"DISSOCIATION AND RACEMISATION STUDIES ON SOME MIXED TRIS BIDENTATE LIGAND COMPLEXES"

THESIS SUBMITTED FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

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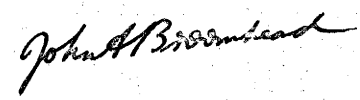
The work in this thesis has been completed in collaboration with Professor F.P. Dwyer. Mr. J.W. Hogarth carried out some preliminary experiments in connection with the preparations published in Inorganic Syntheses; otherwise the work is entirely that of the author.



JOHN A. BROOMHEAD

The following papers have been published:

"Mono complexes of Cr(III), Mn(II), Fe(II), Fe(III), and Ni(II) halides with 1,10-phenanthroline and 2,2'-bipyridine". J.A. Broomhead and F.P. Dwyer. Aust.J.Chem. [2], 14, 250 (1961).

"Resolution of the tris(ethylenediamine) cobalt(III) ion". J.A. Broomhead, F.P. Dwyer and J.W. Hogarth. Inorg. Syntheses. VI. p.183 (1960) (Ed. E.G. Rochow).

"Dextro tris(ethylenediamine) cobalt(III) iodide by a partial asymmetric synthesis". J.A. Broomhead, F.P. Dwyer and J.W. Hogarth. Inorg. Syntheses. VI. p.186 (1960) (Ed. E.G. Rochow).

The following are being prepared for publication:

"The preparation and resolution of the ions $[Ni(phen)(bipy)_2]^{2+}$ and $[Ni(bipy)(phen)_2]^{2+}$". J.A. Broomhead and F.P. Dwyer.

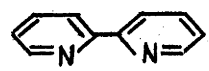
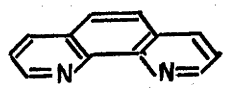
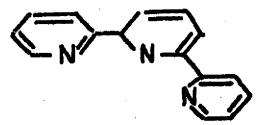
"The mechanisms of racemisation of the ions $[Ni(phen)(bipy)_2]^{2+}$ and $[Ni(bipy)(phen)_2]^{2+}$". J.A. Broomhead and F.P. Dwyer.

"The preparation and resolution of the ions $[Cr(bipy)(ox)_2]^{-}$ and $[Cr(phen)(ox)_2]^{-}$". J.A. Broomhead.

"Racemisation studies on the ions $[Cr(bipy)(ox)_2]^{-}$ and $[Cr(phen)(ox)_2]^{-}$". J.A. Broomhead.

NOMENCLATURE

The naming of compounds in this thesis follows the suggestions given in a review by Fernelius[1]. For the purposes of convenience and simplification the following abbreviations have been used.

Name	Abbreviation	Formula
2,2'bipyridine	bipy	
1,10-phenanthroline	phen	
2,2',2"-terpyridine	trpy	
ethylenediamine	en	$H_2N-CH_2-CH_2-NH_2$
malonate	mal	$CH_2-(COO^-)_2$
oxalate	ox	$(COO^-)_2$
biguanide	bigH.	$(NH_2-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-NH_2)$
dimethylformamide	dmf	$H-CO-N(CH_3)_2$

The term mixed complex will be used when the ligands surrounding the metal ion are not the same kind of molecule e.g. $[Ni(bipy)(phen)_2]^{2+}$, $[Co(en)_2(ox)]^{+}$. The term simple complex will refer to those in which the ligands are the same, e.g. $[Ni(phen)_3]^{2+}$, $[Co(en)_3]^{3+}$.

PREFACE

To date the majority of the investigations of the phenomena and mechanisms of racemisation have been concerned with complexes in which similar ligands are grouped about the central metal ion (e.g. $[Ni(phen)_3]Cl_2$). The purpose of the present work has been to extend the studies to complexes containing different bidentate groups. The complexes $[Ni(bipy)(phen)_2]^{2+}$ and $[Ni(phen)(bipy)_2]^{2+}$ have been chosen because of the large amount of information available about the rates of racemisation and dissociation of the related ions $[Ni(phen)_3]^{2+}$ and $[Ni(bipy)_3]^{2+}$.

An investigation of rates of racemisation and dissociation has been made and used to provide additional information on the mechanisms of racemisation of the nickel(II) phenanthroline and bipyridine systems. For example, if a postulated mechanism included factors common to more than one complex it was examined with both complexes in mind. Hence, a more reliable interpretation becomes possible.

New mono compounds of the metal halides of the first transition series containing the ligands 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2"-terpyridine, and mixed complexes of Cr(III) with 2,2'-bipyridine (or 1,10-phenanthroline) and oxalate ligands, have been prepared and resolved. A study of their kinetics of racemisation has been carried out.

An improved method for the resolution of the $[Co(en)_3]^{3+}$ ion and also a high yield preparation of dextro $[Co(en)_3]I_3$ by means of a second order asymmetric transformation have been described.

Finally, an unusually large activity effect has been found to be present in solutions of the ion $[Co(en)_2(ox)]^{+}$ and any of the

following optically active ions: $[Co(en)_3]^{3+}$, tartrate, and camphorsulphonate. This has made possible the resolution of $[Co(en)_2(ox)]Br$ in good yield by the technique of precipitating the $[Co(en)_2(ox)]^+$ ion as the bromide from a solution containing the above mentioned optically active ions.

CHAPTER ONE

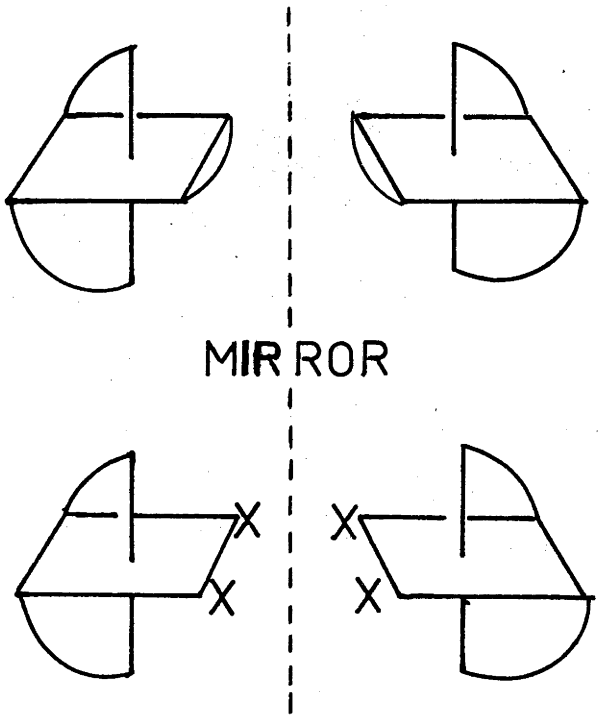
1.0 OPTICAL ACTIVITY IN METAL COMPLEXES.

Certain substances have the property of rotating the plane of polarisation of a beam of plane polarised light, and are said to be optically active. They may be organic or inorganic molecules or ions. Their optical activity may be a property of the molecules themselves or arise from the arrangement of the groups in the crystalline lattice. The last mentioned include quartz, sodium bromate, benzil, and zinc sulphate. When the lattice is destroyed, e.g. by fusion or dissolution, the optical activity is lost. In contrast the optical activity residing in the molecules themselves is, of course, independent of the physical state. These include ammonium d-tartrate, d-methylethylcarbinol, and tris ethylenediamine cobalt(III) chloride.

The condition for optical activity to be present in a substance is the absence of a plane or centre of symmetry. That is, the structure concerned must be non-superimposable upon its mirror image. Optically active carbon compounds are classically asymmetrical but many metal complexes are dissymmetrical and possess some symmetry elements.

The optical rotatory power of a solution is usually expressed in terms of its specific rotation, $[\alpha] = \frac{100\,\alpha}{cl}$. Where α is the rotation in degrees of a solution of the substance at a percent ($^{w}/_{v}$) concentration c in a tube of length l decimetres. The wavelength of the light used must be stipulated and also the temperature as the specific rotation depends on both, though the temperature usually is not a critical factor. In addition, the concentration of solute and the solvent itself can affect the rotation. The most common type of coordination compound

which can exist in optically active forms has the octahedral configuration. Other structures are also known to be capable of resolution e.g. the tetrahderal bis (benzoylacetonato) beryllium(II) complex. In octahedral complexes the most usual structures giving rise to mirror image forms are shown below.



 = bidentate ligand.

X = unidentate ligand.

If the figures on the left side of the mirror plane represent dextro(d) configurations then the right side are the opposite, levo(l) configurations. Substances may be resolved by either chemical or physical means. Easily the most popular method is the formation of a crystalline diastereoisomer. Provided that the racemic substance is an anion or cation, the addition of an oppositely charged optically active ion may produce a crystalline diastereoisomer. For example, the addition of

potassium antimonyl d-tartrate to a solution of $[Ni(phen)_3]Cl_2$ gives an immediate precipitate of the dextro diastereoisomer.[195] Further, an excess of resolving agent will not precipitate the other form which is very soluble. The large difference in solubility of the diastereoisomers in this instance constitutes an ideal method of resolution, separation being achieved in a single operation. Common resolving agents for cationic species include d-tartrate, d-camphorsulphonate, d-bromocamphorsulphonate and even other complex ions such as the d-ethylenediaminetetraacetatocobaltate(III) ion. Werner[4] employed silver d-tartrate to resolve the $[Co(en)_3]^{3+}$ ion the actual diastereoisomer being the chloride d-tartrate salt. (cf. section 4.2). The $[Co(en)_2(NO_2)_2]^+$ ion may be resolved with active potassium ethylenediaminetetraacetatocobaltate(III).[196] Cationic forms of active strychnine, brucine, and α phenylethylamine and the d-$[Ni(phen)_3]^{2+}$ ion[58] have been used for the resolution of anions. Examples are quoted in this work (sections 4.31, 4.32) in which active $[Co(en)_2(ox)]^+$ is used to resolve $[Cr(phen)(ox)_2]^-$ and $[Cr(bipy)(ox)_2]^-$.

It is sometimes possible to make use of a shift in chemical equilibrium in order to get a high yield of one enantiomorph from a solution of the racemate. Provided that racemisation takes place, a resolving agent which will precipitate only one form is needed. For example, the racemic $[Fe(phen)_3]^{2+}$ ion with excess d-antimonyl tartrate yields a precipitate of l-$[Fe(phen)_3]$d(SbO tart)$_2$.$4H_2O$. If the solution is allowed to stand, complete conversion of the racemate to the levo form is obtained.[197] Two other examples of the equilibrium method of resolution are described in this work. One enantiomorph only of the ions

$[Cr(phen)(ox)_2]^-$ and $[Cr(bipy)(ox)_2]^-$ may be readily obtained by using an excess of the resolving agent and allowing to stand. Dextro tris(ethylenediamine)$_{\text{COBALT III}}$chloride d-tartrate prepared by oxidation of the cobalt (II) complex, is produced in over 70 percent yield if the reaction is carried out in aqueous alcohol of such a concentration that only the least soluble diastereoisomer separates. Continuous electron transfer racemisation (p 67) of the l-$[Co(en)_3]^{3+}$ ion via some $[Co(en)_3]^{2+}$ produces more of the d-$[Co(en)_3]^{3+}$ ion which then separates as the diastereoisomer.

Evidence has been obtained showing that the activities of the d and l forms of a substance can be affected to different degrees by the addition of other optically active ions.[186] This provides a method of resolution using the phenomenon called "configurational activity". For example, the solubilities of the enantiomorphs of $[Ru(phen)_3](ClO_4)_2$ are altered when in the presence of d-tartrate or d-bromocamphorsulphonate ion.[193] The difference has been attributed to the different activities of the d and l forms brought about by the optically active environment. A method of resolution based on such a difference involves recrystallising racemic salts from solutions which contain optically active ions. Thus $[Ru(bipy)_3]I_2$ was obtained in an active form by recrystallisation from ammonium d-bromocamphorsulphonate solution.[194] A further example will be described in this work (section 4.3).

Resolution by means of Delepine's method of active racemates[11] is applicable to an isomorphous series of racemic compounds. When a saturated solution of d-$K_3[Ir(ox)_3]$ was added to a saturated solution of dl-$K[Rh(ox)_3]$ a mixed active racemate $dK_3[Ir(ox)_3]$. $lK_3[Rh(ox)_3]$ separated,

and d-$K_3[Rh(ox)_3]$ remained in solution. The "racemate" was active because the different d and l forms present had different rotations.

An interesting new approach to the problem of resolving substances has been suggested[192] and is based on the fact that the d and l forms of $[Co(en)_3]Cl_3$ were found to diffuse at different rates in an optically active solution such as sucrose.

Some time ago Werner obtained preferential crystallisation of one optical form from a solution of the racemate, using an isomorphous optically active crystal as a seed. In this way, the dl$[Cr(en)_2(ox)]^+$ ion was resolved using seeds of d-$[Co(en)_2(ox)]Cl$[4].

A more recent technique is that of selective adsorption of one enantiomorph in preference to the other on an optically active surface such as starch[9], lactose[10], or quartz.[8] At present only partial resolutions have been achieved but the method should be valuable particularly for non-ionic substances. For example, the partial separation into d and l forms of both Cr(III) and Co(III) acetylacetonates on lactose has been reported.[10]

Chemical methods based on differences in the rates of reaction of enantiomorphous forms have been tried as a means of effecting a resolution. For example, circularly polarised light is absorbed to different extents by optical antipodes. This led Jaeger and Berger[101] to attempt to decompose one form of the light-sensitive dl-$K_3[Co(ox)_3]$ by irradiation with circularly polarised light. They were not successful in detecting any activity. In view of the presence of Co(II) in the decomposition products their failure was not surprising. It has been shown[110] that the presence of Co(II) facilitates rapid loss of activity

by an electron-transfer mechanism (section 2.5).

The first resolution ever[7] was accomplished manually after identifying the d and l forms of ammonium d-tartrate from the mirror-image relationships of the crystals. For this method to be possible the enantiomorphs must crystallise so that each unit contains either pure d or pure l molecules, i.e. a racemic mixture in contrast to a racemic compound or solid solution. In addition, the crystals themselves must possess hemihedral facets which permit them to be distinguished from each other. The method is mainly of historical interest but has been applied recently to the resolution of the $Cu(en)_3^{2+}$ ion.[167]

Optical activity in metal complexes has played a part in the history of the metal-ligand bond and it is pertinent to outline this development in the next section.

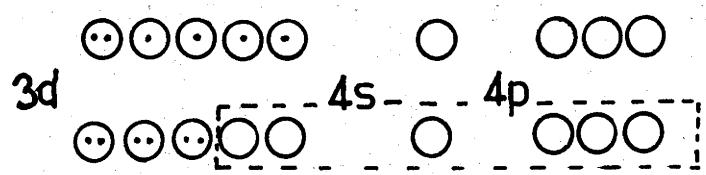
1.1 THE METAL LIGAND BOND.

It was often observed that substitution of one set of ligands for another produced a marked change in the magnetic moment of a complex. It was these changes which provided the so-called magnetic criterion of bond type. Together with the ability of the complex to be resolved and the results of exchange studies, a means was available to classify the type of bond present.

The magnetic criterion may be illustrated in the following way. The ion $Fe(H_2O)_6^{2+}$ is paramagnetic as it contains four unpaired electrons. If the water molecules are replaced by 1,10-phenanthroline the result is a deep-red diamagnetic product. The change in the number of unpaired electron spins is commonly represented in the following way:

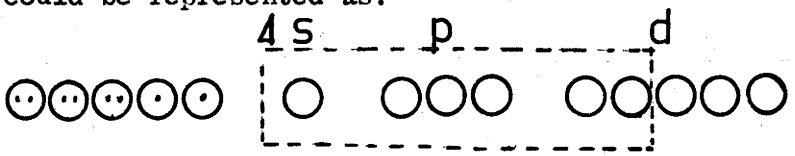
(i) $Fe(H_2O)_6^{2+}$

(ii) $Fe(phen)_3^{2+}$



When the water molecules are replaced by phenanthroline it is the 3d subshell which is most affected. Pauling[15] interpreted the change in magnetism thus:- The iron atom could vacate two 3d orbitals by pairing electrons. Then hybridisation of these two empty d orbitals with the 4s and 4p orbitals could produce six d^2 s p^3 hybrid orbitals, which were directed towards the corners of an octahedron. The hybrid is indicated by the dotted line in (ii). By the magnetic criterion (i) is labelled ionic and (ii) covalent. However, there was room to include a degree of covalent character in an ionic bond and vice-versa.

In addition to the 3d, 4s, and 4p sets of orbitals shown in (i) and (ii) there are, of course, orbitals further removed from the nucleus e.g. 4d, which are referred to as outer orbitals. Some time ago Huggins[18] suggested that these orbitals could be used in forming covalent bonds and he also expected these bonds to be more polar. The complexes which did not have vacant the necessary inner d orbitals could therefore attain some covalent character. For example, the $[Ni(phen)_3]^{2+}$ ion with eight d electrons, was believed to be fairly covalent and use 4s 4 p^3 4 d^2 hybrids. This could be represented as:



Since the orbitals used were further from the nucleus, an outer orbital complex was predicted to be somewhat weaker than the corresponding inner orbital complex as regards bond strength and at the same time more ionic.

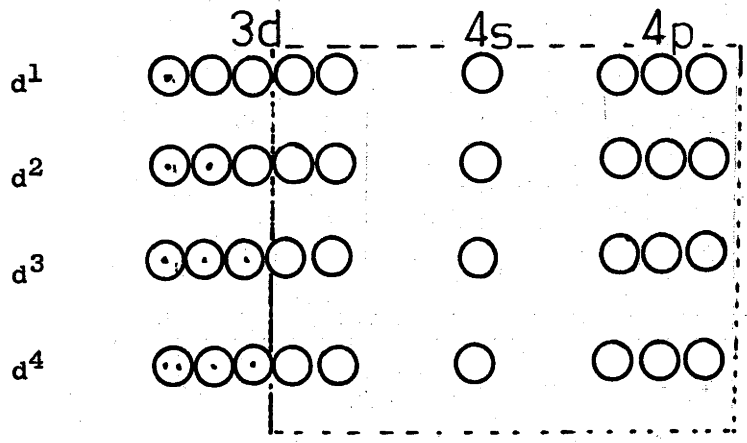
Many compounds classified by the magnetic criterion as covalent were slow to undergo substitution reactions, while others found to be ionic generally reacted rapidly. For example, the $[Fe(phen)_3]^{2+}$ ion was diamagnetic and therefore covalent bonds were present. The blue

$[Fe(phen)_2Cl_2]^0$ was paramagnetic and so was an ionic complex. The reactions of the bis complex were rapid while those of the tris were sluggish. In general, the chemical behaviour here supported the bond classification. On the other hand, the similar $[Ni(phen)_3]^{2+}$ ion was an outer orbital complex, yet it dissociated about 100 times slower than the Fe(II) counterpart.

A classification of bond types on the results of exchange reactions gave general support to the results of magnetic studies as is shown below. In addition, the isolation of optical isomers was taken as evidence for the presence of covalent bonds.[14] For example, Johnson pointed out that all attempts by himself[14], and other workers[43], to resolve the oxalato complexes of Fe(III) and Mn(III) had failed. However, the corresponding Co(III) and Rh(III) compounds had been resolved. As success had only been achieved with the covalent members of this group, the conclusion was drawn that the ionic bonds present in the Fe(III) and Mn(III) compounds could allow rapid racemisation. Exchange data were in agreement with this conclusion. Thus radioactive oxalate ion exchanged rapidly with Fe(III)[45] but not with Co(III).[46]

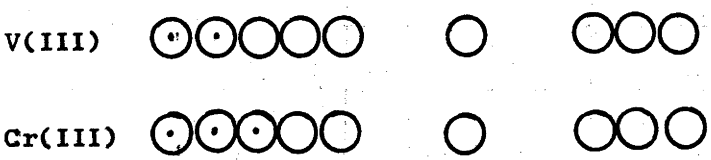
Taube[17] reviewed the position of inner and outer orbital complexes in relation to their reactivity and degree of covalent binding. He classified as labile those complexes that could undergo substitution reactions rapidly and inert those that could not. It was not possible to draw a sharp distinction between these different rate types. He used the ordinary laboratory conditions of temperature and concentration when selecting examples; that is 25°C and 0.1M reactants. It was found that inner and outer orbital bonds could be further subdivided on the basis of rate behaviour. Thus the classes were inner orbital labile, inner

orbital inert, outer orbital labile, and outer orbital inert. There was a sharp distinction in rate behaviour between the inner orbital labile and the inner orbital inert members. This coincided with the filling of all d orbitals by an electron in each and occurred at the d^3 configuration, e.g.



inner orbital d^2 s p^3 hybrids

Thus for configurations d^0, d^1 and d^2 there is a vacant and unused d orbital. This is occupied in d^3 systems. For example, six coordinate complexes of V(III) undergo substitution reactions rapidly while those of Cr(III) do not. The rate behaviour of V(III) makes it a labile complex, while that of Cr(III) leads to the classification inert. It can be seen from their electronic structures that V(III) has a vacant d orbital which is occupied in Cr(III).



Taube showed that though there was a distinct change in lability at this point there appeared to be no evidence to support an abrupt change in the degree of covalent character present. The aquo ions of Al(III),

V(III), Cr(III), Fe(III), and Ga(III) had acid dissociation constants which showed no exceptional interaction for Cr(III), yet this would be expected if the bonding present were more covalent. The reason for the different rates of reaction must lie elsewhere than in the bond strength.

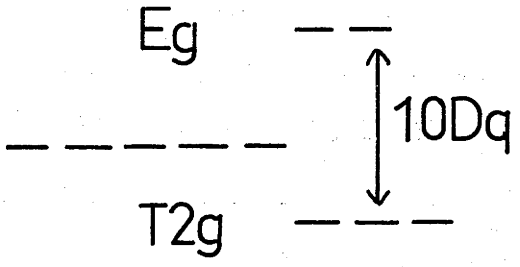
Taube suggested that the vacant d orbital present in the labile members of the inner orbital class could also be the explanation for their rapid reactions. It could be available for further bonding to give a seven coordinate reaction intermediate. A similar mechanism would not be readily available if the d orbitals concerned were filled. For the complexes classified as "outer" orbital labile or "outer" orbital inert, there was a more gradual change in reactivity from one type to the other. It was noted that a decreased lability for an isoelectronic series of similar complexes accompanied an increased charge on the metal. This observation was attributed in part to an increased covalent character in the bonding. Again, when a metal formed both inner and outer orbital complexes it was invariably found that the outer types were labile and the inner ones inert.

The value of Taube's work lay in the attention it focussed on the electronic nature of the metal. A recent approach which can account for the kinetic behaviour of a transition metal ion in terms of the number of d electrons available is given by the ligand field theory (see footnote).

The ligandfield theory originated by Bethe[27] calculates the effect of the electric fields of the ligands on the d orbitals of the metal. In the field-free metal ion the five d orbitals have the same energy. This degeneracy can be removed by the approach of the ligands

N.B. The term ligand field will be preferred to crystal field. Its meaning is less restricted and includes electron delocalisation phenomena.

along the x, y and z axes. Thus in an octahedral complex the d_z^2 and $d_{x^2-y^2}$ orbitals point towards the ligands and are therefore higher in energy compared to the remaining d_{xy}, d_{xz}, and d_{yz} orbitals. The splitting by the ligand field is commonly represented as follows for a symmetrical octahedral complex:

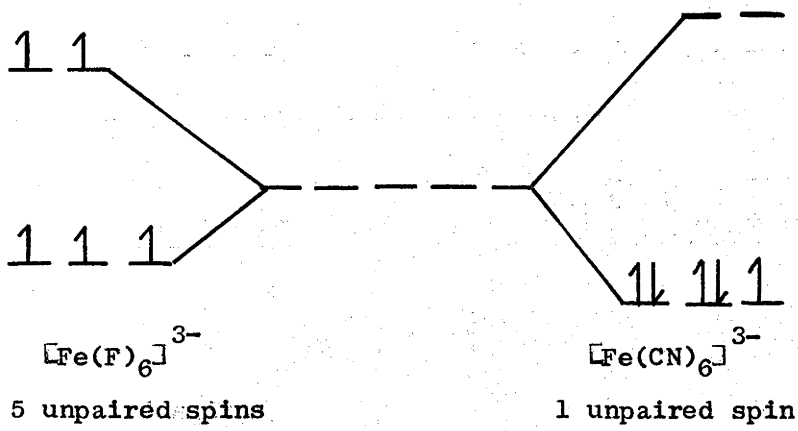


Each horizontal line represents a d orbital. The higher energy Eg set consist of the $d_{x^2-y^2}$ and d_z^2 orbitals while the lower energy T2g set are the three d_{xy} type orbitals. The energy separation between the levels shown is given the value 10 Dq.

Dq is a parameter which may sometimes be calculated. It may also be obtained experimentally from the absorption spectrum using a crystal or solution of the complex. Its magnitude depends upon the field of the ligand and the nature of the central metal ion. Further, a different geometry of the ligands produces a different splitting of the d levels to that shown above, with a different value for Dq.[190] When the common ligands are arranged in order of their Dq values in regular octahedral complexes, the order is found to be almost the same for different metal ions. This is known as the spectrochemical series and proves useful in relating the behaviour of different complexes.

By filling the orbitals of lower energy first, a complex can be made more stable compared to the case of random occupation of the orbitals. The energy gained is known as the ligand field stabilisation energy (L.F.S.E.). For example, in a metal ion with only one d electron the T2g level is occupied and an energy gain of 4Dq would result for an octahedral complex. Similarly, three d electrons in the T2g level would gain 12 Dq of L.F.S.E..

When there are more than three electrons to be accommodated the positions occupied depend on the amount of splitting, that is, on Dq. If the field is weak the electron would find it easier to occupy the Eg level and keep all electron spins parallel so that the configuration is of the high-spin type. When the ligand field is strong the electron finds it easier to pair in the T2g level in spite of the electron repulsion. Thus the magnetic moment is reduced and a low-spin complex results. For example, the $Fe(F)_6^{3-}$ ion is a high-spin complex and the five d electrons each occupy one orbital. When the F^- is replaced by the stronger CN^- field, the paramagnetism of the first substance is greatly reduced. This may be shown diagrammatically thus.



The L.F.S.E. of $[Fe(F)_6]^{3-}$ is zero as the metal ion has all levels equally occupied. In $[Fe(CN)_6]^{3-}$ the L.F.S.E. is approximately 5x4=20 Dq minus the energy required to pair the electrons. It is interesting to consider a series of regular octahedral complexes of the same metal with different ligands. As each set of ligands is replaced by a set of greater field strength, then the separation of the T_{2g} and Eg levels is increased. Though the magnetism changes abruptly it does not mean a discontinuous change in bond type.[16, 32]

Taube's suggestion of a seven coordinated intermediate to explain the lability of inner orbital complexes has been treated by Orgel[16] using the ligand field theory. Thus the T2g orbitals are split into different energy levels by the approach of the ligand, and that orbital in the direction of approach would become the least stable. It is only in the instances of 0, 1, and 2 d electrons that there is still an empty T2g orbital, thus making it possible for reaction to occur without altering the spin multiplicity of the ground state. If there is another T2g electron present, then the field of the approaching group will result in rearrangement of the electrons. Hence, more energy of activation will be required resulting in a decrease in lability compared with the 0, 1 and 2 electron cases.

The idea of a ligand field contribution to the activation energy has been developed by several workers.[35, 36] By making some approximations it was possible to calculate the L.F.S.E. loss (ΔEa) in going from reactants to transition state. In both strong and weak field cases there were found to be good correlations between predicted and observed relative rates. Thus a complex would be expected to react faster

than a similar complex involving the same or a different central metal, if its value of Δ Ea was smallest. Values for Ea are given in reference 35 for electronic configurations with from 0-10 d electrons. Both dissociation and displacement mechanisms are included and the effects of solvent are ignored. In making predictions it is, of course, necessary to note that the absolute rate of any reaction depends upon the entropy as well as the energy of activation. Thus ligand field predictions of relative rates will be satisfactory only when the corresponding entropy terms are also considered.

A recent example of the success of ligand field predictions for reaction rates was given by Ellis and Wilkins.[202] They considered the dissociation of complexes of the type $[M(phen)_3]^{2+}$ and assumed that the transition states were similar and approximated to a square pyramid geometry. The observed activation energies were then compared with the ligand field contributions present. e.g.

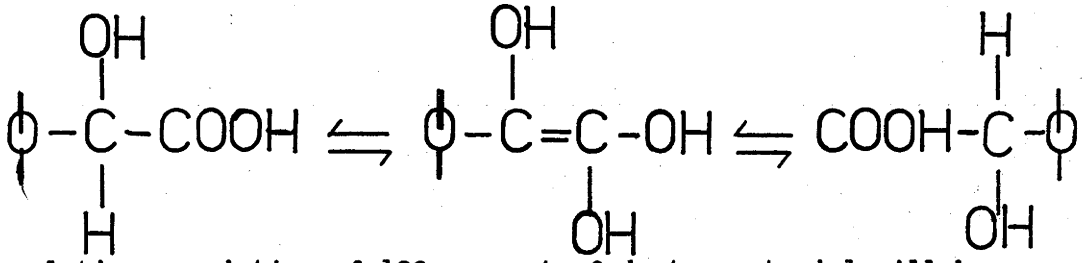
M^{2+}	Ea	ΔEa(Dq)
Fe	32.1	4
Co	20.6	0
Ni	25.2	2
Cu	- fast	-

The value of Dq for bivalent transition metal ions is about 3.0 kcal $mole^{-1}$ and for Ni(II) is 3.5 kcal $mole^{-1}$. It can be seen from the above table that the differences in the Ea's agree fairly well with the Dq differences. A similar calculation of Δ Ea for other transition states (e.g. a trigonal bipyramid) did not give agreement with the observed activation energy differences.

CHAPTER TWO

2.0 RACEMISATION IN METAL COMPLEXES.

The process of racemisation involves the interconversion of enantiomorphs, that is, inversion of configuration. It may be brought about by various agents such as heat, light, dissolution and chemical reaction. For example, l-$[Ni(bipy)_3](ClO_4)_2$ is stable in the solid state for many months but racemises rapidly in solution; l - mandelic acid racemises readily as a consequence of enolisation.[198]



A solution consisting of 100 percent of dextro material will have racemised when 50 percent of this has inverted its configuration. Clearly racemisation occurs in half the time required for complete inversion so that the rate of racemisation is twice the rate of inversion. For inversion of an enantiomorph to take place it is obvious that it must pass through a symmetrical configuration, from which it is then possible for either the dextro or levo variety to form with equal probability. A symmetrical intermediate configuration is the basic requirement in any mechanism postulated to account for racemisation. For instance, the racemisation of the substituted biphenyl 2,2'- diamino 6,6'- biphenyl has been studied by Kistiakowsky and Smith[199] and the optical activity arose from the restricted rotation about the bond joining the benzene rings, which prevented their coplanarity. In solution or in the vapour state the symmetrical intermediate having the rings coplanar was believed to be formed, and this could revert to either enantiomorph with equal chance.

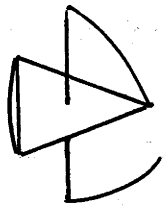
The study of mechanisms of racemisation in octahedral complexes constitutes a major portion of this work and a somewhat detailed account of the history of this branch of coordination chemistry is relevant. In a later chapter an examination of the literature on the racemisation of phenanthroline and bipyridine complexes of nickel(II), and the related iron(III) and iron(II) complexes will be given.

Mechanisms of racemisation in octahedral complexes are conveniently divided into two categories. Either they do not require any net loss of ligand, in which case they are termed intramolecular, or they do require net loss of ligand, in which case they are known as intermolecular mechanisms. Intermolecular mechanisms are readily distinguished from the intramolecular varieties by experiments which measure the rate of ligand exchange. If the rate of exchange is identical with the rate of racemisation then it is concluded that loss in optical activity accompanies the exchange of ligand. Dissociation studies may yield the same information. On the other hand when racemisation proceeds much faster than loss of ligand an intramolecular mechanism must be present. Finally, when racemisation is slower than the rate of ligand exchange, e.g. $[Co(en)_2Cl_2]^+$ ion in water (vide infra), then obviously the act of dissociation does not lead directly to racemisation. The study of the racemisation here requires more detailed information about the dissociation products as there are at least two species contributing to the optical rotation.

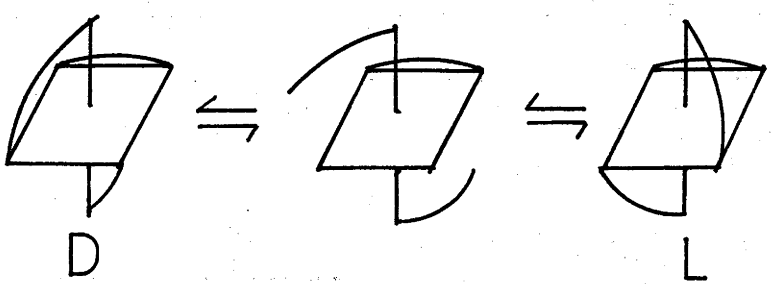
2.1 INTRAMOLECULAR MECHANISMS.

The earliest explanation to account for an observed racemisation was provided by Alfred Werner[6] who suggested that the optical activity of the $[Cr(ox)_3]^{3-}$ ion might be lost as a result of the breaking of at least

one metal–oxygen bond to give a symmetrical trigonal bipyramid* intermediate (I), e.g.



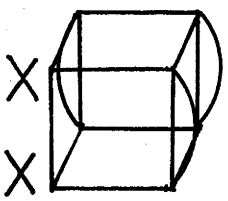
An extension of Werner's proposal was made by Bushra and Johnson[42] who thought that the opening of two chelate rings was necessary. They pointed out that the ion $[Co(en)_3]^{3+}$ did not racemise while $[Co(ox)_3]^{3-}$ did and therefore the ethylenediamine rings did not open as readily as oxalate rings. It was expected that the $[Co(en)_2(ox)]^{+}$ ion should racemise by the opening of the oxalate ring if Werner's mechanism was correct, but they could not verify this since decomposition accompanied loss of activity. However, they reported that the similar $[Cr(en)(ox)_2]^{-}$ ion racemised with the same activation energy as $[Cr(ox)_3]^{3-}$ and proposed that the opening of two oxalate rings, in the following manner, could account for racemisation.



*A trigonal bipyramid intermediate has recently been suggested as a likely mechanism for the racemisation of the cis $[Cr(ox)_2(H_2O)_2]^{-}$ ion.[211]

The mechanisms of racemisation of the ions $[Co(ox)_3]^{3-}$ and $[Cr(ox)_3]^{3-}$ can be conclusively labelled as intramolecular following the results of exchange studies carried out by Long.[46, 45] For both complexes there was no exchange of oxalate in a time sufficient for a racemisation half-life. Subsequent experiments on the rate of oxygen exchange in the $[Cr(ox)_3]^{3-}$ ion demonstrated that all twelve of the oxygens were replaceable.[47] Since the oxalate itself was exchanged much more slowly than the oxygen atoms, it was concluded that the chelate rings opened and closed many times before complete oxalate exchange took place. As the rings have been shown to open, then both the mechanisms of Werner and of Bushra and Johnson could produce some of the loss in activity. It was not possible to account completely for the observed racemisation by these mechanisms as the rate of racemisation was much faster than that of oxygen exchange.

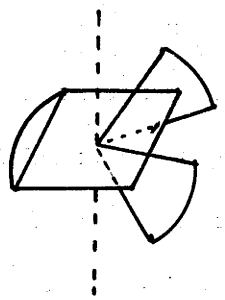
An eight covalent intermediate has been suggested by Charonnet[52] as a further possibility which would be symmetrical and so provide a racemisation path. Solvent molecules could attach themselves in the following way:



The fact that anhydrous $K_3[Cr(ox)_3]$ takes months to racemise but activity is lost in several hours if the dihydrate is used[56] has been explained in this way.

Two other examples of intramolecular mechanisms simply involve a twisting of the metal ligand bonds until a symmetrical structure results. For example, Ray and Dutt[48] could find no evidence of decomposition during the racemisation of the $[Co(bigH)_3]^{3+}$ ion. They did not, therefore, favour a mechanism in which two bonds were broken because the breaking of bonds would introduce the possibility of decomposition. They pictured the intermediate (IV) below formed as a result of the movement of two ligands in opposite directions through 45° in the plane of the bonds.

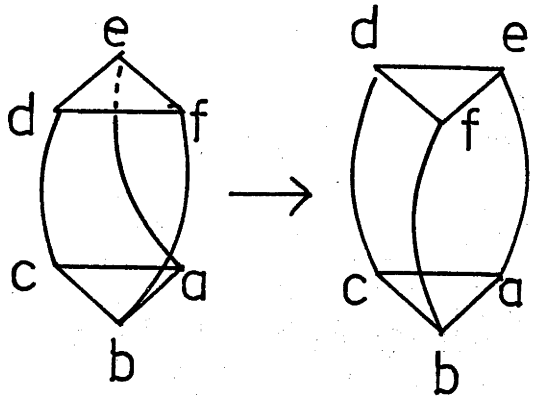
IV



Some support for their mechanism came from infrared measurements which showed that it was less difficult to bend a bond than to stretch one.[200, 201] Bond stretching was the natural preliminary to dissociation. The very low value of the frequency factor (log A 4.16 sec^{-1}) was interpreted as arising from the increase in order required in forming structure (IV).

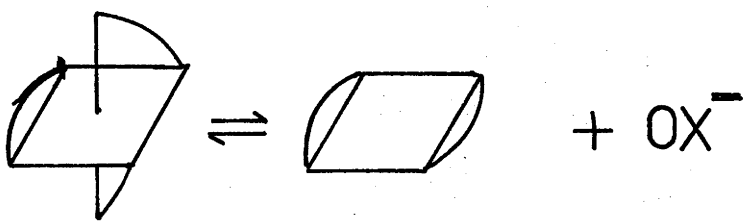
Finally Gehman[54], Seiden[55], and Bailar[56], have independently proposed the same mechanism that can account for both intramolecular racemisation and isomerisation. It was similar to Ray and Dutts' in that bond bending was required. In the following diagram the plane acb is fixed while the parallel plane def is turned through 60 degrees, clockwise, to produce a trigonal prism (V). This is symmetrical for a tris bidentate complex and could lead to racemisation.

V



2.2 INTERMOLECULAR MECHANISMS.

Racemisation attended by complete dissociation of a ligand was suggested by Thomas[43] and Rideal and Thomas[44] to explain the loss in optical rotation of the $[Cr(ox)_3]^{3-}$ ion. Loss of an oxalate in the following manner could form a planar bis complex. Being symmetrical, reattachment of the oxalate resulted in either the d or l product with equal probability. In this example the mechanism is now known to be intramolecular.[45]

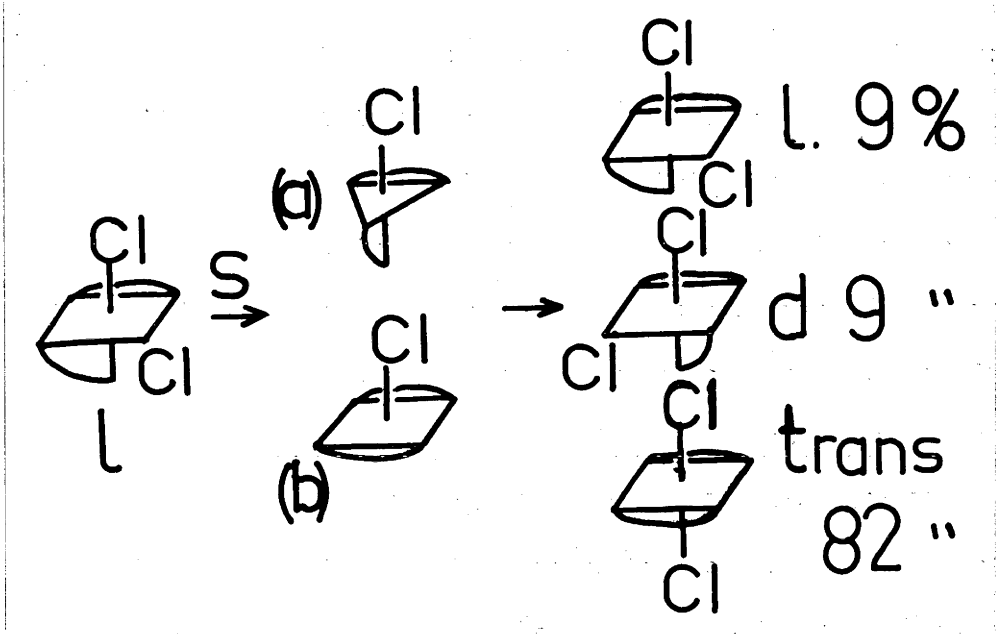


The racemisation of the ions $[Ni(phen)_3]^{2+}$ and $[Ni(bipy)_3]^{2+}$ has been shown to occur by an intermolecular process. The rates of racemisation and dissociation[62,63] are identical within the experimental errors. The rates of dissociation were obtained using exchange[62] and spectrophotometric[63] techniques. The last mentioned method was made possible by the red colour of the tris materials. By working in acid solution the tris complexes may be made to dissociate and the dissociation products were of a different colour to the starting material. It was noted that the presence of excess ligand in an aqueous solution of the complexes did not affect the racemisation rate. Thus the products of dissociation were no longer optically active, otherwise re-formation of the active tris complex would be evident.

e.g. $[Ni(phen)_2(H_2O)_2]^{2+} + phen \rightleftharpoons [Ni(phen)_3]^{2+} + 2H_2O$

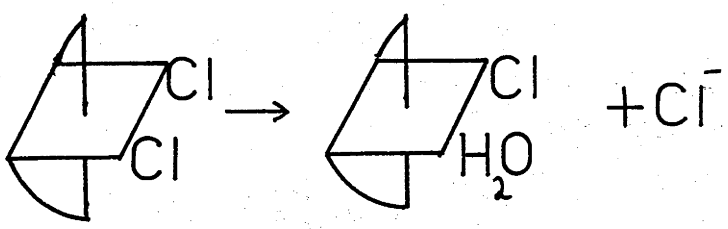
It was concluded that racemisation occurred by loss of ligand to give a bis complex which either racemised rapidly or was already inactive. It could racemise either by further rapid dissociation or by an intramolecular mechanism.

Brown and Ingold[64] found that the rate of chloride exchange in a methanolic solution of optically active cis $[Co(en)_2Cl_2]^+$ ion was the same as the rate of racemisation. They interpreted the mechanism as loss of one chloride ligand and simultaneous formation of an optically inactive product. The possible steric course was suggested as follows, the racemisation being accompanied by partial cis-trans isomerisation.

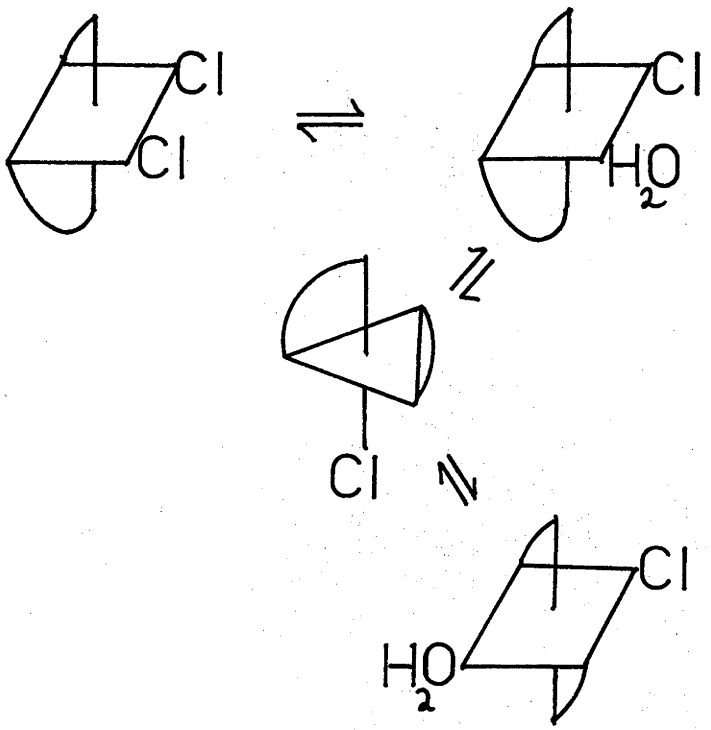


Both (a) and (b) in the diagram have the required symmetrical structure necessary for racemisation to occur. When the chloride ion reattached it was found that most of the product had the trans configuration. In the presence of other ions (eg. CNS^-, Br^-) in methanol, the rate of racemisation of $[Co(en)_2Cl_2]^+$ was unaffected, although the product was now $[Co(en)_2Cl\ X]^+$ where X = CNS^-, Br^-. This observation supported the mechanism depicted, namely a slow and rate determining loss of a chloride ion during which racemisation occurred. By contrast, the same ion in water did not racemise by loss of a chloride ion.

Instead the replacement of the chloride by water produced an optically active ion, cis $[Co(en)_2ClH_2O]^{2+}$ viz:



Thus racemisation need not necessarily follow upon loss of a ligand. The active cis $[Co(en)_2ClH_2O]^{2+}$ ion formed in the above manner racemised much more slowly than the rate at which the remaining Cl^- ion was exchanged[68]. The formation of a similar trigonal bipyramid intermediate (a) as was proposed for the $[Co(en)_2Cl_2]^+$ ion in methanol has been suggested to explain the racemisation. It was thought to be formed by loss of a water molecule. More recent studies[67] on the aquation of $[Co(en)_2Cl_2]^+$ reveal that most of the racemisation could be accounted for by isomerisation. e.g.:



The formation of a trigonal bipyramid by loss of water from the cis-chloraquo complex enables either the cis or trans chloroaquo ion to be obtained. The results of water exchange studies are awaited to check this mechanism. Thus, if water exchange with the trigonal bipyramid intermediate occurs it must exceed the rate of racemisation[70] because some acts of exchange regenerate the original cis configuration and do not produce racemisation. In the related cis $[Co(en)_2Cl\ X]^+$ ion the presence of various ligands (X = NO^-_2 CNS^- and NH_3) produced successively slower rates of racemisation. Upon addition to water there was at first a change in optical rotation to that of the aquo ions $[Co(en)_2H_2O.X]^{2+}$. These then racemised at rates which decreased in the following order $NO^-_2 \sim CNS^- > NH_3$. A similar mechanism of racemisation in which the water was exchanged through a trigonal bipyramid intermediate required that racemisation proceed with greater retention of configuration for the $[Co(en)_2H_2O.NH_3]^{3+}$ than for the $[Co(en)_2H_2O\ NO^-_2]^+$ ion.

Basolo[70] interpreted the order of racemisation rates observed in terms of pi bonding of the p-d type. Thus the Cl^- ion had filled p orbitals which were capable of donating electrons to the cobalt. This should favour rearrangement as it leads to a stabilisation of the trigonal bipyramid intermediate by comparison with the non-pi bonding ligands.

The racemisation of the $[Cr(en)_3]^{3+}$ ion has been accounted for by a direct intramolecular loss in activity together with dissociation to the active cis $[Cr(en)_2(H_2O)_2]^{3+}$ ion which subsequently racemised. The aquation reaction had an activation energy of 24.6 kcal as measured spectrophotometrically[223], compared with 24.30 kcal obtained from the initial mutarotation observed.[222]

2.3 THE EFFECTS OF SPECIFIC IONS ON RACEMISATION RATES.

Various added ions may affect the rates of racemisation of metal complexes but the nature of the role played has not always been easy to interpret. It is convenient to list the complex ions concerned and each will be discussed in turn:

2.31 : $[Cr(ox)_3]^{3-}$

2.32 : $[Co(bigH)_3]^{3+}$

2.33 : $[Ni(phen)_3]^{2+}$ and $[Ni(bipy)_3]^{2+}$

2.34 : $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$

2.35 : $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$

2.31 $[Cr(ox)_3]^{3-}$.

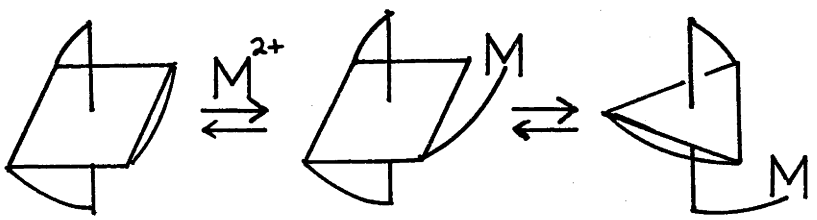
The effects of a considerable number of added ions on the racemisation of this complex have been studied by Beese and Johnson.[91] A selection of their data is given in Table 2.31. All results are at a temperature of 18.2°C. Added ions have been grouped together, depending on the increase in rate constant they produce relative to that in water only. From Table 2.31 it appears that the gross effects are due to the cation and not the anion.

TABLE 2.31

Solution	Concentration (moles/litre)	$\frac{k}{k_{H_2O}}$
HCl	0.01	1.2
$BeSO_4$	"	1.2
$MgCl_2$	"	1.5
$CaCl_2$	"	2.7
$Sr(NO_3)_2$	"	1.6
$BaCl_2$	"	1.7
$MnCl_2$	"	2.4
$Co(NO_3)_2$	"	4.1
$Ni(NO_3)_2$	"	9.1
$CuSO_4$	"	14
$ZnSO_4$	"	6.8
$CdSO_4$	"	2.2
$HgCl_2$	"	1.0
$AgNO_3$	0.10	2.2
$TlNO_3$	"	2.1
$AgNO_3$	0.50	5.5
Li or KCl	"	1.3
K or $(NH_4)_2SO_4$	"	1.5
KOH	0.54	2.8
HCl	0.98	14.3
$(NH_4)_2SO_4$	1.5	2.4
"	3.8	4.6
NH_4NO_3	10.0	2.1
$K_4[Fe(CN)_6]$	0.5	1.6
$[Zn(en)_3]SO_4$	0.01	3.0

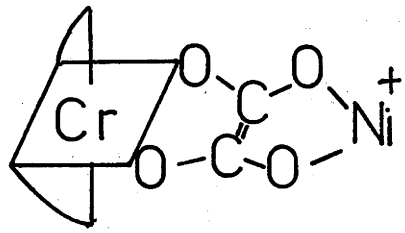
It is now known that the racemisation of the $[Cr(ox)_3]^{3-}$ ion involves an intramolecular process with some bond breaking (section 2.1). Consequently, some attempts have been made to relate these ion effects with the mechanism.

Basolo and Pearson[93] have suggested that the formation of outer sphere complexes between the cations and the anionic $[Cr(ox)_3]^{3-}$ could produce the increase in rates. Further, Carter[94] has noted for the bivalent ions the parallel between accelerated rates and the natural order of stability.[95] There would seem to be two ways in which the ions could be acting. Firstly, by attaching to the free end of a partly dissociated oxalate, they could facilitate rearrangement to a trigonal bipyramid and so lead to an increased racemisation by that path (see below).



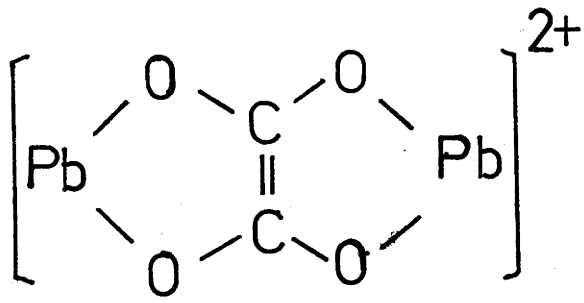
In addition, their presence might tend to weaken the remaining oxalate-metal bond and favour racemisation by an intermolecular mechanism.

Secondly, ions such as Ni^{2+} and Cu^{2+} might be expected to attach themselves to the oxalate ligand in the following manner.



The net result would be competition between the Cr(III) and Ni(II) for the oxalate ligand with a weakening of the chromium-oxygen bond. The increase in racemisation rate could then be understood by any of the two ways just described. It would be interesting to know the effects of these added ions on the rates of ligand exchange and also the relevant energies and entropies of activation.

It is pertinent here to note that structures for oxalato complexes of Zn(II), Cd(II)[204], and Pb(II)[203] have been proposed in which the oxalate group bridges two metal ions, e.g.:



2.32 $[Co(bigH)_3]^{3+}$.

Anions, apart from OH^-, had no effect on the racemisation rate of this complex.[48] The effect of OH^- was accompanied by decomposition and suggests a base hydrolysis reaction.

Cations, particularly when highly charged, were found to markedly retard the racemisation and an explanation based on ion association between cations becomes difficult. The possibility that the additional donor nitrogens on the ligands could bind added metal ions was not consistent with the effectiveness of large complex ions in retarding the rate.[95]

There was a peculiar acid dependence observed as is seen from the results of Ray and Dutt[48] given below.

Solution	Molar Concn.	$k \times 10^5$ (inversion)
H_2O	-	24.8 (= half-life of 46 hrs)
HCl	0.1	Decomposes
"	0.01	545
"	0.001	206
"	0.0005	13.7
"	0.00025	4.04
"	0.0001	No change over 27 hrs.
"	0.00007	16.4
"	0.00005	24.6

It seems probable that there are different protonated forms of $Co(bigH)_3^{3+}$ present at different acidities, which could produce the observed behaviour.

2.33 $[Ni(phen)_3]^{2+}$ and $[Ni(bipy)_3]^{2+}$.

High ionic strength (μ = 7.5) was observed to retard the racemisation of the $[Ni(phen)_3]^{2+}$ ion.[89,90] Also OH^- ion slightly accelerated the racemisation. Large ions, on the other hand, retarded the rates. For example, α naphthalene sulphonate and bromocamphor-sulphonate at concentrations of 2% $^{w}/_{v}$ halved the rate constants for racemisation.[89]

The $[Ni(bipy)_3]^{2+}$ ion was much more sensitive to added ions and marked accelerations of the rate were observed in the presence of OH^-, Cl^-, and F^-, while NO_3^- and $SO_4^=$ had no effect. In contrast to the $[Ni(phen)_3]^{2+}$ ion high ionic strength was without effect but again large ions retarded the racemisation. An acceleration in rate in the presence of nickel(II) chloride has been reported.[61] This can be attributed to the Cl^- ion as it is known that nickel(II) ammonium sulphate is without effect under similar conditions while Cl^- ion accelerates the rate.[89]

The activation energy and log A factors in the presence of Cl^- ions have been measured for the ion $[Ni(bipy)_3]^{2+}$.[112] The results are tabulated below:

	Water	NH_4Cl(3M)
Ea(kcal)	24.1, 21.8*, 21.9†	22.7
log A (sec^{-1})	14.7	13.8
$\Delta S^{\ddagger}$ (e.u.)	6.8, 2.7	2.7

* ref. 63 † ref. 61

Unfortunately no statement can be made regarding the manner in which the Cl^- ion affects the racemisation as the results in water only are not consistent. Davies and Dwyer[90,112] have suggested that the ionic environment affects the racemisation by some modification of the metal ligand bonds.

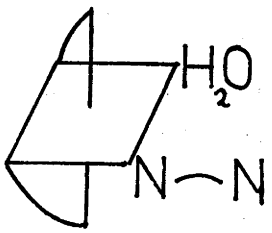
2.34 $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$.

Except for OH^- and large ions, the racemisation and dissociation of both Fe(II) complexes were relatively free from pronounced ion effects.[128] The dissociation displayed a small retardation in the presence of anions or cations at about 1M concentrations, the effectiveness being in the following order:

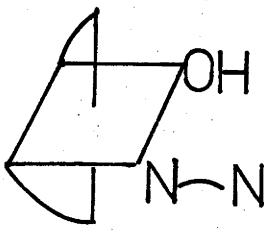
$$HSO_4^- > Cl^- \approx NO_3^- \quad \text{and} \quad H^+ > Li^+ > K^+$$

The diminution in dissociation rate constant was about 10%. It was not possible to detect any changes of this order of magnitude in the racemisation rates as the solutions were intensely coloured and the rotations low. The ion effects were thought to arise in two ways:- for anions by their negative sheath about the complex, and for cations by their alteration in the activity of water.[125]

The acceleration in rates of racemisation and dissociation of the ions $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ in the presence of OH^- ions was accompanied by precipitation. An interpretation of the OH^- ion effect on the dissociation of the $[Fe(phen)_3]^{2+}$ ion has been given in terms of either an SN_2 or an SN_1 mechanism[128]. In the former, attack by H_2O or OH^- was thought to give the following intermediates containing a half-bonded phenanthroline.



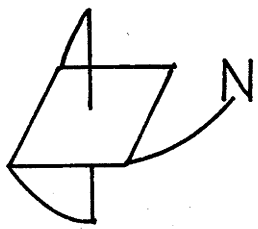
a



b

Intermediate (b) could readily be derived from (a) by proton transfer to an OH^- ion. Racemisation would follow as a result of the dissociation of (a) or (b).

The SN_1 mechanism included the same intermediates as above. In this case (a) and (b) were formed by the reaction of an H_2O molecule or OH^- ion with a partly dissociated complex (c). This scheme could also be applied to $[Fe(bipy)_3]^{2+}$.



C

A quantitative study on the effects of large ions and polyelectrolytes on the racemisation and dissociation of $[Fe(phen)_3]^{2+}$ [127] has disclosed the presence of varying degrees of ionic association. Large cations such as protonated brucine and quinine cause increases in the rates of both dissociation and racemisation. Large anions produce increases or decreases depending specifically on the anion itself. For example, dl-10 camphorsulphonate at low concentrations (0.001M) first gives a slight increase followed

at higher concentrations by a reduction in rate, e.g. 50% at 0.6M added ion concentration. Sodium lauryl sulphate almost doubles the dissociation rate at a concentration of 0.001M. Large ions increased the racemisation rate in general but polystyrene sulphonate decreased the rate by a factor of one half.

The behaviour of large cations could be explained by the presence of their positive field around the $[Fe(phen)_3]^{2+}$ ion held by Van der Waal's attraction.[2] This field might then produce a decreased electron density on the nitrogen and with it faster dissociation. On the other hand the proximity of a positive field, if it can so affect the nitrogen, could surely also affect the metal-ligand pi bond. In this event since the formation of a pi bond tends to make the peripheral atoms negative one would expect a positive field to strengthen the pi bond.

It was suggested that the large anions acted by replacement of a pair of water molecules from between each ligand. Models demonstrated that the three phenanthroline groups jutted out from the centre of the octahedron leaving pockets between each ligand. It was also shown that two water molecules could pack into each pocket to give the whole entity a roughly spherical shape. In agreement with this was the fact that many phenanthroline complexes were known to occur as hexahydrates. The sulphonate group could conveniently replace all three pairs of water molecules from between the ligands. This could lead to slower dissociation since there are now no water molecules to replace the lost ligand. Dialysis experiments[127] showed considerable ion association between polystyrene sulphonate and the $[Fe(phen)_3]^{2+}$ ion.

The rigidity imposed by the linked sulphonate groups could also explain the decreased rate of intramolecular racemisation which was observed.

2.35 $\underline{[Fe(phen)_3]^{3+}}$ and $\underline{[Fe(bipy)_3]^{3+}}$.

In contrast to the divalent iron complexes, high ionic strength increased the racemisation rates of both phenanthroline and bipyridine Fe(III) tris complexes.[89] On the other hand, acid was found to reduce the rate.

The effect of added ions on the dissociation of the Fe(III) complexes of phenanthroline was more pronounced than with the Fe(II) counterparts. As with the last mentioned, H^+, Li^+, and K^+ each produced retarding effects in the order $H^+ > Li^+ > K^+$.[125]

To account for the retardation produced by H^+ the formation of a protonated species $[Fe(phen)_3H]^{4+}$ had been suggested[114], but did not agree with the ability of other positive ions such as Li^+ to retard the rate. The effects on racemisation paralleled those on dissociation and were consistent with the idea of very similar expanded transition states for both racemisation[129] and dissociation. Part of the retardation by cations was thought to arise from a decrease in the activity of water but this could not account completely for the changes since different acid solutions of the same activity gave different rate constants.

The retarding effect produced by anions was believed to be a result of the formation of ion-pairs.[125] The order of effectiveness was $HSO_4^- > Cl^- \sim NO_3^-$ and ion-pairs were detected by small changes in the ultraviolet spectrum of solutions of the $[Fe(phen)_3]^{3+}$ ion in sulphuric, hydrochloric, and perchloric acids.

2.4 THE EFFECTS OF A CHANGE IN SOLVENT ON RACEMISATION RATES.

It has been known for some time that the nature of the solvent may affect the rate of racemisation. Werner[6] reported a retardation in the racemisation of an aqueous solution of $K_3[Cr(ox)_3]$ produced by the addition of acetone. The first study of the temperature dependence of a solvent effect was made by Bushra and Johnson[42] on the racemisation of the $[Cr(ox)_3]^{3-}$ ion in aqueous acetone. Some results are given below:

TABLE 2.4 (BUSHRA AND JOHNSON[64])

Mole fraction acetone	$10^5/\lambda_{inv}$ (*)	Ea(kcal)	log PZ (min^{-1})	$\Delta S^{\ddagger}$ (E.u.)
0	60	15.75	8.05	-32
0.059	13.7	15.60	7.40	-35
0.098	8.6	16.20	7.60	-34
0.144	5.4	18.80	9.30	-26

*Units not specifically quoted are apparently in min^{-1} from the experimental results (temperature 30°.1C.)

$\Delta S^{\ddagger}$ has been calculated via the formula given in section 6.4 (at 300°K.)

The effect of the increased organic component is to retard the rate by raising the energy of activation required. At the same time the entropy term becomes more positive. Aqueous acetone was also observed to retard the racemisation of the $[Cr\ en(ox)_2]^-$ ion. Other solvents such as methanol, ethanol, propanol and 1,4 dioxane were found to reduce the racemisation rate of the $[Cr(ox)_3]^{3-}$ ion.[97]

Preliminary work[85] showed that compared with water the organic solvents methanol, ethanol, propanol, and nitrobenzene

increased the rates of racemisation of the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ ions. Recently their dissociation and racemisation rates were studied in methanol and water-methanol mixtures.[124] The two ions behaved similarly in that the rates of racemisation increased continuously as the methanol content was increased. The rates of racemisation were greater than those of dissociation so that by subtracting the rate of dissociation from the observed racemisation rate, a rate of intramolecular racemisation was obtained. This procedure assumes, of course, that every dissociation produces racemisation. For the $[Fe(bipy)_3]^{2+}$ ion it was shown that an intramolecular process made an increased contribution to the racemisation as the methanol content was increased. In addition, in methanol rich solutions the rate of racemisation was almost independent of the acid concentration, a result consistent with a smaller contribution made by a dissociation mechanism.

The results of a study of the effect of various solvents on the racemisation of the $[Ni(phen)_3]^{2+}$ ion are given below.

TABLE 2. (DAVIES AND DWYER)[85]

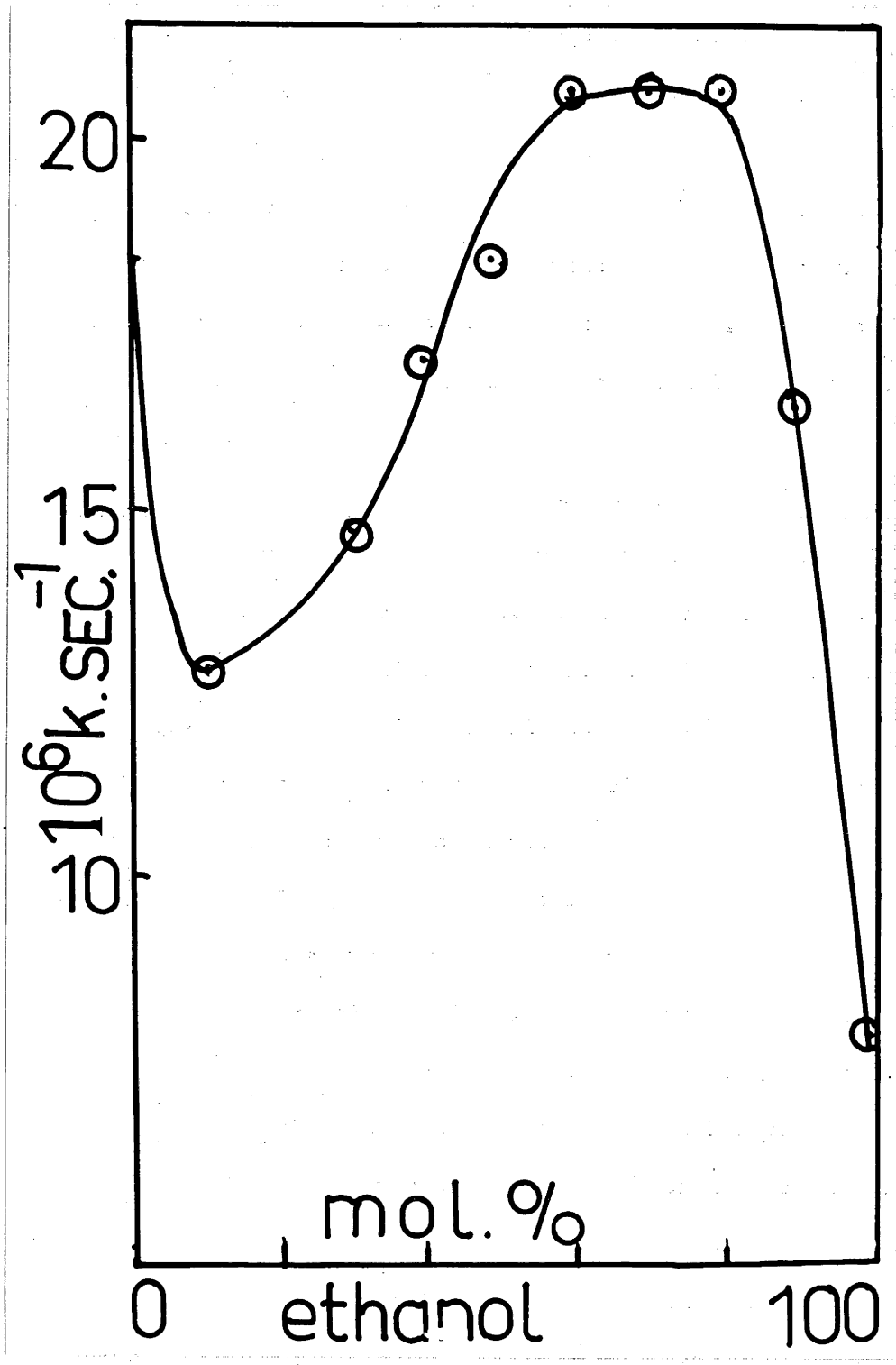
Solvent	Ea(kcal/mole)	$10^4 k$ (min^{-1}) inv.	$\Delta s^{\ddagger}$(e.u.)
Water	13.0 $\pm$ 0.3	3.4	-1.0 ($\pm$ 1.5)
Methanol	11.9 "	2.2	-6.0 "
Ethanol	12.4 "	1.2	-3.8 "
n propanol	12.3 "	1.1	-4.2 "
Acetone	12.7 "	3.0	-2.4 "
Pyridine	13.9 "	4.6	+3.1 "
Nitrobenzene	12.9 "	0.34	-1.5 "
Ethyleneglycol	14.0 "	0.40	+3.6 "

Note: $\Delta s^{\ddagger}$ was calculated as given in Ref. 88.

There was no correlation between the rates and any physical property of the solvent (e.g. dielectric constant). The fact that the rates varied considerably while the energies of activation and log A values remained fairly constant led Davies and Dwyer to favour an intramolecular mechanism. It has since been shown that the rates of racemisation and dissociation are identical in the solvents ethanol, 0.7 mole fraction ethanol-water, and nitrobenzene.[86] Hence dissociation would appear to be a likely mechanism in all the organic solvents tried.

The racemisation rates of the $[Ni(phen)_3]^{2+}$ ion in aqueous organic solvents varied in the manner shown in Figure 2.4 with changing percent organic component. A dual mechanism was thought to operate as it was then believed that racemisation in 0.7 mole fraction ethanol-water was more rapid than dissociation.[37] The behaviour was attributed to a decrease in rate of dissociation and an increase in the rate of intramolecular racemisation as the organic content increased. This explanation did not account for the maxima in the curves. Further, exchange experiments have shown that the rates of racemisation and dissociation in 0.7 mole fraction ethanol-water are the same; therefore a dissociation mechanism must be present.

It has been suggested that the initial decrease in racemisation rate as the organic component was increased could be due to ion-pair formation.[55] Both the ion-pair and the parent complex could then react at different rates. The initial drop due to a change in solvent would be followed by an increase in rate due to the faster dissociation of the ion-pairs. The subsequent decrease in rate would


20
15
10
$10^6 k.SEC.^{-1}$
mol.%
0
ethanol
100

then be a result of the increase in organic solvent on the rate of racemisation of the ion-pair.

It is interesting to investigate what relationships might be present between the energies of activation and entropies of activation for the $[Ni(phen)_3]^{2+}$ ion in the organic solvents and solvent mixtures. Leffler[205] has drawn attention to the implications of a linear relationship between Ea and $\Delta S^{\ddagger}$ in a study of eighty-one organic reactions where solvent or structure of the reactant was varied.

A linear relation between the enthalpy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ of activation could be represented by the following equation known as the isokinetic relationship -

$$\Delta H^{\ddagger} = \alpha + \beta \Delta S^{\ddagger} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where β is the slope of the plot and α the intercept; β has the dimensions of absolute temperature.

The rate of a reaction at any temperature is determined by the free energy of activation ($\Delta F^{\ddagger}$).

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

By substituting for $\Delta H^{\ddagger}$ in (2)

$$\Delta F^{\ddagger} = \alpha + (\beta - T)\Delta S^{\ddagger} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Obviously, when $\beta = T$, $\Delta F^{\ddagger}$ is constant and the rate constants are the same. β is termed the isokinetic temperature. Leffler points out that because a change in solvent or in structure does not alter the rates it is not safe to conclude that there is no effect. It may be that $\beta \doteqdot T$. On the other hand, provided β was sufficiently different to T then a plot of $\Delta H^{\ddagger}$ (equivalent to Ea) against

should be linear only if the mechanism of the reaction was essentially the same. Leffler proposed a temperature difference of at least 20°K.

The following diagram (overleaf) shows the Ea, $\Delta S^{\ddagger}$ plot for the $[Ni(phen)_3]^{2+}$ ion in alcohol solvents (i) and in ethanol-water mixtures (ii). The results were calculated from the work of Davies and Dwyer.[85,89] The slopes of the lines were β= 392 (alcohols) and β = 335 (ethanol-water). These are quite different to $\bar{T}$, the midpoint of the experimental temperature range used, which was 300°K in both cases.

The straight lines obtained indicate the presence of essentially the same mechanism despite the wide variations in the rates - a conclusion that is confirmed by the results of exchange studies.[62] The investigation of the isokinetic relationship was confined to solvents which were of a similar nature. It would not be expected that the relationship would persist when gross changes in solvent were made (e.g. water and nitrobenzene) although the points were still grouped about the same line.

KEY

Figures (i) and (ii)

(1) equals ethanol

(2) " water

(3) " ethyleneglycol

(4) " n propanol

(5) " methanol

Figure (ii)

From top to bottom the points on the line correspond to 5, 10, 40, 70 and 90% mole-fraction ethanol-water mixtures.

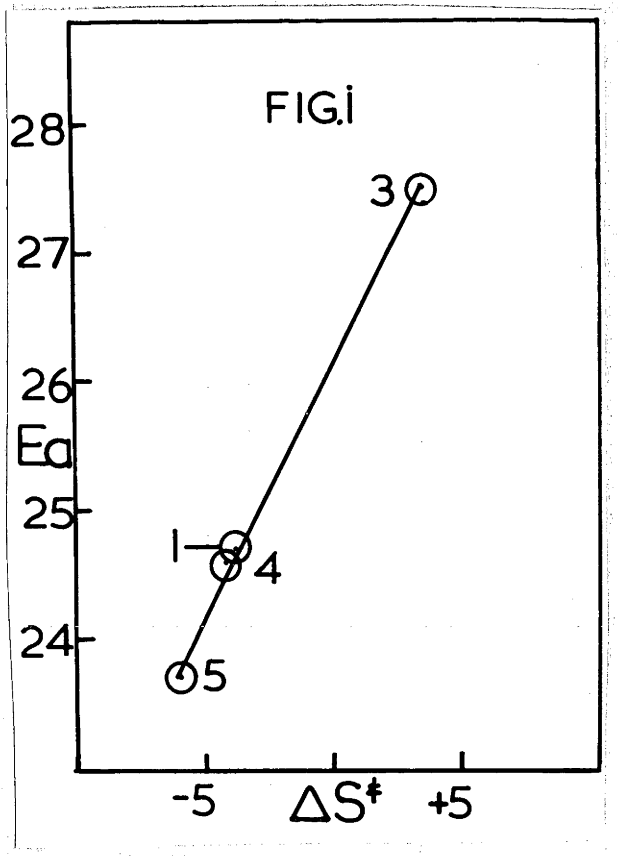


FIG.i
28
27
26
Ea
25
24
3
1
4
5
-5
ΔS‡
+5

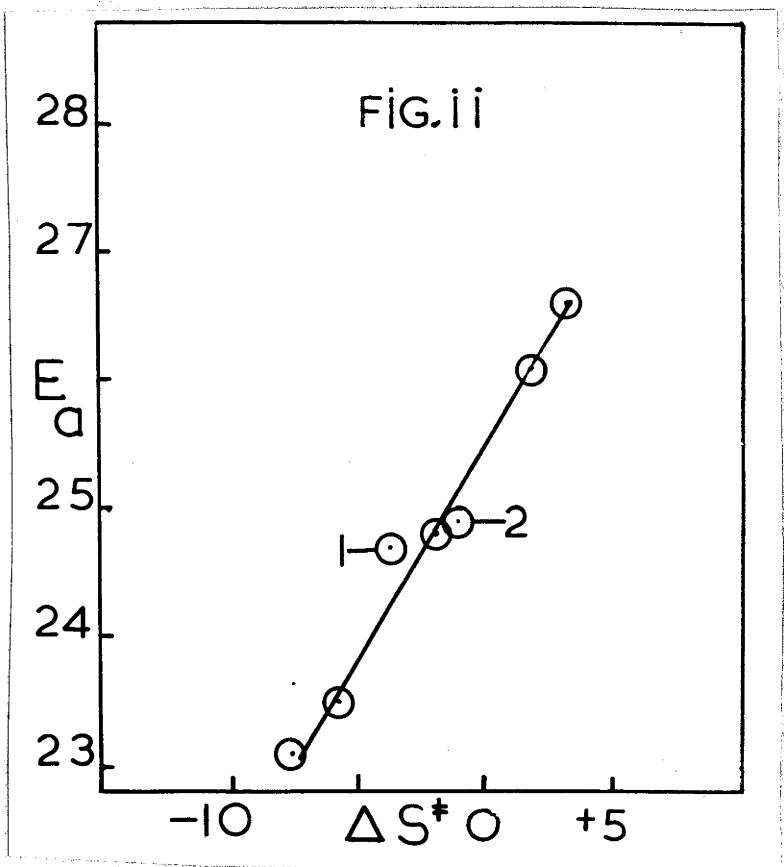


FIG. i i
28
27
Ea
25
24
23
1
2
-10
ΔS‡ 0
+5

2.5 THE EFFECT OF ELECTRON TRANSFER ON RACEMISATION RATES.

Activated charcoal was known to catalyse the racemisation of cobalt(III) complexes.[102,105,108] For example, the optically active $[Co(en)_3]^{3+}$ ion could be boiled in solution with no change in activity but was completely racemised in a few minutes on heating with charcoal.[102] Recent work has shown that the rate of racemisation was largely accounted for by a process of electron transfer[106] to produce the very labile Co(II) complex. The process may be represented by the following equations -

$$d\text{-}[Co(en)_3]^{3+} \xrightarrow[\text{charcoal}]{+e} d\text{-}[Co(en)_3]^{2+} \downarrow \text{rapid racemisation}$$

$$dl\text{-}[Co(en)_3]^{3+} \xleftarrow[\text{charcoal}]{-e} dl\text{-}[Co(en)_3]^{2+}$$

In the present work use is made of the charcoal catalysed racemisation of the $[Co(en)_3]^{3+}$ ion to effect a high yield isolation of one enantiomorph (see section 4.21).

Finally, it has been shown that racemisation can be produced by electron transfer even where the optical forms are stable. Thus when equivalent amounts of $d\text{-}[Os(bipy)_3]^{3+}$ and $l\text{-}[Os(bipy)_3]^{2+}$ were mixed, an inactive solution was obtained.[109] The following electron-transfer equilibrium resulted in complete loss of activity:-

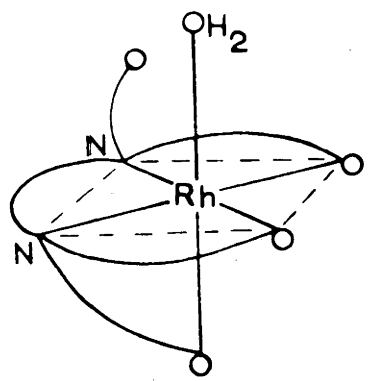
$$l[Os(bipy)_3]^{2+} + d[Os(bipy)_3]^{3+} \rightleftharpoons l[Os(bipy)_3]^{3+} + d[Os(bipy)_3]^{2+}$$

2.6 THE EFFECT OF LIGHT ON RACEMISATION RATES.

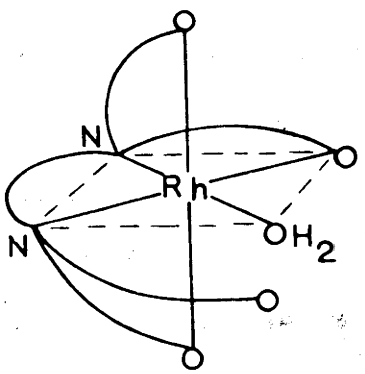
Only two examples were known in which coordination compounds racemised under the influence of light and yet did not, at the same time, suffer decomposition.[110] These were the complexes $d\text{-}K[RhH_2O(EDTA)]$ and $L\text{-}[RhH_2O(l\text{-}PDTA)]H_2O$. (EDTA refers to ethylenediaminetetraacetic acid and l-PDTA to levo propylenediaminetetraacetic acid). Both

complexes were stable in the dark at room temperature though the EDTA complex racemised on heating. Optical activity was lost, however, upon exposure to ultraviolet light, the change being completed in about two hours. The EDTA complex racemised completely while the l-PDTA complex mutarotated. Also the l-PDTA complex regained its activity in three days on storing the solution in the dark but mutarotated upon re-exposure to light. The l-PDTA ligand is stereospecific so that the mutarotated stage must revert to the original configuration. The cycle of rotational changes could be repeated apparently as often as desired.

To account for the racemisation of the EDTA complex, Garvan suggested two possible intramolecular mechanisms. The first was essentially that of Gehman, Bailar, and Seiden (see section 2.1), with the provision that the $[RhH_2O(EDTA)]^-$ complex would have to consist of equal amounts of the following two isomers which also had approximately the same rotating power. This restriction arose since the mechanism proposed converted the d-equatorial isomer into the l-polar form. In the figures below, (XXXI) represents the d-polar isomer and (XXXII) the d-equatorial.



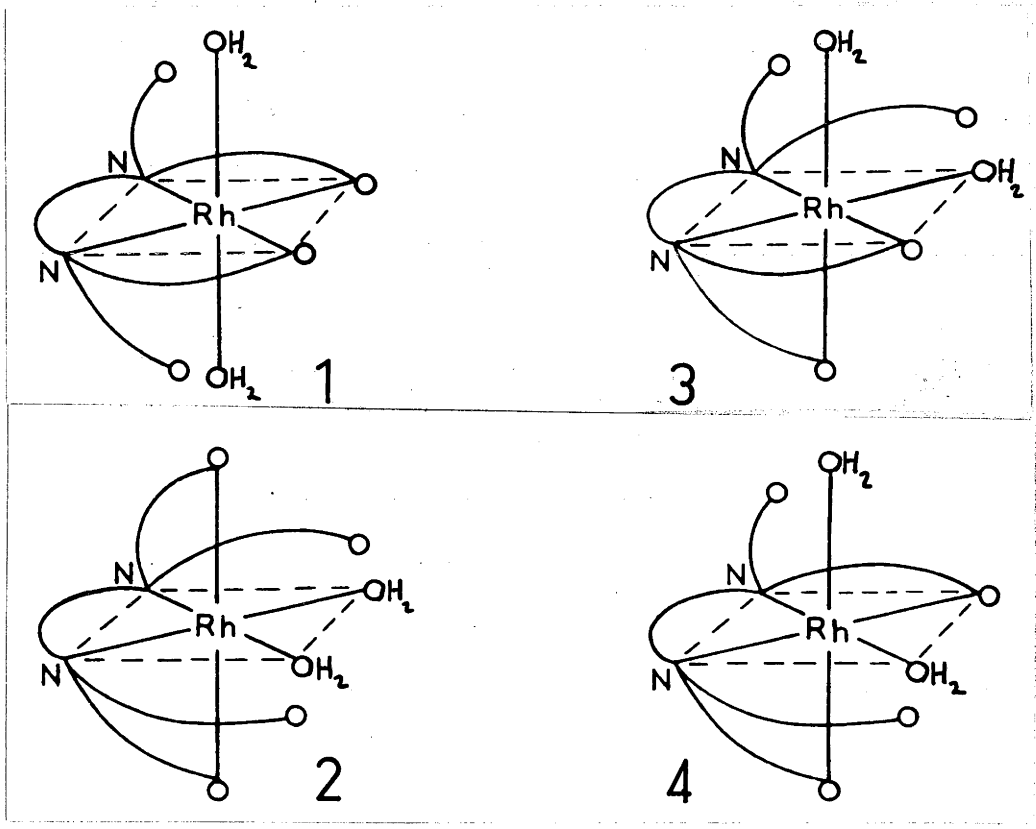
(XXXI)



(XXXII)

In this mechanism the loss in activity was produced by an isomerisation rather than a racemisation.

An alternative hypothesis[110] considered the racemisation to occur via the opening of a second carboxylate ring, with the formation of a diaqua species which then racemised by an intramolecular mechanism. Four isomeric diaqua species were possible (1, 2, 3, 4).



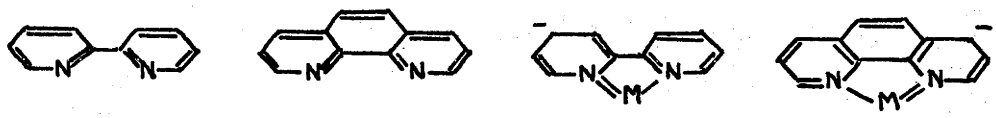
Of these only 1 and 2 were capable of giving a symmetrical intermediate, the others simply produced isomerisation attended by inversion of the equatorial-polar type just mentioned. Information on the rates of H_2O exchange could distinguish between these proposals since the last mentioned involves participation of water by a one-ended detachment of a carboxylate group.

The mutarotation of the P.D.T.A. complex was difficult to explain. There was considerable evidence that steric hindrance prevented the formation of the other form of the complex i.e. D[Rh H_2O(1-PDTA)] and Garvan favoured the formation of diaqua species, which would not be inactive owing to the activity present in the ligand. Examination of the absorption spectrum of both the exposed and unexposed solutions showed them to be practically identical, leading to the conclusion that if diaqua species were formed their absorption spectra must be almost the same as the monoaquated. The same rotational change was observed in the presence of an oxidising agent ($KMnO_4$) thus eliminating the possibility of a Rh(II) complex having been formed. In this event the permanganate would immediately effect oxidation to Rh(III) and the rotation would then return at once to the value prior to exposure. As with the EDTA complex, water exchange data would provide direct evidence of aquation.

The photodecomposition of $K_3[Co(ox)_3]$ has led Jaeger and Berger[101] to attempt an asymmetric synthesis. By using circularly polarised light they hoped to decompose one antipode at a different rate to the other but did not succeed. The presence of cobalt(II), which was formed in the photodecomposition, could rapidly racemise any active tris material by an electron-transfer mechanism (see section 2.5). Consequently, the chance of observing any activity was very slim.[110] An unsuccessful attempt has also been made to effect an asymmetric synthesis with the Rh(III) -EDTA complex[110] by an analogous technique.

2.7 NICKEL AND IRON COMPLEXES OF 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE.

Consideration of the structural formulae below shows that the common feature of the 2,2'-bipyridine (I) and 1,10-phenanthroline (II) molecules is possession of the functional group -N=C-C=N-.



I II III IV

Both ligands are weak bases (I. pK 4.40 II. pK 4.96).[140] Also the bipyridine molecule prefers the trans nitrogen configuration. This has been shown by the dipole moment measurement of 0.91 Debye[72] as against the value of 3.8 Debye expected for the cis configuration. Phenanthroline by comparison has a dipole moment of 4.1 Debye units. Thompson[73] has estimated that the energy difference between the cis and trans forms of bipyridine is about 2-3 kcal.

The ability of structures I and II to coordinate strongly to transition metal ions has been attributed to the formation of double -bonds.[74,75,76] The p orbital of the nitrogen can accept electrons from a d orbital of the metal. As a result structures III and IV could contribute to the resonance hybrid. Of course, the complex as a whole still carried a positive charge. The tris Ni(II) complexes with either ligand are well known and may be readily obtained by mixing the stoichiometric amounts in a solvent such as aqueous ethanol. The optically active forms of $[Ni(bipy)_3]^{2+}$ ion were first obtained by Werner[82] using ammonium d-tartrate as the

resolving agent. A considerably improved resolution was subsequently developed[81], employing the sparingly soluble lattice compound formed with iodide and antimonyl-d-tartrate. A very efficient resolution of the $[Ni(phen)_3]^{2+}$ ion has been achieved using antimonyl d-tartrate which gives complete precipitation of one diastereoisomer only. The corresponding Fe(II) tris complexes have been prepared and resolved by similar methods.[81,215] The Ni(II) and Fe(II) complexes racemise in solution and the mechanisms of racemisation have been studied.

Mechanisms:

Some mention has been made already (section 2.2) concerning dissociation and racemisation studies of the $[Ni(bipy)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ ions. There are marked differences in their racemisation rates and also in their behaviour towards acid. The phenanthroline complex racemises with a half-life of 17 hrs at 25°C independent of acid being present. On the other hand, the bipyridine complex under the same conditions has a racemisation half-life of 5 min. and the rate is accelerated by acid. Davies and Dwyer[84,85,50] studied the racemisation of these complexes under a variety of conditions which included aqueous solution, acid solution, solutions containing different ions (section 2.30), and organic solvents (section 2.4). The failure of an excess of ligand to affect the rates of racemisation was cited as evidence for an intramolecular mechanism.[84,85,61] It was expected that the increased rate of the reverse reaction should produce a slower racemisation according to the following equation (coordinated water being omitted).

$$[Ni(phen)_3]^{2+} \rightleftharpoons [Ni(phen)_2]^{2+} + phen$$

Later workers[63] pointed out that provided the bis complex formed was optically inactive or alternatively rapidly lost its activity, then excess ligand would not affect the observed rate of racemisation. Dissociation studies confirmed the identical nature of both racemisation and dissociation processes in acid solution (cf. section 2.2). Fairly high acidities were needed to effect dissociation since below about 3 molar concentration appreciable re-formation was present. Subsequently, exchange experiments[86] showed that mechanism which involved dissociation of one ligand also accounted for the racemisation in neutral and alkaline solutions up to pH13.

The racemisation of the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ ions was studied several years ago[112] and a considerable amount of work has since appeared on their rates of dissociation,[114,116,117,126] specific ion effects (section 2.3), and solvent effects (section 2.4).

Work on the rates of ligand exchange[113] and acid dissociation[114,116] could not be used satisfactorily in conjunction with the available racemisation data since the conditions were not identical throughout.[115,130] Basolo, Hayes, and Neumann[117] determined both racemisation and dissociation rates under comparable conditions. The dissociation was measured spectrophotometrically in acid solution by following the loss in colour accompanying dissociation of the first ligand. As with the Ni(II) complexes the function of the acid was to prevent the reverse reaction by protonation of the free ligand. Table 2.7 has been taken from Reference 117. The Fe(II) complexes differ from their Ni(II) counter parts in that racemisation takes

place more rapidly than dissociation. By making the reasonable assumption that dissociation of the first ligand would be accompanied by racemisation, Basolo and co-workers attributed the remainder of the racemisation rate constant to an intramolecular mechanism. Thus, by addition of the values shown for intra- and inter-molecular mechanisms the observed racemisation rate constant may be obtained.

TABLE 2.7 (25°C)

	Intramolecular racemisation			Intermolecular racemisation		
	$k(min^{-1})$	Ea (kcal)	$\Delta S^{\ddagger}$ (e.u.)	$k(min^{-1})$	Ea (kcal)	$\Delta S^{\ddagger}$ (e.u.)
$Fe(phen)_3^{2+}$	3.9×10^{-2}	29	21	4.2×10^{-1}	32.1	28
$Fe(bipy)_3^{2+}$	1.6×10^{-2}	26	12	4.7×10^{-2}	27.4	17

For the $[Fe(phen)_3]^{2+}$ ion there was no significant dependence on the acid concentration[125] giving support to the above assumption that racemisation accompanied dissociation. If this were not correct and every dissociation did not lead to racemisation then in the absence of acid the bis complex would be capable of re-forming some active tris. Consequently, the addition of acid should lead to an increase in the observed racemisation rate by elimination of the reverse step. On the other hand, the dependence of the racemisation of the $[Fe(bipy)_3]^{2+}$ ion on acid[117] could be explained by prevention of the reverse reaction, provided it occurred with some retention of configuration. The effect of excess bipyridine on the racemisation in aqueous solution does not appear to have been studied.

Baxendale and George[116] explained the acid catalysed dissociation of the $[Fe(bipy)_3]^{2+}$ complex by an equilibrium:

$$[Fe(bipy)_3]^{2+} + H^+ \rightleftharpoons [Fe(bipy)_3H]^{3+}$$

They assumed that the protonated form reacted more rapidly than the unprotonated form and that at higher concentrations of acid the limiting rate observed was due to the presence of the protonated species. The failure to detect any absorption spectral changes between neutral and acid solutions of the complex led to the following proposal which could account for the acid dependence.[117]

$$(bipy)_2 Fe\langle^{N}_{N}\rangle^{2+} \rightleftharpoons (bipy)_2 Fe\langle^{N}_{N}\rangle^{2+} \rightleftharpoons (bipy)_2 Fe^{2+} + \langle^{N}_{N}\rangle$$

$$\downarrow H^+$$

$$(bipy)_2 Fe\langle^{N}_{NH}\rangle^{+} \xrightarrow{\text{fast}} (bipy)_2 Fe^{2+} + \langle^{N}_{NH}\rangle^{+}$$

Here stepwise dissociation of a bipyridine enables a proton to attach to the free nitrogen and the resulting protonated species was thought to dissociate very rapidly. This path would be more important as the acid concentration was increased and as the protonated species was but a transient intermediate no spectral changes would be expected. A rate expression for the acid dependence could be derived which accounted qualitatively for the observed behaviour but quantitative agreement was not obtained.

Healy and Murmann[212] have concluded that protonated species of the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ ions were present in concentrated perchloric or sulphuric acid solutions, since upon dissolving the red complex chlorides, the solutions changed to a blue colour and became paramagnetic. The changes were reversible on dilution whereupon the red colour was regenerated. If optically active $[Fe(phen)_3]Cl_2$ was used some activity was retained. The

authors excluded the possibility of oxidation having occurred to give formation of the blue Fe(III) complexes, since the changes take place in the presence of Sn^{2+} and $As(OH)_4^-$.

The above evidence, however, is not convincing. Experiments in the present work show that Sn^{2+} did not reduce the blue trivalent $[Fe(bipy)_3](ClO_4)_3$ in concentrated perchloric acid. Similarly, sodium sulphite did not reduce the Fe(III) complex in concentrated sulphuric acid solution. Therefore, a process of oxidation could well account for the colour changes and paramagnetism. Healy and Murmann give the absorption maximum of the blue complex obtained from $[Fe(phen)_3]Cl_2$ as 605 mμ which almost is the same as that reported for the $[Fe(phen)_3]^{3+}$ ion (600 mμ).[125] The reversible nature of the oxidation of the $[Fe(phen)_3]^{2+}$ ion upon dilution of the solution has been noted by Lang.[216] Also the retention of some optical activity is consistent with an oxidation-reduction process.[217]

The available evidence also favours the participation of the proton in a half-bonded intermediate rather than an alternative mode of attachment to the aromatic ring.[116] In the last instance, there seems no reason to prevent phenanthroline attaching a proton in the same way, yet the dissociation and racemisation behaviour of the tris phenanthroline complexes of either Fe(II) or Ni(II) are not acid dependent. The acid dependence is evidently a function of the bipyridine ligand.

The effect of acid on the Fe(III) tris complexes of bipyridine and phenanthroline is opposite to that found for Fe(II), i.e. acid retards the racemisation rates.[129] Also the dissociation of

the $[Fe(phen)_3]^{3+}$ ion is retarded by the presence of acid.[114] A detailed study by Basolo and co-workers[125] showed that the observation was in the category of a specific ion effect since other positive ions also produced a retardation (see section 2.35).

CHAPTER THREE

3.0 MIXED TRISBIDENTATE COMPLEXES.

Mixed complexes of metal ions may be readily prepared provided that the complexes are inert. This applies to a number of transition elements such as Cr(III), Co(III,), Rh(III), etc. although it may happen that the very inertness defeats attempts at preparation. Real problems arise when the complexes of a metal are labile and the thermodynamic stability of the mixed complex is less than one or both of the simple complexes, e.g. -

$$2[Cu(NH_3)_2(en)]^{2+} \rightleftharpoons [Cu(NH_3)_4]^{2+} + [Cu(en)_2]^{2+}$$

The equilibrium then lies far to the right and the equilibrium concentration of the mixed species is very low.

3.1 METHODS OF PREPARATION.

In general, three approaches might be utilised in designing preparations of mixed tris bidentate complexes.

(i) Addition of ligand to the bis or mono complex.

e.g.: $[Cr(en)_2Cl_2]^+ + C_2O_4^{=} \longrightarrow [Cr(en)_2(C_2O_4)]^+ + 2Cl^-$

$[Ni(phen)Cl_2] + 2\ bipy \longrightarrow [Ni(phen)(bipy)_2]\ Cl_2$

(ii) Replacement of ligands.

e.g.: $[Cr(C_2O_4)_3]^{3-} + en \longrightarrow [Cr(en)(C_2O_4)_2] + C_2O_4^{=}$

$[Cr(en)(C_2O_4)_2]^- + en \longrightarrow [Cr(en)_2(C_2O_4)]^+ + C_2O_4^{=}$

$(bipy\ H^+)_2[Ru(phen)Cl_4] \xrightarrow{heat} [Ru(phen)(bipy)_2Cl_2 + 2HCl\uparrow$

(iii) Direct preparation.

e.g.: When cobalt(II) acetate, oxalic acid, and ethylenediamine are taken in stoichiometric proportions in aqueous solution and the mixture oxidised with lead dioxide the complex ions $[Co(en)_2(C_2O_4)]^+$ or

$[Co(en)(C_2O_4)_2]^-$ can be obtained.[134]

For method (i) to be useful the bidentate group(s) present in the bis or mono complex involved must be slow to dissociate relative to the rate of formation of the product. It may be advantageous, as in this work, to change the solvent and/or lower the temperature in order to decrease the rate of dissociation of a mono or bis starting material.

Method (ii) was used by Bushra and Johnson[42] and by Werner.[137] Sometimes more than one ligand may be replaced at a time and a mixture obtained. For example, in the reaction of $[Cr(ox)_3]^{3-}$ with ethylenediamine the insoluble $[Cr(en)_2(ox)][Cr(en)(ox)_2]$ was precipitated.[42]

Method (iii) relied on the availability of the labile Co(II) state. Rapid attainment of equilibrium between the Co(II) complexes was followed by oxidation to the non-labile Co(III) state.

Method (i) was used in this work to prepare the $[Ni(bipy)(phen)_2]^{2+}$ and $[Ni(phen)(bipy)_2]^{2+}$ ions. Contrary to previous ideas[115,139] the dissociation of the Ni(II) mono and bis phenanthroline complexes[121] in aqueous solution was not very rapid, e.g.

Ion	$10^4 k(min^{-1})$	Ea(kcals)
$[Ni(phen)_3]^{2+}$	4.6	25.2
$[Ni(phen)_2]^{2+}$	10.7	23.1
$[Ni(phen)]^{2+}$	5.3	26.2

It was therefore possible to attach two bipyridine ligands to the mono phenanthroline compound to obtain $[Ni(phen)(bipy)_2]Cl_2$ in good yield. A mono starting material was preferred to a bis

because the latter might have been in the trans configuration necessitating rearrangement to the cis during the reaction. The same preparative method was used for $[Ni(bipy)(phen)_2]Cl_2$ starting from $[Ni(bipy)Cl_2]$.

3.2 STABILITY.

The results below constitute what appears to be the only example of equilibrium studies on a mixed tris bidentate complex.[138]

Complex (from Ref.138)	log K(25°C)*
$[Ni(en)_3]^{2+}$	18.28
$[Ni(en)_2(ox)]^{0}$	16.15
$[Ni(en)(ox)_2]^{2-}$	13.02
$[Ni(ox)_3]^{4-}$	8.51

* K refers to the equilibrium, viz.

$$K = \frac{[Ni(en)_2(ox)]}{[Ni(H_2O)_6^{2+}][en]^2[ox^{=}]}$$

Thus successive replacement of ethylenediamine by oxalate produced a less stable complex. A result not surprising if the relative positions of oxalate and ethylenediamine in the spectrochemical series are considered. The Ni(II) mixed complexes prepared in this work were expected to behave very similarly to the simple tris forms since both the bipyridine and phenanthroline ligands were closely related.

3.3 THE PREPARATION AND RESOLUTION OF 1,10-PHENANTHROLINEBIS (2,2'-BIPYRIDINE) NICKEL(II) CHLORIDE 5-HYDRATE AND 2,2'-BIPYRIDINEBIS (1,10-PHENANTHROLINE) NICKEL(II) CHLORIDE 6-HYDRATE.

The method used for the preparation of the mixed complexes $[Ni(bipy)(phen)_2]Cl_2$ and $[Ni(phen)(bipy)_2]Cl_2$ involved first the preparation of the mono compounds $[Ni(bipy)Cl_2]$ and $[Ni(phen)Cl_2]$. The mono complex was then reacted in alcoholic solution with two molecules of the other ligand to yield the mixed complex. The success of this method obviously depends upon the first ligand remaining firmly bound to the nickel. Indeed, with the monobipyridine nickel, some dissociation takes place in the time of the reaction, in spite of the ice-cold conditions employed. This created a complication, since on the addition of phenanthroline, $[Ni(phen)_3]Cl_2$ formed along with the desired $[Ni(bipy)(phen)_2]Cl_2$. e.g.

$$[Ni\ bipy\ Cl_2] \longrightarrow Ni^{2+} + bipy + 2Cl^-$$

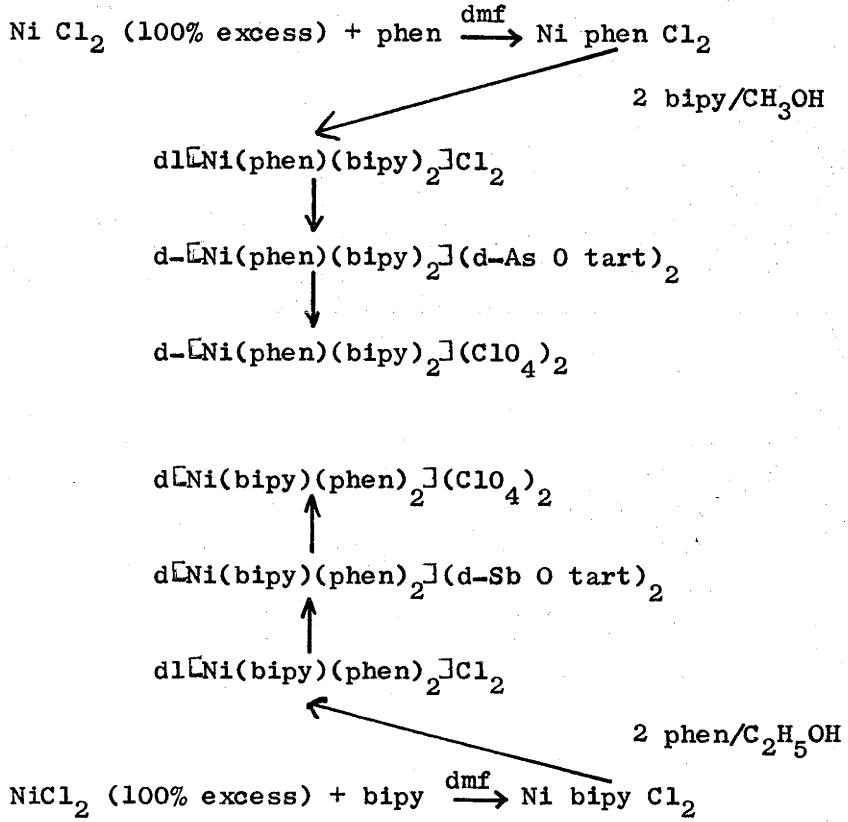
$$Ni^{2+} + 3\ phen \longrightarrow [Ni(phen)_3]^{2+}$$

Furthermore, the mixed ligand complex was resolved with sodium d-antimonyl tartrate, which also resolved the simple tris ion. As a result, the optically active material needed in the racemisation studies was contaminated by another impurity which also racemised. This complicated the interpretation and increased the labour of the kinetic studies.

The preparation of the other mixed complex $[Ni(phen)(bipy)_2]Cl_2$, was not expected to present similar complications as the monophenanthroline nickel(II) ion is known to be much slower to dissociate than its bipyridine analogue.[152] It is true that some $[Ni(bipy)_3]^{2+}$ ion may be formed under the conditions employed, and would be co-resolved along with the mixed complex upon the addition of sodium d arsenyl

tartrate. No anomalous behaviour could be detected in the kinetic studies using this material, and it was concluded that no significant amount of trisbipyridine complex was present.

The reactions used to prepare and resolve both mixed complexes are conveniently summarised below.



3.31 PREPARATIONS.

1,10-Phenanthrolinebis (2,2'- Bipyridine) Nickel(II) Chloride 5 Hydrate.

2,2'-bipyridine (8.1g) was dissolved in methanol (140mls) and 1,10-phenanthrolinedichloronickel(II) (8.0g) (for preparation see section 5.1) added with shaking. The mixture immediately began to turn red, and within half a minute all but a trace of the initial mono complex remained undissolved. The solution was now quickly filtered and the filtrate removed to an ice-bath. Ether (680ml), was gradually added and the

insides of the flask scratched with a glass rod, whereon a pink crystalline product was obtained. This was filtered off at the pump, washed three times with ether and allowed to dry overnight in a desiccator. Yield 16.1g (88%).

Analysis. Calcd. for $[Ni(C_{12}H_8N_2)(C_{10}H_8N_2)_2]Cl_2.5H_2O$

C, 53.94 ; H, 4.77 ; N, 11.79 :

Found C, 53.74 ; H, 4.84 ; N, 11.84 :

2,2'-Bipyridinebis (1,10-Phenanthroline) Nickel(II) Chloride 6 Hydrate.

1,10 phenanthroline hydrate (10.7g), was dissolved in absolute ethanol (90ml); 2,2'-bipyridinedichloronickel(II) (7.7g) (for preparation see section 5.11) was then added, and the flask stoppered and shaken vigorously for six minutes, whereon all but a trace of the green mono complex had dissolved, giving a claret red solution. The latter was filtered and to the filtrate ether (300ml) was added gradually. During this addition, the filtrate was cooled in ice and the insides of the flask were scratched with a glass rod. The pink crystalline produce separated out on the sides of the flask. The product was filtered off at the pump and washed three times with ether, finally being dried in a desiccator overnight. Yield 18.5g. (93%).

Analysis. Calcd. for $[Ni(C_{10}H_8N_2)(C_{12}H_8N_2)_2]Cl_2.6H_2O$

C, 54.00 ; H, 4.77 ; N, 11.1 :

Found C, 54.47 ; H, 4.76 ; N, 11.2 :

3.32 RESOLUTIONS.

N.B. In the following two resolutions it is to be understood that all flasks and solutions were kept well chilled, to reduce the extent of any racemisation and disproportionation that might occur.

The Preparation of Active 1,10-Phenanthrolinebis (2,2'-Bipyridine) Nickel(II) Perchlorate Using Sodium d-Arsenyltartrate.

Sodium d-arsenyltartrate was prepared according to the method of Henderson and Ewing.[174] The resolving agent calls for comment, since repeated recrystallisations from aqueous alcohol gave products for which the specific rotation had the following values (using a 2% solution in a 2dm tube).

$[\alpha]_D$	1st	recrystallisation	$+ 27^\circ$
"	2nd	" "	$+ 26^\circ.5$
"	3rd	" "	$+ 21^\circ$

In addition, the observed rotation of a fresh aqueous solution fell rapidly for about five minutes after mixing and then remained constant. The specific rotations above refer to times when the rotations were constant. Despite the lack of stability in the resolving agent it allows the preparation of active $[Ni(bipy)_2(phen)]^{2+}$ ion in good yield.

A solution of d-arsenyltartrate (4.4g) in ice-water (55ml) was added to a solution of 1,10-phenanthrolinebis (2,2 bipyridine) nickel(II) chloride 5 hydrate (10g) in ice-water (140ml). On scratching, the buff coloured dextro diastereoisomer precipitated. After being cooled in ice for about 1 min. the product was filtered off rapidly at the pump. It was washed well six times with ice-water, then with acetone, and finally dried in a desiccator overnight. Yield 5.3g. The diastereoisomer was split by grinding with sodium perchlorate solution. The pink active complex perchlorate so obtained was filtered off at the pump and washed well with 1% sodium perchlorate, then ice-water, and finally ether. Yield of $d[Ni(bipy)_2(phen)](ClO_4)_2$ 3.3g (33%).

The solid was tested for the complete removal of the resolving agent by using Gutzeit's test for arsenic.[175] Reprecipitation from 90% acetone with sodium perchlorate was sufficient if further purification was needed.

The product racemised rapidly in water but in methanol the racemisation rate was greatly reduced (cf. section 2.4). A 0.1% methanolic solution in a 2dm tube gave respectively α_{5461} + 1.74° and α_D + 1.45° whence $[\alpha]_{5461}$ = +870° and $[\alpha]_D$ = 725°.

<u>The Preparation of Active 2,2'-Bipyridinebis (1,10-Phenanthroline) Nickel(II) Perchlorate Using Sodium d-Antimonyltartrate</u>.

Racemic 2,2'-bipyridinebis (1,10-phenanthroline) nickel(II) chloride 6-hydrate (10g), was dissolved in water (130ml), and sodium d-antimonyltartrate (5g) in water (120ml) added to the cold solution. The buff coloured dextro diastereoisomer precipitated. The mixture was cooled in an ice-bath and the product filtered off at the pump. It was washed well with ice-water and then acetone, before allowing to dry in a vacuum desiccator. Yield 7.3g.

The resolving agent was removed by grinding the diastereoisomer with sodium perchlorate solution. The pink active complex perchlorate so formed was filtered off at the pump, being washed in turn with 1% sodium perchlorate solution, ice-water, and finally ether. Yield 4.7g (45%). A 0.08% solution in methanol in a 2dm tube gave respectively α_{5461} +2.60 and α_D +2.20 whence $[\alpha]^{20}_{5461}$ = +1,625° and $[\alpha]^{20}_D$ = +1,375°.

CHAPTER FOUR

4.0 THE PREPARATION AND RESOLUTION OF POTASSIUM 2,2' BIPYRIDINEDIOXALATO CHROMATE(III) AND POTASSIUM 1,10-PHENANTHROLINEDIOXALATO CHROMATE (III).

Both the above complexes were prepared from the corresponding mono bipyridine or phenanthroline compounds by the addition of two molecules of potassium oxalate in hot aqueous formamide solution. The complexes were isolated as their barium salts and converted to the potassium salts by double decomposition with potassium sulphate. They have been resolved using the optically active $[Co(en)_2(ox)]^+$ ion. The last mentioned was resolved by precipitation as the bromide in the presence of the optically active $[Co(en)_3]^{3+}$ ion. Two new methods for the preparation of active $[Co(en)_3]^{3+}$ have been employed.

4.1 EXPERIMENTAL.

In the preparations described below those quantities in parentheses given first and lettered (a) refer to the 2,2'-bipyridine complex and those lettered (b) refer to the 1,10-phenanthroline counterpart.

All rotations have been measured in a 1dm tube 3-5 minutes after dissolution.

4.11 BARIUM 2,2'-BIPYRIDINE OR 1,10-PHENANTHROLINE DIOXALATO CHROMATE(III).

Potassium oxalate 1-hydrate ((a) 5.5g (b) 6.3g) was dissolved in boiling 1 : 1 formamide-water ((a) 30ml (b) 180ml). To the near boiling solution was added Cr(bipy or phen) Cl_3 dmf* ((a) 5.64g (b) 7g). The mixture was heated for 1½ min. during which the colour changed to a deep-red. The solution was then filtered to remove some grey material

* For preparation see section 5.11.

and barium chloride 2-hydrate (4-5g) in water (10-15mls) added to precipitate the purple-red barium salt. (Yields (a) 6g (b) 7.6g). The barium 2,2'-bipyridine dioxalato chromate(III) could be recrystallised from hot water (700 ml), some insoluble white material (barium oxalate) being filtered off. On adding barium chloride (2g) to the filtrate and cooling in ice a red crystalline product was obtained. This was washed with ice-water then acetone (Yield 4.7g, 67%). A sample of the phenanthroline analogue was purified for analysis by conversion to the potassium salt (see later) and reprecipitated as the barium salt.

Calcd. for $Ba[Cr(C_{10}H_8N_2)(C_2O_4)_2].3H_2O$

C, 35.00 ; H, 2.31%

Found C, 34.90 ; H, 2.27%

Calcd. for $Ba[Cr(C_{12}H_8N_2)(C_2O_4)_2]_2.4H_2O$

C, 37.47 ; H, 2.36; N, 5.47%

Found C, 37.48 ; H, 2.31; N, 5.31%

4.12 BIS(1,10-PHENANTHROLINE) OXALATO CHROMIUM(III) IODIDE.

$[Cr(phen)_2Cl_2]Cl$ was prepared by a method analogous to that described for $[Cr(bipy)_2Cl_2]Cl$[214] except that the brown crystalline product was precipitated by the addition of ether. A solution of potassium oxalate (0.20g, 0.5mol) plus potassium hydrogen oxalate (0.27g, 0.5mol) in about 10ml of water was treated with 0.2N potassium hydroxide to give a pH of 4-5. $[Cr(phen)_2Cl_2]Cl$ (1.5g, 1mol) was then added and the mixture heated to boiling for 5 mins.; during the heating the colour changed slowly to a deep red. Solid potassium iodide (5g) was then added to precipitate a red-brown complex which upon re-crystallisation from boiling water (260ml) yielded 0.8g of orange-red

material. The conductivity of an aqueous solution was 95mhos corresponding to a 1 : 1 electrolyte.

Calcd. for $[Cr(C_{12}H_8N_2)_2(C_2O_4)]I$

C, 49.78 ; H, 2.57 ; N, 8.93%

Found C, 49.86 ; H, 2.80 ; N, 8.75%

4.13 dl-POTASSIUM 2,2'-BIPYRIDINE OR 1,10-PHENANTHROLINEDIOXALATO CHROMATE(III).

The barium salt ((a) 4.7g (b) 7.3g) was suspended in hot water ((a) 40ml (b) 50ml) and the theoretical amount of potassium sulphate required to convert the barium to barium sulphate added. The mixture was heated to boiling and stirred for about 3 mins. The barium sulphate settled out and the mixture was allowed to age $\frac{1}{4}$ hr. on the steam bath before being filtered. The deep-red filtrate was evaporated down to a volume of 40mls and cooled in ice to obtain purple-red crystals of the potassium salt. More product was obtained by evaporating down the mother liquors, adding ethanol and cooling in an ice bath. The crystals were washed with 80% ethanol and finally acetone. They were dried in a vacuum desiccator over calcium chloride. Yields were (a) 4g (b) 4.8g (i.e. ca 65% based on the amount of mono complex).

Calcd. for $K[Cr(C_{10}H_8N_2)(C_2O_4)_2]\frac{1}{2}.H_2O$

C, 38.60 ; H, 2.10 ; N, 6.47%

Found C, 38.68 ; H, 2.27 ; N, 6.45%

Calcd. for $K[Cr(C_{12}H_8N_2)(C_2O_4)_2]$

C, 42.96 ; H, 1.80 ; N, 6.26%

Found C, 42.94 ; H, 1.74 ; N, 6.17%

4.2 THE RESOLUTION OF THE TRIS(ETHYLENEDIAMINE) COBALT(III) ION.

Tris(ethylenediamine) cobalt(III) chloride was first prepared by Werner[4]. Resolution was effected through the chloride d-tartrate which was obtained by allowing the chloride (1mol) to react with silver d-tartrate (1mol). The correct ratio of chloride ion to tartrate ion is important and this has meant that it is necessary to isolate the pure solid chloride, the synthesis of which has been described by Work.[206] In the present method the less soluble diastereoisomer is isolated directly and the expensive and unstable silver d-tartrate is replaced by barium d-tartrate. The addition of activated carbon ensures rapid oxidation of the initial cobalt(II) complex, and eliminates small amounts of by-products of the reaction.

Procedure:

A 500ml filter flask was fitted with a rubber stopper carrying an open glass tube to the bottom of the flask, and 20.4ml of 88.6% w/v ethylenediamine (0.3mol) added*. This was diluted with water (50ml); the mixture was cooled in ice and 10ml of 10 N. hydrochloric acid added**. Cobalt(II) sulphate 7-hydrate, (28.1g; 0.1mol) dissolved in cold water (50ml) was then added, and finally activated charcoal (4g). A rapid current of air was passed for 4 hours. At the end of this time the pH of the mixture was adjusted by the addition of a few drops of either dilute hydrochloric acid or ethylenediamine into the range 7.0-7.5.

* The exact composition of the ethylenediamine should be determined by dilution of a known volume with water and titration with standard acid, using methyl orange as the indicator. It is not necessary to take the concentrations quoted.

** An equivalent amount of weaker or stronger acid can be used.

The mixture was heated in an evaporating dish on the steam bath for ten to fifteen minutes to complete the reaction, cooled and the charcoal filtered off. The charcoal was washed with 20 ml. water. Barium d-tartrate† (0.1mol) was added and the mixture heated on the steam bath with good mechanical stirring for about half an hour. The barium sulphate was filtered off and washed with a little hot water,†† and the orange-red filtrate evaporated to a volume of 50ml. Crystallisation of D-tris(ethylenediamine) cobalt(III) chloride d-tartrate 5-hydrate ensued on cooling and was completed by allowing to stand overnight.* The crystals were filtered off and the filtrate reserved for the isolation of the levo isomer. The crystals were washed with 40% ethanol-water and recrystallised by dissolving in 30-32ml of hot water followed by cooling to room temperature and then in ice. After filtration the crystals were washed with 40% ethanol-water, then with absolute ethanol and air dried. The yield of the optically pure isomer,** $[\alpha]_D$ + 102° was 21g.

Calcd. for $Co(C_2H_8N_2)_3\,Cl.C_4H_4O_6.5H_2O$

C, 23.41 ; H, 7.47%

Found C, 23.30 ; H, 7.44%

† Prepared by mixing solutions of barium chloride 2-hydrate (24.4g 0.1m) and sodium potassium tartrate 4-hydrate, 28.2g (0.1mol) at 90°C, cooling, filtering and washing with warm water. The precipitate and filter paper are added.

†† At equilibrium a small amount of sulphate ion remains in solution. This does not affect the composition of the diastereoisomer that crystallises.

* The solution may be cooled in ice when very small crystals result.

** The values quoted for the specific rotation are 101° (Werner[4]), 103° (Busch[207]).

Dextro Iodide:

The pure chloride-d-tartrate was dissolved in 30ml of hot water, concentrated ammonia solution, (0.5ml) was added, followed with stirring by 35g of sodium iodide dissolved in 15ml of hot water. The iodide crystallises as reddish-orange needles on cooling. Complete crystallisation was effected by cooling in ice for 15 minutes. After filtration the crystals were sucked very dry and washed with ice cold 30% sodium iodide (20ml) to remove tartrate and then with alcohol and acetone. The yield of the air dried product $[\alpha]_D$ + 89°, was 24g (35%).

Calcd. for $Co(C_2H_8N_2)_3\ I_3.H_2O$

C, 11.26 ; H, 4.11%

Found C, 11.43 ; H, 4.01%

Levo Iodide:

The levo tris-(ethylenediamine) cobalt(III) chloride d-tartrate remaining in the solution above was treated with concentrated ammonia solution (0.5ml) and the mixture heated to about 80°C. Solid sodium iodide (35g) was stirred in and the whole cooled in ice. The impure levo iodide was filtered off and washed with ice cold 30% sodium iodide (25ml) and then with alcohol and air dried. Yield 27g. Purification was effected by stirring the whole of the crude material into 65 ml. of water heated to 50°C. The racemate remained undissolved and was filtered off. Sodium iodide (10g) was added to the warm filtrate (50°) and crystallisation allowed to take place. After cooling in ice, the substance was filtered off, washed with alcohol and then acetone and air dried. The yield is 18g (26%), $[\alpha]_D^{\equiv}$ -90°.

Calc. for $Co(C_2H_8N_2)_3\ I_3.1H_2O$

C, 11.26% ; H, 4.11%

Found C, 11.43% ; H, 4.01%

Properties:

Dextro and levo tris-(ethylenediamine) cobalt(III) iodide 1-hydrates crystallise in deep orange needles or rhombs. The racemic phase which separates as the 1-hydrate is much less soluble in water. Racemisation ensues when the substance is heated to 110°C in the solid state in a sealed tube[208] or in aqueous solution in the presence of charcoal[207] and finely divided metals. In the absence of these catalysts solutions in water or dilute acid are stable even at 100°C, Alkali catalyses racemisation and decomposition in hot solution.[4]

4.21 ALTERNATIVE PREPARATION OF DEXTRO TRIS-(ETHYLENEDIAMINE) COBALT(III) IODIDE BY A PARTIAL ASYMMETRIC SYNTHESIS.

$$Co\ Tart. + 2en. \longrightarrow D[Co\ en_2Tart.]^{\circ} \rightleftharpoons L[Co\ en_2Tart.]^{\circ}$$

$$Co\ Tart. + 3en. \longrightarrow D[Co\ en_3]Tart. \rightleftharpoons L[Co\ en_3]\ Tart.$$

$$D[Co\ en_2Tart.]^{\circ} + HCl + O_2 \longrightarrow D[Co\ en_2Tart.]Cl$$

$$L[Co\ en_2Tart.]^{\circ} + HCl + O_2 \longrightarrow L[Co\ en_2Tart.]Cl$$

$$D[Co\ en_2Tart.]Cl + en \longrightarrow D[Co\ en_3]Cl\ Tart.\downarrow$$

$$L[Co\ en_2Tart.]Cl + en \xrightarrow{slow} L[Co\ en_3]Cl\ Tart.\ (soluble)$$

$$D[Co\ en_3]Tart. + HCl + O_2 \longrightarrow D[Co\ en_3]Cl\ Tart.\downarrow$$

$$L[Co\ en_3]Tart. + HCl + O_2 \longrightarrow L(Co\ en_3]Cl\ Tart.\ (soluble)$$

$$L[Co\ en_3]^{3+} + D[Co\ en_3]^{2+} + Cl^- + Tart^{2-} \longrightarrow L[Co\ en_3]^{2+} + D[Co\ en_3]Cl\ Tart.\downarrow$$

The procedure which is illustrated by the above series of reactions combines the stereospecific influence of d-tartrate ion with

a second order asymmetric synthesis in order to obtain almost exclusively the dextro isomer of the tris-(ethylenediamine) cobalt(III) ion.

Bailar and co-workers[209] have shown that the synthesis of d-tartrato-bis-(ethylenediamine) cobalt(III) ion yields unequal amounts of the D and L isomers, and when allowed to react with ethylenediamine an excess of dextro tris-(ethylenediamine) cobalt(III) ion results. Busch[207] crystallised a mixture of D and L $[Co(en)_3]Cl$ d-Tart. until much of the less soluble D-diastereoisomer had separated, and then in the absence of oxygen introduced a little D,L-$[Co\ en_3]Cl_2$. Electron transfer racemisation of the L-diastereoisomer occurred with further separation of the D-diastereoisomer. In this way, more than a 70% yield of the D-$[Co(en)_3]^{3+}$ ion was obtained.

In the present method until oxidation is complete some $[Co(en)_3]^{2+}$ ion is present to bring about electron transfer racemisation. The necessary condition of separation of a solid phase is achieved by performing the reaction in 25-30 % alcoholic solution, in which D-$[Co(en)_3]Cl$ d-Tart. alone is sparingly soluble. Addition of a little activated carbon facilitates oxidation and, as well, ensures rapid equilibrium between the various products.

Procedure:

Solutions of cobalt(II) sulphate 7-hydrate (28.1g 0.1mol) and sodium d-tartrate (23.0g 0.1mol) each dissolved in 50ml of water at 65°C were mixed and stirred. After about a minute purple-red cobalt(II) tartrate separated and the mixture was maintained at 65°C for fifteen minutes then cooled in ice and filtered. The precipitate was washed with 50ml. of ice water, then acetone and air dried. Ethylenediamine,

(20.4ml of 88.6% $^{w}/_{v}$; 0.3mol)* was placed in a 500ml filter flask fitted with a rubber stopper and a wide glass tube for the entry of air. After dilution with water (50ml) and ethanol (30ml)** the solution was cooled in ice. Hydrochloric acid (10ml of 10N. 0.1mol) was now added and the solution cooled to 4-8°C. The cobalt tartrate was added gradually with stirring and a red colour changing to orange was obtained. Finally, animal charcoal (4g) was added and a stream of air‡ sucked through for two hours. The orange diastereoisomer commenced to separate within fifteen to thirty minutes.

The product, mixed with charcoal, is filtered off‡‡ and washed with 40% ethanol (60ml) the washings being discarded. The diastereoisomer is then extracted from the charcoal with successive portions of hot water (60°C)§. The final wash portion should be colourless and usually 300ml will suffice.

The extract is evaporated to a volume of 50ml and on cooling in ice the pure diastereoisomer separates as orange-yellow crystals, $[\alpha]_D = +103^{\circ}$; yield 40-41g or 78-82% on the assumption of complete conversion to one isomer.

Conversion to the iodide $[\alpha]_D = +91^{\circ}$ is effected as in the previous synthesis. The yield is 43-44g or 60-65%.

* The concentrations were not critical but must be known in order to preserve the correct ratio.

** Sufficient to make the final solution 25% by volume of ethanol. It was important that the percentage did not exceed 30% otherwise the D and L tartrates, not the chloride d-tartrate, separated with very poor resolution.

‡ The rate of air flow should be sufficient to keep the charcoal in suspension and prevent blocking of the tube.

‡‡ Addition of sodium iodide to the filtrate yields only a little racemic $[Co(en)_3]I_3$.

§ Care must be taken that the water temperature is not above 60°C or the extraction prolonged, otherwise racemisation is brought about by the charcoal and the yield is lowered.

4.3 THE RESOLUTION OF BIS(ETHYLENEDIAMINE) OXALATO COBALT(III) BROMIDE BY MEANS OF THE TRIS(ETHYLENEDIAMINE) COBALT(III) ION.

Bis(ethylenediamine) oxalato cobalt(III) bromide was prepared by the method of Dwyer and Reid.[210] A sample (8.5g) was converted to the acetate by shaking vigorously with silver acetate (ca.4g) suspended in hot water (73ml, 70°C). The silver bromide was filtered off and to the filtrate was added a solution of dextro tris(ethylenediamine) cobalt(III) acetate*. A solution of potassium bromide (20% $^{W}/_{V}$) was next added gradually in the following portions to precipitate the optically active bromide.

After each addition the crystals precipitated were filtered off from the cold solution and the next portion of potassium bromide added to the filtrate. Each fraction collected was washed well with ice-water. All rotations were measured in the sodium D line using a 0.25% solution in a 1dm tube.

No.	mls. KBr.	Yield of bromide (g)	$[\alpha]_D$
(1)	5	1.3	-796
(2)	3	0.8	-796
(3)	5	1.6	+492
(4)	4	0.3	+236
(5)	5	1.0	+428

Fractions (1) and (2) were combined and recrystallised from hot water (100ml) containing potassium bromide (0.5g). A sample gave $[\alpha]_D$ -812 and the yield was 1.7g corresponding to 40% based on a theoretical yield of 4.25g of the levo isomer. One recrystallisation

* Prepared from the dextro $[Co(en)_3]I_3$(12.9g) (section 4.2) by shaking with silver acetate (ca.10g) in 80ml hot water, filtering off the silver iodide and evaporating down the filtrate to a volume of 18ml.

of fractions (3), (4) and (5) from hot water (90ml) gave 1.5g (35%) of the dextro isomer having $[\alpha]_D$ + 812.

Calcd. for $[Co(C_2H_8N_2)_2(C_2O_4)]Br.H_2O$

C, 19.73 ; H, 4.97%:

Found C, 19.83 ; H, 4.99%

The above resolution was also carried out by replacing the dextro tris(ethylenediamine) cobalt(III) complex with either a 10 percent solution of ammonium d-camphor-10 sulphonate or ammonium d-tartrate. Fractional precipitation and recrystallisation in a manner similar to that described above gave lower yields. (e.g. approximately 20% of each isomer calculated as before). Also the initial precipitates were of opposite sign to the one obtained in the presence of the active $[Co(en)_3]^{3+}$ ion.

4.31 d POTASSIUM 2,2'-BIPYRIDINE DIOXALATO CHROMATE(III).

Racemic potassium 2,2'-bipyridine dioxalato chromate(III) (1.95g) was dissolved in water (25ml). A solution of dextro bis(ethylenediamine) oxalato cobalt(III) chloride 2-hydrate (0.8g in 20ml at 35°C) was added. Immediately, pink needles of the diastereoisomer commenced to separate out. The mixture was cooled in an ice-bath for 1-2 minutes and filtered. The product was washed three times with ice-water and finally with acetone. It was dried in a vacuum desiccator over calcium chloride. Yield 1.13g (38%).*

A 0.1% solution gave $[\alpha]_D$ +890; a 0.02% solution gave $[\alpha]_{5461}$ +1,350.

* An almost quantitative yield of optically active material could be obtained by the addition of more resolving agent and heating the solution; on cooling more diasteroisomer separates. This second order asymmetric transformation could also be carried out on the analogous phenanthroline complex.

Calcd. for d[Co($C_2H_8N_2$)$_2$(C_2O_4)]d[Cr($C_{10}H_8N_2$)(C_2O_4)$_2$]$\frac{1}{2}H_2O$

C, 36.34 ; H, 3.82 ; N, 12.72%

Found C, 36.29 ; H, 3.91 ; N, 12.79%

The diastereoisomer was converted to the potassium salt by grinding with a total of 10mls of 20% potassium iodide in a chilled mortar. The iodide of the resolving agent was filtered off and the filtrate collected in a chilled flask. The potassium salt was precipitated by the gradual addition of cold ethanol* (25mls) accompanied by scratching of the insides of the flask with a glass rod. After cooling in ice for 1-2 minutes the product was filtered off, washed with 95% ethanol and finally acetone. It was dried in a vacuum desiccator over calcium chloride. Yield 0.48g (43%)‡. A 0.1% solution gave $[\alpha]_D$ +670, and a 0.02% solution gave $[\alpha]_{5461}$ + 1,200.

Calcd. for d K[Cr($C_{10}H_8N_2$)(C_2O_4)$_2$]3H_2O

C, 35.17 ; H, 2.95 ; N, 5.87%

Found c, 35.33 ; H, 2.56 ; N, 5.89%

4.32 <u>d POTASSIUM, 1,10-PHENANTHROLINE DIOXALATO CHROMATE(III)</u>.

Racemic potassium 1,10-phenanthroline dioxalato chromate(III) (2g) was dissolved in water (30ml) and to this was added l-bis(ethylenediamine) oxalato cobalt(III) chloride (0.76g) in warm water (20ml; 30°C). On scratching the insides of the flask a pink diastereoisomer was obtained. After cooling in ice, the product was filtered off and washed with ice-water followed by acetone. It was dried in a vacuum desiccator over

* If the addition is completed too rapidly the product will be of small particle size and less pure. On filtration it tends to form a red gum.

‡ Calculated on the basis of a maximum of 1g of each isomer from 2g of racemic starting material.

calcium chloride. Yield 1.04g (35%). A 0.1% solution gave $[\alpha]_D$ + 140.

Calcd. for $l[Co(C_2H_8N_2)_2(C_2O_4)]d[Cr(C_{12}H_8N_2)(C_2O_4)_2]$

C, 39.10 ; H, 3.57 ; N, 12.43%

Found C, 39.07 ; H, 3.47 ; N, 12.38%

The diastereoisomer (1g) was ground in a chilled mortar with 10mls of 20% potassium iodide solution and the iodide of the resolving agent filtered off, the filtrate being collected in a chilled flask. The residue was washed with 4mls of 20% potassium iodide and cold ethanol (30mls) was added gradually to the filtrate and washings to deposit purple-red crystals. After cooling in ice for 3 mins the product was filtered off and washed three times with 95% ethanol followed by acetone. Yield 0.35g. A 0.1% solution gave $[\alpha]_D$ + 790 and a 0.02% solution gave $[\alpha]_{5461}$ + 1,000.

Calcd. for $dK[Cr(C_{12}H_8N_2)(C_2O_4)_2]4H_2O$

C, 37.00 ; H, 3.10 ; N, 5.39%

Found C, 37.33 ; H, 3.17 ; N, 5.46%

Description of New Compounds:

Both potassium 2,2'-bipyridine dioxalato chromate(III) (a) and potassium 1,10-phenanthroline dioxalato chromate(III) (b) crystallise from aqueous alcohol in purple-red needles or rhombs. The active are more soluble than the racemic forms and racemise rapidly in water at ordinary temperatures. The half lives for racemisation are about 50 mins at 25°C. (see later). In the solid state both complexes did not racemise over a period of three months and they were unaffected by light. Their conductivities in aqueous solution were respectively (a) 105 mhos, (b) 94 mhos; corresponding to 1 : 1 electrolytes.

Aqueous solutions of the complexes appear stable to acid but are rapidly decolourised by 1N alkali.

CHAPTER FIVE

5.0 MONO COMPLEXES OF 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE.

In this work particular interest lay in mono bipyridine and phenanthroline complexes of nickel(II). Not only are they used as starting materials in the preparations of the mixed complexes studied but also they are present during the dissociation of the tris species. In addition to nickel, new mono compounds of Cr(III), Mn(II), and Fe(II) are described. Since a review[77] on phenanthroline and bipyridine complexes appeared not long ago it is relevant here to summarise the subsequent literature on mono complexes of the transition elements. By current usage of the term, mono compounds are taken to mean coordination compounds that contain one molecule of a bi-or tridentate ligand. The other coordination positions of the metal may be occupied by water or simple anionic groups such as chloride. It is convenient to discuss the elements under the heading of the first member of the group concerned.

5.01 SCANDIUM AND TITANIUM GROUPS.

No mono complexes are known for these elements.

5.02 VANADIUM GROUP.

A red-brown compound of the formula $[VO\ Cl_3\ bipy]$ containing a weakly held bipyridine has been prepared from $VOCl_3$ and the base in organic solvents such as ethanol.[160] No information was available on the ease of replacement of the different ligands.

5.03 CHROMIUM GROUP.

The carbonyl complex $[Cr(CO)_4\ phen]$, has been prepared from $[Cr(CO)_3(NH_3)_3]$ and phenanthroline.[157a] It decomposes in air forming chromium hexacarbonyl. Similar Mo and W complexes are known.[157b,c,d]

5.04 MANGANESE GROUP.

The paramagnetic $[Mn(CO)_3(phen)]$ complex and also the binuclear $[Mn_2(CO)_8(phen)]$ have been described.[162]

The Re(1) complex $[Re(CO)_3(phen)Cl]$ is known[161] and may be prepared from $[Re(CO)_4NH_3Cl]$ and phenanthroline in alcoholic solution. Recently the red Re(III) mono complex $[Re(phen)Cl_3]$ was reported.[213] It was obtained by chlorine oxidation of the deep-purple binuclear $[(phen)Re_2Cl_4]$. The last mentioned complex was thought to contain both Re(I) and Re(III).

5.05 IRON GROUP.

The Fe(II) complex $[Fe(bipy)Cl_2]$ has been made by the action of heat on the tris material in vacuo[118] but a similar method failed to prepare $[Fe(phen)Cl_2]$. In the present work the mono complexes $[Fe\ B\ Cl_2]$ (where B = bipy, phen or trpy) have been prepared. A discussion of these compounds is given in section 5.16.

Iron II and III mono complexes of the formulae $K_2[Fe(B)(CN)_4]$ described some years ago by Barbieri[164] have recently been investigated and their magnetic properties and spectra studied[163], (B=phen or bipy). They were prepared from the bis iron(II) complex $[Fe(B)_2(CN)_2]$ by prolonged treatment with excess potassium cyanide. Any unchanged bis complex was removed by chloroform extraction before evaporating down the remaining solution to yield the dark orange product. The acid forms were obtained by treating the potassium salt with cold HCl. The Fe(III) complexes were obtained by chlorine oxidation of the corresponding Fe(II) compounds. The evidence for some of these substances was not always convincing. For example, no mention was made of an alternative analysis for the trivalent iron complex $[Fe(phen)_2(CN)_2][Fe(phen)(CN)_4]$ namely $[Fe(phen)_3](Fe(CN)_6]$. Conductivity measurements should

distinguish between the two possibilities.

A yellow complex, $[Fe(phen)Cl_3]$, was obtained when ferric chloride and the base were mixed in non-aqueous solvents.[144,145] The high-spin tetraethylammonium salt of the $[Fe(phen)Cl_4]$ ion has been isolated from acetone-dioxane solvent and had a magnetic moment of 5.9 B.M. corresponding to five unpaired electrons.

Spectrophotometric evidence for the existence of the $[Ru(bipy)]^{3+}$ ion in aqueous solution has recently appeared.[154] The mono complex $H[Ru\ Cl_4B]$[172] (B = bipy or phen) has been used to prepare a number of mixed complexes of the type $[Ru(bipy)(phen)_2]^{3+}$. The bidentate group remains firmly bound under a variety of conditions while the Cl^- ligand can be replaced e.g. Ru(II) and (III) complexes were described in which Cl^- had been replaced by Br^-, OH^-, H_2O, py., and acetylacetone.

Analogous Os(III) and (IV) complexes were known[136] but in general the Cl^- groups in the osmium complexes were not as labile as in the ruthenium counterparts and the variety of compounds prepared was not as large.

5.06 COBALT GROUP.

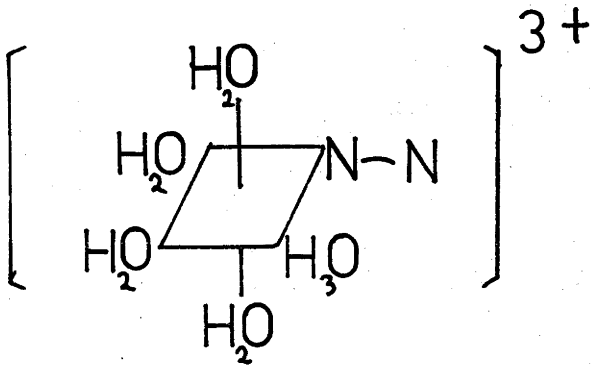
Paglia has prepared cobalt(II) complexes having the formula $[Co(bipy)(CN)_2]$[165] and $[Co(phen)(NO_2)_2]$.[166] Recent exchange studies on the $[Co(phen)]^{2+}$ ion in aqueous solution showed a half-life for ligand exchange of about 1 min. at room temperatures. Also the dissociation of the phenanthroline ligand was catalysed by both acid and base but the mechanism was not investigated.

5.07 NICKEL GROUP.

A study of the dissociation of the $[Ni(phen)]^{2+}$ ion using radioactive nickel[121] showed that rate of loss of the ligand was not very different from the rate of dissociation of the $[Ni(phen)_3]^{2+}$ ion to the bis complex. In the same work the blue solid $[Ni(phen)(H_2O)_4](NO_3)_2$ was prepared by mixing phenanthroline with an excess of nickel nitrate in concentrated aqueous solution. The last mentioned compound had been reported earlier[151] but its existence questioned.[77]

An investigation into the effects of ring substitution on the rates of dissociation of mono nickel(II) phenanthroline and bipyridine complexes has been made by Ellis, Hogg, and Wilkins.[152] For phenanthrolines containing substituents in the 5 position there was a general correlation between dissociation rate constant and the base strength of the ligand. When the substituent was in the 2 position, the dissociation rate increased by a factor of 50 for a methyl group and 1000 for a chloro group. Further, the increased rate arose mainly from a lower activation energy. The results were interpreted for the methyl group in terms of a steric effect. Thus the bonds present were thought to be weaker as the methyl prevented close approach of the phenanthroline nitrogen. On the other hand, steric arguments alone could not account for the even larger increase produced by the chloro group. An additional effect on the metal ligand pi bond was suggested in which the chlorine in the 2 position disrupted the double bond and so accelerated the rate. For 2 chlorophenanthroline the activation energy for dissociation was 7 kcal less than that for the unsubstituted phenanthroline molecule.

The formation rate constant of the $[Ni(phen)]^{2+}$ ion has been shown to increase up till about 0.5N acid and then remain steady. Both the formation and dissociation rates have been studied in acid solution and two mechanisms proposed to account for the hydrogen ion dependence.[149] One, considers protonation of a water molecule in an intermediate formed during stepwise addition of a phenanthroline, viz.



Fast elimination of H_3O^+ would lead to the acid dependence. The second proposal considered the direct reaction of the phenanthrolinium ion with the aquo nickel(II) ion. A half-bonded intermediate was proposed similar to that above except that the proton was attached to the free nitrogen and subsequently was lost before forming the mono complex. Both proposals could account only qualitatively for the acid dependence.

Two forms of $[Ni(phen)(CN)_2]$ have been described.[168] A yellow compound $[Ni(phen)(CN)_2]H_2O$ resulted when potassium cyanide was added to an ice-cold equimolar mixture of aqueous nickel acetate and phenanthroline. If the same reaction was carried out on the steam-bath, lavender $[Ni(phen)(CN)_2](H_2O)_{0.5}$ was obtained. The yellow form had a magnetic moment of 1.7 B.M. and the lavender 2.3 B.M.. The possible existence of bridged structures was recognised.

5.08 COPPER AND ZINC GROUPS.

The equilibria present in solutions of Cu(II) and either bipyridine or phenanthroline have been investigated potentiometrically.[170] In alkaline solution $[Cu(bipy)(H_2O)_2]^{2+}$ can donate two protons to give $[Cu(bipy)(H_2O)(OH)]^{+}$ and $[Cu(bipy)(OH)_2]^{0}$. The $[Cu(bipy)(H_2O)(OH)]^{+}$ complex was not present in appreciable concentrations but rather the dimeric $[(bipy)Cu\langle^{OH}_{OH}\rangle Cu(bipy)]^{2+}$ predominated.

The formation constants for Ag(1) and Cd(II) bipyridine mono complexes have been measured in aqueous alcohol and aqueous dioxane[171] and found to change with the solvent system used.

5.1 EXPERIMENTAL.

In this work mono complexes of 2,2'-bipyridine and 1,10-phenanthroline with the halides of Cr(III), Mn(II), Fe(III), and Ni(II) have been prepared in good yield by reaction of the base with excess of the anhydrous metal halide in boiling dimethylformamide solution. The Fe(II) complexes which could not be prepared satisfactorily in this manner were made in boiling normal hydrochloric acid and salted out with solid calcium chloride. The same method could be used for Ni(II) and Mn(II) monos but the yields were only 50 per cent of the theoretical values compared with 85 per cent using dimethylformamide. Improved methods for the preparation of bis complexes with these ligands have also been developed.

5.11 MONO COMPLEXES OF Fe(III), Mn(II), Cr(III), Ni(II) HALIDES.

The anhydrous halide of the metal, (1.g.), was dissolved completely in dry dimethylformamide, (10ml). A trace of zinc dust was added to effect dissolution of chromium(III) chloride[182], and the

solution then filtered. Phenanthroline, or bipyridine, (1mol.) was added to the hot solution, which was kept agitated while being refluxed. After about a minute, solid commenced to separate, causing violent "bumping". After ten minutes the mixture was cooled to room temperature, the solid collected and washed with cold dimethylformamide, and then dry ether. At this stage the Fe(III) and Mn(II) complexes were pale yellow, the Cr(III) dark green, and the nickel compounds bright green, and contained a molecule of dimethylformamide. At 150° and 10^{-2}mm the Mn(II), Fe(III), and Ni(II) but not the Cr(III) complex lost the solvent of crystallization. The nickel complex became yellow-green after removal of the dimethylformamide.

Calcd.for $Fe(C_{12}H_8N_2)Cl_3$

C, 42.10 ; H, 2.36 ; N, 8.22%

Found C, 42.17 ; H, 2.34 ; N, 8.01%

Calcd.for $Ni(C_{12}H_8N_2)Br_2$

C, 36.1 ; H, 2.0%

Found C, 36.0 ; H, 2.0%

Calcd.for $Ni(C_{12}H_8N_2)Cl_2$

C, 46.5 ; H, 2.6; N, 9.0%

Found C, 46.1 ; H, 2.6 ; N, 9.0%

Calcd.for $Mn(C_{10}H_8N_2)Cl_2$

C, 42.6 ; H, 2.9 ; Cl, 25.2%

Found C, 42.2 ; H, 3.0 ; Cl, 25.2%

Calcd.for $Mn(C_{12}H_8N_2)Cl_2$

C, 47.1 ; H, 2.6 ; N, 9.2%

Found C, 46.7 ; H, 2.6 ; N, 9.1%

Calcd. for $Cr(C_{10}H_8N_2).Cl_3C_3H_7NO$

C, 40.3 ; H, 3.9%

Found C, 39.7 ; H, 4.1%

Calcd. for $Cr(C_{12}H_8N_2).Cl_3C_3H_7NO$

C, 43.8 ; H, 3.7 ; N, 10.2%

Found C, 43.2 ; H, 3.6 ; N, 10.1%

Calcd. for $Ni(C_{10}H_8N_2)Cl_2$

C, 42.0 ; H, 2.9 ; Cl, 24.9%

Found C, 42.0 ; H, 2.8 ; Cl, 24.5%

Calcd. for $Ni(C_{10}H_8N_2)Br_2$

C, 32.1 ; H, 2.2 ; N, 7.5 ; Br, 42.7%

Found C, 32.3 ; H, 2.2 ; N, 7.4 ; Br, 42.5%

5.12 MONO COMPLEXES OF IRON(II) CHLORIDE.

Iron(II) chloride, 4 hydrate (6g, 1mol.) in hydrochloric acid, (IN., 15ml), was heated at 50°-60° with finely divided iron metal (0.5g) to reduce traces of iron(III) chloride. The mixture was filtered into a test-tube filled with carbon dioxide and containing silver wool, (0.2g). After heating to boiling, the solution was decanted on to the base, (0.1mol. phenanthroline, bipyridine or terpyridine), and carbon dioxide passed through the deeply coloured solution while it was boiled for two minutes. Calcium chloride 6-hydrate (13g) was then added, and immediately rose-red crystals of $[Fe(bipy)Cl_2]$ or $[Fe(phen)Cl_2]$, or purple-red $[Fe(trpy)Cl_2]$, commenced to deposit. After two minutes the product was collected, and washed with absolute ethanol containing a drop of hydrochloric acid, followed by absolute ethanol, and finally peroxide free ether, (yields: $[Fe(bipy)Cl_2]$, 56%; $[Fe(trpy)Cl_2]$, 75%; $[Fe(phen)Cl_2]$, 95%.)

Calcd. for $Fe(C_{10}H_8N_2)Cl_2$

C, 42.4 ; H, 2.9 ; N, 9.9%

Found C, 42.4 ; H, 2.9 ; N, 9.8%

Calcd. for $Fe(C_{15}H_{11}N_3)Cl_2$

C, 50.0 ; H, 3.1 ; N, 11.7%

Found C, 50.0 ; H, 3.2 ; N, 11.4%

Calcd. for $Fe(C_{12}H_8N_2)Cl_2$

C, 46.9 ; H, 2.6 ; N, 9.1%

Found C, 46.9 ; H, 2.6 ; N, 9.1%

5.13 BIS COMPLEXES OF Ni(II) HALIDES.

The anhydrous nickel halide (1mol. c 0.4g) was dissolved in hot dimethylformamide (9mls). The base (2mols.) was added, and on heating under reflux the blue solution turned bright green, and green crystals began to deposit. After 5 minutes heating the mixture was cooled to room temperature and filtered. The filtrate was red in colour showing the presence of the tris complex. The produce was washed with dimethylformamide and finally with dry ether. Yields were 55-65% of the theoretical based on the ligand used.

Calcd. for $Ni(C_{10}H_8N_2)_2Cl_2$

C, 54.4 ; H, 3.7 ; Cl, 16.1%

Found C, 54.1 ; H, 3.7 ; Cl, 16.0%

Calcd. for $Ni(C_{10}H_8N_2)_2Br_2$

C, 45.3 ; H, 3.0 ; N, 10.6%

Found C, 45.4 ; H, 3.2 ; N, 10.5%

Calcd. for $Ni(C_{12}H_8N_2)_2Cl_2$

C, 58.8 ; H, 3.3 ; Cl, 14.5%

Found C, 58.9 ; H, 3.4 ; Cl, 14.5%

Calcd. for $Ni(C_{12}H_8N_2)_2Br_2$

C, 49.8 ; H, 2.9 ; Br, 27.6%

Found C, 49.8 ; H, 3.0 ; Br, 27.5%

5.14 PROPERTIES OF THE NEW COMPOUNDS.

All of the substances prepared were coloured, hygroscopic, crystalline solids. Those made in dimethylformamide separated originally with one molecule of the solvent, which could be removed only by heating at 100-150°C/.02mm. With the exception of the chromium compounds all were readily soluble in water and methanol. The complexes $CrphenCl_3$.dmf and $CrbipyCl_3$dmf were stable at 150/0.2mm.

The presence of dimethylformamide can be readily seen from the infra-red spectrum of the liquid which exhibits a strong peak at 1673 cm^{-1} attributed to carbonyl stretching. The figures overleaf consist of the infra-red curves of the following monocomplexes.

Curve (i) $Ni(phen)Cl_2$.dmf

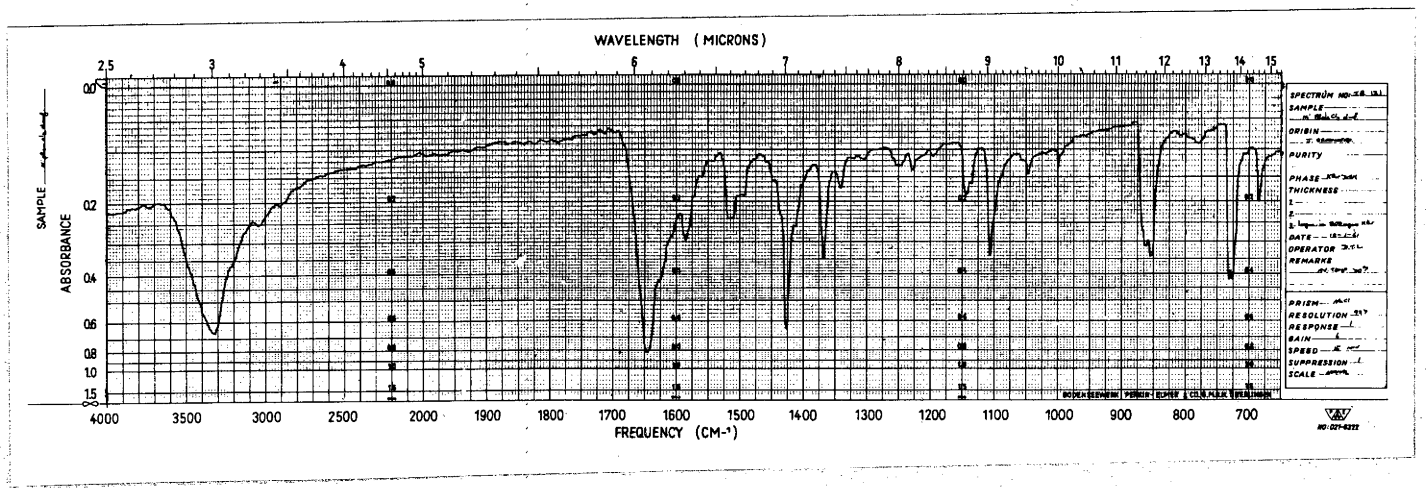
" (ii) $Ni(phen)Cl_2$

" (iii) $Cr(bipy)Cl_3$.dmf

" (iv) $Cr(phen)Cl_3$.dmf

The presence of a carbonyl stretching band, shifted to 1640cm^{-1}, is clearly seen in curves (iii) and (iv). The band is evident at 1645cm^{-1} in curve (i) and is not present in curve (ii). This is consistent with the analytical results on the nickel complexes before and after heating.

The use of the potassium bromide disc technique is known to produce shifts in the infra-red spectrum, but the magnitude of the frequency change observed for the chromium compounds suggests considerable interaction between the dimethylformamide and the metal. This could be a result of complex formation.


WAVELENGTH (MICRONS)
2.5 3 4 5 6 7 8 9 10 11 12 13 14 15
SAMPLE
ABSORBANCE
0.0 0.2 0.4 0.6 0.8 1.0 1.5
4000 3500 3000 2500 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700
FREQUENCY (CM-1)
SPECTRUM NO:
SAMPLE
ORIGIN
PURITY
PHASE
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RESOLUTION
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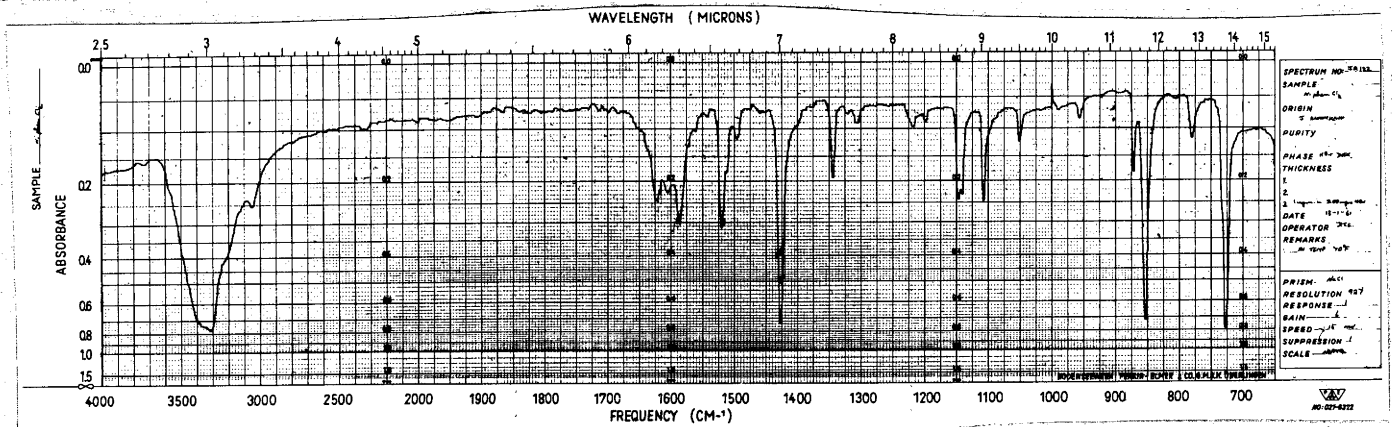
SPEED
SUPPRESSION
SCALE

i


WAVELENGTH (MICRONS)
2.5 3 4 5 6 7 8 9 10 11 12 13 14 15
SAMPLE
ABSORBANCE
0.0 0.2 0.4 0.6 0.8 1.0 1.5
4000 3500 3000 2500 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700
FREQUENCY (CM-1)
SPECTRUM NO:
SAMPLE
ORIGIN
PURITY
PHASE
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RESOLUTION
RESPONSE
GAIN
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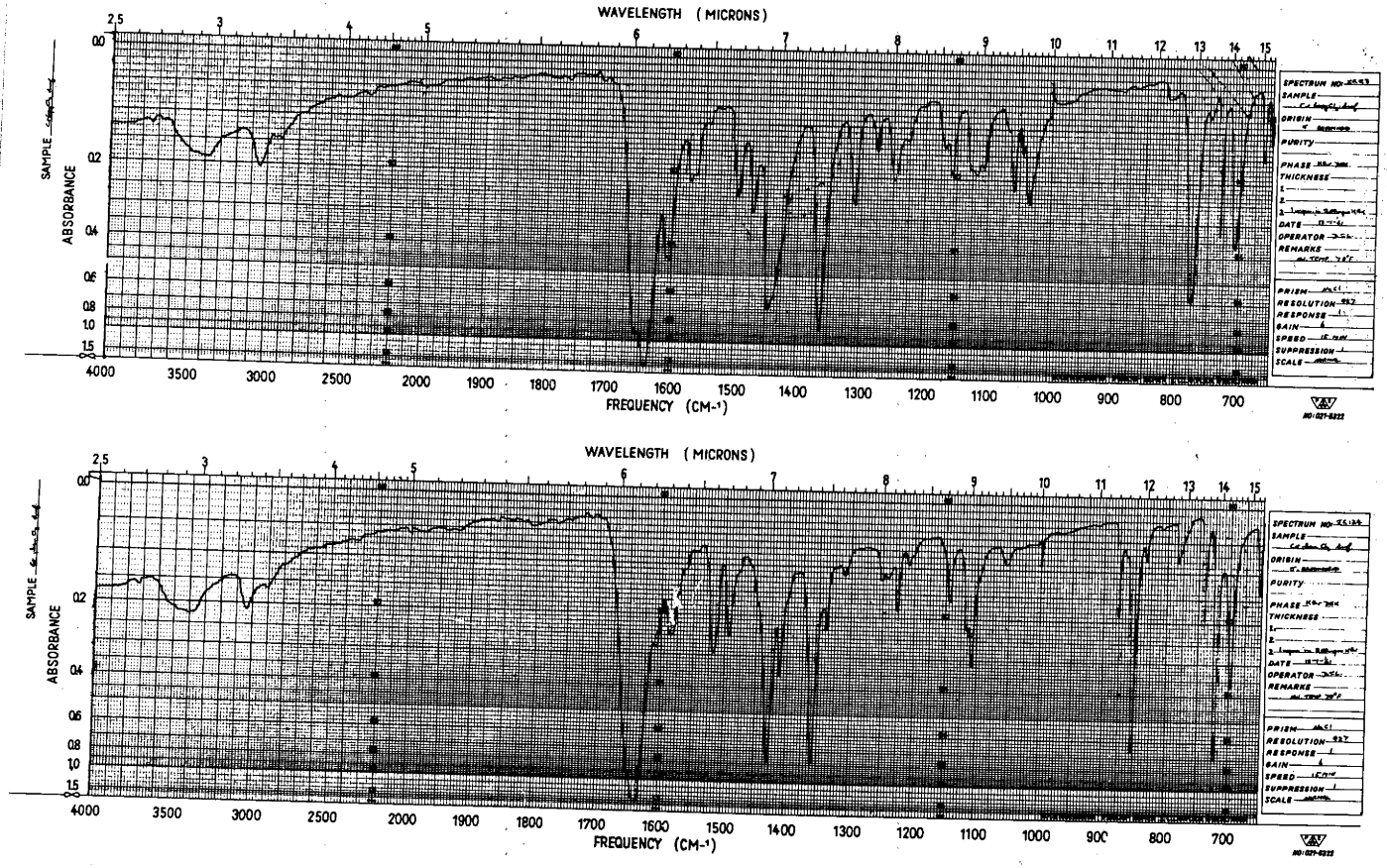
SUPPRESSION
SCALE

ii


WAVELENGTH (MICRONS)
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4
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12
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14
15
SAMPLE
ABSORBANCE
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0.2
0.4
0.6
0.8
1.0
1.5
4000
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3000
2500
2000
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1700
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WAVELENGTH (MICRONS)
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REMARKS
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RESOLUTION
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iii

iv

5.15 MAGNETIC STUDIES.

The magnetic moments of the mono complexes were measured by the Gouy method and calculated from the spin-only formula. The values are recorded below.

Magnetic Moments of Mono Complexes

Substance	(B.M.)	(B.M.) calc.
Cr bipy Cl_3 dmf.	3.77	3.88
Cr phen Cl_3 dmf.	3.72	3.88
Mn bipy Cl_2	5.87	5.92
Mn phen Cl_2	5.83	5.92
Ni bipy Cl_2	3.29	2.83
Ni bipy Br_2	3.52	2.83
Ni phen Cl_2	3.34	2.83
Ni phen Br_2	3.33	2.83
Fe bipy Cl_2	5.72	4.90
Fe phen Cl_2	5.79	4.90
Fe trpy Cl_2	4.60	4.90

5.16 DISCUSSION.

It is well known that whereas the hydrated iron(II) ion is paramagnetic, the tris phenanthroline and bipyridine complexes are diamagnetic, and it is of theoretical interest to determine where the change from high- to low-spin occurs. Dwyer and Basolo[119], showed that the blue $[Fe(bipy)_2Cl_2]$ and $[Fe(phen)_2Cl_2]$ were of the high-spin type, but the red $[Fe(bipy)Cl_2]$, obtained from the bis complex by pyrolysis, was found to have a moment of 1.8 B.M.. The expected moment for low-spin planar Fe(II) is 2.8 B.M., and the low moment was ascribed to metal-metal interaction.

The magnetic moments of all substances showed that they were of the high-spin type. The iron(II) compounds, prepared in hydrochloric acid were rose-red in colour, and gave the rather high values of 5.7 B.M. for the bipyridine complex, and 5.8 B.M. for the phenanthroline complex. These are slightly outside the normal range, (5.0-5.5 B.M.) usually observed.[183] Pyrolysis of $[Fe(bipy)_3]Cl_2$ or $[Fe(bipy)_2Cl_2]$ as described by Basolo and Dwyer[119], gave a dark red solid, (μ= 4.8 B.M.). Both the rose-red and dark-red varieties disproportionated rapidly in methanol and water, but the difference in colour was still evident when both varieties were ground up to the same particle size. The substance may well exhibit dimorphism. All attempts to prepare the variety with the low moment, (1.8 B.M.) failed. It is also significant that 2,2',2"-terpyridine dichloro iron(II), $[Fe(trpy)Cl_2]$ was found to have the normal high moment of 4.60 B.M.. It is concluded that the previous value for the iron(II) mono compound is probably in error. It has usually been found that there is a stepwise decrease in the affinity of a metal ion for the progressive addition of ligands[17], but this order is reversed for the iron(II) phenanthroline and bipyridine systems[114,118], and presumably for the terpyridine system. The paramagnetism of both the mono- and bis-complexes confirms the presence of strong ligand field stabilisation in the diamagnetic tris- species, and is consistent with the reversed order of stepwise ligand affinity.

A 5-covalent distorted trigonal bipyramidal structure probably occurs in dichloro-terpyridine iron(II), analogous to the cadmium, zinc, and copper(II) complexes.[184]

CHAPTER SIX

6.0 THE RACEMISATION OF THE 1,10-PHENANTHROLINEBIS (2,2'-BIPYRIDINE) NICKEL(II) ION AND 2,2'-BIPYRIDINEBIS (1,10-PHENANTHROLINE) NICKEL(II) ION.

Without doubt the nickel(II) tris complexes of phenanthroline and bipyridine are ideal for racemisation studies owing to their high molecular rotations coupled with low extinction coefficients in the wavelengths of light used. By employing a thermostatted polarimeter tube, it becomes a simple matter to follow the change in their optical rotations continuously as a function of time. This technique is possible, of course, only if the light itself does not affect the racemisation. In the work to be described the effects of the following on the racemisation rates have been investigated.

(i) Aqueous solution.

(ii) Ionic strength.

(iii) Acid.

(iv) Base.

(v) Excess ligand.

(vi) Extraneous ions.

(vii) Solvent.

The properties of the mixed complexes resembled those of the trisbipyridine nickel(II) ion rather than the tris phenanthroline nickel(II) ion. For example, the racemisation rates at 25°C in water and in IN HCl are compared in the table below. It is seen that the trisphenanthroline complex racemises much more slowly than the others and that the rates increase with the number of bipyridine ligands present. Also the presence of acid considerably enhances the rate but only if a bipyridine ligand is present.

Complex	$10^2 k(min^{-1})H_2O$	$10^2 k(min^{-1})$ IN.HCl
$[Ni(phen)_3]^{2+}$	0.067	rate unchanged by acid
$[Ni(phen)_2(bipy)]^{2+}$	3.32	11.8
$[Ni(phen)(bipy)_2]^{2+}$	7.81	30.8
$(Ni(bipy)_3]^{2+}$	13.6 (ref. 85)	65

In addition, the $[Ni(bipy)(phen)_2]^{2+}$ ion was anomalous in that the usual first order plot of log optical rotation against time did not give a straight line. The presence of a small amount of optically active $[Ni(phen)_3]^{3+}$ ion in the complex was detected and after the rotations were corrected for this, there was no departure from first order kinetics.

The presence of excess ligand has been reported to be without effect on the racemisation of the ions $[Ni(phen)_3]^{2+}$ and $[Ni(bipy)_3]^{2+}$.[89,61] On the other hand, both mixed complexes displayed slower racemisation rates when in an aqueous solution of bipyridine but not when in aqueous phenanthroline. A reinvestigation of the effect of excess bipyridine on the $[Ni(bipy)_3]^{2+}$ ion in aqueous solution showed that the rate was retarded but phenanthroline again had no effect.

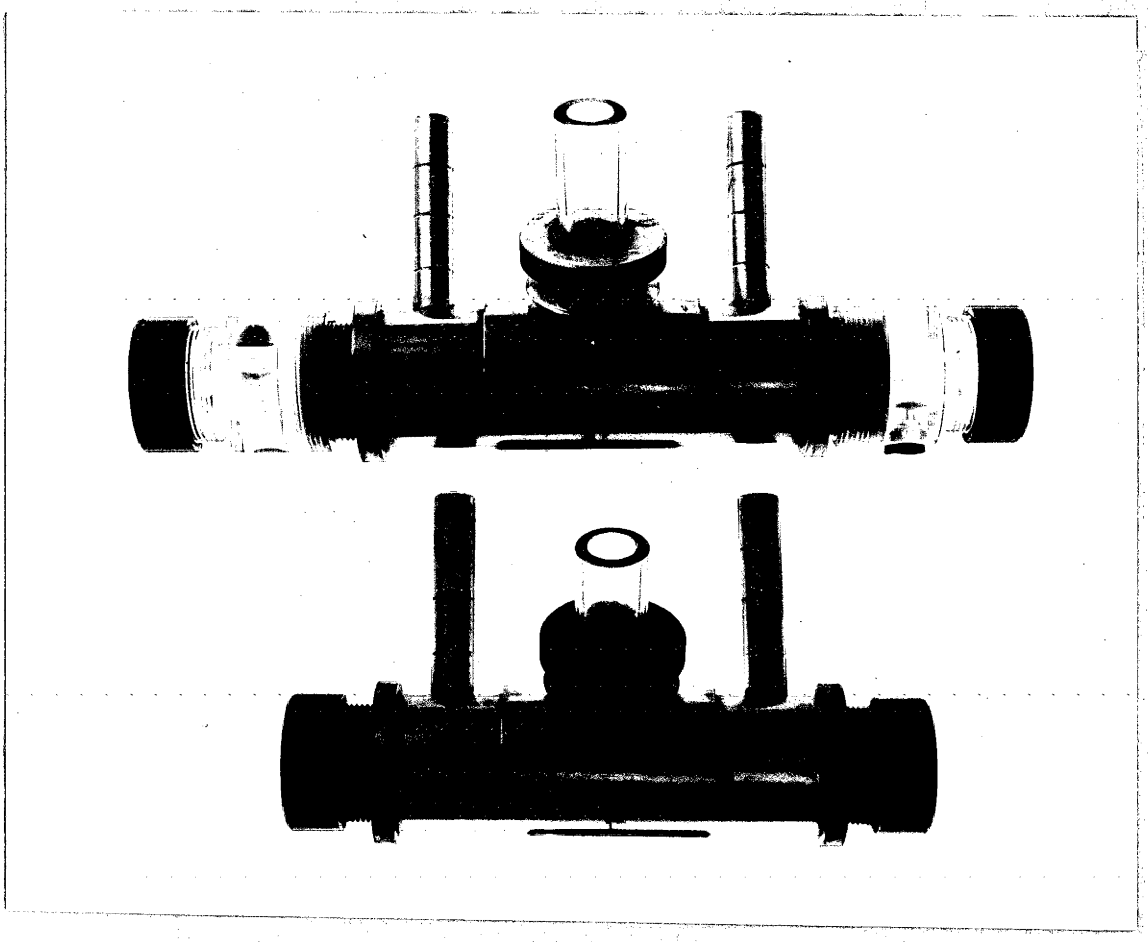
Finally, certain ions such as Cl^- were known to accelerate the racemisation of $[Ni(bipy)_3]^{2+}$ ion and a similar acceleration was found for the mixed complexes.

6.1 EXPERIMENTAL DETAILS - APPARATUS.

A Bellingham and Stanley polarimeter equipped with both mercury and sodium vapour lamps was used. Readings of the rotation could be made to 0.01° with the aid of a vernier. One, two, and four decimetre polarimeter tubes were employed and the temperature was controlled by pumping the water from a constant temperature bath, situated

adjacent to the polarimeter, through the tube jacket. Its temperature at the tube outlet was monitored by means of a thermometer fitted into a well insulated container. In this way, the temperature drop along the tube could be ascertained; the mean value between bath and outlet was recorded as being the temperature of the experiment. The different thermometers employed were calibrated at the National Standards Laboratory, Sydney. Those covering the range 14-30°C were marked in 0.01 degrees while the others used outside this range were marked in 0.02 degree units.

To prevent fogging of the glass windows of the polarimeter tube during the low temperature runs, special double-ends were made. These consisted of perspex extensions to the existing tube, and onto which a second set of glass windows could be screwed. The resulting chamber formed at each end of the polarimeter tube could be dried by inserting a pellet of silica gel, and proved satisfactory in preventing any fogging. A photograph of a tube with double-ends attached appears overleaf alongside that of a second tube having the usual ends.



6.2 EXPERIMENTAL DETAILS - MATERIALS.

All chemicals and solvents employed throughout this work were of analytical reagent quality. The methanol and ethanol were dried by refluxing with calcium metal for 3 hours followed by distillation. The pyridine was also redistilled but the remaining solvents were used without further purification.

The following buffer solutions have been employed in studying the pH dependence of the racemisation rate. Each solution was made to approximately the desired pH and then measured on a Cambridge pH-meter.

No.	pH range	Buffer components	Reference
1	1.81-11.98	H_3PO_4, CH_3COOH and H_3BO_3 titrated with NaOH	177.p365
2	3.56- 5.88	CH_3COOH, CH_3COONa	176.p808
3	6.98	N-Ethyl morpholine (2% $^{v}/_{v}$) titrated with H_2SO_4	-
4	8.06-10.06	H_3BO_3 titrated with NaOH	177.p362
5	0.65- 5.20	HCl, CH_3COONa	176.p808
6	11.82	NaOH, H_3BO_3	177.p364
7	11.75	KH_2PO_4, NaOH	177.p359

6.3 - EXPERIMENTAL DETAILS - METHODS.

To dissolve the nickel complex perchlorate in as short a time as possible it was ground in a mortar with the solvent. The solution obtained was then filtered rapidly and transferred to the polarimeter tube. With runs in which the rates of racemisation were very fast the largest possible initial rotation was secured by first thoroughly chilling all flasks and solvents to be used, since the

rates approximately double for every 5°C rise in temperature. The initial rotations measured were generally within the range of 2-5 degrees rotation, depending upon the time elapsed between solution and measurement. For the slow runs the polarimeter tube plus contents was fully immersed in the constant temperature bath.

With the solution in the polarimeter tube 1-2 minutes generally sufficed before the temperature became constant. This could be decided by the reading of the thermometer at the tube outlet. A reading of the optical rotation was now taken and the stopwatch started at the same time. Sometimes only one reading could be obtained, but if possible four measurements of the rotation were made and the average value recorded. Successive readings were then taken at suitable time intervals. All runs were duplicated unless otherwise stated, and the reaction times were always at least as great as one half-life. The rate constants for racemisation have an accuracy of between 3 and 5% depending on the magnitude and number of measurements possible.

6.4 KINETIC TREATMENT.

Consider an optically active solution. In the process of racemisation one half the optically active molecules invert their configuration. For complete inversion the remainder have also to change, making the rate of racemisation twice the rate of inversion. The process may be represented as follows:

Inversion $\quad d \underset{k_i}{\overset{k_i}{\rightleftharpoons}} l \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$

k_i = inversion rate constant

Racemisation $\quad d \underset{k_r}{\overset{k_r}{\rightleftharpoons}}$ inactive stage $\underset{k_r}{\overset{}{\rightleftharpoons}} l \quad \ldots(2)$

k_r = racemisation rate constant

Let $\quad a$ = initial concentration of active complex

x = amount of antipode formed in time t

Then from (1) $\quad \frac{dx}{dt} = k_i(a-x) - k_i(x)$

$= k_i\,(a-2x)$

Rearranging and integrating $\int \frac{dx}{(a-2x)} = k_i \int dt$

$\frac{-1}{2}\ln(a-2x) = k_i t + \text{constant}$

When $t = 0$, $x = 0$, and the integration constant becomes $\frac{-1}{2}\ln a$

Thus $\quad \frac{-1}{2}\ln(a-2x) = k_i t - \frac{1}{2}\ln a$

$\ln(a-2x) = -2k_i t + \ln a$

$= -k_r t + \ln a \text{ (since } k_r = 2k_i)$

That is $\quad \log (a-2x) = \frac{-k_r}{2.303} t + \log a$

Since α_t, the observed rotation at any time t, is proportional to $(a-2x)$ then a plot of $\log \alpha_t$ on the y axis against t on the x axis should give a straight line of slope $\frac{-k_r}{2.303}$, characteristic of such a first order process. Thus $k_r = 2.303m$, where m = slope.

The temperature dependence of a reaction rate is expressed by the well known Arrhenius formula -

$k = Ae^{\frac{-Ea}{RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$

k = reaction rate constant

A = Arrhenius factor (also called the frequency factor or PZ factor)

Ea = Energy of activation

R = Gas constant

T = Absolute temperature

By taking logs of this relationship we obtain -

$$\ln k = \ln A^{\frac{-Ea}{RT}}$$

$$\text{or } \log k = \log A^{\frac{-Ea}{2.303RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Thus provided log A and Ea can be considered as temperature independent quantities a plot of log k versus $\frac{1}{T}$ gives a straight line of slope $\frac{Ea}{2.303R}$.

Whence $Ea = 2.303\ R \times \text{slope}$ ($R = 1.987$ cal/deg.mole)

$= (4.577 \times \text{slope})$ calories

By substituting a set of values for log k and Ea at a particular temperature, log A can be found.

The entropies of activation have been calculated using the experimentally determined value of log A, and the following formula derived from the theory of absolute reaction rates.[179]

$$k_r = \left\{Ke\ \frac{kT}{h}\ e^{\frac{\Delta S^{\ddagger}}{R}}\right\} e^{\frac{-Ea}{RT}} \quad \ldots\ldots\ldots\ldots(3)$$

Where k = Boltzmanns constant (1.380×10^{-16} ergs/deg-mole)

h = Planck's constant (6.624×10^{-27} erg-sec)

K = The transmission coefficient which allows for the possibility that not all activated complexes which reach the top of the energy barrier will form products.

$\Delta S^{\ddagger}$ = The entropy change between reactants and the activated complex.

The terms inside the brackets in (3) are identified with the A of the simple collision theory. That is -

$$A = Ke\ \frac{kT}{h}\ e^{\frac{\Delta S^{\ddagger}}{R}}$$

taking logs $\ln A = \ln K + 1 + \ln \frac{kT}{h} + \frac{\Delta S^{\ddagger}}{R}$

putting $K = 1$ and with logarithms to the base 10

$$\log A = \frac{1}{2.303} + \log \frac{kT}{h} + \frac{\Delta S^{\ddagger}}{2.303R}$$

$$\Delta S^{\ddagger} = 2.303R\ (\log A - \log \frac{kT}{h} - 0.4343)$$

Note: In this work the rate constants are in min^{-1} and must be converted to sec^{-1} when calculating $\Delta S^{\ddagger}$.

The kinetic parameters Ea and $\Delta S^{\ddagger}$, which are obtained from a study of the temperature dependence, are generally interpreted to mean the following. Ea represent the minimum energy a molecule must possess in order to take part in a chemical reaction. Common values are 10-30 kcals/mole. If the transition state is disordered compared to the initial state then the $\Delta S^{\ddagger}$ value would be expected to be positive. This increased disorder can ensue from such factors as greater ligand freedom and release of solvent molecules in forming the transition state.[180]

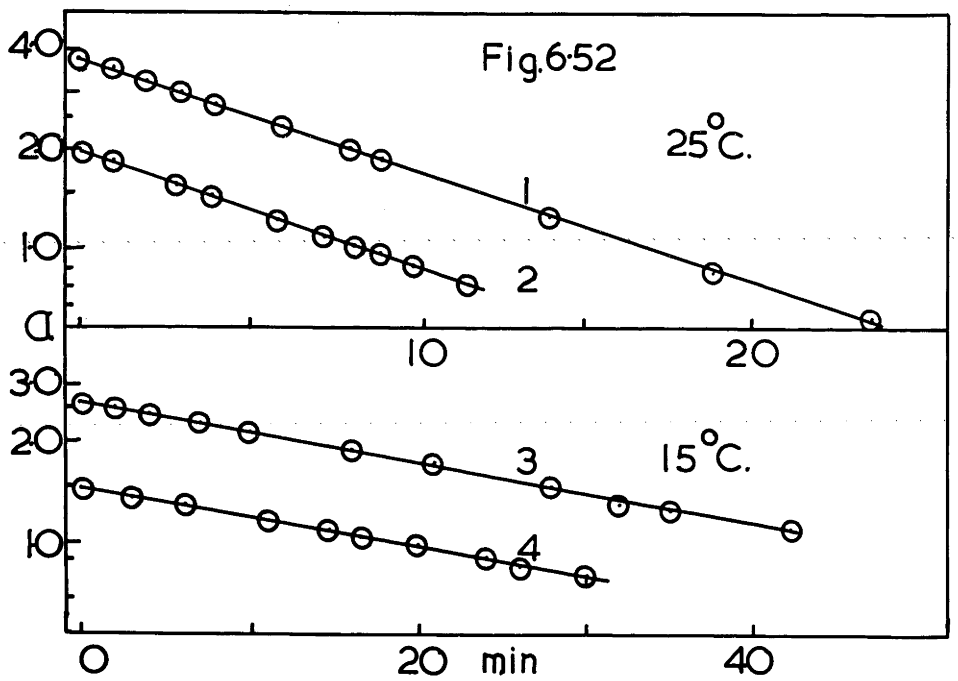
6.5 KINETICS OF RACEMISATION OF 1,10-PHENANTHROLINEBIS (2,2'-BIPYRIDINE) NICKEL(II) PERCHLORATE.

6.51 REACTION ORDER.

By using solutions containing different initial concentrations of complex no significant variation in the rate constants was observed. This behaviour was the same in all the solvents employed. Thus the racemisation followed first order kinetics under all circumstances. This is best shown in the plots below on logarithm ordinate paper of α against time for runs in aqueous solution at different initial concentrations and reaction temperatures.

(1) 0.15% solution at 25°C (3) 0.12% solution at 15°C

(2) 0.08% solution at 25°C (4) 0.06% solution at 15°C



6.52 RACEMISATION IN AQUEOUS SOLUTION.

The primary data from two typical runs at different temperatures are given below. The accompanying plots are in figure 6.521. Their respective slopes are $m = 0.45 \times 10^{-2}$ whence $k_{10^o} = 1.04 \times 10^{-2}$, and $m = 3.39 \times 10^{-2}$ whence $k_{25^o} = 7.81 \times 10^{-2}$ min^{-1}.

Temperature 10°C			Temperature 25°C		
t (mins)	α	logα	t (mins)	α	log α
0	2.61	0.417	0	3.54	0.549
4.5	2.50	0.398	1	3.22	0.508
10	2.30	0.362	2	3.01	0.479
15	2.19	0.340	3	2.76	0.441
21	2.13	0.328	4	2.59	0.413
27.5	1.99	0.299	5	2.38	0.377
33.5	1.85	0.267	6	2.17	0.337
40	1.74	0.241	7.5	1.93	0.285
46	1.64	0.215	8.5	1.82	0.260
55	1.49	0.173	9	1.74	0.241
62	1.38	0.140	9.5	1.67	0.223
72.5	1.24	0.093	10.5	1.55	0.190

The polarimeter tube was often left in the light path throughout a run. Therefore the effect of light on the racemisation rate was checked, as there are known examples where it influences the reaction (see section 2.6). An aqueous solution of the complex was kept in darkness between readings, and the rate constant obtained was identical with that of an exposed solution under the same conditions.

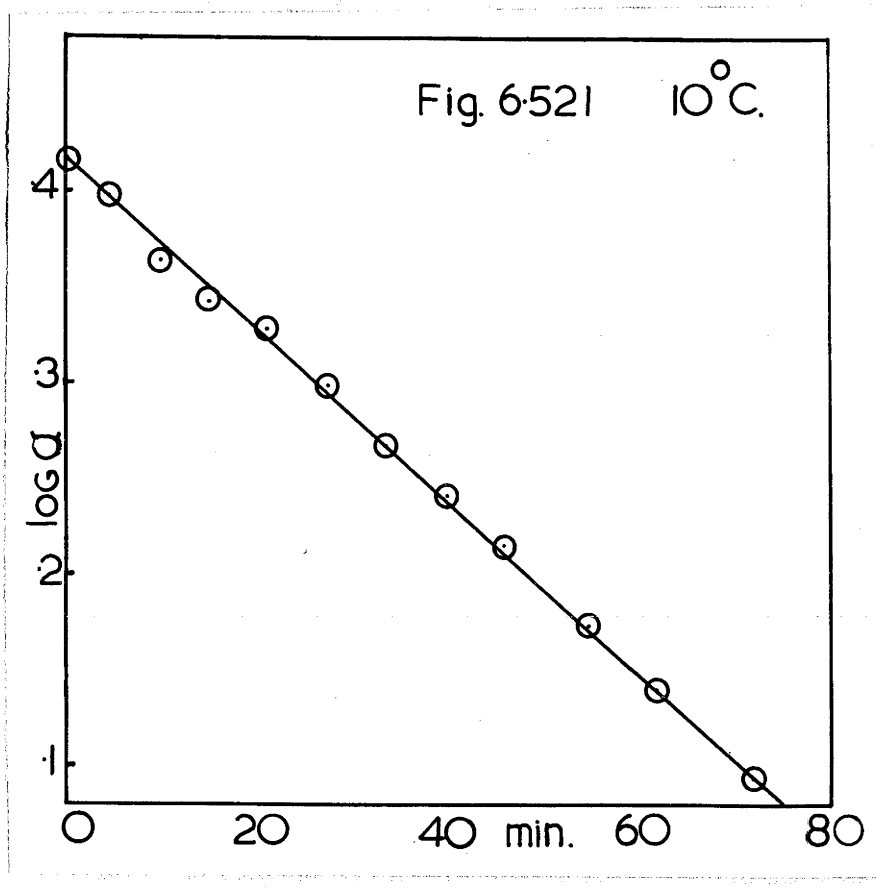


Fig. 6·521
10°C.
4
3
2
1
log a
0
20
40
min.
60
80

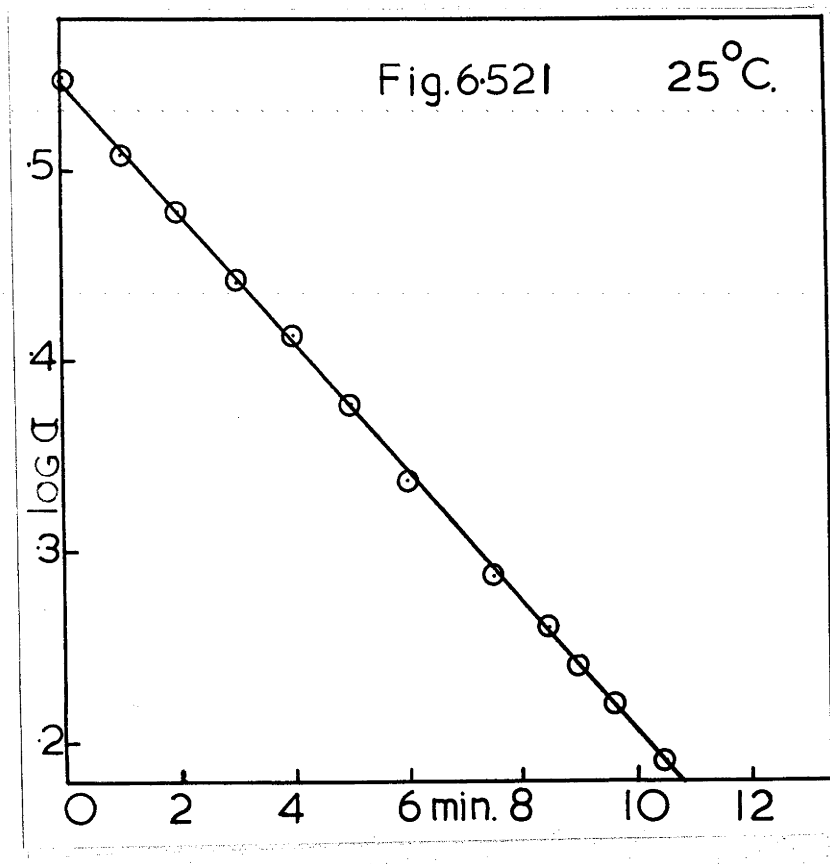
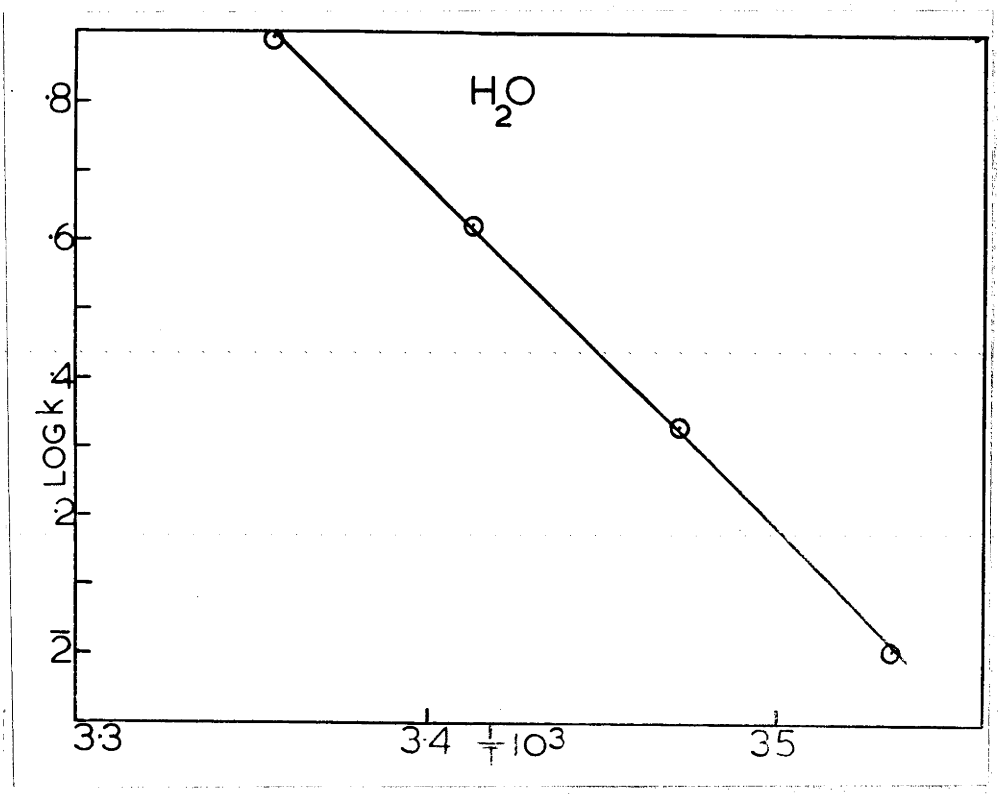


Fig. 6·521
25°C.
5
4
3
2
log a
0
2
4
6
min.
8
10
12

The results of determinations of the rate constants at different temperatures appear below. From the slope Ea = 22.9 kcals, log A = 13.9 sec^{-1}, $\Delta S^{\ddagger}$ = + 3.1 e.u.

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10	283	3.534	1.01	$\bar{2}$.004
15	288	3.472	2.14	$\bar{2}$.334
20	293	3.413	4.17	$\bar{2}$.620
25	298	3.356	7.81	$\bar{2}$.893



6.53 IONIC STRENGTH.

The effect of the ionic strength (μ), was determined in ammonium sulphate solution and the values of the rate constants are given below. Within the experimental accuracy there was no significant dependence. A similar observation had been made for $[Ni(bipy)_3]^{2+}$ ion though the $[Ni(phen)_3]^{2+}$ ion showed an ionic strength retardation.[89]

Solution	Temperature (°C)	$10^2 k(min^{-1})$
H_2O	25	7.81 ± 0.24
H_2O	20	4.17 ± 0.12
$(NH_4)_2SO_4$, $\mu = 1$	25	7.64 ± 0.24
" " "	20	4.02 ± 0.12
" " $\mu = 3$	25	7.42 ± 0.24

6.54 RACEMISATION IN ACID SOLUTION.

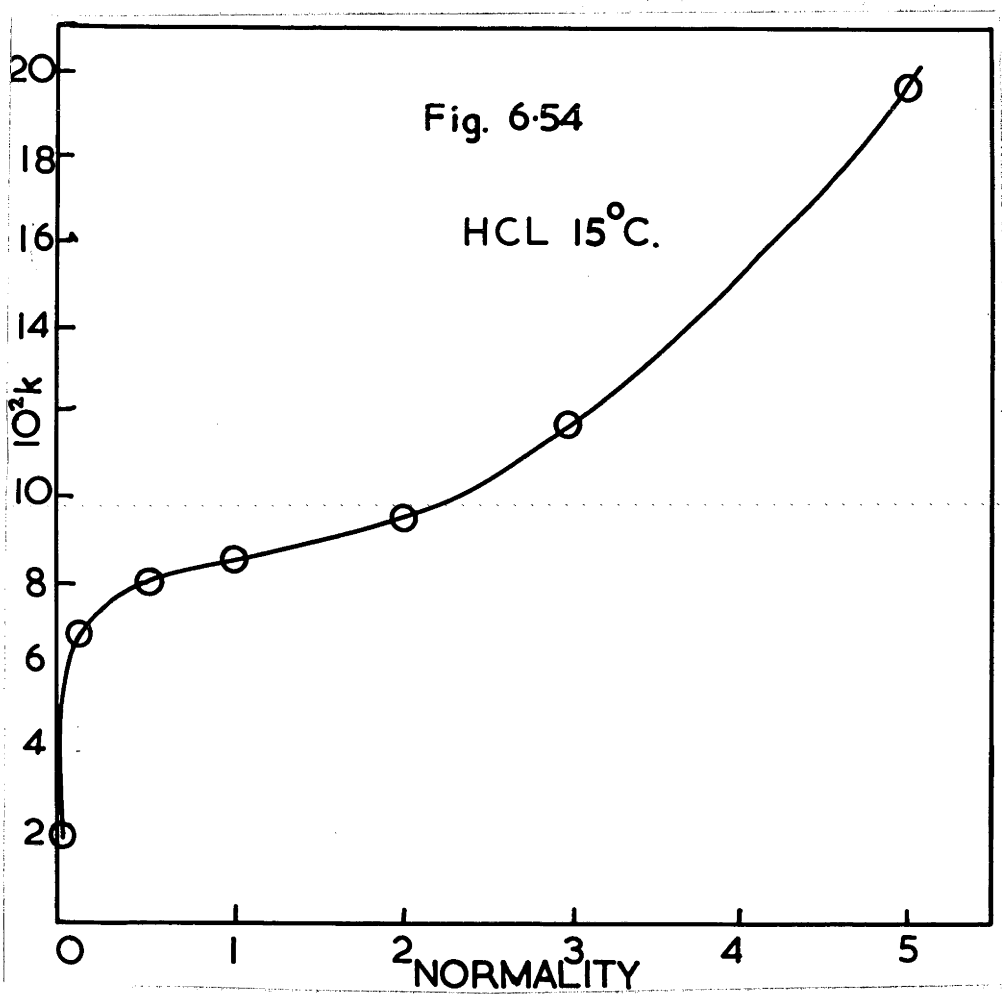
The racemisation rate was increased considerably in acid media, the increase being accompanied by noticeable decolorisation of the solution at the higher acid concentrations (i.e. those greater than 2 normal). The acid dependence was investigated in hydrochloric and sulphuric acids respectively. Table 6.54 gives some results for the former at 15°C. The data are graphed in figure 6.54.

TABLE 6.54

HCl Concentration	$10^2 k\ (min^{-1})$
0.1 N	6.89
0.5 N	8.05
1.0 N	8.56
2.0 N	9.40
2.98N	11.7
5.0 N	19.7
H_2O	2.14

The temperature dependence of the rates has been studied for comparison with dissociation results. The values and kinetic parameters are given in the succeeding pages. It will be seen that the acid acts by lowering the activation energy compared to the value in water, and that there are but slight effects on the entropy term. The temperature dependence graphs are included to show the fit of the data.

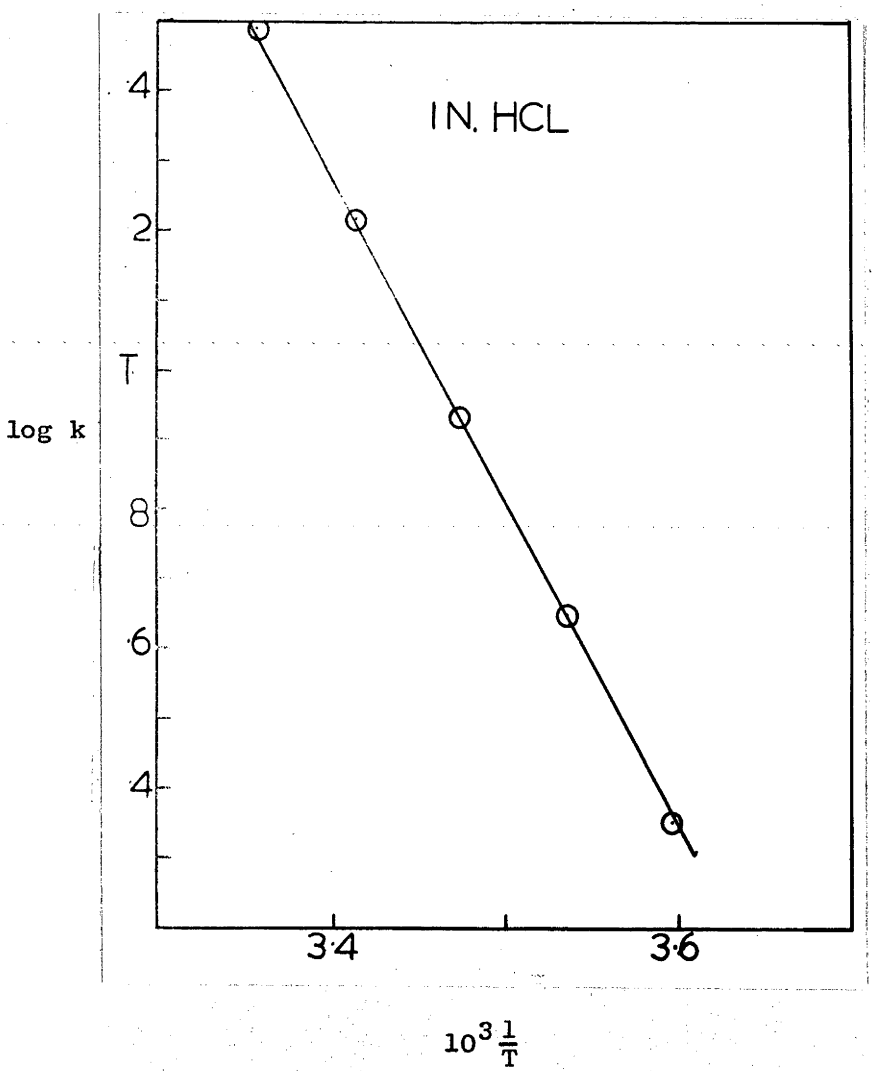
Acid Dependence of $[Ni(phen)(bipy)_2]^{2+}$ at 15°C



The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 1 Normal Hydrochloric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
5.15	278.15	3.595	2.24	$\bar{2}.350$
10.0	283	3.534	4.44	$\bar{2}.647$
15.0	288	3.472	8.56	$\bar{2}.933$
20.0	293	3.413	16.5	$\bar{1}.218$
25.0	298	3.356	30.8	1.489

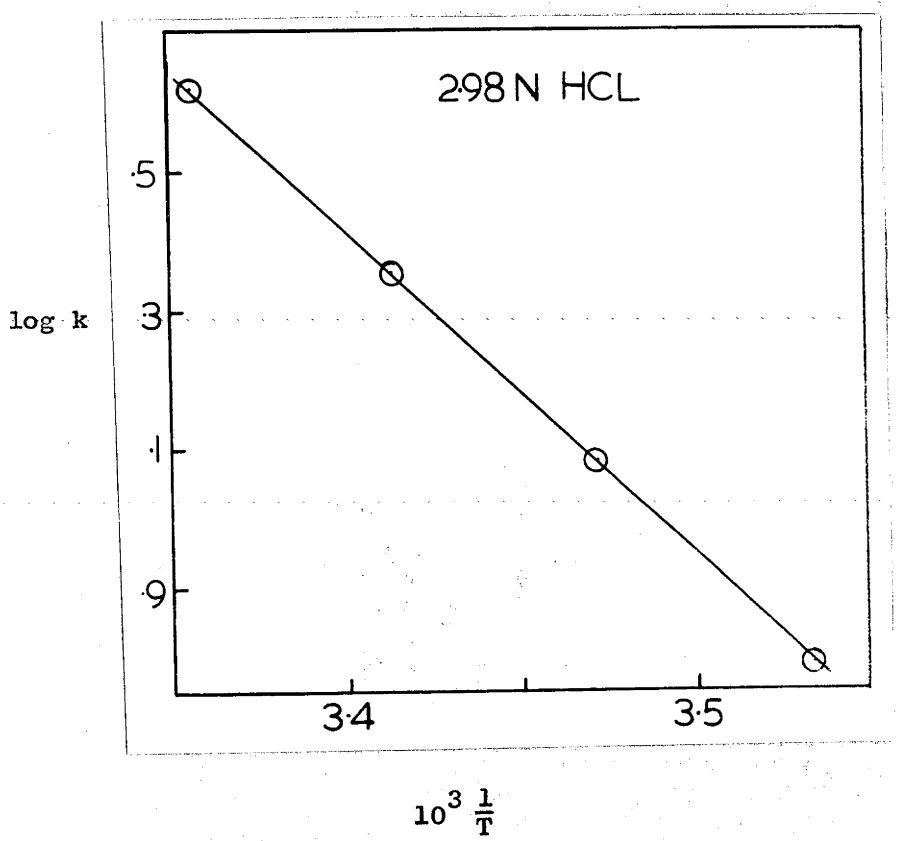
Ea = 21.6 kcals; log A = 13.53 sec^{-1}; $\Delta S^{\neq}$ = + 1.4 e.u.



The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 2.98 Normal Hydrochloric Acid

^{o}C	$T(^{o}K)$	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.0	283	3.534	6.14	$\bar{2}.788$
15.0	288	3.472	12.0	$\bar{1}.079$
20.0	293	3.413	22.4	$\bar{1}.350$
25.0	298	3.356	41.2	$\bar{1}.615$

Ea = 21.2 kcals/mole; log A = 13.36 sec^{-1}; $\Delta S^{\neq}$ = + 0.64 e.u.



The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 5 Normal Hydrochloric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
5.0	278	3.597	5.5	$\bar{2}.740$
10.0	283	3.534	10.3	$\bar{1}.013$
15.0	288	3.472	19.7	$\bar{1}.295$
20.0	293	3.413	36.0	$\bar{1}.556$

Ea = 20.4 kcals/mole; log A = 12.99 sec^{-1}; $\Delta S^{\ddagger}$ = -1.1 e.u.

The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 5 Normal Sulphuric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
5.0	278	3.597	4.82	$\bar{2}.683$
10.0	283	3.534	9.30	$\bar{2}.969$
15.0	288	3.472	17.7	$\bar{1}.248$
20.0	293	3.413	33.5	$\bar{1}.525$

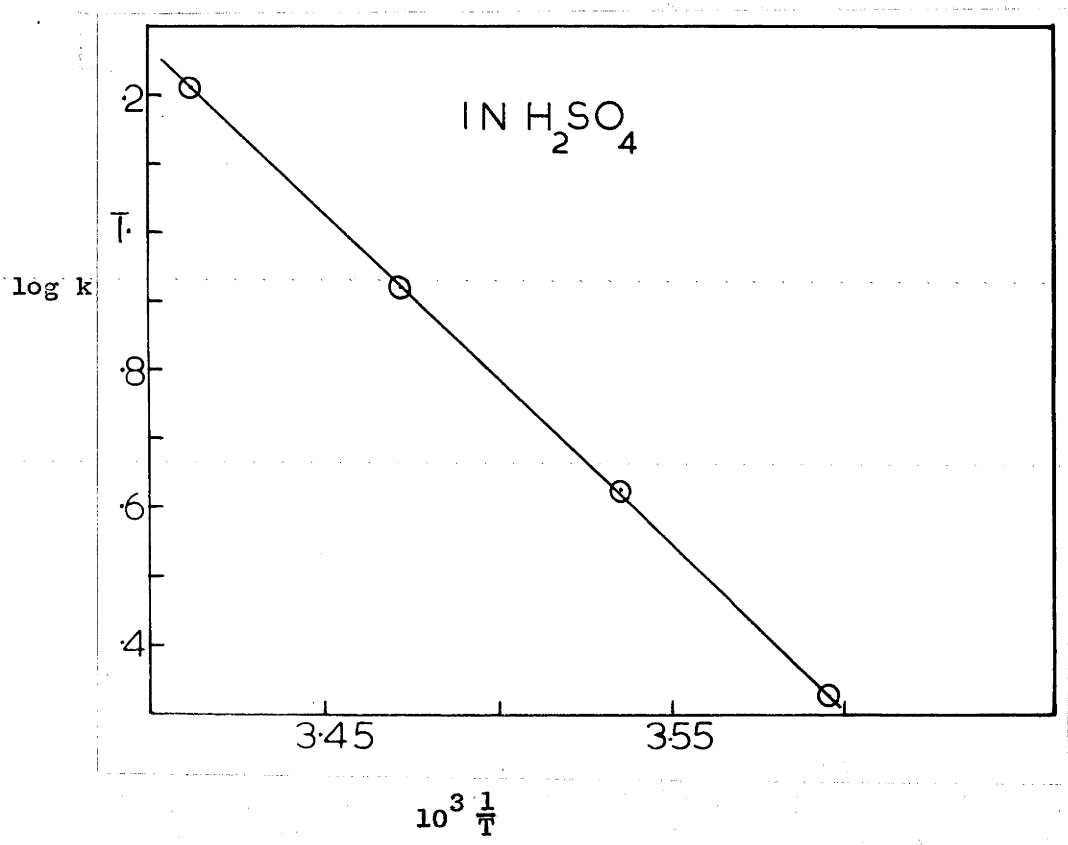
Ea = 20.9 kcals/mole; log A = 13.32 sec^{-1}; $\Delta S^{\ddagger}$ = + 0.46 e.u.

For corresponding graphs see section 7.2.

The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 1 Normal Sulphuric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
5.15	278.15	3.595	2.12	$\bar{2}.326$
9.9	282.9	3.535	4.22	$\bar{2}.625$
15.0	288	3.472	8.29	$\bar{2}.919$
20.0	293	3.413	16.3	$\bar{1}.212$

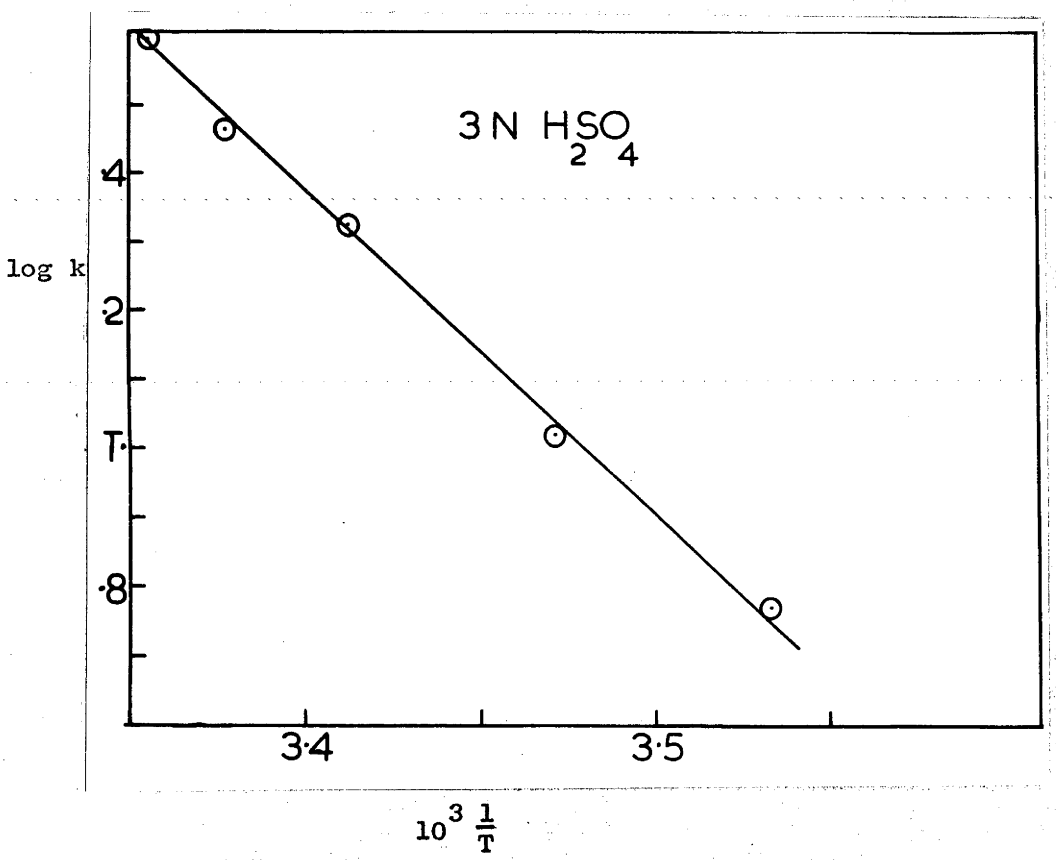
Ea = 22.3 kcals/mole; log A = 14.08 sec^{-1}; $\Delta S^{\neq}$ = + 3.9 e.u.



The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 3 Normal Sulphuric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.0	283	3.534	5.87	$\bar{2}.769$
15.0	288	3.472	10.4	$\bar{1}.017$
20.0	293	3.413	21.1	$\bar{1}.323$
23.0	296	3.378	29.0	$\bar{1}.462$
25.0	298	3.356	39.4	$\bar{1}.596$

Ea = 21.4 kcals/mole; log A = 13.53 sec^{-1}; S = + 0.46 e.u.



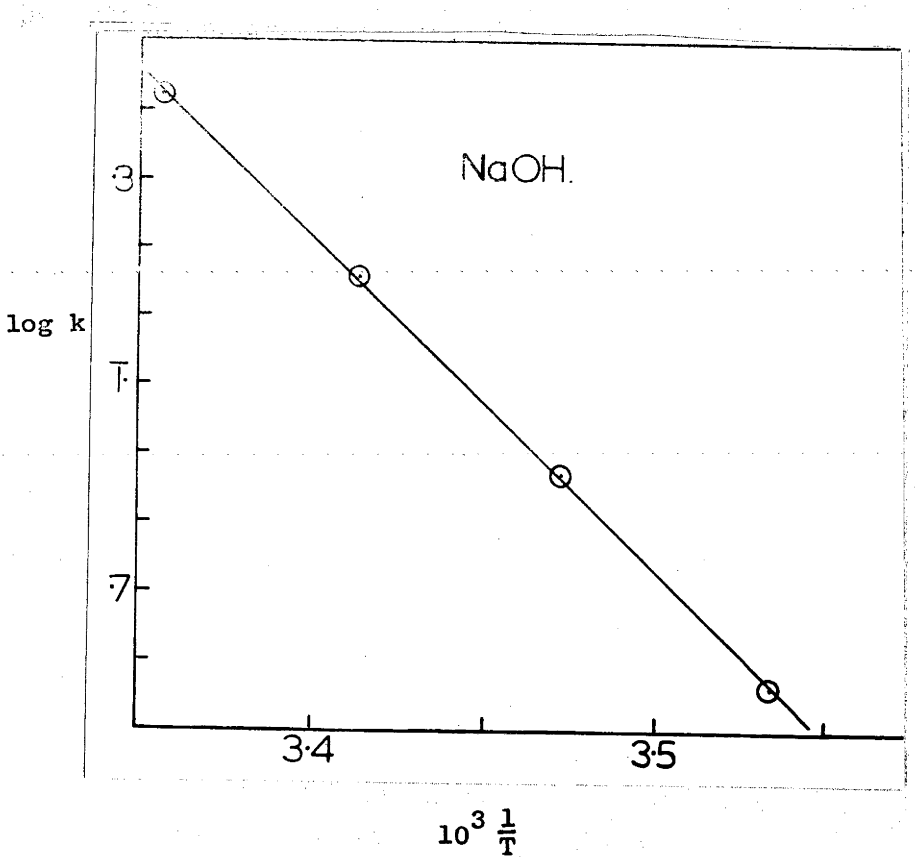
6.55 RACEMISATION IN BASIC SOLUTION.

Sodium hydroxide increases the racemisation rate over that in water. Thus $k(H_2O$ at $20^oC) = 4.17 \times 10^{-2}$ min^{-1} while $k(0.098N$ NaOH at $20^oC) = 14.5 \times 10^{-2}$ min^{-1}. The rate increased with the hydroxide ion concentration and the temperature dependence studies show that the increased rate was accompanied by a lower activation energy. The results are given overleaf.

The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 0.098 N Sodium Hydroxide Solution

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.0	283	3.534	3.68	$\bar{2}.566$
15.0	288	3.472	7.49	$\bar{2}.875$
20.0	293	3.413	14.5	$\bar{1}.161$
25.0	298	3.356	26.3	$\bar{1}.420$

Ea = 22.0 kcals/mole; log A = 13.78 sec^{-1}; $\Delta S^{\ddagger}$ = + 2.6 e.u.

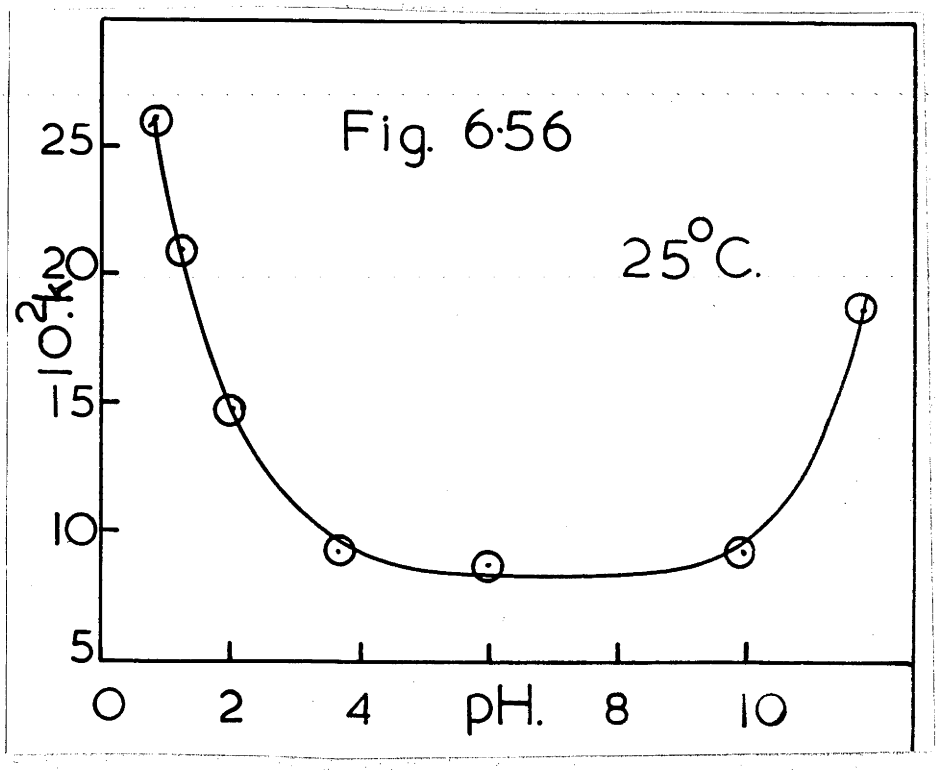


6.56 THE EFFECT OF pH.

Buffer solutions as described in section 6.2 were employed and determinations of the rate at 25°C over the pH range 0.9-11.8 made. Figure 6.56 illustrates the results which are given in Table 6.56.

TABLE 6.56

Buffer solution number (see 6.2)	pH	$10^2 k(min^{-1})$
5	0.90	26.0
5	1.46	21.0
1	2.20	14.9
2	3.56	8.5
1	6.04	9.0
4	10.06	8.7
1	11.50	15.8
6	11.82	18.5



6.57 THE EFFECT OF EXCESS LIGAND.

In water, the racemisation rate was retarded by excess 2,2'-bipyridine but not by excess 1,10-phenanthroline. For instance, at a ligand concentration of 0.005 M and complex concentration of 0.002 M the 2,2'-bipyridine reduced the rate constant from $(7.81 \pm .24).10^{-2}$ to $(7.20 \pm .24).10^{-2}$ min^{-1} at 25°C. Under similar conditions 1,10-phenanthroline was without effect. The same was true at 10°C. Table 6.57 and Figure 6.57 give the temperature dependence of the racemisation for a 0.002 M aqueous solution of complex which was 0.023 M with respect to 2,2'-bipyridine (points enclosed by circles). The points for racemisation in water (shown by a dot) and in saturated phenanthroline (shown by a cross) are also included in Figure 6.57.

TABLE 6.57

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	$10^3 k(min^{-1})$ H_2O	log k (excess bipy)
10.0	283	3.534	8.55	10.1	$\bar{3}.932$
15.0	288	3.472	17.1	21.4	$\bar{2}.233$
20.0	293	3.413	34.6	41.7	$\bar{2}.539$
24.8	297.8	3.358	65.5	-	$\bar{2}.816$

It appears that the observed retardation in the racemisation rate arises from a simple mass law retardation.

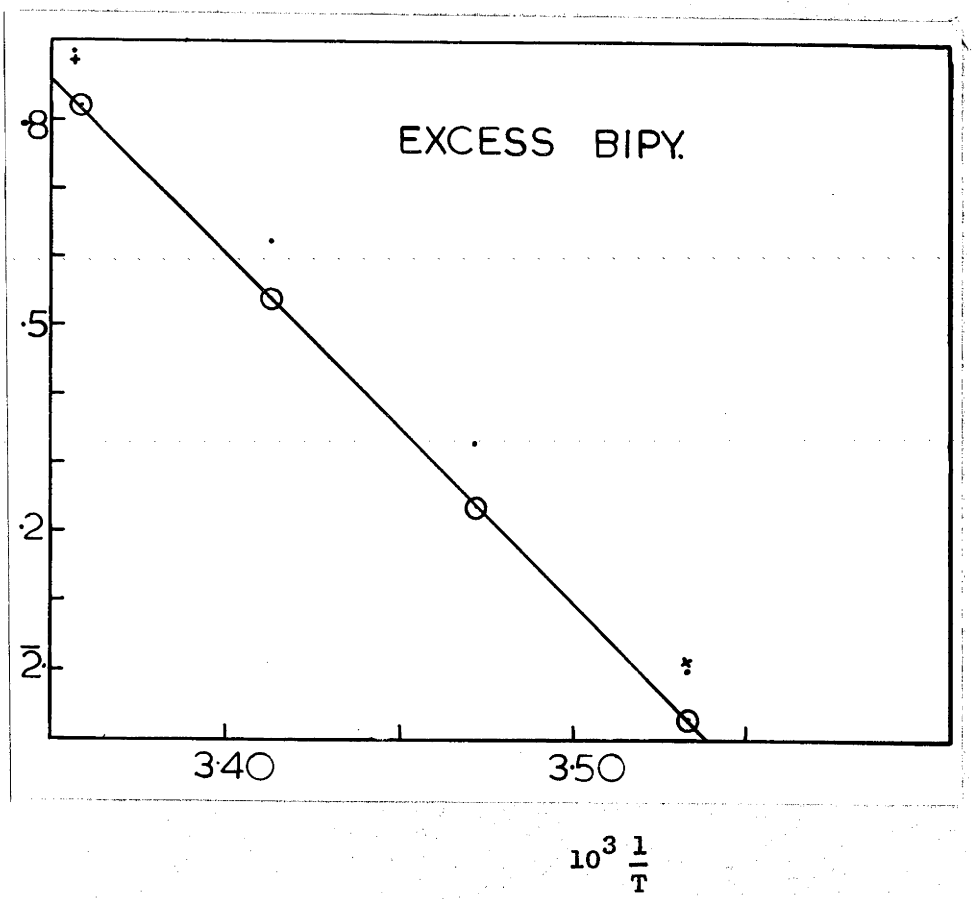
The effect of excess ligand was also studied for certain organic solvents. In formamide, nitrobenzene, and 60% mole fraction ethanol–water no change in the rate constant with excess ligand was observed. However, in 11.8% mole fraction ethanol-water a retardation by bipyridine was found. The results overleaf are for a temperature

of 25°C and complex concentration of 0.002 M.

Although the rate in the presence of excess phenanthroline is lowered the extent is not significant.

11.8% mole fraction ethanol-water (containing a 20:1 ratio of ligand to complex)	$10^2 k(min^{-1})$	$10^2 k(min^{-1})$ (without excess ligand)
bipy present	5.31 ± 0.20	7.11 ± 0.20
phen present	6.81 ± 0.20	7.11 ± 0.20

FIGURE 6.57



6.58 THE EFFECTS OF EXTRANEOUS IONS.

Nickel(II) sulphate (0.16 M) was without effect on the racemisation rate. Chloride ions increased the rate of racemisation as the results below demonstrate.

Solution	Concentration	$10^2 k(min^{-1})$ at 25^oC
NH_4Cl	2 M	9.55
"	1 M	9.41
"	0.5 M	9.10
H_2O	-	7.81

6.6 THE EFFECT OF SOLVENT CHANGES.

All the organic solvents tried reduced the rate of racemisation compared to that in water, the greatest effects being observed with solvents of low coordinating ability. e.g. Nitrobenzene reduced the rate constant at 25^oC from 7.8×10^{-2} min^{-1} in water to 1.56×10^{-4} min^{-1}, while formamide reduced it to 2.04×10^{-2} min^{-1}. The results and temperature dependence plots for the following solvents are given in the succeeding pages. The alcoholic solvents are shown to change both the energy and entropy terms while the others mainly exert their influence on the entropy. For comparison the values in water only are included.

(i) Methanol (Dried as in section 6.2)

(ii) Ethanol " " " " "

(iii) Pyridine " " " " "

(iv) Formamide

(v) Glacial acetic acid

Note: The complex perchlorate was very soluble in methanol, pyridine, and formamide, but soluble with difficulty in ethanol and glacial acetic acid.

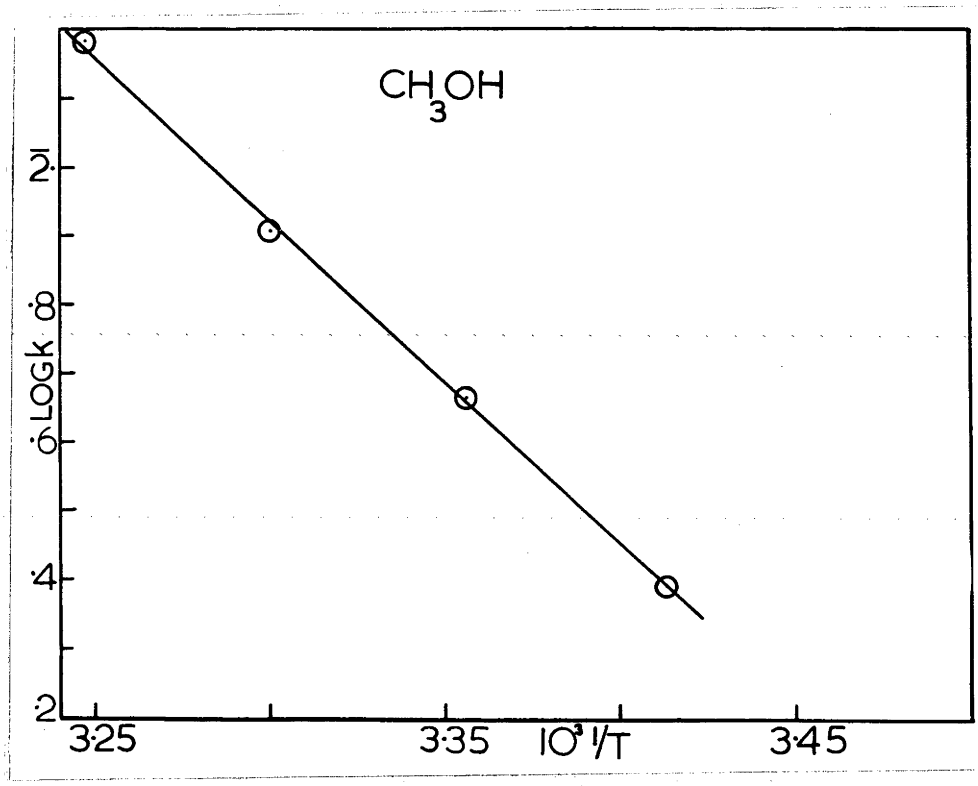
The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in Methanol

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})H_2O$
20.0	293	3.413	0.247	$\bar{3}$.393	4.17
25.0	298	3.356	0.462	$\bar{3}$.665	7.81
30.0	303	3.300	0.805	$\bar{3}$.906	-
35.0	308	3.247	1.53	$\bar{2}$.185	-

Ea = 21.5 kcals/mole; log A = 11.64 sec^{-1}; $\Delta S^{\ddagger}$ = - 7.2 e.u.

In water:

Ea = 22.9 kcals/mole; log A = 13.90 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.1 e.u.



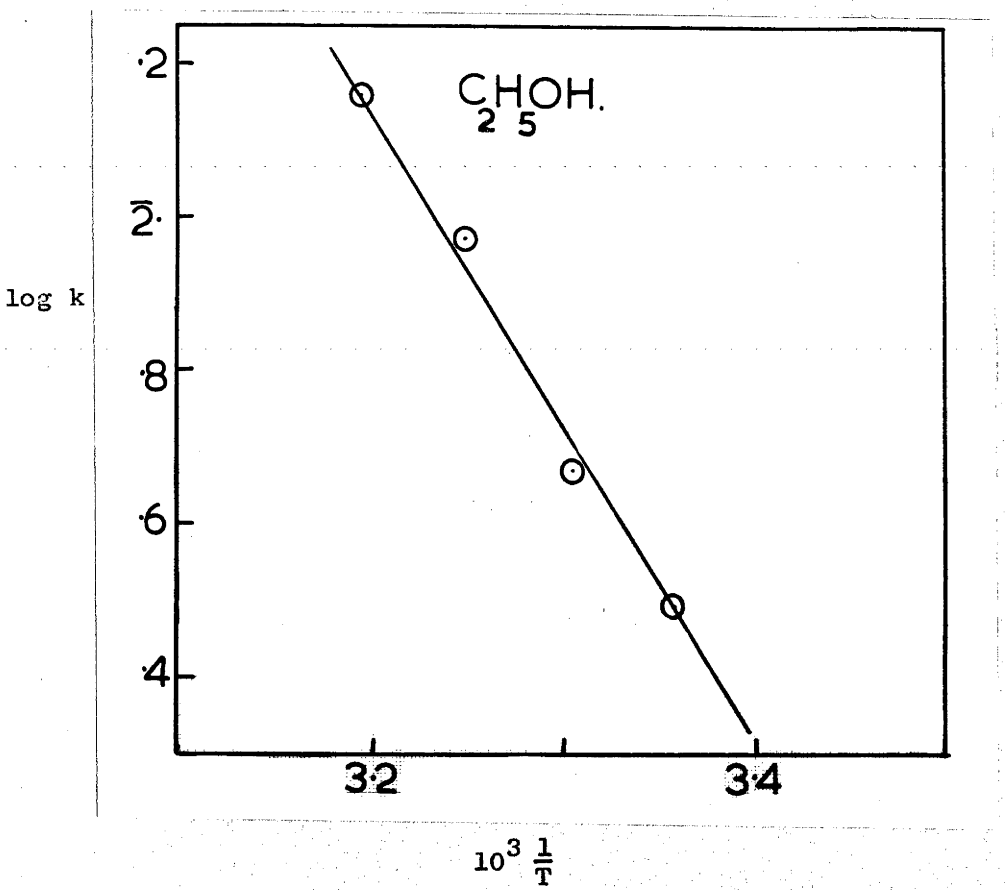
The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in Ethanol

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})H_2O$
25.0	298	3.356	0.307	$\bar{3}$.487	7.81
29.8	302.8	3.303	0.459	$\bar{3}$.662	-
34.8	307.8	3.249	0.932	$\bar{3}$.969	-
40.0	313	3.195	1.43	$\bar{2}$.155	-

Ea = 18.9 kcals/mole; log A = 9.58 sec^{-1}; $\Delta s^{\ddagger}$ = -16.7 e.u.

In water:

Ea = 22.9 kcals/mole; log A =13.90 sec^{-1}; $\Delta s^{\ddagger}$ = + 3.1 e.u.



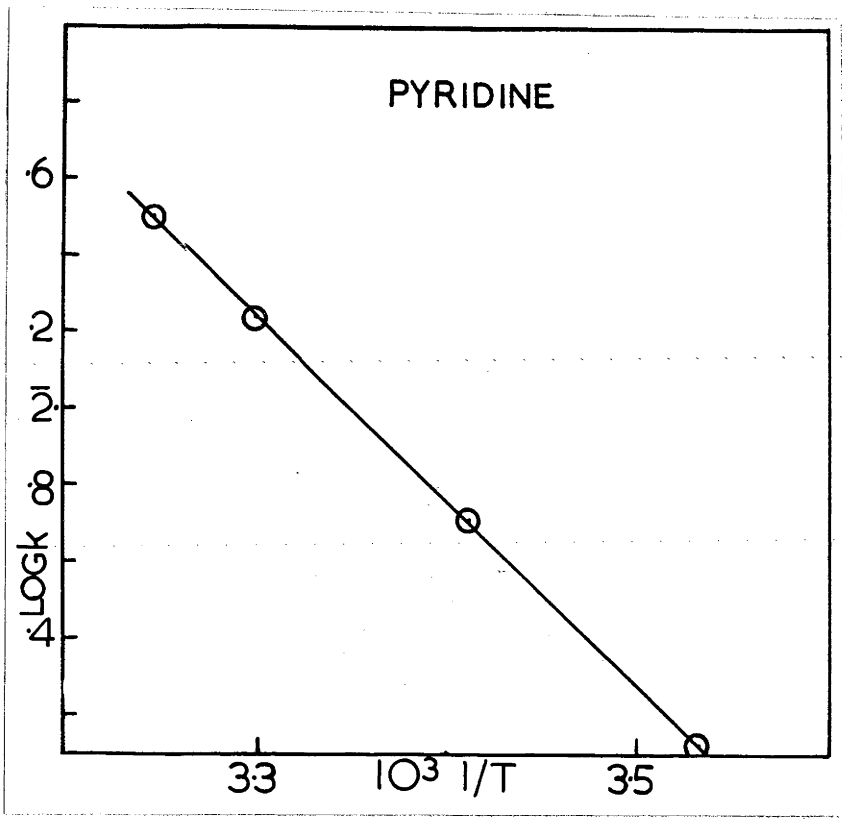
The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in Pyridine

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})H_2O$
10.0	283	3.534	0.133	$\bar{3}.124$	1.01
20.0	293	3.413	0.505	$\bar{3}.703$	4.17
30.0	303	3.300	1.73	$\bar{2}.238$	-
34.8	307.8	3.249	3.19	$\bar{2}.503$	-

Ea = 22.1 kcals/mole; log A = 12.41 sec^{-1}; $\Delta S^{\ddagger}$ = - 3.7 e.u.

In water:

Ea = 22.9 kcals/mole; log A = 13.9 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.1 e.u.



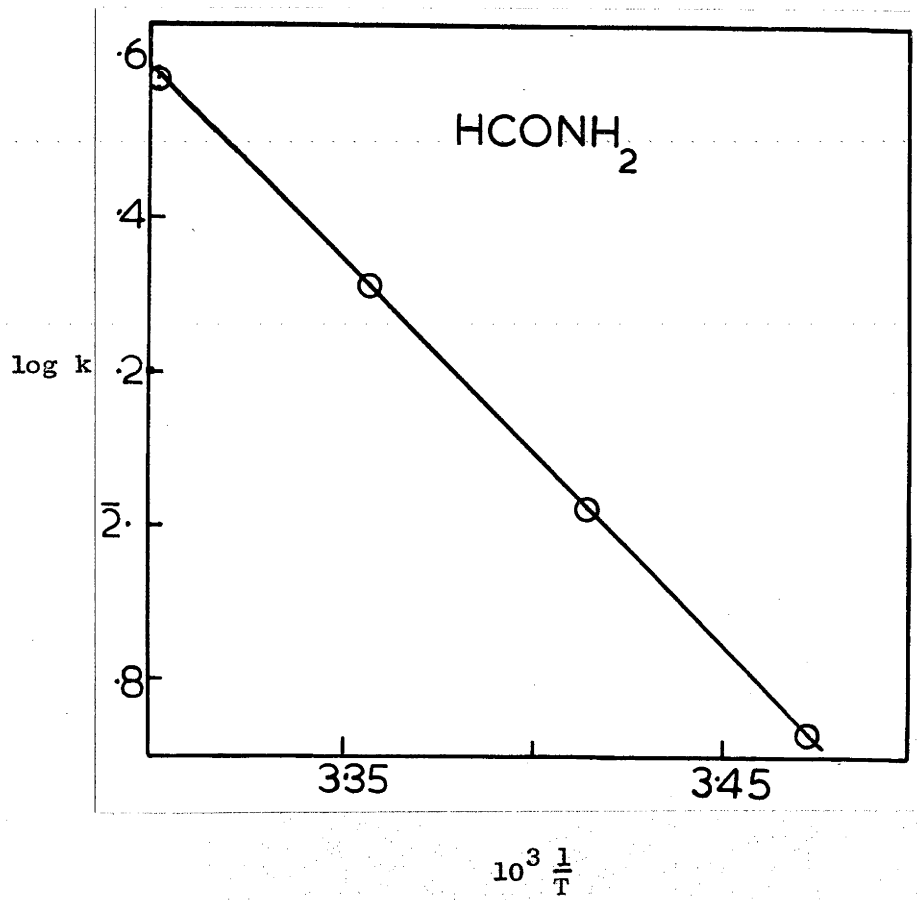
The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in Formamide

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})H_2O$
15.0	288	3.472	0.537	$\bar{3}.730$	2.14
20.0	293	3.413	1.05	$\bar{2}.021$	4.17
25.0	298	3.356	2.04	$\bar{2}.310$	7.81
29.9	302.9	3.301	3.80	$\bar{2}.580$	-

Ea = 22.8 kcals/mole; log A = 13.23 sec^{-1}; $\Delta S^{\ddagger}$ = + 0.1 e.u.

In water:

Ea = 22.9 kcals/mole; log A = 13.9 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.1 e.u.



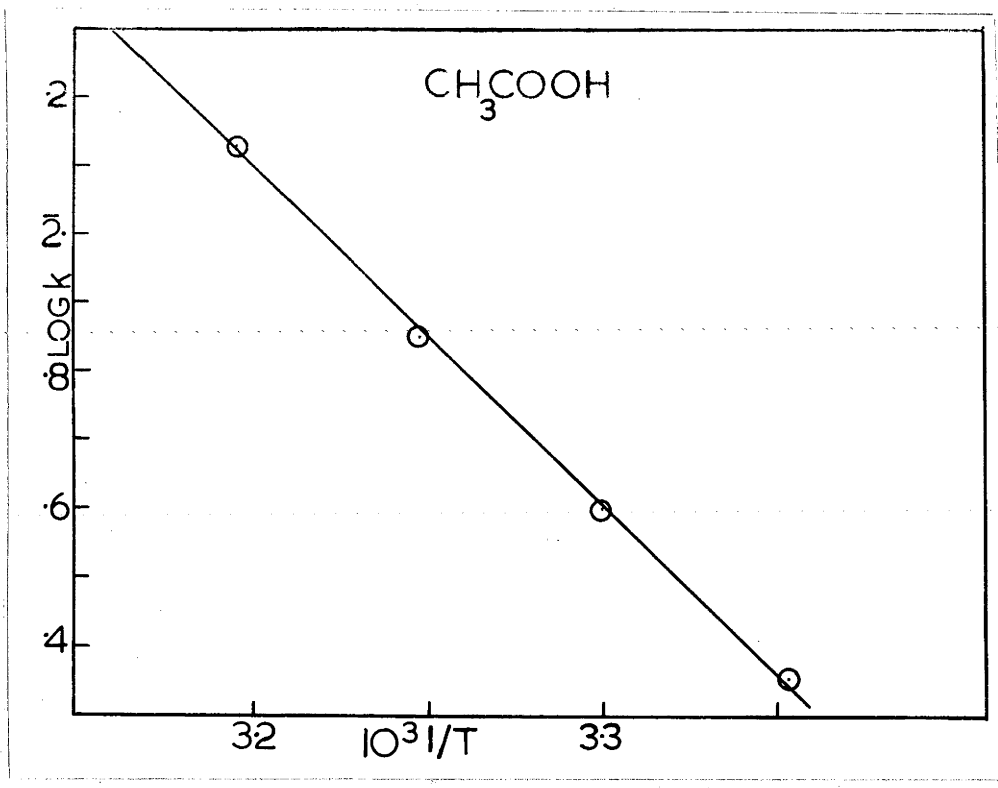
The Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in Glacial Acetic Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k	$10^3 k(min^{-1})H_2O$
25.0	298	3.356	2.26	$\bar{3}.354$	78.1
29.9	302.9	3.301	4.01	$\bar{3}.603$	-
34.8	307.8	3.249	7.10	$\bar{3}.851$	-
39.8	312.8	3.197	13.6	$\bar{2}.134$	-

Ea = 22.3 kcals; log A = 11.90 sec^{-1}; $\Delta S^{\ddagger}$ = - 6.0 e.u.

In water:

Ea = 22.9 kcals; log A = 13.9 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.1 e.u.



6.61 RACEMISATION IN AQUEOUS ETHANOL.

Previous work on the simple tris complexes in aqueous ethanol solutions had shown a peculiar variation in the rate constants with changing percent organic component (e.g. see Fig. 2.4). For $[Ni(phen)(bipy)_2]^{2+}$ the results of the determination of the rate constant at 25°C for various ethanol-water mixtures are shown in Table 6.61. Fig. 6.91 illustrates the data graphically. It is seen that following an initial decrease between 11.8% and 19.7% the rate constant changes very little until the ethanol content reaches 100%. An almost identically shaped curve was obtained in the previous work with the $[Ni(bipy)_3]^{2+}$ ion (see Fig. 6.91).

The temperature dependence of racemisation in the solvent of composition 39.7% mole fraction ethanol-water has been measured; the results are included in Table 6.61. The first effect upon the addition of ethanol is a small increase in the activation energy leading to a slower racemisation. This is followed at high ethanol concentration by a decrease in the activation energy but does not result in an increased rate because at the same time the entropy of activation becomes more negative.

TABLE 6.61

Solvent	$10^2 k(min^{-1})$
H_2O	7.81
11.8% mole fraction ethanol-water	7.11
19.7% " " " "	1.81
39.7% " " " "	1.73
60.6% " " " "	1.72
80.5% " " " "	1.18
Ethanol	0.307

Temperature Dependence in 39.7% Ethanol-Water

^oC	^oK	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k
15.0	288	3.472	4.25	$\bar{3}.628$
20.0	293	3.413	8.76	$\bar{3}.943$
25.0	298	3.356	17.3	$\bar{2}.238$
30.0	303	3.300	32.6	$\bar{2}.513$

Ea = 23.7 kcals/mole; log A = 13.8 sec^{-1}; $\Delta S^{\ddagger}$ = + 2.6 e.u.

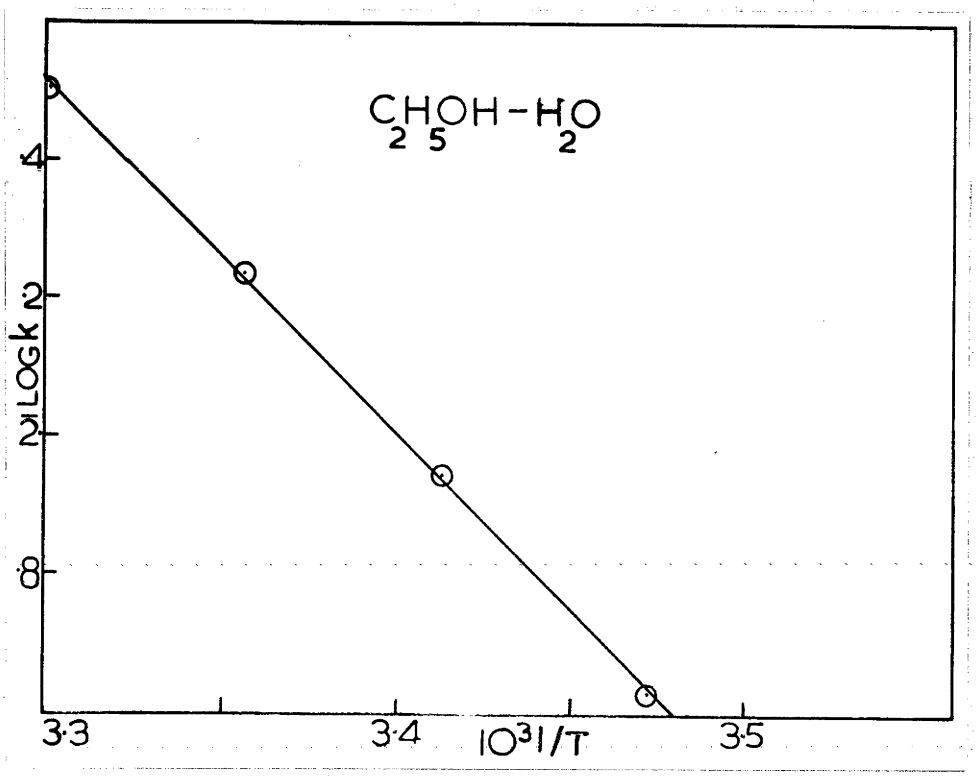
In water:

Ea = 22.9 kcals/mole; log A = 13.9 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.1 e.u.

In ethanol:

Ea = 18.9 kcals/mole; log A = 9.58 sec^{-1}; $\Delta S^{\ddagger}$ = -16.7 e.u.

Temperature Dependence in 39.7% Ethanol-Water



6.7 KINETICS OF RACEMISATION OF 2,2'-BIPYRIDINE BIS (1,10-PHENANTHROLINE) NICKEL(II) PERCHLORATE.

The Order of the Reaction.

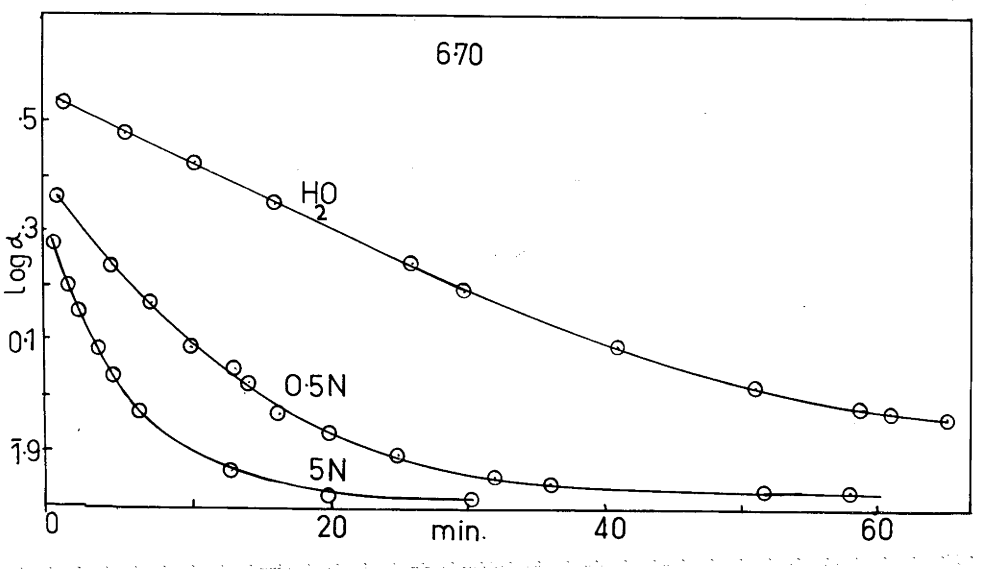
The usual first order plot of log optical rotation versus time did not give a straight line. Instead, a curve was obtained irrespective of whether the solvent was water or acid. In figure 6.70 curve (I) refers to an aqueous solution and curve (2) to 0.5 normal sulphuric acid. Higher acid concentrations gave curves which differ from (2) only in that their initial slopes were steeper and this effect increases with the acid concentration (5N sulphuric acid curve 3). Provided that the initial concentration was kept constant all the curves became coincident at the later portion of the graph.

It is obvious that the analyses given for $[Ni(bipy)(phen)_2]Cl_2$ could also apply to a 1:2 mixture of $[Ni(bipy)_3]Cl_2$ and $[Ni(phen)_3]Cl_2$. Fortunately, the subsequent resolution employed conditions under which only the $[Ni(phen)_3]^{2+}$ ion would yield a precipitate. Thus the optically active perchlorate obtained from the diastereoisomer could contain $[Ni(phen)_3](ClO_4)_2$ in addition to $[Ni(bipy)(phen)_2](ClO_4)_2$. The method of preparation of the latter also makes the tris phenanthroline complex a likely impurity (see section 3.3).

A first order rate constant of 6.4×10^{-4} min^{-1} could be calculated from the later part of the curves in figure 6.70. This was in agreement with the published value of 6.7×10^{-4} min^{-1} [60a] for the $[Ni(phen)_3]^{2+}$ ion. Accordingly, the data were treated using the reasonable assumption that the complex contained a certain amount of optically active $[Ni(phen)_3](ClO_4)_2$. The published values for the

FIGURE 6.70

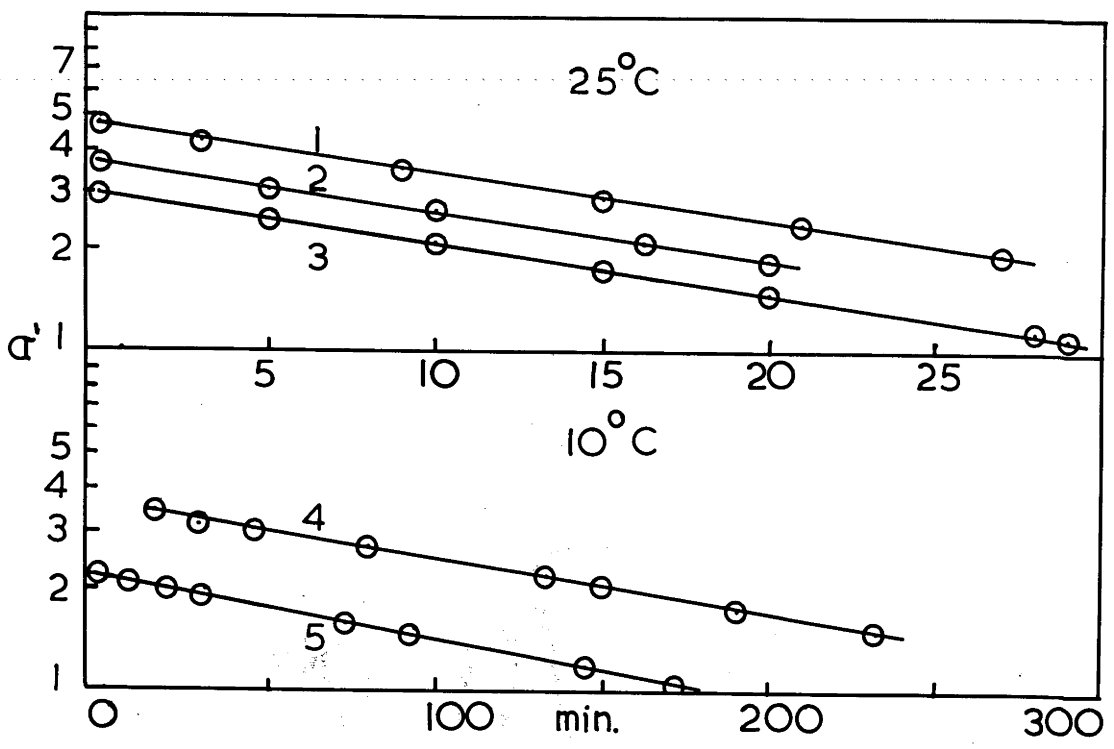
Temperature 25°C



rate constants of the trisphenanthroline compound were used[60a, 89], together with the rotation values at the later times. The value of the initial rotation due to the $[Ni(phen)_3]^{2+}$ ion could then be calculated and was of the order of 0.6 degree for a 0.1% solution in a 4dm tube. A correction (C), was next subtracted from the observed rotations (α), and a plot of $\log \alpha'$ ($= \alpha - C$) against time gave excellent straight lines. In some experiments, it was necessary to allow for the racemisation of the trisphenanthroline complex. For example, in the organic solvents the change in C due to racemisation was appreciable and could be readily calculated at any time t from the usual formula $k = \frac{2.303}{t} \log \frac{C_o}{C}$.

The figure below shows the plots of α' against time on logarithmic ordinate paper at different temperatures and initial concentrations. In the figure, the concentrations are:

(1) 75mg/50ml; (2) and (3) 40mg/50ml; (4) 25mg/50ml; (5) 50mg/50ml.



6.71 RACEMISATION IN AQUEOUS SOLUTION.

The primary data from a typical determination of the racemisation rate constant at 25°C are shown in Table 6.71 and the accompanying first order plot in Figure 6.71. From the slope k is 3.32×10^{-2} min^{-1}.

The kinetic parameters have been evaluated from the measurements of k at different temperatures (Table 6.711), via the slope of the log k versus $\frac{1}{T}$ plot (Figure 6.711)

TABLE 6.71

t(min)	α	$\alpha' = \alpha - 0.65$	$\log \alpha'$
0	4.31	3.66	0.564
2	4.06	3.41	0.533
4	3.89	3.24	0.511
6	3.63	2.98	0.474
8	3.44	2.79	0.446
10	3.25	2.60	0.415
12	3.10	2.45	0.389
14	2.93	2.28	0.358
16	2.78	2.13	0.328
18	2.66	2.01	0.303
20	2.51	1.86	0.270
22	2.39	1.74	0.241
24	2.30	1.65	0.218
26	2.19	1.54	0.188

FIGURE 6.71

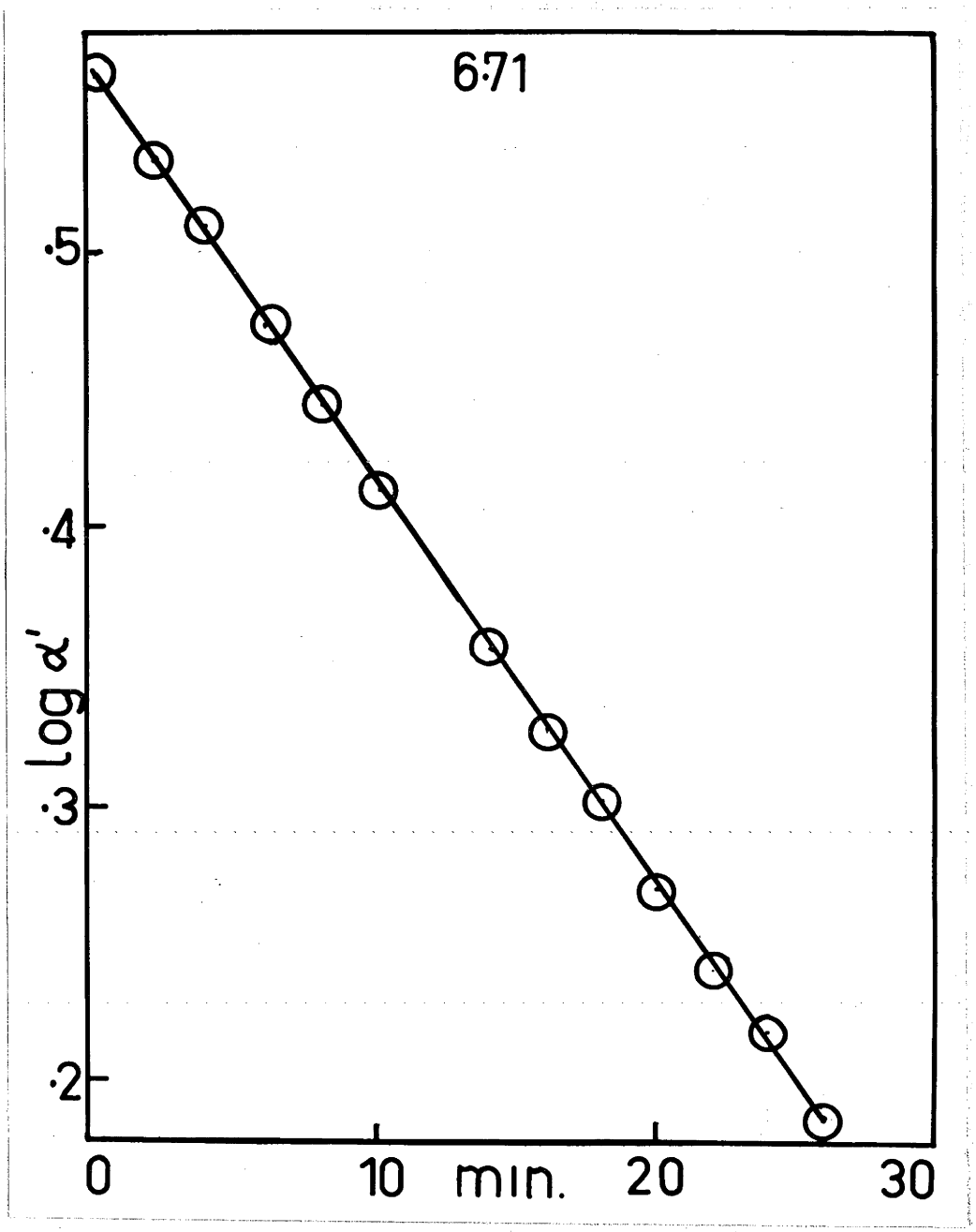


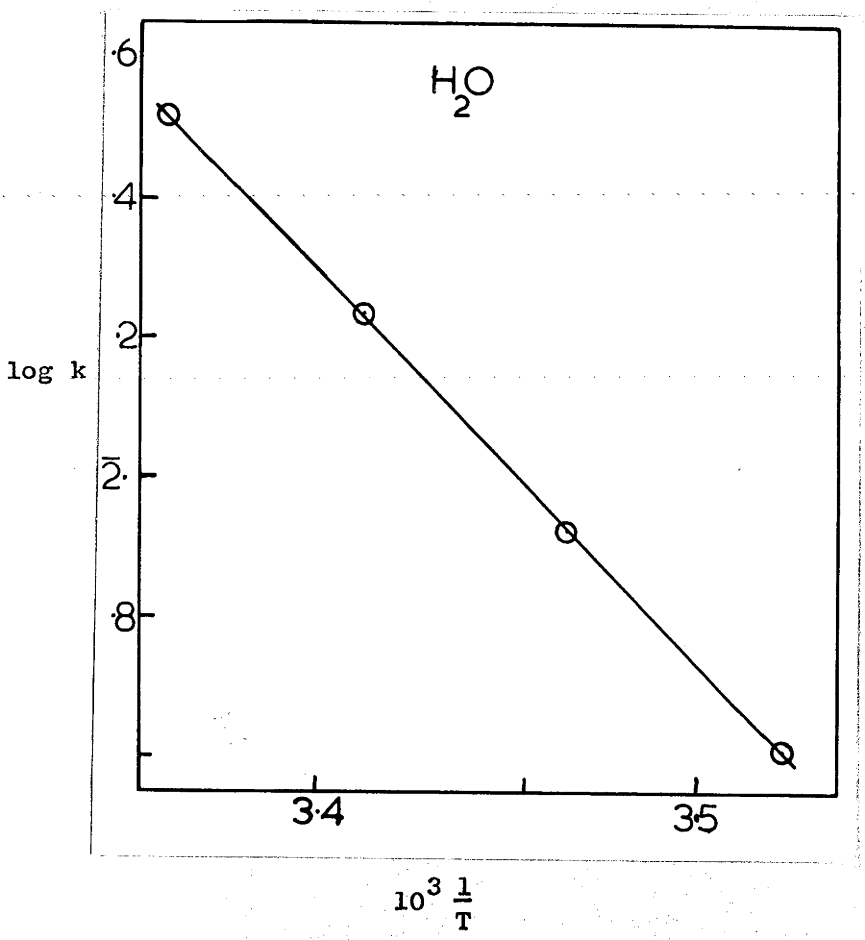
TABLE 6.711

The Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in Water

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.0	283	3.534	0.407	$\bar{3}.610$
15.0	288	3.472	0.840	$\bar{3}.924$
20.0	293	3.413	1.72	$\bar{2}.236$
25.0	298	3.356	3.32	$\bar{2}.521$

Ea = 23.6 kcals/mole; log A = 14.05 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.8 e.u.

FIGURE 6.711



6.72 IONIC STRENGTH.

Solutions of high ionic strength had no appreciable effect on the rate constant for racemisation, as the following results demonstrate.

Solution	Ionic Strength	$k(min^{-1})$
$(NH_4)_2SO_4$	3	3.31×10^{-2} (25°C)
" "	2	3.34×10^{-2} (25°C)
$NaNO_3$	2	3.32×10^{-2} (25°C)
"	2	1.68×10^{-2} (20°C)
H_2O	-	3.32×10^{-2} (25°C)
"	-	1.72×10^{-2} (20°C)

6.73 RACEMISATION IN ACID SOLUTION.

The dependence of the rate of racemisation of the $[Ni(bipy)(phen)_2]^{2+}$ ion upon the acid concentration is clearly shown in the graph of the following data for hydrochloric acid at 25°C (Figure 8 points marked with a cross). Analogous results were obtained with sulphuric acid.

Acid Concentration	Hydrochloric $10^2k(min^{-1})$	Sulphuric $10^2k(min^{-1})$
0.005 normal	5.02	-
0.01 "	6.28	-
0.10 "	9.94	9.37
0.50 "	11.3	10.8
1.00 "	11.8	11.4
1.98 "	13.6	13.6
2.98 "	16.3	16.6
4.00 "	21.9	21.8
5.00 "	27.6	27.6

For certain acid concentrations a detailed study of the temperature dependence has been made the results being given in the following pages. The plots of log k against $\frac{1}{T}$ are given later together with the dissociation results (section 7.321[185] the circles designate racemisation values).

By comparing the racemisation results in acid with those for water only, (Table 6.711), it is apparent that the increased rate in acid solution arises from a lower energy of activation.

The Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in Hydrochloric Acid

5 Normal

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
5.0	278	3.597	2.37	$\bar{2}.375$
10.0	283	3.534	4.71	$\bar{2}.673$
15.0	288	3.472	8.95	$\bar{2}.952$
20.0	293	3.413	17.6	$\bar{1}.246$
25.0	298	3.356	27.6	$\bar{1}.441$

Ea = 21.6 kcals/mole; log A = 13.53 sec^{-1}; $\Delta S^{\ddagger}$ = + 1.4 e.u.

2.98 Normal

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
25.0	298	3.356	16.3	$\bar{1}.212$
20.0	293	3.413	8.55	$\bar{2}.932$
15.0	288	3.472	4.49	$\bar{2}.652$
10.0	283	3.534	2.25	$\bar{2}.352$

Ea = 22.1 kcals/mole; log A = 13.65 sec^{-1}; $\Delta S^{\ddagger}$ = + 2.0 e.u.

The Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in Hydrochloric Acid

1 Normal

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.0	283	3.534	1.69	$\bar{2}.228$
15.0	288	3.472	3.33	$\bar{2}.522$
20.0	293	3.413	6.59	$\bar{2}.819$
25.0	298	3.356	11.8	$\bar{1}.072$

Ea = 22.2 kcals/mole; log A = 13.57 sec^{-1}; $\Delta S^{\ddagger}$ = + 1.6 e.u.

The Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 1 Normal Sulphuric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.0	283	3.534	1.60	$\bar{2}.204$
15.0	288	3.472	3.12	$\bar{2}.494$
20.0	293	3.413	5.99	$\bar{2}.777$
25.0	298	3.356	11.4	$\bar{1}.057$

Ea = 21.9 kcals/mole; log A = 13.35 sec^{-1}; $\Delta S^{\ddagger}$ = + 0.6 e.u.

The Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 1.97 Normal Sulphuric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
25.0	298	3.356	13.6	$\bar{1}.134$
20.0	293	3.413	6.64	$\bar{2}.822$
14.8	287.8	3.475	3.33	$\bar{2}.522$
10.0	283	3.534	1.69	$\bar{2}.228$

Ea = 23.1 kcals/mole; log A = 14.25 sec^{-1}; $\Delta S^{\ddagger}$ = 4.7 e.u.

(for accompanying graph see section 7.321)

The Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 5 Normal Sulphuric Acid

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
5.0	278	3.597	2.07	$\bar{2}.316$
10.0	283	3.534	3.99	$\bar{2}.601$
15.0	288	3.472	7.94	$\bar{2}.900$
20.0	293	3.413	15.1	$\bar{1}.179$
25.0	298	3.356	27.6	$\bar{1}.441$

Ea = 24.1 kcals/mole; log A = 13.37 sec^{-1}; $\Delta S^{\ddagger}$ = + 0.7 e.u.

(for accompanying graph see section 7.321)

6.74 RACEMISATION IN BASIC SOLUTION.

The presence of hydroxide ions produced an increase in the racemisation rate compared to that in water (see below). The increased rates were accompanied by a lowering of the activation energy (Table 6.741).

Temperature 25°C

Solution	$10^2 k(min^{-1})$
H_2O	3.32
0.1 N KOH	10.1
0.5 N "	10.5
2.5 N "	18.1

TABLE 6.741

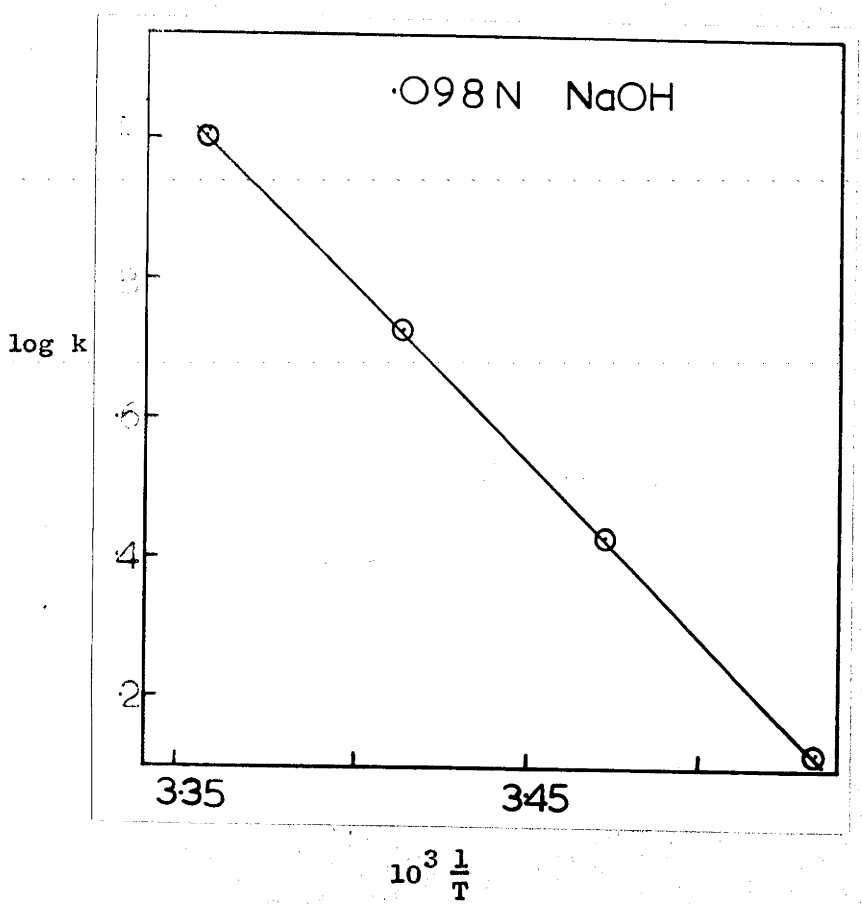
The Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 0.098 N Sodium Hydroxide

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.0	283	3.534	1.33	$\bar{2}.124$
15.0	288	4.472	2.69	$\bar{2}.430$
20.0	293	3.413	5.34	$\bar{2}.728$
25.0	298	3.356	10.1	$\bar{1}.004$

Ea = 22.8 kcals/mole; log A = 13.93 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.3 e.u.

In water:

Ea = 23.6 kcals/mole; log A = 14.05 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.8 e.u.



6.75 THE EFFECT OF pH.

Buffer solutions as described in section 6.2 were used to determine the effect of pH on the racemisation rate. Some of the buffers contained chloride ions which themselves slightly accelerated the rates. Accordingly a small correction to the rate constant first obtained has been made by subtracting the increment known to arise from the chloride ion concentration. At 25°C and a concentration of 0.2g ions litre^{-1} of Cl^- the correction amounts to 0.33×10^{-2} min^{-1}.

The data from which figure 6.75 has been drawn are given in Table 6.75. Over the range 3.56 - 9.00 pH units the rate constant was independent of hydrogen ion concentration.

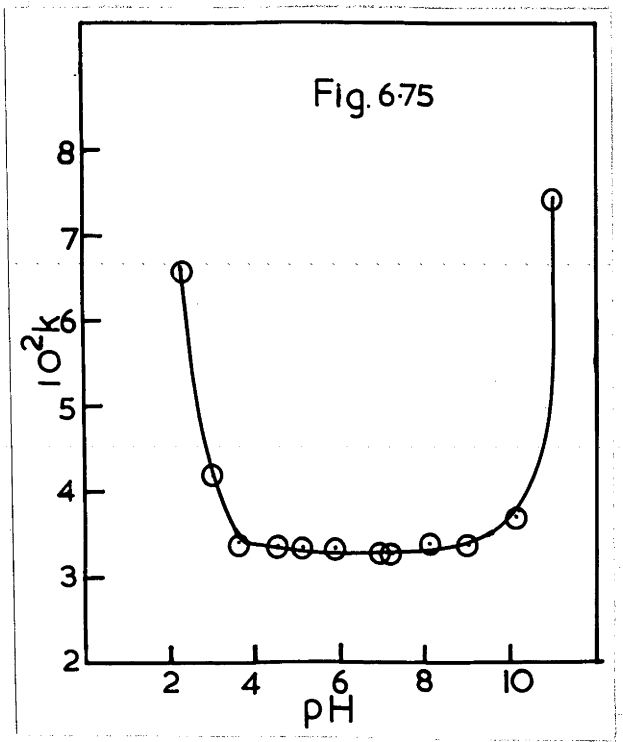


TABLE 6.75

Temperature 25°C

Buffer Number*	pH	$10^2 k(min^{-1})$
5	2.30	6.57
5	3.00	4.17
2	3.56	3.36
2	4.51	3.36
1	5.05	3.31
2	5.88	3.32
3	6.98	3.28
1	7.20	3.22
4	8.06	3.37
4	9.00	3.36
4	10.06	3.68
1	11.00	7.42

*See section 6.2

6.8 THE EFFECT OF EXCESS LIGAND.

The complex ion $[Ni(bipy)(phen)_2]^{2+}$ behaved in a manner analogous to $[Ni(phen)(bipy)_2]^{2+}$. Thus excess 2,2'-bipyridine reduced the racemisation rate in water, while a similar amount of 1,10-phenanthroline did not. Table 6.80 gives results for various solvents. The complex concentration was 0.001 M. It is seen that bipyridine also reduced the rate in 11.83% mol. fraction ethanol-water but not in the 30.15% or 100% solutions. Throughout there was no deviation from first order kinetics. Discussion of these results is deferred until all the results have been presented.

TABLE 6.80

Solution	Temperature (°C)	k(min^{-1})
Water	25	$3.32 \pm .12 \times 10^{-2}$
"	20	$1.72 \pm .05 \times 10^{-2}$
bipy (0.0064M)	25	$2.90 \pm .08 \times 10^{-2}$
" (0.028M)	25	$2.39 \pm .07 \times 10^{-2}$
phen (0.005M)	25	$3.28 \pm .12 \times 10^{-2}$
" "	20	$1.64 \pm .05 \times 10^{-2}$
ethanol	25	$10.0 \pm .3 \times 10^{-4}$
ethanol + bipy (0.0064M)	25	$9.9 \pm .3 \times 10^{-4}$
87.65% mol. fraction ethanol-water	25	$4.10 \pm .1 \times 10^{-3}$
87.65% mol. fraction + phen (0.01M)	25	$4.07 \pm .1 \times 10^{-3}$
30.15% mol. fraction ethanol-water	25	$6.47 \pm .2 \times 10^{-3}$
30.15% mol. fraction + bipy (0.0064M)	25	$6.48 \pm .2 \times 10^{-3}$
11.83% mol. fraction ethanol-water	25	$2.88 \pm .10 \times 10^{-2}$
11.83% mol. fraction + bipy (0.0064M)	25	$2.56 \pm .10 \times 10^{-2}$
methanol	25	$1.98 \pm .06 \times 10^{-3}$
methanol + bipy (0.0128M)	25	$2.01 \pm .06 \times 10^{-3}$
methanol + phen (0.0256M)	25	$2.05 \pm .06 \times 10^{-3}$
0.5 N HCl	25	$11.3 \pm .3 \times 10^{-2}$
0.5 N HCl + bipy (0.0128)	25	$11.2 \pm .3 \times 10^{-2}$

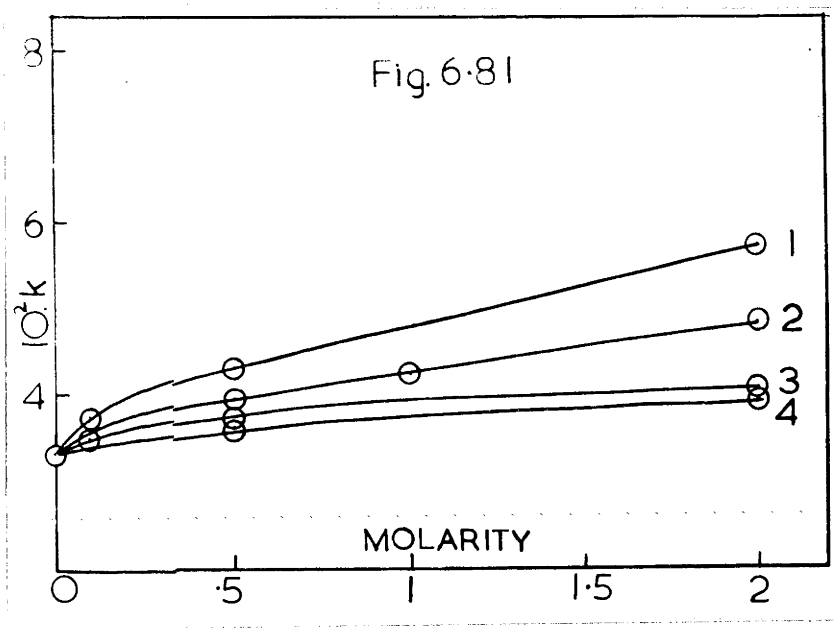
6.81 THE EFFECT OF ADDED MOLECULES OR IONS.

Table 6.81 gives the rate constants for an aqueous solution of $[Ni(bipy)(phen)_2]^{2+}$ ion in the presence of various added molecules or ions. Throughout the temperature was 25°C and the complex concentration 0.001M.

The largest effects are produced by the ions F^-, Cl^-, Br^-, and NO_2^- and are shown graphically in Figure 6.81. The halide ions were present as their ammonium salts and the NO_2^- as sodium nitrite. The measured pH's of the solutions were within the range 5.5-8.5 wherein the rate constant was independent of pH (see Figure 6.75). A similar acceleration in the racemisation rate of $[Ni(bipy)_3]^{2+}$ ion has been noted previously[60b] in the presence of Cl^- ion.

TABLE 6.81

Added Substance	Molar Concentration	$10^2k(min^{-1})$
Water	-	$3.32 \pm .12$
phenylenediamine	0.028	3.28 "
" "	0.056	3.28 "
glycine	0.028	3.36 "
"	0.28	3.52 "
"	1.0	3.73 "
potassium oxalate	0.028	3.47 "
ammonium acetate	1.0	3.67 "
pyridine	0.028	3.36 "
nickel ammonium sulphate	0.01	3.40 "
" " "	0.1	3.34 "
lithium nitrate	0.24	3.36 "
potassium chloride	0.006	3.38 "



(1) $NaNO_2$

(2) NH_4Cl

(3) NH_4F

(4) NH_4Br

6.9 THE EFFECT OF SOLVENT CHANGES.

All solvent changes produced a decrease in the racemisation rate compared to the rate in water at the same temperature, an observation found also for the $[Ni(phen)(bipy)_2]^{2+}$ ion. The results of temperature dependence measurements are given in the following pages for the solvents listed below. The values in water are included for comparison.

(i) Methanol.

(ii) Ethanol.

(iii) Pyridine.

(iv) Formamide.

(v) Nitrobenzene.

Note: The complex perchlorate was very soluble in all solvents except ethanol. It was insoluble in glacial acetic acid.

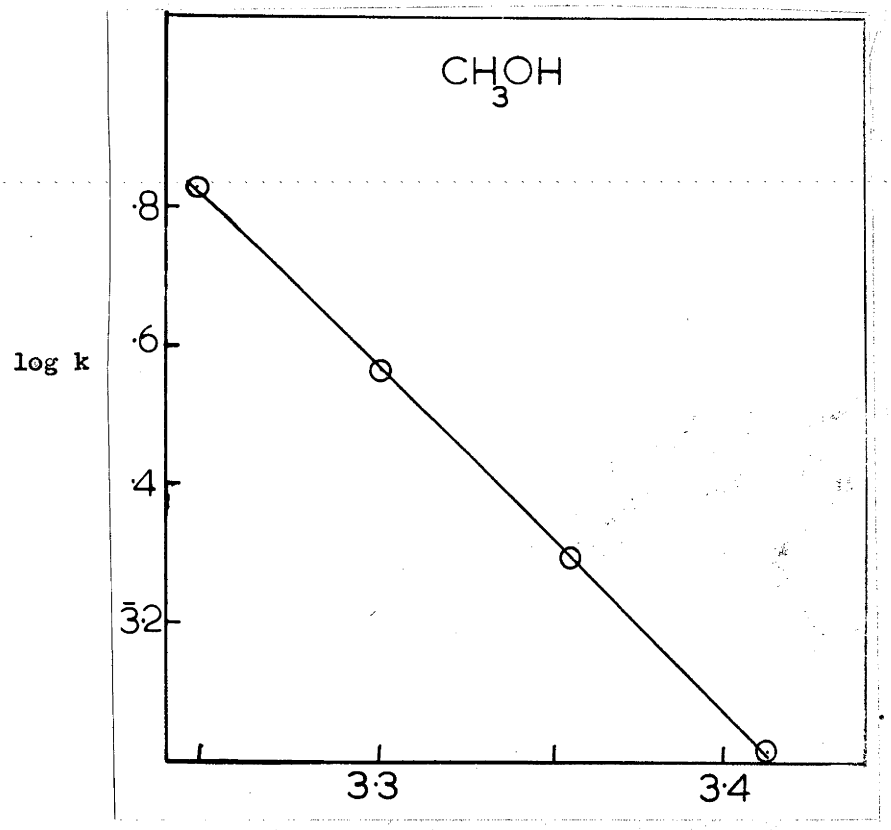
The Racemisation of the $[Ni(bipy)(phen)_2]^{2+}$ ion in Methanol

°C	T(°K)	$10^3 \frac{1}{T}$	$10^4 k(min^{-1})$	log k	$10^4 k(min^{-1})H_2O$
20.0	293	3.413	10.4	$\bar{3}.017$	172
25.0	298	3.356	19.8	$\bar{3}.297$	332
29.9	302.9	3.301	36.8	$\bar{3}.566$	-
34.8	307.8	3.249	67.9	$\bar{3}.832$	-

Ea = 22.7 kcals/mole; log A = 12.19 sec^{-1}; $\Delta S^{\ddagger}$ = - 4.7 e.u.

In water:

Ea = 23.6 kcals/mole; log A = 14.05 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.8 e.u.



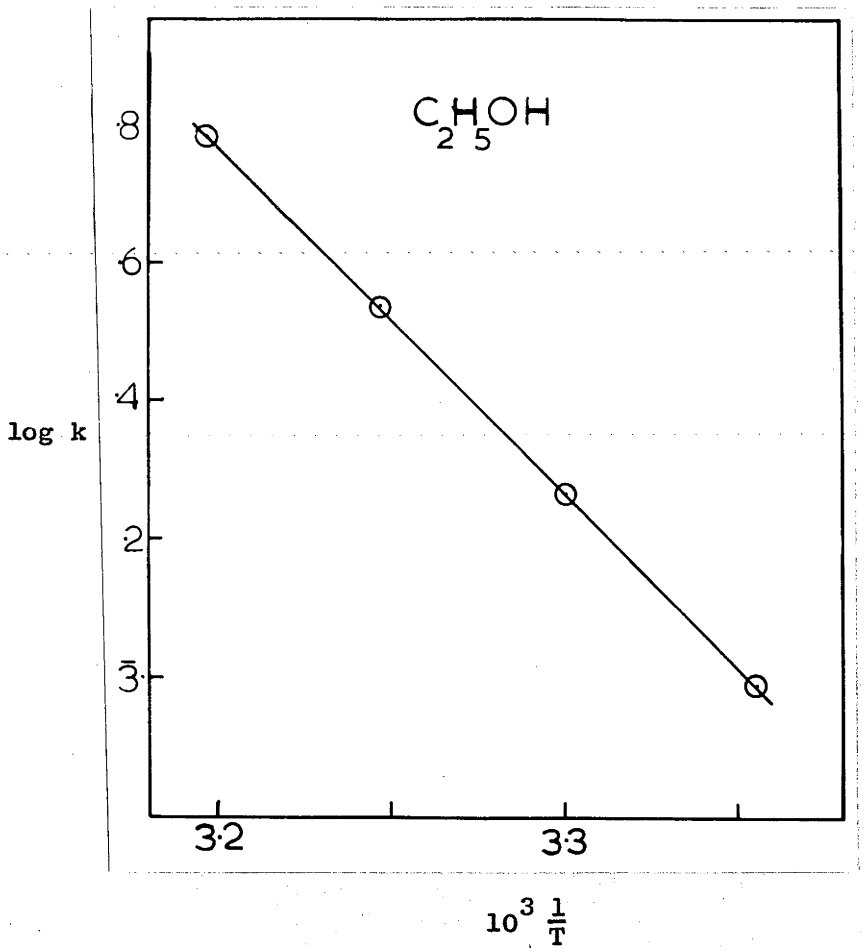
The Racemisation of the $[Ni(bipy)(phen)_2]^{2+}$ ion in Ethanol

°C	T(°K)	$10^3 \frac{1}{T}$	$10^4 k(min^{-1})$	log k	$10^4 k(min^{-1})H_2O$
25.0	298	3.356	9.72	$\bar{4}.988$	332
29.9	302.9	3.301	18.3	$\bar{3}.263$	-
35.0	308	3.247	34.5	$\bar{3}.538$	-
39.8	312.8	3.197	61.0	$\bar{3}.785$	-

Ea = 23.1 kcals/mole; log A = 12.13 sec^{-1}; $\Delta s^{\ddagger}$ = - 5.0,e.u.

In water:

Ea = 23.6 kcals/mole; log A = 14.05 sec^{-1}; $\Delta s^{\ddagger}$ = + 3.8 e.u.



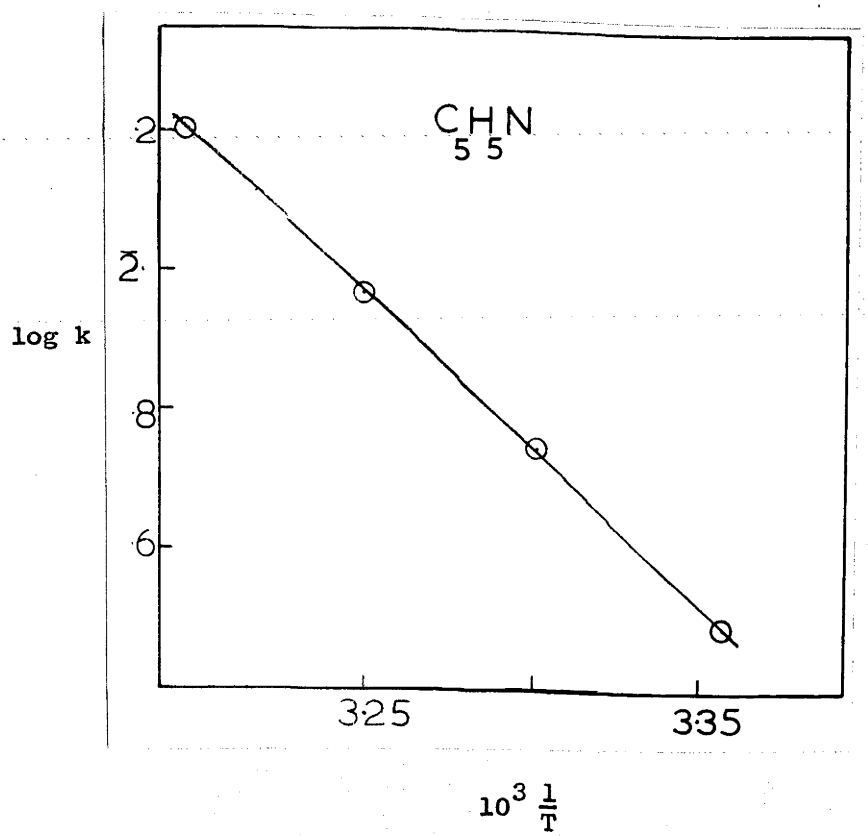
The Racemisation of the $[Ni(bipy)(phen)_2]^{2+}$ ion in Pyridine

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k	$10^3 k(min^{-1})H_2O$
25.0	298	3.356	3.04	$\bar{3}.483$	33.2
29.9	302.9	3.301	5.55	$\bar{3}.744$	-
34.8	307.8	3.249	9.30	$\bar{3}.969$	-
39.8	312.8	3.197	16.3	$\bar{2}.212$	-

Ea = 20.9 kcals/mole; log A = 11.01 sec^{-1}; $\Delta S^{\ddagger}$ = - 10.1 e.u.

In water:

Ea = 23.5 kcals/mole; log A = 14.05 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.8 e.u.



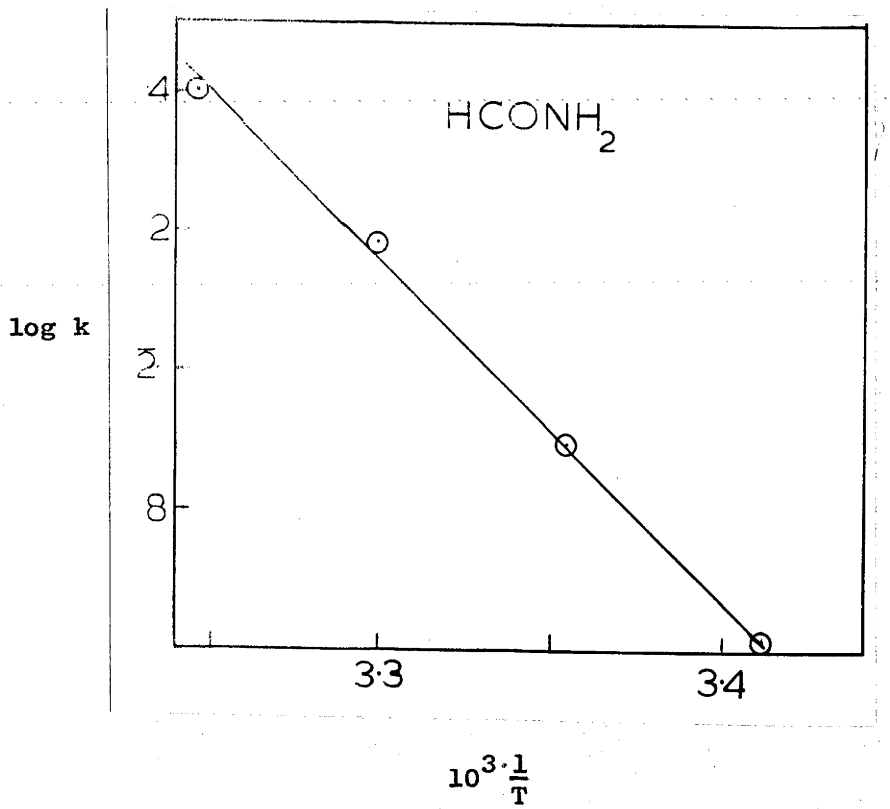
The Racemisation of the $[Ni(bipy)(phen)_2]^{2+}$ ion in Formamide

^{o}C	$T(^{o}K)$	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k	$10^3 k(min^{-1})H_2O$
20.0	293	3.413	4.10	$\bar{3}.613$	17.2
25.0	298	3.356	7.87	$\bar{3}.896$	33.2
29.9	302.9	3.301	15.4	$\bar{2}.188$	-
35.0	308	3.247	25.3	$\bar{2}.403$	-

Ea = 22.6 kcals/mole; log A = 12.64 sec^{-1}; $\Delta s^{\ddagger}$ = - 2.7 e.u.

In water:

Ea = 23.6 kcals/mole; log A = 14.05 sec^{-1}; $\Delta s^{\ddagger}$ = + 3.8 e.u.



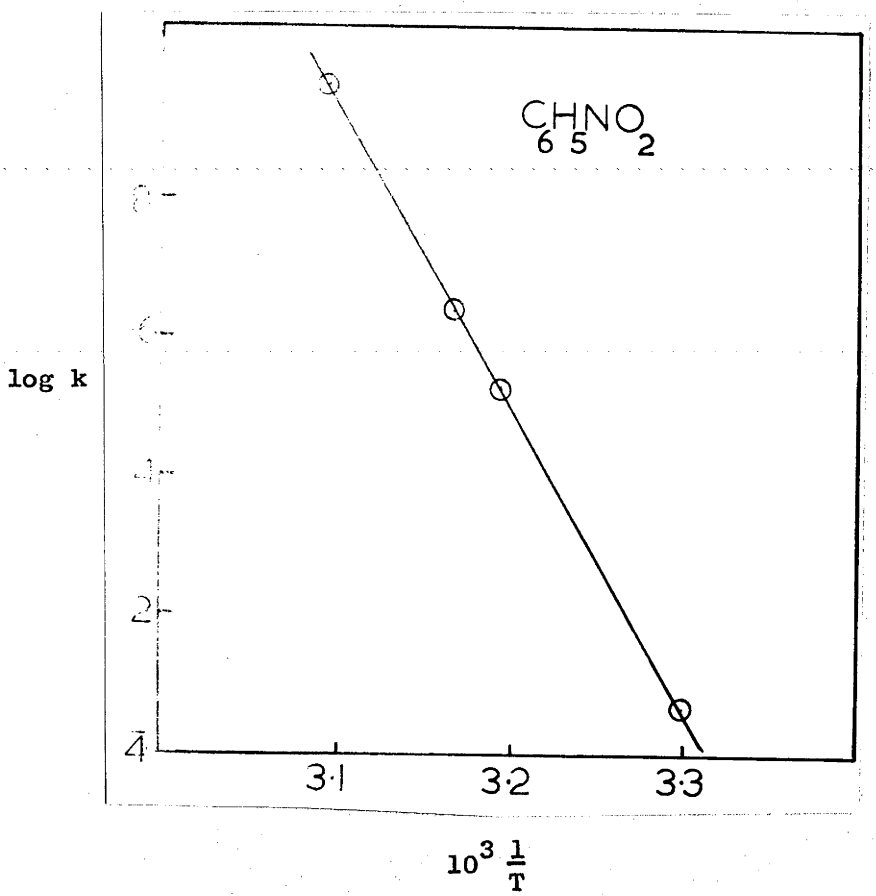
The Racemisation of the $[Ni(bipy)(phen)_2]^{2+}$ Ion in Nitrobenzene

°C	T(°K)	$10^3 \frac{1}{T}$	$10^4 k(min^{-1})$	log k
29.9	302.9	3.30	1.17	$\bar{4}.068$
40.1	313.1	3.194	3.36	$\bar{4}.526$
42.8	315.8	3.167	4.35	$\bar{4}.639$
50.0	323.0	3.096	9.27	$\bar{4}.967$

Ea = 19.8 kcals/mole; log A = 8.56 sec^{-1}; $\Delta S^{\ddagger}$ = - 21.3 e.u.

In water:

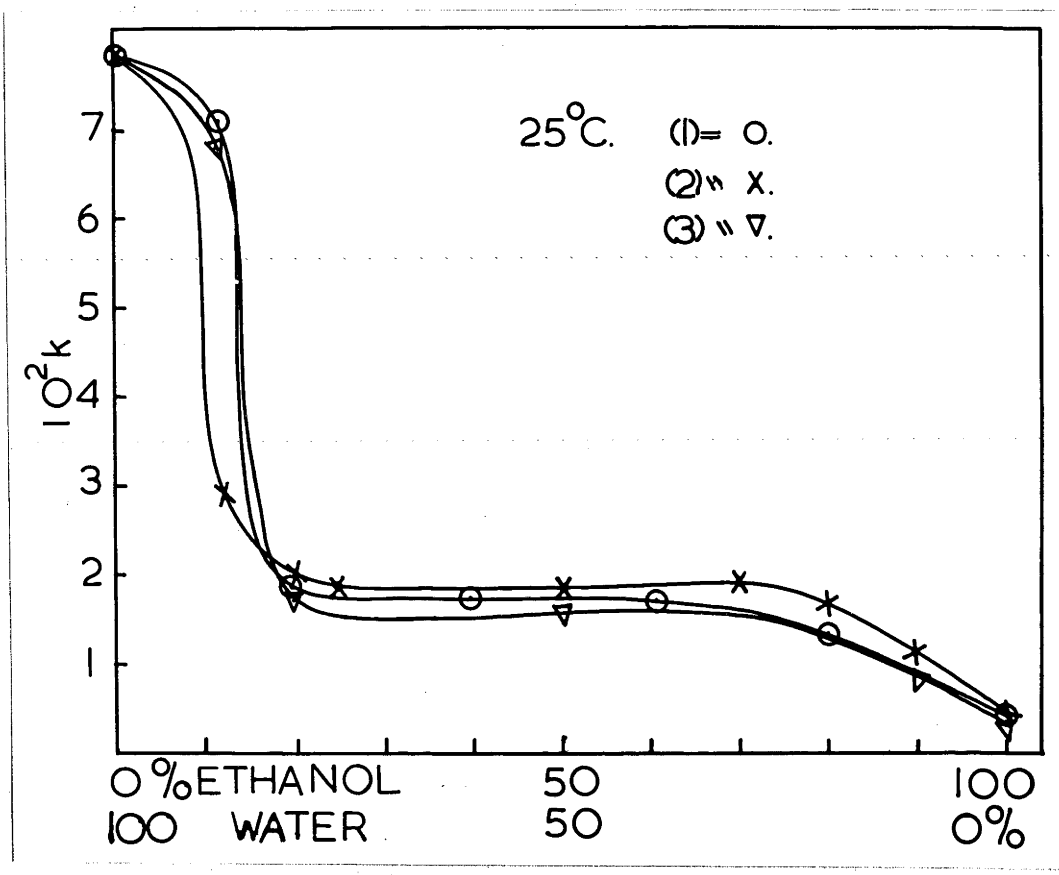
Ea = 23.6 kcals/mole; log A =14.05 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.8 e.u.



6.91 RACEMISATION IN AQUEOUS ETHANOL.

The shape of the plot of rate constant at 25°C against percent mole fraction ethanol-water was almost identical with those obtained for the $[Ni(bipy)_3]^{2+}$ and $[Ni(phen)(bipy)_2]^{2+}$ ions. Figure 6.91 shows the data for the $[Ni(bipy)(phen)_2]^{2+}$ ion (2) from Table 6.91 plotted together with similar data for the $[Ni(bipy)_3]^{2+}$ (3) and $[Ni(phen)(bipy)_2]^{2+}$ (1) ions. The first points of each set have been made coincident to illustrate the close similarity present.* The corresponding curve for the $[Ni(phen)_3]^{2+}$ ion is different (Chapter 2, Figure 2.4) and exhibits a peak at about 70% mole fraction ethanol-water.

FIGURE 6.91



* SEE OVERLEAF

TABLE 6.91

Percent Mol. Fraction Ethanol	$10^2 k(min^{-1})$ at 25°C
Nil	3.32
11.8	2.88
19.7	0.679
30.2	0.647
39.7	0.638
49.8	0.668
60.6	0.656
69.4	0.630
80.5	0.535
87.7	0.410
100	0.0972

For the 39.7 percent mol-fraction ethanol water mixture the temperature dependence of the rates has been studied and is given overleaf. An increase in ethanol content was found to reduce the rates by making the entropy of activation more negative.

Note: The rate constants for the $[Ni(phen)_2(bipy)]^{2+}$ and $[Ni(bipy)_3]^{2+}$ ions have been multiplied by the factors $\frac{7.81}{3.32}$ and $\frac{7.81}{13.6}$ respectively. The factors used are the relative values of the racemisation rate constants in water at 25°C, viz:

$[Ni(bipy)_3]^{2+}$ 13.6 min^{-1} (reference 89)

$[Ni(phen)(bipy)_2]^{2+}$ 7.81 min^{-1} (table 6.61, p.120)

$[Ni(bipy)(phen)_2]^{2+}$ 3.32 min^{-1} (table 6.91 above)

The Racemisation of the $[Ni(bipy)(phen)_2]^{2+}$ Ion in 39.7% Mol-Fraction Ethanol-Water

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k
20.0	293	3.413	3.02	$\bar{3}.480$
25.0	298	3.356	6.38	$\bar{3}.805$
30.0	303	3.300	12.4	$\bar{2}.093$
34.8	307.8	3.249	21.0	$\bar{2}.322$

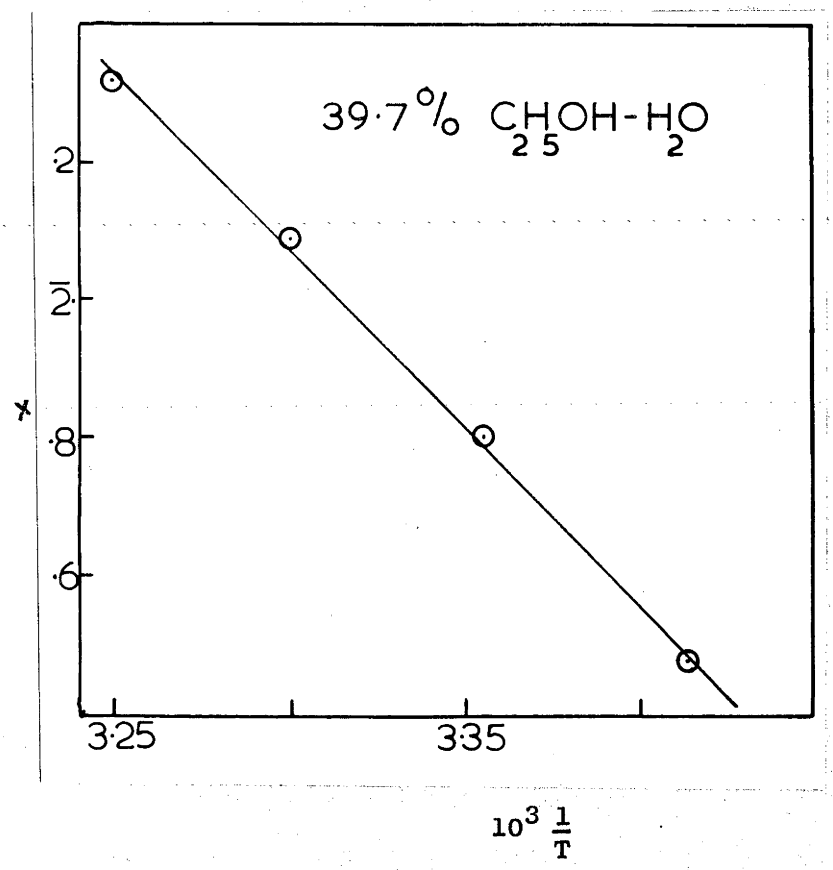
Ea = 23.3 kcals/mole; log A = 13.13 sec^{-1}; $\Delta S^{\ddagger}$ = - 0.4 e.u.

In water:

Ea = 23.6 kcals/mole; log A = 14.05 sec^{-1}; $\Delta S^{\ddagger}$ = + 3.8 e.u.

In ethanol:

Ea = 23.1 kcals/mole; log A = 12.13 sec^{-1}; $\Delta S^{\ddagger}$ = - 5.0 e.u.



6.92 SUMMARY.

The following table summarises the general racemisation behaviour of the mixed complexes. (Temperature 25°C unless otherwise stated). The results in organic solvents are given in Chapter 8 (Table 8.3).

Solvent	$10^2 k(min^{-1})$	Ea(kcals/mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
	[Ni(phen)(bipy)$_2$]$^{2+}$ Ion		
Water	7.81 ± 0.24	22.9	+ 3.1
1N HCl	30.8 ± 0.12	21.6	+ 1.4
5N HCl (at 20°C)	36.0 ± 0.16	20.4	- 1.1
0.098N NaOH	26.3 ± 0.12	22.0	+ 2.6
ionic strength = 1	7.64 ± 0.24	-	-
0.023 M bipy	7.20 ± 0.24	-	-
1M NH_4Cl	9.41 ± 0.32	-	-
	[Ni(bipy)(phen)$_2$]$^{2+}$ Ion		
Water	3.32 ± 0.12	23.6	+ 3.8
1N HCl	11.8 ± 0.36	22.2	+ 1.6
5N HCl	27.6 ± 0.90	21.6	+ 1.4
0.098N NaOH	10.1 ± 0.30	22.8	+ 3.3
ionic strength = 2	3.32 ± 0.12	-	-
0.028 M bipy	2.39 ± 0.07	-	-
1M NH_4Cl	4.42 ± 0.12	-	-

CHAPTER SEVEN

7.0 THE DISSOCIATION OF THE $[Ni(phen)(bipy)_2]^{2+}$ AND $[Ni(bipy)(phen)_2]^{2+}$ IONS IN ACID SOLUTION.

The dissociation of the mixed ligand complexes may be effected in acid solution in an analogous manner to that described for the simple tris complexes (section 2.2). The acid concentration employed governs the rate as well as the extent of dissociation taking place. In the acid solutions shown below the following equations were found to represent the dissociation processes, water molecules being omitted.

$$[Ni(phen)(bipy)_2]^{2+} \xrightarrow{5N\ acid} [Ni(phen)]^{2+} + 2\ bipy \quad .....(1)$$

$$[Ni(bipy)(phen)_2]^{2+} \rightleftharpoons^{acid} [Ni(phen)_2]^{2+} + bipy \quad .....(2)$$

$$bipy + H^+ \rightleftharpoons bipy\ H^+$$

Equation (1) applies only at about 5N acidities and at lower concentrations a bis complex, presumably the $[Ni(bipy)(phen)]^{2+}$ ion, may be detected. Equation (2) applies at all the acid concentrations used. The $[Ni(phen)_2]^{2+}$ complex formed is slow to dissociate[121], consequently the reverse of equation (2) can take place in spite of the large amount of acid present. This leads to a metastable equilibrium as represented by equation (2). A true equilibrium is precluded by the further dissociation of the $[Ni(phen)_2]^{2+}$ ion. A similar re-formation reaction is known to occur with the simple tris complexes[63], but as it does not become appreciable until a late stage in the dissociation it may be neglected in the kinetic treatment. For the mixed complexes the experiments show that re-formation cannot be neglected and the results are interpreted using an opposed first and second order reaction scheme.

7.1 ABSORPTION SPECTRA.

The Beckmann DK2 or Shimadzu recording spectrophotometers have been employed to obtain the spectra shown in Figure 7.1. In all measurements freshly prepared aqueous solutions (0.02M) were used in 1cm cells. The visible spectra of the mixed complexes were not only very similar but also closely resembled the spectra of the simple tris compounds.[63]

The spectra of the Ni(II) bis and mono complexes prepared in this work (section 5.1) are shown in Figure 7.11 and the positions of the absorption maxima are in agreement with previous results.[63] The green bis complexes $[Ni(phen)_2Cl_2]$ and $[Ni(bipy)_2Cl_2]$ were observed to turn pale blue on wetting with water and subsequently to dissolve completely giving blue solutions. The conductivity of a 10^{-3}M solution of $[Ni(phen)_2Cl_2]$ was 232mhos corresponding to a 2:1 electrolyte and consistent with replacement of the Cl^- ligands by H_2O.

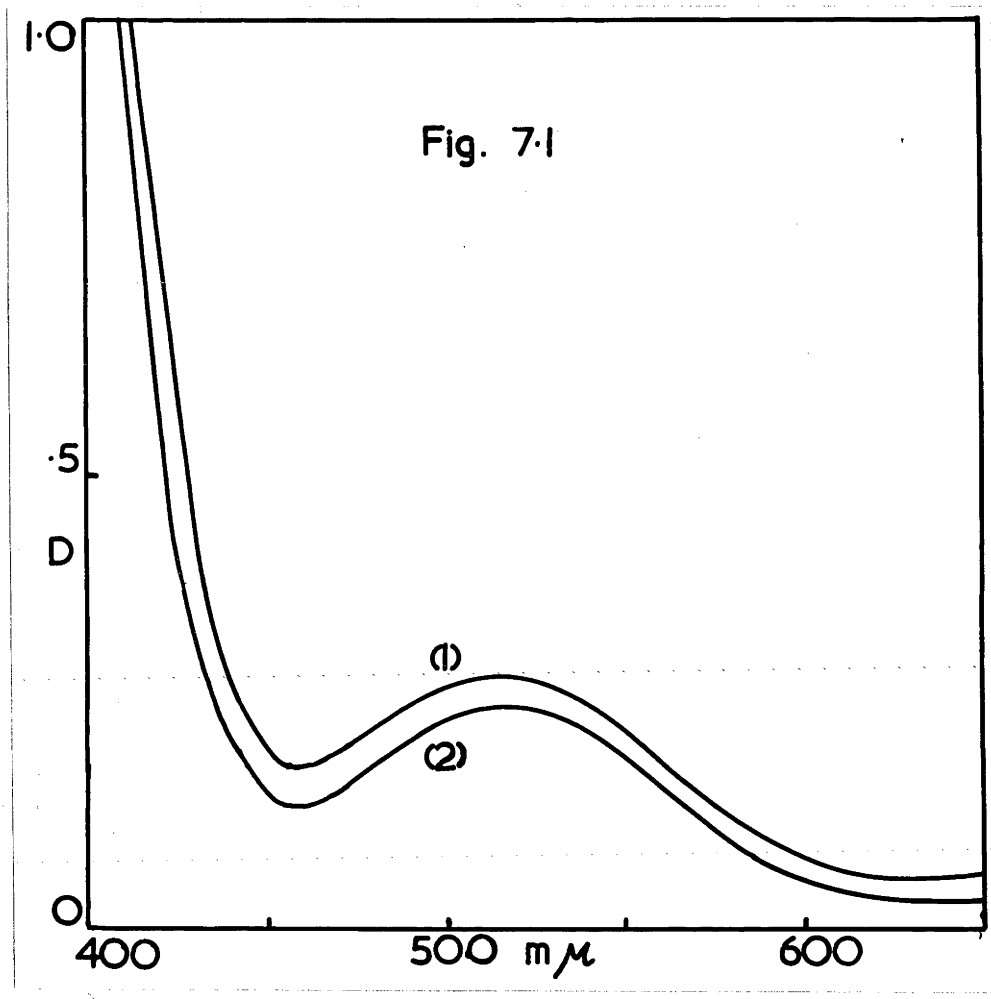
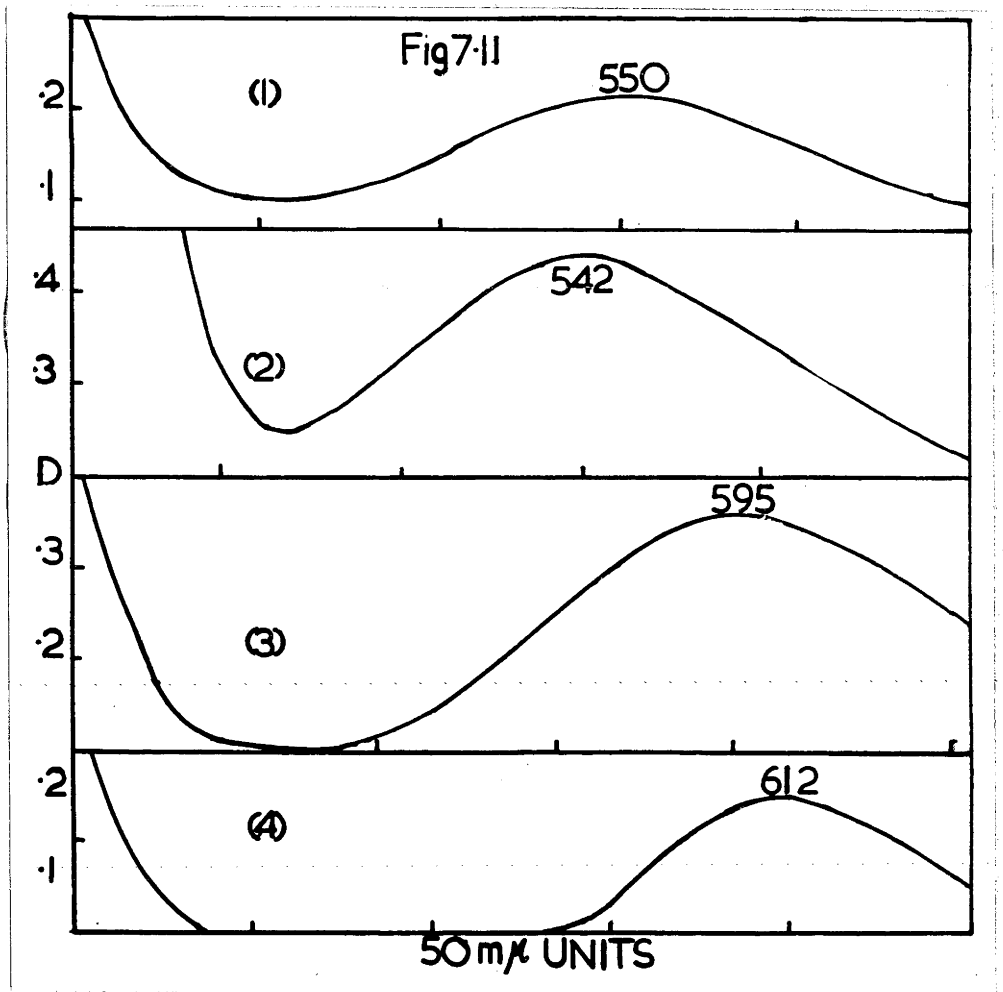


Fig. 7·1

(1) $[Ni(phen)(bipy)_2]Cl_2 \cdot 5H_2O$ (0.02M)

(2) $[Ni(bipy)(phen)_2]Cl_2 \cdot 6H_2O$ (0.02M)



(1) [Ni(phen)$_2$Cl$_2$]

(2) [Ni(bipy)$_2$Cl$_2$]

(3) [Ni(bipy)Cl$_2$]

(4) [Ni(phen)Cl$_2$]

7.11 THE EFFECT OF ACID ON THE VISIBLE ABSORPTION SPECTRUM OF THE $[Ni(phen)(bipy)_2]^{2+}$ ION.

The peak at 515mμ present in a neutral solution of the tris complex (Figure 7.1) disappears in 3 normal sulphuric acid (Figure 7.12, curve 1) and a smaller peak at 540mμ appears. The last mentioned could be attributed to the presence of a bis complex since both simple bis complexes absorb in the vicinity of 540mμ and if the mixed bis complex were present it would be expected to behave similarly.

In an acid concentration of 5 normal (Figure 7.12, curve 2) the maximum has shifted to 600mμ the region where both the mono complexes absorb. It is noteworthy that the red colour of the complex persists in acid solutions up to 2 normal but at higher acid concentrations the solution turns blue. The studies show that dissociation of the $[Ni(phen)(bipy)_2]^{2+}$ ion gives predominantly a bis complex until the acid normality exceeds 3 after which a mono complex is obtained.

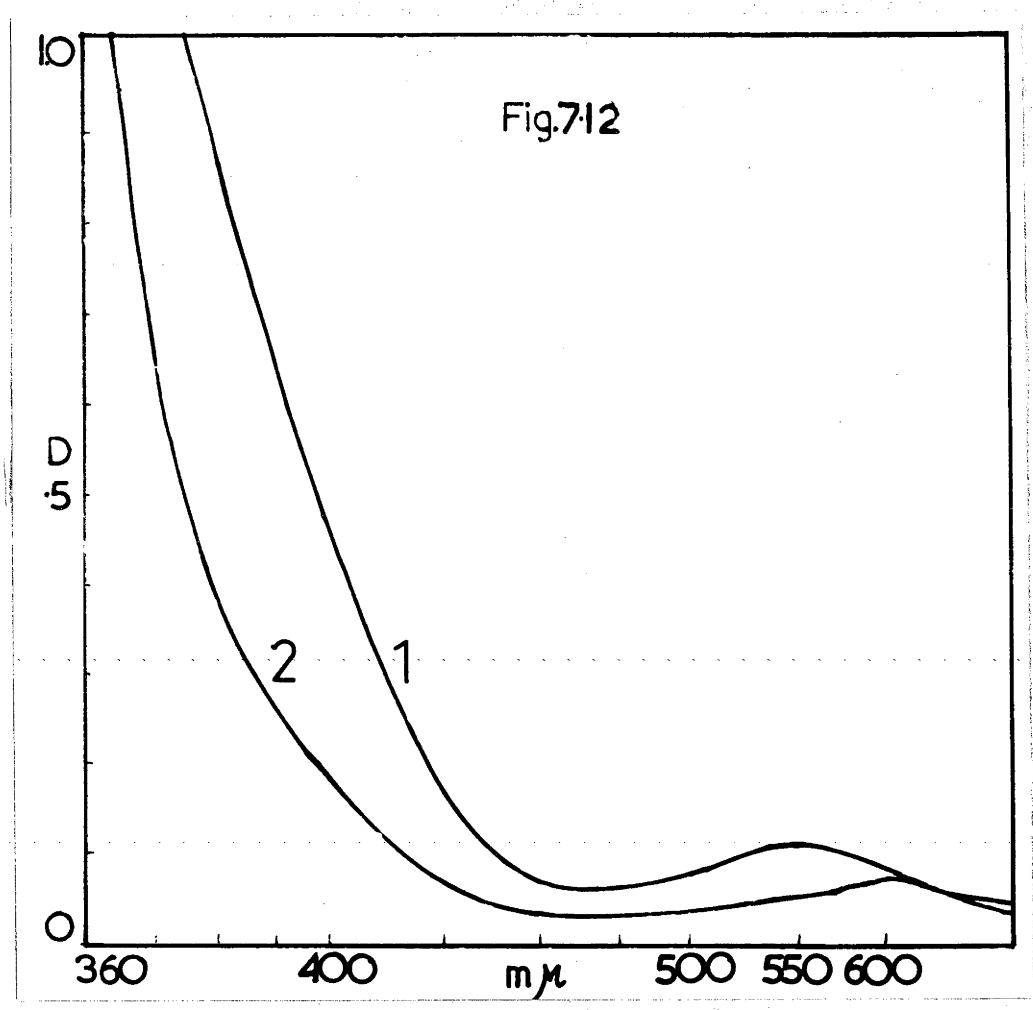


Fig. 7·12

7.12 THE EFFECT OF ACID ON THE VISIBLE ABSORPTION SPECTRUM OF THE $[Ni(bipy)(phen)_2]^{2+}$ ION.

The change in optical density with time for the $[Ni(bipy)(phen)_2]^{2+}$ ion in 2.98N hydrochloric acid is shown in Figure 7.13, zero time being measured from the moment of dissolution. A peak of 550mμ is evident and following the initial rapid change the spectrum alters very little. At the lower acid concentrations (less than 3N), the solution appears red but at higher normalities the colour changes to blue and the maximum (550mμ) corresponds to the $[Ni(phen)_2]^{2+}$ ion. It is concluded that the bis complex was present in all the acid solutions studied.

7.13 THE EXTINCTION COEFFICIENTS.

Preliminary experiments with each mixed tris complex at wavelengths of 400, 420, 440, and 520mμ showed that owing to an inadequate change in optical density, only the first two were suitable for quantitative rate measurements over a range of acid concentrations (viz. 1-5N). In addition, for solutions of less than 1N the extent of dissociation was insufficient for accurate measurement.

To simplify the calculations almost all readings were made at the one wavelength (viz. 400mμ). As the curve at this wavelength is steep it was necessary to use small band-widths so as to maintain accuracy. The slit was generally set at about 0.02mm and corresponded to a band-width of 0.2mμ.

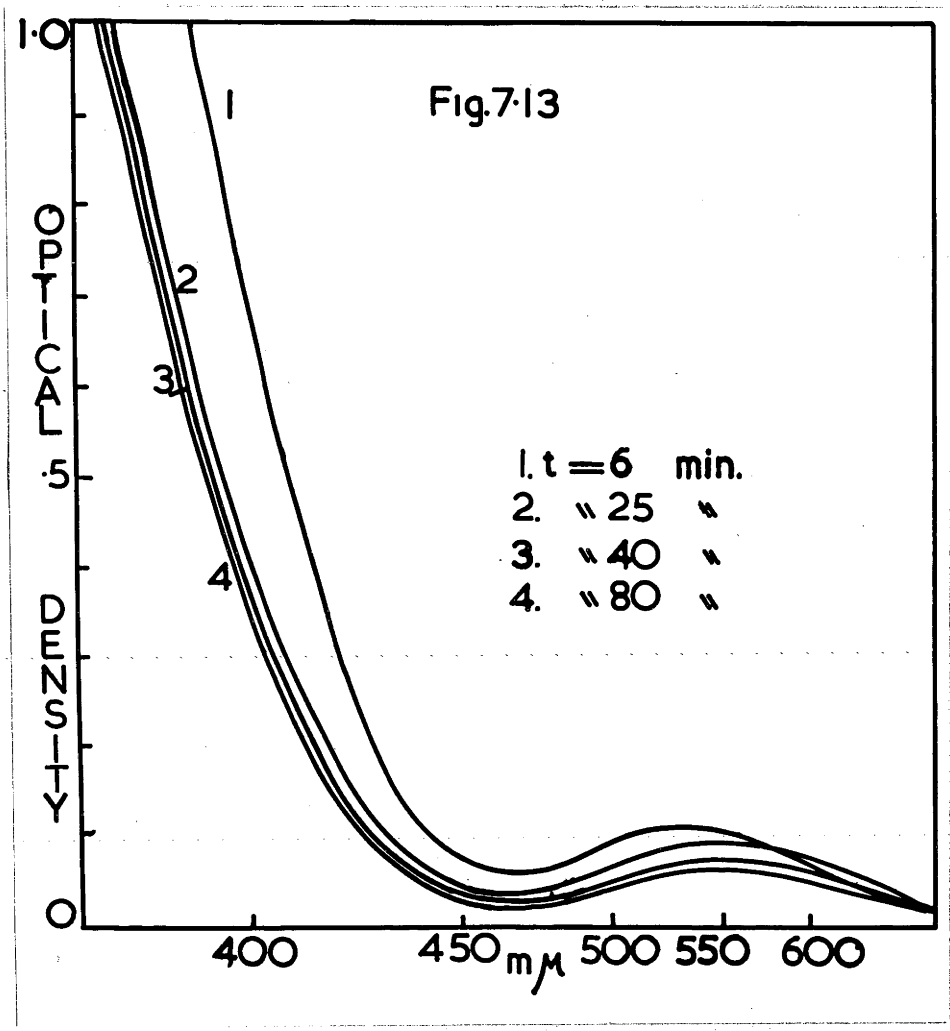


Fig.7·13
1·0
·5
0
OPTICAL DENSITY
1
2
3
4
1. t = 6 min.
2. " 25 "
3. " 40 "
4. " 80 "
400
450
mμ
500
550
600

The extinction coefficients were calculated from the usual formula, D = ect where

D = the optical density

e = the molar extinction coefficient

c = the molar concentration

t = the cell thickness in cms (here 1cm)

The optical densities of freshly prepared solutions of different molar concentrations were measured as quickly as possible and the extinction coefficients so obtained are shown below. Where possible the effect of acid on the optical density was determined. Thus for $[Ni(phen)_2Cl_2]$ and $[Ni(phen)Cl_2]$ acid did not alter the extinction coefficients. It was not possible to measure all the complexes in acid media as those containing bipyridine dissociated rapidly.

MOLAR EXTINCTION COEFFICIENTS

Species	Times Determined	Extinction Coefficients 400mμ	420mμ
$[Ni(bipy)(phen)_2]Cl_2$	4	88.1 ± 0.9	37.4 ± 0.8
$[Ni(phen)(bipy)_2]Cl_2$	3	99.3 ± 0.5	32.4 ± 0.6
$[Ni(phen)_2Cl_2]$	6	12 ± 0.5	4.5 ± 0.8
$[Ni(bipy)_2Cl_2]$	3	22 ± 1	-
$[Ni(phen)Cl_2]$	3	5.7 ± 0.2	3.0 ± 0.2
$[Ni(bipy)Cl_2]$	3	12.3 ± 0.5	7.6 ± 0.5
$bipy.H^+$	3	1.2 ± 0.02	0
$phen.H^+$	3	0.59 ± 0.02	0.45 ± 0.02
$Ni(H_2O)_6$	3	4.9 ± 0.02	2.5 ± 0.02

It was necessary to make a correction to the optical densities of $[Ni(bipy)(phen)_2]Cl_2$ for the $[Ni(phen)_3]Cl_2$ impurity present. From

the racemisation studies the rotation due to the $[Ni(phen)_3]I_2$ present in $[Ni(bipy)(phen)_2]I_2$ was known. Hence the percent impurity and corrected extinction coefficients could be calculated.

The use of the more soluble chloride was preferred to the iodide and it was assumed that the same relative amount of $[Ni(phen)_3]Cl_2$ impurity was present in the racemic $[Ni(bipy)(phen)_2]Cl_2$ as was found for the active iodide. This assumption was reasonable as conversion of racemic chloride to active iodide gives almost the theoretical yield. Within the experimental errors the extinction coefficients were identical for either iodide or chloride and the chloride has been used throughout this work.

7.14 BEER'S LAW.

Sample experiments to check the validity of Beer's law for the systems encountered are shown below. The agreement is reasonable as disproportionation reactions could not be eliminated although the solutions were cold and measured immediately after dissolution.

Solution A :	$[Ni(bipy)(phen)_2]Cl_2$	0.00265M
Solution B :	$[Ni(phen)_2Cl_2]$	0.0102M
Solution C :	$[Ni(phen)(bipy)_2]Cl_2$	0.00267M
Solution D :	$[Ni(phen)Cl_2]$	0.026M

Solution	Optical Density (400mμ) Observed	Calculated
3 ml A + 5 ml B	0.171 ± 0.002	0.164 ± .005
4 ml A + 4 ml B	0.186 ± 0.002	0.178 ± .004
5 ml A + 3 ml B	0.202 ± 0.002	0.192 ± .003
3 ml C + 5 ml D	0.187 ± 0.002	0.192 ± .003
4 ml C + 4 ml D	0.195 ± 0.002	0.207 ± .003
5 ml C + 3 ml D	0.216 ± 0.002	0.221 ± .004

7.15 EXPERIMENTAL METHODS.

The rates of dissociation were measured by means of a Shimadzu spectrophotometer set at a wavelength of 400mμ and slit widths of about 0.02mm. This instrument is a copy of the well-known Beckmann model D.U.. As far as possible readings were kept within the range 20-80% transmission to give maximum accuracy of reading. Water from a constant temperature bath was circulated through both the specially constructed cell-holder and a jacket which surrounded the cell-holder compartment. The temperature of the water after it had left the cell-holder was measured with a thermometer calibrated in hundredths of a degree centigrade. The reaction temperature could be maintained constant to within 0.1°C at 20° and 25°C and within 0.2°C at other temperatures. To prevent fogging of the cells at low temperatures tubes of silica-gel were stored in the cell compartment.

The rapid dissociation rates of both complexes necessitated the following technique. A weighed amount of the complex chloride (generally about 0.1g) was transferred to a stoppered chilled test-tube containing a suitable volume (20ml) of the required acid. It was then shaken vigorously to bring about complete solution of the complex in from 1-4 minutes. The solution was next poured into the dried 1cm cell and readings of the optical density begun as soon as the temperature of the water leaving the cell-holder was constant. To begin a run the stopwatch was started and measurements were taken continuously, all runs being repeated at least once.

7.2 KINETICS OF DISSOCIATION OF 1,10-PHENANTHROLINEBIS (2,2'-BIPYRIDINE) NICKEL(II) CHLORIDE.

The Order of the Reaction.

When the $[Ni(phen)(bipy)_2]^{2+}$ ion dissociates in acid solution the following consecutive reactions can take place. (Co-ordinated water is omitted).

$$[Ni(phen)(bipy)_2]^{2+} \xrightarrow{k1a} [Ni(phen)(bipy)]^{2+} + bipy \quad (1a)$$

$$[Ni(phen)(bipy)_2]^{2+} \xrightarrow{k1b} [Ni(bipy)_2]^{2+} + phen \quad (1b)$$

$$[Ni(phen)(bipy)]^{2+} \xrightarrow{k2a} [Ni(phen)]^{2+} + bipy \quad (2a)$$

$$[Ni(phen)(bipy)]^{2+} \xrightarrow{k2b} [Ni(bipy)]^{2+} + phen \quad (2b)$$

$$[Ni(bipy)_2]^{2+} \xrightarrow{k2c} [Ni(bipy)]^{2+} + bipy \quad (2c)$$

$$[Ni(phen)]^{2+} \xrightarrow{k3a} Ni^{2+} + phen \quad (3a)$$

$$[Ni(bipy)]^{2+} \xrightarrow{k3b} Ni^{2+} + bipy \quad (3b)$$

Of course the free ligands in the above sets of reactions will be protonated in the acid solution. The optical density of a solution at time t, say, is the sum of the optical densities of all species present. Therefore in 1cm cells we have -

$$Dt = e_1c_1 + e_2c_2 + e_3c_3 \ldots + e_nc_n$$

Dt is the optical density at any time t of a solution containing 1, 2, 3, ... n different species with extinction coefficients e_1, e_2, e_3, ... e_n and concentrations c_1, c_2, c_3, ... c_n.

The change in Dt with time is given by:

$$\frac{dDt}{dt} = e_1 \frac{dc_1}{dt} + e_2 \frac{dc_2}{dt} + e_3 \frac{dc_3}{dt} \ldots + e_n \frac{dc_n}{dt}$$

The interpretation of the results has been simplified by considering some assumptions about the rate constants of the three sets of reactions listed. This treatment is analogous to that used by earlier

workers for the simple tris complexes.[63]

All the intermediate complexes proposed in the reactions above save the $[Ni(bipy)(phen)]^{2+}$ ion have been prepared as their chlorides (sections 5.11, 5.13). A reasonable value of the extinction coefficient for $[Ni(bipy)(phen)]^{2+}$ was necessary for trial calculations of the dissociation data. Therefore, a value obtained by averaging those for $[Ni(bipy)_2]^{2+}$ and $[Ni(phen)_2]^{2+}$ has been used, i.e. $-\frac{1}{2}(22 + 12)$ or 17. The assumptions are as follows:

Assumption (i) - Reactions in set 1 slow, sets 2 and 3 fast.

Assumption (ii) - Reactions in set 1 fast, sets 2 and 3 slow.

Assumption (iii) - Reactions in sets 1 and 2 fast, set 3 slow.

In addition, re-formation reactions may have to be considered, particularly in 1 and 2 normal acids where the spectrophotometric measurements show that dissociation is obviously incomplete (section 7.11).

Assumption (i).

Here -

$$[Ni^{2+}] = [phen\ H^+] = \tfrac{1}{2}[bipy\ H^+] = [tris]_o - [tris]$$

where the brackets refer to concentrations. $[\,]_o$ refer to initial times.

Also -

$$Dt = e_{tris}[tris] + e_{Ni^{2+}}[Ni^{2+}] + e_{bipy\ H^+}[bipy\ H^+] + e_{phen\ H^+}[phen\ H^+]$$

Substituting the following abbreviations, viz. -

$e_{tris} = T$; $e_{Ni^{2+}} = n$; $e_{bipy\ H^+} = b$; $e_{phen\ H^+} = p$; $[tris]_o = c_o$; and $[tris] = C$,

we obtain -

$$Dt = Tc + n(c_o - c) + 2b(c_o - c) + p(c_o - c)$$

For a first order process $c = c_o e^{-kt}$ where k is the rate constant and t the time.

Therefore -

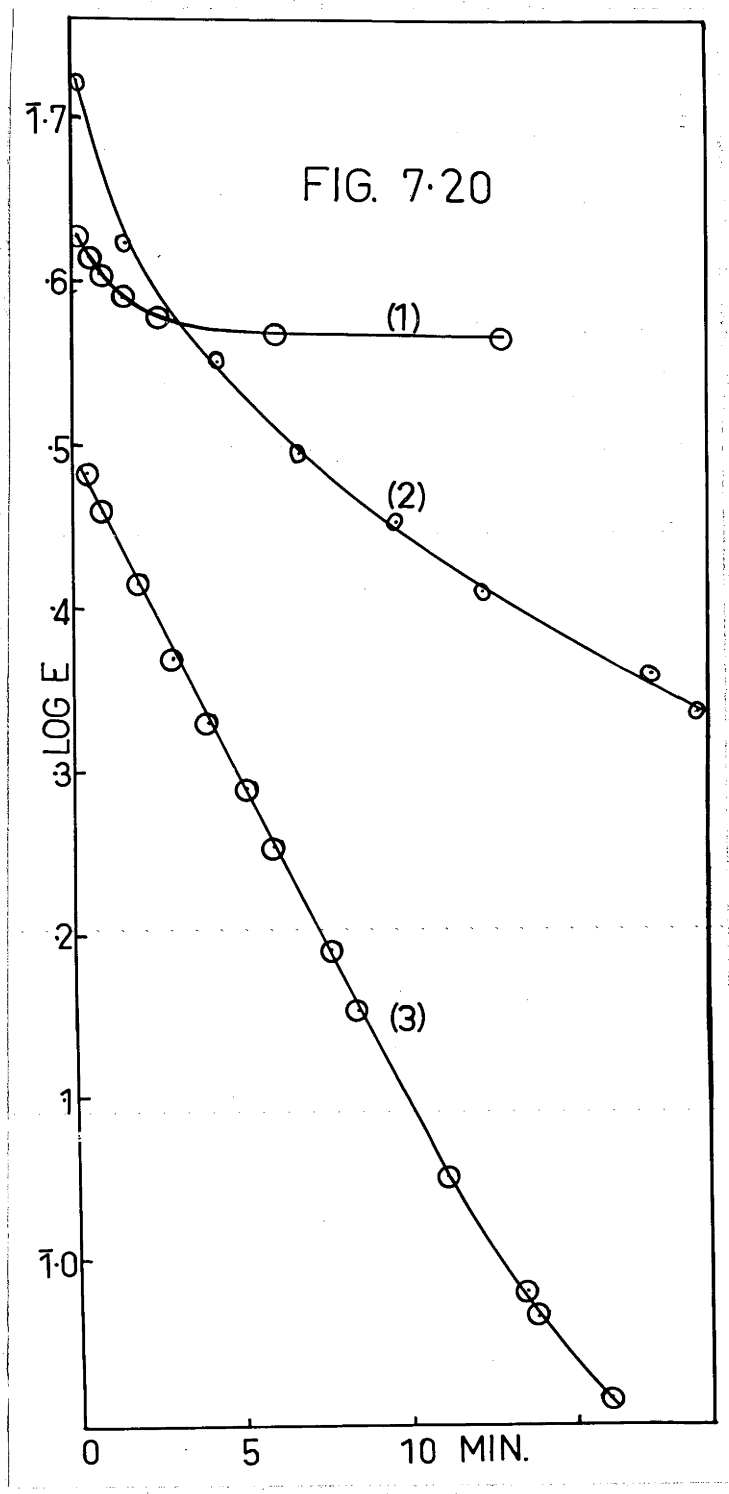
$$Dt = Tc_o e^{-kt} + (n + 2b + p)c_o - (n + 2b + p)c_o e^{-kt}$$

$$Dt - (n + 2b + p)c_o = [Tc_o - (n + 2b + p)c_o]e^{-kt}$$

Taking logs -

$$\ln\ Dt - (n + 2b + p)c_o = \text{constant} - kt$$

Thus a plot of $\log_{10}$ of the left hand side of this equation (log E) against a time abscissa should give a straight line of slope $-\frac{k}{2.303}$. Figure 7.20 gives some results for various sulphuric acid concentrations at different temperatures.

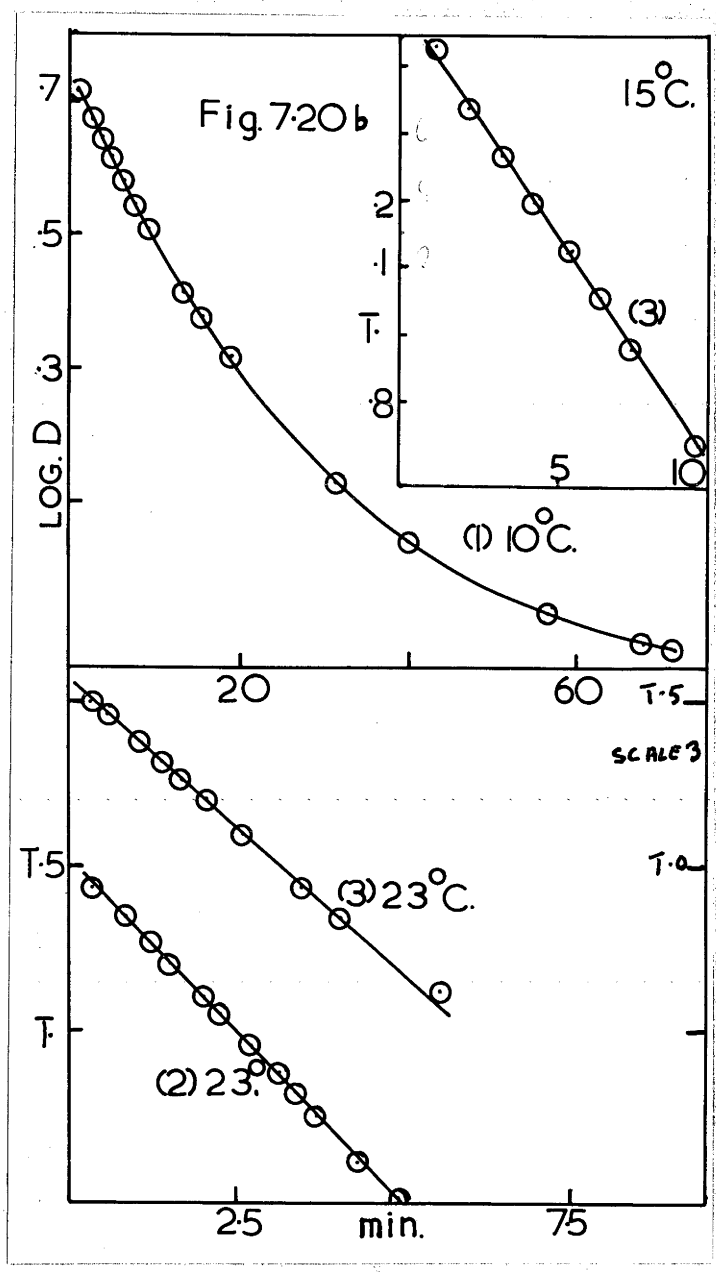


(1) 0.5N H_2SO_4 at 25°C. (2) 3N H_2SO_4 at 10°C. (3) 5N H_2SO_4 at 10°C.

Similar curves were obtained with hydrochloric acid although here the curving takes place at somewhat later times. Certainly for the two lower acid concentrations the assumption made is incorrect. On the other hand if the acid concentration is increased to 3 normal the graph remains linear for a half-life period and with further increases in the acidity good straight lines are obtained. Figure 7.20b gives some results at 10^{o}, 15^{o}, and $23^{o}C$. The primary data are also given (Table 7.20b).

As the plots do not show flattening out over the whole acid range, that observed at lower acidities cannot be due to the presence of an impurity such as the $[Ni(phen)_3]^{2+}$ ion. It did not seem reasonable to include a reverse reaction such as -

$$[Ni(phen)(bipy)_2]^{2+} \rightleftharpoons Ni^{2+} + phen + 2\ bipy$$



(1) 2.98N HCl

(2) 5.0N HCl

(3) 5.0N H_2SO_4

TABLE 7.20b

Dissociation of $[Ni(phen)(bipy)_2]^{2+}$ in 5 normal acids calculated by assumption (i). $[tris]_o$ equals 0.702×10^{-2} M.

H_2SO_4 at 15°C				HCl at 23°C			
t(min)	Dt	(Dt-.55)	log (Dt-.55)	t(min)	Dt	(Dt-.55)	log (Dt-.55)
0 s	0.514	0.459	$\bar{1}$.662	0 s	0.371	0.316	$\bar{1}$.500
18 s	.491	.436	.640	22 s	.326	.271	.433
31 s	.477	.422	.625	50 s	.279	.224	.350
57 s	.449	.394	.596	1-13	.241	.186	.270
1-15	.425	.370	.568	1-30	.215	.160	.204
1-44	.395	.340	.532	2-0	.183	.128	.107
2-0	.379	.324	.511	2-15	.169	.114	.057
2-22	.360	.305	.484	2-42	.146	.091	$\bar{2}$.959
2-50	.335	.280	.447	3-05	.131	.076	.881
3-25	.305	.250	.398	3-22	.121	.066	.820
4-03	.275	.220	.342	3-39	.111	.056	.748
4-21	.264	.209	.320	4-15	.095	.040	.602
5-0	.242	.187	.272	9.45	.059	.004	$\bar{3}$.602
5-27	.228	.173	.238	15-0	.057	.002	.301
7-03	.187	.132	.121				
9-16	.149	.094	$\bar{2}$.973				
11-20	.124	.069	.839				
13-15	.107	.052	.716				
15-05	.098	.043	.634				
17-20	.091	.036	.556				

TABLE 7.20b (Contd.)

5N H_2SO_4 at 23°C				2.98N HCl at 10°C			
t(min)	Dt	(Dt − 0.055)	log (Dt − 0.055)	t(min)	Dt	(Dt − 0.055)	log (Dt − 0.055)
0 s	0.398	0.343	$\bar{1}$.535	0	0.520	0.465	$\bar{1}$.668
18 s	.364	.309	.490	2	.451	.396	.598
33 s	.339	.284	.453	3	.429	.374	.573
1-02	.289	.234	.369	4-08	.402	.347	.540
1-22	.259	.204	.310	5	.385	.330	.519
1-40	.236	.181	.256	6-30	.360	.305	.484
2	.211	.156	.193	8	.336	.281	.449
2-18	.191	.136	.134	9-35	.314	.259	.413
2-33	.178	.123	.090	12-10	.280	.225	.352
2-58	.160	.105	.021	14	.262	.207	.316
3-26	.140	.085	$\bar{2}$.929	16	.245	.190	.279
4-0	.124	.069	.839	19	.221	.166	.220
5-30	.096	.041	.613	22-20	.197	.142	.152
6-09	.090	.035	.544	24-54	.185	.130	.114
7-24	.079	.024	.380	31	.160	.105	.021
				40	.139	.084	$\bar{2}$.924
				56-40	.121	.066	.820
				68-15	.116	.061	.785

Assumption (ii).

Here -

$$[\text{mixed bis}] = [\text{bipy H}^+] = [\text{tris}]_o - [\text{tris}]$$

Also -

$$Dt = Tc + mb\,[\text{mixed bis}] + b\,[\text{bipy H}^+]$$

where mb = the extinction coefficient of the mixed bis complex and the other terms are as defined for assumption (i).

Therefore -

$$Dt = Tc + (mb + b)(c_o - c)$$

$$= Tc + (mb + b)c_o - (mb + b)c$$

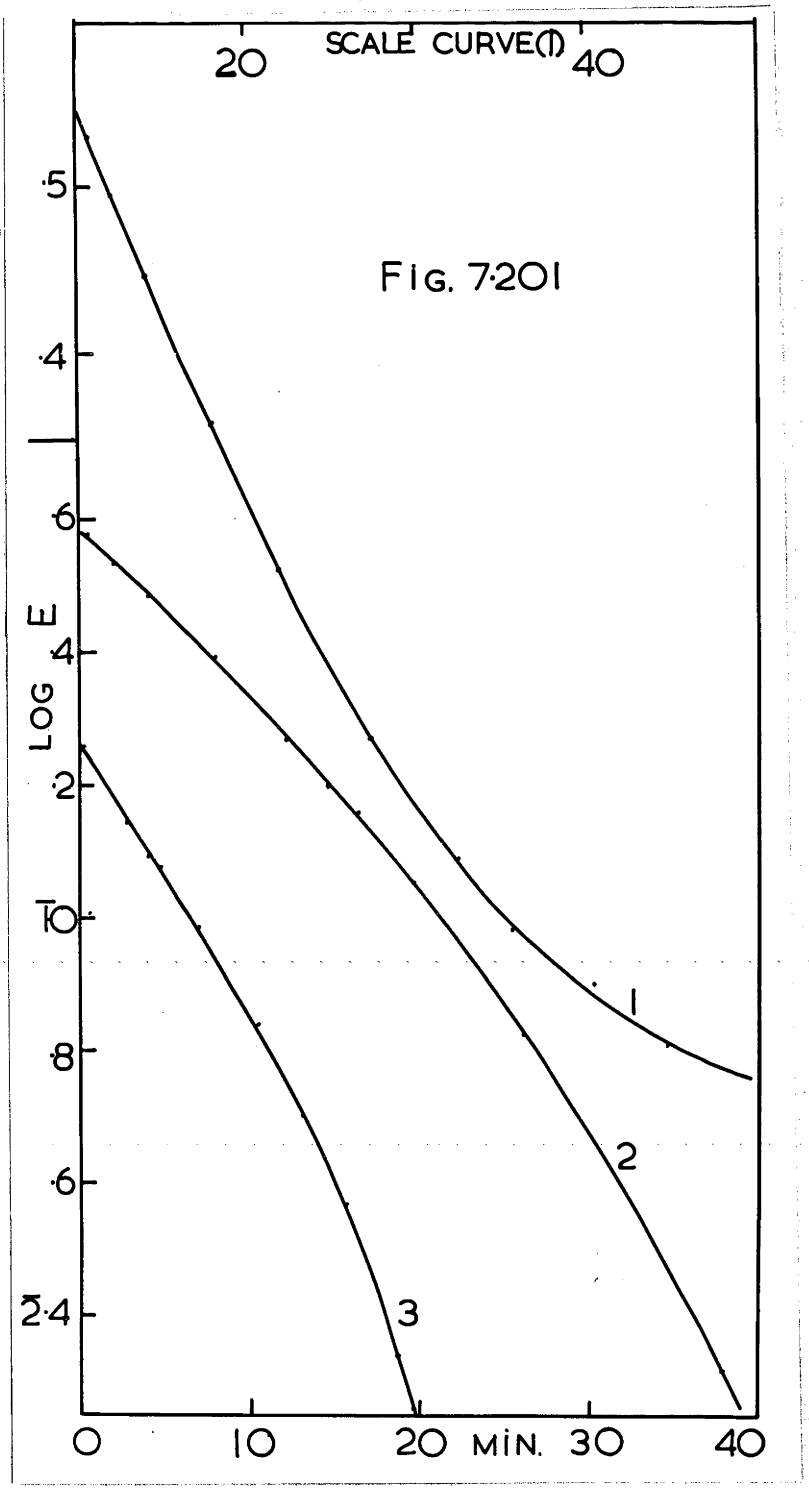
$$= (T - mb - b)c_o e^{-kt} + (mb + b)c_o$$

$$Dt - (mb + b)c_o = (T - mb - b)c_o e^{-kt}$$

Taking logs -

$$\ln[Dt - (mb + b)c_o] = \ln(\text{constant}) - kt$$

Thus a plot of $\log_{10}[Dt - (mb + b)c_o]$ against a time abscissae should give a straight line of slope $-\frac{k}{2.303}$. Figure 7.201 illustrates some examples under various conditions. It is evident that no linear relationship prevails. Again the reverse reaction could well be producing the flattening out of the curve.



Using assumption (ii)

(1) 3N H_2SO_4 at 5°C; (2) 2.98N HCl at 20°C; 5.0N HCl at 5°C.

Considering assumption (ii) but taking into account the reverse reaction we have:

$$\text{tris} \underset{k^1}{\overset{k}{\rightleftharpoons}} \text{bis} + \text{ligand}$$

If c_o is the initial concentration of tris complex and x the amount of bis formed in time t, then

$$\frac{dx}{dt} = k(c_o - x) - k^1x^2 \quad \text{.....(1)}$$

and at equilibrium

$$x = x_e, \frac{dx}{dt} = 0$$

Thus -

$$k(c_o - x) = k^1x_e^2$$

and substituting for k^1 in (1)

$$\frac{dx}{dt} = k\left\{(c_o - x) - \frac{(c_o - x_e)}{x_e^2}x^2\right\}$$

This equation may be integrated, in a rearranged form[180], using the method of partial fractions to give:

$$\ln \frac{c_ox_e + x(c_o - x_e)}{c_o(x_e - x)} = k\frac{(2c_o - x_e)}{x_e}t$$

It can be seen that plotting $\log_{10}\frac{c_ox_e + x(c_o - x_e)}{c_o(x_e - x)}$ as ordinate against t should give a straight line of slope

$$m = \frac{k(2c_o - x_e)}{2.303\ x_e}$$

$$\text{i.e.} \quad k = \frac{2.303\ x_e.m}{(2c_o - x_e)}$$

To check this assumption the optical density was treated in the following manner -

$$Dt = T(c_o - x) + (mb + b)x$$

Since it is known that the bis bipyridine nickel complex dissociates rapidly to the metal ion in acid solution[63], the presence of the alternative mixed bis complex is assumed here.

Thus -

$$Dt = 99.3\,(c_o - x) + (17 + 1.2)x$$

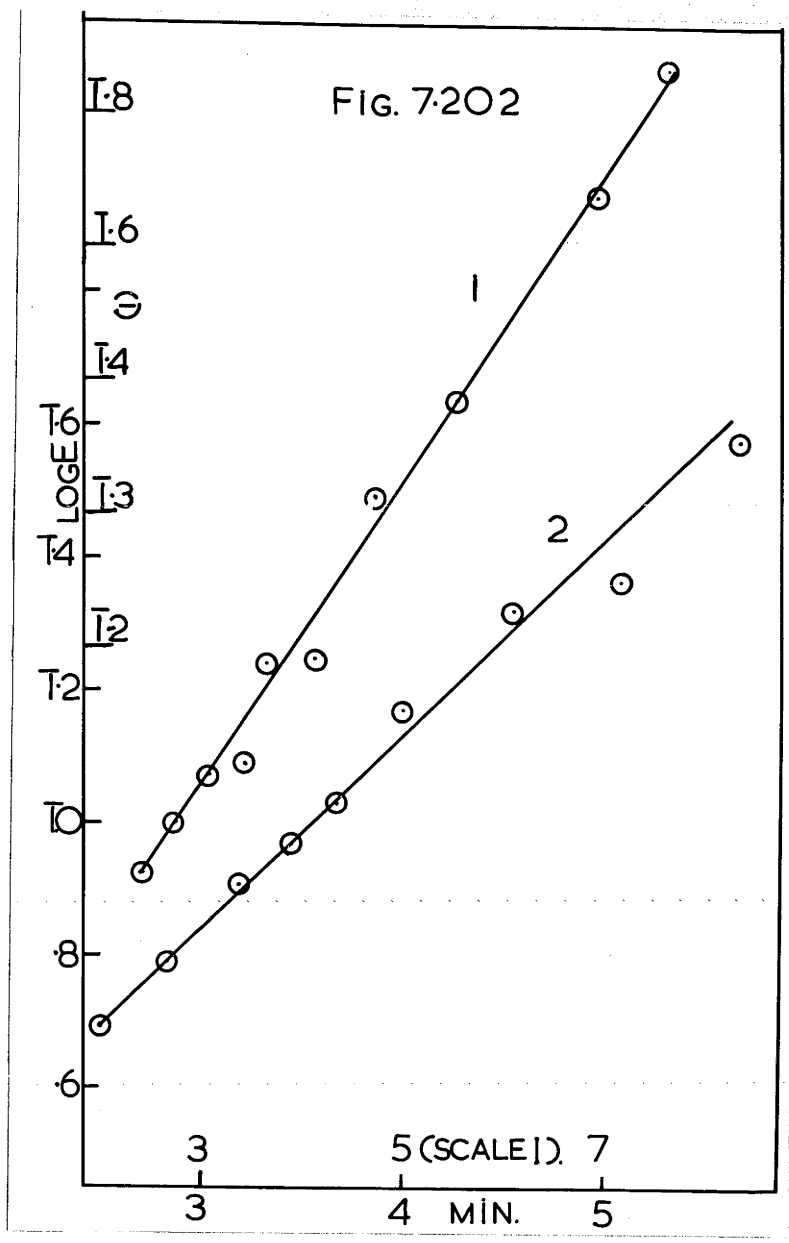
$$= 99.3\,c_o - 99.3x + 18.2x$$

$$= 99.3\,c_o - 81.1x$$

$$x = \frac{99.3\,c_o - Dt}{81.1}$$

However, in acids of normality greater than two the quantity Dt decreases to a value which makes $x > c_o$, which is impossible.

On the other hand, in one and two normal acids reasonable straight line graphs were obtained, samples of which are given in Figure 7.202. The rate constants calculated from their respective slopes were 33.7×10^{-2} min^{-1} in 1 normal HCl and 46×10^{-2} min^{-1} in 2 normal acid both at 25°C. Unfortunately, the maximum change in optical density which could be measured was 0.1 units. This was considered to be too small to warrant a quantitative study at the lower acid concentrations but the results indicate that a reaction of the opposed first and second order might be present.



$$E = \frac{c_o x_e + x(c_o - x_e)}{c_o (x_e - x)}$$

(1) 1N HCl at 25°C; (2) 2N H_2SO_4 at 25°C.

Assumption (iii).

Here -

$$[\text{monophen}] = \tfrac{1}{2}[\text{bipy } H^+] = [\text{tris}]_o - [\text{tris}]$$

Also -

$$Dt = Tc + m[\text{monophen}] + b[\text{bipy } H^+]$$

where -

m = the extinction coefficient of the mono phenanthroline complex.

It is known that the monobipyridine complex dissociates very rapidly in acid solution[63] but the monophenanthroline complex does not[120]. Consequently only the latter was assumed to be present. Therefore -

$$Dt = Tc + (m + 2b)(c_o - c)$$

$$\simeq Tc + (m + 2b)c_o - (m + 2b)c$$

Then -

$$Dt - (m + 2b)c_o = (T - m - 2b)c_o e^{-kt}$$

taking logs -

$$\ln [Dt - (m + 2b)c_o] = \ln (\text{constant}) - kt$$

Thus a plot of $\log_{10} [Dt - (m + 2b)c_o]$ against a time abscissae should yield a straight line of slope $-\frac{k}{2.303}$.

Assumptions (i) and (iii) gave rise to almost identical expressions for the corrected optical density, e.g. when $c_o = 0.702 \times 10^{-2}$ M, (i) gave Dt - 0.055 and (ii) gave Dt - 0.057. Fortunately, the visible absorption spectrum in 5N acid (section 7.11) disclosed the presence of a mono complex which could only be $Ni(phen)^{2+}$ since the dissociation of $Ni(bipy)^{2+}$ in acid solution was known to be very fast. Therefore, assumption (iii) was used to calculate the rate constants. Some results employing different initial

concentrations of complex in 5N acids at 15°C are given below:

c_o	$10^2 k$ HCl	$10^2 k$ H_2SO_4
0.702	21.6	18.3
0.351	21.6	19.3
0.176	21.9	18.4

The dissociation of the $[Ni(phen)(bipy)_2]^{2+}$ ion is conveniently summarised here. Thus in acid solutions of below 3N the change in optical density was not sufficient for reasonably accurate measurements to be made. An approach using an opposed first and second order reaction scheme could be fitted to the observations and it was concluded that appreciable re-formation was present.

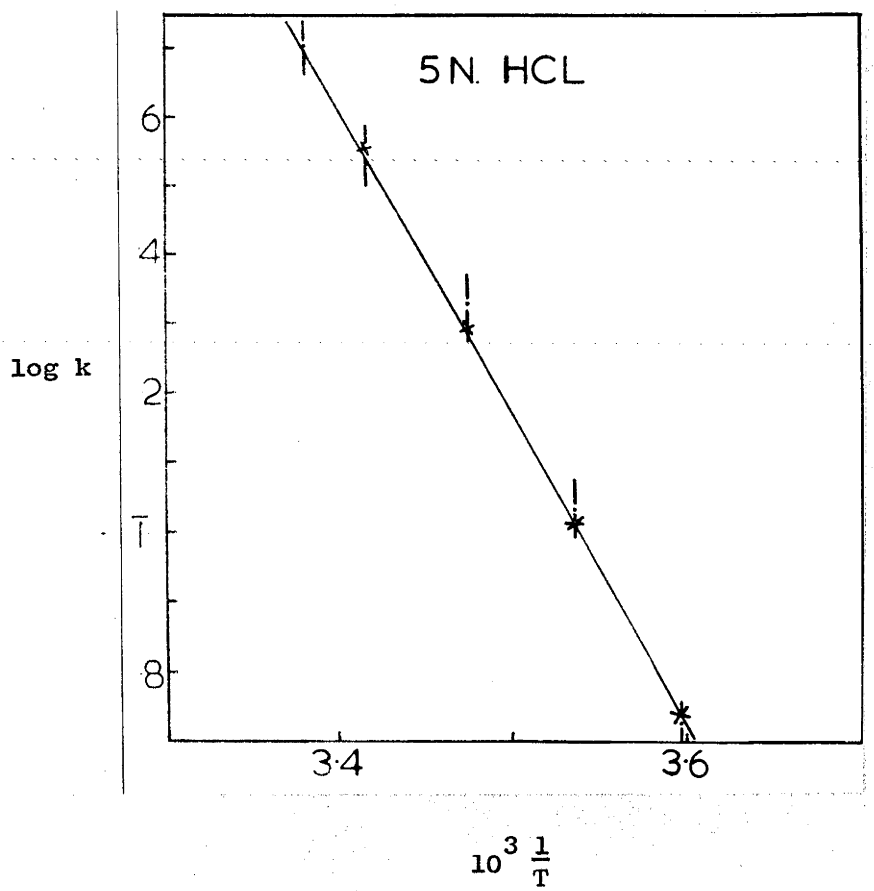
In 5N acids rapid dissociation to the $Ni(phen)^{2+}$ ion was consistent with the observations. First order rate constants and their temperature dependences are given in the succeeding pages; for convenience the racemisation results are included. It is evident that the two processes are the same within the experimental errors. (In the figures, racemisation values are shown by an x, dissociation values by a dot, and the error in the dissociation by a vertical line).

Dissociation and Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 5 Normal Hydrochloric Acid

		Dissociation		Racemisation	
°C	$10^3 \frac{1}{T}$ (°K)	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})$	log k
5.0	3.597	5.32	$\bar{2}.726$	5.50	$\bar{2}.740$
10.0	3.534	10.8	$\bar{1}.033$	10.3	$\bar{1}.013$
15.0	3.472	21.6	$\bar{1}.335$	19.7	$\bar{1}.295$
20.0	3.413	34.9	$\bar{1}.543$	36.0	$\bar{1}.556$
23.0	3.378	50.9	$\bar{1}.707$	-	-

Dissociation: Ea = 20.3 kcals/mole; log A = 12.88 sec^{-1};
$\Delta S^{\ddagger}$ = - 1.6 e.u.

Racemisation: Ea = 20.4 kcals/mole; log A = 12.99 sec^{-1};
$\Delta S^{\ddagger}$ = - 1.1 e.u.

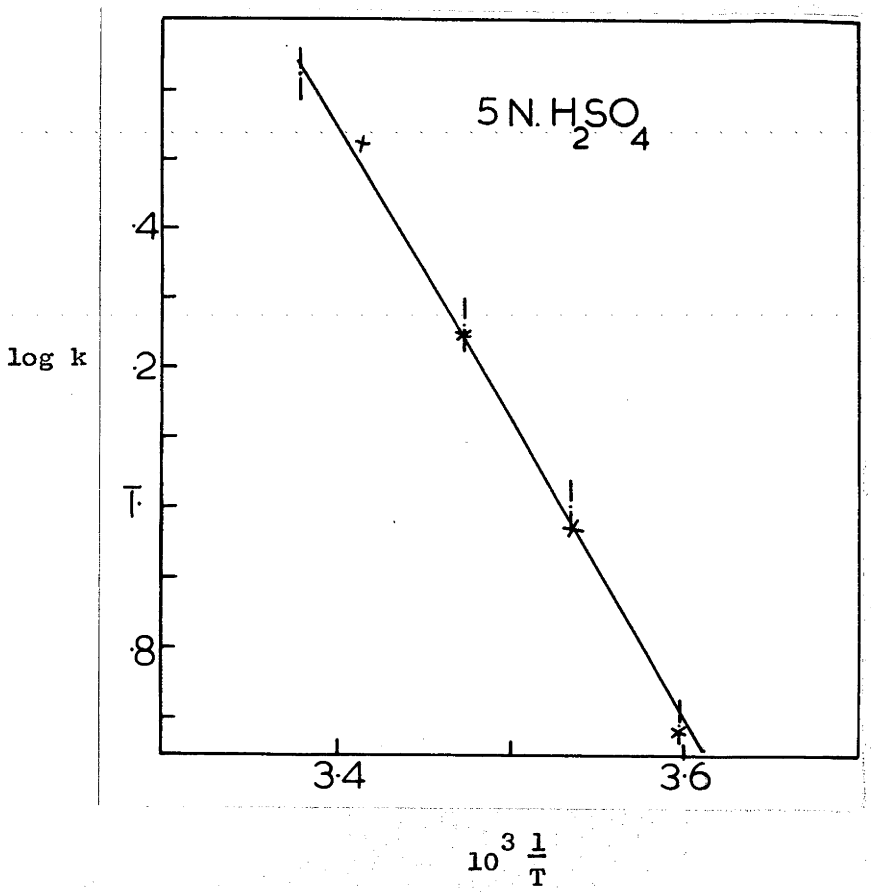


Dissociation and Racemisation of $[Ni(phen)(bipy)_2]^{2+}$ in 5 Normal Sulphuric Acid

		Dissociation		Racemisation	
°C	$10^3 \frac{1}{T}$ (°K)	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})$	log k
5.0	3.597	4.88	$\bar{2}.688$	4.82	$\bar{2}.683$
10.0	3.534	10.0	$\bar{1}.000$	9.30	$\bar{2}.969$
15.0	3.472	18.3	$\bar{1}.261$	17.7	$\bar{1}.248$
20.0	3.413	31.2	$\bar{1}.494$	33.5	$\bar{1}.525$
23.0	3.378	42.1	$\bar{1}.625$	-	-

Dissociation: Ea = 19.4 kcals/mole; log A = 12.15 sec^{-1};
$\Delta S^{\ddagger}$ = - 4.9 e.u.

Racemisation: Ea = 20.9 kcals/mole; log A = 13.32 sec^{-1};
$\Delta S^{\ddagger}$ = + 0.5 e.u.



7.3 KINETICS OF DISSOCIATION OF 2,2'-BIPYRIDINE BIS (1,10-PHENANTHROLINE NICKEL(II) CHLORIDE.

Note: The presence of a small amount of the $[Ni(phen)_3]^{2+}$ ion was detected in the racemisation studies. In view of the almost quantitative conversion of racemic $[Ni(phen)_3]^{2+}$ complex into the active form it was reasonable to assume that a similar amount of the $[Ni(phen)_3]^{2+}$ ion was present in the racemate used for the dissociation studies. Accordingly, a correction has been made to the optical densities by subtracting the calculated optical density due to the $[Ni(phen)_3]^{2+}$ ion,

$$\text{i.e. } Dt = D_{observed} - D_{[Ni(phen)_3]^{2+}}$$

A treatment analogous to that given for $[Ni(phen)(bipy)_2]^{2+}$ (section 7.2) uses the same sets of equations to represent the dissociation except that equations (1b) and (2c) refer to $[Ni(phen)_2]^{2+}$ in place of $[Ni(bipy)_2]^{2+}$. For a first order process similar assumptions concerning the relative rates have been made and yield the following corrected optical densities. The abbreviations used are the same as defined previously (page 159). In addition, bp is used for the extinction coefficient of the $[Ni(bipy)(phen)]^{2+}$ ion.

Assumption (i) -

$$Dt - (n + b + 2p)c_o$$

Assumption (iia) -

$$Dt - (bp + p)c_o$$

Assumption (iib) -

$$Dt - (mb + p)c_o$$

A plot of $\log_{10}$ of the corrected optical density for each assumption against a time abscissae should give a straight line if the assumption made was correct. Figure 7.30 shows the graphs for each assumption. The upper set were obtained in 1N HCl at 15°C and the lower set in 5N HCl at 15°C. It may be seen that no linear relationships were obtained.

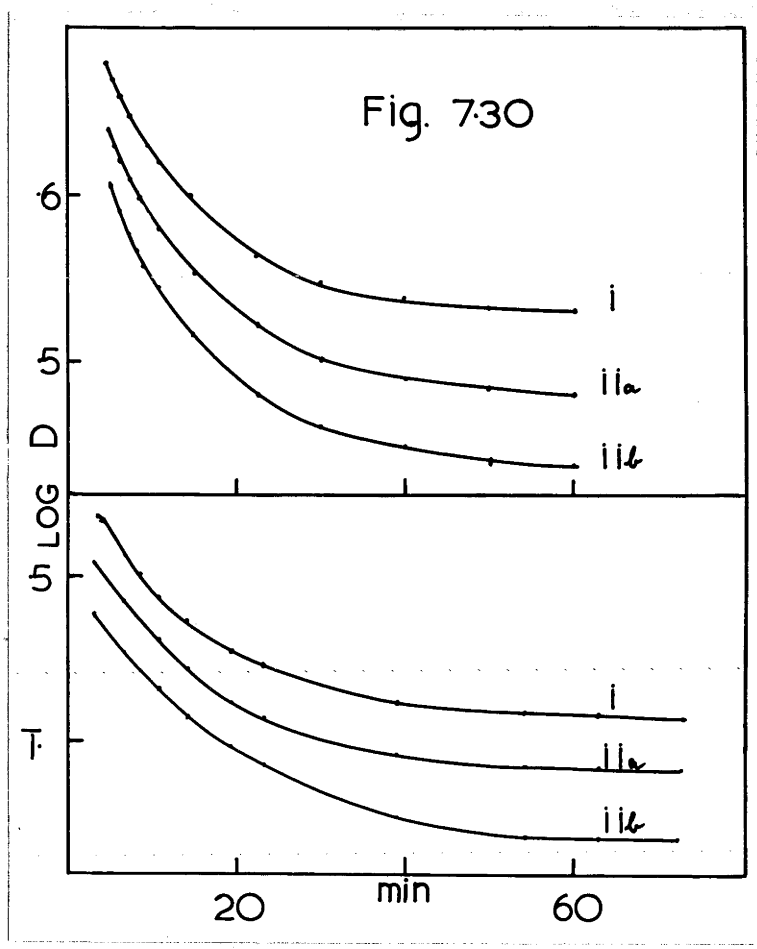


Fig. 7·30
6
5
LOG D
i
iia
iib
5
T·
i
iia
iib
20
min
60

The visible absorption spectra of the complex in acid solution (section 7.13) suggested that at least for acidities less than 3N re-formation could occur. It has been observed for the simple tris complexes, that appreciable re-formation takes place in solutions of less than 3N acidity[63]. Therefore, a trial of the data according to an opposed first and second order scheme was carried out. The derivation of the rate equation has already been given (page 168).

7.31 TREATMENT OF DATA.

Equations (1) and (2) below represent the possible dissociations in acid solution.

$$[Ni(bipy)(phen)_2]^{2+} \longrightarrow [Ni(phen)_2]^{2+} + bipy \quad .....(1)$$

$$[Ni(bipy)(phen)_2]^{2+} \longrightarrow [Ni(bipy)(phen)]^{2+} + phen \quad .....(2)$$

The free ligands will be present mainly as their protonated forms. Using the nomenclature defined earlier the corrected optical densities at time t are given by the following:

$$Dt = T(c_o - x) + (bp + b)x \quad .....(1)$$

$$Dt = T(c_o - x) + (mb + p)x \quad .....(2)$$

Substitution of the numerical values for the extinction coefficients and re-arranging gives:

$$Dt\ x(1) = \frac{88.1\ c_o - Dt}{74.9}\ ;\quad x(2) = \frac{88.1\ c_o - Dt}{70.5}$$

The values found for x were used to plot the graph of $\log \left\{ \frac{c_o x_e + x(c_o - x_e)}{c_o (x_e - x)} \right\}$ versus time. Unfortunately, it was not possible to distinguish between assumptions (1) and (2). In the results which follow x has been obtained from (1).

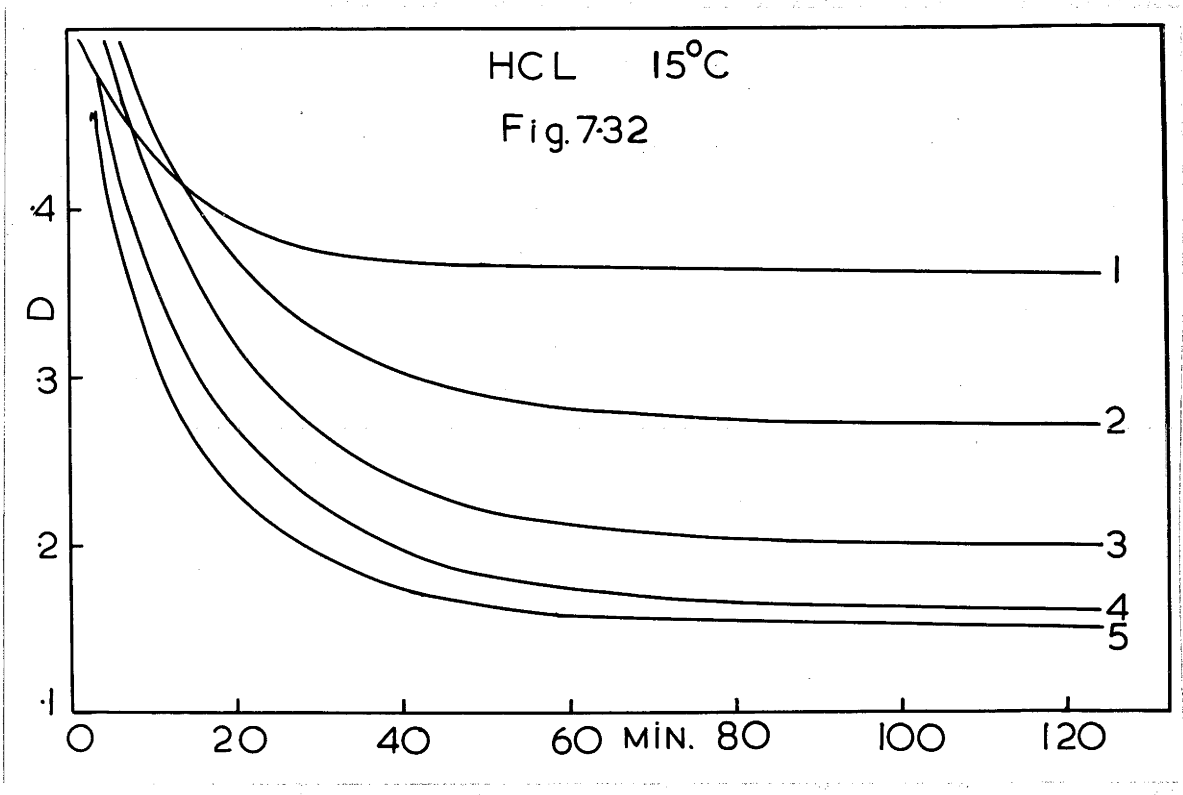
It is noteworthy that a blue crystalline solid could be isolated from a solution of the tris complex in 3N acid (cf. section 7.1).

Analysis gave : $[Ni(C_{12}H_8N_2)_2(H_2O)_2]Cl_2.3H_2O$

Calcd. C, 49.64 ; H, 4.65 ; N, 9.65%

Found C, 49.70 ; H, 4.09 ; N, 9.53%

The curves in Figure 7.32 illustrate the method used to determine the "equilibrium" value of the optical density for solutions of varying acid concentrations. Following the initial decrease the optical density continued to change at a much slower rate. In practice, if the time interval between the initial reading and the horizontal portion of the graph was, say, 40 min., it was found that over the next 40 min. the optical density would change very little, (i.e. by about 2%). The value of the optical density at the mid-point of this horizontal portion was used as a reasonable estimate of the "equilibrium" position and could be repeated with a precision of about 2%. A sample calculation of the first order rate constant is shown below for a 1N HCl solution at 15 $\pm$ 0.2°C. The data used are given in Table 7.321 and Figure 7.321. Some results in 5N HCl at 10°C are also included.



(1) 1N HCl

(2) 1.98N HCl

(3) 2.98N "

(4) 3.98N "

(5) 5N HCl

Sample Calculation 7.321.

$$c_o = 0.622 \times 10^{-2} M$$

Dt = D(observed) - 0.029 where 0.029 is the tris impurity correction.

$$x = \frac{88.1\, c_o - Dt}{74.9}$$

$$= \frac{(88.1 \times 0.622 \times 10^{-2}) + 0.029 - D(\text{observed})}{74.9}$$

$$= \frac{0.577 - D\ \text{observed}}{74.9}$$

$x_e = 0.266 \times 10^{-2}$ and the slope (m) of the plot $\log_{10} \frac{c_o x_e + x(c_o - x_e)}{c_o (x_e - x)}$ versus time (Figure 7.321) is $m = 5.02 \times 10^{-2}$

Thus -

$$k = \frac{2.303\ m\ x_e}{(2c_o - x_e)}$$

$$= \frac{2.303 \times 5.02 \times 10^{-2} \times 0.266 \times 10^{-2}}{0.978 \times 10^{-2}}$$

$$= 3.14 \times 10^{-2}\ \text{min}^{-1}$$

Similarly in 5N HCl at 10°C -

$m = 2.07 \times 10^{-2}$ whence $k = 3.87 \times 10^{-2}\ \text{min}^{-1}$

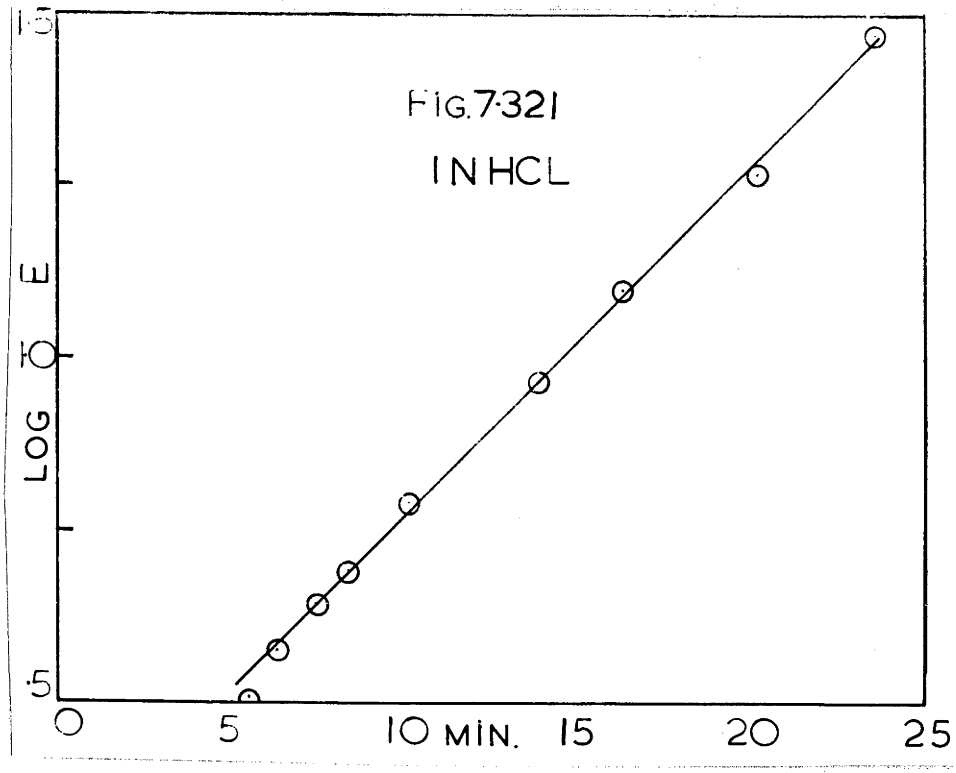


Fig. 7·321
1 N HCL
LOG E
·5
0
5
10 MIN.
15
20
25

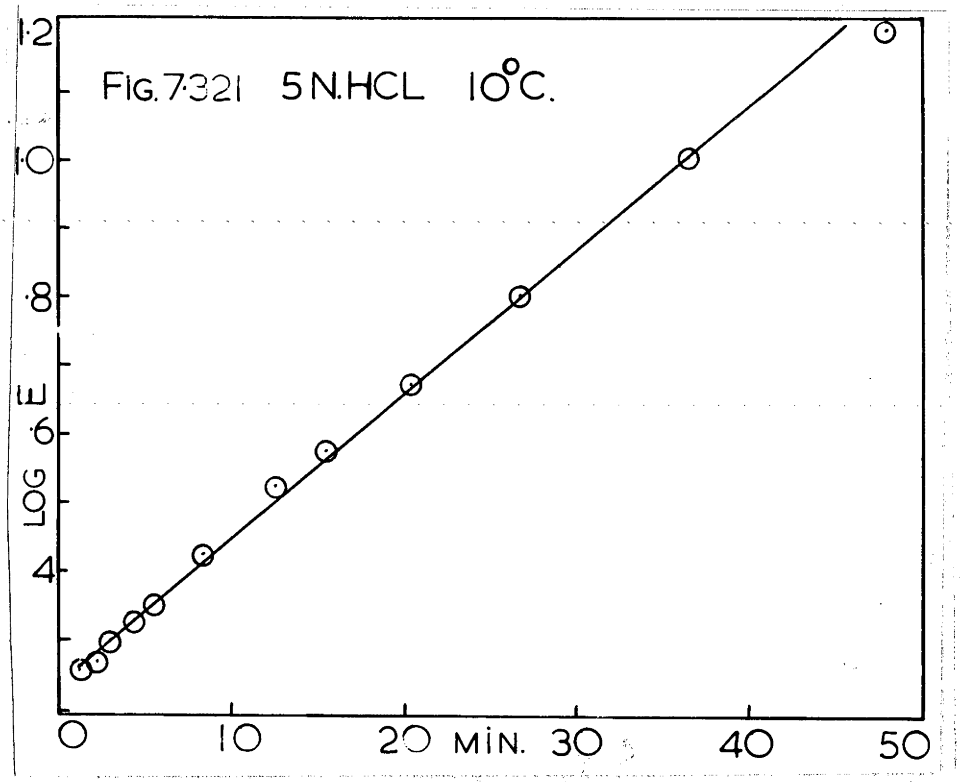


Fig. 7·321 5 N.HCL 10°C.
LOG E
·4
·6
·8
1·0
1·2
0
10
20 MIN.
30
40
50

TABLE 7.321

1 Normal HCl at 15 $\pm$ 0.2°C

t(min)	D_{obs}	$0.577-D_{obs}$	$x \times 10^2$	$\frac{x_e-x}{\times 10^2}$	$\frac{c_o(x_e-x)}{\times 10^5}$	$\frac{x(c_o-x_e)}{\times 10^5}$	$\frac{c_o x_e+x(c_o-x_e)}{\times 10^5}$	$\frac{c_o x_e+x(c_o-x_e)}{c_o(x_e-x)} = E$	log E
5-33	0.460	0.117	0.156	0.110	0.684	0.555	2.21	3.23	0.509
6-20	0.450	0.127	0.170	0.096	0.597	0.605	2.26	3.78	0.578
7-25	0.441	0.136	0.182	0.084	0.522	0.648	2.30	4.41	0.644
8-21	0.435	0.142	0.190	0.076	0.473	0.676	2.33	4.92	0.692
10-05	0.424	0.153	0.204	0.062	0.386	0.726	2.38	6.17	0.790
13-55	0.410	0.167	0.223	0.043	0.267	0.794	2.45	9.18	0.963
16-20	0.402	0.175	0.234	0.032	0.199	0.833	2.49	12.5	1.097
20-10	0.394	0.183	0.244	0.022	0.137	0.869	2.52	18.4	1.265
23-35	0.388	0.189	0.252	0.014	0.087	0.897	2.55	29.3	1.467
27	0.380	0.197	0.263						
37	0.379	0.198	0.264						
60	0.375	0.202	0.270						

TABLE 7.321 (Contd.)

5 Normal HCl at 10 ± 0.2°C

t(min)	D_{obs}	$0.577-D_{obs}$	$x \times 10^2$	$\frac{x_e-x}{\times 10^2}$	$\frac{c_o(x_e-x)}{\times 10^5}$	$\frac{x(c_o-x_e)}{\times 10^5}$	$\frac{c_o x_e+x(c_o-x_e)}{\times 10^5}$	$\frac{c_o x_e+x(c_o-x_e)}{c_o(x_e-x)} = E$	log E
0	0.440	0.137	0.183	0.374	2.33	0.119	3.58	1.54	0.188
1-15	0.402	0.175	0.234	0.323	2.01	0.152	3.62	1.80	0.255
2-10	0.390	0.187	0.250	0.307	1.91	0.163	3.63	1.90	0.279
2-55	0.384	0.193	0.258	0.299	1.86	0.168	3.63	1.95	0.290
4-22	0.365	0.212	0.283	0.274	1.70	0.184	3.65	2.14	0.330
5-32	0.355	0.222	0.296	0.261	1.62	0.192	3.66	2.25	0.352
8-18	0.330	0.247	0.330	0.227	1.41	0.215	3.68	2.60	0.415
12-30	0.296	0.281	0.375	0.182	1.13	0.244	3.71	3.27	0.515
15-30	0.279	0.298	0.398	0.159	0.99	0.259	3.72	3.77	0.576
20-24	0.256	0.321	0.429	0.128	0.80	0.279	3.74	4.70	0.672
26-45	0.231	0.346	0.462	0.095	0.59	0.300	3.77	6.37	0.804
36-30	0.205	0.372	0.497	0.060	0.37	0.323	3.79	10.2	1.007
48	0.189	0.388	0.518	0.039	0.24	0.337	3.80	15.7	1.196
95	0.163	-	-						
160	0.160	-	x_e = .557						

Rate constants calculated in the manner shown were independent of the initial concentration over the acid range employed. Some results at 25°C are given in Table 7.322.

TABLE 7.322

Acid	$10^2 C_o$	$k(min^{-1})$
0.5N HCl	0.498	0.10
" "	0.995	0.11
1N HCl	0.744	0.11
" "	0.622	0.11
3N HCl	1.82	0.14
" "	0.622	0.15
5N HCl	0.498	0.27
" "	0.747	0.27

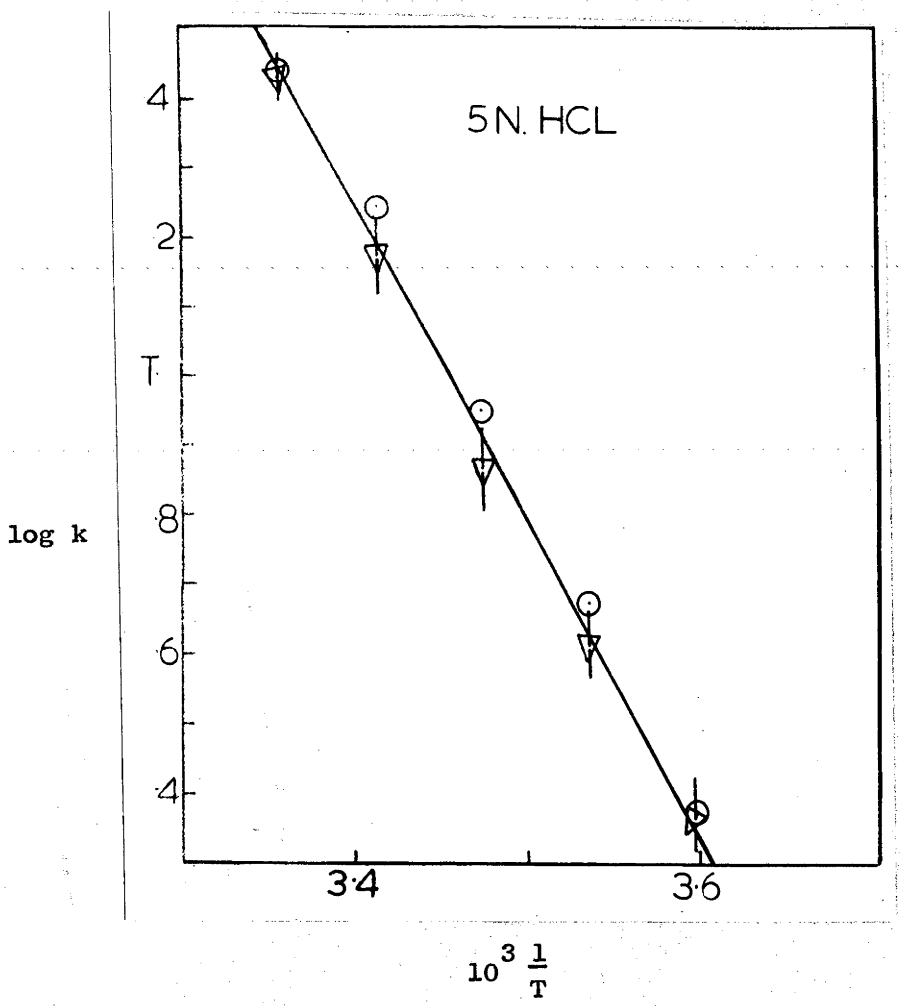
The activation energies, frequency factors, and entropies of activation have been calculated from the results of temperature variation studies given in the following pages. The method of calculation used has been described (section 6.4). Included are the racemisation results under the same conditions. In the figures those points enclosed by circles represent racemisation values and their vertical diameters give the errors. Corresponding dissociation results are shown by triangles and their errors by vertical lines. It is evident that within the experimental errors the results are the same for both dissociation and racemisation.

Dissociation and Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 5 Normal Hydrochloric Acid

		Dissociation		Racemisation	
^oC	$10^3 \frac{1}{T}$ (^oK)	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})$	log k
25.0	3.356	27.0	$\bar{1}.431$	27.6	$\bar{1}.441$
20.0	3.413	14.9	$\bar{1}.173$	17.6	$\bar{1}.246$
15.0	3.472	7.27	$\bar{2}.862$	8.95	$\bar{2}.952$
10.0	3.534	4.10	$\bar{2}.613$	4.71	$\bar{2}.673$
5.0	3.597	2.36	$\bar{2}.373$	2.37	$\bar{2}.375$

Dissociation: Ea = 21.0 kcals/mole; log A = 13.01 sec^{-1};
$\Delta S^{\ddagger}$ = - 1.0 e.u.

Racemisation: Ea = 21.6 kcals/mole; log A = 13.53 sec^{-1};
$\Delta S^{\ddagger}$ = + 1.4 e.u.

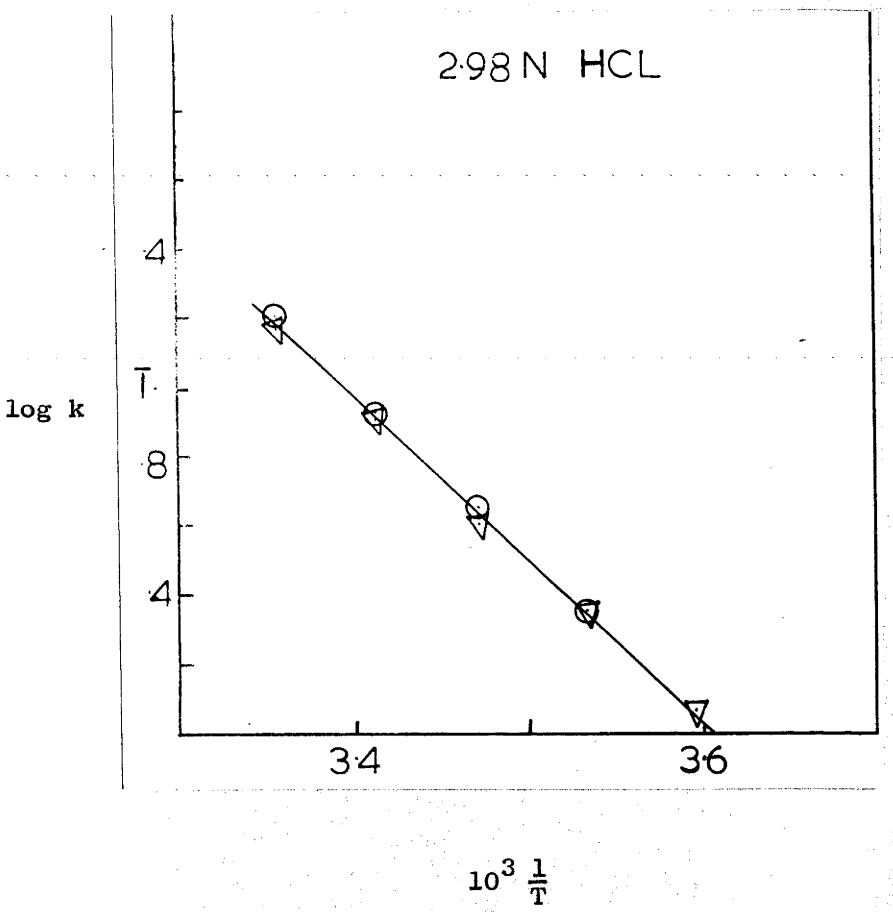


Dissociation and Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 2.98 Normal Hydrochloric Acid

		Dissociation		Racemisation	
°C	$10^3 \frac{1}{T}$ (°K)	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})$	log k
25.0	3.356	14.9	$\bar{1}.173$	16.3	$\bar{1}.212$
20.0	3.413	8.02	$\bar{2}.904$	8.55	$\bar{2}.932$
15.0	3.472	4.03	$\bar{2}.605$	4.49	$\bar{2}.652$
5.0	3.597	1.16	$\bar{2}.065$	-	-

Dissociation: Ea = 21.4 kcals/mole; log A = 13.10 sec^{-1};
$\Delta S^{\ddagger}$ = - 0.6 e.u.

Racemisation: Ea = 22.1 kcals/mole; log A = 13.65 sec^{-1};
$\Delta S^{\ddagger}$ = + 2.0 e.u.

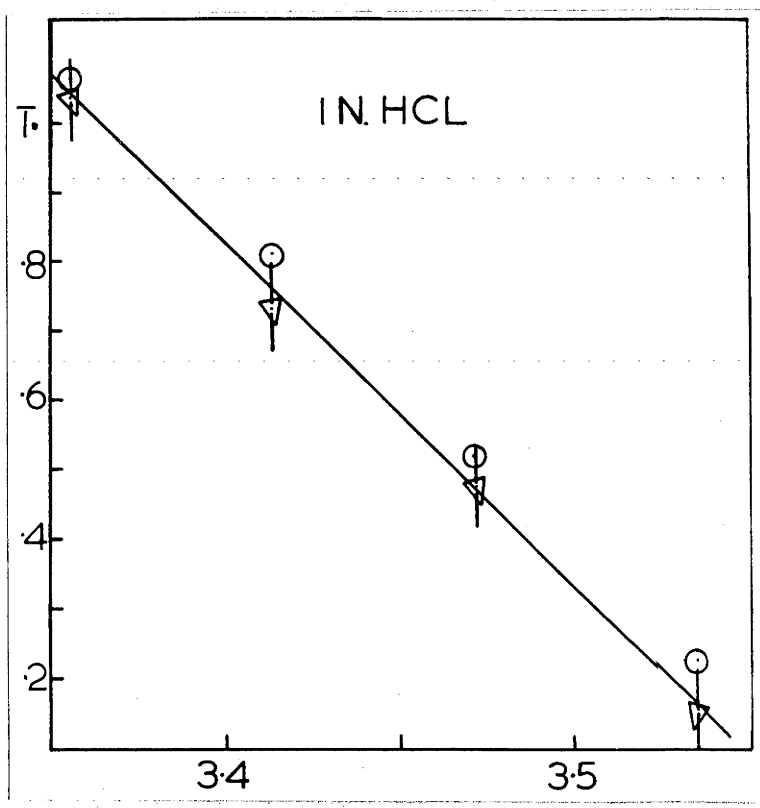


Dissociation and Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 1 Normal Hydrochloric Acid

		Dissociation		Racemisation	
°C	$10^3 \frac{1}{T}$ (°K)	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})$	log k
25.0	3.356	11.0	$\bar{1}.041$	11.8	$\bar{1}.072$
20.0	3.413	5.41	$\bar{2}.733$	6.59	$\bar{2}.819$
15.0	3.472	3.01	$\bar{2}.479$	3.33	$\bar{2}.522$
10.0	3.534	1.44	$\bar{2}.158$	1.69	$\bar{2}.228$

Dissociation: Ea = 22.7 kcals/mole; log A = 13.88 sec^{-1};
$\Delta S^{\ddagger}$ = + 3.0 e.u.

Racemisation: Ea = 22.2 kcals/mole; log A = 13.57 sec^{-1};
$\Delta S^{\ddagger}$ = + 1.6 e.u.



log k

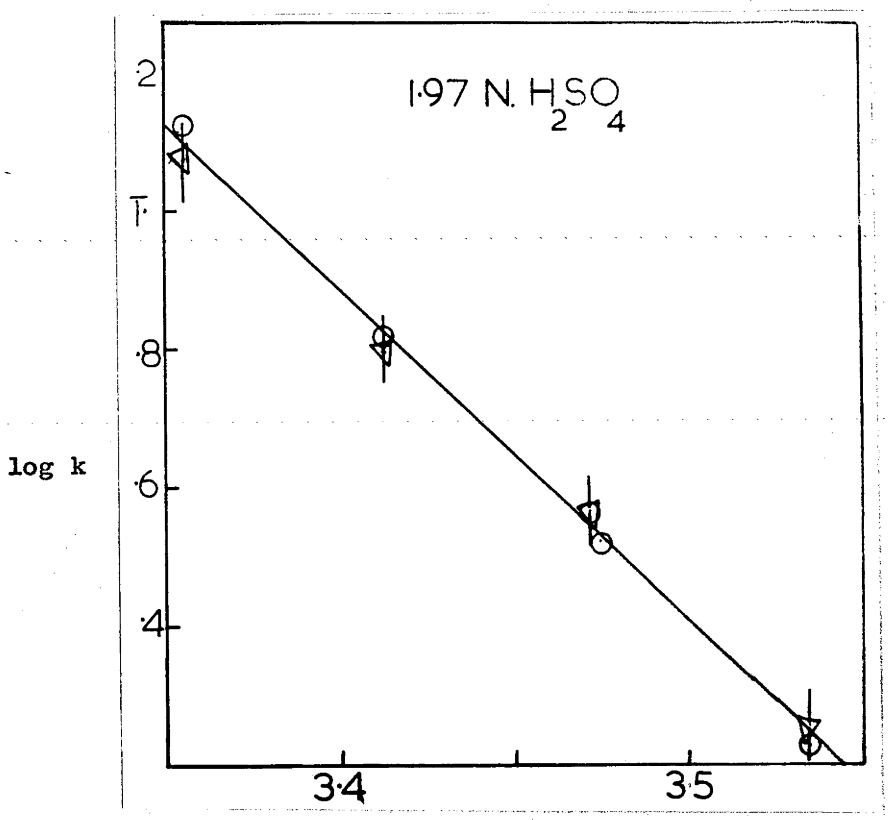
$10^3 \frac{1}{T}$

Dissociation and Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 1.97 Normal Sulphuric Acid

		Dissociation		Racemisation	
^{o}C	$10^3 \frac{1}{T}$ (^{o}K)	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})$	log k
25.0	3.356	12.0	$\bar{1}.079$	13.6	$\bar{1}.134$
20.0	3.413	6.35	$\bar{2}.803$	6.64	$\bar{2}.822$
15.0	3.472	3.72	$\bar{2}.571$	3.33 ($14^{o}.8$)	$\bar{2}.522$
10.0	3.534	1.80	$\bar{2}.255$	1.69	$\bar{2}.228$

Dissociation: Ea = 21.3 kcals/mole; log A = 12.95 sec^{-1};
$\Delta S^{\ddagger}$ = - 1.2 e.u.

Racemisation: Ea = 23.1 kcals/mole; log A = 14.25 sec^{-1};
$\Delta S^{\ddagger}$ = + 4.7 e.u.

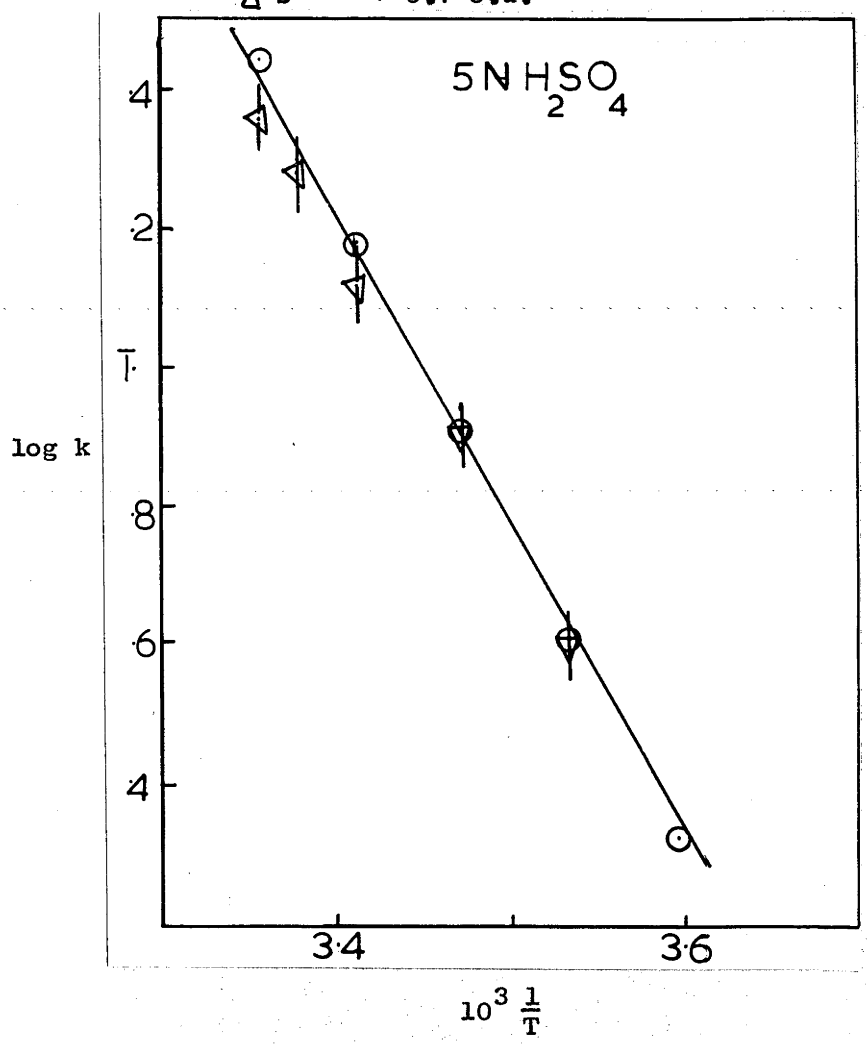


Dissociation and Racemisation of $[Ni(bipy)(phen)_2]^{2+}$ in 5 Normal Sulphuric Acid

		Dissociation		Racemisation	
°C	$10^3 \frac{1}{T}$ (°K)	$10^2 k(min^{-1})$	log k	$10^2 k(min^{-1})$	log k
25.0	3.356	22.5	$\bar{1}.352$	27.6	$\bar{1}.441$
23.0	3.378	19.0	$\bar{1}.279$	-	-
20.0	3.413	13.0	$\bar{1}.114$	15.1	$\bar{1}.179$
15.0	3.472	8.10	$\bar{2}.909$	7.94	$\bar{2}.900$
10.0	3.534	4.02	$\bar{2}.604$	3.99	$\bar{2}.601$

Dissociation: Ea = 19.9 kcals/mole; log A = 12.21 sec^{-1};
$\Delta S^{\ddagger}$ = - 4.6 e.u.

Racemisation: Ea = 21.4 kcals/mole; log A = 13.37 sec^{-1};
$\Delta S^{\ddagger}$ = + 0.7 e.u.



7.4 ERRORS.

Racemisation:

The measurements of the racemisation rate constants could be repeated with a precision of $\pm$ 2% and have an accuracy of within $\pm$ 5% for both complexes studied. The following method has been used in making an estimate of the errors. When two numbers were added or subtracted the error in the result was approximately given by the sum of the errors in the separate numbers. When two numbers were multiplied together or divided the error was approximately given by the sum of the percentage errors.[219] The error in the measurement of the slopes has been obtained by the method suggested by Livingstone.[218] The errors in the Ea and $\Delta S^{\ddagger}$ values for the racemisation results are estimated as $\pm$ 0.6 kcal and $\pm$ 2 e.u..

Dissociation:

Successive determinations of the rate constants for both mixed tris complexes had a precision of within $\pm$ 5%. The accuracy varied from about $\pm$ 8% for the $[Ni(phen)(bipy)_2]^{2+}$ ion to about $\pm$ 15% for the $[Ni(bipy)(phen)_2]^{2+}$ ion. For the last complex the results were most accurate at the higher acid concentrations where there was the greatest change in optical density. Moreover, the method used to calculate the first order rate constants for the $[Ni(bipy)(phen)_2]^{2+}$ ion involved the difference, viz. $x_e - x$, of two experimentally determined quantities and further enhanced the errors present. The respective errors in Ea and $\Delta S^{\ddagger}$ were $\pm$ 0.9 kcal/mole and $\pm$ 3 e.u. for the $[Ni(phen)(bipy)_2]^{2+}$ ion and $\pm$ 1.5 kcal/mole, $\pm$ 5 e.u. for the $[Ni(bipy)(phen)_2]^{2+}$ ion. These figures can be regarded as order of magnitude quantities only and the best evidence for parity in the

dissociation and racemisation results is given by the graphical representation. Here the fit to the same line is obtained by either experimental method and with one exception there is random scattering of the points. The exception (1N HCl) could be ascribed to a larger than average systematic error.

CHAPTER EIGHT

8.0 NICKEL COMPLEXES - DISCUSSION OF RESULTS.

The experimental work will be discussed under these headings -

8.1 Reaction mechanisms in acid solution.

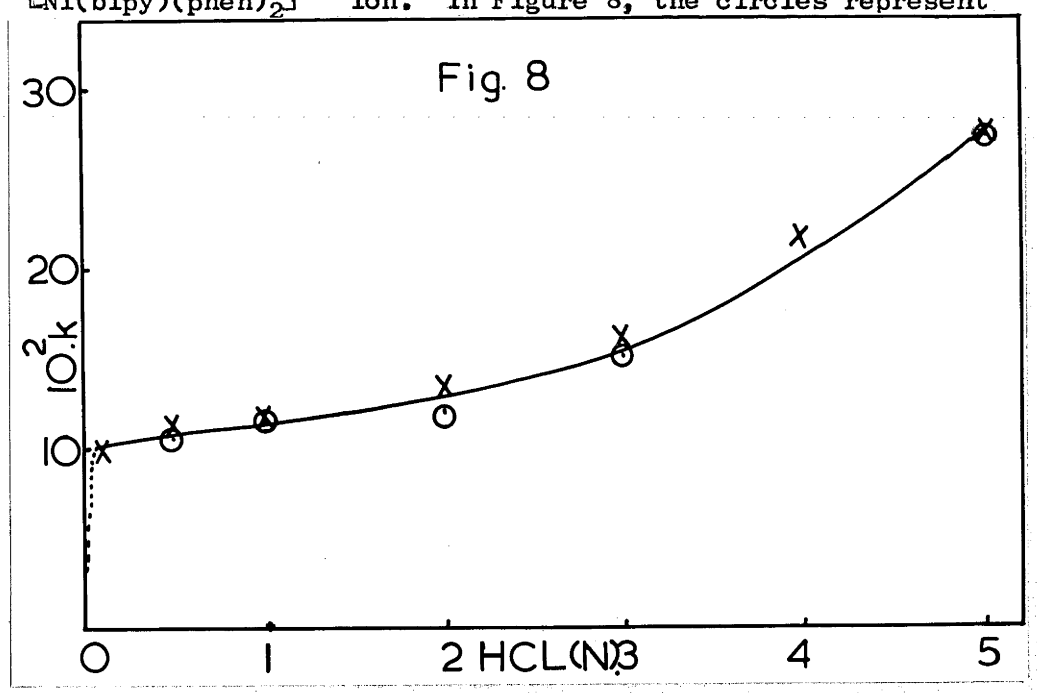
8.2 Reaction mechanisms in aqueous solutions.

8.3 Reaction mechanisms in organic solvents.

8.1 REACTION MECHANISMS IN ACID SOLUTIONS.

In the temperature range studied the rates of dissociation and racemisation of the $[Ni(phen)(bipy)_2]^{2+}$ ion in 5N acid are identical within the experimental errors. The same is true for $[Ni(bipy)(phen)_2]^{2+}$ over the acid range 1-5 normal. It is concluded therefore, that racemisation takes place by dissociation mechanisms.

It is evident that both racemisation and dissociation rates are markedly increased by the concentration of acid present. The dependence of both rates on the acidity is shown for the $[Ni(bipy)(phen)_2]^{2+}$ ion. In Figure 8, the circles represent



dissociation values and the crosses those for racemisation. A similar graph was obtained earlier for the racemisation of the $[Ni(phen(bipy)_2]^{2+}$ ion (see Chapter 6, Figure 6.54). An explanation is sought which will account for -

(a) racemisation by a dissociation process;

(b) the acid dependence of this process;

(c) the relationship of the results of those of previous investigations.

The complex ions are conveniently referred to as -

(o) $[Ni(phen)_3]^{2+}$

(i) $[Ni(phen)_2(bipy)]^{2+}$

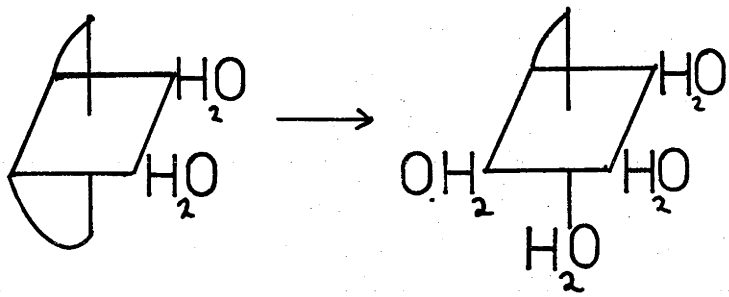
(ii) $[Ni(phen)(bipy)_2]^{2+}$

(iii) $[Ni(bipy)_3]^{2+}$

In the racemisation of the mixed ligand complexes the operation of a dissociation mechanism requires that either a phenanthroline or a bipyridine group be lost first. Since the results of previous work show that the rates of racemisation and dissociation for (iii) are markedly acid dependent while those for (o) are not, it is reasonable to conclude that the bipyridine in (i) and (ii) produces the acid dependence observed. It is also likely, in view of the dissociation mechanisms known for (iii), that a bipyridine ligand is the first to dissociate.

For complex (i) loss of a bipyridine leaves behind the more slowly dissociating $[Ni(phen)_2(H_2O)_2]^{2+}$ ion. In accordance with the previous interpretation this is either already inactive or rapidly loses its activity.[63] The result is racemisation.

For complex (ii) loss of a bipyridine must result in the formation of a mixed bis complex and if this is inactive or rapidly loses its activity, racemisation follows. Alternatively, loss in activity might arise from further rapid dissociation of the active bis to give the inactive mono complex, e.g.



It was not possible to obtain dissociation data in solutions of less than 0.5N acid. From the continuous nature of the plot it appears that dissociation parallels racemisation down to 0.1N acid. In the range 0.1-2N the racemisation increases by a relatively small amount but outside this the changes are more pronounced. The Ea and $\Delta s^{\ddagger}$ values in the acids employed are given in the following table. It is seen that the activation energy decreases with increasing acid concentration though this is partly compensated by a more negative entropy of activation.

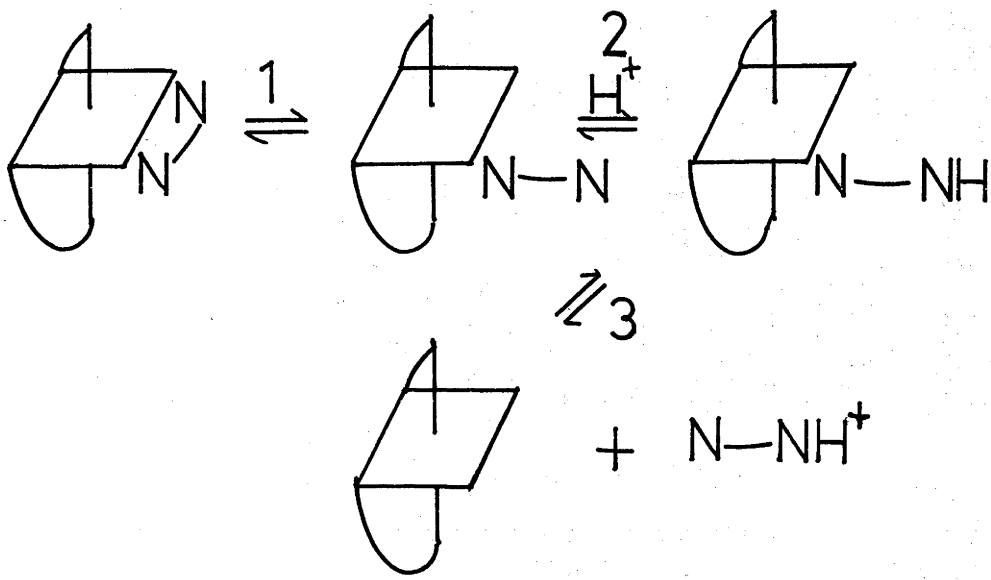
$[Ni(bipy)(phen)_2]^{2+}$

Acid normality	HCl Racemisation Ea kcals mole^{-1}	HCl Racemisation $\Delta S^{\ddagger}$ e.u.	HCl Dissociation Ea kcals mole^{-1}	HCl Dissociation $\Delta S^{\ddagger}$ e.u.	H_2SO_4 Racemisation Ea kcals mole^{-1}	H_2SO_4 Racemisation $\Delta S^{\ddagger}$ e.u.	H_2SO_4 Dissociation Ea kcals mole^{-1}	H_2SO_4 Dissociation $\Delta S^{\ddagger}$ e.u.
1.0	22.2	+1.6	22.7	+3.0	21.9	+0.6	-	-
1.97	-	-	-	-	23.1	+4.7	21.3	-1.2
2.98	22.1	+2.0	21.4	-0.6	-	-	-	-
5	21.6	+1.4	21.0	-1.0	21.4	+0.7	19.9	-0.6

$[Ni(phen)(bipy)_2]^{2+}$

Acid normality	HCl Racemisation Ea kcals mole^{-1}	HCl Racemisation $\Delta S^{\ddagger}$ e.u.	HCl Dissociation Ea kcals mole^{-1}	HCl Dissociation $\Delta S^{\ddagger}$ e.u.	H_2SO_4 Racemisation Ea kcals mole^{-1}	H_2SO_4 Racemisation $\Delta S^{\ddagger}$ e.u.	H_2SO_4 Dissociation Ea kcals mole^{-1}	H_2SO_4 Dissociation $\Delta S^{\ddagger}$ e.u.
1.0	21.6	+1.4	-	-	22.3	+3.9	-	-
3.0 (2.98 HCl)	21.2	0.6	-	-	21.4	+0.5	-	-
5.0	20.4	-1.1	20.3	-1.6	20.9	+0.5	19.4	-5.0

The dissociation mechanism proposed may be illustrated as follows where N-N represents a bipyridine ligand.

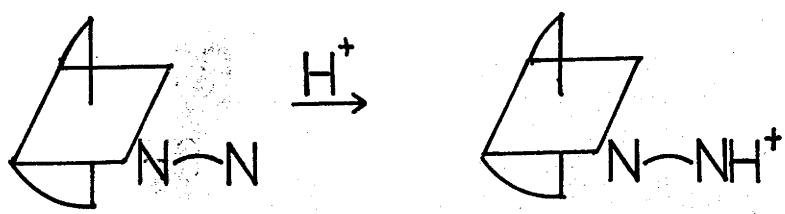


It is reasonable to assume that the ligands dissociate step-wise. Stage (1) represents a reversible reaction between the tris complex and a partly dissociated intermediate. Partial dissociation as here envisaged must precede complete dissociation; the alternative being the very unlikely three-centred reaction involving the simultaneous rupture of two metal-nitrogen bonds. Thus the dissociation in step (1) would be expected to take place with all four complexes under discussion. However, for (o) the nitrogen would be held in the vicinity of the metal after bond-breaking has occurred, owing to the rigid nature of the phenanthroline ligand. Thus re-formation of the original tris configuration would be favoured compared with step (2).

On the other hand, step (2) would be expected to proceed much more readily where a bipyridine molecule was concerned. Not being rigid it could permit one end to detach and move further away from the positive field of the metal. Thus a hydrogen ion from the solution could attach to the free nitrogen. At stage (3) the positive charge on the bipyridine would distribute over the whole ligand, and weaken the remaining metal-nitrogen bond so that dissociation follows. The possibility of a direct attack by a proton on the undissociated tris complex is thought unlikely as a similar attack could take place with $[Ni(phen)_3]^{2+}$ but here no acid dependence is observed.

Evidently the bis complex formed on dissociation of one bipyridine group must be either optically inactive or racemise rapidly.[63] Otherwise not only excess bipyridine but also excess phenanthroline should retard the racemisation in aqueous solution.

The proposed mechanism is consistent with the lowering in activation energy found as the acid concentration increases. The tendency for the entropy terms to become more negative might be identified with a decreased number of particles in the transition state, e.g.



In view of the experiments carried out in this work (see section 2.7, page), the results of Healy and Murmann[212] on the behaviour of $[Fe(bipy)_3]^{2+}$ and related ions in concentrated acids are open to serious doubts and cannot be taken as evidence against half-bonded intermediates. In addition, the rates of dissociation of the $[Fe(bipy)_3]^{2+}$ and $[Ni(en)_3]^{2+}$ [244] ions are acid dependent, and both contain ligands capable of a one-ended detachment in the manner suggested.

Finally, the possibility that the acid dependence results from attachment of a proton to the heterocyclic ring is not consistent with the acid independent dissociation of $[Ni(phen)_3]^{2+}$. Moreover, $[Fe(phen)_3]^{2+}$ displays only a slightly acid dependent dissociation rate. It is difficult to see why a proton should not just as readily attach to a phenanthroline as to a bipyridine ligand if the attachment is of this type.

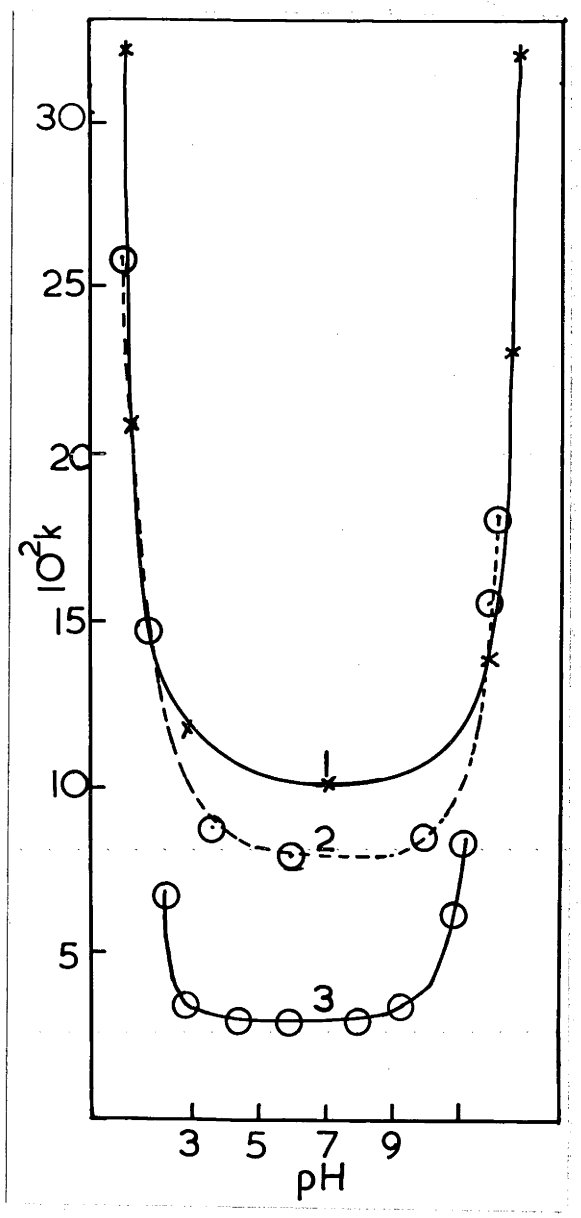
The table below summarises the available data in 5 normal hydrochloric acid at 25°C. The k values are taken from the racemisation figures and reference 89.

	Complex	$10^2 k(min^{-1})$	Ea(kcals $mole^{-1}$)	$^{*}\Delta S^{\ddagger}$ (e.u.)
(o)	$[Ni(phen)_3]^{2+}$	0.06	25.0	-0.6
(i)	$[Ni(phen)_2(bipy)]^{2+}$	27.6	21.6	1.4
(ii)	$[Ni(phen)(bipy)_2]^{2+}$	66.0	20.4	-1.1
(iii)	$[Ni(bipy)_3]^{2+}$	very fast	-	-

* calculated as in section 6.4.

The presence of at least one bipyridine ligand in the complex increases the rate in acid solution by lowering the activation energy, as required by the proposed mechanism. Unfortunately (iii) has not been studied as fully as the other members of the set, no doubt owing to the rapidity of its reactions in acid solution at the usual temperatures. It was possible to utilise the results of Schweitzer and Lee[63] to obtain the pH dependence curve (iii) shown in Figure 8.1. The similarity of complexes (i), (ii), and (iii) is clearly demonstrated in their racemisation behaviour over the pH range.

FIGURE 8.1



(1) $[Ni(bipy)_3]^{2+}$ ion.

(2) $[Ni(bipy)_2(phen)]^{2+}$ ion.

(3) $[Ni(bipy)(phen)_2]^{2+}$ ion.

The sharp increase in rate observed at an acid concentration of about 10^{-2}M could be explained by the formation of a half-bonded, protonated intermediate, which then racemised rapidly. In addition, a further effect could be present. It has been pointed out (sections 6.57, 6.8) that excess bipyridine retards the racemisation rate in aqueous solution. Contrary to earlier work[60] excess bipyridine was also found to retard the racemisation of the $[Ni(bipy)_3]^{2+}$ ion. For example in water at 10°C the rate constant was reduced from $(1.86 \pm 0.08) \times 10^{-2}$ to $(1.62 \pm 0.07) \times 10^{-2}$ min^{-1} in the presence of 0.028M bipyridine. Therefore, as re-formation takes place with some retention of configuration, the addition of acid would reduce the free bipyridine concentration and so contribute to the increase in racemisation rate (but cf 8.2, the amount of re-formation with retention of configuration in neutral solution is thought to be very small).

The racemisation and dissociation rates are seen to continue to increase as the acid concentration exceeds 3 normal (Figures 6.54, 8.0). The dissociation results indicate that the bipyridine group re-attaches in 3 normal and also in 4 and 5 normal acids, though in the last two the extent is comparatively small. The increased rate above 3 normal could be understood in terms of the reduced rate of the reverse reaction, the bipyridine being present largely as the $(bipy\ H_2)^{2+}$ ion.[221] Finally, it might be more appropriate to treat the high acid concentrations as equivalent to a change in solvent and the rate variations explained on this basis.

8.2 REACTION MECHANISMS IN AQUEOUS SOLUTIONS.

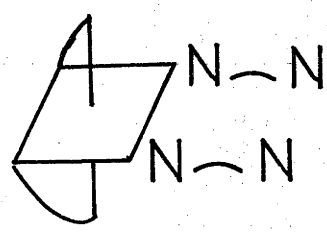
In the absence of direct information on the rates of dissociation in aqueous solution the conclusions regarding mechanisms of racemisation in this solvent must remain open to question. Analogy with the simple complexes and the results just discussed for the mixed complexes makes it not unlikely that the dissociation mechanism persists. In a dissociation mechanism in aqueous solution the stepwise detachment of a bipyridine ligand has been suggested. Consequently, upon a one-ended detachment of a bipyridine, water molecules could occupy the vacant site on the metal. They prevent re-attachment so that when the second metal-ligand bond breaks dissociation follows. Such a process, of course, could contribute to the racemisation in acid solution also and may be applied to both the complexes.

In an analogous manner it is possible to interpret the effects of certain ions on the racemisation rates (sections 6.58, 6.81). For example, complexes (i), (ii), and (iii) in basic solutions of pH greater than ten show a marked increase in rate while complex (o), which contains no bipyridine ligands, is only slightly affected even in 1M potassium hydroxide. It is proposed that a half-bonded intermediate could be involved here in which the strongly nucleophilic OH^- ion attaches to the vacant site and so prevents re-attachment of the free nitrogen. On the breaking of the second metal-nitrogen bond dissociation and racemisation take place. The increased rates are found to be a consequence of the lower activation energy required. (cf. Cl^- ion section 2.33).

Alternatively the OH^- ion could attack the complex, either before or at the half-bonded stage, in a bimolecular mechanism to produce dissociation and racemisation. There seems to be no reason, however, why the $[Ni(phen)_3]^{2+}$ ion should not also suffer such an attack by OH^- ion.

The increase in racemisation rate observed in the presence of either NO_2^-, Cl^-, Br^- or F^- ions may be explained by a mechanism similar to that proposed for OH^- ion. That is, the ions could attach to the metal at the half-bonded stage and favour complete loss of ligand. The above ions have no effect on the racemisation of complex (o), in agreement with the absence of bipyridine ligands which can readily half-bond.

For both mixed complexes bipyridine, but not phenanthroline, produces a retardation in the racemisation rate which is attributed to a mass-law retardation. It could be envisaged as a re-attachment via one end of a bipyridine to the site left vacant in a half-bonded intermediate. At this stage the intermediate may be represented as follows:



Retention of configuration takes place as one half-bonded ligand can lead to re-formation of the active tris complex upon dissociation of the other. Molecular models show that it is not possible to attach a phenanthroline group at the half-bonded stage, thus account-

ing for the failure of excess phenanthroline to affect the rates. This results from the rigid nature of phenanthroline, which leads to steric hindrance involving a nitrogen atom belonging to an attached ligand and one of the phenanthroline nitrogens. On the other hand the more flexible bipyridine group can twist one ring relative to the other and remove this steric hindrance to reattachment.

A specific effect with ions such as Ni^{2+} might be expected on the basis of the mechanism proposed. It should be possible to produce accelerated racemisation rates as a consequence of the metal ion attaching itself to the free end of a half-bonded bipyridine. At the maximum concentration of nickel employed (0.16M) there was no significant effect on the racemisation rate constant in water. Higher concentrations were not practical as it became impossible to see through the polarimeter tube.

It might also be expected that the presence of metal ions which are capable of reaction with bipyridine could increase the racemisation rate by affecting the rate of the reverse reaction. However, the failure to observe an increased rate need not be surprising as it is not necessary for the re-formation reaction to occur with 100% retention. It appears more probable that in the absence of added bipyridine the amount of re-formation taking place with retention is very small.

There was no significant effect with other bidentate ligands on the racemisation rates at concentrations of the same order as used for bipyridine (Table 6.81). It would be necessary for an added ligand to react with the half-bonded intermediate at a rate compar-

able to that of the bipyridine group in order to produce an optically active product and so affect the racemisation rate. Evidently this does not take place.

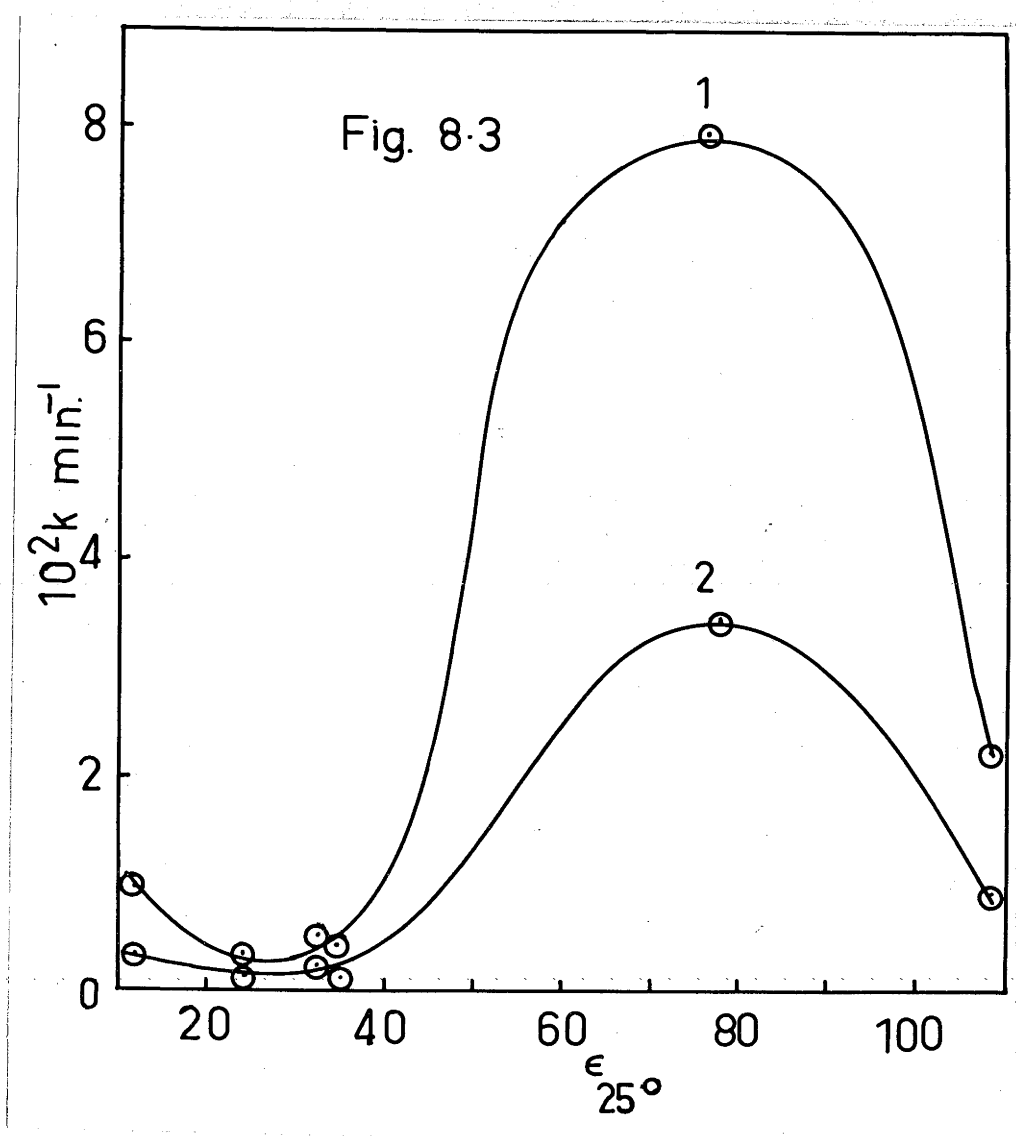
8.3 REACTION MECHANISMS IN ORGANIC SOLVENTS.

Table 8.3 summarises the results for both mixed complexes in the solvents used. It may be seen (Figure 8.3), that the racemisation rates do not vary in any simple way with the dielectric constant (ε) of the solvent. Similar observations have been made for the simple tris complexes (Section 2.4). The results are not surprising as there are obvious differences between the solvents used, for example structure of the solvent molecules and their ability to coordinate.

An examination of Table 8.3 shows that the decreased rates in organic solvents compared to the rates in water are a result of more negative entropies of activation. The energies of activation are seen to decrease. An interpretation of the entropy changes may be given in terms of the dissociation mechanism already proposed for acid solutions. There would then appear to be two factors in opposition. Firstly, those contributing to an increase in entropy, which may be set out as follows:

(a) The formation of a half-bonded intermediate suggests a transition state having an increased freedom of movement of the ligands and therefore greater entropy.

(b) A molecular model of the $[Fe(phen)_3]^{2+}$ complex ion has shown the presence of three major pockets in between the ligands, in which water molecules can fit to give a fairly compact spherical aggregate.[127] A similar



(1) $Ni(phen)(bipy)_2(ClO_4)_2$

(2) $Ni(bipy)(phen)_2(ClO_4)_2$

aggregate should be possible for the nickel complexes. Therefore in water, and perhaps other solvents, a positive entropy increment could arise from the release of solvent from the initial aggregate in forming the transition state.

TABLE 8.3

RACEMISATION IN VARIOUS SOLVENTS

$[Ni(bipy)(phen)_2]^{2+}$

Solvent	log A (sec^{-1})	Ea(kcals)	$\Delta S^{\ddagger}$ e.u.	ε 25°C	$10^2 k(min^{-1})$ 25°C
water	14.05	23.6	3.8	78.5	3.32
39.7% ethanol-water	13.13	23.3	-0.4	-	0.638
ethanol	12.13	23.1	-5.0	24.3	0.0972
methanol	12.19	22.7	-4.7	32.6	0.198
formamide	12.64	22.6	-2.7	109	0.787
pyridine	11.01	20.9	-10	12.3	0.304
nitrobenzene	8.56	19.8	-21	35.0	0.0069

$[Ni(phen)(bipy)_2]^{2+}$

water	13.90	22.9	3.1	78.5	7.81
39.7% ethanol-water	13.79	23.7	2.6	-	1.73
ethanol	9.58	18.9	-16.7	24.3	0.307
methanol	11.64	21.5	-7.2	32.6	0.462
formamide	13.23	22.8	+0.1	109	2.04
pyridine	12.41	22 .1	-3.7	12.3	0.977
glacial acetic acid	11.90	22.3	-6.0	6.2	0.226

Those factors which, on the other hand, could contribute to an entropy decrease, are set out below:

(c) If the mechanism involves partial dissociation it is reasonable to expect the formation of a more polar transition state tending to "freeze" solvent molecules.

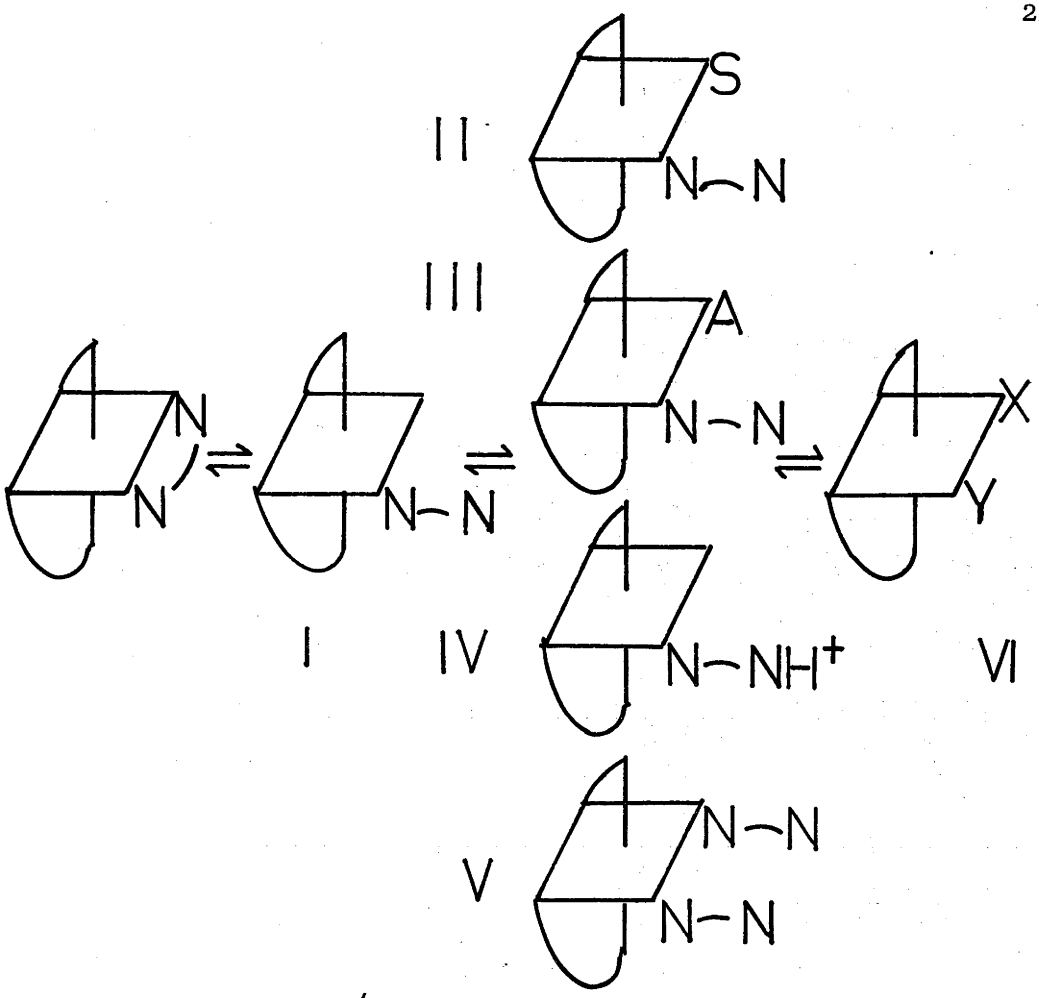
(d) Certain of the solvents used are known to form complexes with the transition metal ions, e.g. $[Ni(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, and $[Ni(py)_4]^{2+}$. In a dissociation mechanism it is probable that the solvent would interact with the vacated site on the metal, the degree of interaction depending to a first approximation on the ability of the solvent molecule to coordinate. The binding of a solvent molecule in this way could result in an entropy decrease.

The effects of a change in solvent on the racemisation rates may be approximately correlated with the coordinating power of the solvent. For example, the order of decreasing racemisation rate is as follows for both mixed complexes in various solvents: water > formamide > pyridine > methanol > ethanol > nitrobenzene ~ glacial acetic acid. The same sequence was obtained for the $[Ni(bipy)_3]^{2+}$ complex while the order for $[Ni(phen)_3]^{2+}$ placed pyridine before water.[89] On the other hand, the somewhat analogous iron complexes $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ are known to racemise faster in nitrobenzene than in water, and an intramolecular mechanism is believed to operate in both solvents.

In the absence of a dissociation mechanism the complexes could racemise in organic solvents by any of the intramolecular

methods discussed earlier (Section 2.1). For example, a mechanism of the Ray and Dutt type could be correlated with the negative entropies of activation found. The absence of a retarding effect by excess bipyridine when in organic solvents could be accounted for by an intramolecular mechanism. Also the effect of organic solvent on the participation of water molecules in a half-bonded intermediate may be important. Excess bipyridine produces a small retardation in rate in 11.83% mole fraction ethanol-water but no effect at higher ethanol concentrations. A consideration of Figure 6.91 (page 144) shows that at higher ethanol concentrations the racemisation rate decreases quite suddenly and then remains almost unaffected by further increased alcohol content. In addition, the shapes of the plots for complexes (i), (ii), and (iii) are quite different from that of complex (o) (Figure 2.4). Provided that one bipyridine ligand is present then it appears that there are features common to the racemisation mechanisms, since they are affected so similarly by changes in solvent composition. Unfortunately, measurements of the activation energies and entropies in 39.7% ethanol-water do not exhibit any parallelisms between the complexes. Thus the retardation in racemisation rate found for (i) could be attributed to a more negative entropy but for (ii) the retardation is attended by a higher activation energy.

The proposed dissociation mechanism which applies to both complexes may be summarised as follows:



X, Y = solvent and/or solute molecules or ions.

(In species (II), (III), S = solvent and A = an anionic group).

The first dissociation to a half-bonded stage (I) would normally be followed by return to the starting configuration. In the presence of acid rapid reaction of (IV) may account for the accelerated rate. Loss in activity would result by the rapid racemisation of (VI) or alternatively, by (VI) having the trans configuration. Effects on the rate by S and A could occur via species (II) and (III) while (V) would be expected to favour return to the original configuration and so account for the small retardation observed with excess bipyridine.

CHAPTER NINE

9.0 THE RACEMISATION OF THE $Cr(bipy)(ox)_2^-$ AND $Cr(phen)(ox)_2^-$ IONS.

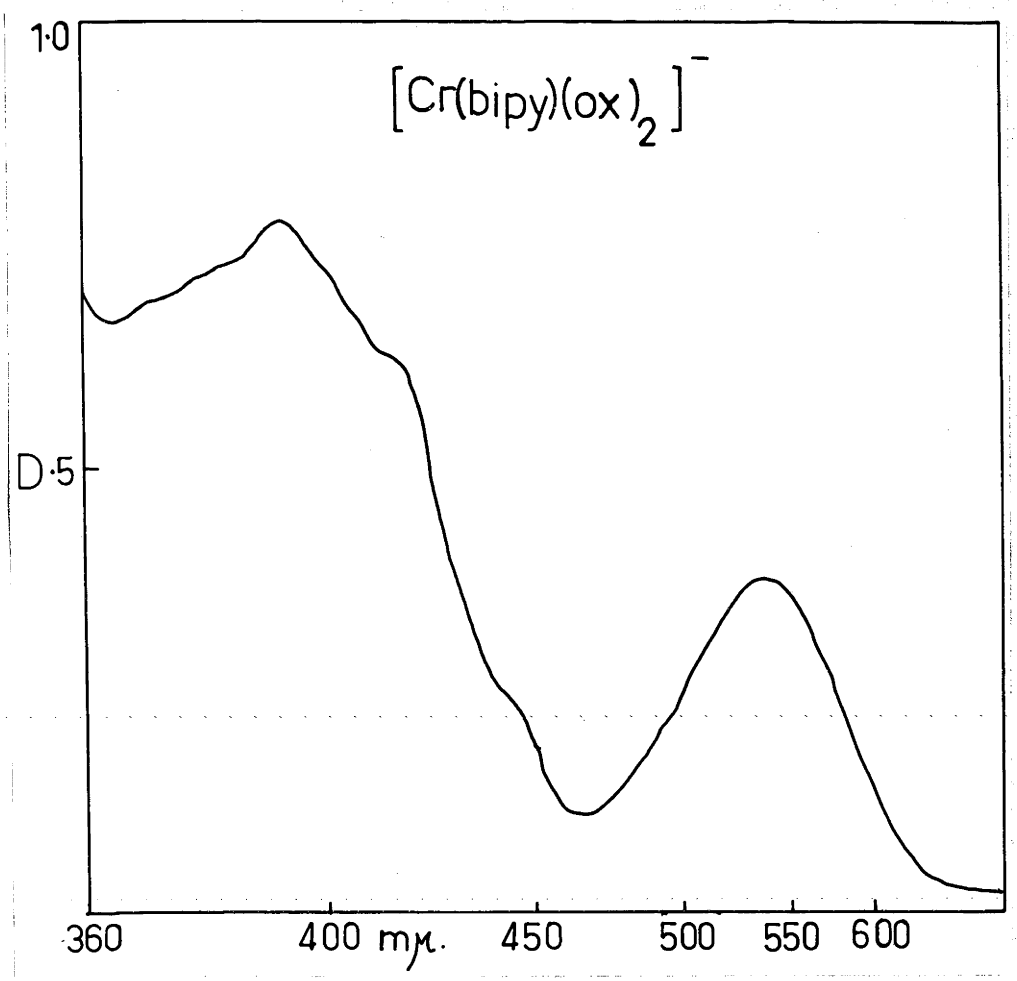
A discussion of the general historical background to the racemisation of Cr(III) complexes has already been given (Chapter 2).

9.1 ABSORPTION SPECTRA AND ROTATORY DISPERSION.

The visible absorption spectra are shown in Figure 9.1 for aqueous solutions of the complexes at concentrations of 0.0044M. Curve i corresponds to $K[Cr(bipy)(ox)_2]$ and curve ii to $K[Cr(phen)(ox)_2]$, (cell thickness = 1cm). Curve iii shows the optical rotatory dispersion of active $K[Cr(bipy)(ox)_2]$. A similar curve was also obtained for the phenanthroline complex (not shown). The largest rotations are given at wavelengths of about 470 and 555 mμ. The sodium yellow line (589 and 589.6 mμ) proved satisfactory for rate measurements.

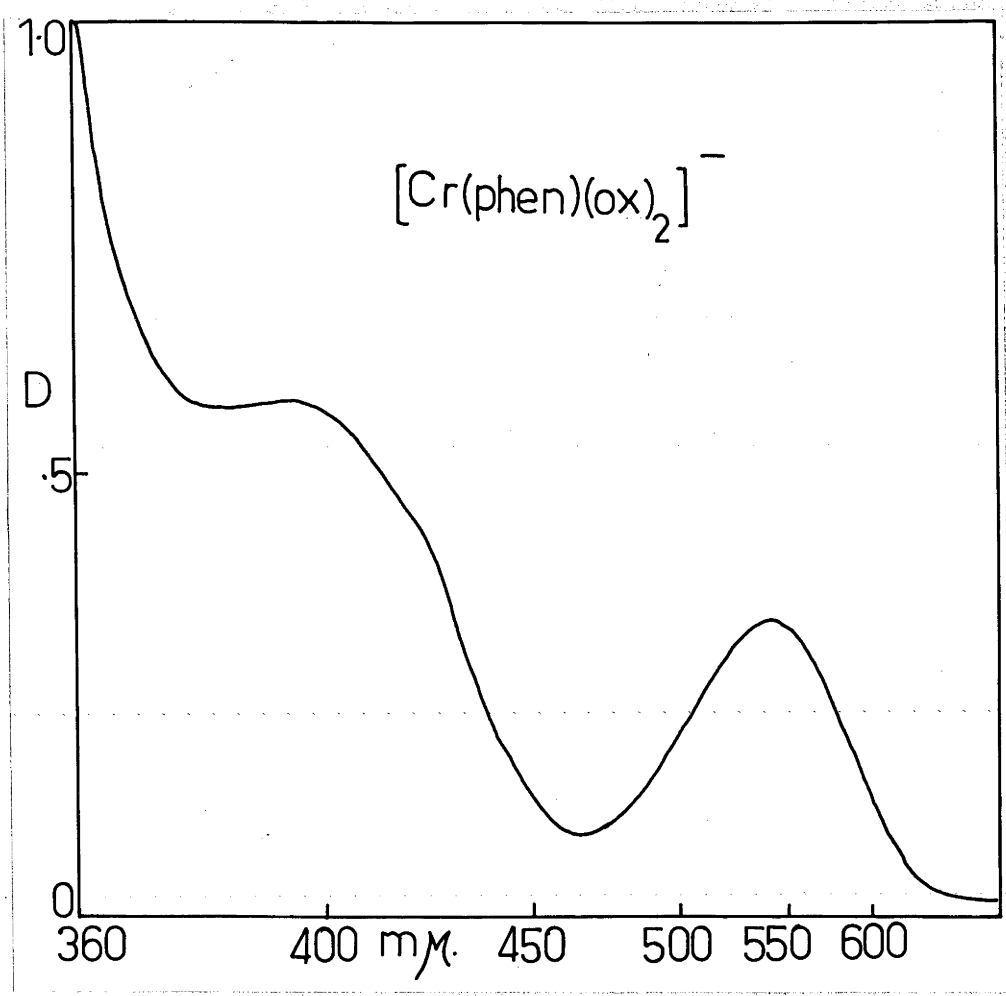
FIGURE 9.1

(i).



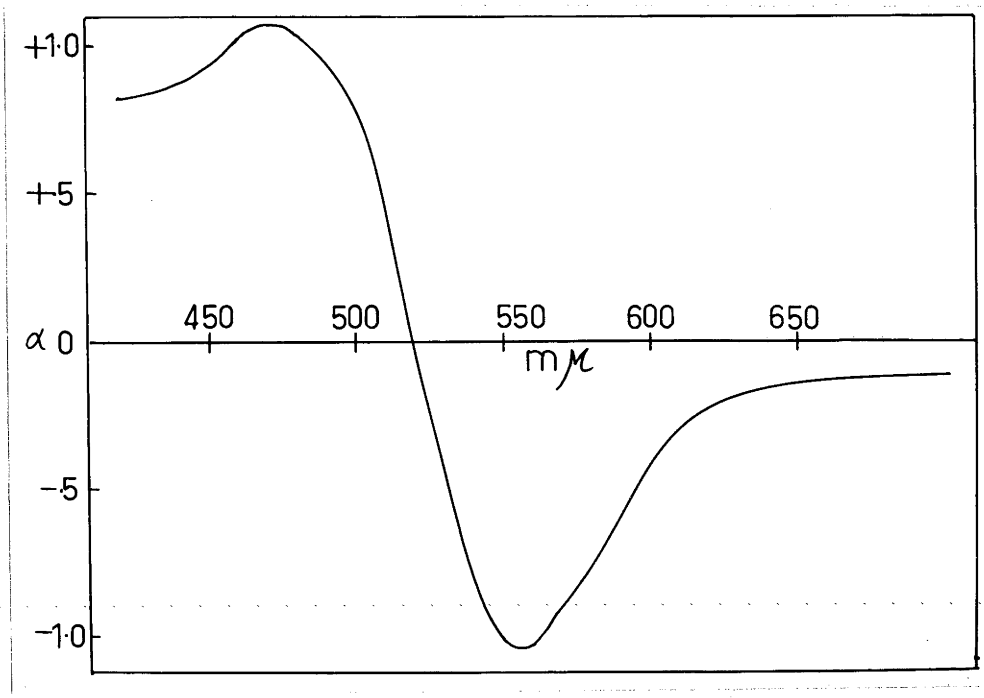
9.1

ii



9.1

iii



9.2 KINETIC STUDIES.

Measurements of the rates of racemisation were made by a technique analogous to that already described (Section 6.3).

The plot of log α-Z against a time abscissae gave good straight lines for both complexes. From the slopes first-order rate constants were calculated (Section 6.4), and found to be independent of the initial concentrations over the temperature ranges employed. Table 9.2 gives some results in aqueous solvent at different initial concentrations together with some typical runs which are plotted in Figure 9.2.

TABLE 9.2

Racemisation Data for the $[Cr(bipy)(ox)_2]^-$ Ion In Water at 25 ± 0.1°C

(Z = tube zero reading)

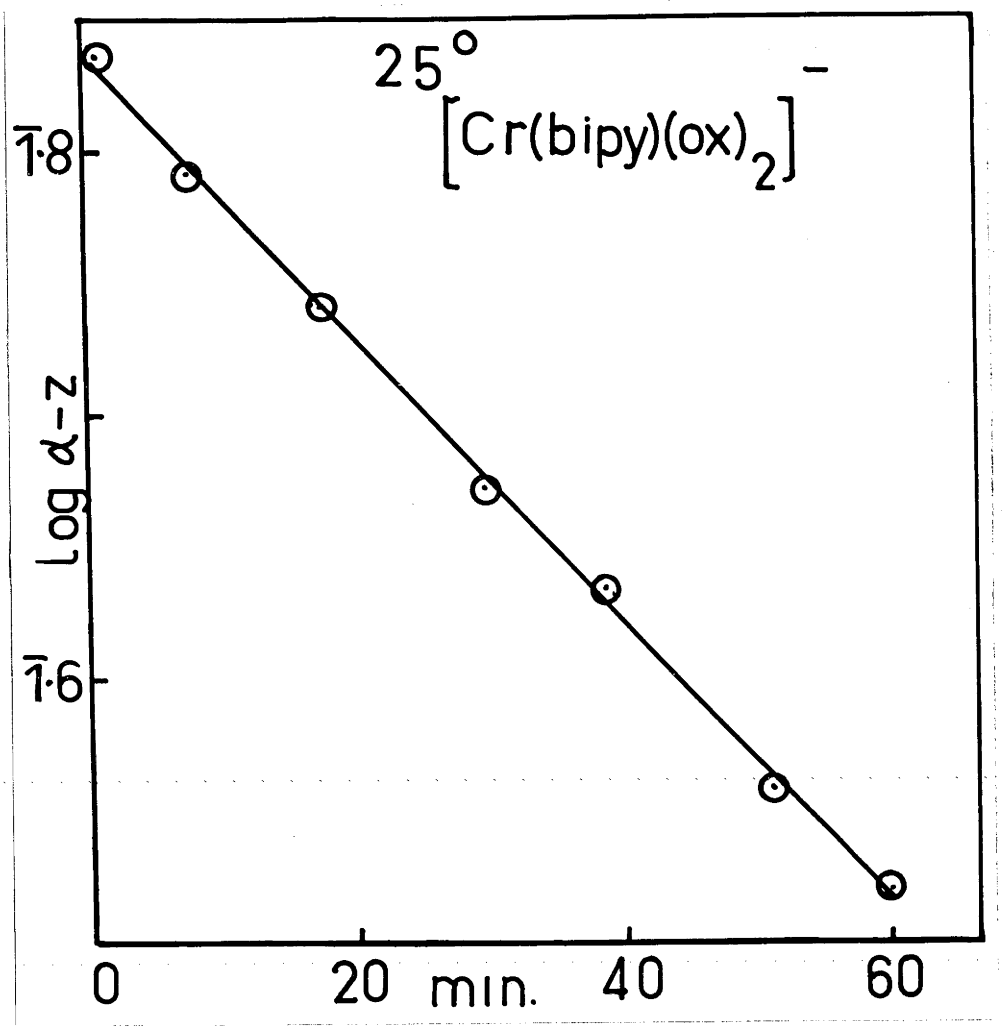
t(mins)	α	$(\alpha - Z)$	$\log (\alpha - Z)$
0	0.98	0.69	$\bar{1}.839$
7.5	0.91	0.62	.792
17	0.84	0.55	.740
29.5	0.75	0.46	.663
38.5	0.72	0.43	.634
51	0.65	0.36	.556
60	0.62	0.33	.519

From the slope $m = 5.35 \times 10^{-3}$, $k_{rac} = 2.303\ m$ or $12.3 \times 10^{-3}\ min^{-1}$

Racemisation Data for the $[Cr(phen)(ox)_2]^-$ Ion In Water at 20 ± 0.1°C

t(mins)	α	$(\alpha - Z)$	$\log (\alpha - Z)$
26.5	1.24	0.94	$\bar{1}.973$
31	1.18	0.88	.945
40	1.12	0.82	.914
52	1.02	0.72	.857
66	0.96	0.66	.820
80	0.88	0.58	.763
105	0.78	0.48	.681
119	0.71	0.41	.613
131.5	0.68	0.38	.580
145	0.64	0.34	.532

From the slope $m = 3.60 \times 10^{-3}$, $k_{rac} = 2.303\ m$ or $8.30 \times 10^{-3}\ min^{-1}$


25°
[Cr(bipy)(ox)2]−
Log a-x
1̄·8
1̄·6
0
20 min.
40
60

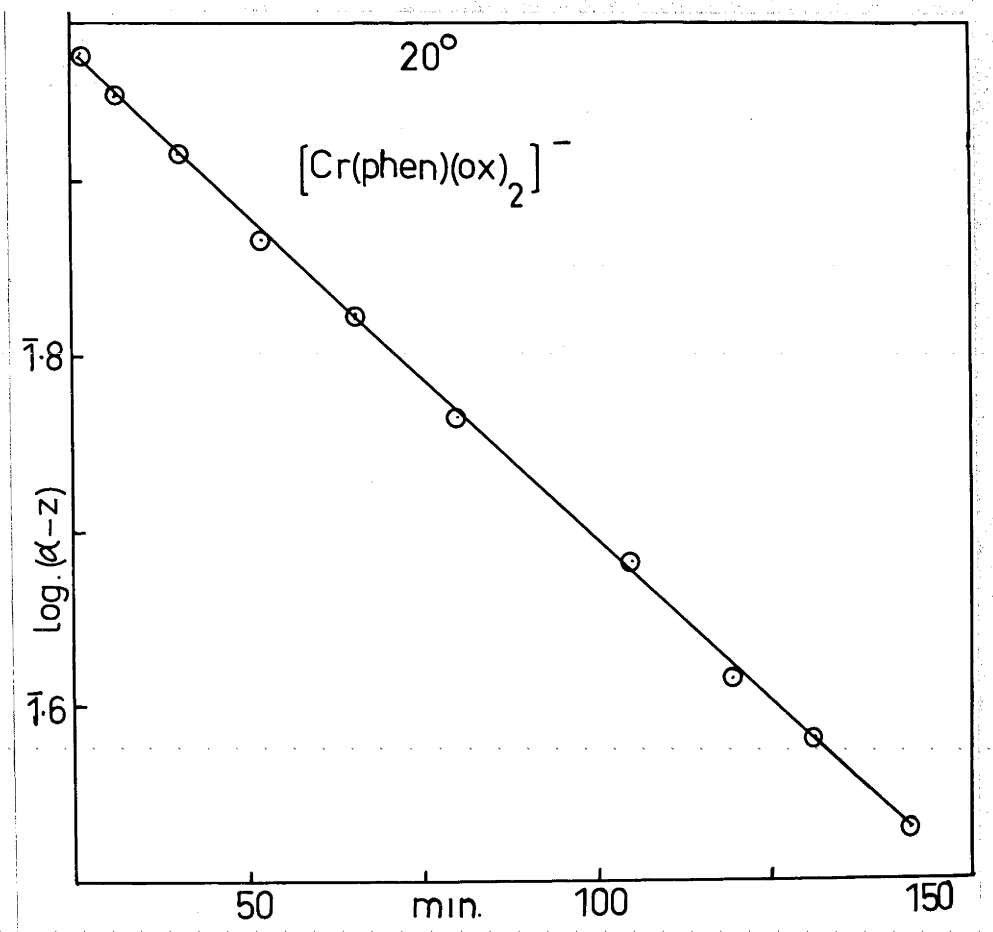

20°
[Cr(phen)(ox)2]⁻
log.(a−z)
1̄·8
1̄·6
50
min.
100
150

TABLE 9.2 (Contd.)

Initial Concentration (mg/25ml H_2O)	Temperature (deg. C)	$10^3 k_{rac}(min^{-1})$ $K[Cr(bipy)(ox)_2]$	$K[Cr(phen)(ox)_2]$
13	20	5.95 ± 0.19	8.46 ± 0.27
6.5	20	6.10 ± 0.19	-
30	20	-	8.51 ± 0.27
15	35	30.5 ± 1	38.2 ± 1
30	35	29.2 ± 0.9	37.1 ± 1

The effects of light, ionic strength, and pH have been studied together with the temperature dependence of the rates in neutral, acid, and alkaline solutions.

9.21 KINETIC STUDIES - THE EFFECT OF LIGHT.

Light itself has been found to affect the racemisation rates of metal complexes and in particular those of Cr(III). (See Section 2.6). Therefore, the effect of the sodium yellow light employed was studied by simply comparing the rate constants obtained for solutions when continuously exposed, with those of solutions kept in the dark between readings. For both complexes light had no effect. In addition, solid samples of the active potassium salts were stored in the daylight and dark respectively, their specific rotations being measured from time to time. In an interval of three months there was no loss in activity for either sample.

9.22 THE EFFECT OF pH:

The racemisation rate constants obtained over the pH scale range are shown in Table 9.22. (The buffer solutions used were the same as described earlier (Section 6.2)). It was not always possible to avoid the presence of ions known to have specific effects

but their concentrations could be kept comparatively low (~0.2M).

It was found that both complexes were sensitive to changes in pH in the alkaline region, while only slight increases were observed in acid solutions. Measurements of the energies and entropies of activation show that the increased rates arise mainly from a lowering of the activation energy.

TABLE 9.22

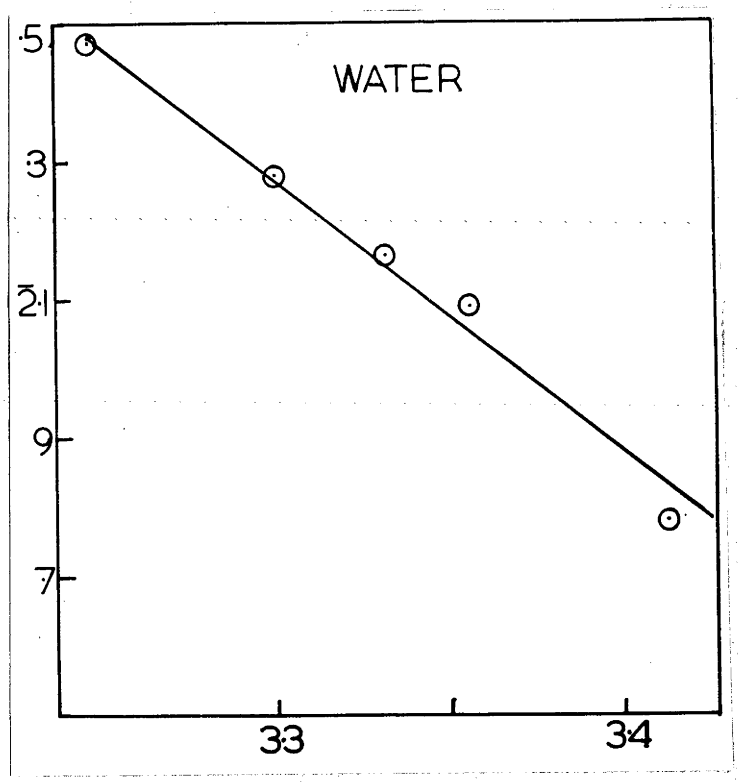
(Temperature 25°C)

Buffer Solution Number (See 6.2)	pH	$10^3 k_{rac}(min^{-1})$ $[Cr(bipy)(ox)_2]^-$	$[Cr(phen)(ox)_2]^-$
5	0.90	14.5	17.7
5	2.20	11.9	13.7
2	4.22	11.2	-
2	6.04	12.7	15.8
1	7.65	30.4	-
4	7.80	31.1	-
4	8.20	51.2	53.7
4	8.80	71.1	-
1	11.5	74.8	79.8
7	11.75	77.2	79.6
(in 0.01g NaOH)	12.3	-	83.8

The Racemisation of the $[Cr(bipy)(ox)_2]^-$ Ion in Water

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k
20.0	293	3.413	6.10	$\bar{3}.785$
25.0	298	3.356	12.4	$\bar{2}.093$
30.0	303	3.300	19.2	$\bar{2}.283$
35.0	308	3.247	29.8	$\bar{2}.474$

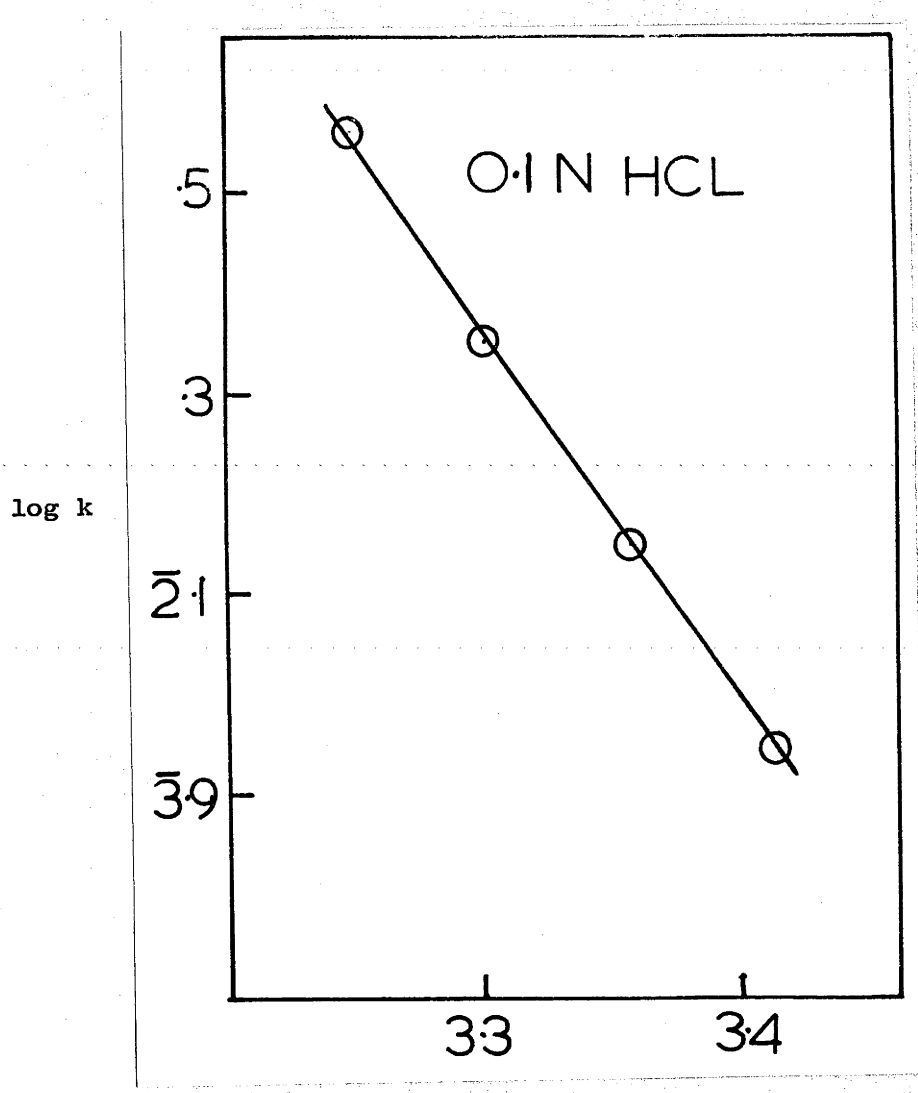
Ea = 18.1 kcal/mole; log A = 9.56 sec^{-1}; $\Delta S^{\ddagger}$ = - 16.8 e.u.



The Racemisation of the $[Cr(bipy)(ox)_2]^-$ Ion in 0.1N HCl

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k
20.0	293	3.413	8.70	$\bar{3}.940$
25.0	298	3.356	13.8	$\bar{2}.140$
30.0	303	3.300	22.1	$\bar{2}.344$
34.9	307.9	3.248	35.8	$\bar{3}.554$

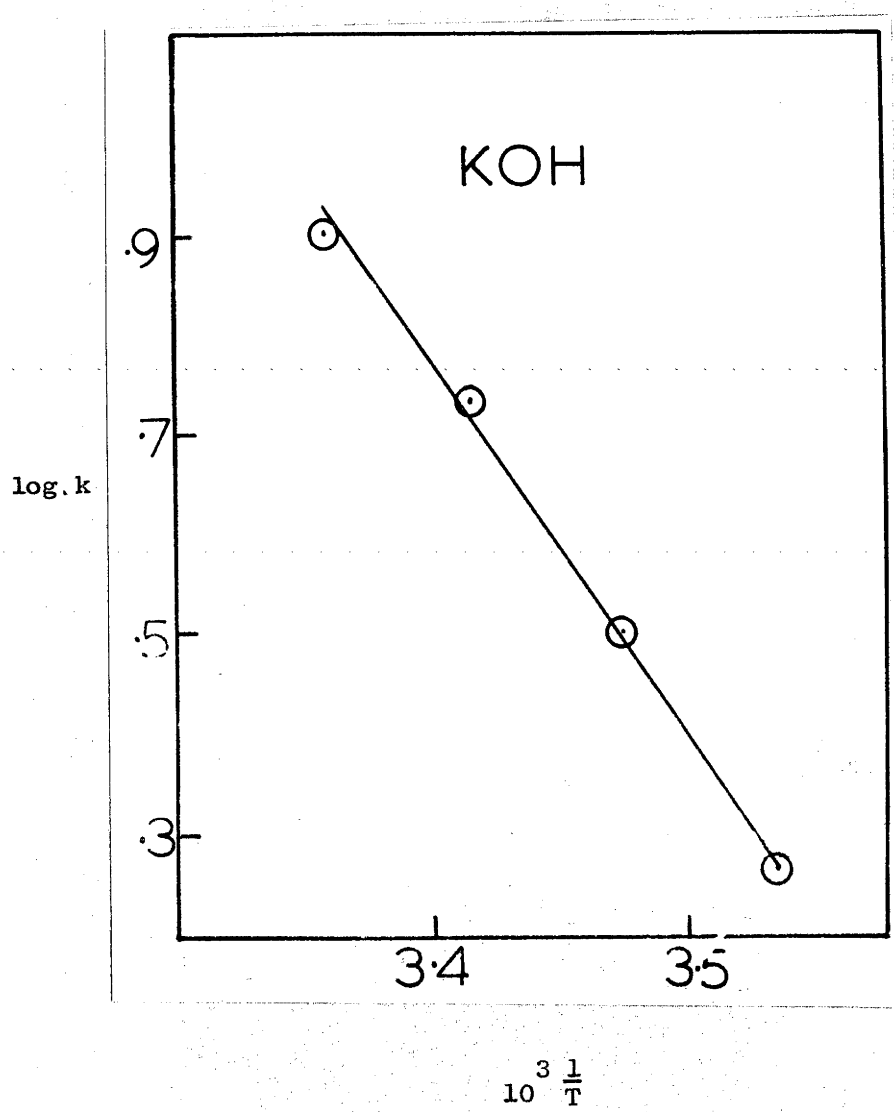
Ea = 16.9 kcal/mole; log A = 8.78 sec^{-1}; $\Delta S^{\ddagger}$ = - 20.3 e.u.



The Racemisation of the $[Cr(bipy)(ox)_2]^-$ Ion in 0.09N KOH

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.1	283.1	3.532	1.82	$\bar{2}.260$
15.0	288	3.472	3.13	$\bar{2}.496$
20.0	293	3.413	5.39	$\bar{2}.732$
25.0	298	3.356	7.91	$\bar{2}.898$

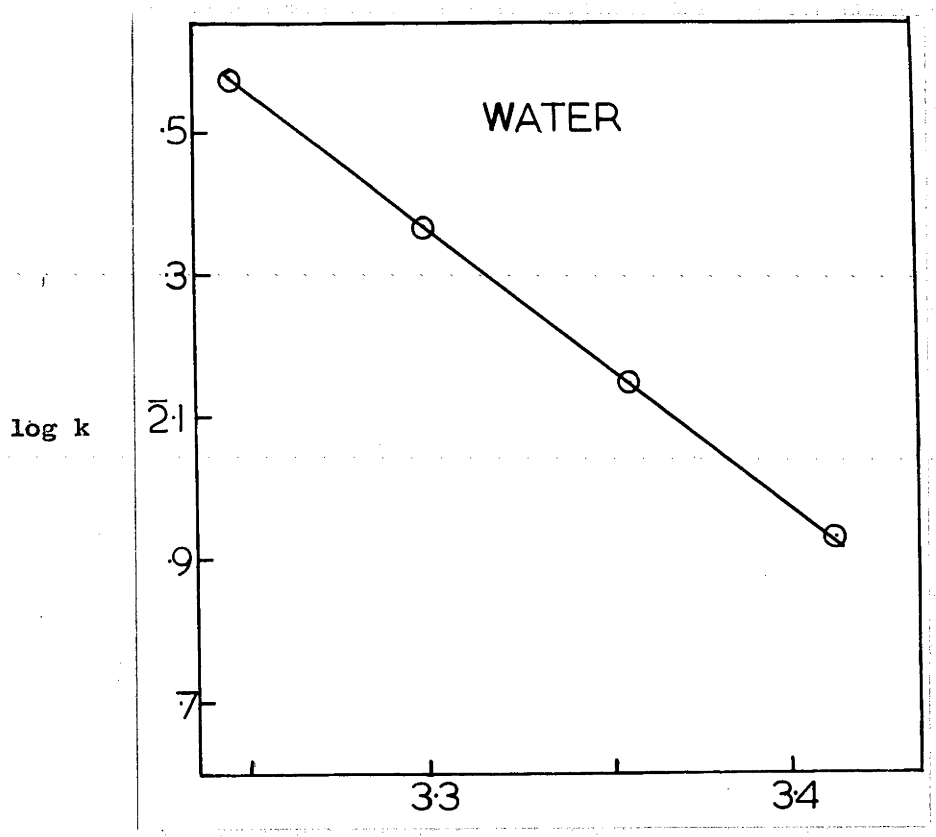
Ea = 16.9 kcal/mole; log A = 9.54 sec^{-1}; $\Delta S^{\ddagger}$ = - 16.8 e.u.



The Racemisation of the $[Cr(phen)(ox)_2]^-$ Ion in Water

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k
20.0	293	3.413	8.47	$\bar{3}.928$
25.0	298	3.356	13.9	$\bar{2}.143$
30.0	303	3.300	23.3	$\bar{2}.367$
35.0	308	3.247	37.8	$\bar{2}.578$

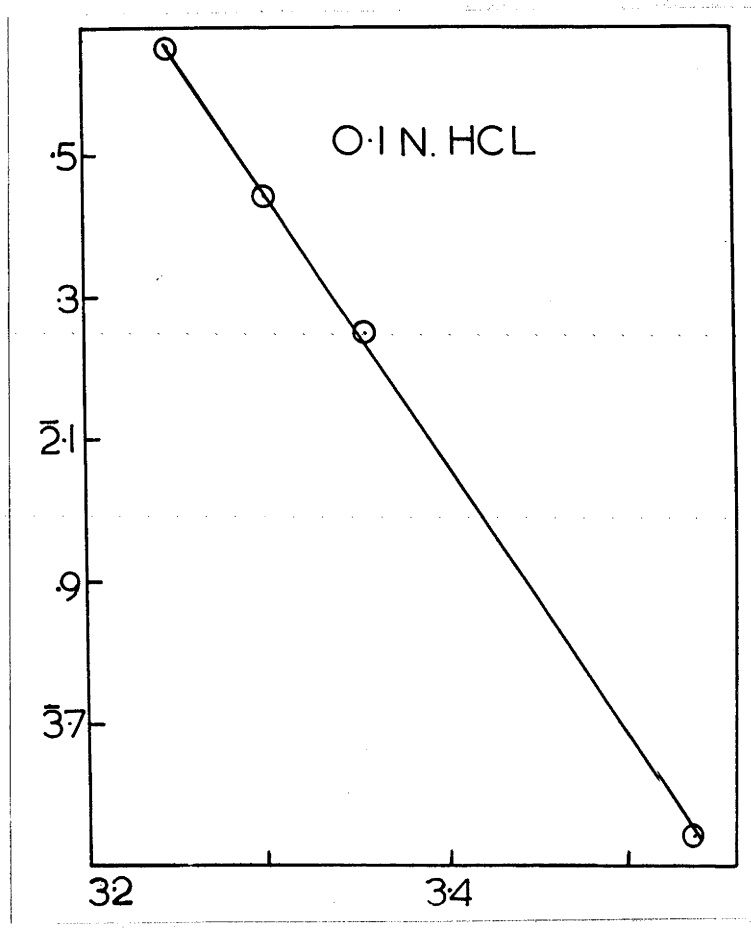
Ea = 18.0 kcal/mole; log A = 9.6 sed^{-1}; $\Delta S^{\ddagger}$ = - 16.6 e.u.



The Racemisation of the $[Cr(phen)(ox)_2]^-$ Ion in 0.1N HCl

°C	T(°K)	$10^3 \frac{1}{T}$	$10^3 k(min^{-1})$	log k
10.0	283	3.534	3.47	$\bar{3}.540$
25.0	298	3.356	17.8	$\bar{2}.250$
30.0	303	3.300	27.6	$\bar{2}.441$
34.9	307.9	3.248	44.9	$\bar{2}.652$

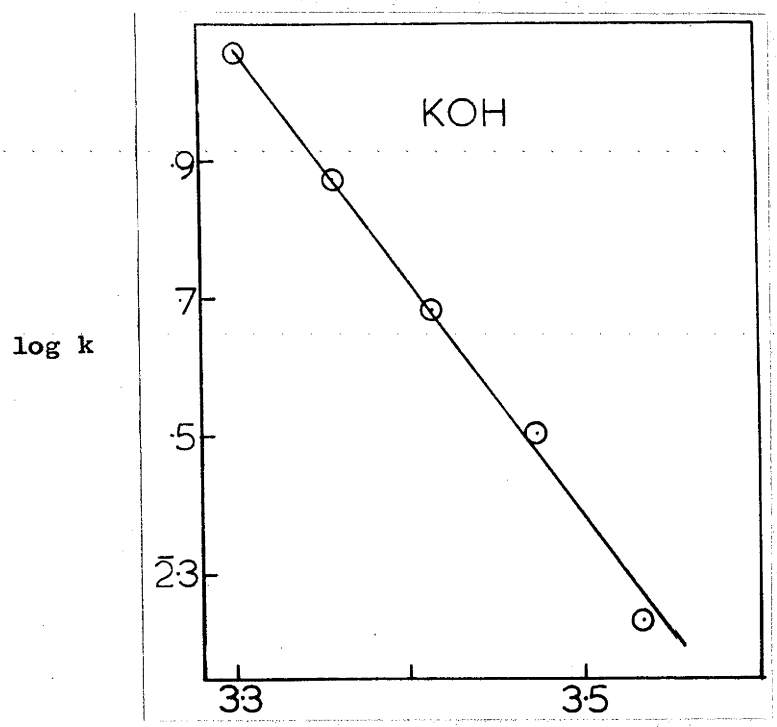
Ea = 17.9 kcal/mole; log A = 9.55 sec^{-1}; $\Delta S^{\ddagger}$ = - 16.7 e.u.



The Racemisation of the $[Cr(phen)(ox)_2]^-$ Ion in 0.09N KOH

°C	T(°K)	$10^3 \frac{1}{T}$	$10^2 k(min^{-1})$	log k
10.1	283.1	3.532	1.71	$\bar{2}.233$
15.0	288	3.472	3.19	$\bar{2}.504$
20.0	293	3.413	4.82	$\bar{2}.684$
25.0	298	3.356	7.48	$\bar{2}.874$
30.0	303	3.300	11.4	$\bar{1}.058$

Ea = 15.8 kcal/mole; log A = 8.66 sec^{-1}; $\Delta S^{\ddagger}$ = - 20.9 e.u.



9.23 THE EFFECT OF ADDED IONS.

The following table gives the effects of solutions of different ionic strengths on the racemisation rates at 25°C.

Solution	Ionic Strength	$10^3 k(min^{-1})$ $K[Cr(bipy)(ox)_2]$
H_2O	-	12.4 ± 0.6
KNO_3	1	11.9 ± 0.6
KCl	1	11.9 ± 0.6
		$K[Cr(phen)(ox)_2]$
H_2O	-	13.9 ± 0.6
KNO_3	1	16.2 ± 0.7
"	0.5	13.8 ± 0.6
KCl	0.5	15.7 ± 0.6
"	0.25	" "
NH_4NO_3	0.5	15.9 ± 0.8
$NH_4(CH_3COO)$	"	23.3 ± 1

It may be seen that there is a small ionic strength acceleration for the $[Cr(phen)(ox)_2]^-$ ion coupled with small specific ion effects.

9.3 CHROMIUM COMPLEXES - DISCUSSION.

In the absence of corresponding ligand exchange data it is only possible to make some comparisons between the racemisation results of the two Cr(III) complexes, and indicate what mechanisms appear to be the most likely. The table overleaf shows the kinetic parameters obtained for various solutions. The rate constants have an accuracy of within ± 5%.

Solvent	$[Cr(bipy)(ox)_2]^-$			$[Cr(phen)(ox)_2]^-$		
	$10^3 k\ min^{-1}$ (25°C)	Ea kcal	$\Delta S^{\ddagger}$ e.u.	$10^3 k\ min^{-1}$ (25°C)	Ea kcal	$\Delta S^{\ddagger}$ e.u.
H_2O	12.4 ± 0.6	18.1	-16.8	13.9 ± 0.7	18.0	-16.6
0.1N HCl	13.8 ± 0.7	16.9	-20.3	17.8 ± 0.9	17.9	-16.7
0.09N KOH	79 ± 4	16.9	-16.8	75 ± 4	15.8	-20.9

In water the two complex ions have activation energies and entropies that are identical within the experimental errors. Their similarity in rate behaviour extends to acid and alkaline solutions making it reasonable to suppose that the mechanisms used might not differ very much. In alkaline solution the increased rates are attended by a change in colour from red to green and evidently a base hydrolysis reaction contributes to the observed rate.

Substitution of a phenanthroline ligand for a bipyridine hardly affects the rate constants and suggests that it is probably the oxalate groups that are concerned in the racemisation process. Bushra and Johnson[42] have studied the related ions $[Cr(en)(ox)_2]^-$ and $[Cr(ox)_3]^{3-}$ and found activation energies of 15.8 kcals/mole in both cases (with log A 8.9 and 8.05 sec^{-1} respectively). Their studies did not include acid or alkaline solutions. An intramolecular mechanism has been demonstrated for the $[Cr(ox)_3]^{3-}$ ion and bond-breaking is known to contribute to the observed rate. A Common mechanism of racemisation could be envisaged for the $[Cr(bipy)(ox)_2]^-$ and $[Cr(phen)(ox)_2]^-$ ions in which a one-ended detachment of one or two oxalate rings is followed by reattachment

to give either d or l forms with equal probability (cf. Section 2.1).

A mechanism of the Ray and Dutt type in which no bonds are broken could also account for the racemisation. It is interesting to consider the likelihood of this occurring in Cr(III) complexes. On electrostatic grounds the movement of a pair of ligands in opposite directions through 45 degrees in the plane of the bonds should be facilitated by the absence of T2g electrons. In such movement the ligand field must interact with these electrons and the degree of interaction would be related to the number of electrons present. This would be expected to have a destabilising effect on the intermediate in the Ray and Dutt mechanism, and for a given metal ion the mechanism would be expected to be less favourable as the negative field of the ligand increased. It may be noted that both the $[Co(ox)_3]^{3-}$ and $[Cr(ox)_3]^{3-}$ ions racemise in part by intramolecular mechanisms possibly of the Ray and Dutt type. The $[Co(ox)_3]^{3-}$ ion, with configuration $(T2g)^6$, has an activation energy of 26 kcals $mole^{-1}$ which is approximately 10 kcals greater than the $[Cr(ox)_3]^{3-}$ ion (configuration $(T2g)^3$).*

It is also noteworthy that the intramolecular racemisation of the ions $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ is thought to be

* Dissociation to a 5 covalent square pyramid intermediate as required, say, in a half-bonded mechanism, could lead to an activation energy difference of this order of magnitude.[2] In a strong field Cr(III) loses 2Dq of L.F.S.E. compared with 4Dq for Co(III). Dq has a value of 5-6 kcals for the trivalent metal ion hydrates[3] and a similar figure would be expected for the oxalate ligand leading to an activation energy difference of $2Dq \approx 10$-12 kcals.

preceded by expansion to a high spin excited state.[130a, 49] The last mentioned involves removal of electrons from the T2g level and so would facilitate the Ray and Dutt racemisation process believed to be present.

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