SUBSTITUTION REACTIONS
IN SOME TRANSITION METAL
CHELATE COMPOUNDS.

by

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INTRODUCTION

(i) Substitution Reactions.

The term substitution, may be used to describe a reaction involving the replacement of one metal by another, or one ligand by another, in a transition metal complex.[a]

The terms, exchange and displacement, may be used to describe such substitution reactions in which no net transfer of charge occurs. The reactions may involve either,

(a) constituents of a chemically similar nature (isotopic exchange), eg.

$$A + A^{*}X \rightleftharpoons AX + A^{*}$$

where A may be either a metal ion or ligand, in solution,

or

(b) constituents of a chemically dissimilar nature (non-isotopic exchange), eg.

$$B + AX \rightleftharpoons BX + A$$

where B and A may be either chemically dissimilar metal ions or ligands. Further, many authors have further differentiated such reactions by use of the following general terms,

(a) Exchange reaction when applied to an isotopic substitution,

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[a] charged or uncharged species.

or

(b) Displacement reaction when applied to a non-isotopic substitution.

In this thesis, the terms exchange and <u>re</u>placement will be used to describe such isotopic and non-isotopic substitutions, respectively. The term <u>re</u>placement will be used, to distinguish a non-isotopic substitution, from a reaction involving a displacement mechanism of substitution. (see p3). Reactions involving a net transfer of charge (atom or group transfer) within the system, have become known as oxidation-reduction or electron-transfer reactions. Where necessary these terms will be used to describe such reactions.

In recent years, the study of substitution reactions in solution, has been considerably influenced by the detailed application of kinetic and thermodynamic measurements. Prior to 1950, little kinetic data was sought to support the mechanisms of substitutions, in inorganic complexes, and the qualitative data derived from the study of such systems was taken to extreme limits. The rates of substitution reactions may vary greatly, depending on a number of factors, eg. pH, solvent properties, added basic and acidic anions, variations in the bond type of complexes due to changes in the central metal atoms or ligands, or steric factors. The magnitudes of these effects will be discussed in some detail later in this thesis.

In many substitution reactions, where stable intermediates cannot be isolated and examined, the kinetic order and the energy of activation of the system are of prime importance in any attempt to define a possible mechanism for the reaction.

(ii) Types of Mechanisms.

(a) Displacement.

Collisional mechanisms of substitution, require that the energy of collision, derived from the "merging" of the free[a] and complexed species to form the transition state(1), must be great enough to simultaneously break the required number of bonds, for substitution to occur. Such a mechanism would require a bimolecular rate determining step, and would involve a high energy of activation for many complexes, in which a number of bonds need be broken to effect substitution.

A displacement mechanism of substitution, as classified by Basolo and Pearson,(2) involves a bimolecular rate determining step in which the coordination number of the complexed metal is increased by one, in the transition state. These authors classified such reactions as S_E2 (metal substitution) and S_N2 (ligand substitution), using the terminology of Hughes and Ingold.(3) In addition, it must be remembered that overall second-order kinetics in a reaction, do not necessarily require a bimolecular collisional mechanism, nor in fact an increased coordination number of the metal ion

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[a] solvated metal ion or ligand.

in the transition state. However, they require that the rate determining step of the reaction does not depend solely upon the concentration of only one reactant.

The mechanisms of collision and displacement, can for most purposes be considered identical. In each case, when considering either metal or ligand substitution, equal importance is placed upon bond breaking in the initial complexed species, and bond making in the final complex, eg. in the metal exchange reaction

$$M^{*} + L\ M \xrightarrow{k_1} M^{*}\text{---}L\text{---}M \longrightarrow M^{*}L + M$$

the rate determining step k_1, involves both bond breaking in L–M (the initial complex) and bond making in M^{*}–L (the final complex). Wilputte-Steinert, Fierens and Hannaert,(4) discussed the concepts of bond breaking and bond making in describing many organic substitution reactions.

The term collision, as used by authors, to describe the mechanisms of substitution reactions in many inorganic complexes (see later), implied little more than that second-order kinetics were found for the systems under examination. This led to the use of the term, collisional mechanism, for many substitution reactions in which first order kinetics were not found.

In this thesis, the terms displacement and collision, will be used to describe the probable mechanisms of those reactions in which bimolecular rate determining steps may be postulated on the basis of available experimental and theoretical data.(52)

The mechanism may involve the simultaneous (collision) or stepwis (displacement) rupturing of the bonds, to effect substitution.

(b) Dissociation and Recombination (S_E1 or S_N1).

For such a mechanism of substitution, the rates of exchange or replacement of a metal ion or ligand in a complex, must necessarily depend upon the rates of ionization of the ligands in that complex. If overall first-order kinetics are found for a substitution reaction, the rate determining step may be one of dissociation of the complex. If the rates of ionization of the ligands are slow, then the rates of substitution of either the central metal or ligands in that complex, will be correspondingly slow. Such a substitution reaction, providing the dissociation of the ligands is rate determining, may be expected to proceed by a dissociation mechanism.

Complexes containing polydentate ligands may show dissociation of one or more metal-to-ligand bonds without the complete dissociation of the complex into free ligands and metal ions. Basolo and Pearson(2a) have suggested a stepwise dissociation mechanism to explain the low activation energies found for the isotopic metal ion exchanges with N,N'-ethylenebis(salicylideneiminato)copper(II)(5) and N,N'-1,2-phenylenebis(salicylideneiminato)cobalt(II)[a] (6) systems. (23 and 17 K.cals. respectively).

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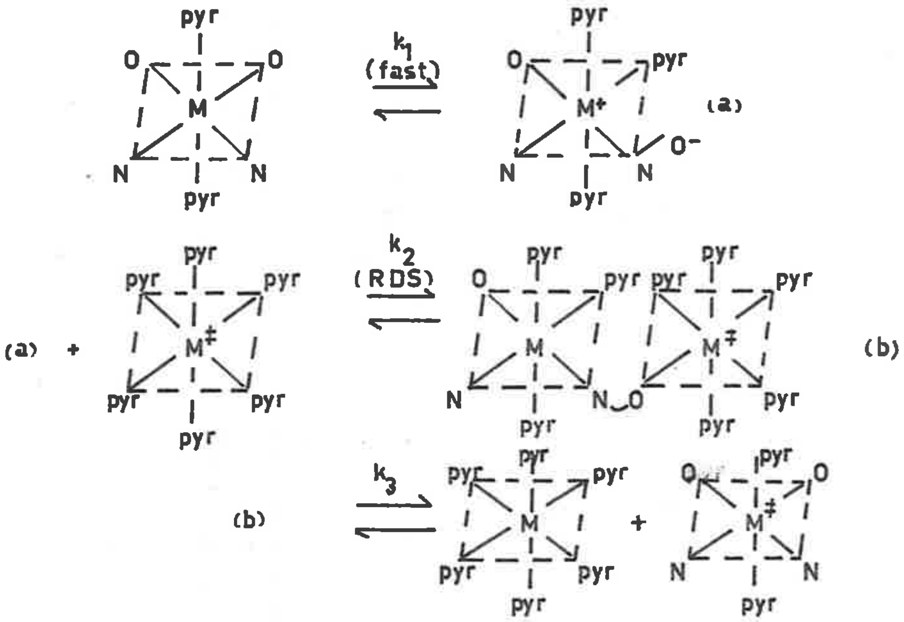
[a] cobalt(II) (salophen).



The observed second-order kinetics in these systems, do not necessarily require a collisional mechanism of substitution, wherein all four bonds of the quadridentate ligand must be broken simultaneously to effect metal exchange. However, the observed kinetics do require that the rates of dissociation of the ligands, from the complex, are not rate determining. Basolo and Pearson postulate an initial, rapid, partial dissociation of the chelate, followed by a rate-determining bimolecular reaction between free metal ion and the partially dissociated chelate, which may be considered as a zwitter-ion. Accordingly, this type of mechanism may be termed, displacement. Similarly, the rate of substitution of ferric ions in $[Fe(EDTA)]^-$ was found to be hydrogen ion dependent,(7) probably involving the stepwise dissociation or uncoiling of one, two and then three carboxylate groupings from the sexadentate ligand. A similar pH dependence on the rate of replacement was found in the $Cu^{+2}-\left[Cd(EDTA)\right]^{-2}$ system.(8)

(iii) The interpretation of data from Substitution reactions.

Prior to 1952, many of the rates of substitution reactions derived from studies of the replacements or exchanges of central metal ions and ligands in complexes, had been used to assess what was commonly called the "stability" of the complex.

The term "stability", used somewhat loosely by many authors, implied little more than that the complex was or was not resistant to substitution, and in fact in many cases the thermodynamic stabilities (stability constants,K) of the complexes, derived from studies in solution, were not known.

On the basis of some qualitative rates of exchange, further attempts to correlate with the type of bond in a complex were made, using as a criteria for bond type, the general inertness to chemical attack, and the magnetic criteria of Pauling.(9)

In most cases, it was found that a readily dissociable complex, showing ionic bonds on the Pauling view, showed a rapid rate of substitution for all its constituents. Conversely, a complex showing covalent bonds substituted very slowly or not at all.

The experimental conditions of such substitution reactions varied greatly in many cases, and the criterion of rapid substitution, and hence ionic bonding, was that

complete substitution should occur within the time of mixing and separating of the reactants.
Some limitations were placed by Taube(10) upon the experimental conditions that could be used in establishing such a criterion of substitution, viz. complete replacement in the time of mixing (1 minute, c = 0.1M and T = 25°C). Any reactions slower than these were taken as indicating covalently bonded complexes.

Bis(salicylaldehydato)cobalt(II), was found by West,(11 to undergo complete exchange with cobalt(II) ions in pyridine, in the time of separation (40 secs.). Magnetic measurements on this compound, made by Tyson and Adams,(12) indicated that the metal-oxygen bonds were ionic in character (μ= 4.5B.M.). The oxygen inactive form of N,N'-ethylenebis(salicylideneiminato) cobalt(II)[a] was found by Calvin and Barkelew(13) to be paramagnetic to the extent of one unpaired electron, indicating covalent metal-ligand bonds in the Pauling terminology. This complex underwent complete exchange with cobalt(II) ions, under similar conditions, in the time of separation (6 mins.).(6) Kinetic measurements at lower temperatures,(6) showed that cobalt(II)(salen) was in fact less susceptible to metal exchange than the salicylaldehyde complex.

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[a] cobalt(II) (salen)

However, these examples serve to indicate the necessity for some common parameter, other than a time of substitution, for the assessment of bond type in a complex. Obviously, when measurable a comparative rate constant is needed.

A discussion of the comparative merits of metal ion and ligand substitution is relevant.

Stranks and Wilkins(14) and later Basolo and Pearson(2b) both agreed that the probability of metal ion exchange in the system,

$$ML_n + M^{*\,a+} \rightleftharpoons M^{*}L_n + M^{a+}$$

was less than the corresponding ligand exchange reaction,

$$ML_n + L^{*} \rightleftharpoons ML^{*}_n + L$$

Their discussion based essentially on energetic considerations, certainly holds for complexes containing unidentate ligands.

Metal ion exchange, in such systems, would require the rupture of four or six metal-ligand linkages, depending upon the coordination number of the metal ion, and independent of the mechanism.

Ligand exchange would involve the breaking of one and only one metal-ligand bond, irrespective of the coordination number of the complexed metal and the mechanism of substitution.

Ligand exchange may be complicated in complexes containing metals of low coordination number. The ability of such complexes to form higher coordinated species in solution, by association with one or more ligands, may lead to erroneous conclusions being drawn from such ligand substitution studies.

In fact, the exchange of mercury(II) with $(HgCN)^{+1}$ is slow,(15) indicating a $(HgCN)^{+1}$ species in solution resistant to exchange.

However, the corresponding ligand exchange reaction $(HgCN)^{+1}$-$[CN^{*}]^{-1}$, may be expected to be complicated by the formation of the higher coordinated $Hg(CN)_2$ species in solution. The $Hg(CN)_2$-$[CN^{*}]^{-1}$ exchange is known to be rapid.(16)

The use of radioactive tracers has shown that no exchange of platinum(IV) ions occurs between $[Pt^{*}Cl_6]^{-2}$ and either cis-$[Pt(NH_3)_2Cl_4]$(17) or $[Pt(NH_3)_2Cl_2]^{+2}$ (18), while exchange does occur in the systems $[PtCl_6]^{-2}$-$[Cl^{*}]^{-1}$(19) and $[PtBr_4]^{-2}$-$[Br^{*}]^{-1}$(20). The breaking of six Pt-Cl linkages, and the rupturing of four Pt-ligand bonds in $[Pt(NH_3)_2Cl_2]^{+2}$, then recombination of the groupings around platinum after exchange, was expected to require too great an energy of activation for metal substitution to occur.

It is more probable that unidentate ligands can be substituted than the central metal ion, irrespective of the mechanism involved.

When considering the ease of substitution in complexes containing other than unidentate ligands, a different situation may arise depending upon the nature of the ligands and the coordination number of the complexed metal, in solution.

A collisional mechanism of substitution requires that all the bonds from a polydentate ligand to the central metal ion must be broken simultaneously for ligand substitution to occur, while for metal substitution, all the bonds from all the ligands to the central metal must be broken to effect substitution, just as in the case of a complex containing unidentate ligands.

As before, the probability of metal ion substitution appears unfavourable energetically and statistically, compared with ligand substitution, particularly when considering metals whose coordination number is greater than two, in complexes containing bidentate ligands. However, it does seem likely that the substitutions of quadridentate ligands in complexes containing metals with a coordination number of four, would be as difficult a process energetically as substitutions of the central metals. In both cases, four bonds need be broken, simultaneously in collision, or stepwise in dissociation or displacement.

In fact, there is no *a priori* reason to suggest that both mechanisms may not be operating simultaneously, or that a mechanism intermediate between displacement (S_E2 or S_N2) and dissociation (S_E1 or S_E1) may not be operating. Gold(21) has discussed the existence of mechanisms intermediate between S_N1 and S_N2 for many reactions. Finally, it must be remembered that for many substitution reactions where the isolation of a stable intermediate is not possible, the mechanisms of substitution are discussed on the basis of kinetic measurements.

The final chosen mechanism must agree with all the existing data, but in many cases it is not possible to allocate one particular mechanism to a reaction. An assignment of a mechanism made on the basis of pure displacement or pure dissociation may be incorrect.

Taube(10) in 1952, was the first to seriously question the validity of using a rate of substitution as a measure of the thermodynamic stability of a complex. He introduced the concepts of lability (rapid exchange) and inertness (little or no exchange) when referring to substitution. Further, a slower rate of substitution did not necessarily imply greater stability of one complex compound compared with another.

Perhaps one of the most striking discrepancies between exchange rates and thermodynamic stabilities, where both of these are known, exists in the case of the metal cyano complex ion systems. Adamson, Welker and Volpe(16) found that cyanide ion exchanged very rapidly with $[Ni(CN)_4]^{-2}$ and $[Hg(CN)_4]^{-2}$, while very slow exchanges of cyanide were found with the $[Fe(CN)_6]^{-4}$ (22) and $[Fe(CN)_6]^{-3}$ (16) complex ions. However, the dissociation constants for all these ions were found to be very low, indicating high stability, eg. K diss.$_{[Hg(CN)_4]^{-2}} = 10^{-42}$ and K diss.$_{[Fe(CN)_6]^{-3}} = 10^{-44}$.

Taube first pointed out the need for a clear distinction between the stability constant K, of a complex, for the reaction,

$$M^{a+} + nL \rightleftharpoons ML_n$$

$$K = \frac{ML_n}{M^{a+} \quad L^n}$$

and the <u>rate of attainment</u> of that equilibrium position. That is, he made the distinction between a kinetic and thermodynamic factor (stability constant), and pointed out that there need be no correlation between them.

The lack of correlation between the rate of attainment of equilibrium and the value of K, may best be illustrated by the following example. The stability constants K, for $[CrCl]^{+2}$ and $[FeCl]^{+2}$, at 25°C ($\mu = 0.3$), were found by Bjerrum(23) and Rabinowitch and Stockmayer(24) to be 0.2 and 5.0 respectively, indicating greater stability for the chloro-ferric ion than for the chloro-chromic species. However, it was found that the rate of dissociation of the $[FeCl]^{+2}$ species, in acid solution, was in fact greater than that of the $[CrCl]^{+2}$ ion.

It follows from Taube's distinction between stability and lability, that if the overall rate of dissociation of a complex is rapid, then metal and ligand substitution will be fast, and the system labile to substitution.

Further, Taube classified the complexes as inert or labile, depending upon the electronic structures of the complexed metal ions. On his classification, all octahedral d^2sp^3 or sp^3d^2 orbital complexes, containing metals with d^0, d^1 or d^2 configurations were labile to substitution, whereas those inner-orbital complexes containing metals having three or more d electrons were all inert to substitution.

The presence of a vacant lower d orbital, in those complexes containing metals with 0, 1 and 2 d electrons, greatly facilitated the formation of a transition state, of increased coordination number, by the acceptance of the donor electrons from the free metal ion or ligand.

Taube's classification of labile complexes, made entirely on qualitative interpretations of substitution reactions using the valence-bond theory, parallels the S_E2 and S_N2 mechanisms of displacement developed by Basolo and Pearson(2). These latter authors tabulated the differences in Crystal Field Stabilization Energies (C.F.S.E.),(25) for all d^n electronic structures for both S_E1 or S_N1 and S_E2 or S_N2 mechanisms of substitution, on the basis of forming either, a square pyramid (dissociation), or pentagonal bipyramid (displacement) transition state, from an initial octahedral structure. Their quantitative calculations indicated a preferential displacement mechanism for substitution in complexes containing d^0, d^1 and d^2 metals, and a preferred dissociation mechanism for complexes containing metals with three or more d electrons.

In fact, for d^0, d^1 and d^2 configurations, both five and seven coordinated transition states have C.F.S.E.[8] greater than those of the initial octahedral structure for d^1 structures, $[\Delta E_a = -0.57$ Dq (5 coord.) and $\Delta E_a = -1.28$ D (7 coord.)$]$. ΔE_a represents the difference in C.F.S.E. between the initial and transition state.

It is interesting to note that complexes containing d^8 metals are predicted to react slowly by either mechanism. Both transition states involve a loss of C.F.S.E., in fact, $[2.00$ Dq (5 coord.) and 4.26 Dq (7 coord.)$]$.

On the basis of the crystal field theory, nickel(II) complexes are predicted to react more slowly than their corresponding copper(II) complexes, irrespective of the mechanism of substitution. Further, copper(II) compounds show a gain in C.F.S.E. in passing from an octahedral configuration to a square pyramid transition state ($\Delta E_a = -3.14$ Dq), but a loss of C.F.S.E. in passing from octahedral to a pentagonal bipyramid state ($\Delta E_a = 1.07$ Dq.)

On the basis of these quantitative calculations, substitution reactions of complexes containing copper(II) and nickel(II) would be expected to proceed by a dissociative mechanism, with copper(II) compounds reacting the faster .

Excellent agreement between rates of substitution and the electronic structures of the central metal ions is found for a number of reactions involving nickel(II) and copper(II) compounds.

Popplewell and Wilkins(26) found that the exchange of ethylenediamine in $[Ni(en)_3]^{+2}$ proceeded by a S_N1 dissociation mechanism, with a $t_{1/2} = 5$ secs. at 0°C. However the same authors found that the $[Cu(en)_2]^{+2}$- en^* exchange proceeded immeasurably fast under similar conditions.

Further, Tanaka and Sakuma(27) found that the reaction between nickel(II) ions and ethylenediaminetetra-acetic acid, in acetate buffer (pH 3.8-5.2), could proceed by four independent paths, however the rate constant of formation of $[Ni(EDTA)]^{-2}$ was much smaller than that of the corresponding copper complex,(28)

$$Cu^{+2} + (EDTA)^{-4} \rightleftharpoons [Cu(EDTA)]^{-2}$$

It must be remembered that all quantitive calculations, based on the crystal field theory, completely ignore any covalent contributions.

By definition, the crystal field theory should only apply to ionically bonded compounds.

The difference between the thermodynamic and kinetic aspects of substitution should be taken a little further. When considering pure isotopic exchange

$$A^* + AX \underset{}{\overset{k_1}{\rightleftharpoons}} A^*X + A$$

where A may be either a ligand or metal ion in solution, the theory of reaction rates(29) enables calculations of $\Delta F^{\neq}$ and $\Delta S^{\neq}$ to be made for the systems concerned, using the observed forward rate constants (k_1) and the activation energies obtained from studies of the variation of k_1 with temperature. The values of $\Delta F^{\neq}$ and $\Delta S^{\neq}$ obtained, the free energies and entropies of activation, give some measure of the ease of formation of the transition state, and therefore a measure of the ease of substitution.

Chemically, the products of such isotopic reactions are indistinguishable from the reactants, and for these systems, the overall heat of reaction ΔH will be zero, the standard free energy change ΔG^o, always small and negative, derived from the small positive entropy of mixing.

Because such reactions, irrespective of the types of complexes, have negligible standard free energy changes, Stranks and Wilkins(14) agreed that the rates of substitution in such systems would give a measure of the bond type in the complexes concerned.

However, the restriction must be made that a similar mechanism is operating for each reaction being compared. A similarity in the energy of activation and the order of the reaction, between systems being compared, could be taken as a criterion for a similar mechanism in each case.

In addition, any comparison of activation energies and rate constants, and therefore $\Delta F^{\neq}$ and $\Delta S^{\neq}$, for different

AX systems (X different) would have to be made in the same solvents with the same A^* species, if information regarding bond type was wanted.

When considering non-isotopic replacements,

$$B + AX \rightleftharpoons BX + A$$

where B and A may be either metal ions or ligands, a more difficult situation arises when interpreting overall physical measurements on such systems.

The standard free energy change $-\Delta G^o$, for such a reaction will be much larger in passing from the less stable AX species to a more stable BX species ($K_{eq.} > 1$). The value of $-\Delta G^o$ is then some measure of the comparative stabilities of AX and BX as such.

It must be emphasized, that the rates of substitution in such reactions need bear no direct relation to the dissociative stabilities of the complexes themselves.

However, a measure of the activation energies involved in such systems will give some indication of the ability of AX to undergo replacement.

If measurements are made in the same media, under the same conditions of concentration and temperature to ensure the consistency of species B, metal complexes with different ligands X, can be compared semi-quantitatively, and similarities of mechanism may be disclosed because of similarities in kinetic and energetic measurements.

Overall measurements of ΔH and ΔS^o embrace all the products and reactants in the replacement reactions, and interpretations of these results may have little bearing upon the relative stabilities of the complexes themselves.

In addition, when considering metal ion substitutions, the free metal ion in solution, has previously been considered as one readily capable of losing its inner-sphere coordination molecules, ie. attached solvent molecules, derived from an easily dissociable metal salt in a solvent of relatively low coordinating power. This in fact is rarely the case, particularly in non-aqueous solvents of low dielectric constant where complete dissociation of the metal salt may not occur. The use of a higher dielectric constant solvent would involve stronger metal-solvent interaction, with the possible result of forming a kinetically unfavourable species. Thus, the rate of exchange between a metal ion and a non-charged inner chelate, would be expected to be greater in a solvent of low, than in one of high dielectric constant, assuming complete dissociation and a similar mechanism of substitution.

In view of the limited information existing on studies of metal ions, particularly transition metal ions, in non-aqueous solvents eg. (dissociation data), substitution reactions with water soluble complexes are widely used as a means of assessing reaction pathways with a general insight into the chemistry of the transition metals.

Similarly, ligand substitution reactions have become increasingly important in studies of substitution reactions, because solvation effects in all solvents are expected to play a much smaller part, even with charged ligands, than they do with metal ions.

The results of such experiments are more easily interpreted.

(iv) Substitution reactions in some transition metal Complexes.

In the following pages, a more detailed review of the experimental work related to the subject matter in the earlier sections of this thesis, will be discussed.

These examples have been divided into two classes, first,

(a) Those metal and ligand substitutions in which data has been found to support the bond types, "stabilities" etc. of the transition metal complexes, and secondly,

(b) Those metal and ligand substitution reactions in which quantitative data, derived from extensive kinetic, stereochemical and related studies, has been used to support the probable reaction mechanisms of substitution.

(a) The elucidation of possible reaction mechanisms of metal substitutions in transition metal complexes, has received little attention, experimentally. There are a few quantitative studies of this type,most of which will be mentioned under (b) above, however their numbers are small compared with similar ligand substitution reactions. This is not surprising upon consideration of the number of difficulties which may accompany the interpretations of the results of such metal substitution reactions, as mentioned in section (iii) of this thesis.

Nevertheless, many of the earlier studies were confined to metal exchanges and replacements, the results of which were taken as evidence of bond type and "stability", as previously discussed.

Many complexes containing bidentate ligands have been shown to undergo rapid metal ion exchange. The results of some of these studies are given in Table I (p.22).

Rapid metal exchanges were taken as indicating weak bonds in the Pauling view, and were supported by magnetic evidence in some cases, eg. cobalt(II)(11) and nickel(II)(33) complexes.

However, certain complexes containing bidentate ligands were found to be inert towards metal exchange. Tris(O-phenanthrolin iron(II) found to contain covalent metal-ligand bonds by Cambi and Cagnasso(34), showed slow exchange with ferrous ions in aqueous solution,(35)(36) that is, a complex containing covalent bonds ($3d^2 4s4p^3$) by the valence bond theory, exchanged slowly. Further, some correlation between the slow cobalt(II) ion exchange in bis-(4:4'-dicarbethoxy-3:3'-5:5'-tetramethyl-dipyrromethene)cobalt(II), and the expected covalent character of the Co - N bonds, has been found by West(11).

However, ferriheme, found by Pauling and Coryell(37) to contain "ionic" bonds on the basis of its magnetic moment

Table I

Metal Exchange Reactions with Complexes containing bidentate ligands.

Exch.complex	Solvent	Result	Ref.
Bis(acetylacetonate)zinc(II)	pyridine	rapid exch. (30 secs.)	(30)
Bis(8-quinolinate)zinc(II)	pyridine	rapid exch. (0.5 mins.)	(31)
Bis(sal-anilinate)cobalt(II)	pyridine	complete exch. ($<$ 50 secs.)	(11)
Bis(salicylaldoximate)cobalt(II) (oxygen inactive form)	pyridine	complete exch. ($<$ 18 mins.)	(11)
Bis(acetylacetonate)cobalt(II)	pyridine	complete exch. ($<$ 2 mins.)	(11)
Bis(acetylacetonate)copper(II)	chloroform	exch. (2 mins)	(32)
Bis(salicylaldehydate)copper(II)	pyridine	exch. (15 secs.)	(5)
Bis(sal-anilinate)copper(II)	pyridine	exch. (15 secs)	(5)
Bis(salicylaldehydate)nickel(II)	methyl cellosolve	exch. (5 mins.)	(33)
Bis(salicylaldoximate)nickel(II)	methyl cellosolve	exch. (5 mins.)	(33)

of 5.8 BM, showed no exchange with ferric ions in 95% ethanol.(32)(36) In fact, ferrihemoglobin,(32)(38) pheophytin iron(III)(36) and tetraphenyl porphyrin iron(III)(36) were all found to undergo negligible exchanges with ferric ions. The lack of correlation between bond type and exchange rate is splendidly illustrated in the ferriheme complex. Ruben and coauthors(36) suggested that in such "fused-ring" structures, where the small central metallic ion was surrounded by a closed porphyrin ring, that for metal exchange to occur, the four metal-nitrogen bonds must be broken simultaneously. However, they suggested that the tris-(<u>O</u>-phenanthroline)iron(II) metal exchange may occur by a stepwise dissociation or uncoiling of the ligands although these authors had no quantitative evidence to support such a theory. Similar negligible exchange rates, to those found in the porphyrin iron(III) systems, were found for the isotopic metal exchanges in pheophytin copper(II)(36) and in the cobalt(II)(11) and zinc(II)(31) phthalocyanine systems. In fact, Atkins and Garner,(31) upon the examination of a number of zinc chelates found only the coplanar phthalocyanine compound inert towards zinc metal exchange in pyridine solution.

Metal <u>re</u>placements have been found to occur in some porphyrin complexes. Phillips(39) has reviewed a number of such studies. Caughey and Corwin(40), examined the relative rates of metal <u>re</u>placements of a number of aetoporphyrin(II) complexes. These authors have suggested that the metal(II) aetoporphyrin stabilities lie in the order $Co^{+2} < Ni^{+2} > Cu^{+2} > Zn^{+2}$ This sequence was based upon the relative rates of metal replacements from the complexes, by sulphuric-acetic acid mixtures. They found that aetoporphyrin nickel(II) reacted more slowly than aetoporphyrin copper(II) towards acid decomposition. Although Caughey and Corwin realised the difficulties of comparing rates and stabilities, as discussed by Taube,(10) the position of nickel(II) with respect to copper(II), in the rate of reaction, had been shown previously to ~~exist~~ occur in the isotopic metal exchanges for a number of quadridentate planar chelates.

The exchanges of metal ions, in complexes containing quadridentate ligands, have been shown to proceed at rates much slower than those of metal exchange reactions in complexes containing bidentate ligands, with similar donor atoms, eg. it has been shown that the exchange of cobalt(II) in cobalt(II) (salen)(6) proceeds at a much slower rate than the exchange of cobalt(II) in bis(salicylideneanilinate)cobalt(II). Similar differences in the rates of exchange of complexes containing quadridentate ligands and bidentate ligands have been shown to exist in some copper(II) complexes.(5)

Duffield and Calvin(5) found that copper(II) ions exchanged with N,N'-ethylenebis(salicylideneiminate)copper(II)[a] at a

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[a] N,N'-ethylenebis(salicylideneimine) = (salen).

measurable rate in pyridine. However, Hall and Willeford(41) found negligible exchange of nickel(II) ions and nickel(II)(salen) under comparable conditions.
Similar negligible metal ion exchanges were found for the N,N'-1,2-phenylenebis(salicylideneiminato)nickel(II)[a] and N,N'-ethylenebis(1-methyl-3-oxobutylideneiminato)nickel(II) systems.(41) However, Pfeiffer(42) found complete replacement of nickel(II) by copper(II) in nickel(II)(salen), in boiling pyridine. If some correlation existed between stability and lability, for these metal exchange reactions, the substitution reactions of copper(II) complexes would be expected to be slower than those of the corresponding nickel(II) complexes. This follows from the well known stability constant series for metal ion complexes, viz. $Cu^{+2} > Ni^{+2} > Co^{+2}$ etc.,(43-45) and also from the replacement studies on the metal(II) complex systems made by Pfeiffer.(42)

Barnes and Dorough(46) found complete replacement of zinc(II) by copper(II) in tetraphenyl porphyrin zinc(II), while Caughey and Corwin(40) found no replacement of zinc(II) by copper(II) in aetoporphyrin zinc(II). The presence of the large phenyl groupings, in the former compound, does not allow the attainment of a coplanar structure because of steric interference with the porphyrin ring. This has the result of further weakening the bonding, through non-planarity,

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[a] N,N'-1,2-phenylenebis(salicylideneimine) = (salophen)

thereby allowing metal replacement to occur.

The large standard free energy changes associated with replacement reactions, further distinguishes between the total replacement of zinc by copper in tetraphenyl porphyrin-zinc(II)(46), and the non-exchange of zinc ions in phthalocyanine zinc(II);(31) also the total replacement of nickel(II) by copper(II) in nickel(II)(salen),(42) and the non-exchange of nickel(II) in this compound.(41)

Caughey and Corwin(40) emphasized the effects of solvent coordination upon bond type in aetoporphyrin(II) compounds. They found that the magnitudes of the shifts in the wave lengths of the visible absorption bands for nickel(II), copper(II) and zinc(II) compounds, in acetic acid-pyridine mixtures, increased in that order ie. Ni > Cu > Zn.

They concluded, that in such stable "fused-ring" structures, where changes in the bond type due to solvent interaction were small, that nickel(II) complexes were in fact more stable than the corresponding copper(II) complexes.

Further, Miller and Dorough(47) studied the reaction of pyridine with magnesium(II), zinc(II), copper(II) and nickel(II) derivatives of $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin, spectrophotometrically. These authors found that the copper monopyridinate compound had an association constant of 0.05 (30°C), about the same as that of the nickel(II) derivative.

Clark and Odell(48) studied the exchanges of ligands in a number of nickel(II) chelates. They found rapid ligand

exchange in the system, bis(salicylaldoximato)nickel(II) - (salicylaldoxime), but zero exchange in the systems nickel(II)(salen) - (salen) and nickel(II)(salophen) - (salophen) Their results indicated that some correlation existed between ligand exchange and the electronic structure of the central nickel(II) atom, at least for a number of systems.
Muto(49) reported the results of a number of quadridentate ligand replacement reactions of some copper(II) complexes. His results indicated that ligand replacements occurred in the reactions,

$$\mathrm{Cu(II)(salophen)} \;+\; \mathrm{(salen)} \rightleftharpoons \mathrm{Cu(II)(salen)} \;+\; \mathrm{(salophe}$$

$$\mathrm{Cu(II)(salophen)} \;+\; \mathrm{(en)} \rightleftharpoons \mathrm{Cu(II)(salen)} \;+\; \mathrm{(O\text{-}phen)}$$

This is of interest in view of the work of Duffield and Calvin(5) who found that the isotopic metal exchange in the system copper(II)(salen) - copper(II) was in fact much faster than the exchange copper(II)(salophen) - copper(II).

(b) Bailar(50), Taube(10), Basolo(51) and Stranks and Wilkins(14) have reviewed the possible reaction mechanisms whereby metal ions and ligands, in transition metal complexes, may be exchanged or replaced.
It must be remembered that kinetic measurements alone, do not give the reaction pathway unambiguously, in fact Basolo and Pearson,(2a) Moore(52) and Frost and Pearson(53) have made clear the distinction between the experimental (order) and theoretical (molecularity) aspects of a reaction. There is no clear cut

distinction between an $S_E1(S_N1)$ or $S_E2(S_N2)$ mechanism on the basis of kinetic measurements alone. The influence of stereochemistry and other factors upon the type of mechanism(s) involved has been fully discussed by several authors.(50)(51)(54)(55) However, it must be repeated that the final chosen mechanism $S_E1(S_N1)$ or $S_E2(S_N2)$, must agree with all the available evidence, in particular, the evidence observed from any kinetic measurements made on the system. The following pages review some of the experimental and theoretical results which have been used to elucidate the possible mechanisms of substitution reactions in inorganic transition metal complexes.

(i) Ligand Substitution Studies.

Basolo, Pearson and coworkers have published a series of papers investigating mainly the ligand substitution reactions of cobalt(III) complexes and have shown how the nature of the transition state can influence the mechanism of ligand substitution.

An S_N1CB[a] mechanism of dissociation was supported for the base hydrolysis of cis and trans - $[Co(en)_2Cl_2]Cl$ on the observed rapid rates for these reactions and as a result of the dependence of the rate of hydrolysis with structural changes in the complexes. Moreover, the authors supported an

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[a] S_N1CB = substitution, nucleophilic, unimolecular, conjugate base.

S_N1CB mechanism of substitution for the base hydrolysis of all complex ions of cobalt(III). However, the observed high rates of hydrolysis of chloroamido and chlorohydroxo complexes of cobalt(III), led Pearson and Basolo$^{(57)}$ to introduce the concept of π bond stabilization, in the transition state. The suspected pK_a values of the conjugate bases, $[Co(NH_3)_4NH_2Cl]^{+1}$ and $[Co(NH_3)_3NH_2OH]Cl$ respectively, did not fully explain their ease of formation and reactivity.

Previously an S_N2 displacement mechanism of substitution, had been supported by Brown, Ingold and Nyholm$^{(58)}$ for the acid hydrolysis of $[Co(NH_3)_5\substack{Cl\\Br\\NO_3}]^{+2}$ on the available kinetic evidence.$^{(59)(60)(61)(62)}$

In fact, Brown, Ingold and Nyholm$^{(58)}$ were of the opinion that substitution reactions of cobalt(III) ions proceeded by a dual mechanism involving both dissociation and displacement pathways.

Later an S_N1 dissociation mechanism for acid hydrolysis of cobalt(III) ions was supported by Basolo, Pearson and coworkers$^{(63)(64)(65)}$ as a result of the dependence of the rate of aquation, with structural and steric properties of the bidentate ligand (LL), in the compound trans- $[Co(LL)_2Cl_2]^{+1}$ These authors suggested the formation of a penta-coordinated square pyramid transition state for these acid hydrolysis reactions.

Primarily, Pearson and Basolo$^{(57)}$ were confronted by experimental results which indicated that the rates of base hydrolysis of cobalt(III) ions were larger in complexes containing saturated ligands capable of donating electrons to the cobalt $3d^6$ electronic nucleus. Accordingly, they discussed the stereochemical requirements for π bonding (ligand → metal), in the transition state, from two viewpoints,

(a) The influence of such π bonding upon the dissociation of a ligand and its effect upon the stability of the resulting transition state.

(b) The amount of π bonding possible for such $3d^6$ systems, using the orbital overlap considerations developed by Craig, Maccoll, Nyholm, Orgel and Sutton.(66)

On comparison of the three possible structures for a central cobalt(III) ion, viz.

(i) trigonal bipyramid.

(ii) square pyramid d^2sp^2

(iii) a d^2p^3 hybridized structure,

Basolo and Pearson(57) found only (i) agreed fully with their experimental results and the theoretical energetic and π bonding concepts.

The repulsion, between filled non-bonding d_{xy}, d_{yz} and d_{zx} orbitals of the central metal ion and the filled p orbitals of the amido group in the conjugate base $\left[Co(NH_3)_4NH_2Cl\right]^{+1}$, has the effect of facilitating the release of a chloride ion, with the accompanying rearrangement to a trigonal bipyramid transition state, which is stabilized by ligand → metal π bonding involving the donation of a free electron pair from the amido nitrogen to the empty $d_{x^2 - y^2}$ orbital of the cobalt(III) ion.

Further, the observed first order kinetics involving comparatively rapid conjugate base dissociation as the rate determining step, could be explained on the basis of forming a five coordinated species of increased stability due to π bonding.

The effects of a variety of nucleophilic reagents upon the kinetics, stereospecificity and the rates of exchange of chloride ions in $[Pt(NH_3)_2Cl_2]$, $[Pt\ en\ Cl_2]$ and $[Pt(NH_3)_3Cl]Cl$, has been examined in an attempt to elucidate a possible reaction mechanism of substitution.(67) The reactions of these platinum(II) compounds were classified by the authors as substitutions in octahedral complexes. The ability of such coplanar structures, in solution, to coordinate solvent, reactant and added anions etc. above and below the plane, is well known.(68)(69)(70)(71)

Accordingly, Banerjea, Basolo and Pearson proposed a reaction mechanism whereby substitution reactions in such platinum complexes could be explained. Primarily, they considered two factors in assessing the stability of the probable transition state,

(i) The extent of π bonding using an extension of the trans-effect theories of Chatt(72) and Orgel.(73)

(ii) The differences in C.F.S.E. between the square planar reactant and the proposed transition state.[a]

With certain limitations, they proposed a dissociation mechanism of the tetragonal complex, in which the two groupings above and below the plane moved closer, and facilitated the removal of the chloride ion, by repulsion, with an accompanying rearrangement, after dissociation, to a trigonal bipyramid transition state, stabilized by π bonding. However, unlike cobalt(III), platinum(II) has a d^8 electronic structure. Accordingly, if the concept of π bonding in the transition state was to be maintained, the added stabilization from π bonding must result from the donation of electrons from the filled d orbital of platinum(II) to an unoccupied d or p orbital on the ligand. Therefore, only unsaturated ligands, eg. $SC(NH_2)_2$,$(NO_2)^{-1}$, would react rapidly with platinum complexes of this type. This was in agreement with the experimental results found.

A detailed examination of the kinetics of the exchange of chloride ions with trans- $[Pt(pyr)_2Cl_2]$ in a variety of solvents,(74) enabled the authors to classify the reactions into three groups, depending upon the observed order

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[a] The authors fully realized the limitations of using the C.F.S.E. for a square planar reactant, when they admitted a tetragonal structure in solution.

of the reaction with respect to R_4NCl^* , the source of free chloride ions.

In benzene, methyl cyanide and acetone, the observed kinetics indicated first order dependence on both [complex] and $[R_4NCl^*]$. Further, slow rates of chloride exchange were found in high dielectric constant solvents. The free chloride ion, produced by the complete dissociation of R_4NCl^*, in such solvents, was stabilized by solvation thereby forming a kinetically unfavourable species for exchange. Conversely, in low dielectric constant solvents, higher rates of exchange were observed.

The authors discussed the anomalous position of methyl cyanide, a strong π bonding solvent in which slow rates of exchange were observed, with respect to its peculiar behaviour on coordination.(75) The C≡N grouping is known to coordinate above and below the plane of the platinum(II) complex, in a parallel arrangement, thereby hindering its distance of approach and its ability to facilitate in the dissociation of ligands.

Quagliano and Schubert(54) have shown how various trans-effect theories can predict the stereochemical course of substitution reactions of planar complexes of platinum. Further, S_N2 displacement mechanisms have been proposed for these substitutions, by some authors,(72)(73)(76) in particular Chatt and his coworkers(72) who used a π bonding theory to account for the substitutions of such square planar complexes by S_N2 displacement mechanisms.

Thus, the mechanism(s) of ligand substitutions in platinum complexes is still uncertain. The Basolo and Pearson reaction mechanism requires an initial tetragonal structure in solution; if such a structure may be conceived on the evidence available, a dissociation S_N1 mechanism appears attractive.

It has been suggested that the dissociation mechanisms of exchange and racemization of $\left[Ni(1{:}10\ phen)_3\right]^{+2}$ are the same,(77) on the basis of the identical values of the rate constants, for the $\left[Ni(1{:}10\ phen)_3\right]^{+2}$ – (1:10 phenanthroline) ligand exchange $k_{exch.}$(77), and the pH independent acid dissociation and racemization reaction k_a, of $\left[Ni(1{:}10\ phen)_3\right]^{+2}$ (78)

Moreover, it was found that the removal of one phenanthroline ligand facilitated both exchange and racemization. The dissociation rates measured by means of the ligand exchange experiments were found to be first order in the nickel complex and zero order in the free 1:10 phen ligand.

Such a dissociation path for exchange was found to persist in the non-aqueous solvents, ethyl alcohol and nitrobenzene.

It is of interest to note that Davies and Dwyer(79) measured the rates of racemizations of $\left[Ni(1{:}10\ phen)_3\right]^{+2}$ and $\left[Ni(dipyr)_3\right]^{+2}$ in some non-aqueous solvents, and suggested from the similarities in activation energies and pZ-factors in all solvents used, that an intra-molecular mechanism of racemization operated in contrast to that in water.

(ii) Metal Substitution Studies.

The exchanges of tetracyano nickelate ion with certain amino acid complexes of nickel(II) have been examined kinetically.(80) The rates of exchange of nickel(II) between the two species were found to be little affected by either,

(i) added neutral salt,

(ii) charge of the amino acid complex,

(iii) molecular weight of the acid complex.

The results indicated that the nature of the complexing agent, was more important than charge etc., for the determination of the rate of substitution in these complexes. From the observed second order kinetics (dependence of the rate of exchange on the concentration of both reacting species) for the $\left[Ni(CN)_4\right]^{-2}$ - $\left[Ni(glycinate)_2\right]$ exchange, the authors suggested a collisional mechanism of substitution. However, the observed activation energy (17.3 K cals) seems unusually small to involve the breaking of eight or ten relatively strong bonds, instantaneously.

The exchange of $\left[1{:}10(phen)\right]$ between $\left[Ni(1{:}10phen)_3\right]^{+2}$ and the free ligand in solution, was found to have an activation energy of 25.2 K.cals.(77) This exchange was found to proceed by an S_N1 dissociation mechanism, involving the complete fission of only one phenanthroline molecule from the complex. ie. the breaking of two bonds.

It seems that the observed energy of activation in the nickel(II)(glycinate)exchange may disagree with a collisional mechanism on energetic grounds. Perhaps a mechanism of substitution similar to the one suggested by Basolo and Pearson(2a) for the copper(II)(salen) exchange, may be applicable to the systems examined by Calkins and Hall.(80)

Collisional mechanisms of substitution for the metal exchanges in copper(II)(salen)(5) and cobalt(II)(sal<u>o</u>phen)(6) were proposed by the authors on the grounds of the second order kinetics observed for these systems. As discussed earlier the interpretations of these kinetic measurements have been revised by Basolo and Pearson.(2a)

An expression for the rate of substitution, which included five terms, four of which were dependent upon pH, was found for the exchange of nickel(II) ions and $[Ni(EDTA)]^{-2}$ (81) Five activated complexes were found to be present in the reaction, the mechanism of exchange involving a preliminary equilibria between H^+ and $[Ni(EDTA)]^{-2}$, followed by both unimolecular dissociation of a protonated complex and bimolecular collision and exchange with nickel(II) ions.

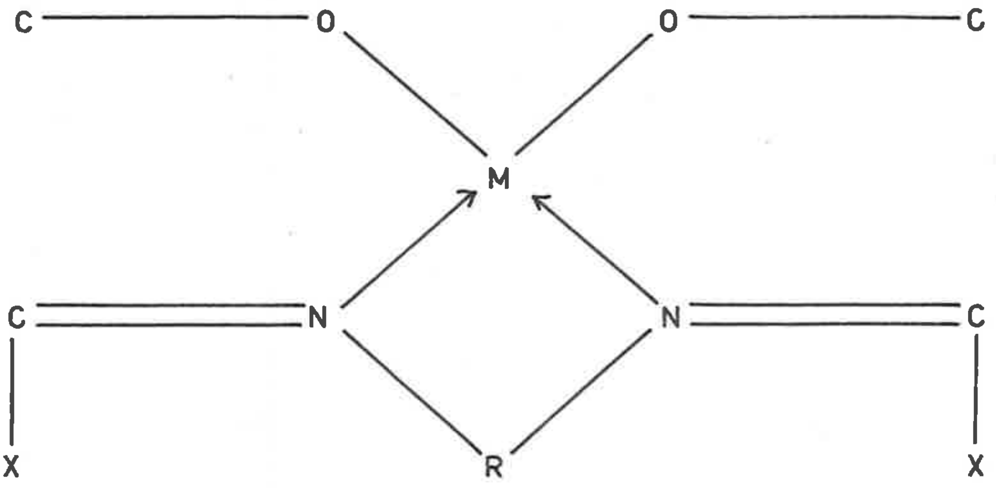
It was suggested, from the similarity of the rates of racemization and the rates of iron(II) exchange in tris-(2,2'-dipyridyl)iron(II) and tris-(1:10 phenanthroline) iron(II)(11), that the racemization processes of these ions may be brought about by the dissociations of the complexes.(35)

Kinetic measurements have been used to elucidate the probable reaction mechanism(s) for the <u>re</u>placement of lead(II) by copper(II) ions in $[Pb(EDTA)]^{-2}$ (28) A mechanism(s) similar to the one proposed for the replacement reaction,

$$Pb^{+2} + [Zn(EDTA)]^{-2} \rightleftharpoons [Pb(EDTA)]^{-2} + Zn^{+2} \quad (82)$$

was established by the authors,(28) involving four reaction pathways.

The research presented in this thesis is concerned with some kinetic studies of metal replacement reactions involving quadridentate chelate compounds of nickel(II), copper(II) and cobalt(II), with ligands of the type shown in Fig.II.



R = alkyl or aryl group.

Fig.II.

The primary object of the work involved an examination of the mechanism(s) of replacement of nickel(II) from such complexes, according to the reaction

$$Cu^{+2} + Ni(II)(chelate) \rightleftharpoons Ni^{+2} + Cu(II)(chelate)$$

The effect of varying the solvent, the type of copper salt used, and the influence of added electrolytes upon the rates of these replacements have been examined.

Further, the replacement of cobalt(II) from cobalt(II)(salen), by several divalent transition metal ions in pyridine, has also been studied.

In addition, the ultra violet and visible absorption spectra of a number of copper(II) salts and nickel(II) chelates have been examined in various non aqueous solvents, in an attempt to determine the nature of the reacting species in such replacement reactions.

METAL SUBSTITUTION REACTIONS WITH N,N'-ethylenebis(salicylideneiminato)cobalt(II)

(i) The relation between the metal ion and the rate and equilibrium position of the reaction.

The systems studied may be represented by the reaction,

$$M^{+2} + Co(II)(salen) \rightleftharpoons M(II)(salen) + Co^{+2}$$

Cobalt(II)(salen) labelled with Co^{60} was used in the experiment. The course of reaction was followed by measuring the amount of radioactive cobalt released as cobalt(II) ions in the system. Four such substitutions were examined and the results of these given in Table II.

Cobalt(II) ions in cobalt(II)(salen) were found to undergo substitution by other metal ions at 25°C, in pyridine. Under similar conditions of concentration the relative rates of substitution and final equilibrium positions were as follows:

(a) rapid <u>re</u>placement by copper(II) ions, equilibrium position, 96%,

(b) slow <u>re</u>placement by nickel(II) ions, equilibrium position, 78%,

(c) rapid exchange with cobalt(II) ions, equilibrium position, 50%,

(d) rapid replacement with zinc(II) ions, equilibrium position, 16%.

Relative to the cobalt(II) exchange, the observed equilibrium positions for these substitutions, obey the expected order of metal complex stabilities,[a] viz. Cu $>$ Ni $>$ Zn. However, the slow replacement found with nickel(II) ions, compared with the rapid exchange with cobalt(II), may be taken as evidence for a complete lack of correlation between the rates of substitution and the expected stabilities of the complexes formed, as a result of these reactions.

Pfeiffer and coworkers(42) carried out a similar investigation with a number of (salen) complexes, however these authors were content with the determination of a stability series only, kinetic measurements on the system were not attempted.

They found a relative series of metal complex stabilities, in the order $Cu^{+2} > Ni^{+2} > VO^{+2}$, $Fe^{+2} > Zn^{+2} > Mg^{+2}$, based upon the extent of the reaction,

$$M^{+2} \quad + \quad M'(II)(salen) \quad \underset{}{\overset{\text{pyridine}}{\xrightleftharpoons{115^{\circ}C}}} \quad M(II)(salen) \quad + \quad M'^{+2}$$

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[a] No data is available on the stability constants of these chelates in any solvents.

Table II

The substitution of cobalt^{60}(II) from cobalt^{60}(II)(salen)

T = 25.0 ± 0.1°C   Solvent = pyridine   Concn. = 2.6×10^{-3}
$= [M^{+2}] = [\text{complex.}]$

Substituting cation	Salt	Activity counts/300secs [Complex]	[^{60}Co]$^{+2}$	Reaction time (hours)	% Substitution.
Cu^{+2}	acetate monohydrate	101	2171	0.05	96
		136	1847	0.20	93
		129	2355	1.00	95
		102	2338	2.50	96
		98	2396	5.00	96
Ni^{+2}	acetate tetrahydrate	4035	648	0.25	14
		4433	1452	0.50	25
		4774	2344	1.00	33
		3888	2520	1.50	39
		3444	3743	2.50	52
		3043	4938	3.75	62
		2607	7419	5.25	74
		1568	5419	9.50	77
		1906	6763	10.50	78
		1632	6689	24.20	81

Substituting cation	Salt	Activity counts/300secs.		Reaction time (hours)	% Substitution
		[Complex]	$[^{60}Co]^{+2}$		
Co^{+2}	acetate tetrahydrate	3248	3410	0.05	51
		2697	2816	0.19	51
		2800	3241	0.50	53
		2930	2790	1.00	50
		2498	2571	5.50	51
Zn^{+2}	acetate dihydrate	5613	1086	0.05	16
		4677	694	0.25	13
		5742	799	0.75	12
		4767	829	1.50	15
		5890	1155	3.00	16
		5694	1049	5.00	16
		6680	1297	8.75	16

(i) The activities of both fractions have not been corrected for the incomplete extraction of either the complex or metal(II) ion, but the rapidity of substitution or otherwise is evidenced directly from the uncorrected results.

The activity under the heading Complex $[Co^{60}(II)(salen)]$ is the activity remaining in the solvent ($CHCl_3$) which would normally extract all the unreacted chelate, while that under $(^{60}\mathrm{Co})^{+2}$ is the activity of the water extracted $(^{60}\mathrm{Co})^{+2}$ salt after reaction.

(ii) % Substitutions are calculated on the basis of the activity appearing in the aqueous fraction, ie.

$$\%\ \text{substitution} = \frac{\text{counts/300 secs of aqueous fraction}}{\text{counts/300 secs of (aq. + organic) fraction}} \times 100$$

(iii) All activities were counted for a sufficient time to give a Standard Percentage Error (E%)(83) of better than 3%, and were corrected for background activity.

The stability sequence above parallels the stability constant series,(43)(44)(45) except for the positions of iron(II) and zinc(II). Pfeiffer found complete replacement of zinc(II) by iron(II) in zinc(II)(salen), chemical analysis of the reaction products showing no unchanged zinc(II)(salen). However, no replacement of iron(II) by zinc(II) in iron(II)(salen) was observed. Further, equilibrium positions were found for many systems eg.,

$$^{a}\,\mathrm{Ni(II)(salen)} \quad + \quad \mathrm{VO^{+2}} \quad \overset{\approx 30\%}{\rightleftharpoons} \quad \mathrm{VO(IV)(salen)} \quad + \quad \mathrm{Ni^{+2}}$$

$$\mathrm{VO(IV)(salen)} \quad + \quad \mathrm{Fe^{+2}} \quad \overset{>50\%}{\rightleftharpoons} \quad \mathrm{Fe(II)(salen)} \quad + \quad \mathrm{VO^{+2}}$$

$$\mathrm{Fe(II)(salen)} \quad + \quad \mathrm{VO^{+2}} \quad \overset{<50\%}{\rightleftharpoons} \quad \mathrm{VO(IV)(salen)} \quad + \quad \mathrm{Fe^{+2}}$$

West(6) found that the exchange of cobalt(II) ions in cobalt(II)(salophen) proceeded by a second-order reaction, presumably involving a bimolecular rate determining step and a collisional or displacement mechanism of substitution. No detailed kinetic measurements on the exchange of cobalt(II) ions and cobalt(II)(salen) are available to support a possible reaction mechanism of substitution, however it was found exchange was complete in less than 6 minutes at 30°C [0.0121M Co(II)(salen), 0.0057M Co(II)(acetate)](6). Studies carried out by the present author showed complete exchange

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[a] Complete replacement was observed for the back reaction,

$$\mathrm{VO(IV)(salen)} \quad + \quad \mathrm{Ni^{+2}} \quad \longrightarrow \quad \mathrm{Ni(II)(salen)} \quad + \quad \mathrm{VO^{+2}}$$

of cobalt(II) in cobalt(II)(salen) in less than 3 minutes at 25°C [0.0026M each reactant].
Some evidence for a bimolecular (S_E2) rate determining step may be obtained from the marked dependence of the rate of *re*placement of cobalt(II) from the complex, upon the electrophilic nature of the incoming metal ion.(2) This is most marked when comparing the slow *re*placement by nickel(II) with the rapid exchange of cobalt(II) ions.

Calvin and Barkelew(13) found that cobalt(II)(salen), *in the solid state*, was paramagnetic to the extent of one unpaired electron, indicating a square planar, covalently bonded complex. This would imply, at least in the solid state, that the four cobalt-ligand bonds in the complex would be strong in the Pauling view ($3d4s4p^2$)(9) or indicate a strong-field planar structure for the complex on Crystal Field grounds.(2c) If, as suggested by Stranks and Wilkins,(14) a strict correlation between the rate of exchange and bond type can be made, such a rapid metal exchange in cobalt(II)(salen would not be expected, unless the bonding in this compound is modified to some extent, in solution.
In addition, on the basis of calculations made by Basolo and Pearson(2a) of the activation energies of substitution reactions of strong-field "square planar" (tetragonal) complexes (by S_N1 and S_E1 mechanisms), cobalt(II) complexes of this type are predicted to react more slowly than either their corresponding

nickel(II) or copper(II) complexes,[a] in fact the calculated order for the rates of reaction is given as $Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+}$ However, the isotopic metal exchange of copper(II) in copper(II)(salen)(5) has been shown to proceed at a much slower rate than the corresponding cobalt(II) exchange, under comparable conditions. This is in direct contradiction to the calculated rates on the basis of the Crystal Field approach, for "square planar" (tetragonal) reactant molecules on the basis of a dissociation mechanism.

Evidence for solvent interaction with the complexes

(a) Cobalt(II)(salen).

Tsumaki(84) has isolated a chloroform addition compound of this chelate which would imply at least a five coordinated structure for the complex in that solvent. Further, the magnetic susceptibilities of oxygenated and pyridinated forms of cobalt(II)(salen) have been reported.(13) Diehl and coworkers(85) investigated the oxygen-carrying properties of this complex and later Diehl and Hach(86) reported the preparation of aquo-dicobalt(II)(di-salen) in which reference to the formation of chloroform and pyridine addition compounds was made. In fact, it was found that the method of preparation used by these workers(86) yielded a binuclear compound in which a molecule of water acted as a bridging group between

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[a] This assumes a strict parallel between the activation energies and rates of reaction, a correlation which may be taken only qualitatively.

the two cobalt atoms in the molecule, each of which was surrounded by a quadridentate molecule of the Schiffs base. The complex, as prepared by Diehl and Hach, absorbed oxygen in the solid state, the addition of oxygen yielding a compound in which the coordination number of each cobalt(II) atom in the complex was thought to be six.(86)
The sample of complex used in the substitution experiments reported in this thesis was prepared by the method of West.(6) The material prepared in this manner did not react with oxygen, <u>in the solid state</u>. (see EXPERIMENTAL)

It seems reasonable to suggest, from the evidence presented above, a six coordinated structure for the complex in the strong coordinating solvent pyridine, the structure involving two molecules of solvent, one above and one below the plane of the complex, thereby producing a C.F.S.E. equivalent to that of a weak field octahedral or tetragonal structure in solution.(2)(2c) Assuming then a bimolecular rate determining step for the exchange reaction, an assumption not unreasonable on the evidence presented on p.44,45, then such a rapid exchange may be explained on the basis of a displacement mechanism of substitution, whereby a pentagonal bipyramid transition state is formed (from an initial tetragonal complex in solution) involving a net gain of C.F.S.E. (ΔE_a = -2.56 Dq)(2)

(b) <u>Nickel(II)(salen)</u>

No spectroscopic or other evidence, for solvent interaction with this complex, has been found,(41)(87)(88) although some evidence for partial solvation of the complex was reported by Basolo and Matoush(89) who isolated a pyridine addition compound of this chelate containing 0.372 moles of pyridine per mole of nickel(II)(salen). However, no isotopic metal or ligand exchange was found for this chelate in pyridine solution,(41)(48) under comparable conditions as those used for copper(II) and cobalt(II) exchanges. However, although nickel(II) complexes are predicted to react more slowly than those of their corresponding copper(II) complexes, on Crystal Field calculations,(2)(2a) by both $S_E1(S_N1)$ and $S_E2(S_N2)$ mechanisms, this does not explain the observed lack of exchange of nickel(II) and (salen) in nickel(II)(salen) at room temperature.(41)(48) This matter will be examined further when discussing the replacement of nickel(II) ions from the complex, in the following sections of this thesis.

(c) Copper(II)(salen)

Spectroscopic evidence for solvent interaction with copper(II)(salen) in pyridine has been reported,(90) however, Tanaka(91) was unsuccessful in an attempt to isolate a pyridine addition compound. In fact, the latter author suggested from the similarities in the visible absorption spectra of copper(II)(salen) in pyridine and benzene, that solvent interaction with the chelate did not occur in either of these solvents. However, addition compounds of copper(II) (salen) with acids and phenols have been isolated.(92)

Waters and Hall(93) as a result of studies on the solid absorption spectra, of a number of copper(II) chelates, including copper(II)(salen), found that those complexes with green colours e.g. copper(II)(salen), by analogy with their spectra in solution,(90) contained copper(II) atoms with coordination numbers of greater than four.
Later, X-ray studies(94) supported a dimeric structure for copper(II)(salen) in the solid state, with two Cu – O bonds binding the two units of the dimer, each molecule thereby containing two copper(II) atoms, each with coordination numbers of greater than four.
Similarly, colour and, solution and solid spectra, were compared for a number of brown and violet copper(II) complexes.(90)(93) The results indicated that such chelates contained copper(II) atoms with coordination numbers of four. A green solution of copper(II)(salen) in pyridine, compared with the resulting purple solutions of the complex in alcohol and chloroform, does not only suggest dissociation of the solid chelate into single units containing copper(II) atoms with coordination numbers of four, in the latter solvents, but indicates, either,

(a) solvent interaction with copper(II)(salen) in pyridine,

or

(b) an unchanged dimeric structure for the complex in this solvent.

However, by analogy with solid copper acetate, which is known to be dimeric in the solid state(95)(96), but found to dissociate in pyridine, but not in ethanol or dioxan solutions,(97) it seems likely that solvent interaction with copper(II)(salen) in pyridine does occur, producing a weak-field octahedral structure in solution. [cf. cobalt(II)(salen)]. Therefore, the observed slow but measureable copper(II) exchange in this chelate, involving second order kinetics,(5) and a suggested bimolecular rate determining step,(2a) may be explained on the basis of forming a seven coordinated transition state, from an initial weak-field octahedral structure, involving a loss of C.F.S.E. of 1.07 Dq.(2)

The predicted order of the rates of reaction, and those observed in the metal exchanges, may be summarized as follows in Table III, p.51.

Table III

The rates of metal exchange in nickel(II), copper(II) and cobalt(II) (salen) complexes in pyridine.

Complex	Mechanism	Observed rate	Ref.	Predicted rate on C.F.S.E. calculations	ΔE_a
Nickel(II) (square planar)	S_E1	negligible	(41)	slow	10.42Dq 6.28Dq
weak field octahedral	S_E2	negligible	(41)	slow	4.26Dq
	S_E1	negligible	(41)	slow	2.00Dq
Copper(II) weak field octahedral	S_E2	slow but measurable	(5)	slow	1.07Dq
Cobalt(II) weak field octahedral	S_E2	rapid	(6)	rapid	-2.56D

The values of ΔE_a have been taken from the calculations made by Basolo and Pearson(2)(2a)

Some correlation between the observed rates of exchange and those predicted on the basis of theoretical calculations, using the electrostatic approach, can be seen to exist for these essentially covalently bonded (salen) chelates. The results of Table IV show that the ease of replacement is not solely a function of the metal ion, but may depend strongly upon the actual replacing species.

(ii) The effect of the type of nickel salt upon the rate of replacement.

The results of replacement experiments with cobalt(II)(salen), using different nickel salts, show that the order of the rates of replacement is nickel acetate (anhydrous) $>$ nickel acetate (tetrahydrate) and nickel perchlorate (dihydrate).
The data for these experiments is given in Table IV.
The slower rate exhibited in the perchlorate substitution compared with the anhydrous acetate replacement, may be due to the formation of a different nickel(II) species in solution.

No data is available relating to the dissociation constant(s) of nickel acetate in pyridine [$\varepsilon_{(25^{\circ}\mathrm{C})} = 12.0$(98a)] however ion-exchange and potentiometric investigations of nickel acetate in aqueous solution have indicated the existence of both $(\mathrm{NiOAc})^{+1}$ and $\mathrm{Ni(OAc)_2}$ species in solution at $[\mathrm{AcO^-}] \leqslant 0.5\mathrm{M}$(99) However, E.M.F. measurements made by other workers,(100) have indicated that the first stage of dissociation of nickel acetate, in water, is complete.
The dissociation constant of nickel oxalate in water at 25°C is given as $K_{\mathrm{dissconst.}} = 0.05 \times 10^{-4}$ (101)
Further, the dissociation constants of a number of inorganic and organic salts in pyridine have been listed.(98b) These have values ranging from $K_{\mathrm{dissconst.}} = 1 \times 10^{-3} - 1 \times 10^{-5}$.

Table IV

The replacement of cobalt^{60}(II) ions from cobalt^{60}(II)(salen) by nickel(II) ions

T = 25.0 ± 0.1°C Solvent = pyridine

Salt	Concn. in moles l^{-1} $[Ni^{+2}] = [complex]$	Activity counts/300secs.		Reaction time (hours)	% Replacement
		[Complex]	$[^{60}Co]^{+2}$		
acetate (tetrahydrate)	2.6×10^{-3} M	see Table II.			
perchlorate (dihydrate)	2.6×10^{-3} M	6280	1182	0.07	15
		5197	1431	0.18	22
		4963	1725	0.50	26
		4090	1937	1.00	32
		2945	2575	2.50	47
		3444	3433	4.00	50
		3587	4393	5.50	55
		4160	4953	7.60	54
		3241	4212	9.00	57
		3588	4946	10.00	58
acetate (anhydrous)	2.6×10^{-3}	3197	2742	0.25	46
		2559	4316	0.50	63

Salt	Concn. in moles l^{-1} $[Ni^{+2}] = [complex]$	Activity counts/300secs.		Reaction time (hours)	% Replacement.
		[Complex]	$[^{60}Co]^{+2}$		
acetate (anhydrous)	2.6×10^{-3} M	1878	6378	1.00	77
		1015	6985	3.00	87
		984	8111	4.50	89
		851	7439	6.50	90
		785	6970	8.00	90
acetate (anhydrous)	1.3×10^{-3} M	2621	984	0.25	27
		2927	2042	0.50	41
		1928	2587	1.00	57
		1173	2980	2.00	72
		855	4261	4.25	83
		598	4468	6.00	88
		497	4037	9.00	89

(i) % Replacements have been calculated in a similar manner to those given in Table II.

It would appear that nickel acetate in pyridine at the concentrations used in the replacement experiments ($1.3 - 2.6 \times 10^{-3}$ M), would at least exist to some degree as the free solvated nickel(II) ion in solution.

$Ni(ClO_4)_2pyr_6$ has been isolated,(102) and presumably $Ni(pyr)_{4 \text{ or } 6}$ exists in solution to some extent. Conductance experiments on nickel perchlorate dihydrate in pyridine,(103) indicate that the degree of dissociation of nickel perchlorate in this solvent is of the same magnitude as that in furfural ($\varepsilon_{20^\circ C} = 41.9^{(104)}$), which was found to be an excellent ionizing solvent for transition metal perchlorates.

During substitution studies a white precipitate of ($pyr\ HClO_4$) was slowly precipitated, which implied the formation of a hydroxide ion in solution, which may form an ion such as $(Ni\ OH\ pyr_x)^{+1}$

Such an anion participating in a substitution reaction would require great reorganization of its attached groups, particularly the hydroxide group, than would a single ion bearing only solvent molecules, and hence a slower rate of substitution may be expected.

The exact nature of the species present in the hydrated acetate replacement is in doubt, however it is not unreasonable to suggest a similar hydroxy pyridinated nickel(II) ion as above.

The similarity in the initial rates of replacement, using the hydrated acetate and perchlorate salts tends to support this assumption, although the equilibrium positions absberved in both of these experiments were widely different. [58% perchlorate (dihydrate) and 78% acetate (tetrahydrate)]. A complete examination of the solid formed during the hydrated perchlorate replacement was not attempted. Some addition product $[Ni(ClO_4)_2pyr_6]$ may have been precipitated, thereby decreasing the amount of nickel(II) available for substitution.

However, the results do show the variation in the rate of substitution with the nature of the nickel salt used. This may be expected if the rate determining step of the reaction depended upon the nature of the nickel(II) species in solution, as well as the cobalt(II) complex. Such evidence further supports a bimolecular rate determining step for these replacement reactions.

A similar dependence on the rate of substitution with the type of copper salt used has been shown to exist in the reaction involving the replacement of nickel(II) by copper(II) in nickel(II)(salen). The results of these experiments are given in the following chapter.

METAL REPLACEMENT REACTIONS WITH

N,N'-ethylenebis(salicylideneiminato)nickel(II).

[nickel(II)(salen)].

The reaction between copper(II) ions and nickel(II)(salen) has been studied in various non-aqueous solvents. The overall reaction may be represented by the general equation,

$$Cu^{+2} \quad + \quad Ni(II)(salen) \rightleftharpoons Cu(II)(salen) \quad + \quad Ni^{+2}$$

The course of the reaction was followed by taking samples of reaction mixtures at various time intervals, and measuring the concentration of unreacted copper(II) ions, in each sample.
A colorimetric method of analysis was used which involved the reduction of copper(II) to copper(I) ions, then development of the violet copper(I) complex with 2,2'-Diquinolyl.(105)
A more detailed description of the experimental procedures used in the colorimetric determinations is given in the EXPERIMENTAL section.

The various factors which have been shown to influence the rates of reaction will be discussed under the following headings viz.,

A. The effect of the type of copper(II) salt used, together with the effects of added salts and water.

B. The effect of varying the solvent.

The following sections present and discuss the experimental results obtained from the studies.

Measurements were made of the initial rates of reaction, in order to avoid difficulties which arose as the

reactions proceeded, due to the increased velocity of the back replacement reaction of nickel(II) ions with copper(II)(salen), or any side reactions.
The rates were obtained from graphs of copper(II) concentrations (mole l^{-1}) versus time (t in hours). The slopes of the tangents to these curves at t=0, being taken as the initial rates of disappearance of copper(II) ions from the systems.
The upper and lower limits set for the rates of reaction, represent the graphical errors involved in obtaining the slopes from the rate curves, at t=0. Similarly, the upper and lower limits given for the rate constants and other physical values, represent the errors involved in graphical procedures.

The kinetics of the replacement reactions between copper(II) ions and nickel(II)(salen), in methyl cellosolve and ethyl alcohol, have been examined. The results are included in this chapter.

Representative tables of replacement experiments and rate graphs are given throughout the following sections.

A. The effect of type of copper(II) salt etc., upon the initial rate of replacement.

The reactions of three copper(II) salts with nickel(II)(salen) were studied viz., copper(II) perchlorate (hexahydrate), copper(II) acetate (monohydrate) and anhydrous copper(II) chloride.

These reactions were found to proceed at convenient rates for measurement at 60 - 70°C, in 2-methoxy ethanol (methyl cellosolve), at concentrations used in the replacement experiments. This solvent was chosen as the reaction medium because it was an excellent solvent for all the reactants, it possessed a high boiling point (124.3°C),(106) and was chemically stable.(107) Further, Hall and Willeford used the solvent when examining the metal exchange reaction of nickel(II) ions with nickel(II)(salen).(41)

Table V presents the experimental results obtained from the replacement experiments using the above three copper(II) salts.

The calculated rates have been summarized in Table VI.

Upon examination of Table VI, the initial rates of disappearance of copper(II) ions may be seen to depend strongly upon the type of copper(II) salt used. The initial rates increase in the order, acetate (monohydrate) $<$ chloride $<$ perchlorate (hexahydrate).

Table V

The Replacement of nickel(II) ions by copper(II) ions in N,N'-ethylenebis(salicylideneiminate)nickel(II).

Solvent: 2-methoxy ethanol $T = 70.0 \pm 0.1^{\circ}C$

Salt	(1)	(2)	(3)	Time t (hrs)
$Cu(ClO_4)_2 \cdot 6H_2O$	0.598	0.00118	0.00012	0.10
	0.542	0.00107	0.00023	0.20
	0.502	0.00099	0.00031	0.30
	0.427	0.00085	0.00045	0.50
	0.366	0.00073	0.00057	0.70
	0.299	0.00059	0.00071	1.00
	0.050	0.00009	0.00121	10.00
	0.020	0.00004	0.00126	24.00
$CuCl_2$	0.692	0.00119	0.00011	0.20
	0.632	0.00109	0.00021	0.40
	0.610	0.00105	0.00025	0.50
	0.538	0.00093	0.00037	0.80
	0.515	0.00089	0.00041	1.00
	0.482	0.00083	0.00047	1.20
	0.451	0.00078	0.00052	1.50
	0.422	0.00073	0.00057	1.80
	0.367	0.00064	0.00066	$\left\{\begin{matrix}3.00\\8.00\end{matrix}\right\}$

Table V (contd.)

Salt	(1)	(2)	(3)	Time t (hrs)
$Cu(CH_3COO)_2H_2O$	0.773	0.00255	0.00005	0.10
	0.764	0.00252	0.00008	0.20
	0.752	0.00249	0.00011	0.30
	0.737	0.00244	0.00016	0.50
	0.720	0.00238	0.00022	0.80
	0.710	0.00235	0.00025	1.00
	0.697	0.00231	0.00029	1.40
	0.690	0.00228	0.00032	2.00
	0.295	0.00093	0.00167	18.00 60.00

Legend for Table V.

Concentration (a) of reacting species after mixing in mole l^{-1}.

$[Cu(II)salt] = [Ni(salen)] = (a)$

For: $Cu(ClO_4)_2.6H_2O$ and $CuCl_2 = 1.30 \times 10^{-3}M$;

$Cu(CH_3COO)_2.H_2O = 2.60 \times 10^{-3}M$.

(1) Optical density of extracted Cu(I)2,2'-Diquinolyl.

(2) Copper(II) concentration remaining at time t in mole l^{-1} $= (a - x)$.

(3) Concentration of Copper(II) ions reacted after time t = (x

(i) The optical density of the solutions containing the Cu(I)2,2'-Diquinolyl complex gave a direct measure of the concentrations of free copper(II) ions, after time t. Standard copper(II) solutions were prepared for each substitution experiment and were subjected to the same extraction procedures as the samples taken from the reaction mixtures. (see EXPERIMENTAL). Using graphs of copper concentration (mole l^{-1}) versus optical density, at a fixed wave length, the concentrations of free copper(II) ions in the reaction mixtures could be obtained.

(ii) The rate curves obtained from plots of x versus t are shown in Figs.III, a,b, and c, for these experiments.

Table VI

Initial Rates of Replacement of nickel(II) ions from nickel(II) (salen) by copper(II), in methyl cellosolve.

T = 70.0 ± 0.1°C.

Salt	Concns.(a) Of reactants in mole l^{-1}	Equilibrium position	Rate R.10^7(sec^{-1}mole l
$CuClO_4.6H_2O$	1.30×10^{-3}M	> 97%	3.8 ± 0.1
$CuCl_2$	1.30×10^{-3}M	50%	1.8 ± 0.05
$Cu(CH_3COO)H_2O$	2.60×10^{-3}M	64%	1.3 ± 0.05

THE REASON FOR THE DIFFERENCES IN THE INITIAL RATES BETWEEN THE REACTIONS INVOLVING DIFFERENT COPPER SALTS, MAY BE DUE TO THE VARYING ABILITIES OF THE ANIONS, IN THESE SALTS, TO

The reaction between Copper(II) salts and nickel(II)(salen), in methyl cellosolve, at 70°C

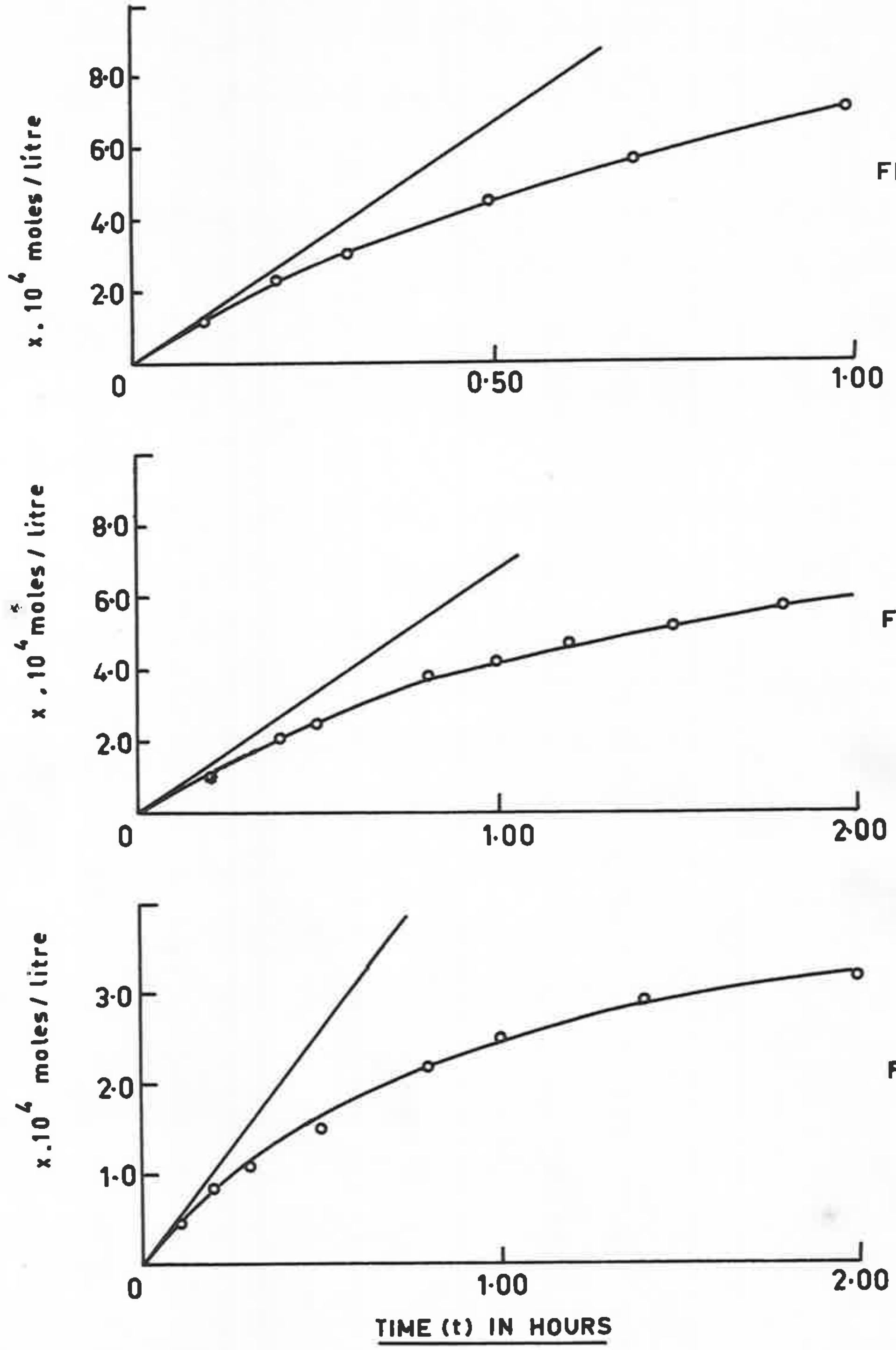

FIG IIIa

FIG III b

FIG III c

FIG III (a) PERCHLORATE (b) CHLORIDE (c) ACETATE

COMPLEX WITH FREE COPPER(II) IONS OR NICKEL(II)(SALEN), THUS PRODUCING SPECIES, OTHER THAN SOLVATED COPPER(II) IONS AND TETRACOORDINATED NICKEL(II) CHELATE MOLECULES, WHICH CAN TAKE PART IN THE REPLACEMENT REACTIONS, AT DIFFERENT RATES.

It is relevant to review the evidence for interaction of anions or solvent molecules, with square planar nickel(II) derivatives, and copper(II) ions.

(i) The behaviour of nickel(II) complexes, in solution.

As discussed on p.48, spectral and magnetic evidence suggests the existence of a diamagnetic structure for nickel(II)(salen), in pyridine.(87)(88) Further, Hall and Willeford found no spectral evidence to support possible solvent interaction of the chelate with methyl cellosolve.(41)

Meller and his coworkers,(108)(109) upon the examination of a number of tetracoordinated nickel(II) complexes,[a] found a correlation between the magnetic moments of some of these compounds, and their absorption spectra, in solution. They found that diamagnetic compounds had an absorption spectrum dissimilar to that of the free chelating base, with a strong absorption band occurring at about 4000 Å. However, these complexes paramagnetic in the solid

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[a] tetracoordinated in the solid state.

state, showed an absorption spectrum similar to that of the free base.

The spectrum of nickel(II)(salen) in solution, is characteristic of a diamagnetic chelate, on this basis.(87) Further work enabled Willis and Mellor(88) to explain several important exceptions to the correlation previously drawn. They postulated for various nickel(II) complexes that equilibria existed between planar and octahedral forms of the complexes, in pyridine, and between planar and tetrahedral forms of the complexes in chloroform eg. bis(salicylaldoximato)nickel(II).

Clark and Odell(87) upon examination of the visible absorption spectra of six nickel(II) chelates, in solution, found the existence of a temperature dependent equilibria between diamagnetic and paramagnetic forms of N,N'-1,2,-phenylenebis(salicylideneiminato)nickel(II)[a] and bis(salicylaldiminato)nickel(II) in pyridine and bis(N-methylsalicylideneiminato)nickel(II) in alcohol and dioxan. They proposed the formations of paramagnetic disolvate adducts for these compounds to explain their spectral and magnetic characteristics, but declined to comment on the configuration of bis(N-methylsalicylideneiminato)nickel(II) in chloroform and methylbenzene, where although solution spectral evidence was characteristic of a diamagnetic structure, magnetic measurements

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[a] nickel(II) (salophen).

indicated the existence of a temperature <u>in</u>dependent diamagnetic-paramagnetic equilibria.

Clark and Odell concluded that no change in the magnetic moment or absorption spectrum of nickel(II)(salen) in either methanol or pyridine occurred, although a small bathochromic displacement in the position of 4000 Å band was found in pyridine, compared with methanol. However, the authors chose to ignore this and proposed a $3d4s4p^2$ square planar configuration for the complex, in both of these solvents.

Basolo and Matoush(89) concluded from studies on the magnetic moment of diamagnetic bis-(formylcamphor)-ethylenediimine nickel(II),[a] in a number of methylbenzenes, that the paramagnetism exhibited in solution was not due to the formation of tetrahedral nickel(II) compounds.

Sacconi, Paoletti and Del Re,(110) upon the examination of the magnetic, spectrophotometric and electron moment properties of some (N-alkylsalicylideneiminato)nickel(II) chelates in various "non-coordinating" solvents eg. benzene, and upon examination of the dipole moments of these chelates in the molten state; proposed the existence of trans, planar "outer-orbital" ($4s4p^24d$)(111)(112) structures to account for the paramagnetism observed in solution, or upon melting.

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[a] diamagnetic in the solid state.

Clark and O'Brien(113) upon a spectral examination of (N-methylsalicylideneiminato)nickel(II), in a number of solvents, proposed the formation of,

(a) a tetragonal dipyridine adduct,

(b) a temperature dependent equilibria between a diamagnetic planar and a paramagnetic, tetragonal configuration, in alcohol,

(c) a temperature independent equilibria between paramagnetic tetrahedral and square planar configurations in benzene and chloroform.

Maki(114) and Ballhausen and Liehr(115) have recently discussed the spectra and magnetic properties of nickel(II) complexes, using both theoretical considerations based on Ligand Field calculations and experimental spectra. These workers proposed, independently, that it was possible *to assign square planar configurations to paramagnetic Nickel(II) compounds*, and further, that no tetrahedral model was consistent with both the spectral and magnetic properties of nickel(II) complexes.

Ballhausen and Liehr(115) calculated that paramagnetic nickel(II) complexes should show no crystal-field bands in the visible and infra-red regions.

The spectra of paramagnetic nickel(II) chelate compounds, obtained by Mellor(108)(109) did not show such bands in the visible region. However, nickel(II)(salen) has a maximum band in the region of 4000 Å, of considerable intensity.(87)

In fact, Maki(114) has calculated the theoretical spectrum of nickel(II)(salen) assuming no solvent interaction, and found that the theoretical calculation was in good agreement with the spectrum found by experiment.

The effects of a variety of solvents upon the visible and ultraviolet absorption spectra of $(PtCl_4)^{-2}$ and $(PtBr_4)^{-2}$ led Harris, Livingstone and Reece(116) to propose the following series of decreasing coordinating abilities of the solvents, with the complexes, viz., $H_2O > CH_3CN > CH_3OH > (CH_3)_2CO > CH_3NO_2 > (CH_3CO)_2O > C_6H_5NH_2$.
In addition, shifts in the wavelength of the 4000 Å band of K_2PtCl_4 in various solvents, led Pearson, Gray and Basolo(74) to propose varying degrees of solvent interaction for this complex, depending upon the magnitude of the wavelength shift.

It has been proposed that nickel(II)(salen), in solution, remains essentially a square planar molecule.(87) However, in view of the recent suggestion by Waters and Hall,(90) that the complex becomes solvated in pyridine, but maintains its diamagnetic electronic configuration, the absorption spectrum of the complex, in solvents of varying coordinating abilities was measured, in anattempt to disclose the true configurations, in such media.
These results are given in Table VII p.69.

Table VII

The effects of different solvents upon the position and intensity of the 4000 Å band of nickel(II)(salen).

Concn. of $[Ni(II)(salen)] = 1.04 \times 10^{-4} M$ Temperature = 20°C

Solvent	Position of max.band in Å	Optical density	Position o max.band in Å (87)
Pyridine	4170	0.720	4140
Acetonitrile	4115	0.665	not examined
Dioxan	4105	0.639	"
Methyl cellosolve	4100	0.668	"
Ethyl alcohol	4100	0.637	"
Methyl alcohol	not examined	-	4020

Clark and O'Brien(113) characterized a similar band around 4000 Å, found in the spectrum of bis(N-methylsalicylideneiminate)nickel(II) in various solvents, as being due to electronic transitions within the conjugated system containing the nickel-ligand bonds.

Therefore, if solvent or anion interaction with nickel(II)(salen) occurs, through coordination with the nickel(II) ion, it may be expected that the 4000 Å band should show some change in the position and/or intensity of absorption. Conversely, if no change in the position and/or intensity of the maximum band is observed, it may be expected that solvent and anion interaction with the complex would be non-existent or so very weak as to maintain the crystal-field of a diamagnetic, tetracoordinated complex, in solution.

The spectrum of nickel(II)(salen) in pyridine, shows a small bathochromic shift in the position of the 4000 Å band, compared to the wavelength in other solvents. (Table VII)

Clark and Odell,(87) obtained a similar bathochromic displacement. (Table VII).

However, the small shift in wavelength and intensity of absorption of the maximum band of nickel(II)(salen) in pyridine; compared with the complete change in the spectrum of nickel(II)(salophen) in pyridine, compared to other solvents (Table VIII p. 71 .), affords evidence for the existence of an essentially diamagnetic, tetracoordinated structure, for the former compound, in all of the solvents examined.

Nickel(II)(salophen) in pyridine, is known to be paramagnetic(89) and has therefore been considered to have an octahedral configuration due to the attachment of two pyridine molecules.

The difference between the spectrum of this nickel(II) chelate in pyridine and other solvents, is most marked.

(Table VIII p.71).

Table VIII

The effects of different solvents upon the spectrum of nickel(II)(salophen).

Concn. of $\left[\mathrm{Ni(II)(salophen)}\right] = 4.00 \times 10^{-5}$M   Temperature = 20°C

Solvent	Positions of max.bands (Å)		Positions of max.bands in Å (87)
Pyridine	3500,3850,4150,4475.	(4)	3840,4450 (only two reported.)
Acetonitrile	3790,4825	(2)	not examined
Dioxan	3820,4900	(2)	not examined
Methyl cellosolve	3785,4775	(2)	not examined
Methyl alcohol	not examined	(-)	3720,4700

The difference between the spectrum of nickel(II)(salophen) in pyridine, andother solvents, does not necessarily mean that a change in configuration for this complex does not occur upon dissolving it in other media. However, it may be taken as evidence for less solvent-complex interaction in these other weaker coordinating solvents.

Therefore, although the spectral evidence supports the existence of a diamagnetic, presumably square planar molecule for nickel(II)(salen) in methyl cellosolve, the small change in wavelength and intensity of maximum absorption found for the complex in pyridine compared to other solvents, may be significant.

Such a change in the wavelength of maximum absorption, which is outside experimental error, may be taken as indicative of at least weak pyridine-complex interaction.
In addition, if crystal-field calculations can be applied with any certainty to the substitution reactions of nickel(II) complexes,(2)(2a) upon the weakening of one metal-ligand bond, prior to dissociation of the complex, solvent-chelate interaction may be expected to increase, and in so doing possibly facilitate in the dissociation of a ligand.
Such a hypothesis cannot be completely ignored, even when considering the replacement reactions in methyl cellosolve, which is expected to be a weaker coordinating agent than pyridine.

The suggestion by Waters and Hall(90) that nickel(II)(salen) is solvated in solution, may be correct. It is difficult to predict the magnitude of the change in the spectrum of diamagnetic, square planar complexes,[a] upon dissolving them in different solvents. If the change in coordination number is accompanied by a change in the magnetic moment of the complex, it may be expected that a complete change in the spectrum would occur, as is the case with nickel(II)(salophen). However, nickel(II)(salen) is known

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[a] solid chelate.

to be diamagnetic in pyridine solution.(87-89) Therefore, the small change in the spectrum, found in pyridine, may be evidence for the existence of a tetragonal configuration or weak solvent-complex interaction, in solution.

The spectrum of nickel(II)(salen) in methyl cellosolve, in the presence of excess perchlorate, acetate and chloride ions has been examined.

The results of these spectral investigations are given in Table IX.

Table IX

The effects of added anions upon the position and intensity of the 4000 Å band of nickel(II)(salen), in methyl cellosolve.

Temperature = 20°C

Added salt	concn. of added salt in mole l^{-1}	concn. of [nickel(II) chelate] in mole l^{-1}	posn. of max. band in Å	Optica densit
		1.30×10^{-4}M	4100	0.880
sodium acetate (anhydrous)	1.30×10^{-2}M	1.30×10^{-4}M	4100	0.860
sodium chloride (anhydrous)	1.30×10^{-2}M	1.30×10^{-4}M	4100	0.855
magnesium perchlorate (anhydrous)	1.30×10^{-2}M	1.30×10^{-4}M	4100	0.860

The same wavelength and intensity of maximum absorption, within experimental error, are found for the complex, in the presence of these anions. Such results indicate that anion interaction with the four-coordinated nickel(II) complex, in solution, is non-existent or very weak.

Therefore, the results of the spectral investigations of nickel(II)(salen), in various solvents and in the presence of excess anions, indicate that this complex shows a characteristic spectrum indicative of a diamagnetic, square planar or weakly tetragonal structure, in solution.

(ii) The types of copper(II) species in solution.

In order to propose a mechanism(s) of reaction it is necessary to obtain information about the nature of the reactant species, in solution.

In the present work the spectra of copper(II) salts in various organic solvents have been compared with the spectrum of the aquated copper(II) ions, in order to obtain information about the types of copper(II) species existing in the various solvents.

However, it is necessary that the interpretations of the spectral changes found upon examination of the absorption spectra of various transition metal(II) salts, in organic solvents, be treated with care.

(1) Hydrated copper(II) salts have been used in many of the replacement reactions discussed in this thesis, and further it cannot be assumed that normal purification techniques will remove all the water from the solvents used. Therefore, it is probable that in many cases the concentration of water in the solvents employed may exceed the concentrations

of the reactants used in the experiments. These latter concentrations are of the order of 1.0 x 10^{-3}M. Jørgensen and Bjerrum(117)(118) have attributed changes in the spectra of neodymium chloride and cobalt(II) nitrate in aqueous-alcohol mixtures, to the replacement of alcohol solvate molecules by water molecules.
In fact, the consecutive formation constants of aquo-neodymium ions in alcoholic solutions have been calculated, assuming such a hypothesis. Therefore, in the systems examined by the present author, it may be expected that competition between water and solvent molecules for reaction with the metal ions, would occur.

(2) For hydrated salts and anhydrous salts, auto-complex formation may also occur, giving rise to complex anions containing the metal, in solution.
In this respect, Katzin and coworkers,(119)(120) have attributed the changes in the absorption spectra of some metal salts in various non-aqueous solvents and water-alcohol mixtures as being due to cation-anion interactions ie. complex-ion formation, and not necessarily solvent replacements. Jørgensen and Bjerrum(121) have replied by proposing that anion effects may be superimposed upon solvent replacement effects.

Because of a lack of data relating to the dissociation and association constants of transition metal(II) salts, in organic solvents, the comparison of rate data with the types of copper(II) species in solution, has proven difficult.

However, the following sections attempt to correlate the rates of replacement with the types of copper(II) species, in solution, using data derived from spectral and conductivity investigations.

(a) Copper(II) perchlorate (hexahydrate) in methyl cellosolve.

The replacement of nickel(II) from nickel(II)(salen) using copper(II) perchlorate (hexahydrate) was found to proceed almost to completion (97% at equilibrium) at 70°C (Table V p.61.)

This indicates a large negative standard free energy change in passing from the less stable nickel(II)(salen) to the more stable copper(II)(salen), and supports the existence of copper(II) species, in solution, capable of undergoing almost quantitative replacement with the nickel complex.

In addition, the reaction mixtures at equilibrium are coloured violet; the colour also given by solid copper(II)(salen) dissovled in methyl cellosolve.

Waters and Hall(90) consider that violet solutions are given by copper(II)(salen) and similar compounds, in non-coordinating solvents, and that the colour is indicative of four coordination in solution of such compounds.

1. Kinetics of the reactions between copper(II) perchlorate (hexahydrate) and nickel(II)(salen) in methyl cellosolve.

In an attempt to discover the possible reaction mechanism(s) for this replacement reaction, the reaction order with respect to each reactant was measured.

The rate expression for this reaction may be written thus:

$$R = k\left[Cu^{+2}\right]^{x} . \left[Ni(II)(salen)\right]^{y}$$

where x represents the dependence of the rate on the copper(II) concentration, and y the dependence of the rate on the nickel(II)(salen) concentration.

Writing the same expression in logarithmic form,

$$\log R = \log k + x \log\left[Cu^{+2}\right] + y \log\left[Ni(II)(salen)\right]$$

Since k is a constant at constant temperature, x can be evaluated from the slope of a plot of log $\left[Cu^{+2}\right]$ versus log R in a series of experiments in which the concentration of the nickel(II) complex is kept constant. y can then be evaluated in a corresponding manner by plotting log $\left[Ni(II)(salen)\right]$ versus log R and measuring the slope of the line. Tables X and XI (p.79) give the results of such experiments, while Figs. IV and V show the graphical dependence of the rates with the concentration of copper(II) perchlorate and nickel(II)(salen), respectively.

Upon examination of Fig.IV, it may be seen that the line joining the points 4,5 and 6 (see Table X) has a slope of approximately 1, indicating first-order dependence

of the reaction on the concentration of copper(II) perchlorate (hexahydrate), below 1.30×10^{-3}M.
However, points 1,2 and 3 (see Table X) lie in a straight line of slope = 0, indicating that at these higher concentrations of copper(II) perchlorate, the reaction rate is independent of the concentration of the copper(II) species, in solution.

Fig.V shows the result of the dependence of the rate of replacement upon the concentration of Ni(II)(salen) . A line of slope = 1 appears on each figure for comparison with the slope of the experimental curves. The reaction appears first-order with respect to the concentration of the nickel(II) complex, over the concentration range examined.
[7.80×10^{-3} - 6.50×10^{-4}M Ni(II)(salen)].
The change in the slope in Fig.IV would seem to be directly related to the changing nature of the copper(II) species in solution, with concentration.

Table X

Dependence of the Initial Rate of Replacement on the concentration of Copper(II) perchlorate (hexahydrate).

T = 71.1 ± 0.1°C   Solvent: methyl cellosolve

Concn. [Cu(II) salt] in mole l^{-1}	log $[Cu^{+2}]$	Concn. [Ni(II)(salen)] in mole l^{-1}	Rate $R.10^3$ hrs^{-1} mole l^{-1}	log R
1. 5.20×10^{-3}M	-2.284	1.30×10^{-3}M	2.61	- 2.583
2. 3.90×10^{-3}M	-2.409	1.30×10^{-3}M	2.72	- 2.565
3. 2.60×10^{-3}M	-2.584	1.30×10^{-3}M	2.70	- 2.568
4. 1.30×10^{-3}M	-2.886	1.30×10^{-3}M	2.12	- 2.674
5. 0.98×10^{-3}M	-3.011	1.30×10^{-3}M	1.56	- 2.808
6. 0.65×10^{-3}M	-3.187	1.30×10^{-3}M	1.06	- 2.975

Table XI

Dependence of the Initial Rate of Replacement on the concentration of nickel(II)(salen).

T = 71.1 ± 0.1°C   Solvent: methyl cellosolve.

Concn. [Ni(II)(salen)] in moles l^{-1}	log[Ni(II)(salen)]	Concn. [Cu(II) salt] in moles l^{-1}	Rate $R.10^3$ hrs^{-1} $mole\ l^{-1}$	log R
7.80×10^{-3}M	−2.108	1.30×10^{-3}M	9.80	−2.009
5.20×10^{-3}M	−2.284	1.30×10^{-3}M	7.10	−2.149
2.60×10^{-3}M	−2.584	1.30×10^{-3}M	4.61	−2.336
1.30×10^{-3}M	−2.886	1.30×10^{-3}M	2.12	−2.674
0.65×10^{-3}M	−3.187	1.30×10^{-3}M	0.80	−3.097

Kinetics of the replacement in methyl cellosolve at 71.1°C

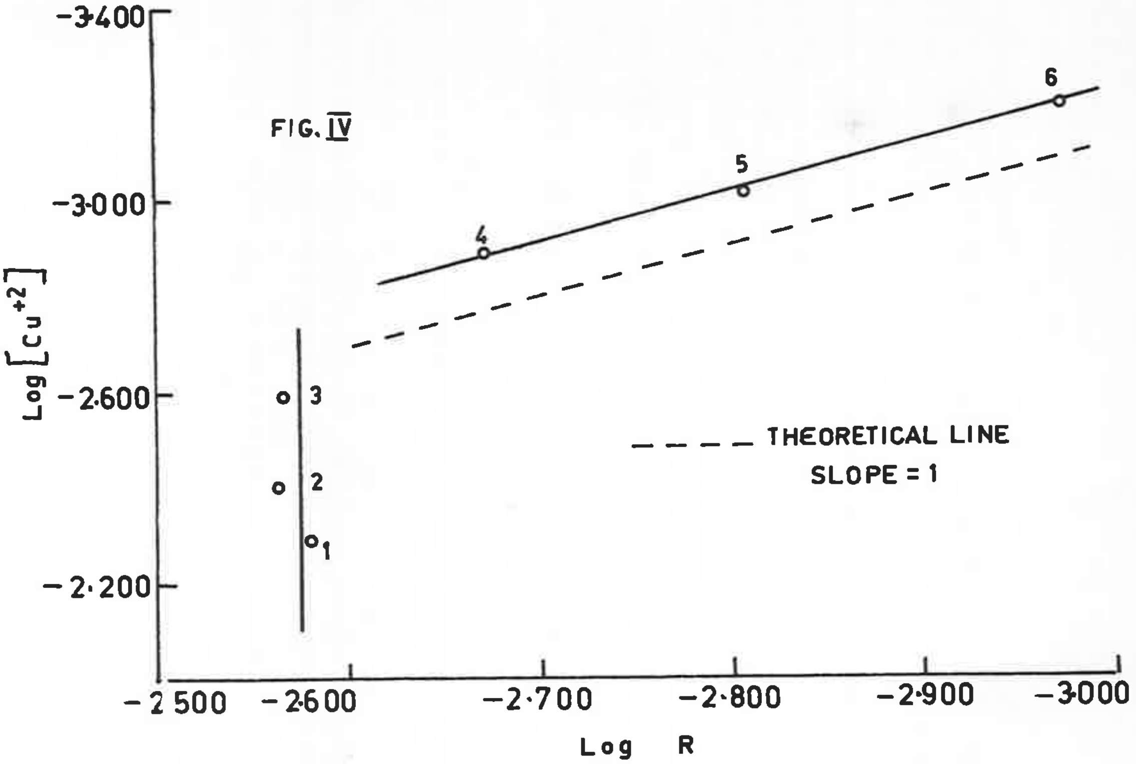

FIG. IV

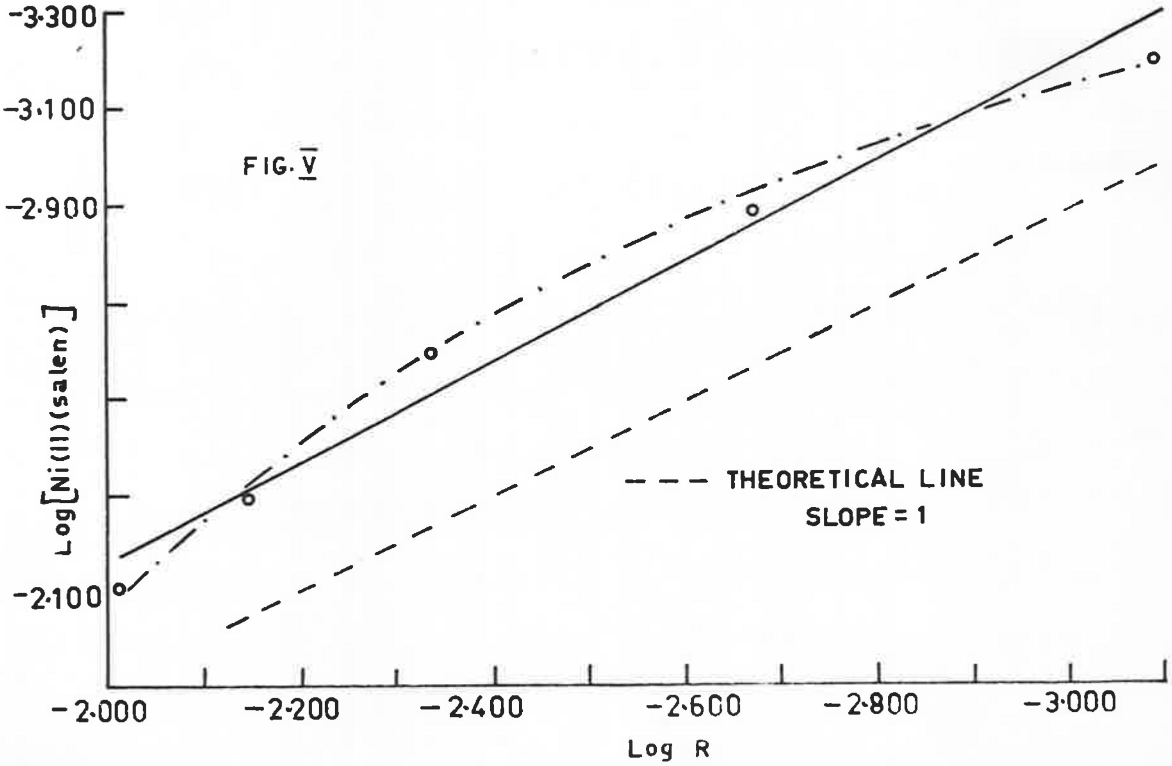

FIG. V

2. The type of copper(II) species formed upon dissolving copper(II) perchlorate (hexahydrate), in methyl cellosolve.

Transition metal perchlorates are known to dissociate almost completely in water,(98c) however in order to determine the type(s) of copper(II) species obtained on dissolving copper(II) perchlorate (hexahydrate) in methyl cellosolve, the ultraviolet absorption spectrum of this solution was examined.

Copper(II) perchlorate($6H_2O$) in water absorbs strongly at wavelengths below 2100 Å. The band is thought to be due to the non-associated copper(II) ion.(98c)

However, the ultraviolet absorption spectra of copper(II) perchlorate (hexahydrate) in methyl cellosolve, shows a broad maximum band in the region 2200 - 2400 Å, the wavelength and intensity of maximum absorption depending strongly upon the temperature of the solution. The results of these spectral investigations are given in Table XII, p.82.

No information is available on the dissociation constants of transition metal(II) perchlorates in organic solvents, however $AgClO_4$ and $[(n\text{-}C_4H_9)_4]N.ClO_4$ have dissociation constants of 1.91×10^{-3}, (pyridine $\varepsilon_{25°C} = 12.0$) and 9.58×10^{-3}(acetone $\varepsilon_{25°C} = 20.4$), respectively.(98b). These figures indicate a considerable degree of association, possibly ion-pair formation, for these salts in pyridine and acetone.

Table XII

The wavelength and intensity of maximum absorption of copper(II) perchlorate (hexahydrate) in methyl cellosolve.

(1)	(2)	(3)	Temperature
1.30×10^{-3}M	2320 - 70	1.990	Room temp.
1.04×10^{-3}M	2330 - 80	1.805	
0.98×10^{-3}M	2330 - 80	1.760	
0.65×10^{-3}M	2330 - 70	1.374	
0.33×10^{-3}M	2330 - 80	0.760	
0.26×10^{-3}M	2330 - 80	0.639	
1.30×10^{-3}M	2250 - 90	1.486	T = 67.0 ± 0.5°C
1.04×10^{-3}M	2250 - 90	1.260	
0.98×10^{-3}M	2250 - 90	1.190	
0.65×10^{-3}M	2250 - 90	0.832	
0.33×10^{-3}M	2250 - 90	0.464	

1.30×10^{-3}M Copper(II) perchlorate (hexahydrate) in water shows no maximum absorption band in the region 2100 - 2400 Å.

The optical density of the solution at 2100 Å = 1.316.

Legend for Table XII

(1) Concentration of $[Cu^{+2}]$ in mole l^{-1}.

(2) Wavelength Å of maximum absorption.

(3) Optical density.

If, as suggested, the absorption band corresponding to the non-associated copper(II) ion, occurs at wavelengths below 2100 Å (98c), the broad maximum observed in the spectrum of copper(II) perchlorate in methyl cellosolve in the region 2200 - 2400 Å, may be taken as indicative of the presence of a different species to that found in water.

Ion-pair association ie. $(CuClO_4)^{+1}$, may be expected to exist even at 70°C, in this solvent of relatively low dielectric constant, ($\varepsilon_{25^\circ C} = 15.96$)(122), although such association may be expected to be less than at room temperature.(98c)

Further, the failure to obey Beer's Law, over the concentration range examined, tends to support the existence of a changing species with dilution, indicative of the presence of ion-pair dissociation, at lower concentrations.

However, in this respect Jørgensen(118) attributed departures from Beer's Law in the spectra of some copper(II) salts in the infra-red region, to the high absorption of the solvent at the wavelengths used.

Methyl cellosolve absorbs strongly in the ultra violet region, therefore the failure to obey Beer's Law may be explained on this basis. However, the shift in the wavelengths of the maximum absorption band, at high temperatures, towards the far ultraviolet (corresponding to a shift towards the spectrum of $Cu(ClO_4)_2.6H_2O$ in water), and a corresponding decrease in the intensity of absorption at the maximum, may be taken as evidence for partial dissociation, at 70°C, of the associated species present in solution.

Further, as the concentrations of copper(II) perchlorate (hexahydrate) increase, it may be expected that ion-pair association will also increase. In fact, above 1.30 x 10^{-3}M, the reaction appears zero-order with respect to copper(II) perchlorate, and the reaction is overall first-order. (Fig.IV)

This may be taken as evidence for the existence of kinetically unfavourable copper(II) species,[a] above 1.30 x 10^{-3}M copper(II) perchlorate (hexahydrate), such that the rate-determining step of the reaction may be one involving dissociation of the complex.

In view of the low concentration used in the replacement experiment with copper(II) perchlorate, (1.30 x 10^{-3}M each reactant. Table V Fig.IIIa), and the temperature of reaction, it may be assumed that non-associated copper(II) ions are present to some extent, in solution.

This supposes the existence of free perchlorate ions in the reaction mixtures. However, the presence of such ions were found to have no effect upon the spectrum of nickel(II)(salen) in methyl cellosolve. (Table IX p.73). Therefore, it must be assumed that anion interaction with the partially dissociated nickel(II) complex, if such exists in solution, will

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[a] kinetically unfavourable = copper(II) species, in solution, which react at slower rates than the unassociated cation.

be very small and the rate of replacement found in this reaction, using copper(II) perchlorate (hexahydrate), should be little effected by the interaction of perchlorate ions with the nickel(II) complex.

A series of experiments designed to correlate the rate of replacement with the types of copper(II) species, in solution, were completed. The results of these are discussed below.

3. The effects of added salts and water upon the initial rate of replacement.

The rates of reactions between ions and neutral molecules can for most purposes, at very low concentrations, be expected to be independent of ionic strength.(53a) However, it has been shown that sodium chloride and sodium perchlorate have opposite effects upon the activity coefficient of γ-butyrolactone, and that these effects may be correlated with the changes observed in the rates of hydrolysis of the lactone in the presence of these electrolytes.(123) But in cases where evidence for complex formation between an ionic reactant and added electrolyte has been found, the quantitative agreement between the rate and ionic strength may disappear.(124)

Such a lack of correlation between the rates and ionic strengths may be expected upon the addition of perchlorate salts to the reaction system under consideration in this thesis. Perchlorate ion addition may be expected to increase ion-pair formation between copper(II) ions and perchlorate ions, whereby the rate of replacement may be expected to decrease, if the free solvated copper(II) ion can be assumed the most kinetically favourable species for reaction. (see later).

The results of Table XIII(p.88) indicate that the rates of replacement of nickel(II) ions decrease upon the addition of nickel(II) perchlorate and sodium perchlorate. The concentrations of the added salts were chosen so as to keep an approximate constant ionic strength for the two experiments. (see p.88.).
However, the addition of a thirty-fold excess of sodium perchlorate is found to decrease the initial rate of replacement to a greater extent than that of a ten-fold excess of nickel(II) perchlorate (hexahydrate).
This tends to support the assumption made earlier that increased ion-association, involving the copper(II) species, through an increase in the concentration of perchlorate ions, produces a species which is less able to undergo the replacement reaction than the simple solvated copper(II) ions.

The effect of added nickel(II) perchlorate may be expected to produce a similar effect in "binding" the copper(II) ions, although ion-association may be expected to be less because of the lower concentration of this salt added.
The calculated rates support the assumptions although the presence of the nickel(II) ion may be expected to increase

Table XIII

The effects of added salts and water upon the initial rates of replacement of nickel(II) in nickel(II)(salen) by copper(II) in methyl cellosolve

T = 71.1 ± 0.1°C

Added component	Concn. of added component in mole l^{-1}	Concn. of each reactant in mole l^{-1} $[Cu^{+2}]=[Ni(II)(salen)]$	Ionic strength of soln. [a]	Rate $R.10^7$ ($sec^{-1} mole\ l^{-1}$)
(a) -	-	$1.30 \times 10^{-3}M$	0.004	5.8 ± 0.2
(b) H_2O	0.093M	$1.30 \times 10^{-3}M$	0.004	4.4 ± 0.2
(c) $Ni(ClO_4)_2.6H_2O$	0.013M	$1.30 \times 10^{-3}M$	0.043	4.0 ± 0.2
(d) $NaClO_4$	0.039M	$1.30 \times 10^{-3}M$	0.043	2.7 ± 0.1

---

[a] The ionic strengths of the solutions have been calculated on the basis of stoichiometric concentrations, $\mu = \frac{1}{2}\sum C_i Z_i^2$ (29a) ie. assuming complete dissociation of all species present in solution. Such an assumption is by no means valid. However, although the absolute values given are incorrect, such a method of calculation may serve as a worthwhile qualitative comparison of ionic strengths, providing the dissociation constants of the salts used are of the same order.

the rate of the back reaction. However, comparisons of the initial rates of replacement, in both cases, limit the effect considerably.

The effect of added water (Table XIII (b)) is to decrease the rate of substitution. Two suggestions may be made to explain such a decrease in the rate of replacement.

First, an increase in the concentration of water will produce a corresponding increase in the number of free copper(II) ions to which water is coordinated, since it may be expected that water is a stronger coordinating agent than methyl cellosolve.
The aquated ions may react much less readily with nickel(II) (salen), since solvent molecules must be lost from the copper(II) ions during the replacement reaction and the more firmly held are such molecules to the metal ion, the slower the rate of the reaction should be.

An alternative explanation may be as follows. Additional water may increase ion-association between copper(II) and perchlorate ions, in a manner similar to that postulated by Sykes(125) for the interaction between ferric ions and perchlorate ions in aqueous solution. Here the water molecules facilitate the attachment of perchlorate ions to the ferric ion. If a similar reaction, between copper(II) ions, perchlorate ions and water, takes place in the system copper(II) perchlorate-nickel(II)(salen), additional water will increase copper(II) ion-association and therefore slow the rate of replacement, if the free solvated copper(II) ion can be considered the most kinetically favourable species, for reaction.

Thus, at the concentration used in the replacement reaction between copper(II) perchlorate (hexahydrate) and nickel(II)(salen), viz. 1.30 x 10^{-3}M (Table V), it seems evident that both free solvated copper(II) ions and ion-pairs ie. $(CuClO_4)^{+1}$, exist in solution.

4. Determination of the Energy and Entropy of Activation for the reaction between copper(II) perchlorate (hexahydrate) and nickel(II)(salen), in methyl cellosolve.

The energy of activation for the replacement experiment was calculated as $E^{\neq} = 24.6 \pm 1.0$ Kcals/mole^{-1}. (see Table XIV and Fig. VIII). The rate constants k, in hrs^{-1}mole 1^{-1}, were evaluated at five temperatures by assuming the reaction to be first-order with respect to both the copper(II) salt and nickel(II)(salen), at 1.30 x 10^{-3}M each reactant. (see Figs IV and V).
The plot of $\frac{1}{a-x}$ versus time (in hours), for each kinetic experiment gave the expected overall second-order reaction, straight line relationship. (Figs. VI and VII).

The entropy of activation $\Delta S^{\neq}$, for the reaction, was calculated from the equations of the theory of absolute reaction rates(29c) viz.,

Table XIV

The replacement of nickel(II) ions by copper(II) ions in N,N'-ethylenebis(salicylideneiminate)nickel(II), using copper(II) perchlorate ($6H_2O$)

Solvent: methyl cellosolve

Concn.(a) of reacting species in mole l^{-1} = 1.30 x 10^{-3}M

$[\text{Cu(II)salt}] = [\text{Ni(II)(salen)}]$.

Temp.	(1)	(2)	(3)	(4)	$\frac{1}{a-x}$
83.1 ± 0.1°C	0.05	0.577	0.00104	0.00026	962
	0.15	0.398	0.00072	0.00058	1390
	0.25	0.301	0.00054	0.00076	1850
	0.40	0.223	0.00040	0.00090	2510
	0.50	0.193	0.00035	0.00095	2870
	24.00	0.040	0.00007	0.00123	-
76.9 ± 0.1°C	0.10	0.456	0.00102	0.00028	980
	0.20	0.394	0.00086	0.00044	1160
	0.40	0.272	0.00059	0.00071	1700
	0.50	0.236	0.00051	0.00079	1960
	0.70	0.197	0.00042	0.00088	2380
	0.90	0.152	0.00032	0.00095	3125
	24.00	0.038	0.00007	0.00123	-

Table XIV (contd.)

Temp.	(1)	(2)	(3)	(4)	$\frac{1}{a-x}$
71.1 ± 0.1°C	0.10	0.516	0.00110	0.00020	909
	0.30	0.408	0.00087	0.00043	1150
	0.50	0.332	0.00071	0.00059	1410
	0.70	0.271	0.00058	0.00072	1720
	0.90	0.235	0.00051	0.00079	1960
	24.00	0.037	0.00009	0.00121	-
65.1 ± 0.1°C	0.10	0.560	0.00123	0.00007	813
	0.30	0.481	0.00106	0.00024	943
	0.50	0.418	0.00092	0.00038	1090
	0.70	0.367	0.00081	0.00049	1240
	1.00	0.314	0.00070	0.00060	1430
	1.50	0.247	0.00055	0.00075	1820
	24.00	0.050	0.00012	0.00118	-
58.1 ± 0.1°C	0.20	0.604	0.00116	0.00014	862
	0.40	0.561	0.00108	0.00022	926
	0.70	0.505	0.00098	0.00032	1020
	1.10	0.454	0.00088	0.00042	1140
	1.60	0.387	0.00075	0.00055	1330
	48.00	0.038	0.00008	0.00122	-

(i) The concentrations of unreacted copper(II) ions were calculated in a similar manner to those given in Table V.

(ii) The plot of $\frac{1}{a-x}$ versus t gave a straight line for each of these reactions, the slope of the line being equal to the rate constant k (hrs^{-1}mole l^{-1})(29b) These plots are shown in Figs. VI and VII.

(iii) The energy of activation for the system has been calculated from the Arrhenius relation viz.,

$$\frac{d\ln k}{dT} = \frac{E}{RT^2} \quad (29b)$$

The plot of log k v $\frac{1}{T^{\circ}K}$ gave a straight line (Fig.VIII), from which the energy of activation, $E^{\neq} = 2.303$ slope (cals/mole^{-1}), was calculated.

Legend for Table XIV

(1) Time (t) in hours.

(2) Optical density of extracted Cu(I) 2,2'-Diquinolyl.

(3) Copper(II) concentration remaining at time t in mole l^{-1} = (a - x).

(4) Concentration of copper(II) ions reacted after time t = (x).

Evaluation of the rate constants for the replacements in methyl cellosolve.

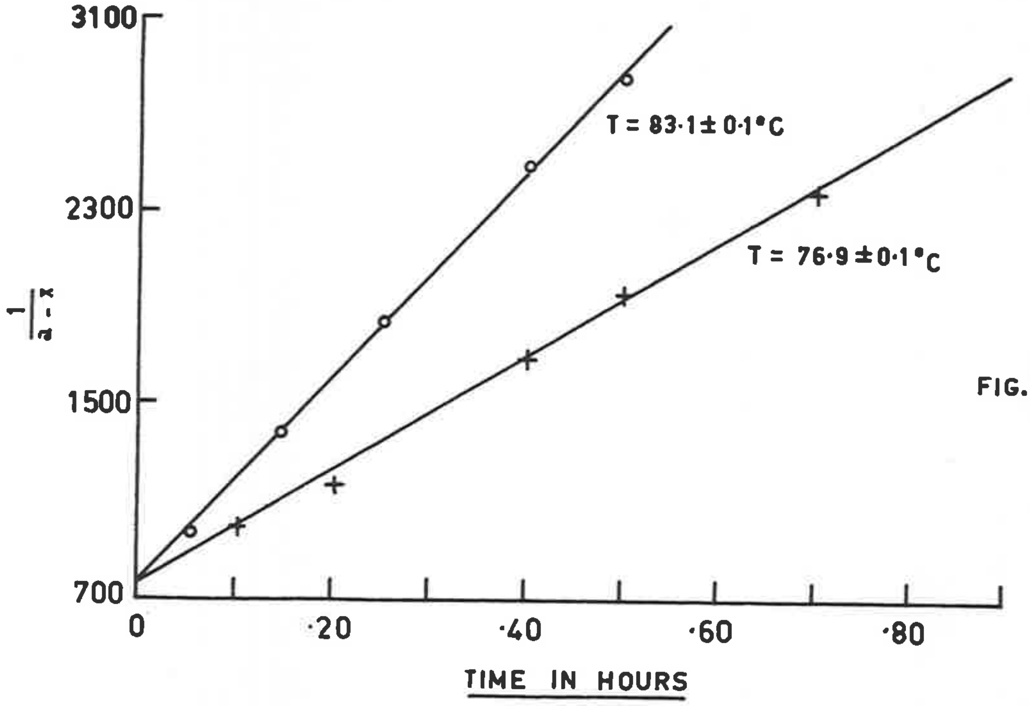

FIG. VI

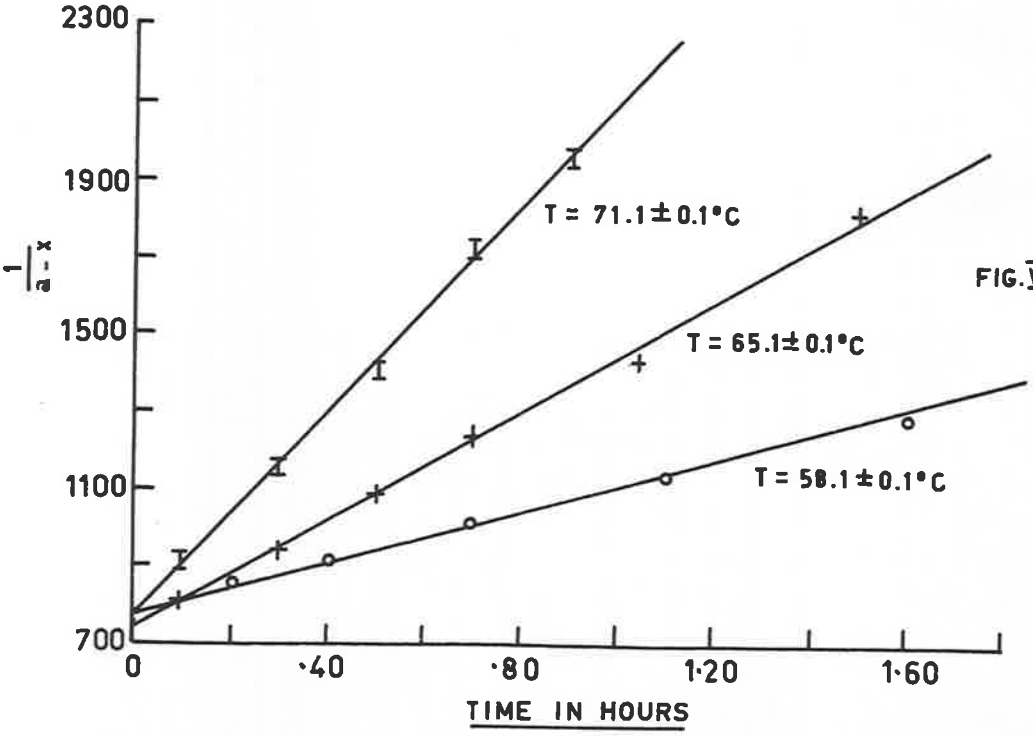

FIG. VII

Activation energy for the replacement, in methyl cellosolve.

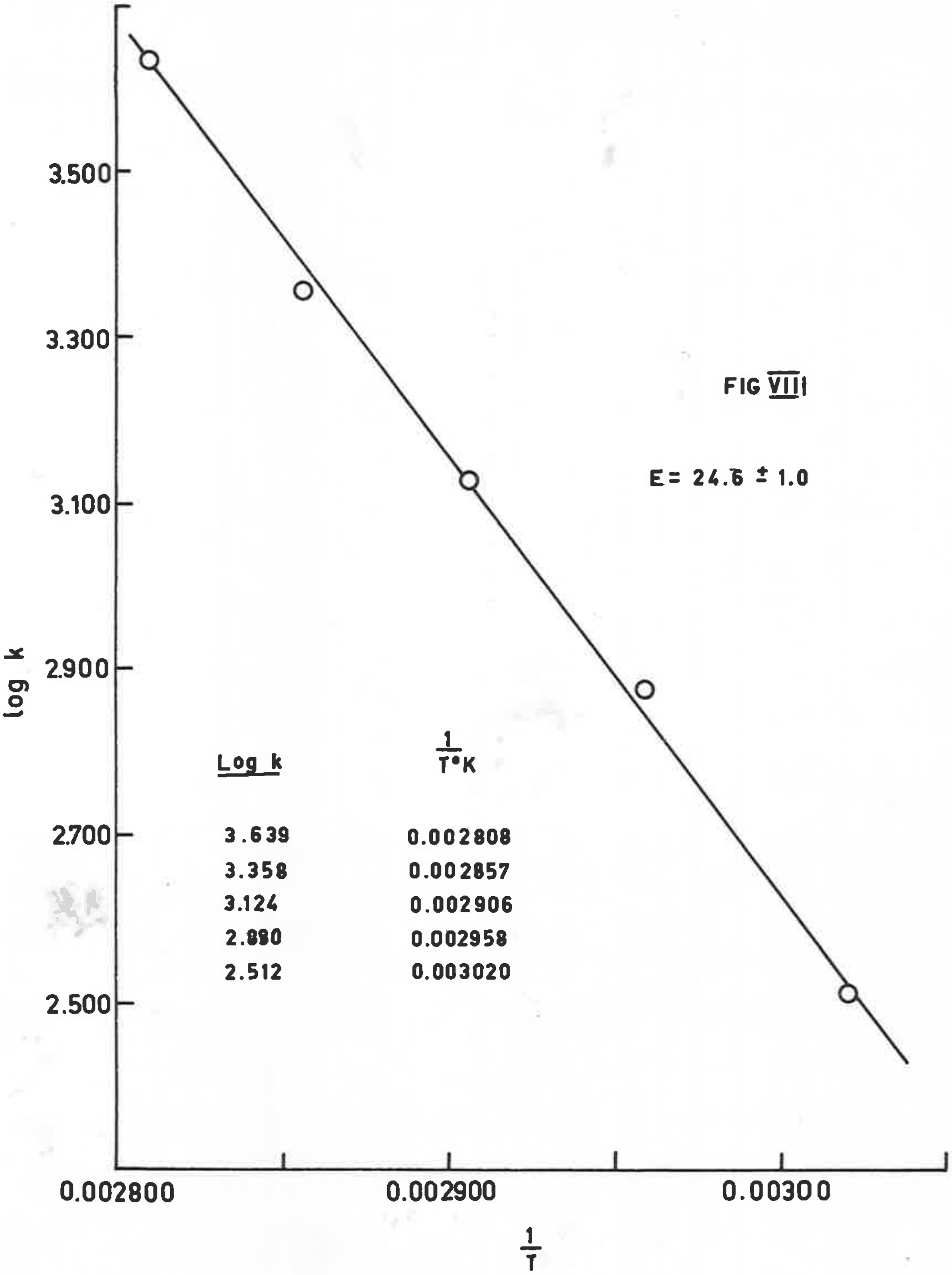

FIG VIII

E = 24.6 ± 1.0

Log k	$\frac{1}{T°K}$
3.639	0.002808
3.358	0.002857
3.124	0.002906
2.880	0.002958
2.512	0.003020

$$\Delta S^{\neq}\,(\text{e.u.}) = \frac{\Delta H^{\neq} + RT \ln \dfrac{k_r h}{kT}}{T}$$

where k_r = rate constant in <u>$\text{sec}^{-1}\,\text{mole}\ l^{-1}$</u>

$\Delta H^{\neq} = E^{\neq} - RT$

The value of $\Delta S^{\neq}$ was found to be 8 ± 2 e.u.
These results will be discussed with the data obtained from the kinetic studies in ethyl alcohol.

(b) <u>Copper(II) acetate (monohydrate) in methyl cellosolve</u>.

The reaction between copper(II) acetate and nickel(II) (salen) in methyl cellosolve at 70°C, was found to exhibit a slower rate of <u>rep</u>lacement than the reaction using copper(II) perchlorate, and also a different equilibrium position. (Table VI)

Copper(II) acetate in the solid state is known to be dimeric.(95)(96) Magnetic susceptibility measurements have indicated the existence of undissociated dimer molecules in ethanol and dioxan solutions.(97)

The ultraviolet absorption spectrum of copper(II) acetate (monohydrate) in ethanol, methyl cellosolve and dioxan has been examined.
One broad maximum absorption band was found in all three solvents, the positions of the maxima being as follows, 2460 Å (dioxan, green solution), 2460Å (ethanol, green solution) and 2430 Å (methyl cellosolve, green solution). The similarities

in the spectra and colour of the solutions, in these solvents of different dielectric constants, may be taken as evidence for the existence of undissociated dimer molecules of copper(II) acetate, in methyl cellosolve, at room temperature.

Some dissociation of the dimeric species may be expected at 70°C, therefore it may be assumed that, in solution, under the conditions of the replacement experiment (see Table V), the following species may exist viz. $[\mathrm{Cu(OAc)_2}]_2$, $[\mathrm{Cu(OAc)_2}]$, $[\mathrm{Cu(OAc)}]^{+1}$ and Cu^{+2}, each bearing a number of solvent molecules.

The slow rate of replacement found, compared to the reaction using copper(II) perchlorate (hexahydrate), may then be explained by the existence of copper(II) species, in solution, less able to take part in the replacement experiment. The existence of an equilibrium position greatly removed from 100% reaction (viz. 64%), may be correlated with competitive reactions involving different copper(II) species, in the following manner.

1. $$\begin{array}{llll} [\mathrm{Cu(OAc)_2}]_2 & & & \\ [\mathrm{Cu(OAc)_2}] & +\ \mathrm{Ni(II)(salen)} + \text{solvent} & \rightleftharpoons & \mathrm{Cu(II)(salen)} \\ [\mathrm{Cu(OAc)}]^{+1} & & & +\ \tfrac{1}{2}\,\mathrm{Ni}^{+2} + \tfrac{1}{2}[\mathrm{Ni(OAc)}\ ]^{-(a-2)} \\ \mathrm{Cu}^{+2} & & & +\ \text{solvent} \end{array}$$

2. $$[\mathrm{Cu(OAc)}_a]^{-(a-2)} + [\mathrm{OAc}]^{-1} \rightleftharpoons [\mathrm{Cu(OAc)}_{a+1}]^{-(a-1)}$$

3. $$[\mathrm{Ni(OAc)}_a]^{-(a-2)} + [\mathrm{OAc}]^{-1} \rightleftharpoons [\mathrm{Ni(OAc)}_{a+1}]^{-(a-1)}$$

where $a = 0, 1, 2$ etc.

The formation constants for the reactions between copper(II) and nickel(II) ions with acetic acid, in aqueous solution, under similar experimental conditions have been calculated.

For copper(II), the values are log K_1 = 1.65, log K_2 = 1.0, log K_3 = 0.36(126) and for nickel(II), log K_1 = 0.67, log K_2 = 0.58.(99)

The complexing ability of acetate ions with copper(II) ions, is seen to be much larger than that with nickel(II) ions. Therefore, if such a comparison can be applied to the system in the replacement reaction, reaction 2 (p.95) can be expected to proceed to a much larger extent than reaction 3, and further, reaction 2 may be expected to compete with the group of reactions 1., hence slowing the rate of the forward reaction, thus allowing the back reaction between nickel(II) and copper(II)(salen) to be more pronounced, at equilibrium.

(c) Copper(II) chloride (anhydrous) in methyl cellosolve.

The reaction between copper(II) chloride and nickel(II)(salen) was found to reach equilibrium (50%) within about 3 hours, at 70°C (see Table V). The slow rate of replacement and the position of equilibrium of this reaction compared to the perchlorate system may be explained on the basis of interaction of free chloride ions with the copper(II) ions, in solution.

1. Interaction of chloride ions with copper(II) ions, in methyl cellosolve.

Several authors have proposed the existence of the complex species $(CuCl)^{+1}$, $CuCl_2$, $(CuCl_3)^{-1}$ and $(CuCl_4)^{-2}$ in aqueous solution,$^{(127-130)}$ while the formation constants for these species in acetone solution have been calculated ($K_1 = 4.10$, $K_2 = 3.08$, $K_3 = 1.57$, $K_4 = 0.12$)$^{(131)}$. The figures indicate that $(CuCl)^{+1}$, $CuCl_2$ and $(CuCl_3)^{-1}$ predominate, in this solvent. Further, autocomplexes of the type $Cu(CuCl_3)_2$ and $Cu(CuCl_4)$ have been proposed in aqueous-alcoholic solutions.$^{(132}$ In addition, magnetic susceptibility studies on the colour changes of copper(II) chloride in aqueous and HCl solutions support complex-ion formation in these systems, and indicate an increase in complex-ion formation with an increase in concentration of copper(II) chloride, chloride ions and solution temperature.$^{(133)}$ Colour changes associated with the breaks in the magnetic susceptibility versus concentration curves of copper(II) chloride in methanol and ethanol support the existence of complex-ion formation, of the type $[CuCl_3]^{-1}$ and $[CuCl_4]^{-2}$ in the solvents.$^{(134)}$

Because of the high temperature used in the chloride replacement, and the relatively low dielectric constant of the solvent, complex-ion formation may be expected to be high.

Aqueous solutions of copper(II) chloride, at high concentrations of chloride, copper(II) chloride and at high temperatures, show yellow-green colours indicating the various complex ions found under these conditions.

Solutions of copper(II) chloride in methyl cellosolve also show yellow-green colours, and such colourations support the existence of complex-ion species in methyl cellosolve, under the conditions of the replacement reaction.

In order to test the effect of added chloride ions upon the rate of replacement, a ten-fold excess of lithium chloride was added to the reaction mixture.

The results are given in Table XV.

Table XV

The effect of added chloride ions upon the rate of replacement of nickel(II) ions from nickel(II)(salen), using copper(II) chloride.

Solvent: methyl cellosolve T = 70.0 ± 0.1°C.

Added salt	Concn. of added salt in mole l^{-1}	Concn. of reactants in mole l^{-1} $[CuCl_2]=[Ni(II)(salen)]$	Rate (t=0) $R.10^7$ (sec^{-1} mole l^{-1})	% Equilibrium
-	-	1.30×10^{-3}	1.8 ± 0.1	50%
LiCl(anhydrous)	1.30×10^{-2}	1.30×10^{-3}	1.5 ± 0.1	39%

It may be seen from Table XV, that although the rates of replacement are roughly of the same order, the equilibrium positions observed, differ considerably.

Added chloride ions would be expected to increase complex-ion formation in the solution of copper(II) chloride in methyl cellosolve, producing species which are less "kinetically favourable" for reaction eg. $(CuCl)^{+1}$ etc., compared with the simple solvated copper(II) ions.

Näsänen(135) has shown that the effect of added chloride ions upon the ultraviolet absorption spectrum of copper(II) perchlorate (hexahydrate) in water, indicates the formation of the complex-ion, $(CuCl)^{+1}$.

In a solvent of lower dielectric constant, such as methyl cellosolve, considerable association may be expected.

Therefore, the slower rate of <u>re</u>placement in the copper(II) chloride reaction, and the observed 50% equilibrium position found for this reaction, compared with that involving copper(II) perchlorate, may be explained as follows.

The reactions occurring in the system may be written thus,

$$1.\quad Cu^{+2}(me.cell)_x + Ni(II)(salen) \rightleftharpoons Cu(II)(salen) + \tfrac{1}{2}Ni^{+2}(me.cell)_x + \tfrac{1}{2}\left[NiCl_4\right]^{-(a-2)}$$

$$2.\quad \left[CuCl_a\right]^{-(a-2)} + Ni(II)(salen) \rightleftharpoons Cu(II)(salen) + \tfrac{1}{2}\left[NiCl_a\right]^{-(a-2)} + \tfrac{1}{2}Ni^{+2}(me.cell)_x$$

$$3.\quad \left[CuCl_a\right]^{-(a-2)} + Cl^- \rightleftharpoons \left[CuCl_{a+1}\right]^{-(a-1)}$$

$$4.\quad \left[NiCl_a\right]^{-(a-2)} + Cl^- \rightleftharpoons \left[NiCl_{a+1}\right]^{-(a-1)}$$

where $a = 0, 1, 2, 3, 4$.

The existence of many chloro complexes of copper(II) and cobalt(II) have been proposed, in both aqueous and organic

solvents.(136) However, the complexing ability of nickel(II) with chloride appears to be less than that of cobalt(II), at least in octan-2-ol,(137) although Gill and Nyholm(138) have presented evidence in favour of the complex-ion species $[NiCl_4]^{-2}$, existing in organic solvents.
Generally, the complexing ability of chloride ions with nickel(II) is less than that with copper(II) ions.(136)

Therefore, considering the reactions 1,2,3, and 4 (p.99), the equilibrium constant for reaction 3 may be expected to be greater than that for reaction 4, and further as the replacement reactions 1 and 2 continue, the ratio copper(II) ions/chloride ions, becomes smaller.
Thus, reaction 3 may be expected to compete more effectively with reactions 1 and 2 as the substitution reaction proceeds.
Such a situation does not require that the higher complexes eg. $[CuCl_3]^{-1}$ and $[CuCl_4]^{-2}$ can not take part in the substitution reaction directly.

The change in the position of equilibrium when using copper(II) chloride alone, and in the presence of lithium chloride, compared with the almost quantitative replacement when using copper(II) perchlorate (Table VI and Table XV), may then be explained by the fact that a greater concentration of free copper(II) ions are "bound up" in the form of the chloride species.
The rate of the forward reaction using the chloride salt, may be expected to be slowed down, due to complex formation with

the free copper(II) ions. The back reaction will be less affected by chloride ions due to two factors.
First, nickel(II) does not form chloride complexes as readily as copper(II), and secondly, the reverse reaction will be aided by the ready association of chloride ions with the copper(II ions released from copper(II)(salen), in the back reaction.
The full reaction may be represented by a dynamic system of the equilibria, represented by equation 1-4 (p.99)

2. Determination of the Energy and Entropy of Activation for the reaction between copper(II) chloride and nickel(II)(salen) in methyl cellosolve.

The rate constants for the reactions, at three temperatures, were obtained from the relationship

$$k = \frac{x_e}{2t\ a\ (a-x_e)} \quad \ln \frac{x(a-2x_e) + ax_e}{a(x_e - x)}$$

This is the equation for the calculation of the forward rate constant for a second-order reaction, opposed by one of the same order,(29b)

where k = rate constant in $hrs^{-1}mole\ l^{-1}$.

t = time in hours.

a = initial concn. of the reactants, in mole l^{-1}, where the initial concns, of the reactants are equal.

x = decrease in concn. of each reactant after time t.

x_e = amount changed at equilibrium, in mole l^{-1}.

The plots of log $\left[\frac{x(a-2x_e) + ax_e}{a(x_e - x)}\right]$ or log $[a]$ versus time (t), gave straight lines for each of the reactions. (Fig.IX).

The rate constant k, for each reaction, was calculated from the slope of the line, such that,

$$k = \frac{2.303\ x_e}{2.a(a - x_e)}\ .\text{slope} \quad (\text{hrs}^{-1}\text{mole l}^{-1})$$

The calculated rate constants have been tabulated in Table XVI.

The forward rate constants were then used to determine the activation energy of the reaction between copper(II) chloride and nickel(II)(salen), in methyl cellosolve. The plot of log k versus $\frac{1}{T^\circ K}$ is shown in Fig.X, from which the activation energy E $^{\neq}$, for the reaction, was calculated as 21.0 Kcals./ mole l

Table XVI

The Rate constants and related physical values for the reaction between copper(II) chloride and nickel(II)(salen).

Solvent: methyl cellosolve

Concn.(a) of reacting species $[Cu^{+2}]=[Ni(II)(salen)]$	Temperature	Rate constant k, in $\text{hrs}^{-1}\text{mole l}^{-1}$	Activation Energy E $^{\neq}$ in Kcals/ mole.
2.60×10^{-3}M	70.0 ± 0.1°C	547 ± 20	21.0 ± 1.0
2.60×10^{-3}M	61.0 ± 0.1°C	230 ± 5	
2.60×10^{-3}M	53.0 ± 0.1°C	111 ± 5	

Evaluation of the rate constants and energy of activation for the reaction between copper(II) chloride and nickel(II)(salen), in methyl cellosolve.

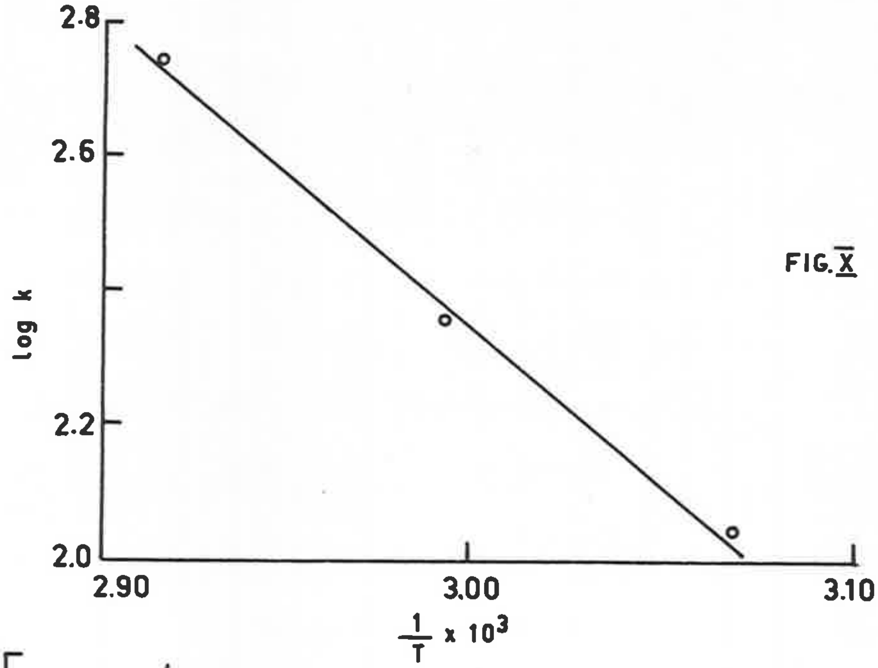

FIG. X

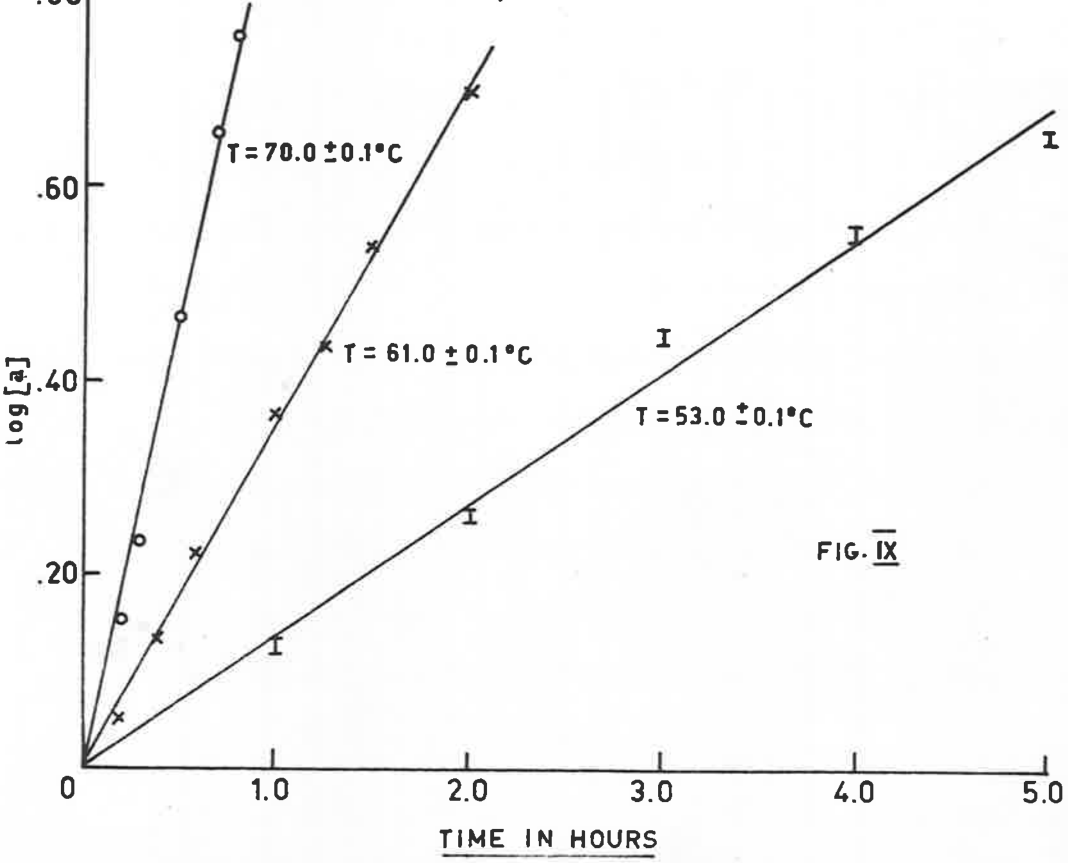

FIG. IX

Summary of the experiments using the copper(II) salts.

The complexing ability of anions in aqueous solution is known to increase in the order, perchlorate $<$ nitrate $<$ acetate $<$ chloride.(139)

It is significant that the equilibrium positions observed in the three replacement experiments given in Table VI, may be correlated with the abilities of the anions to undergo coordination with the copper(II) ion viz.,

[97%(perchlorate), 64%(acetate), 50%(chloride)].

Further, it seems probable in view of the previous discussion, that the most kinetically favourable component for reaction, is the free solvated copper(II) ion.

Pearson, Gray and Basolo(74) have suggested that the free solvated anion is the active reagent in a nucleophilic exchange reaction. If such a suggestion is correct, similarly it may follow that the non-associated cation ie. the free solvated ion, is the more favoured species for metal substitution reaction, than an ion-pair or undissociated metal salt. The evidence presented in this chapter supports this view.

Therefore, it may be expected that faster rates of metal replacement will be observed using metal salts with large dissociation constants than with salts of low dissociation constants, in the same solvent.

Therefore, a correlation between the observed rates of replacement and the expected rates on the basis of the hypothesis suggested above, may be expected. Such a correlation is presented in Table XVII.

Table XVII

The types of copper(II) species present in the replacement experiments, in methyl cellosolve, at 70.0 ± 0.1°C.

Salt	Most probable reacting component	Expected reaction Rate	Observed Rate $R.10^7$ in(sec^{-1} mole l^{-1})
$Cu(ClO_4)_2 6H_2O$	Cu^{+2}, $(CuClO_4)^{+1}$	fast	3.8 ± 0.1(1.30×10^{-3}M)
$CuCl_2$	$(CuCl)^{+1}$, Cu^{+2} $CuCl_2$	slow	1.8 ± 0.05(1.30×10^{-3}M
$Cu(CH_3COO)_2$	$[Cu(CH_3COO)_2]$ $(Cu\ OH\ pyr_x)^{+1}$ etc.	slow	1.3 ± 0.05(2.60×10^{-3}M

B. The effect of varying the solvent.

The rates of reactions between ions and neutral molecules are expected to be larger in solvents of lower dielectric constant.(140) It has been proposed that such a correlation would not necessarily be expected if the rates were measured in different media instead of in mixtures of two solvents.(53a)

However, Basolo and coworkers have found a correlation between the rate of chloride exchange with trans-$[Pt(pyr)_2Cl_2]$, upon examining the substitution in different solvents.(74)

The rate of replacement of nickel(II) in nickel(II)(salen) has been found to markedly depend upon the type of copper(II) salt used in the reaction. It is also influenced by added salts where anions can coordinate with copper(II) ions.

The extent of coordination between copper(II) ions and anions will depend upon the dielectric constant of the solvent used, while the ability of a given solvent to solvate a copper(II) ion will depend not only upon the dielectric constant but also the coordinating ability of the solvent, which may not necessarily parallel the dielectric constant eg. pyridine, ($\varepsilon_{25°C} = 12.0$) and methanol ($\varepsilon_{25°C} = 32.6$)

In the study of the effects of solvents on the rate of reaction, the salt expected to show the smallest amount of anion-cation interaction viz. copper(II)perchlorate (hexahydrate) was used, except for the experiments in pyridine and dioxan, in which its low solubility prevented its use. Six solvents, ranging in dielectric constant from 2 to 37 (25°C) were used and some correlation between the rate of replacement of nickel(II) ions and the dielectric constant of the solvent was found.

However, the correlation was in direct contradiction to the results of Basolo and coauthors,(74) who found an increased rate of exchange with a decrease in the dielectric constant of the solvent, for the exchange of chloride ions with $[Pt(pyr)_2Cl_2]$.

In the reactions with nickel(II)(salen), it has been found that the rates of replacement increase with an increase in the dielectric constant of the solvent.

The results of these experiments are given in Table XVIII (p.107)

Table XVIII

The rates of replacement of nickel(II) ions from nickel(II)(salen), by copper(II) ions, in various solvents.

Solvent	$\varepsilon_{25^\circ C}$	Salt	C	Concn. in mole l^{-1} [Cu(II)salt] = [Ni(II)(salen)] = (a)	Temp. T ± 0.1°C	Initial Rate. $R.10^{7}$ ($sec^{-1} mole\ l^{-1}$)
Dioxan	2.2	CH_3COO^{a}	-	5.00×10^{-4} M	65.1	≪1.2 (35% substitution in 24.0 hours)
Pyridine	12.0	CH_3COO^{a}	green	1.00×10^{-2} M	25.2	30% in 48 hours
		CH_3COO^{a}	brown	1.30×10^{-3} M	70.0	1.2 ± 0.05
		Cl^{-}	brown	1.30×10^{-3} M	70.0	1.6 ± 0.05
Methyl cellosolve	15.96	ClO_4^{e}	violet	1.30×10^{-3} M	70.0	3.8 ± 0.1
Ethanol	24.3	ClO_4^{e}	violet	1.30×10^{-3} M	48.2	4.0 ± 0.1
Methanol	32.6	ClO_4^{e}	violet	1.30×10^{-3} M	48.2	4.3 ± 0.1
Acetonitrile	36.7	ClO_4^{e}	green	5.00×10^{-4} M	15.9	≫4.3 (Equilib. 44% reached in 0.05 hours)

Legend for Table XVIII

(A) a = $Cu(CH_3COO)_2.H_2O$, b = $CuCl_2$,

c = $Cu(ClO_4)_2.6H_2O$

(B) C = Colour of equilibrium mixtures.

(C) ε = Dielectric constant of the solvent.

(i) Copper(II) acetate (monohydrate) in dioxan.

Because of the limited solubilities of many copper(II) salts in dioxan, copper(II) acetate (monohydrate) was employed for the experiments in this solvent. As discussed earlier (p.50) this salt remains undissociated in dioxan, however at 65°C, partial dissociation may be expected, although in view of the low dielectric constant of the solvent it is possible that the main constituents would be $[Cu(CH_3COO)_2]_2$ and $[Cu(CH_3COO)_2]$ and $[Cu(CH_3COO)]^{+1}$. Such species in solution, may be considered "kinetically unfavourable" for the reaction, compared with the solvated copper(II) ions, and therefore the observed slow rate of replacement, is not unexpected.

(ii) Copper(II) acetate (monohydrate) in pyridine.

Copper(II) perchlorate tetrapyridinate has been isolated,(102) and this addition compound is insoluble in pyridine. Therefore, the acetate and chloride salts were employed in the experiments involving pyridine as solvent. Electrical conductance experiments on copper(II) acetate in pyridine have shown that the conductance increases with dilution.(141) Further, solvates of the type $Cu(CH_3COO)_2pyr_4$ have been isolated.(142)

Magnetic measurements have indicated the existence of single molecules, rather than dimers of copper(II) acetate, in pyridine.(97) On the available evidence it is unlikely that complete dissociation of $[Cu(CH_3COO)_2]$ occurs, in pyridine, even at the temperature used in the replacement experiment. As discussed on p.52, the dissociation constants of a number of salts in pyridine have been measured, the values ranging from 1×10^{-3} to 1×10^{-5},(98b) indicating that the solvent does not permit extensive dissociation.

In aqueous solution, conductivity measurements on copper(II) acetate (where dissociation of the dimeric solid compound is known to occur(97)), have indicated the existence of three ions viz. $(CuOAc)^{+1}$, $(OAc)^{-1}$ and solvated copper(II) ions, the dissociation constant of the ion-pair being very small.(143) These ions may also be expected to occur in pyridine solution.

During the replacement experiment at 70°C, the reaction mixtures turned brown.

Mason and Mathews(144) observed the formation of a brown solution in pyridine, when metallic copper was left in pyridine and the solution exposed to the air, for a long period of time. No explanation of this phenomena was given.

In the replacement experiments, the hydrated copper(II) salt was used, and further no rigorous precautions were taken to exclude oxygen from the reaction mixtures, although stoppered vessels were used (see EXPERIMENTAL).

Mason and Mathews(144) noted no brown colouration when oxygen was excluded from the system.

The formation of the brown colour, produced in the reaction between copper(II) ions and nickel(II)(salen), could be due to an ion such as $(CuOH\ pyr_x)^{+1}$.

The rate curve for this reaction is shown in Fig.XI.

The equilibrium position for the replacement reaction, at 70°C, corresponded to 84% reaction. No attempt was made to investigate fully the constitution of the brown species, so the replacement reaction in pyridine, at high temperature, was not examined further.

However, the replacement of nickel(II) ions from nickel(II)(salen) using copper(II) acetate (monohydrate) was examined at room temperature. A brown colouration did not develop during this reaction, the colour of the initial solution of copper(II) acetate in pyridine being blue-green, and the final equilibrium mixtures, dark green.

It was found that 30% substitution had occurred in 48 hours ($T = 25.2 \pm 0.1^{\circ}C$, $[Cu(II)\ salt] = [Ni(II)(salen)] = 1.00 \times 10^{-2}M$)

Further an equilibrium position of about 70% substitution was reached in approximately 150 hours.

A solution of nickel(II) acetate in pyridine at a concentration corresponding to that existing in the equilibrium mixtures proved a light green colour, and the much darker green of the equilibrium mixtures obtained from the experiment was taken to indicate the existence of solvated copper(II)(salen) molecules, as discussed on p.50.

If the solvent can facilitate the dissociation of a complex molecule, (as proposed by Basolo, Pearson and coworkers(74) for the substitution reactions of platinum complexes) such a solvated copper(II)(salen) molecule may be expected to be

The reaction between copper(II) salts and nickel(II)(salen) in pyridine, at 70°C.

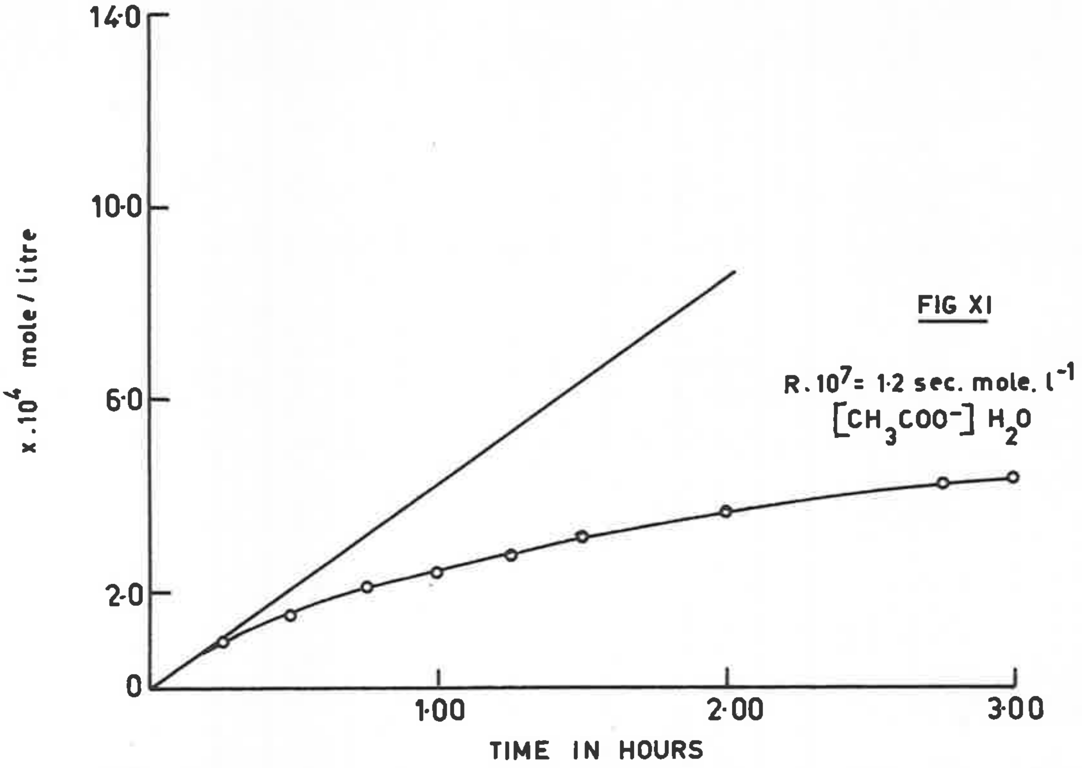

FIG XI

$R.10^7 = 1{\cdot}2$ sec. mole. l^{-1}

$[CH_3COO^-]$ H_2O

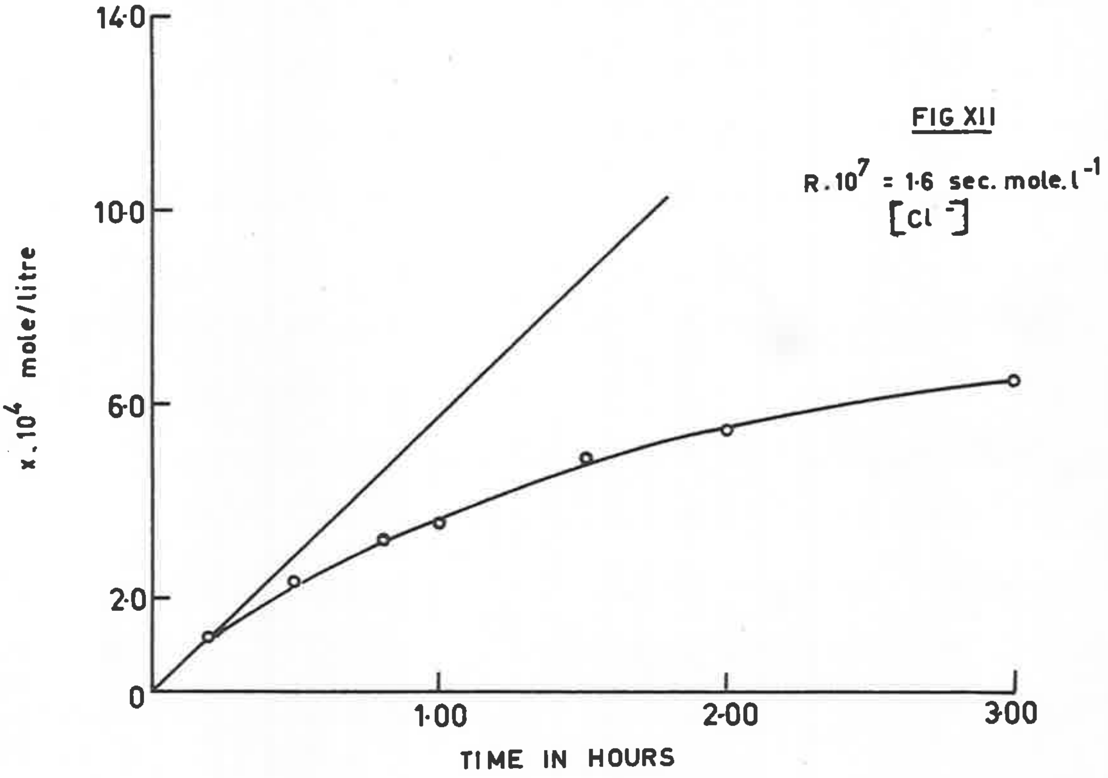

FIG XII

$R.10^7 = 1{\cdot}6$ sec. mole. l^{-1}

$[Cl^-]$

more labile towards metal replacement than the non-solvated copper(II) chelate.

However, the purple colours found for the reaction mixtures, at equilibrium, for the reactions in methyl cellosolve and alcohol(see later), when using the hydrated perchlorate salts, indicate the possible existence of a non-solvated complex, in these solvents.

The nearly complete replacement found for the forward reactions, using copper(II) perchlorate in these solvents, supports the assumption that such four-coordinated copper(II) complexes are inert towards metal substitution by nickel(II) ions ie. the "back" reaction or reverse reactions do not occur to any measureable extent.

(iii) Copper(II) chloride (anhydrous) in pyridine.

Molecular weight studies on this salt in pyridine, at room temperature, indicate the presence of undissociated copper(II) chloride molecules and the colour of such solutions are blue.(145)

Further, addition compounds of the type $CuCl_2pyr_2$ and $2CuCl_3pyr_3$ have been isolated.(144)

A brown colouration, similar to the one found in the experiment, using the hydrated acetate, was produced in the reaction mixtures after some 30 minutes, at 70°C.

The similarities in the initial rates of replacement, using the chloride and acetate salts, (Table XVIII p.107) supports

the existence of copper(II) component(s), in both systems capable of undergoing substitution at similar rates eg. $[\mathrm{Cu\ OH\ pyr_x}]^{+1}$.
An equilibrium position of 78% substitution was found, which may be explained assuming the existence of a solvated copper(II)(salen) molecule capable of undergoing replacement with nickel(II) ions, as postulated in the case of the substitution reaction involving copper(II) acetate, in pyridine.
The plot of x versus t for this reaction is shown in Fig.XII.

(iv) Copper(II) perchlorate (hexahydrate) in methyl cellosolve.

The existence of free solvated copper(II) ions and the ion-pairs $(\mathrm{CuClO_4})^{+1}$, has been proposed in such a system (see p.90). The faster rate of replacement found in this solvent, compared with the reactions in pyridine and dioxan, where copper(II) acetate and chloride were used, may be explained by proposing that the copper(II) species in methyl cellosolve are more "kinetically favourable" for reaction than the species occurring in pyridine ($[\mathrm{Cu\ OH\ pyr_x}]^{+1}$), or dioxan ($[\mathrm{Cu(OAc)_2}]_2$).

(v) Copper(II) perchlorate (hexahydrate) in ethanol and methanol.

It has been proposed that cation-anion interaction occurs in solutions of copper(II) perchlorate in aqueous-ethyl alcohol.(119) However, it may be suggested that ion-pair association in these solvents would be less than that expected in methyl cellosolve, upon comparison of the dielectric constants of these media. (Table XVIII p.107) Therefore, the faster rates of replacement found in ethyl and methyl alcohol compared to methyl cellosolve, may be related to the larger amounts of free solvated copper(II) ions present in the alcohols compared with methyl cellosolve.

1. Kinetics of the reaction between copper(II) perchlorate (hexahydrate) and nickel(II)(salen), in ethyl alcohol.

In an attempt to discover the possible reaction mechanism for the replacement reaction, the reaction order with respect to each reactant was measured. The method used was similar to that employed for the substitution reactions examined in methyl cellosolve. (p.77 - 78)

Table XIX (p.116) shows the dependence of the initial rates of replacement on the concentration of copper(II) perchlorate (hexahydrate).

Table XX (p.116) shows the dependence of the initial rates of replacement on the concentration of nickel(II)(salen).

Figs.XIII and XIV show the plots of log $[Cu^{+2}]$ versus log R and log [Ni(II)(salen)] versus log R for these systems.

The replacement was found to be first-order with respect to each reactant, below 1.30×10^{-3}M.

A line of slope = 1 appears on each figure for comparison with the slopes of the experimental curves.

The rate constants for the reactions at three different temperatures have been evaluated from plots of $\frac{1}{a-x}$ versus t. The calculated rate constants are given in TableXXI, together with the activation energy and the entropy of activation for the reactions in ethanol.

Included in Table XXI are the rate constants and energies and entropies of activation for the replacement reactions in methyl cellosolve, using the chloride and perchlorate salts.

Table XIX

Dependence of the Initial Rate of Replacement on the concentration of Copper(II) perchlorate (hexahydrate).

T = 48.2 ± 0.1°C Solvent: Ethyl alcohol

Concn. $[Cu^{+2}]$ in mole l^{-1}	log $[Cu^{+2}]$	Concn. [Ni(II)(salen)] in mole l^{-1}	Rate $R.10^4$ $hrs^{-1} mole\ l^{-1}$	log R
1. $3.25 \times 10^{-4}M$	-3.488	$1.30 \times 10^{-3}M$	2.50	-3.602
2. $6.50 \times 10^{-4}M$	-3.187	$1.30 \times 10^{-3}M$	7.20	-3.143
3. $9.75 \times 10^{-4}M$	-3.011	$1.30 \times 10^{-3}M$	11.7	-2.932
4. $1.30 \times 10^{-3}M$	-2.886	$1.30 \times 10^{-3}M$	17.3	-2.762

Table XX

Dependence of the Initial Rate of Replacement on the concentration of nickel(II)(salen).

Concn. [Complex] in mole l^{-1}	log [Ni(II)(salen)]	Concn. $[Cu^{+2}]$ in mole l^{-1}	Rate $R.10^4$ $hrs.^{-1} mole\ l^{-1}$	log R
$3.25 \times 10^{-4}M$	-3.488	$1.30 \times 10^{-3}M$	3.90	-3.409
$6.50 \times 10^{-4}M$	-3.187	$1.30 \times 10^{-3}M$	9.30	-3.032
$9.75 \times 10^{-4}M$	-3.011	$1.30 \times 10^{-3}M$	12.7	-2.896
$1.30 \times 10^{-3}M$	-2.886	$1.30 \times 10^{-3}M$	17.3	-2.762

Kinetics of the replacement in ethanol at 48.2°C.

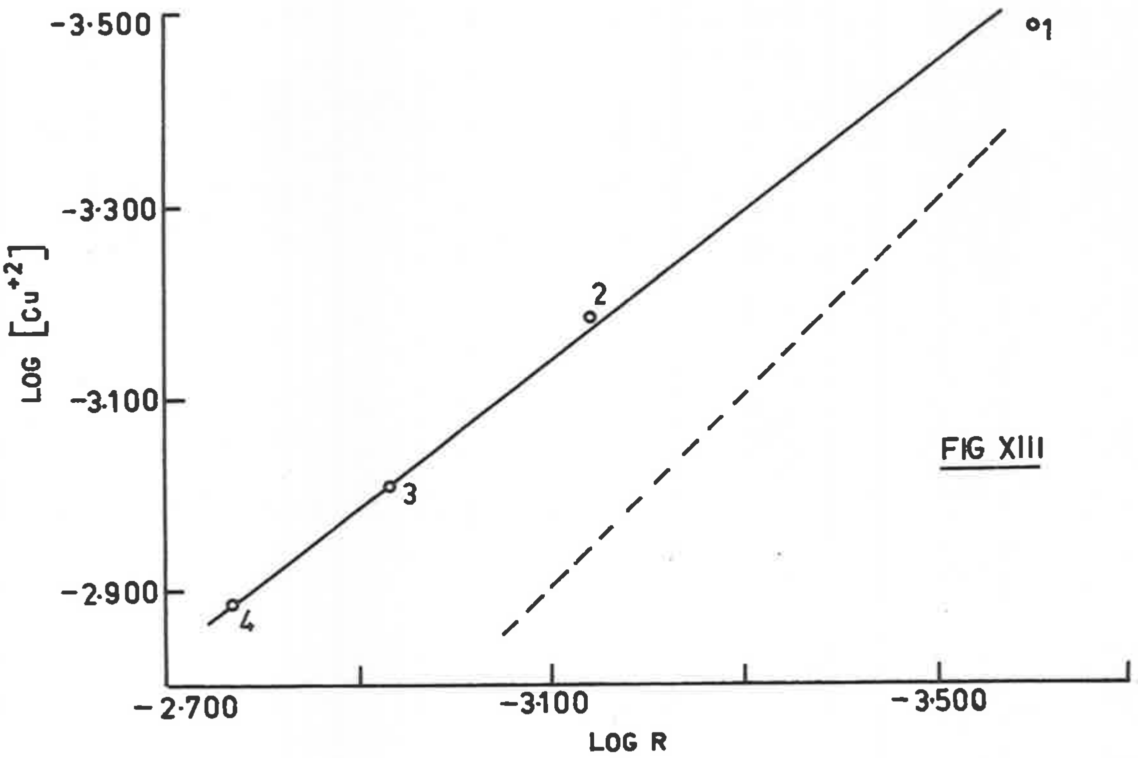

FIG XIII

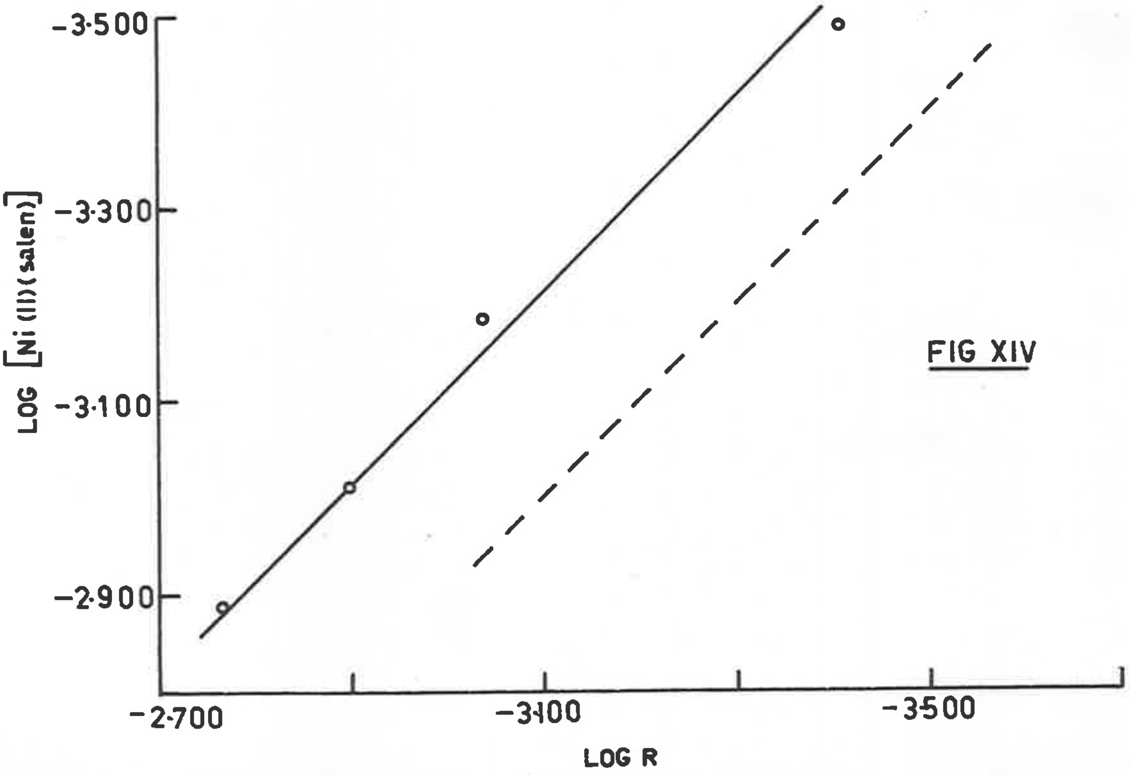

FIG XIV

Table XXI

The replacement of nickel(II) ions from nickel(II)(salen) by copper(II) ions, in ethyl alcohol and methyl cellosolve.

Solvent and Salt	Concn.(a) of reacting species. [Cu(II)salt]=[Ni(II)(salen)]	Rate constant $k.10^{-2}$ $(hrs^{-1} mole\ 1^{-1})$	Temp. T ± 0.1°C.	$E^{\neq}$ (Kcals/mole^{-1}) $E^{\neq}$ ± 1.0	$\Delta S^{\neq}$ e.u ± 2
Ethyl alcohol					
$Cu(ClO_4)6H_2O$	$1.30 \times 10^{-3}M$	28.2	65.1	17.3	-10
		14.5	56.2		
		7.2	48.2		
Methyl cellosolve					
$Cu(ClO_4)_26H_2O$	$1.30 \times 10^{-3}M$	43.5	83.1	24.6	8
		22.8	76.9		
		13.3	71.1		
		7.6	65.1		
		3.3	58.1		
Methyl cellosolve					
$CuCl_2$	$2.60 \times 10^{-3}M$	5.5	70.0	21.0	-
		2.3	61.0		
		1.1	53.0		

Stranks(146) has compiled a table of published kinetic studies of substitution reactions of complexes, of the transition metals. Upon examination of this table it is found that the activation energies calculated for many of these reactions, in almost all instances, both for exchange and replacement reactions, are in the range 15-25 Kcals/ mole l^{-1}.

In addition, the entropies of activation $\Delta S^{\neq}$ for the metal exchange reactions, $[Ni(CN)_4]^{+2}$ - [Ni(glycinate)] and $[Ni(CN)_4]^{-2}$ - [Ni(serinate)] in water, are -11 and -8 e.u. respectively.(80) These are the only entropy changes that seem to have been reported for such metal substitution reactions, between ions and neutral molecules.

The value of -10 e.u. calculated for the replacement reaction in ethyl alcohol is of the same order of magnitude as those found for the nickel(II) exchange reactions.

The positive entropy of activation (8 ± 2 e.u.) associated with the replacement reaction using copper(II) perchlorate (hexahydrate), in methyl cellosolve, may be correlated with the "sloughing off" of the anions (attached to the copper(II) species), in forming the transition state.

As given on p.94, the calculation of $\Delta S^{\neq}$ from the equations of the theory of absolute reaction rates, incorporates the absolute value of the rate constant.

The rate constants obtained for the reactions in methyl cellosolve, may be expected to be overall values associated with the reactions between different copper(II) species and nickel(II)(salen). Therefore, the calculation of $\Delta S^{\neq}$, using the observed rate constants, may well give a misrepresentation of the entropy changes, expected for such a reaction, in methyl cellosolve.

However, it is significant that, the positive entropy change for the reaction in methyl cellosolve, compared with the negative value for the reaction in ethyl alcohol, parallels the expected order of complex-ion association with the copper(II) ions, in these solvents.

(vi) Copper(II) perchlorate (hexahydrate) in acetonitrile.

A number of solvates of transition metal halides with acetonitrile, have been isolated.(149)

The visible absorption spectra of a number of transition metal salts, including $Cu(ClO_4)_2 6H_2O$, in N,N-dimethylformamide ($\varepsilon_{25°C}$ = 36.71(98a)) have been examined.(139) The spectra of these compounds in this solvent differ from the spectra exhibited in aqueous solution.

Therefore, it is probable that some degree of ion-pair formation does occur in acetonitrile, the dielectric constant of which is very similar ($\varepsilon_{25°C}$ = 36.7). At the concentrations used in the replacement experiment viz. 5.00×10^{-4}M, ion-pair formation may be expected to be relatively low compared with the association expected in methyl cellosolve.

Although the rate of *re*placement of nickel(II) in nickel(II)(salen) is rapid, the reaction goes only to 44% to the right ($T = 15.9 \pm 0.1^{\circ}C$). Such an observed equilibrium position is difficul~~a~~t to correkate with the types of species, in solution. It may be expected that the free solvated copper(II) ions and the ion-pairs $[CuClO_4]^{+1}$, exist in solution. Such species have been shown to undergo nearly quantitative *re*placement with nickel(II)(salen), in methyl cellosolve. However, the colours of the equilibrium mixtures obtained in the reaction in acetonitrile were green, and similar to those obtained from reactions in pyridine. Such colourations are considered to indicate the presence of a solvated copper(II) complex, produced during the *re*placement reaction.(p.50)

(a) Some qualitative experiments with copper(II)(salen).

(1) Copper(II)(salen) was prepared by adding an acetonitrile solution of the Schiffs base to copper(II) perchlorate (hexahydrate) dissolved in acetonitrile. A green solution was produced. Similar reactions in alcohol and methyl cellosolve yielded violet coloured solutions. Similarly, when solid, green copper(II)(salen) was dissolved in acetonitrile, a violet coloured solution resulted.

(2) A solution, containing 2.22×10^{-4}M copper(II)(salen) and 2.78×10^{-4}M nickel(II)(salen) in acetonitrile, was prepared.

Such a solution corresponded in composition to the equilibrium mixtures obtained in the replacement experiment.

The colour of this solution was brown-red, quite dissimilar to the green colour of the reaction equilibrium mixtures.

The green solution found on mixing copper(II) perchlorate and (salen) in acetonitrile, and, for the equilibrium mixtures in the replacement experiments, may indicate that a solvated copper(II) (salen) molecule is produced in such reactions.

However, it appears likely that a four-coordinated complex results on dissolving solid copper(II)(salen) in acetonitrile.

(b) The replacement of copper(II) ions in copper(II) (salen) by nickel(II) ions.

The substitution reaction between the violet solution of copper(II)(salen) and nickel(II) perchlorate (hexahydrate), in acetonitrile, was found to reach equilibrium (14% reaction) in 120 hours. ($T = 15.9 \pm 0.1°C$, $[Ni(II)\ salt] = [Cu(II)(salen)] = 5.00 \times 10^{-4} M$).

It is evident from these results that the replacement of the central metal atom of the four coordinated copper(II (salen) molecule can only occur to a slight extent.

This further supports the assumption that the copper(II)(salen) complex produced by the replacement of nickel(II) ions in nickel(II)(salen) is different in structure to that obtained on dissolving solid copper(II)(salen) in acetonitrile.

C. The mechanism of replacement of nickel(II) ions from nickel(II)(salen) by copper(II).

There are at least two types of mechanisms of replacement which may be tentatively suggested,

(i) A dissociation mechanism in which the rate determining step involves a slow, unimolecular dissociation of the nickel(II) complex, followed by a rapid reaction with copper(II) to form copper(II)(salen).

However, such a reaction may not necessarily exhibit first-order kinetics.(53)

(ii) A displacement mechanism of replacement, in which the rate-determining step of the reaction would be one involving a bimolecular reaction between the copper(II) species and nickel(II)(salen), to form a transition state in which the coordination number of the complexed metal ion is increased by one. Such a reaction need not necessarily exhibit second-order kinetics.(53)

The kinetics of the replacement reactions in methyl cellosolve and ethanol below 1.30 x 10^{-3}M, exhibit overall second-order kinetics. Further, the rates of replacement in methyl cellosolve, and the rates of replacement of nickel(II) ions in nickel(II)(salen), in different solvents, were found to markedly depend upon the types of copper(II) species, in solution.

These factors support the existence of a bimolecular rate-determining step, for the reaction, rather than a mechanism in which the dissociation of the nickel(II) complex, is rate-determining and unimolecular.

Spectroscopic and magnetic evidence points to nickel(II)(salen) existing, in solution, as a square planar molecule, either without attached solvent molecules, or, with very loosely bound solvent molecules, such that the Crystal Field remains essentially that of a diamagnetic (strong field) square planar molecule.

On this basis, a proposed displacement mechanism requires the formation of a five-coordinated transition state.

Basolo and Pearson$^{(2a)}$ have tabulated Activation Energies for the reaction of square planar complexes, calculated on the basis of Crystal Field Energy changes. However, such calculations are based on the assumption that tetragonal structures, in solution, have C.F.S.E. equivalent to those of square planar molecules, and therefore the values listed refer to the dissociation of a six-coordinated complex (with a C.F.S.E. equivalent to that of a square planar molecule), into a five-coordinated transition state. Such a calculation should approximate to the ΔE_a for a displacement mechanism, involving a four-coordinated reactant molecule.

Such calculations show that the loss of C.F.S.E. in passing from a nickel(II) tetragonal reactant molecule (ie. square planar) to a five-coordinated square pyramid transition state, involves a loss in C.F.S.E. of 6.28 Dq.

Calculations, made from d-orbital energies for Crystal Fields of different geometries,(2c) indicate a loss in C.F.S.E. of 13.62 Dq, for a strong-field nickel(II) complex, in passing from a square planar reactant to a trigonal plane transition state ie. with dissociation of the quadridentate chelating agent at one point, thus forming a three coordinate state for the central nickel(II) atom, prior to reaction with a copper(II) ion.

It would appear, despite the errors in the energy values given, for the d-orbitals for other configurations than octahedral, that such a dissociative step would be most unlikely, and would moreover, be expected to give a slow reaction which could become rate-determining, and if unimolecular, could therefore possibly exhibit first-order kinetics.

By either mechanism, dissociation of a four-coordinated complex, or a bimolecular reaction resulting in the formation of a five-coordinated transition state, the substitution reactions of square planar d^8 nickel(II) complexes are predicted to be slower than those of the corresponding solvated copper(II) and cobalt(II) complexes, on the basis of Crystal Field calculations. This is in agreement with the results of the metal exchange reactions,(5)(6)(41) as discussed in Chapter I of this thesis.

(1) Basolo and Pearson(2a) have suggested a reaction mechanism to account for the second-order kinetics and observed activation energies for the copper(II)(salen) and cobalt(II)(salophen) metal exchange reactions.(p.5-6). However, such mechanisms presuppose the existence of tetragonal structures for the complexes, in pyridine. Similar kinetics and activation energies were found for the replacement reactions with nickel(II)(salen), in methyl cellosolve and alcohol.

It may be suggested on this basis, that a similar mechanism may operate in the replacement reactions with nickel(II)(salen), to that proposed by Basolo and Pearson(2a) for the cobalt(II) and copper(II) metal exchange reactions.

However, as previously discussed, the loss in C.F.S.E. in passing from a four coordinated reactant to a three coordinated transition state, is very high, and such a reaction step would be energetically unfavourable, and therefore, would not be expected to proceed to any great extent. Such a situation may account for the observed lack of metal exchange in nickel(II)(salen), at room temperature.(33)(41) At such a temperature, the dissociation of the reactant complex may be expected to be very small in the low dielectric constant media used to examine these reactions viz., methyl cellosolve and pyridine, and further, if such a reaction path persists a low rate of dissociation may be expected.

The Basolo and Pearson mechanism (p.6) requires an initial fast, partial dissociation of the nickel(II) complex.

(a) Such a dissociation may be expected to be enhanced in solvents of high dielectric constant, thus increasing the rate of replacement, in such solvents relative to solvents of low dielectric constants.
This is in agreement with the experimental results found. (Table XVIII p.107).

(b) It may be expected that the Ni - O linkages are broken in such a dissociative step, rather than the Ni - N bonds. The N atoms would be held rigidly in position by the ethylene bridge, thus increasing their strength relative to the Ni - O linkages.

(c) After rupture of these bonds, attachment of the copper(II) ion to the O^- ion may be expected (as shown in the diagram presented on p.6), thus making the stepwise breaking of subsequent bonds in the chelate much easier, and after further reactions these attach themselves to the copper(II) ion, thereby forming the copper(II)(salen) molecule.

(2) An alternative mechanism, may be that the approach of the copper(II) ion to the nickel(II)(salen) molecule, can aid the dissociation of the nickel-ligand bonds, particularly a Ni – O bond, by forming a linkage of the type Cu – O – Ni, as shown in Fig.A.

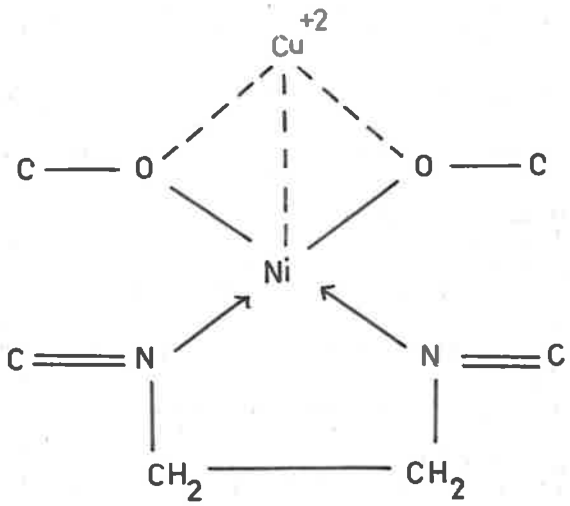

Fig. A.

Such a mechanism would involve a three coordinated oxygen atom in the system. Three coordination for oxygen is known in stable units eg. H_3O^+, and similar oxonium derivatives.(148)

In such a reaction mechanism, the copper(II) ions upon approaching the complex would aid dissociation by sharing the electrons of the oxygen atom, thus weakening the force of attachment of the oxygen atom to the nickel(II) atom ie. bonding function of the oxygen atom would be transferred from the nickel(II) atom to the incoming copper(II) ion.

The next step would involve one nitrogen atom attaching itself to the copper(II) ion, followed by the rupture of the other

Ni - N bond, until a trigonal plane configuration is formed about the copper(II) ion.

The last step would involve the rupturing of the final Ni - O linkage, and the forming of the copper(II)(salen) molecule, thus leaving the nickel(II) ion, in solution, bearing solvent and/or anion molecules.

The ability of the Ni - O linkage to dissociate, would be enhanced in solvents of high dielectric constant, and therefore the rate expected to increase, in agreement with the experimental results, for the replacements in such solvents. (Table XVIII p.107).

Such a mechanism would not be considered as either dissociation or displacement in the terminology of Basolo and Pearson;(2) as it does not involve a unimolecular dissociative step, which is rate-determining; nor does it involve an increased coordination number for the nickel(II) ion in the transition state (shown in Fig.A) expected for a displacement mechanism, unless weak Cu - Ni bonds can be postulated.

However, it may be expected that the rate of replacement would depend upon the concentration of the copper(II salt used, and upon the natures of copper(II) species, in solution. Such a dependence has been found for the replacement reactions in nickel(II)(salen).

It is significant that solvent-complex interaction may be postulated for copper(II)(salen) and cobalt(II)(salen), in pyridine, and that these complexes exhibit measurable rates of exchange at room temperature. Such solvation, in changing the configuration of the complex, would also be expected to relax the Crystal Field of the chelate, thus weakening the bonds prior to dissociation. Therefore a substitution reaction involving a solvated complex may be expected to occur more readily than one involving the corresponding non-solvated chelate.

Such a situation has been found for the replacement reactions with nickel(II)(salen), in acetonitrile and pyridine, compared with those in methyl cellosolve and alcohol.

(1) The replacement reaction in acetonitrile was found to reach an equilibrium position of 44% substitution, in less than 0.05 hour.

The fast rate of replacement (cf. that in other solvents) may be explained on the basis of the existence of a large percentage of kinetically favourable copper(II) ions capable of reacting and also by the high dielectric constant of the solvent capable of facilitating dissociation of nickel(II)(salen).

It has been shown that a probable solvated copper(II)(salen) molecule is produced, in the reaction, capable of undergoing replacement with nickel(II) ions to such an extent that the equilibrium position observed in the reaction supports the view that solvated copper(II)(salen) is less stable than the non-solvated nickel(II)(salen) molecule.

The replacement reaction in pyridine is slower than that in acetonitrile. This may be correlated with the existence of a larger percentage of kinetically unfavourable copper(II) species in this solvent, compared with acetonitrile (as discussed on p.111 - 112).

However, it may be expected tha an equilibrium position of <50% substitution would be observed for this reaction, if the suggestion that solvated copper(II)(salen) is less stable than the four coordinated nickel(II) complex, is correct.

The observed 70% equilibrium position found for the replacement reaction in pyridine, may be associated with the inability of the nickel(II) species, produced in the replacement experiment, to undergo reaction with copper(II)(salen) to the same extent as the free solvated nickel(II) ions produced in the reaction in acetonitrile. That is, the back reaction is impeded by nickel(II) ions entering into a competitive reaction with acetate ions, thus producing a dynamic equilibria in this reaction system, similar to that of the copper(II) chloride/acetate - nickel(II)(salen) reaction, in methyl cellosolve.

The nearly complete forward replacements found in alcohol and methyl cellosolve, when using copper(II) perchlorate (hexahydrate), where four-coordinated copper(II) complexes are expected to be produced, further supports the suggestion that such non-solvated copper(II) complexes will not undergo substitution reactions to the same extent as their corresponding solvated chelates.

Hall and Willeford(41) upon examination of the metal exchange reactions of a number of other nickel(II) complexes, found that in nearly all instances, those chelates which became solvated in solution, underwent rapid exchange at room temperature. Such solvent interaction with a chelate, above and below the planes of the complex, has been suggested to facilitate the dissociation of a ligand.(74) Therefore, it may be expected that an increased rate of substitution would result. (cf. corresponding non-solvated chelate). However, nickel(II)(sal<u>o</u>phen), found inert towards metal exchange at room temperature, is known to be paramagnetic and presumed to have an octahedral configuration, in solution. (see p.70)
Such a situation is difficult to reconcile with the hypothesis suggested above, as this would imply that exchange should proceed at a measureable rate, at room temperature. However, the copper(II) and cobalt(II) (sal<u>o</u>phen) complexes were found to be more inert towards metal exchange than the derresponding (salen) compounds.(5)(6) However, for the copper(II) and cobalt(II) chelates, solvent-chelate interaction may be expected to exist, suggesting perhaps that the effect of solvent interaction with nickel(II)(sal<u>o</u>phen) is not sufficient to outweigh the strength of the Ni - ligand bonds in the

complex, and therefore make it as inert towards metal exchange, as nickel(II)(salen).
Further, the magnetic moment of nickel(II)(salophen) in pyridine, is not that expected for a completely spin-free nickel(II) ion(88) ie. 3.2 B.M., indicating that some percentage of the nickel(II) complex molecules exist in square planar configurations.

The reaction mechanism is expected to be similar whether solvation occurs or not. However, the weakening of the bonds prior to dissociation, and therefore the rate of replacement, is expected to be greater in solvated nickel(II) complexes. Further, the stabilities of the four and six coordinated complexes are expected to be different, as shown in the case of copper(II)(salen) in acetonitrile and pyridine compared with the complex in methyl cellosolve and alcohol.

METAL REPLACEMENT REACTIONS WITH SOME NICKEL(II) CHELATES.

The metal exchange reactions of a number of nickel(II) chelate complexes have been examined by Hall *et al*(33)(41)

These workers found that those nickel(II) compounds, paramagnetic in solution, and which on the Pauling terminology(9) or "outer-orbital"(111)(112) concept, indicated the presence of ionic bonds, exchanged their central nickel(II) atoms at measurable rates, at room temperature; the exception being nickel(II)(salophen), as previously discussed. (p.132). However, those nickel(II) chelate complexes, diamagnetic in the solid state and in solution eg. nickel(II)(salen), showed no exchange of nickel(II) ions, at room temperature. Therefore, it was of interest to examine the ease of replacement of nickel(II) ions by copper(II) ions, in some of the diamagnetic chelates, to determine,

(1) their rates of replacement,

(2) the stabilities of the nickel(II) chelates relative to those of the corresponding copper(II) complexes.

If the rates of metal replacements can be correlated with the bond strengths of the metal-ligand linkages, in a similar manner to that suggested by Stranks and Wilkins,(14) for exchange reactions, then the different rate of replacement found in one nickel(II) chelate compound, compared with another, may be correlated with the relative strengths of the metal-ligand bonds.

The initial rates of replacement of nickel(II) ions from the diamagnetic nickel(II) chelates, by copper(II) ions, were determined in a similar manner to those given in Chapter II, for the replacement reactions, involving nickel(II)(salen).

Methyl cellosolve was used as the solvent for all the replacement experiments, because it dissolved all the nickel(II) complexes readily. Copper(II) perchlorate (hexahydrate) was used as the source of the copper(II) species. The copper(II) species produced in this medium have been shown to react nearly quantitatively with nickel(II)(salen) (see Tables V and VI).

(1) N,N'-1,2-phenylenebis(salicylideneiminato) nickel(II) [nickel(II)(salophen)]

The replacement of nickel(II) ions from nickel(II)(salophen) by copper(II) ions was found to proceed almost to completion (95%), in about 60 hours, at 71°C, in methyl cellosolve (1.30×10^{-3}M each reactant), indicating that the copper(II)(salophen) produced in the reaction is more stable than the reactant nickel(II) chelate.

The initial rates of replacement of nickel(II) ions from nickel(II)(salophen) at 71° and 77°C are given in Table XXII. Also included are the rates of replacement of nickel(II) ions from nickel(II)(salen), at the same temperatures.

Table XXII

The rates of replacement of nickel(II) ions from nickel(II)(salen) and nickel(II)(salophen), in methyl cellosolve.

Complex.	Temp T ± 0.1°C	Initial Rate $R.10^7$ ($sec^{-1} mole\ l^{-1}$)
Ni(II)(salen)	76.9	11.3 ± 0.3
Ni(II)(salophen)		1.8 ± 0.05
Ni(II)(salen)	71.1	5.8 ± 0.2
Ni(II)(salophen)		0.92 ± 0.04

$$\left[\text{Cu(II) salt}\right] = \left[\text{Ni(II) complex}\right] = 1.30 \times 10^{-3}\text{M}$$

Figs XVa and XVb show the graphs of x versus t for the nickel(II)(salen) and nickel(II)(salophen) replacements, at 76.9°C, from which the initial rates of replacement were calculated.

The initial rates of replacement of nickel(II) ions from nickel(II)(salen) are greater than those for the replacement reactions with nickel(II)(salophen) (Table XXII). If the rates of metal replacements can be correlated with the bond strengths of the metal-ligand linkages, then the slower rates of replacement found with nickel(II)(salophen) indicate the existence of stronger metal-ligand bonds in this complex than in nickel(II)(salen).

As discussed on p.70, nickel(II)(salophen) exhibits paramagnetism in pyridine solution,(89) and such magnetic behaviour may be taken as indicating the presence of "ionic

Replacement reactions with some nickel(II) chelates at 76.9°C

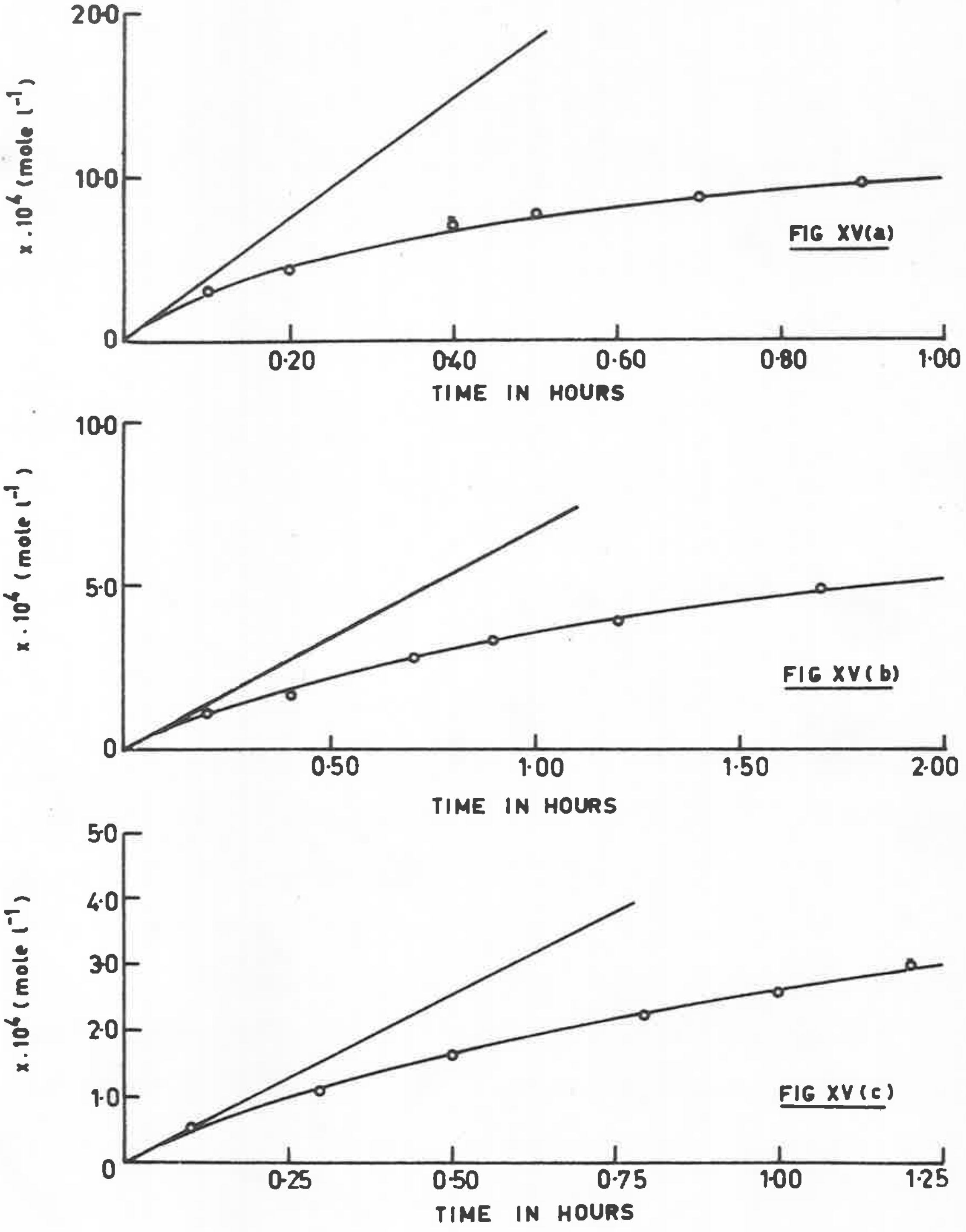

FIG XV (a) nickel(II)(salen) (b) nickel(II)(salophen) (c) nickel(II)(salpn) bonds" [cf. diamagnetic character of nickel(II)(salen) in pyridine.]

Further, the spectrum of nickel(II)(salophen) in acetonitrile, dioxan, methyl alcohol and methyl cellosolve shows two maximum absorption bands in the region 3200 - 4900 Å, while the spectrum in pyridine solution shows four maximum absorption bands, in the same wavelength region (Table VIII p.71).

As discussed on p.71, such a dissimilarity in the spectrum of nickel(II)(salophen) in various solvents, may be due to the presence of stronger solvent-complex interaction in pyridine than in other solvents.

In addition, the paramagnetism exhibited in pyridine solution has been shown to decrease with increase in temperature,(87) indicating less solvent-complex interaction at higher temperatures. The weak solvent-complex interaction in methyl cellosolve, at room temperature, may be expected to be weaker at 70-80°C, the temperatures used in the replacement experiments. Therefore, the ability of the solvent, at high temperatures, to facilitate the dissociation of nickel(II)(salophen) is expected to be small.

The slower rates of metal replacement in nickel(II)(salophen) compared with nickel(II)(salen) may be explained by the existence of stronger Ni-ligand bonds in the former compound.

Calvin and Duffield(5) and West(6) both found that the rates of metal exchange in copper(II)(salophen) and

cobalt(II)(sal<u>o</u>phen) respectively, were smaller than these of the metal exchanges in the corresponding (salen) complexes. West(6) explained the slower rate of exchange found in cobalt(II)(sal<u>o</u>phen), to that in cobalt(II)(salen), by the increased "stability" of the (sal<u>o</u>phen) complex, arising from the conjugated nature of the ring systems present in this compound. The word "stability", used by West(6) implied bond strength, rather than dissociative stability.
Therefore, the strengths of the metal-ligand linkages in nickel(II)(sal<u>o</u>phen) may also be expected to be greater than those in nickel(II)(salen), on the same basis.
No such conjugation of the chelate rings is possible in nickel(II)(salen) because of the single C-C bond in the ethylene grouping.
Hence the slower rates of metal <u>re</u>placement found in nickel(II) (sal<u>o</u>phen) compared to those in nickel(II)(salen) may be related to the strengths of the metal-ligand linkages.

(ii) <u>N,N'-1,2-propylenebis(salicylideneiminato) nickel(II)</u> [<u>nickel(II)(salpn)</u>]

The <u>re</u>placement of nickel(II) ions from nickel(II) (salpn) using copper(II), was found to proceed almost to completion (95%), in about 70 hours, in methyl cellosolve, at 76.9°C (1.30×10^{-3}M each reactant). The initial rate of <u>re</u>placement at 76.9°C, was calculated as $R.10^7 = 3.9$ (sec^{-1} mole l^{-1}) [cf. nickel(II)(salen) $R.10^7 = 11.3$ (sec^{-1}mole l^{-1})]
The graph of x versus t for the nickel(II)(salpn) <u>re</u>placement

is given in Fig.XV(c).

The slower rate of substitution, produced by the introduction of a methyl group on the ethylene bridge, may be similar to the effect discussed by Wilkins(149) for the rate of dissociation of $\left[Ni(pn)_2\right]^{+2}$ compared with $\left[Ni(en)_2\right]^{+2}$. Wilkins suggested that the slower rate of dissociation of $\left[Ni(pn)_2\right]^{+2}$ than $\left[Ni(en)_2\right]^{+2}$ lay in the changed pZ factor, thus implying a steric factor operating in the case of the dissociation of $\left[Ni(pn)_2\right]^{+2}$. Further, the rate of exchange of nickel(II) ions with $\left[Ni(tetrameen)_2\right]^{+2}$ [a] is less than that with $\left[Ni(en)_2\right]^{+2}$, under similar conditions.(149) However, it is difficult to see how steric factors can make dissociation more difficult for the (salpn) complex compound than the (salen) chelate. Models fail to show any effect of steric hindrance on the ability of nickel(II)(salpn) to dissociate.

The chelating tendencies of 1,2-propylenediimine and ethylenediimine with nickel(II), are of the same order,(150)(151) indicating that the stabilities of the nickel(II) species formed from these bases, are not widely different.

The explanation of the slower rate of <u>re</u>placement found in nickel(II)(salpn) compared to that in nickel(II)(salen)

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[a] tetrameen = $NH_2.CH_2.CH_2.CH_2.CH_2.NH_2$

may lie in the decreased ability of the (salpn) chelate to dissociate, due to the presence of the CH_3 grouping.

(iii) (a) N,N' ethylenebis(1-methyl-3 oxobutylideneiminato nickel(II) [nickel(II)(acacen)], and

(b) N,N'-1,2-propylenebis(1-methyl-3 oxobutylideneiminato) nickel(II) [nickel(II)(acacpn)].

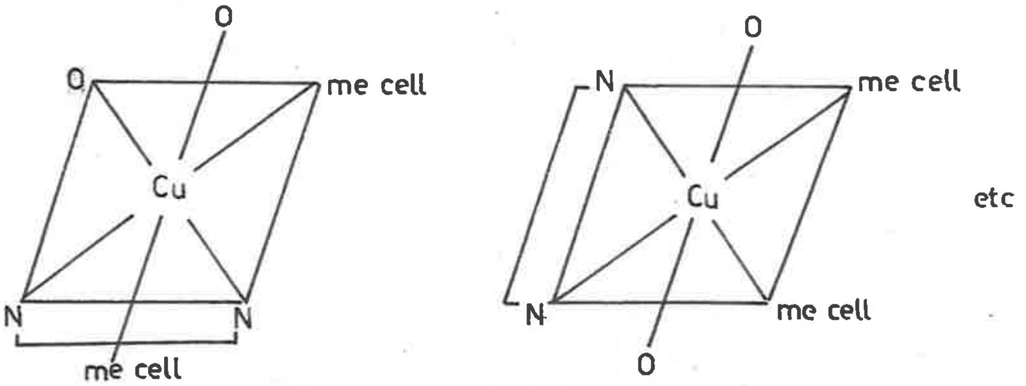
The reaction between nickel(II)(acacen) and copper(II) perchlorate (hexahydrate) in methyl cellosolve, was found to reach equilibrium (22% substitution) in about 8 hours, at 71.1°C (1.30×10^{-3}M each reactant).
The initial rate of replacement was calculated as $R.10^7 = 0.39$ ($sec^{-1} mole\ l^{-1}$) [cf. nickel(II)(salen) $R.10^7 = 5.8$ ($sec^{-1} mole\ l^{-1}$)].

The reaction between copper(II) and nickel(II)(acacpn) has been shown to reach equilibrium (40% substitution) in about 20 hours, at 71.1°C in methyl cellosolve.
The initial rate of reaction has been calculated as $R.10^7 = 0.17$ ($sec^{-1} mole\ l^{-1}$) [cf. nickel(II)(acacen) $R.10^7 = 0.39$ ($sec^{-1} mole\ l^{-1}$)].

The equilibrium positions found for the replacement reactions with the substituted acetylacetone chelates indicate that the copper(II) complexes produced as a result of the substitution reactions are less stable than those of the reactant nickel(II) chelates. Further, the slower rates of substitution found for these nickel(II) acetylacetone chelates, compared with the salicylaldehyde complexes, may indicate the existence of stronger metal-ligand linkages in the former compounds than are present in the latter chelates.

The situation with the low percentage substitutions is similar to the copper(II)-nickel(II)(salen) replacement reactions in acetonitrile. In this experiment, evidence was produced to support the existence of a different copper(II)(salen) species produced in the reaction in acetonitrile than in other solvents ie. a solvated copper(II) molecule capable of undergoing replacement more easily than the corresponding four coordinated (salen) complex produced in other solvents. It is difficult to support the existence of strong solvent-complex interaction with copper(II)(acacen) and copper(II)(acacpn), in methyl cellosolve, at 70°C.
However, the copper(II) complexes produced as a result of the replacement reactions with nickel(II)(acacen) and nickel(II)(acacpn) may not be the planar molecules expected for such reactions.

Morgan and Main-Smith(152) have prepared five isomers of $[Co(NH_3)_2C_{12}H_{18}O_2N_2]Cl$. This means that the acetylacetone molecule can twist itself in a variety of ways, and further may imply that it would be possible to produce a copper(II)(acacen) complex, in solution (as a result of the substitution of nickel(II)(acacen)), which is tetragonal in configuration, perhaps containing two solvent molecules in its arrangement, eg.



Further, Morgan and Main-Smith(152) have isolated a green monohydrate of copper(II)(acacen), possibly containing a copper(II) atom with a coordination number of five. (cf.Waters and Hall(90)(93) - colour-spectra correlation p.49).

If a similar mechanism of reaction to that suggested for the replacement reactions of nickel(II)(salen), can be applied to the nickel(II)(acacen) systems, such a reaction step implies that on the approach of the copper(II) atom, to form the transition state in the replacement reaction with nickel(II) (acacen), the oxygen atoms tend to bond partially to the copper(II) and partially to the nickel(II) atom in the complex. Such a situation was expected to facilitate dissociation of the complex (p.128).

Such bonding in the transition state may involve bringing the oxygen atoms out of the plane of the complex, after which the remaining portion of the substitution reaction would involve succesive ruptures of the metal-donor bonds in a similar manner to that proposed for the replacement reactions of nickel(II)(salen).

The net result would be to twist the tetracoordinate complexing agent out of the normal planar arrangement associated with nickel(II)(acacen).

A similar situation may arise with the salicylaldehyde chelates, but the rigid nature of the salicylaldehyde rings would be against any stable configuration for the copper(II) complex, in methyl cellosolve, other than a square planar state.

Such a non-planar strained configuration for the copper(II)(acacen) molecule, produced in the substitution reactions, should be more susceptible to substitution with nickel(II) ions, and hence the extent of the back reaction, [nickel(II) + copper(II)(acacen)], increased. Such a situation does explain the observed equilibrium position for the replacement experiment with nickel(II)(acacen).

The replacement reaction with nickel(II)(acacpn) was found to reach an equilibrium position of 40% substitution. The presence of the acetylacetone grouping will again allow a certain degree of freedom in forming the copper(II)(acacpn) complex (as above), however, such twisting of the tetracoordinate base may be expected to be impeded by the steric effect of the methyl grouping on the ethylene bridge.

Models indicate that steric hindrance may be quite marked for the (acacpn) chelates.

However, the observed larger reaction (40%) compared with the (acacen) (22%), may be explained on the basis of less twisting of the tetracoordinate base in forming the copper(II) derivative(s), thereby forming a copper(II)(acacpn) molecule less susceptible to replacement by nickel(II) ions, than the copper(II)(acacen) molecule produced in the copper(II)-nickel(II)(acacen) substitution.

The rates of replacement of nickel(II) ions from nickel(II)(acacen) and nickel(II)(acacpn) are less than those in the salicylaldehyde chelates (see p.141) under similar conditions.

Martell et al,(153)(154) have examined the infra-red, ultra-violet and visible absorption spectra, of a number of metal(II) chelates of substituted acetylacetones.

Ueno and Martell(153) found that the positions of the metal specific absorptions in copper(II)(acacen) occurred at lower frequencies than those in nickel(II)(acacen).

In a later paper, Ueno and Martell(155) suggested that no relationship should exist between the shifts of the metal specific absorptions and the kinds of metals in the complexes. However, several authors,(156-159) including Thomas and Martell,(159) have used infra-red measurements to predict the relative strengths of the metal-ligand bonds in metal(II) complexes. Stavos, Curran and Quagliano,(158) proposed that the Ni - N bonds were stronger than the Cu - N bonds in the salicylaldiimine chelates, on the basis of the shifts in the frequencies of the metal specific absorption bands.

If the shifts in the metal specific absorptions can be correlated with the strengths of the bonds, the work of Ueno and Martell(153) indicates that the Ni - ligand bonds in nickel(II)(acacen) are stronger than the corresponding Cu - ligand bonds in copper(II)(acacen). Such a situation may also explain the position of equilibrium in the replacement experiment copper(II) - nickel(II)(acacen).

No solvent interaction with nickel(II)(acacen) has been reported, on the basis of visible absorption spectral measurements in various solvents,(41) however Ueno and Martell(154 concluded from studies of the ultraviolet and visible absorption spectra of a number of substituted copper(II) acetylacetone chelates, in methanol, that these compounds contained covalent metal-ligand bonds.
No information is available on the spectrum of copper(II)(acacen) in various solvents.

Duffield and Calvin(6) upon examination of the metal exchange reactions of copper(II)(salen) and copper(II)(acacen), found that the former compound exhibited the faster rate of exchange. These workers proposed that the lower "stability" of copper(II)(salen), compared with copper(II)(acacen) was due to interference with the chelate benzenoid resonance by requirement that the benzene ring of salicylaldehyde, in copper(II)(salen), be quinoidal.
A similar situation may be expected with nickel(II)(acacen) and nickel(II)(salen) complexes. As discussed earlier (p.139) such a relative decrease in "stability" may be correlated with the bond strengths.
Therefore, the slower rate of nickel(II) replacement in

nickel(II)(acacen), compared with nickel(II)(salen), may be explained.

The slower rate of replacement found for the (acacpn) reaction, compared with the (acacen) system, may be explained by the fact that carbon substitution on the ethylenediimine bridge may result in the formation of a complex less able to dissociate, as was the case with nickel(II)(salpn) and nickel(II)(salen).

(v) N,N'-ethylenebis(3-methoxy-salicylideneiminato) nickel(II) [nickel(II)(3-oMe salen)]

The reaction between copper(II) perchlorate (hexahydrate) and nickel(II)(3-oMe salen), in methyl cellosolve at 71.1°C, was found to go nearly to completion (93% substitution) in 36 hours (1.30 x 10^{-3}M each reactant).
The initial rate of replacement was calculated as $R.10^7 = 2.7$ ($sec^{-1} mole\ l^{-1}$), compared with the initial rate of replacement in nickel(II)(salen) viz. [$R.10^7 = 5.8$ ($sec^{-1} mole\ l^{-1}$)] under similar reaction conditions.
The slower rate of replacement found in the methoxy compound supports the existence of stronger nickel-ligand bonds in this compound, compared to those in nickel(II)(salen).

The presence of a methoxy grouping in nickel(II)(3-oMe salen), ortho to the hydroxy group (see Fig.B), may be expected to increase the electron density on the C atom (1), adjacent to the hydroxy grouping, because of the strong -I effect of the methoxy grouping.(160) Such an increase in electron density, will be relayed to the adjacent oxygen atom, giving it a more negative charge, which in turn may be expected to increase the strength of the Ni – O linkage.

Such an increase in the strength of metal-ligand bonding would be expected to result in a slower rate of replacement for this compound, compared to nickel(II)(salen), in agreement with the experimental results.

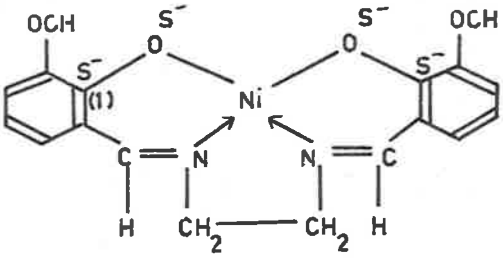


Fig. B.

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EXPERIMENTAL

I Radiochemical Techniques.

(a) Radioactive cobalt.

This was supplied by the United Kingdom Atomic Energy Authorities (Amersham), as the isotope Co^{60}, in a solution of carrier cobalt(II) chloride.

(b) Labelled N,N'-ethylenebis(salicylideneiminate) cobalt^{60}(II).

(i) N,N'-ethylenebis(salicylideneimine).

3-4 ccs of ethyl alcohol were added to 24.4g (0.2 M) of salicylaldehyde, the mixture then poured into 6.0g (0.1 M) of anhydrous ethylenediamine containing a little ethyl alcohol. The mixture was stirred and allowed to crystallize. The product was then recrystallized twice from boiling ethyl alcohol and collected as fine, bright yellow plates.

(ii) N,N'-ethylenebis(salicylideneiminate)cobalt^{60}(II)

N,N'ethylenebis(salicylideneimine)(5.3g 0.02 M) was dissolved in ethyl alcohol (120ccs) and placed in a 500cc flask F, as shown in diagram 1.

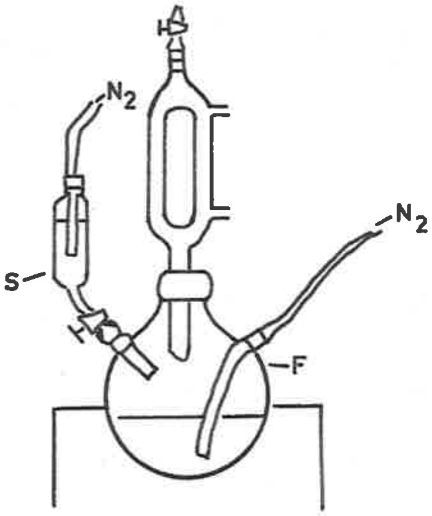

Diagram 1.

Oxygen free nitrogen, (produced by bubbling Cylinder nitrogen through two acid-chromous chloride bubblers, the solutions being prepared by the reduction of acid-chromic chloride with zinc amalgam),(1) was bubbled through the yellow solution of the free base for about 30-40 minutes, the solution meanwhile heated on a water-bath to about 60-70°C.

Cobalt(II) acetate tetrahydrate (5.0g 0.02M), to which was added a small amount of radioactive cobalt^{60}(II) chloride, was heated to boiling with ethyl alcohol (90ccs) until all the solid had been converted to a pink, amorphous powder, which was probably cobalt hydroxide or a basic

cobalt(II) acetate since the solid was insoluble in water. The cobalt(II) mixture was then placed in the separating funnel S and nitrogen passed through it for about 30 minutes, while deoxygenation of the free base solution in F was carried out simultaneously.
The cobalt(II) suspension was then added dropwise to the reaction flask, nitrogen bubbling through the flask continuously. The solid dissolved giving a deep-red solution. Heating was continued for a further 30 minutes with nitrogen passing continuously through the system.

The flask was then allowed to cool, when small maroon prisms (4.3g) were isolated, after filtering the cold solution under a nitrogen atmosphere.
The product was sucked dry on a Buchner flask, nitrogen passing continuously. By this preparation, the solid cobalt^{60}(II) complex was found to be unreactive towards oxygen, under atmospheric conditions.$^{(2)}$

(Found: C, 59.07; H, 4.57; N, 8.35; Co, 17.8 (by combustion). Calc. for $Co[C_{16}H_{14}N_2O_2]$; C, 59.1; H,4.34; N, 8.61; Co, 18.1%).

(c) Substitution Reactions.

The substitution reactions of this complex were studied in pyridine solution, with the exclusion of oxygen. Cobalt(II)(salen) was first prepared by Tsumaki, Pfeiffer, Breith and Lübbe$^{(3)}$.

The complex prepared by these workers showed a tendency to turn brown on exposure to air.

Tsumaki(4) showed this to be due to the absorption of oxygen, by the solid crystalline material.

Calvin and coworkers(5) found that samples of the complex could be prepared which either did or did not absorb oxygen, depending on the method used for synthesis.

The method of West(2) was used to prepare the sample of cobalt(II)(salen), which was used in these studies. The complex prepared in this manner did not absorb oxygen, in the solid state, but underwent oxygen absorption in solutions of organic solvents.

West(2) examined the metal(II) exchange of cobalt(II)(salen) in pyridine, and in the presence of oxygen. He proposed the existence of $[\mathrm{Co(II)(salen)}](O_2)$ or $[\mathrm{Co(II)(salen)}]_2(O_2)$ or a cobaltic complex of (salen) eg. $[\mathrm{Co(III)(salen)}]^+$, or in fact a mixture of these complexes, in solution.

Therefore, in order to examine the substitution reactions of cobalt^{60}(II)(salen), an apparatus was designed so as to study the reactions under nitrogen. This is shown in Diagram (II) p.v.

Oxygen was removed from cylinder nitrogen by passage through two acid-chromous chloride bubblers(1) (as given on p.ii). These bubblers were followed by one containing concentrated sulphuric acid, then a caustic potash tower (for drying purposes) and finally a pyridine bubbler to saturate the

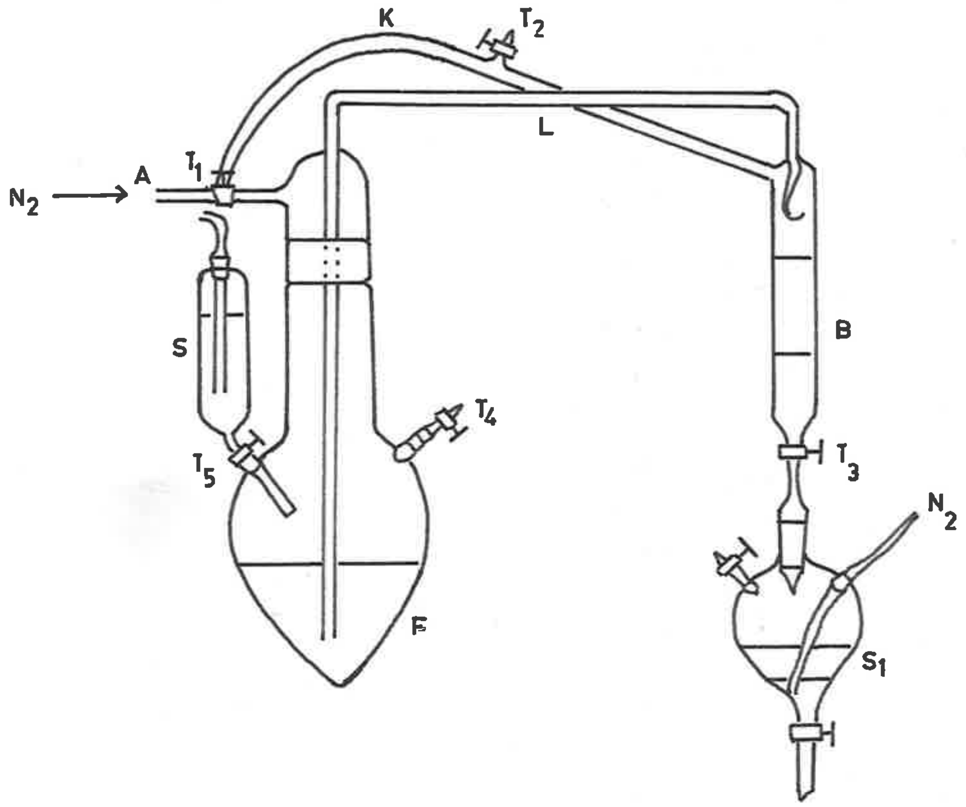

Diagram (II)

the nitrogen stream in order to replace pyridine lost by the bubbling action in the reaction flask F.

A weighed amount of the cobalt^{60}(II) complex in a thin walled glass tube, was dropped into a known volume of pyridine in F. Nitrogen had been bubbling through the pure solvent for some time (15-20 minutes) previously, in order to remove all oxygen from the reaction medium.

The glass tube containing the Co^{60}(II)(salen) was broken and the mixture swirled to dissolve the solid. Nitrogen was kept bubbling for a further 15 minutes.

The reaction vessel was clamped inside a conventional, electrically regulated thermostat water bath, kept at 25° ± 0.1°C, in such a way that the "bulb" of the flask F, was completely immersed. The burette B was outside the bath.

Meanwhile, an equal volume of the metal(II) salt solution in pyridine, at a concentration equal to that of the cobalt(II) complex solution in F, had nitrogen passed through it for some 15-20 minutes.

Purified nitrogen enters the system at A and by manipulation of taps T_1,T_2,T_3 and T_4, may flow through K, B and L, into the reaction flask F.

After the reacting metal(II) salt solution had been added through T_5, the vessel was shaken to ensure thorough mixing. The time when the required volume of solution S had been added, was considered as zero-time for the reaction.

Samples of the reaction mixture in F were taken at various time intervals, by passing nitrogen into the flask F with T_4 closed and forcing the sample through L into the burette B. When the required volume appeared in B, any solution held in L was forced back into the flask F by suitable manipulation of the taps T_1 T_2 and T_4. The required 5cc sample was then delivered from the graduated burette B into the separating funnel S, which contained 25cc of deoxygenated chloroform and 25cc of air-free water. The contents were shaken, under nitrogen, to effect a separation.

Chloroform extracts of cobalt(II)(salen) became brown fairly rapidly even with the precautions taken, due to possible absorption of oxygen from the air. Therefore, only one extraction was made for each sample.

The chloroform and aqueous layers were made up to 50ccs. with absolute alcohol, and aliquots taken and counted.

(d) Measurement of radioactivity.

(i) Geiger tubes.

Measurements of radioactivity were made on solutions using a Skirted Type Liquid Counter Geiger tube (20th.Century, Electronic Ltd. Type M12), of 10cc. capacity. The operating potential of each tube used was given by the manufacturers. In order to reduce the background count the tubes were fitted into a circular lead tower with a removable lead cover. A thickness of 1.5 ins. of lead served to reduce the background to about one-quarter of the value found when unprotected.

(ii) Preparation of Samples for Counting.

Aliquots of the solution obtained after the separation procedure were poured into the Counting tubes. The tubes were filled until the Geiger tube was covered. An increase in the volume of the solution above this mark made no appreciable difference to the number of counts obtained.

(iii) Counting.

Counting was carried out using an Automatic Scaler, Type N530 D (Ekco Electronics Ltd.). Background corrections were the only ones applied to the counts obtained. These were determined by one hour counts on each "counting day". Such corrections were of the order 30 counts/100 secs, A decay correction was unnecessary with Co^{60}(5.3 yrs.) Density corrections were not applied in view of the semi-quantitative kinetic approach of this work.

(e) Purification of Solvents.

(i) Pyridine.

B.D.H. or Anax Pyridine was dried by refluxing over KOH pellets, followed by fractional distillation whenever required. The b.pt. fraction 114.5-115.5°C was collected for use.

(ii) Chloroform.

This was purified by fractionally distilling it through an 18" Dufton column. The b.pt. fraction 60.5-61.0°C was collected for use.

(iii) Water.

De-ionized water was used for all experiments.

(f) Metal(II) Salts.

Analytical Reagent copper(II) acetate (monohydrate) and zinc(II)acetate (dihydrate) were used for the copper(II) and zinc(II) metal replacement reactions with cobalt(II)(salen). B.D.H. hydrated nickel(II) acetate was purified by recrystallization twice from water-acetic acid mixtures.

The green crystals obtained were analysed for nickel by the pyridine-ammonium thiocyanate gravimetric method.(6)

(Found: Ni, 23.4; 22.9% by $[Ni(C_5H_5N)_4](CNS)_2$.
Calc. for $Ni(CH_3COO)_2\ 4H_2O$ Ni, 23.6%).

Pure anhydrous nickel(II) acetate was prepared by dehydrating the pure tetrahydrate (from above) at 100°C, in an Abderhalden apparatus. The anhydrous acetate obtained was stored over silica gel in a desiccator, ready for use.

Nickel(II) perchlorate (dihydrate) was made by treating basic nickel(II) carbonate with 60% perchloric acid. The carbonate was produced by mixing togetheraqueous solutions of A.R. nickel chloride and A.R. sodium carbonate.

The green solution formed on dissolving the basic carbonate in perchloric acid was then slowly evaporated on a water-bath, kept at about 80°C.

The green needles produced were then recrystallized twice from ice-cold water and collected and dried quickly between filter papers.

They were stored over silica gel in a vacuum desiccator.

Nickel(II) analysis using pyridine-ammonium thiocyanate gravimetric procedure indicated that the perchlorate had the formula $Ni(ClO_4)_2\ 2H_2O$. (Found: Ni, 19.6, 19.3% by $[Ni(C_5H_5N)_4](CNS)_2$.
Calc. for $Ni(ClO_4)_2\ 2\ H_2O$ Ni 20.0%).

Cobalt(II) aceatate (tetrahydrate) was purified by recrystallizi

B.D.H. hydrated cobalt(II) acetate twice, from glacial acetic acid-water mixtures.

Cobalt(II) analysis carried out on the red crystalline product indicated the formula, $Co(CH_3COO)_2\ 4H_2O$.

(Found: Co, 23.2, 23.5%, by $[Co(C_5H_5N)_4](CNS)_2$(6a)
Calc. for $Co(CH_3COO)_2\ 4H_2O$ Co, 23.7%.)

II Substitution Reactions with N,N'ethylenebis (salicylideneiminate) nickel(II) [nickel(II)(salen)].

(a) Preparation of N,N'ethylenebis(salicylideneiminate) nickel(II)

This chelate was first prepared by Tsumaki, Pfeiffer, Breith and Lübbe.(3)

(i) Preparation of bis(salicylaldehydate)nickel(II).

An aqueous solution of nickel(II) acetate (tetrahydrate)(5.0g 0.02M) was added to freshly distilled salicylaldehyde (4.9g 0.04M), dissolved in a little alcohol. The green solid was filtered, and washed with alcohol several times. It was used in (ii) below, without further purification.

(ii) Preparation of nickel(II)(salen).

3.0g of finely ground bis(salicylaldehydate)nickel(II was made into a paste with alcohol. 15cc of 10% ethylenediamine were added and the mixture stirred, The paste was then warmed for one hour on a water-bath, after which the orange condensation product was washed with alcohol and ether. The orange chelate was purified by recrystallization, twice from chloroform, once from glacial acetic acid and finally dissolved in pyridine and precipitated with ether, The pure chelate was dried in an oven at 70–80°C for one hour.

(found: C, 59.22; H, 4.59; N, 8.58;
Calculated for $Ni(C_{16}H_{14}N_2O_2)$: C, 59.13; H 4.34; N 8.62)

(b) Metal(II) Salts.

A.R. copper(II) acetate (monohydrate) was used in the replacement experiments.

Anhydrous copper(II) chloride was prepared from A.R. copper(II) chloride (dihydrate) by heating the hydrated compound in a Abderhalden apparatus, at 100°C. The anhydrous brown copper(II) salt, prepared in this manner, was stored in a desiccator over silica gel.

Copper(II) perchlorate (hexahydrate) was prepared in a similar manner to that of hydrated nickel(II) perchlorate. Basic copper(II) carbonate, prepared by mixing aqueous solutions of A.R. copper(II) chloride and A.R. sodium carbonate, was treated with 60% perchloric acid, until the basic carbonate dissolved to give a dark blue solution. The solution was then filtered, and evaporated almost to dryness on a water-bath, kept at about 80°C. The blue crystals were then filtered off and recrystallized twice from ice-cold water. They were stored in a desiccator over silica gel, No loss of weight or change in colour of the copper(II) perchlorate occurred when kept for several months, in such a manner. Analysis on the compound prepared in this way was found to agree with the formula $Cu(ClO_4)_2.6H_2O$.

(Found: Cu, 20.60%; 20.55%; 20.46% as $[Cu(C_5H_5N)_2](CNS)_2$
Calc. for $Cu(ClO_4)_2.6H_2O$, Cu 20.69%).

The "added salts" used in the experiments described in Chapter II viz. LiCl, $NaClO_4$ etc were A.R. or recrystallized

B.D.H. reagents.

(c) Purification of Solvents.

(i) Pyridine.

This solvent was purified by the method outlined on p(viii).

(ii) Ethyl Alcohol.

Absolute alcohol was dried by refluxing over KOH pellets for several hours, followed by fractional distillation through an 18" Dufton column. The b.pt.fractions 77.5 - 78.0°C was collected.

The alcohol purified in such a manner was passed through a Vapour Refractometer, Model 154. A small peak due to water was obtained in the chromatogram, however this was estimated at 0.5% of the total alcoholic content.

(iii) Methyl Alcohol.

B.D.H. Spectroscopic methyl alcohol was used without further purification. Gas chromatogram analyses indicated a very small amount of impurity present (water approx. 0.1%).

(iv) 2-Methoxy ethanol (methyl cellosolve).

Commercial methyl cellosolve was dried by refluxing over anhydrous barium oxide for several hours, followed by fractional distillation through an 18" Dufton column. The boiling point fraction 123.5 - 124.5°C was taken.

(v) Acetonitrile.

Acetonitrile (B.D.H.) was dried by distilling it from P_2O_5 in an all glass apparatus closed with a P_2O_5 tube, some five or six times, until the colour of the oxide remained unchanged. The final distillate from this procedure was then distilled from anhydrous potassium carbonate, the b.pt. fraction 81.0 - 82.0°C collected. Finally, the acetonitrile was distilled alone, and the pure solvent collected; b.pt. range 81.5 - 82.0°C.

The solvent after purification was used almost immediately for the replacement reactions.

(vi) Dioxan.

One litre of Purified Dioxan (L.Light Ltd.), 14mls. of conc. HCl and 100mls. of water were refluxed for 6-12 hours, while a slow stream of nitrogen was bubbled through the solution to remove the acetaldehyde. The cold solution was treated with KOH pellets with shaking until some remained undissolved. The aqueous layer was then run off and most of the water was removed by keeping the solution over KOH pellets for a further 24 hours.

The solution was then refluxed over excess sodium wire for a further 10-12 hours, until the reaction ceased and the sodium remained bright. Finally, the dioxan was distilled from sodium and the b.pt. fraction 101.0 - 101.5°C collected.

(vii) Water.

Conductivity water was used for the separation and analytical procedures used in the replacement experiments with nickel(II)(salen) and other nickel(II) complexes.

(viii) Chloroform, used in the separation procedures, was purified by distillation.

(d) Substitution Reactions.

The method used to follow the replacement reactions wit nickel(II)(salen) and other nickel(II) complexes, is described below.

The reactions were carried out in glass reaction vessels having the shape of an inverted "Y", with a ground glass socket bearing a stopper at the top. In one arm of the vessel was placed 5mls. of the metal(II) salt solution, while in the other arm, 5mls. of the nickel(II) chelate solution. The concentrations of the two solutions placed in the arms of the reaction vessels were equal, and of such values, that on mixing, the desired concentration for the experiment was obtained. The reaction vessels were then placed in the thermostated bath overnight, so as to allow the solutions to come to temperature equilibrium.
The reactions were started by inverting and vigorously shaking the vessels. At the initial time of mixing (time = 0) a stopwatch was started.

At various time intervals (time = t), the vessels were taken from the thermostat and plunged into an ice-water bath, so as to "stop" the reaction. After some 30secs. in the ice-water bath, 5ml. samples of the reaction mixtures were taken, and run into 15ccs. of chloroform and 15ccs. of water, in a separating funnel. Separation of the chelate and metal ion components was effected by shaking the funnel vigorously. The complexes extracted into chloroform while the free copper(II and nickel(II) ions remained in the aqueous solution.[a] The aqueous layer was then run into a 50ml. beaker, 20cc. of A.R. sodium acetate - A.R. acetic acid-water buffer (pH 4.63) added, and the whole made up to 50ml. in a volumetric flask.

The solution was then ready for the estimation of the concentration of copper(II) ions.

Reactions in Acetonitrile.

For the replacement reaction in this solvent it was not necessary to cool the reaction mixtures in an ice-water bath, because of the low temperature used for this substitution reaction. ($T = 15.9 \pm 0.1^\circ C$).
Samples of the reaction mixtures and standard solutions were taken directly from the reaction vessels and run into $CHCl_3/H_2O$ mixtures in separating funnels, all being maintained at 16°C.
The time (t) of reaction was taken as the time when the contents of the separating funnel were first shaken.

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[a] Separation of the chelate and metal ion components, when using pyridine as a solvent, proved difficult. A brown layer was produced at the interface of the chloroform and aqueous layers on shaking the funnel. However, as such a brown layer occurred on treating both the reaction mixtures and standard copper(II) solutions, and further, since the same techniques were used in the separation procedures etc., the error of separation was assumed constant.

Preparation of N,N'-ethylenebis(salicylideneiminato)-copper(II). [copper(II)(salen)].

The method used for the preparation of copper(II)(sale
was analogous to the one used for the nickel(II) complex (p xi).
A.R. copper(II) acetate (monohydrate) was used as the salt, in the preparation of bis(salicylaldehydato) copper(II).
Copper(II)(salen) made by this method was recrystallized three times from chloroform. The dark green crystals obtained were dried in an oven, at 80°C, for two hours.

(found: C, 58.52; H, 4.47; N, 8.21;
calc. for $Cu(C_{16}H_{14}N_2O_2)$: C, 58.30; H, 4.29; N, 8.49).

The sample of hydrated nickel(II) perchlorate, used in the replacement reaction between nickel(II) ions and copper(II)(salen), was prepared by an analogous method to that of the dihydrate (p.ix).
However, nickel(II) analysis using pyridine-ammonium thiocyanate indicated that the perchlorate had the formula $Ni(ClO_4)_2.6H_2O$.

(e) Analysis of the Aqueous layer for copper(II).

Copper was estimated colorimetrically using 2,2'-Diquinolyl(Cuproine) as the reagent.(7) Depending upon the concentration used in the experiments, a known volume of an aqueous extract was placed in a separating funnel.
A few crystals of A.R.Hydroxylamine Hydrochloride were added, to reduce the copper(II) ions to copper(I) ions, then 15ml. of 0.02% Cuproine in redistilled B.D.H. iso-amyl alcohol, were added.
The funnel was shaken for some minutes, after which the violet organic layer was run out into a 20ml. volumetric flask. The aqueous aliquot was re-extracted with a further 3ml. of the 0.02% Cuproine solution, after which the organic layer was run into the volumetric flask. The violet solution was then made up to the mark with pure iso-amyl alcohol.

In all experiments, irrespective of the molarity of the reactants used in the substitution experiments and the volume of the aqueous extract taken, the second extraction was found to remove the remaining copper(I) ions, as the Cu(I)-2,2'-Diquinolyl complex.
The optical densities of the violet solutions were read at 5400 Å,(7) on a Unicam S.P. 500 Spectrophotometer, using 1cm.silica cells.

To prepare the standard curves of copper(II) concentration versus optical density, solutions containing copper(II) ions corresponding to 0%, 20%, 50% and 80% substitution were made from each copper(II) reactant solution eg. if the initial concentration of the copper(II) solution used in the substitution experiment was 2.60 x 10^{-3}M, four solutions corresponding to 1.30 x 10^{-3}M, 1.04 x 10^{-3}M, 6.50 x 10^{-4}M and 2.60 x 10^{-4}M were prepared, by appropriate dilution of the copper(II) reactant solution.

These four solutions were then subjected to the same procedures (eg. kept in the water-bath overnight, cooled, 5ml. samples taken etc.), as those of the reaction mixtures, and the optical densities of the extracted Cu(I)-2,2'-Diquinolyl-iso-amyl alcohol solution taken, at 5400Å.

A typical standard optical density versus copper(II) concentration plot is shown in Fig.1. The graph shown is for the $Cu(ClO_4)_2.6H_2O$ - Ni(II)(salen) replacement in methyl cellosolve, at 71.1°C (1.30 x 10^{-3}M each reactant). The concentrations of free copper(II) ions in the reaction mixtures were then read directly from the standard graphs.

The volume of the aqueous extract was chosen, for each concentration, so as to give a maximum optical density of the violet solution ie. (0% substitution or 100% copper(II) ions), in the region of 0.6 - 0.7. When the concentration of copper(II) after mixing was 1.30 x 10^{-3}M, 20ml. of the aqueous extract was found suitable to give such an optical density maximum of 0.6 or 0.7. Similarly, when the concentration of copper(II) after mixing, in the reaction, was 5.20 x 10^{-3}M, 5ml. of the aqueous extract gave a reading

Standard optical density versus concentration graph.

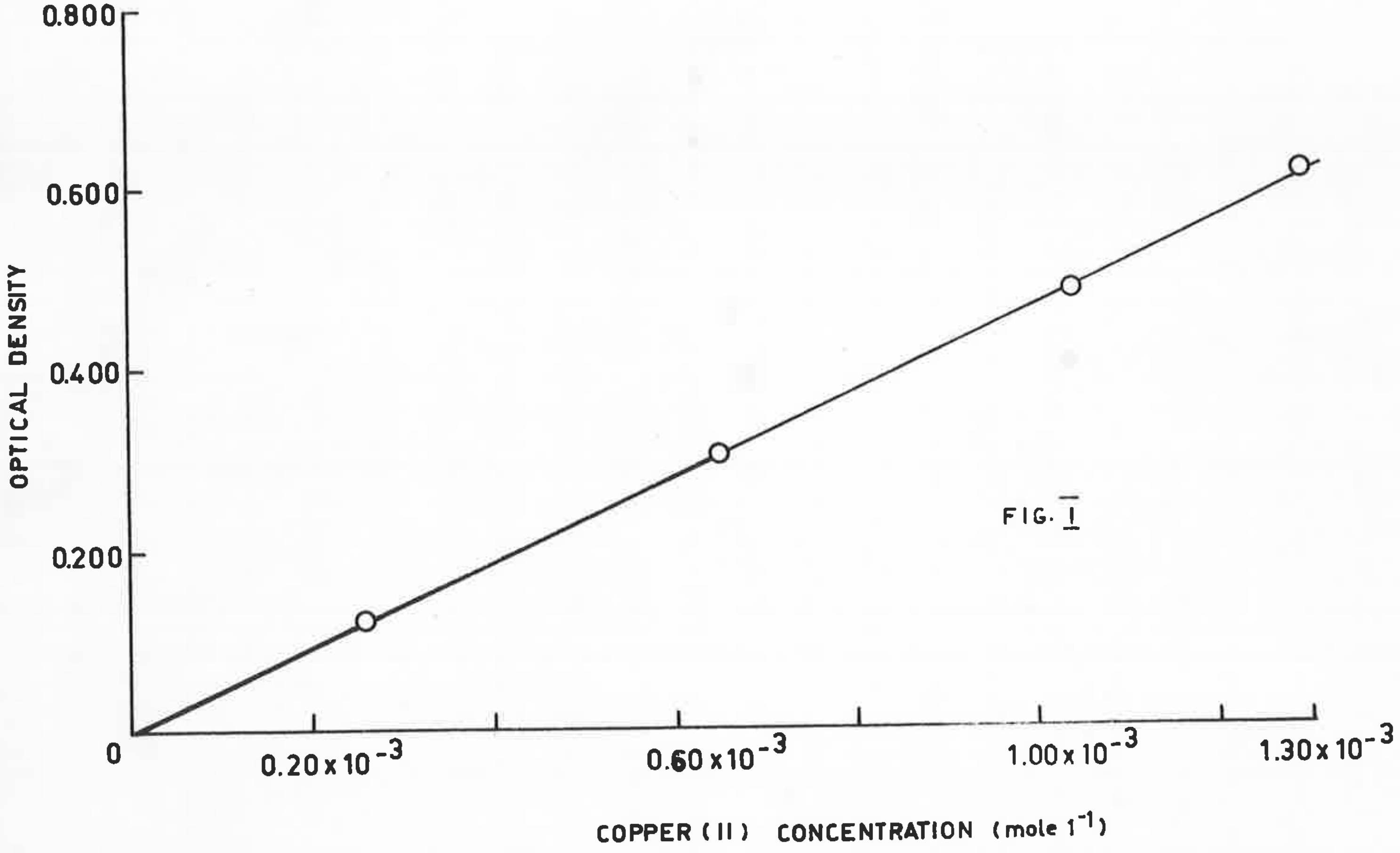

FIG. I

corresponding to 0.6 or 0.7 for 0% substitution, etc.

Extraction of copper(II)(salen) into the aqueous layer.

Solutions of 1.30 x 10^{-3}M copper(II)(salen) in alcohol, pyridine and methyl cellosolve were made up. 5ml. of each of the solutions were taken and run into 15cc. of chloroform and 15cc. of water, contained in separating funnels. The contents of the funnels were shaken, and the aqueous layers separated, after which the solutions were tested for copper(II) ions with 2,2'-Diquinolyl. No violet colours were produced from the solutions of the copper(II) complex in alcohol and methyl cellosolve, however a slight violet colouration resulted on testing the aqueous layer as a result of the extraction of the pyridine solution.
The concentration of copper(II) ions, measured in this way, was found to be $<$ 2% of the total copper(II) content. No corrections were made to the calculations of the initial rates of the replacement experiments, when using pyridine as a solvent.

Measurement of Spectra.

All spectra were measured on a Unicam S.P. 500 Spectrophotometer, using silica cells. A constant temperature cell housing (S.P. 570) was used for all spectra taken at high temperatures. The cell compartment, supplied with heating liquid by a thermostat water-bath, could be maintained at a given temperature between 25°-80°, ± 0.5°C.

III. Substitution Reactions with other nickel(II) complexes.

Preparation of Nickel(II) Complexes.

a. Preparation of N,N'-1,2-phenylenebis(salicylideneiminato)[nickel(II)(salophen)].

This compound was first prepared by Tsumaki, Pfeiffer, Breith and Lübbe(3). This preparation is given below.

2.0gm. of bis(salicylaldehydato)nickel(II) and 1.5gm. of o-phenylenediamine were mixed to a thick paste, in alcohol. The mixture was warmed for one hour on a water-bath. The green colour of bis(salicylaldehydato)nickel(II) disappeared and the colour became deep red-brown after some 30 minutes. The precipitate was filtered off and washed with alcoholic ether.

It was purified, by first dissolving it in chloroform and reprecipitating with ether, and then recrystallizing from glacial acetic acid.

The dark red crystals were dried in an oven at 70-80°C.

(Found: C, 63.85; H, 3.80; N, 7.37;
Calc. for Ni($C_{20}H_{14}N_2O_2$): C, 64.38; H, 3.79; N, 7.51).

(b) Preparation of N,N'-ethylenebis(1-methyl-3-oxobutylideneiminato)nickel(II) [nickel(II)(acacen)]

(i) Preparation of the Schiffs base.

10.0g (0.1M) of acetylacetone in 4-5cc of absolute alcohol were added to 3.0gm. (0.05M) of anhydrous ethylenediamine. The resulting light yellow solid was filtered off and recrystallized twice from absolute alcohol.

(ii) Preparation of nickel(II)(acacen).

2.2gm. (0.01M) of the Schiffs base were dissolved in a little alcohol, and added to a solution of 2.5gm.(0.01M) of nickel acetate (tetrahydrate) in aqueous alcohol. The mixture was heated for some 30 minutes on a water-bath, after which the red solid was filtered off and recrystallized three times from absolute alcohol.

(Found: C, 52.09; H, 6.51; N, 10.14.
Calc. for $Ni(C_{12}H_{18}O_2N_2)$ C, 51.29; H, 6.46; N, 9.97)

(c) Preparation of N,N'-1,2-propylenebis(acetylacetoneiminate)nickel(II) [nickel(II)(acacpn)]

(i) Preparation of the Schiffs base.

10.0gm (0.01M) of acetylacetone in 4-5cc. of absolute alcohol were added to 3.7gm. of 1,2-propylenediamine. The resulting light yellow solid was filtered off and recrystallized twice from absolute alcohol.

(ii) Preparation of nickel(II)(acacpn)

2.4gm. (0.01M) of the Schiffs base were dissolved in a little alcohol and added to a solution of 2.5gm. of nickel(II) acetate (tetrahydrate) dissolved in aqueous-alcohol. The red solid produced was filtered and recrystallized three times from absolute alcohol.

(Found: C, 53.62; H, 6.78; N, 9.63;
Calc. for Ni($C_{13}H_{20}O_2N_2$) C, 52.93; H, 6.84; N, 9.49.)

(d) Preparation of N,N'-1,2-propylenebis(salicylideneiminate) nickel(II) [nickel(II)(salpn)]

(i) Preparation of N,N'-1,2-propylenebis(salicylideneimine).

12.2gm. (0.1M) of salicylaldehyde were dissolved in a small amount of absolute alcohol and added to 3.7gm. (0.05M) of 1,2-propylenediamine. The yellow solid was filtered off and recrystallized once from absolute alcohol.

(ii) Preparation of nickel(II)(salpn)

2.8gm. (0.01M) of N,N'-1,2-propylenebis(salicylideneimine) were dissolved in a little alcohol and added to 2.5gm. (0.01M) of nickel(II) acetate (tetrahydrate) dissolved in aqueous-alcohol. The red solid formed was heated on a water-bath for 30 minutes, then filtered, and recrystallized twice from chloroform and once from glacial acetic acid. Final purification was effected by dissolving it in pyridine and re-precipitating with ether.
The orange-red solid was dried in an oven at 70-80°C for one hour.

(Found: C, 59.82; H, 4.92; N, 8.38
Calc. for Ni($C_{17}H_{16}O_2N_2$) C, 60.23; H, 4.76; N, 8.27)

(e) Preparation of N,N'-ethylenebis(3-methoxysalicylideneiminato) nickel(II). [nickel(II)(3-oMe salen)]

(i) Preparation of N,N'-ethylenebis(3-methoxysalicylideneimine.).

12.2gm. (0.1M) of 3-methoxysalicylaldehyde(o-vanillin) in 5cc. of absolute alcohol were added to 3.0gm. (0.05M) of ethylenediamine. The solid was filtered off and recrystallized twice from alcohol.

(ii) Preparation of nickel(II)(3-oMe salen)

3.3gm (0.01M) of N,N'-ethylenebis(3-methoxysalicylideneimine) were dissolved in absolute alcohol and 2.5gm (0.01M) of nickel acetate (tetrahydrate) in aqueous-alcohol, added. The red crystals produced were heated on a water-bath, at 60-70°C, for two hours.
They were filtered, and washed three times with boiling alcohol and twice with boiling water.
The red crystals were dried in an oven at 60-70°C.

(Found: C, 56.67; H, 4.77; N, 7.44;
Calc. for $Ni(C_{18}H_{18}O_4N_2)$ C, 56.15; H, 4.72; N, 7.28)

Substitution Reactions.

The method used to study the replacement reactions using these five complexes was similar to that used to study the reactions of nickel(II)(salen).
For each of the reactions given in Chapter III, standard optical density versus concentration curves were drawn, from

which the concentrations of free copper(II) ions, in the reaction mixtures, could be read.

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Substitution Reactions in some Transition Metal Chelate Compounds.

Summary of the Thesis presented by W.W.FEE for the degree of Ph.D at the University of Adelaide.

The substitutions of cobalt(II) ions in N,N'-ethylenebis(salicylideneiminato)cobalt(II), by copper(II), nickel(II), cobalt(II) and zinc(II) ions have been examined, in pyridine. The equilibrium positions found for the replacement experiments have been correlated with the expected stabilities of the chelates produced as a result of such substitution reactions viz. Cu(II) > Ni(II) > Zn(II), in stability.
Further, the rates of replacement of cobalt(II) ions from N,N'-ethylenebis(salicylideneiminato)cobalt(II) by nickel(II) have been found to depend upon the types of nickel(II) species, present in solution.

The rates of replacement of nickel(II) ions from N,N'-ethylenebis(salicylideneiminato)nickel(II) by copper(II) ions, in methyl cellosolve, at 70°C, have been shown to depend upon the types of copper(II) salts used for the reactions, and to be influenced by added salts. Spectral measurements have been used to identify the types of copper(II) species and nickel(II) complexes, present in solution.
The rate of replacement of nickel(II) was found to be greater in solvents of higher dielectric constant. Such a result has been correlated with the nature of the copper(II)

species in solution, and upon the increased ability of nickel(II)(salen) to dissociate in higher dielectric constant solvents.

Two mechanisms of reaction, for the replacement of nickel(II) ions from nickel(II)(salen), have been proposed, on the available experimental data and on the basis of Crystal Field calculations.

The rates of replacement of nickel(II) ions by copper(II) ions from a number of diamagnetic nickel(II) chelate compounds have been correlated with the bond strengths of the nickel-ligand linkages or with the effects of substituents upon the rates of dissociation of the nickel(II) complexes.