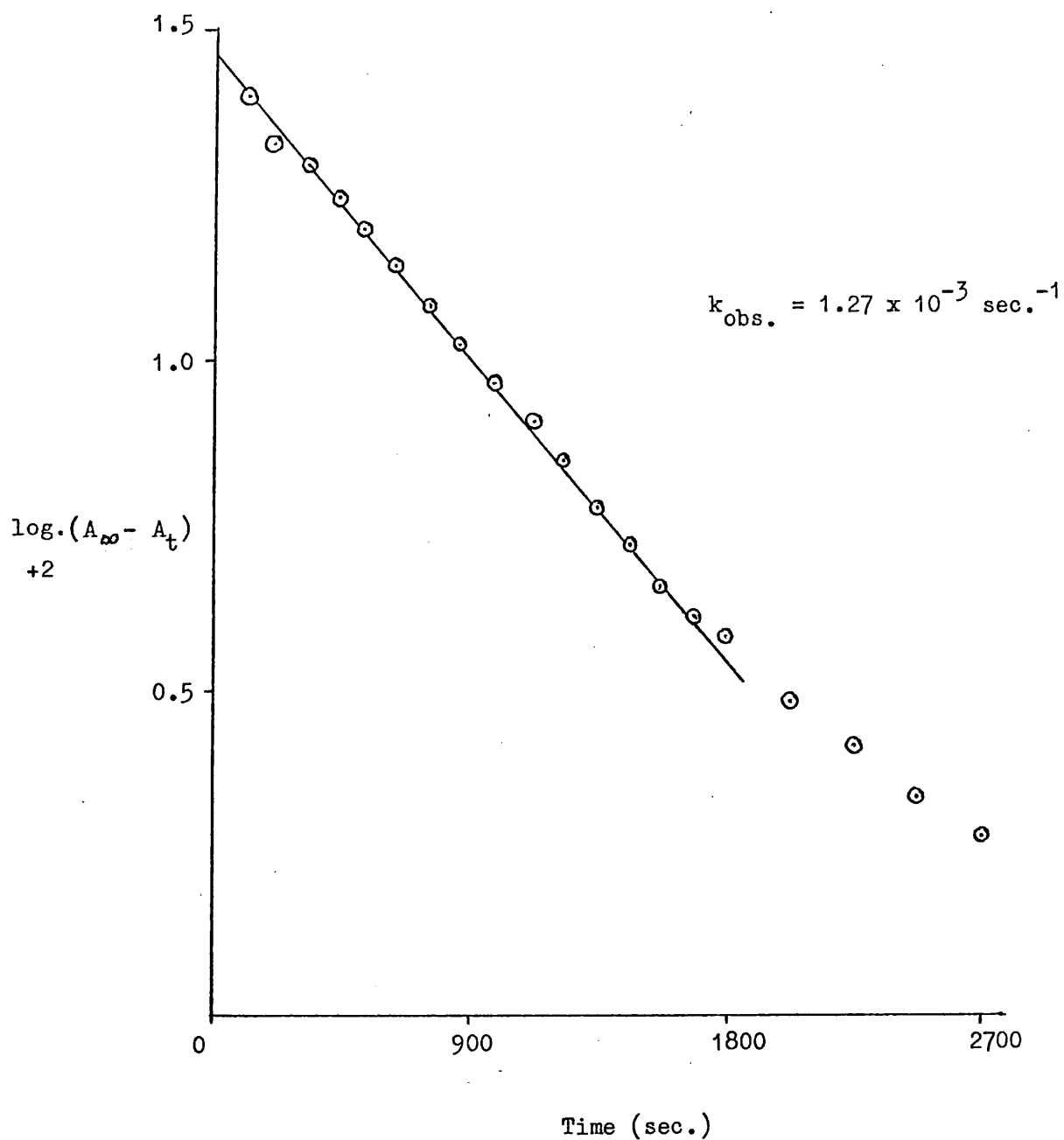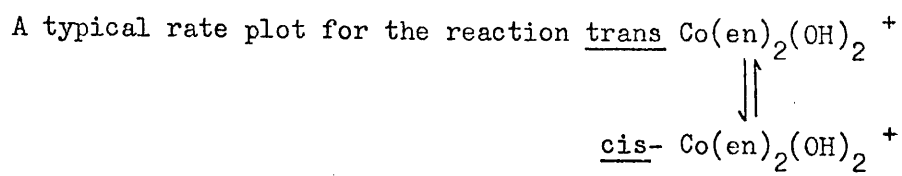
complex = 9.22mM

OH^- = 0.067M

Temp. = 59.1°

Table 1.

Observed Spectrphotometric Rate Constants, $k_1 + k_{-1}$, for the Isomerisation of the cis- and trans- $[Co(en)_2(OH)_2]^+$ Cations.

Temp. (°C)	[Complex] (mM)	$10^4 k_{obs}$ (sec.$^{-1}$)	γ (a) (cm.$^{-1}$)	ε_∞ (c) [OH] = .067M
59.1	92.2	11.0	27,000	73.5
59.1	92.2	10.9	27,000	73.5
59.1	92.2	12.0	27,000	73.5
59.1	92,2	12.7	27,000	73.5
59.1	92.2	10.7	27,000	73.4
50.8	6.95	4.61	27,000	73.4
50.8	6.95	4.41	27,000	73.3
50.8	6.95	4.99	27,000	73.4
50.8	6.95	3.77	27,000	73.4
50.8	6.95	4.29	27,000	73.3
50.8	6.95	5.00	19,230	68.8
25.5	9.80	.0077	19,230	71.3
25.5	9.80	.0075	19,230	72.0
24.8	10.5 (b)	.0065	19,230	70.5

(a) reaction was followed at the given wavelength

(b) $[OH] = 1M$

(c) Value of the extinction coefficient of the cis-dihydroxo product.

$$k_{obs.} = k_1 + k_{-1} \qquad \qquad (2)$$

$$K_{eq.} = \frac{k_1}{k_{-1}} \qquad \qquad (3)$$

Since $k_{obs.}$ and $K_{eq.}$ may be obtained experimentally, k_1 and k_{-1} can be calculated.

The equilibrium constants, average values of the final molar extinction coefficients and the final percentage of cis complex, at varying temperatures are given in Table 2. Some literature values are included for comparison.

Table 2.

Position of Equilibrium for the Isomerisation of the

$$\left[Co(en)_2(OH)_2\right]^+ \text{ Ions.}$$
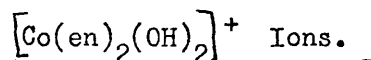
Temp. (^{o}C)	ε_∞(taken at 27,000cm.$^{-1}$)	%cis
~ 70	73.3	38 (a)
~ 60	73.5	39
~ 50	74.5	41
35	73.8	39 (b)
25	75.7	45 (c)

(a) from ref. 4

(b) from ref. 2

(c) from ref. 1

$\Delta H^{\ddagger} = 28.5$ kcal. mole^{-1}
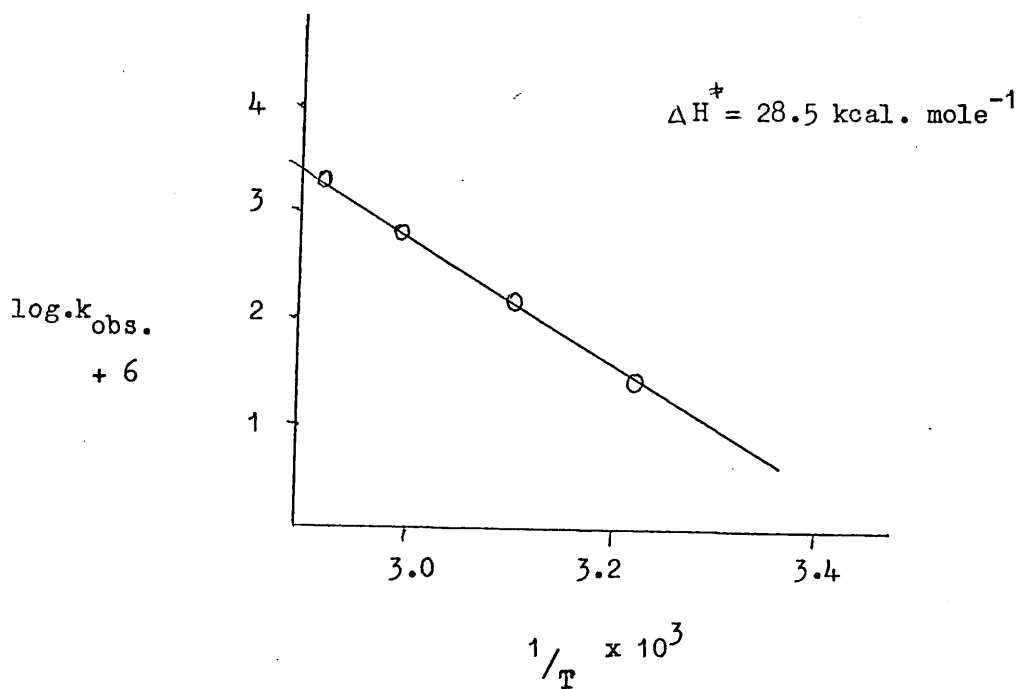
Figure ii.

Arrhenius plot for the isomerisation of trans→cis $[Co(en)_2(OH)_2]^+$ (k_1)

$\Delta H^{\ddagger} = 29.5$ kcal.mole^{-1}

Figure iii.

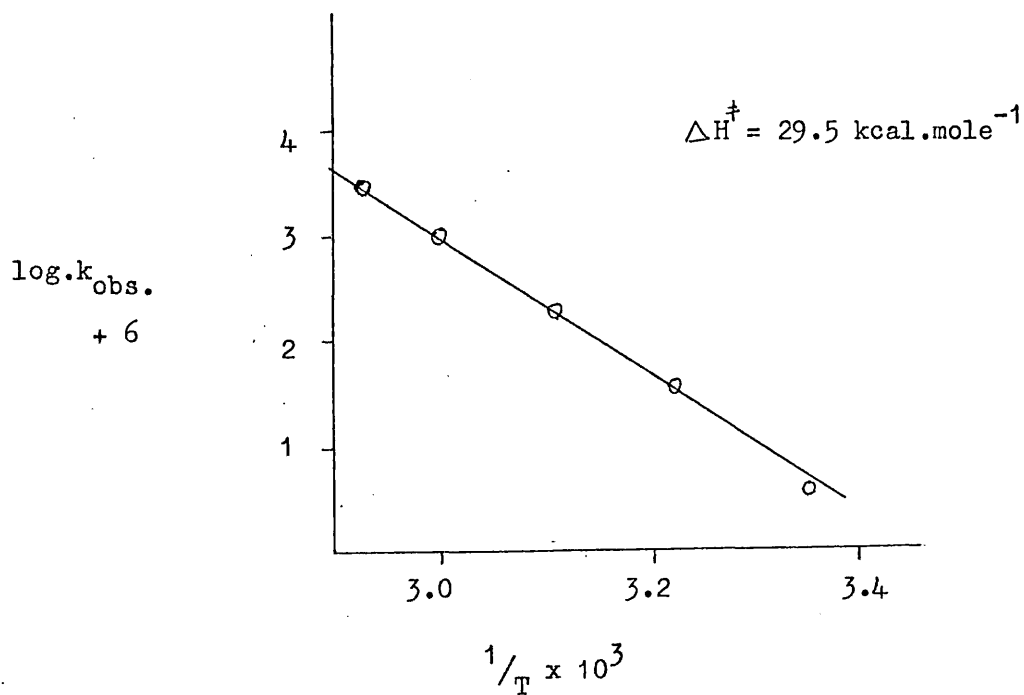Arrhenius plot for the isomerisation of cis→trans $[Co(en)_2(OH)_2]^+$ (k_{-1})

It may be observed from the Arrhenius plots that when $\log k_1$ (Fig. ii) and $\log k_{-1}$ (Fig.iii) are plotted against the reciprocal of the absolute temperature, straight line graphs are obtained. The activation energies for the cis to trans change and for the trans to cis isomerisation are 29.5 and 28.5kcal.mole^{-1}, respectively.

Discussion.

The results shown herein and those reported in the literature[2,3] indicate that the rate of isomerisation of the dihydroxobis(ethylenediamine)cobalt(III) cation is unaffected by changes in the concentration of alkali and changes in the ionic strength.

From their investigations on the exchange of labelled, coordinated $^{18}OH^-$, with solvent, Kruse and Taube[3] have shown that the rate of exchange of the cis- $\left[Co(en)_2(OH)_2\right]^+$ isomer is almost ten times faster than the rate of the cis $\longrightarrow$ trans isomerisation, the values being 3.0×10^{-5} and 3.7×10^{-6} sec.$^{-1}$ at $24.95°$, respectively. It was also observed that only a fraction of the solvent exchanged with the complex for each act of isomerisation. This must mean that the cis- $\left[Co(en)_2(OH)_2\right]^+$ reacts mainly with retention of configuration.

The isomerisation of the diaquo species is slow[3] and is thought to occur via acid hydrolysis(see Section IV, p. 65). At pH 7-8 the hydroxoaquo species is formed and the rate of isomerisation is markedly increased.[2,3] At a still higher pH the dihydroxo cation is formed and the rate of isomerisation again becomes slow.

There are several ways in which solvent may be exchanged in neutral solution and in basic solution, but from the kinetics it is not possible to distinguish between them.[5]

From isotopic studies it is impossible to differentiate between

for instance, aquation of the hydroxoaquo species and the base-catalysed hydrolysis of the diaquo species at pH 7-8. Similarly, from the present evidence it may not be distinguished between spontaneous cobalt-oxygen fission and base catalysis in the hydrolysis of the hydroxoaquo cation at pH 7-8.

Gillard[6] has suggested that the fast isomerisation of the $\left[Co(en)_2(OH)(OH_2)\right]^{2+}$ cation is due to the formation of a pre-equilibrium ion pair, in which a hydroxyl group links the hydroxo and aquo ligands (Fig. iv).
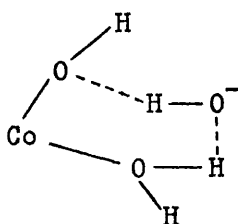
Fig. iv.

This type of mechanism would appear to be unlikely to occur in the isomerisation of the dihydroxo species, since this undergoes isomeric change at a much slower rate.

One mechanism which may be postulated for the dihydroxo isomerisation is one which involves the opening of the ethylenediamine linkage. This has been suggested for $\left[Co(en)_2(OH)NH_3\right]^{+}$,[7] where isomerisation takes place without exchange of the attached hydroxo group. It was thought that under the influence of the strong positive inductive effect of the hydroxo group, the cobalt-ethylenediamine linkage is severed and then this re-attacks the cobalt atom (Fig. v). This ring opening mechanism has also been used in the explanation of the ^{18}O exchange with all twelve oxygen atoms in $\left[Cr(C_2O_4)_3\right]^{3-}$,[8] under conditions where there is no exchange between the coordinated and ionic oxalate.

trans- $[Co(en)_2(OH)NH_3]^+$
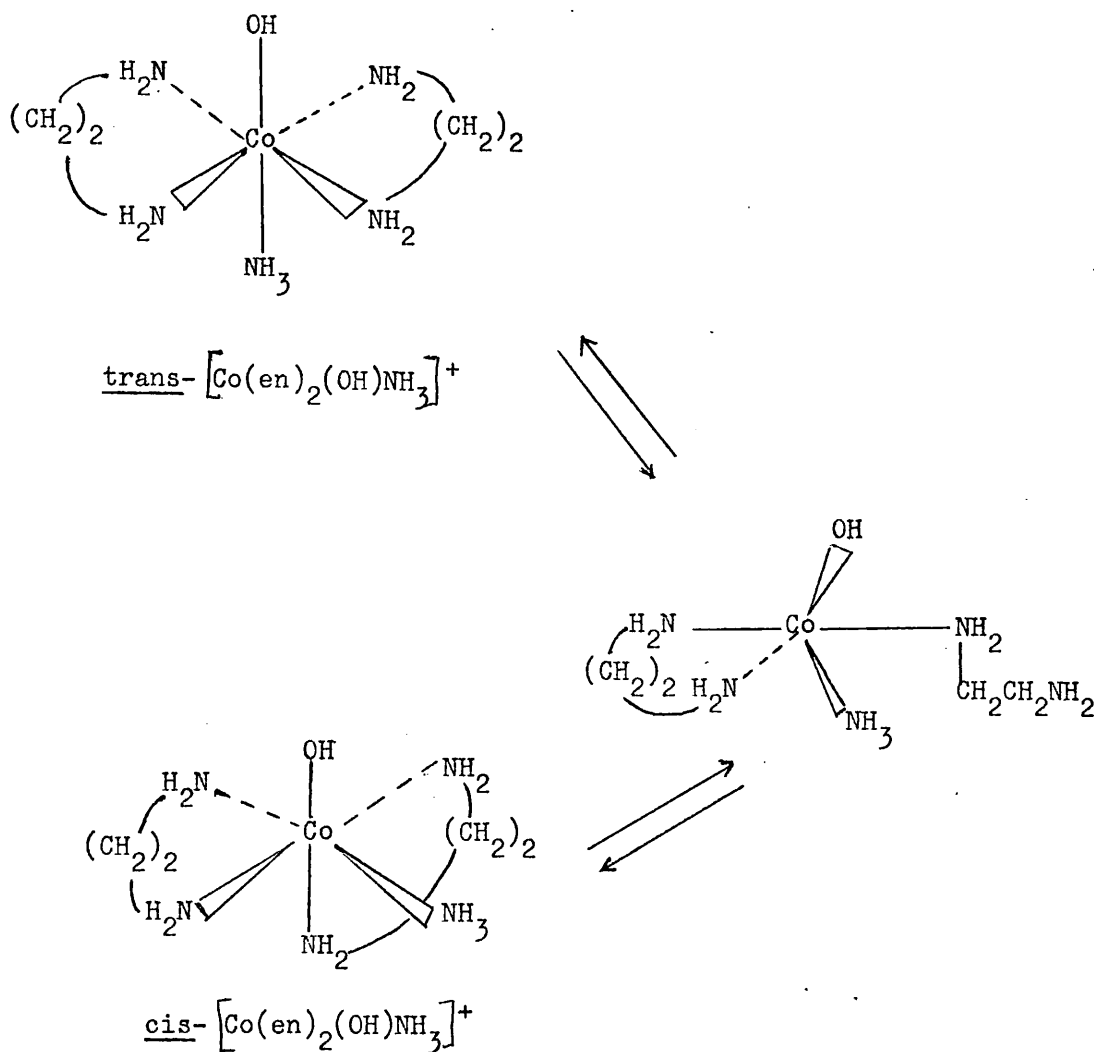
cis- $[Co(en)_2(OH)NH_3]^+$

Figure V.

Tobe et al.[7] suggested that the isomerisation and oxygen

exchange observed in the $[Co(en)_2(OH_2)NH_3]^{3+}$ system could occur

via a ring opening process, accompanied by a bimolecular attack

of hydroxyl ions on the the complex. It is necessary to stipulate

that the coordination position left vacant by the cobalt-nitrogen

cleavage cannot be filled by a solvent molecule, if isomerisation

is to occur without water exchange. However, it is difficult to

believe that the active intermediate has time to rearrange before

it reacts with a solvent molecule, as the cation will be surrounded

by a solvent shell. This type of mechanistic path was also proposed

in the base hydrolysis of $[Cr(C_2O_4)(OH_2)_2]^-$,[8] where it is the

cobalt-oxalato oxygen bond that is broken. Later studies[9] have

demonstrated that the opening of the oxalato group, by cobalt-oxygen bond fission takes place with the uptake of a hydroxyl group.[10]

In the base hydrolysis of complexes of the type $\left[Co(en)_2(OH)X\right]^+$ [11] the strength of the cobalt-X bond has been assumed to be the determining factor for the type of mechanism which will occur. When X is weakly bonded, e.g. for the chloro, bromo, and isothiocyanato ligands, a hydrolysis mechanism is more probable, with X being replaced, initially, by the solvent, rather than direct replacement by an hydroxyl ion. When X is strongly bonded, e.g. ammino or hydroxo, ring opening is thought to be the major factor contributing to the isomerisation.

If the isomerisation of the dihydroxo species is actually due to the base-catalysed hydrolysis of the hydroxoaquo complex[12] as previously mentioned (p. 50), via a five-coordinate intermediate, then it is the aquo ligand which will be removed in the rate determining step. This will occur as the aquo ligand is not able to π- bond to the metal atom as strongly as the hydroxo ligand. Considering this to take place, then the five-coordinate intermediate would be identical to the intermediate obtained in the base-catalysed hydrolysis[11] of $\left[Co(en)_2(OH)X\right]^+$ when X^- = chloro, bromo, or isothiocyanato. The latter reaction, however, proceeds with 100% steric change, but the former reaction proceeds mainly with retention of configuration.

Two mechanisms are possible for the isotopic exchange observed in the dihydroxo complex. One such mechanism, involving the formation of a tetragonal pyramidal intermediate, would allow exchange without change in configuration. Since isomerisation proceeds with little exchange, the above intermediate does not appear reasonable. Exchange could occur via a five-coordinate

trigonal bipyramidal intermediate formed by the loss of one of the hydroxo ligands. The remaining hydroxo group could stabilise the intermediate by the donation of π - electrons to the cobalt atom. It is necessary to restrict the entry of the incoming ligand to the same side as the leaving group. This restriction is quite feasible[11] as the hydroxyl group, on leaving the complex, will disturb the solvation shell allowing entry of the incoming solvent group. Proton transfer from the incoming group to the departing hydroxo ligand would further facilitate bond breaking(Fig. vi).
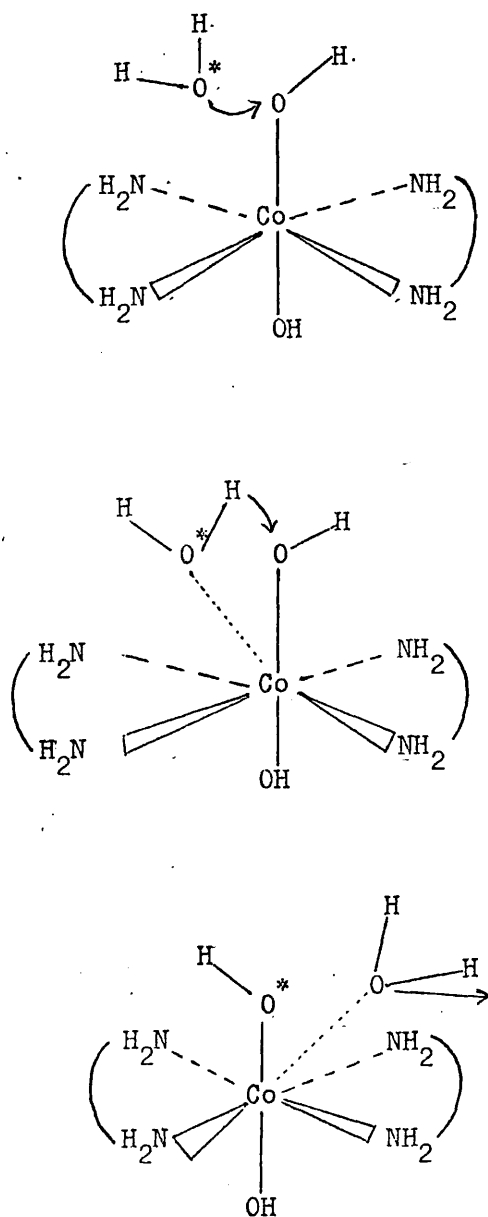

Figure vi .

Oxygen exchange of cis- $\left[Co(en)_2(OH)_2 \right]^{+}$ by water attack and proton transfer.

Alternatively, exchange could be occurring with a bimolecular attack, by hydroxide ions or water, in which instance there would be a significant contribution to the activation energy from bond making. This mechanism is similar to that which operates in rhodium complexes,[13] where the ligand-metal bonds possess considerably more covalent character than the ligand-metal bonds in cobalt complexes. The hydrolysis reactions of the rhodium(III) chloroammino complex[13] occurs with almost 100% retention of configuration. Strong σ- bonding from the two hydroxo groups and the four amine ligands may make the cobalt(III) centre, in this case, very similar to the rhodium(III) centre.

An intramolecular mechanism which would permit isomerisation without exchange is the Bailar 'twist' mechanism.[14] The hydroxo group has a high inductive effect via σ- bonding and also possesses π-antibonding properties,[15] together with low ligand field strength.[16] These factors would appear to weaken the cobalt-nitrogen bond, facilitating cleavage of the cobalt-ethylenediamine linkage. However, the cobalt-oxygen bonds would also tend to be weakened due to repulsive π- bonding. As the cation contains four nitrogen donors and two hydroxo ligands, the conditions for the 'twist' mechanism would appear to be present. The twisting mechanism has been analysed by Serpone and Fay[17] and may be discussed in terms of four imaginary 'C_3' axes (Fig. vii).

The mechanism involves the displacement through 120° of the three coordinated atoms on the lower octahedral face, with respect to the three donor atoms on the upper face. The twisting may be performed about any of the four 'C_3' axes, in both clockwise and anticlockwise directions. The mechanism is further explained in figures viii - x.

Figure vii.

View of <u>cis</u>-[Co(en)$_2$X$_2$] along a 4-fold axis, with the 4 imaginary C$_3$ axes.
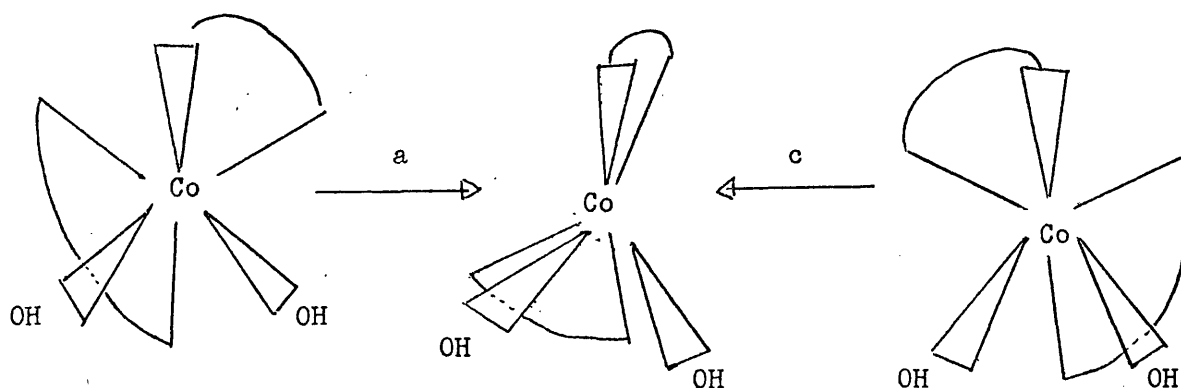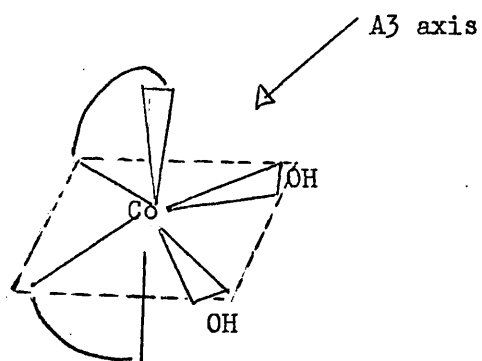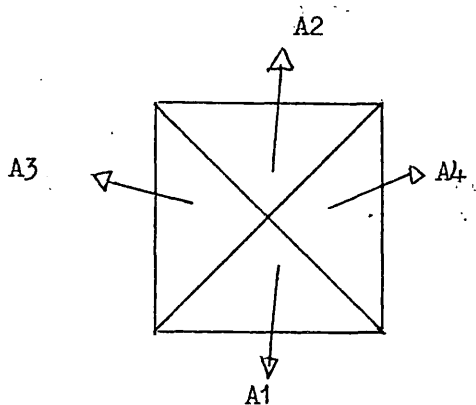
Figure viii.

Racemisation of [Co(en)$_2$(OH)$_2$]$^+$ by rotation about the A3 axis, <u>via</u> a trigonal prism.

    a - anticlockwise;   c - clockwise

A1 axis
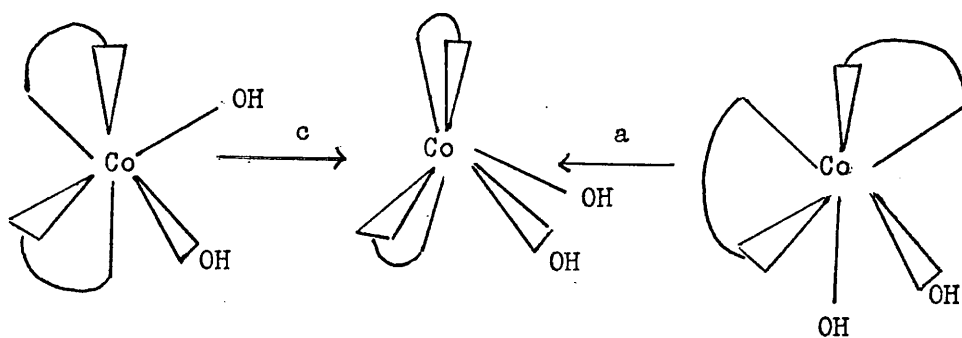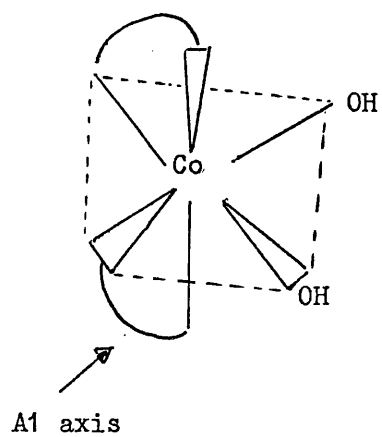
Figure ix.

Racemisation of $[Co(en)_2(OH)_2]$ by rotation about the axes A1 and A2, <u>via</u>

a trigonal prism.

a - anticlockwise; c - clockwise

A2 axis

(A)

(B)   trans   (B)
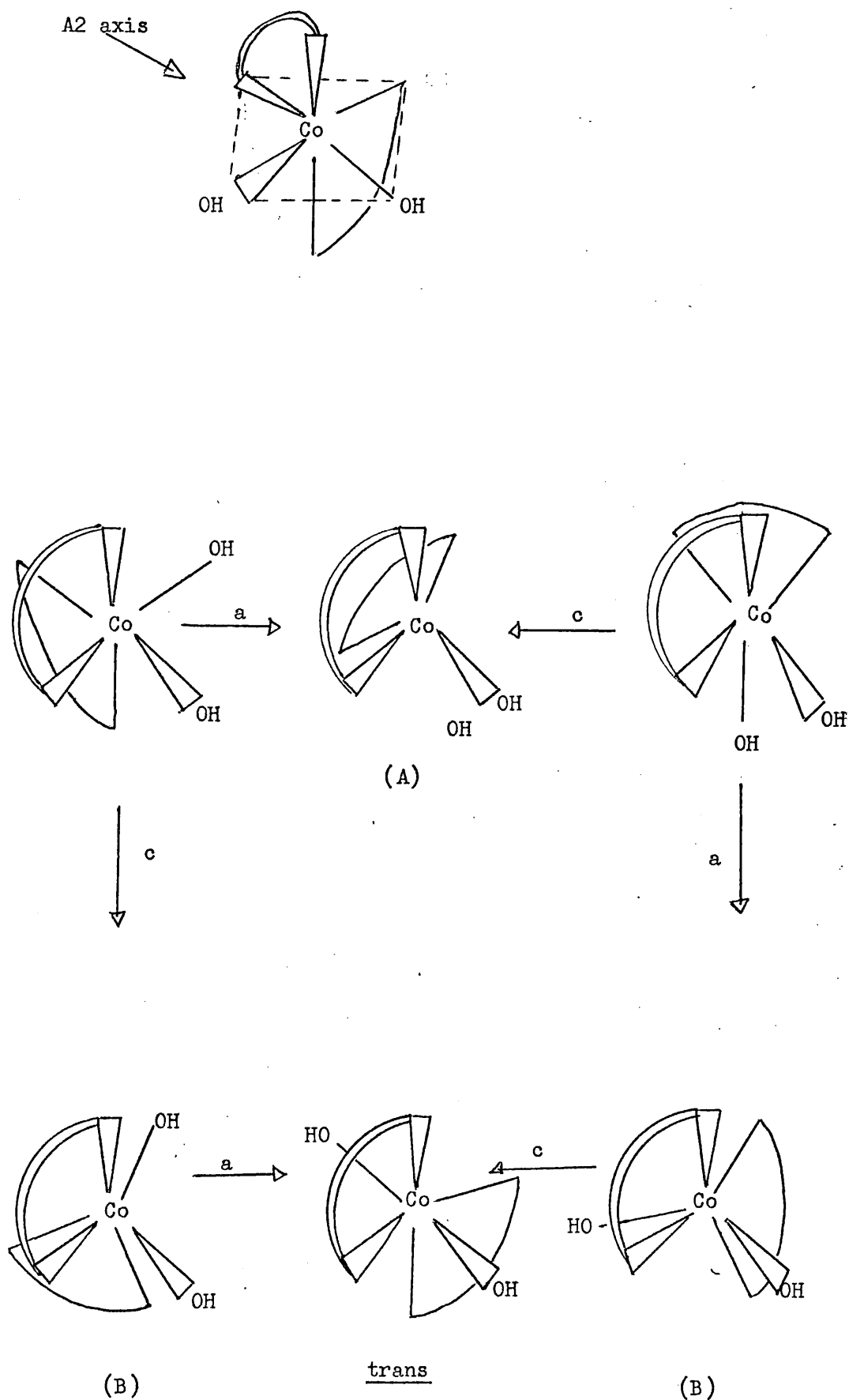
Figure x.

Racemisation of $[Co(en)_2(OH)_2]^+$ by rotation about the A1 and A2 axes, via trigonal prism (A); isomerisation via trigonal prism (B). a - anticlockwise; c - clockwise

The isomerisation of the dihydroxotriethylenetetraminecobalt(III) system[18] has also been discussed in terms of this type of intramolecular rearrangement.

Very recently, Bradley has suggested that the racemisation of cis-dialkoxybis(acetylacetonato)titanium(IV) complexes[19] occurs by a 'twist' mechanism, as it was observed that the activation energy required increased with the size of the alkoxy group.

The lability of the $[Co(cyclam)(OH)(OH_2)]^{2+}$ (where cyclam = 1,4,8,11-tetra-azacyclotetradecane) has been ascribed to an intramolecular proton transfer from the nitrogen to the oxygen atom,[20] With a secondary amine this would lead to a change of configuration at the nitrogen atom, and allows steric change without disruption of the octahedral symmetry. If steric change were unfavourable intramolecular interaction would assist a change about the central cobalt atom.

Thus, an intramolecular 'twist' mechanism would seem to be consistant with the data obtained in the isomerisation of the dihydroxobis(ethylendiamine)cobalt(III) system.[4]

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·SECTION IV.

Isomerisation Reactions of the Diaquobis(ethylenediamine)cobalt(III) Cations.

Introduction.

The series of <u>cis</u> and <u>trans</u> diaquobis(ethylenediamine)cobalt(III) complexes was originally prepared by Werner[1] as the trihalide. The nitrate, sulphate, dithionate, and thiocyanate were later produced.[2] It was observed that the <u>trans</u> complexes were frequently contaminated with small amounts of the <u>cis</u> isomer. Later studies[3] investigated the absorption spectra of the two isomers in acidic solution, at 0°. This temperature was employed to minimise the amount of <u>trans</u> to <u>cis</u> isomerisation, which was found to be quite rapid at room temperature.

The first study on the rate of the <u>trans</u> to <u>cis</u> isomerisation[4] was carried out in dilute nitric acid solution at 25°, starting with the <u>trans</u>-$\left[Co(en)_2(OH_2)_2\right](NO_3)_3$. The observed first order rate constant was 1.25×10^{-5} sec.$^{-1}$ and the equilibrium constant was observed to be 58. It was found that the observed rate was reproducible only when the same batch of starting material was used. In the presence of a charcoal catalyst the rate of conversion of the <u>trans</u> species to the <u>cis</u> isomer was shown to be ten times faster than the rate in the absence of the catalyst.[4] It was suggested that the isomerisation was catalysed by the formation of small amounts of cobalt(II).

Later studies[5,6] disputed the value of the rate constant obtained by Bjerrum and Rasmussen, suggesting that the starting material was contaminated with the more labile hydroxoaquo complex.

Several different methods of preparing the <u>trans</u> and <u>cis</u> diaquo ions were used in another study[5] and it was found that the observed values of the rate constants for isomerisation did not

differ appreciably, if the original compound used was very pure.

The rates of exchange of isotopically labelled coordinated water ($H_2^{18}O$) with solvent water, in the cis- and trans-$[Co(en)_2(OH_2)_2]^{3+}$ cations have been reported.[6] The exchange rate of the trans isomer was slightly higher than that of the cis isomer, being 1.13×10^{-5} and $7.3 \times 10^{-6} sec^{-1}$, respectively, at $24.95°$. It was also reported[6] that for each act of trans to cis isomerisation, approximately one coordinated water molecule exchanged with the solvent molecules. The rate of cis exchange was much greater than both the cis to trans isomerisation and the rate of racemisation of the optically active cis-diaquo species (Table 1). This must mean that the cis isomer is reacting mainly with retention of configuration. As such it is reacting in a way common to cis isomers which undergo base hydrolysis. Trans isomers tend to react with change in configuration.[7]

Table 1.

Exchange and Isomerisation Rates of the cis- and trans-$[Co(en)_2(OH_2)_2]^+$ Cations.

|	Temp. ($°C$)	$HClO_4$ (M)	$10^6 k$ (sec^{-1})	
cis exchange	24.95	0.8	7.3	(a)
cis→trans isomerisation	24.95	1.0	0.17	(a)
cis→trans isomerisation	25.2	0.41	1.1	(b)
trans exchange	24.95	0.8	11.3	(a)
trans→cis isomerisation	24.95	1.0	6.7	(a)
trans→cis isomerisation	25.2	0.41	12.0	(b)

(a) taken from ref. 6.   (b) from the present work

This lack of rearrangement by the cis isomer may be explained on the basis of ligand to metal π-bonding stabilising the tetragonal pyramidal intermediate.[8] The ligand donates π-electrons to the vacant 4p orbital in the Co(III) ion, thus gaining stabilisation energy. The interaction would be small as the energy of the 4p orbital is relatively high. If one of the negative ligands were removed, however, the energy of the p level would be lowered and the interaction would increase. When a ligand is removed from the x axis, it is the p_x orbital which loses most energy, relative to the p_y and p_z orbitals. As may be seen in Fig.i, only a ligand cis to the removed group may form a π-bond with the p_x orbital. The trans ligand may only bond with the p_y or p_z orbitals.

Similarly, in terms of the molecular orbital theory[8] the π-electrons on the ligand may overlap with a vacant d^2sp^3 hybridised orbital, only if the ligand occupies a cis position relative to the departing ligand. Thus the formation of a tetragonal pyramid may be stabilised by π-bonding when the octahedral species has the two active groups in a cis position to oneanother. (Fig.ii) However, if the ligand possessing π electrons is trans to the leaving group, direct interaction is not possible with the vacant metal orbital. The trans intermediate may undergo rearrangement to a trigonal bipyramid, thus permitting the donation of ligand π electrons to the vacant dx^2-dy^2 metal orbital, in the trigonal plane. (Fig.iii) If the coordinated water is to act as a π electron donor, it must be trigonally hybridised in the transition state.[9]

It may be seen from the present study that the cis and trans isomers of diaquobis(ethylenediamine)cobalt(III) react as would be predicted on the basis of the π-bonding theories out-lined above.
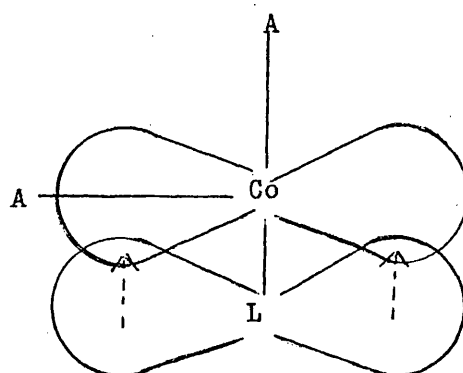
(a) <u>cis</u> isomer
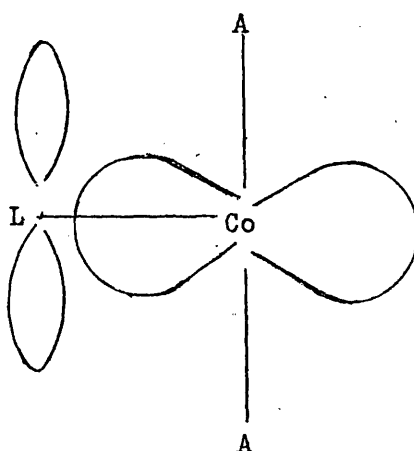
(b) <u>trans</u> isomer

<u>Figure i.</u>

Overlap (a) and lack of overlap (b) of the filled p orbital of L with

the vacant p orbital on the metal, in the tetragonal pyramidal

intermediate resulting from the dissociation of CoA_4LX. The two other

A ligands are omitted for the sake of clarity.
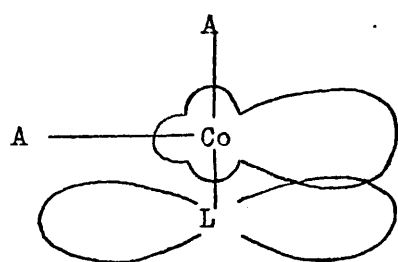
(a) <u>cis</u> isomer.

(b) <u>trans</u> isomer.
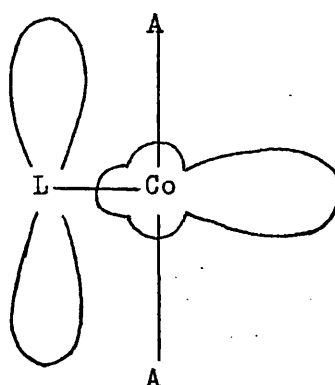
Figure ii.

Overlap (a) and lack of overlap (b) of the filled p orbital on L with the vacant d^2sp^3 orbital on the cobalt, in the tetragonal pyramidal intermediate resulting from the dissociation of CoA_4LX.
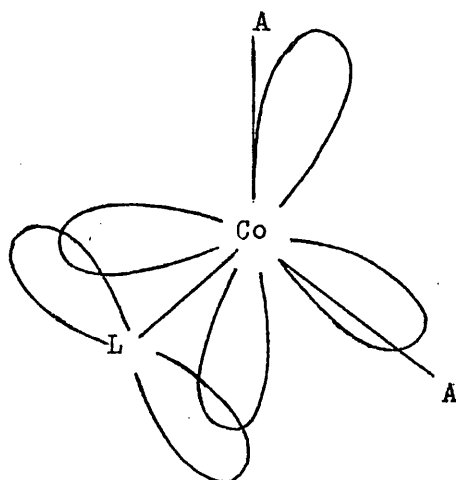
Figure iii.

Overlap of filled p orbital on L with vacant $d_{x^2-y^2}$ on the metal centre when the 5-coordinate intermediate resulting from the dissociation of CoA_4LX rearranges to form a trigonal bipyramid.

The isomerisation of the _trans_-$[Co(en)_2(OH_2)_2]^{3+}$ complex to the _cis_ isomer, in acidic solution, may be considered an aquation reaction i.e. the replacement of a coordinated ligand, in this case water, by a molecule of solvent water.

There are many reports in the literature on the acid-catalysed aquation of bis(ethylenediamine)cobalt(III) complexes, containing fluoro[10]azido,[11] nitro,[12] carbonato,[13] and sulphato[13] ligands. In these it has been found that the rate of aquation increases disproportionately with increasing acid concentration. Studies on the $[Co(en)_2F_2]^+$ complex[10] showed that its rate of acid hydrolysis was slower than that of its $[Co(en)_2Cl_2]^+$ analogue. Unlike the latter, the reaction of the difluoro complex was acid catalysed. It was thought that the catalysis was due to the greater basicity and hydrogen bonding tendency of the fluoride ion, compared with that of the chloride ion. Protonation of the fluoro ligand would weaken the cobalt-fluorine bond to give a more reactive species. Staples[11] observed that the acid hydrolysis of the _cis_- and _trans_- $[Co(en)_2(N_3)_2]^+$ occurred mainly with retention of configuration, and that at high perchloric acid concentrations the increase in rate was much greater than the increase in acid concentration justified. It was suggested that an SN2CA mechanism was operating. Again in the acid hydrolysis of $[Co(en)_2(NO_2)_2]^+$ disproportionately large increase in the rate with increasing concentration of acid were observed.[12] For this a mechanism was proposed involving, as the rate determining step, attack by water on the protonated complex.

It is generally considered that acid catalysis will be observed in the replacement of two different types of ligands:[16]

      1. those which are strongly basic or possess a high
         tendency to hydrogen bonding

2. flexible multi-dentate ligands or multi-dentate

basic ligands, e.g. bipyridyl, ethylenediamine,

and ethylenediaminetetraacetic acid, where

protonation of the ligand assists its removal

from the metal ion.

There are few reports in the literature concerning the optically

active cis-diaquobis(ethylenediamine)cobalt(III) cation. An

approximate value for the half-life of racemisation[14] of the cis

isomer is given as 50days at room temperature. This permits an

estimate of $1.6 \times 10^{-7} sec^{-1}$ for the specific rate of loss of optical

activity.

Experimental.

In contrast to the procedure in previous studies[4,5,6] the diaquo

ion was obtained by the acid hydrolysis of the carbonatobis(ethylene-

diamine)cobalt(III) perchlorate, thus avoiding contamination with

trans- $\left[Co(en)_2(OH)(OH_2) \right]^{2+}$, which occurs in the preparation of

the trans-diaquo complex.

Preparation of Reaction Solutions.

(a) Isomerisation

The reaction solutions for the isomerisation, both in dilute and

in concentrated perchloric acid, were prepared in the following

manner.

When the carbonato complex is dissolved in perchloric acid

solution, carbon-dioxide is evolved and the cis-diaquo ion generated.[15]

On the addition of alkali the cis-dihydroxobis(ethylenediamine)cobalt(III)

cation is produced, with full retention of configuration.[15] This,

on gentle warming, converts to the equilibrium mixture of 46% cis-

and 54% trans-$\left[Co(en)_2(OH)_2\right]^+$.[4,6,17] A known excess of perchloric acid was then added giving a mixture of 46% cis- and 54% trans-diaquo ions. The subsequent trans to cis isomerisation was followed spectrophotometrically.

(b) Racemisation.

The addition of perchloric acid to the optically active $\left[Co(en)_2CO_3\right]$ ClO_4 solid, generates a solution of the optically active cis-diaquo ion, with full retention of configuration.[15]

Kinetic Measurements.

(a) Isomerisation

(i) A known volume of 46% cis/54%trans equilibrium mixture of $\left[Co(en)_2(OH)_2\right]^+$ and a known volume of standard perchloric acid were placed on either side of a divided, stoppered flask. The flask was then placed in a thermostatting bath, maintained at the required temperature. The reaction was started by shaking the flask, thus mixing the reactants. The resulting solution was rapidly transferred to a 1cm silica cell, which was then placed in a thermostatted cell compartment in the spectro-photometer.

(ii) A known volume of the dihydroxo equilibrium mixture was placed in a 1cm silica cell contained in the thermostatted cell compartment of the spectrophotometer. The run was intiated by the addition of a known volume of standard perchloric acid, maintained at the same temperature, to the cell. The reactants were then mixed by shaking and the change in optical absorbance recorded on the spectrophotometer.

(b) Racemisation Measurements

Since the racemisation of the cis-diaquo ion has been observed to be rather slow[14] at 25°, a known weight of (+) or (-)$\left[Co(en)_2CO_3\right]ClO_4$

was dissolved in a known volume of standard perchloric acid and 2ml. samples were placed in glass ampoules which were then sealed and suspended in a thermostatting bath, maintained at the required temperature. At recorded time intervals the samples were removed and rapidly cooled in ice. The optical rotation of the sample was recorded at $22,940cm.^{-1}$ (436nm.). The optical rotatory dispersion spectrum of the sample was also recorded.

Instrumentation.

The isomerisation of trans- $\left[Co(en)_2(OH_2)_2 \right]^{3+}$ was followed at $20,100cm.^{-1}$ on a Unicam S.P.800 spectrophotometer using:

    a. an S.P.850 scale expansion unit and a Kent
       slave recorder.

    b. an S.P.825 fixed-wavelength repetitive scan
       unit.

Alternatively, the spectra were scanned over the range 15,000 - $35,000cm.^{-1}$ (667 - 286nm.) at known time intervals.

The optical rotation was measured on an automatic recording Zeiss polarimeter at $22,940cm.^{-1}$ (436nm.), using a tube of 0.5dm. path length.

The ORD spectra were recorded on Perkin Elmer Model P23 spectropolarimeter, using a tube of 0.4999dm. path length.

Measurement of Temperature.

All temperatures were measured using thermometers previously calibrated at the National Physical Laboratories. In the isomerisation reactions the temperature was measured in the reaction mixture. For the racemisation experiments, the temperature of the thermostatting bath was taken as the reaction temperature.

Results.

Isomerisation - dilute acid.

Kruse and Taube[6] found that the rate of isomerisation of the trans- isomer to the cis-diaquo isomer appeared to be independent of acid concentration up to ~1M acid, and that the rate was unaffected by changes in the ionic strength. The present work confirms these observations, although the specific rates obtained differ (Table 2).

First order plots were obtained by plotting log $\frac{(A_\infty - A_t)}{(A_\infty - A_0)}$ v.time and the observed rate constant calculated from the following equation:

$$\underline{trans-} \left[Co(en)_2(OH_2)_2\right]^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underline{cis-} \left[Co(en)_2(OH_2)_2\right]^{3+}$$
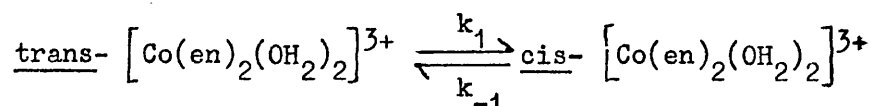
then

$$k_{obs.} = k_1 + k_{-1} = 2.303 \; \log \frac{(A_\infty - A_t)}{(A_\infty - A_0)} \; t \quad sec.^{-1}$$

where A_∞ = absorbance at infinite time

A_t = absorbance at time t

A_0 = absorbance at time t = 0

Bjerrum and Rasmussen[4] in their studies of the diaquo system, observed that the equilibrium coefficient, at 25°, was 58. This indicates that the equilibrium mixture contains 98.3% of the cis-diaquo isomer and 1.7% of the trans- isomer. Kruse and Taube[6] used this value in their calculations although they noted that, under strong illumination, almost 30% of the trans isomer existed at equilibrium. In this study the position of equilibrium appeared to temperature dependent, the final amount of cis isomer varying between 90 - 97%. Unfortunately, this is

Table 2.

Observed Spectrophotometric Rate Constants Obtained in the Isomerisation

Reaction $trans\text{-}[Co(en)_2(OH_2)_2]^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}[Co(en)_2(OH_2)_2]^{3+}$,
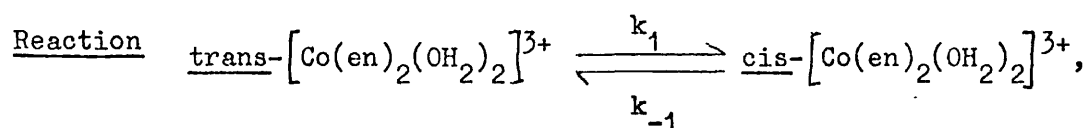
in Dilute Perchloric Acid Solution.

Temp. (°C)	[Complex] (mM)	[HClO$_4$] (M)	$10^4 k_{obs.}$ (sec.$^{-1}$)	
67.4	9.02	0.41	40.2	
67.4	9.02	0.41	42.2	
67.4	9.02	0.41	40.7	
67.4	9.02	0.20	41.8	
58.4	9.02	0.41	15.1	
58.4	9.02	0.41	14.8	
58.4	9.02	0.41	15.3	
54.3	9.21	0.48	8.07	
53.1	5.00	0.32	7.68	
48.0	9.02	0.41	3.20	
48.0	9.02	0.41	3.30	
47.3	10.6	0.50	3.10	
46.6	9.21	0.48	2.50	
46.6	9.21	0.48	2.90	
46.6	9.21	0.48	2.90	
45.7	12.1	0.58	2.35	
45.7	5.06	0.45	2.40	
39.4	9.02	0.41	.768	
39.4	9.02	0.41	.743	
39.4	9.02	0.41	.770	
38.8	9.21	0.48	.768	
38.8	9.21	0.48	.767	
37.5	10.0	1.00	.40	(ref. 6)
33.6	5.06	0.30	.533	
31.1	5.06	0.30	.441	
25.2	9.02	0.41	.130	
25.0	10.0	0.05	.125	(ref. 4)
24.95	10.0	1.00	.068	(ref.6)

in a region where the observed equilibrium constant will change

rapidly with small changes in concentration of the product, thus

affecting the calculation of the cis to trans rate of isomerisation.
as is shown in Table 4 p.75.

The higher value reported[+] for the observed rate constant

at $25°$, 1.25×10^{-5} sec.$^{-1}$, compared with that reported by

Kruse and Taube, 7.0×10^{-6} sec.$^{-1}$, was thought, by the latter,

to be caused by a contribution from the highly labile

hydroxoaquo species,[5,6] due to a low concentration of acid. The

result obtained in the present work, 1.20×10^{-5} sec.$^{-1}$, agrees

with the former result, despite a ten-fold increase in the

acid concentration.

Isomerisation - concentrated acid.

The kinetic runs in concentrated perchloric acid gave excellent

first - order rate plots at all acid concentrations, up to 90%

reaction. A typical plot is shown in Fig. iv and the observed

rate constants are given in Table 3.

A plot of the observed first-order rate constant against

acid concentration was markedly curved (Fig. v). Very large

increases in $k_{obs.}$ were found above an acid concentration of

8M. The large increases in the rate of isomerisation are

parallelled by the increase in the rate of water exchange between

the $\underline{\text{trans-}}\left[\text{Co(en)}_2(\text{OH}_2)_2\right]^{3+}$ and the solvent water at high

acid concentrations.[6]

The UV and visible spectrum of the product was identical

with that obtained from the isomerisation in dilute acid. This

is in agreement with recently published work on the cis /trans

equilibrium of the diaquobis(ethylenediamine)cobalt(III) ion

in concentrated perchlorate media. It was found[24] that sodium

perchlorate had no effect on the percentage of the cis- and trans-

isomers which existed at equilibrium. A previous study[25] employing

Temp. = 26.8°

[complex] = 8.32mM

$[HClO_4]$ = 7.73M
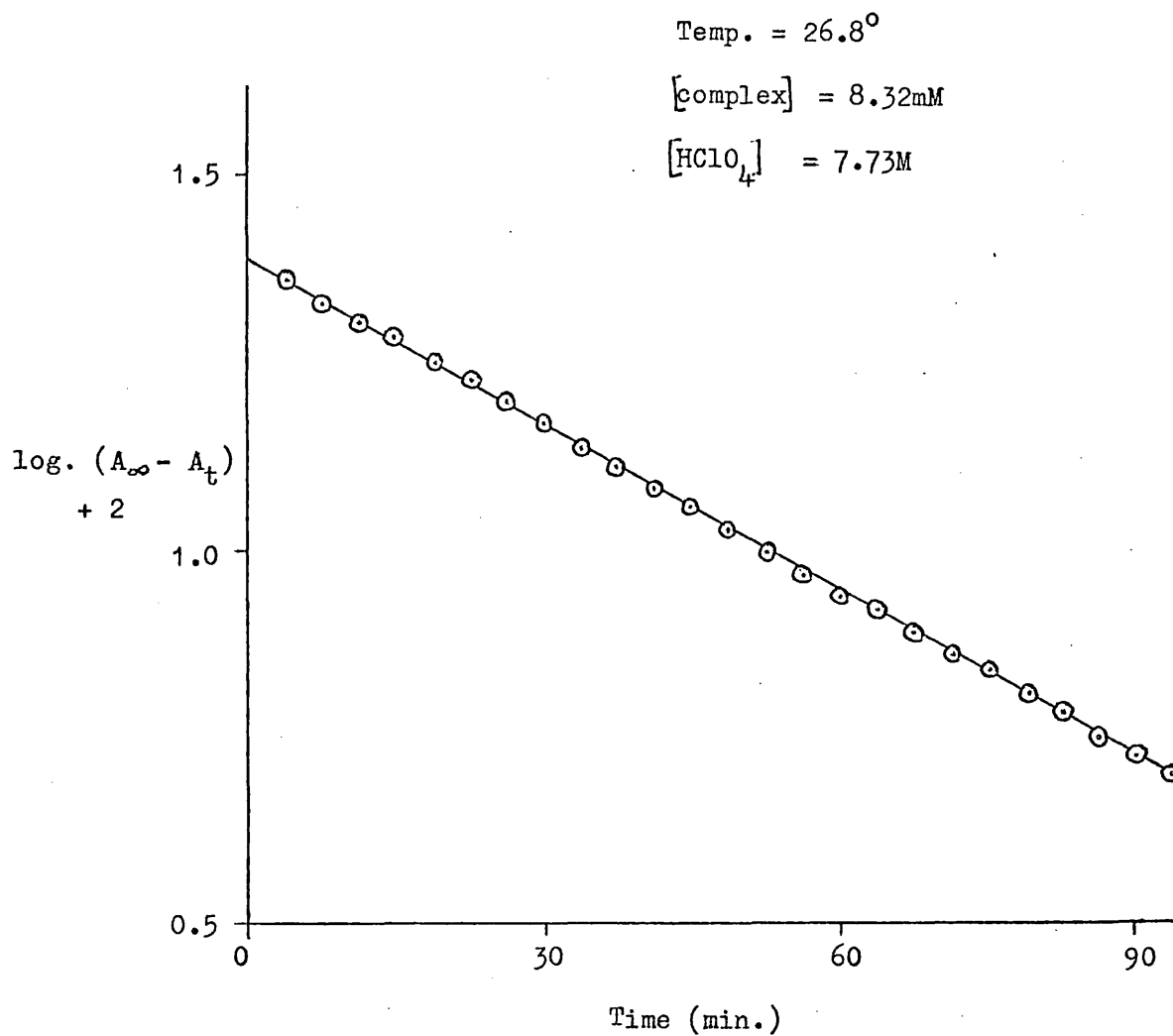
Figure iv.

Rate plot obtained in the isomerisation of <u>trans-</u>$[Co(en)_2(OH_2)_2]^{3+}$ in concentrated perchloric acid.

Table 3.

Observed Spectrophotometric Rate Constants Obtained in the Isomerisation

Reaction trans-$\left[Co(en)_2(OH_2)_2\right]^{3+}$ $\rightleftharpoons$ cis-$\left[Co(en)_2(OH_2)_2\right]^{3+}$
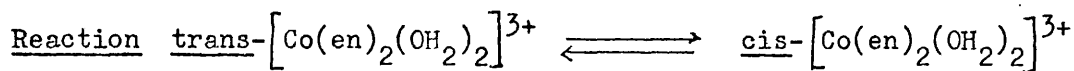
in Concentrated Perchloric Acid Solution.

Complex = 8.32 mM

Temp. = 26.8° unless otherwise stated

	$\left[HC10_4\right]$ (M)	$10^4 k_{obs.}$ (sec.$^{-1}$)	
	9.64	23	
	9.64	27	
	9.64	19	
	9.64	21	
	9.06	9.6	
	9.06	9.7	
	9.06	1.1	
Temp.= 14.0°	9.06	1.3	
Temp.= 14.0°	9.06	1.4	
Temp.= 14.0°	9.06	1.4	
Temp.= 4.5°	9.06	0.29	
Temp.= 4.5°	9.06	0.29	
Temp.= 4.5°	9.06	0.30	
	8.43	4.4	
	8.43	5.3	
	8.43	4.7	
	7.73	2.8	
	7.73	3.2	
	7.22	2.9	
	7.22	2.7	
	7.22	3.0	
	5.91	0.65	
	5.91	0.65	
Temp.= 24.95°	5	0.21	(from ref. 6)
	4.81	0.46	
	4.81	0.45	

Temp. = 26.8°

[complex] = 8.32mM

$10^3 k_{obs.}$

[HClO$_4$] (M)

Figure v.

Plot of observed rate constant against acid concentration for the isomerisation of <u>trans-</u> $[Co(en)_2(OH_2)_2]^{3+}$ in concentrated perchloric acid.

proton magnetic resonance techniques, had suggested that a greater amount of the _trans_ isomer existed, at equilibrium, in highly concentrated perchlorate media.

Racemisation.

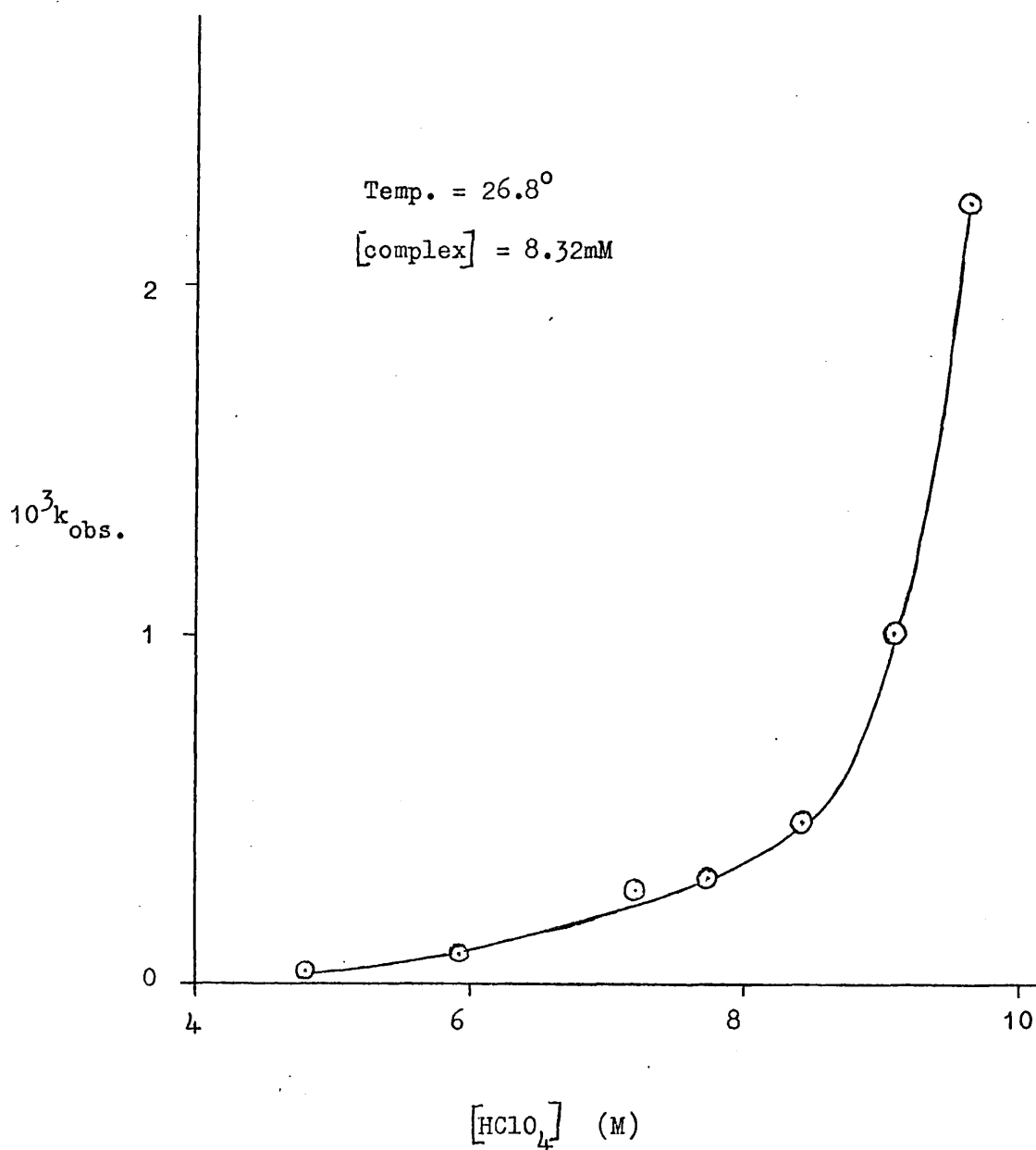The rate of loss of optical activity was observed to be very slow, but by plotting log ($\alpha_t - \alpha_\infty$) _v_. time (where α_t = optical rotation at time t, α_∞ = optical rotation at time t = ∞) good first order plots were obtained. The results are given in Table 4. The specific rate constants for the _cis_ to _trans_ isomerisation are included for comparison.

A set of typical ORD spectra, obtained during racemisation, are shown in Fig. vi.

Table 4.

Observed Rates of Racemisation of the Optically Active cis-$\left[Co(en)_2(OH_2)_2\right]^{3+}$, in Dilute Perchloric Acid Solution.

Temp.	[Complex]	[HClO_4]	$k_{rac.}$	$k_{c \to t}$ (calculated)
(°C)	(g/100ml)	(M)	(sec.$^{-1}$)	(sec.$^{-1}$)
54.2	0.16	0.048	4.32×10^{-5}	1.4×10^{-5}
54.2	0.17	0.048	4.39×10^{-5}	"
40.2	0.17	0.021	4.21×10^{-6}	1.8×10^{-6}
40.2	0.17	0.021	4.40×10^{-6}	"
40.2	0.17	0.048	4.33×10^{-6}	"
26.6	0.05	0.021	4.25×10^{-7}	2.0×10^{-7}
26.6	0.19	0.021	4.28×10^{-7}	"
25	-	-	1.7×10^{-7} (a)	

(a) from ref. 14.

(b) calculated using $K_{eq.}$ = 58[4]. The following results are obtained by employing the experimentally observed equilibrium constants.

T (°C)	54.2	40.2	26.6
$k_{c \to t}$ sec.$^{-1}$	8.1×10^{-5}	7.9×10^{-6}	1.0×10^{-6}
$K_{eq.}$	9	11	17

Figure vi.

ORD spectra obtained in the racemisation of $(-)cis-[Co(en)_2(OH_2)_2]^{3+}$ in dilute acid solution.
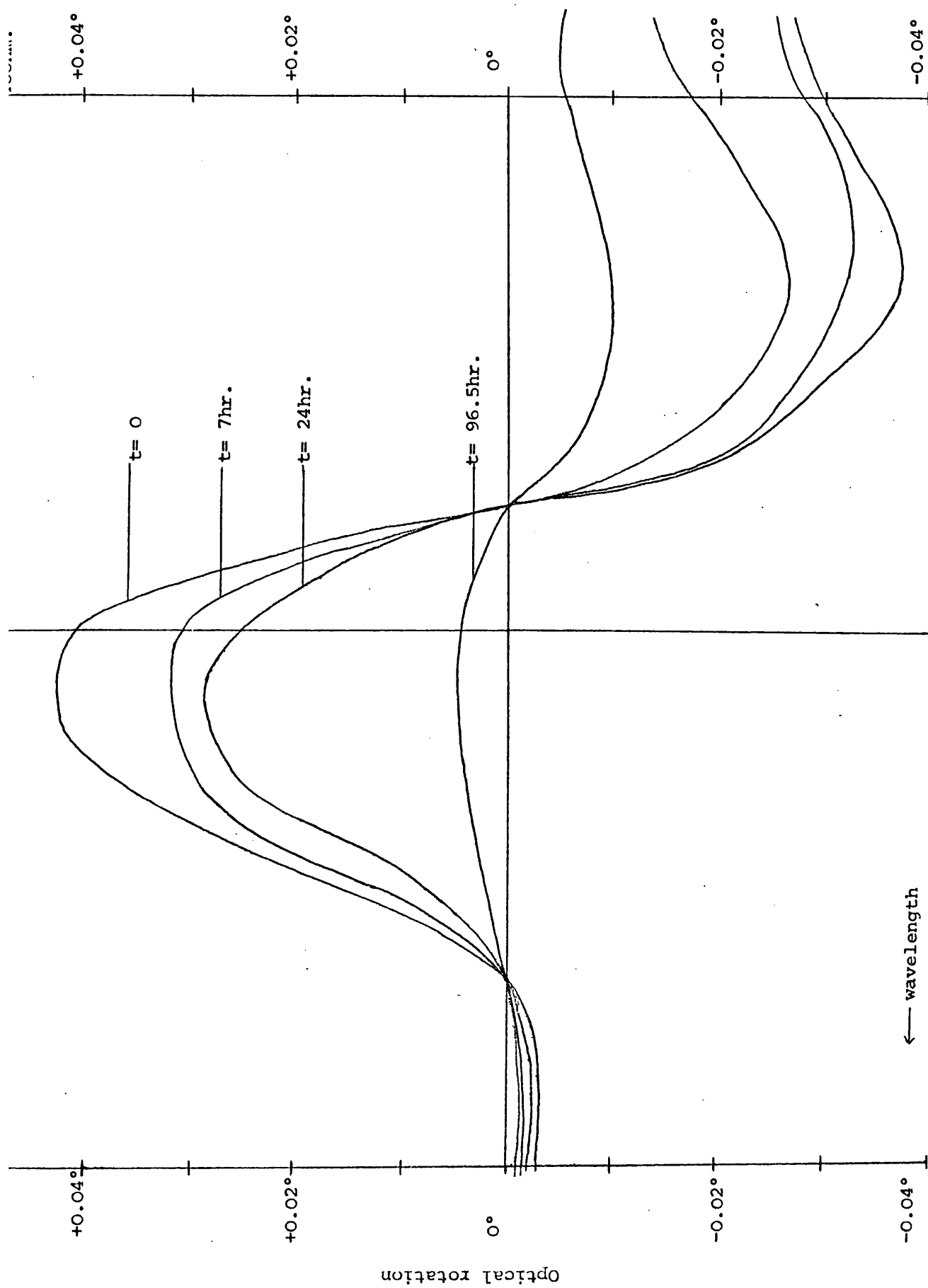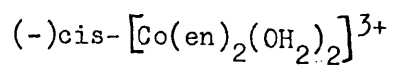
Discussion.

In the studies on the exchange of isotopically labelled coordinated water, $H_2^{18}O$, with solvent water[6] it was found that approximately one molecule of solvent exchanged with one of the coordinated water ligands for each act of _trans-_ to _cis-_ isomerisation. This result could be explained on the basis of an intermediate of coordination number five, which is then rapidly attacked by water to form the six-coordinated product (SN1). The loss of a proton releases electrons which could stabilise an intermediate of lower coordination number. There are two possible structures for a five-coordinate intermediate. A tetragonal pyramid would allow exchange but not isomerisation, whereas a trigonal bipyramid would permit both exchange and isomerisation. Thus, the structure of the intermediate for isomerisation _via_ an SN1 mechanism would be a trigonal bipyramid. The position of attack by the incoming nucleophile is in the trigonal plane since the metal atom will be most easily accessible at an angle of 120° and a minimum of atomic motion is required to regenerate the octahedron.[17] The trigonal plane also contains a vacant dx^2-dy^2 orbital thus further facilitating nucleophilic attack.[17]

However, the isotopic exchange could also be explained by assuming an intermediate of increased coordination number. This intermediate would then lose a water molecule to reform the six-coordinated product. Such a mechanism (SN2) would also permit isomerisation.

The large increase in the rates of isomerisation and the decrease in the enthalpy of activation (see Table 6 p.80) in concentrated acid, relative to those in dilute acid, may be explained on the basis of the incomplete tetrahydration of the protons in concentrated perchloric acid.[19] Thus,it may be more

relevant to consider the relationship of the water activity to the rate of isomerisation, since the present work was carried out in a region where the activity of water is decreasing rapidly.

Following work on a large number of acid-catalysed reactions Bunnett[19] proposed the relationship:

$$\left[\log k_{obs.} + H_o\right] = \omega \log a_w + constant \tag{1}$$

where

$k_{obs.}$ is the observed rate constant

H_o is the Hammett acidity function

a_w is the water activity

ω represents a parameter, which describes the way in which a reaction is catalysed by a strong mineral acid.

Reactions were classified according to their ω value as follows:

1. negative, water is not involved in the rate determining step.

2. $0 < \omega < 3$, water is acting as a nucleophile in the rate determining step.

3. $\omega > 3$, water is acting as a proton transfer agent in the rate determining step.

If $\log k_{obs.} + H_o$ v. $\log a_\omega$ is then plotted, the slope gives a value of $\omega = +1.3$, indicating that water is acting as a nucleophile in the rate determining step. This would seem to suggest that an SN2 mechanism is operating in the isomerisation of the trans- $\left[Co(en)_2(OH_2)_2\right]^{3+}$ species, at high acid concentrations.

The general applicability of Bunnett's equation[19] (eqn. 1) has been doubted[20] although several authors have recently employed

it to clarify the mechanism of the acid catalysed aquation of

cis- and trans-$\left[\text{Co(en)}_2(\text{N}_3)_2\right]^+$ in concentrated perchloric acid[11]

and the acid catalysed hydrolysis of trans-$\left[\text{Co(en)}_2(\text{NO}_2)_2\right]^+$ in

a large variety of strong mineral acids.[12] In the above studies

it was found that the increase in the rate of aquation was

much greater than the increase in the concentration of acid could

be expected to produce. The value of the parameter, w , in

Bunnett's equation was consistent with the attack of water on the

protonated complex as the rate determining step.

Alternatively, since not all the protons in concentrated acid

are tetrahydrated, the proton may be more strongly attracted

to the coordinated water, which could bond the proton to it

through the lone pair of electrons on the oxygen. This would

weaken the cobalt-oxygen bond and facilitate the formation of a

five-coordinated intermediate, increasing the rate of isomerisation

and lowering the enthalpy of activation.

A comparison between the rate of cis to trans isomerisation

and the rate of loss of optical activity, leads to the conclusion

that the racemisation occurs via the formation of the trans-

$\left[\text{Co(en)}_2(\text{OH}_2)_2\right]^{3+}$ isomer as shown below:

$$(+) \text{ cis-}\left[\text{Co(en)}_2(\text{OH}_2)_2\right]^{3+} \rightleftharpoons \text{trans-}\left[\text{Co(en)}_2(\text{OH}_2)_2\right]^{3+}$$

$$\updownarrow$$

$$(-) \text{ cis-}\left[\text{Co(en)}_2(\text{OH}_2)_2\right]^{3+}$$
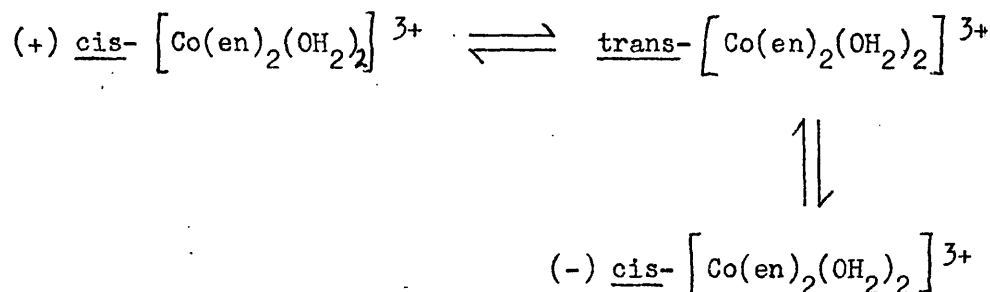
The postulated mechanism for the loss of optical activity of the

cis-diaquo ion i.e. via a trans- intermediate, may be explained

on the basis of either an SN1 or an SN2 mechanism. In an SN1

process, inversion cannot take place directly via a five-

coordinated intermediate as only retention of configuration
or loss of optical activity are possible. If the intermediate
is a tetragonal pyramid retention of configuration will result
(Fig. vii(a)). A trigonal bipyramid, however, could explain the
loss of optical activity, as a mixture of isomers would be produced
(Fig. vii(b)). Thus, the loss of optical activity may be due to
the formation of a trans- product or to the formation of a
racemic mixture of the cis- isomer.

An SN2 process involving the formation of a seven-coordinated
intermediate would lead to the production of the cis- isomer,
with full retention of optical activity and also to the formation
of the trans- isomer (fig. viii).

At this point it may be instructive to consider the respective
enthalpies and entropies which are presented in Table 6.

Table 6.

Kinetic Parameters Obtained from the Reactions of the $[Co(en)_2(OH_2)_2]^{3+}$ Cation.

Reaction.	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal.deg.$^{-1}$mole^{-1})
Dilute acid.		
trans → cis isomerisation	28.0	12.1
cis → trans isomerisation	29.4	13.4
racemisation	29.2	8.1
Concentrated acid.		
trans → cis isomerisation	25.5	12.1

Crystal field effects appear to favour a low value of ΔH when the intermediate is a tetragonal pyramid, whereas a trigonal bipyramidal intermediate would tend to produce a high enthalpy of activation.[21] It has been suggested that high entropies of activation may be diagnostic of a trigonal bipyramidal intermediate.[22] The similarity between the enthalpies of activation of the isomerisation (cis → trans) and for the racemisation of the optically active cis- isomer viz. 29.4 and 29.2 kcal./mole respectively, would seem to indicate that the loss of optical activity does indeed proceed via the formation of the trans- species.

It was thought that the isomerisation and exchange reactions of the diaqo ions could be explained by assuming the formation of two tetragonal pyramidal intermediates[6] one from the cis isomer and the other from the trans isomer. This would permit isotopic exchange to occur. The intermediate subsequently rearranged to form a trigonal bipyramid, which would allow isomerisation to occur. If this mechanism is operating it is difficult to explain the higher enthalpy of activation obtained in the trans exchange experiment relative to that obtained in the trans- to cis- isomerisation, viz. 30.6 and 28.0 kcal./mole, respectively.

From a study of the steric course of aquation of compounds of the type $\left[Co(en)_2ACl\right]^{n+}$, it was concluded that 'whether or not the trigonal bipyramidal form of the intermediate will develop is determined in the transition state and not by subsequent rearrangement of a square pyramid'.[23]

A lower value for the trans- exchange would have been predicted if this reaction proceeded via a tetragonal pyramidal intermediate.

The values of ΔH for the <u>trans</u> to <u>cis</u> isomerisation and <u>cis</u> to <u>trans</u> change in high concentrations of acid are less than those obtained for the isomerisations occurring in dilute acid. This, as previously suggested (p. 79) may be attributed to the greater attraction of the proton to the coordinated water molecule which would lower the energy required to form the reactive intermediate.

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<center>SECTION V.</center>

The Isomerisation of the Aquoisothiocyanatobis(ethylenediamine)cobalt(III)

<center>Cation in Concentrated Perchloric Acid Solution.</center>

Introduction.

It has been reported [1,2,6] that in dilute perchloric acid solution

each of the aquoisothiocyanatobis(ethylenediamine)cobalt(III) isomers

undergoes conversion to the other. This occurs at a rate which is

independent of the acid concentration, up to ∼1M. It was originally

suggested that at late stages of the isomerisation, an aquation reaction

involving the replacement of the isothiocyanato ligand by a second

water molecule took place. This aquation, however, is retarded by the

presence of hydrogen ions and at acidities of 0.01M or higher, becomes

negligible.

A later study [2] examined the rate of exchange of isotopically

labelled solvent, $H_2^{18}O$, with both the cis and the trans isomers

and concluded that the exchange was accompanied by change of

configuration. It was also observed that the trans isomer exchanges

at a slightly faster rate than the cis isomer. This higher rate of

exchange for the trans isomer was explained in terms of the effect of

the ligand trans to the departing aquo ligand. The isothiocyanato

ligand is able to release electrons and this will facilitate the

removal of the ligand trans to it. In the case of the trans isomer

this will be the coordinated water molecule, whereas in the cis

isomer it is the ethylenediamine ligand which will be affected.

The isomerisation of $\left[Co(en)_2(OH_2)NCS\right]^{2+}$ may be considered to

be an aquation reation, or acid hydrolysis, where the aquo ligand

is being replaced by another water molecule.

A study on the acid hydrolysis of cis- and trans- $\left[Co(en)_2ClNCS\right]^+$

and cis- and trans- $\left[Co(en)_2BrNCS\right]^+$ showed that the cis isomers were

considerably more reactive than the trans isomers. The activation energies for the aquation of cis- $\left[Co(en)_2ClNCS \right]^+$ and cis- $\left[Co(en)_2BrNCS \right]^+$ were found to be 20.8 and 23.1 kcal.mole^{-1} respectively, whereas those of the corresponding trans isomers were 30.4 and 30.1 kcal.mole^{-1}, respectively. It was also observed that the cis isomers reacted with 100% retention of configuration, but that the trans isomers reacted with considerable steric change. The trans-$\left[Co(en)_2ClNCS \right]^+$ and trans-$\left[Co(en)_2BrNCS \right]^+$ gave 50-70% and 45% cis- $\left[Co(en)_2(OH_2)NCS \right]^{2+}$, respectively. It was thought that the difference in reactivities could be explained by considering the ease with which the cis and trans isomers may form a stable five-coordinate intermediate.[3]

The coordinated isothiocyanato ligand may be represented as

$$X \text{------} Co \text{------} \overset{+}{N} \equiv C \text{---} \overset{-}{S}$$
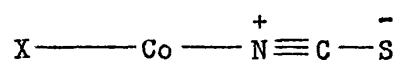
The positive charge on the nitrogen would be expected to induce the withdrawal of electrons from the cobalt atom. There is also a positive electromeric effect as the sulphur atom may release electrons which would then facilitate the cleavage of the cobalt-ligand bond

$$X \text{------} Co \text{---} \overset{+}{N} \equiv C \text{---} \overset{-}{S}$$
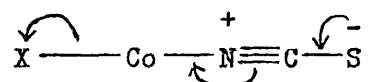
The latter effect was assumed to be more important in determining the mechanism which takes place during aquation. The large differences in the reactivities of the cis and trans isomers were also attributed to the ease of electron donation from the isothiocyanato ligand to the orbital left vacant by the departing ligand, as the electron donation would be important in establishing the stability of the 5-coordinate intermediate.

When the NCS$^-$ group is cis to the outgoing ligand, there is adequate overlap without any change in the relative positions of the

five remaining ligands. This will produce a square pyramidal intermediate, which may then be attacked by water to reform the <u>cis</u> product. In the <u>trans</u> isomer, direct orbital overlap is only possible by the intermediate rearranging to a trigonal bipyramid.

The lability of the <u>cis</u>- $\left[Co(en)_2 ClNCS \right]^+$ may be attributed to the ability of the <u>cis-iso</u>thiocyanato group to orientate a water molecule, which may then form a very weak hydrogen bond with the chloro ligand and assist its dissociation. If the aquation proceeds through a tetragonal pyramidal intermediate, this could account for the increased lability. This would be consistent with the relatively low activation energy ($20.8 kcal.mole^{-1}$), as a low activation energy is thought to be diagnostic of an intermediate of this structure.[8]

The racemisation of the optically active <u>cis</u>-$\left[Co(en)_2 ClNCS \right]^+$ has been studied.[3] A mechanism involving the formation of the <u>trans</u> compound as the active intermediate was proposed, as the rate of the <u>cis</u> $\longrightarrow$ <u>trans</u> isomerisation is of the same order of magnitude as the observed rate of loss of optical activity.

Experimental.

Perparation of Reaction Solutions.

A known weight of solid <u>trans</u>- $\left[Co(en)_2 (OH)NCS \right]$ SCN was dissolved in a minimum of water and the solution passed through an ion exchange column containing Amberlite I.R.400 in the hydroxide form. This removes the free thiocyanate ions, as they tend to interfere with the isomerisation of the $\left[Co(en)_2 (OH)NCS \right]^+$.[2] The <u>trans</u>- $\left[Co(en)_2 (OH_2)NCS \right]^{2+}$ was obtained by acidifying the <u>trans</u>-$\left[Co(en)_2 (OH)NCS \right]^+$ elluent with dilute perchloric acid, to pH 3. The aquo solution was then made up to a known volume using distilled water.

Method of Mixing.

A known volume of the above reaction solution was added to a known amount of standard perchloric acid contained in a 1cm. silica cell, in the thermostatted cell compartment of a Unicam S.P.800 spectrophotometer. The change in absorbance, of the reaction mixture, with time, was recorded at ~20,410 cm.$^{-1}$ (490nm.) or over the range 15,000 – 35,000cm.$^{-1}$ (667 – 286nm.) as previously described in Section IV, p. 68

Measurement of Temperatures

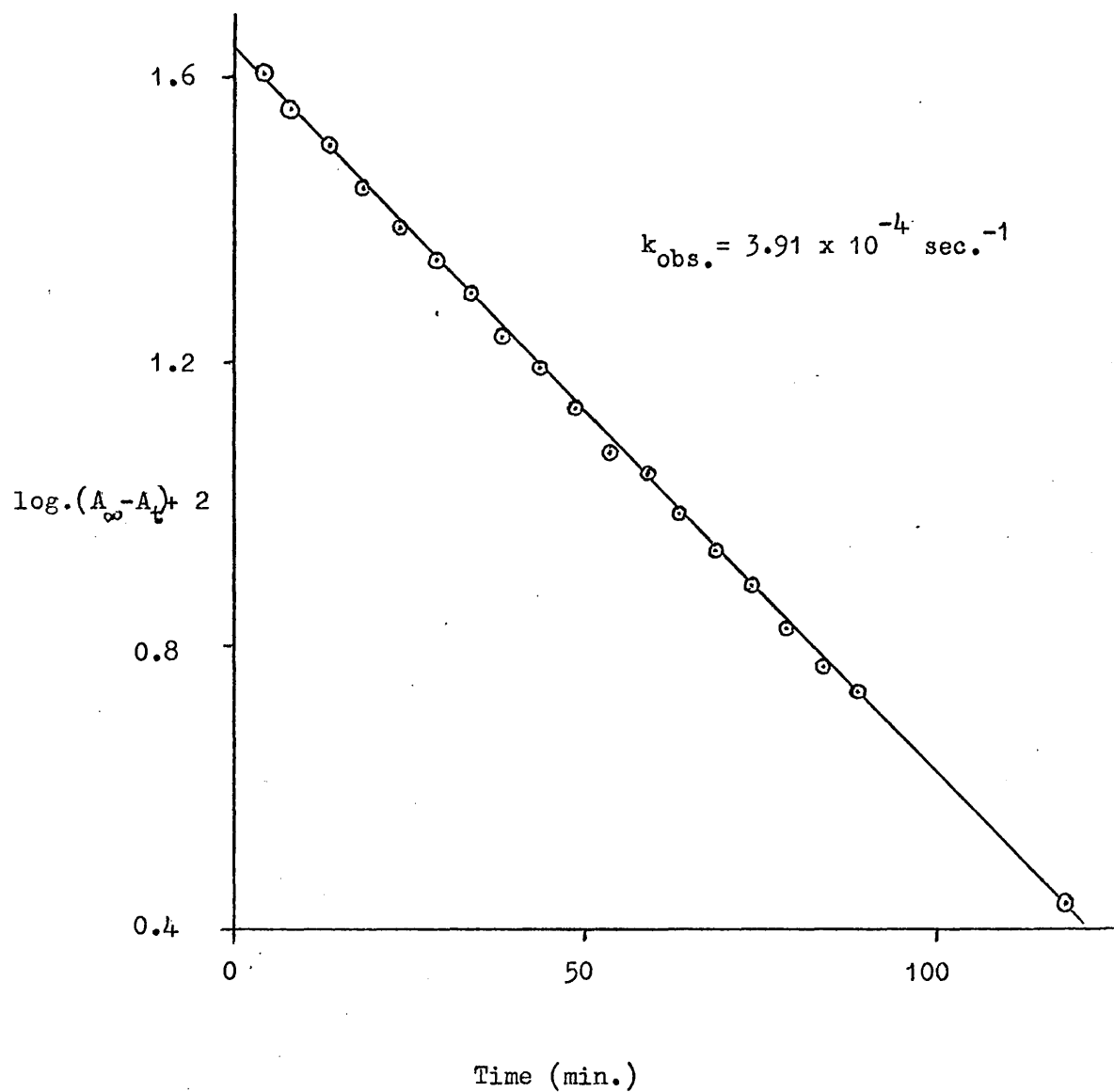Temperatures were recorded as described in Section IV, p. 68

Results.

Straight line first-order plots were obtained when log $(A_\infty - A_t)$ was plotted against time, for up to 90% reaction (Fig.i) First-order rate constants were calculated as previously shown(p.69). The percentage of the cis isomer at equilibrium was calculated from the equation below:-

$$\%cis = \frac{\Sigma_{cis} - \Sigma_{final}}{\Sigma_{cis} - \Sigma_{initial}} \times 100$$

where Σ_{cis} is the molar extinction coefficient of the pure cis-$[Co(en)_2(OH_2)NCS]^{2+}$

Σ_{final} is the molar extinction coefficient of the equilibrium mixture

$\Sigma_{initial}$ is the molar extinction coefficient of the solution at time = 0

Figure i.

A typical rate plot obtained for the reaction <u>trans-</u> $\left[\text{Co(en)}_2(\text{OH}_2)\text{NCS}\right]^{2+}$

<u>cis-</u> $\left[\text{Co(en)}_2(\text{OH}_2)\text{NCS}\right]^{2+}$

$k_{obs.} = 3.91 \times 10^{-4} \text{ sec.}^{-1}$

Time (min.)

$\left[\text{complex}\right]$ = 4.60mM

$\left[\text{HClO}_4\right]$ = 8.02M

Temp. = 46.0°

The observed rate constants of the <u>trans-</u>$\left[Co(en)_2(OH_2)NCS\right]^{2+}$ isomerisation at various concentrations of perchloric acid, are presented in Table 1, together with some literature values for the observed rates in dilute acid. The percentage of <u>cis</u> product is also included.

<div align="center">Table 1.</div>

<u>Observed Spectrophotometric Rate Constants Obtained in the Isomerisation</u>

<u>of the</u> <u>trans-</u>$\left[Co(en)_2(OH_2)NCS\right]^{2+}$ <u>Cation in Perchloric Acid</u>

<div align="center"><u>Solution.</u></div>

<u>Temp.</u> ($^{\circ}$C)	$\left[\underline{HClO_4}\right]$ (M)	$10^5\underline{k}_{obs.}$ (sec.$^{-1}$)	%<u>cis</u> product	$\left[Complex\right] = 4.60mM.$ Reaction followed at $\gamma = 20,350cm.^{-1}$
37.0	8.02	10.6	73	
37.0	8.02	11.7	77	
37.0	8.02	11.4	77	
37.0	8.02	10.9 (a)	80	
37.0	8.02	11.1 (a)	80	
37.0	7.20	6.52	79	
37.0	7.20	5.99	77	
37.0	7.20	6.66	85	
37.0	6.40	4.09	76	
37.0	6.40	3.96	77	
37.0	6.40	3.93	76	
37.0	5.64	2.80	75	
37.0	5.64	2.69	72	
37.0	5.64	3.07	72	
37.0	4.02	1.04	-	
37.0	4.02	1.03	-	
43.0	8.02	27.6 (b)	78	

Table 1. (contd.)

Temp. (°C)	$[HClO_4]$ (M)	$10^5 k_{obs.}$ (sec.$^{-1}$)	%cis product	
46.0	8.02	39.1 (b)	79	
46.0	8.02	39.1 (b)	80	
46.0	8.02	41.1 (b)	80	
56.0	8.02	186 (b)	82	
56.0	8.02	165 (b)	78	
56.0	8.02	175 (b)	82	
53.5	pH 3	4.96	-	(ref. 6)
54.9	pH 3	5.92	-	(ref. 6)

(a) $[Complex] = 2.30$ mM

(b) Reaction followed at 20,550cm.$^{-1}$

When the observed first-order rate constant was plotted against the acid concentration a curve was obtained (Fig. ii). The equilibrium constant for the isomerisation in concentrated acid is between 4 and 5, which agrees well with that obtained in dilute acid solution viz. ~5.[3]

An Arrhenius plot of log $k_{obs.}$ v.the reciprocal of absolute temperature (Fig. iii) permits an estimate of 29.9kcal.mole^{-1} for the activation energy of the process. This figure is slightly smaller than those which have been obtained in dilute acid i.e. 33.3[2] and 30.7[7]kcal.mole^{-1}

The entropy of the system in concentrated acid solution is calculated to be 17.6e.u., compared with 20.7e.u. in dilute perchloric acid.[2]
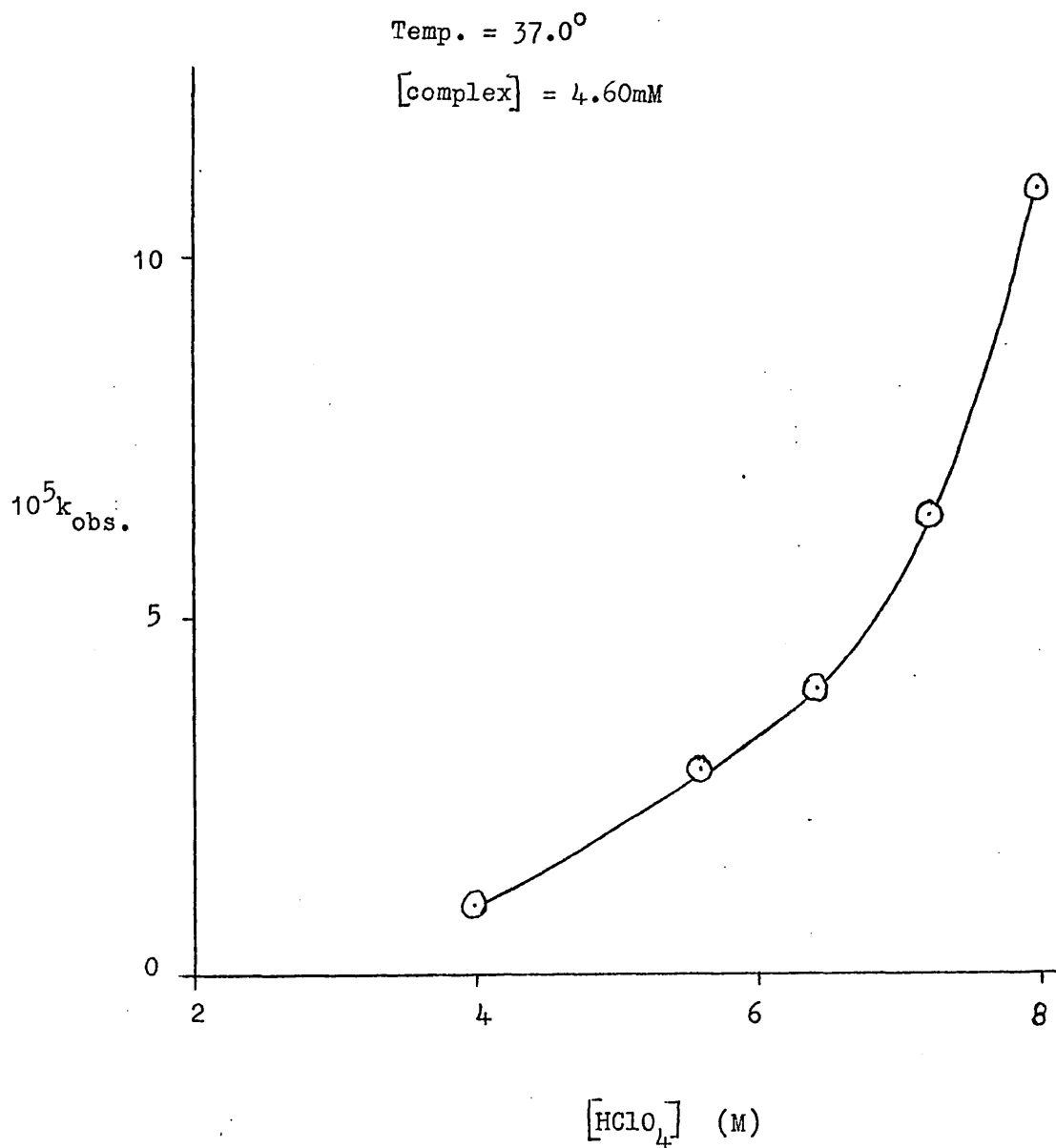
Temp. = 37.0°

[complex] = 4.60mM

Figure ii.

Variation of rate constants with concentration of acid in the

isomerisation of <u>trans-</u> [Co(en)$_2$(OH$_2$)NCS]$^{2+}$

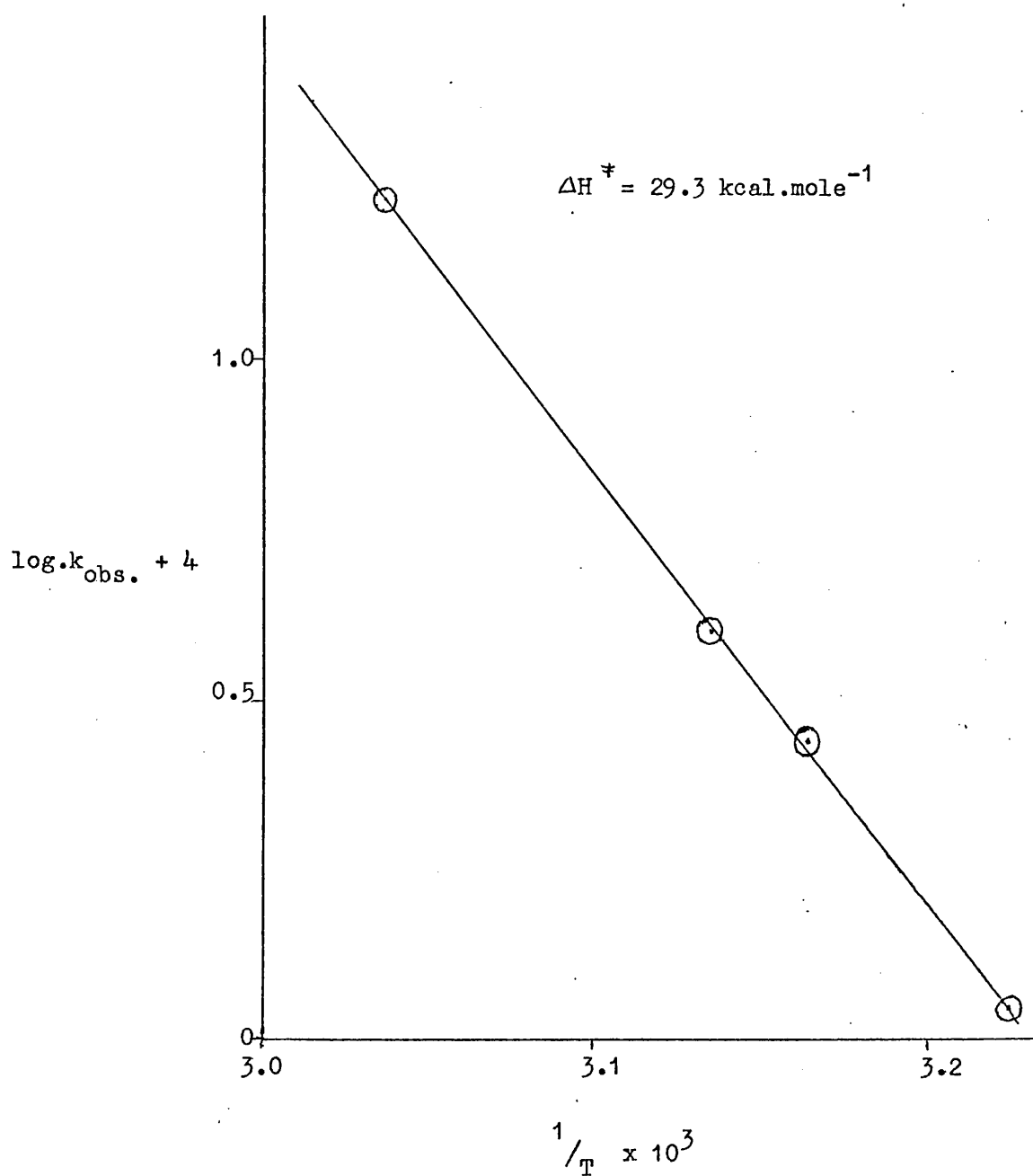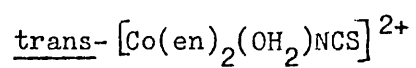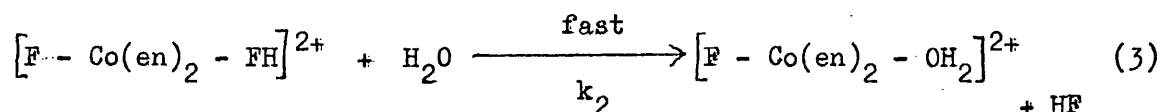$\Delta H^{\neq} = 29.3$ kcal.mole^{-1}

Figure iii.

Arrhenius plot obtained for the isomerisation of

trans- $[Co(en)_2(OH_2)NCS]^{2+}$

<u>Discussion.</u>

Since $\omega = +2.9$ a possible mechanism for the isomerisation of the <u>trans-</u>$\left[Co(en)_2(OH_2)NCS\right]^{2+}$ cation is that of an attack, by water, on the protonated complex as the rate determining step. This type of mechanism was first discussed by Basolo <u>et al.</u> in the acid hydrolysis of the difluorobis(ethylenediamine)cobalt(III) complex. The rate of aquation was found to be acid-catalysed, increasing disproportionately with decrease in pH. This reaction path is summarised in equations 1 - 3 and gives

$$\left[F - Co(en)_2 - F\right]^+ + H_2O \xrightarrow[\text{k}_1]{\text{slow}} \left[F - Co(en)_2 - OH_2\right]^{2+} + F^- \quad (1)$$

$$\left[F - Co(en)_2 - F\right]^+ + H^+ \xrightleftharpoons{\text{instantaneous}} \left[F - Co(en)_2 - FH\right]^{2+} \quad (2)$$

$$\left[F - Co(en)_2 - FH\right]^{2+} + H_2O \xrightarrow[\text{k}_2]{\text{fast}} \left[F - Co(en)_2 - OH_2\right]^{2+} + HF \quad (3)$$
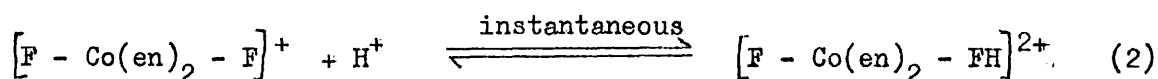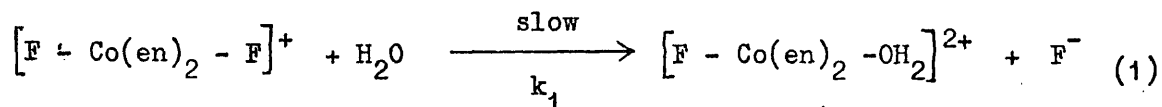
This produces a rate equation of the form

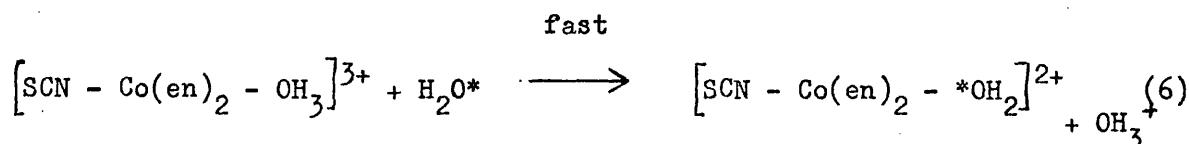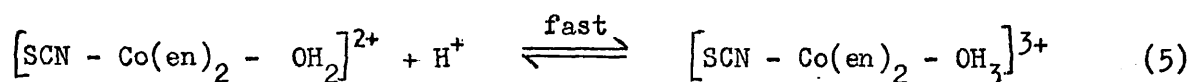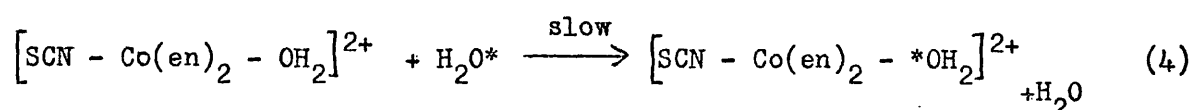$$k_{obs.} = k_1 \left[Co(en)_2F_2^+\right] + k_2 k_{eq.} \left[Co(en)_2F_2^+\right]\left[H^+\right]$$

where $k_{eq.}$ is the equilibrium constant in equation 2.

If this type of mechanism is to be applied to the present work, it is necessary to assume that the aquo ligand is the leaving group and not the <u>iso</u>thiocyanato ligand. This is reasonable as the presence

of acid reduces the dissociation of the isothiocyanato ligand and also as no trace of the cis- or trans-diaquo isomers was observed during the isomerisation of the trans-aquoisothiocyanato complex. The spectra of the diaquo ions are quite distinct from those of the cis- and trans- $\left[Co(en)_2(OH_2)NCS \right]^{2+}$ species (Fig. iv).

The reaction scheme suggested for the present work is as follows:-

(solvent water is shown as H_2O^*)

$$\left[SCN - Co(en)_2 - OH_2 \right]^{2+} + H_2O^* \xrightarrow{\text{slow}} \left[SCN - Co(en)_2 - {}^*OH_2 \right]^{2+}_{+H_2O} \qquad (4)$$

$$\left[SCN - Co(en)_2 - OH_2 \right]^{2+} + H^+ \underset{\xrightarrow{\hspace{1cm}}}{\overset{\text{fast}}{\rightleftharpoons}} \left[SCN - Co(en)_2 - OH_3 \right]^{3+} \qquad (5)$$

$$\left[SCN - Co(en)_2 - OH_3 \right]^{3+} + H_2O^* \xrightarrow{\text{fast}} \left[SCN - Co(en)_2 - {}^*OH_2 \right]^{2+}_{+\ OH_3^+} \qquad (6)$$

At low concentrations of acid the equilibrium reaction (eqn. 5.) cannot be significant and this will cause the substitution reaction (eqn. 6) to be negligible. The major path for isomerisation in dilute acid will be that shown in equation 4. In dilute acid there are sufficient water molecules for all the protons to be tetrahydrated[5] but in concentrated acid ($\sim$7 - 8M.) there are insufficient water molecules for complete tetrahydration of the protons.

As previously mentioned, the isothiocyanato ligand may be able to orientate the water molecules in its vicinity, further decreasing the number available for proton hydration. This may account for the disproportionate rate increase occurring at a lower acid concentration ($\sim$6M.) than is found in the diaquo system (Section IV p. 71). In the
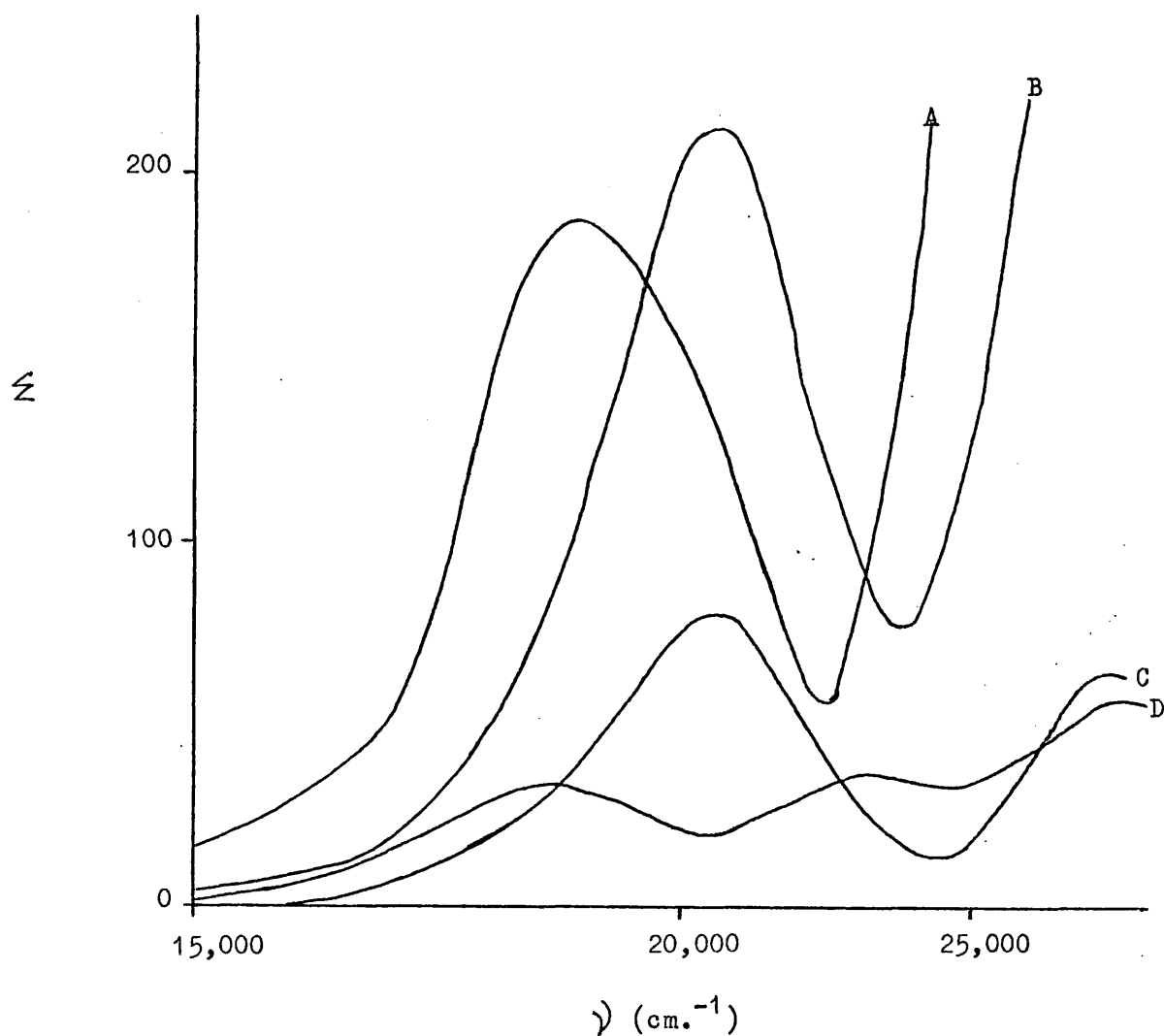
Figure vi.

UV and visible spectra of (A) trans- $[Co(en)_2(OH_2)NCS]^{2+}$;

(B) cis- $[Co(en)_2(OH_2)NCS]^{2+}$; (C) cis- $[Co(en)_2(OH_2)_2]^{3+}$ and

(D) trans- $[Co(en)_2(OH_2)_2]^{3+}$

latter system the extra large increases in the rate of isomerisation with increasing acid concentration start to occur at ~8M.

It is also possible that the isothiocyanato ligand is protonated, Co - N - C - S - H$^+$, thus weakening the cobalt-nitrogen bond to form $\left[Co(en)_2(OH_2)\right]^{3+}$ as the five-coordinate intermediate. Previous studies[2] have shown that the UV and visible reaction spectra for the trans to cis isomerisation of $\left[Co(en)_2(OH_2)NCS\right]^{2+}$ do not give a distinct isosbestic point in the presence of added thiocyanate ions. In the present work clean isosbestic points were obtained, pointing to the conclusion that there are no free thiocyanate ions in solution. From this it may be inferred that it is the aquo ligand and not the isothiocyanato ligand which is removed to form the reactive intermediate.

In dilute acid the major path for isomerisation is the direct replacement of a coordinated water ligand by a molecule of solvent water. The high positive entropy of the system (17.6e.u.) indicates that the most probable structure of the intermediate is a trigonal bipyramid. This may be formed by the slow rate-determining removal of the aquo ligand and the subsequent attack, by water, on this active intermediate. A trigonal bipyramidal structure would yield statistically 67% of the cis isomer and 33% of the trans isomer, rather less than the experimentally observed proportions, these being ~80% and 20% respectively.

In concentrated acid the formation of an intermediate of reduced coordination number would be assisted by the protonation of the aquo ligand, as this will weaken the cobalt-oxygen bond. This weakening would increase the rate of isomerisation.

The thiocyanato group possesses a large dipole moment, due to the ligand to metal π bonding[5] and this acts in the opposite direction to its net charge. This may cause an electrostatic attraction of water molecules, which would then be in a good position to attack the 5-coordinate intermediate, immediately adjacent to the isothiocyanato ligand. The cis-$\left[Co(en)_2(OH_2)NCS\right]^{2+}$ isomer would then be produced

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SECTION VI.

A Preliminary Investigation into the Substitution Reactions of the Sulphitobis(ethylenediamine)cobalt(III) Complexes.

Introduction.

Cobalt(III) is a d^6 ion and as such its complexes were considered to be fairly inert to ligand substitution. The sulphito complexes, however, exhibit a very marked lability. This was originally thought to be due to the possibility of $d\pi - d\pi$ bonding between the cobalt ion and the coordinated sulphur atom, which would stabilise the formation of the five coordinate intermediate. The lability is now thought to arise from a ligand to metal donation of charge through the σ bond. [2]

The sulphite ion has been reported to form complexes with a number of transition metals.[3-5] In many compounds it acts as a unidentate ligand, bonding through the sulphur atom. Complexes in which the sulphite ion acts as a bidentate ligand, bonding through two oxygen atoms have also been prepared. [6]

Strong sulphito compounds are usually formed with class (b) metals. Class (a) metals were originally defined by Ahrland et al. [7] as those metals which form stable compounds with the first ligand atom in each periodic group, e.g. N, O, F, etc. Class (b) metals were said to be those forming stable compounds with the second or subsequent donor atom in the periodic group. The concept of class (a) and class (b) compounds has been expanded and redefined by Pearson in his theory of hard and [8] soft acids and bases.

A hard acid (class (a) acid) is said to possess small size, high positive charge and with valence electrons that are not easily distorted or removed. A soft acid (class (b) acid) is one in which the acceptor atom has a large size, small positive or zero charge and easily polarised valence electrons. Cobalt(III) is considered to be a hard acid.

A soft base has a large negative charge and easily polarised electrons whereas the opposite is true for a hard base. Hard acids tend to form complexes with hard bases. Similarly, soft bases tend to complex with soft acids. The sulphito group may be considered to be a borderline case, acting as a hard or soft base according to the reaction conditions.

The lability of the sulphito complexes of cobalt(III) may be explained by the _trans_ effect which is strong in sulphur bonded complexes. In the amminosulphito complexes of platinum(II),[10] ethylenediamine will replace the two ammino groups in the _cis_ compound, but this substitution does not occur in the _trans_ compound. The _trans_ effect is known to be dependent on the following factors:[9]

1. the dipole moment

2. the induced dipole moment

3. the polarisability of the ligand

4. the charge and size of the ligand

5. the degree of metal-ligand π bonding.

Although a relative order of the strength of the _trans_[11] effect has been formulated for a number of ligands, much of the data is based on product yields, which have been obtained under varying conditions.
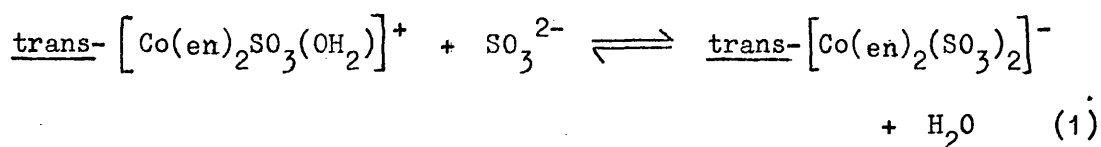
The _trans_ labilising influence of the sulphito group was observed [12] in a study of the kinetics and mechanisms of some amminosulphitocobalt(III) complexes. This study was concerned with the substitution by nucleophilic ligands _viz._ OH^-, NO_2^-, CN^-, SCN^- into complexes of the type $\left[Co(NH_3)_4SO_3X\right]$ where $X = NH_3$, OH^-, NO_2^- or SCN^-. These reactions were extremely fast necessitating the use of stopped flow techniques. Stranks and Yandell observed that the rate of nucleophilic substitution in a cobalt(III) complex is accelerated by the presence of sulphite ions. [13] Reaction half lives of seconds or less were recorded for the $\left[Co(NH_3)_4SO_3X\right]$ compounds at 25°, which is at least 10^3 times shorter than for typical substitution reactions of cobalt(III) complexes. A dissociative mechanism was suggested (SN1(limiting)) for these reactions, in which the generated intermediate exists for a sufficient length of time to discriminate, kinetically, between different nucleophiles. An analogous effect was observed in the substitution reactions of _trans-_ $\left[Co(CN)_4(SO_3)_2\right]^{5-}$ which undergoes ready aquation to produce _trans-_ $\left[Co(CN)_4SO_3(OH_2)\right]^{3-}$. [14, 15]

In a study of the reactions of the _trans_-aquosulphitobis(dimethyl-glyoximato)cobalt(III) complex, substitution of the water ligand by azide, bisulphite, iodide, pyridine or thiosulphate gives a second order rate constant. Substitution by sulphite or thiocyanate, however, appeared to proceed _via_ an SN1(lim.) mechanism. It was concluded that the high lability of the sulphito complexes was not completely attributable to metal to ligand π bonding. [2]
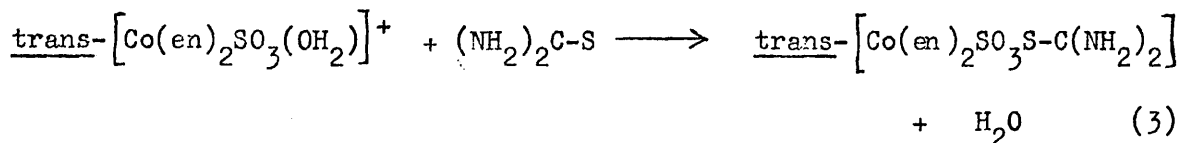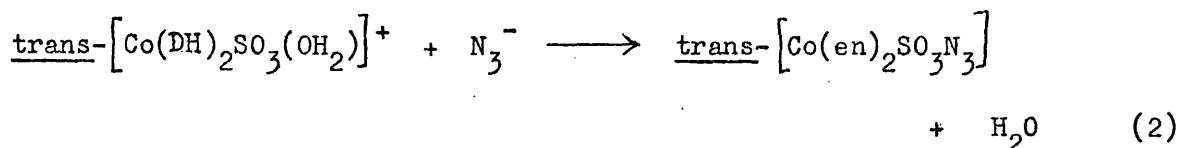
Recently, it has been stated that the rapid substitution rates [16] observed for the aquosulphitocobalomin system, could be explained on the basis of a ligand to metal donation of charge. This transfer of charge could be through the sulphur-metal σ bond. This conclusion was based on a consideration of the reactions of $\left[Co(DH)_2I(OH_2)\right]^{2+}$. [2] This complex is relatively inert towards substitution, despite the

similarity of the iodide ion to the sulphite ion in possessing low electronegativity and high polarisability. This would suggest that the π bonding is not a major factor contributing to the lability of the sulphito complexes.

As stated above the sulphito ligand directs an attacking nucleophile into a position <u>trans</u> to it and this was again observed in the substitution reaction illustrated in equation 1.[13]

$$\underline{trans\text{-}}\left[Co(en)_2SO_3(OH_2)\right]^+ \;+\; SO_3^{2-} \;\rightleftharpoons\; \underline{trans\text{-}}\left[Co(en)_2(SO_3)_2\right]^-$$
$$+ \; H_2O \qquad (1)$$

Here the <u>trans</u>-disulphito complex is produced by a dissociative mechanism, whereas the reactions shown in equations 2 and 3 proceed through an associative mechanism.[2]

$$\underline{trans\text{-}}\left[Co(DH)_2SO_3(OH_2)\right]^+ \;+\; N_3^- \;\longrightarrow\; \underline{trans\text{-}}\left[Co(en)_2SO_3N_3\right]$$
$$+ \; H_2O \qquad (2)$$

$$\underline{trans\text{-}}\left[Co(en)_2SO_3(OH_2)\right]^+ \;+\; (NH_2)_2C\text{-}S \;\longrightarrow\; \underline{trans\text{-}}\left[Co(en)_2SO_3S\text{-}C(NH_2)_2\right]$$
$$+ \; H_2O \qquad (3)$$

Due to the difficulties of obtaining free sulphite ions in solution, the reaction in eqn. 1 was performed at pH 8. At this value less than 3% of the sulhpite ions are converted to bisulphite ions. Since, however, the bisulphite substitutes at a rate similar to the sulphite ion, it was assumed that this would have a negligible effect on the reaction rate. At pH 8 the reaction described in equation 4 occurs, <u>viz</u> deprotonation of the water ligand.

$$\left[Co(en)_2SO_3(OH_2)\right]^+ \;+\; OH^- \;\longrightarrow\; \left[Co(en)_2SO_3OH\right] \;+\; H_2O \qquad (4)$$
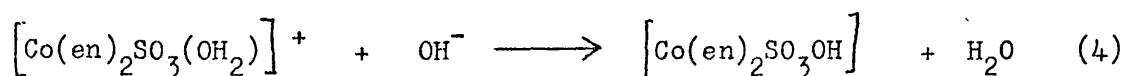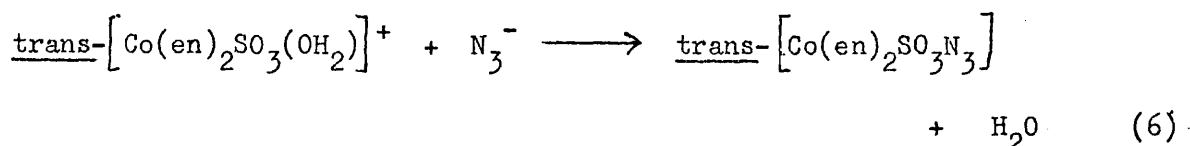
The hydroxosulphito complex is approximately 50 times less labile than the corresponding aquo complex and was hence also assumed to leave the reaction rate unaffected.

- The sulphite substitution reaction shown in equation 5 was also studied.[13]

$$[Co(en)_2SO_3OH] \;+\; SO_3{}^{2-} \longrightarrow [Co(en)_2(SO_3)_2]^- \;+\; OH^- \qquad (5)$$
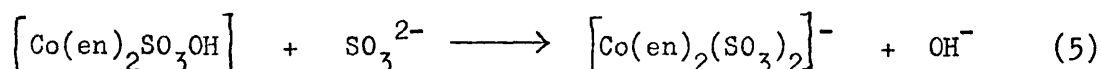
An activation energy of 16.5 kcal. mole^{-1} was obtained for reaction 1 and a value of 21.2 kcal. mole^{-1} was recorded for the hydroxosulphito complex substitution (eqn. 5).

The reaction in equation 6 at pH = 8, is extremely rapid at 25° and

$$\underline{trans\text{-}}[Co(en)_2SO_3(OH_2)]^+ \;+\; N_3^- \longrightarrow \underline{trans\text{-}}[Co(en)_2SO_3N_3]$$
$$+\; H_2O \qquad (6)$$

the first order rate constant is given as 13.6sec.$^{-1}$.[13]

$H_2{}^{18}O$ exchange experiments, at pH 8, on the aquosulphito complex showed that exchange was complete within 2 minutes at 25°.[18]
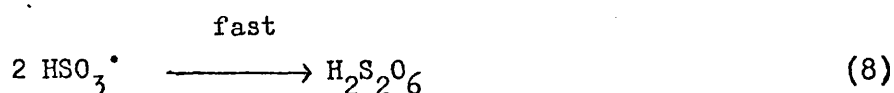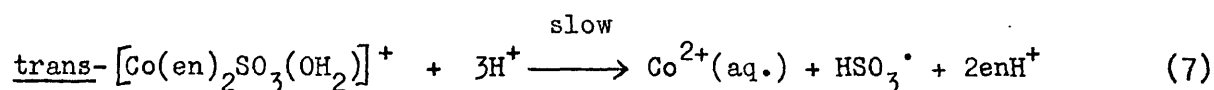
The <u>cis</u> sulphito compounds are not as labile as the <u>trans</u> series. Comparitive rates for three reactions of the <u>cis</u> and <u>trans</u>-disulphito complexes are given in Table 1.

Table 1. [13]

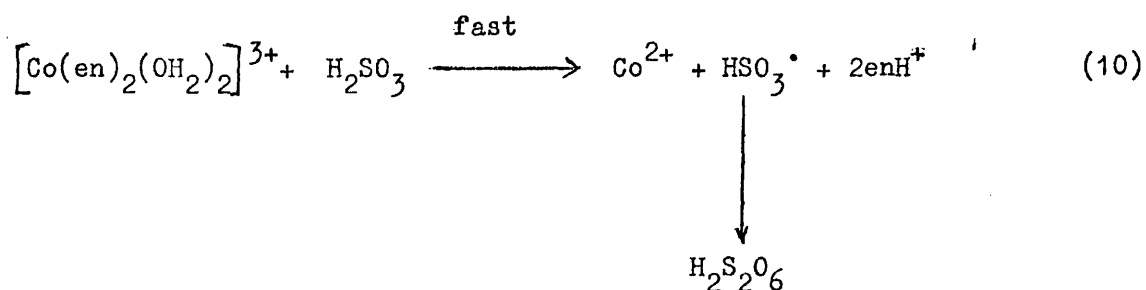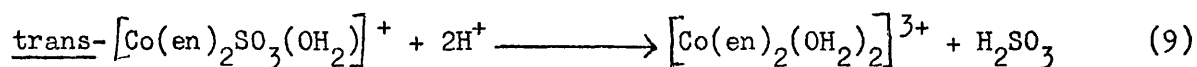|	$\underline{trans\text{-}}[Co(en)_2(SO_3)_2]^-$	$\underline{cis}\text{-}[Co(en)_2(SO_3)_2]^-$
Acid hydrolysis	very fast	$t_{\frac{1}{2}} = 840$ min. at 25°
Base hydrolysis	$t_{\frac{1}{2}} = 53$msec.	$t_{\frac{1}{2}} > 10^7$sec.
$^{35}SO_3{}^{2-}$ exchange at 25°	exchange incomplete after 10sec., but complete after 2min.	No exchange after 10min.

A report on the reaction of trans- $\left[Co(en)_2SO_3(OH_2)\right]^+$ at high acid

concentrations has been published.

In perchloric acid (up to ~7M) trans- $\left[Co(en)_2SO_3(OH_2)\right]^+$

disproportionates as shown in equations 7 and 8, at a rate equal to

3.6×10^{-4} sec.$^{-1}$ at $73°$.[19]

$$\text{trans-}\left[Co(en)_2SO_3(OH_2)\right]^+ + 3H^+ \xrightarrow{\text{slow}} Co^{2+}(aq.) + HSO_3^\bullet + 2enH^+ \qquad (7)$$

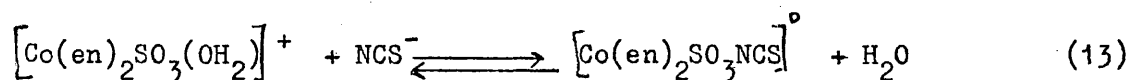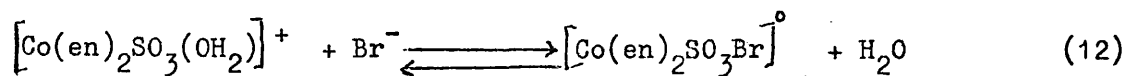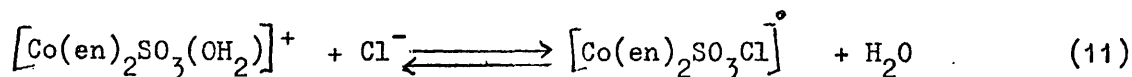$$2\,HSO_3^\bullet \xrightarrow{\text{fast}} H_2S_2O_6 \qquad (8)$$

The reaction in eqn. 8 may be prevented by the addition of a radical

scavenger such as oxygen or ferrous ions. The reaction is acid catalysed,

protonation of the complex being complete at 1M acid concentration. The

observed rate constant varies directly with the water activity in

the perchloric acid. This reaction may be considered to be an internal

oxidation/reduction reaction as the complex contains an oxidant

$(Co^{(III)}(en)_2)$ and a reductant (SO_3^{2-}). Although these are directly

bonded the complex is normally inert to internal oxidation/reduction

and to disproportionation.

An alternative route was suggested and this is demonstrated in equations

9 and 10.

$$\text{trans-}\left[Co(en)_2SO_3(OH_2)\right]^+ + 2H^+ \longrightarrow \left[Co(en)_2(OH_2)_2\right]^{3+} + H_2SO_3 \qquad (9)$$

$$\left[Co(en)_2(OH_2)_2\right]^{3+} + H_2SO_3 \xrightarrow{\text{fast}} Co^{2+} + HSO_3^\bullet + 2enH^+ \qquad (10)$$

$$\downarrow$$

$$H_2S_2O_6$$

However, $[Co(en)_2(OH_2)_2]^{3+}$ reacts too slowly with a mixture of perchloric acid and sodium sulphite, therefore this type of hydrolysis/redox reaction cannot be occurring.

In the present study the formation constants for the reactions between aquosulphitobis(ethylenediamine)cobalt(III) and chloride, bromide, and thiocyanate ions were obtained over a range of temperatures.

$$[Co(en)_2SO_3(OH_2)]^+ + Cl^- \rightleftharpoons [Co(en)_2SO_3Cl]^0 + H_2O \qquad (11)$$

$$[Co(en)_2SO_3(OH_2)]^+ + Br^- \rightleftharpoons [Co(en)_2SO_3Br]^0 + H_2O \qquad (12)$$

$$[Co(en)_2SO_3(OH_2)]^+ + NCS^- \rightleftharpoons [Co(en)_2SO_3NCS]^0 + H_2O \qquad (13)$$

The pK_b of the hydroxosulphitobis(ethylenediamine)cobalt(III) complex was obtained for the reaction

$$[Co(en)_2SO_3OH]^0 + H^+ \longrightarrow [Co(en)_2SO_3(OH_2)]^+ \qquad (14)$$
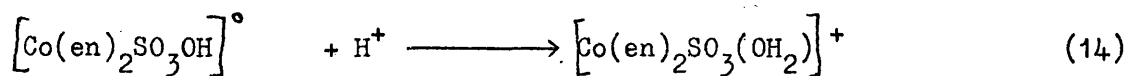
The pK_a of the aquosulphitobis(ethylenediamine)cobalt(III) cation was also calculated from the reaction

$$[Co(en)_2SO_3(OH_2)]^+ + OH^- \longrightarrow [Co(en)_2SO_3OH]^- + H_2O \qquad (15)$$
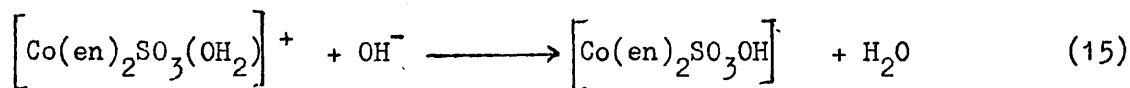
Other preliminary studies were made involving the acid and base hydrolysis of the cis- and trans-$[Co(en)_2(SO_3)_2]^-$ and the reaction between $[Co(en)_2SO_3(OH_2)]^+$ and hydroxide ions. The rates were too rapid to be followed using conventional techniques and the investigations were curtailed in favour of a study of the systems which have been discussed in the preceding sections.

Experimental.

Equilibrium studies.

The reaction of $\left[Co(en)_2SO_3(OH_2)\right]^+$ with chloride, bromide, and

thiocyanate ions was performed at constant ionic strengths of 1M,

4.1M and 0.5M respectively. A study of the reaction between the

aquosulphito complex and sodium iodide was not pursued as it was found

that a redox reaction producing Co(II) took place.

Preparation of Reaction Solutions.

A known weight of $\left[Co(en)_2SO_3(OH_2)\right]ClO_4$ was dissolved in a known

volume of water. Various concentrations of incoming ligand were prepared

by dissolving a recorded weight of NaCl, NaBr or NaNCS in water.

Constant ionic strength was maintained using $NaClO_4$. AnalaR NaCl and

NaBr were employed in these studies. The sodium thiocyanate was

standardised using a solution of silver nitrate as the primary standard

and ferric ammonium sulphate as the indicator. Sodium perchlorate

was standardised by allowing a known volume of $NaClO_4$ solution to

pass through an ion exchange column containing Amberlite IR-400 in

the acid form. The elluent was titrated with borax as the primary standard.

The indicator used was methyl red.

Method of Mixing.

The two reactants were mixed in known proportions in small

sample bottles and transferred to 1 cm. silica cells contained in the

thermostatted cell compartment of a Unicam SP 500 spectrophotometer.

The optical density of each solution was recorded at the selected

wavelength, having allowed 10 - 15 minutes for the solution to reach

complete thermal equilibrium.

This was repeated at several temperatures for each concentration

of incoming ligand.

Instrumentation.

Preliminary studies were performed on a Unicam SP800 spectro-photometer, but more accurate absorbances were obtained as stated above.

Measurement of Temperatures.

Temperatures were taken in the thermostatted cell compartment of the Unicam SP 500, using thermometers previously standardised at the National Physical Laboratories.

Results.

Method of Calculation

A certain amount of difficulty was encountered in the calculation of the equilibrium constants. This arose from the impossibility of obtaining, experimentally, the extinction coefficients of the product. This results from the reversible nature of the reaction. Stranks has reported similar difficulties in calculating the equilibrium constant for the reaction shown in equation 16.

$$\left[Co(en)_2SO_3(OH_2)\right]^+ + SO_3^{2-} \rightleftharpoons \left[Co(en)_2(SO_3)_2\right]^- + H_2O \qquad (16)$$
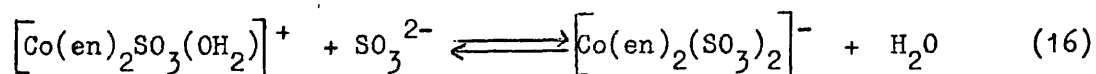
In the present work the equilibrium constants were obtained as follows:

At a particular wavelength

$$A_{(observed)} = A_{(reactant)} + A_{(product)}$$

$$= (c-x).\epsilon_{(reactant)} + x.\epsilon_{(product)} \qquad (17)$$

where A = absorbance

x = product concentration at equilibrium

ϵ = molar extinction coefficient

If the reaction given in equation 11 is considered then the

equlibrium constant will be of the form

$$K_{eq.} = \frac{\left[Co(en)_2SO_3Cl\right]\left[H_2O\right]}{\left[Co(en)_2SO_3(OH_2)^+\right]\left[Cl^-\right]}$$

From equation 17 the product concentration may be obtained by

estimating the value of $\lessgtr_{(product)}$. The concentration of the two

reactants <u>viz.</u> $\left[Co(en)_2SO_3(OH_2)\right]^+$ and Cl^- at equilibrium may be found

by subtracting the product concentration from their original respective

values.

It was found that if a range of extinction coefficients were taken

for the product, the calculated equilibrium constant increased with

increases in the concentration of the incoming ligand. A point was reached

where the equilibrium constant began to decrease with continued

increases in the ligand concentration. Graphs of $K_{eq.}$ (calcd.) $\underline{v.}$
the extinction coefficient of the product were plotted and a series

of intersecting curves were obtained. A typical set are shown in figure i.

The point of mutual intersection gave the value of the equilibrium constant

and the extinction coefficient of the product.

Tables 2 -4 give the equilibrium constants calculated at

various temperatures and differing ligand concentrations.

The thermodynamic constants for the equilibria are given in

Table 5.

Figure i.

Set of intersecting curves obtained in the calculation of the molar
extinction coefficient of the product from the reaction between NaCl and
$[Co(en)_2SO_3(OH_2)]^+$
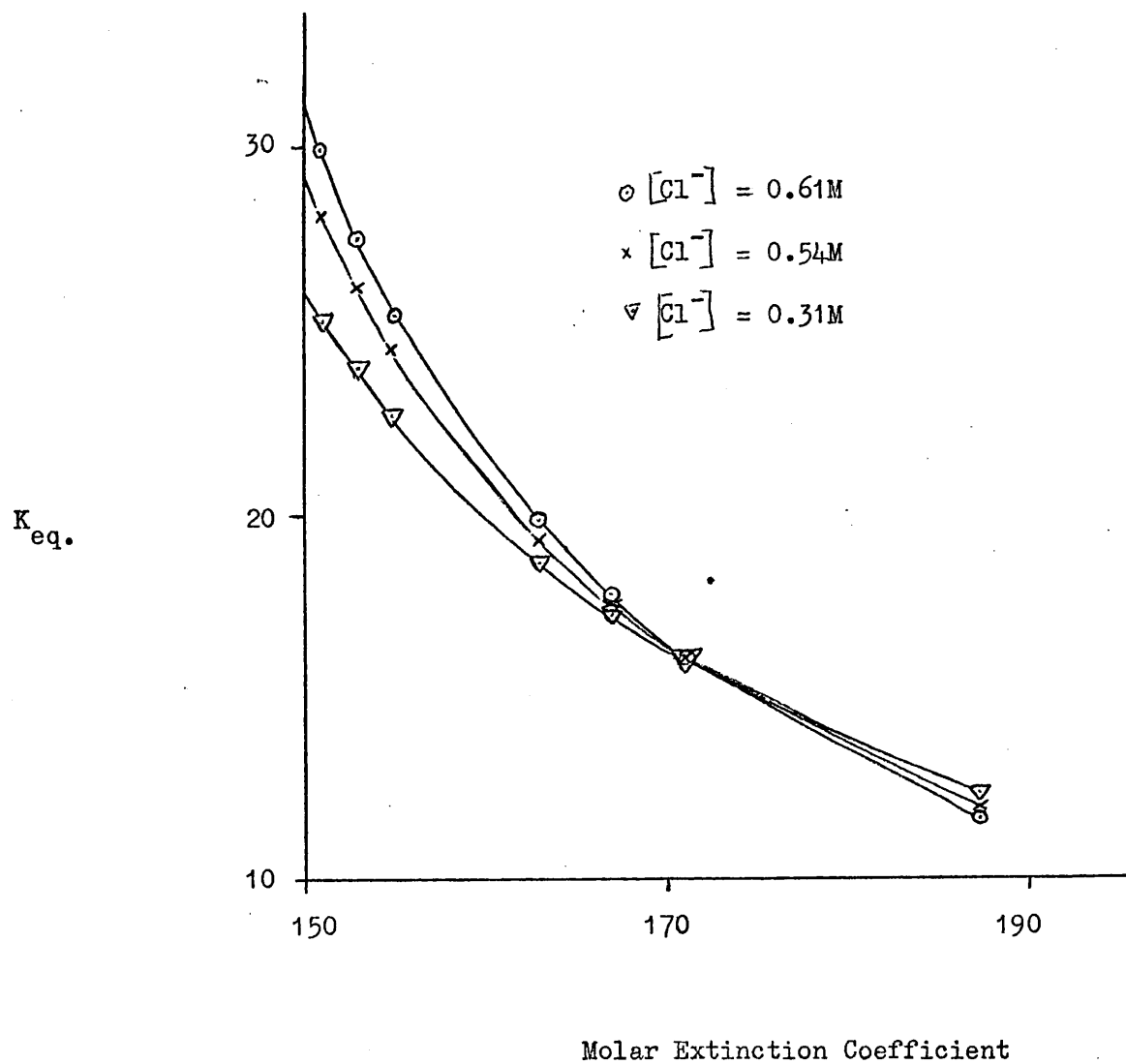
Table 2.

Equilibrium Constants Obtained Spectrophotometrically for the Reaction of trans-$[Co(en)_2SO_3(OH_2)]^+$ with Chloride Ions.

$[Complex] = 1.20mM$

Ionic strength = 1.0M

Wavelength at which reaction followed = 20,000cm.$^{-1}$ (500nm)

Temp. (°C)	$[Cl^-]$ (M)	$K_{eq.}$
5.4	0.61	12.7
5.4	0.54	12.9
5.4	0.31	9.8
24.5	0.61	15.2
24.5	0.54	15.7
24.5	0.31	16.2
36.4	0.98	21.7
36.4	0.61	20.3
36.4	0.54	17.1
36.4	0.31	20.7

Table 3.

Equilibrium Constants Obtained Spectrophotometrically for the Reaction of trans-$[Co(en)_2SO_3(OH_2)]^+$ with Bromide Ions.

$[Complex] = 1.62mM$

Ionic strength = 4.1M

Wavelength at which reaction was followed = 20,000cm^{-1} (500nm)

Temp. (°C)	$[Br^-]$ (M)	$K_{eq.}$
5.4	2.60	14.4
5.4	1.30	14.5
5.4	1.30	14.5
22.1	2.60	25.7
22.1	1.30	26.0
22.1	1.30	25.8
35.5	2.60	35.1
35.5	1.30	35.6
35.5	1.30	35.2
45.8	2.60	40.0
45.8	1.30	42.4
45.8	1.30	40.3

Table 4.

Equilibrium Constants Obtained Spectrophotometrically for the

Reaction of trans-$[Co(en)_2SO_3(OH_2)]^+$ with Thiocyanate Ions.

$[Complex]$ = 2.43 mM

Ionic strength = 0.5 M

Wavelength at which reaction was followed = 21,800cm.$^{-1}$ (460nm)

Temp. (°C)	$[NCS^-]$ (10^3M)	10^4 K_{eq}
15.7	0.1	5.38
15.7	0.19	5.22
24.1	4.8	1.72
24.1	0.1	2.38
24.1	0.19	3.62
37.2	4.8	1.32
37.2	0.1	1.56
37.2	0.19	3.00
43.2	4.8	1.22
43.2	0.1	1.16
43.2	0.19	1.93

Table 5.

Thermodynamic Parameters Obtained in the Equilibrium Studies of

$[Co(en)_2SO_3(OH_2)]^+$ with Cl^-, Br^-, and NCS^- Ions.

Complex product.	ΔH (kcal. mole^{-1})	ΔS (cal.deg.$^{-1}$ mole^{-1})	ΔG (kcal.mole^{-1})
$[Co(en)_2SO_3Cl]^0$	2.28 $\pm$ 1	22.1	- 1.8 $\pm$ 1
$[Co(en)_2SO_3Br]^0$	4.65 $\pm$ 1	13.7	- 1.94 $\pm$ 1
$[Co(en)_2SO_3NCS]^0$	- 8.96 $\pm$ 0.5	- 9.3	- 6.2 $\pm$ 0.5

pH Titrations.

Hydrochloric acid, previously standardised against sodium
hydroxide with phenolphthalein as the indicator, was added dropwise
to an aqueous solution of the $[Co(en)_2SO_3OH]$. This was contained in a
three-necked flask, through one of which nitrogen was passed into the
reaction vessel. This performed the two-fold task of excluding air
from the reaction mixture and also of mixing the reactants. The central
neck held the burette containing the HCl and the third neck held the
combined electrode and a metal stirrer to ensure complete mixing of
the reactants. The pH of the solution was recorded ~10 seconds after
each addition of acid. Nitrogen was bubbled through the solution before
and during the titration to ensure the mixture was oxygen free.

Boiled conductivity water was used throughout the titrations and
for making up the solutions.

Instrumentation.

The pH measurements were recorded on a Pye Cambridge Dynacap
pH meter using a combined glass/calomel electrode.

Calculations.

pK_b values were calculated using the equation

$$pH = \tfrac{1}{2}(pK_w - pK_b - \log c)$$

where

    pH is the pH at the observed end point

    $pK_w = -\log K_w$ and K_w = Dissociation constant for water

    $pK_b = -\log K_b$ and K_b = Association constant of the base

    c = concentration of the complex

    pK_a values were calculated using the equation

$$pH = \tfrac{1}{2}(pK_w - pK_a - \log c)$$

where

    $pK_a = -\log K_a$ and K_a = Dissociation constant for the acid

Results.

The pK_a and pK_b values are given in Table 6 for the compounds $\left[Co(en)_2SO_3(OH_2)\right]^+$ and $\left[Co(en)_2SO_3OH\right]$, respectively.

Table 6.

(A) pKa values for $\left[Co(en)_2SO_3(OH_2)\right]^+$

$\left[\underline{Complex.}\right]$ (10^3M)	$\underline{pK_a}$	$T = 25.0° \pm 0.5°$
1.18	9.77	
11.3	9.47	
11.3	9.54	

(B) pK_b values for $\left[Co(en)_2SO_3OH\right]^0$

$\left[\underline{Complex.}\right]$ (10^2M)	$\underline{pK_b}$	$T = 25.0° \pm 0.5°$
1.23	9.16	
1.23	9.11	
1.38	9.13	
1.68	9.17	
1.12	9.15	
0.25	9.01	

Discussion.

The relative stabilities of the complexes formed in the reactions studied (equations 11 - 13) may be discussed in terms of the theory of hard and soft acids and bases.

Although equilibrium constants are frequently taken as a measure

of hardness or softness, the temperature dependence of these constants makes enthalpy changes a better basis for correlation.
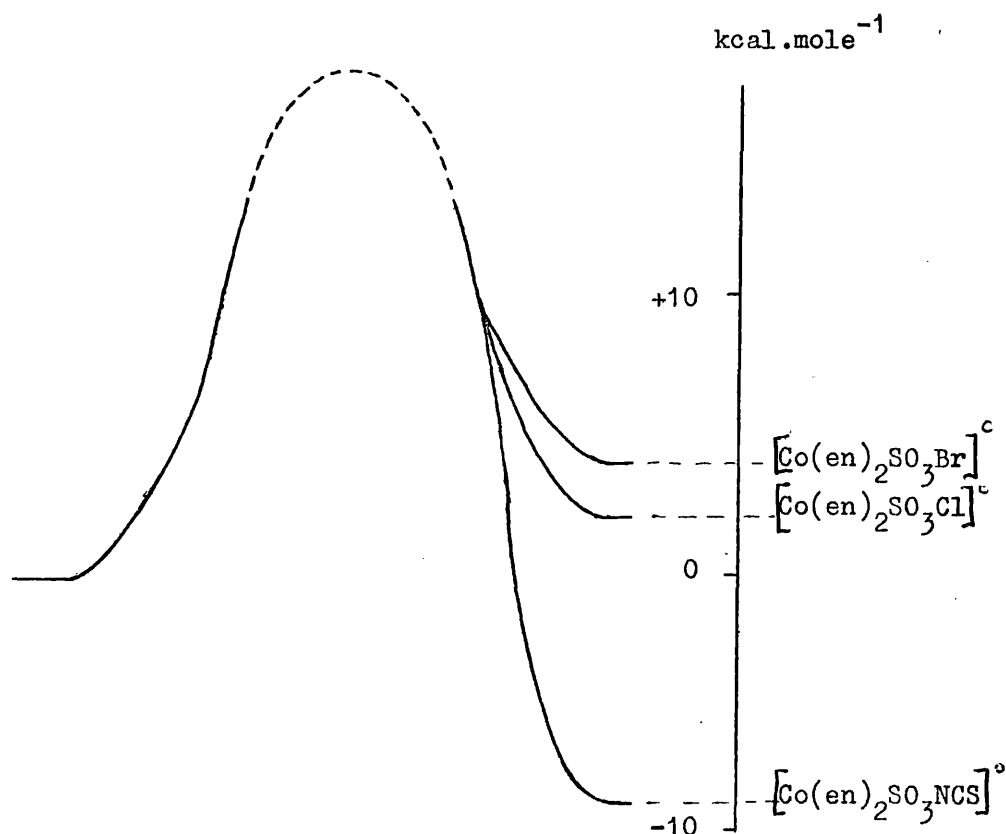
The results are presented schematically in figure ii.

Figure ii.

The chloro- and bromo- complexes may be considered to be of approximately equal stability, whereas the thiocyanato complex is clearly more stable than both.

The data for the classification of hard and soft bases was obtained mainly from reactions in the gas phase and from liquid phase reactions using non-polar solvents. As water is a polar solvent, it may lower the basicity of the anion and hence increase the tendency towards soft character. This would, perhaps, explain the proximity in the stabilities of the chloro- and bromo- complexes. The chloride ion is usually considered to be hard and the bromide ion to be a borderline base. Here, possibly because of hydration of the chloride ion, their

basicities are almost equal with respect to the $\left[\text{Co(en)}_2\text{SO}_3(\text{OH}_2)\right]^+$

cation. On the principle that soft bases form their most stable complexes

with soft acids, and since the thiocyanate ion is thought to

possess soft character, the intermediate $\left[\text{Co(en)}_2\text{SO}_3\right]^+$ must

exhibit the properties of a soft acid.

The <u>trans</u>-sulphito complexes of cobalt(III) resemble the vitamin

B_{12} complexes as they both display a strong <u>trans</u>-labilising effect

and their five coordinated intermediates possess reasonable stability.

The order of formation constants, at room temperature, obtained

by Pratt and Thorpe[20] was identical with that reported in the

present work <u>viz.</u> $NCS^- \gg Br^- > Cl^-$. This indicates that the

bromo complex has a slightly greater stability than the chloro complex.

It has been shown, from the enthalpy data, that in fact the relative

stabilities are reversed.

The pK_a value obtained compares favourably with that recently reported[15]

in the literature, these being 9.6 and 9.45 respectively.

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SECTION VII.

Preparation of Compounds.

The purity of the compounds was established, unless otherwise stated, by comparing the UV and visible spectra of the complex with that of a fully authenticated sample.

trans-$[Co(en)_2Cl_2]Cl$.
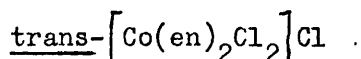
This compound, the starting material for many of the following preparations, was prepared by the published method[1] without further modification.

A 10% solution of ethylenediamine (600g) was added to cobaltous chloride hexahydrate (160g in 150ml of water) and air drawn through the solution for twelve hours. Concentrated hydrochloric acid (350ml) was then added and the solution was then evaporated on a steam bath until a crust had formed on the surface. After standing over night, the dark green trans-$[Co(en)_2Cl_2]Cl.HCl$ was filtered off and washed with ethanol and ether. The HCl of crystallization was removed by drying the compound at ∼110°. The trans-$[Co(en)_2Cl_2]Cl$ was produced as a dull green powder.
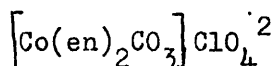
$[Co(en)_2CO_3]Cl$[2]
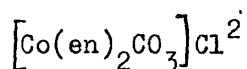
A solution of cobaltous chloride hexahydrate (80g in 100ml of water) and dilute hydrochloric acid (667ml of 1M) was deaerated using carbon dioxide gas. Anhydrous ethylenediamine (40ml) was then added and the solution rapidly heated to 80°. Oxidation to the Co(III) state was achieved by the addition of lead dioxide (60g) and heating the solution, at 80°, for three hours. The solution was then filtered and lithium carbonate (48g) added to the filtrate. The reaction mixture

was maintained at 30° for half an hour on a water bath and the solution

again filtered. The filtrate was evaporated, at 60°, in a stream

of air to 480ml. The excess carbonate ions were removed by the addition

of calcium chloride hexahydrate (20g dissolved in the minimum

quantity of water) and filtering off the precipitated calcium

carbonate.

Twice the volume of ethanol was added to the solution obtained

after the removal of the calcium carbonate, and the mixture cooled

in ice. On cooling, $[Co(en)_2CO_3]Cl$ was precipitated as a red powder.

The powder was filtered off, dissolved in water (310ml at 48°)

and reprecipitated by the addition of ethanol (620ml).

The purified product was filtered off, washed with ethanol and

dried in air.

$[Co(en)_2CO_3]ClO_4$ [2]

This was prepared by grinding a solution of $[Co(en)_2CO_3]Cl$ (27.5g

in the minimum amount of water) with solid sodium perchlorate (12.2g).

The resulting $[Co(en)_2CO_3]ClO_4$ was filtered off and recrystallized from

hot water.

cis-$[Co(en)_2(NO_2)_2]NO_2$ [3]
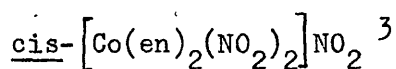
A 10% solution (aqueous) of ethylenediamine (48g) was added to

potassium hexanitritocobaltate (20g) and the mixture heated, with stirring,

to 70° on a water bath. The yellow hexanitritocobaltate salt

dissolved to give a brown solution. This was rapidly filtered and the

warm filtrate was then placed in an ice bath. On cooling cis-$[Co(en)_2(NO_2)]^+$

was precipitated as the nitrate. The yellow powder was then filtered

off and washed with 50% aqueous ethanol, ethanol and acetone and

dried in air.

Resolution of the cis-$\left[Co(en)_2(NO_2)_2\right]^+$ Cation.

The cis-$\left[Co(en)_2(NO_2)_2\right]NO_2$ prepared above was disolved in water

(12g in 50ml) by shaking, at 60°. A solution of potassium d-antimony

tartrate (7g in 25ml of water), at 75°, was added to the dinitrito

compound and the mixture thoroughly shaken. The mixture was then rapidly

cooled to 25°. The yellow diastereoisomer, $\ell\left[Co(en)_2(NO_2)_2\right]d\left[SbOC_4H_2O_4\right]$

was precipitated and the mixture allowed to stand, at 25°, for

exactly 10 minutes, with occasional shaking. The precipitate was

then filtered off and the filtrate, which contained the $d\left[Co(en)_2(NO_2)\right]^+$

isomer was set aside for further use.

The diastereo isomer was washed with 50% aqueous ethanol, ethanol

and acetone and air dried.

Ammonium bromide (2g) was added to the filtrate and the mixture

was allowed to stand, at 20 - 25°, for 5minutes only. The impure

$d\left[Co(en)_2(NO_2)_2\right]Br$ was filtered off and washed with iced water (10ml).

The precipitate and filter paper were then transferred to a flask and

shaken with water (35ml) at 55°. Freshly precipitated silver chloride

(4g), prepared from silver nitrate and dilute hydrochloric acid, was

added and the shaking continued for a further 3 minutes. The silver

halides were then filtered off and washed with warm water (5ml).

Ammonium bromide (1.5g) was added to the filtrate and the solution

allowed to stand for 10 minutes at 20 - 25°.

The pure $d\left[Co(en)_2(NO_2)_2\right]Br$ was filtered off, washed with 50%

aqueous ethanol, ethanol and acetone and dried in air.

A 0.41% solution of the pure $d\left[Co(en)_2(NO_2)_2\right]Br$, contained in

a 2dm path length tube, gave an optical rotation $\left[\alpha\right]_D = + 0.36^\circ$,

$\therefore$ a 0.5% solution would give a rotation $\left[\alpha\right]_D = +0.44^\circ$. The

literature value for a 0.5% solution is given as $\left[\alpha\right]_D = +0.44^\circ$ (2dm

path length tube)

The previously prepared diastereoisomer (5.5g) was then ground with water (30ml) and sodium iodide (7g) added. The mixture was shaken for 2 minutes and the $\ell\text{-}[Co(en)_2(NO_2)_2]I$ filtered off and washed with iced water (15ml). The precipitate was then transferred to a flask and shaken with water (30ml) at 55°. Freshly prepared silver chloride (4g) was then added and the mixture shaken for 3 minutes after which the silver halides were removed by filtration. The precipitate was washed with hot water (5ml) and ammonium bromide added to the filtrate (3g). The solution was cooled in an ice bath. The yellow $\ell\text{-}[Co(en)_2(NO_2)_2]Br$ was filtered off, washed with 50% aqueous ethanol (10ml), ethanol and acetone, and finally dried in air.

A 0.42% solution gave an optical rotation $[\alpha]_D = -0.37^\circ$ (2dm path length tube), i.e. a 0.5% solution would produce a rotation of $[\alpha]_D = -0.44^\circ$. The literature value[4] for a 0.5% solution is given as $[\alpha]_D = -0.44^\circ$ (2dm path length tube).

$Ca[Co(en)(C_2O_4)_2]_2\cdot 4H_2O$ [5]
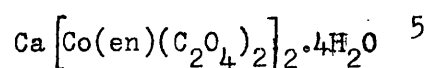
This was prepared by the addition of a solution of cobaltous acetate (10g in 50ml of water) to a hot solution of potassium oxalate monohydrate (28.5g in 50ml of water, maintained at 80°). Ethylenediamine hydrochloride (5.8g) was dissolved in the solution and the resulting solution was then rapidly heated to boiling point. Lead dioxide (25g) was then added and the mixture boiled with stirring for a further 30 minutes. The hot solution was filtered and the filtrate diluted to 200ml with water. Oxalic acid (9g) was added and the solution boiled for for 15 minutes. The hot solution was again filtered and cooled to room temperature. On cooling, concentrated hydrochloric acid (50ml) was added to the solution. Calcium chloride hexahydrate (25g in the minimum quantity of water) was added, the sides of the container scratched, and the mixture allowed to stand for 5 minutes only.

The precipitated $Ca\left[Co(en)(C_2O_4)_2\right]_2$ was filtered off, washed with 1M HCl and ethanol and air dried. The complex was further freed from calcium oxalate impurities by suspension in 1M HCl at 40° and filtration whilst still warm.

The purified product was then washed with warm 1M HCl, ethanol and acetone and dried in air.

$Na\left[Co(en)(C_2O_4)_2\right]$ [5]
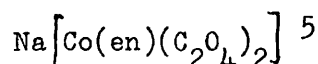
A hot solution (65°) of the calcium bis(oxalato) salt (25g in 50ml of water), prepared above, containing sodium oxalate (6.2g) was heated rapidly to boiling and the heating continued, with stirring, for 15 to 20 minutes. After this the mixture was cooled and the precipitated calcium oxalate removed by filtration.

The filtrate was evaporated on a steam bath and after cooling additional calcium oxalate was again removed by filtering the solution. Ethanol was added to the filtrate until precipitation of the dark red sodium ethylenediaminebis(oxalato)cobaltate was complete. The complex was filtered off, dissolved in warm water and reprecipitated by the addition of ethanol. The purified $Na\left[Co(en)(C_2O_4)_2\right]$ was filtered off, washed with ethanol and dried in air.

Resolution of $Na\left[Co(en)(C_2O_4)_2\right]$ [5]
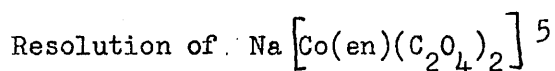
This was prepared by a modification of the method formerly employed.[5]

A mixture of silver acetate (3.3g) in water (50ml) was mechanically stirred at 55 - 60° and $d\text{-}\left[Co(en)_2(NO_2)_2\right]Br$ (4.8g) added. Stirring was continued for 10 minutes and the silver bromide was then filtered off. $Na\left[Co(en)(C_2O_4)_2\right]$ (7.5g) was added to the filtrate and the solution stirred for 5 minutes, after which the purple/brown diastereoisomer, d $\underline{cis\text{-}}\left[Co(en)_2(NO_2)_2\right]^+ l\left[Co(en)(C_2O_4)_2\right]^-$ was precipitated. This was filtered off, ground with sodium iodide (6g)

and the resulting d-<u>cis</u> $\left[Co(en)(NO_2)_2\right]I$ removed by filtering. Ethanol was then added to the filtrate, until precipitation of the ℓ-$Na\left[Co(en)(C_2O_4)_2\right]$ started. The solution was then cooled in ice. The purple crystals of the ℓ isomer were filtered off, washed with ice-cold water and ethanol, and dried in the air.

The d-$Na\left[Co(en)(C_2O_4)_2\right]$ was obtained in a similar manner from the filtrate produced after removal of the diastereoisomer. Sodium iodide (6g) was added and the d-cis-dinitrito complex filtered off as the iodide. Ethanol was added to the filtrate until observable crystallization of the d-$Na\left[Co(en)(C_2O_4)_2\right]$ occurred. This was then filtered off and treated as for the ℓ isomer.

However, since at this stage the isomers exhibited only a small amount of optical activity, the resolution was repeated using the semi-resolved d-$Na\left[Co(en)(C_2O_4)_2\right]$ isomer, rather than the optically inactive $d\ell$-$Na\left[Co(en)(C_2O_4)_2\right]$ complex. A more reasonable separation of the optically active isomers was then obtained.

For the ℓ isomer $\quad \left[\alpha\right]_D = -326^0$

$\qquad\qquad d$ isomer $\quad \left[\alpha\right]_D = +490^0$

Literature value $\quad \left[\alpha\right]_D = \pm500^0$

Resolution of $\left[Co(en)_2CO_3\right]Cl.$ [2]

An aqueous solution of carbonatobis(ethylendiamine)cobalt(III) chloride (5.7g in 30ml of water) was cooled to 5^0 and d-$Na\left[Co(en)(C_2O_4)_2\right]$ (4.5g) stirred into the solution. After 5 minutes the diastereoisomer ℓ-$\left[Co(en)_2CO_3\right]^+d$-$\left[Co(en)(C_2O_4)_2\right]^-$ was filtered off, washed with ice-water (30ml), acetone and air dried. The report in the literature[2] states that d-$\left[Co(en)_2CO_3\right]^+d$-$\left[Co(en)(C_2O_4)_2\right]^-$ was obtained at this point. The results obtained in this study are in agreement with later work.[6]

The diastereoisomer was ground with ice (30ml) and sodium perchlorate (12g) and the precipitated ℓ-$[Co(en)_2CO_3\ ClO_4]$ removed by filtration. The optically active isomer was recrystallized from hot water.

To the filtrate, obtained after the removal of the diastereoisomer, was added sodium perchlorate (12g) and the precipitated d-$\{Co(en)_2CO_3\}ClO_4$ was filtered off and recrystallized from hot water.

The d-$Na[Co(en)(C_2O_4)_2]$ may be recovered from the filtrates remaining after removal of the d and ℓ $[Co(en)_2CO_3]^+$ isomers, by the careful addition of ethanol.

The following specific rotations were obtained:

ℓ-$[Co(en)_2CO_3]ClO_4$ $\qquad$ $[\alpha]_D = -500°$

d-$[Co(en)_2CO_3]ClO_4$ $\qquad$ $[\alpha]_D = +1310°$

Literature value[2] $\qquad$ $[\alpha]_D = \pm1300°$

trans-$[Co(en)_2ClNCS]SCN$ [7]
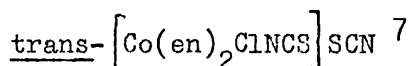
A solution of potassium thiocyanate (6.8g in 50ml of water) was added to a slightly warmed solution of trans-$[Co(en)_2Cl_2]Cl$ (20g in 30ml of water). The light green trans-$[Co(en)_2Cl_2]SCN$ was immediately precipitated, but after heating on a water bath, this dissolved to give a violet solution. On cooling for 2 hours, the cis-$[Co(en)_2ClNCS]Cl$ precipitated was removed by filtering and the trans-$[Co(en)_2ClNCS]SCN$ obtained from the filtrate by the addition of potassium thiocyanate (6.8g). The purple salt was filtered off and recrystallized from warm water.

trans-$[Co(en)_2(OH)NCS]SCN$ [8]
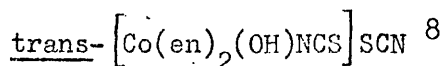
Sufficient concentrated sodium hydroxide was added to the solid trans-$[Co(en)_2ClNCS]SCN$ to form a smooth paste. The red paste

was then very gently heated on a water bath, until a deep orange
solution was formed. This on cooling, deposited deep orange/brown
crystals of the trans-$\left[Co(en)_2(OH)NCS\right]$ SCN. These were filtered off
and recrystallized from dilute potassium hydroxide solution.

trans-$\left[Co(en)_2(OH)(OH_2)\right](ClO_4)_2$ [9]
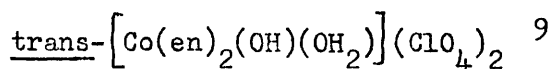
This was prepared by a modification of the method of Baldwin,
Chan and Tobe.[10]

The chloride form of the trans-$\left[Co(en)_2Cl_2\right]^+$ was used instead
of the nitrate. Since the chloride is considerably more soluble than the
nitrate, this removed the need to concentrate the elluent by freeze
drying.

A concentrated solution of the trans-$\left[Co(en)_2Cl_2\right]Cl$ was
passed through an ion exchange column containing Amberlite IR 400
in the hydroxide form. The elluent containing cis- and trans-
$\left[Co(en)_2(OH)_2\right]OH$ was adjusted to pH 7 with 72% perchloric acid. The
trans-$\left[Co(en)_2(OH)(OH_2)\right](ClO_4)_2$ crystallized out on cooling in an ice
bath. The complex was filtered off and washed with acetone and dried in
the air.

trans-$\left[Co(en)_2ClSO_3\right].H_2O$
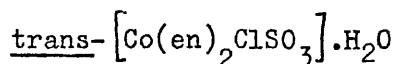
trans-$\left[Co(en)_2Cl_2\right]Cl$ (2.8g) was dissolved in the minimum quantity
of water, at 30°, and anhydrous sodium perchlorate added (1.3g). On
gentle warming the solution became brown and a red/brown precipitate
appeared on cooling. The trans-$\left[Co(en)_2ClSO_3\right].H_2O$ was filtered off
and washed with methanol and ether and air dried.

Found: C, 15.7; H, 5.7; and S, 10.3%

Calcd. C, 15.3; H, 5.7; and S, 10.0%

trans-$\left[\text{Co(en)}_2(\text{OH}_2)\text{SO}_3\right]\text{ClO}_4$ 11
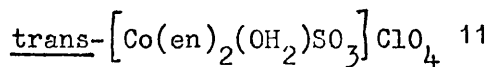
This was prepared by the addition of an aqueous solution of

sodium perchlorate (2g in the minimum amount of water) to trans-

$\left[\text{Co(en)}_2\text{ClSO}_3\right]\text{H}_2\text{O}$ (3g again in the minimum quantity of water). Almost

immediately the yellow/brown crystals of $\left[\text{Co(en)}_2(\text{OH}_2)\text{SO}_3\right]\text{ClO}_4$ began

to be precipitated. The complex was filtered off, washed with

ethanol and ether, and dried in air.

Found: C, 12.6; H, 5.0%

Calcd.   C, 12.8; H, 4.8%

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Mechanism of the Reactions of Dihydroxobis(ethylenediamine)cobalt(III) Cations in Highly Basic Aqueous Solution

BY M. E. FARAGO, B. A. PAGE, AND C. F. V. MASON

The rates of isomerization and of the racemization of the $Co(en)_2(OH)_2^+$ ions have been measured over the temperature range 25–70°. The observed rates are independent of hydroxide concentration. The activation energies for the *cis* → *trans* change and for the *trans* → *cis* change are 29.5 and 28.5 kcal mol^{-1}, respectively. The activation energy for the racemization is not constant over the temperature range. The mechanisms of oxygen exchange with solvent and of stereochemical change are discussed. The mechanism of the latter is intramolecular, and it is proposed that a twisting process is the most likely one.

Introduction

Three studies of the system containing the *cis*- and *trans*-Co(en)$_2$(OH)$_2$$^+$ ions are reported in the literature.[1-3] Bjerrum and Rasmussen[1] investigated the

(1) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).
(2) J. Y. Tong and P. E. Yankwich, *J. Am. Chem. Soc.*, **80**, 2664 (1958).
(3) W. Kruze and H. Taube, *ibid.*, **83**, 1280 (1961).

equilibrium and estimated the rate constant for *cis* ⇌ *trans* isomerization at 25°. Tong and Yankwich[2] showed that the rate of isomerization at 35° was independent of hydroxide concentration between 1.0 and 0.0005 *M*.

In a more detailed study Kruze and Taube[3] found that during the *cis* ⇌ *trans* isomerization of the Co-

(en)₂(OH)₂⁺ cations only a fraction of one oxygen exchanges for each act of isomerization. They found that the energy of activation was not constant over the temperature range 14–37° and suggested that isomerization involves two paths: one corresponding to breaking of a cobalt–oxygen bond and the other to cobalt–nitrogen bond fission. Both paths permit isomerization, but only Co–O bond fission leads to oxygen exchange with solvent.

This paper presents a study of the racemization and isomerization of $Co(en)_2(OH)_2^+$ ions in highly basic media over an extended temperature range.

Experimental Section

In order to exclude difficulties resulting from impurities in preparation,[1,2] the cis- and trans-dihydroxo species were generated in solution from [Co(en)₂CO₃]ClO₄ and trans-[Co(en)₂OH-(OH)₂](ClO₄)₂, respectively. The cis-Co(en)₂(OH)₂⁺ species was obtained by acid hydrolysis of [Co(en)₂CO₃]ClO₄ and subsequent addition of alkali. Both acid hydrolysis and proton removal take place with full retention of configuration.[4] [Co(en)₂CO₃]ClO₄ was prepared from an aqueous solution of the chloride[4] by the addition of sodium perchlorate and was recrystallized from warm water. Anal. Calcd for C₅H₁₆ClCoN₄O₇: C, 17.7; H, 4.8; N, 16.5. Found: C, 17.6; H, 4.6; N, 16.8. The complex, resolved by Dwyer's method,[4,5] had [α]D ±1250°.

trans-Co(en)₂(OH)₂⁺ was generated in solution by dissolving trans-[Co(en)₂OH(OH₂)](ClO₄)₂ in alkali.[6] (The authors thank Dr. M. L. Tobe for a sample of this compound.)

Spectrophotometric Runs. Method A.—A known weight of rac-[Co(en)₂CO₃]ClO₄ was dissolved in a known excess of standard perchloric acid and 0.5 ml of this solution v   .   .   .   .   .   .   known volume of standard sodium hydroxide in a thermostated 1-cm silica cell. The change of absorbance at 27,000 or at 19,200 cm⁻¹ was recorded on either a Unicam SP 700 or SP 800 spectrophotometer. The latter was fitted with a scale expansion unit and external recorder. Cell temperatures were measured with a thermocouple and checked against standard NPL thermometers.

Spectrophotometric rate constants were calculated from the formula

$$k_1 + k_{-1} =$$

$$(2.303/t) \log [(D_0 - D_\infty)/(D_t - D_\infty)] \sec^{-1}$$

where D_t was the absorbance after t seconds and D_0 was the absorbance at the time of the first reading (which was arbitrarily taken as zero time). By extrapolation back to time of mixing the molar extinction coefficients of pure cis-Co(en)₂(OH)₂⁺ were 103 and 93 at 27,000 and 19,200 cm⁻¹, respectively (lit.[1] values 103.6 and 93).

Method B.—A known weight of trans-[Co(en)₂OH(OH₂)]-(ClO₄)₂ was dissolved in standard sodium hydroxide solution thermostated to the desired temperature. The solution was transferred to the thermostated cell in the spectrophotometer. The procedure was then as in method A.

Method C.—A known weight of trans-[Co(en)₂OH(OH₂)]-(ClO₄)₂ was dissolved in standard sodium hydroxide solution, and samples were placed in sealed tubes in a thermostat. These were withdrawn at known time intervals and the absorbance at 19,200 cm⁻¹ was measured using a Unicam SP 500 spectrophotometer. The extinction coefficients of trans-Co(en)₂(OH)₂⁺ were found to be 53.0 and 53.7 at 19,200 and 26,300 (lit.[1] values 53.0 and 53.9).

(4) F. P. Dwyer, A. M. Sargeson, and T. K. Reid, J. Am. Chem. Soc., **85**, 1215 (1963).
(5) F. P. Dwyer, A. M. Sargeson, and F. L. Garvan, ibid., **83**, 1285 (1961).
(6) M. E. Baldwin, S. C. Chan, and M. L. Tobe, J. Chem. Soc., 4637 (1961).

Method D.—The procedure was as in method C, except that the contents of each tube was run into an excess of standard perchloric acid and the absorbance (now of the Co(en)₂(OH₂)₂³⁺ species) was measured at 20,000 cm⁻¹. The extinction coefficients of trans-Co(en)₂(OH₂)₂³⁺ were found to be 32.5, 33.1, and 55.8 at 18,200, 22,500, and 28,900 cm⁻¹, respectively (lit.[1] values 32.8 and 33.2, respectively, for the first two peaks).

Polarimetric Runs.—(−)D-[Co(en)₂CO₃]ClO₄ was dissolved in standard perchloric acid and neutralized with a known excess of standard sodium hydroxide. A sample was placed in a thermostated tube in a Zeiss photoelectric polarimeter. Readings of the rotation at 436 nm were taken at known time intervals.

Results

The results of the spectrophotometer runs are given in Table I.[7] It is evident from these results that the variation in the position of equilibrium is outside experimental error, although this is large.[8] The average values of ϵ_∞ and per cent cis at equilibrium have been calculated at the temperatures ∼70, ∼60, ∼50, 37.5, and ∼25° and are shown in Table II, together with some literature values. The rate of loss of optical activity is shown in Table III.

It can be seen that the cis → trans change cannot fully account for the loss of optical activity. The specific rate constants k_1(cis → trans) and k_{-1}(trans → cis) were calculated using the position of equilibrium shown in Table II. The constant k_1 was then subtracted from k_p to give k_r, the racemization rate: k_r is then .   .   .   .   .   The results are
.   .   .   .   .
The results in Table IV .   .   .   W   .   .   .   ..enius plots in Figure 1. It can be seen that log k_1 and log k_{-1} vs. the reciprocal of the absolute temperature give straight-line plots whereas log k_i vs. $1/T$ gives a curve. The variations of k_1 and k_{-1} with temperature fit the Arrhenius equations

$$k_1 = 2.1 \times 10^{16} \exp(-29,500/RT) \sec^{-1}$$

$$k_{-1} = 3.1 \times 10^{15} \exp(-28,500/RT) \sec^{-1}$$

Discussion

The results of this investigation and those in the literature[1–3] show that the rates of oxygen exchange with solvent, the isomerization, and the racemization of the dihydroxo cations are independent of hydroxide concentration and of ionic strength. The loss of optical activity cannot be accounted for entirely by the cis → trans change.

Kruze and Taube[3] have shown that during the cis ⇌ trans isomerization only a fraction of one oxygen exchanges for each act of isomerization and that the exchange rate of the cis isomer is about eight times faster than the cis → trans rate. Most of the oxygen exchange must therefore take place with retention of

(7) The proposed equilibrium between the trans species is: trans-Co(en)₂-(OH)₂²⁺ + Cl⁻ ⇌ Co(en)₂ClOH²⁺ + OH⁻; see E. A. Dittmar and R. D. Archer, J. Am. Chem. Soc., **90**, 1468 (1968). However this reaction has been shown not to take place: M. E. Farago, B. Page, and M. L. Tobe, Inorg. Chem., **8**, 388 (1969). The isomerization of Co(en)₂(OH)₂⁺ ions is not catalyzed by chloride; neither does coordinated chlorine in trans-Co(en)₂-ClOH⁺ exchange with chloride ion in basic media.

(8) The fact that the per cent of cis product is independent of wavelength and of initial configuration indicates that this is a real effect and not just a consequence of variation of ϵ_m with temperature.

TABLE I

OBSERVED SPECTROPHOTOMETRIC RATE CONSTANTS, $k_1 + k_{-1}$,
FOR THE ISOMERIZATION OF THE *cis*- AND *trans*-$Co(en)_2(OH)_2{}^+$ IONS

Starting isomer	Method[a]	Temp, °C	[Complex], mM	[NaClO₄],[b] M	[OH⁻], M	$k_1 + k_{-1}$, sec⁻¹	ν,[c] kK	ε∞
cis	A	71.0	9.84	0.015	0.0681	5.5 × 10⁻³	27.0	73.3
cis	A	71.0	9.84	0.015	0.0515	5.4 × 10⁻³	27.0	73.3
cis	A	68.0	4.25	0.025	1.33	4.30 × 10⁻³	19.2	68.0
cis	A	68.0	8.50	0.033	1.26	3.83 × 10⁻³	19.2	67.5
cis	A	61.0	7.20	0.022	0.044	1.68 × 10⁻³	27.0	73.6
cis	A	61.0	7.20	0.022	1.27	1.65 × 10⁻³	27.0	73.6
cis	A	61.0	7.20	0.022	3.31	1.64 × 10⁻³	27.0	74.0
trans	B	59.1	9.22	0.00	0.067	1.20 × 10⁻³	27.0	73.5
trans	B	59.1	9.22[d]	0.00	0.067	1.30 × 10⁻³	27.0	73.5
trans	B	50.8	6.95	0.00	0.067	4.4 × 10⁻⁴	27.0	73.4
trans	B	50.8	6.95[d]	0.00	0.067	4.5 × 10⁻⁴	27.0	73.4
trans	B	50.8	6.95[d]	0.00	0.067	4.5 × 10⁻⁴	19.2	68.8
trans	D	50.7	8.00[e]	0.00	0.050	4.4 × 10⁻⁴	20.0	...
cis	A	49.3	9.84	0.015	0.0681	3.81 × 10⁻⁴	27.0	74.5
cis	A	37.5	9.84	0.015	0.0681	6.5 × 10⁻⁵	27.0	75.0
cis	A	37.5	9.84	0.015	0.0515	6.4 × 10⁻⁵	27.0	75.5
trans	B	25.5	9.80	0.00	0.067	7.68 × 10⁻⁶	19.2	71.3
trans	C	24.8	10.5	0.00	1.00	6.52 × 10⁻⁶	19.2	70.5
cis	A	24.6	10.6	0.046	2.32	6.40 × 10⁻⁶	19.2	...
cis	C	24.0	10.6	0.046	2.32	6.32 × 10⁻⁶	19.2	71.5

[a] See text. [b] NaClO₄ produced as product of neutralization. [c] Reaction followed at this wave number. [d] In presence of 0.353 *M* NaCl.[7] [e] In presence of 0.40 *M* NaCl.[7]

TABLE II

POSITION OF EQUILIBRIUM FOR THE ISOMERIZATION
OF THE $Co(en)_2(OH)_2{}^+$ IONS

Temp, °C	ε∞ (27 Kk)	% cis	ε∞ (19.2 Kk)	% cis	Av % cis
~70	73.3	38	67.7	37	37.5
~60	73.5	39			39
~50	74.5	41	68.8	40	40.5
37.5	75.2	42			42
37.5[a]					46[a]
35[b]	73.8	39	69.5	40	39.5[b]
~25			71.1	45	45
24.95[a]					46[a]
25.0[c]	75.7	45	71.4	45	45[c]
14.4[a]					46[a]

[a] From ref 3. [b] From ref 2. [c] From ref 1.

TABLE III

OBSERVED FIRST-ORDER RATE CONSTANTS (k_D) FOR THE LOSS OF
OPTICAL ACTIVITY OF THE $(-)$D-$Co(en)_2(OH)_2{}^+$ ION

Temp, °C	[Complex], mM	[NaOH], M	$10^4 k_D$, sec⁻¹
69.4	7.6	0.259	69.9
60.8	4.1	0.855	19.0
60.8	5.0[a]	0.855	19.0
60.8	7.8	0.259	19.9
49.3	8.0	0.259	4.16
37.2	7.5	0.259	0.692
24.8	9.9	0.259	0.0936

[a] Run carried out in presence of free ethylenediamine.

configuration, and most of the isomerization without exchange of oxygen with the solvent. It was suggested[3] that one path for isomerization involves opening of the ethylenediamine chelate ring. This mechanism has also been suggested[9] for the isomerization of the Co-$(en)_2NH_3OH^{2+}$ cations, where rearrangement has been shown to take place without exchange of any of the attached ligands.

(9) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).

TABLE IV

SPECIFIC RATE CONSTANTS (SEC⁻¹) FOR THE ISOMERIZATION AND
INVERSION OF THE $Co(en)_2(OH)_2{}^+$ IONS

Temp, °C	$10^4(k_1 + k_{-1})$	% cis[a]	$10^4 k_1$	$10^4 k_{-1}$	$10^4 k_D$	$10^4 k_i$
69.4	53[b]	37.5	33.1	19.9	69.9	18.4
61.0	16.5	39.0	10.1	6.44	19.0	4.45
49.3	3.81	40.5	2.27	1.54	4.16	0.945
37.5	0.644	42.0	0.374	0.270	0.692	0.159
24.8	0.0652	45.0	0.036	0.029	0.0936	0.0288

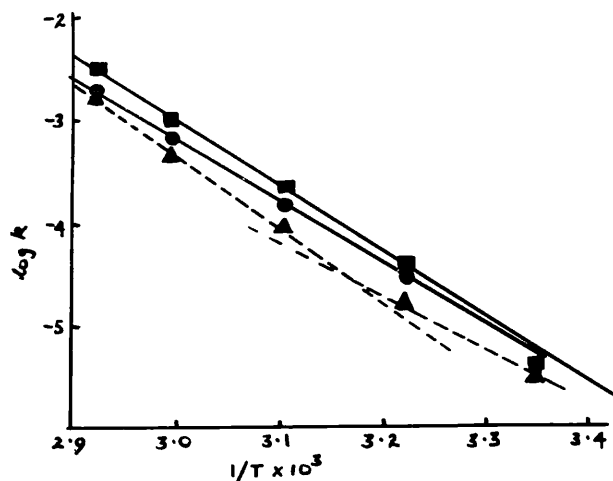[a] At equilibrium. [b] By interpolation.

Figure 1.—Arrhenius plots for isomerization and racemization of $Co(en)_2(OH)_2{}^+$: ■, $k(cis \rightarrow trans)$; ●, $k(trans \rightarrow cis)$; ▲, k(inversion).

It was pointed out by Tobe[9] that for complexes of the type $Co(en)_2XOH^{n+}$, the strength of the Co–X bond determines which of two reactions takes place. These reactions can be hydrolysis where X is lost (X = Cl, Br, or NCS) or ring opening where X is strongly bound (X = NH₃, OH).

In acid solution the diaquo ions $Co(en)_2(OH_2)_2^{3+}$ isomerize with water exchange, by slow acid hydrolysis.[3] In neutral solution (pH 7–8) the cations are in the form of the hydroxoaquo species $Co(en)_2OH(OH_2)^{2+}$, and the reactions become much more rapid.[2,3] In highly basic media, the isomerization becomes slow again and independent of hydroxide concentration.

There are several ways in which oxygen could be exchanged for solvent in neutral and basic media. It is not possible, however, from the kinetics to distinguish[10] (i) between aquation of the hydroxoaquo species and base-catalyzed hydrolysis of the diaquo species (at pH 7–8) or (ii) between spontaneous Co OH fission and base-catalyzed hydrolysis of the hydroxoaquo species (in basic media). However, in basic solution the lack of effect of ionic strength or of base concentration and the fact that oxygen exchange with solvent takes place with retention of configuration lead to the conclusion that the reaction is spontaneous Co–OH fission. If the reaction were base-catalyzed hydrolysis of $Co(en)_2OH(OH_2)^{2+}$ via formation of an amide group, water would be the leaving group (less strongly σ bonded). The trigonal-bipyramidal intermediate would then be identical[11] with that for the base hydrolysis of complexes of the type $Co(en)_2OHX^+$. Where $X = Cl$ or Br, this reaction takes place in the *trans* isomer with almost 100% steric change.[12] In the case of the dihydroxo cations, however, reaction must take place with retention of configuration.

Exchange of Oxygen with Solvent.—A possible mechanism for the exchange of oxygen with solvent would be the formation, by dissociation of OH^-, of a trigonal bipyramid stabilized by π bonding[13a] from the remaining hydroxo ligand. Intermediate A is likely to be formed from both *cis* and *trans* starting materials[13b] (intermediate B cannot readily be formed from the *trans* isomer). In order to reduce steric retention via intermediate A, it is necessary to restrict the entry of OH^- (or H_2O) to near the leaving group.

An alternative mechanism would be a bimolecular attack by hydroxide or water or a dissociation in which there is a contribution from bond making, as in rhodium(III) complexes.[14] Bonds between ligands and Rh-(III) are on the whole more covalent than those to Co-(III). Strong σ bonding of the two hydroxide ligands and the four amine groups may make the cobalt(III) center, in this instance, more like rhodium(III).

Whether there is appreciable bond making or not in the transition state, the incoming group must enter *cis* to the leaving group. It would be expected that a leaving hydroxide group would greatly disturb the solvent shell on that side, allowing easy entry for the incoming group. If the incoming group were solvent
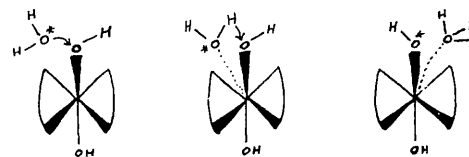

Figure 2.—Oxygen exchange of *cis*-$Co(en)_2(OH)_2^+$ by water attack and proton transfer.

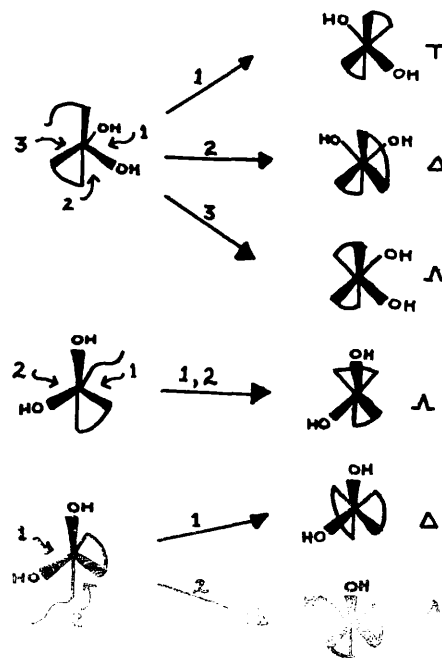Figure 3.—Isomerization and racemization of $Co(en)_2(OH)_2^+$ via a trigonal bipyramid formed by cobalt–nitrogen fission, starting from Λ *cis*.

water, then a proton transfer from the incoming group to the departing hydroxyl group would result in further bond weakening and facilitate bond breaking (Figure 2).

Stereochange by Intramolecular Mechanism.—There are two possible mechanisms for stereochange without exchange of oxygen with the solvent: twist or bust. In the former none of the six cobalt–ligand bonds is broken, whereas in the latter, cobalt–nitrogen bond fission occurs. Stereochange via the opening of an ethylenediamine chelate ring would result from the trigonal-bipyramidal intermediates shown in Figure 3.

The first intermediate in Figure 3 allows isomerization whereas racemization can occur through both the first and the last intermediates. So that isomerization should not be accompanied by exchange of oxygen with solvent, it is necessary that the coordination position be left vacant and not filled by a water molecule. Although this mechanism has been suggested in the diaquobis(oxalato)chromium(III) system,[15] the ring opening of the carbonato group, by cobalt–oxygen fission,[16] is found to take place with the uptake of an OH group.[17]

(10) C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968).

(11) R. B. Jordan and A. M. Sargeson, *ibid.*, **4**, 433 (1965).

(12) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1531 (1962).

(13) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, New York, N. Y., 1967: (a) p 186; (b) p 263.

(14) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

(15) J. Agett, I. Mawston, A. C. Odell, and B. E. Smith, *J. Chem. Soc.*, A, 1413 (1968).

(16) C. A. Andrade and H. Taube, *J. Am. Chem. Soc.*, **86**, 1328 (1964).

(17) H. Scheidegger and G. Schwarzenbach, *Chimia* (Aarau), **19**, 169 (1965); M. E. Farago, *Coord. Chem. Rev.*, **1**, 66 (1966).

The hydroxide ligand has a high inductive effect operating through the σ bond, π-antibonding properties,[18] and low ligand field strength.[19] The high inductive effect is responsible for the low pK_a of the amino group.[13a] The weakening of the Co–N bonds by this effect alone would tend to favor a *bust* mechanism; however, the Co–O bonds, in addition, would tend to be weakened by the repulsive π bonding. It seems possible that in compounds of cobalt(III) containing four nitrogen donors and two hydroxide ligands there are favorable conditions for the twist mechanism. An intramolecular mechanism has also been suggested for isomerization in the dihydroxotriethylenetetraminecobalt(III) series.[20]

Three twist mechanisms for octahedral chelate complexes have been proposed by Rây and Dutt,[21] Bailar,[22] and Springer and Sievers.[23] It has been pointed out[23] that the Rây and Dutt and the Springer and Sievers twists are special cases of the Bailar twist and that they will give transition states which differ only in the orientation of the chelate rings about the trigonal prism.[24]

The four trigonal prismatic transition states which result from the twisting of a species of the type Co-(en)₂X₂ are shown in Figure 4. Springer and Sievers' twist is represented by I, and that of Rây and Dutt by II and III. These three intermediates permit intramolecular *cis* → *cis* changes. Only the fourth which may exist in mirror image forms permits *cis* ⇌ *trans* changes.
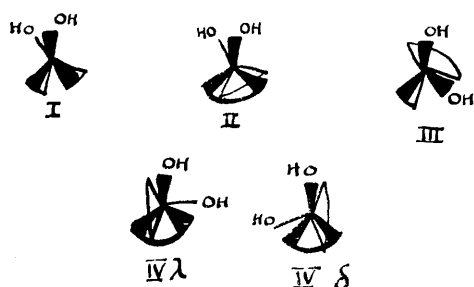
Figure 4.—Four trigonal-prismatic transition states resulting from the twist of species of the type Co(en)₂X₂.

Serpone and Fay[24] have analyzed the twisting mechanism and this analysis is extended below. Following their numbering,[24] the four *imaginary* C_3 axes of a complex of the type *cis*-Co(en)₂X₂ are shown in Figure 5.

The twisting mechanism involves the displacement of three of the donor atoms on one octahedral face (the lower) through 120°, with respect to the three donor atoms of the upper octahedral face. The twisting
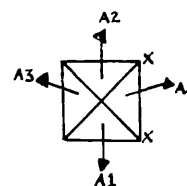
(18) C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, pp 24, 51.

(19) W. E. Hatfield, J. F. Anders, and L. J. Rivela. *Inorg. Chem.*, 4, 1088 (1965).

(20) E. Kyono, L. J. Boucher, and J. C. Bailar, *J. Am. Chem. Soc.*, 37, 4458 (1965).

(21) P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, 20, 81 (1948).

(22) J. C. Bailar, *J. Inorg. Nucl. Chem.*, 8, 165 (1958).

(23) C. S. Springer and R. E. Sievers, *Inorg. Chem.*, 5, 852 (1967).

(24) N. Serpone and R. C. Fay, *ibid.*, 6, 1835 (1967).

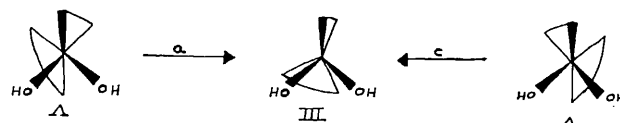Figure 5.—View of *cis*-Co(en)₂X₂ along a fourfold axis showing four imaginary C_3 axes: A1, A2, A3, A4.

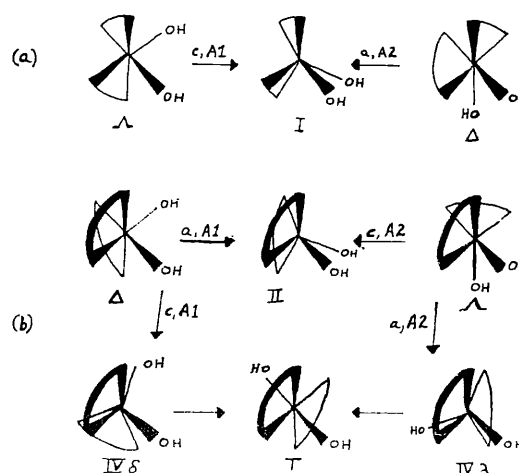Figure 6.—Racemization of Co(en)₂(OH₂)⁺ by rotation about axes A3 and A4, *via* trigonal prism III.

Figure 7.—Steric change of Co(en)₂(OH)₂⁺ by rotation about axes A1 and A2: (a) racemization *via* trigonal prism I; (b) racemization *via* trigonal prism II and isomerization *via* trigonal prism IV.

process may be carried out about any of the four imaginary axes in Figure 5 and may be in a clockwise (c) or an anticlockwise (a) direction. (Anticlockwise (rather than the more usual counterclockwise) is used in order to make the abbreviations comprehensible.) The starting material may be *cis* Λ,[25] *cis* Δ, or *trans;* the axis may be A1, A2, A3, or A4; and the transition state may be any of the prisms I, II, III, or IV shown in Figure 4. Rotation about the axis A3 or A4, which results in racemization *via* intermediate III, is illustrated in Figure 6. Starting from the Λ enantiomer an anticlockwise rotation about either A3 or A4 produces first intermediate III and then the mirror-image Δ enantiomer. Conversely a clockwise rotation of the Δ form about A3 or A4 produces the Λ form. Rotation about the axis A3 or A4 does not permit *cis* ⇌ *trans* changes.

Figure 7 shows twists around axis A1 or A2. The Λ isomer may only rotate about axis A1 in a clockwise direction and the Δ isomer is restricted to anticlockwise rotation about axis A2. These twists produce race-

(25) The nomenclature used for absolute configuration is that of T. S. Piper, *J. Am. Chem. Soc.*, 83, 3908 (1961).

mization *via* intermediate I and are illustrated in Figure 7a. The Λ isomer may twist about axis A2, however, in both clockwise and anticlockwise directions (Figure 7b), giving racemization and isomerization *via* intermediates II and IV, respectively. Similarly the Δ isomer rotates about axis A1 in both directions. It should be noted that the isomerization (*cis* ⇌ *trans*) process goes by way of IV, which is either IVδ or IVλ, which give rise to or are evolved from the Δ or Λ *cis* form, respectively.

The data in Figure 1 now seem consistent with a twist mechanism. Isomerization is *via* one type of intermediate, IV, whereas racemization may involve three intermediates, all of which make a contribution to the over-all reaction. The extent of the contribution varies with temperature and, hence, the variable energy. Recently Bradley[26] has suggested a *twist* mechanism in the racemization of *cis*-dialkoxybis(acetylacetonato)-titanium(IV) complexes, where the activation energy tends to increase with the bulk of the alkoxy group.

Intramolecular Interactions between Ligands.—Recently two types of interaction have been suggested: one for the Co(cyclam)OH(OH₂)²⁺ system[10] and one for the *cis*-Co(en)₂OH(OH₂)²⁺ system.[21] For the latter compound, Gillard[27] has attempted to link the large Cotton effect of *cis*-Co(en)₂OH(OH₂)²⁺ with its fast iso........................ a preequilibrium ion pair, ... the aquo and hydroxo .... Such a preequilibrium would however give kinetics indistinguishable from that of the reaction of the Co-

(26) D. C. Bradley and C. E. Holloway, *J. Chem. Soc., A*, 282 (1969).
(27) R. D. Gillard, *ibid., A*, 1945 (1968).

(en)₂(OH)₂²⁺ species (*vide infra*), and neither racemization nor the isomerization of this latter compound is fast.

Tobe[10] has suggested that in complexes containing a secondary nitrogen, the fast isomerization of complexes of the type CoA₄OH(OH₂)²⁺ (where A = cyclam or tren) involves an intramolecular proton transfer from nitrogen to oxygen. With a secondary amine the exchange process would lead to inversion of configuration on the nitrogen. Such an inversion would allow steric change to take place in the octahedral moiety, and if this steric change is unfavored, then the intramolecular interaction would facilitate steric change about the cobalt.

There seems to be no *a priori* reason why such an interaction should not occur with a primary nitrogen. It seems possible therefore that the intervention of a water molecule between the aquo and hydroxo groups of *cis*-Co(en)₂OH(OH₂)²⁺ could hold the coordinated hydroxide in such a position that one of the lone pairs points toward the hydrogen of a neighboring amine. An intramolecular proton jump would thus be facilitated, producing an amido group and steric change about the cobalt.

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The Base Hydrolysis of
trans-Chlorohydroxobis(ethylenediamine)-cobalt(III) Cations

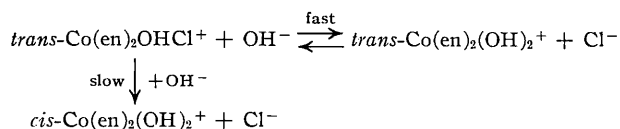By M. E. Farago, B. Page, and M. L. Tobe

CONTRIBUTION FROM THE WILLIAM RAMSAY
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BEDFORD COLLEGE, LONDON, N.W.1, ENGLAND

The Base Hydrolysis of trans-Chlorohydroxobis(ethylenediamine)cobalt(III) Cations

BY M. E. FARAGO, B. PAGE, AND M. L. TOBE

In a recent paper,[1] Dittmar and Archer have re-examined the kinetics and steric course of the base hydrolysis of $trans$-Co(en)$_2$OHCl$^+$ (en = ethylenediamine) and claimed to have shown that there is a fast and reversible stereoretentive loss of chloride that is accompanied by a slow, irreversible formation of the cis-dihydroxo product, *i.e.*

$$trans\text{-Co(en)}_2\text{OHCl}^+ + \text{OH}^- \underset{fast}{\rightleftharpoons} trans\text{-Co(en)}_2\text{(OH)}_2{}^+ + \text{Cl}^-$$

$$\text{slow} \downarrow +\text{OH}^-$$

$$cis\text{-Co(en)}_2\text{(OH)}_2{}^+ + \text{Cl}^-$$

They reach this conclusion because a computer-controlled spectrophotometric analysis indicates that, almost immediately after adding alkali to a solution of [$trans$-Co(en)$_2$OHCl]Cl, approximately 9% of the complex is present as $trans$-Co(en)$_2$(OH)$_2{}^+$ and that the concentration of this species *decreases* as the reaction proceeds.

They therefore suggest that the work of Chan and Tobe,[2] who appear to have reported only the rate of formation of the cis-Co(en)$_2$(OH)$_2{}^+$ product, is in error and that, far from reacting relatively slowly and with considerable steric change, $trans$-Co(en)$_2$OHCl$^+$ is very labile and undergoes base hydrolysis mainly with retention of configuration. In view of this startling result and the implications that it raises in connection with the general consideration of the mechanism of base hydrolysis of these cobalt(III) complexes, we have applied two very simple tests which these authors failed to report. Our observations are given in this note.

Experimental Section

$trans$-Chlorohydroxobis(ethylenediamine)cobalt(III) chloride monohydrate was prepared from [$trans$-Co(en)$_2$Cl$_2$]Cl by a previously published method.[3] The spectrum of an acidified aqueous solution was completely identical with that of a fully characterized sample over the whole wavelength range studied (300–800 mμ).

$trans$-Hydroxoaquobis(ethylenediamine)cobalt(III) perchlorate was prepared by a modification of the method of Baldwin, Chan, and Tobe.[3] The $trans$-dichloro complex was provided as the chloride, which is much more soluble than the nitrate so that the use of a much more concentrated solution (10 g/25 ml of

water) removed the need to concentrate the acidified effluent by freeze-drying. In fact, when the alkaline effluent, containing [cis- and $trans$-Co(en)$_2$(OH)$_2$]OH, was neutralized to pH 7 with 72% perchloric acid, the $trans$-hydroxoaquo perchlorate crystallized out on cooling in an ice bath. The purity of this sample was also established by comparing the spectrum of an acidified aqueous solution with that of a fully characterized, authentic specimen.

Isomerization Kinetics.—Two standard spectrophotometric methods were used to follow the reaction. In the first, a known amount of solid complex was added to the solution containing the other reagents previously brought to the reaction temperature and the reaction followed *in situ* with a thermostated spectrophotometric cell housing. The reaction was started in the same way in the second method but aliquot portions were withdrawn from time to time and the reaction stopped in acid. The spectra of these solutions were then measured at leisure.

Tracer Studies.—A weighed amount of the complex [$trans$-Co(en)$_2$OHCl]Cl·H$_2$O was added to a solution of 0.04 M Na^{36}Cl (obtained from H^{36}Cl from the Radiochemical Center, Amersham, England) and 0.16 M NaOH, previously brought to 0° in an ice–water bath. Samples of 5.00 ml were withdrawn at known times and pipetted into 5 ml of 1.44 M perchloric acid. The volume of the solution was made up to 25.00 ml and the absorption spectrum was measured in order to assess the extent of the reaction. A concentrated solution of sodium tetraphenylborate (*ca.* 1–2 ml) was then added dropwise and, with sufficient care, green [$trans$-Co(en)$_2$H$_2$OCl][B(C$_6$H$_5$)$_4$]$_2$ could be precipitated in a pure form. If too much precipitant was used or if the mixture was allowed to stand too long, the precipitate was contaminated. This is especially true at the later stages of the reaction. The complex was filtered off and washed with water until no significant activity could be detected in the washings. The dried tetraphenylborate was dissolved in 10.0 ml of acetone and the spectrum was measured immediately in order to confirm the purity and establish the concentration. The solution was then transferred to a liquid counter and the activity was measured with a Dynatron Radio Ltd. SC 200 scaling unit. A 0.2-ml quantity of the original chloride–hydroxide reaction solution was diluted to 10.0 ml with acetone and its activity was determined in the same way. Spectra were measured with a Unicam SP 800 recording spectrophotometer.

Results and Discussion

If the Dittmar–Archer mechanism is correct, one would expect to find that, when chloride is added to an alkaline solution of $trans$-Co(en)$_2$(OH)$_2{}^+$, 91% of the complex should be converted very rapidly to $trans$-Co(en)$_2$OHCl$^+$. This should then change to the cis-Co(en)$_2$(OH)$_2{}^+$ cation at a rate that is equal to the apparent rate of base hydrolysis of an authentic sample of the $trans$-chlorohydroxo complex. Thus, the mechanism predicts a chloride-catalyzed isomerization of the dihydroxo species. However, since the cis-dihydroxo complex does not appear to react with chloride and since the equilibrium mixture has been shown to contain 56% $trans$ and 44% cis complex (independent of [OH]),[4] it is difficult to reconcile this mechanism with the laws of thermodynamics.

We find that, on adding sodium chloride (0.35 M) to a solution of $trans$-Co(en)$_2$(OH)$_2{}^+$ (0.01 M, provided as the hydroxoaquo perchlorate) in sodium hydroxide solution (0.07 M), there is no change in the spectrum over a period of at least 25 min at 0°, nor is there any change in the spectrum of portions of the reaction mixture that have been acidified after various periods of

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time up to 25 min at 0°. The spectrum remains identical with that of *trans*-Co(en)₂(H₂O)₂³⁺ and is quite different from that of the *trans*-Co(en)₂H₂OCl²⁺ cation. Under these reaction conditions the proposed anation of the *trans*-dihydroxo complex to the *trans*-chlorohydroxo intermediate should have been complete in a few seconds and the chlorohydroxo intermediate should have been 80–90% converted to the *cis*-dihydroxo complex in this time. However, in order to induce any change in the spectrum within a reasonable time, it was necessary to raise the temperature. At 50.8°, samples withdrawn from time to time, cooled, and acidified gave a set of spectra with isosbiestic points at 551, 446, 385, and 348 mμ which were fully consistent with those of mixtures of *cis*- and *trans*-Co(en)₂(H₂O)₂³⁺⁴ and were essentially identical with spectra obtained under the same conditions but in the absence of chloride. The spectrophotometric change followed a first-order rate law and the rate constant was independent of the wavelength and independent of the concentration of hydroxide and chloride. The value obtained, 4.4×10^{-4} sec⁻¹, is identical with that reported in the absence of chloride.[4–7]

The second test of the Dittmar–Archer mechanism arises from the reversibility of the fast stereoretentive base hydrolysis. This would require that the *trans*-Co(en)₂OHCl⁺ cation exchanges its chloride rapidly with free chloride ions in solution. We therefore took a solution of [*trans*-Co(en)₂OHCl]Cl in alkali, under similar conditions to those reported by Dittmar and

Archer, except for the presence of Na³⁶Cl, and, after stopping the reaction at various stages, isolated the unreacted complex as [*trans*-Co(en)₂H₂OCl][B(C₆H₅)₄]₂. The data reported in Table I indicate that, even after there has been considerable base hydrolysis, there is no significant exchange of the chloride in the unreacted complex.

TABLE I

Uptake of ³⁶Cl in Unreacted *trans*-Co(en)₂OHCl⁺ at 0°[a]

Time, sec	% reaction	$10^{-2} \times$ specific activity of [*trans*-Co(en)₂H₂OCl][B(C₆H₅)₄]₂, counts/mmol min	% exchange
40	13	7.8	0.26
60	18	6.9	0.23
90	29	9.5	0.32
180	38	10.9	0.36

[a] Initial [complex] = 0.050 M; [NaCl] = 0.04 M; initial [OH⁻] = 0.16 M; specific activity of Cl*⁻ = 1.08×10^6 counts/mmol min.

Thus we have been unable to find any evidence that supports the mechanism of Dittmar and Archer and can only assume that their observation of the rapid formation of *trans*-Co(en)₂(OH)₂⁺ is the consequence of the overrefinement of their data by means of a computer. Therefore, there is no reason to change significantly the original data for the rates and steric course of the base hydrolysis of *trans*-Co(en)₂OHCl⁺.[2]

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THE MECHANISM OF THE REACTIONS OF COBALT(III)
COMPLEXES IN HIGHLY ACIDIC AND HIGHLY BASIC MEDIA

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Abstract

The cis $\rightleftharpoons$ trans isomerisation and the loss of optical activity of the $[Co\ en_2(OH_2)_2]^{3+}$ ions have been studied in aqueous acid solution up to 10 M perchloric acid concentration. The activation parameters in dilute acid are cis $\rightarrow$ trans: $\Delta H^{\ddagger}$ = 29.4 kcal mole^{-1}, $\Delta S^{\ddagger}$ = 13.4 e.u., trans $\rightarrow$ cis : $\Delta H^{\ddagger}$ = 28.0 kcal mole^{-1}, $\Delta S^{\ddagger}$ = 12.1 e.u. cis inversion, $\Delta H^{\ddagger}$ = 29.2 kcal mole^{-1}, $\Delta S^{\ddagger}$ = 8.1 e.u. In concentrated acid the enthalpy of activation for the trans $\rightarrow$ cis change becomes 25.5 kcal mole^{-1} and $\Delta S^{\ddagger}$ is 12.8 e.u. The acid catalysis of the isomerisation is discussed in terms of the bonding of a proton to a coordinated water molecule, thus weakening the metal-oxygen bond. The base-catalysed aquation of $[Co\ en_2(C_2O_4)]^{+}$ is also discussed, where the steric course of the reaction changes from 100% cis $[Co\ en_2(OH)_2]^{+}$ product in slightly basic media to 50% steric change in 4 M alkali. The mechanism is discussed in terms of the effect of the medium upon the formation and subsequent reaction of a five-coordinate intermediate.

Introduction

There are reports in the literature of the acid-catalysed aquation of cobalt bisethylenediamine complexes containing fluoro [1], azido [2] , and nitro [3] groups. The explanation of acid catalysis has been in terms of the attraction of a proton to a particular ligand and the consequent weakening of that metal-ligand bond.

Acid catalysis of the cis $\rightleftharpoons$ trans equilibration has been reported for several complexes of the type $[\text{Co en}_2 \text{ X H}_2\text{O}]^{n+}$, where X is isothiocyanato [4] , azido [2] and aquo [5] .

In these acid-catalysed reactions the acid seems to affect most the kinetics, which would indicate that the acid catalysis is involved in the formation of the five-coordinate intermediate, rather than in its subsequent fate.

In concentrated hydroxide solutions, however, both the kinetics and the stereochemical course of the reaction may be different from those in dilute basic solution. For example, Bailar and his co-workers [6, 7] have found that the stereochemical course of the base hydrolysis of $[\text{Co en}_2\text{Cl}]^+$ changes from overall retention of configuration to overall inversion in concentrated hydroxide. The results have been discussed [6, 7] in terms of a special orientation of the hydroxide brought about by ion-pairing in the concentrated solution, in such a way as to give inversion.

We shall discuss in this paper the reaction in concentrated solution of the diaquo ions $[\text{Co en}_2(\text{OH}_2)_2]^{3+}$ and in concentrated alkali of the oxalato complex $[\text{Co en}_2\text{C}_2\text{O}_4]^+$.

Experimental and Results

Studies of the $[\text{Co en}_2(\text{OH}_2)_2]^{3+}$ system. Taube and Kruse [5] studied the cis $\leftrightarrow$ trans isomerisation and water exchange in the two isomeric species. We have extended the isomerisation data over a

larger range of temperatures and acidities, and have measured the rate of loss of optical activity of the resolved cis ion.

In order to exclude difficulties resulting from impurities in preparations [8] all species were evolved from $[Co\ en_2CO_3]ClO_4$.

Spectrophotometric studies

A known weight of $[Co\ en_2CO_3]ClO_4$ was dissolved in a known excess of perchloric acid (to give $[Co\ en_2(OH_2)_2]ClO_4$). To this was added a known excess of hydroxide and the solution was warmed to equilibrate [9] giving 60% trans $[Co\ en_2(OH)_2]^+$. A known small volume of this solution was added to a known volume of standard perchloric acid in a 1 cm thermostated cell (species now 40% cis and 60% trans $[Co\ en_2(OH_2)_2]^{3+}$). The change of absorbance during the reaction to give $\sim 95\%$ cis $[Co\ en_2(OH_2)_2]^{3+}$ was measured at 20,100 cm^{-1} or spectra were scanned from 15,000 cm^{-1} to 40,000 cm^{-1} at known time intervals.

Polarimetric studies

$(-)_D$ $[Co\ en_2CO_3]ClO_4$ was dissolved in standard perchloric acid. 2 ml aliquots were placed in sealed tubes in a thermostat. At known time intervals samples were removed and the rotation was measured at 436 nm.

Using the observed equilibrium quotient of 58 (in agreement with Bjerrum [8a]) the specific rates coefficients k_c (cis $\rightarrow$ trans), k_t (trans $\rightarrow$ cis) were calculated. It can be seen that the cis $\rightarrow$ trans reaction cannot fully account for the loss of optical activity. This coefficient (k_c) was subtracted from k_r to give twice the inversion rate for cis $[Co\ en_2\ (OH_2)_2]^{3+}$.

Table 1   Observed spectrophotometric rate constants $(k_c + k_t \text{ sec}^{-1})$ for the cis $\leftrightarrow$ trans isomerisation of the $[\text{Co en}_2(\text{OH}_2)_2]^{3+}$ ions. $[\text{H}^+]$ varies between 0.21 and 0.48 M

Temp. $^\circ$C	Complex m M	10^4k obs sec^{-1}
26.6	7.0	0.12
38.8	9.2	0.77
39.4	9.21	0.77
40.2	7.0	1.05
45.4	12.1	2.4
46.6	9.2	2.8
47.3	9.2	3.0
67.4	9.2	4.1

Table 2   Observed polarimetric rate constants $(k_r \text{ sec}^{-1})$ for the loss of optical activity of the cis $[\text{Co en}_2(\text{OH}_2)_2]^{3+}$ ion

Temperature $^\circ$C	26.6	40.2	54.2
$10^6 \, k_r \text{ sec}^{-1}$	0.43	4.2	4.3
$10^6 \, k_i \text{ sec}^{-1}$	0.11	1.2	1.45
$10^6 \, k_c \text{ sec}^{-1}$	0.20	1.78	1.36

The rate of isomerisation in high acid concentration

The results are shown in Table 3.

Table 3   Observed spectrophotometric rate constants ($k_c + k_t$ sec^{-1}) for the cis $\longleftrightarrow$ trans isomerisation of the $[Co\ en_2(OH_2)_2]^{3+}$ ions in perchloric acid. Complex concentration = 8.6 m M

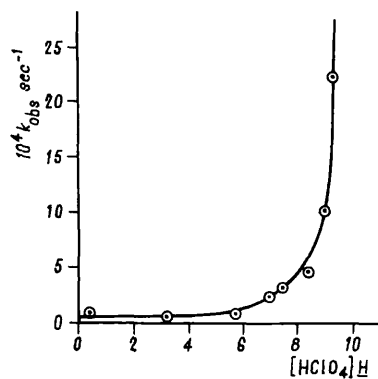| Temp. ^{o}C	$[H^+]$ M	$10^4 k$ obs sec^{-1}
4.5	9.06	0.29
14.0	9.06	1.42
26.8	9.64	22.5
26.8	9.06	10.1
26.8	8.43	4.7
26.8	7.73	3.01
26.8	7.22	2.9
26.8	5.91	0.67

Fig. 1   Variation of k obs sec^{-1} with acid concentration

Discussion

Acid hydrolysis

The results of Kruse and Tobe [5] show that (i) in the trans $[Co\ en_2(OH_2)_2]^{3+}$ ion, one molecule of water exchanges with solvent for every act of isomerisation and (ii) the rate of water exchange in the cis isomer is some two powers of ten faster than either its iso-merisation or its inversion. This must mean that the cis isomer is reacting with full retention of configuration most of the time. It is thus behaving in a way typical of cis isomers of the type $[Co\ en_2\ XY]$ in general [11] , (trans isomers react with some rearrangement of con-figuration). This stereochemical pattern has been discussed in terms of π bonding [11] . A ligand in a cis position which is a π donor, having a filled p orbital, can effectively π bond in a square pyramid-al intermediate whereas a trans group cannot.

If the coordinated water molecule is to act as such a donor it must be trigonally hybridised, at least in the transition state when it has a pair of p electrons [12] ,(it thus becomes very similar to the amido group).

Kruse and Taube suggested that the reactions of the diaquo ions could be explained by the formation of two tetragonal pyramidal intermediates, one from cis and one from trans, and an activated complex, perhaps a trigonal bipyramid which would allow isomerisation.

In an analysis of activation parameters and steric courses of aquations of complexes of the type $[Co\ en_2X\ Cl]^{n+}$, Tobe [13] has come to the conclusion that "whether or not the trigonal bipyramidal form of the intermediate will develop is determined in the transition state and not by subsequent rearrangement of a square pyramid". Taube also pointed out that high entropies of activation may be diagnostic of an incipient trigonal bipyramidal intermediate. The entropies of activa-tion in the diaquo system are all high positive values. It seems likely therefore that these ions are acting via trigonal bipyramids, with the cis isomer picking up a solvent water molecule to give a product with complete retention of configuration most of the time.

Acid-catalysed reaction

Fig. 1 shows that in high concentrations of perchloric acid the isomerisation is accelerated. This increase in rate is paralleled by the rate of water exchange in both the cis and trans isomers [5] .

It can be seen that the catalysis starts to be very noticeable above about 8 M perchloric. Bell [14] has concluded that protons in perchloric acid up to 8 M are tetrahydrated, and Bunnett [15] has suggested that in 8 M $HClO_4$ there is insufficient water for all the protons to be tetrahydrated. In such solutions the protons will then be likely to seek the coordinated water molecules and it is suggested that the coordinated water in concentrated acid is able to accept a proton to its lone pair and in doing so the metal-oxygen bond is weakened. This means that the formation of the five-coordinate intermediate is facilitated; this is reflected in a decrease in the activation energy of about 4 kcal $mole^{-1}$.

Base hydrolysis

The base hydrolysis of cobalt bisethylenediamine complexes has been discussed [16] in terms of the trigonal bipyramidal intermediates produced in an SNICB [9(b), 17] mechanism, and this discussion has been recently extended. The possible trigonal bipyramids are shown in Fig. 1. The cis isomer is able to form either intermediate A or B, whereas for the trans starting material only inter-mediate trigonal bipyramid can be formed easily. The extraction of the proton from the amine to give the amido group is represented ⊖ .

The product of the base hydrolysis of $[Co\ en_2 C_2 O_2 (OH)]$ in dilute b⁻ ⌐ is racemic cis $[Co\ en_2 (OH)_2]^+$. It is then possible that the reaction goes via intermediate B solely, giving equal quantities of ∧ and Δ product. If any cis is produced from intermediate A, which has retentive configuration, then this must be compensated for by net inversion from B.
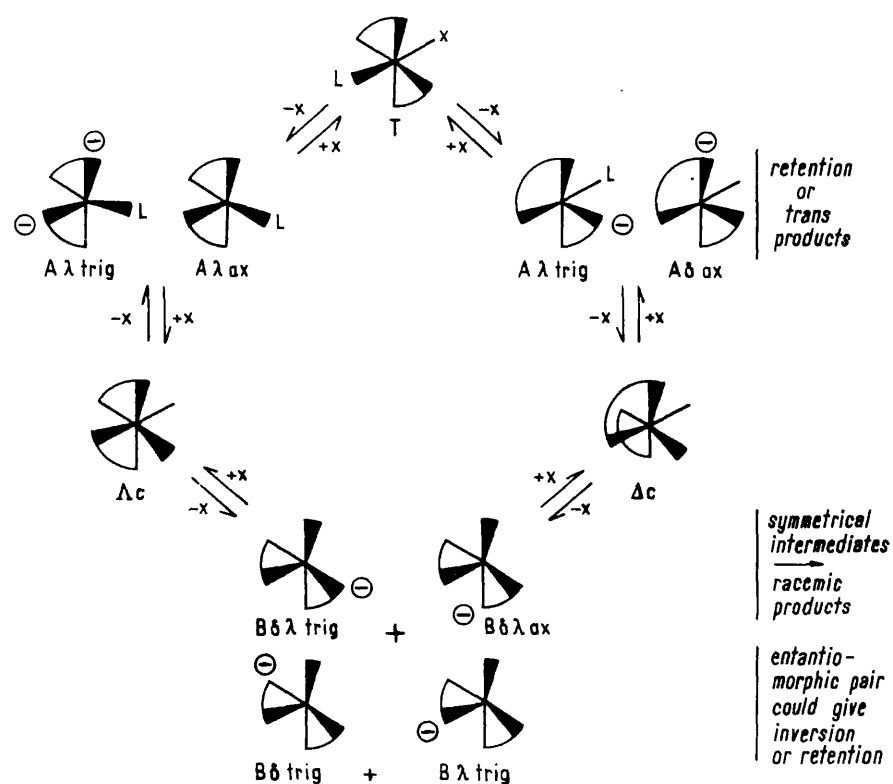
Fig. 2

In concentrated alkali the products become approximately equal amounts of cis and trans product. For an SNICB mechanism, intermediate A must be formed to produce trans product, and if it gives only trans product then intermediate B must still produce racemic cis. Any production of retentive cis via trigonal bipyramid must again be accompanied by a compensating net inversion from intermediate B.

We can now define two extreme cases.

(a)	(b)
Intermediate B always produced equal amounts of retentive and inverted cis product, i. e. B λ δ trig is the most likely.	Intermediate A gives cis product accompanied by net inversion from B so that total cis is racemic.
Intermediate A is formed <u>only</u> at high concentrations of base and gives trans product.	At high base concentration intermediate A gives trans product, with a corresponding decrease in net inversion from intermediate B.
Change of medium alters distribution of intermediates	Change of medium alters position of incoming group in trigonal bipyramid

Case (b) amounts to an ion pairing mechanism and the change in steric course of the base hydrolysis of the $[Co\ en_2Cl_2]^+$ ion has been explained in these terms.

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