AN INVESTIGATION INTO THE KINETICS AND MECHANISM OF THE HYDROLYSIS REACTIONS OF SOME COMPLEXES OF COBALT III

A thesis presented for the Degree
of Doctor of Philosophy
in the
University of London
by
Caroline Faith Vibert Pearce

Chemistry Department,
Bedford College,
University of London.

September, 1967.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

ABSTRACT

The mechanism of the base hydrolysis of the carbonato- and oxalato-bisethylenediaminecobalt III ions was investigated by measuring the rate of base hydrolysis spectrophotometrically under varying conditions. The steric changes accompanying the reaction was also followed by measurement of the change of optical activity during the reaction. In conjunction with this the rate of racemisation of the cis(-) dihydroxobisethylenediaminecobalt III ion was measured. Mechanistic paths are discussed.

For comparative purposes the rate of base hydrolysis of the carbonatobis(1,10-phenanthroline)cobalt III ion was investigated. Further work using 1,10-phenanthroline as a ligand consisted of an investigation into the compounds formed between cobalt, chlorine and phenanthroline.

The infrared spectra of the dichloro-, carbonato-, oxalato-, malonato- and cyclobutane 1,1'dicarboxylatobis-(1,10-phenanthroline)cobalt III complexes are recorded.

ACKNOWLEDGEMENTS

The author would like to thank her supervisor, Dr. M.E. Farago for her invaluable advice, guidance and helpful criticism.

The author is also indebted to Professor P.B.D. de la Mare for his continued interest and for the provision of laboratory facilities.

Thanks are also due to Dr. M.M. Harris for the use of the Zeiss Polarimeter and to Westfield College for the use of their spectropolarimeter.

The award of a University of London Postgraduate Studentship is gratefully acknowledged.

CONTENTS

PART I: INTRODUCTION

PART II: RESULTS AND DISCUSSION

PART III: EXPERIMENTAL

OBJECT OF THE INVESTIGATION

The replacement reactions of many monodentate ligands by hydroxide have been reported in the literature,(17) and their steric courses and reaction paths have been formulated.

The replacement of bidentate ligands however, has been less fully studied.(59, 100, 134) The object of the present work therefore was to clarify the steric course and formulate mechanistic paths for hydroxide substitution in compounds of the type $[Coen_2X]^+$ where X was either of the bidentate ligands carbonate or oxalate.

The reaction can be divided into two parts:

a) Initial dechelation of the ligand X

$$[Coen_2X]^+ + OH^- \longrightarrow [Coen_2(OH)(X)]^0$$

b) Removal of ligand X

$$[Coen_2XOH]^0 + OH^- \longrightarrow [Coen_2(OH)_2]^+ + X^{2-}$$

Steric changes are possible in both stages. The initial tris chelated ion necessarily has a cis configuration prohibiting cis-trans isomerisation, but the other two ions can both undergo racemisation and isomerisation. Further, the isomerisation (58, 96) and racemisation of the final product, the $[Coen_2(OH)_2]^+$ ion can be studied separately.

$$cis[Coen_2(OH)_2]^+ \rightleftarrows trans[Coen_2(OH)_2]^+$$

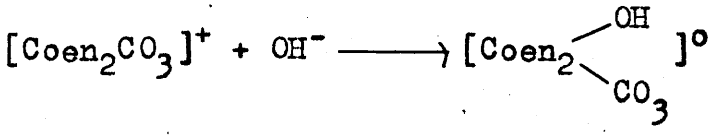
In order to obtain further data relevant to the mechanistic course, the complex $[Cophen_2CO_3]^+$ was studied. The 1,10 phenanthroline ligand lacks hydrogen atoms attached to the coordinated nitrogen atoms, so that any mechanism which utilises such hydrogen atoms is prohibited. No cis trans isomerisation of the $[Cophen_2(OH)_2]^+$ ion has been found. The trans isomers of this complex have not been characterised and are thought not to exist.

SUMMARY OF THE RESULTS AND CONCLUSIONS

1. The racemisation of the cis(-)$[Coen_2(OH)_2]^+$ ion is faster than the isomerisation, both processes being independent of the hydroxide concentration. Several mechanistic paths are involved. A path involving the dechelation of the ethylenediamine is postulated to account for the rapid racemisation relative to the isomerisation.

2. The base hydrolysis of the $[Coen_2CO_3]^+$ ion proceeds in two stages:

a) Initial dechelation of the carbonate.



$$[Coen_2CO_3]^+ + OH^- \longrightarrow [Coen_2\begin{smallmatrix}OH \\ CO_3\end{smallmatrix}]^0$$

At high base concentration the dechelation process proceeds by a mechanism first order in hydroxide. The variation of the second order rate constant with temperature fits the Arrhenius equation:

$$k_2 = 2{\cdot}9 \times 10^{15}\ e^{21,600/RT}\ \text{l mole min.}^{-1}$$

At all concentrations the rates of mutarotation were found to be the same as the rates of dechelation. Cobalt-oxygen bond fission is postulated with an S_N1 CB or S_N2 ion pair mechanism.

At low base concentrations an acid catalysed reaction path is also present.

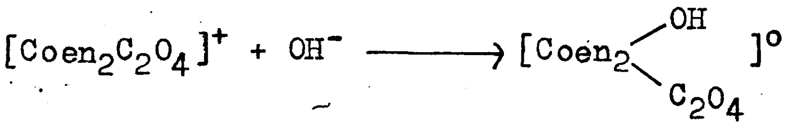
b) Removal of carbonate

$$[Coen_2CO_3OH]^0 + OH^- \longrightarrow [Coen_2(OH)_2]^+ + CO_3^{2-}$$

The rate of loss of carbonate varies with the wavelength at which the loss was measured. The loss of optical activity was slower than the decomposition. Several different species are undergoing decomposition, racemisation and isomerisation at different rates.

3. The base hydrolysis of the $[Coen_2C_2O_4]^+$ ion proceeds in two stages:

a) Initial dechelation of the oxalate.



$$[Coen_2C_2O_4]^+ + OH^- \longrightarrow \left[Coen_2\begin{matrix} OH \\ C_2O_4 \end{matrix}\right]^0$$

The dechelation is found to proceed by a mechanism first order in hydroxide. The variation of the second order rate constant with temperature fits the Arrhenius equation:

$$k_2 = 3{\cdot}6 \times 10^{12}\ e^{-17,700/RT}\ \text{l.mole min.}^{-1}$$

The reaction is much faster than for the $[Coen_2CO_3]^+$ ion.

b) Removal of oxalate

$$[Coen_2C_2O_4OH]^o + OH^- \longrightarrow [Coen_2(OH)_2]^+ + C_2O_4^{2-}$$

Above 1 M sodium hydroxide, the variation of the first order rate constant with temperature fits the Arrhenius equation:

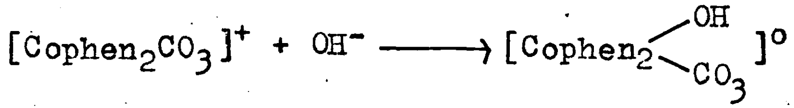
$$k_1 = 2{\cdot}74 \times 10^{11}\ e^{-15,300/RT}\ \text{min.}^{-1}$$

The rate of loss of optical activity was found to be identical to the rate of removal of oxalate. At high temperature the reaction proceeds by a mechanism first order in hydroxide, an S_N1 CB mechanism is postulated.

At low temperatures and base concentrations the reaction proceeds by a mechanism second order in hydroxide. The mechanism is envisaged as a synchronous attack by hydroxide at the cobalt and the formation of an ion pair of the hydroxide with the oxalate.

4. The base hydrolysis of the $[Cophen_2CO_3]^+$ ion proceeds in two stages:

a) Initial dechelation of the carbonate



$$[\mathrm{Cophen_2CO_3}]^+ + \mathrm{OH^-} \longrightarrow [\mathrm{Cophen_2}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{CO_3}\end{smallmatrix}]^\circ$$

Qualitatively the rate of dechelation appears to become slower with decrease in ionic strength and hydroxide concentration.

b) Removal of carbonate

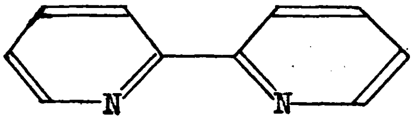
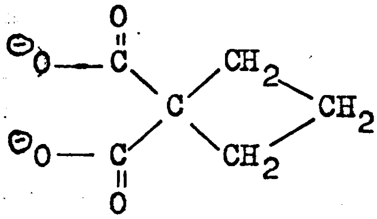
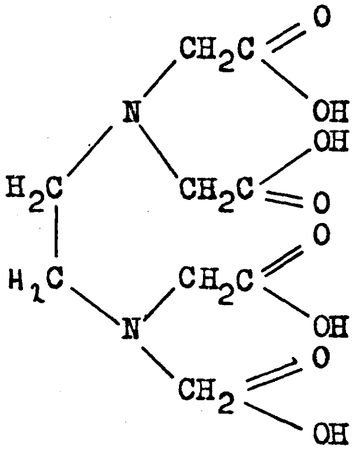
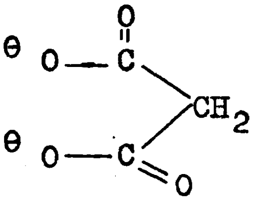
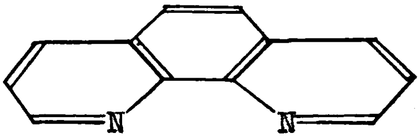
$$[\mathrm{Cophen_2CO_3OH}]^\circ + \mathrm{OH^-} \longrightarrow [\mathrm{Cophen_2(OH)_2}]^+ + \mathrm{CO_3}^{2-}$$

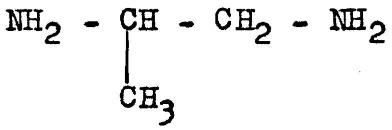
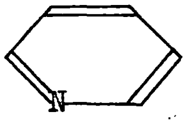
The rate of loss of carbonate is independent of the hydroxide concentration but catalysed by the presence of chloride ions. An electron transfer mechanism is postulated.

5. The infrared spectra of the dichloro-, carbonato-, oxalato-, malonato-, and cyclobutane 1, 1' dicarboxylatobis(1,10-phenanthroline)cobalt III ions show that the complexes are stabilised through the development of a partial Co-N double bond by conjugation with the π electrons on 1,10-phenanthroline.

6. The compound of cobalt, chlorine and phenanthroline termed 'the green chloride' contains the tetrahedral CoII ion, $[\mathrm{CoCl_4}]^{2-}$.

GLOSSARY OF ABBREVIATIONS FOR LIGANDS

Abbreviation	Name	Formula
bipy	2,2'-bipyridyl	
cB	cyclobutane 1, 1'dicarboxylate	
en	ethylenediamine	$NH_2\ CH_2\ CH_2\ NH_2$
EDTA	ethylenediamine-tetraacetic acid	
mal	malonate	
phen	1,10-phenanthroline	

Abbreviation	Name	Formula
pn	propylenediamine	 $NH_2 - \underset{\substack{\vert \\ CH_3}}{CH} - CH_2 - NH_2$
py	pyridine	
trien	triethylenetetramine	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$

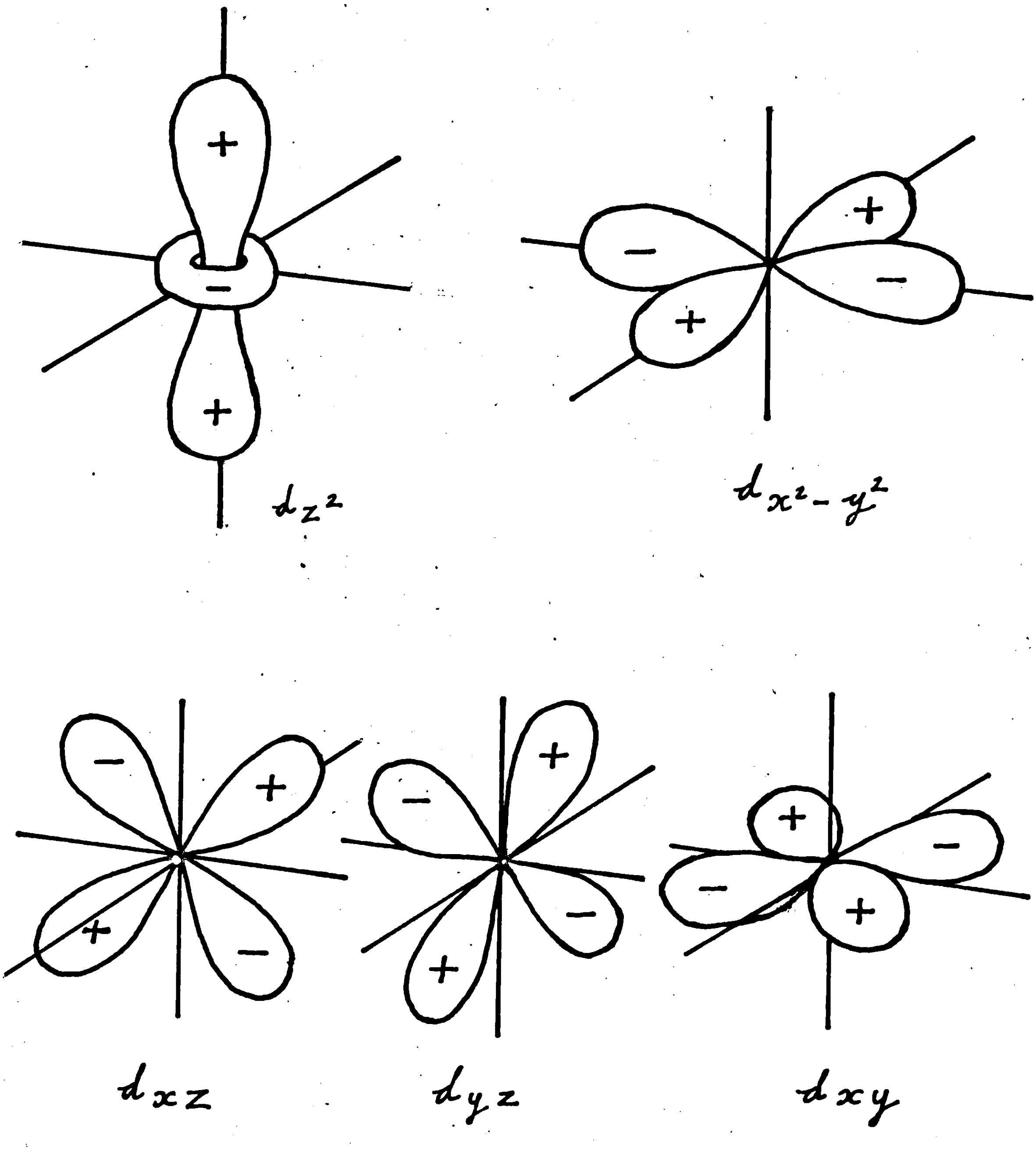
PART 1. INTRODUCTION

1. Crystal Field Theory

Crystal field theory was first formulated by H. Bethe(20) who studied the interactions between metal ions and ligands in a purely electrostatic sense by considering the ligands as point charges. The possibility of any orbital overlap was ignored. The theory was later modified(115) to account for partial orbital overlap and covalence and this modified theory is known as the ligand field theory. Molecular orbital theory considers the interactions purely in terms of molecular orbitals.

In a neutral environment the d orbitals of a metal ion all have equivalent energy, but in a negatively charged environment they are no longer equivalent. If this environment is supplied by six similar ions, these ions will be arranged symmetrically around the metal ion and form an octahedron. The concentration of charge in the d_{xy}, d_{yz} and d_{zx} orbitals project between the negative charges of the ligands, and the concentration in the d_{z^2} and $d_{x^2-y^2}$ orbitals projects directly towards

DIAGRAM I.



d_{z^2} $d_{x^2-y^2}$

d_{xz} d_{yz} d_{xy}

The "Shapes" of d Orbitals.

the ligands, thereby having a higher energy. These are shown in diagram 1.

~~Since there is no net change in energy~~ The destabilisation energy of $d_{x^2-y^2}$ and d_{z^2} orbitals is equivalent to the stabilisation energy of the d_{zx}, d_{zy}, d_{yx} orbitals. The former are known collectively as the e_g orbitals and the latter as the t_{2g} orbitals and the difference 10 D_q or Δ is the ligand field strength.

Reduction in symmetry from octahedral (O_h) will cause further splitting in the energy levels of the orbitals. The changes due to tetragonal distortion are shown in diagram 2.

2. Electronic Structure and Spectra in Co III Complexes

All cobalt III complex ions are derived from the octahedral arrangement. Diagram 3 shows a simplified energy level diagram for Co III, a d^6 ion (45) with increasing ligand field strength.

The ^5D and ^1I terms refer to the two lowest energy terms arising in the absence of a ligand field. The letters I and D refer to the total orbital angular momentum and the numbers to the spin angular momentum. In the presence of a ligand field, these terms are split

DIAGRAM 2.

RELATIVE CHANGES OF ENERGY OF d ORBITALS IN DIFFERENT ENVIRONMENTS.

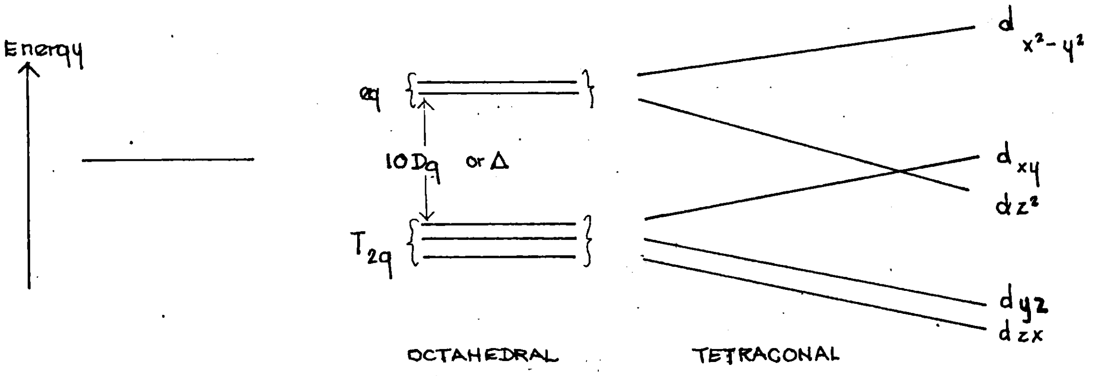
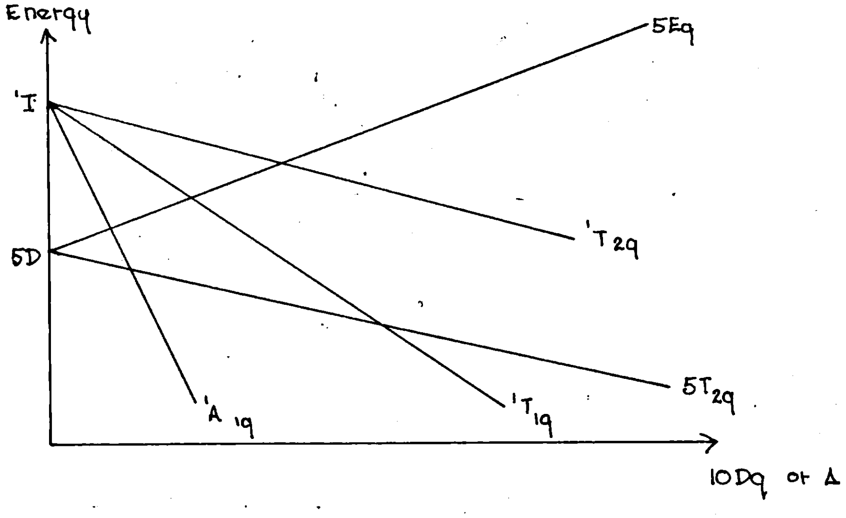


DIAGRAM 3.

ENERGY LEVEL DIAGRAM FOR A COBALT III ION.

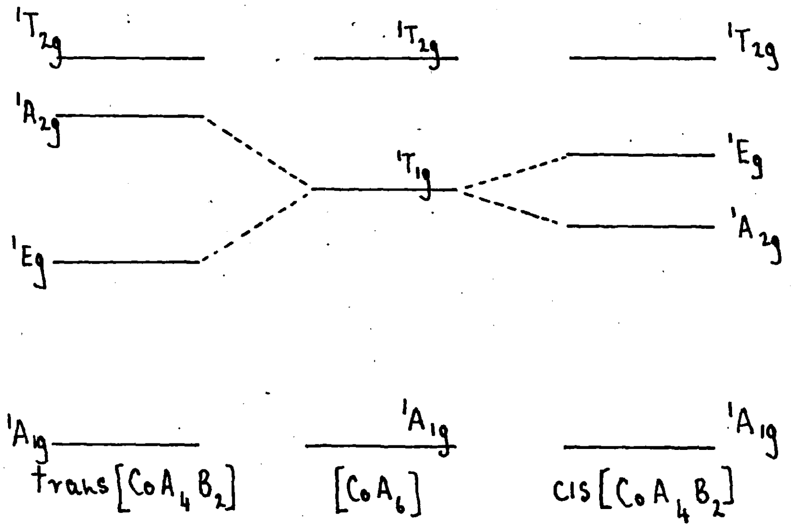


into terms of lower symmetry, T states being triply degenerate, E states doubly degenerate and A states non degenerate. With the increase in ligand field strength the $^1A_{1g}$ state quickly becomes the lowest energy state, the ground state. This results in diamagnetic complexes since there are no unpaired electrons. The one exception to this is the $[CoF_6]^{3-}$ ion, which is paramagnetic with four unpaired electrons, the ground state being $^5T_{2g}$. No transitions take place between levels arising from the ^5D state and the ^1I state since this would involve the violation of the selection rule, $\Delta L = 0, \pm 1$, where L is the total orbital angular momentum.

The visible absorption spectrum arises from transitions from the $^1A_{1g}$ ground state to excited states. Often two absorption bands are found, caused by transitions to the $^1T_{1g}$ and $^1T_{2g}$ excited states where $\Delta L = 0$. These transitions are very weak (extinction coefficients are of the order of 50 to 150) since the transitions are formally forbidden in the free ion due to the <u>Laporte Selection rule</u>. This states that transitions which involve the redistribution of electrons within a single quantum shell are forbidden. However if the compound lacks a centre of symmetry or a centre of symmetry during the molecular vibrations then there will be some mixing of d and p orbitals which then allows a transition to take place.

The complex $[Co(NH_3)_6]^{3+}$ has O_h symmetry. Many complexes have lower symmetry caused by further splitting of the energy levels. The complex $[Coen_3]^{3+}$ is an octahedral complex with D_3 symmetry. For complexes of the type cis and trans $[CoA_4B_2]$ the $^1T_{1g}$ level is further split due to the lowering of the symmetry, C_{2v} in the cis complex and D_{4h} in the trans complex. This is shown in diagram 4.

Diagram 4: The Splitting of the $^1T_{1g}$ energy level on lowering the symmetry



The splitting of the ${}^1T_{1g}$ state is twice as great for a trans complex than for a cis.

Ballhausen (10) has shown that this result is predictable by consideration of the tetragonal contribution to the crystalline field potential $\mathcal{V}_T$. This was defined as

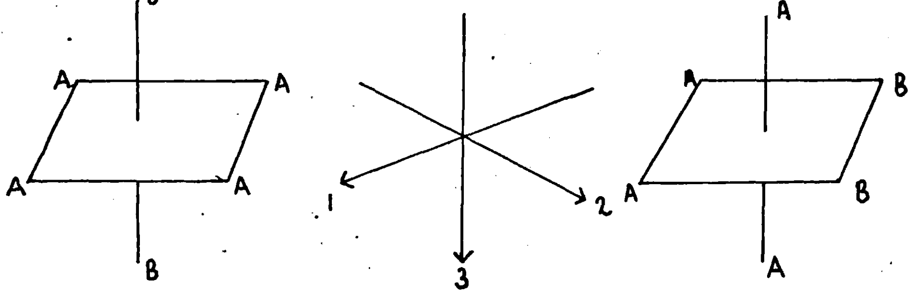
$$\mathcal{V}_T = \left(\frac{\mu_1 + \mu_2}{2} - \mu_3\right) f_{(x,y,z)}$$

at a point $f_{(x,y,z)}$ where μ_1, μ_2 and μ_3 are the sums of the charges on the x, y and z axes of the complex. In a tetragonal field $\mu_1 = \mu_2 \neq \mu_3$. Therefore

$$\mathcal{V}_T = (\mu_1 - \mu_3)\, f_{(x,y,z)}$$

Diagram 5 shows the configurations of the cis and trans isomers of the $[CoA_4B_2]$ complex.

DIAGRAM 5.



trans $[CoA_4B_2]$

$\mu_1 = \mu_2 \neq \mu_3$

cis $[CoA_4B_2]$

$\mu_1 = \mu_2 \neq \mu_3$

The tetragonality parameter $(\mu_1 - \mu_3)$ will be different in the two cases :-

1) for trans $[CoA_4B_2]$,

$\mu_1 = 2q_A$ where q_A is the charge due to group A and q_B the charge due to group B.

$\mu_3 = 2q_B$

$\mu_1 - \mu_3 = 2(q_A - q_B)$

2) for cis $[CoA_4B_2]$,

$\mu_1 = q_A + q_B$

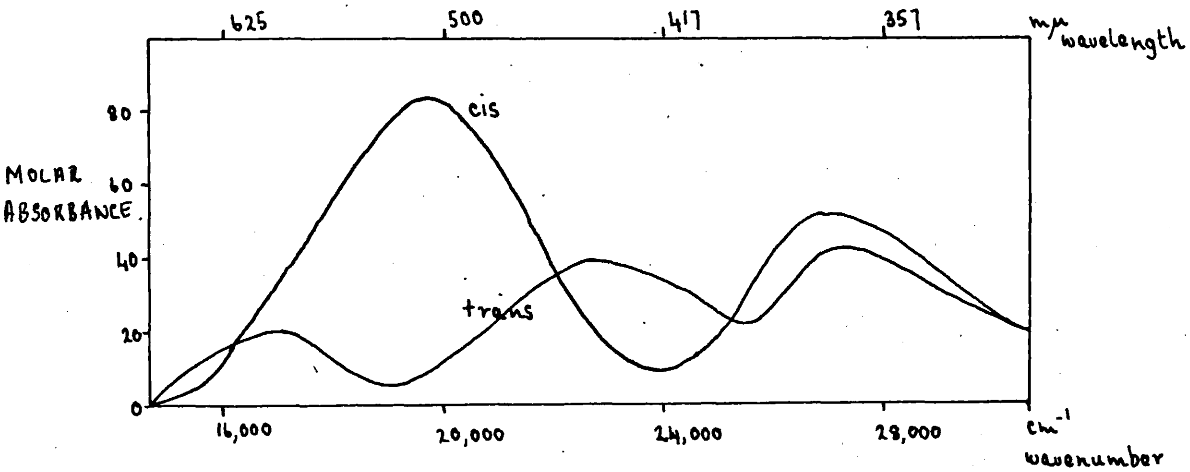
$\mu_3 = 2q_A$

$\mu_1 - \mu_3 = (q_A - q_B)$

Therefore the tetragonal splitting in the trans complex is twice that of the cis and the level order is inverted as shown in diagram 4.

This is found in practice and is shown in diagram 6 for the cis and trans $[Coen_2F_2]^+$ ion. (45)

Diagram 6: Visible Absorption spectra for the cis and trans $[Coen_2F_2]^+$ ions.



The absorption band in both the cis and trans complexes at 28,000 cm^{-1} corresponds to the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. In the cis complex the $^1T_{1g}$ is not split sufficiently for two different transitions to be seen, one transition is seen at 20,000 cm^{-1} corresponding to the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition. This is not so in the trans complex where 2 weak transitions are seen at 17,000 cm^{-1} and 23,000 cm^{-1}. These correspond (12, 92) to the $^1A_{1g} \longrightarrow {}^1E_g$ and the $^1A_{1g} \longrightarrow {}^1A_{2g}$.

In general, absorption in a cis complex is greater than in a trans complex since the cis isomer lacks a centre of symmetry.

3. Kinetic Application of crystal field theory.

It is found that substitution reactions of cobalt III complexes are relatively slow, and so in general can be measured by standard techniques such as spectrophotometry. Substitution reactions of some other transition metals are found to be much faster and cannot be measured by the same techniques. Taube qualitatively systematised the two types of rates of substitution by calling slow reacting complexes inert and fast reacting complexes labile. He correlated the rates with the electronic arrangement of the d orbitals. Complexes of the first transition series which have at least one completely empty 3d orbital (inner d orbital) eg. Sc III and Ti II react fast and so are known as labile. Complexes which have no empty 3 d orbitals such as Cr III and Co III react slowly thus being classified as inert.

The importance of crystal field stabilisation in determining the rates of reactions has been developed in a more quantitative fashion by Basolo and Pearson.(17) They calculated the crystal field stabilisation energy (C.F.S.E.) for various numbers of electrons for a regular octahedral complex in weak and strong fields and also for a square pyramid and a pentagonal bipyramid. The latter two are used as approximations to the activated complex for S_N1 and S_N2 mechanisms and, as far as crystal field effects are concerned, a trigonal bipyramid is always less favourable than a square pyramid. The difference between the original octahedral and final C.F.S.E. is considered as a contribution to the total activation energy, ΔE_a. A large value of ΔE_a implies a slow reaction and a small value a fast reaction. The most affected ions are the d^3, spin coupled d^6 and d^8 ions. This results in the observed slow reactions of Cr III and Co III.

4. Optical Activity

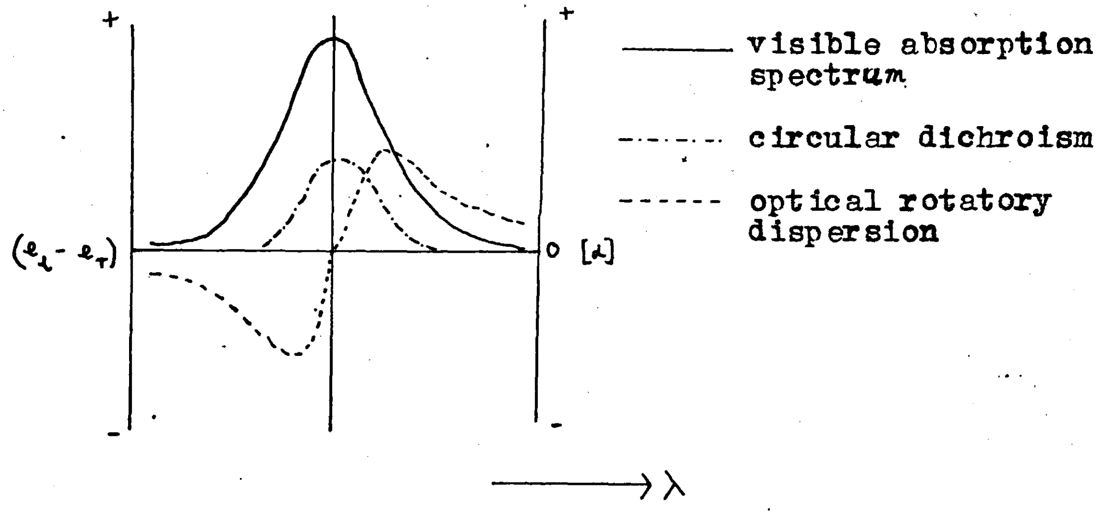
Optical activity is associated with molecules containing an asymmetric centre or overall asymmetry and lacking a plane and centre of symmetry. This results in two related phenomena, <u>optical rotatory dispersion</u> and <u>circular dichroism</u>.

Optical rotatory dispersion is the ability of the molecule to rotate the plane of plane polarized light. It is found to vary with wavelength and each asymmetric centre gives rise to an S curve in its region of light absorption. This curve is known as the optical rotatory dispersion curve or the Cotton Effect. The rotation, α, at any wavelength λ is given by

$$(\alpha)_\lambda = \frac{\pi}{\lambda}(n_l - n_r)$$

where n_r and n_l are the refractive indices for right and left circularly polarized light respectively. Plane polarized light can be considered to be made up of right and left circularly polarized light.

Diagram 7: Positive Cotton Effect



Since right and left circularly polarized light are absorbed to different extents the resultant light will no longer be plane polarized but elliptically polarized.

This phenomenon is known as circular dichroism; its magnitude is expressed by the ellipticity, $e_l - e_r$, the difference in circular dichroic absorption:

$$e_l - e_r = \frac{4\pi}{\lambda} (K_l - K_r) \log e.$$

where K_l and K_r are the absorption indices for left and right circularly polarized light.

The origin of both phenomena arises from the interaction of the electromagnetic light radiation with the valence electrons.(142) When the amplitude of the light becomes close to the natural amplitude of the electron, the electron is polarized and induces an electric field. This results in refraction since $n^2 = e$ (Maxwell's law) where e is the strength of the electric field and n, the refractive index, is different for left and right circularly polarized light. When the light amplitude is exactly equal to that of the electron, exchange of energy takes place resulting in zero rotation and, on further increasing the amplitude, the rotation is reversed due to change in phase. This results in the S shaped dispersion curve.

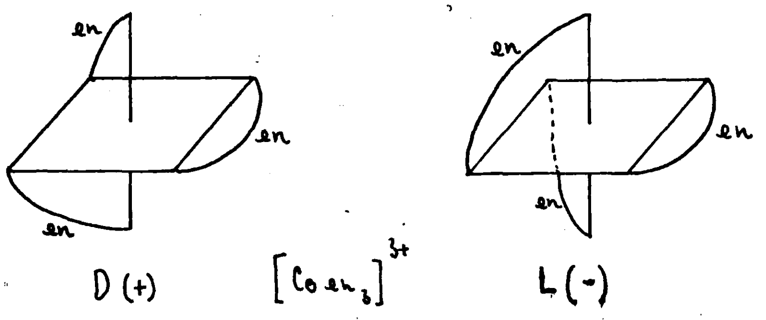
Optical rotatory dispersion and circular dichroism can be used to correlate the configurations of related dissymmetric molecules and so follow the steric course of reactions. Circular dichroism has been used to deduce symmetry elements and electronic energy levels. (109)

5. Optical Activity in cobalt III complexes

Optical activity is exhibited in cobalt III complexes when the structure of one isomer is nonsuperposable on its mirror image and the molecule as a whole lacks a plane and centre of symmetry.

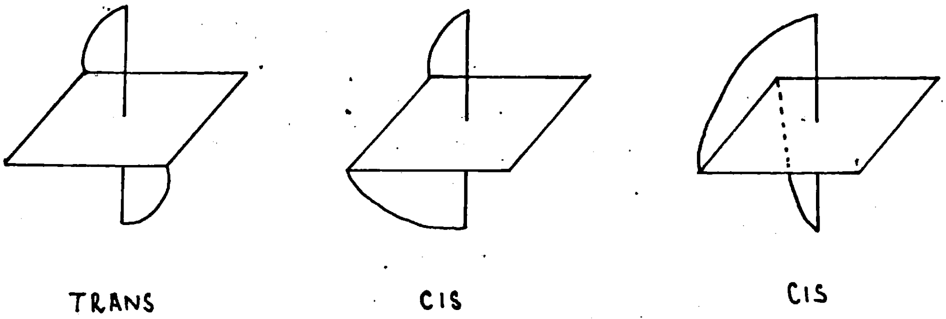
Optical activity among octahedral complexes was first demonstrated by Werner. He resolved (145) the $[Coen_3]^{3+}$ ion by making use of the large difference in solubility of the diastereoisomers in the form of the chlorotartrate or the bromotartrate, $[Coen_3]^{3+}Cl(C_4H_4O_6)$. The two forms are shown in diagram 8.

Diagram 8



Complexes containing two bidentate chelate ligands and two unidentate ligands can exist in cis and trans forms. Two optically active forms of the cis isomer exist.

Diagram 9: Isomers of a bisbidentate chelate compound



The complex will also exhibit optical activity if one of the atoms in the ligand is asymmetric. An asymmetric carbon centre is present in propylenediamine, so the complex $[Copn(NH_3)_4]^{3+}$ owes its activity to the carbon atom alone. However, the optical activity of cis $[Copn_2(NH_3)_2]^{n2+}$ will be due not only to the asymmetric carbon atom but also to the overall asymmetry.

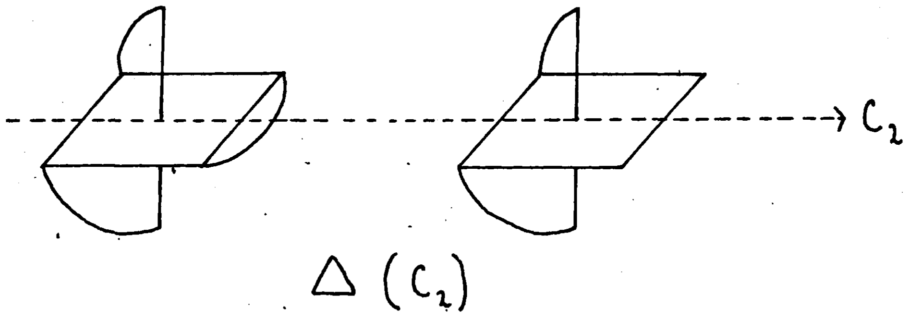
Recently the $[Co(NH_3)_4(CH_3NHCH_2COO)]^{2+}$ where $CH_3NHCH_2COO^-$ = sarcosine has been resolved. (14) Here the activity is due to the asymmetry of the coordinated nitrogen. The coordination stabilises the proton on the asymmetric nitrogen and prevents the rapid inversion which is responsible for the isolation of racemic quaternary ammonium salts.

The actual nomenclature used for relating and distinguishing configuration has been the subject of much discussion. Originally two enantiomers were distinguished by their rotation (+) or d and (-) or l at the Na_d line. This is still commonly used. The symbols D and L are used to describe absolute configuration relative to a standard substance, e.g., D(+) $[Coen_3]^{3+}$ ion. This is only relative nomenclature and is dependent on the absolute configuration of D(+) $[Coen_3]^{3+}$. The problem of nomenclature inherent in the relative position of the ligands has been examined fully (35) as a purely topological problem of chirality, where chirality expresses the necessary and sufficient conditions for the existence of isomers. From a numerical system of arranging the groups around the central metal atom a series of rules were set out which allowed the nomenclature of the absolute configuration to be fixed. These are called R and S where the R configuration corresponds to the

D(+) $[Coen_3]^{3+}$ shown by X-ray analysis.

The configurations of many bisethylenediamine complexes have been related to the helix described by the chelate ligands of the $[Coen_3]^{3+}$ about the major axis C_3. This chirality is left handed for the D(+) $[Coen_3]^{3+}$ ion and this isomer has been designated Λ using the convention first introduced by Piper.(103, 122) But complexes with a C_3 symmetry are much less common than with C_2 symmetry as in cis $[Coen_2X_2]^{n+}$. The configuration of such a complex can be considered about an imaginary C_3 axis but the chirality can also be related to its own real C_2 axis and this results in a change of chirality. Thus for example the designation for the D(+) $[Coen_3]^{3+}$ is both Λ (C_3) and Δ (C_2), depending on which reference axis is considered. Since this work deals mainly with bisethylenediamine complexes, the designation of Δ and Λ are made with reference to the C_2 axis.

Diagram 10: C_2 Axis in a bisbidentate chelate complex



It is also found that if the helical distribution of several complexes is the same, then they all have the same general shape for their optical rotatory dispersion curves. Some of these are shown in Figure 1.

However the values obtained for the (-) $[\mathrm{Coen_2CO_3}]^+$ ion and for the (-) and (+) $[\mathrm{Coen_2(C_2O_4)}]^+$ ions were larger than the reported values (pages 263, 268).

This allows the formation of a general empirical rule; (66) For monomeric complexes of cobalt III containing two or three five-membered or smaller chelate rings, the enantiomer having a dominantly positive Cotton Effect for the longest wavelength spin allowed d-d transition absorption band has the D configuration.

The absolute structure of the Δ $[\mathrm{Coen_3}]^{3+}$

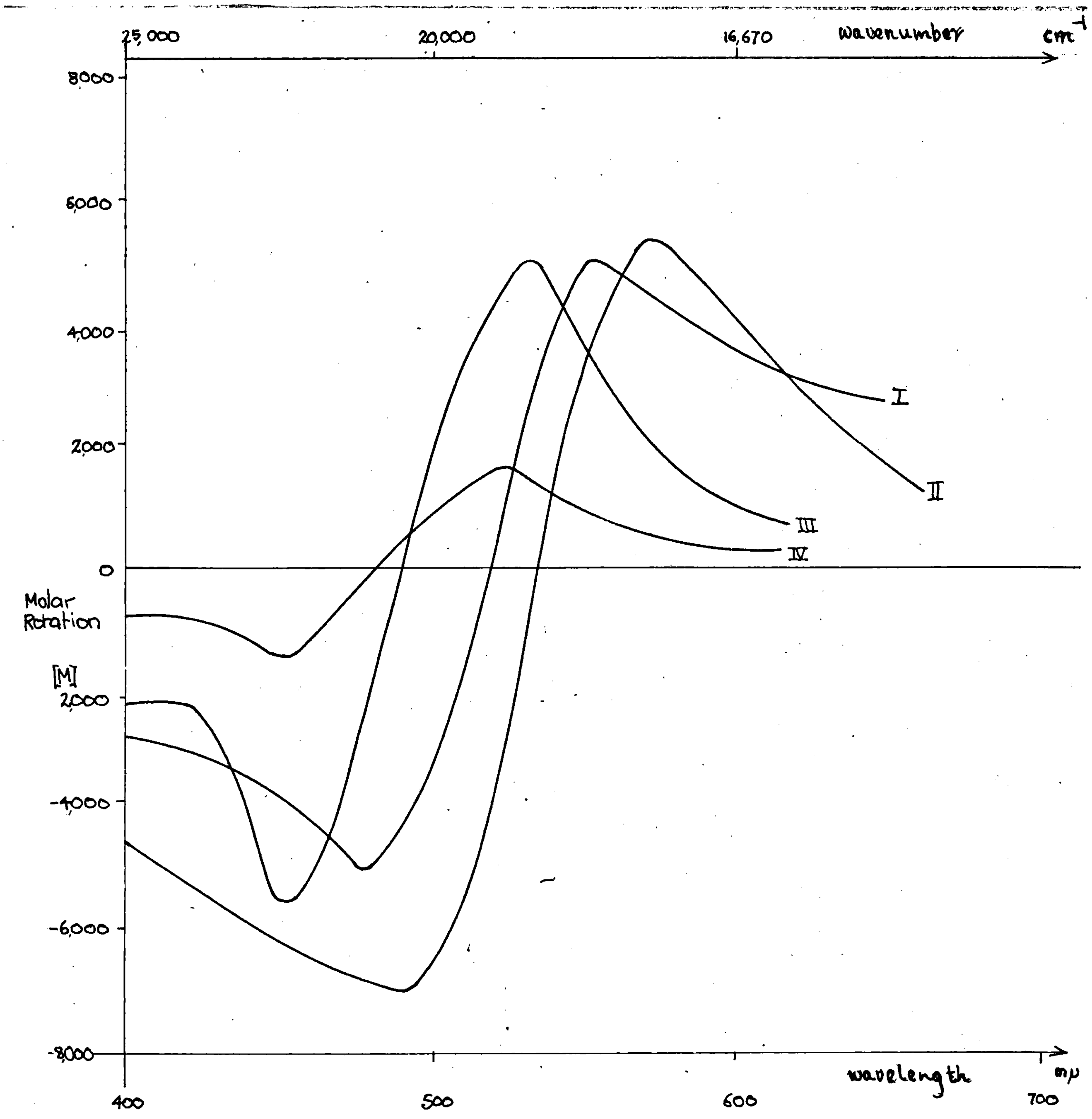
FIGURE · 1

ROTATORY DISPERSION CURVES OF SOME

$\Delta\,[Coen_2\,X]^{n+}$ COMPLEXIONS [from references 107, 128]

I $[Coen_3]^{3+}$, II $[Coen_2\ CO_3]^{+}$ $(\times 1/3)$ III $[Coen_2\ C_2O_4]^{+}$

IV $[Coen_2(H_2O)_2]^{3+}$



ion has been measured by X-Ray crystallography, the D (Δ) and L (-) isomers have been previously shown (page 28). Therefore the absolute structure of all compounds which can be related to this ion can be found. The extensions of this correlation into the cisbisdiamine series is less certain and more definite information can be obtained from the circular dichroism curves. Circular dichroism is especially valuable when the optical rotatory dispersion curve is complicated by a number of overlapping absorption bands, since, due to the more local effect of the circular dichroism, very much less overlap is obtained in the latter.

That there is any connection between the Cotton Effect and the absolute configuration has been questioned.(109) If the optical activity is ascribed solely to the distortion of the ligand atoms, their orbitals or their charges from their octahedral distribution then there is no necessary correlation. These theories require that the chelate atoms not directly bonded to the metal, such as hydrogen and nitrogen in ethylenediamine, are electronically inert and serve in a mechanical capacity only to produce the distortions required.

Experimentally this is not supported. X-ray diffraction studies on Δ $[Co(en)_3]^{3+}$ show that the displacement of the nitrogen atoms from the octahedral position is small. Deuteration studies on the same complex suggest that the electronic states connected by transitions giving rise to absorption bands are affected by the N-H bond. They also suggest that the sign of the charge transfer circular dichroism band depends on the right (k') or left (k) handed conformation of the N-C-C-N chain. (page 53). These theories also require that the ligand field parameter, 10 Dq, as measured by the energy of the long wavelength absorption band should be smaller in the $[Co(en)_3]^{3+}$ ion than in the $[Co(NH_3)_6]^{3+}$ ion. This is due to the displacement of the nitrogen atom reducing the overlap of the nitrogen lone pair σ orbital and the e_g orbitals of the metal ion. In practice the reverse is found to happen showing that the t_{2g} metal ion electrons are delocalised into the antibonding σ orbitals spanning the whole ethylenediamine chain. The decrease in energy of the t_{2g} electrons results in an increase in 10 Dq.

Therefore the optical activity of a complex containing chelated ethylenediamine rings does not arise solely from mechanical distortion effects. It arises from the mixing of the d-d transitions of the metal ion with charge transfer transitions of the ligand σ electrons to the e_g orbitals of the metal and of metal t_{2g} electrons to the antibonding σ orbitals of the ligand in the delocalised d electron model.

The lower symmetry of the bisethylenediamine cobalt III complexes relative to the O_h symmetry of the $[Co(NH_3)_6]^{3+}$ and the D_3 symmetry of the $[Coen_3]^{3+}$, causes a greater number of weaker transitions. For complexes of the type $[Coen_2L_2]^{3+}$ four circular dichroism bands are found. (109) If L is a unidentate ligand, two bands are associated with each light absorption band and if L is a bidentate ligand one band is found associated with the short wavelength absorption and three with the long wavelength absorption. From measurement of the position and strength of these bands, information has been obtained concerning the symmetry and configuration of the complex. For example, cis Δ $[Coen_2(NH_3)_2]^{3+}$ is found to have a symmetry which approximates to the D_3 symmetry of $[Coen_3]^{3+}$. At the other extreme cis Δ $[Coen_2(CN)_2]^+$ has a C_{2v} symmetry. (109) Other complexes have symmetries intermediate between the two extremes. The optical activity is correlated with configuration by measuring the rotational strength of the A(Ea) transition arising from the breakdown of the T_{1g} octahedral symmetry. The rotational strength of this transition is found to have a positive value for complexes which have the same absolute configuration as the $\Delta\,[Coen_3]^{3+}$ ion.

These methods of comparing absolute configuration were at first found to agree in general with an earlier empirical method which was suggested by Werner.(144) He assigned the same absolute configuration to compounds which gave the less soluble (+) α bromocamphorsulphonate salt. These were all found to have a positive major circular dichroism band except for the less soluble isomer of cis $[Coen_2(NH_3)(NO_2)]^{2+}$ which gave a negative circular dichroism band. Therefore the solubility method for relating configurations is unreliable.

Gillard (63) has shown that this case is not unique. Table 1 shows a comparison of the sign of the configuration of the less soluble diastereoisomers and the sign of the same isomer given by the Cotton Effect.

TABLE 1

Complex	Less soluble (+) BCS	Positive Cotton Effect
$[Coen_2(NO_2)_2]^+$	(+)	(+)
$[Coen_2(NCS)(NO_2)]^+$	(-)	(+)
$[Coen_2(NCS)_2]^+$	(-)	(+)
$[Coen_2(NH_3)(NO_2)]^{2+}$	(-)	(+)
$[Coen_2(NH_3)(NCS)]^{2+}$	(+)	(+)

He also pointed out that reactions which occur without metal ligand bond breakage, retain their original configuration. This can be used for relating configuration, although it is of limited value as the number of reactions occurring without metal ligand bond breakage is small. These include isothiocyanate - ammine conversions.

$$cis[Coen_2(NCS)_2]^+ \longrightarrow cis[Coen_2(NCS)(NH_3)]^{2+}$$

$$\longrightarrow cis\ [Coen_2(NH_3)_2]^{3+}$$

6. The Walden Inversion

Originally it was found by Bailar and Auten (9, 55) that the configuration of the product, $[Coen_2CO_3]^+$

formed by treating (-) $[Coen_2Cl_2]^+$ with carbonate ion depended on the nature of the carbonate ion. With mercury, potassium or insufficient silver carbonate the (+) $[Coen_2CO_3]^+$ ion was formed, but with excess silver carbonate the (-) $[Coen_2CO_3]^+$ ion was produced. Further it was found that the configuration of the product was dependent on the length of time the (-)$[Coen_2Cl_2]Cl$ solution was allowed to stand before reacting with silver carbonate. This suggests some form of aquo intermediate. Since Mathieu had shown that (-) $[Coen_2Cl_2]^+$ and (+) $[Coen_2CO_3]^+$ had the same sign for their circular dichroism it is likely that their configurations are the same. The following reaction sequence was suggested:

$$\begin{tikzcd}
\Lambda\ [Coen_2Cl_2]^+ \arrow[r, "dry\ Ag_2CO_3"'] \arrow[d, "H_2O"] & \Delta[Coen_2CO_3]^+ \arrow[d, "HCl\ (alc.)"] \\
\Lambda\ [Coen_2H_2OCl]^{2+} \arrow[d, "K_2CO_3"] & \Delta\ [Coen_2H_2OCl]^{2+} \arrow[d, "HCl\ (alc.)"] \\
\Lambda\ [Coen_2CO_3]^+ & \Delta\ [Coen_2Cl_2]^+
\end{tikzcd}$$

Very few inversions are found to take place, the other main example(8) being the reaction of l cis

$[Coen_2Cl_2]Cl$ in liquid ammonia where inversion is found to take place at low temperature.

$$\Lambda[Coen_2Cl_2]Cl + NH_3 \longrightarrow \Delta[Coen_2NH_3Cl]Cl_2$$

$$\Delta[Coen_2NH_3Cl]Cl_2 + NH_3 \longrightarrow \Delta[Coen_2(NH_3)_2]Cl_3$$

As the temperature increases the proportion of non inverted product increases.

The common factor to the two reactions is the use of a basic reagent. This was demonstrated by Dwyer who treated cis (-) $[Coen_2Cl_2]CH_3COO$ with two moles of silver ion followed by two moles of sodium hydroxide.(55) Since the dihydroxo product racemises quickly, the configuration was immediately frozen by the addition of carbonate which forms an optically stable product.

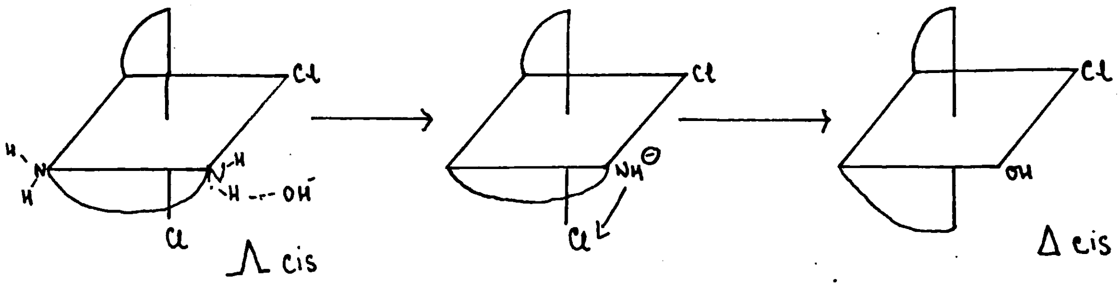
$$\Lambda[Coen_2Cl_2]^+ \xrightarrow[2OH^-]{} \Delta[Coen_2(OH)_2]^+ \xrightarrow[CO_3^{2-}]{} \Delta[Coen_2CO_3]^+$$

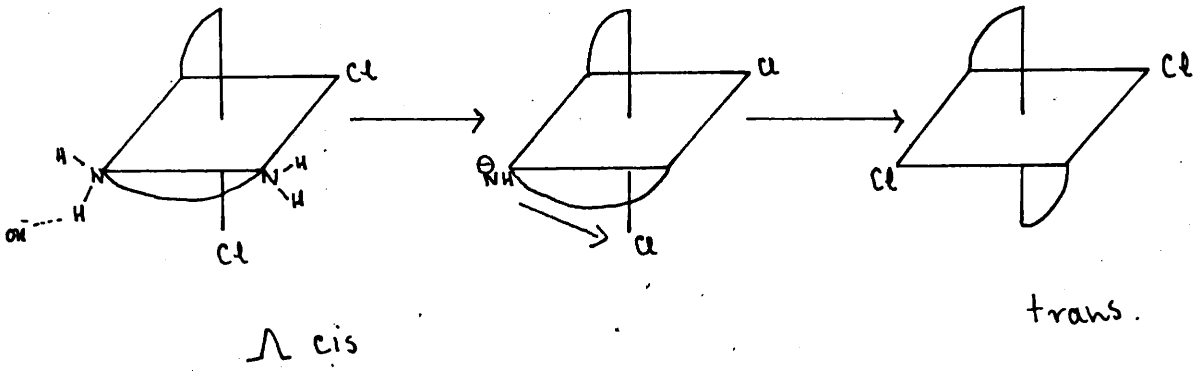
Inversion will occur also in the absence of silver ions if the concentration of base is sufficiently high.(3) Bailar suggested that the cause of inversion is the removal of a proton from the complex. If the complex has been in the solution long enough to aquate, the proton will be removed from the coordinated water and no inversion will occur.

$$\Lambda[\mathrm{Coen_2Cl_2}]^{+} + \mathrm{H_2O} \longrightarrow \Lambda[\mathrm{Coen_2(H_2O)Cl}]^{2+} + \mathrm{Cl}^{-}$$

$$\Lambda[\mathrm{Coen_2(H_2O)Cl}]^{2+} + \mathrm{OH}^{-} \longrightarrow \Lambda[\mathrm{Coen_2OHCl}]^{+} + \mathrm{H_2O}$$

If the proton is removed from the nitrogen of the coordinated ethylenediamine, this nitrogen may then move to an adjacent corner of the octahedron, displacing the chloride from the coordination sphere. The vacant position left by the nitrogen will be filled by the solvent hydroxide ions. The product will have either an inverted cis or a trans configuration depending on which nitrogen has lost a proton.



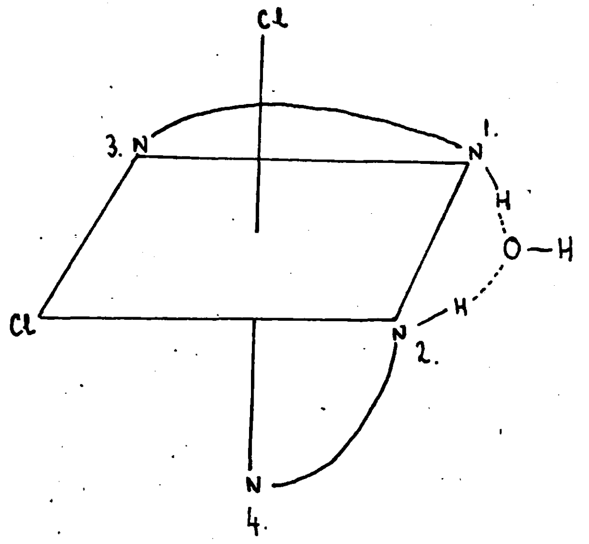


This invokes a new general mechanism for base hydrolysis at low base concentrations, whereby rapid aquation is followed by proton removal.

An alternative mechanism also suggested by Bailar(24) agrees with a normal S_N1CB process at low concentration but involves the formation of ion pairs at high hydroxide concentration.

The ion pair is visualised as being formed on the side of the complex which is more positive. Once the ion pair has been formed the reaction can proceed either by an S_N1CB mechanism or by an S_N2 mechanism. The intermediate is shown in Diagram 11.

Diagram 11: Intermediate ion pair to account for inversion



For an S_N1CB mechanism, a proton is extracted from either the N1 or N2 nitrogen with a simultaneous lengthening of the cobalt - chloride bond and hydroxide attack at the 1, 2 edge.

For an S_N2 mechanism a trans displacement is involved.

7. Racemisation Mechanisms in octahedral complexes

The rate of loss of optical activity varies greatly with the compound being considered. From the results of many investigations of racemisation two mechanistic pathways have been suggested, the intermolecular and intramolecular mechanisms.

Intermolecular Mechanism

During an intermolecular process, one of the ligands becomes completely dissociated.

$$M(AA)_3 \rightleftharpoons M(AA)_2 + AA$$

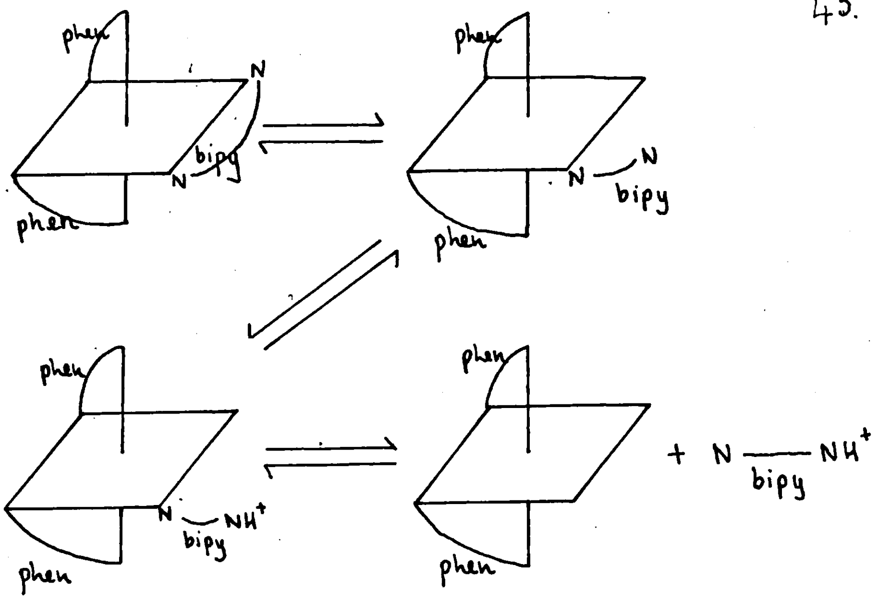
The formation of this intermediate allows rearrangement and thus loss of optical activity. If the rate of dissociation and racemisation are the same, then the two processes are accomplished by the same mechanism. At first sight the presence of excess chelating ligand might be expected to retard the racemisation rate. This is inconclusive, since if the intermediate was symmetrical or lost its activity very quickly it would be unaffected by excess chelating reagent.

This type of mechanism is used to explain the racemisation of several complexes, among them the tris-(1,10-phenanthroline)-nickel II, tris-(2,2' bipyridyl)-nickel II and the (2,2' bipyridyl)bis (1,10-phenanthroline) nickel II ions. For the homogeneous ligand nickel II complexes an optically inactive intermediate can be envisaged: (13)

$$(+)\ [Ni(AA)_3]^{2+} \rightleftharpoons \begin{array}{l}\text{optically}\\ \text{inactive}\\ \text{intermediate}\end{array} \rightleftharpoons (-)\ [Ni(AA)_3]^{2+}$$

The exact nature of the intermediate has not been defined. It is possible to imagine a cis diaquo complex, $[Ni(AA)_2(H_2O)_2]^{2+}$ which would racemise rapidly or the inactive trans diaquo complex.

For the (2,2' bipyridyl)bis(1,10-phenanthroline)nickel II ion, the mechanism suggested (18,19) for acid solutions involves a two-stage removal of the non rigid bipyridine ligand.



This two-stage process is impossible for the $[Ni(phen)_3]^{2+}$ ion since the rigid structure of 1,10-phenanthroline prevents it acting as a unidentate ligand and so, for an intermolecular process, the dissociation has to take place in one step.

The effect on the racemisation rate on changing the solvent has been studied(26) in the case of the tris-(1,10-phenanthroline)nickel II ion. In ethanol-water medium the racemisation at first decreased, then increased and finally decreased as the ethanol content was raised. Similar behaviour was found in methanol-water and acetone-water systems. When a graph of the entropy of activation $\Delta S^{\ddagger}$ against the energy of activation $\Delta H^{\ddagger}$ was plotted it was found to be linear.

This fits the relation:

$$\Delta H^{\ddagger} = \alpha + \beta \Delta S^{\ddagger}$$

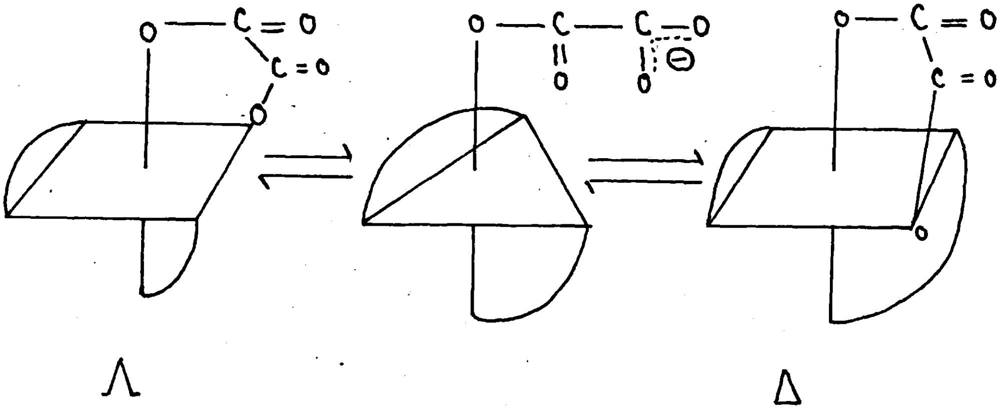
where β is defined as the isokinetic temperature and has the dimensions of absolute temperature. α is the measure of the intercept and has no physical meaning.

Leffler has shown(102)that, provided the mid-point of the temperature range was sufficiently different from β, then a linear relationship was diagnostic of the same mechanism irrespective of solvent. Since a dissociation mechanism is known to take place in aqueous solution it can be assumed that it takes place in all solvents, the mechanistic pathway not being a solvation process.

Intramolecular mechanism

a) Chelate ring cleavage mechanism

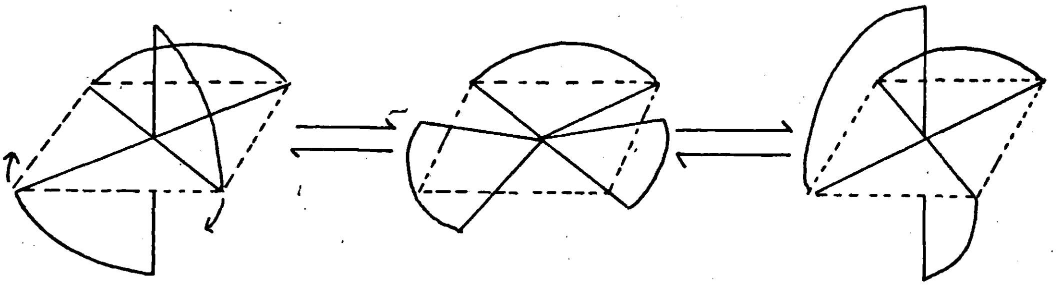
There is no complete dissociation of ligands during an intramolecular racemisation. This does not exclude a pathway where there is ring cleavage, the bidentate chelate functioning as a unidentate group. This idea has been used to explain(11) the racemisation of the ~~tris~~-oxalatochromium III ion, $[Cr(C_2O_4)_3]^{3-}$. It was found that the rate of oxalate exchange with unchelated carbon^{14} labelled oxalate was slower than the racemisation, suggesting an intramolecular mechanism. Further oxygen^{18} experiments showed that all 12 oxygens exchange with the solvent water and the rate of exchange is faster than the oxalate exchange but slower than the racemisation. The chelate ring must open and close several times before the departure of the oxalate group and this suggests that the racemisation takes place by chelate ring cleavage.



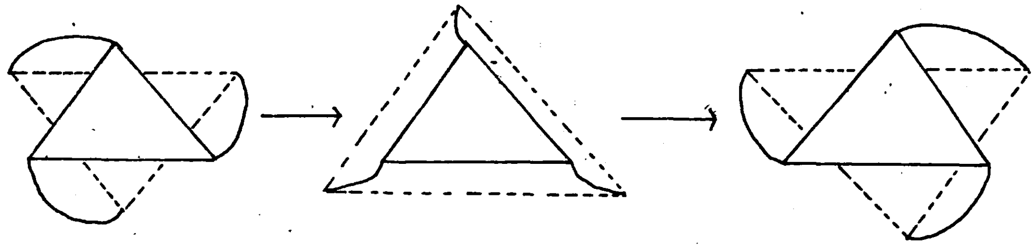
b) <u>Twist mechanism</u>

Three different intramolecular racemisation mechanisms not involving bond rupture have been postulated. (135).

The first of these was suggested by Rây and Dutt. Considering a tris bidentate chelate compound this mechanism can be imagined by fixing one of the rings in space and rotating the two remaining rings 90° in opposite directions about axes perpendicular to their respective planes and passing through the metal ion.

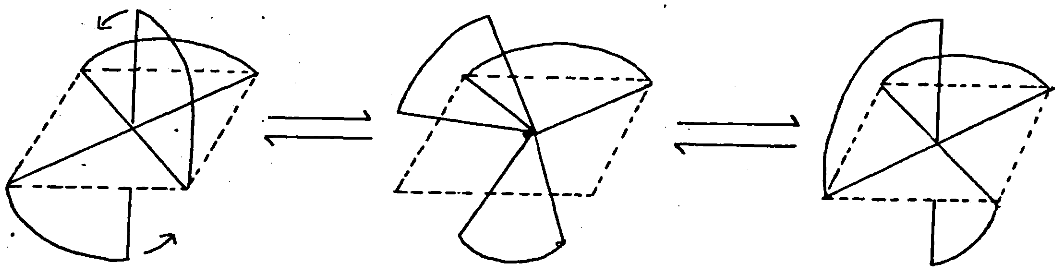


The Bailar (7) twist involves the rotation of the three metal donor bonds about the C_3 axis in a counterclockwise direction.



The main difference between these two twist mechanisms is that in the former the internal chelate ring angles do not change, but they do in the latter.

Much more recently Springer and Sievers (135) suggested a third mechanism. Here, while imagining one ring to remain stationary, the two remaining rings revolve past each other continually changing their planes. The front faces of the octahedron rotate through 120° simultaneously but independently about axes passing perpendicularly through their face centres.



Λ (C_2) TRANSITION STATE. Δ(C_2)

This is in contrast to the Rây and Dutt mechanism where the two rings rotate past each other in their own planes.

The Rây and Dutt mechanism and Springer and Siever mechanism do not allow change in the internal chelate ring angle and thus are found to be specific cases of the Bailar twist where changes in the ring angle occur.

There is no conclusive experimental evidence for distinguishing between the three mechanisms and it is likely that in reality the mechanism lies somewhere between the extreme cases discussed. For rigid chelate rings, as in the case of 1,10-phenanthroline a fixed chelate ring angle mechanism is preferred. Conversely the Bailar twist mechanism is more suitable for non-rigid chelates like 22' bipyridine.

Experimentally it is found that for tris-(1,10-phenanthroline)iron II ion racemisation is ten times faster than dissociation. A twist mechanism must be involved since 1,10-phenanthroline cannot function as a monodentate ligand. For the tris-(22' bipyridine)iron II ion,(14) racemisation is again faster than dissociation, suggesting racemisation proceeds both by inter-and intramolecular processes.

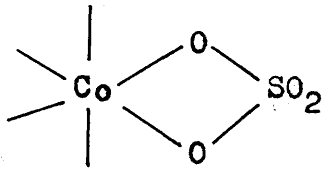
8. The Effects of ring formation on complex stability

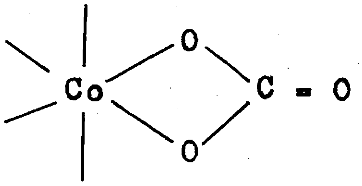
Chelated complexes are found to be more stable than their non chelated analogues. The equilibrium constant for the reaction:

$$ML_n + mX \rightleftharpoons mX_m + nL$$

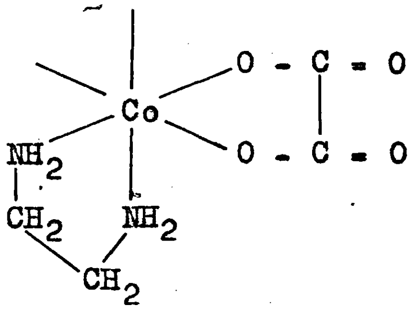
where n unidentate ligands are replaced by m multidentate ligands has been shown to be greater than unity.(17) The stability of complexes with related multidentate ligands also increases with the number of chelate rings formed, provided there are no restrictions introduced by steric strain.

Four-membered rings are relatively rare in mononuclear complexes due to the strain imparted by the unusual bond angles. They are found in the sulphato and carbonato groups complexes when these act as bidentate ligands.

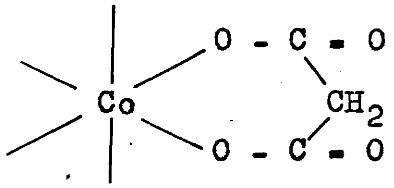




Generally five and six-membered rings are much more stable. Ethylenediamine itself forms a five-membered ring as also does the oxalate ion.



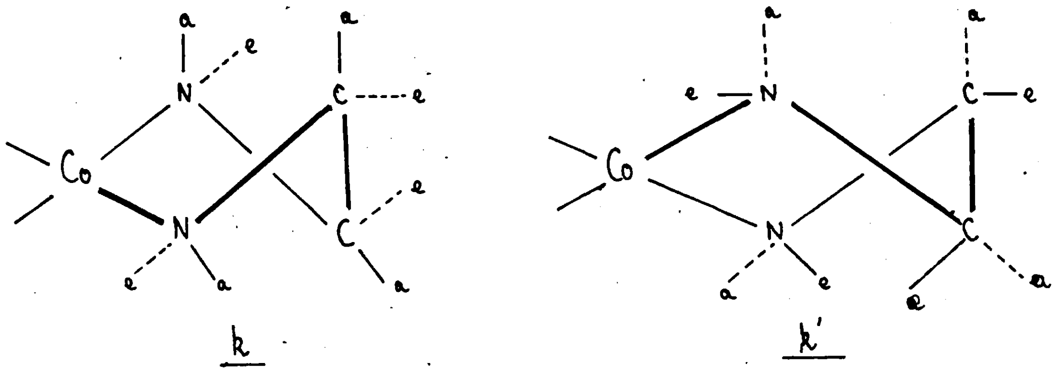
Commonly five-membered rings are more stable than six. Ethylenediamine and 1,2 diaminopropane complexes are more stable than those of 1,3 diaminopropane. By consideration of acid properties the planar oxalato ligand ring would also be expected to be more stable than the malonato ligand, its six-membered non-planar ring analogue.



In practice this is not always true due to the reducing properties of the oxalate group.

The most stable puckered conformation of the ethylenediamine ring allows the hydrogens on the adjacent ring atoms to be almost completely staggered, giving gauche conformations.(43) This tends to minimise the energy of the cyclic structure and outweighs the energy increase due to the diminution of the N - Co - N angle from the ideal 90° to 81°. Two conformations of the gauche form are possible.(128)

Diagram 12: Conformations of the ethylenediamine-cobalt ring



a and e show the axial and equatorial hydrogen atoms. These are mirror images and designated k and k'. Four possible combinations of the three ethylenediamine rings in $[Coen_3]^{3+}$ are possible. These are kkk, kkk', kk'k', k'k'k' and have different stabilities.

The physical evidence (65) for the conformations comes partly from X-ray crystallographic structural determinations. It was initially thought that infra-red studies on the variation in the stretching frequencies between axial and equatorial substituents would yield information. The infra-red evidence for the ethylenediamine complexes was found to be inconclusive although in favour of a gauche conformation. (65) This has been confirmed by X-ray diffraction studies on the $[Coen_3]^{3+}$

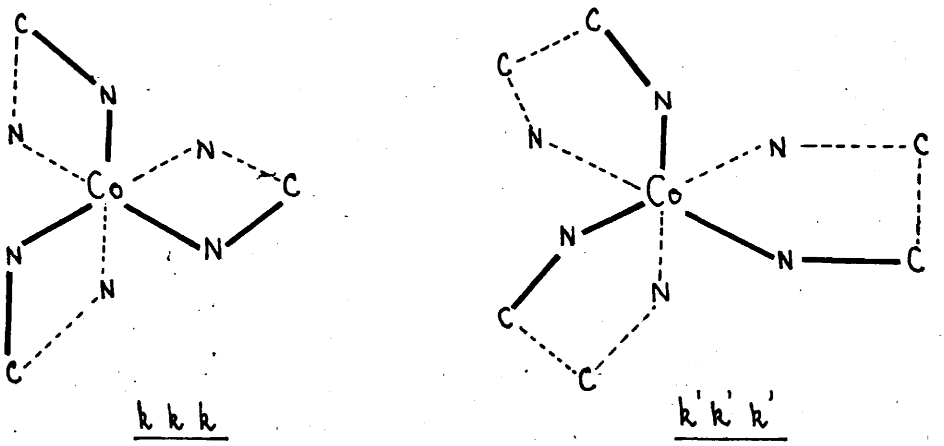
ion and on some trans $[Coen_2X_2]^+$ ions where X = Cl^-, Br^-. The conformations of the rings are found to be gauche and these, together with the actual conformations of the rings, are shown in Table 2.

TABLE 2

Compound	Conformation of diamine	Relation of rings
trans $[Coen_2Cl_2]Cl$	gauche	k k'
trans $[Coen_2Br_2]Br$	gauche	k k'
Δ $[Coen_3]Br_3H_2O$	gauche	kkk

Diagram 13 shows the kkk and k'k'k' forms of the Δ $[Coen_3]^{3+}$ ion. The kkk has been shown to be the more stable and this might be predicted since the non-bonded interactions between the axial hydrogens of the amino group and the ring carbons are smaller. The C-C axis is eclipsed in the k k k form and staggered in the k'k'k' form.

Diagram 13: The k k k and the k'k'k' forms of the $\Delta[Coen_3]^{3+}$ ion viewed along the three-fold axis of symmetry



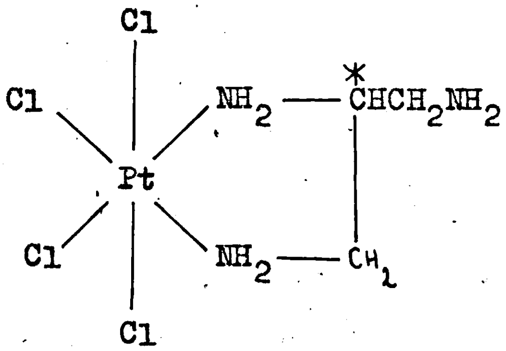
k k k   k'k'k'

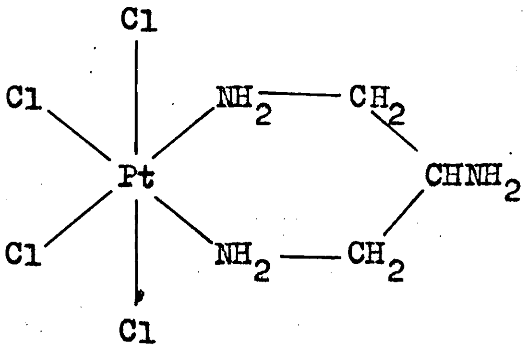
The reverse is found in the Λ $[Coen_3]^{3+}$ ion where the k'k'k' conformation is the most stable.

In a recent review by Sargeson(119) the use of NMR spectroscopy and circular dichroism in conformational analysis has been discussed. If the Δ $[Coen_3]^{3+}$ ion adopts the k k k conformation, the theoretical carbon proton spectrum should show three equivalent sets of A_2B_2 lines. In fact only one broad line is observed which is probably due to the complex being partly in the k k k' form in solution. The idea of a mixture of conformers has also been suggested to account for the presence of large positive and small negative circular dichroism bands associated with the first ligand field band in solution. However this explanation is at variance with the fact that the difference between the positive and negative circular dichroism bands for the Δ $[Co(+)pn_3]^{3+}$ ion is even larger. This ion is constrained to exist purely in the k k k form, showing that the Δ ion must give rise to both the positive and negative circular dichroism bands. If the k k k' form only gives rise to a positive curve the variation in magnitude of the negative band can be explained by assuming the presence of some k k k' form.

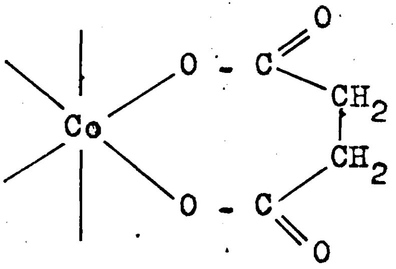
Similarly with the six-membered ring analogue the most stable conformation is the puckered chair form. In this case the hydrogens on adjacent atoms are less well staggered and interactions between axial and equatorial hydrogens are significant. This destabilisation factor outweighs the fact that the N - Co - N angle is not forced from 90°.

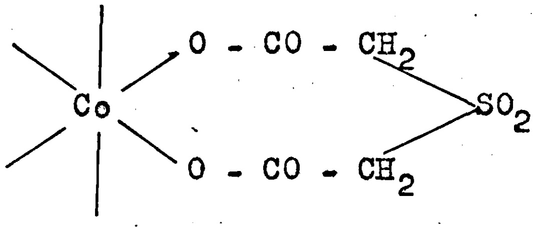
In practice it is found that if a ligand theoretically has the alternative of forming either a five or six-membered ring, the five-membered ring is formed. This was shown by the resolution (104) of 1,2,3,triaminopropanetetrachloroplatinum IV. The smaller ring has an asymmetric carbon whereas the larger one is symmetrical.





Seven and eight-membered rings are very uncommon in aqueous solution, although there are reports of succinato (49) and sulphonyldiacetato (125) complexes.





All attempts to repeat this work failed due to the formation of polymeric oils. In non-aqueous solution, such as alcohol it has been possible to isolate chelate rings with up to nine-members. This dependency of ring size on solvent occurs since water is a sufficiently good coordinating agent to prevent the formation of large unstable rings. The instability of the ligands of the diamine series can be predicted due to the compressions and eclipsing of the hydrogens on adjacent ring atoms which would be introduced.

9. Substitution Mechanisms in octahedral complexes

The theory of the mechanisms of substitutions in octahedral complexes was first developed by Ingold (83) as an extension to his theories applying to a tetrahedral carbon atom. The system was likened to nucleophilic substitution at a saturated aliphatic carbon atom. Thus the substitution can be stoichiometrically represented as:

$$M\text{-}X + Y^- \longrightarrow M\text{-}Y + X^-$$

where M-X represents the metal complex, M being the metal centre and Y^- the attacking nucleophile. Mechanistically the substitutions were divided into two classes, the S_N1 [substitution nucleophilic unimolecular] and the S_N2 [substitution nucleophilic bimolecular]. In the former a slow rate determining heterolysis is followed by the rapid addition of the substituting nucleophile.

$$M\text{-}X \longrightarrow M^+ + X^-$$

$$M + Y^- \longrightarrow MY$$

In the latter the reaction takes place in one bimolecular step involving the partial formation of a new metal-ligand bond synchronous with the weakening of the bond joining the metal to the departing nucleophile.

$$Y^- + M\text{-}X \longrightarrow Y\ldots M\ldots X \rightarrow YM + X^-$$

In an S_N2 substitution, the rate of substitution should be dependent on the nucleophilic character of the incoming ligand, Y^-, whereas in an S_N1, the rate should be independent of Y^-.

Ideas of mechanism can be obtained by studying the change in rate by varying the structure of the complex, by following the stereochemical course, by isotopic labelling and by changing the solvent.

These ideas were developed and extended by Basolo and Pearson (17), since reactions often occurred which appeared to fit a mechanism intermediate between the two extremes. Thus the classification was enlarged to four classes:

a) S_N2. The rate step involves equal bond breaking in M-X and bond making in M-Y.

b) S_N2 (lim). The rate step only involves bond making as in M-Y.

c) S_N1 (lim). Definite evidence for an intermediate of reduced coordination number can be found.

d) S_N1. Definite evidence of an intermediate of reduced coordination number cannot be found but requirements for a dissociative process are otherwise fulfilled.

Recently, mechanistic ideas concerning these substitutions have been widened in the work of Langford and Gray. (98) The classification so far developed has been based on the molecularity of the rate determining step in the overall stoichiometry. This emphasises the importance of the molecularity which may not be the most significant feature of the reaction. In a bimolecular reaction in solution, the reacting molecules are caught together in a solvent cage during rapid energy transfer. The system cannot be expected to remain in this highly activated state for more than one exchange. This is called a case of 'accidental bimolecularity' since the new ligand happens to occupy the appropriate place in the solvation shell and may not necessarily have made any contribution to the activation energy of the reaction. Therefore it is possible to have a mechanism which is bimolecular in the stoichiometric sense but which is related to a unimolecular case since the intimate mechanism seems to be more like a unimolecular process.

The mechanistic scheme has been based on the type of stoichiometry which is important in ligand substitutions. Three possible pathways can be envisaged:

a) Dissociative D. The leaving ligand is lost in the first step producing an intermediate of reduced coordination number which may be detected by its selective reactivity.

b) Associative A. The entering ligand adds in the first step forming an intermediate of increased coordination number.

c) Interchange I. The leaving group is moving from the inner to outer coordination sphere at the same time as the entering group is moving from outer to inner. There is no intermediate where the primary coordination number of the metal is modified.

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

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

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

The interchange process is divided into two subdivisions. Associative Interchange, I_a, occurs when the activation energy is mostly affected by the incoming ligand. Dissociative Interchange, I_d, occurs when the activation energy is not affected by the incoming ligand.

This nomenclature can be seen to correspond closely to the previous one. Thus the D mechanism corresponds to the S_N1(lim) and the A mechanism to the S_N2(lim). In the more recent nomenclature emphasis has been moved not only from the molecularity of the reaction but also from the nucleophilicity of the attacking ligand. Although the majority of substitutions are nucleophilic there is always the possibility of back donation of electrons from the metal, provided there are empty orbitals on the ligand, which makes the electronic movement a two way process.

10. Substitution Mechanisms in cobalt III complexes

For cobalt III complexes in aqueous solution it is found that for all anions, other than the hydroxide ion, the substituting rate is independent of the substituting nucleophile. For every system examined the reaction proceeds through two steps. In the first step the original ligand is replaced by a water molecule, an acid hydrolysis reaction. In the second step the coordinated water is replaced by a ligand, an anation reaction.

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + X^-$$

$$[Co(NH_3)_5H_2O]^{3+} + Y^- \longrightarrow [Co(NH_3)_5Y]^{2+} + H_2O$$

In no case has an anionic ligand been replaced directly by another without going through an intermediate aquo complex.

Hydroxide substitution

For cobalt III complexes in aqueous solution it is found that the hydrolysis rate is accelerated greatly by the presence of hydroxide ion, even when the ion is present in low concentration. In investigations of monosubstitutions with hydroxide ion, the reaction is found generally to have overall second order kinetics, first order with respect to complex and first order with respect to hydroxide.

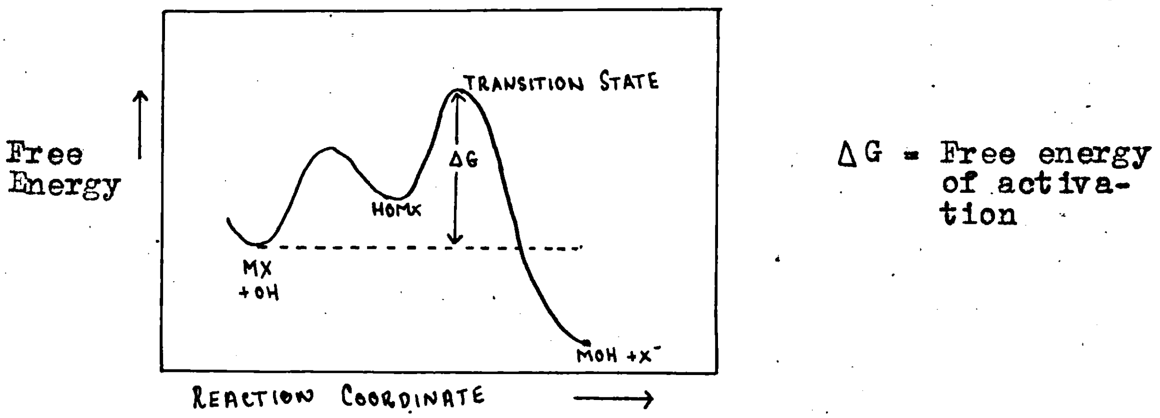
One mechanism, first suggested by Ingold and his associates,(84,138) is a bimolecular process whereby the hydroxyl ion displaces the X group. This can be classified either as an S_N2(lim), the A process or as an S_N2, the I_a process.

$$OH^- + [Co(NH_3)_5X]^{2+} \longrightarrow [HO...Co(NH_3)_5...X]^+ \longrightarrow [Co(NH_3)_5OH]^{2+} + X^- \quad (1)$$

Rate = $k_2[OH^-][complex]$

A distinction can be made between the I_a and A process by consideration of the energy profile.

<u>Diagram 14:</u> <u>Energy profile for an associative type of reaction of the type $OH^- + MX \longrightarrow HOMX \longrightarrow MOH + X^-$</u>



The intermediate can only be detected if it is stable enough to accumulate. If the concentration of either of the reactants is increased, then a position will be reached where all the complex will be converted into the intermediate. The reaction will now be unimolecular, since the decomposition of the intermediate will now be observed. At high concentrations departure from second order kinetics will be observed and the limiting law will be a first order process. This is diagnostic of an A process where the only other possibility is an I_a process. For this there will be no accumulation of intermediate and so no departure from second order kinetics.

Another mechanism, first proposed by Garrick,(18,64) suggests a rapid deprotonation of the complex to form the conjugate base, followed by a slow heterolysis resulting in the formation of a five coordinate intermediate. With the rapid addition of water, the product is then formed.

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{K}{\rightleftharpoons} [Co(NH_3)_4NH_2X]^+ + H_2O \qquad (2)$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow{k} [Co(NH_3)_4NH_2]^{2+} + X^- \qquad (3)$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \longrightarrow [Co(NH_3)_5OH]^{2+} \qquad (4)$$

This is the S_N1CB mechanism, a dissociative D process. Further if the conjugate base reacts directly with water, then an S_N2 CB mechanism results.

$$[Co(NH_3)_4NH_2X]^+ + H_2O \longrightarrow [Co(NH_3)_5OH]^{2+} + X^-$$

A second order kinetic form can also arise from a conjugate base mechanism.

From (3)

$$\text{Rate} = k\,[\text{conjugate base}]$$

From (2)

$$[\text{Conjugate base}] = K\,[\text{Conjugate acid}]\,[OH^-]$$

Also,

$$[\text{Total complex}] = [\text{Conjugate acid}] + [\text{Conjugate base}$$

$$[\text{Conjugate base}] = K[OH^-][\text{Total complex} - \text{conjugate base}]$$

$$= \frac{K[OH^-][\text{Total complex}]}{1 + k[OH^-]}$$

Therefore,

$$\text{Rate} = \frac{k\,K[OH^-][\text{Total complex}]}{1 + K[OH^-]}$$

When $K\,[OH^-] \ll 1$,

$$\text{Rate} = k\,K\,[OH^-]\,[\text{Complex}]$$

The expected first order kinetics with respect to hydroxide are obtained. However, when the hydroxide concentration is put up so that $K\,[OH^-] \gg 1$

$$\text{Rate} = k\,[\text{Complex}]$$

All the complex is in the form of the conjugate base and a first order limiting law is obtained.

In aqueous solution solvent participation is an integral part of any substitution reaction due to its good coordinating ability.

Experiments by Tobe(139) carried out in non aqueous solvents have elucidated the mechanistic ideas of solvent participation in the reaction. It was hoped that by using non aqueous solvents,participation of the solvent in the substitution would be eradicated. The substitution was found to be dependent on the formation of outer sphere complexes. In order to find the molecularity of the reaction the concentration of the entering anion must be such that the reaction of the free ion can be measured. Providing the entering anion is in sufficiently low quantities so that only the free complex and a 1:1 outer sphere complex is present,extrapolation of the results can lead to molecularity determinations. If there is a pathway dependent on the entering group, the reaction is bimolecular,but if an independent pathway is found the reaction may be unimolecular. The same ambiguity concerning unimolecularity arises in non aqueous as in aqueous solvents. For the exchange reaction of the dichlorobisethylenediamine cobalt III ion in methanol, a term in the rate law is found involving only the free ion. Since the lability of the methanol is insufficient to allow the complex to be an intermediate in the substitution, a genuine unimolecular reaction is being followed.

11. Experimental Mechanistic Evidence

Clearly the mechanisms cannot be distinguished by kinetic measurements alone.

For amine complexes containing N - H bonds, the rate of base hydrolysis is often as much as 10^6 times faster (16) than the hydrolysis in acid. This supports an S_N1CB mechanism since, when there are no acidic protons present, the rate of base hydrolysis is very slow. The base hydrolysis rate for the trans dinitro 2 2'.bisbipyridinecobalt III ion is independent of base concentration.

Further evidence for the S_N1CB mechanism is found from the fact that in general the rate of hydrogen exchange (16) is found to be about 10^5 times faster than the rate of hydrolysis supporting a rapid deprotonation equilibrium.

However, work done on the exchange in hexamminocobalt III and oxalatotetramminocobalt III ions does not support this conclusion. (22) The loss of deuterium from $[Co(ND_3)_6]^{3+}$ and $[Co(ND_3)_4(C_2O_4)]^+$ was studied and found to be specifically catalysed by hydroxide ion.

In general,

$$XND_2D^{n+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XND_2^{(n-1)+} + OHD \qquad (5)$$

$$X = [Co(ND_3)_5],\ n = 3$$

$$= [Co(ND_3)_3(C_2O_4)],\ n = 1$$

$k_1 \gg k_{-1}$ since the reaction is first order with respect to hydroxide ion. The reversal of equation (5) can involve not only OHD but also OHH, and since [OHH] $\gg$ [OHD], the equation cannot be a preequilibrium but must be the rate controlling step.

When the reaction is carried out in dry dimethyl sulphoxide, (121) there is good evidence for a five coordinate intermediate species. For the reaction of the type

$$\text{trans } [Coen_2NO_2Cl]^+ + Y^- \longrightarrow \text{trans } [Coen_2NO_2Y]^+ + Cl$$

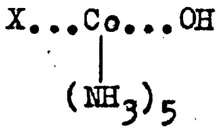
$$Y^- = NO_2^-,\ CNS^-,\ N_3^-$$

only catalytic amounts of hydroxide are needed to cause a rapid reaction. For a given concentration of hydroxide, the reaction is independent of the concentration of the nucleophile in the system. Also the reaction between trans $[Coen_2NO_2OH]^+$ and Y^- is slow. This suggests that all three reactions go through the common intermediate $[Coen(en\text{-}H)NO_2]^+$.

However the extrapolation of this evidence to aqueous solutions is questionable.

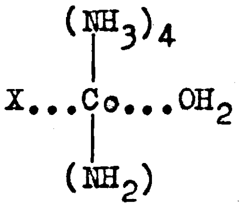
Although the conjugate base may be sufficiently long lived in non-hydroxylic solvents, it has been suggested (39) that in water, proton transfer from the solvation sphere would take place sufficiently rapidly to prevent dissociation, since the proton can move via the Grotthuss process without displacing a water molecule.

Oxygen ^{18} studies on the halopentammine-cobalt III ions, $[Co(NH_3)_5X]^{2+}$, also support the S_N1CB mechanism for chlorine, bromine and iodine and the S_N2CB mechanism for fluorine. (72) It was found that the final $O^{16}:O^{18}$ ratio in the product was independent of X. If an S_N2 or S_N2CB mechanism occurs, the composition of the respective intermediates will cause the isotopic fraction to vary.



$$X\ldots\underset{(NH_3)_5}{\underset{|}{Co}}\ldots OH$$

S_N2



$$X\ldots\underset{(NH_2)}{\underset{|}{\overset{(NH_3)_4}{\overset{|}{Co}}}}\ldots OH_2$$

S_N2 CB

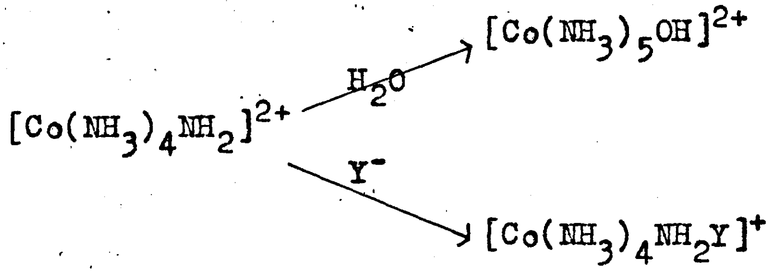
where X = F

Only in the case of fluorine was this found.

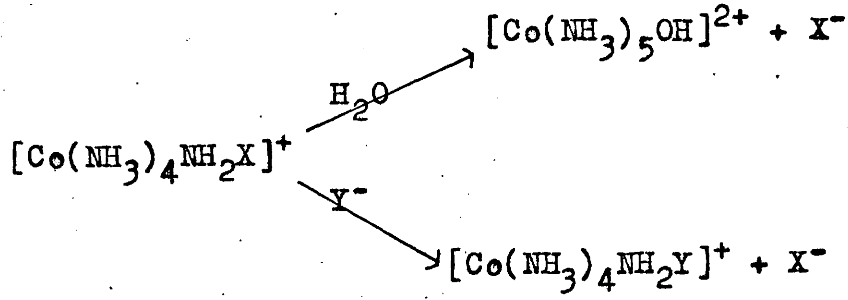
Studies on the acid hydrolysis (73) of $[Co(NH_3)_5N_3]^{2+}$, suggested that the formation of a five coordinate intermediate $[Co(NH_3)_5]^{3+}$ accounted for both the formation of some $[Co(NH_3)_5X]^{2+}$, where $X^- = Cl^-$, Br^-, NO_3^-, SCN^-, and the increase in rate in the presence of X^-. However, studies (119) on the change in molar absorbencies as the reaction proceeds showed that no competition reaction took place, the formation of $[Co(NH_3)_5X]^{2+}$ being due to the rapid anation of the aquo complex. The intermediate $[Co(NH_3)_5]^{3+}$ is less stable than the intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ formed during the base hydrolysis. Evidence for the conjugate base intermediate has been obtained from competition studies.

Experiments (32) carried out on the substituted cobaltpentammines, $[Co(NH_3)_5X]^{2+}$ where $X^- = Cl^-$, Br^-, I^-, NO_3^-, in the presence of added anions, $Y^- = N_3^-$, SCN^-, CH_3COO^-, SO_4^{2-}, PO_4^{3-} was found to lead to the formation of some $[Co(NH_3)_5Y]^{2+}$. The ratio of the two ions $[Co(NH_3)_5Y]^{2+}$:$[Co(NH_3)_5OH]^{2+}$ was found to be independent of the hydroxide concentration and dependent on the concentration of Y^-. This result suggests an S_N1 CB mechanism and not an S_N2 or S_N2 CB mechanism where there should be some dependency on the leaving group X^-.

S_N1 CB



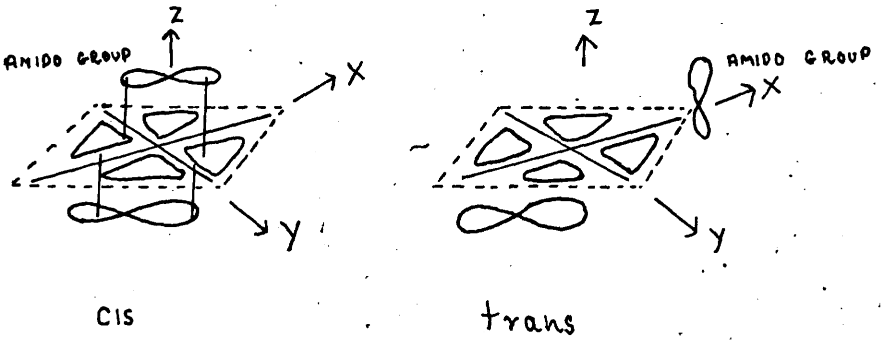
S_N2 CB



The S_N2 mechanism leads exclusively to the hydroxo product.

The fast S_N1 CB mechanism can be ascribed (120) to repulsive π type interaction between the filled p orbitals of the nitrogen in the amido group and the filled d_{xy} type orbitals on the metal atom. This repulsion provides the driving force for, say the loss of chloride in the cis and trans $[Coen_2Cl_2]^+$.

More recently quantum mechanical arguments have been suggested (36) in evidence for an S_N2 mechanism. This work has been carried out on the cis and trans $[Coen_2Cl_2]^+$ ions. It is found that the trans complex reacts faster than the cis. For the conjugate base intermediate there would be interaction between the filled p orbitals of the nitrogen on the amido group and the filled d_{xy} orbital on the metal ion.



This would provide the driving force for the departing chloride and it would be expected that the trans compound would react more slowly than the cis as the π type of interaction cannot be developed and transmitted in the former. Therefore the driving force has been postulated to originate from the two filled non σ bonded p orbitals of the inert chloride.

Rates of hydroxide substitution were measured (39) in the series $[Co(NH_3)_5X]^{2+}$ where $X^- = F^-, Cl^-, Br^-, I^-$

and it was found that the order of the rates was $F^- < Cl^- < Br^- < I^-$ which is the same order as is found in substitution at a saturated aliphatic carbon atom. As the substitution in these carbon systems is thought to go by an S_N2 process, the cobalt substitution was thought to go by a similar process.

12. The S_N2 ion pair mechanism

An S_N2 ion pair mechanism has also been suggested for the hydrolysis of the $[Co(NH_3)_5Cl]^{2+}$ ion, the $[Co(NH_3)en_2Cl]^{2+}$ ion and for the $[Co(NH_3)trienCl]^{2+}$ ion. (37)

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{K}{\rightleftharpoons} ([Co(NH_3)_5Cl]^{2+}\ OH^-)$$

$$([Co(NH_3)_5Cl]^{2+}\ OH^-) \xrightarrow[slow]{k} ([Co(NH_3)_5OH]^{2+}Cl^-)$$

$$([Co(NH_3)_5OH]^{2+}\ Cl^-) \xrightarrow[fast]{} [Co(NH_3)_5OH]^{2+} + Cl^-$$

from which the following rate law was calculated, assuming the hydroxide was in large excess;

$$\frac{1}{k_{obs}} = \frac{1}{K\ k\ [OH']} + \frac{1}{k}$$

The standard rate plot of $k_{obs.}$ against hydroxide showed a departure from linearity at very low base concentrations (0·03M). The plot of the reciprocal of the observed rate constant against the reciprocal of the hydroxide concentration gave a straight line and this was understood as being diagnostic of ion pair formation. The rate law would also fit a dissociative process, the value of K being the acid dissociation constant. The value of K was found to decrease along the series $(NH_3)_5$, $(NH_3)(en)_2$, and (NH_3)(trien). It was suggested that this supports an ion pair mechanism since the increase in the size of the molecule will decrease the possibility of ion pair formation. From examination of molecular models it becomes apparent that the increase in chelation has little effect on the accessibility of the reaction site, the region of the Co - Cl bond, to the hydroxide, where the actual exchange must take place. The citation of the ion pair formation constants of the $[Coen_3]^{3+}$ being smaller than those for the $[Co(NH_3)_6]^{3+}$ complex are of little relevance, since they both have higher charge and no one dominant reaction site for the formation of the ion pair. Therefore for an ion pair mechanism the K values should not vary significantly.

It was also argued that a conjugate base mechanism would require the reverse order of change in the value of K, the acid ionisation constant. These would be expected to increase with increase in chelation. The evidence for this hypothesis is from platinum IV complexes, where the constants are measurable, and also from the rate of deuterium exchange being greater for the $[Coen_3]^{3+}$ complex than for the $[Co(NH_3)_{6\cancel{5}}]^{3+}$. There is no direct evidence for the acidity constant for the pentammine series, although it is generally accepted that the value cannot be greater than 10^{-14}. The presence of an ammonia group in each of the three complexes cis to the reaction centre might be expected to govern the base formation and so the values of K would again be expected to be approximately constant. The actual value of the observed rate constants increases markedly along the series $(NH_3)_5$, $(NH_3)(en)_2$, $(NH_3)(trien)$.

The values of K could be considered to remain approximately constant (4·1 to 2·1), the small variations being due to the difference in the ligands altering the environment and not altering any fundamental concept of the course of the reaction. This does not help distinguish between the two mechanisms being considered.

A further possibility in considering ion pair formation is the role of the non coordinating perchlorate ion which is present in order to maintain the ionic strength constant. It has been suggested by Winstein (148) that the leaving group in the ion pair is replaced by perchlorate, thereby stabilising the intermediate for solvolysis. This produces a specific acceleration due to the perchlorate.

$$\begin{tikzcd}
{[(NH_3)_5Co\text{-}Cl]^{2+}} \arrow[r, leftrightharpoons] & (NH_3)_5Co^{3+}\ldots Cl^- \arrow[r, leftrightharpoons, "ClO_4^-"] & (NH_3)_5Co^{3+}\ldots ClO_4^- + Cl^- \arrow[d, "OH^-"] \\
 & & {[(NH_3)_5Co(OH)]^{2+}}
\end{tikzcd}$$

If this theory and the reaction mechanism proposed by Chan are both valid, a retardation should be found, relative to the rate in the presence of perchlorate, by carrying the reaction out in the presence of other anions, e.g. chloride or bromide, these being necessary to keep the ionic strength constant. Furthermore these rates should be the same.

Throughout the work by Chan there is no mention of the complex concentration. The assumption that in 0·03M hydroxide the hydroxide is present in large excess is non-verifiable. This is an essential assumption to the production of the rate law.

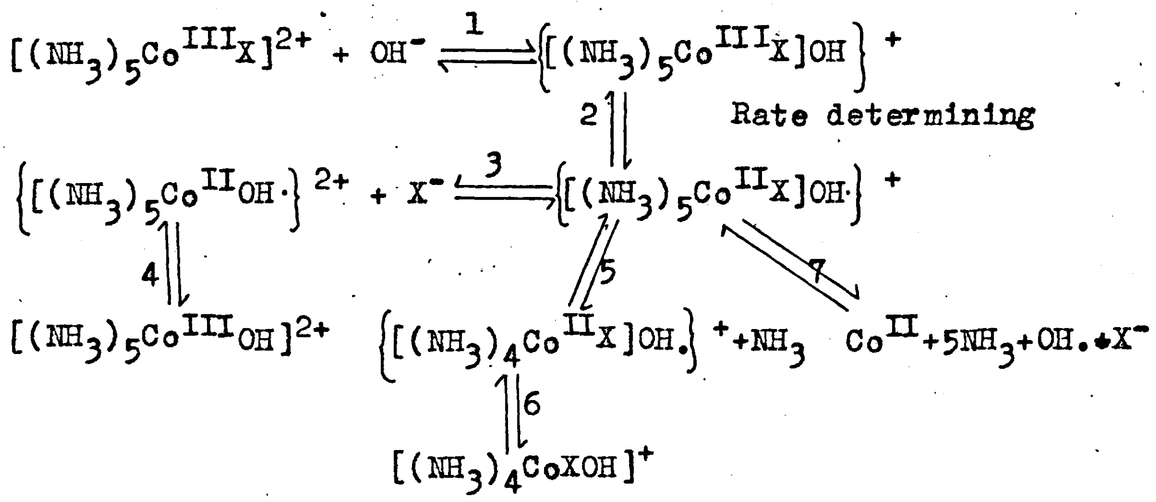
Further, there is always the possibility that a consecutive reaction is going on, resulting in the formation of ammonia and cobalt III hydroxide.

$$[Co(NH_3)_5Cl]^{2+} + 3OH^- \longrightarrow Co(OH)_3 + 5NH_3 + Cl^-$$

This has been found in other base hydrolyses of the cobaltpentammines, notably the $[Co(NH_3)_5NO_2]^{2+}$. (99)

13. The Electron Transfer Mechanism

In a recent paper (67) by Gillard all the evidence in support of an electron transfer mechanism has been assembled. He suggests that the rate determining step in the reaction is the formation of a cobalt II intermediate with a hydroxyl radical.



$$\begin{tikzcd}
{[(NH_3)_5Co^{III}X]^{2+} + OH^-} \arrow[r, shift left, "1"] & {\left\{[(NH_3)_5Co^{III}X]OH\right\}^+} \arrow[l, shift left] \arrow[d, shift left, "2", "\text{Rate determining}"'] & \\
{\left\{[(NH_3)_5Co^{II}OH\cdot]\right\}^{2+} + X^-} \arrow[r, shift left, "3"] \arrow[d, shift left, "4"'] & {\left\{[(NH_3)_5Co^{II}X]OH\cdot\right\}^+} \arrow[l, shift left] \arrow[u, shift left] \arrow[d, shift left, "5"] \arrow[dr, "7"] & \\
{[(NH_3)_5Co^{III}OH]^{2+}} \arrow[u, shift left] & {\left\{[(NH_3)_4Co^{II}X]OH.\right\}^+ + NH_3} \arrow[u, shift left] \arrow[d, shift left, "6"] & {Co^{II} + 5NH_3 + OH. + X^-} \\
& {[(NH_3)_4CoXOH]^+} \arrow[u, shift left] &
\end{tikzcd}$$

The mechanism is dependent on the initial formation of ion pairs and the electron transfer could be expected to be hindered by the presence of solvent.

Reactions 5 and 6 are found not to take place, the predominant path being 3 and 4, whilst sometimes path 7 has been shown to exist.

However, he points out that hydroxyl radicals would not be expected to exist freely in solution, only in cases where reaction 7 is known to take place. When ammonia is liberated, such as during the hydrolysis of the benzoatopentamminecobalt III, free radicals would be expected. It might be possible to confirm the presence of these by electron spin resonance studies. The presence of radicals has been looked for in many reactions of this type and not been found. (71) This does not (47) necessarily mean radicals are absent since if they were very short-lived and in low concentration they would be undetectable by electron spin resonance.

The rate determing step involves electron transfer from the hydroxyl ion to the cobalt, the ease of transfer depending on the ease of reduction of the Co(III) to cobalt(II). The electron affinities for Cr(III), Co(III), Ru(III) and Rh(III) are given on page 97.

Co(III) having the highest value would be expected to react fastest which is indeed what is found. However, it is also found that Ru(III) reacts considerably faster than Rh(III) which is unexpected from the values of electron affinity. See page 97.

14. Stereochemical change accompanying substitutions

Stereochemical changes are often observed during substitution reactions. Racemisation, isomerisation, retention and inversion have all been observed. Examples of these are given in Table 3 (page 81). It can be seen that in basic substitution, rearrangement always occurs, unlike aquation where retention is fairly common. The analysis of the products is complicated since the products themselves may undergo racemisation and isomerisation. However, if the ratio of the isomeric products does not change during the course of the reaction, the ratio observed is a direct consequence of the substitution.

These results can be analysed using either an S_N1 dissociative mechanism or an S_N2 associative mechanism.

TABLE 3

Steric course of some substitution reactions. (17, 118)

Reactant	Reagent	Product	% cis product		
			$\Lambda + \Delta$	Λ	Δ
cis$[Coen_2NO_2Cl]^+$	H_2O, $HClO_4$	$[Coen_2NO_2H_2O]^{2+}$	100		
trans$[Coen_2NO_2Cl]^+$	H_2O, $HClO_4$	$[Coen_2NO_2H_2O]^{2+}$	-		
trans$[Coen_2NCSBr]^+$	H_2O	$[Coen_2(H_2O)NCS)]^{2+}$	45		
cis$[Coen_2(NO_2)Cl]^+$	OH^-	$[Coen_2(NO_2)OH]^+$	66		
trans$[Coen_2(NO_2)Cl]^+$	OH^-	$[Coen_2(NO_2)OH]^+$	6		
cis$[Coen_2(NH_3)Cl]^{2+}$	OH^-	$[Coen_2(NH_3)OH]^{2+}$	84		
trans$[Coen_2(NH_3)Cl]^{2+}$	OH^-	$[Coen_2(NH_3)OH]^{2+}$	76		
Λ cis$[Coen_2(OH)Cl]^+$	OH^-	$[Coen_2(OH)_2]^+$		61	36
trans$[Coen_2(OH)Cl]^+$	OH^-	$[Coen_2(OH)_2]^+$	94		
Λ cis$[Coen_2Cl_2]^+$	OH^-	$[Coen_2Cl(OH)]^+$		21	16
trans$[Coen_2Cl_2]^+$	OH^-	$[Coen_2Cl(OH)]^+$	5		
Λ cis$[Coen_2(NCS)Cl]^+$	OH^-	$[Coen_2(NCS)OH]^+$		56	24
trans$[Coen_2(NCS)Cl]^+$	OH^-	$[Coen_2(NCS)OH]^+$	76		
trans$[Coen_2ClBr]^+$	OH^-	$[Coen_2Cl(OH)]^+$	5		

S_N2 mechanism

This mechanism leads to the production of a seven coordinate intermediate which can be visualised as a pentagonal bipyramid. The stereochemistry will be determined by the initial direction of the attack of the entering group. The attacking group, Y, can either attack adjacent to the departing group, cis attack, or opposite to the departing group, trans attack. The effect of this on an optically active isomer is shown in Figure 2. A cis attack leads to retention of configuration whereas during a trans attack re-arrangements are possible. If the attack by Y takes place at a trans edge, then the group already at that position, A, must shift to the position being vacated by the leaving group X.

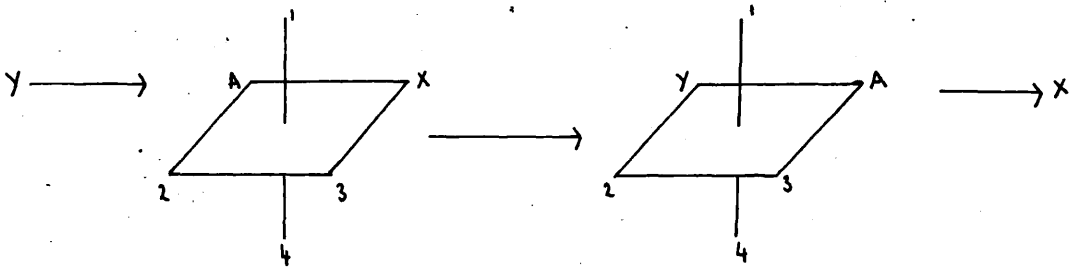
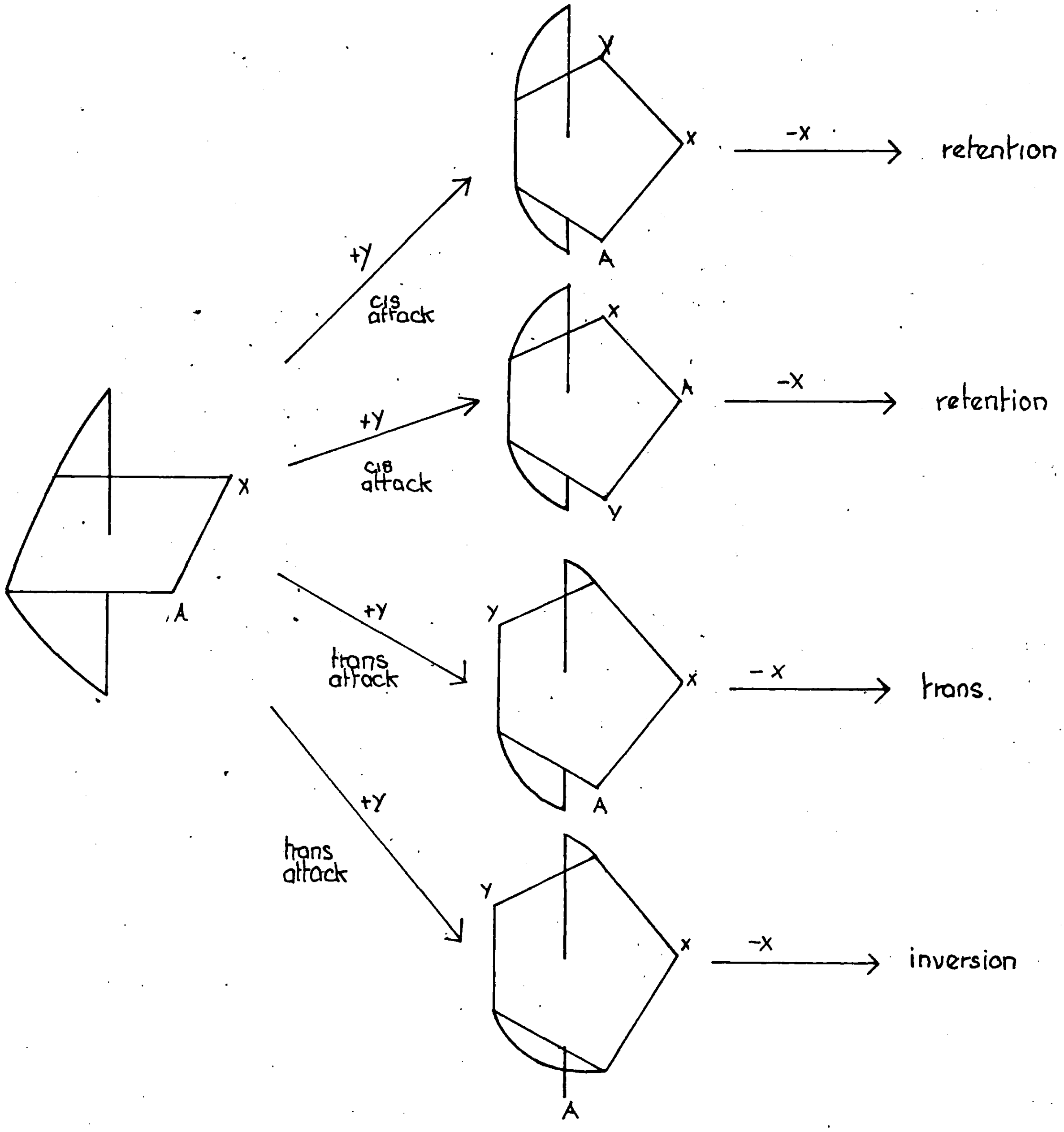


FIGURE 2.

BIMOLECULAR SUBSTITUTION INTO AN OPTICALLY ACTIVE ISOMER.



This process, implicit in an S_N2 reaction, was called 'edge displacement' by Brown, Ingold and Nyholm. (31) The stereochange is not affected by the positions of Y, A and X but only by the position of some unaffected group. The position of X and Y relative to this group determines whether the compound is called d or l, cis or trans. There is no fundamental difference between the conversions d $\rightleftharpoons$ l, cis $\rightleftharpoons$ trans. Considering the unaffected group B, then

a) If B is at 1. d $\rightleftharpoons$ l (if compound optically active as in $[Coen_2X_2]^+$)

b) B is at 2. trans ⟶ cis.

c) B is at 3. cis ⟶ trans.

d) B is at 4. d $\rightleftharpoons$ l.

Edge displacement can also explain lack of stereochange, since if the groups at 1 and 4 can be superposed by rotation then there will be no stereochange.

The relative rates of substitution in the reaction :-

$$[Coen_2AX]^{n+} + OH^- \longrightarrow [Coen_2AOH]^{n+} + X^-$$

where X = Cl^-, Br^-.

A = OH^-, N_3^-, NCS^-, Cl^-, NO_2^-, NH_3.

have been rationalised (85) by considering the inductive, electromeric and conjugative effects of the non-labile orientating group A. Thus the strong electron withdrawing properties of the NO_2^- and N_3^- result in a slow cis substitution with retention of configuration. The electron donating properties of the OH^-, and NCS^- induce a slow trans attack and Cl^- or Br^- induce a rapid cis replacement with retention of configuration since only relatively small changes in bdnding take place on going to the transition state.

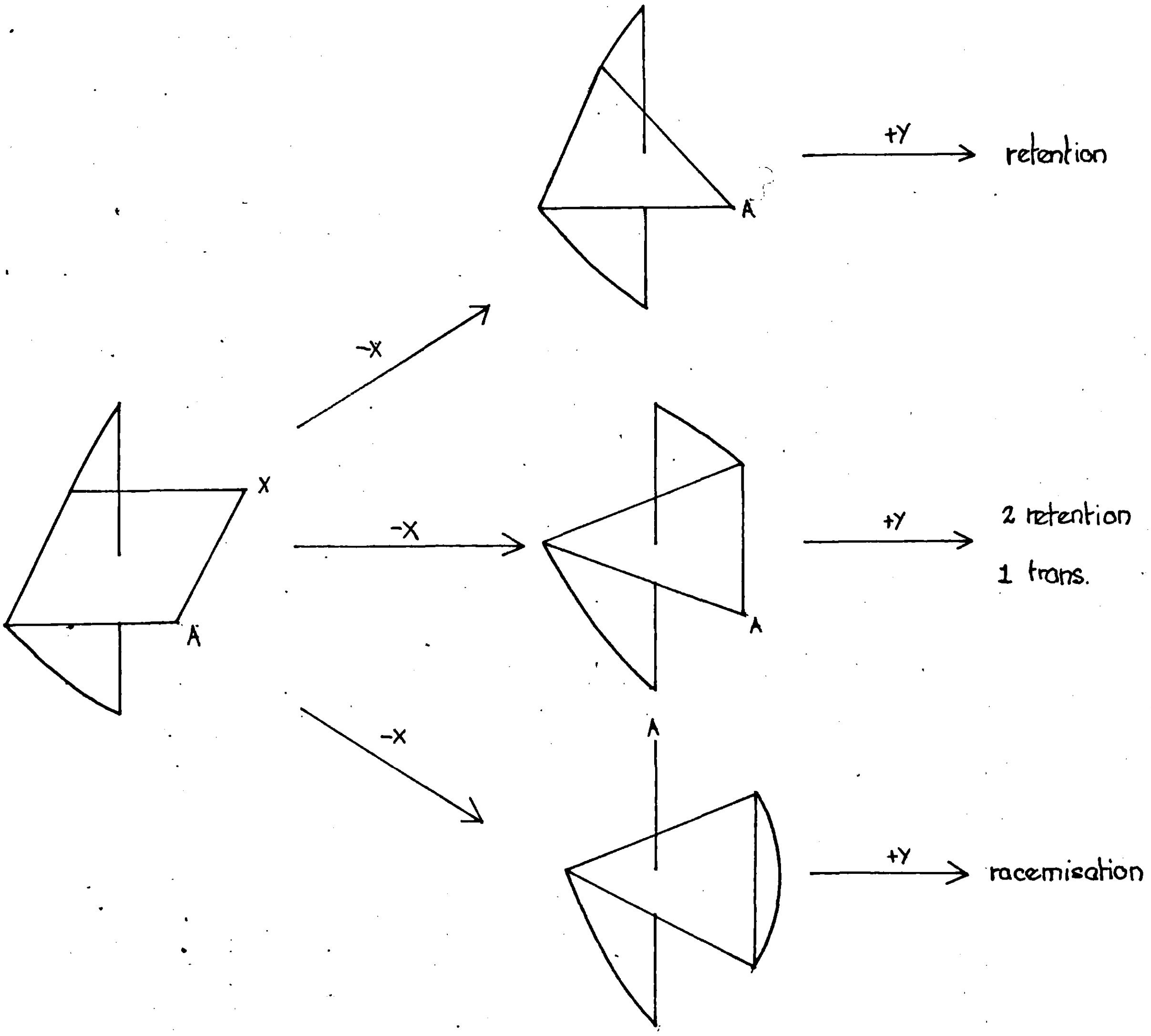
S_N1 mechanism

An S_N1 mechanism produces a five coordinate intermediate. This can be visualised either as a tetragonal pyramid or as a trigonal bipyramid, as is shown for an optically active isomer in Figure 3. It can be seen that in the case of the tetragonal pyramid, substitution will take place with retention of configuration. For a trigonal bipyramid rearrangement takes place and ideal statistical ratios for the three isomers can be calculated.

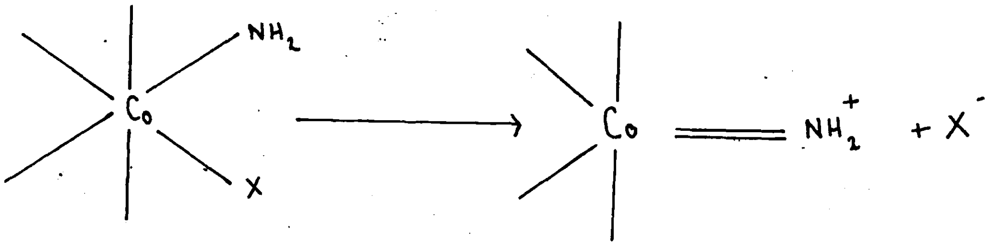
Since rearrangement always occurs during base hydrolysis, the intermediate must be a trigonal

FIGURE 3.

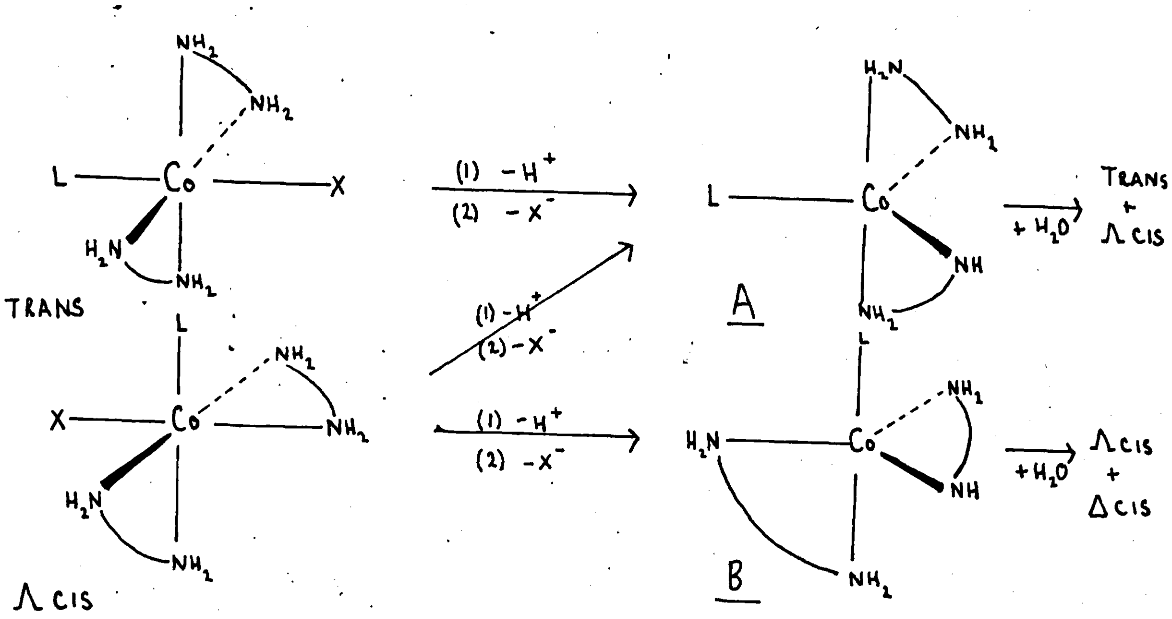
UNIMOLECULAR SUBSTITUTION INTO AN OPTICALLY ACTIVE ISOMER.



bipyramid. This agrees with the hypothesis (117) that this structure is stabilised by the π bonding of the electron pair of the amido nitrogen which must be in the same trigonal plane as the vacant $d_{x^2-y^2}$ orbital on cobalt III.



Basolo and Pearson (118) have analysed the isomeric products formed from the base hydrolysis of many cis and trans cobalt III complexes. Assuming an S_N1 CB mechanism, they calculated the fractions of the two possible intermediates produced from the cis and trans forms with the minimum of atomic motion.



There is one common intermediate, A, and one intermediate which is specific to the cis form. Out of this analysis two stereochemical rules emerge.

a) The cis isomer must never give less cis product than the trans form.

b) The % retention of configuration by a cis substrate must be greater than, or equal to, the % of intermediate. A times the fraction of cis product from A.

Rule (a) can be seen to be obeyed by the examples given in Table 3. This is good evidence for an S_N1 CB process.

It has also been pointed out (90) that if a five coordinate intermediate is formed, then the concentrations of the isomeric products should be independent of the departing group. This is found to be so, as in the example of trans[Coen$_2$ClBr]$^+$ and trans[Coen$_2$Cl$_2$]$^+$. In both cases five % of the cis product ion, [Coen$_2$Cl(OH)]$^+$ is formed. (page 81).

The stabilisation of the pentacoordinate intermediate could also be achieved by the interaction of a filled p orbital of the fixed ligand L with the empty d orbital. (70) This is only possible when the ligand is in the trigonal plane, i.e. in the case of the intermediateA. Further, the two effects can be considered together by imagining a conjugated system involving both L and the amido group. In practice the percentage of A formed during the hydrolysis of [Coen$_2$LX]$^{n+}$, X - Cl$^-$, Br$^-$, OH$^-$, is as follows:-

L	NO_2^-	N_3^-	Br^-	NH_3	Cl^-	NCS^-
%	34	40-50	60	67	66-74	84

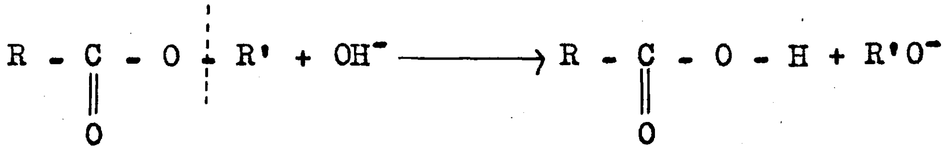
Since the nitro group is an electron acceptor the low percentage supports the theory. The other results can also be rationalised to support the theory. Ammonia is not a π donor. The unexpectedly high percentage is explained by its acid properties being stronger than ethylenediamine, thus resulting in its greater likelihood of it being in the trigonal plane. The remaining ligands are all π donors and occur in the accepted order of increase in ability with the exception of the thiocyanate ion. This high value is thought to be due to the linear nature of the thiocyanate ion. Thus in general it would appear that the fixed ligand L affects the percentages of intermediates formed.

15. Bond Cleavage during the hydrolysis of complexes containing the carboxyl group

In all the discussion so far the emphasis has been placed on the effect of the ligands on the reaction of the metal complex. The emphasis can be shifted so that the major interest is centred on the influence the metal ion has on the reactivity of the groups attached to it. Thus a group such as the $Co(NH_3)_5^{3+}$ can be considered as a Lewis acid, in the same way as a methyl group or a proton. When the coordinated ligand contains a carboxyl group the whole molecule can be considered likened to an organic ester; RCOOR', for example for the $[Co(NH_3)_5COOCF_3]^{2+}$, R = $Co(NH_3)_5$, R' = CF_3.

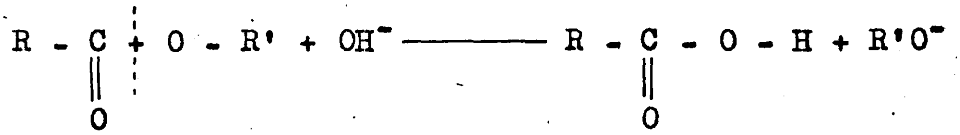
As in the hydrolysis of esters it is possible that bond fission can take place in one of two places:

1) <u>Alkyl bond fission</u>



$$R-\underset{\underset{O}{\|}}{C}-O\;\vdots\;R' + OH^- \longrightarrow R-\underset{\underset{O}{\|}}{C}-O-H + R'O^-$$

2) <u>Acyl bond fission</u>



$$R-\underset{\underset{O}{\|}}{C}\;\vdots\;O-R' + OH^- \text{———} R-\underset{\underset{O}{\|}}{C}-O-H + R'O^-$$

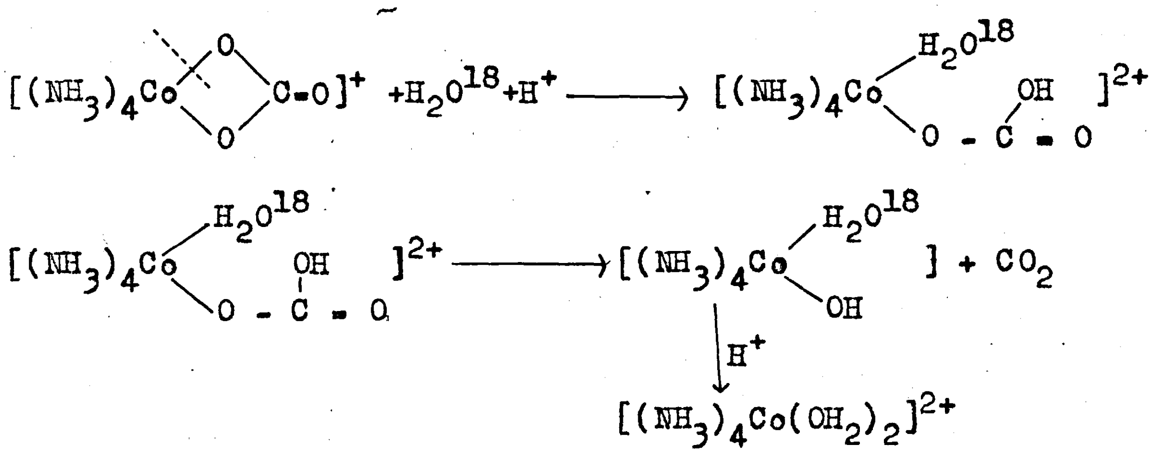
If the reaction is carried out in the presence of solvent labelled with oxygen^{18} it is possible to tell where bond fission occurs.

During the acid hydrolysis of the carbonatopentammine ion, (81) there is no oxygen^{18} incorporated into the aquopentammine product ion.

$$[(NH_3)_5Co-O\vdots COOH]^{2+}+H_2O^{18}+H^+ \longrightarrow [(NH_3)_5Co-OH_2]^{3+}+CO_2$$

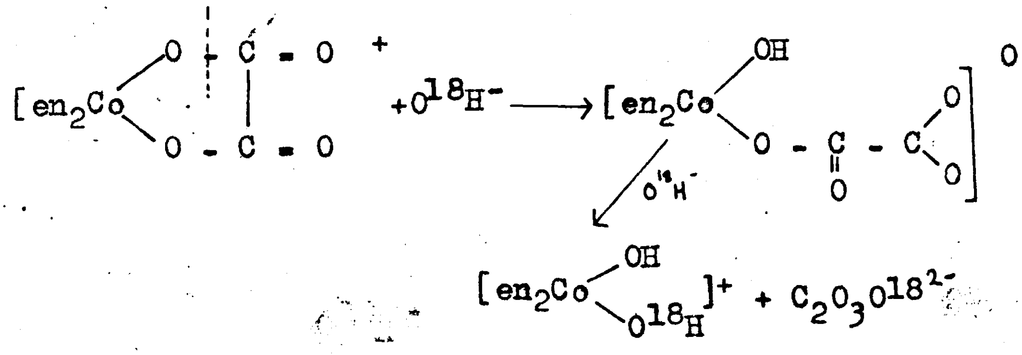
When the carbonatotetrammine ion is studied (124) only 50% of the oxygen incorporated comes from the solvent labelled oxygen^{18}. This suggests that during the dechelation of the tetrammine, a cobalt-oxygen bond is broken.

With the complete removal of the carbonate, a carbon-oxygen bond is broken. This can be explained on the following mechanism:



During the second stage, there is no transfer of oxygen from the solvent, simply the removal of carbon dioxide.

On alkaline hydrolysis of oxalatobisethylenediaminecobalt III ion, the reverse is found.(134) These results have been interpreted to suggest that the dechelation process takes place by carbon oxygen fission and the subsequent removal of the oxalate by coablt oxygen fission.



This is supported by work (6) on the hydrolysis of the $[Co(NH_3)_5O_2CCO_2]^+$ where only cobalt oxygen bond breaking occurs.

$$[(NH_3)_5\text{-}Co\text{-}O_2\ CCO_2]^+ + O^{18}H^- \longrightarrow [(NH_3)_5Co\text{-}O^{18}H]^{2+} + C_2O_4^{\ 2-}$$

Originally it was thought (33) that there was a gradual shift in the bond breaking position from cobalt oxygen to oxygen carbon, with increasing electron withdrawing power of the R group in the $RCOO^-$ ligand in complexes of the form $[(NH_3)_5CoOOCR]$ where R = CH_3, CH_2Cl, ~~Cl~~, CCl_3, CF_3. The explanation being the competition of carbonyl addition with the S_N1 CB mechanism. That this is not always a complete explanation was shown by further work (91) on the base hydrolysis of the trifluoroacetatopentamminecobalt III ion, $[Co(NH_3)_5(CF_3COO)]^{2+}$, where it was found that there are two reaction paths, one first order in hydroxide and the other second order.

$$\text{Rate} = k'\ [OH^-] + k''\ [OH^-]^2$$

The oxygen tracer experiments showed that the k' path takes place with cobalt oxygen fission and the k" path with carbon oxygen fission. The k' path being dominant at high temperature and low base concentration and the k" path at low temperature and high base concentration.

These two reaction paths have also been found (88) in the hydrolysis of the $[\mathrm{Coen_2(C_2O_4)}]^+$ ion.

The interpretation given of the position of bond breaking, assuming only one reaction path first order in oxalate, may not be generally valid.

The rate equation, rate = k' $[\mathrm{OH^-}]$ + k" $[\mathrm{OH^-}]^2$ was also found (111) in the base hydrolysis of the $[\mathrm{Rh(NH_3)_5OCOR}]^{2+}$ where $\mathrm{RCOO^-}$ is formate, acetate or substituted acetate. No oxygen exchange experiments have yet been reported.

When the base hydrolysis of the complex ions in the series cis and trans $[\mathrm{Coen_2(OCOAr)_2}]^+$ where Ar = $\mathrm{C_6H_5}$, $\mathrm{pCH_3OC_6H_4}$, m $\mathrm{ClC_6H_4}$, m $\mathrm{FC_6H_4}$, m $\mathrm{NO_2C_6H_4}$ was investigated (82) no oxygen^{18} was incorporated in the product and there was no reaction path second order in hydroxide found.

$$\text{Rate} = k' [\mathrm{OH^-}]$$

This may be a specialised case of the more general form

$$\text{Rate} = k' [\mathrm{OH^-}] + k'' [\mathrm{OH^-}]^2$$

The latter pathway is favoured by powerful electron withdrawing agents in the carboxylato ligand and the lack of such effects may be one reason why the second term is unimportant. Another reason may be due to the low base concentration (maximum 0.02 M) and temperature, 25° at which the reaction was carried out.

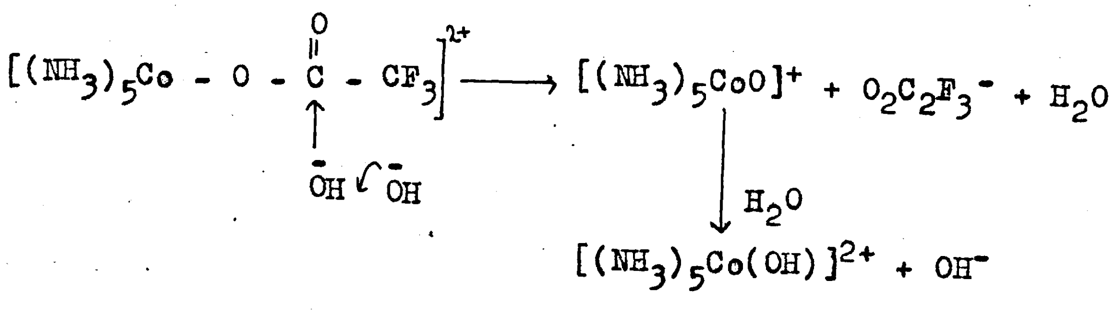
The k' path of the hydrolysis of the $[Co(NH_3)_5(CF_3COO)]^{2+}$ ion is thought to go through a conjugate base mechanism.

$$[Co(NH_3)_5(CF_3COO)]^{2+} + OH' \rightleftharpoons [Co(NH_3)_4(NH_2)(CF_3COO)]^{+} + H_2O$$

$$[Co(NH_3)_4(NH_2)(CF_3COO)]^{+} \longrightarrow [Co(NH_3)_4(NH_2)(OH_2)]^{2+} + CF_3COO^-$$

$$[Co(NH_3)_4(NH_2)(OH_2)]^{2+} = [Co(NH_3)_5OH]^{2+}$$

A possible mechanism for the k" path involves attack by OH^- at the carbonyl carbon followed by a second OH^- removing the proton from the first. The process is concerted, the low activation energy being consistent with strong bond making in the activated complex.



$$\left[(NH_3)_5Co - O - \overset{\overset{O}{\|}}{\underset{\underset{\bar{O}H \curvearrowleft \bar{O}H}{\uparrow}}{C}} - CF_3\right]^{2+} \longrightarrow [(NH_3)_5CoO]^{+} + O_2C_2F_3^{-} + H_2O$$

$$\downarrow H_2O$$

$$[(NH_3)_5Co(OH)]^{2+} + OH^-$$

16. The base hydrolysis of cobalt III complexes compared to other metal octahedral complexes

Due to their relative ease of preparation and inert nature in substitution reactions, cobalt III complexes have been the most thoroughly studied metal complexes at the present time. The halogenopentammine complexes of rhodium III,(86, 5) ruthenium III, (27) chromium III and iridium III (132, 97) have been made, as have also the diacidobisethylenediamine complexes of chromium III, rhodium III, (86) ruthenium III,(30) and iridium III.(46)

The most striking feature arising from comparative studies was that, like Co III, the base hydrolysis for the Ru III complexes is very much faster (27) than the acid hydrolysis, whereas for Cr III and Rh III (87) the rates of hydrolysis in acid and base are relatively slow and comparable. Very little work has been done in the case of iridium III but the base hydrolysis of $[Ir(NH_3)_5OCOCF_3]^{2+}$ proceeds at a rate substantially (111) the same as for the $[Rh(NH_3)_5OCOCF_3]^{2+}$ ion, and for $[Ir(NH_3)_5Br]^{3+}$ the base hydrolysis is slower than in the rhodium complex.

Table 4 compares some properties of some metal ions.

TABLE 4

Comparison of some properties of some metal ions

Property.	Cr^{3+}	Co^{3+}	Ru^{3+}	Rh^{3+}
Electronic Configuration	$3d^3$	$3d^6$	$4d^5$	$4d^6$
$k(OH^-)/k(H_2O)$ at 25° for $[M(NH_3)_5Cl]^{2+}$	$2x10^2$	$5x10^5$	$2x10^6$	$4x10^3$ at 80°
pK_a $[M(NH_3)_5H_2O]^{3+}$ at 25°	5·2	5·7	4·2	5·9
CFAE for a trigonal bipyramid	5·74Dq	11·48Dq	8·90Dq'	11·48Dq'
CFAE for coordination number 7	1·80Dq	3·63Dq	1·14Dq'	3·63Dq'
Electron affinity, ev [3rd ionisation potential of metal]	29·5	35·5	31	33

The form of reactivity can be discussed on the basis of the S_N1 CB mechanism as for cobalt.

$$[M(NH_3)_5Cl]^{2+} + OH^- \xrightleftharpoons{\text{fast}} [M(NH_3)_4NH_2Cl]^+ + H_2O \qquad (1)$$

$$[M(NH_3)_4NH_2Cl]^+ \xrightarrow{\text{slow}} [M(NH_3)_4NH_2]^{2+} + Cl^- \qquad (2)$$

$$[M(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [M(NH_3)_5OH]^{2+} \qquad (3)$$

For the Co III the stability of the five co-ordinate intermediate is mainly due to rearrangement to a trigonal bipyramid with π bonding from the amido group.

$$H_2\overset{\curvearrowright}{N} - Co \overset{\curvearrowright}{-} Cl \longrightarrow H_2N^{+} = Co + Cl^{-}$$

Any factor which favours the formation of the amido base will cause a high rate of base hydrolysis. The pK_a values of the acid dissociation, reaction 1, are too small to be measured but the pK_a of the $[M(NH_3)_5H_2O]^{3+}$ ion has been measured as is shown in Table 4. It can be seen that Ru III is the strongest, with Cr III next. This is partly explainable by consideration of the crystal field destabilisation on production of the amide group from the amine. This would be smaller for Ru III and Cr III due to their partially filled t_{2g} sub shells.

Once the base is formed the stability will depend on the ability to rearrange to a trigonal bipyramid so that ligand to metal π bonding can occur. This is estimated by considering the ease of reduction of the metal, $M^{3+} \longrightarrow M^{2+}$ which is in the order $Co > Rh > Ru > Cr$.

Loss of crystal field stabilisation on going from the octahedral ground state to the transition state must also be considered. This is called the crystal field activation energy (CFAE) and the figures are shown in Table 4. Ligand repulsions and π bonding favour a trigonal bipyramid intermediate whereas crystal field effects oppose it. The crystal field splitting in the second row transition elements Dq' is about 50% greater than in the first, so a trigonal bipyramid is likely for Co III and Cr III but unlikely for Rh III and Ru III.

The high rate of base hydrolysis of Ru III can be rationalised best as a seven coordinate intermediate with no rearrangement since the tendency to π bond is small, although the amido group is easily formed, since the loss of crystal field stabilisation is small. The high rate of base hydrolysis of Co III is due to the ease of reduction whilst the low rate of Cr III is due to reduction taking place with very great difficulty. The low rate for Rh III is explained by the low acidity and the large crystal field effects.

An S_N2 mechanism has also been proposed by Chan for the $[Rh(NH_3)_5X]^{2+}$ ions where X = Cl^-, Br^-, I^-.(38) He compares the Rh III systems to aromatic hydrocarbons since in both systems the lowest unfilled energy orbitals are accessible for bonding purposes. Since the rate decreases $Cl^- > Br^- > I^-$ which is the same pattern as for aromatic hydrocarbons which are known to substitute by an S_N2 process, the substitution in the rhodium series must also be S_N2. The same argument has been applied for Co III (page 74) where Co III complexes are likened to aliphatic carbon systems.

PART II. RESULTS AND DISCUSSION

1. RACEMISATION OF THE CIS (-) $[Coen_2(OH)_2]^+$ ION

Method

Optically active $[Coen_2CO_3]ClO_4$ was dissolved in standard perchloric acid, the $[Coen_2(H_2O)_2]^{3+}$ ion was immediately formed with complete retention of configuration.(55) On the subsequent addition of sodium hydroxide, the $[Coen_2(OH)_2]^+$ ion was instantaneously formed.

$$[Coen_2CO_3]^+ + 2H_3O^+ \longrightarrow [Coen_2(H_2O)_2]^{3+} + CO_2 + H_2O$$

$$[Coen_2(H_2O)_2]^{3+} + 2OH^- \longrightarrow [Coen_2(OH)_2]^+ + H_2O$$

The solution was placed in a jacketted thermostatted polarimeter tube in a Zeiss Polarimeter and readings of the rotation at 436 mμ were taken at various time intervals.

Calculation

The rate constants ($k_{1(rac.)}$) were obtained from the equation:

$$k_{1(rac.)} = \frac{2.303 \log_{10}(\alpha_t - \alpha_\infty)}{t}$$

where α_t is the rotation at time t and α_∞, in this case zero, is the rotation on the completion of the reaction. $k_{1(rac.)}$ was obtained graphically from a graph of the log of the rotation plotted against time. The slope measures the rate, a specimen first order rate plot is shown in graph 1.

Results

Table 5 shows, the observed first order rate constants for the rate of loss of optical activity of the cis (-) $[Coen_2(OH)_2]^+$ ion at various temperatures. No inversion or mutarotation was observed and the rate was found to be independent of the hydroxide concentration and excess ethylenediamine.

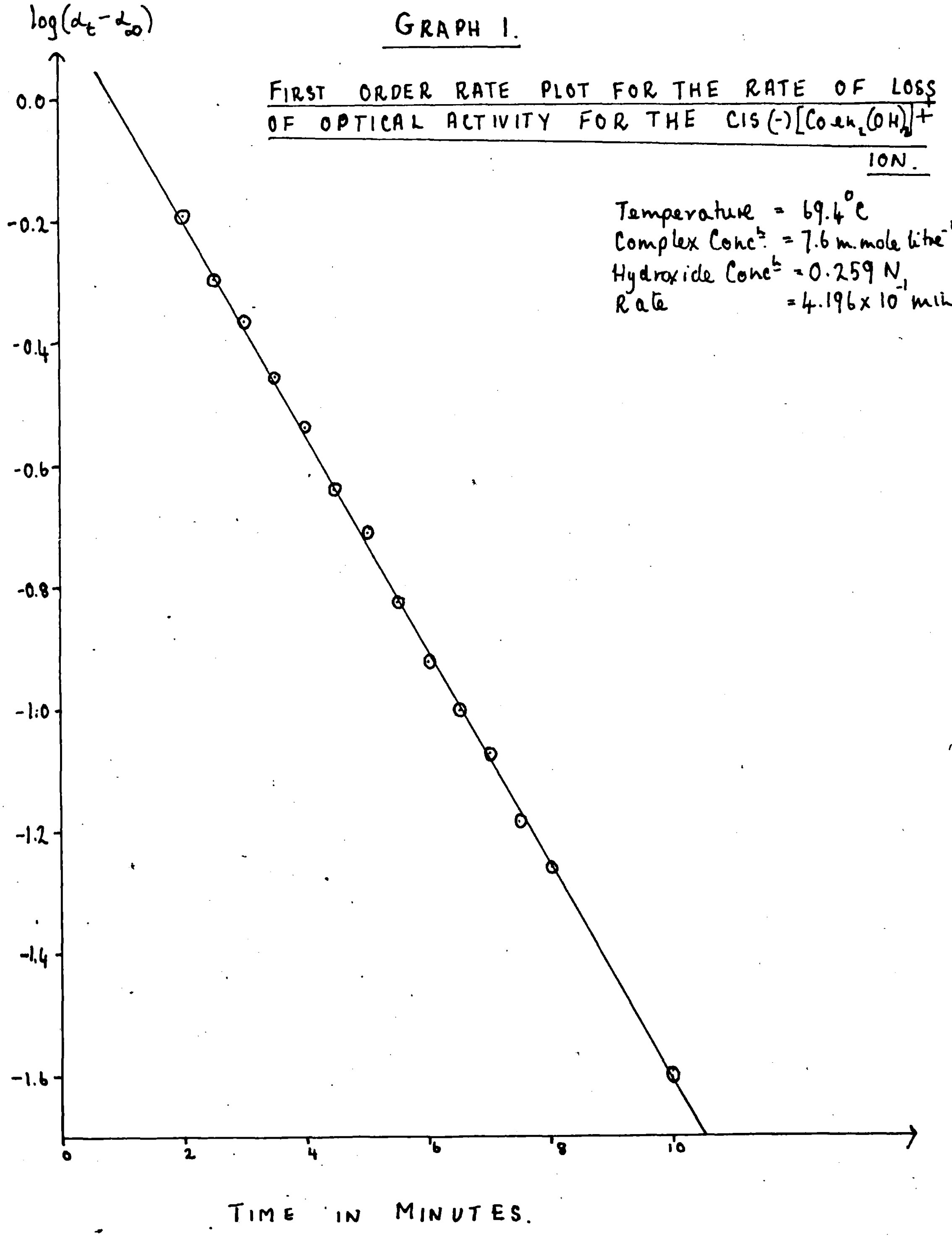
Several workers (21,96,58,141) have studied the cis/trans isomerisation spectrophotometrically.

$$(\pm)\ \text{cis}\ [Coen_2(OH)_2]^+ \underset{k_t}{\overset{k_c}{\rightleftarrows}} \text{trans}\ [Coen_2(OH)_2]^+$$

Graph 2 shows an Arrhenius plot of $\log_{10}k'$, where $k' = k_c + k_t$ [illegible] against the reciprocal of the absolute temperature. The racemisation rates are slightly slower than the combined isomerisation rates. The position of equilibrium cis trans does not change with temperature, the ratio (K) k_c/k_t was found to be 0·80 by Bjerrum and Rasmussen(21) and 0·85 by Kruse and Taube. (96) By using the relation $K = k_c/k_t$ in addition to the relation $k' = k_c + k_t$ the values of k_c were calculated. The racemisation rate and isomerisation rate, both k' and k_c are compared in Table 6, the racemisation being very much faster than the isomerisation. The isomerisation only partially accounts for the loss of optical activity.

GRAPH I.

FIRST ORDER RATE PLOT FOR THE RATE OF LOSS OF OPTICAL ACTIVITY FOR THE CIS(-)$[Co\,en_2(OH)_2]^+$ ION.



Temperature = 69.4°C
Complex Conc^n. = 7.6 m.mole litre^{-1}
Hydroxide Conc^n = 0.259 N
Rate = 4.196×10^{-1} mins^{-1}

TABLE 5

OBSERVED FIRST ORDER RATE CONSTANTS FOR THE LOSS OF ACTIVITY OF THE (-) cis $[Coen_2(OH)_2]^+$ ION

Measured at 436 mμ. Sodium hydroxide = 0·259 N

Temperature °C	Complex Conc. m.mole litre^{-1}	k_1(rac.) min.$^{-1}$
69·4	7·6	$4{\cdot}196 \times 10^{-1}$
60·8 [a]	4·1	$1{\cdot}142 \times 10^{-1}$
60·8 [a,b]	5·0	$1{\cdot}142 \times 10^{-1}$
60·8	7·8	$1{\cdot}196 \times 10^{-1}$
49·3	8·0	$2{\cdot}495 \times 10^{-2}$
37·2	7·5	$4{\cdot}174 \times 10^{-3}$
24·8	9·9	$5{\cdot}614 \times 10^{-4}$

a. Sodium hydroxide = 0·855 N

b. Run carried out in the presence of 0.5 ml. ethylenediamine.

GRAPH 2.

ARRHENIUS PLOT FOR THE RACEMISATION AND ISOMERISATION OF THE CIS (-) $[Co\,en_2(OH)_2]^+$ ION.

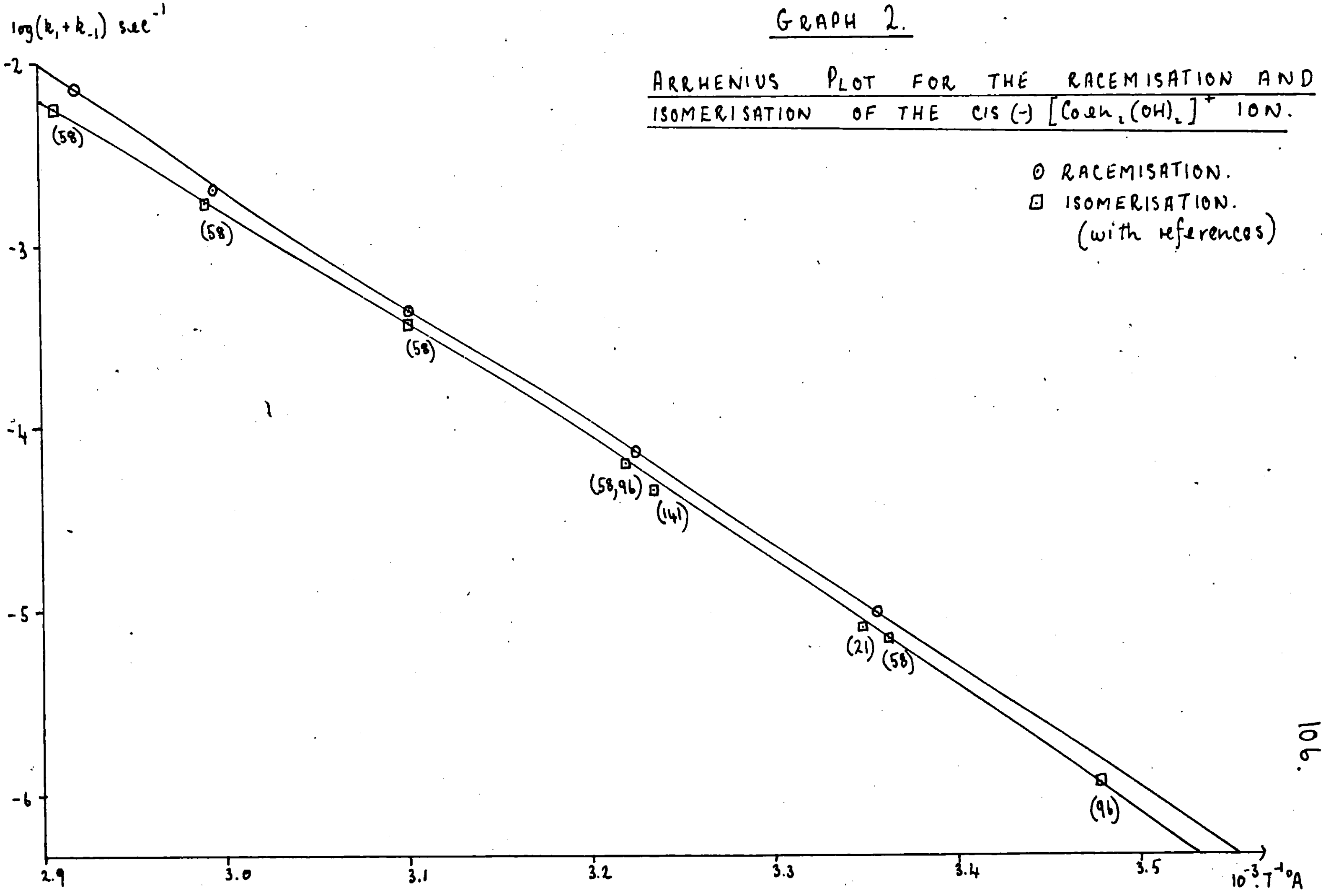


TABLE 6

COMPARISON OF THE RACEMISATION AND ISOMERISATION (CIS TO TRANS) RATES FOR THE $[Coen_2(OH)_2]^+$ ION

Temperature °C	k_{1}(rac.) min.$^{-1}$	k_1' min.$^{-1}$	k_{1c} min.$^{-1}$	Ref. for k_1'
14·4		7·0x.10^{-5}	3·2x10^{-5}	96
24·8	5·614x10^{-4}			
24·95		4·0x10^{-4}	1·8x10^{-4}	96
25·0		4·57x10^{-4}	2·11x10^{-4}	21
35·03		2·59x10^{-3}	1·96x10^{-3}	141
37·2	4·184x10^{-3}			
37·5	-	3·86x10^{-3}	1·78x10^{-3}	58
49·3	2·495x10^{-2}	2·28x10^{-2}	1·05x10^{-2}	58
60·8	1·196x10^{-1}			
61·0		9·90x10^{-2}	4·59x10^{-2}	58
69·4	4·196x10^{-1}			
71·0		3·30	1·524	58

DISCUSSION

The isomerisation of the cis and trans $[Coen_2(OH)_2]^+$ ion has been extensively studied by Kruse and Taube. (96) They found that an equilibrium mixture of the two ions was obtained which was independent of the temperature. An intramolecular mechanism was postulated since the rate was found to be independent of the hydroxide concentration above a concentration of about 0•01 N, Below this concentration the reaction is complicated by the presence of $[Coen_2(OH)(H_2O)]^{2+}$, and this is expected to racemise faster than $[Coen_2(OH)_2]^{2+}$. They suggested that the reaction did not proceed through a single mechanism since lack of linearity was obtained in the Arrhenius plot, (page 106). Measurements over an increased temperature range support this conclusion.(58) Further, in the oxygen 18 exchange studies it was found that only a fraction of oxygen exchange occurred per ion for each act of isomerisation. Two different reaction paths were suggested, one being the breaking of a Co(III) - OH bond and the other being the breaking of the Co(III) - NH_2 bond in the activated complex. The two processes may reasonably be considered to compete, the lability of the Co-O bond being decreased by the loss of a proton from the water to bring it into the range of the lability of the $Co-NH_2R$ bond. Thus two different transition states or intermediates exist and these may be visualised as trigonal bipyramids, although a transition state with coordination number 7 involving direct attack in a bimolecular way is also possible. A tetragonal pyramid is impossible as this would result in retention of configuration. They suggested two consecutive transition states or intermediates.

From the present measurements on racemisation rates it is apparent that some other reaction path must be present since the racemisation rate is so much faster than the isomerisation rate. The racemisation can be considered either as a direct inversion

$$(+)\ [Coen_2(OH)_2]^+ \overset{k_1''}{\rightleftarrows} (-)\ [Coen_2(OH)_2]^+$$

or involving an inactive intermediate.

$$(+)[Coen_2(OH)_2]^+ \overset{k_1'}{\rightleftarrows} \begin{matrix}\text{inactive}\\ \text{intermediate}\end{matrix} \rightleftarrows (-)[Coen_2(OH)_2]^+$$

Then $k_1' = 2k_1''$ since two original (+) isomers on dissociation give two optically inactive molecules which can regenerate one (+) and one (-) molecule.

It is not possible to tell which process is being carried out. If the actual racemisation is twice as slow it will still be faster than the isomerisation rate.

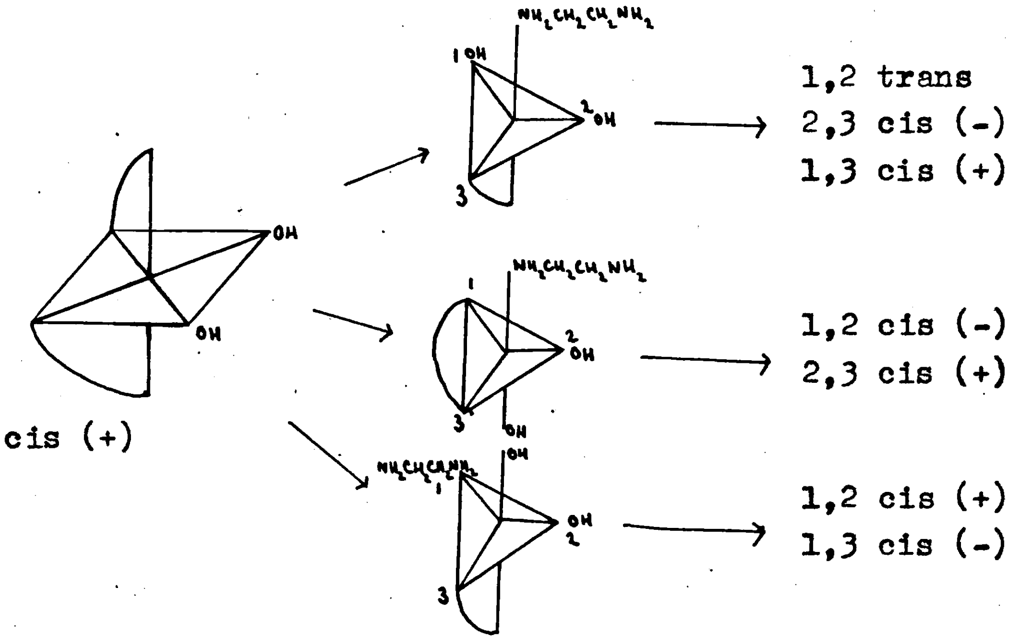
a) Direct inversion

Since the reaction has been shown to be independent of hydroxide concentration there can be no cobalt-oxygen bond fission.

Dechelation of the ethylenediamine ring is postulated. Complete removal of the ethylenediamine does not occur since the rate is independent of excess ethylenediamine. This dechelation is plausible due to the strong electromeric effect of the hydroxide group.

This dechelation has been proposed by Martin and Tobe (106) to account for the isomerisation of the $[Coen_2NH_3(OH)]^{2+}$ ion. They postulated a general rule for reactions of complexes of the type $[Coen_2A(OH)]^+$ in aqueous solution. When A is less strongly bound than ethylenediamine, aquation occurs and A is replaced. When A is more strongly bound than ethylenediamine, isomerisation takes place by the dechelation of the ethylenediamine ring.

The possible trigonal bipyramid intermediates are



The production of all three intermediates would account for the fast racemisation relative to the slow isomerisation since only the first intermediate can produce the trans isomer.

An intramolecular twist mechanism may also be responsible for the fast rate of racemisation compared to isomerisation. Any twist mechanism can only give racemisation and no isomerisation.

b) Inactive intermediate

Dechelation of both ethylenediamine rings would result in a intermediate, symmetric between the two enantiomeric forms. On reforming the ethylenediamine rings both the (+) and (-) isomers would be formed. This seems less likely than a single dechelation.

2. THE BASE HYDROLYSIS OF THE CIS $[Coen_2CO_3]^+$ ION

RESULTS

a) Spectrophotometric measurements on the base hydrolysis of the $[Coen_2CO_3]^+$ ion

Instrumentation

All the measurements were carried out on Unicam SP.700 and 800 spectrophotometers. Preliminary work was carried out on the SP.800, the spectrum scanned from 15,000 to 45,000 cm.$^{-1}$ at various time intervals. This allowed the position of maximum change in optical density to be determined. The majority of the kinetic work was carried out on the SP.700.

Stoichiometry

The reaction was found to take place in two stages. The first corresponding to an initial dechelation first proposed by Harris (79, 100) and the second to the complete removal of the carbonate.

$$[Coen_2CO_3]^+ + OH^- \longrightarrow [Coen_2CO_3OH]^0$$

$$[Coen_2CO_3OH]^0 + OH^- \longrightarrow [Coen_2(OH)_2]^+ + CO_3^{2-}$$

General method

The alkaline solution was placed in 1 cm. silica cells in the thermostatted cell compartment of the instrument and left for 10 minutes to thermally equilibrate. The run was commenced by pipetting a solution of the complex into the alkali and shaking, the total volume of the sample being 3 ml.

The ionic strength was kept constant at 0·167 N with sodium perchlorate. Sodium chloride was also used and found to make no difference to the rate.

Temperature control

For temperatures above 50°, an electric thermostat was used and for temperatures between 20° and 50° a water thermostat was used. The temperature of the cell compartment was measured using a galvanometer, the accuracy of which was not more than $\pm 0{\cdot}5^{\circ}$.

Scale expansion unit

At 25° the observed change in optical density is very slight and slow. Therefore the runs were carried out on the SP.800 since this instrument is fitted with a scale expansion unit, a scale expansion factor of five being used. The observed changes were now sufficient to calculate the rate constants although the accuracy was diminished.

First stage of the reaction

$$[Coen_2CO_3]^+ + OH^- \longrightarrow [Coen_2CO_3OH]^o$$

Graphs 3 and 4 show the spectrophotometeric changes which occur during this stage of the reaction. This is characterised by a large increase in absorption between 29,000 and 36,700 cm.$^{-1}$ and isosbestic points at 44,100, 36,700, 29,000, 26,700, 24,900 and 23,600 cm.$^{-1}$ There is also an initial change in the ultraviolet spectrum. The reaction was followed at 30,000 cm.$^{-1}$ where the initial increase in absorption is followed by a decrease when the second stage of the reaction becomes significant. The time corresponding to maximum absorption becomes shorter and the maximum less pronounced with increase in hydroxide concentration and temperature.

The rate of the ring opening reaction was calculated by the Guggenheim method (62) since it was impossible to obtain an ∞ value for this part of the reaction. It has been shown (62) that

$$kt + \ln (D-D') = \text{constant}$$

where k is the rate constant and t the ~~constant~~ time when the optical density is D and D' the optical density at time t + Δ where Δ is a constant time interval.

interval between two optical densities D and D'. Thus, provided the time interval Δ is kept constant, the gradient of the graph t against ln (D-D') will give the rate constant. A specimen plot is shown in graph 5. Table 7 gives the first order rate constants $k_{[1]obs}$ for the reaction calculated in this way. Due to the small changes in optical density the results at 25·7° are inherently inaccurate and the limits of the values obtained are given. Graph 6 shows the changes with hydroxide concentration of k_{1obs}.

Second stage of the reaction

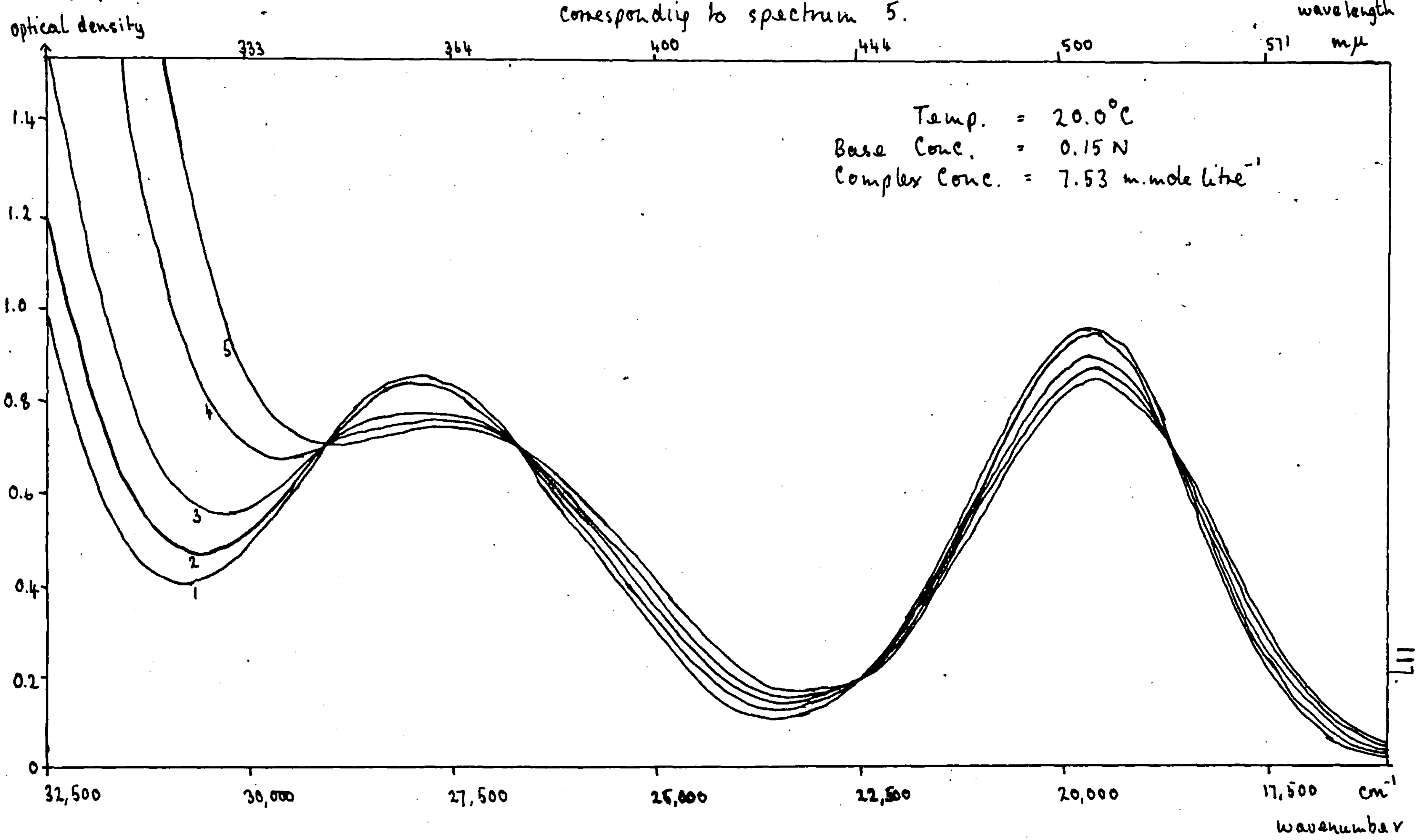
$$[\mathrm{Coen_2CO_3OH}]^{0} + \mathrm{OH^-} = \mathrm{cis/trans}\ [\mathrm{Coen_2(OH)_2}]^{+} + \mathrm{CO_3}^{2-}$$

This part of the reaction was measured at 19,230 cm.$^{-1}$ and not at 30,000 cm.$^{-1}$ In all cases the cis/trans isomeric mixtures were formed, the reaction rates being considerably slower than the cis/trans isomerisation of the $[\mathrm{Coen_2(OH)_2}]^+$. At lower temperatures and higher base concentrations the formation of the cis isomer would be expected. The extinction coefficients are given in Table 8 .

GRAPH 3.

SPECTROPHOTOMETRIC CHANGES OCCURING DURING THE BASE HYDROLISIS OF THE $[Co\,en_2CO_3]^+$ ION.

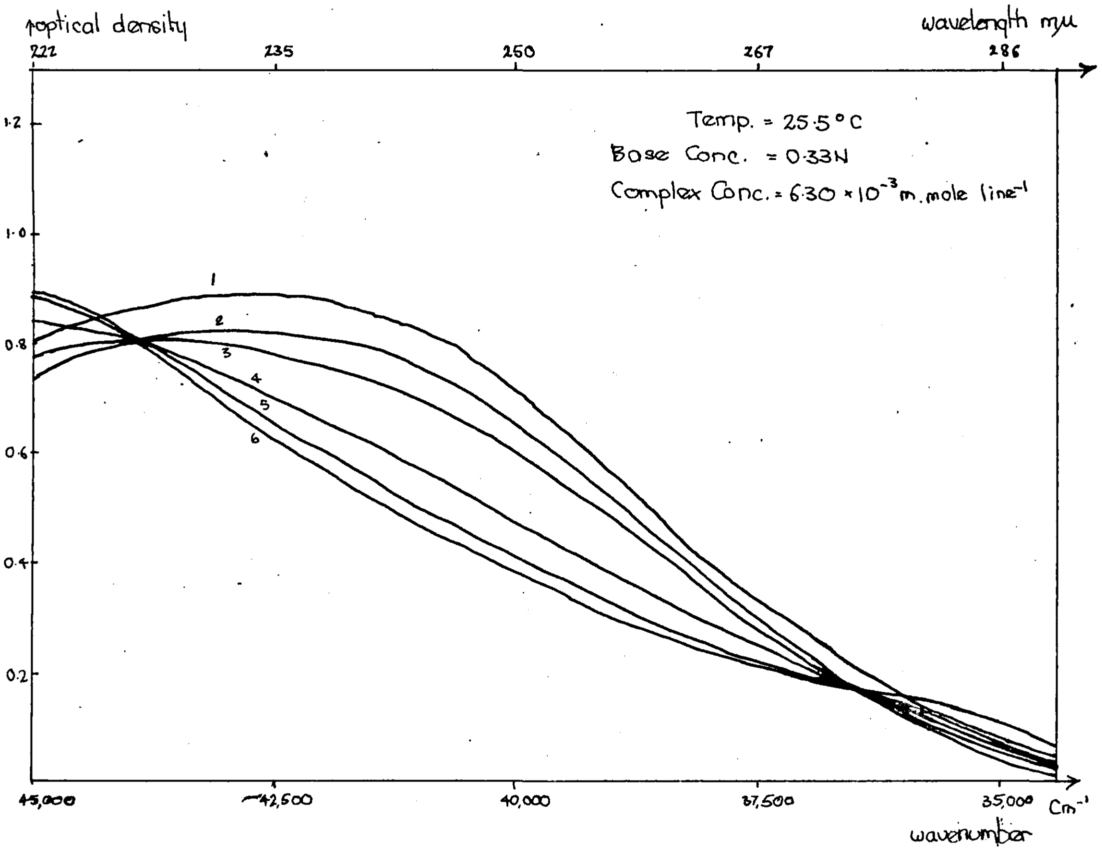
1., Spectrum at beginning of reaction. 2,3,4,5 spectra at increasing lengths of time, the longest time (130 mins) corresponding to spectrum 5.



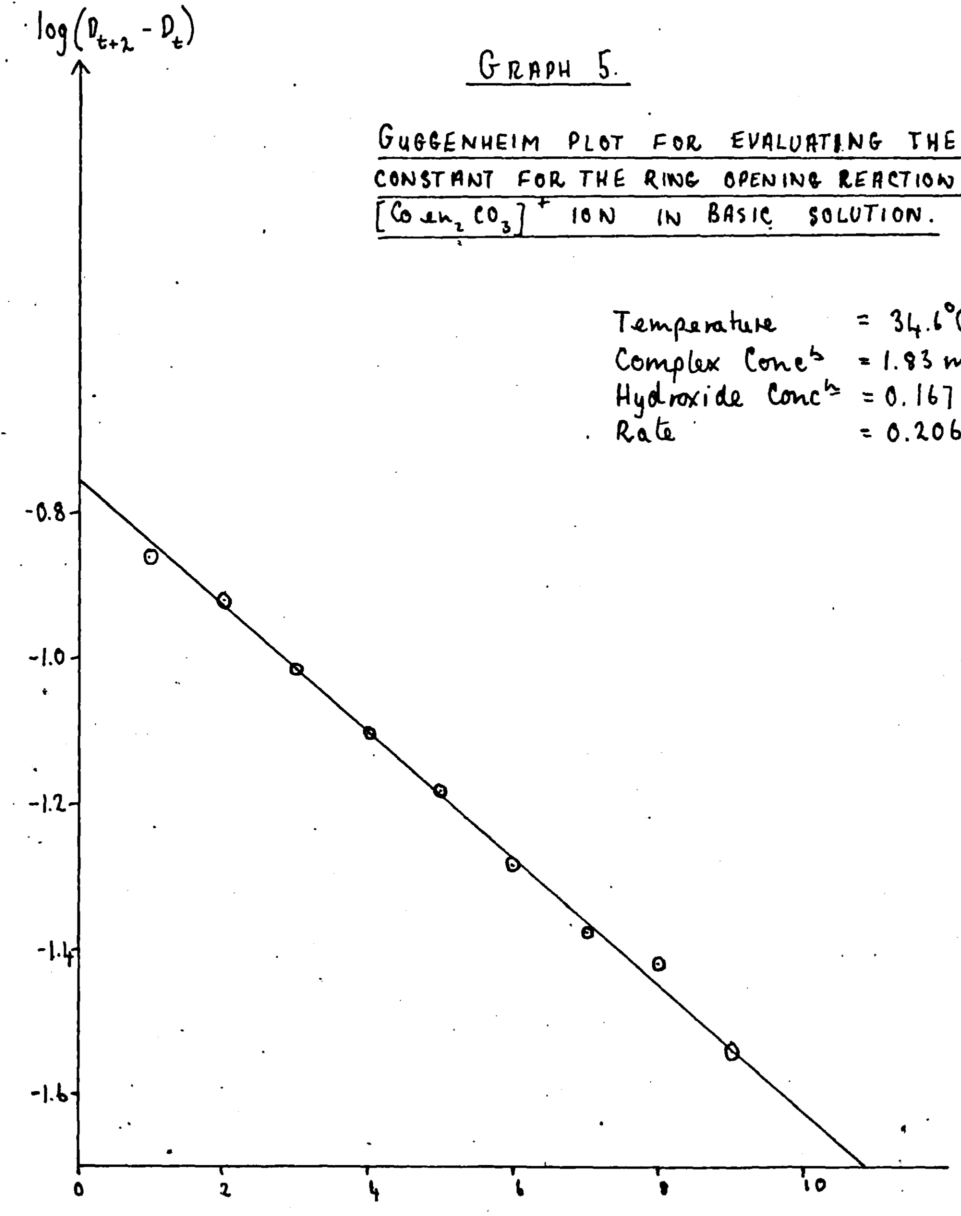
Temp. = 20.0°C
Base Conc. = 0.15 N
Complex Conc. = 7.53 m.mole litre⁻¹

GRAPH 4.

SPECTROPHOTOMETRIC CHANGES OCCURING DURING THE BASE HYDROLYSIS OF THE $[Coen_2CO_3]^+$ ION



1. Spectrum before addition of base.
2. Spectrum immediately after addition, of base
3, 4, 5 and 6. Spectra at increasing lengths of time, the longest time (30 minutes) corresponding to spectrum 6.



GRAPH 5.

GUGGENHEIM PLOT FOR EVALUATING THE RATE CONSTANT FOR THE RING OPENING REACTION OF THE $[Co\,en_2\,CO_3]^+$ ION IN BASIC SOLUTION.

Temperature = 34.6°C
Complex Concn = 1.83 m.mole litre^{-1}
Hydroxide Concn = 0.167 N
Rate = 0.206 mins^{-1}

[2 minute time interval used]

TABLE 7.

First order rate constants for the ring opening reaction

Temperature °C	[NaOH] N	Complex Conc. m.mole litre^{-1}	$k_{[1]}$obs. min.$^{-1}$
53·0	0·167	3·24	1·305
	0.150		1.162
	0·133		1·091
	0.117		0.960
	0·100		0·823
	0·083		0·648
	0·067	3·17	0·591
	0·053		0·503
	0·047		0·496
	0·040		0·478
	0·033		0·472
44·5	0·167	2·86	0·481
	0·133		0·378
	0·100		0·282
	0·067		0·233
	0·033		0·210
34·6	0·167	1·83	0·206
	0·133		0·168
	0.100		0.127
	0·067		0·087
	0·033		0·067

[continued over]

TABLE ⌉ - continued

Temperature °C	[NaOH] N	Complex Conc. m.mole $litre^{-1}$	$k_{[1]}$obs. $min.^{-1}$	
25·7	0·167	3·18	0·066 - 0·063	
	0·150		0·061 - 0·058	
	0·133		0·057 - 0·053	
	0·100		0·042 - 0·040	
	0·083		0·035 - 0·032	
	0·067		0·028 - 0·025	
	0·050		0·026 - 0·024	
	0·033		0·011 - 0·016	

GRAPH 6.

OBSERVED FIRST ORDER RATE CONSTANTS FOR THE RING OPENING REACTION OF THE $[Co\,en_2\,CO_3]^+$ ION AGAINST BASE CONCENTRATION.

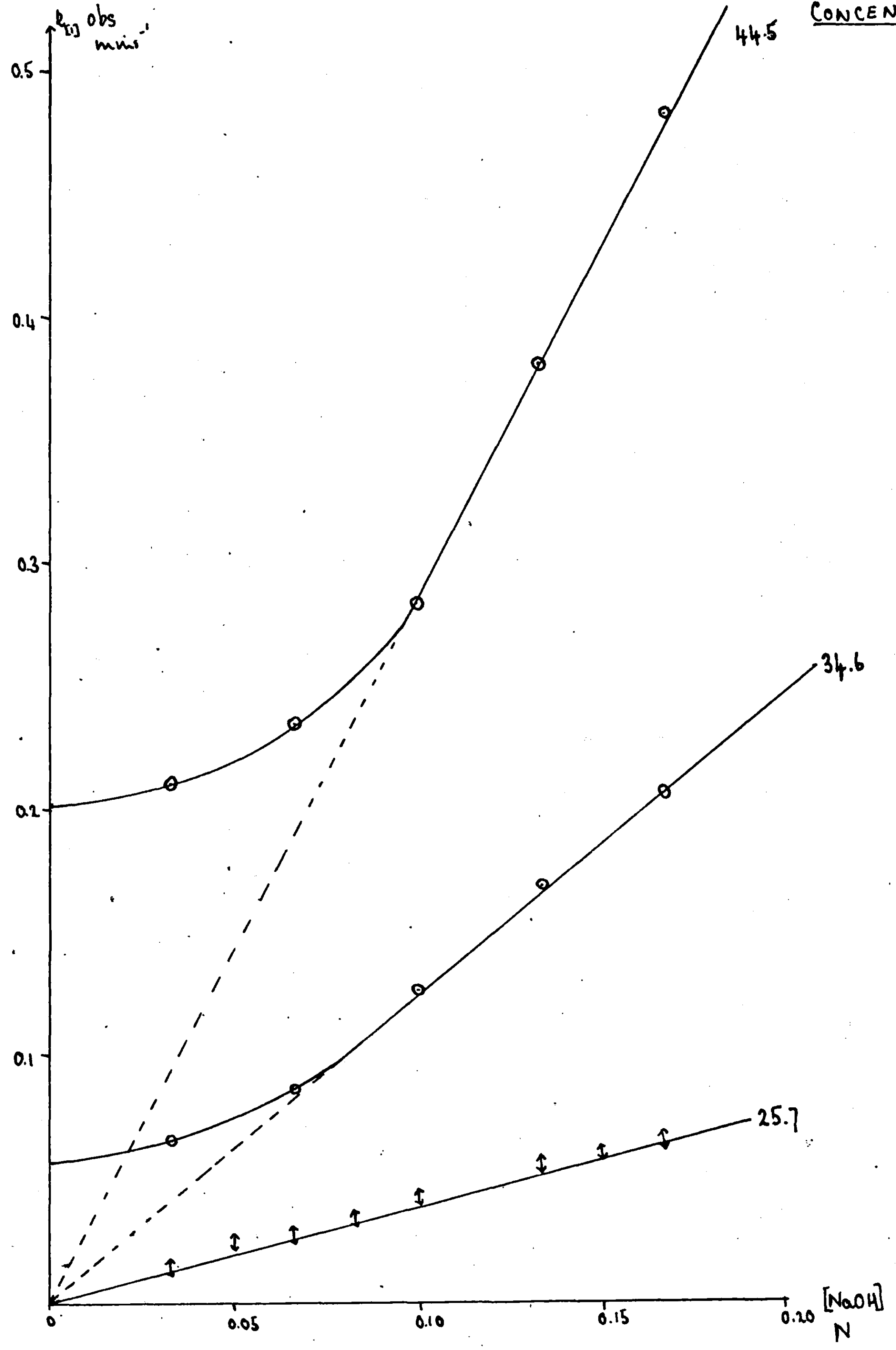


TABLE 8.

Extinction Coefficients for the $[Coen_2CO_3]^+$, cis$[Coen_2(OH)_2]^+$ and cis/trans equilibrium $[Coen_2(OH)_2]^+$ ions

Wave-length mμ	Wave-number cm.$^{-1}$	Extinction coefficients		
		$[Coen_2CO_3]^+$	cis$[Coen_2(OH)_2]^+$	cis/trans $[Coen_2(OH)_2]^+$
333	30,000	59	40	34
520	19,230	131	96	63

The values for the dihydroxo ions at 520 mμ agree with those found by Bjerrum and Rasmussen.(21) Graph 7 shows the spectrophotometric changes during this part of the reaction. The rate constants were evaluated graphically from

$$k_{1obs}t = \frac{2{\cdot}303 \log_{10}(D_t - D_\infty)}{t} + C$$

where D_t and D_∞ are the measured optical densities at time t and when the reaction is complete ($t = \infty$).
and C = constant.

Graph 8 shows a typical plot of $\log_{10}(D_t - D_\infty)$ against time, t.

The rate constants are listed in Table 9 and graph 9 shows the change in rate constant with hydroxide concentration.

The values of the Arrhenius paramaters measured at various base concentrations are shown in Table 10.

TABLE 10

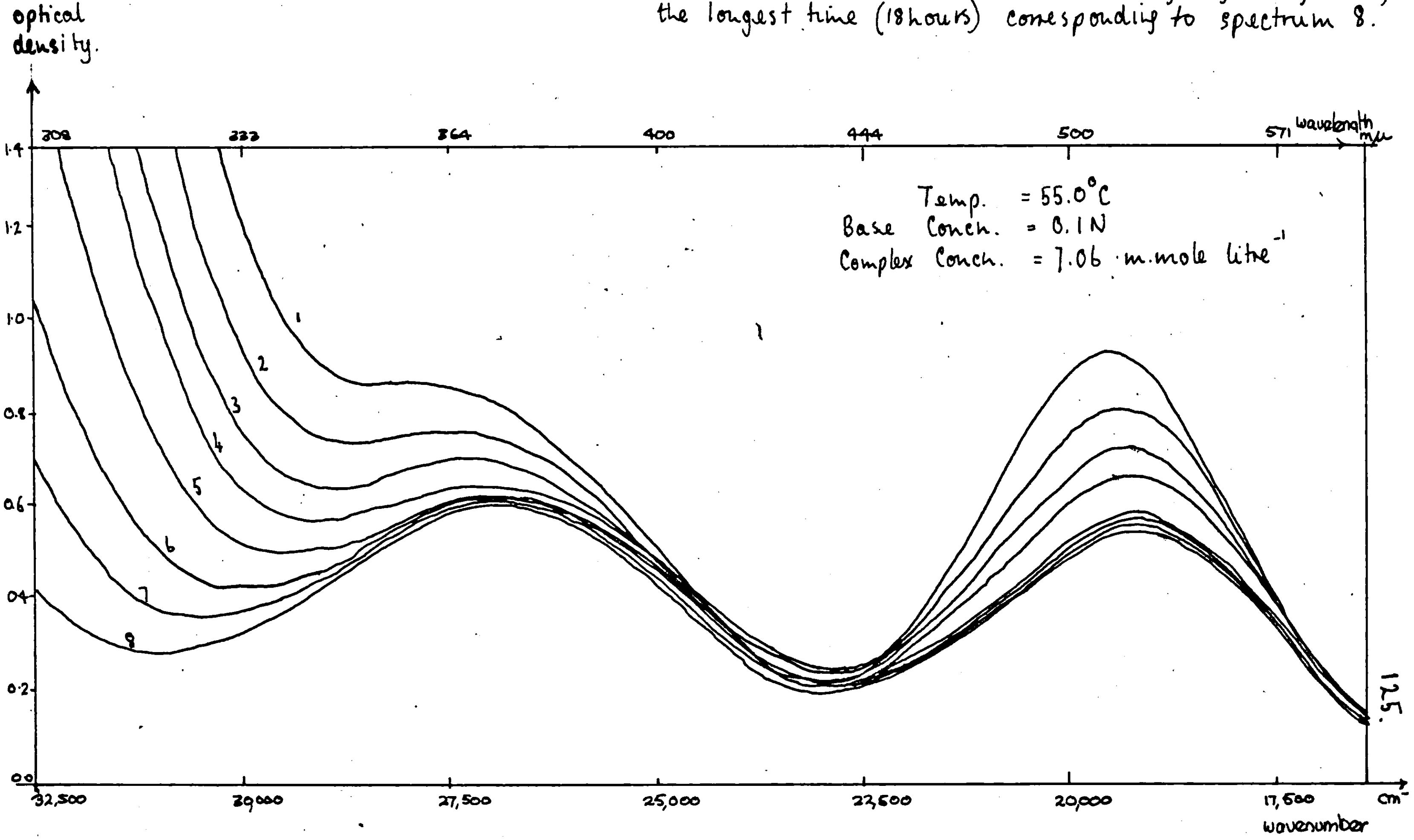
Variation in activation energy with base concentration for the second stage of the base hydrolysis of the $[Coen_2CO_3]^+$ ion

NaOH N	Activation energy k.cals/mole	Probability factor
0·167	21·0	$8 \cdot 23 \times 10^{14}$
0·100	22·2	$4 \cdot 89 \times 10^{13}$
0·033	24·1	$5 \cdot 37 \times 10^{14}$

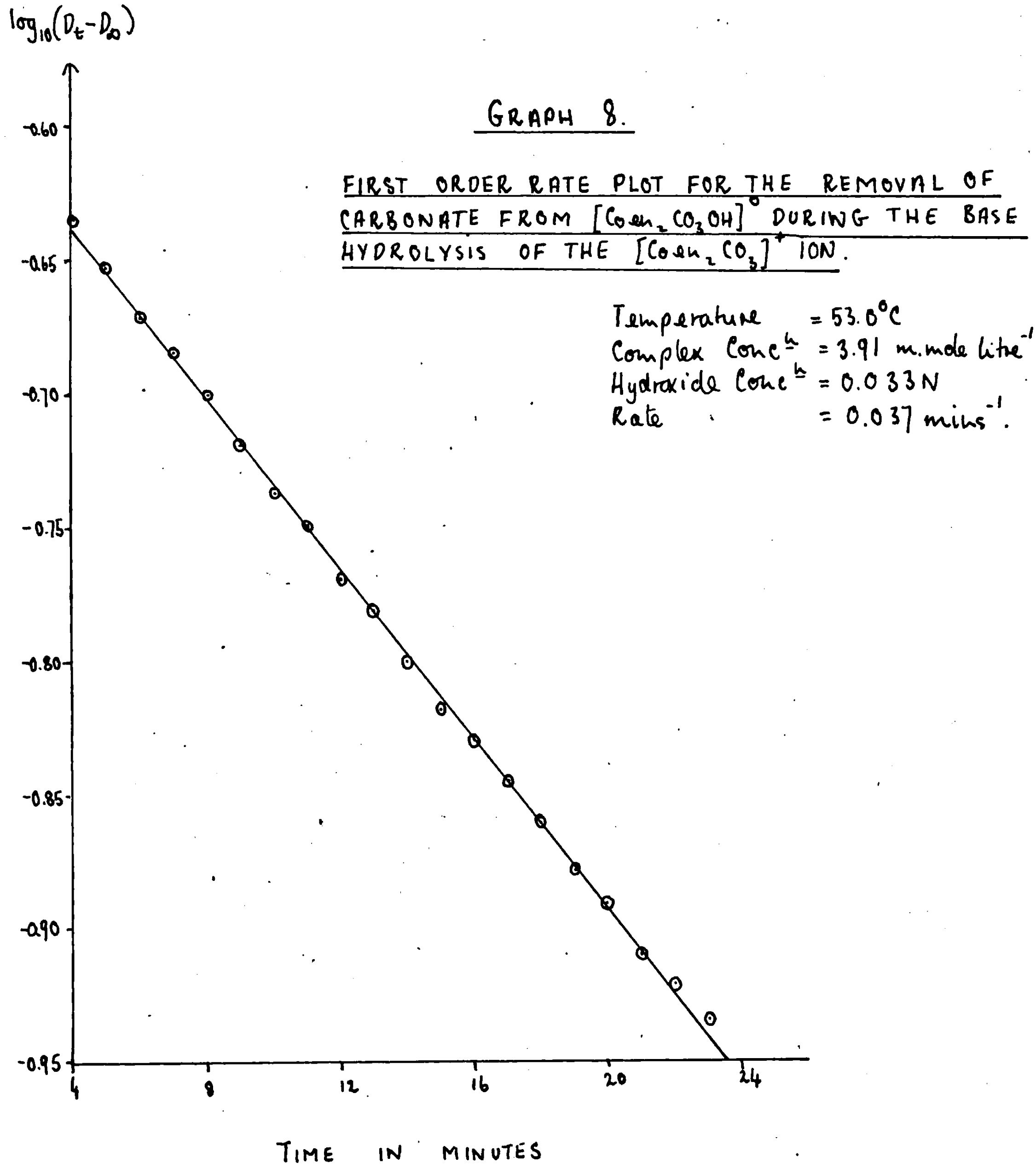
GRAPH 7.

SPECTROPHOTOMETRIC CHANGES OCCURING DURING THE BASE HYDROLYSIS OF THE $[Coen_2CO_3]^+$ ION.

1, Spectrum after 2.5 mins reaction time. 2,3,4,5,6,7 and 8 spectra at increasing lengths of time, the longest time (18 hours) corresponding to spectrum 8.



Temp. = 55.0°C
Base Conch. = 0.1 N
Complex Conch. = 7.06 m.mole litre⁻¹



GRAPH 8.

FIRST ORDER RATE PLOT FOR THE REMOVAL OF CARBONATE FROM $[\text{Co en}_2\text{CO}_3\text{OH}]^0$ DURING THE BASE HYDROLYSIS OF THE $[\text{Co en}_2\text{CO}_3]^+$ ION.

Temperature = 53.0°C
Complex Concn = 3.91 m.mole litre^{-1}
Hydroxide Concn = 0.033N
Rate = 0.037 mins^{-1}.

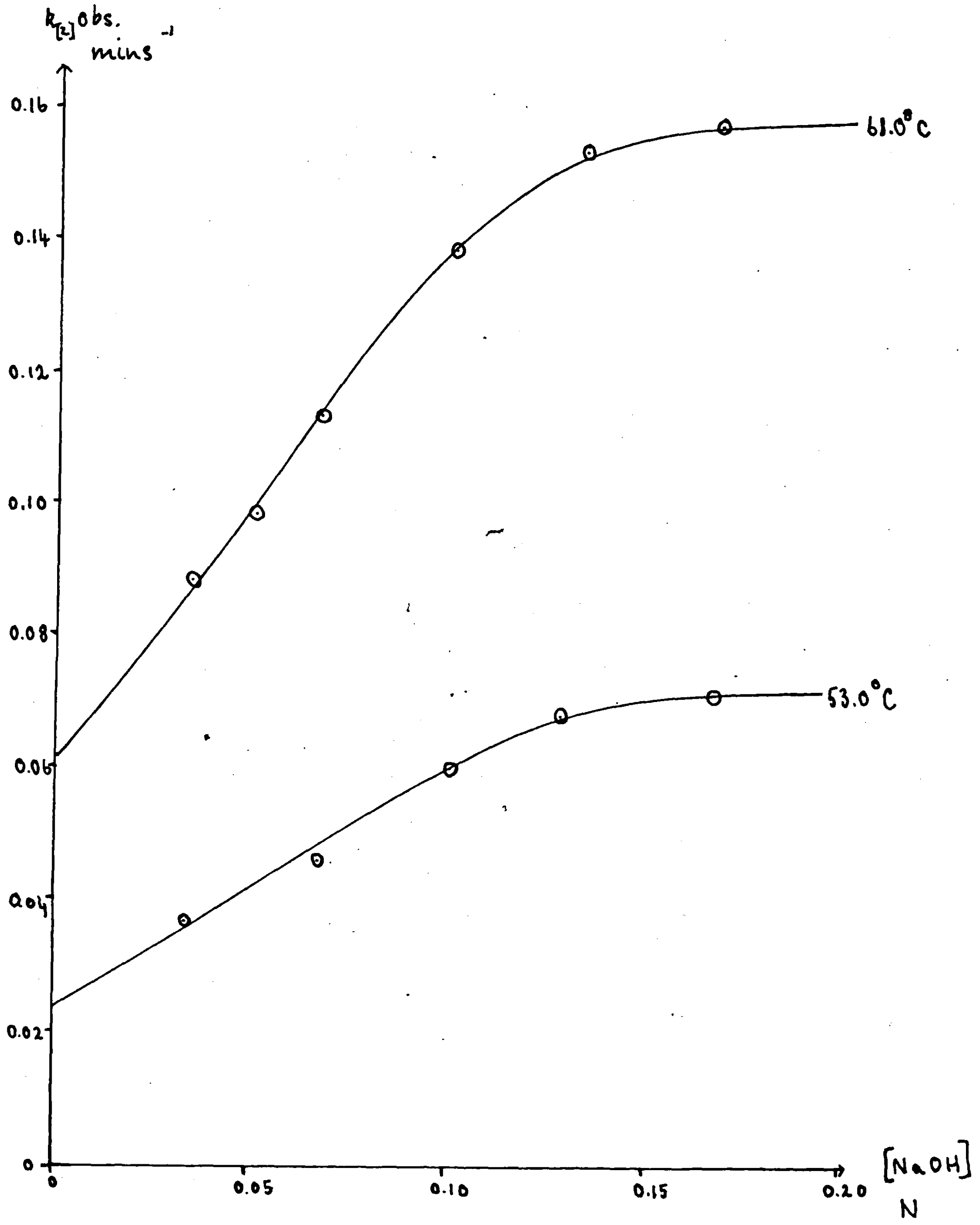
TABLE 9.

First-order rate constants for the second stage of the reaction

Temperature $^{\circ}C$	[NaOH] N	Complex Conc. m.mole litre^{-1}	$k_{[1]}$obs. min.$^{-1}$
71·0	0·167	4·80	0·380
	0·133		0·362
	0·100		0·355
	0·067		0·340
	0·050	3·10	0·311
	0·033	4·80	0·248
61·0	0·167	3·91	0·157
	0·133		0·154
	0·100		0·139
	0·067		0·113
	0·050	6·02	0·099
	0·033	3·91	0·089
53·0	0·167	3·91	0·071
	0·133		0·069
	0·100		0·060
	0·067		0·046
	0·033		0·037

GRAPH 9.

OBSERVED FIRST ORDER RATE CONSTANTS FOR THE SECOND STAGE OF THE BASE HYDROLYSIS OF THE $[Co\,en_2\,CO_3]^+$ ION AGAINST BASE CONCENTRATION.



Reaction in neutral solution

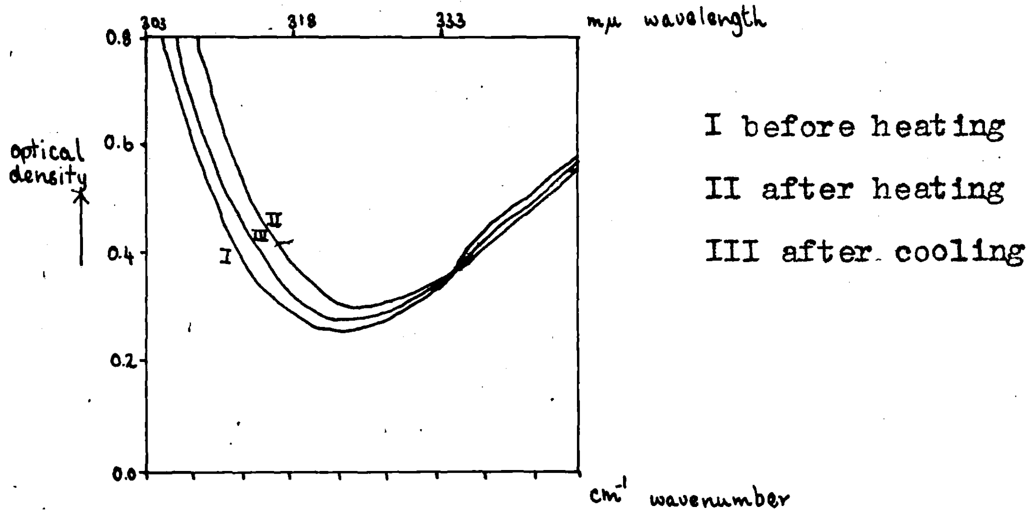
When the spectrum of a neutral solution (pH 7·02) of $[Coen_2CO_3]Cl$ was taken before and after heating to 80° for 10 minutes a significant increase in absorption is seen around 30,000 cm.$^{-1}$ whereas there is very little change elsewhere in the spectrum. This is shown in Diagram 15. The rise in absorption is due to the temperature dependent formation of $[Coen_2CO_3OH]^o$. Once this is formed there are two possible reactions which can occur on cooling. These are the complete removal of the carbonate and the reversible formation of the chelated carbonate.

$$[Coen_2CO_3]^+ \rightleftarrows [Coen_2CO_3OH]^o \longrightarrow [Coen_2(OH)_2]^+$$

Since the spectrum decreases on cooling but does not return to the original spectrum it would appear that both reactions take place.

DIAGRAM 15

Ultra violet spectrum of a neutral solution of $[Coen_2CO_3]Cl$ before and after heating



For the neutral rate the activation energies were calculated from the extrapolation of rates at known base concentration to zero.

Ring opening reaction, activation energy = 21•8 k.cals/mole

Removal of carbonate activation energy = 22•2 k.cals/mole

b) The rate of loss of optical activity accompanying base hydrolysis

Stoichiometry

The loss of optical activity was found to take place in two stages in a similar way as found spectrophotometrically. The first stage is due to the dechelation of the carbonate and the second to the complete removal of the carbonate.

$$[\mathrm{Coen_2CO_3}]^+ + \mathrm{OH^-} \longrightarrow [\mathrm{Coen_2CO_3OH}]^0 \qquad (1)$$

$$[\mathrm{Coen_2CO_3OH}]^0 + \mathrm{OH^-} \longrightarrow [\mathrm{Coen_2(OH)_2}]^+ + \mathrm{CO_3}^{2-} \qquad (2)$$

Method

Optically active $[\mathrm{Coen_2CO_3}]\mathrm{ClO_4}$ was dissolved in standard sodium hydroxide solution. The solution was placed in a jacketted polarimeter tube of a Zeiss polarimeter and readings of the rotation were taken at various time intervals at 436 mμ (22,940 cm.$^{-1}$)

Results

At high temperatures racemisation was observed, whilst at low temperatures an initial mutarotation was found prior to the racemisation. The mutarotation was ascribed to the ring opening reaction (1) and the racemisation to the complete removal of the carbonate (2). As in the spectrophotometric measurements the ring opening reaction was too fast to measure at high temperatures. The rate constants for the racemisation process were calculated as on page 101 . For the mutarotation the rate constants were also obtained graphically using an ∞ value obtained by the extrapolation to zero time, the line corresponding to the rate of racemisation. This was first done by Basolo, Matoush and Pearson.(15) Graph 10 shows the first order rate plot of the log of the rotation against the time t. Table 10 shows the observed first order rate constants for the rate of loss of optical activity. Graphs 11 and 12 show the change with hydroxide concentration of $k_{[1]\text{mut.}}^{\text{obs.}}$ and $k_{[1]\text{rac.}}^{\text{obs.}}$ respectively.

For the ring opening stage of the reaction the activation energy was calculated using the first order rate constants at various base concentrations for both spectrophotometric and polarimetric rates. It was also calculated from the second order rate constants. In all cases the activation energy was found to be 21·6 k.cals/mole. The variation of the second order rate constant with temperature fits the Arrhenius equation:

$$k_2 = 2{\cdot}9 \times 10^{15}\ e^{-\frac{21,600}{RT}}\ \ 1\ mole^{-1}\ min^{-1}$$

Within the experimental error this is the same as that found by Farago;(59)

$$k_2 = 2{\cdot}6\ 10^{15}\ e^{(-22,000/RT)}\ 1\ mole^{-1}\ min^{-1}$$

Since the ionic strength was not the same in the two series of measurements, the ring opening must be independent of the ionic strength.

The activation energy for the second stage of the reaction was also found to be independent of base concentration and had the value of 29·4 k.cals/mole.

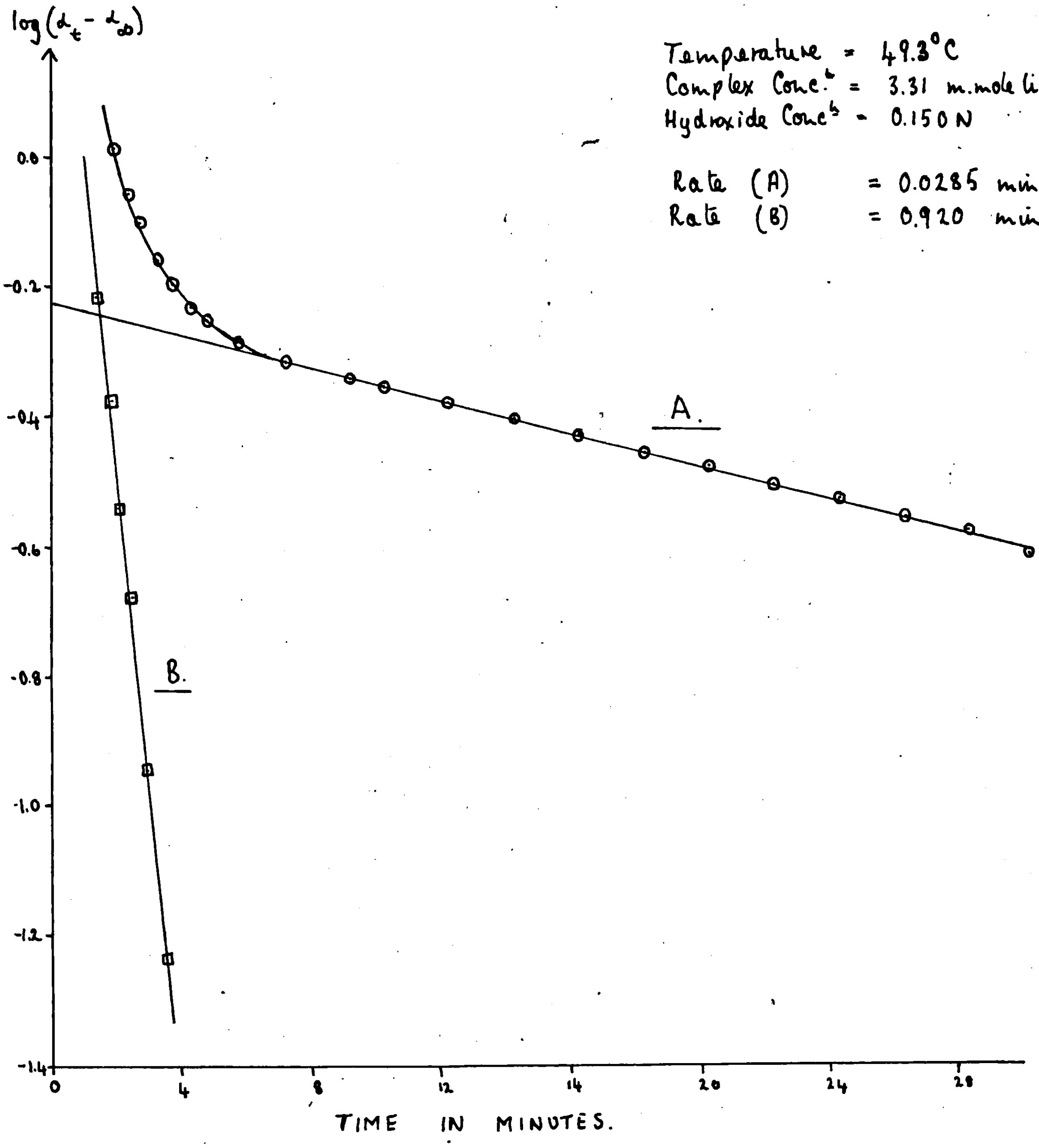
$$k_1 = 2{\cdot}95 \times 10^{18}\ e^{-29,400/RT}\ \ 1\ mole^{-1}\ min^{-1}$$

Rate of loss of optical activity in neutral solution

The rate of loss of optical activity was measured at neutral solution buffered at pH 7 at room temperature using a perchloric acid collidine buffer. No mutarotation was observed but a slow racemisation. The rate constants were evaluated graphically by the method used previously and these are shown in Table 11 .

GRAPH 10.

FIRST ORDER RATE PLOT FOR THE RATE OF LOSS OF OPTICAL ACTIVITY ACCOMPANYING THE BASE HYDROLYSIS OF THE $[Co\,en_2CO_3]^+$ ION.



Temperature = 49.3°C
Complex Concⁿ = 3.31 m.mole litre^{-1}
Hydroxide Concⁿ = 0.150 N

Rate (A) = 0.0285 mins^{-1}
Rate (B) = 0.920 mins^{-1}

A. α_∞ = 0
B. α_∞ obtained by extrapolation of A to zero time.

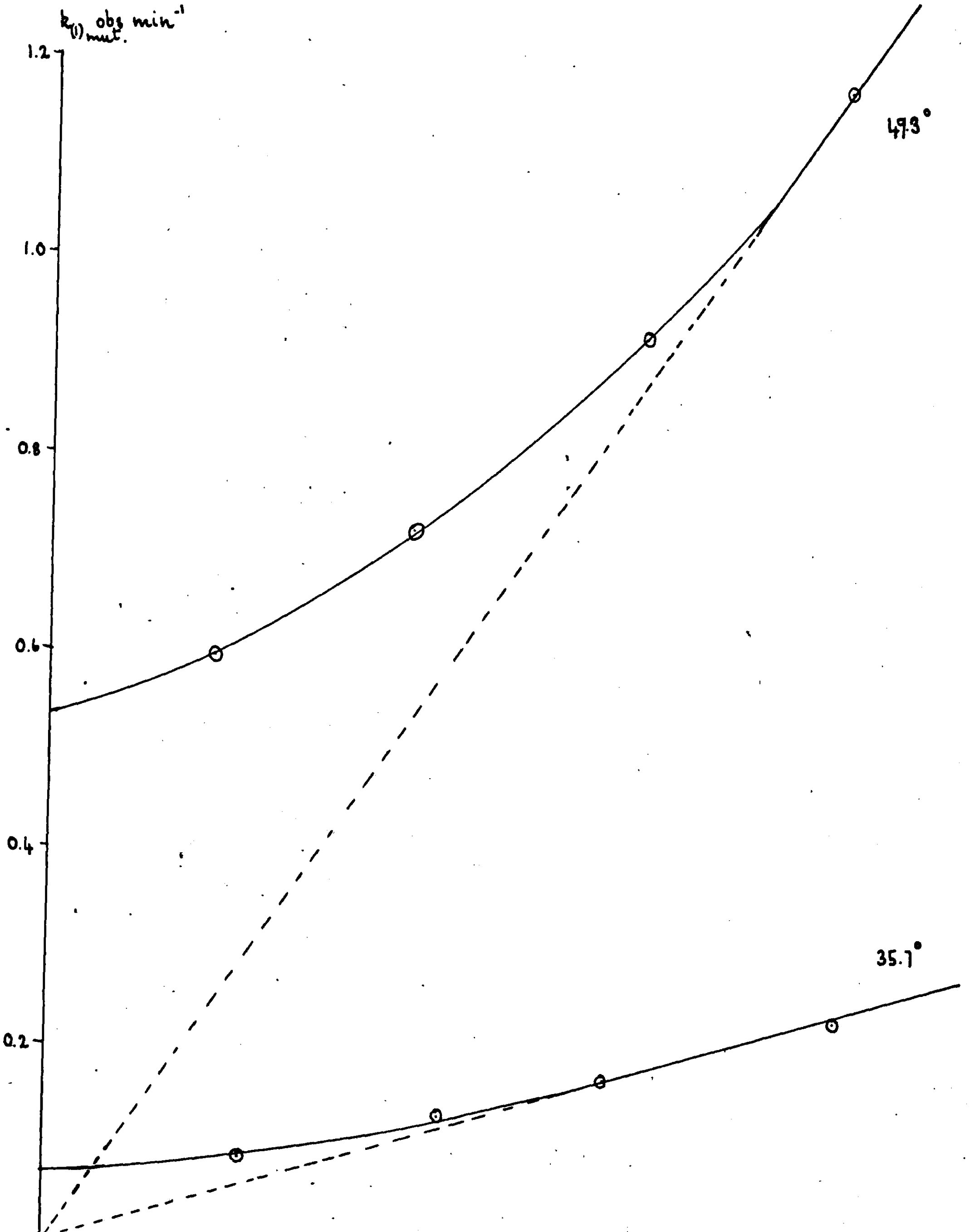
TABLE 10.

Observed first order rate constants for the mutarotation and racemisation occurring during the base hydrolysis of $[Coen_2CO_3]^+$ ion

Temperature °C	[NaOH] N	Complex Conc. m.mole litre^{-1}	$k_{[1]}$obs. (mutarotation) min.$^{-1}$	$k_{[1]}$ obs. (racemisation) min.$^{-1}$
66•8	0•20	6•91		0•324
66•9	0•15	2•57		0•284
66•9	0•10	6•64		0.250
66•9	0•05	7•18		0•193
49•3	0•20	7•77	1•176	0•0319
49•3	0•15	3•31	0•920	0•0285
49•3	0•10	6•35	0•721	0•0245
49•3	0•05	6•64	0•593	0•0193
35•7	0•20	5•26	0•224	0•00444
35•7	0•15	3•04	0•168	0•00404
35•7	0•10	4•78	0•130	0•00355
35•7	0•05	3•39	0•083	0•00289

GRAPH II.

OBSERVED FIRST ORDER RATE CONSTANTS FOR THE MUTAROTATION OF THE $[Co\,en_2\,CO_3]^+$ ION AGAINST BASE CONCENTRATION



GRAPH 12.

OBSERVED FIRST ORDER RATE CONSTANTS FOR THE LOSS OF OPTICAL ACTIVITY OF THE $[Co\,en_2\,CO_3]^+$ ION IN BASIC SOLUTION AGAINST BASE CONCENTRATION.

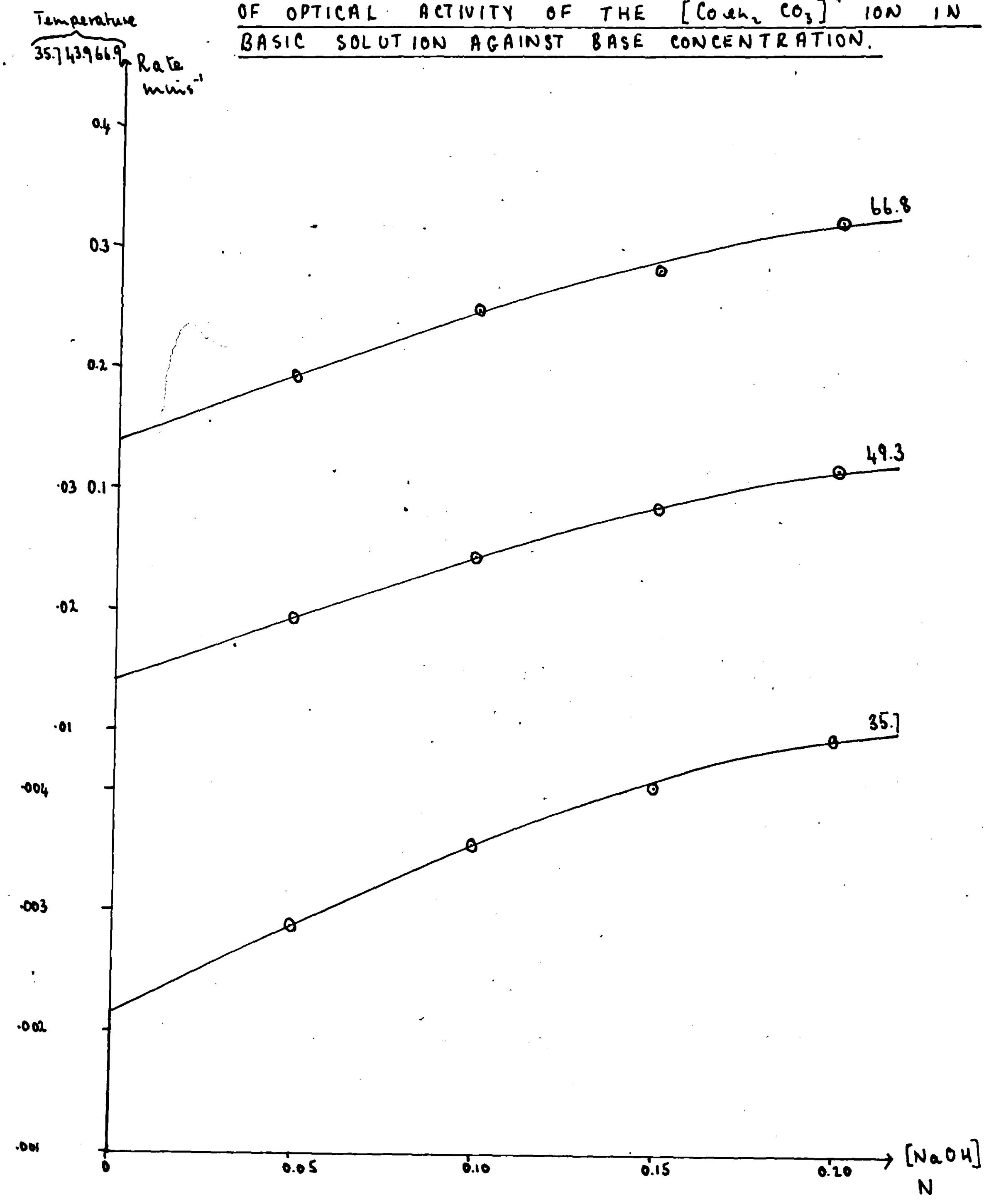


TABLE 11.

Observed first order rate constants for the loss of optical activity of the $[Coen_2CO_3]^+$ ion in neutral solution

Temperature ^oC	Complex Conc. m.mole litre^{-1}	k obs. min.$^{-1}$
66·8	3·75	0·0770
66·7	3·10	0·0762
49·7	2·98	0·0106
49·5	3·16	0·0106
35·6	2·22	0·00141
35·6	1·36	0·00152

The Arrhenius equation was found to be

$$k_1obs = 1{\cdot}82 \times 10^{16}\ e^{-27,000/RT}\ 1\ mole\ min^{-1}$$

DISCUSSION

1. Stoichiometry

The overall stoichiometry of the reaction under the conditions studied is given by:

$$[Coen_2CO_3]^+ + 2OH^- = cis/trans\ [Coen_2(OH)_2]^+ + CO_3^{2-} \qquad (1)$$

While following the course of the reaction spectrophotometrically it became clear that the reaction falls into two distinct parts, characterised by an initial rise in absorption around 30,000 cm.$^{-1}$ (333 mμ) followed by a decrease. This was interpreted as an initial dechelation followed by the complete removal of carbonate,

$$[Coen_2CO_3]^+ + OH^- = [Coen_2CO_3OH]^0 \qquad (2)$$

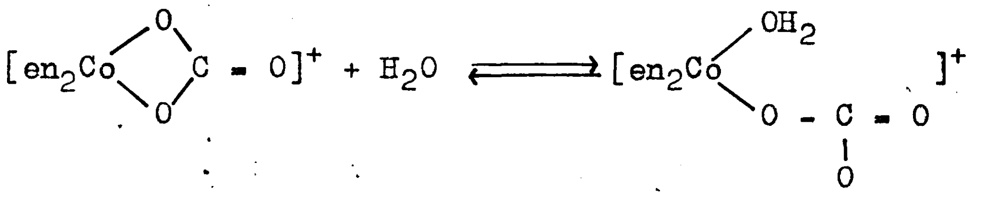
$$[Coen_2CO_3OH]^0 + OH^- = cis/trans\ [Coen_2(OH)_2]^+ + CO_3^{2-} \qquad (3)$$

Due to the chelated nature of the carbonate it would be expected that the cis dihydroxo ion would be formed initially and this would isomerise to form the cis/trans equilibrium mixture.

$$cis\ [Coen_2(OH)_2]^+ \rightleftharpoons trans\ [Coen_2(OH)_2]^+ \qquad (4)$$

2. The nature of the $[Coen_2CO_3]^+$ ion in aqueous solution

Since the carbonate chelate exists as a highly strained four-membered ring it was thought that, in aqueous solution, there might be an equilibrium with the non-chelated form:

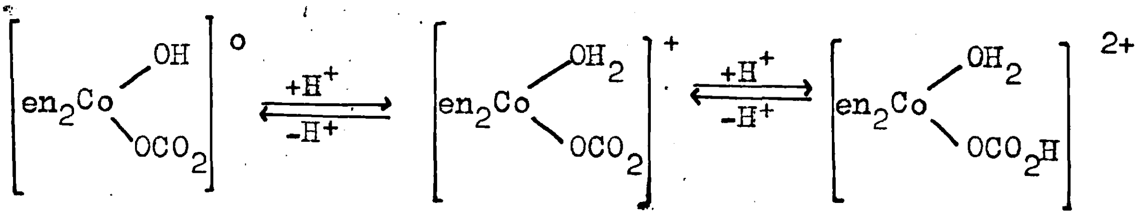

(6)

$$[en_2CoCO_3H_2O]^+ + H_2O \rightleftharpoons [en_2CoOHCO_3]^0 + H_3O^+ \qquad (7)$$

This would account for small changes in pH which occur when the complex is dissolved.

Work carried out on the carbonate exchange rate can be explained by considering the equilibrium to be dominantly to the right, i.e. existing in the non-chelated form. When the exchange equilibrium for the $[Co(NH_3)_4CO_3]^+$ ion was studied(136) using uncomplexed carbonate labelled with carbon 14 it was found that the equilibrium constant was 0·875 at 0°. This deviation from the ideal value of unity was explained by assuming modifications in the vibrational frequencies of the carbonate on chelation. However, it was found(149) that for the $[Coen_2CO_3]^+$ ion the exchange equilibrium was only slightly less than one (0.99). The vibrational frequencies appear to be unmodified, suggesting that there is no chelation of the carbonate. This is the same result as for the $[Co(NH_3)_5CO_3]^+$ ion,(79) the non-chelated carbonate group being almost identical structurally with a free carbonate ion.

Scheidegger and Schwarzenbach have pointed out(130) that the unchelated complex must be able to act both as a proton donor and proton acceptor.



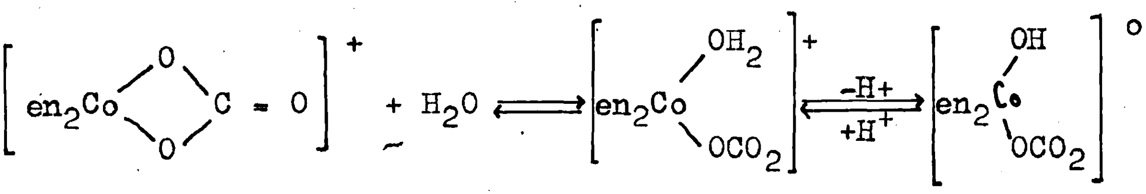
(8)

By addition of acid and alkali in a flow apparatus the complex was shown to be aprotic between pH 3 and pH 11. Readings were taken after 5×10^{-3} secs. which is sufficient time for equilibration of reactions involving protons but insufficient time for decomposition to set in. Therefore the complex must exist in the chelated form at 20^{o} . In the course of the present work, i.e. the change in rate of the ring opening reaction with change in base concentration (reaction 2), it was found that, at temperatures greater than 25°, the ring opening reaction does take place in neutral solutions, page 122. Additional evidence was obtained by the increase in absorbance around 30,000 $cm.^{-1}$ of a neutral solution of the complex on heating. On cooling the absorbance decreased but the original spectrum was not reattained showing that some reaction had taken place.

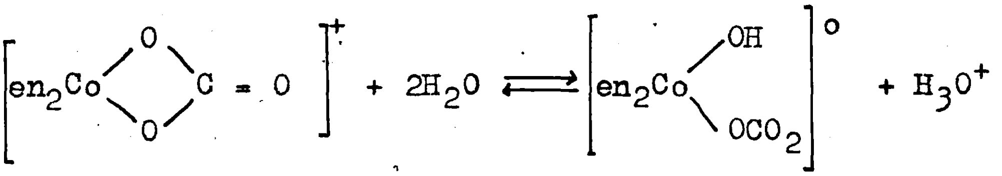
Since the measurements of Sheidegger and Schwarzenbach were carried out at 20° no reaction or ring opening would be expected to take place.

The exchange equilibrium constant of the $[Coen_2CO_3]^+$ ion with uncomplexed carbonate labelled with carbon 14 at 25° is 0·99, which is higher than might be expected assuming an almost completely chelated form at 25°. For the $[Co(NH_3)_4CO_3]^+$ ion the exchange equilibrium is 0·875 at 0·0° and 0·999 at 30.0°, the increase with temperature being due to the presence of some unchelated complex, the equilibrium being governed by the temperature.

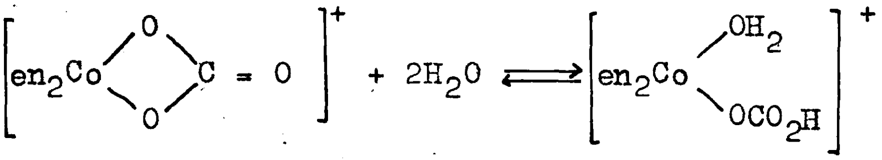
Several different reactions can be responsible for the formation of a ring open species in neutral solutions:



(9)



(10)



(11)

A solution of the optically active $[Coen_2CO_3]^+$ ion undergoes loss of optical activity in aqueous solution. As well as the racemisation of the $(-)[Coen_2CO_3]^+$ ion other processes involving all the species in solution result in the loss of optical activity.

3. The acid hydrolysis of the $[Coen_2CO_3]^+$ ion

The acid catalysed hydrolysis of this ion has been studied spectrophotometrically (140) in the pH range 2·4 to 3·0 and as a result of these measurements it was postulated that the reaction may go through one of the following reaction paths:

$$[Coen_2CO_3]^+ + H_2O \longrightarrow$$

$$[Coen_2CO_3H]^{2+} + H_2O \longrightarrow$$

$$[Coen_2CO_3H]^{2+} + H_3O^+ \longrightarrow$$

Alternatively it was suggested that both the protonated and unprotonated forms are present in significant concentrations with a rapid equilibrium being maintained between the two:

$$[Coen_2CO_3]^+ + H_3O^+ \rightleftharpoons [Coen_2CO_3H]^{2+} + H_2O$$

Other work done (78) over a larger pH range (1 to 5) resulted in the proposal of the following mechanism:

$$[\mathrm{Coen_2CO_3}]^+ + \mathrm{H_2O} \rightleftharpoons [\mathrm{Coen_2(H_2O)(OCO_2)}]^+ \qquad (1)$$

$$[\mathrm{Coen_2(H_2O)(OCO_2)}]^+ + \mathrm{H}^+ \rightleftharpoons [\mathrm{Coen_2(H_2O)(OCO_2H)}]^{2+} \qquad {}^1/\mathrm{K} \quad (2)$$

$$[\mathrm{Coen_2(H_2O)(OCO_2)}]^+ + \mathrm{H_2O} \xrightarrow{k_1} [\mathrm{Coen_2(OH)(H_2O)}]^{2+} + \mathrm{HCO_3}^-$$

$$[\mathrm{Coen_2(H_2O)(OCO_2H)}]^{2+} + \mathrm{H_2O} \xrightarrow{k_2} [\mathrm{Coen_2(H_2O)_2}]^{3+} + \mathrm{HCO_3}^-$$

$$[\mathrm{Coen_2(H_2O)(OCO_2H)}]^{2+} + \mathrm{H_3O}^+ \xrightarrow{k_3} [\mathrm{Coen_2(H_2O)_2}]^{3+} + \mathrm{H_2CO_3}$$

This is similar to the first reaction scheme except for the assumption of the opening of the carbonato chelate by the inclusion of a water molecule. If it is accepted that the equilibrations of reactions (1) and (2) are very rapid as compared to the aquations, then the total rate constant is given by:

$$k = \frac{k_1K + k_2(\mathrm{H}^+) + k_3(\mathrm{H}^+)^2}{K + (\mathrm{H}^+)}$$

where K is the equilibrium constant for reaction (2). This has been evaluated with the aid of a computer and found to fit the observed rate constants.

Very much more recently a slightly different mechanism resulting in the same rate law has been suggested: (89

$$[\mathrm{Coen_2CO_3}]^+ + \mathrm{OH^-} \rightleftarrows [\mathrm{Coen_2OHCO_3}]^0 \qquad K_0$$

$$[\mathrm{Coen_2OHCO_3}]^0 + \mathrm{H^+} \rightleftarrows [\mathrm{Coen_2OHCO_3H}]^+ \qquad {}^1/k_1$$

$$[\mathrm{Coen_2OHCO_3H}]^+ + \mathrm{H_2O} \xrightarrow{k_1} [\mathrm{Coen_2OH(H_2O)}]^{2+} + \mathrm{HCO_3^-}$$

$$[\mathrm{Coen_2OHCO_3H}]^+ + \mathrm{H^+} \rightleftarrows [\mathrm{Coen_2(H_2O)CO_3H}]^{2+} \quad {}^1/k_2$$

$$[\mathrm{Coen_2(H_2O)CO_3H}]^{2+} + \mathrm{H_2O} \xrightarrow{k_2} [\mathrm{Coen_2(H_2O)_2}]^{3+} + \mathrm{HCO_3^-}$$

$$[\mathrm{Coen_2(H_2O)CO_3H}]^{2+} + \mathrm{H_3O^+} \xrightarrow[k_3]{} [\mathrm{Coen_2(H_2O)}]^{3+} + \mathrm{H_2CO_3}$$

$$\text{rate} = \frac{k_1K_2 + k_2[\mathrm{H^+}] + k_3[\mathrm{H^+}]^2}{\frac{K_1K_2}{K_0K_w} + [\mathrm{H^+}]}$$

where $K_w = [\mathrm{H^+}]\,[\mathrm{OH^-}]$

The assumption is that the bicarbonato species is much more reactive than the carbonato species.

The rate constants k_1, k_2, and k_3 were calculated from the rate equation using the observed hydrolysis rate and the values of the equilibrium constants K_0, K_1 and K_2 found by Scheidegger and Schwarzenbach.(130) The rates obtained were found to be very similar to those found by Harris and Sastri.(78) Also the values of

k_1 and k_2 are in reasonable agreement with the analogous hydrolysis rate constants for $[Co(NH_3)_5CO_3H]^{2+}$.

Scheidegger and Schwarzenbach (130) examined the system by carrying out the acid base titrations using a flow apparatus. In this way they found that the protons initially attack the hydroxo ligand and subsequently attack the carbonato ligand. In acid solution the initial reaction involves attack by water on the cobalt whilst in alkaline solution the initial attacking species involves the hydroxyl ion.

The ring opening reaction

$$[Coen_2CO_3]^+ + OH^- \longrightarrow [Coen_2CO_3OH]^0$$

During the present investigation the rate of ring opening and the rate of mutarotation were found to be identical indicating that the rate of change of optical activity is due to the ring opening. Thus, the reaction must take place without extensive rearrangement, although there may be some formation of the racemic ion. Under the present conditions it is not possible to distinguish between partial racemisation and complete retention. Since the isomerisation reaction

$$\text{cis } [Coen_2CO_3OH]^0 \rightleftharpoons \text{trans}[Coen_2CO_3OH]^0$$

has been shown to have a half-life of about nine days (130) it is not significant in the present investigation.

The graph of $k_{1obs.}$ against added hydroxide concentration (page 121) shows that there is one reaction path first order in hydroxide. At low concentrations a departure from linearity occurs indicating some other reaction path. If a reaction involving a neutral species was occurring simultaneously with a base catalysed reaction it would occur at all base concentrations and an intercept giving the neutral rate would be found. Since no such intercept is found the departure from linearity is due, not to a neutral species as suggested from the equations on page 143 , but to an acid species since the departure from a second order rate decreases with increase in base concentration. An acid catalysed path may be stoichiometrically represented as

$$[Coen_2CO_3]^+ + H_3O^+ \longrightarrow [Coen_2CO_3H_3O]^{2+}$$

but, as before it cannot necessarily be considered as mechanistically satisfactory.

Mechanistic course

Base catalysed path

a) Cobalt-oxygen bond fission

Cobalt-oxygen bond fission has been postulated by Taube (6) and more recently by Farago (59) and can be explained on the basis of an S_N1 CB mechanism.

$$[Coen_2CO_3]^+ + OH^- \underset{}{\overset{fast}{\rightleftarrows}} [Coen(en\text{-}H)CO_3]^o + H_2O$$

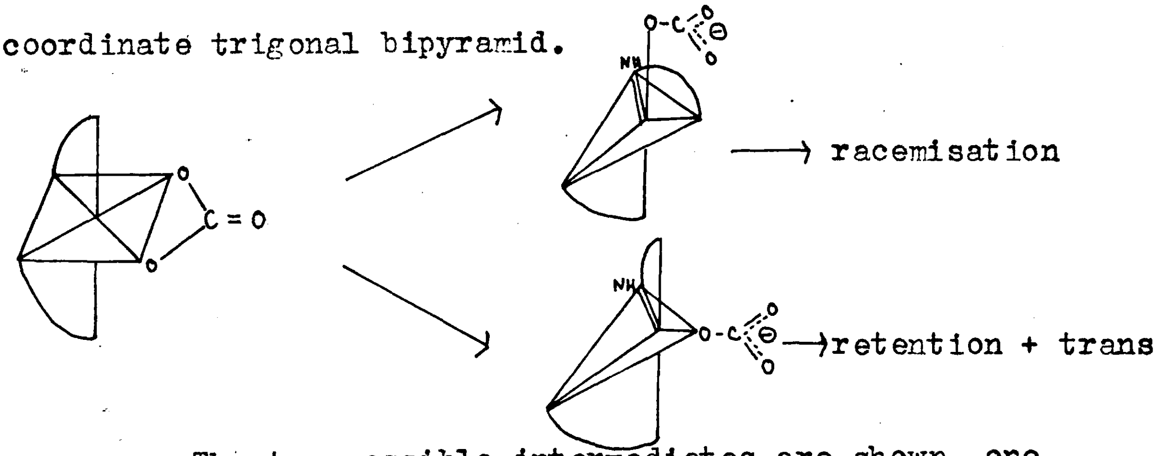
$$[Coen(en\text{-}H)CO_3]^o \xrightarrow{slow} [Coen(en\text{-}H)CO_3]^o$$

$$[Coen(en\text{-}H)CO_3]^o + H_2O \xrightarrow[fast]{} [Coen_2CO_3OH]^o$$

Farago (59) has previously found that, with increase in base concentration, the reaction rate becomes independent of base which is expected if an S_N1 CB mechanism is operative.

Graph 4 (page 118) shows that there is a large initial decrease in absorption in the ultraviolet spectrum with the maximum becoming less pronounced and shifting very slightly to longer wavelength. The two possible explanations are either rapid proton removal with the formation of the conjugate base or rapid ion pair formation. Rapid proton removal results in a decrease in absorption and a shift in maximum absorption to longer wavelength. Ion pair formation results in an increase in absorption (17) with the maximum again being shifted to longer wavelength. Since a decrease in absorption is found a rapid proton removal is more likely, supporting an S_N1 CB mechanism. A decrease in the absorption spectrum of the complexes $[[Pt(NH_3)_6]Cl_4$, $[Pt(NH_3)_5Cl]Cl_3$, $[Pt(NH_3)_5OH]Cl_3$ and $[Pt(NH_3)_4(OH)_2]Cl_2$ on the addition of sodium hydroxide has been accounted for in this way.(72a)

In the S_N1 CB mechanism the rapid formation of the conjugate base is followed by the slow rate determining dechelation of the carbonato group to form the monodentate chelate. The formation of the conjugate base is accompanied with rearrangement to form a five coordinate trigonal bipyramid.



The two possible intermediates are shown, one leading to retention and trans configuration and the other leading to racemisation. The intermediate leading to trans configuration would be more stable since the lone pair of electrons on the oxygen attached to the cobalt may be partially donated into the cobalt $d_{x^2-y^2}$ orbital providing the donor group is in the xy plane. Since the reaction is known to go with retention of configuration (partial or complete) there must be preferential attack at the same position as dechelation, to obtain the observed configuration and also to account for the lack of trans isomer. This preferential attack could result in an I_d process rather than a pure D process (page 61). Instead of the dissociation of the conjugate base being unaffected by environment as in a D process, it is assisted by the entry of water in an I_d process, although the activation energy is still largely governed by the dissociation. The degree of bond breaking in the transition state is still more important than that of bond making.

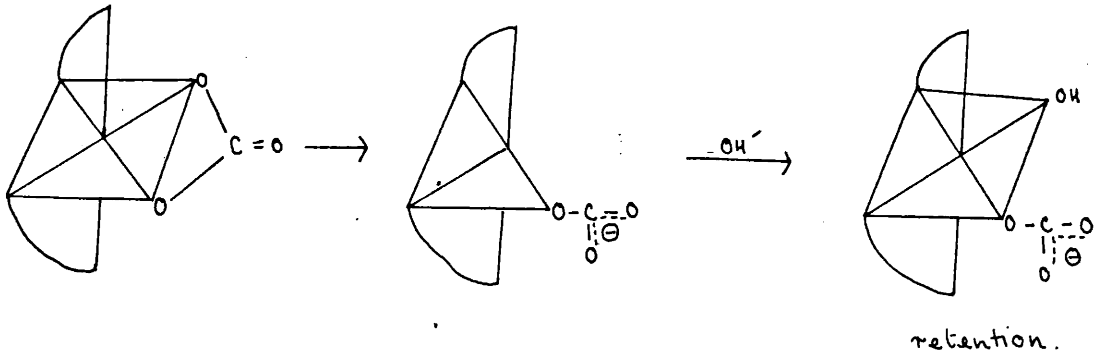
Alternatively the initial change in the ultraviolet spectrum shown in graph 4 (page 118) could be explained by the rapid formation of a reactive ion pair species, although an increase in absorption would be expected whereas a decrease is found.

$$[\mathrm{Coen_2CO_3}]^+ + \mathrm{OH^-} \xrightarrow[\text{fast}]{} [\mathrm{Coen_2CO_3}]^+.\mathrm{OH^-}$$

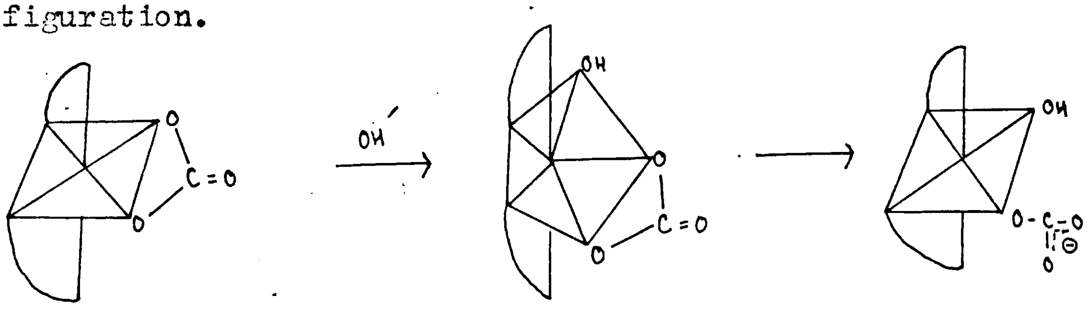
$$[\mathrm{Coen_2CO_3}]^+.\ \mathrm{OH^-} \xrightarrow[\text{slow}]{} [\mathrm{Coen_2CO_3OH}]^0$$

No change in rate was found when sodium perchlorate was replaced by sodium chloride showing that there are no specific anion effects.

Retention of configuration may be due to attack on a tetragonal pyramid intermediate. This is unlikely since the stabilisation induced by the formation of an amido base results in the trigonal bipyramid intermediate since the amido nitrogen must be in the same trigonal plane as the vacant $d_{x^2-y^2}$ orbital on the cobalt.



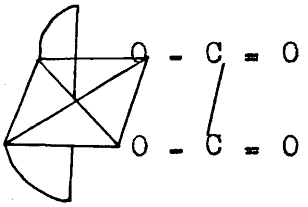
An S_N2 mechanism with cis attack adjacent to the carbonate would also explain the retention of configuration.



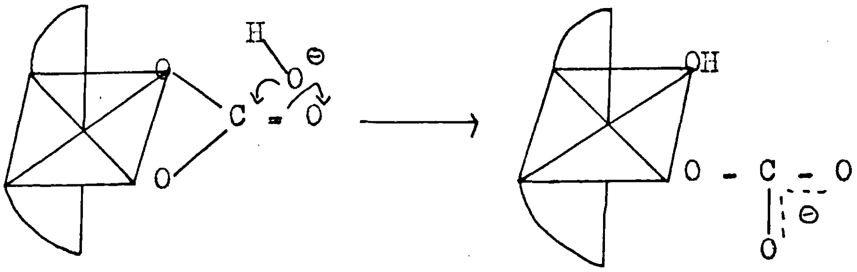
An S_N2 mechanism and trans attack is not prohibited and would result in the production of both cis isomers and the trans isomers. Specific attack in a cis position is likely due to hydrogen bonding between the carbonate and the solvent water.

b) Carbon-oxygen bond fission

Carbon-oxygen fission has been shown to take place during the dechelation of the oxalate ligand.(134)



Several factors favour carbon-oxygen bond fission. The inductive effect of the carbonyl group renders the carbon electropositive and thus liable to attack and also the carbon is more accessible than the cobalt. As there is no metal ligand bond fission there is no stereo change.



A limiting rate at high hydroxide concentrations is unlikely if the reaction proceeds by hydroxide attack on carbon giving carbon-oxygen bond fission. The dechelation during the acid hydrolysis of the $[Co(NH_3)_4CO_3]^+$ has been shown (124) to proceed by cobalt-oxygen bond fission. It is unlikely that carbon-oxygen bond fission occurs in the present context.

Conclusion

The reaction proceeds by a mechanism involving cobalt-oxygen bond fission. This can either be an S_N1 CB or S_N2 ion pair mechanism.

Acid Catalysed Path

As stated on page 144., the most likely stoichiometry consists of an equilibrium

$$[Coen_2CO_3]^+ + H_3O^+ \rightleftharpoons [Coen_2CO_3H]^{2+} + H_2O$$

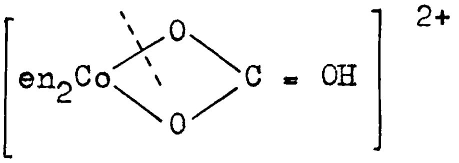
The actual dechelation takes place by two different processes.

$$[Coen_2CO_3]^+ + H_3O^+ \longrightarrow [Coen_2CO_3H_3O]^{2+}$$

$$[Coen_2CO_3H]^{2+} + H_2O \longrightarrow [Coen_2CO_3H.H_2O]^{2+}$$

or $$[Coen_2CO_3H]^{2+} + H_3O^+ \longrightarrow [Coen_2CO_3H\ H_3O]^{3+}$$

Again there are the two possibilities for the position of bond fission. If the reaction proceeds in a similar fashion to the acid hydrolysis of the $[Co(NH_3)_4CO_3]^+$ ion then a cobalt-oxygen bond is broken. (see page 92).



In keeping with other acid hydrolysis processes a slow dissociative process is followed by the rapid addition of water.

Second stage of the base hydrolysis

Published results on this reaction

Previous spectrophotometric measurements (59) were carried out at 30,000 cm.$^{-1}$ Higher hydroxide concentrations were used, the final product formed being the cis $[Coen_2(OH)_2]^+$ ion. The reaction was found to be first order with respect to hydroxide throughout the ~~temperature~~ hydroxide range studied (3·71 M to 0·276 M) and the variation of the rate constant with temperature fitted the Arrhenius equation:

$$k_2 = 1{\cdot}9 \times 10^{13}\ e^{-24,000/RT}\ \text{l.mole min.}^{-1}$$

The reaction was suggested to occur with carbon-oxygen bond fission.

Results in the present work

The observed first order rate constants at 19,230 cm.$^{-1}$ do not show a first order dependency on the hydroxide concentration except over a very limited range, graph 9, page 128 . A neutral rate was obtained. With increasing base concentration a first order rate was very soon superseded by a rate independent of hydroxide concentration. (0.167 N at 53^{o}). In all cases the cis/trans equilibrium mixture of the product ion, $[Coen_2(OH)_2]^+$, was obtained.

In the previous measurements at 30,000 cm.$^{-1}$ a first order rate was found. Reactions carried out under identical conditions at 19,230 cm.$^{-1}$ and 30,000 cm.$^{-1}$ confirmed that the measured rate is dependent on the wavelength. The rate measured at 30,000 cm.$^{-1}$ was considerably slower than that measured at 19,230 cm.$^{-1}$, as has been found previously.(59)

The reaction path previously postulated by Farago (59) will be operative and be the dominant reaction path at high base concentrations. At low base concentrations other species will be present in solution which cannot be detected spectrophotometrically but will provide alternative reaction paths. Since there is also a neutral rate the following reaction paths are postulated to occur with both carbon-oxygen and cobalt-oxygen bond fission.

$$[Coen_2CO_3OH]^0 + H_2O \longrightarrow [Coen_2(H_2O)OH]^{2+} + CO_3^{2-}$$

$$[Coen_2CO_3H_2O]^+ + OH^- \longrightarrow [Coen_2(H_2O)OH]^{2+} + CO_3^{2-}$$

$$[Coen_2OHOCO_2H]^+ + OH^- \longrightarrow [Coen_2(OH)_2]^{\cancel{2}+} + HCO_3^{\cancel{2}-}$$

These species only differ in the position of the proton.

At low base concentrations it is possible to have more acidic species and the same reaction paths which are postulated under acid hydrolysis (page 144) are possible since an intercept is obtained on the rate axis when the hydroxide concentration is zero.

Steric course

The rate of loss of optical activity was found to have a different variation with base than the spectrophotometric rates (Graph 12, page 137) and also to be slightly slower. This favours the reaction path involving carbon-oxygen bond fission as this must necessarily go with retention of configuration. The activation energy was also found to be greater. The rate of loss of optical activity does not proceed by the same mechanism as the base hydrolysis. As suggested by Harris (79) it would appear that there are a variety of species present which are racemising, isomerising and decomposing with steric change by various independent reaction paths. The following reactions, each contributing to the inactive solution are suggested:

$$(-)[Coen_2CO_3OH]^o \rightleftharpoons (+)[Coen_2CO_3OH]^o$$

$$(-)[Coen_2CO_3OH]^o + OH^- \longrightarrow (\mp)[Coen_2(OH)_2]^+ + CO_3^{2-}$$

$$(-)[Coen_2CO_3OH]^o + H_2O \longrightarrow (\mp)[Coen_2(H_2O)OH]^+ + CO_3^{2-}$$

$$(-)[Coen_2(OH)_2]^+ \rightleftharpoons (+)[Coen_2(OH)_2]^+$$

Conclusions

At low base concentrations several reaction paths are responsible for the formation of the cis/trans equilibrium mixture of the product ion, $[Coen_2(OH)_2]^+$. The rate of loss of optical activity is found to have a higher activation energy and to be slower than the base hydrolysis showing that reactions are responsible for the rate of loss of optical activity which are not responsible for the formation of the product ion.

At high base concentration the dominant reaction path is first order in hydroxide and involves carbon-oxygen bond fission.(59)

3. THE BASE HYDROLYSIS OF THE CIS $[Coen_2C_2O_4]^+$ ION

a) Spectrophotometric measurements on the base hydrolysis of the $[Coen_2C_2O_4]^+$ ion

Stoichiometry

As in the case of the $[Coen_2CO_3]^+$ ion the reaction was found to take place in two stages, an initial dechelation of the oxalate ligand followed by its complete removal. The cis $[Coen_2(OH)_2]^+$ ion isomerises so that an equilibrium mixture of the cis and trans isomers is formed.

$$[Coen_2C_2O_4]^+ + OH^- \longrightarrow [Coen_2C_2O_4OH]^o$$

$$[Coen_2C_2O_4OH]^o + OH^- \longrightarrow cis[Coen_2(OH)_2]^+ + C_2O_4{}^{2-}$$

$$cis[Coen_2(OH)_2]^+ \rightleftharpoons trans[Coen_2(OH)_2]^+$$

At low temperatures the last two reactions are inseparable.

General method of measurement

A similar method was used as in the case of the $[Coen_2CO_3]^+$ ion. The base concentrations employed were higher rising to a maximum of 3.4 N. The ionic strength was kept constant with sodium chloride at 3·4 N. Sodium nitrate and sodium dithionate were both tried and found to have an inhibiting effect on the reaction. Graph 13 shows the spectrophotometric changes which occur during the reaction.

Temperature control

For temperatures above 20° the same method was used as for the $[Coen_2CO_3]^+$ ion. Below 20° a methanol thermostat was used with a heat exchanger filled with "drikold". At temperatures below 5° nitrogen was passed through the cell compartment to prevent condensation.

First stage of the ~~transition~~ reaction

$$[Coen_2C_2O_4]^+ + OH^- \longrightarrow [Coen_2C_2O_4OH]^0$$

This is characterised by an increase in absorption around 30,000 cm.$^{-1}$ This increase is slight, the production of the maximum optical density being much faster than for $[Coen_2CO_3]^+$ ion. Graph 14 shows the changes in optical density over the first ten minutes of the reaction at 33,000 cm.$^{-1}$ at various temperatures. The rate constants were calculated by the Guggenheim method (page 115) using the changes in optical density at 33,000 cm.$^{-1}$ Graph 15 shows a sample

Guggenheim plot. In general the errors present in the rate constants given in Table 12. are largely due to the small fast changes in optical density, the range of the values obtained being given.

At 3.33 N sodium hydroxide the variation in rate constant with temperature fits the Arrhenius equation :-.

$$k_1 = 1{\cdot}2 \times 10^{13}\ e^{-17,700/RT}\ \text{min}^{-1}$$

$$k_2 = 3{\cdot}6 \times 10^{12}\ e^{-17,700/RT}\ \text{l. mole min.}^{-1}$$

Second stage of the reaction

$$[Coen_2C_2O_4OH]^o + OH^- \longrightarrow cis[Coen_2(OH)_2]^+ + C_2O_4{}^{2-}$$

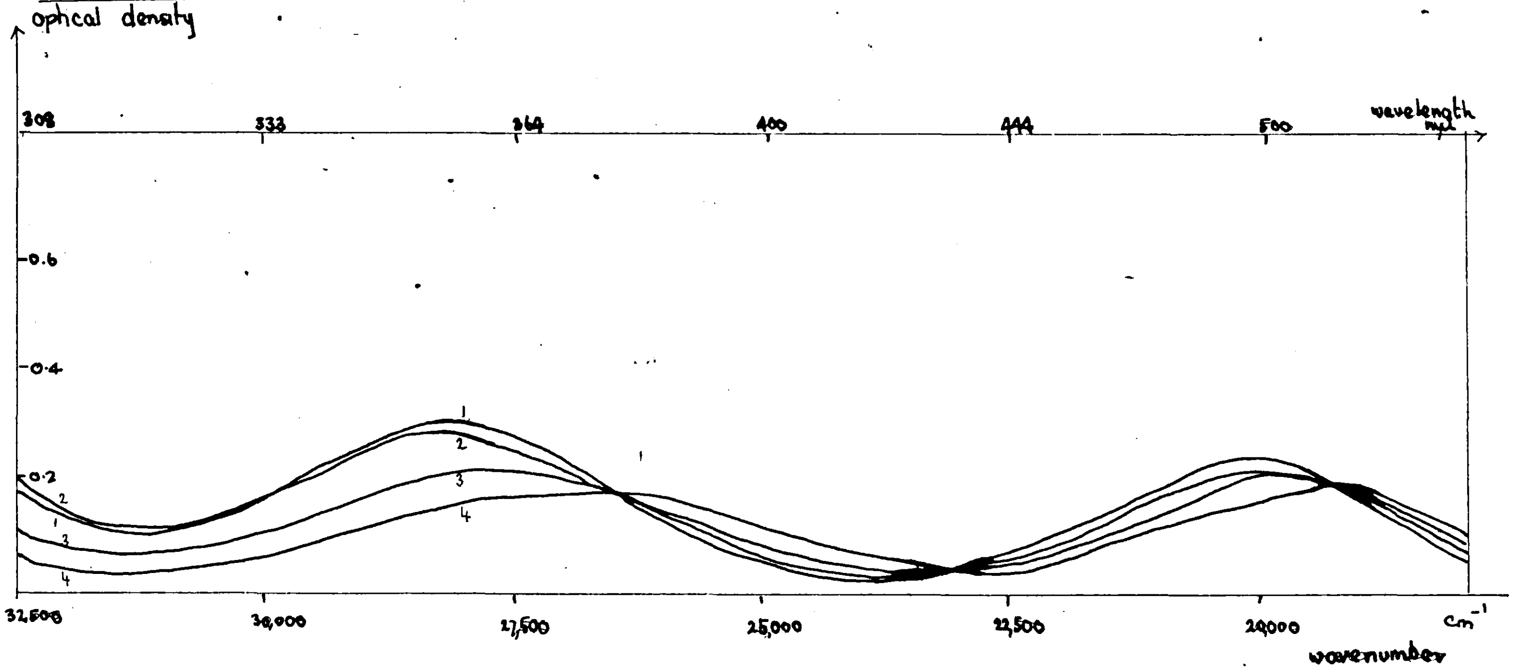
$$cis[Coen_2(OH)_2]^+ \rightleftharpoons trans[Coen_2(OH)_2]^+$$

This is characterised by a decrease in absorption around 33,000 cm.$^{-1}$ and isosbestic points at 26,600, 22,250 and 19,200 cm.$^{-1}$

The products of the reaction (either the cis or cis/trans dihydroxo ions) vary with the reaction conditions used. The measured extinction coefficients are shown in Table 13. (page 167).

GRAPH 13

SPECTROPHOTOMETRIC CHANGES OCCURING DURING THE BASE HYDROLYSIS OF THE $[\mathrm{Co\,en_2C_2O_4}]^+$ ION.



1. initial spectrum

2 spectrum after 3 minutes

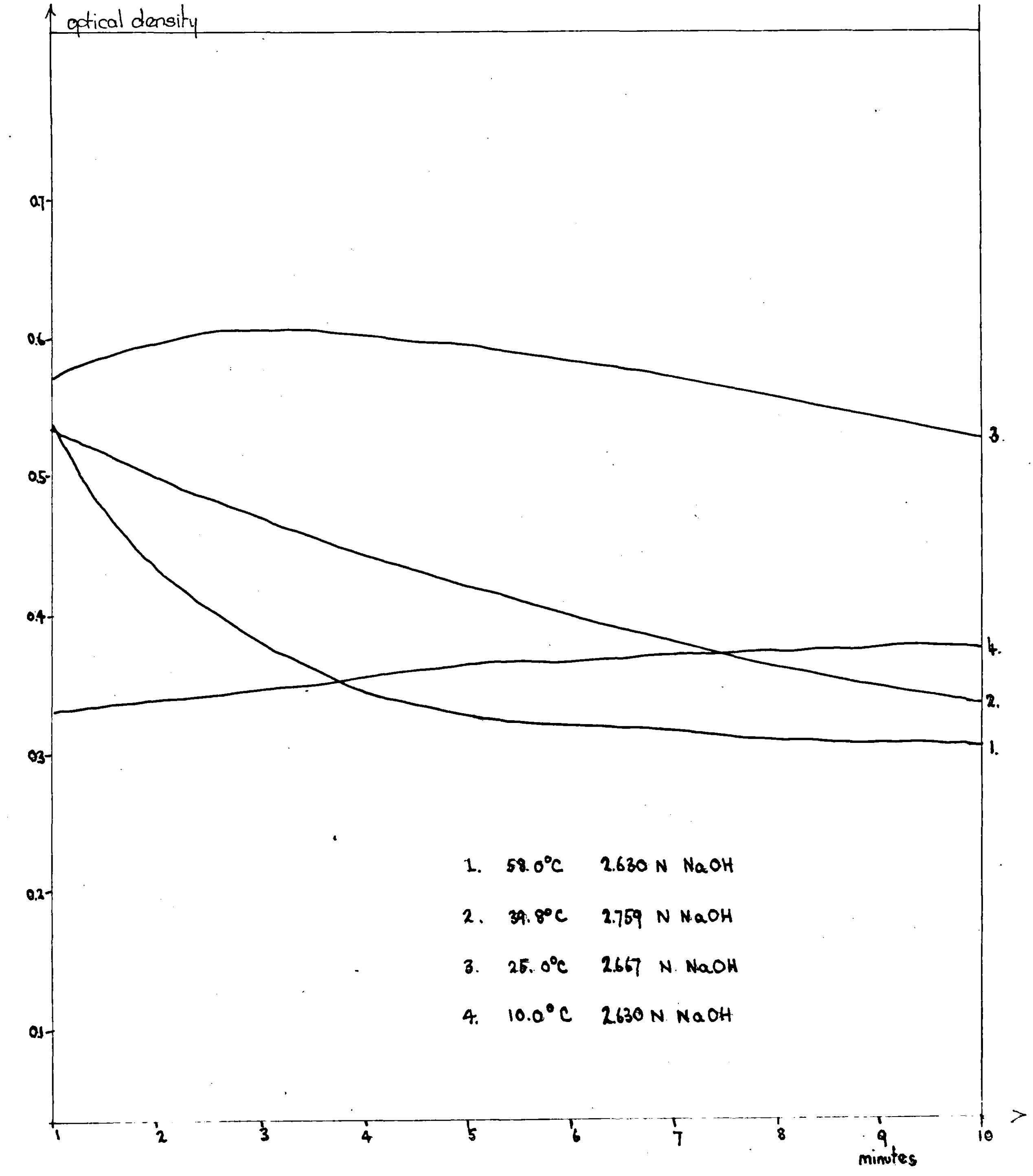
3 intermediate spectrum.
4 final spectrum.

25°C, 2.41 N NaOH

1.4 m.mole litre⁻¹ complex.

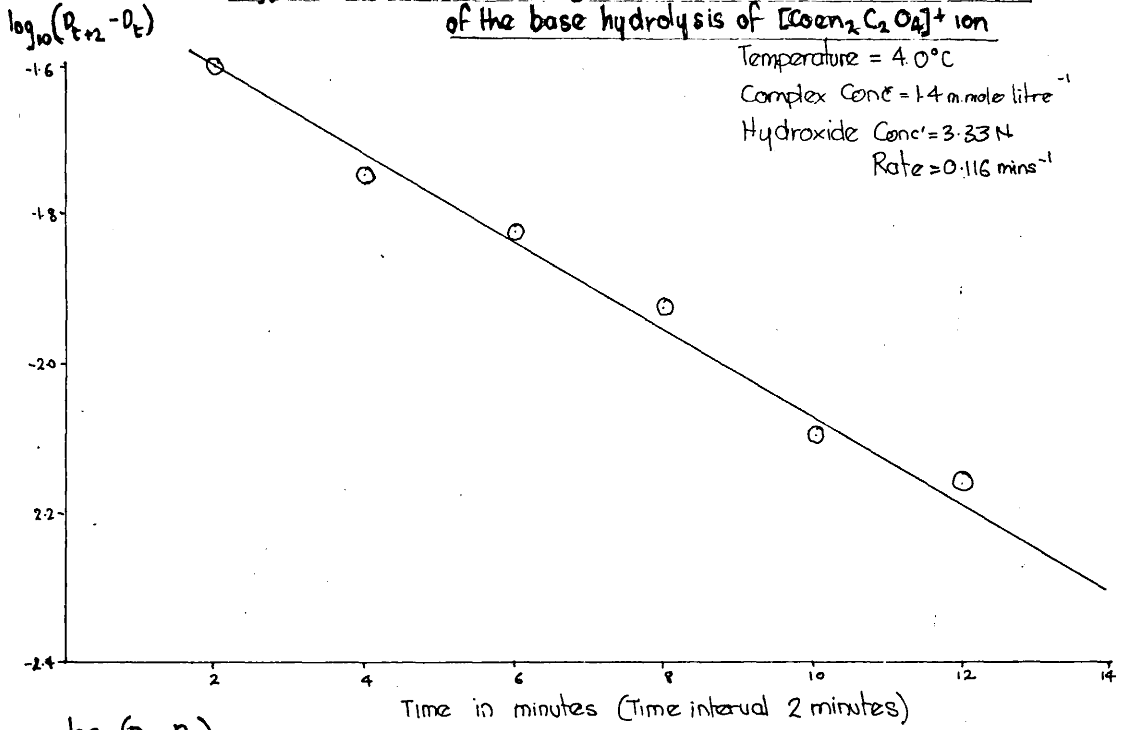
GRAPH 14.

Spectral changes occuring during the first 10 minutes of the base hydrolysis of the $[Coen_2(C_2O_4)]^+$ ion at 33,000 cm^{-1}



GRAPH 15.

Guggenheim plot for evaluating the rate constant for the first stage of the base hydrolysis of $[Coen_2C_2O_4]^+$ ion



Temperature = 4·0°C

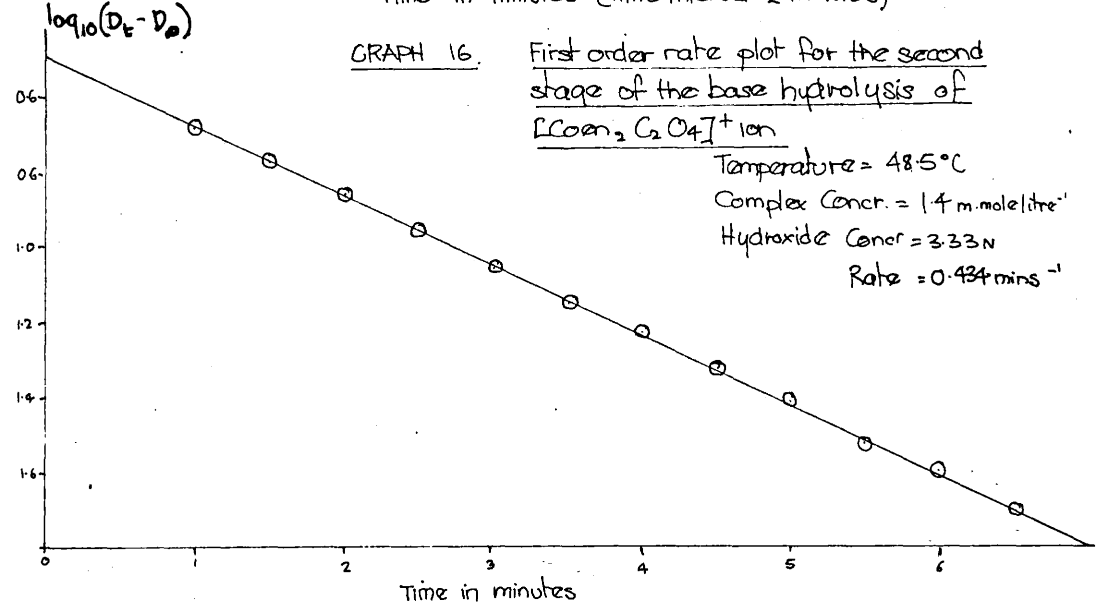
Complex Conc^n = 1·4 m.mole litre^{-1}

Hydroxide Conc^n = 3·33 N

Rate = 0·116 mins^{-1}

GRAPH 16.

First order rate plot for the second stage of the base hydrolysis of $[Coen_2C_2O_4]^+$ ion



Temperature = 48·5°C

Complex Concr. = 1·4 m.mole litre^{-1}

Hydroxide Concr = 3·33 N

Rate = 0·434 mins^{-1}

TABLE 12.

Observed first order rate constants and second order rate constants for the first stage of the hydrolysis of the $[Coen_2C_2O_4]^+$ ion

Temperature °C	NaOH N	$k_{[1]}$ obs. min.$^{-1}$	k_2(obs.) moles^{-1}min.$^{-1}$
25·0	3·398	1·511 - 1·241	0·321
	2·667	0·965 - 0·702	0·313
20·0	3·333	0·635 - 0·588	0·184
	2·667	0·293 - 0·257	0·136
10·0	3·333	0·283 - 0·215	0·075
	2·667	0·215 - 0·185	0·075
8·0	3·333	0·223 - 0·186	0·062
	3·000	0·149 - 0·130	0·047
	2·667	0·058 - 0·052	0·021
4·0	3·333	0·129 - 0·116	0·037
	2·667	0·113 - 0·073	0·035
	2·000	0·034 - 0·030	0·016

TABLE 13

Extinction coefficients for the $[Coen_2C_2O_4]^+$, cis $[Coen_2(OH)_2]^+$ and cis/trans equilibrium $[Coen_2(OH)_2]^+$ ions

Wave-number cm.$^{-1}$	Wave-length mμ	Extinction Coefficients		
		$[Coen_2C_2O_4]^+$	cis$[Coen_2(OH)_2]^+$	cis/trans $[Coen_2(OH)_2]^+$
33,000	303	115	50	44
20,000	500	113	85	65

The values obtained at 20,000 cm.$^{-1}$ agree with the literature values.(21) Bjerrum and Rasmussen (21) found that the values for the cis/trans equilibrium in the near ultraviolet are too high which is probably due to small amounts of ultraviolet absorbing biproducts. Because of this the experimentally obtained final extinction coefficients were used throughout the calculations. First order rate constants were calculated in the same way used for the $[Coen_2CO_3]^+$ ion, page 123 . Graph 16 shows one of the first order rate plots. The rate constants found are shown in Table 14 . The table also shows whether the product consists of the cis isomer or the equilibrium mixture of the cis and trans isomers. The nature of the products depends on the relative rate of the loss of oxalate compared to the cis/trans isomerisation rate. The rate of loss of oxalate is dependent on the base concentration whereas the isomerisation is independent. Therefore cis/trans equilibrium mixtures are obtained when the rate of loss of oxalate is slow, i.e. at low temperatures and base concentrations. At high temperatures and base concentrations the cis isomer is obtained. This is illustrated in the Arrhenius plots shown in Graph 17. The activation energy is independent of the base concentration above 1N NaOH within the experimental limits and has a value of 15·3 k. cals/mole. The variation of the first order rate constant with temperature fits the Arrhenius equation

$$k_1 = 2{\cdot}74 \times 10^{-11}\ e^{-15,300/RT}\ \text{min.}^{-1}$$

The Arrhenius plot for the isomerisation of the $[Coen_2(OH)_2]^+$ ion is also shown. This has a higher activation energy, about 30 k. cals/mole. With increase in temperature the rate of the isomerisation becomes faster than the rate of loss of oxalate as has been qualitatively predicted. Thus at 59° and 1.0N sodium hydroxide the rate of production of cis $[Coen_2(OH)_2]^+$ is the same as the rate of the cis/trans isomerisation.

TABLE 14.

Observed first order rate constants for the second stage of the hydrolysis of the $[Coen_2(C_2O_4)]^+$ ion in water

Complex conc. = 1.4 m.mole litre^{-1} approximately for all runs.

Temperature °C	NaOH N	$k_{[1]}$ obs. min.$^{-1}$	Isomeric composition of $[Coen_2(OH)_2]^+$ product ion.
72·0	3·000	1·640	cis
	2·333	1·060	"
	1·667	0·630	"
	1·333	0·515	"
	1·000	0·349	"
	0·400	0·156	"
	0·333	0·115	"
	0·200	0·069	"
	0·100	0·032	"
58·0	3·287	0·696	cis
	2·630	0·449	"
	1·973	0·294	"
	1·315	0·179	"
	0·658	0·086	cis/trans
	0·066	0·011	"
48·5	3·330	0·434	cis
	2·667	0·207	"
	2·000	0·128	"
	1·333	0·049	"
	1·000	0·031	"
	0·067	0.012	cis/trans

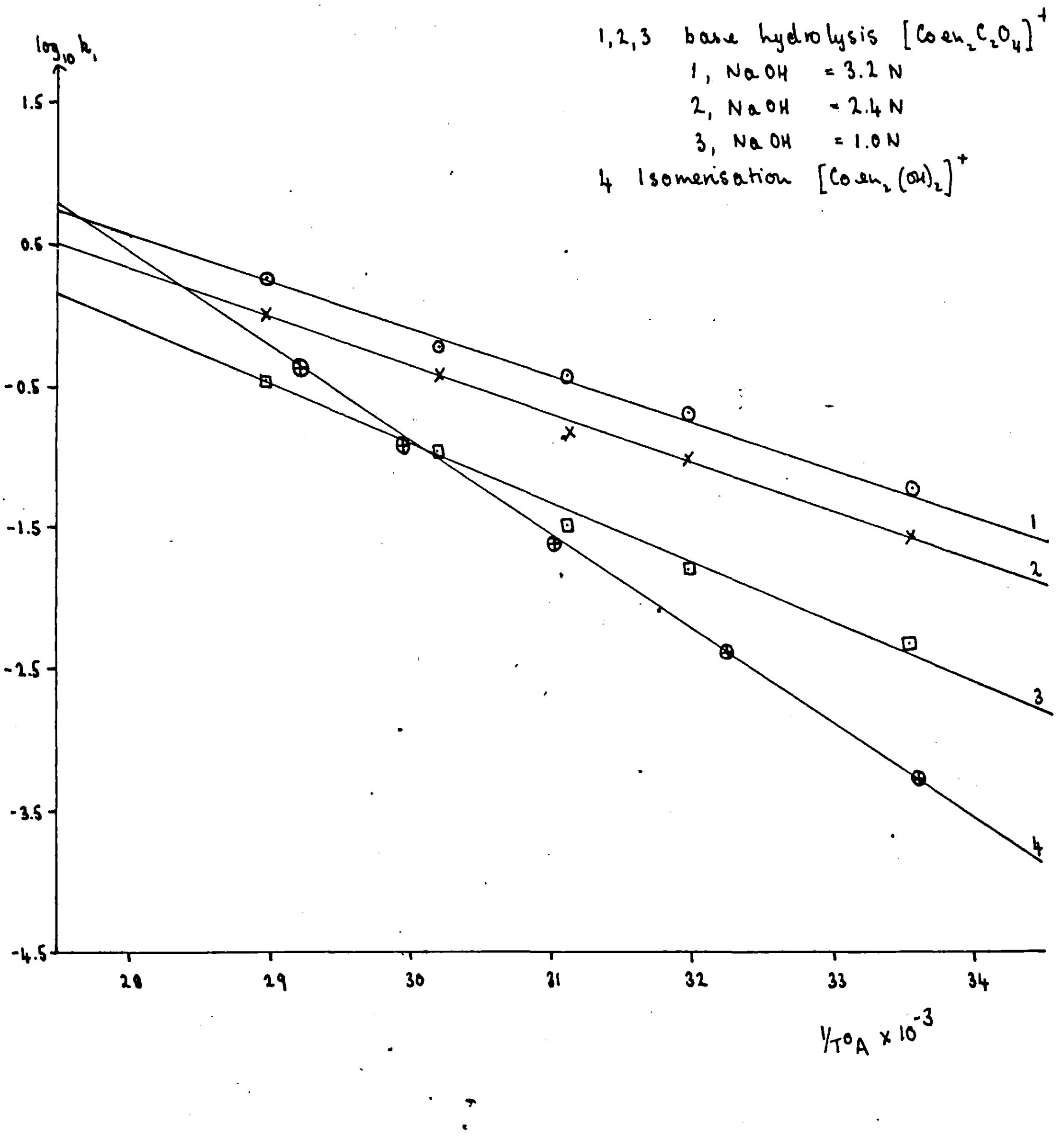
[continued over]

TABLE 14 - continued

Temperature °C	NaOH N	$k_{[1]}$ obs. min.$^{-1}$	Isomeric composition of $[Coen_2(OH)_2]^+$ product ion
39·8	3·448	0·273	cis/trans
	3·103	0·199	"
	2·759	0·148	"
	2·414	0·101	"
	2·069	0·067	"
	1·724	0·043	"
	1·303	0·022	"
25·0	3·398	0·078	cis/trans
	3·059	0·053	"
	2·719	0·039	"
	2·379	0·028	"
	2·069	0·020	"
	1·400	0·009	"

GRAPH 17

ARRHENIUS PLOT FOR THE SECOND STAGE OF THE BASE HYDROLYSIS OF THE $[\mathrm{Co\,en_2\,C_2O_4}]^+$ ION AND FOR THE ISOMERISATION OF THE $[\mathrm{Co\,en_2(OH)_2}]^+$ ION.



The reaction was also found to be independent of the presence of sodium chloride and sodium oxalate. These rate constants are shown in Table 15 .

TABLE 15

Rate constants for the second stage of the reaction

Temperature = 58·2° C

Complex Conc. = 5·62 m.mole litre^{-1}

NaOH N	NaCl N .	$Na_2C_2O_4$	Rate min.$^{-1}$
2·67	0·67	absent	0·546
2·67	-	absent	0·558
2·67	0·67	present	0·558

The rate constants were also measured using D_2O as solvent instead of H_2O. The rates were found to be unaffected by change in solvent and are shown in Table 16 . Graph 18 shows the change in the observed rate constant both in H_2O and D_2O with hydroxide concentration.

TABLE 16.

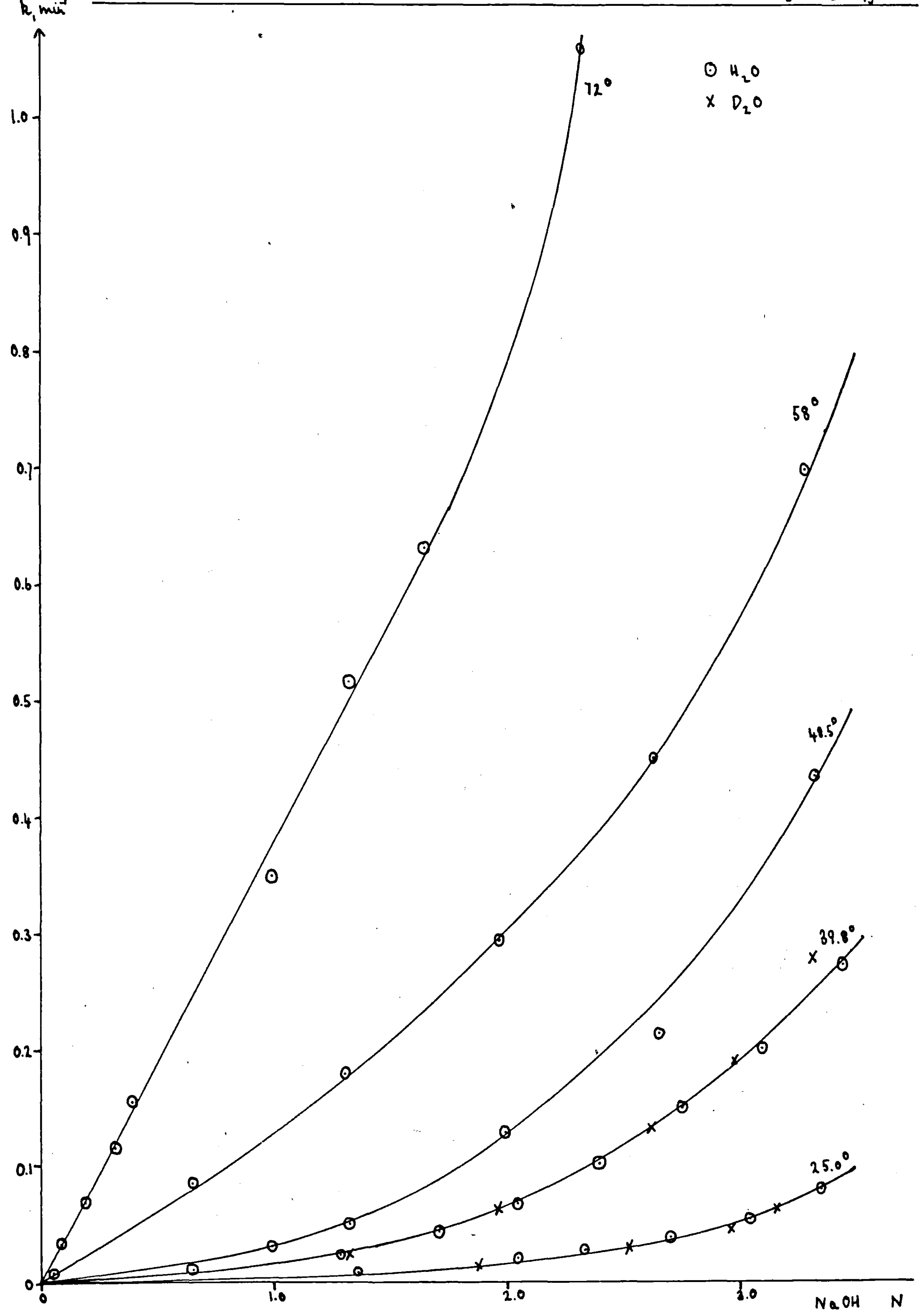
Observed first order rate constants for the second stage of the hydrolysis of the $[Coen_2C_2O_4]^+$ ion in deuterium oxide solvent resulting in the production of the cis/trans equilibrium mixture of the $[Coen_2(OH)_2]^+$

Complex conc. = 1·4 m.mole litre^{-1} approximately for all runs

Temperature °C	NaOH N	$k_{[1]}$ obs min.$^{-1}$
39·8	3·325	0·278
	2·993	0·189
	2·660	0·129
	1·994	0·062
	1·329	0·022
25·0	3·165	0·060
	2·939	0·046
	2·532	0·030
	1·899	0·014

GRAPH 18

CHANGE IN THE OBSERVED RATE CONSTANT WITH BASE CONCENTRATION FOR THE SECOND STAGE OF THE BASE HYDROLYSIS OF THE $[\mathrm{Co\,en_2\,C_2O_4}]^+$ ION.



b) The rate of loss of optical activity occurring during base hydrolysis

Stoichiometry

The rate of loss of optical activity was found to take place in one stage. This was due to the complete removal of the oxalate from the complex.

$$[\text{Coen}_2\text{C}_2\text{O}_4\overset{\text{OH}}{\wedge}]^0 + \text{OH}^- \longrightarrow [\text{Coen}_2(\text{OH})_2]^+ + \text{C}_2\text{O}_4{}^{2-}$$

Under the experimental conditions used the cis/trans equilibrium mixture of the $[\text{Coen}_2(\text{OH})_2]^+$ ions was always formed. No initial mutarotation was observed. Spectrophotometrically the initial ring opening has been shown to be rapid but should be observable at low temperatures. The lack of mutarotation may be due to the rotation of the $[\text{Coen}_2\text{C}_2\text{O}_4]^+$ being qualitatively similar to that of other cobalt III complexes whereas for the $[\text{Coen}_2\text{CO}_3]^+$ the rotation is much larger. This is shown on page 33 , Any initial mutarotation will be much smaller.

Results

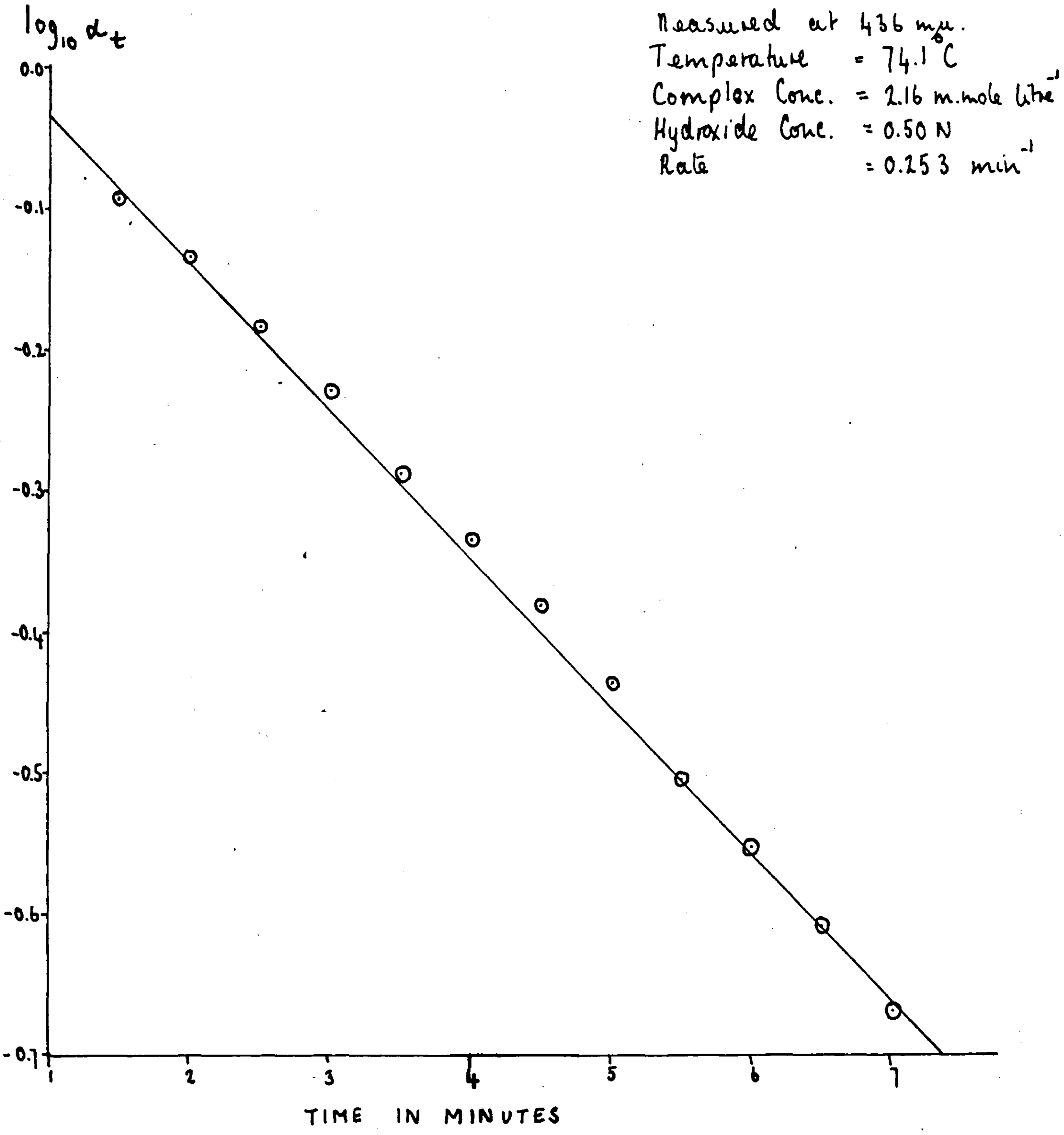
The rate of racemisation was measured at various temperatures and base concentrations in a similar way as described for the $[\text{Coen}_2\text{CO}_3]^+$ ion.

Graph 19 shows a sample rate plot and Table 17 gives the rate constants. The ionic strength was kept constant at 4N. The base concentration could not be taken as high as in the spectrophotometric measurements as the base would corrode the polarimeter tube.

The activation energy was shown to vary with the base concentrations as shown in graph 20. This variation together with the probability factors is shown in Table 18 .

GRAPH 19.

FIRST ORDER RATE PLOT FOR THE RATE OF LOSS OF OPTICAL ACTIVITY DURING THE BASE HYDROLYSIS OF THE (-)$[Co\,en_2C_2O_4]^+$ ION.



Measured at 436 mμ.
Temperature = 74.1°C
Complex Conc. = 2.16 m.mole litre^{-1}
Hydroxide Conc. = 0.50 N
Rate = 0.253 min^{-1}

TABLE 17

Observed first order rate constants for the loss of optical activity accompanying the base hydrolysis of the (-) $[Coen_2(C_2O_4)]^+$ ion resulting in the formation of the cis/trans equilibrium mixture of the $[Coen_2(OH)_2]^+$ ion

Temperature °C	NaOH N	Complex conc. m.mole $litre^{-1}$	$k_{[1]}$ obs. $min.^{-1}$
74·1	0·500	2·05	2·53 x 10^{-1}
	0·250	1·99	1.04 x 10^{-1}
	0·125	2·01	4·73 x 10^{-2}
58·8	0·500	1·88	3·24 x 10^{-2}
	0·250	2·13	1·25 x 10^{-2}
	0·125	2·04	5·38 x 10^{-3}
49·0	1·000	2·05	2·92 x 10^{-2}
	0·500	2·04	9·31 x 10^{-3}
	0·250	2·25	3.38 x 10^{-3}
38·6	0·500	2·18	2·57 x 10^{-3}
	0·250	1·78	7·93 x 10^{-4}
	0·125	1·98	2·40 x 10^{-4}
24·9	0·500	2·05	5·76 x 10^{-4}
	0·250	1·78	1·20 x 10^{-4}

GRAPH 20

ARRHENIUS PLOT FOR THE RATE OF LOSS OF OPTICAL ACTIVITY OF THE cis (-) $[Co\,en_2\,C_2O_4]^+$ ION DURING BASE HYDROLYSIS AND FOR THE RACEMISATION OF THE $[Co\,en_2\,(OH)_2]^+$ ION.

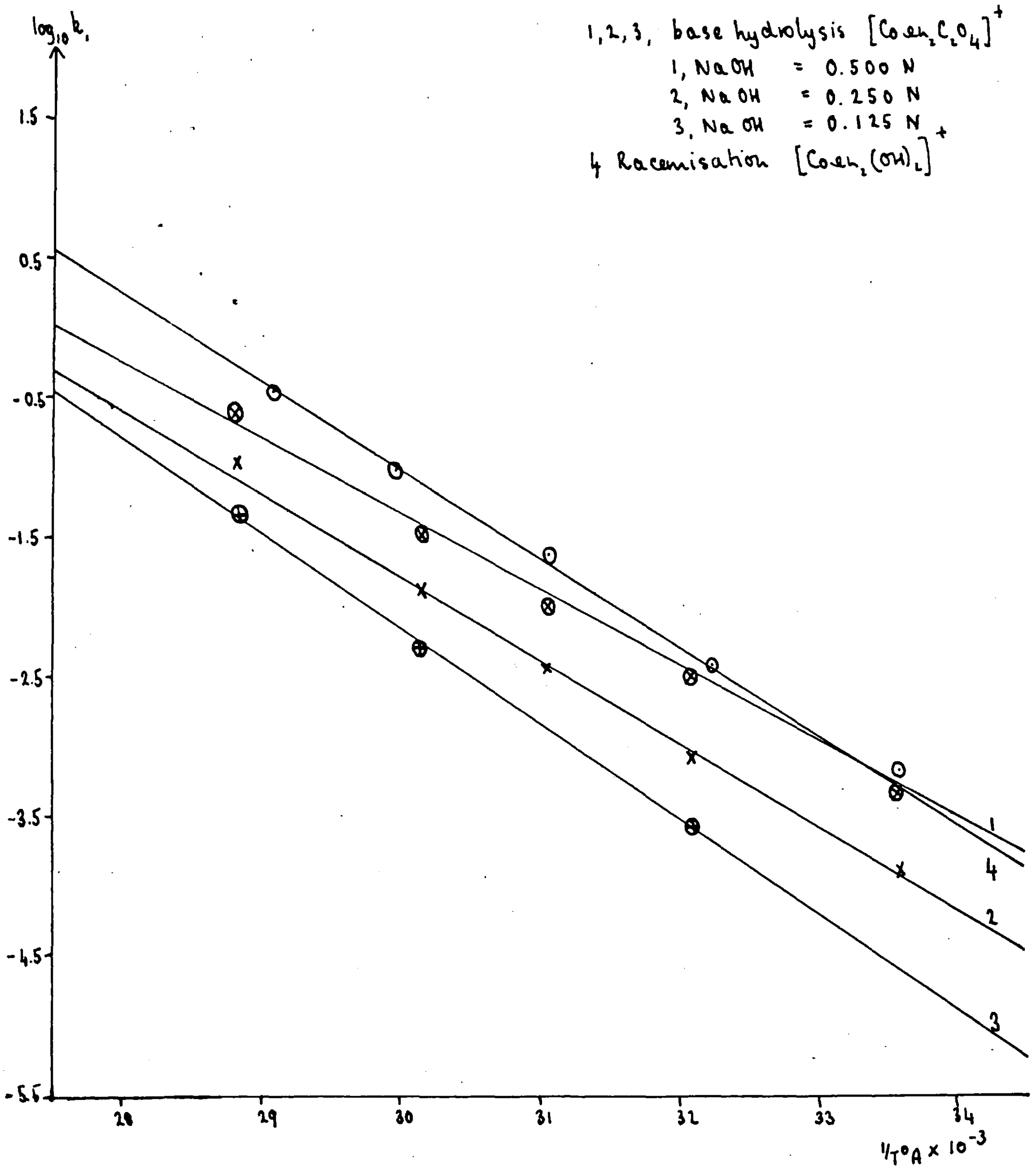


TABLE 18.

Variation in activation energy with base concentration for the rate of loss of optical activity during the base hydrolysis of the $[Coen_2C_2O_4]^+$ ion

NaOH N	Activation Energy k. cals/mole	Probability factor
0·500	22·7	$3·8 \times 10^{14}$
0·250	27·7	$2·2 \times 10^{16}$
0·125	30·8	$1·4 \times 10^{18}$

The variation of rate with temperature previously found fits the Arrhenius equation:-

$$k_2 = 6·5 \times 10^{19} e^{-38,000/RT} \text{ l mole sec.}^{-1} \quad (134)$$

c) Spectropolarimetric measurements

The majority of the polarimetry was carried out at 436 mμ. The reaction was also followed at 365, 405, 546 and 578 mμ and the rate was found to be independent of the wavelength used.

The change in the optical rotatory dispersion curve was also measured during the course of the reaction.

Method

Cis (-) $[Coen_2C_2O_4]I$ was dissolved in standard sodium hydroxide which was placed in a thermostatted water bath. At intervals samples were withdrawn and the reaction quenched by running into standard hydrochloric acid. The formation of the diaquo complex proceeds with full retention of configuration and is also optically stable.(55) The samples were frozen in "drikold" and later unfrozen in order for the optical rotatory dispersion curves to be measured. These are shown in graph 21.

The molar rotation, $[\phi]$, is given by

$$[\phi] = \frac{\text{deflexion} \times \text{molar concentration} \times \text{instrumental constant}}{100}$$

and the amplitude, a, by

$$a = -\frac{(\text{min.}[\phi] + \text{max.}[\phi])}{100}$$

The first order rate constant was evaluated graphically from

$$k = \frac{2{\cdot}303}{2}\,\frac{\log_{10}a}{t}$$

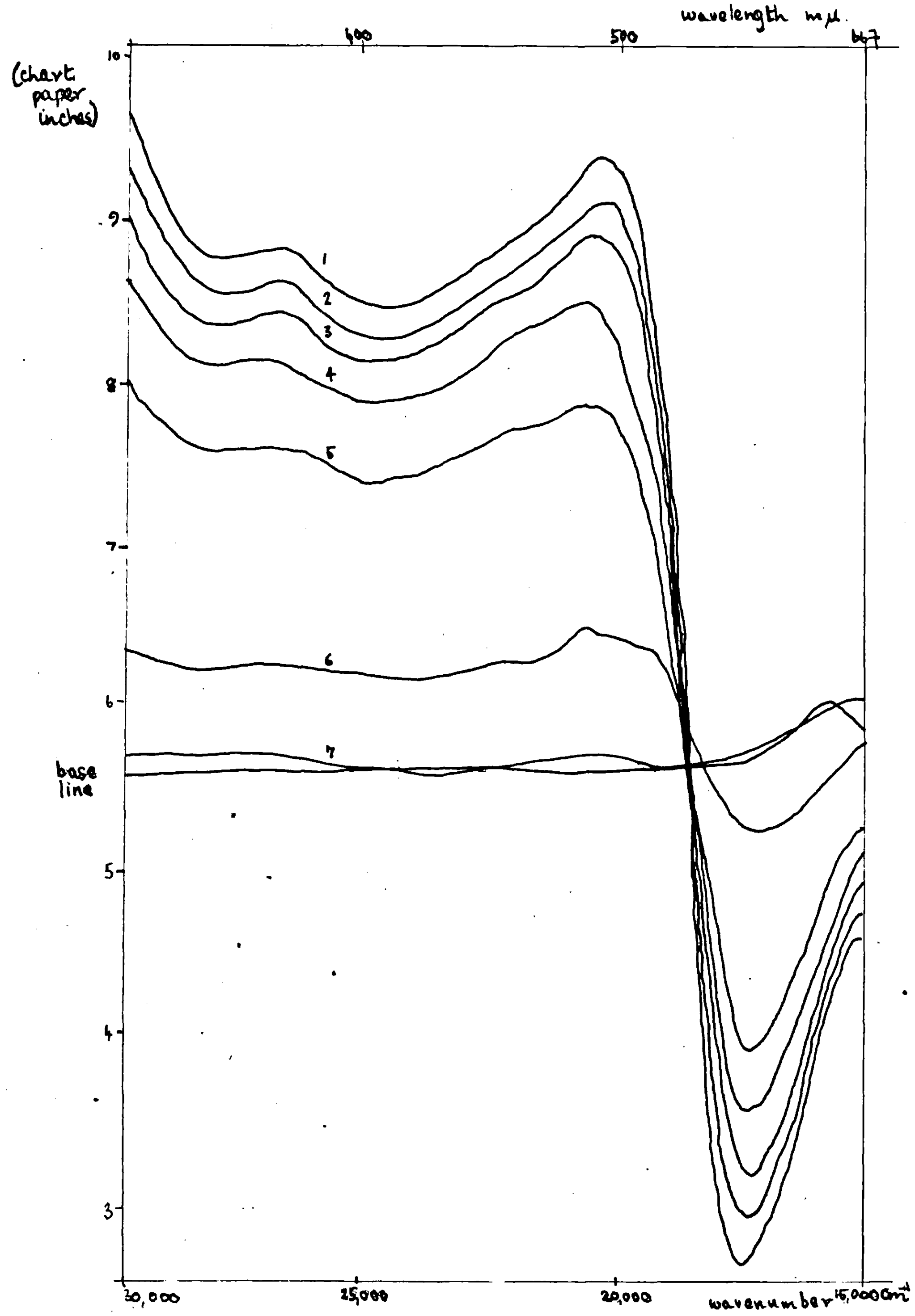
where t is the time for the measured amplitude. This is shown in graph 22.

GRAPH 21.

OPTICAL ROTATORY DISPERSION CURVES DURING THE BASE HYDROLYSIS OF CIS (-)[Coen$_2$ (C$_2$O$_4$)]$^+$ ION. 45.8°C.

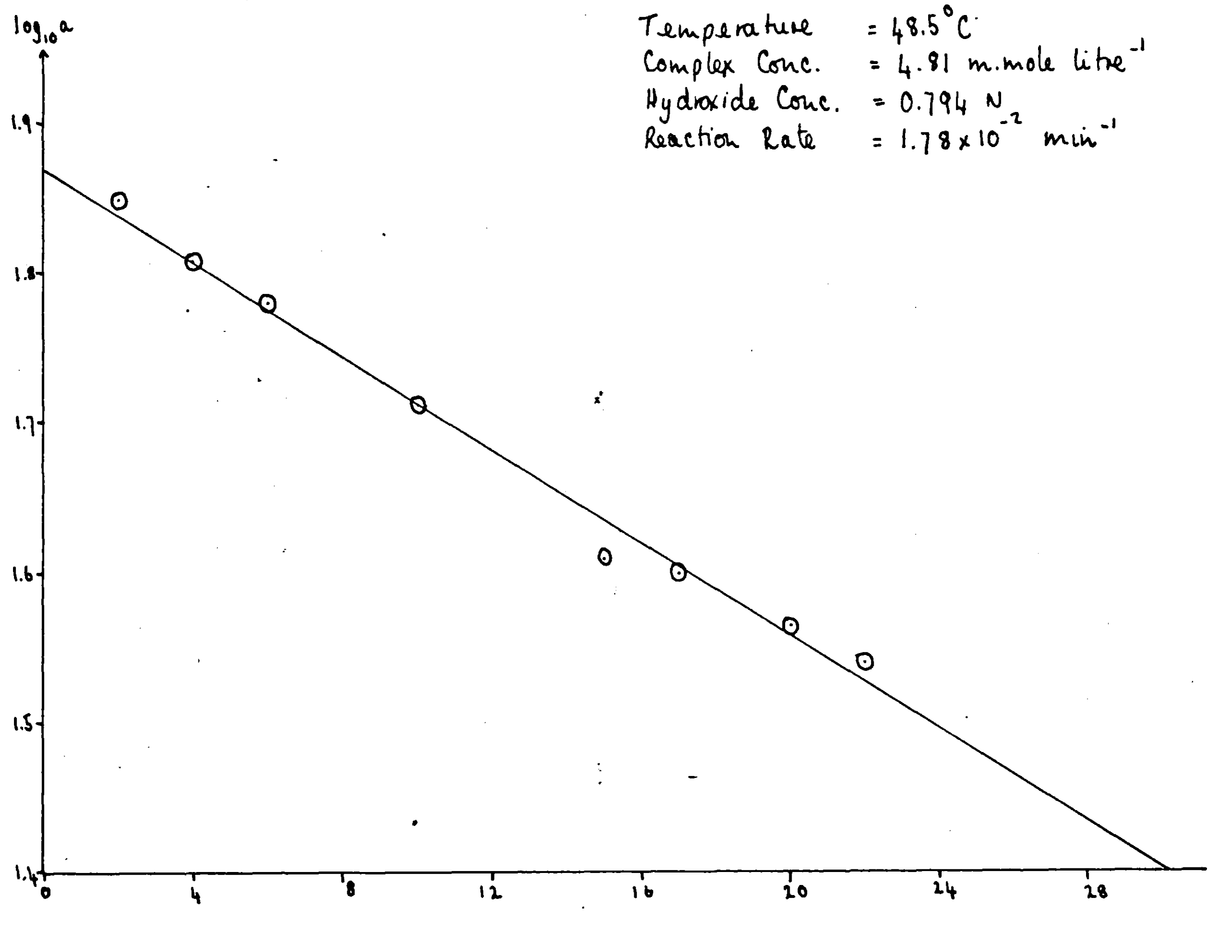
1. two minutes 2. four minutes 3. six minutes 4. ten minutes

5. seventeen minutes 6. 3½ hours 7. 24 hours.



GRAPH 22

FIRST ORDER RATE PLOT FOR THE RATE OF LOSS OF AMPLITUDE DURING THE BASE HYDROLYSIS OF THE CIS (-) $[\mathrm{Co\,en_2\,C_2O_4}]^+$ ION.



Temperature = 48.5°C
Complex Conc. = 4.81 m.mole litre^{-1}
Hydroxide Conc. = 0.794 N
Reaction Rate = 1.78×10^{-2} min^{-1}

Result

Temperature = 48·5° C

$[Coen_2C_2O_4]I$ = 4·81 m.mole litre^{-1}

Hydroxide conc. = 0·794 N

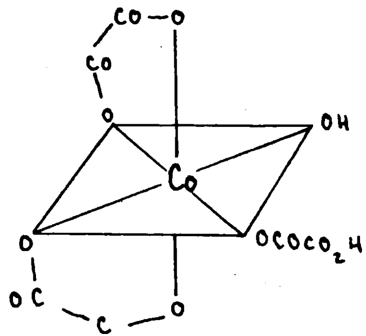
Reaction rate = 1·78 x 10^{-2} min^{-1}

This is of the order of the predicted rate from the polarimetric rate constants.

Discussion

1. The nature of the $[Coen_2C_2O_4]^+$ ion in aqueous solution

The nature of the ion $[Coen_2C_2O_4]^+$ in aqueous solution has been less thoroughly studied than in the case of $[Coen_2CO_3]^+$ and the only evidence for the open ring form comes from studies on the $[Co(C_2O_4)_3]^{3-}$ ion. McCaffery and Mason (108) showed from circular dichroism measurements that in solution the ion exists partly in the form



The fully chelated ion has D_3 symmetry while in the open ring form the symmetry has been reduced to C_2. Due to this decrease in symmetry a C_2 complex may have two or three circular dichroism bands in the higher energy ligand field absorption band whereas a D_3 complex can only give one. The ion which is represented formally by the formula $[Co(C_2O_4)_3]^{3-}$ is found to give two circular dichroism bands.

Gillard, Graham and Fenn (60) assign the same open ring form from studies on the part played by water in the crystal lattice. They deduced from infrared and thermogravimetric measurements that some of the water of crystallisation was involved in the first coordination sphere. The ion was found not to be isomorphous with the trisoxalates of aluminium, vanadium, iron, or chromium. These latter trisoxalates have been shown to have a trisbidentate form from X-ray studies. The cobalt (III) trisoxalate ion is isomorphous with the rhodium trisoxalate which, from nuclear magnetic resonance studies (123) on the potassium salt has been given the formula :-

$$K_6[Rh(C_2O_4)_3][Rh(C_2O_4)_2(HC_2O_4)(OH)]8H_2O.$$

The evidence for the trisoxalate ion may not be relevant to the monooxalatebisethylenediaminecobalt III ion. Table 19 compares some of the properties of the 4 relevant complexes.

TABLE 19.

Comparison of some properties of the ions, $[Coen_3]^{3+}$, $[Coen_2C_2O_4]^+$, $[Coen\ (C_2O_4)_2]^-$ and $[Co(C_2O_4)_3]^{3-}$

Formal representation of ion	$[Coen_3]^{3+}$	$[Coen_2C_2O_4]^+$	$[Coen_2(C_2O_4)_2]^-$	$[Co(C_2O_4)_3]^{3-}$
Stability in acid (77)	Stable	Stable after boiling for 1 hr. 1M acid	Stable	Light sensitive decomposition
Stability in base	Ion pair formation, (17) substitution above 70° (61)	Slow substitution	Slow substitution	Decomposition
Racemisation in aqueous solution (17)	No racemisation after 1 day at 90°	No racemisation after 5 days at 18°	$t_{1/2}$ = 7·5 hr, at 99°	$t_{1/2}$ = 66 mins. at 37·5°
Water of crystallisation	$(NO_3)_3^-$ none. Cl_3^- 5	Br^- salt none	Na^+ salt 1·0	K_3^+ salt (60) 3·5

Circular dichroism considerations are inapplicable to the mixed ligand complexes since the symmetry is initially reduced below D_3.

It would appear that there is a stabilising factor due to the non-reacting ligand.

From the current kinetic measurements the open ring non-chelated form of the oxalate ligand in neutral solution is unlikely since there is no rate for the reaction in neutral solution. Further the bromide salt crystallises with no water of crystallisation, unlike the $[Co(C_2O_4)_3]^{3-}$ ion where the water of crystallisation is thought to play an integral part in the first coordination sphere.

Previous work on the base hydrolysis of the $[Coen_2C_2O_4]^+$ ion

Sheel, Meloon and Harris $^{(134)}$ studied the reaction at 71°. They found that the rate of loss of optical activity, decomposition and oxalate exchange reactions all have identical second order kinetics fitted by the rate law:

$$R = k\ ([Coen_2C_2O_4]^+)\ (OH^-)$$

They suggested that the rate determining step was the dechelation of the oxalate ligand with subsequent rapid steps resulting in the formation of a cis/trans equilibrium mixture of the dihydroxy species. The dechelation takes place by carbon-oxygen bond fission and the complete removal of oxalate by cobalt-oxygen bond fission (page 92).

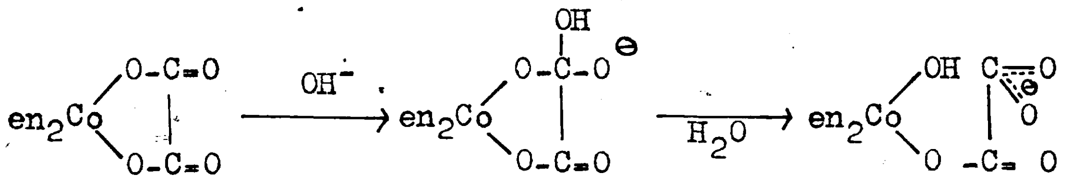
First stage of the reaction

$$[\mathrm{Coen_2C_2O_4}]^+ + \mathrm{OH^-} \longrightarrow [\mathrm{Coen_2C_2O_4OH}]^0$$

Within the experimental limitations, the reaction is found to be first order in hydroxide following the rate equation:

$$R = k_1\ (\mathrm{OH^-})$$

at constant complex concentration. It has been suggested previously that the dechelation takes place with carbon-oxygen bond fission. An S_N2 mechanism is proposed with attack by the hydroxyl group on the carbon. As in the case of the carbonato complex this mechanism is favoured both by the accessibility of the carbon relative to the cobalt and by the inductive effect of the carbonyl group rendering the carbon electropositive.



A slow rate determining addition is followed by rapid carbon oxygen bond fission.

No measurable change in the optical rotation was observed during the dechelation process showing that there is complete retention of configuration, agreeing with the proposed carbon-oxygen bond fission since, there being no bond fission at the asymmetric cobalt centre, there can be no steric change. Reaction paths resulting in formation of $(\pm)[Coen_2C_2O_4OH]^o$ and trans$[Coen_2C_2O_4OH]^o$ are inoperable.

This is contrasted to the analogous carbonato dechelation reaction which is postulated to proceed with cobalt-oxygen bond fission, the rate reaching a maximum at high hydroxide which does not occur in the oxalato case. Both the dechelation processes proceed with retention of configuration. The difference in mechanism is due to the relative lack of steric strain in the 5 membered oxalato chelate ring compared to the four-membered carbonato ring. Also the stronger acid properties of the oxalato group render the carbon of the oxalate group more susceptible to attack.

It has not been found possible to support the hypothesis that this is the rate determining step in the reaction sequence. Indeed at 71° it can be considered as a rapid pre-rate determining step, the rate at this temperature being completely due to the rate of loss of oxalate.

Second stage of the reaction

The rate of the reaction measured spectrophotometrically was found to be the same as the rate of loss of optical activity. With increase in base concentration the activation energy becomes less and reaches a limiting value of 15.3 kcals/mole at 1N sodium hydroxide. The activation energy at 0.5 N NaOH was found to be the same whether measured spectrophotometrically or polarimetrically, i.e. 22.7 k.cals/mole.

Kinetic form

A first order kinetic plot is not found except at 72° with base concentrations less than 2N. In this region the second order kinetics are the same as found by Sheel et. al.(134)

The deviations from a standard first order rate plot may be due to the very high hydroxide concentrations employed, since at concentrations greater than 1M, the basicity of the solution increases more rapidly than the stoichiometric concentration of base. The concept of the acidity function in strongly basic aqueous solution has recently been reviewed by Rochester.(126) H_-, the acidity function for a given basic solution is the measure of the ability of that solution to abstract a proton from an electrically neutral weakly acidic molecule.

$$SH + OH^- \rightleftharpoons S^- + H_2O$$

$$H_- = pK_{SH} + \log_{10}\frac{[S^-]}{[SH]}$$

where pK_{SH} = acid ionisation constant for **SH.** $[SH]$ and $[S^-]$ are the concentrations of the acid and its conjugate base respectively. The H_- scale has been established for aqueous sodium hydroxide by Schwarzenbach and Sulzberger,(133) at 20° assuming $H_- = 14$ when $[NaOH] = 1$ M. The values they obtained are shown in Table 20. These measurements are not generally applicable at any temperature due to the change in the ionisation constant of water with temperature.

$$H_- = pK_w + \log_{10}[OH^-] + \log_{10}\frac{f_{SH}f_{OH^-}}{f_{S^-}a_w}$$

where f denotes activity coefficient and a activity. Below 1 M NaOH the last term approximates to zero giving the "ideal" expression of H_-. The value of $pK_w + \log_{10}[NaOH]$ at 20° and 58° are shown in Table 20.

TABLE 20.

Experimental and "Ideal" H_- values for sodium hydroxide

[NaOH]	$pK_w + \log_{10}$[NaOH]	$pK_w + \log_{10}$[NaOH]	H_-
M	58°	20°	20°
1	13.03(ref 75)	14.17	14.00
2	13.33	14.47	14.36
3	13.51	14.65	14.64
4	13.63	14.77	14.93

The ideal values of H_- at both 20° and 58° change more slowly than the experimental values at 20°. In the absence of any information about the variation with alkali concentration and temperature of the solute activity coefficients f_{SH} and f_{S^-} and any experimental values other than temperatures the experimental scale at 20° was used.

If the reaction is considered to go by the mechanism:

$$SH + OH^- \longrightarrow S^- + H_2O$$

$$\text{where } [S^-] \ll [SH]$$

$$S^- \xrightarrow{k'} \text{products}$$

for which the experimental rate constant, k_{obs}, is given by

$$k_{obs.} = -\,(1/[SH])\,(d[SH]/dt)$$

$$= k'\,([S^-]/[SH])(f_{S^-}/f^{*}) \qquad (2)$$

where * the transition state.

Assuming $f_{SH}/f^{*} = f_{SH}/f_{S^-}$

and by combining (1) and (2)

$$\log_{10} = \log_{10}k'\ K_{SH} + H_-$$

If this theory is operational a plot of $\log_{10}k_{obs}$ should be a linear function of H_- with unit slope.

Graphs 23 and 24 show the plots of H_- against $\log_{10}k_{obs}$ at the various experimental temperatures. At 72° and 58° straight line graphs with unit gradient are obtained. The theory is valid, the reaction proceeds by an S_N1 CB mechanism.

$$[Coen_2C_2O_4OH]^o + OH^- \overset{\text{rapid}}{\rightleftarrows} [Coen(en\text{-}H)C_2O_4OH]^- + H_2O$$

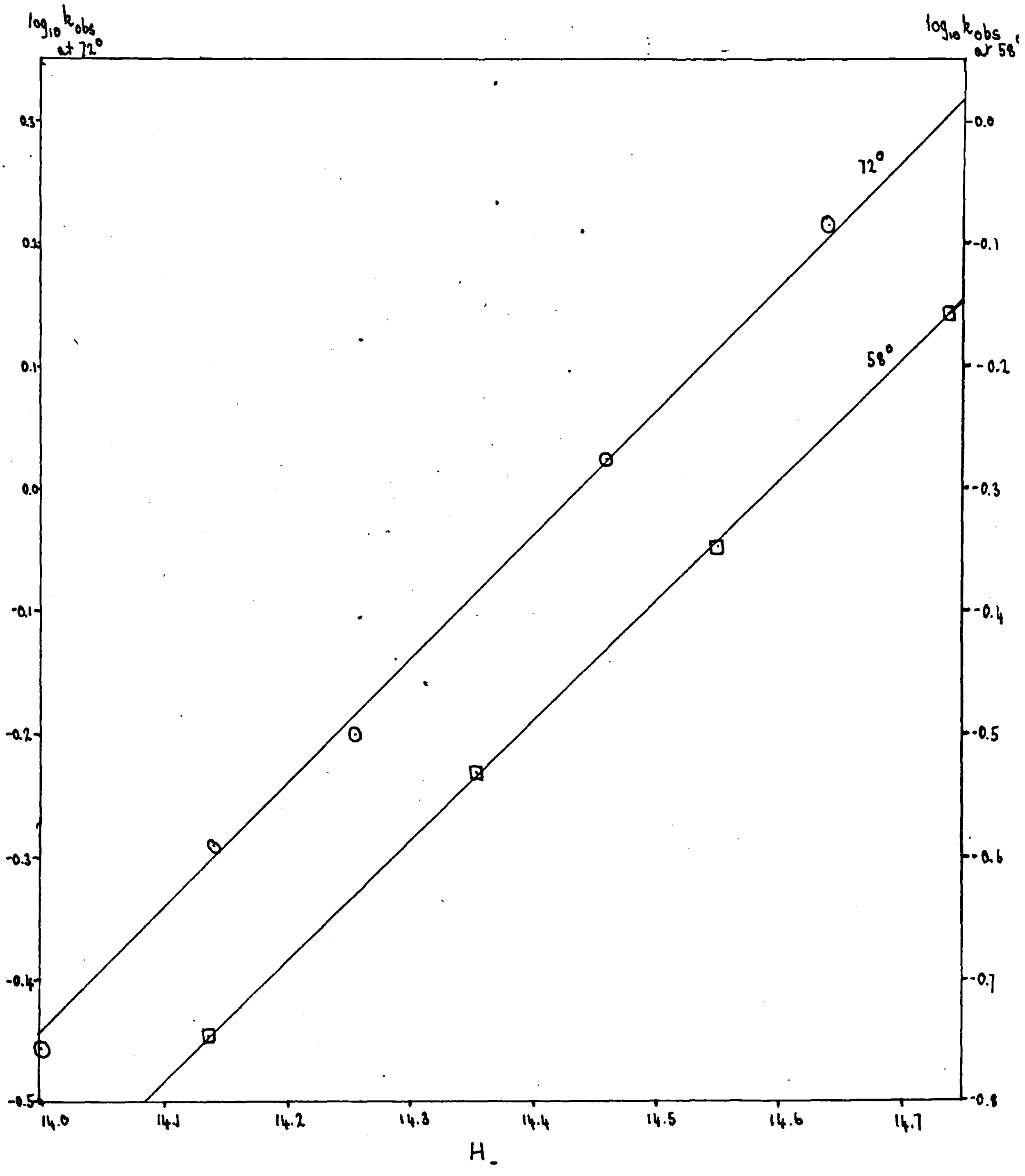
$$[Coen(en\text{-}H)C_2O_4OH]^- \xrightarrow{\text{slow}} [Coen(en\text{-}H)OH]^+ + C_2O_4{}^{2-}$$

$$[Coen(en\text{-}H)OH]^+ + H_2O \longrightarrow [Coen_2(OH)_2]^+$$

Additional evidence is found by the independence

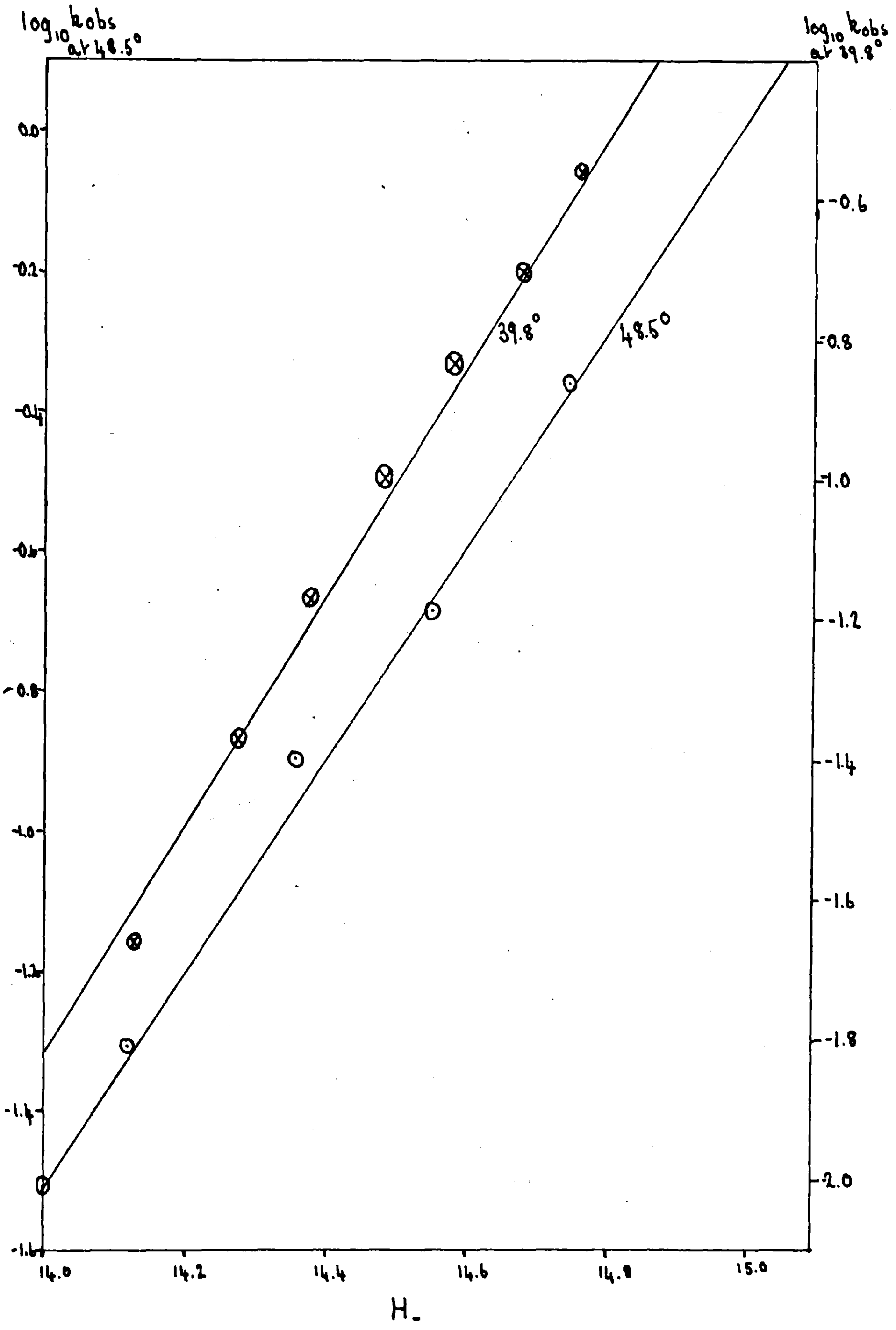
GRAPH 23

CHANGE IN $LOG_{10} k_{OBS}$ WITH H_- FOR THE SECOND STAGE OF THE BASE HYDROLYSIS OF THE $[Co\,en_2C_2O_4]^+$ ION.



GRAPH 24

CHANGE IN $\log_{10} k_{obs}$ WITH H_- FOR THE SECOND STAGE OF THE BASE HYDROLYSIS OF THE $[Co\,en_2C_2O_4]^+$ ION.



of rate on the presence of excess oxalate. It has also previously been suggested that the reaction proceeds by cobalt-oxygen fission.(134)

However at the lower experimental temperatures although graphs of H_ against $\log_{10}$ obs. give linear plots, the gradient of these plots are no longer unity. These are shown in Table 21 .

TABLE 21.

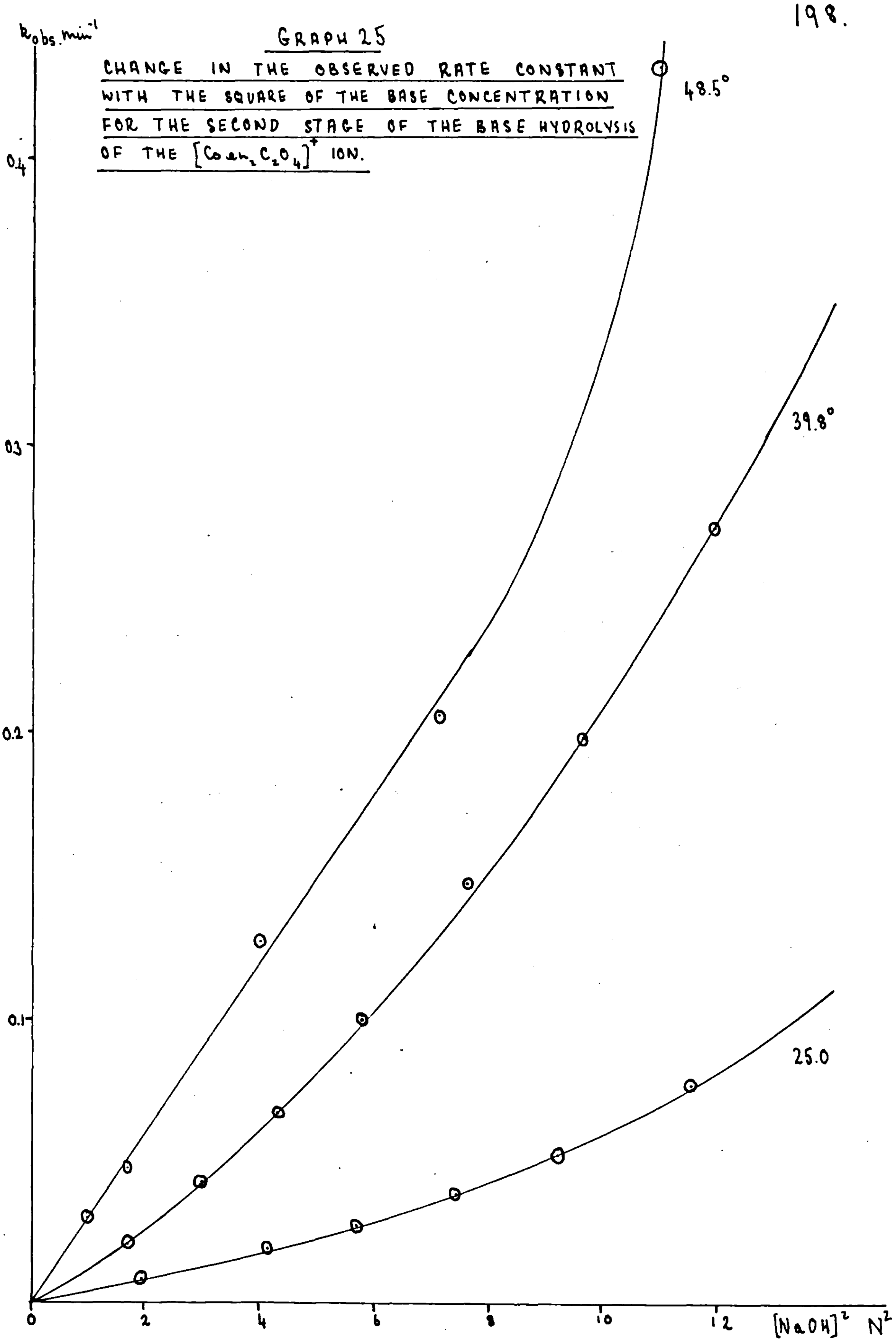
Variation of gradient of graph $\log_{10} k_{obs}$ against H_-

Temperature °C	Gradient
48.5	1.52
39.8	1.64
25.0	1.52

A simple S_N1 CB mechanism cannot provide a complete mechanistic view. Further if an S_N1 CB mechanism was exclusively operating at these temperatures a change in rate would be predicted on changing the solvent from water to deuterium oxide. The rates of both acid and base hydrolysis of the $[Co(NH_3)_5Cl]^+$ ion are slower (18) in D_2O than in H_2O. By analogy to the effect of deuteration on the base hydrolysis of diacetone alcohol the reaction would be expected to go faster if a pre-equilibrium proton transfer was involved. Since the ion, $[Co(NH_3)_5Cl]^+$ is only weakly acidic there is probably a large isotope effect on its acid ionisation constant as on the ionic product of water and consequently the deuterated system will react more slowly.

No solvent isotope effect was found at 25° and 39·8° and, together with the non-unit gradient of the graph $\log_{10}k_{obs}$ against H_-, shows that there is some other reaction path not involving a deprotonation equilibrium available for the decomposition. Further, the reaction products are the cis/trans equilibrium mixture of the $[Coen_2(OH)_2]^+$ ion.

A reaction path proceeding by a mechanism involving higher order with respect to hydroxide is postulated. Plots of the observed rate constants against the square of the hydroxide are shown in graph 25. At low concentrations these graphs are seen to be linear whilst at high concentrations the departure from linearity may be due to the basicity increasing more quickly than the stoichiometric concentration of base rather than to the presence

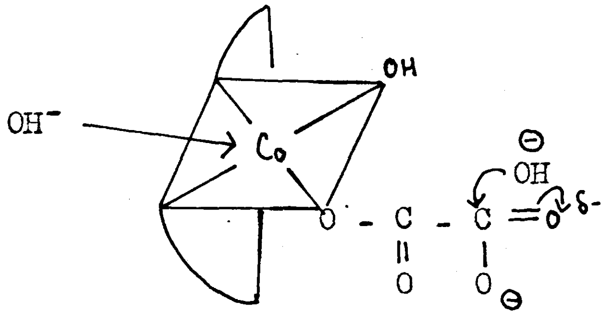


GRAPH 25

CHANGE IN THE OBSERVED RATE CONSTANT WITH THE SQUARE OF THE BASE CONCENTRATION FOR THE SECOND STAGE OF THE BASE HYDROLYSIS OF THE $[Co\,en_2C_2O_4]^+$ ION.

of any other reaction path.

An assisted substitution is postulated whereby hydroxide attack occurs synchronously at the cobalt with hydroxide addition to the carbon non-bonded to the cobalt.



The associative attack is eased due to the formation of the tetrahedral carbon on the original planar oxalate carbon. Once the transition state has been reached the final dissociation takes place rapidly. The initial direction of the hydroxide attack at the cobalt has not yet been defined.

The order of the reaction with respect to hydroxide was found from the gradient of the graph $\log_{10}$[NaOH] against $\log_{10}k_1$ obs. These are shown in Table 22.

TABLE 22.

Variation in hydroxide order with temperature for the reaction stoichiometrically represented as $[Coen_2C_2O_4OH]^0 + OH^- \longrightarrow [Coen_2(OH)_2]^+ + C_2O_4^{2-}$

Temperature °C	Order
72•0	1•07
58•0	1•10
48•5	1•58
39•8	2•53
25•0	2•23

A maximum order is reached at 38•8° showing that the reaction is proceeding by a mechanism both first order and second order in hydroxide. At 48•5° the first order reaction path is becoming dominant whilst at 72° it is the only significant reaction path. If the Arrhenius parameters for the two processes are similar, the reaction second order in hydroxide would be dominant at high base concentration which was not found. The activation energies must be of equivalent values since straight line Arrhenius plots were obtained and it was impossible to separate the rate constants for the two processes. The decrease in importance of the second order reaction path with temperature must be due to a large probability factor relative to the first order reaction path. As a trimolecular process is postulated it is very likely that the probability factor is extremely high. It can be seen to increase with decreasing base concentration, (Table 18 page 180).

Steric course of the reaction

Sheel et al (134) found that the base hydrolysis occurred at the same rate as the loss of optical activity and suggested that the two processes proceed by identical mechanisms. They postulated the rate determining step to be the initial dechelation.

In the present work it was found that the rate of base hydrolysis of the intermediate $[Coen_2C_2O_4OH]^0$ containing the non-chelated oxalate group proceeded at the same rate as the rate of loss of optical activity. At high temperatures the racemic cis $(\pm)[Coen_2(OH)_2]^+$ ion is formed.

$$cis(-)[Coen_2C_2O_4OH]^0 + OH^- \text{———} cis(\pm)[Coen_2(OH)_2]^+ + C_2O_4^{2-}$$

The rates are the same, therefore the rates of isomerisation and racemisation of the intermediate ion, $[Coen_2C_2O_4]^o$ must be slow compared to the decomposition rate.

$$cis(-)[Coen_2C_2O_4OH]^o \rightleftharpoons cis(+)[Coen_2C_2O_4OH]^o$$

$$cis[Coen_2C_2O_4OH]^o \rightleftharpoons trans[Coen_2C_2O_4OH]^o$$

These have been shown to be slow in the case of the carbonato ion.(130)

At low temperatures the production of the $trans[Coen_2(OH)_2]^+$ ion also occurs which can be formed either by the isomerisation of the cis product ion or by direct substitution into the intermediate, $[Coen_2C_2O_4OH]^o$.

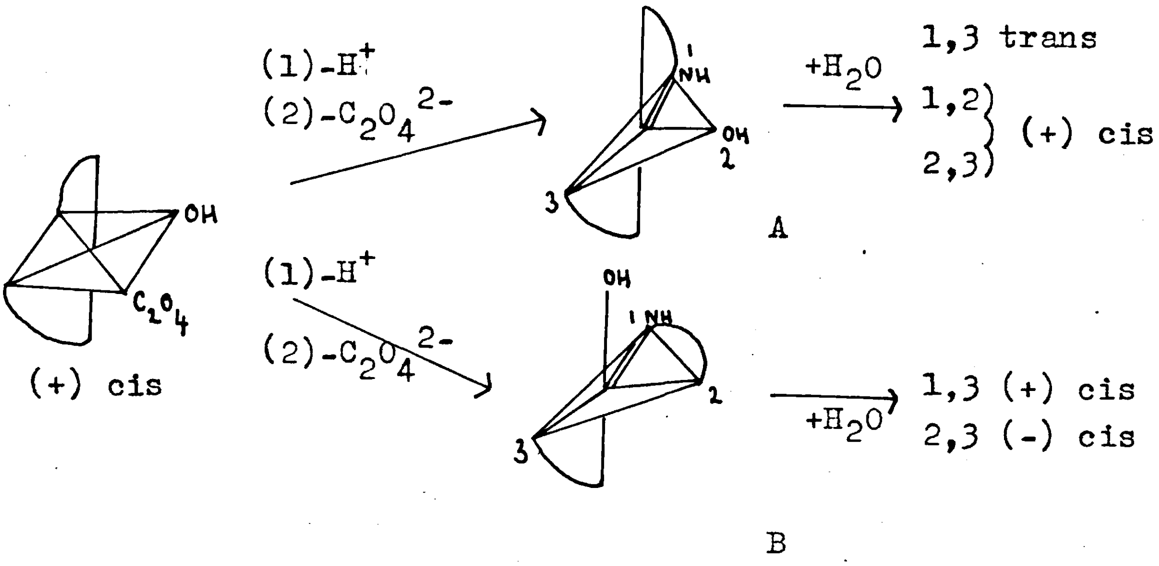
$$cis[Coen_2(OH)_2]^+ \rightleftharpoons trans[Coen_2(OH)_2]^+$$

$$cis(-)[Coen_2C_2O_4OH]^o + OH^- \longrightarrow trans[Coen_2(OH)_2]^+ + C_2O_4^{2-}$$

As a second reaction path has been shown to be present at low temperatures the second reaction occurs in conjunction with the first.

The S_N1 CB mechanism

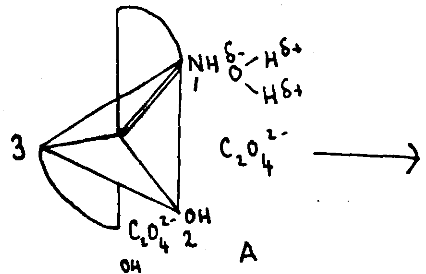
The formation of a trigonal bipyramid is necessarily accompanied by loss of optical activity. There are two possible intermediates -



Basolo and Pearson (118) have analysed the stereoisomeric products from both the cis and trans isomers of complexes of the type $[Coen_2OHX]^+$ and concluded that 50% of B is formed when $L = Cl^-$ and 60% when $L = Br^-$. Since the oxalate group is larger than both the chloride and bromide ions these percentages may not be relevant but suggest that there will be some formation of B.

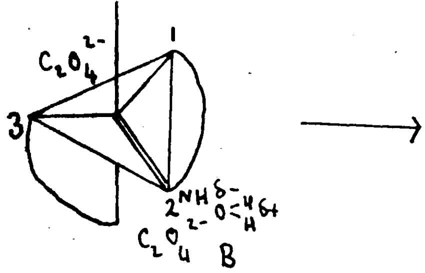
Chan and Tobe (40) suggest that as the hydroxide is capable of donating a second pair of electrons to the cobalt when in the trigonal plane, intermediate A is so much more stable than B that the latter can be ignored.

In this reaction there is demonstrably racemic cis and no trans isomers formed. The production of some intermediate B seems more likely. Tobe and Chan (40) discuss the orienting effect of the leaving group. The leaving group influences the direction of attack of the incoming ligand thereby directing the steric course. As well as the hydroxide group, the leaving oxalate group is also capable of donating electrons to the cobalt when in the trigonal plane and so will depart from the trigonal plane, the position from which it leaves being sterically hindered. However the dipolar character of the incoming water results in its orientation between the departing oxalate and the imino nitrogen. The intermediates are considered in conjunction with their environment, (the two possible positions of the oxalate are shown in each case):



A

1,2 (+) cis
2,3 (+) cis (if imino nitrogen considered to be at position 3).



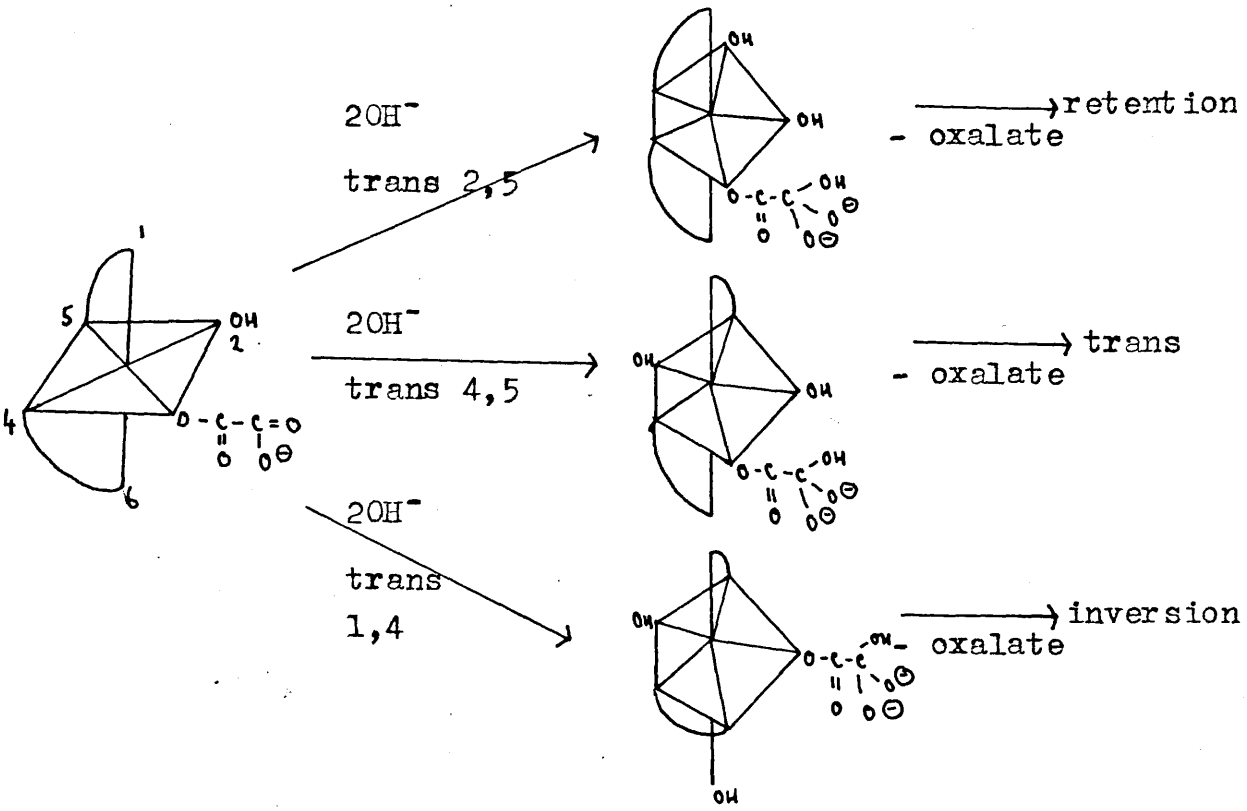
B

1,3 (+) cis
2,3 (-) cis

In intermediate A, attack in the 1,3 position will be further hindered due to the relative crowding of the ethylenediamine rings. The intermediates form the observed racemic cis $(\pm)[\mathrm{Coen}_2(\mathrm{OH})_2]^+$.

Steric course of reaction path second order in hydroxide

The reaction path second order in hydroxide is considered as an associative mechanism while not necessarily implying the equivalent importance of bond making and bond breaking in the transition state. The steric course is considered on the basis of a seven coordinate intermediate. Hydroxide attack adjacent to the oxalate is unlikely due to the bulky nature of the oxalate, and the high concentration of negative charge. Only trans attack is envisaged.



This reaction path is only significant at low temperatures where the production of racemic cis and trans$[Coen_2(OH)_2]^+$ ions occurs. The presence of all three intermediates accounts for the observed hydrolysis being the same as the rate of loss of optical activity.

4. THE BASE HYDROLYSIS OF THE $[Cophen_2X]^+$ ION

$X = CO_3^{2-}, C_2O_4^{2-}$, mal, CB.

a) $[Cophen_2X]Cl$, $X = C_2O_4^{2-}$, mal, CB

In all three cases the complexes decompose in the presence of base with the formation of black cobalt oxide, CoO(OH). The speed of decomposition depends on the base concentration. For a 0.5 N base strength, decomposition is instantaneous for the $[Cophen_2mal]Cl$ complex and complete in about 10 minutes for the $[Cophen_2CB]Cl$ complex. Both these complex ions are stable in neutral aqueous solution. Graph 26 shows the visible absorption spectrum for the $[Cophen_2CB]Cl$ complex.

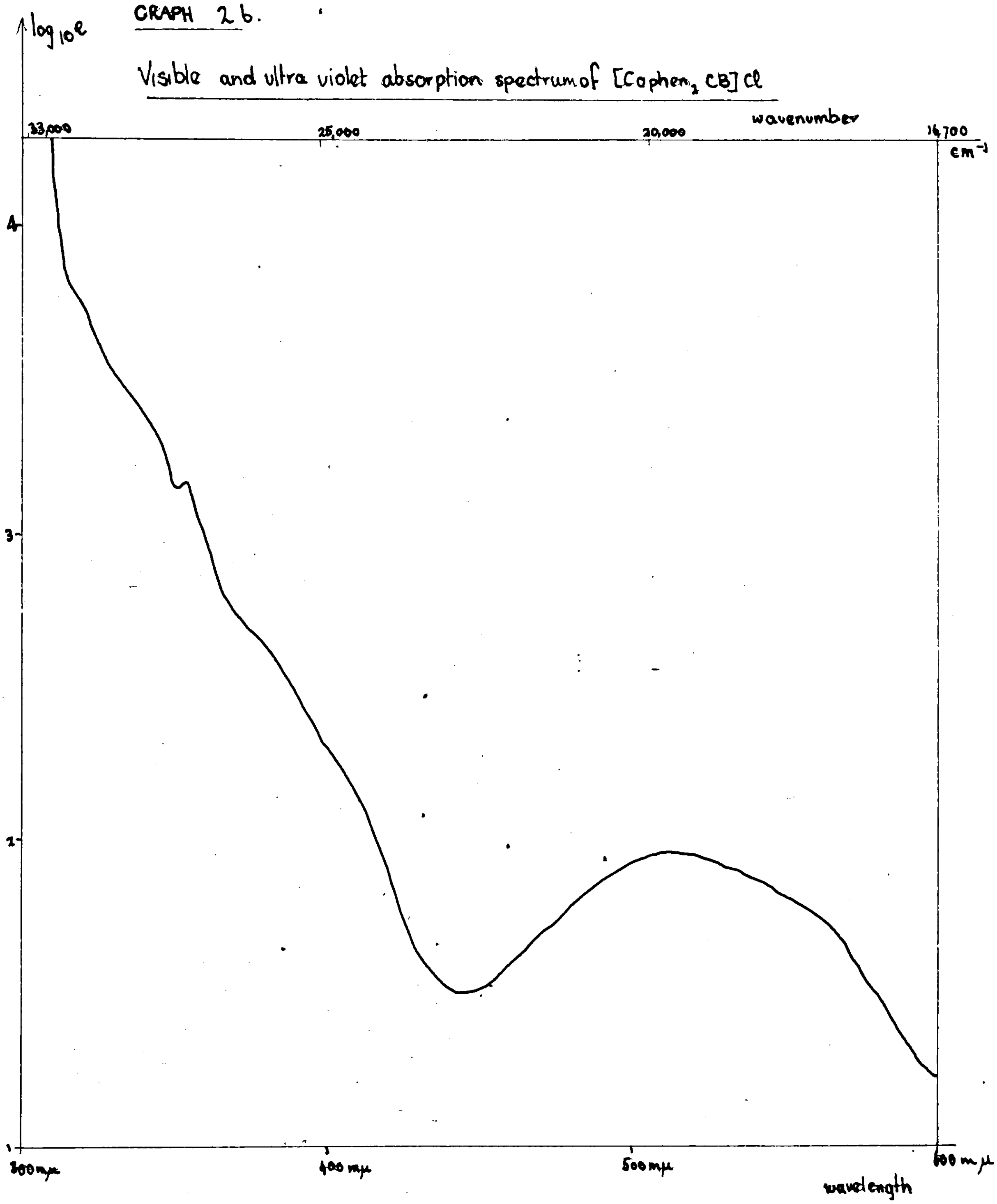
Although the $[Cophen_2C_2O_4]Cl$ complex is stable in neutral solution in the absence of light, it decomposes in light both in the solid state and in aqueous solution. A cobalt II complex, $Cophen_2Cl_2$, is formed which is an insoluble flesh coloured powder.

b) $[Cophen_2CO_3]Cl$

This complex is unaffected by light and stable in the solid state. It is also stable in aqueous

GRAPH 2b.

Visible and ultra violet absorption spectrum of [Cophen$_2$ CB] Cl



solution insofar as its absorption spectrum does not change over a period of days at room temperature.

Stoichiometry

Slow substitution takes place with the formation of the $[Cophen_2(OH)_2]^+$ ion.

$$[Cophen_2CO_3]^+ + 2OH^- = [Cophen_2(OH)_2]^+ + CO_3^{2-}$$

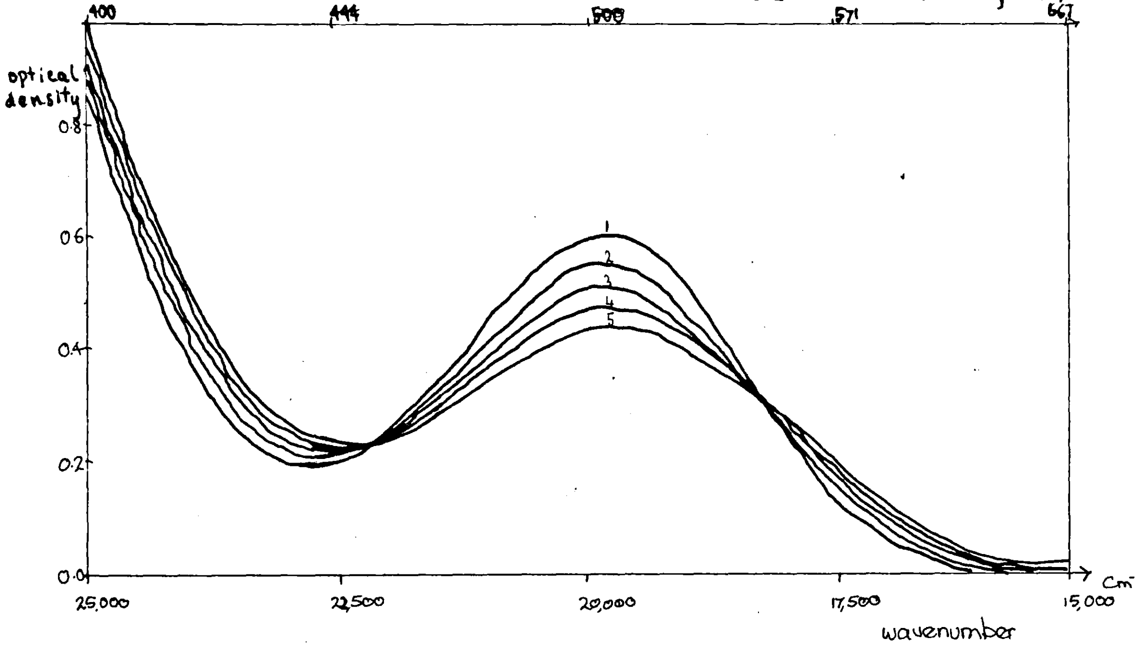
At 520 mμ (19,230 cm.$^{-1}$) the initial extinction coefficient is 114·8 and the final extinction coefficient is 79·5. The extinction coefficients are the same as those given by Ablov and Palade (2,3) for the $[Cophen_2CO_3]^{2+}$ and $[Cophen_2(OH)_2]^+$ ions respectively.

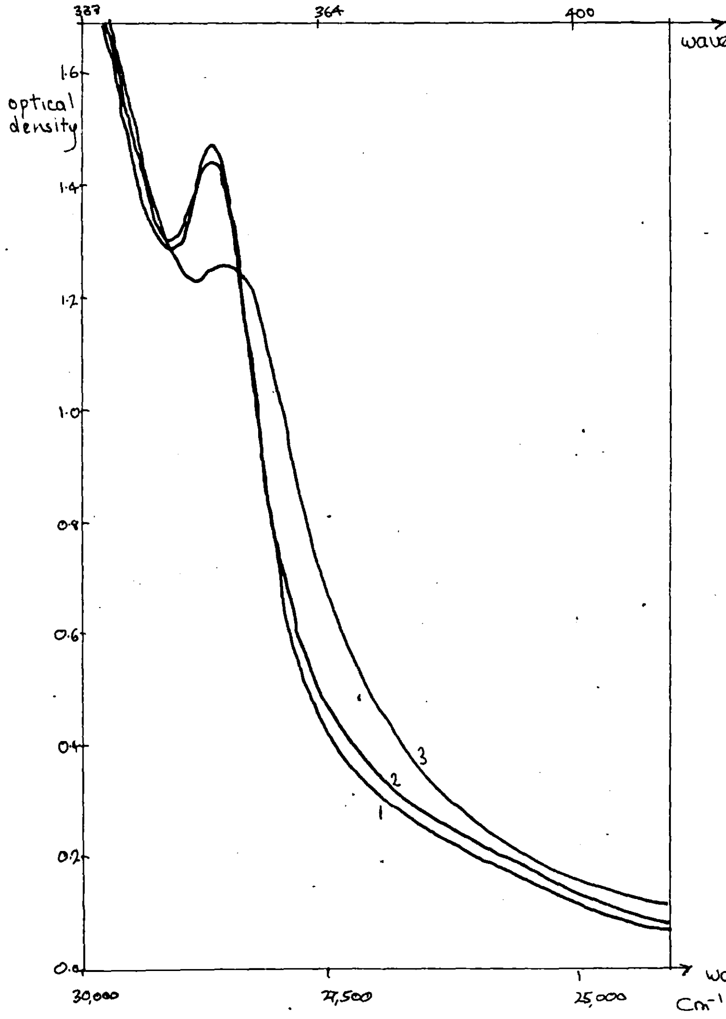
Method

The same general method was used as in the cases of the $[Coen_2CO_3]^+$ and $[Coen_2C_2O_4]^+$ complex ions. Initially the spectrum between 15,000 and 30,000 cm.$^{-1}$ (667 and 333 mμ) was measured at room temperature at various reaction time intervals as shown on graphs 27 and 28. The changes which occur are characterised by isosbestic points at 18,200, 22,200 and 28,400 cm.$^{-1}$ The actual rates were measured at 19,230 cm.$^{-1}$

GRAPH 27

SPECTROPHOTOMETRIC CHANGES OCCURING DURING THE BASE HYDROLYSIS OF THE [Cophen$_2$CO$_3$]$^+$ ION, 25,000 - 15,000 CM^{-1}





GRAPH 28.

SPECTROPHOTOMETRIC CHANGES OCCURING DURING THE BASE HYDROLYSIS OF THE [Cophen$_2$CO$_3$]$^+$ ION.
24,000-30,000 CM^{-1}

1. Initial spectrum

2, 3, 4, &5 graphs showing the spectral changes accompanying base hydrolysis of the [Cophen$_2$ CO$_3$]$^+$ion. The solution in 27 is about 300 times more dilute than in 28.

In some cases sodium chloride was used to maintain the ionic strength. Sodium perchlorate could not be used as its presence resulted in the immediate formation of a flesh coloured precipitate.

Results

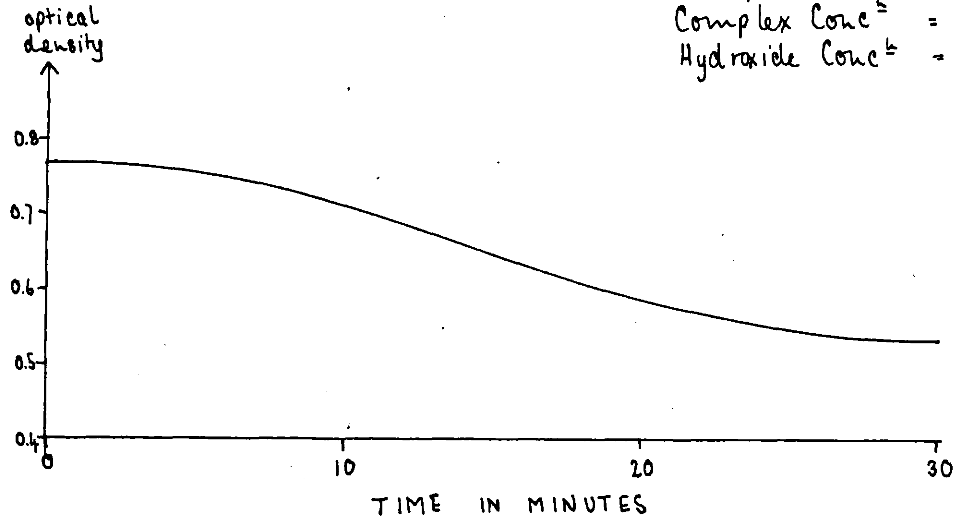
Graph 29 show the observed changes of optical density accompanying the base hydrolysis at 19,230 cm.$^{-1}$ Characteristic of this is the initial lack of change of optical density over the first 1 to 5 minutes of reaction time at both low ionic strength and hydroxide concentration. The rate constants were evaluated in the same manner as for the $[Coen_2CO_3]^+$ ion described on page 123 . Graph 30 shows an example of a first order rate plot. The initial lack of linearity corresponds to the initial lack of change in optical density. Table 23 gives the observed first order rate constants, and the length of time of the initial lack of change of optical density.

If the temperature or concentration is put up, then decomposition sets in, for example with a 0·167 N basic solution decomposition sets in at 65° and for a 0·20 N solution at 50°. The result of cutting the hydroxide concentration to half the complex concentra-

GRAPH 29

OBSERVED CHANGE IN OPTICAL DENSITY ACCOMPANYING THE BASE HYDROLYSIS OF THE $[Co\,phen_2\,CO_3]^+$ ION.

Temperature = 35.5°C
Complex Conc^{n} = 6.72 m.mole litre^{-1}
Hydroxide Conc^{n} = 0.167 N



GRAPH 30.

FIRST ORDER RATE PLOT FOR THE BASE HYDROLYSIS OF THE $[Co\,phen_2\,CO_3]^+$ ION.

Temperature = 35.5°C
Complex Conc^{n} = 6.72 m.mole litre^{-1}
Hydroxide Conc^{n} = 0.167 N
Rate = 0.128 min^{-1}

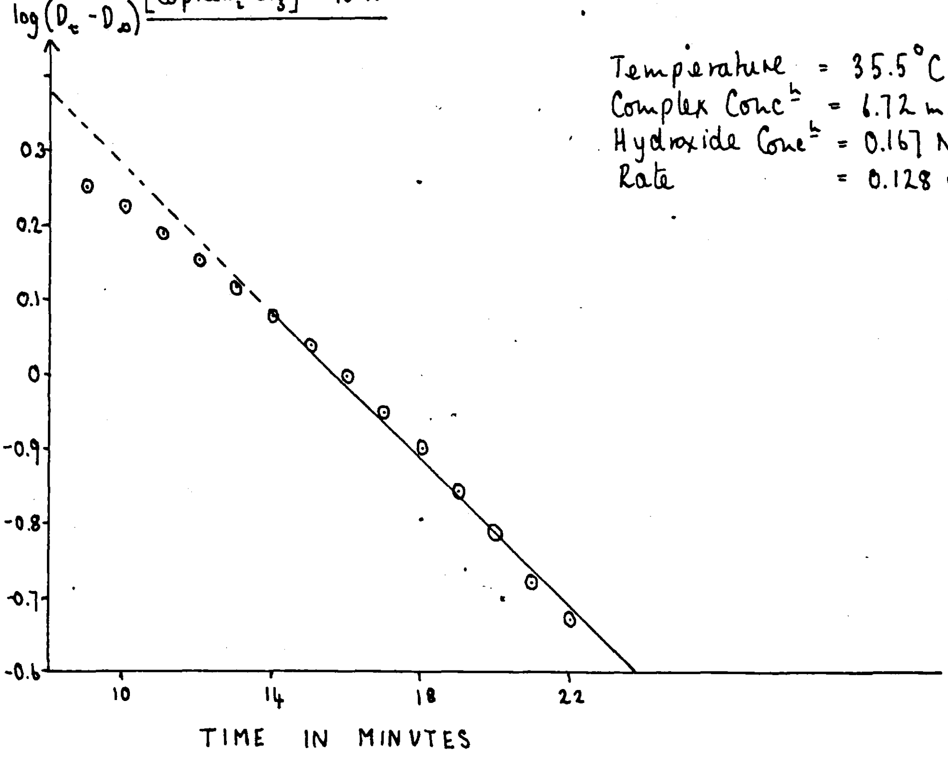


TABLE 23

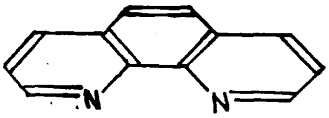
OBSERVED FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF THE $[\mathrm{Cophen_2CO_3}]^+$ ION

Temperature °C	Time length of initial constant optical density min.	Ionic strength N	[NaCl] N	[NaOH] N	Complex Conc. m.mole litre^{-1}	k_1 obs. min.$^{-1}$
35·5	2	0·167	-	0·167	6·72	0·128
	2	0·167	-	0·167	4·70	0·125
	3	0·133	-	0·133	6·72	0·133
	4	0·133	-	0·133	5·71	0·166
	3	0·100	-	0·100	4·51	0·091
	5	0·100	-	0·100	4·17	0·085
	2	0·167	0·067	0·100	5·49	0·115
	1	0·167	0·067	0·100	8·19	0·137
	4	0·167	0·034	0·133	3·31	0·089
24·5	0	0·267	-	0·267	4·49	0·101
	"	"	"	"	"	0·105
	0	0·267	0·133	0·133	3·59	0·179
	"	"	"	"	"	0·179
	0	0·267	0·200	0·067	3·95	0·172
	"	"	"	"	"	0·172

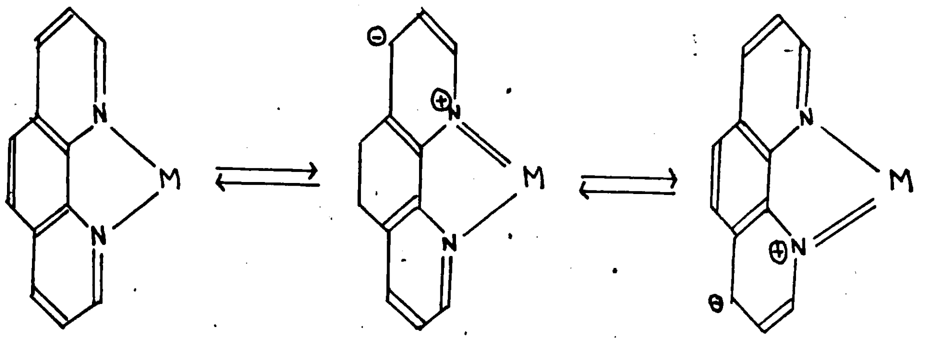
tion results on no observable reaction except a very slow decomposition.

Discussion

1,10 phenanthroline forms stable complexes with many metals. These have been reviewed by Brandt et al. (25) 1,10 phenanthroline is a planar rigid aromatic molecule in which the nitrogen atoms are easily coordinated to a metal with little internal bond distortion.



It is a weak base and the complexes are unexpectedly stable from consideration of the N - N distance which is 2·88.Å whereas the intermolecular radii of the nitrogen atoms is 3·14 Å. This stability has been rationalised by Burstall and Nyholm (34) by analogy with diarsine complexes. They suggested that the stability was due to the production of partial double bonds between the metal and the nitrogen resulting in the formation of resonance hybrids;



Therefore it has been suggested that electron attracting substituents, such as a nitro group, attached to the para carbon atom where the negative charge is located would further stabilise the complex by increasing the degree of double bonding.

From infra red studies on $[Fephen_2(NCS)_2]$ and $[Fephen_2(NCSe)_2]$ it has been shown (95) that strong back π bonding from the iron to the nitrogen on the phenanthroline occurs only in the $^1A_1$ ground state and not in the $^5T_2$ state. Since practically all Co III complexes exist on the $^1A_1$ ground state the assumption of a strong back π bonding is valid for these complexes. [also see page 137].

In general, metal complexes of a high oxidation state of a metal cannot be formed by direct combination of the ligand and the metal, only by oxidation of the corresponding lower oxidation state complex. For iron complexes the different colours of the two complexes make the reaction suitable for use as a redox indicator.

$$[\mathrm{Fephen_3}]^{2+} \underset{+e}{\overset{-e}{\rightleftarrows}} [\mathrm{Fephen_3}]^{3+}$$

deep red — light blue

"ferroin" — "ferriin"

In the present work all the complexes were made from the $[\mathrm{Cophen_2Cl_2}]^+$ ion which itself was made by oxidising with chlorine the Co II complex.

$$[\mathrm{Cophen_2Cl_2}]^{0} \xrightarrow{-e} [\mathrm{Cophen_2Cl_2}]^{+}$$

No Co III bisphenanthroline complexes have been resolved so far, although there is a report of the partial resolution of the $[\mathrm{Cophen_3}]^{3+}$, (page 284). Lack of success in resolving cis $[\mathrm{Cophen_2Cl_2}]^+$ can be explained by the rapid aquation the compound undergoes in aqueous solution, which would be expected to be accompanied by racemisation. Attempts at resolving $[\mathrm{Cophen_2CO_3}]^+$ lead to the formation of insoluble $[\mathrm{Co(II)phen_2Cl_2}]^{0}$.

1,10 phenanthroline was used as a ligand since it lacks hydrogen atoms directly bound to the coordinating nitrogen. If the conjugate base mechanism is in general operative, it is impossible here, and the hydrolysis should therefore be slow and independent of base concentration. Further, since there is no cis/trans isomerisation, [but see pages 242-252] the cis $[Cophen_2(OH)_2]^+$ ion will be formed solely, unlike the ethylenediamine system where an equilibrium mixture of the cis and trans isomers is found.

The $[Cophen_2CO_3]^+$ ion yielded the cis $[Cophen_2(OH)_2]^+$ ion on hydrolysis. Although the system was not exhaustively analysed, the rates obtained were substantially independent of the hydroxide concentration in the presence of chloride ion provided the ionic strength was kept constant. In the absence of added chloride the reaction went more slowly. There appears to be some ion catalysis, whether of a general or specific nature, which has not been investigated.

The complex is stable in aqueous solution as shown by the lack of change in the visible spectrum over a period of two days, although it is possible that some other species with an exactly similar spectrum is being formed. On the addition of alkali there is no immediate change in absorption at 520 mμ, but absorption starts to decrease after afew minutes. The initial lack of change in absorption spectra could be explained by the formation of the hydroxocarbonato species provided this has the same spectrum as the carbonato species. By analogy with the bisethylenediamine complex this is reasonable since the spectral region where the absorption $[Coen_2CO_3OH]$ is different to that of the $[Coen_2CO_3]^+$ ion is, in the phenanthroline complex, obscured by the strong change transfer band of the phenanthroline.

At higher ionic strengths this initial lack of change was very much shorter and undetectable when an ionic strength equivalent to 0·267 N was used.

$$[Cophen_2CO_3]^+ + OH^- \longrightarrow [Cophen_2CO_3(OH)]^o$$

The formation of the cis dihydroxospecies then takes place with the removal of the carbonate.

$$[Cophen_2CO_3(OH)]^o + OH^- \longrightarrow [Cophen_2(OH)_2]^+ + CO_3^{2-}$$

No rates of the initial dechelation have been measured, although qualitatively the rate appears to become slower with decrease in ionic strength and hydroxide concentration.

The rates which are quoted (Table 23 , page 213) refer to the complete removal of the carbonate. The loss of α hydrogen atoms may be responsible for the rate being little affected by variation in base but this loss does not result in a slow rate relative to the $[Coen_2CO_3]^+$ as shown in Table 24 .

TABLE 24.

RELATIVE RATES FOR THE $[Coen_2CO_3]^+$ and $[Cophen_2CO_3]^+$ IONS.

	[NaOH] N	Temperature ^oC	Rate mins.$^{-1}$
$[Coen_2CO_3]^+$	0·167	61·0	0·157
$[Cophen_2CO_3]^+$	0·167	35·5	0·128

Further chloride ion has no accelerating effect on the ethylenediamine complex. This is most obvious at high ionic strength measurements (0·267 N) where comparable measurements were not taken for the ethylenediamine system.

Clearly the mechanism of the phenanthroline complex must be different from that of the ethylenediamine complex as it was also noted that the rate of acid hydrolysis is not significantly slower than the rate of basehydrolysis, the other basic criterion for a S_N1CB mechanism.

The substitution in the phenanthroline complex may go by an electron transfer mechanism. Phenanthroline, as well as being a good σ donor due to the presence of the sp^2 donor orbitals on the nitrogen, can also function as an electron acceptor due to the presence of delocalised π orbitals of the aromatic system. Thus it can stabilise a cobalt II ion. A cobalt II ion may be formed as an intermediate and the reaction can be considered to take place by the reaction sequence proposed by Gillard. (page 78).

$$\begin{tikzcd}
{[phen_2Co^{III}(OH)CO_3]^0 + OH^-} \arrow[r, leftrightarrow] & {\{[phen_2Co^{III}(OH)CO_3]OH\}^-} \arrow[d, leftrightarrow] \\
{[phen_2Co^{II}(OH)(OH.)] + CO_3^{2-}} \arrow[d] \arrow[r, leftrightarrow] & {\{[phen_2Co^{II}(OH)CO_3]OH.\}^-} \\
{[phen_2Co^{III}(OH)_2]^+} &
\end{tikzcd}$$

There is fairly good evidence for this mechanism from a general consideration of phenanthroline complexes. The critical factor is for the cobalt II complex to be sufficiently stable to allow exchange of ligands between the inner and outer coordination spheres. Measurements on the oxidation potential (76) of the system $[Cophen_3]^{2+}$/ $[Cophen_3]^{3+}$ show that the cobalt II complex is the more stable. It has also been shown (57) that the dissociation rate of [Cophen$_3$]$^{2+}$ is very much faster than for [Cophen$_3$]$^{3+}$ since [Cophen$_3$]$^{2+}$ catalyses the exchange of [Cophen$_3$]$^{3+}$ with uncomplexed carbon 14.

A variation on this electron transfer mechanism which can be considered is a cobalt II catalysed substitution with cobalt II being present as an impurity in catalytic amounts in the original complex. The two mechanisms do not substantially differ only in the initial production of cobalt II. A variable amount of the catalytic impurity could also account for the erratic nature found in the results. A cobalt I^{I} impurity providing a catalytic pathway was first suggested (56) to account for the exchange of [Cophen$_3$]$^{3+}$ in neutral solution. In acid solution there was no exchange and the rate in neutral solution was found to vary with the sample of complex. Although electron transfer between CoII and Co III complexes is generally slow it is not so in this case. The general slowness is explained by imagining a large environmental change between Co II and Co III which makes further readjustment improbable. However in the case of phenanthroline the readjustment of environment is considerably eased due to the π electron cloud of the aromatic system. In the absence of any Co II ion the exchange reaction of $[Cophen_3]^{3+}$ in neutral solution is slow which is unremarkable since it is a diamagnetic inner orbital complex. Further, no exchange is observed for $[Coen_3]^{3+}$ with C^{14} labelled ethylenediamine whereas in the presence of catalytic amounts of Co II a slow but measurable exchange is found.

This electron transfer mechanism does not explain the observed catalysis by sodium chloride. From the present evidence it is impossible to say whether this acceleration is of a specific or general nature. The chloride ion may stabilise the ion pair complex, decreasing the activation energy and thereby accelerating the rate determining electron transfer process. The nature of this stabilisation is uncertain. Just as chlorine may be used to oxidise cobalt II, the chloride may reduce cobalt III as has been demonstrated (61) in the case of trans $[Copy_4Cl_2]Cl$. When this is dissolved in water the following reaction takes place.

$$\text{trans } [Copy_4Cl_2]Cl \rightleftarrows CoII + py + Cl_2$$

The cobalt II is unusually labile, the chloride ion may be acting in a similar way in this instance.

On the basis of this electron transfer mechanism it is quite surprising that a Co III complex is the final product. When the other complexes in this series were examined [Cophen$_2$(C$_2$O$_4$)]Cl, [Cophen$_2$mal]Cl, [Cophen$_2$CB]Cl, a black precipitate of cobalt II oxide were formed. The last two complexes differ from the first in being stable in light. The [Cophen$_2$(C$_2$O$_4$)]$^+$ ion rapidly decomposed to form [Cophen$_2$Cl$_2$]^0, the cobalt III being reduced, (4) to the cobalt II by the oxalate group.

In general agreement with chelate ring stability, it was shown (4) that the five-membered ring incorporating the oxalate group is more stable than the six-membered ring. The malonate group can be replaced by nitrite at room temperature by reaction with alkali metal nitrite solutions whilst with the oxalato complex no replacement occurs. Attempts to make the succinato complex were unsuccessful due to the low stability of the seven-membered ring.

5. INFRA RED SPECTRA OF BIS 1,10 PHENANTHROLINE COBALT III COMPLEXES

a) Production of spectra

All the spectra were taken by the disc method using potassium bromide as a matrix media. The spectrum for 1,10 phenanthroline hydrate corresponds closely to the published spectra (116, 131) taken in nujol. Therefore the grinding and compression involved in the production of a plate cannot critically change the nature of the sample. A further potential inherent difficulty in the production of a disc is that ion interchange with the potassium bromide matrix will take place. (44) In order to reduce this to a minimum the spectra were taken immediately the disc had been formed and again 20 minutes later. Only in the case of the [Cophen$_2$mal]Cl was any change in the spectrum observed. In general, ion interchange does not take place. Unsatisfactory spectra were uniformly obtained using the mulling method; the mulling agents tried were nujol, hexachlorobutadiene and Kel F no.3. The range of the spectra (650-5000 cm.$^{-1}$) was governed by the range of the SP 200 since this was the only instrument on which it was possible to use discs.

b) 1,10 Phenanthroline metal complex spectra

Schilt and Taylor were the first authors (131) to attempt investigations and correlations on the infra red spectra of several 1,10 phenanthroline metal complexes. Other papers have more recently appeared (95) on these complexes but none on bis 1,10 phenanthroline cobalt III complexes.

The vibrational frequencies observed in the region studied arise exclusively from the ligand part of the complex. There have been no systematic studies on the vibrational frequencies of 1,10 phenanthroline but according to Bellamy (19) many generalisations based on studies of benzene derivatives can be applied to heterocyclic aromatic compounds. It has been observed (93) that although there are considerable differences in the hydrogen deformation vibrations, the out of plane hydrogen deformation vibrations appear to be like those of benzene compounds containing additional substituents. The normal vibrations of hetero-aromatic compounds have been divided into two classes:

a) those in which the hydrogen atoms move relative to the heavy skeleton;

b) those in which each C-H or N-H group moves as a unit. Since similar masses are involved, the substitution of N for CH would have little effect on the normal vibrations of the class (b).

In general, if n hydrogen atoms are attached to a planar ring, there will be 3n CH type modes and in each group the n modes will be coupled. The fundamental absorption bands corresponding to the three classes occur in different parts of the spectrum: CH stretching near 3000 cm.$^{-1}$, in plane CH bending in the region 1300-1000 cm.$^{-1}$ and out of plane CH bending in the region 1000-700 cm.$^{-1}$

Infra red spectra

The position and intensities of the infra red bands in the spectra of 1,10 phenanthroline hydrate and some of its complexes are given in Tables 25 and 26 Graphs 31, 32 and 33.

The700-900 cm.$^{-1}$ region

In phenanthroline and its complexes two strong bands appear at about 710 and 855 cm.$^{-1}$ This is the number expected since there is one group of two and two groups of three adjacent hydrogen atoms in the ring system.

TABLE 25.

INFRA RED STRETCHING FREQUENCIES IN THE 4000-700 cm.$^{-1}$ REGION FOR phenH_2O, CIS [Cophen$_2$Cl$_2$]Cl AND THE GREEN CHLORIDE

phenH_2O	CIS [Cophen$_2$Cl$_2$]Cl	Green Chloride	Band Assignments
695 (d)$^+$			
735 (vs)	710 (vs)	710 (vs)	out of plane motion of H atoms on heterocyclic rings
	720 (sh)	720 (sh)	
	745 (w)	750 (w)	
779 (w)	780 (wd)	780 (wd)	
840 (sh)	841 (vs)		
854 (vs)	855 (vs)	845 (vs)	out of plane motion of H atoms on the centre ring
989 (w)			
	1030 (vw)	1030 (m)	ring breathing modes
1090 (m)	1090 (w)		
	1100 (w)		
1135 (m)	1140 (m)	1140 (wd)	
1210 (w)	1215 (m)	1220 (m)	

[continued on next page]

TABLE 25. [continued]

$phenH_2O$	Cis $[Cophen_2Cl_2]Cl$	Green Chloride	Band assignments
	1310 (wd)	1310 (md)	
1342 (m)	1340 (m)	1340 (wd)	
1400 (sh)	1410 (m)	1410 (s)	
1420 (vs)	1420 (vs)	1425 (vs)	C = C stretching vibrations
		1455 (w)	
1480 (w)	1480 (w)	1490 (w)	
1497 (sh)			
1508 (s)	1515 (s)	1515 (s)	ring frequency
1555(m)	1555 (w)		
	1570 (m)	1570 (m)	
1580 (m)	1600 (w)	1595 (m)	ring frequency
1630 (w)	1630 (w)	1620 (w)	
1640 (w)	1640 (w)	1640 (w)	
	1700 (w)		
3050 (sh)	3050 (sh)	3000 (m)	C - H stretching vibration
3390 (sd)	3390 (sd)	3350 (sd)	Antisymmetric and symmetric O - H stretching modes

+ s = strong; m = medium; w = weak; d = diffuse;
v = very; sh = shoulder.

TABLE 26.

INFRA RED STRETCHING FREQUENCIES IN THE 4000-700 cm.$^{-1}$ REGION FOR [Cophen$_2$CO$_3$]Cl, [Cophen$_2$C$_2$O$_4$]Cl, [Cophen$_2$mal]Cl and [Cophen$_2$CB]Cl

[Cophen$_2$CO$_3$] Cl	[Cophen$_2$C$_2$O$_4$] Cl	[Cophen$_2$mal] Cl	[Cophen$_2$CB] Cl	Assignments
710 (vs)	710 (vs)	710 (vs)	710 (vs)	out of plane motion of H atoms on heterocyclic ring
745 (vw)	745 (vw)	740 (vw)		
755 (vw)		750 (vw)	750 (vw)	
785 (wd)	780 (w)	785 (w)	790 (vw)	
	795 (s)			v (O-C=O) + (M-O)
830 (m)		810 (vw)		
855 (vs)	855 (vs)	855 (vs)	855 (vs)	out of plane motion of H atoms on centring
	855 (vw)			vs (C-O) + (O-C=O)
		980 (w)		
	1030 (vw)	1040 (vw)		
	1090 (vw)			ring breathing modes
	1105 (vw)	1110 (vw)	1100 (m)	
1150 (m)	1145 (m)	1150 (m)	1140 (m)	
1200 (m)		1210 (m)	1200 (m)	
1220 (m)	1220 (m)	1220 (m)	1220 (m)	

[continued on next page]

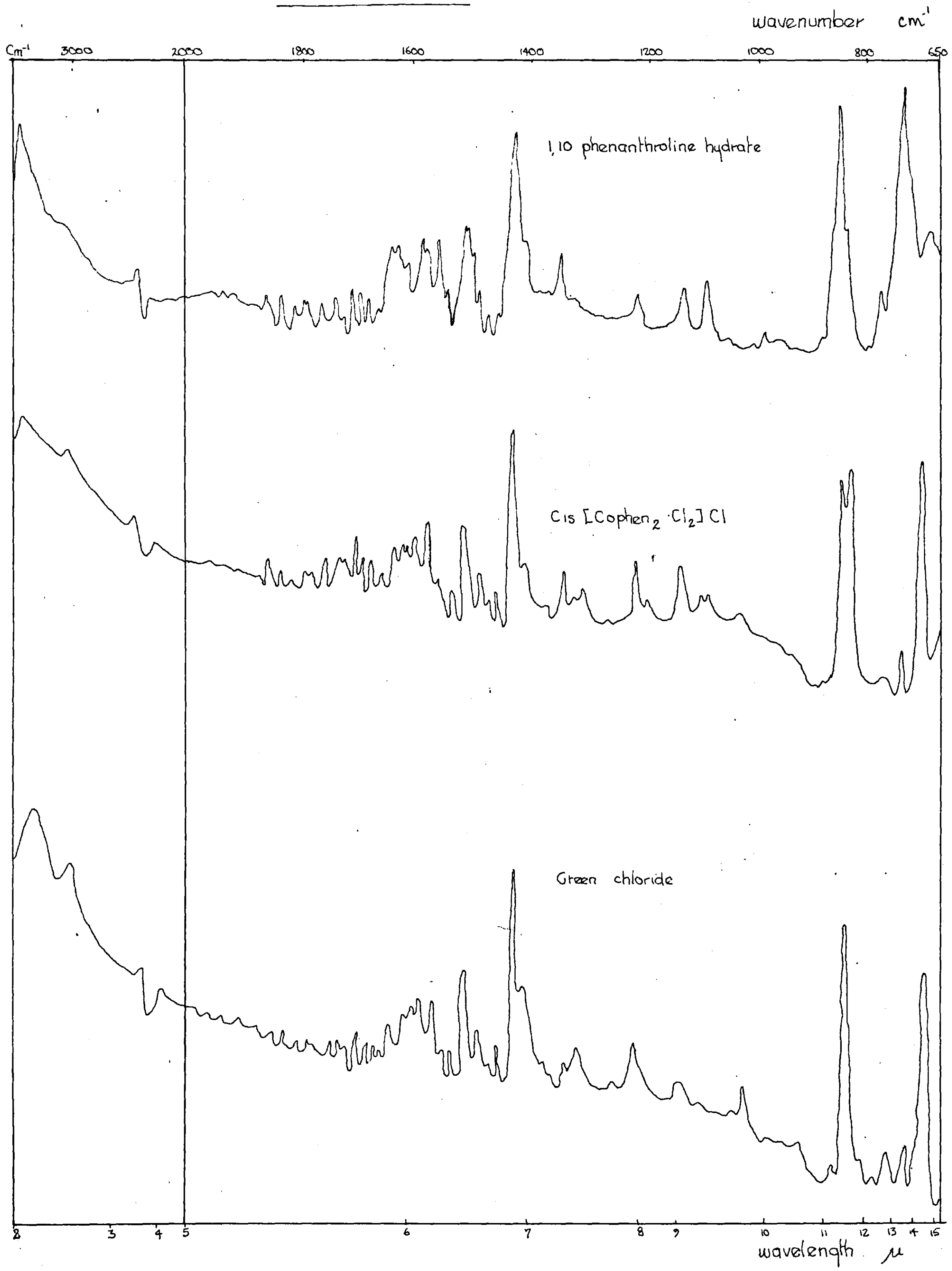
TABLE 26. [continued]

[Cophen$_2$CO$_3$]Cl	[Cophen$_2$C$_2$O$_4$]Cl	[Cophen$_2$mal]Cl	[Cophen$_2$CB]Cl	Assignments
1240 (s)				
1310 (wd)	1315 (m)	1320 (m)		
1340 (w)	1340 (s)	1345 (s)	1345 (s)	
	1370 (vs)	1390 (vs)	1350 (vs)	vs(C-O)+v(C-C)
1410 (sh)	1410 (sh)	1410 (vs)	1410 (s)	
1425 (vs)	1425 (vs)	1435 (vs)	1425 (vs)	C=C stretching vibration
1460 (w)	1455 (w)	1460 (w)	1455 (w)	
1490 (w)	1490 (w)	1495 (w)	1490 (w)	
1520 (s)	1508 (s)	1525 (s)	1520 (s)	ring frequency
1555 (sh)	1550 (w)	1550 (w)	1540 (w)	
1570 (m)	1570 (m)	1560 (sh)	1560 (sh)	
1600 (sh)	1600 (w)	1580 (sh)	1580 (sh)	ring frequency
		1610 (vs)	1610 (vs)	v as (C=O)
1630 (vs)	1630 (m)	1635 (vs)	1630 (vs)	
1650 (vs)	1660 (vs)			v as (C=O)
	1690 (vs)	1680 (sh)		v as(C=O)
3050 (m)	3050 (m)	3050 (m)	3050 (m)	C-H stretching vibration
3400 (sd)	3350 (sd)	3450 (sd)	3400 (sd)	Antisymmetric and symmetric O-H stretching mode

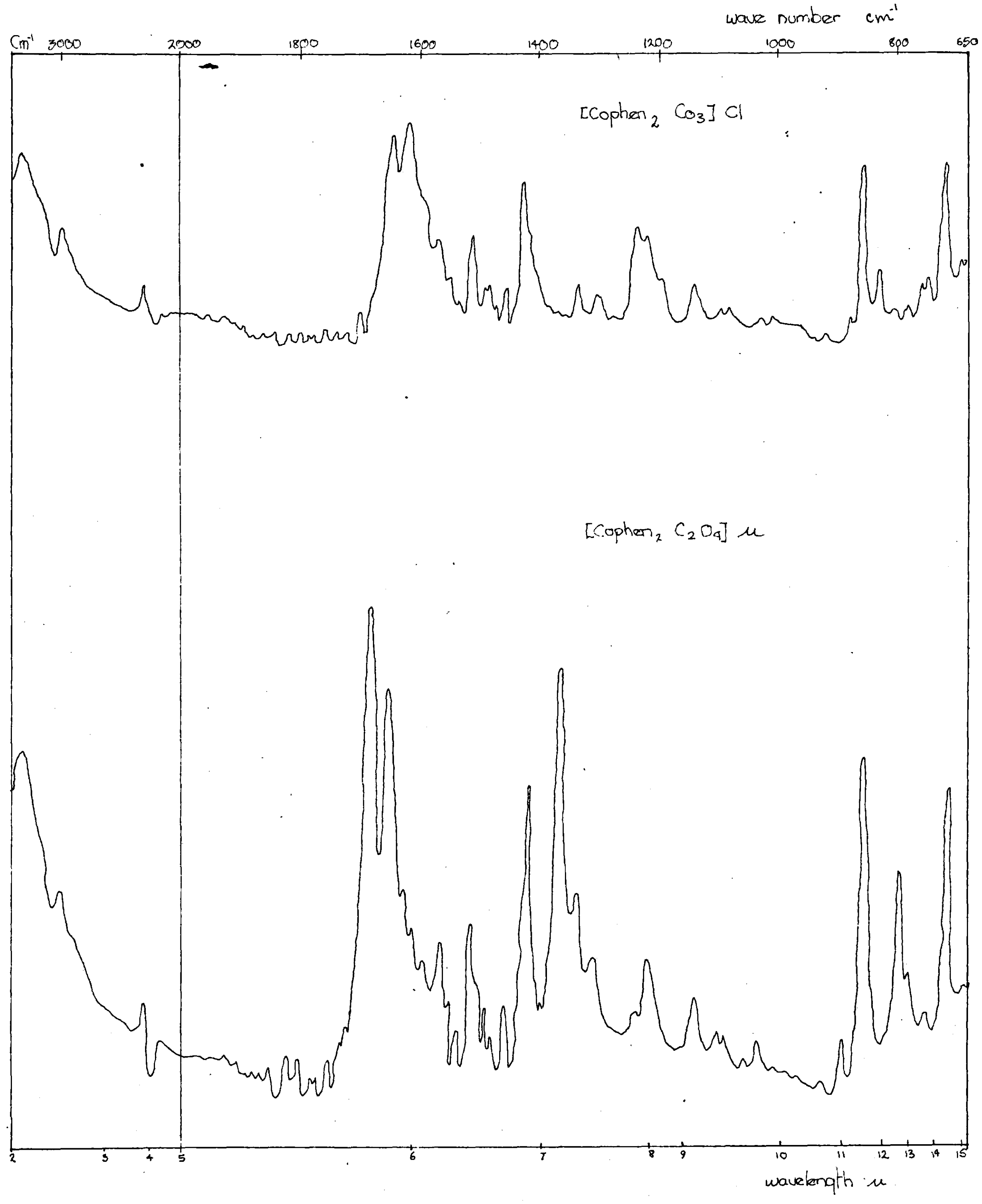
s = strong; m = medium; w = weak; d = diffuse; v = very; sh = shoulder.

GRAPH 31

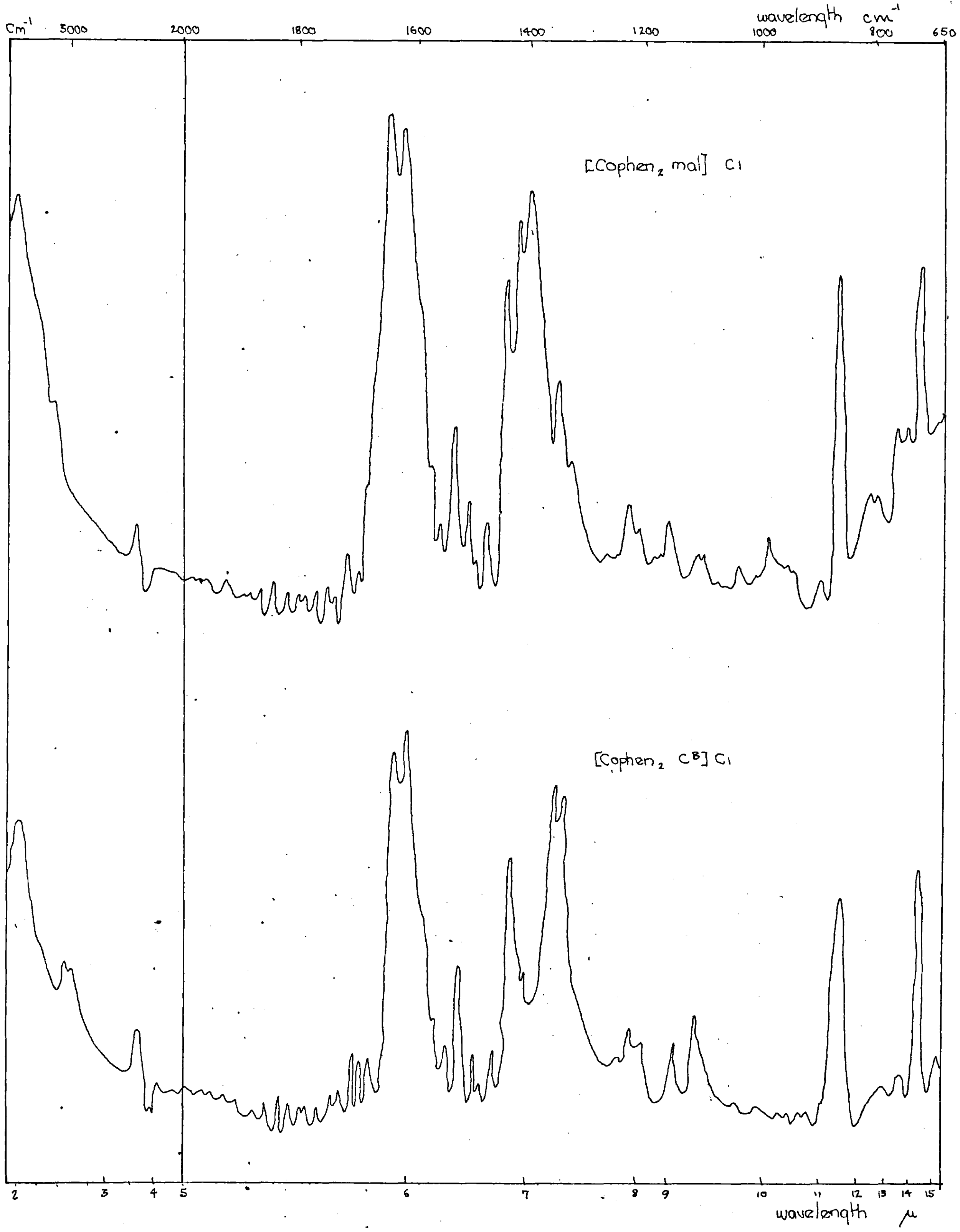
INFRA RED SPECTRA



GRAPH 32
INFRA RED SPECTRA



GRAPH 33
INFRA RED SPECTRA



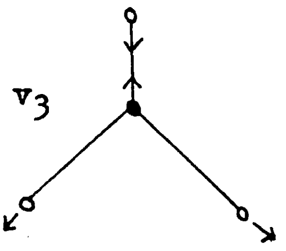
In hydrocarbons, the frequency shifts upwards as the number of adjacent atoms in a group decreases. On this basis, the 710 cm.$^{-1}$ is assigned to the out of plane motion of the hydrogen atoms on the heterocyclic rings and the 850 cm.$^{-1}$ to the hydrogens on the centre ring. Other weak bands in the region due to the phenanthroline have not been unambiguously assigned but probably arise from out of plane hydrogen motions other than the one in which all the atoms move in phase. An alternative explanation is also given, see page 237.

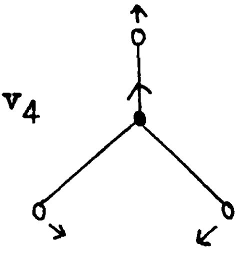
Some of the vibrations are due to the presence of the carboxylate ligand. In $[Cophen_2C_2O_4]Cl$ bands are observed at 795 cm.$^{-1}$ and 885 cm.$^{-1}$ and, by analogy, these are assigned to the sum of the deformation frequency O - C = O with the Co - O stretching frequency and to the sum of the deformation O - C = O with the C - O symmetric stretch frequency.

The 1125-1400 cm.$^{-1}$ region

The phenanthroline chelate frequencies are not well characterised in this region but it has been suggested that they may arise from in plane hydrogen deformation motions or possibly ring vibrations. There are three main bands in this area, 1140, 1220 and 1342 cm.$^{-1}$, the position of which remain sensibly constant. In addition to the bands due to the phenanthroline ligand, there also occurs in the dicarboxylato complexes a band at about 1370 cm.$^{-1}$ which has been assigned to the sum of the symmetric C - O frequency and the C - C frequency.

The spectrum of the [Cophen$_2$CO$_3$]Cl is unique in this series in having a strong band at 1240 cm.$^{-1}$ On coordination the symmetry of the carbonate group is reduced from D_{3h} in the free ion to C_s on monochelation and C_{2v} on bichelation. This results in the doubly degenerate vibrations, v_3 and v_4 splitting into two separate bands.





The effect is qualitatively similar in both cases but much larger in the case of bichelation. (114) The splitting of the v_3 band (occurring at 1500 cm.$^{-1}$ in sodium carbonate) results in the observed component at 1240 cm.$^{-1}$, the other component occurring at about 1640 cm.$^{-1}$ where the spectrum is too complicated for any unambiguous assignment.

Chelation of an oxalate group results in nine infra red active bands, but apart from the C - O bands these have not been assigned. Empirical band assignments have been made for many trisoxalato metal complexes by comparison with the spectrum of N_2O_4.(113) However this comparison is not completely satisfactory since in a chelate system, coupling between various vibrational modes is expected. Band assignments have also been made as the result of normal coordinate analysis on the free oxalate ion, but again the same reservations must be made about the applicability of this to chelate systems. The bands here have been assigned by comparison to the $[Co(C_2O_4)_3]^+$ ion.

The 1400 - 1650 cm.$^{-1}$ region

The most intense absorption is contained in this region since, not only are there characteristic ring frequencies of phenanthroline, but also absorptions due to the carbonyl group. The discernable ring frequencies occur at 1420, 1508 and 1580 cm.$^{-1}$, the latter two bands being displaced to longer wavelength on coordination. Other ring frequencies at 1630 and 1640 cm.$^{-1}$ tend to be obscured on complexing by the very much stronger asymmetric vibration due to the carbonyl group between 1610 and 1690 cm.$^{-1}$, the exact position depending upon the particular complex. The band at 1630 cm.$^{-1}$ may also be due to the H - O - H bending mode due to the presence of lattice water.

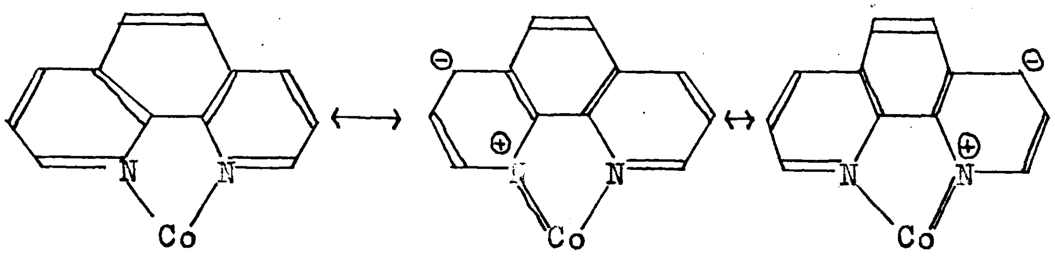
The 3000 cm.$^{-1}$ region

All the complexes considered exist as hydrates. This results in an intense diffuse band at about 3400 cm.$^{-1}$ due to the antisymmetric and symmetric O - H stretching modes. In addition to this band there is also present a band at 3050 cm.$^{-1}$ due to C - H stretching frequency.

The nature of the Cobalt-Nitrogen bond

Metal ligand stretching frequencies are of particular interest since they provide direct information about the coordinate bond. In complexes containing heterocyclic ligands, the metal nitrogen frequency is usually below 300 cm.$^{-1}$ and so could not be measured directly in this work, although this is subject to some debate. (42, 110)

It has been suggested (34) that the conjugation of π electrons on the phenanthroline is further delocalised by the development of a partial double bond of the Co - N.



I II III

If this is the position on chelation then the ring frequencies should be much weaker. Indeed the 1497 cm.$^{-1}$ band in the phenanthroline hydrate is missing on chelation. This bond is assigned to strong coupling between the C - C and C - N stretching vibrations. However the band at 1508 cm.$^{-1}$, thought to be due to the same cause is still present although shifted to longer wavelengths.

The same resonance form can be used in the interpretation of the C - H bending modes. (95) The three pairs of C - H bending modes become inequivalent if there is a significant contribution of resonance forms like II and III. Thus the single peak becomes split into three, 710, 720 and 745 cm.$^{-1}$ as is observed for the cis $[Cophen_2Cl_2]Cl$ and the green chloride. Splitting is also observed in the carboxylato complexes although there is no band at 720 cm.$^{-1}$ but, except for the oxalato complex, a weak band is found around 750 cm.$^{-1}$

It seems likely that the resonance forms shown exert a stabilising influence on the complex.

6. COMPOUNDS OF COBALT, PHENANTHROLINE AND CHLORINE

Historical Introduction

The first compounds to be made in this group were $[Cophen_3]Cl_3$ and $[Cophen_3]Cl_2$. More recently the $[Cophen_2Cl_2]Cl$ was made and this preparation has been repeated in the present study, (page 219).

1) Assignment of the cis configuration to the $[Cophen_2Cl_2]Cl$ complex

This grey purple crystalline powder was assigned a cis configuration by Ablov. (1) This assignment was based on the colour being similar to the violet cis $[Coen_2Cl_2]Cl$. No isomeric salts were isolated although the violet complex was heated for some time with concentrated hydrochloric acid. Under the same conditions the violet cis $[Coen_2Cl_2]Cl$ is converted to the green trans $[Coen_2Cl_2]Cl$.

It was also shown (2) that the $[Cophen_2Cl_2]^+$ ion undergoes aquation in solution, but with sufficient hydrochloric acid the rate of aquation is so decreased that the absorption curve only coincides with that of the $[Cophen_2(H_2O)_2]^{3+}$ ion after 90 hours of heating.

These mild aquation conditions exclude the possibility of isomerisation and therefore the $[Cophen_2Cl_2]^+$ ion formed must be assigned the cis configuration since the $[Cophen_2CO_3]^+$ ion gives the same $[Cophen_2(H_2O)_2]^{3+}$ ion on acidification.

2) The green chloride

The formation of this chloride is described on page 280 . It was originally thought to be the trans $[Cophen_2Cl_2]^+$ ion, the trans $[Coen_2Cl_2]^+$ ion also being green. In nitrobenzene a green solution was found whilst in water a pink solution was formed due to rapid aquation, the trans structure being confirmed by the isolation of trans $[Cophen_2(H_2O)_2][Cr(NH_3)_2(SCN)_4]$. (25)

Later Ablov suggested (1) that the green chloride was an intermediate aquation product, $[Cophen_2(H_2O)Cl]$, since on drying the characteristic grey purple crystals of cis $[Cophen_2Cl_2]Cl$ were formed.

Experimental

The cis $[Cophen_2Cl_2]Cl$ and green chloride were isolated as described on page 279 . As well as these two compounds, two other solids were isolated from the solution by partial evaporation and the addition of a

1:1 solution of alcohol and ether. The results of physical measurements carried out on these compounds are shown in Table 27.

Discussion

1) Possibility of cis and trans isomers

The assignment of cis and trans stereochemistry has been carried out on the basis of physical measurement. There is no immediate factor, such as steric hindrance which prevents the $[\text{Cophen}_2\text{Cl}_2]^+$ ion as existing in cis and trans isomeric forms.

a) Ultra violet and visible spectroscopy

It has been shown (page 13) that in the region of ligand field absorption bands, cis complexes absorb more strongly than trans. The visible absorption maximum to which a cis configuration has been assigned occurs at a longer wavelength than for the trans. Cis $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ is purple and trans $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ is green. Similarly cis $[\text{Rhen}_2\text{Cl}_2]\text{Cl}$ is yellow and trans $[\overset{\text{Rh}}{\text{Co}}\text{en}_2\text{Cl}_2]\text{Cl}$ is orange.

In the case of phenanthroline complexes, the large charge transfer band due to the phenanthroline obscures the position where the short wavelength ligand field band would be expected, although a shoulder at 350 mμ is often found. Therefore any structural assignment has to be made on the basis of the band which occurs at about 370 mμ, As has been previously stated the purple crystalline [Cophen$_2$Cl$_2$]$^+$ ion has been assigned the cis structure because of its colour. In the absence of any other isomer with which to compare it, this evidence is inconclusive.

The concept of more ~~intense~~ deep colour being diagnostic of a trans complex has been used in the assignment of the [Irphen$_2$X$_2$]$^+$ ion, X$^-$ = Cl$^-$, Br$^-$. This is shown in Table 28.

TABLE 28. (41)

STEREOCHEMISTRY OF [Irphen$_2$X$_2$]$^+$ IONS ON THE BASIS OF COLOUR.

X$^-$	Colour	Stereochemistry
Cl$^-$	Yellow	cis
Cl$^-$	Reddish-orange	trans
Br$^-$	Orange	cis
Br$^-$	Reddish-brown	trans

TABLE 21.

SOME PHYSICAL PROPERTIES OF THE FOUR COMPOUNDS ISOLATED DURING THEPREPARATION OF CIS$[\text{Cophen}_2\text{Cl}_2]$Cl

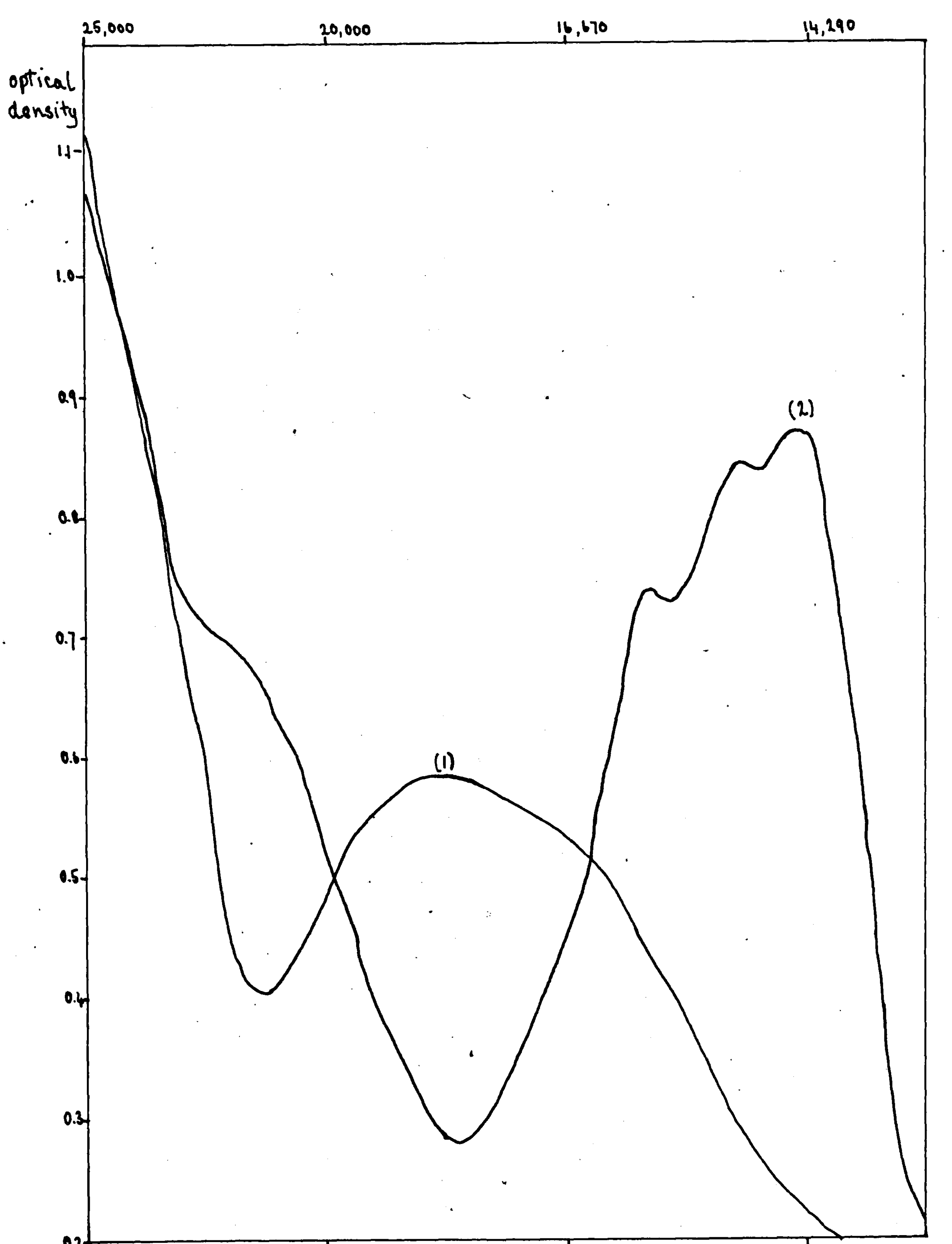
Number	932	1080	1079	1012
Colour in solid	bright green	dark grey	greypurple	dark purple
Analysis %C	49·22	45·33	47·37	48·06
%H	3·72	3·79	4·04	3·85
%N	9·71	8·34	9·01	9·27
%Cl	17·53		22·38	18·01
Colour in aqueous solution	yellow	orange	bright pink	dirty cherry
Visible reflectance spectrum				
λ max. mμ	695, 670 635, 475	695, 670 635, 550	550	550
O.D.	·875, ·845 ·740, ·650 (sh) (graph 34, page 246)	·905, ·905 ·885, ·680	·590	·590 (graph 34, page 246)
λ min. mμ.	550	475	475	475
O.D.	·290	·630	·430	·405
Visible solution spectrum	slight change on standing (graph 35, page 247)	slight change on standing	change	change
isosbestic points mμ	505	-	520, 455	540
$\lambda_{\text{max.}}$ mμ	465 (sh)	509	515 (initial and final)	540 (initial and final)
$\lambda_{\text{min.}}$ mμ	-	465	465(initial and final)	470(initial) 459(final)

TABLE 27. (Continued)

	932	1080	1079	1012
Infra red spectrum out of plane motion of H atoms on centre ring.	850(s)	850(s) 855(sh)	845(s) 855(s)	845(s) 855(s)
Solubility in nitrobenzene	slightly soluble	slightly soluble	insoluble	insoluble
Magnetism	paramagnetic			diamagnetic
Stability in aqueous sodium hydroxide	decomposes, yellow solution, gradually darkening.	decomposes	slow change	slow change
Stability in conc. hydrochloric acid	bright green solution (graph 35, page 247)	pale green solution	pale pink solution (not very soluble)	insoluble

GRAPH 34

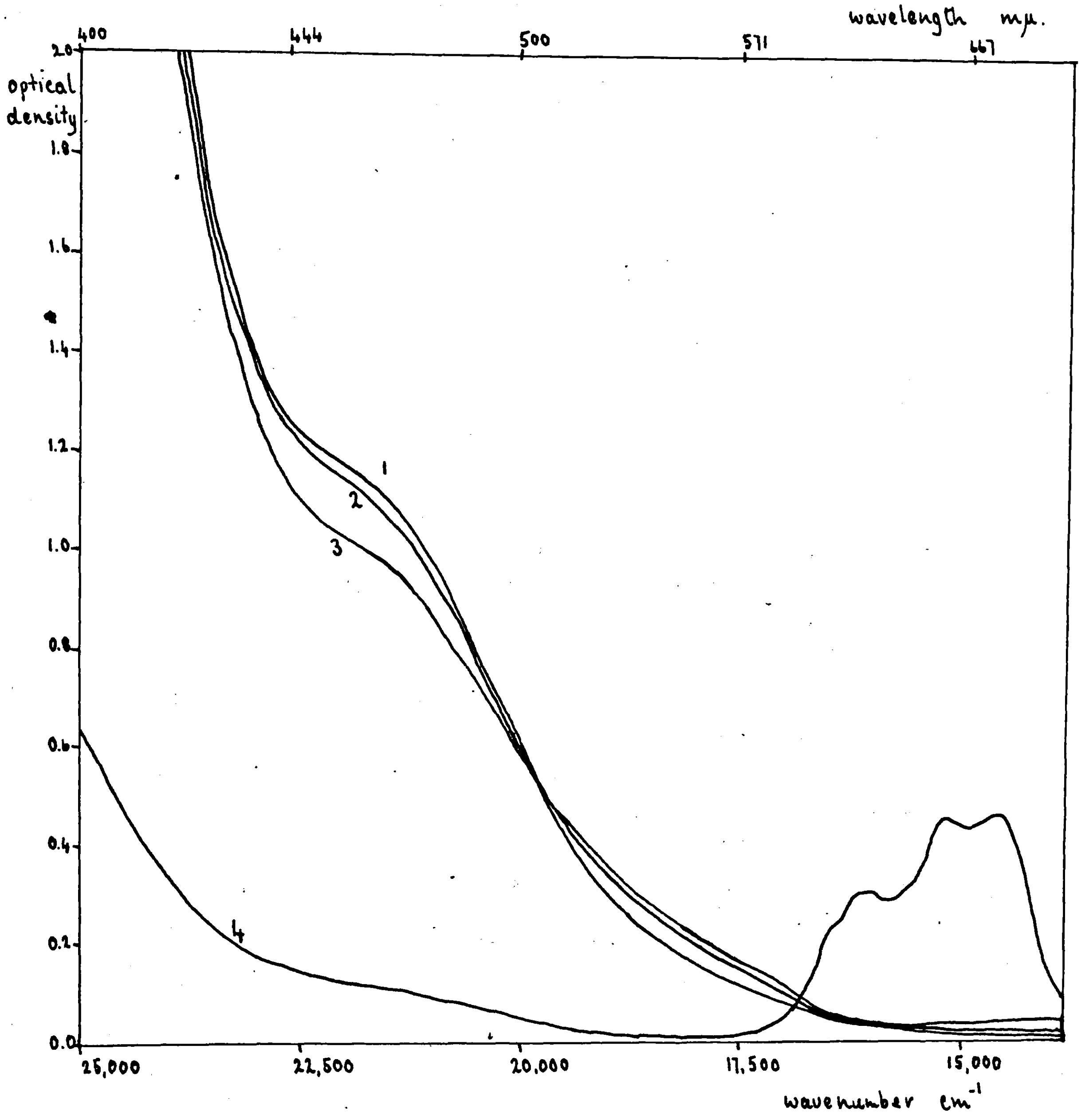
SOLID STATE REFLECTANCE SPECTRA FOR CIS[$Cophen_2Cl$]Cl (1) AND THE GREEN CHLORIDE (2).



GRAPH 35

SPECTRA OF THE GREEN CHLORIDE IN WATER.

1, immediately on formation of solution.
2, 3, spectra at increasing lengths of time.
3. after 30 minutes when there is no further change.
4. spectra of the same solution after dilution (about 300 times) and acidification with concentrated hydrochloric acid.



Further the molecular conductivities indicated they were 1:1 electrolytes.

On the basis of colour alone it would appear that the green chloride might be the trans isomer. However this is not supported since the compound was found to be paramagnetic and gave a solid state spectrum indicating the presence of the tetrahedral Co II ion, $[CoCl_4]^{2-}$, (graph 34 , page 246).

b) Infra red spectroscopy

This has been successfully applied to the study of the cis and trans isomers of bisethylenediamine cobalt III and rhodium III complexes. In general the cis isomers show a splitting of the NH_2 assymmetric deformation while in the trans complex there is no splitting. These are shown in Table 29.

TABLE 29.

SPLITTING OF THE ASSYMMETRIC DEFORMATION FREQUENCY IN COMPLEXES OF THE TYPE $[Men_2Cl_2]^+$ M = Co, Rh, from refs. 112, 86.

M	Stereochemistry	Frequency cm.$^{-1}$
Co	trans	1596 (s)
Co	cis	1630,(m), 1561 (s)
Rh	trans	1600
Rh	cis	1570 , 1625

The situation in bisphenanthroline complexes is less easily interpreted since, in general, it is found that metal phenanthroline complexes are all very similar (131) and in these particular complexes the only major difference found in the spectra occurred in the splitting of the frequency which has been assigned to the out of plane motion of the H atoms on the central aromatic ring, at about 850 cm.$^{-1}$ This splitting agrees with the cis structure assigned by Ablov. (1) The $[\mathrm{Rhphen_2Cl_2}]^+$ ion has been made (68) and this has been assigned the trans structure. It has one sharp peak at 850 cm.$^{-1}$ There are no reports of the cis rhodium complex.

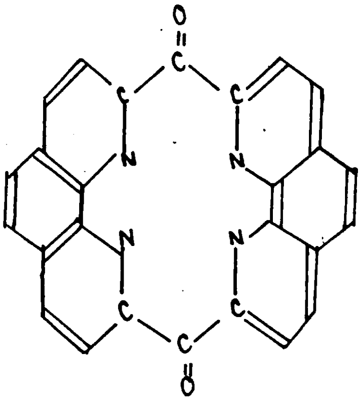
c) <u>Steric considerations</u>

The major reason for doubting the existence of compounds of the general type trans $[\mathrm{Cophen_2X_2}]^+$ where X is a monodentate ligand comes from the possible steric interactions between the two and nine hydrogen atoms which are necessarily planar. However, it has been found that the distance between two nitrogen atoms on neighbouring phenanthroline groups is 2·88 Å which is less than the sum of the intermolecular radii of the nitrogen atoms, 3·14 Å. Therefore it might seem that this should lower the stability of the complexes although in fact phenanthroline complexes are in general stable. Any interaction between the hydrogens cannot be a major cause of disallowing the formation of the complex.

For rhodium, only trans [Rhphen$_2$Cl$_2$]Cl has been claimed to be characterised. (68) (and 69) With the increase in size of the Rh III ion (ionic radius 0·69 Å) from Co III (ionic radius 0·29 Å) an increase in stability of the trans complex would be expected if the instability in the case of Co III is due to the interactions as suggested. The size increases only slightly on passing from rhodium to iridium, (atomic radius increases from 1·34 Å to 1·35 Å). Iridium is the only member of the triad for which both cis and trans complex ion of the type [M phen$_2$Cl$_2$]$^+$ have been formulated.

The trans stereochemistry of the [Rhen$_2$Cl$_2$]$^+$ ion is assigned due to its likeness to its bipyridyl analogue which in turn is given its structure from consideration of its electronic spectrum. (68) Previously the assignment had been based firstly on the splitting of the in - phase out of plane CH vibrations of the bipyridyl allegedly due to the cis configuration and later on the formation of an adduct with hydrogen chloride, indicating a trans configuration. There seems little reason why the cis isomer should not also be made.

Theoretically it is possible that the carbon at the two position on a phenanthroline molecule can be linked to that at the two position on a second molecule through a carbonyl group. If this is done in both the two and nine position then a planar quadridentate cyclic ligand is formed which could only be coordinated in a manner resulting in a similar structure to a trans phenanthroline complex.



If this ligand could be coordinated to the central cobalt then there is no reason why the trans $[Cophen_2Cl_2]^+$ complex ion should not also exist.

From steric considerations the stability of the cis form relative to the trans in the series $[\mathrm{Cophen_2X_2}]^+$, $X^- = Cl^-$, Br^-, I^- might be expected to decrease in the order $Cl > Br > I$, the bulky iodide having the least tendency to form a cis complex. The $[\mathrm{Cophen_2Br_2}]^+$ ion has been made but there are no reports of the $[\mathrm{Cophen_2I_2}]^+$ ion although the isothiocyanato complex has been made. (1)

d) Resolution of the cis isomer

This would prove a cis stereochemistry. However lack of resolution cannot be taken to indicate a trans structure.

Every attempt to resolve the $[\mathrm{Cophen_2Cl_2}]\mathrm{Cl}$ complex failed (pages 284 - 287). This is due either to a trans configuration or to a rapid racemisation. In either case rapid aquation is shown to take place by following the spectrophotometric changes which occur when the ion is dissolved in water.

2. The nature of the green chloride

The analysis, colour and infra red spectrum favour a trans Co III ion, $[\mathrm{Cophen_2Cl_2}]^+$ ion. The reflectance spectrum and paramagnetism show that it is a Co II complex containing the tetrahedral $[CoCl_4]^{2-}$ ion. See graph 34, page 246. Further, in aqueous solution a slow aquation takes place but on acidification with concentrated hydrochloric acid a bright green solution containing the $[CoCl_4]^{2-}$ ion is formed. This is similar to the behaviour of $[Co(H_2O)_6]Cl_2$ which is pink in water and bright blue on acidifcation with concentrated hydrochloric acid.

In aqueous solution the $[Co(H_2O)_6]^{2+}$ ion has been shown (13) to be in equilibrium with small amounts of tetrahedral $[Co(H_2O)_4]^{2+}$ ion. This provides a pathway for the formation of the $[CoCl_4]^{2-}$ ion from the original octahedral complex in the presence of concentrated hydrochloric acid or the precipitation of this ion from a strongly acid solution.

Reduction of phenanthroline cobalt III complexes take place readily so this cobalt II complex can either be considered to be formed by reduction from Co III or merely as a biproduct from the original $CoCl_2.6H_2O$ which was mainly oxidised for the preparation of cis $[Cophen_2Cl_2]Cl$.

Another complex ion containing phenanthroline must also be present since such a high proportion of the compound is carbon. It was not found possible to find an analysis to fit the results. Some trial analyses are shown in Table 30.

TABLE 30

THEORETICAL ANALYSES FOR SOME COBALT, PHENANTHROLINE AND CHLORINE COMPLEXES

%	C	H	N	Cl
Found (before heating)	49·22	3·27	9·71	17·53
(after heating)	44·30	4·60	8·60	16·30
$[Cophen_2Cl_2]Cl3H_2O$	49·72	3·82	9·66	18·34
$[Cophen\ Cl_4][CoCl_4]$-$[Cophen_3]$	48.79	2.72	9.49	24.02
$[Cophen_2Cl_2]_2[CoCl_4]$	48.79	2.72	9.49	24.02
$[Cophen_2(H_2O)_2][CoCl_4]$	43.92	3.08	6.34	21.60
$[Cophen_3][CoCl_4]$	48·00	2·68	9·315	23·62
$[Cophen_3]_2[CoCl_4]_3$-$[Cophen_2Cl_2]6H_2O$	49·25	3·27	9·57	21·2

Conclusion

Of the four compounds made, the first corresponds to the green chloride (932), the last (1012), cis [Cophen$_2$Cl$_2$]Cl and the remaining two are mixtures . (1080 and 1079) are mixtures of the green chloride and cis {Cophen$_2$Cl$_2$]Cl.

No unambiguous evidence has been obtained as to whether the [Cophen$_2$Cl$_2$]Cl complex exists in the cis or the trans form, although in general the evidence favours a cis configuration.

The green chloride contains the [CoCl$_4$]$^{2-}$ ion which rapidly aquates in aqueous solution. There is also present a complex ion containing phenanthroline but the exact nature remains unknown. There is also the possibility of chlorination on the phenanthroline rings and of the presence of phenanthrolinium hydrochloride.

Further work is required.

PART III: EXPERIMENTAL

1. PREPARATION AND RESOLUTION OF SOME BISETHYLENEDIAMINE AND RELATED COBALT III COMPLEXES

cis d,l $[Coen_2(NO_2)_2]NO_2$

This compound was prepared in the same way as in Inorganic Synthesis. (80) A 10% aqueous solution of ethylenediamine was added to sodium cobaltinitrite. The mixture was stirred on a steam bath until a temperature of 70° was obtained. At this temperature the reaction occurred as was shown by the dissolving of the sodium cobaltinitrite to form a dark brown solution. After filtering, the filtrate was allowed to cool in an ice salt bath and on scratching brown crystals of the cis compound were formed. These were filtered off and air dried.

cis d $[Coen_2(NO_2)_2]Br$ and cis l $[Coen_2(NO_2)_2]Br$ (51)

Solutions of cis d,l $[Coen_2(NO_2)_2]NO_2$ and d antimony potassium tartrate were mixed and the resulting mixture cooled under running water to room temperature. The solution was surrounded by ice and after 10 minutes of scratching, crystals of the diastereoisomer, l $[Coen_2(NO_2)_2]$ d $SbOC_4H_4O_6$ began to separate out. Crystallisation was allowed to continue for 10 minutes before filtering.

The d $[Coen_2(NO_2)_2]Br$ was extracted from the filtrate by the addition of ammonium bromide. On scratching orange crystals began to separate and crystallisation was allowed to continue for 5 minutes before the impure d $[Coen_2(NO_2)_2]Br$ was collected on a Buchner and washed with ice cold water.

The precipitate of the diastereoisomer was washed with 50% aqueous ethanol, ethanol and air dried. It was transferred to a mortar and ground with water and sodium iodide, and after about 2 minutes the l $[Coen_2(NO_2)_2]$ I separated out leaving the antimony potassium tartrate in solution.

Both isomers were purified by shaking with silver chloride, thus forming the soluble $[Coen_2(NO_2)_2]Cl$. After the removal of the silver halides, the $[Coen_2(NO_2)_2]^+$ ion was reprecipitated by the addition of ammonium bromide. After filtration, the salts were washed with 50% aqueuous ethanol, ethanol, acetone and air dried.

Rotations

Found: l $[Coen_2(NO_2)_2]Br$ $[\alpha]_D = -43.6^\circ$

d $[Coen_2(NO_2)_2]Br$ $[\alpha]_D = +39.7^\circ$

Literature value: $[\alpha]_D = \pm 44^\circ$

cis d,l $Ca[Coen_2(C_2O_4)_2]_2$ (54)

Cobalt acetate was added to a hot solution of potassium oxalate.. After addition of ethylenediamine hydrochloride a deep red solution was obtained which, after the addition of lead IV oxide, was heated and stirred for 30 minutes. Boiling at ~~this~~ a later stage was found to result in the extensive precipitation of calcium oxalate. The hot alkaline solution was filtered, diluted, and oxalic acid added slowly. Hydrochloric acid was added to make the solution approximately 2N, followed by a strong solution of calcium chloride. Crystallisation commenced immediately and was allowed to continue for 2 minutes before filtration. Longer crystallisation caused much calcium oxalate to separate. The dark red powder was washed with 2N hydrochloric acid and alcohol. It was further freed from calcium oxalate by suspending in 2N hydrochloric acid at 40° and filtering while warm. The powder was washed with acid, water, alcohol and acetone and air dried.

cis d,l $Na[Coen(C_2O_4)_2]H_2O$

Solutions of the calcium salt and sodium oxalate were mixed at 60° and boiled for twenty minutes. The mixture was cooled and filtered and evaporated on a steam bath for 30 minutes. After cooling and filtering, precipitation of the sodium salt as a dark purple crystalline solid was effected by the slow addition of ethanol. The compound was recrystallised from hot water.

cis d $Na[Coen(C_2O_4)_2]H_2O$ and cis l $Na[Coen(C_2O_4)_2]H_2O$

d$[Coen_2(NO_2)_2]Br$ (11 g.) in 60 ml. water was mechanically stirred to 60° for 10 minutes with silver oxalate (11 g.). The solution was filtered hot and a solution of $Na[Coen(C_2O_4)_2]$ (11 g.) in 30 ml. of water was immediately added. There was an immediate colour change and on cooling in ice and stirring a brown precipitate of the diastereoisomer, $[Coen(C_2O_4)_2][Coen_2(NO_2)_2]$, was formed. Precipitation was allowed to continue for 5 minutes, the mixture then being filtered and the precipitate washed with ice cold water.

The precipitate of the diastereoisomer was ground with sodium iodide (11 g.) and water (50 ml.). This resulted in the precipitation of d $[Coen_2(NO_2)_2]$ I which was removed by filtration. The d $Na[Coen(C_2O_4)_2]$ was precipitated by the slow addition of alcohol with stirring in ice. The purple crystals were separated by filtration, washed with ice cold water, alcohol and air dried.

Sodium iodide (11 g.) was added to the filtrate after the removal of the diastereoisomer. On stirring d $[Coen_2(NO_2)_2]I$ separated. This was filtered off and the purple crystals of l $Na[Coen(C_2O_4)_2]$ precipitated by the slow addition of alcohol to the ice cold filtrate. The crystals were filtered, washed with ice cold water, alcohol and air dried.

<u>Reactions</u>:

d $Na[Coen(C_2O_4)_2]$	$[\alpha]_{5791}$	= 218·0
l $Na[Coen(C_2O_4)_2]$	$[\alpha]_{5791}$	= - 90·0
Literature value:	$[\alpha]_D$	= ± 500

In practice it was found to be more accurate to take some of the rotations of the highly coloured solutions at the mercury yellow line (5791 Å) and not at the sodium D line (5890).

cis d,l [Coen$_2$CO$_3$] Cl

The method of preparation was that used by Dwyer, Sargeson and Reid. (55)

A solution of cobalt chloride and hydrochloric acid was deaerated using a continuous stream of carbon dioxide at room temperature. After the slow addition of ethylenediamine the mixture was rapidly heated to 80°, lead dioxide added and the carbon dioxide stopped. The mixture was maintained at 80° for three hours with stirring. The hot solution was filtered, lithium carbonate added slowly to the filtrate and the filtrate maintained at 80° on a water bath for 30 minutes. The alkaline solution was again filtered and the filtrate evaporated in a stream of air at 60°. Free carbonate was removed by filtration after the addition of a solution of calcium chloride. Twice the volume of ethanol was added to the warm solution. On being cooled in ice, red crystals of [Coen$_2$CO$_3$] Cl were formed. These were filtered and freed from small quantities of [Coen$_3$]Cl$_3$ by dissolving in water and reprecipitating by the addition of alcohol. The crystals were washed with alcohol and air dried.

Analysis of $[Coen_2CO_3]Cl$

Analysed	% Calculated	% Found
Carbon	21·87	21·92
Hydrogen	5·87	5·80
Nitrogen	20·40	20·62

cis d,l $[Coen_2CO_3]\ ClO_4$

When a solution of cis d,l $[Coen_2CO_3]$ Cl is ground with solid sodium perchlorate, precipitation of the cis d, l $[Coen_2CO_3]\ ClO_4$ takes place. This was filtered off, recrystallised from hot water and air dried.

Analysis of $[Coen_2CO_3]\ ClO_4$

Analysed	% Calculated	% Found
Carbon	17·74	17·61
Hydrogen	4·76	4·56
Nitrogen	16·54	16·83

cis d $[Coen_2CO_3]ClO_4$ and cis l $[Coen_2CO_3]\ ClO_4$

cis d, l $[Coen_2CO_3]$ Cl (5·7 g.) was dissolved in water (30 ml.) and cooled to 5°. d Na $[Coen(C_2O_4)_2]$ (4·5 g.) was stirred in. The mixture was scratched, stirred and after 5 minutes pink crystals of the diastereoisomer , l $[Coen_2CO_3]d[Coen(C_2O_4)_2]$ were filtered off. The precipitate was washed with ice cold water (30 ml.), acetone and air dried.

The diastereoisomer was ground with ice, about 30 ml. and sodium perchlorate (12 g.). Pink crystals of l $[Coen_2CO_3]ClO_4$ were immediately formed. These were filtered off and recrystallised from water. The d $Na[Coen(C_2O_4)_2]$ was recovered by the slow addition of alcohol to the filtrate after the removal of l $[Coen_2CO_3]ClO_4$.

The filtrate from the precipitation of the diastereoisomer was ground with sodium perchlorate which resulted in the precipitation of d $[Coen_2CO_3]ClO_4$. This was filtered off and recrystallised from hot water.

Rotations

l $[Coen_2CO_3]ClO_4$	$[\alpha]_D = -1459$
d $[Coen_2CO_3]ClO_4$	$[\alpha]_D = +1252$
Literature value:	$[\alpha]_D = \pm 1250$

The two optical isomers were obtained in the same way as in the literature report (55) except that the negative isomer was obtained where the positive one was reported and vice versa.

d,l K[Co(EDTA)]. (51)

An aqueous solution containing cobalt chloride, potassium acetate and disodium ethylenediaminetetraacetate was heated to nearly boiling. A 3% solution of hydrogen peroxide was added to the solution. On the addition of alcohol, silvery violet crystals of d,l K[Co(EDTA)] were precipitated. After filtering these were washed with alcohol and air dried.

d K [Co(EDTA)] and l K [Co(EDTA)] (53)

d $[Coen_2(NO_2)_2]$ I was converted to the chloride by vigorously shaking with silver chloride and water at 60°. The silver halides were removed by filtration and d, l K [Co(EDTA)] added to the filtrate. On cooling in ice with scratching crystals of the diastereoisomer, d $[Coen_2(NO_2)_2]$ l [Co(EDTA)] were formed. Crystallisation was allowed to continue for 5 minutes before filtering. The diastereoisomer was washed with 50% aqueous alcohol, alcohol and air dried.

The diastereoisomer was treated with water, and potassium iodide. On stirring the insoluble d $[Coen_2(NO_2)_2]$ I was formed and was removed by filtration. Alcohol was slowly added to the filtrate with stirring. The l K [Co(EDTA)] separated out and after 5 minutes was filtered off, washed with 50% aqueous alcohol, alcohol, acetone and air dried.

Potassium iodide was also added to the filtrate obtained from the removal of the diastereoisomer. On scratching the insoluble d $[Coen_2(NO_2)_2]I$ was formed and removed by filtration. Precipitation of d K [Co(EDTA)] was effected by the slow addition of alcohol. This was filtered, washed with 50% aqueous alcohol, alcohol and air dried.

Rotations:

Found:	l K [Co(EDTA)]	$[\alpha]_{5791}$ = - 286
	d K [Co(EDTA)]	$[\alpha]_{5791}$ = + 248
Literature value:		$[\alpha]_{5461}$ = ± 1000

cis d,l $[Coen_2(C_2O_4]C_2O_4H$

This was obtained from a modified method of Werner's.(146) $[Coen_2CO_3]Cl$ (2 g.) was dissolved in water (30 ml.). Freshly precipitated silver oxide was added (2 g.) and the whole stirred and filtered. Oxalic acid (2 g.) was added and the whole heated on a water bath. After the cessation of effervescence, the solution was removed from the water bath and left for a few days. $[Coen_2(C_2O_4)]C_2O_4H$ was precipitated and this was removed by filtration, washed with alcohol and ether and air dried.

Analysis of $[Coen_2(C_2O_4)]C_2O_4H$

Analysed	% Calculated	% Found
Carbon	26·98	26·93
Hydrogen	4·84	5·00
Nitrogen	15·73	15·81

cis d,l $[Coen_2(C_2O_4)]Br$

$[Coen_2(C_2O_4)]C_2O_4H$ was ground with potassium bromide and water. The mixture was filtered and the grinding repeated. The mixture was again filtered and the solid dried with alcohol and acetone. The pink $[Coen_2(C_2O_4)]Br$ was recrystallised from water.

Analysis of [$Coen_2(C_2O_4)$]Br

Analysed	% Calculated	% Found
Carbon	20·76	20·65
Hydrogen	4·65	4·80
Nitrogen	16·14	16·03

cis d [$Coen_2(C_2O_4)$]I and cis l [$Coen_2(C_2O_4)$]Br (54)

cis d,l [$Coen_2(C_2O_4)$]Br (2·6 g.) in water (15 ml.) was heated to 65° and shaken with silveracetate (1·7 g.) for 10 minutes. The silver halides were filtered off and the precipitate washed with hot water (5 ml.). l K [Co(EDTA)] (1·5 g.) was added to the solution at 60° and the diastereoisomer, d [$Coen_2(C_2O_4)$] l [Co(EDTA)] began to separate immediately when the mixture was cooled to room temperature.

The diastereoisomer was separated by filtration, washed with ice cold water, alcohol and air dried. After grinding with water and potassium iodide (1·5 g.) the d [$Coen_2(C_2O_4)$]I separated out and was filtered off and recrystallised from hot water.

Ammonium bromide (2·5 g.) in water (5 ml.) was added to the filtrate after the removal of the diastereoisomer. The pink l [$Coen_2(C_2O_4)$]Br immediately began to separate out and was filtered and recrystallised from hot water.

Rotations:

Found: d $[\mathrm{Coen_2(C_2O_4)}]\mathrm{I}$ $[\alpha]_{5791} = +794$

l $[\mathrm{Coen_2(C_2O_4)}]\mathrm{Br}$ $[\alpha]_{5791} = -951$

Literature values:

d $[\mathrm{Coen_2(C_2O_4)}]\mathrm{I}$ $[\alpha]_D = +720$

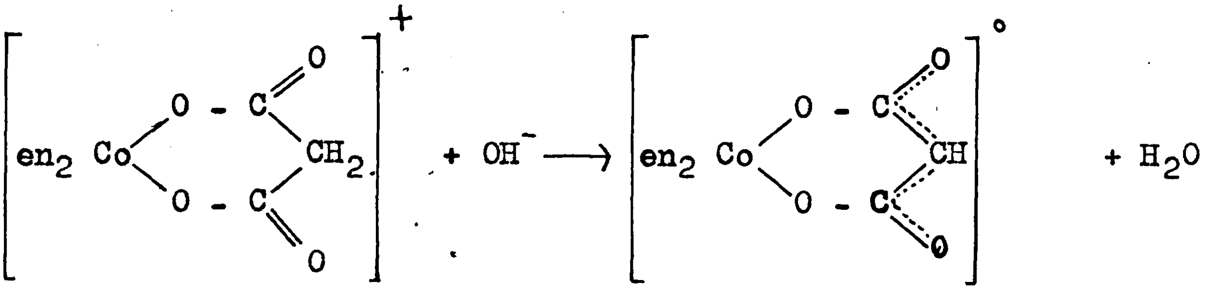
l $[\mathrm{Coen_2(C_2O_4)}]\mathrm{Br}$ $[\alpha]_D = -820$

2. INVESTIGATION INTO THE PREPARATION OF SOME BISETHYLENEDIAMINEDICARBOXYLATOCOBALT III COMPLEXES

During the consideration of the structural effect of the carbonato and oxalato ligands on the hydrolysis mechanisms it became clear that it would be informative to try using different dicarboxylic acids. The malonato complex has already been studied(59) and so attempts were made to introduce the following acids into the complex:

1)	diethylmalonic acid.	$(C_2H_5)_2C(COOH)_2$
2)	cyclobutane 11'dicarboxylic acid,	$(CH_2)_3C(COOH)_2$
3)	isopropylidenedimethylmalonic acid,	$(CH_3)_2C{-}C(COOH)_2$
4)	succinic acid	$(CH_2)_2(COOH)_2$
5)	dibromosuccinic acid	$(CHBr)_2(COOH)_2$
6)	maleic acid	$(CH)_2(COOH)_2$
7)	thiodiacetic acid	$S(CH_2COOH)_2$

The first three acids are substituted malonic acids. The hydrolysis of the bisethylenediaminemalonatocobalt III ion involves the removal of a methylenic proton to form a resonance stabilised unreactive intermediate. (59)



This mechanism would be impossible for the substituted malonic acids.

The coordination of succinic acid, dibromosuccinic acid and maleic acid would result in seven-membered ring formation as in the work of Duff. (49) Thiodiacetic acid would result in an eight-membered ring as was obtained by Price and Brazier (125) using sulphonyldiacetic acid although when they tried with thiodiacetic acid they obtained the double salt, $S(CH_2CO_2)_2CoS(CH_2CO_2)_2en_2.H_2O$.

In the first six cases the same method of preparation was used and this was based on the preparation by Werner (147) of the bisethylenediaminemalonatocobalt III ion.

Method

$[Coen_2CO_3]Cl$ (2 g.) was dissolved in 30 ml. of water. Freshly precipitated silver oxide (1 g.) was added. The mixture was stirred and filtered. Two equivalents of acid were added and the solution heated on a water bath at a temperature not exceeding 50° for 10 minutes with stirring. Effervescence occurred. The solution was cooled and covered and allowed to stand in the refrigerator overnight.

Half the solution was removed, alcohol and acetone were added slowly with stirring, resulting in the formation of a thick pink oil.

In general the solution remaining in the refrigerator also gradually turned into a thick pink oil. This ~~were~~ was thought to be a polymeric species.

However, in the case of cyclobutane 1 1'dicarboxylic acid (CB), the addition of alcohol after two months resulted in the formation of pink crystals. These were filtered, washed with water, acetone and air dried.

Analysis of $[Coen_2CB]CBH.3H_2O$

Analysed	% Calculated	% Found
Carbon	37•63	37•09
Hydrogen	7•12	6•81
Nitrogen	10•98	10•81

This compound was shown to contain the $[Coen_2CB]^+$ ion and not the $[Coen_2(H_2O)_2]^{3+}$ by measurement of the visible spectrum. The measured extinction coefficients are compared with those known for the cis $[Coen_2(H_2O)_2]^{3+}$ ion in Table 30 .

TABLE 30

EXTINCTION COEFFICIENTS FOR THE $[Coen_2CB]^+$ and $[Coen_2(H_2O)_2]^{3+}$ IONS

Wavelength mμ	Extinction Coefficients	
	$[Coen_2CB]^+$	cis$[Coen_2(H_2O)_2]^{3+}$(21)
370	67•8	57•0
380	54•5	44•2
480	72•9	76•2
492	79•9	80•9
520	69•2	62•7

A slightly different method was tried for thiodiacetic acid.

Thiodiacetic acid complex

Thiodiacetic acid (2·5 g.) was dissolved in a minimum of hot water and $[\mathrm{Coen_2CO_3}]\mathrm{ClO_4}$ (2 g.) was added slowly. After cooling in ice and adding methanol and acetone the mixture was left in the refrigerator overnight. The semi-solid oil that was formed was filtered and immediately placed in a vacuum de~~s~~siccator. The compound proved to be of an oily consistency which precluded any physical measurements.

3. INVESTIGATION INTO THE PREPARATION OF SOME BIS-ETHYLENEDIAME DICARBOXYLATORHODIUM III COMPLEXES

Attempts were made to make the carbonato and oxalatobisethylenediamine rhodium III ions.

The starting materials used were cis and trans dichlorobisethylenediaminerhodium III nitrate made by the method of Johnson and Basolo. (86).

Method

Rhodium trichloride, ethylenediaminedihydrochloride, and potassium hydroxide were refluxed with water until a clear red solution was obtained. The refluxing was continued with the slow addition of potassium hydroxide solution. The golden yellow solution was evaporated to half volume on a steam bath. Concentrated nitric acid was added and after about 30 minutes yellow crystals of trans $[Rhen_2Cl_2]NO_3$ separated. On leaving the solution for three days crystals of cis $[Rhen_2Cl_2]NO_3$ separated.

Both isomers were recrystallised by dissolving in hot water and reprecipitating by the addition of cold concentrated nitric acid. The bright yellow crystals were washed with dilute nitric acid, water, acetone, ether and air dried.

Analysis of trans $[Rhen_2Cl_2]NO_3$

Analysed	% Calculated	% Found
Carbon	13·67	13·74
Hydrogen	4.60	4.71
Nitrogen	19·99	19·82

Analysis of cis $[Rhen_2Cl_2]NO_3$

Analysed	% Calculated	% Found
Carbon	13·67	13·88
Hydrogen	4·60	4·79
Nitrogen	19·99	19·85

Method tried for preparation of $[Rhen_2CO_3]NO_3$

cis $[Rhen_2Cl_2]NO_3$ (0·15 g.), K_2CO_3 (0.06 g.), 1N KOH, water (1·5 ml.) and absolute alcohol (0·5 ml.) were heated with stirring on a water bath until complete dissolution had occurred. Sodium iodide was added and the whole left in the refrigerator overnight. No precipitation occurred and the addition of alcohol resulted in the formation of a white solid.

Method tried for the preparation of $[Rhen_2C_2O_4]NO_3$

And excess of oxalic acid was added to a solution containing cis $[Rhen_2Cl_2]NO_3$.

The mixture was refluxed for 10 minutes with 10 ml. of ethanol. The solution was then allowed to stand. After filtering off excess oxalic acid the solution was left in the refrigerator overnight. Crystals were formed which were washed with dilute nitric acid, ethanol, ether and air dried.

Analysis

Analysed	% Calculated for $[Rhen_2(C_2O_4)]NO_3$	% Calculated for $[Rhen_2Cl_2]NO_3$	% Found
Carbon	19•31	13•67	13•92
Hydrogen	4•32	4•59	4•72
Nitrogen	17•77	19•99	19•00

The compound is probably $[Rhen_2Cl_2]NO_3$.

It has been shown (143) that the presence of ethanol is essential for the conversion of $[Rhen_2Cl_2]^+$ to $[Rhen_2AA]^+$ where AA is an L amino acid. Solutions of $[Rhen_2Cl_2]NO_3$ containing no ethanol underwent no reaction with amino acids even after hours of heating. The conversion in the presence of ethanol was explained by assuming the presence of a labile complex of rhodium formed by reduction with ethanol. Further both the cis and trans $[Rhen_2Cl_2]^+$ ion yields $[Rhen_2AA]^+$ ion showing that the trans complex is isomerised easily.

It might be possible to prepare the complex oxalate and carbonate in the presence of ethanol with more prolonged heating and a higher proportion of ethanol.

4. PREPARATION OF BIS 1,10 PHENANTHROLINE COBALT III COMPLEXES

cis d,l $[Cophen_2Cl_2]Cl$

This compound, the starting material for the preparations, was made by the method developed by Ablov. (1) Cobalt chloride was heated with 1,10 phenanthroline hydrate on a heating mantle with water for 15 minutes. The sides of the flask were washed down with water and a fine pink precipitate of $CoCl_2 2phen\ 3\frac{1}{2}H_2O$ was formed. The mixture was cooled and oxidised by passing in chlorine for 1½ hours with frequent shaking. After this time, the pink solid had been completely transformed into a dark grey solid. This was filtered off using a sintered glass crucible, washed with hydrochloric acid and air dried.

The compound was recrystallised by dissolving 9g in 130 ml. of water and heating on a water bath. 25 ml. of concentrated hydrochloric acid was added and on standing crystals of cis dichlorobis 1,10 phenanthrolinecobalt III chloride were formed. Complete precipitation of these grey green crystals from a pink solution took about a week.

Analysis of $[Cophen_2Cl_2]Cl.3H_2O$

Analysed	% Calculated	% Found
Carbon	49.72	48.06
Hydrogen	3.82	3.85
Nitrogen	9.66	9.27
Chlorine	18.34	18.01

To some of the filtrate from the precipitation of the dichloro product a 1:1 mixture of meths and ether was added, which resulted in the precipitation of a bright green powder. Recrystallisation of the bright green powder was attempted from hot water. A small quantity of concentrated hydrochloric acid was added and, on allowing to stand at room temperature, a small quantity of grey green crystals were formed.

Analysis of the green chloride

Analysed	% Found	(After heating to 130° for 3 hours) - % Found
Carbon	49.22	44.3
Hydrogen	3.72	4.6
Nitrogen	9.71	8.6
Chlorine	17.53	16.3

cis d,l [$Cophen_2CO_3$]Cl (2)

[$Cophen_2Cl_2$]Cl (3 g.) and analar sodium carbonate (3 g.) were heated together on a water bath with water. With stirring, complete dissolving was effected. Sodium chloride (2 g.) was added to the hot solution and the whole stirred. On cooling in ice bright pink crystals of [$Cophen_2CO_3$]Cl separated out and these were filtered off and air dried.

The crystals were recrystallised twice by dissolving in hot water, filtering, adding sodium chloride (1 g.) and cooling in ice. Finally the compound was washed with ice cold water and air dried.

Analysis of [$Cophen_2CO_3$]Cl.$5H_2O$

Analysed	% Calculated	%Found
Carbon	49.63	50.55
Hydrogen	4.33	4.38
Nitrogen	9.26	9.24

cis d,l [$Cophen_2C_2O_4$]Cl

[$Cophen_2Cl_2$]Cl was ground with excess freshly prepared silver oxide and water. After filtration oxalic acid was added and the whole stirred on a boiling water bath for 10 minutes. Sodium chloride was added to the hot solution and the solution cooled in ice. Bright pink crystals were formed which were filtered off and recrystallised by dissolving in hot water, adding sodium chloride and cooling in ice.

In light the crystals very quickly changed from red to yellow with the formation of a Co II compound. This rendered them unsuitable for quantitative work.

cis d, l [Cophen$_2$mal]Cl

The malonate complex was made in an exactly similar way to the oxalate complex using malonic acid instead of oxalic acid. Bright pink crystals were formed which were recrystallised from water on the addition of sodium chloride.

Analysis of [Cophen$_2$mal]Cl.6H$_2$O

Analysed	% Calculated	% Found
Carbon	48·77	48·96
Hydrogen	4·55	4·51
Nitrogen	8·43	8·44
Chlorine	5·33	5·51

cis d, l $[Cophen_2CB]Cl$

The cyclobutanell'dicarboxylato complex was made in a similar way as the malonate and oxalate complexes but using cyclobutane 1 1'dicarboxylic acid. Pink crystals were obtained which were recrystallised as before.

Analysis of $[Cophen_2CB]Cl.\ 3\frac{1}{2}H_2O$

Analysed	% Calculated	% Found
Carbon	54•60	54•44
Hydrogen	4•43	4•01
Nitrogen	8•38	8•62

5. ATTEMPTED RESOLUTIONS OF BIS 1, 10 PHENANTHROLINE COBALT III COMPLEXES

There are several known examples of optically active tris and bis 1,10 phenanthroline metal complex ions. The (+) antimonyl and (+) arsenyl tartrate ions have been used to resolve $[Ni(phen)_3]^{2+}$, (94) $[Fe(phen)_3]^{2+}$,(50) $[Ni(phen)_2(bipy)]^{2+}$ (28) and $[Ru(phen)_2py_2]^{2+}$.(23) However, until recently, there have been no reports of direct resolution of tervalent metal complexes, isomers have been obtained by the oxidation of the corresponding bivalent complex. The resultion of the $[Co(phen)_3]^{3+}$ ion was attempted(56) using sodium (+) tartrate, sodium (+) antimonyl tartrate and α bromocamphor π sulphonic acid as the resolving agents. The lack of resolution was accounted for by the very high solubility of the salt resulting in the need for extensive evaporation for isolation.

Recently the resolution of the $[Co(phen)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ ions was achieved(101) by the use of silver (+) antimonyl tartrate on $[Co(phen)_3]^{3+}$ and also by the oxidation by chlorine of a mixture of cobalt chloride, potassium (+) antimonyl tartrate and 1,10 phenanthroline. The success of this method was explained by the use of a suspension and not a solution during oxidation.

a) Attempted resolution of cis d,l [Co(phen)$_2$CO$_3$]Cl

[Co(phen$_2$)CO$_3$]Cl (0.77 g.) was dissolved in 10 ml. of ice cold water and d Na[Coen(C$_2$O$_4$)$_2$] was stirred in. This was allowed to stand for three minutes and then filtered. The precipitate was flesh coloured and ground with sodium perchlorate and water. This mixture was filtered. The filtrate was colourless and precipitate flesh coloured, suggesting the compound was insoluble and identical to the original precipitate. The rotation was zero, the compound probably being a Co II compound, [Cophen$_2$Cl$_2$]^0 as described by Ablov. (4) Alcohol was added to the original filtrate and this resulted in the precipitation of the purple d Na[Coen(C$_2$O$_4$)$_2$] leaving a red solution.

b) Attempted resolution of cis d, l [Cophen$_2$Cl$_2$]Cl

1) Using potassium (+) antimonyl tartrate

[Cophen$_2$Cl$_2$]Cl (0·5 g.) was dissolved in 10 ml. of water at room temperature and cooled in ice. Potassium (+) antimonyl tartrate (0·3 g.) was added and the mixture stirred and left in the refrigerator overnight. An olive green precipitate was formed which was filtered and washed with ice cold water and acetone and air dried. The filtrate was returned to the refrigerator. The precipitate was very insoluble but had a positive rotation.

Yield = 0·5 g.

The precipitate (0·2 g.) was mechanically stirred for 10 minutes with conc. HCl (10 ml.). The green precipitate dissolved and a pale violet one was formed. The mixture was filtered through a sintered glass funnel and the precipitate was washed with conc. HCl, dilute HCl and acetone and air dried. This violet precipitate was optically inactive.

2) Using the ammonium salt of α bromocamphor π sulphonic acid

This resolution was carried out in the same way as case 1). The blue green diastereoisomer was produced much faster, extensive precipitation had taken place after standing in ice for 30 minutes. The violet powder was formed in the same way as in the first instance and this was again found to be inactive.

3) Oxidation of Co II complex in the presence of potassium (+) antimonyl tartrate

The oxidation was carried out in the same way as in the preparation of the cis d, l $[Co(phen)_2Cl_2]Cl$ as on page 279. Potassium (+) antimonyl tartrate (6.48 g.) was added to a mixture of $CoCl_2.6H_2O$ (4.76 g.) and 1, 10 phenanthroline (7.92 g.). Small quantities of grey green crystals were formed as before, but these proved to be inactive. In addition to the grey green crystals a green powder was also formed, which is probably a cobalt II compound.

6. PHYSICAL MEASUREMENTS

1. Ultra violet and visible spectroscopy

Solution spectra were measured on Unicam SP 500, 700 and 800 spectrophotometers using 1 cm silica cells.

Solid state spectra were measured on a Unicam SP 500 fitted with a special reflectance attachment.

2. Infra red spectroscopy

All measurements were taken on a Unicam SP 200 spectrophotometer, from 5000 - 650 cm.$^{-1}$ Discs were made with potassium bromide and the spectra were taken immediately in order to cut down the possibility of ion interchange. The reference beam was fitted with an attenuator in order to cut down its intensity. The instrument was calibrated for wavelength against a standard polystyrene spectrum.

3. Polarimetry

All measurements were taken on a Zeiss Polarimeter at 436 mμ using a jacketted thermostatted 1 dm polarimeter tube. The instrument was also capable of measurement at 365, 405, 546 and 578 mμ.

4. Spectropolarimetry

The measurements were taken on a Bellingham and Stanley/Bendix Ericcson automatic recording spectropolarimeter.

BIBLIOGRAPHY

1. A.V. Ablov, Rus.J.Inorg.Chem., 1961, 6, 157.
2. A.V. Ablov and D.M. Palade, Rus.J.Inorg.Chem., 1961, 6, 306.
3. Idem., ibid., 1961, 6, 567.
4. Idem., ibid., 1962, 7, 1304.
5. S.Anderson and F. Basolo, J.Am.Chem.Soc., 1960, 82, 4423.
6. C.A. Andrade and H. Taube, J.Am.Chem.Soc., 1964, 86, 1328.
7. J.C. Bailar Jr., J.Inorg.Nucl.Chem., 1958, 8, 165.
8. Idem., "Mechanisms of Inorganic Reactions", Adv. in Chem., 49, A.C.S. 1965, page 5.
9. J.C. Bailar and W. Auten, J.Am.Chem.Soc., 1934, 56, 774.
10. C.J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill Book Co. Ltd., 1962, page 107.
11. F. Basolo, Survey of Prog. in Chem., 1964, 2,3~~2~~4.
12. F. Basolo, C.J. Ballhausen and J. Bjerrum, Acta. Chem.Scand., 1955, 9, 810.
13. F. Basolo, J.C. Hayes and H.M. Neumann, J.Am.Chem. Soc., 1953, 75, 5102.
14. Idem., ibid., 1954, 76, 3807.
15. F. Basolo, W.R. Matoush and R.G. Pearson, J.Am. Chem.Soc., 1956, 78, 4883.
16. F. Basolo, J.W. Palmer and R.G. Pearson, J.Am.Chem. Soc., 1960, 82, 1073.

17. F. Basolo and R.G. Pearson, "Mechanisms in Inorganic Reactions", John Wiley, 1958, chapter 3.

18. Idem., Adv.Inorg. and Radiochem., 1961, 3, 25.

19. L.J. Bellamy, "Infra red spectra of complex molecules", Methuen and Co., 1958.

20. H. Bethe, Ann.Physik., 1929, [5], 3, 133.

21. J. Bjerrum and S.E. Rasmussen, Acta Chem.Scand., 1952, 6, 1265.

22. H. Block and V. Gold, J.Chem.Soc., 1959, 966.

23. B. Bosnich and F.P. Dwyer, Aust.J.Chem., 1966, 19, 2229.

24. L.J. Boucher, E. Kyuno and J.C. Bailar, J.Am.Chem. Soc., 1964, 86, 3656.

25. W.W. Brandt, F.P. Dwyer and E.C. Gyarfas, Chem.Revs., 1954, 959.

26. J.A. Broomhead, Aust.J.Chem., 1963, 16, 1886.

27. J.A. Broomhead, F. Basolo and R.G. Pearson, Inorg. Chem., 1964, 3, 826.

28. J.A. Broomhead and F.P. Dwyer, Aust.J.Chem., 1962, 15, 453.

29. Idem., ibid., 1963, 16, 51.

30. J.A. Broomhead and L.A.P. Kane-Maguire, J.Chem.Soc., (A) 1967, 546.

31. D.D. Brown, C.K. Ingold and R.S. Nyholm, J.Chem.Soc., 1953, 2673.

32. D.A. Buckingham, I.I. Olsen and A.M. Sargeson, J.Am.Chem.Soc., 1966, 88, 5443.

33. C.A. Bunton and D.R. Llewellyn, J.Chem.Soc., 1953, 1692.

34. F.H. Burstall and R.S. Nyholm, J.Chem.Soc., 1952, 3570.

35. R.S. Cahn, C.K. Ingold and V. Prelog, Angew.Chem., 1966, 5, 385.

36. S.C. Chan, Nature, 1966,212~~09~~, ~~1~~815.

37. Idem., J.Chem.Soc., (A) 1966, 1124.

38. Idem., Aust.J.Chem., 1967, 20, 61.

39. S.C. Chan, K.Y. Hui, J. Miller and W.S. Tsang, J.Chem.Soc., 1965, 3207.

40. S.C. Chan and M.L. Tobe, J.Chem.Soc., 196~~5~~3, ~~3207~~5700.

41. B. Chiswell and S.E. Livingstone, J.Inorg.Nucl.Chem., 1964, 26, 47.

42. R.J.H. Clark, J.Chem.Soc., 1963, 1377.

43. E.J. Corey and J.C. Bailar, J.Am.Chem.Soc., 1959, 81, 2620.

44. F.A. Cotton, "Modern Coordination Chemistry", ed. J. Lewis and R.G. Wilkins, Interscience, 1960, page 328.

45. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", John Wiley and Sons Ltd., 1966, page 875.

46. M. Delépine, Nouveau Traité de Chemie Minérale, 19, 465, Masson, Paris, 1958.

47. W.T. Dixon, Personal communication.

48. F. Douvillé, C. Duval and J. Lecomte, Bull.soc.chim. France, 1942, 9, 548.

49. J.C. Duff, J.Chem.Soc., 1921, 119, 385.

50. F.P. Dwyer and E.C. Gyarfas, J.Proc.Royal Soc. N.S. Wales, 1949, 83, 263.

51. F.P. Dwyer, E.C. Gyarfas and D.P. Mellor, J.Phys. Chem., 1955, 59, 296.

52. F.P. Dwyer and F.L. Garvan, "Inorganic Synthesis", VI, page 195, ed. E. Ruchow.

53. Idem., ibid., page 192.

54. F.P. Dwyer, I.K. Reid and F.L. Garvan, J.Am.Chem. Soc., 1961, 83, 1285.

55. F.P. Dwyer, A.M. Sargeson and I.K. Reid, J.Am.Chem. Soc., 1963, 85, 1215.

56. P. Ellis, R.G. Wilkins and M.J.G. Williams, J.Chem. Soc., 1957, 4457.

57. P. Ellis and R.G. Wilkins, J.Chem.Soc., 1959, 299.

58. M.E. Farago, unpublished results.

59. Idem., Coordination Chem.Revs., 1966, 1, 66.

60. R.H. Fenn, A.J. Graham and R.D. Gillard, Nature, ~~213,~~ 1967, 213, 1012.

61. J.A. Friend and E.K. Nunn, J.Chem.Soc., 1958, 1567.

62. A.A. Frost and R.G. Pearson, "Kinetics and Mechanism", John Wiley, 1961, page 49.

63. K. Garbett and R.D. Gillard, J.Chem.Soc., 1965, 6084.

64. F.J. Garrick, Nature, 1937, 139, 507.

65. R.D. Gillard, Chem. Revs., 1965, 65, 612.

66. Idem., Chem. in Britain, 1967, 3, 206.

67. Idem., J.Chem.Soc., A, 1967, 917.

68. R.D. Gillard, J.A. Osborn and G. Wilkinson, J.Chem. Soc., 1965, 1951.

69. R.D. Gillard and G. Wilkinson, J.Chem.Soc., 1964, 1640.

70. M. Green, J.Chem.Soc., A, 1967, 762.

71. Idem., personal communication to Dr. M.E. Farago.

72. M. Green and H. Taube, Inorg.Chem., 1963, 2, 948.
72a. A.A. Grunberg and G.P. Faerman, Z. anorg. u. allg. Chem., 1930, 193, 193
73. A. Haim and H. Taube, Inorg.Chem., 1963, 2, 1199.

74. B. Halpern, A.M. Sargeson and K.R. Turnbull, J.Am. Chem.Soc., 1966, 88, 4630.

75. H.S. Harned and R.A. Robinson, Trans.Farad.Soc., 1940, 36, 976.

76. C.M. Harris and S.E. Livingstone, "Chelating Agents and Metal Chelates", Academic Press, 1964, page 112.

77. G.M. Harris, ref. 8, page 151.

78. G.M. Harris and V.S. Sastri, Inorg.Chem., 1965, 4, 263.

79. J.S. Holden and G.M. Harris, J.Am.Chem.Soc., 1955, 77, 1934.

80. H.F. Holtzclaw, D.P. Sheetz and B.D. McCarty, "Inorganic Synthesis", IV, page 178, ed.J.C. Bailar.

81. J.P. Hunt, A.C. Rutenberg and H. Taube, J.Am.Chem. Soc., 1952, 74, 268.

82. G. Illuminati and F. Monacelli, J.Inorg.Nucl.Chem., 1967, 29, 1265.

83. C.K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, 1953.

84. Idem., Weizmann Memorial Lecture, 1958.

85. C.K. Ingold, R.S. Nyholm and M.L. Tobe, Nature, 1962, 194, 344.

86. S.A. Johnson and F. Basolo, Inorg.Chem., 1962, 1, 925.

87. S.A. Johnson, F. Basolo and R.G. Pearson, J.Am.Chem. Soc., 1963, 85, 1741.

88. R.B. Jordan, C.A. Andrade and H. Taube, Proc.Symp. Coordin.Chem., Tihany, Hungary, 1964, 381.

89. R.B. Jordan and D.J. Francis, Inorg.Chem., 1967, 6, 1605.

90. R.B. Jordan and A.M. Sargeson, Inorg.Chem., 1965, 4, 4353.

91. R.B. Jordan and H. Taube, J.Am.Chem.Soc., 1966, 88, 4406.

92. C.K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, 1962.

93. A.R. Katritzky, Quart.Revs., 1959, 13, 353.

94. G.B. Kauffman and H.T. Takahashi, J.Chem.Ed., 1962, 39, 481.

95. E. König and K. Madeja, Spectrochim.Acta., 1967, 23A, 45.

96. W. Kruse and H. Taube, J.Am.Chem.Soc., 1961, 83, 1280.

97. A.B. Lamb and L.T. Fairhall, J.Am.Chem.Soc., 1923, 45, 378.

98. C.H. Langford and H.B. Gray, "Ligand Substitution Processes", W.A. Benjamin Inc., 1965, chapter 3.

99. G.C. Lalor and J. Lang, J.Chem.Soc., 1963, 5620.

100. G. Lapidus and G.M. Harris, J.Am.Chem.Soc., 1963, 85, 1223.

101. C.S. Lee, E.M. Gorton, H.M. Neumann and H.R. Hunt, Inorg.Chem., 1966, 5, 1397.

102. J.E. Leffler, J.Org.Chem., 1955, 20, 1202.

103. J.I. Leggard and B.E. Douglas, J.Am.Chem.Soc., 1966, 88, 2697.

104. F.G. Mann, J.Chem.Soc., 1928, 890.

105. B. Martin, W.R. McWhinnie and G.M. Waind, J.Inorg. Nucl.Chem., 1961, 23, 207.

106. D.F. Martin and M.L. Tobe, J.Chem.Soc., 1962, 1388.

107. J.P. Mathieu, Bull.soc.chim.France, 1936, 3, 469.

108. A.J. McCaffery and S.F. Mason, Proc.Chem.Soc., 1962, 388.

109. A.J. McCaffery, S.F. Mason and B.J. Norman, J.Chem. Soc., 1965, 5094.

110. W.R. McWhinnie, J.Inorg.Nucl.Chem., 1965, 27, 2573.

111. F. Monacelli, J.Inorg.Nucl.Chem., 1967, 29, 1079.

112. M.L. Morris and D.H. Busch, J.Am.Chem.Soc., 1960, 82, 1521.

113. K. Nakamoto, "Infra red spectra of inorganic and coordination compounds", John Wiley, 1963.

114. K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, J.Am.Chem.Soc.; 1957, 79, 4904.

115. L.E. Orgel, J.Chem.Phys., 1955, 23, 1819.

116. L. Pabon, Ph.D. Thesis, London, 1965.

117. R.G. Pearson and F. Basolo, J.Am.Chem.Soc., 1956, 78, 4878.

118. Idem., Inorg.Chem., 1965, 4, 1522.

119. R.G. Pearson and J.W. Moore, Inorg.Chem., 1964, 3, 1334.

120. R.G. Pearson, R.A. Munson and F. Basolo, J.Am.Chem. Soc., 1958, 80, 504.

121. R.G. Pearson, H.H. Schmidtke and F. Basolo, J.Am. Chem.Soc., 1960, 82, 4434.

122. T.S. Piper, J.Am.Chem.Soc., 1961, 83, 3908.

123. A.L. Porte, H.S. Gutowsky and C.M. Harris, J.Chem. Phys., 1961, 34, 66.

124. F.A. Posey and H. Taube, J.Am.Chem.Soc., 1953, 75, 4099.

125. T.S. Price and S.A. Brazier, J.Chem.Soc., 1915, 107, 1367.

126. C.H. Rochester, Quart.Revs., 1966, ~~4~~, 20, 511.

127. F.J.C. Rosotti, "Modern Coordination Chenm." ed. J. Lewis and R.G. Wilkins, Interscience, 1960, page 57.

128. A.M. Sargeson, "Chelating Agents and Metal Chelates", ed. F.P. Dwyer and D.P. Mellor, Academic Press, 1964, chapter 5.

129. A.M. Sargeson, "Transition Metal Chemistry", vol.3, ed. R.L. Carlin, Edward Arnold Ltd. p.303

130. H. Scheidegger and G. Schwarzenbach, Chimia, 1965, 19, 169.

131. A.A. Schilt and R.C. Taylor, J.Inorg.Nucl.Chem., 1959, 9, 211.

132. H.H. Schmidtke, Inorg.Chem., 1966, 5, 16~~8~~82.

133. G. Schwarzenbach and R. Sulzberger, Helv.Chim.Acta, 1944, 27, 348.

134. S. Sheel, D.T. Meloon and G.M. Harris, Inorg.Chem., 1962, 1, 170.

135. C.S. Springer and R.E. Sievers, Inorg.Chem., 1967, 6, 852.

136. D.R. Stranks and G.M. Harris, J.Phys.Chem., 1952, 56, 906.

137. T.J. Swift, Inorg.Chem., 1964, 3, 526.

138. M.L. Tobe, Sci. Progress, 1960, 48, 483.

139. M.L. Tobe, ref. 8, page 7.

140. J.Y. Tong, E.S.A. Keen, and B.B. Hall, Inorg.Chem., 1964, 3, 1103.

141. J.Y. Tong and P.E. Yankwich, J.Am.Chem.Soc., 1958, 80, 2664.

142. L. Velluz, M. Legrand and M. Grosjean, "Optical Circular Dichroism", Academic Press, 1965.

143. J.F. Waller, J. Hu and B.E. Bryant, J.Inorg.Nucl. Chem., 1965, 27, 2371.

144. A. Werner, Arch.de.Sci.Phys. et Nat., 1911, 32, 457.

145. Idem., Ber., 1912, 45, 121.

146. Idem., Ann de Chem., 1912, ~~55,~~ 386, 11.

147. Idem., ibid., 1912, ~~79,~~ 386, 19.

148. S. Winstein and A.H. Fainberg, J.Am.Chem.Soc., 1958, 80, 459.

149. P.E. Yankwich and J.E. McNamara, J.Chem.Phys., 1952, 20, 1325.