MECHANISTIC STUDIES IN RUTHENIUM CHEMISTRY

By

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A thesis presented for the degree

Doctor of Philosophy

in

The University Of Aston in Birmingham

October 1979

SUMMARY

MECHANISTIC STUDIES IN RUTHENIUM CHEMISTRY

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Submitted for the degree of PhD. October 1979

The studies described in this thesis are predominantly concerned with the investigation of possible starting compounds of use in preparative ruthenium chemistry. Especially with those compounds which might lead conveniently to the formation of compounds of interest in mechanistic and photochemical studies.

The synthesis of various Schiff base complexes of ruthenium (ll) and (lll) using the ligand N, N'-ethylenebis (salicylideneimine) has been studied. Some complexes containing different unidentate ligands have been prepared and examined. The behaviour of bis(triphenylphosphine)-N,N'-ethylenebis(salicylideneminato)ruthenium (ll) in alcohol or acetonitrile as solvent has been studied spectrophotometrically, as has the irradiation of bis(triphenylphosphine) N,N-ethylenebis(salicylideneiminato)ruthenium (ll) in inert and air atmosphere.

The preparation of water soluble sulphonated phthalocyanine was attempted and the treatment of this water soluble ligand with different metal ions including ruthenium (ll) examined. This time consuming topic has not been taken to its limits since it has proved impossible to obtain reliable analytical results, which are necessary for the characterization of products.

The preparation of the ethanolic blue solution obtained by the reduction of ruthenium trichloride using hydrogen and Adams catalyst has been investigated. The rate of formation of the blue solution and the effect of temperature and various concentration of catalyst have been studied spectrophotometrically, and attempts made to utilize the solutions preparatively.

Various procedures were attempted for the preparation of dichlorotetrakisdimethylsulphoxideruthenium (ll) complexes as readily available intermediates. These are described as also are the results of kinetic and mechanistic studies on the claimed red isomer, which undergoes a slow isomerization in alcoholic solution.

Key words

Ruthenium
Phthalocyanine
Schiff base
Dimethyl sulphoxide

This work was carried out between 1976-1979 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

M. Hekmat

M.Hekmat

TO MY MOTHER AND TO THE MEMORY OF MY FATHER

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Dr.J.D.Miller for his supervision.

I should also like to thank Professor W.R.McWhinnie for many helpful discussions.

My thanks go to the members of the technical staff in the Department of Chemistry in the University of Aston for help in obtaining spectra and analytical data.

I am most grateful to Mrs. C.Shabani for typing the manuscript.

Finally, I am indebted to Pars University for a reserch assistantship.

NAME	ABBREVIATION
Schiff base	SBH_2
N,N'ethylenebis(salicylideneimine)	Sal_2enH_2
N,N'-ethylene(salicylideneimine)	SalenH
N,N'ethylenebis(penta-2,4,-dione-monoimine)	$acac_2enH_2$
Phthalocyanine	PC
Dimethyl sulphoxide	DMSO
Dimethyl sulphide	DMS

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CHAPTER ONE

(1.1.1) GENERAL INTRODUCTION

Since most of the work in this thesis is concerned with compounds of ruthenium the major part of this introductory chapter will be concerned with a brief description of the relevant chemistry of ruthenium.

Ruthenium is one of the six platinum metals, occuring immediately below iron in Group VIII of the periodic classification.

Mn	Fe	Co	Ni	Cu	
Te	Ru	Rh	Pd	Ag	platinum metals.
	Os	Ir	Pt	Av	

it has

Atomic number	44
Atomic weight	101.1
Electronic configuration	$4d^7 5S^1$

Ruthenium was found by F Wohler$^{(1)}$ to occur as the mineral laurite, RuS_2 or $(Ru,Os)S_2$ in the platinum washings from the Transvaal,Borneo and Oregon. H. Debray and C.Claus, observed that the ruthenium favours the osmiridium. When ruthenium is required, it is usually extracted from osmiridium. Ruthenium-syserskite has 18.3 percent of ruthenium; and ruthenium neujanskite 4.7 to 13.4 percent. Osmiridium is an alloy of osmium and iridium containing small proport-

tions of rhodium and ruthenium. In some cases, about 6 percent of ruthenium is present. E. Fremy(1) and H. St. C. Deville and H. Debray found that when osmiridium is roasted in air or oxygen, much of ruthenium is volatized as oxide which can be easily reduced to the metal by heating it in a current of hydrogen. C. Claus(1) obtained ruthenium from osmiridium, by washing the powdered mineral with hydrochloric acid, and then heating to low redness its mixture with sodium chloride in a current of moist chlorine. The aqueous extract of the cold mass was concentrated, mixed with a few drops of ammonia and heated, where-upon osmium and ruthenium dioxides were precipitated. The precipitates of these oxides were washed with nitric acid, and heated with acid in a retort until the free acid and osmic acid had distilled over. The dry contents of the retort were fused with potassium hydroxide, and the cold mass dissolved in cold water. The clear liquid, separated from the sediment, was neutralized with nitric acid, when black ruthenium dioxide was precipitated. The washed and dried oxide, when reduced in hydrogen, furnished powdered ruthenium.
O.W.Gibbs(1) recommended removing iridium and rhodium from the solution with other platinum metals by treatment with cobalt trichloride which precipitates $[Co(NH_3)_6]$ $[IrCl_6]$ and $[Co(NH_3)_6]$ $[RhCl_6]$.(1)

Ruthenium is a hard white metal, insoluble in mineral acids and in aqua regia. Ruthenium reacts with fused sodium hydroxide to give sodium ruthenate Na_2RuO_4. It also combines with oxygen and chlorine on heating, to give mainly RuO_2 and $RuCl_3$ respectively.

C. Claus dissolved ruthenium sesquioxide or ruthenium hemitrioxide Ru_2O_3 in hydrochloric acid, and evaporated the solution to dryness to obtain ruthenium trichloride $RuCl_3$. W.R.Crowell and D.M.Jost(1) found that solutions of ruthenium compounds in hydrochloric acid are reduced by potassium iodide to the tervalent state. L.Wohler and P.Blaz obtained only trichloride by the action of chlorine on finely divided ruthenium between 380° and 420°, and L. Wohler and co-workers, by heating the chloroperruthenite in hydrogen and 400°C. A. Joly heated ruthenium in chlorine and found that the transformation to trichloride incomplete, but if the chlorine be mixed with carbon monoxide, chlorination readily occurs at 350°. The trichloride is also produced when the tetroxide is dissolved in chlorine water, and the solution evaporated.

The modern precious metals industry produces a commercial normally called 'commercial ruthenium trichloride' which is in fact Ru IV compounds which contain both oxygen and chlorine attached to ruthenium but Ru:Cl ratio is approximately 1:3. This material is the normal material for most preparations and for convenience is called ruthenium trichloride, which is not a very good name for it, since it is in fact misleading and is only part of the complete designation.

The trichloride is hygroscopic, and is readily soluble in water, and in alcohol. The concentrated aqueous solution is brown but when diluted, it is orange-yellow. A. Joly(1) reported that if the aqueous solution be evaporated to a syrupy mass, on cooling, it solidifies to a reddish brown mass of ruthenium hydrotetrachloride $2RuCl_3.HCl.H_2O$ and when gently heated it forms a black mass of the $2RuCl_3.3H_2O$, which yields a brown solution with cold water.

The chemistry of ruthenium is characterized by the large number of oxidation states that it can assume in its compound. We may divide these into:

-2,0,(1),2	3,4	5,6,7,8
low	usual	high

The low oxidation states are obtained almost exclusively in combination with ligands which have strong π -acceptor properties, i.e., those which have unoccupied orbitals of suitable energy and symmetry, and which can overlap effectively with filled d-orbitals on the metal. By this back donation method a large build up of negative change on the metal due to the σ-donation of the ligand is avoided.

The complexes of Ru (11) are nearly all octahedral and kinetically inert. The fact that they are diamagnetic indicates that they contain the low spin d^6 Ru (11) ion, the six electrons fill the T_2g level which is lower on account of splitting of the 4d orbitals by the ligand field.

The complexes of Ru (111) are fairly numerous, but the number of different types is rather small. Examples Fluoro, Chloro, Bromo but no Iodo complexes are known. Those complexes with oxygen ligands well characterized like acetylacetonate and oxalates, the +4 state for ruthenium is also quite common. The tetrahalides $Ru\ x_4$ (x = F, Cl) are known. A number of compounds are known which contain Ru (IV) atoms linked by oxygen bridges like Ru_2OCl_6, $K_4\ Ru_2OCl_{10}\ .H_2O$. The high valency states of ruthenium are found almost exclusively in combination with oxygen or fluorine.

As this thesis deals mainly with ruthenium (11) chemistry, a brief review of the field is appropriate.

Ruthenium (11) ammine complexes are known, e.g. $Ru(NH_3)_6\ Cl_2$,(2) as very air sensitive orange crystals formed by the zinc reduction of "ruthenium trichloride" in the presence of ammonia; $[Ru(NH_3)_5]^{2+}$ or $[Ru(NH_3)_5(H_2O)]^{2+}$ formed by the reduction of ruthenium (111) Penta-ammino species.(3) Ruthenium trichloride was claimed to form a hydrazine complex but subsequent work(4) has shown that the compound is in fact the ruthenium (11) species $[Ru(NH_3)_5N_2]Cl_2$. Similar complexes with various amines are known, e.g. $[Ru(en)_3]^{2+}$ (5) being made by treating ruthenium trichloride with zinc and ethylenediamine; the non ionic compounds $Ru(Py)_4Cl_2$ (6) $Ru(Phen)_2X_2$ (7,8) and $Ru(bi\ Py)_2X_2$ (7,8) have also been made.

A large group of ruthenium (11) chemistry involves the phosphine carbonyl complexes. A very versatile precursor for the formation of ruthenium carbonyl phosphines and ruthenium carbonyls generally is the red solution formed by passing carbon monoxide through a refluxing solution of ruthenium trichloride. Addition of phosphine PEt_3 to this solution gives trans-$RuCl_2(CO)_2(PEt_3)_2$ (9); the Cis-isomer can be made by heating the trans isomer in solution.

Refluxing the red solution with stannous chloride formed the anionic species $[RuCl_2(CO)_2(SnCl_3)_2]^{2-}$ which reacted with pyridine to form $Ru(Py)_2(CO)_2(SnCl_3)_2$; with diethyl sulphide the cation $[Ru(Et_2S)_3(CO)_2(SnCl_3)]^+$ was formed (10). Treatment of the red solution with dithiocarbonates or tetra-alkylthiuram disulphides resulted in the formation of the monocarbonyls and dicarbonyls $Ru(R_2NCS_2)_2(CO)$ and $Ru(R_2NCS_2)_2(CO)_2$ depending on the reaction conditions (11). With thiophenol the red solution formed dicarbonyl $Ru(C_6H_5S)_2(CO)_2$ (11). The red carbonyl solution was found to react slowly at room temperature to yield the chloro bridged species $[\mathrm{RuCl_2(CO)(C_7H_8)}]_2$(12) with norbornadiene or with cyclo-octal 1, 5 dien, on refluxing.

An interesting group of ruthenium (11) and ruthenium (0) olefin compounds comprises the π-cyclopertadienyl species, ruthenocene $\mathrm{Cp_2Ru}$(13) and, of perhaps more synthetic chemical importance, the mono-π-cyclopentadienes. The latter are derived from $[\mathrm{CpRu(CO)_2}]_2$,(14) by way of the iodide π-$\mathrm{CpRu(CO)_2I}$ or the anion $[\pi\text{-}\mathrm{CpRu(CO)_2}]^-$(15) to give the alkyl and hydrido compounds π-$\mathrm{CpRu(CO)_2R}$, where R is H, $\mathrm{CH_3}$ or $\mathrm{C_2H_5}$. With the sodium salt, $\mathrm{Na}[\pi\text{-}\mathrm{CpRu(CO)_2}]$, a series of fluoro compounds is reacted to give species of the form CpRu(CO)X, where X is $\mathrm{CF = CF\text{-}CF_3}$, $\mathrm{CycloC_6H_9}$ etc.......

Not very many stable diene complexes of ruthenium have been characterized. The strongly chelating dienes, cyclo-octa 1, 5 diene and bicyclo 2, 2, 1-hepta 2, 5 diene, react with ruthenium (111) halides reducing them and forming the polymeric complexes $[\mathrm{RuX_2(diene)}]_n$, where X is Cl, Br or I.(16) The halogen bridges were cleaved by p-toluidine giving the compound $\mathrm{RuX_2(diene)(P\text{-}toluidine)_2}$. Powell and Shaw(17) reacted the cyclo-octadien polymer $[\mathrm{RuCl_2(C_8H_{12})}]_X$ with an allyl Gringard to give the monomeric species formed halogen bridges dimers with allyl halides to give $\mathrm{Ru_2X_2(allyl)_2(diolefin)_2}$.

Anhydrous ruthenium trichloride reacted under Friedel-Crafts conditions with benzene to form the cation $[(\pi\text{-}C_6H_6)_2Ru]^{2+}$ isolated as its perchlorate.(18)

There has, however, in recent years been a marked increase in the number and variety of ruthenium (111) and ruthenium (11) complexes with soft bases. PEt_2Ph and $AsEt_2Ph$ were found(19) to react with ruthenium trichloride to form $Ru(MEt_2Ph)_3Cl_3$, and the arsine analogue $AsMeph_2$ has also been made.(20) Recently Chatt and co-workers(21) have generalised the preparation of RuP_3X_3; where P represents a phosphine such as PEt_2Ph, PMe_2Ph, PPh_3 and X is Cl or Br; by reacting ruthenium trichloride in ethanol and concentrated hydrochloric acid with phosphine for very short reaction times.

Complexes of the group VIII metals, particularly the platinum metals, have been used as catalysts for a variety of homogeneous(22) and heterogeneous reactions, ruthenium systems generally seem to have been less studied than rhodium and palladium counterparts. The current interest in ruthenium complexes as hydrogenation catalyst increase interest in this metal.

I do not propose to quote any further examples since this particular aspect of ruthenium chemistry is not immediately related to the material in this thesis.

The remainder of this introduction will give a more specific account of the work I have done. Our studies are predominantly concerned with the investigation of possible alternative starting compounds in preparative ruthenium chemistry, especially those compounds conveniently lead to the formation of compounds of interest in mechanistic and photochemical studies.

Triphenylphosphine reacts with ruthenium trichloride to give markedly different products depending on the reaction conditions. Addition of two equivalents of the phosphine to ruthenium trichloride in an alcohol results in $Ru(PPh_3)_2Cl_3$(alcohol), triphenyl arsine gives analogous compounds(23) using an excess of triphenylphosphine with very short reaction time in methanolic hydrochloric acid, Chatt(21) made the ruthenium (111) compound $Ru(PPh_3)_3Cl_3$. By refluxing ruthenium trichloride and excess triphenylphosphine in methanol the ruthenium (11) species $Ru(PPh_3)_3Cl_2$ is obtained.(23) The interaction of dichlorotris (triphenylphosphine) ruthenium (11) with sodium salts of various Schiff bases leads to complexes of the type trans-$RuL(PPh_3)_2$ for the quadridentate bifunctional ligands and $RuL_2(PPh_3)_2$ for the bifunctional ligands.(24) These ruthenium (11) compounds were found in this work to be useful precursors. The interaction of dichlorotris(triphenylphosphine)ruthenium (11) with various reagents have been studied and the resulting complexes were formed like $RuCl_2(RCN)_2(PPh_3)_2$, $RuCl_2(amine)_2(PPh_3)_2$

$Ru(\beta$- diKet$)_2(PPh_3)_2$, $Ru(OCOR)_2(PPh_3)_2$.(25)

Ruthenium (11) phthalocyanine has been reported by Kreuger and Kenney.(26) It forms adducts with aniline and O-toluidine containing six molecule of base.

In the preparation of phthalocyanine compounds simple metal salts are heated with phthalodinitrile, phthalic acid, phthalimide or phthalamide producing water insoluble compounds. We have attempted to prepare the metal phthalocyanines by different means trying to prepare the complete ligand first and then to insert the metal into the ligand.

The so called "blue ruthenium chloro complexes" or the "blue ruthenium (11) chloride" have been the subject of many investigations over the last 25 years. This was first noted by Fourcnoy and Vauquelin in 1804(27) who ascribed it to a compound of osmium. Claus(28) observed in 1845 that when ruthenium trichloride was heated with strong reducing agents such as metallic zinc, a deep blue solution was obtained. Various suggestions as to the entities in solution have been made, that of $RuCl_4^{2-}$ by Jorgenson,(29) being noted by Adamson(30) and Halpern.(31) The work reported here consists of the preparation of the ethanolic blue solution by reducing ruthenium trichloride using hydrogen and Adams catalyst.

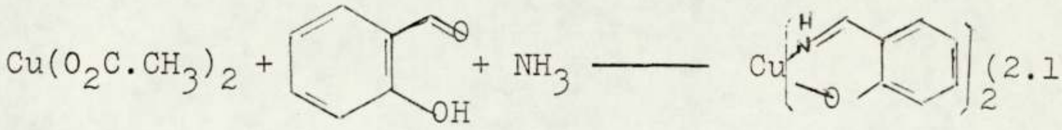
Many dimethyl sulphoxide (DMSO) complexes of transition elements have been reported.(32,33,34) Some dimethyl sulphoxide (DMSO) and dimethyl sulphide (DMS) of ruthenium $[Ru(DMSO)_6]X_3$ (X = Cl, ClO_4) and red isomers of M $[Ru(DMSO)_4Cl_2]$ [M = Na, Bu_4N] (Bu_4N = tetrabutylammonium), $[Ru(DMS)_3Cl_3]$ and $[Ru(DMS)_3Cl_3]_2$ have been prepared by T.Bora and M.M.Singh.(35) Dichloro tetrakisdilmethylsulphoxide Ru (11) was also prepared by the hydrogeration of ruthenium trichloride in dimethylsulphoxide(36) and also it was prepared by Wilkinson and co-workers and used as a potentially useful material.(37)

Preparation of dichlorotetrakisdimethylsulphoxideRuthenium (11) is attempted in this thesis and some mechanistic investigation was carried out on the reported red isomer.(35)

CHAPTER TWO

(2.1.1.) INTRODUCTION: SCHIFF BASE AS A LIGAND

The preparation in 1804 by Eitting(38) of the first Schiff base complex, bis(salicylideneiminato)copper(11), , by the reaction of copper (11) acetate and salicylaldehyde in aqueous ammonia (Equation 2.1) led to the extensive development of the chemistry of these ligands with transition metals.



(2.1)

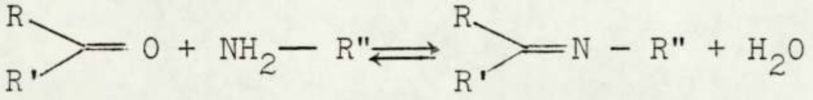
Interest in this area has been stimulated not only by the desire to form new complexes which may have interesting stereochemistry or different donor atoms, but also in the use of these complexes as biological models for vitamine B_{12} and as reversible oxygen carriers. It was found that Co-(Sal_2en) could act as an oxygen carrier.(40)

However, it is apparent from the literature that while the first row transition metals have been covered in great depth the second and the third row elements have been almost neglected. In the case of ruthenium this is particularly surprising considering the amount of interest shown in ruthenium chemistry. In fact the only reports in this area deal with a few simple preparations. Consequently, the present study was undertaken in order to react several ruthenium compounds with the more common tetradentate Schiff base ligands, and investigate the reactions of the resultant complexes.

The reactions carried out here aim predominately to yield 6 - Co-ordinate products with the Schiff base occupying four co-ordinate sites and with various other ligands occupying the other positions.

Before discussing the present work it is, however, necessary to present a brief review of Schiff base complexes.

A Schiff base is defined as the product formed by condensation of an organic carbonyl compound with a primary amine (Equation 2.2), to produce a compound containing a carbon-nitrogen double bond. The lone pair of electrons on the nitrogen has basic properties which enables the formation of stable complexes, although it is usual for there also to be present in the molecule a functional group to allow formation of a 5 or 6 membered ring by chelating to the metal atom.



$$\mathrm{RR'C{=}O + NH_2{-}R'' \rightleftharpoons RR'C{=}N - R'' + H_2O} \qquad (2.2)$$

Although the first Schiff's base complexes were prepared by Eitting and Schiff(40), it was not until later that the first synthetic study of the chemistry of this type of ligand was carried out by Pfeiffer and his co-worker from 1931-1942.(41) They produced a large number of complexes of transition metals with ligands from o-aminobenzaldehyde, salicylaldehyde and pyrole - 2 - aldehyde.

Since then many papers have been published. The most recent comprehensive review to be published is that of Chakrovorty, Holm and Everett(42) which covered the literature to the end of 1964.

Schiff's base complexes have been prepared by a number of methods. Most of these methods only been applied to salicylideneimine ligands but could be extended to other Schiff bases with acidic protons. These Schiff bases derived from pyridine-2-aldehyde are prepared differently as they contain no acidic protons.(43,44,45,46,47,48,49,50,51,52)
(H_2SB = Schiff Base)

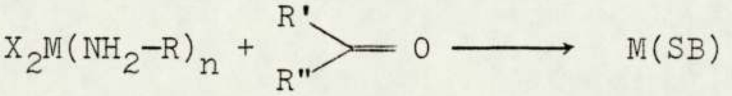
a) $LMX_2 + H_2(SB) \longrightarrow LM(SB) + 2HX$ (2.3)

This method is relatively uncommon but has been shown for the reaction of TiX_4 (where X = Cl(53) or isopropoy)(54) with H_2Sal_2en and are best formulated $\left[Ti(SB)\right] X_2$.

b) $M(Salicylaldehyde)_2 + RNH_2 \longrightarrow M(SB)_2 + H_2O$ (2.4)

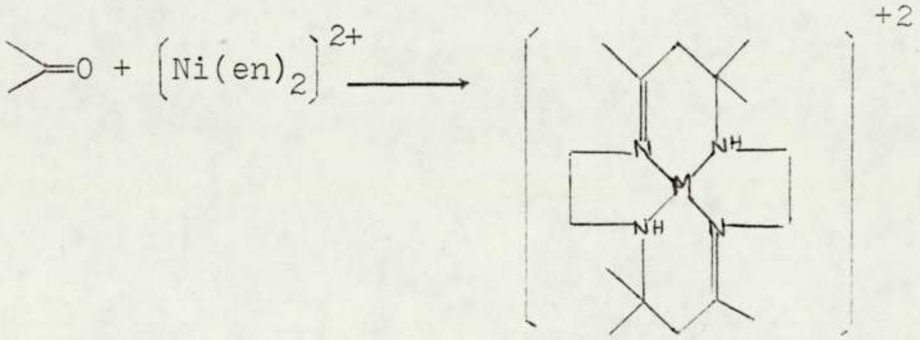
First discovered by Schiff,(40) this method found great use primarily among the first row transition metal complexes(41) eg. tri(salicylaldehyde)-chromium (111)with primary amines yields the expected product but with ethylenediamine forms the ligand $\overset{-}{O}.C_6H_4-C = N-CH_2-CH_2-NH_2$ to give Cr $(Salen)_2X$.(55)

c) the converse(56) reaction has also been shown to be used



$$X_2M(NH_2-R)_n + \begin{matrix} R' \\ \\ R'' \end{matrix}\!\!>\!= O \longrightarrow M(SB)$$ (2.5)

Using M = Ni, Cu a variety of complexes has been prepared. The simple condensation of salicylaldehyde and $Ni(en)_2Cl_2$ in pyridine yielded the expected product $Ni(Sal_2en)$.(57) However a similar reaction using (catechol) (1,3-propanediamine)nickel(11), and salicylaldehyde led to retention of the chatechol and co-ordination of the Schiff base formed only through the nitrogens of the $C = N^{(58)}$. Curtis$^{(59)}$ has studied the reaction of various amine complexes with acetone and other aliphatic carbonyl componds and formed macrocyclic ligands e.g.


(2.6)

d) $LMX_n + RNH_2 + HR'C = O + Base \longrightarrow LM(SB)_n$ (2.7)

This Schiff base is preformed in situ, then equivalent amounts of NaOH, NaOAC, Et_3N or KOBut are added together with the metal precursor. This is by far the most common method and is particularly useful for ligands which are not readily isolated pure.$^{(60)}$ It is not, however, of use if non-aqueous conditions are required except when Et_3N has been used on a base. This is the method employed in the original work described in this thesis.

e) $M(CO)_x + H_2(SB) \longrightarrow M(SB)(CO)_y + H_2 + CO$ (2.8)

Under forcing conditions, such as prolonged refluxing in dimethyl formamide transition metal binary carbonyls react with Schiff bases and oxidation of the metal occurs with formation of the M(SB) complexes. For ruthenium $[Ru\ (Sal_2en)\ (CO)]_2$ and cis-$Ru(Salphen)_2\ (CO)_2$ are formed with M = Fe, Mn only the $M(Sal_2en)$ complexes are formed$^{(61)}$ but molybdenum hexacarbonyl yields $[Mo\ O(Sal_2en)]_2\ O$ was formed.$^{(62)}$

f) $LMX_2 + M'(SB) \longrightarrow LM(SB) + 2M'X$ (2.9)

In these reactions the salt of the Schiff base is preformed either by reaction with Tl (OH)(63), NaH(64), LiOEt(65) which can then be isolated pure and used for reactions under anhydrous conditions. It would seem to be a good method for reactions in non-aqueous solvents.

By far the greatest interest has been shown in the Chemistry of salicylideneimine complexes as compared to the other Schiff base ligand types. This is possibly a consequence of the ready synthesis of the deportonated Ligands.

These complexes are able to serve as models for biological systems, in particular for the reversible addition of dioxygen, discovered in 1938, when it was found that Co-(Sal_2en) would act as an oxygen carrier.(39) The nature of this dioxygen species has been widely studied(66) and the final species formed has been found to be [BCo(Sal_2-en)]$_2$ O_2 (where B is a base such as dmf or pyridine) where the dioxygen bonds as a μ- peroxo species(67) and a mechanism has been proposed(68) involving a monomeric BCo(Sal_2en) O_2 paramagnetic species. The reactions of other M (Sal_2en) complexes with oxygen have been covered in general review on these compounds by Hobday and Smith(69) although none have been found to act as reversible oxygen carriers. The general field has very recently been reviewed by Martell and McLendon.(70)

Because of the wide range of amines and substituted salicylaldehyde available, much detailed work has been carried out on the stereochemistry of the Schiff base complexes. Calligaris(71) et al. have reviewed the stereochemistry of complexes containing tetradentate Schiff bases and illustrate the various possible conformations of Sal_2en in octahedral complexes as either a) planar tetradentate, b) non-planar tetradentate, c) bisbidentate and d) planar tetradentate bridging through the oxygen atoms. The four types are illustrated in the Fig. 2.1.

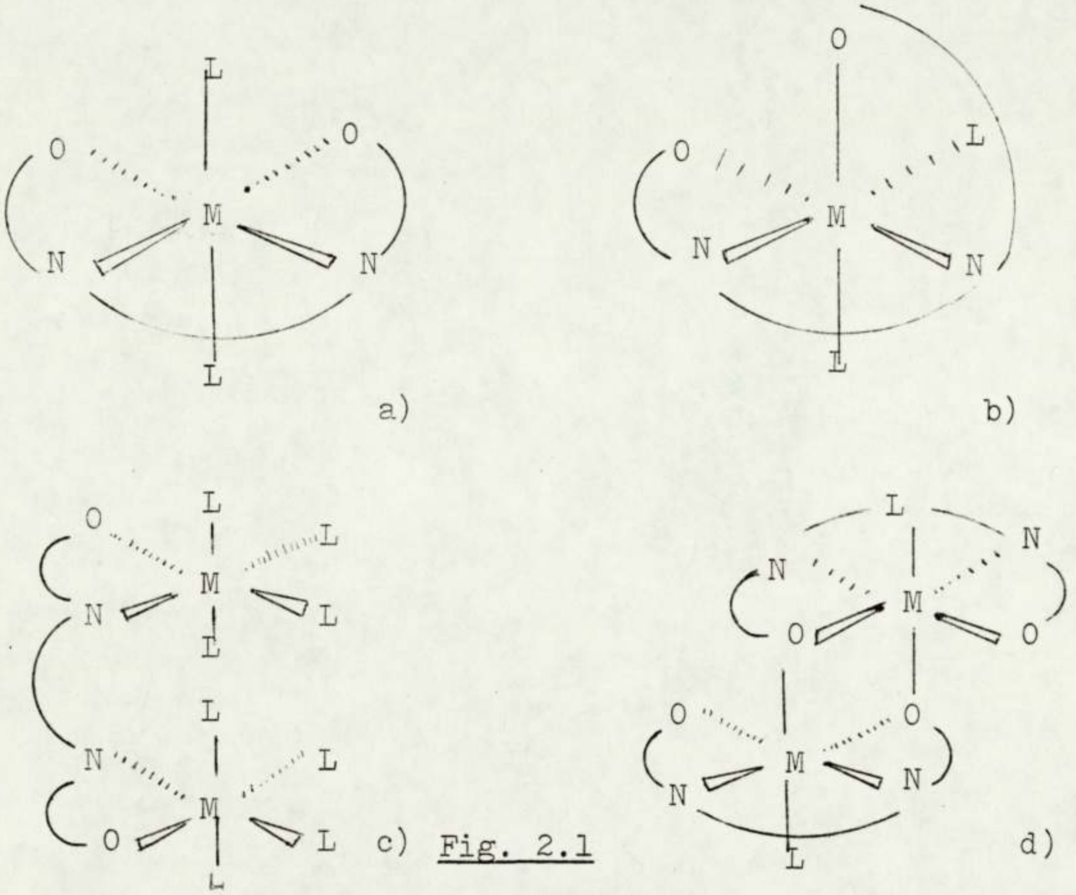


Fig. 2.1

By far the commonest is type a) with the ligand basically planar.

Most complexes of the form $M(Sal_2en)$ have this monomeric structure, e.g., M = Co, Fe, Mn, Cu which were all isolated initially by Pfeiffer. Type b) is less common, although an increasing number of examples has been found of the form M (Sal_2en) L_2, type c) has been shown to exist in Co_2 $[(3 - MeOSal)_2en]_3$ (72) which has both non-planar and bisbidentate Schiff base ligands. A similar structure has been proposed for $Ln_2 \cdot (Sal_2en)_3$ (73) (Ln = lanthanide). Type d) was first recognised in the "inactive" form of $[Co\ (Sal_2en)]_2$ (74) ie. that which does not uptake dioxygen, but has also been found in $[Fe\ (Sal_2en)Cl_2]$ (75) and proposed in $[Ru\ (Sal_2en)\ (CO)]_2$. (61)

The stereochemistry of the first row transition metal bisbidentate and quadridentate Schiff base complexes have been extensively studied because of the possibility of structural change (Fig. 2.2)

$$\text{Planar} \rightleftarrows \text{tetrahedral} \qquad (2.2)$$

In the magnetic properties of the complex, mainly due to steric effects. Holm and his co-workers have studied the subject comprehensively (76) and shown that while Ni (11) preferentially forms planar complexes, Co (11) preferentially forms tetrahedral complexes, and so by making the ligand such that the preferred conformation is no longer the lowest energy state it is then possible to form planar Co (11) complexes and tetrahedral Ni (11) complexes, e.g., $Co(SalMe)_2$ and $Ni(Sal\text{-}isopropyl)_2$ (77) although in a lot of these cases the system is complicated by association to form 5 and 6 co-ordinate species. The resultant stereochemical changes effect pertubations in the magnetic properties of the complexes. This also occurs in Sal_2en

and pyrrole-2-aldimine complexes where increasing the number of methylene groups results in Cu (11) and Ni (11) complexes with no structure changes, but in Co (11) increasing the methylene bridge length to 7-10 methylenes results in a change to a tetrahedral structure.(78)

Co (Sal_2en) complexes have also been widely studied since the discovery of σ—Co alkyl bonds in vitamine B_{12}.(79)

Of course, by substituting functional groups containing acidic protons or basic nitrogens in the amine such that chelation is possible, a large number of complexes have been prepared with not only N and O as donor atoms but also S, P and Se, sometimes resulting in interesting stereochemistries and polymerisation. These areas have been reviewed recently by Bertrand(80) and Hodgson.(81)

Finally, in industry, Schiff base complexes have been used to stabilise polyolefins(82) and as additives in the petroleum industry,(83) although these appear to be fairly small scale uses.

EXPERIMENTAL PROCEDURE

(2.2.1) PREPARATION OF BIS-SALICYLIDENIMINE-ETHYLENEDIIMINE (84)

Anhydrous ethylenediamine (60g) was added slowly to salicylaldehyde (224g). Considerable heat was evolved during the reaction, with the result that the water formed was boiled. The product solidified on cooling to a yellow-coloured product. The product was crystallized from hot water. The product is soluble in acetone, nitromethane, tetrahydrofuran and hot ethanol.

Analysis Found	71.5%C	5.8%H	10.4%N	
Expected for Sal_2en	72.1%C	5.2%H	10.5%N	$C_{16}H_{14}N_2O_2$

(2.2.2.) PREPARATION OF BIS-ACETYLACETONE-ETHYLENEDIIMINE (84)

This compound was prepared in an analogous manner to the previous experiment.

Analysis Found	64.1%C	8.0%H	12.4%N	
Expected for $acac_2en$	64.2%C	8.9%H	12.5%N	$C_{12}H_{20}N_2O_2$

(2.2.3) REACTION BETWEEN COMMERCIAL RUTHENIUM TRICHLORIDE AND BIS-SALICYLIDENEIMINE-ETHYLENEDIIMINE

Commercial ruthenium trichloride (1g) was dissolved in stirred ethanol (100ml) and the solution was then heated under reflux for two hours. After the solution had turned to a green colour, indicating the presence of ruthenium in a lower oxidation state(85), a mixture of bis-salicylideneimine-ethylenediimine (1.08g) and triethylamine (1.1 ml) in ethanol was added. The reaction mixture was refluxed for approximately 60 hours, then the mixture was cooled and filtered. The crude dark blue product was extracted with acetonitrile for 18 hours in a soxhlet apparatus. A black solid (A) (1g) and a green solution were obtained. The solution was concentrated and on addition of diethyl ether produced the same green material (B) as was obtained from evaporating to dryness of the extracted acetonitrile solution. The product was washed and dried under vacuum.

Analysis

Found	(A)	36.0%C	3.7%H	22.8%Cl	7.7%N
	(B)	43.0%C	4.2%H	17.2%Cl	7.3%N
Expected for $[Ru(Sal_2en)]_2[RuCl_6]$		36.6%C	2.5%H	20.4%Cl	5.4%N
Expected for $[Ru(Sal_2en+H)Cl_2]$		43.0%C	3.19%H	16.2%Cl	6.3%N

(2.2.4) REACTION OF RUTHENIUM TRICHLORIDE WITH BIS-SALICYLIDENEIMINE-ETHYLENEDIIMINE AND SODIUM HYPOPHOSPHITE

Ruthenium trichloride (1g) was refluxed in ethanol (400ml) for an hour. Sodium hypophosphite (0.2g) was dissolved in water (10ml) and then added to the reaction mixture, which was then refluxed for a further 20 hours. The brown precipitate (C) formed was filtered off and washed with cooled ethanol. Yield 0.24g. Addition of ether to the filtrate produced a green precipitate (D) which was washed with diethyl ethere & dried in vacuo. Complete evaporation of filtrate gave a dark solid which was extracted with benzene in a soxhelt apparatus. The dark green/black solid (E) which was the major product was insoluble in benzene (0.95g).

Analysis

Found (C)	26.5%C	3.5%H	8.9%Cl	7.0%N	1.9%P
(D)	28.3%C	3.1%H	8.2%Cl	6.6%N	9.0%P
(E)	45.4%C	7.9%H	17.3%Cl	7.5%N	1.7%P

Expected for
$Ru(Salen)Cl.H_2PO_4$ ———
29.4%C 3.2%H 8.7%Cl 6.9%N 7.6%P

Compound E looks to be the same as compound B mentioned above with phosphine contamination.

(2.2.5) REACTION OF RUTHENIUM TRICHLORIDE WITH BIS-SALICYLIDENEIMINE-ETHYLENEDIIMINE IN THE PRESENCE OF TRIETHYLAMINE

Rutenium trichloride (0.5g) was dissolved in ethanol (250 ml) and refluxed under nitrogen for 2 hours. A mixture of bis-salicylideneimine (0.52g) and triethylamine (5ml) in ethanol (100ml) was then added and the reaction mixture was refluxed under nitrogen for 2 days. A black precipitate (F) was formed (0.05g). The brown filtrate did not show any sensitivity to air when exposed to air for 20 hours. Its volume was reduced, but attempts to produce precipitate by adding organic solvents were unsuccessful. On complete evaporation of the solvent a brown solid was obtained which was washed with water and dried in vacuo . It was dissolved in methanol, the solution filtered and a solid was obtained by evaporating to dryness (G)

Analysis

Found	(F)	37.8%C	3.8%H	12.7%Cl	4.9%N
	(G)	52.8%C	5.5%H	7.0%Cl	8.1%N

(2.2.6) REACTION OF TRICHLORO-HEXAKIS-DIMETHYLSULPHOXIDE RUTHENIUM(111) WITH BIS-SALICYLIDENEIMINE-ETHYLENEDIIMINE

Trichloro-hexakis-dimethylsulphoxide (0.5g) was suspended in acetonitrile (100ml) and a mixture of bis-salicylideneimine-ethylenediimine (0.2g) in acetonitrile (20ml) was added and the reaction mixture was heated under reflux. After three hours the colour of the mixture had changed from light yellow to light green. The clear solution was filtered and the addition of dry benzene to the concentrated solution caused a light green precipitate to form. This product is very sensitive to air it was washed with very small amounts of cold acetonitrile and dried under vacuum. The product is soluble in water and slightly soluble in ethanol.

Analysis

28%C	4.3%H	22.4%Cl	6.3%N	16.8%S

IR in NuJol: 3450Cm^{-1},2920,2980,1600,1400,1300,1100,1020,
420,380 Cm^{-1}

conductivity for 8.8 x 10^{-2}g/lit of the product in acetonitrile is equal to 24.15 ohm.$^{-1}$g.$^{-1}$Cm^{+2}. Because of its sensitivity no magnetic measurement was carried out.

(2.2.7) PREPARATION OF DICHLORTRIS(TRIPHENYLPHOSPHINE) RUTHENIUM(11)(86)

This compound was prepared accordingly to the literature method(86). Ruthenium trichloride (o.6g) was dissolved in methanol (150ml), filtered, and then refluxed for 5 minutes under nitrogen. After cooling, triphenylphosphine (6.0g) was added in ratio of 6 moles of tripheylphosphine per mole of ruthenium trichloride and the solution is again refluxed under nitrogen, washed several times with degassed ether, and dried under vacuum. The yield was 2.7g.

Analysis

Found	67.9%C	4.9%H	7.1%Cl	10.0%P
Expected for $Ru(PPh_3)_3Cl_2$	67.6%C	4.7%H	7.4%Cl	10.3%P

(2.2.8) PREPARATION OF TRANS-N,N'-ETHYLENE-BIS(PENTANE-2,4-DIONEMONOIMINATO)-BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11)(87)

Dichlorotristriphenylphosphineruthenium(11), (1g)in dry benzene (20ml) and bisacetylacetone-ethylenediimine (0.24g) and triethylamine (0.42ml) was refluxed under nitrogen for 5 hours. The solution was filtered to remove triethylamine hydrochloride. Dedarated methanol (80ml) was added to the filtrate and it refluxed for a further 4 hours.

An orange crystalline solid was isolated, which was recrystalized from acetone.

Analysis

Found	68.5%C	5.7%H	3.8%N	6.9%P
Expected for Ru(acac$_2$en)(PPh$_3$)$_2$	67.6%C	6.1%H	3.2%N	7.2%P

(2.2.9) PREPARATION OF DICHLOROMONO-PROTONATED-N,N'-ETHYLENE-BIS(PENTANE-2,4-DIONEMONOIMINATO)-TRIPHENL-PHOSPHINE RUTHENIUME(11),

Trans-N,N'-ethylenebis(pentane-2,4-dionemonoiminato) bis(triphenylphosphine)ruthenium(11) (0.5g) was dissolved in methanol (50ml) and lithium chloride (1g) was dissolved in methanol (50g) was added to the mixture. The mixture was heated under reflux for 20 hours. The brown solution was filtered and an attempt to produce precipitate using organic solvents was unsuccessful. Evaporation of the solvent gave a greenish brown residue which was washed with water and ether and dried in vacuo.

Analysis

Found	55.4%C	4.6%H	11.0%Cl	4.3%N	4.5%P
Expected for [Ru(acac$_2$en+H)(PPh$_3$)]Cl$_2$	54.6%C	5.4%H	10.7%Cl	4.2%N	4.7%P

(2.2.10) REACTION OF TRIS-TRIPHENYLPHOSPHINE-DICHLORO-RUTHENIUM(11) WITH BISACETYLACETON-ETHYLENEDIIMINE IN ETHANOL

Bis-acetylaceton-ethylenediimine (0.2g) was dissolved in ethanol (50ml) and excess triethylamine was added to the mixture. The mixture was heated to boiling point and tris-triphenylphosphine-dichlororuthenium (11) added. Air was drawn through the hot suspension for two days, the brown solution was filtered. An attempt to obtain precipitate by concentrating filtrate was unsuccessful. On complete evaporation a brown residue was left which was washed with benzene and ether and dried in vacuo.

Analysis

Found 49.5%C 5.9%H 10.1%Cl 6.4%N 15.7%P

(2.2.11) AERIAL OXIDATION OF TRANS-N,N'-ETHYLENE-BIS (PENTANE-2,4-DIONEMONOIMINATO)BIS(TRIPHENYLPHOSPHINE) RUTHENIUM(11) IN BENZENE

Trans-N,N'-ethylene-bis(Pentane-2,4-dionemonolminato) bis(triphenylphosphine)ruthenium(11) (0.2g) was dissolved in benzene (150ml). The solution turned green immediately and the mixture was left overnight. Attempts to produce precipitate from concentrated solutions by adding organic solvents were unsuccessful. Evaporation of the solvent gave a black/green residue which was washed with ether and dried in vacou. The precipitate is soluble in benzene, ethanol, acetone and is insoluble in water.

Analysis

Found 31.0%C 3.6%H 7.7%N 3.4%P

IR in KBr 3600,1600,1500,1440,1400,520,460 Cm^{-1}

(2.2.12) PREPARATION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) (87)

This compound was prepared according to the method described in reference (87). Tris(triphenylphosphine) dichlororuthenium(11) (4.79g) was dissolved in dry benzene (80ml) under nitrogen. A mixture of Bis-salicylideneimine-ethylenediimine (1.44g) and triethylamine (1.5g) was added and the reaction mixture was refluxed under nitrogen for 5 hours. The solution was filtered to remove triethylamine hydrochloride. Deareated methanol 150ml was added to filtrate and refluxed for a further 4 hours. On cooling, purple crystals were filtered under nitrogen and washed with deareated methanol and ether and dried in vacuo.

Analysis

Found 70.5%C 5.0%H 3.1%N 7.1%P

Expected for $Ru(Sal_2en)(PPh_3)_2$ 70.1%C 4.9%H 3.1%N 6.9%P

(2.2.13) PREPARATION OF DICHLORO-DIPROTONATED N,N'-ETHYLENEBIS(SALICYLALDIMINATO)TRIPHENYLPHOSPHINE RUTHENIUM(111) UNDER NITROGEN

Trans-N,N'-ethylenebis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.2g) and lithium chloride (1g) was suspended in degassed ethanol (150ml) under nitrogen. The reaction mixture was refluxed for 3 days. The reddish brown solution was filtered under nitrogen and it was found to be very sensitive to air. Complete evaporation of the solvent produced a reddish brown solid. It was washed with degassed ether and water under nitrogen and dried in vacuo.

Analysis

Found	58.8%C	4.1%H	9.2%Cl	3.3%N	6.8%P
Expected for $Ru(Sal_2enH_2)(PPh_3)(Cl_2)$	58.0%C	4.3%H	10.1%Cl	4.0%N	4.4%P

(2.2.14) PREPARATION OF DICHLORO-MONO-PROTONATED N,N' ETHYLENEBIS(SALICYLALDIMINATO)TRIPHENYLPHOSPHINE-RUTHENIUM(111) IN AIR.

Trans-N,N'-etylenebis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.2g) was dissolved in ethanol (150ml) and when a green solution was produced lithium chloride (1g) was added and the reaction mixture was heated under reflux for two days. The mixture was filtered to remove excess lithium chloride. On complete evaporation of solvent a green residue was obtained which was washed with water and dried and then washed with ether and dried in vacuo.

Analysis

Found	60.9%C	5.4%H	11.4%Cl	3.8%N	5.1%P
Expected for $Ru(Sal_2enH)(PPh_3)_2(Cl)_2$	58.0%C	4.3%H	10.1%Cl	4.0%N	4.4%P

(2.2.15) PREPARATION OF N,N'-ETHYLENEBIS(SALICYLALDIMINATO)TRIPHENYLPHOSPHINEAMMINE-RUTHENIUM(11) UNDER NITROGEN

Trans-N,N'-ethylenebis(salicylaldiminato)bis(triphenylphosphineruthenium(11) (0.2g) was dissolved in degassed ethanol (100ml) and degassed ammonia (2ml) was added to the mixture. The resultant reaction mixture was refluxed under nitrogen for ten hours. On addition of ammonia (1ml) to the cherry coloured solution a precipitate was produced. The precipitate was collected under nitrogen and washed with degassed water. It was found to be soluble in ether, chloroform, benzene and acetonitrile. These solutions turned green in a few seconds on exposure to air.

Analysis

Found	63.4%C	5.2%H	6.2%N	5.0%P
Expected for $Ru(Sal_2en)(PPh_3)(NH_3)$	63.1%C	4.9%H	6.5%N	4.79%P

IR in NuJol 3350 cm^{-1}

The absorption spectrum of a freshly prepared solution of this compound in ethanol ($1.36 \times 10^{+4}$ mole) shows a small peak at 700 nm ($\epsilon = 2.27 \times 10^{+3} mole^{-1} cm^{-1}$) & three maxima at 495 nm (ε = 1.5 x 10^{+3}mole^{-1}cm^{-1} 400 nm) (ε = 1.6 x 10^{+2}mole^{-1}cm^{-1}and 360 nm (ε = 1.5 x 10^{+3}mole^{-1} cm^{-1}) with time the intensity of the small peak at 700 nm is increased (ε = 3.8 x 10^{+3}mole^{-1}cm^{-1}) and the peak at 495 nm decreases to a very small shoulder and a peak at 340 nm (ε = 1.52 x 10^{+2}mole^{-1}cm^{-1})develops. Conductivity of the freshly prepared solution (1.36 x 10^{+4}mole) in acetonitrile is 10.30 Ohm^{-1}.mol^{-1}.Cm^{-1}.

(2.2.16) REACTION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) WITH AMMONIA IN ATMOSPHERIC CONDITIONS

Trans-N,N'ethylenebis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.2g) was dissolved in ethanol (80ml) and stirred for half an hour. Ammonia (5ml) was added to the green solution and the reaction mixture was refluxed for two days. The dark green mixture was cooled and a black precipitate (H) was filtered and washed with ethanol and ether and dried in vacuo. Upon addition of diethyl ether to the concentrated filtrate, a dark green precipitate (I) was formed, which was filtered off and washed with ether. It is soluble in water, dimethylsulphoxide and slightly in acetonitrile.

Analysis

Found	(H)	42%C	3.1%H	7.8%N	4.7%P
	(I)	22.6%C	3.3%H	7.7%N	5%P

(2.217) PREPARATION OF TRANS N,N'-ETHYLENEBIS(SALICYLALDIMINATO)TRIPHENYLPHOSPHINE(PYRIDINE)RUTHENIUM(11) UNDER AN ATMOSPHERE OF NITROGEN

Trans-N,N'-ethylenebis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.2g) was suspended in degassed ethanol (80ml) under nitrogen and degassed pyridine (2ml) was added and the reaction mixture was heated under reflux under nitrogen for two days. On filtration reddish brown precipitate was collected and washed with deareated water under nitrogen and dried in vacuo. The product is soluble in ether, benzene and solutions immediately turn to a green colour on exposure to air.

Analysis				
Found	65.1%C	5.3%H	5.6%N	4.8%P
Expected for Ru(Sal$_2$en)(PPh$_3$)^2(pyridine)	64.5%C	4.7%H	5.9%N	4.3%P

IR in NuJol 3350 Cm^{-1}, 1550 Cm^{-1}.

The absorption spectra of a freshly prepared solution (1.24 x 10^{+4}mole^{-1}cm^{-1}shows a maxima at 700 nm (ε=1.5 x 10^{+3}mole^{-1}cm^{-1}which increases with time (ε = 6.4 x 10^{+3} mole^{-1}cm^{-1})and a maxima at 480 nm (ε = 3.5 x 10^{+3}mole^{-1}cm^{-1}) disappears with time and two maximum at 400 nm (ε = 1.7 x 10^{+2}mole^{-1}cm^{-1}and 350 nm (ε = 1.68 x 10^{+2}mole^{-1}cm^{-1})which the first one with time disappears and the second one slightly decreases (ε = 1.6 x 10^{+2}mole^{-1}cm^{-1}. Conductivity of freshly prepared solution in acetonitrile

(1.24 x $10^{-4}\bar{M}^{-1}Cm^{-1}$ is 10,70 $Ohm^{-1}.mole^{-1}.Cm^{-1}$ and for a aged solution is 10.52 $Ohm^{-1}.mole^{-1}.Cm^{-1}$.

(2.2.18) REACTION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) WITH PYRIDINE

Trans-N,N'-ethylenebis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.2g) was dissolved in ethanol (80ml) and stirred for one hour to produce a deep green solution then pyridine (2ml) was added and the reaction mixture was refluxed for 2 days. The greenish brown solution was filtered. An attempt to produce precipitate by concentrating the solution was unsuccessful. Attempts to produce precipitate by adding organic solvents were also unsuccessful. On complete evaporation brown solid was formed which was washed with diethyl ether The precipitate is soluble in water, conductivity for 8.8 x 10^{-2}g/lit of this product is 67.1 $Ohm^{-1}.g^{-1}.Cm^{+.2}$.

Analysis
Found 65.8%C 4.9%H 5.2%N 6.8%P

(2.2.19) PREPARATION OF -N,N'-ETHYLENEBIS(NITROSALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM (11) UNDER NITROGEN

Trans-N,N'-ethylene bis(salicylaldiminato)bis-(triphenylphosphine)ruthenium(11) (0.2g) and sodium nitrite (1g) in degassed ethanol under nitrogen were refluxed together for 2 days. Excess sodium nitrite was removed by filtration under nitrogen and addition of diethyl ether to the concentrated solution cause the deposition of more sodium nitrite. On complete evaporation a light brown precipitate was formed, filtered off and washed with ether and dried and then with water and dried in vacuo.

Analysis

Found 66%C 4.5%H 4.5%N 8.0%P 0.5%Na

Expected for

$Ru(NO_2Sal_2en)(PPh_3)_2$ 66.4%C 4.6%H 4.4%N 6.8%P

IR in NuJol 1800 Cm^{-1}.1630 Cm^{-1}

Using brown solid in ESR technique g⊥=1.98 and g‖=1.80 is obtained. Conductivity of 4.8×10^{-4} molar of this product in acetonitrile is 13.83 $Ohm^{-1}.mol^{-1}.Cm^{-1}$.

(2.2.20) PREPARATION OF TRANS-N,N'-ETHYLENEBIS-(NITROSALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE) RUTHENIUM(11).

Trans-N,N'-ethylene-bis(salicylaldiminato)bis (triphenylphosphine)ruthenium(11) (0.2g) was dissolved in ethanol (80ml) and stirred for 1 hour to produce a green solution. Sodium nitrite (1g) was added and the reaction mixture was refluxed for 2 days. The brown solution was filtered and on addition of diethyl ether on concentrated solution more sodium nitrite was deposited. On complete evaporation of solvent the brown product was collected, washed with ether and water and dried in vacuo.

Analysis

Found	65%C	4.3%H	4.6%N	6.5%P	0.3%Na
Expected for $Ru(NO_2Sal_2en)(PPh_3)_2$.	66.4%C	4.4%H	4.6%N	6.8%P	-

Using the ESR technique for the brown solid g⊥ = 1.98 and gll = 1.80 are obtained. Conductivity of 4.8×10^{-4} molar of this product in acetonitrile is 13.8 $Ohm^{-1}.mol^{-1}.Cm^{-1}$.

(2.2.21) REACTION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) WITH SODIUM NITRATE UNDER NITROGEN.

Trans-N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) and sodium nitrate (1g) in degassed ethanol under nitrogen were refluxed for 2 days. Excess sodium nitrate was removed by filtration under nitrogen and the addition of diethyl ether to the concentrated solution cause the deposition of more sodium nitrate. On complete evaporation purple crystals were formed, filtered off and washed with ether and dried and then water and then dried in vacuo. This reaction was not successful and starting materials were separated.

Analysis

Found	69.6%C	5.0%H	3.1%N	7.1%P
Expected for $Ru(Sal_2en)(PPh_3)_2$	70.1%C	4.9%H	3.1%N	6.9%P

(2.2.22) PREPARATION OF TRIPHENYLPHOSPHINEOXIDE(88)

A mixture of triphenylphosphine (8.0g) and ethylpyruvate (7.08g)was heated at 140°C for one hour. By vacuum distillation triphenylphosphine oxide was isolated (5g).

Analysis

Found	79%C	5.3%H	11.3%P
Expected for $C_{18}H_{15}OP$	77.6%C	5.3%H	11.1%P

(2.2.23)PREPARATION OF TRANS-N,N'ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINEOXIDE)RUTHENIUM(11)

Triphenylphosphine oxide (0.1g) and trans-N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.2g) was dissolved in degassed ethanol and refluxed under nitrogen for 2 days. No precipitate was found on filtration. The filtrate was evaporated completely and a red precipitate was found which was washed with degassed ether under nitrogen. The product gave a green solution immediately on dissolution in methanol.

Analysis

Found	69.1%C	5.0%H	3.3%N	7.2%P
Expected for Ru(Sal$_2$en)(Ph$_3$PO)$_2$	67.6%C	4.7%H	3.0%N	6.7%P

IR no obvious change in spectrum compared with IR of starting material was observed. Conductivity 2.3 x 10^{-4}molar of this product in methanol is equal to 4.3 Ohm^{-1}.mol^{-1}.Cm^{-1}.

(2.2.24) REACTION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(ll) WITH ETHANOL AT ROOM TEMPERATURE

Trans-N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(ll) (1g) was suspended in ethanol (300ml) and stirred for 2 days at room temperature and then filtered. Attempts to produce precipitate by adding organic solvents to the concentrated solution were unsuccessful. The solvent was removed to complete dryness in low temperature. The green product was washed with ether. Attempts to determine the molecular weight by vapour pressure osmometry were unsuccessful for ethanol and chloroform solutions because of low concentration can be achieved. In benzene an apparent molecular weight of 378±25, was determined even though only dilute solutions could be obtained.

Analysis

Found	65.3%C	4.9%H	3.4%N	5.1%P
Expected for $[Ru(Sal_2en).PPh_3]_2O$	64.0%C	4.6%H	4.4%N	4.9%P
Expected for $[Ru(Sal_2en)_2(PPh_3)_2]_2O_2$	63.2%C	4.5%H	4.3%N	4.8%P

IR same as IR of parent material, this green product is paramagnetic with $\chi = 65.1x10^{-6}$ using the Faraday method for measurements. g1 = 1.89 and g11 = 1.8 are obtained from the ESR spectrum of the undiluted powder. Conductivity of product in ethanol is 12.28 $Ohm^{-1}.mole^{-1}.Cm^{-1}$. (2.02 x 10^{-4}molar in ruthenium)

(2.2.25) REACTION OF TRANS-N,N'-ETHYLENEBIS(SALCYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) WITH ETHANOL

Trans N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11), (1g) was refluxed in ethanol (200ml) for one week and the hot suspension

Analysis

Found 48.6%C 3.5%H 6.5%N 1.8%P

g⊥ = 1.87 and gll = 1.80 are obtained from the ESR spectrum of the undiluted powder. IR of this dark green compound is very similar to the starting material. It is very soluble in chloroform and is slightly soluble in ethanol and benzene and is insoluble in water.

B) Trans-N,N'-ethylene-bis(salicylaldiminato)bis (triphenylphosphine)ruthenium(ll), (0.5g) was dissolved in acetonitrile (300ml) and after two hours when the mixture was completely green, it was filtered and the solution was then left for three days during which time a precipitate formed. This was separated using a centrifuge, washed with diethyl ether and dried in vacuo.

Analysis

Found 46.5%C 3.5%H 6.2%N 1.1%P

IR of this compound is similar to the IR of the starting material. g⊥ = 1.88 and gll = 1.81 are calculated from ESR spectrum of undiluted powder. This product is only soluble in benzene.

was filtered and filtrate was evaporated to dryness and the dark brown product washed with ether. Attempts to determine the molecular weight by vapour pressure osmometry in ethanol, chloroform and benzene were unsuccessful because low concentration can be achieved.

Analysis

Found	63.5%C	5.0%H	3.6%N	6.2%P
Expected for $Ru(sal_2en)(PPh_3)_{1.5}$	67.8%C	4.8%H	3.7%N	6.1%P

The conductivity of product (2.0×10^{-4} molar) in ruthenium in ethanol is equal to 10.07 $Ohm^{-1}.mole^{-1}.Cm^{-1}$. $g_{\perp} = 1.95$ and $g_{\parallel} = 1.80$ are obtained from ESR spectrum of undiluted powder. IR of the brown compound is same as IR of tris(triphenylphosphine)dichlororuthenium(11).

(2.2.26) REACTION OF TRANS-N,N'-ETHYLENE BIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) WITH ACETONITRILE

A)

The named compound (0.5g) was dissolved in acetonitrile (300ml) and after one hour it was filtered and the addition of diethyl ether caused a green precipitate to form. This collected using centrifuge and washed with ether and dried in vacuo.

PHOTOCHEMISTRY OF SCHIFF BASES:

(2.2.27) IRRADIATION OF TRANS-N,N'-ETHYLENEBIS (SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM (11) IN NITROGEN ATMOSPHERE

The above compound (0.5g) was irradiated as a solid under nitrogen atmosphere using a photoflood lamp (1000 watts) for two weeks. The product was washed with degassed ether under nitrogen. No changes were observed in its colour and infrared spectrum.

Analysis

Found	69.8%C	5.0%H	3.1%N	7.1%P
Expected for $Ru(Sal_2en)(PPh_3)_2$	70.1%C	4.7%H	3.1%N	6.9%P

(2.2.28) IRRADIATION OF TRANS-N,N'-ETHYLENE-BIS (PENTANE)-2,4-DIONEMONOIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) IN NITROGEN ATMOSPHERE

Above experiment was carried out for this compound and no changes were observed and the product was identified as the starting material.

Analysis

Found	68.0%C	6.0%H	3.2%N	6.9%P
Expected for $Ru(acac_2en)(PPh_3)_2$	67.5%C	6.0%H	3.2%N	7.1%P

No changes was observed in its infrared compare to starting material.

(2.2.29) IRRADIATION OF TRANS-N,N'-ETHYLENEBIS (SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM (11) IN AIR

The above compound (0.5g) was irradiated with a photoflood lamp (1000 watts) for more than ten days. Its colour changed from purple to dark brown. It was washed with diethyl ether and a black product was obtained.

Analysis

Found	63.8%C	4.3%H	3.2%N	6.2%P
Expected for $[Ru(Sal_2en)(PPh_3)]_2O_2$	63.2%C	4.5%H	4.3%N	4.8%P

The IR of the product was very similar to the starting material. Attempts to determine the molecular weight by vapour pressure osmometry were unsuccessful for benzene, ethanol and chloroform, because of low concentration can be achieved. $g\perp = 1.90$ and $g\parallel = 1.79$ are obtained using solid samples in ESR thenique. This compound is slightly soluble in nitromethane and acetonitrile. This material was used as a starting material for (2.2.33)(2.2.34)and (2.2.35)preparations.

(2.2.30) IRRADIATION OF TRANS-N,N'-ETHYLENE-BIS (SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM (11) IN BENZENE UNDER NITROGEN

The above compound (0.5g) was dissolved in degassed benzene (100ml) & the green solution was irradiated in nitrogen using a photoflood lamp (1000 watts) for 5 days. The solution was filtered under nitrogen and filtrate was evaporated to complete dryness and the reddish brown product was washed with deareated ether and dried in vacuo.

Analysis

Found 47.7%C 3.3%H 5.4%N 7.3%P

(2.2.31) IRRADIATION OF TRANS-N,N'-ETHYLENEBIS (SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM (11) IN BENZENE

Trans-N,N'-ethylene bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.5g) was dissolved in benzene (100ml) and the green solution was irradiated in 5 days. The mixture was filtered and an attempt to produce precipitate on concentrated solution was unsuccessful and on complete evaporation of solvent a greenish brown product was washed with diethyl ether and dried in vacuo.

Analysis

Found 57.4%C 4.0%H 4.1%N 7.6%P

Expected for

Ru.Salen.Ph_3P 61.4%C 5.1%H 5.3%N 5.8%P

No obvious changes were observed in its infrared spectrum. Conductivity of (1.66×10^{-4} molar) of the product in acetonitrile is 20.2 $Ohm^{-1}.g^{-1}.cm^{+2}$

(2.2.32) IRRADIATION OF TRANS-N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM (11) WITH LITHIUM CHLORIDE IN ETHANOL

Trans-N,N' — ethylene-bis(salicylaldiminato)bis (triphenylphosphine)Ruthenium(11), (0.2g) and lithium chloride (1g) were dissolved in ethanol (200ml). The reaction mixture was irradiated using a photoflood lamp (1000 watts) for one week. The mixture was filtered to remove excess of lithium chloride and an attempt to produce precipitate using organic solvents on concentrated solution were unsuccessful. On complete evaporation a green product was obtained which was washed with water and dried and then with water and dried in vacuo.

Analysis

Found	57.3%C	4.1%H	6.6%Cl	3.9%N	4.9%P
Expected for Ru(Sal_2en)(PPh_3)Cl	61.3%C	4.3%H	5.3%Cl	4.2%N	4.7%P

(2.2.33) REACTION OF SODIUM NITRITE AND THE PRODUCT OF THE REACTION (2.2.29)

The product of reaction (2.2.29)(0.4g) was treated with sodium nitrite(1g) in ethanol (100ml) and the reaction mixture was heated under reflux for 24 hours. The brown solution was filtered to remove excess sodium nitrite & addition of diethylether deposited more sodium nitrite. On complete removal of solvent light brown product was collected which was washed successively with ether and water and dried in vacuo, over phosphorus pentoxide very low yield.

Analysis

Found	63.8%C	5.1%H	3.8%N	6.3%P	10%Na
Expected for $Ru(NO_2.Sal_2en)(PPh_3)_2$	66.4%C	4.6%H	4.4%N	6.8%P	

IR 1800 Cm^{-1} and 1600 Cm^{-1}. gl = 1.9 and gll = 1.8 are obtained using the product as a solid in ESR technique.

(2.2.34) REACTION OF AMMONIA WITH THE PRODUCT WHICH WAS OBTAINED IN REACTION (2.2.29)

The product of the reaction (2.2.29)(0.4g) was suspended in ethanol (100ml) and ammonia (3ml) was added and the solution was refluxed for 3 days. The green solution was filtered. The volume of the filtrate was reduced and some precipitate was formed which was washed with ether. On complete evaporation more product was found. Both precipitates had identical elemental analysis and IR spectra .

Analysis

Found	60.0%C	4.2%H	4.3%N	8.0%P

(2.2.35) REACTION OF PYRIDINE WITH THE PRODUCT OF REACTION (2.2.29)

The above product (0.4g) was dissolved in ethanol (100ml) and pyridine (2ml) was added and the reaction mixture was refluxed. No precipitate was found on filteration. Addition of diethyl ether on concentrated solution produced some green precipitate which was washed with ether and dried in vacuo.

Analysis

Found 67.2%C 5.8%H 5.5%N 6.4%P

IR: very small changes was observed in finger print part of spectrum.

SPECTROPHOTOMETRIC STUDIES

KINETIC STUDIES

(2.2.36)

Trans-N,N'-ethylene bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (1.68×10^{-4} mole) was dissolved in ethanol (10ml) and using spectrophotometer optical density changes at a fixed wavelength of 700 nm. The change of concentration with time was followed using thermostated cell holders. This experiment was repeated using freshly prepared thermostated solutions at different temperatures, from these data, rate constants were calculated. (Table (1))

(2.2.37)

Different concentrations of trans-N,N'-ethylenebis (salicylaldiminato)—bis(triphenylphosphine)ruthenium (11) were prepared and optical density changes using thermostated cell holders were measured at a fixed wave length (700nm) and fixed temperature 40°C, from which the rate constants were calculated. (Table (2))

(2.2.38)

Quantities of trans-N,N'-ethylene-bis(salicylaldiminato)—bis(triphenylphosphine)ruthenium(11) (2.8×10^{-4}mole) were dissolved in 10ml aliquots of $10^{-1}$and 10^{-3}mole solutions of triphenylphosphine in ethanol at fixed wave length 700 nm and fixed temperature 40°C. The optical density changes were measured in a thermostated spectrophotometer with time. The rate constants were calculated and the effect of triphenylphosphine was considered.

(2.2.39)

Trans-N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (1.68×10^{-4}mole) was dissolved in acetonitrile. Optical density changes immediately were measured at fixed wave length 700 nm at different temperatures using thermostated cell holders and the rate constants were calculated.

(2.2.40)

Portions of trans-N,N'-ethylene-bis(salicylaldiminato) bis(triphenylphosphine)ruthenium(11) (1.68×10^{-4}mole) were dissolved in different concentrations of triphenylphosphine in acetonitrile at a fixed wavelength 700 nm and constant temperature 40°C. The optical density changes were immediately measured using thermostated cell holders and the rate constants were calculated.

EQUILIBRIUM STUDIES

(2.2.41)

A solution of trans-N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (0.002g) in ethanol (100ml) was prepared and was left for 5 days. The colour of the solution changed from green to reddish-brown. 5ml of the above stock solution were diluted with 3ml of 10^{-3}mole and 7,10ml of 10^{-2}mole and 5,7 and 10ml of 10^{-1}mole of triphenylphosphine solution in acetonitrile and the volume of the samples were made up to 15ml using ethanol. These new solutions were left one week to reach complete equilibrium at fixed temperature 40°C and optical densities were measured using a thermostate cell holder at two different wave length 750 nm and 395 nm. (Table (5))

(2.2.42)

Trans-N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) (1.6×10^{-4}mole) were dissolved in 2,4,6,8,10 ml 10^{-3}mole and 2,4,6, 8,10 ml 10^{-2}mole and 2,4,6,8,10 ml 10^{-1}mole solution of triphenylphosphine in acetonitrile and left at a fixed temperature 40°C in a thermostat bath for one week, but because of the occurrence of precipitation, equilibrium studies in acetonitrile were unsuccessful.

(2.3.1) DISCUSSION AND RESULTS

While it has proved possible to prepare many new Schiff base complexes of ruthenium, only for the phosphine containing complexes were the reactions easy and they lead to unequivocally identifiable products. Using tris(triphenylphosphine)dichloro ruthenium(Il) as a starting material is convenient and leads to the preparation of such compounds as Ru(Sal$_2$en)(PPh$_3$)(NH$_3$), Ru(Sal$_2$en)(Pyridine), Ru (NO$_2$.Sal$_2$en)(PPh$_3$)$_2$, Ru(Sal$_2$en)(Ph$_3$PO)$_2$, Ru(Sal$_2$en + H)(PPh$_3$)(Cl$_2$) and Ru(acac$_2$en + H)(PPh$_3$)Cl$_2$. These compounds were prepared after prolonged refluxing of dichlorotris(triphenylphosphine) ruthenium(ll) and the desired ligands in a suitable solvent under nitrogen, followed by the collection of the products under nitrogen. The physical and chemical properties of these compounds are described briefly in experimental part.

Ru(NO$_2$.Sal$_2$en)(PPh$_3$)$_2$ was prepared using two different routes with the starting complexes in the oxidation state (ll) and (lll). The ESR spectrum of this compound is shown in Fig (2.1) and gl=1.98 and gll=1.80 were calculated each time, which is comparable with the figures quoted in the literature.(87) Values of gl=2.18 and gll=1.92 are given for Ru(Sal$_2$en)(Cl)(PPh$_3$).

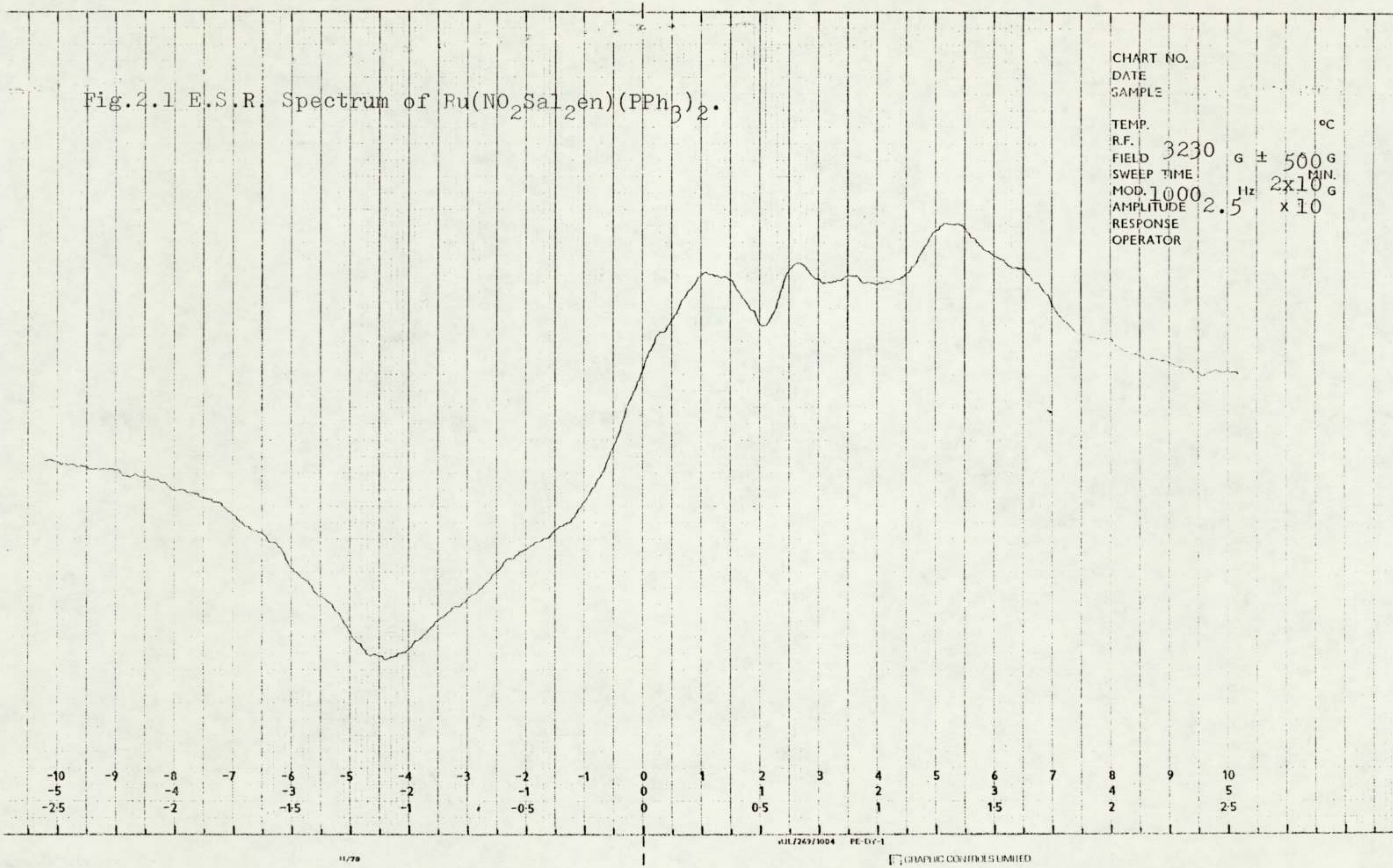


Fig.2.1 E.S.R. Spectrum of $Ru(NO_2Sal_2en)(PPh_3)_2$.

Alternative ruthenium compounds,where used as initial reagents,gave much lower product yields as well as mixtures of complexes from which separation of pure compounds was rather difficult. An attempt to prepare different Schiff base Ru (11) complexes using commercial ruthenium trichloride as starting material was not very successful because of the limited range of reducing agents suitable for the production of the desired oxidation state of ruthenium under the relevent experimental conditions. Refluxing ruthenium trichloride(85) for a while in ethanol to produce the green solution which has been reported(85) previously to produce ruthenium in lower oxidation states leads to the formation of mixtures and products containing ruthenium in more than one oxidation state. Reaction of bis-salicylideneiminethylenediimine with the green ethanolic solution of ruthenium trichloride in presence of triethylamine gives a crude product which after being extracted with acetonitrile in a soxhlet apparatus produces a black solid whose analysis suggests a formula of $[Ru^{111}Sal_2en]_2[Ru^{1V}Cl_6]$. Using ruthenium trichloride and sodium hypophosphite as a reducing agent always resulted in phosphorus contamination. There is the possibility that the ligand has been cleaved to produce a tridentate ligand which can be characterized from low C:N ratio in analysis. The green ethanolic solution derived from commercial ruthenium trichloride after being refluxed with bis(salicylideneimine-ethylenediimine) in presence of sodium hypophosphite, followed by the addition of diethyl ether to the green solution which was obtained after filtration produced green precipitate (D)whose analysis fits to the formula of Ru(Salen)Cl.PO_4H_2. That is, the C:N ratio is found to be approximately 9:2 rather than 16:2 as the original Sal_2en ligand requires.

Reaction of ruthenium trichloride and bis-salicylideneiminethylenediimine in presence of a base in ethanol, as previously mentioned in experiment (2.2.3), produced a green compound (B) and black product (A). Because the black product (A) was the major product and was obtained in high yield, exploratory work was carried out on this material. These studies were undertaken before analytical data become available, and therefore before $RuCl_6$ was suspected to be present. Nonetheless they provide support for the idea that ruthenium is present in more than one form.

Compound (A) treated with freshly precipited silver oxide in water and shaken for one day gives no silver chloride precipitate. This means that no simple chloride anion is present even though the percentage of chlorine is high. When compound (A) is refluxed in water for a few hours and the solution then filtered, a new black precipitate and a green solution are obtained, the elemental analysis of this new black solid differs from that of the starting solid containing much less C,Hand N.

The green solution does not yield any precipitate with silver nitrate. When compound (A) treated with aqueous sodium hypophosphite and refluxed for a few hours, a very black green solid is formed which is insoluble in all organic and inorganic solvents. Treatments of (A) with excess hydrazine yields a brown insoluble solid, while treatment of (A)with sodium borohydride in ethanol under nitrogen produces an insoluble reddish brown compound, treatment of (A) with 1N sodium hydroxide solution produces a dark brown solution. Addition of 1 N hydrochloric acid to this solution gives a green precipitate, which can be collected and washed with water.

The elemental analysis of all these compounds were obtained, but do not seem to fit any reasonable and simple formulae. The infrared spectra of all the derivatives of the black product differ little from that of the parent product. Further work on this and other similar products, was suspended because of the uncertain information being obtained. Efforts were concentrated on those compounds subsequently discussed. However, it might be profitable for a future worker to retain to the investigation of these dark products.

Studies of the visible spectra of trans-N,N'-ethylene bis(salicylaldiminato)bis(triphenylphosphine)ruthenium (11) in ethanol and acetonitrile suggests a new branch of research in this area. The purple crystals of this Ru (11) compound give a green solution immediately on dissolution in methanol, ethanol, benzene or chloroform in air. In acetonitrile the colour changes from purple to green slower than in other solvents.

The absorption spectra of these solutions are similar in character to that of the characterized Ru (11) compound. This green colour does not appear when degassed solvents are used, and the solutions are prepared under an atmosphere of nitrogen. Following the visible spectra of this compound in ethanol over a prolonged time interval shows that further reactions occur. Dissolution of the compound in ethanol is slower than in other solvents. When this compound was dissolved in ethanol ($1.68\mathrm{x}10^{-4}$ mole) a peak is initially observed at 750 nm ($\varepsilon = 1.42 \times 10^{3} \mathrm{mole}^{-1}.\mathrm{Cm})^{-1}$ which disappears with time.

A shoulder at 500 nm ($\varepsilon = 6.2\text{x}10^{2}\text{mole}^{-1}.\text{Cm}^{-1}$) intensifies with time ($\varepsilon = 1.19\text{x}10^{3}\text{mole}^{-1}.\text{Cm})^{-1}$ and a maximum at 345 nm ($\varepsilon = 6.11\text{x}10^{3}\text{mole}^{-1}.\text{Cm})^{-1}$ also increases with time ($\varepsilon = 7.3\text{x}10^{3}\text{mole}^{-1}.\text{Cm})^{-1}$ Fig (2.2). These changes are very slow at room temperature and no isosbestic point in the visible spectra of the ethanolic solution is observed. When this solution is left at room temperature for 24 hours it gradually turns to a brown solution. Ethanol seems to be the only solvent in which the trans N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) forms such a brown solution. Kinetic and equilibrium studies were undertaken both to investigate the formation of this brown solution and to help in the characterization of the compounds involved. At a fixed wave length of 700 nm the optical density changes with time were measured. Plotting optical densities against time and measuring gradients to obtain $\frac{dD}{dt}$ allows one to plot $-\frac{dD}{dt}$ against D, where D represents optical density. Such a graph shows $-\frac{dD}{dt}$ increasing to a maxima around $(D-D_{\infty}) = \frac{1}{2}(D_0-D_{\infty})$, this observation suggests an autocatalytic reaction of the form

$$A + B \xrightarrow{k} 2B \qquad (2.10)$$

This equation obeys the differential equation (2.11)

$$-\frac{dA}{dt} = k.B.A = k.A(Ao - A) \qquad (2.11)$$

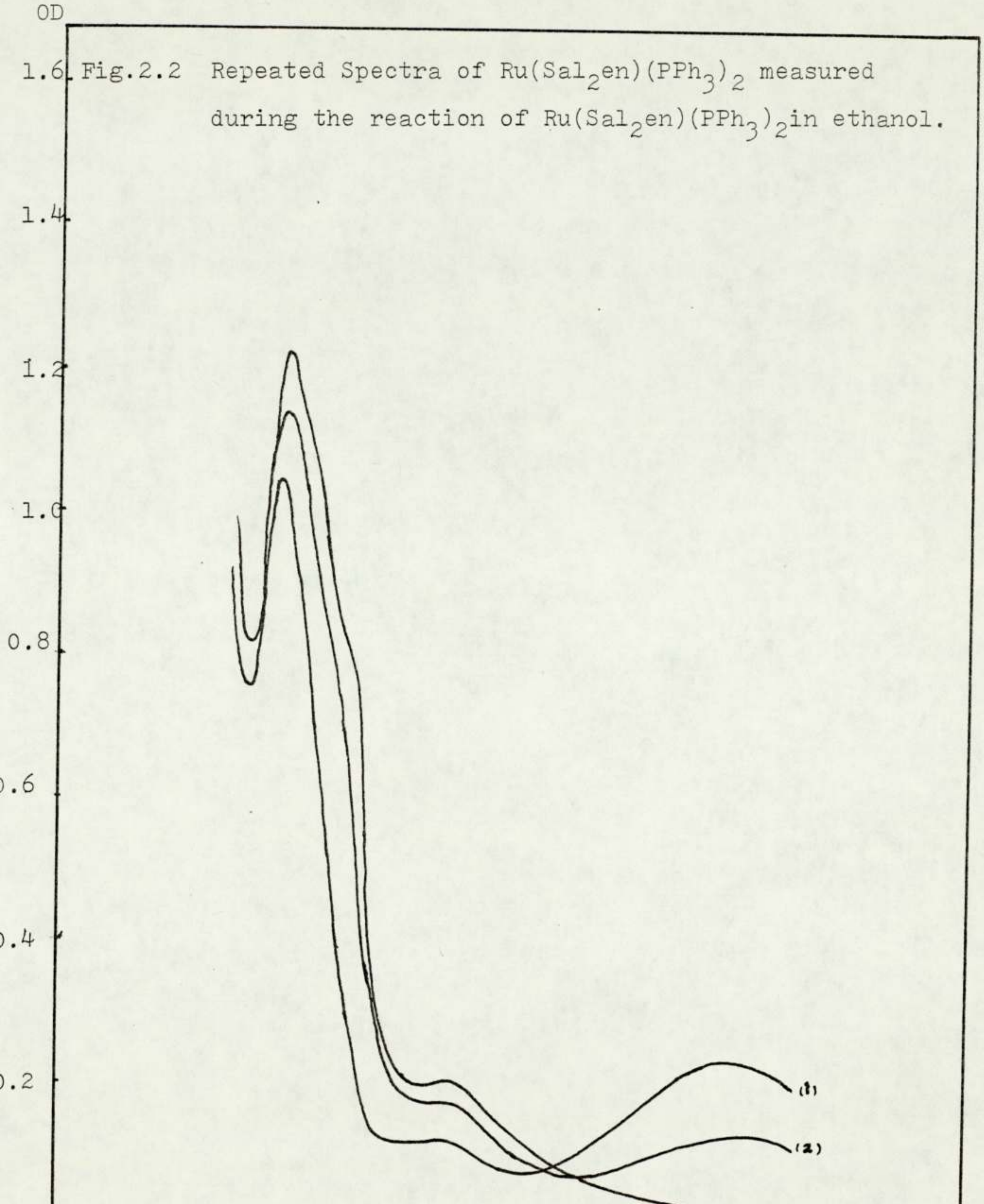


Fig.2.2 Repeated Spectra of $Ru(Sal_2en)(PPh_3)_2$ measured during the reaction of $Ru(Sal_2en)(PPh_3)_2$ in ethanol.

and plotting $-\frac{dD}{dt}$ against $(D - D_\infty)(D_0 - D)$ shows a reasonable but not perfect fit to the experimental curve. The integrated rate equation being

$$\frac{1}{(A_0-B_0)}.\ln\left\{\frac{A_0(B_0+B)}{B_0(A_0-B)}\right\} = kt \qquad (2.12)$$

and a plot of $\log\left(\frac{D - D_\infty}{D_0 - D}\right)$ is reasonably linear with time but not perfectly so, especially early on. Of course, equation (2.10) will never start without some B appearing somehow. It could have come in a very slow side reaction, in which case equation (2.12) would have been perfect. More likely we could have

$$A \xrightarrow{k_1} B \qquad (2.13)$$

$$A + B \xrightarrow{k_2} 2B \qquad (2.14)$$

this is described by the equation (2.15)

$$\frac{A_0 - A}{A_0} = \frac{\rho(1 - e^{-xt})}{\rho + e^{-xt}} \qquad (2.15)$$

where $\rho = \frac{k_1}{k_2A_0}$ and $x = (1+\rho)k_2A_0$

rearrangement of equation (2.15) gives the form:

$$-\alpha t = \beta + \log_{10}\left\{\frac{D - D_\infty}{Z - D}\right\} \qquad (2.16)$$

where $Z = D_0 + \frac{\rho}{\varepsilon}$

taking three points equally spaced in time and using equation (2.17) it is possible to estimate Z, since then :

$$\frac{(D_2-D_\infty)(Z-D_1)}{(D_1-D_\infty)(Z-D_2)} = \frac{(D_3-D_\infty)(Z-D_2)}{(D_2-D_\infty)(Z-D_3)} \qquad (2.17)$$

the function $\log_{10} \frac{(D-D_\infty)}{Z-D}$ can now be plotted against time, and Z can be refined to give the best straight line. This procedure results in a very good fit over the entire reaction and from this plot k_{obs} can be calculated. (Full equations are described in appendix (1)). The fit is insensitive to small changes in Z, and so it was felt to be unnecessary to devise a full, least square's programme for the computation of best values of the constants.

TABLE (2.1)

VARIATION OF RATE CONSTANT AT DIFFERENT TEMPERATURE AT FIX WAVELENGTH AND CONCENTRATION

T

T/K^o	Con/mole	Z	D_0	D_∞	k/sec^{-1}	λnm	solvent
333	$1.68x10^{-4}$	0.95	0.45	0.095	$5.03x10^{-4}$	700	EtoH
323	"	0.6	0.52	0.09	$2.74x10^{-4}$	"	"
313	"	0.49	0.42	0	$1.9x10^{-4}$	"	"
303	"	0.52	0.45	0.138	$5.3x10^{-5}$	"	"

The scheme outlined above shows that rate constants should be independent of initial concentrations of trans-N,N'-ethylene(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) . As it can be seen this is not the case, and there is a small variation of the rate constant with initial concentration of the compound. When $\frac{1}{k_{obs}}$ is plotted against the square of the initial ruthenium concentration a good straight line is produced that a slight development in the mechanistic scheme above and summerised as equation (2.13) and (2.14) is necessary.

A similar and likely scheme would be of the following form.

$$E \overset{K_0}{\rightleftharpoons} A + 2L \qquad (2.18)$$

$$A \xrightarrow{k_1} B \qquad (2.19)$$

$$A + B \xrightarrow{k_2} 2B \qquad (2.20)$$

$$C \overset{K_3}{\rightleftharpoons} B + 2L \qquad (2.21)$$

If according to the equlibria (2.18) and (2.21) dissociation occurs, we would expect that the rate constant will vary with the initial concentration of the compound and because this is the fact, so the value for the Z will change slightly. If these equilibria lie far over in favour of the dissociated form then L approximates to 2A, with no excess L added.

It should be possible to distinguish between the dissociation of one or two ligands by plotting the function $\frac{Z - D_\infty}{k_{obs}}$ against either $L + A_0$ or $\left[L+2A_0\right]^2$ When these two graphs are produced both show reasonable linearity, although the square function appears to be a better fit, therefore it is deduced that in the two equilibria both ligands identified as L are lost. Full equations are set out in appendix 2.

The data of Table (2.1) produces a good straight line for an Arrhenius Plot giving an activation energy equal to - 66.1 K.J.mol^{-1}. Also using data from Table (2.2) a plot of concentration against the reciprocal of the rate constants produced straight line with gradient equal to 1.54 x 10^{-7}mole.sec and intercept equal to - 5.4 x 10^{-4}mole.

Fig. (2.3) shows the optical density changes with time when different amounts of triphenylphosphine in ethanol are added. Considering the data for trans-N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine) ruthenium(11) in a 10^{-3}M solution of triphenylphosphine in ethanol, a curve of $\frac{dD}{dt}$ against D with a maximum around 50% reaction is again produced. Gradients were drawn to get $\frac{dD}{dt}$ and subsequently when $\frac{dD}{dt}/(D_0-D)$ was plotted against D, straight line was obtained. A graph of log $(\frac{Z - D}{D + D_\infty})$ against time gives a good straight line from which k_{Obs} can be calculated. Therefore it confirms the equations (2.18-2.20). Data is collected together in Table (2.3).

We know that for the simple scheme:

$$A \xrightarrow{k_1} B \qquad (2.22)$$

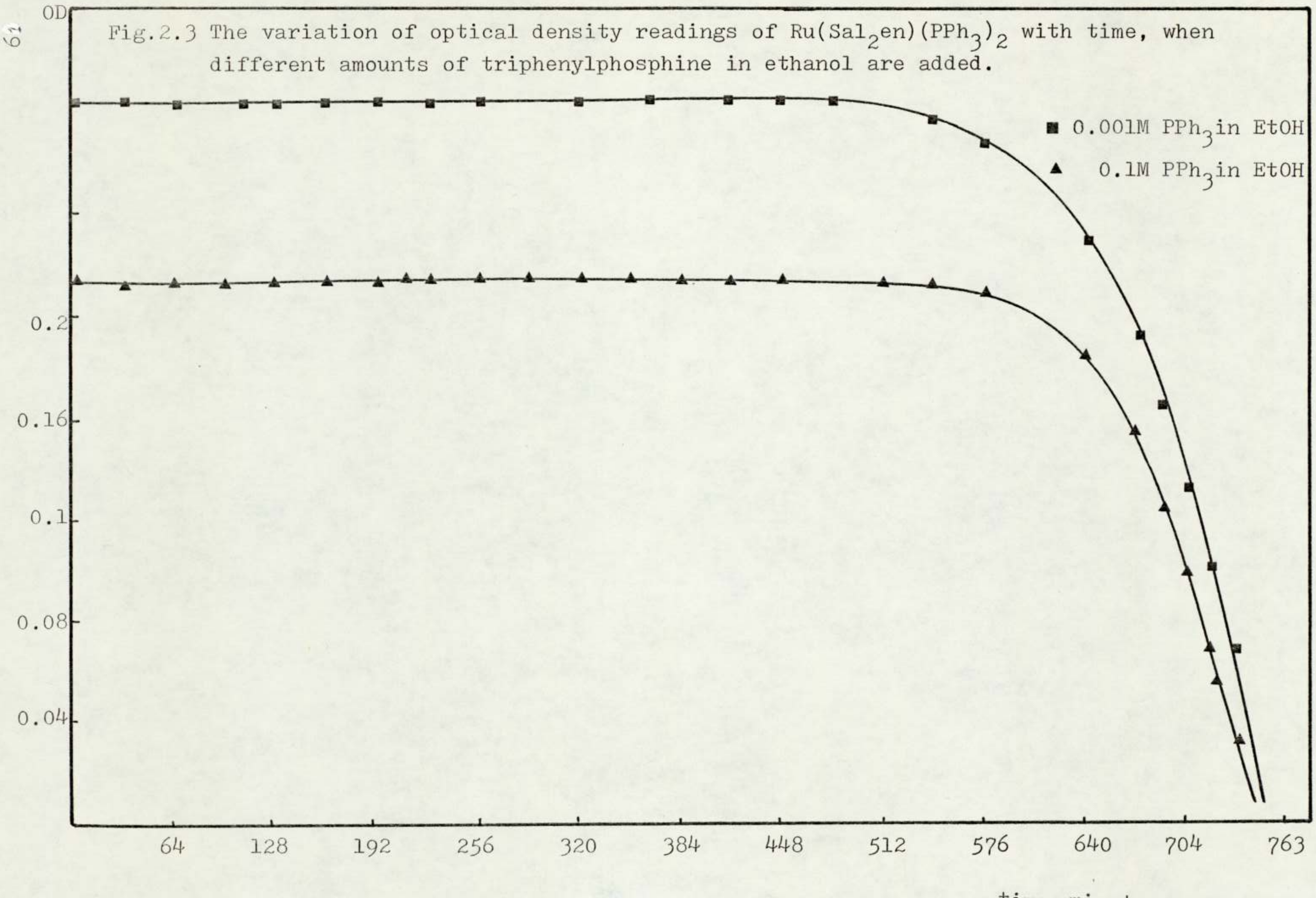


Fig.2.3 The variation of optical density readings of $Ru(Sal_2en)(PPh_3)_2$ with time, when different amounts of triphenylphosphine in ethanol are added.

TABLE (2.2)

VARIATION OF CONCENTRATIONS AT CONSTANT TEMPERATURE AND WAVE LENGTH

T/K^{o}	Conc/M	Z	D_0	D	k/sec^{-1}	λ/nm	solvent
313	$1.12x10^{-4}$	0.28	0.28	0.085	$2.08x10^{-4}$	700	EtOH
313	$1.68x10^{-4}$	0.49	0.42	0	$1.9x10^{-4}$	700	EtOH
313	$2.02x10^{-4}$	0.73	0.7	0.165	$1.84x10^{-4}$	700	EtOH
313	$2.8x10^{-4}$	1.21	1.09	0	$1.67x10^{-4}$	700	EtOH

TABLE (2.3)

VARIATION OF RATE CONSTANTS WITH DIFFERENT CONCENTRATIONS OF TRIPHENYLPHOSPHINE IN ETHANOL

Ru/M	Ph_3P/EtOH M	k/sec	Z
$2.86x10^{-4}$	10^{-1}	$1.29x10^{-2}$	0.725
$2.86x10^{-4}$	10^{-3}	$1.8x10^{-2}$	0.235

$$A + B \xrightarrow{k_2} 2B \qquad (2.23)$$

When k_1 becomes negligible, then $\log \left(\frac{D_0 - D}{D - D_\infty} \right)$ becomes a linear function of time. Many attempts were made to study the effect of triphenylphosphine in ethanol in concentration range 10^{-2}M and 10^{-4}M on trans-N,N'-ethylene-bis(salicylaldiminato)-bis(triphenylphosphine) ruthenium(11) , but unfortunately they were uninformative. No optical density changes were observed with time, indicating that no product even in small amounts was produced. There is the possibility that the addition of triphenylphosphine prevents the dissociation of the starting compound and makes the cleavage of Ru-P bond more difficult. In an attempt to overcome these problems a small amount of product was allowed to form before free triphenylphosphine in ethanol was added. Again the experiment was unsuccessful as reaction ceased, when the phosphine was added.

In attempting equilibrium studies, sets of experiments were carried out using different concentrations of triphenylphosphine solution in ethanol data are quoted in Table (2.4). It can be seen that triphenylphosphine has little or no effect on progress of equilibrium, although the quantative observation was made that it reduced the rate at which equilibrium is obtained.

From the equilibrium and kinetic studies shown in Table (2.4) it seems that when trans-N,N'-ethylene-bis(sali-

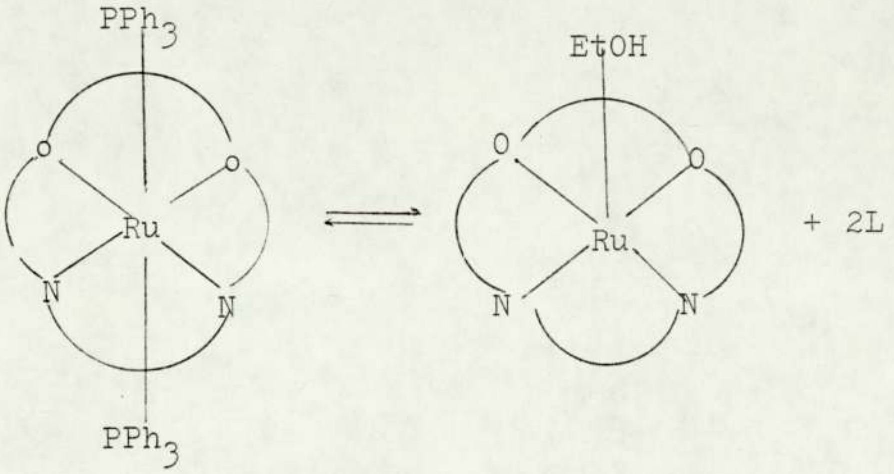
TABLE (2.4)

EFFECT OF DIFFERENT CONCENTRATION OF TRIPHENYLPHOSPHINE IN ETHANOL AT FIX TEMPERATURE AND WAVELENGTH IN EQUATION STUDIES Ru = 1.68×10^{-4}M IN ETHANOL AS A SOLVENT

t = 40°

PPh_3/M	0.1	0.07	0.05	0.01	0.007	0.003
D(initial)	0.04	0.05	0.038	0.03	0.04	0.038
D(final)	0.15	0.16	0.16	0.16	0.17	0.16

cylaldiminato)bis(triphenylphosphine)ruthenium(11) dissolves in ethanol, it is oxidized very rapidly and ruthenium takes the oxidation state (111). The bond between triphenylphosphine and ruthenium seems extraordinary easy to break, and so there is the possibility that one or both of the triphenylphosphine ligands will come off and produce'A' in equation (2,18)



(A)

'A' could then change to a non planar tetradentate b) or bisbidentate c) form depending on activation energies of the products and then follows by an autocatalytic reaction certainly all the evidence suggests that the compounds symbolized by A and B are isomers.

Attempts were made to isolate the brown and green compounds as solids, as described in the experimental parts (2.2.24) and (2.2.25) even although one can never be certain that what is isolated as a solid has the same composition as the solute. Infrared spectra of these two solid compounds are very similar to that of the trans-N,N'-ethylene-bis(salicylaldiminato)bis (triphenylphosphine)ruthenium(11) and no differences are observed between the ESR spectra of these two brown and green compounds. They show similar g factors and have the same magnetic susceptibilities. Attempts, using vapour pressure osmometry, to determine the molecular weights of the green and brown compounds in ethanol and chloroform were not successful since only low concentration can be achieved producing very low reading. Again in benzene only low concentration can be achieved and an accurate determination is difficult. However, attempts at determination yield an apparent molecular weight of 378 ± 25 for the green compound in benzene, which suggests that for each mole of ruthenuim approximately three particles are produced in benzene at these low concentrations. Therefore in benzene at low concentrations the green material is best regarded as monomeric complex which loses its two phosphine ligands almost completly. The molecular weight determination in benzene for the brown compound was impossible because of its still lower solubility. The pH of a 2.4×10^{-6}M solution of the green compound is 9.8. The same concentration of the brown compound gives a value of 8.1 compared to the measured pH of pure ethanol 9.11.

Attempts to follow changes in the infrared spectrum of the green solution as it changes to brown were not very informative since changes were detected. These observations suggest that the green and brown materials are closely related isomers.

INVESTIGATION OF TRANS-N,N'-ETHELENE BIS(SALICYLALDIMINATO)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(11) IN ACETONITRILE

When the visible spectrum of the compound in acetonitrile (2.24×10^{-4}M) is examined, a shoulder is observed at 700 nm ($\varepsilon = 9.3 \times 10^{2}$mole.C m.$^{-1}$)which rapidly increases with time ($\varepsilon = 3.2 \times 10^{3}$mole.Cm^{-1}) and a shoulder around 460 nm slightly increases and shifts to a higher wavelength of 500 nm. Two peaks at 395 nm ($\varepsilon = 7.2 \times 10^{3}$mole.Cm^{-1}) and 345 nm ($\varepsilon = 7.03 \times 10^{+3}$mole.Cm^{-1}) are initially present, the first of which disappears with time while the second one increases with time ($\varepsilon = 8.3 \times 10^{3}$mole.Cm $^{-1}$) Fig.(2.4) As can be seen from the absorption spectra no isobestic point occurs. The changes with time imply a sequence such as:

$$F \xrightarrow{k_1} G \xrightarrow{k_2} H \qquad (2.24)$$

and two different steps are suggested. $F \longrightarrow G$ corresponds to the formation of the green colour. Following the changes at a fixed wavelength (700 nm) shows that the first step is much faster than the second step. For each step separate plots of log

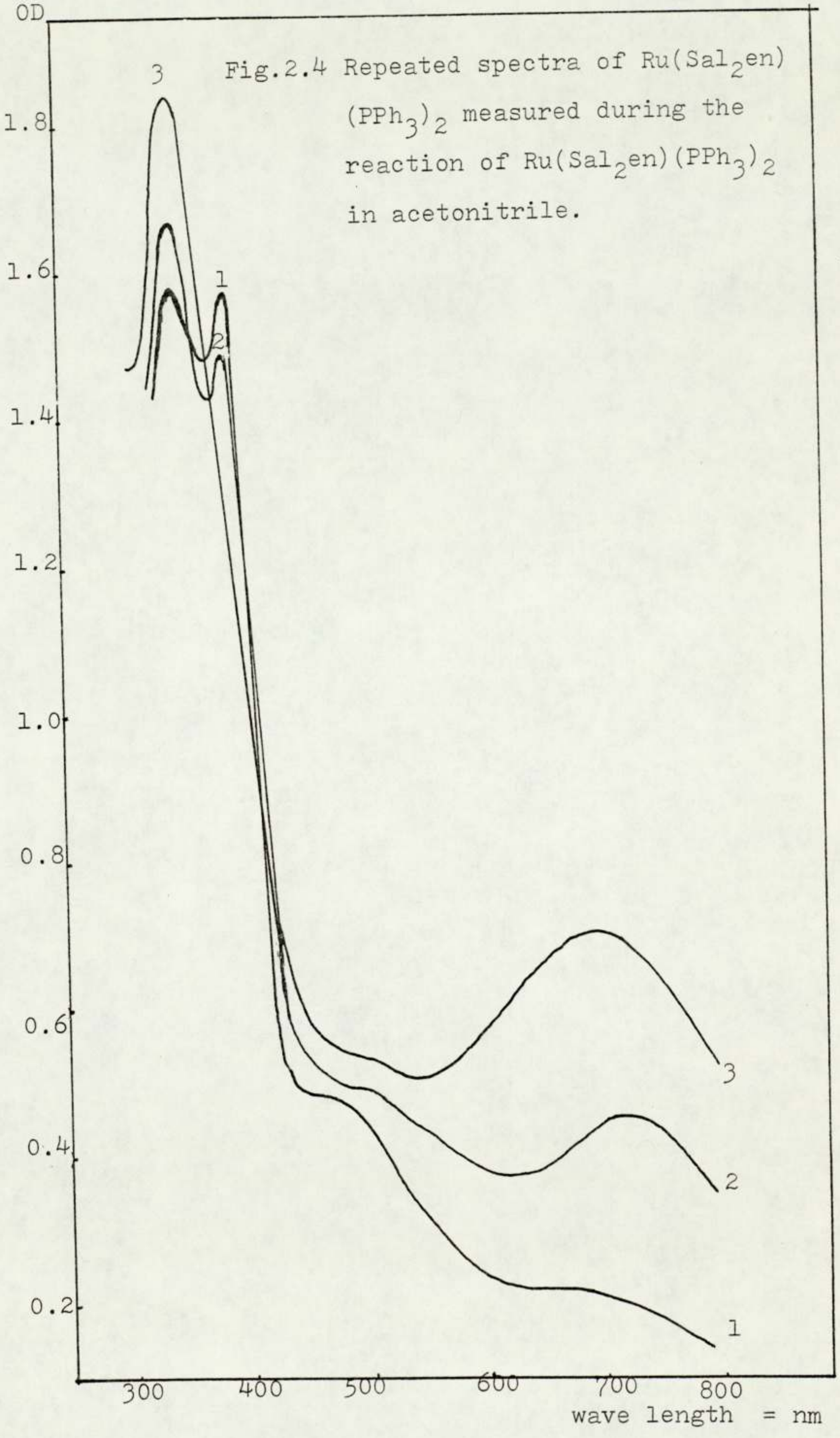


Fig.2.4 Repeated spectra of $Ru(Sal_2en)(PPh_3)_2$ measured during the reaction of $Ru(Sal_2en)(PPh_3)_2$ in acetonitrile.

TABLE (2.5)

VARIATION OF FIRST RATE CONSTANT WITH TEMPERATURE IN ACETONITRILE

T/K	Ru/M	k/sec^{-1}
323	1.68x10^{-4}	4.9x10^{-3}
318	1.68x10^{-4}	5.7x10^{-3}
313	1.68x10^{-4}	6.14x10^{-3}
308	1.68x10^{-4}	8.4x10^{-3}
303	1.68x10^{-4}	9.8x10^{-3}
298	1.68x10^{-4}	1.18x10^{-2}
295	1.68x10^{-4}	1.35x10^{-2}
A * 323	1.68x10^{-4}	3.9x10^{-4}
〃	〃	4.1x10^{-4}
〃	〃	4.2x10^{-4}

A * Reaction carried out under the oxygen atmosphere acetonitrile having been previously saturated by bubbling pure oxygen through it.

TABLE (2.6)

VARIATION OF THE SECOND RATE CONSTANTS WITH TEMPERATURE

T/K	Ru/M	k_2/sec^{-1}
303	1.68x10^{-4}	9.59x10^{-5}
308	1.68x10^{-4}	1.13x10^{-4}
313	1.68x10^{-4}	1.25x10^{-4}
318	1.68x10^{-4}	1.4x10^{-4}
323	1.68x10^{-4}	1.6x10^{-4}
328	1.68x10^{-4}	1.8x10^{-4}

$(D_\infty - D)$ against time were prepared and thus k_1 and k_2 calculated at different temperatures. Tables (2.5 and 2.6).

Plots of log k against the reciprocal of temperature for the first and second steps produce straight lines with activation energies equal - 171.8 K.J.mole^{-1} and 19.1 K.J.mole^{-1} successively.

Considering equation (2.24) for the two step we can write:

$$G = G_0 . e^{-k_1 t}$$

$$F = \frac{k_1 G_0}{k_2 - k_1} \quad (e^{-k_1 t} - e^{-k_2 t})$$

$$H = G_0 \left(1 - \frac{k_2 . e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right)$$

and if we define

$$D = \alpha' G + \beta' F + \gamma H$$

and

$$D_\infty - D_0 = \gamma G_0$$

we will find that

$$\frac{D_\infty - D}{D_\infty - D_0} = e^{-k_1 t} \left(\frac{(k_2 - k_1)}{k_1 - k_2} - \alpha \right) + e^{-k_2 t} . \left(\frac{k_1 (1 - \beta)}{k_1 - k_2} \right)$$

α is obviously small since D_0 must be small, so if assume

$$D_0 = 0$$

$$\alpha = 0$$

so

$$\frac{D_\infty - D}{D_\infty} = e^{-k_1 t}\left(\frac{k_2 - k_1\beta}{k_1 - k_2}\right) + e^{-k_2 t}\left(\frac{k_1(1-\beta)}{k_1 - k_2}\right)$$

and if $k_1 \gg k_2$ then towards the end of reaction

$$\frac{D_\infty - D}{D_\infty} = e^{-k_2 t}\left(\frac{k_1(1+\beta)}{k_1 - k_2}\right) = (1-\beta).e^{-k_2 t}$$

then we can write:

$$\log(D_\infty - D) = \log(D_\infty(1-\beta)) - k_2 t$$

and a plot of $\log(D_\infty - D)$ against time gives k_2 and β can be calculated since

$$\beta = \frac{D_\infty \ (\text{for } G \longrightarrow H)}{D_\infty \ \ \text{for } G \longrightarrow H \longrightarrow F}$$

plot of $\left(1 - \frac{D}{D_\infty}\right)$ also give a good straight line for all points when plotted against $\beta.e^{-k_1 t} + \frac{k_1}{k_2}.e^{-k_2 t}$

The effect of various concentrations of triphenylphosphine in acetonitrile on the first step at constant temperature was considered in Table (2.7).

It is obvious that different concentrations of triphenylphosphine do not change the rate constant of the first step. The effect of a wide range of triphenylphosphine concentrations on the optical density for the second step is too small to allow any slight variation to be detected. As described in the experimental part, equilibrium studies using acetonitrile are unsuccessful because of precipitation.

TABLE (2.7)

VARIATION OF FIRST CONSTANT WITH DIFFERENT CONCENTRATION OF TRIPHENYLPHOSPHINE IN ACETONITRIL

T/K	Ru/M	Ph_3P/M	k/sec^{-1}
3.13	$1.64x10^{-4}$	0.0005	$6.9x10^{-3}$
3.13	$1.64x10^{-4}$	0.007	$6.9x10^{-3}$
3.13	$1.64x10^{-4}$	0.007	$6.89x10^{-3}$
3.13	$1.64x10^{-4}$	0.01	$5.9x10^{-3}$
3.13	$1.64x10^{-4}$	0.05	$6.8x10^{-3}$
3.13	$1.64x10^{-4}$	0.07	$5.7x10^{-3}$
3.13	$1.64x10^{-4}$	0.1	$6.04x10^{-3}$
3.13	$1.64x10^{-4}$	0	$6.2x10^{-3}$

Substitution reactions on both Ru (11) and Ru (111) complexes are usually slow.(89) This means that oxidation of Ru (111) compounds by the majority of oxidizing agents is outer sphere e.g. ceric ion. Molecular oxygen however, normally behaves as an inner sphere oxidising agent. If oxygen is going to oxidize Ru (11) compounds in the usual inner sphere process, then for the majority of the systems one would expect the oxidation to be slow, since it is very difficult for oxygen to replace existing ligands. Since we observe a very rapid reaction the most likely conclusion is then either we have a ligand which comes off the ruthenium very rapidly allowing a rapid substitution and hence a rapid inner sphere process; or a rapid outer sphere process which is not usual for oxygen. There are claimed to be one or two examples of outer sphere oxidation using molecular oxygen. B.R.James has claimed one or two in literature.(90) Of these two possibilities we would tend to favour the inner sphere rapid process, since there is evidence that the ligand comes off. However, a third possibility must also be considered. It is known that for some compounds there is the possibility of oxidation of ligand. Such a process could result initially in the oxidation of an activated ligand followed then by movement of electrons within the complex. So the net result is that ruthenium is oxidized.

Oxidation of organic ligand is not detected, no signs of protonated ligand are detected in its infrared. It proves that the oxidized ligand is not present in the final product, however, if the ligand had initially been oxidized and then subsequently reduced by the ruthenium which is thus oxidized to Ru (111), the final form of the ligand would have the same. This has been claimed for iron system with ethylenediamine as a ligand(91).

Since we have the evidence from elsewhere of rapid loss of phosphine the inner sphere process seems to be the most likely one. The observation that the process is slower in acetonitrile compared to ethanol, also supports this deduction.

If we were dealing with an outer sphere process then it is difficult to see why the change of solvent should have much effect. If there is the possibility of the oxidation of the ligand, then there is no obvious reason why there should have been a change. If, however, the initial loss of the phosphine ligand is required, then it is easily possible to imagine that the initial loss involves the replacement of phosphine by solvent molecule, and acetonitrile a different ligand to ethanol would react at a different rate. If that is true then the different rate of loss of triphenylphosphine could account for the slower net oxidation. The only exception there is, is that in benzene in which the oxidation is fast, while to a first approximation benzene is not expected to believe as a ligand. There is the possibility that the rate is slower for acetonitrile than ethanol because acetonitrile is a better ligand and competes with oxygen for the free site, but benzene won't compete, therefore the rate is faster.

When acetonitrile, presaturated with oxygen is used in pure oxygen atmosphere, the rate constant for the first observed step remains constant within experimental error, which indicates that molecular oxygen does not effect the rate of this reaction in acetonitrile. There is the possibility then that either there is a rapid irreversible process involving oxygen before the rate determining step or alternatively use a sequence of two reactions, the first slow reaction which could be the loss of triphenylphosphine and that then would be followed by rapid reaction with oxygen. If we have two steps.

$$A \xrightarrow{k'} B \xrightarrow{k''} C$$

and step A ⟶ B is the slow step, the rate of formation of C is determined by the rate of formation of B and anything which is involved in B ⟶ C does not appear in the rate equation. The second alternative is considered to be the more likely, since it is very difficult to imagine that, if oxygen were involved in replacing triphenylphosphine directly, there would not be some degree of reversibility in the reaction.

Clearly we do not have enough evidence to distinguish definately between these alternative possibilities although my own preference is for the inner sphere process.

Attempts were made to isolate the compounds produced during the first and second steps when acetonitrile is used as a solvent. The full details of their isolation are described in experiments (2.2.26a) and (2.2.26b). These two products have identical elemental analysis and infrared spectra. The ratio of carbon to nitrogen is 9:1, which is very close to the expected ratio for Sal_2en and the amount of phosphorus is also very low. However, the analytical data do not appear to be consistent within any simple formula which can be envisaged. Repeat preparations gave the same results.

Since the kinetic studies show the rate of the reaction to be unaffected by the present of added triphenylphosphine, it is reasonable to suppose that the products of the first and second step contain the same number of triphenylphosphine ligands but we do not know how much.

In the infrared spectra of these two compounds no signs of acetonitrile is detected and up to now not a reasonable formula can be suggested for these two products, which may well be isomers.

INTERPRETATION OF PHOTOCHEMICAL RESULTS

Investigation was carried out to find a compound from which the preparation of new compounds would be easy. Consideration of the N,N'-ethylene bis(salicylaldiminato)bis(triphenylphosphine)ruthenium(11) properties suggested that it might be a very good starting material after being subjected to irradiation. One might expect it to lose one or two triphenylphosphine due to irradiation in air. When the above compound is irradiated in air as a solid for several days, a black product is obtained which was washed with ether and dried in vacuo. The molecular weight determination using vapour pressure osmometer was not successful because of low solubility. The compound was used as a starting material for other preparations which unfortunately did not yield pure products. Treatment of this material with ammonia, pyridine or sodium nitrite produced mixtures whose element analyses do not fit to any sensible formulae. Similarly irradiation of N,N'-ethylene-bis(salicylaldiminato)bis(triphenylphosphine) ruthenium(11) in presence of the desired ligands as the mixed of solids or in suitable solvents were not successful.

CHAPTER THREE

3.1.1) INTRODUCTION: PHTHALOCYANINE AS A LIGAND

The first recorded preparations of phthalocyanines were all accidential. In 1907 Braun and Tcherniac(92) reported that molten o-cyanobenzamide turned green and gave a small quantity of a blue,alcohol-insoluble, substance. The product obtained in this way is now known as metal-free phthalocyanine Fig (3.1).

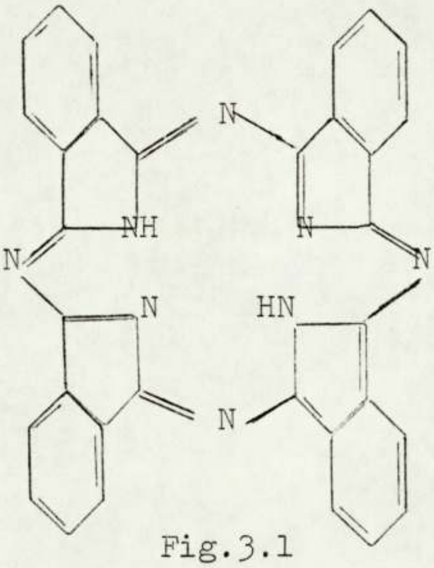


Fig.3.1

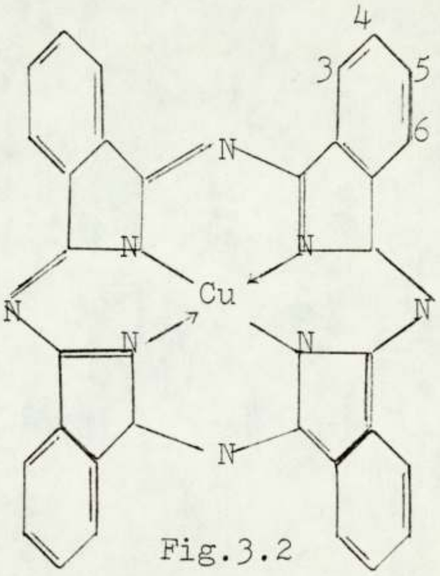


Fig.3.2

In 1927, De Diesbach and Von Der Weid(93) prepared copper phthalocyanine Fig(3.2) although several years were to elapse before the constitution was determined by two methods. Firstly, by analogy with previous experiments with dibromoxylenes(94), O-dibromobenzene was heated with cuprous cyanide in pyridine at 200°C, but gave a blue product rather than the expected phthalonitrile. The same blue product was also obtained by heating phthalonitrile (which was therefore the likely intermediate in the first process) with cuprous bromide in pyridine at reflux temperature. This second process is obviously an improvement on the first and yields of about 70% of the theoritical can be obtained. They observed the remarkable stability of their product to heat, concentrated alkali and concentrated sulphuric acid.

In 1928, at Grangemouth, Scotland, at the works of Messrs. Scottish Dyes Ltd., traces of a dark blue insoluble complex were noticed in the iron vessels used to prepare phthalimide from phthalic anlydride(94) and ammonia(95). This product was subsequently shown to be ferrous phthalocyanine. Since then literally thousands of patents and publications concerning the phthalocyanines have appeared. It is possible that the phthalocyanies have been the subject of more physical studies than any other single class of compounds, partly as a result of their unique structure and partly because of their high thermal and chemical stability.

The classic studies elucidating the structure of the phthalocyanines were carried out in the early 1930's under the direction of Sir Patrick Linstead. Linstead and his colleagues(95,96,97,98,99,100,101) showed that phthalocyanine Fig. (3.10PC) contained a ring system of four isoindol units linked by aza nitrogen atoms. It is therefore closely related to the naturally occuring porphyrins, but having aza rather than methine corner links. Fig. (3.3 and 3.4)

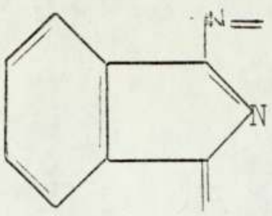


Fig.3.3

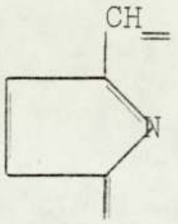


Fig.3.4

The analogy to the porphyrins makes the under-standing of the chemical and physical behaviour of the phthalocyanines especially important in the long term investigation of material life processes. The two central hydrogen atoms of structure(102) are replaceable by a wide range of metals and metalloids. The compounds so obtained are usually insoluble in common solvents, but have some slight solubility in higher boiling aromatic solvents such as quinoline, chlorobenzene and chloronaphthalene. The complexes are all intensely coloured purple, blue or green compounds with a beautiful red reflex. Most of them are thermally very stable and many will sublime unchanged at 400°C/10^{-6}mm. Copper phthalocyanine has been shown(103) to be stable at 900°C in vacuo.

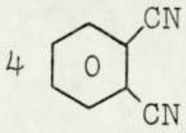
Metal free phthalocyanine exists in three polymorphic forms (α, β, and γ)(104), while most other phthalocyanines exist in two (α and β)(105). The polymorphic forms differ in their infrared spectra, x-ray diffraction(105,106,107) and conductivity. Although phthalocyanines in which the central metal ion has an oxidation state of 2 are the most common, complexes are known in all oxidation states from 0 to 6, phthalocyanine manganese complexes, for example, are known in oxidation states 0,1,2,3,4,(97,108,109,110).

Phthalocyanines exhibit varying stabilities towards solution in concentrated sulfuric acid. Virtually all the complexes are freely soluble in this acid, but some such as Pc·Cu and Pc·Ni are reprecipitated unchanged upon dilution, where as others, for example, Pc·Ca and $Pc\cdot Na_2$ are demetallated. The product, metal-free phthalocyanine $Pc\cdot H_2$, is itself slowly decomposed in concentrated sulfuric acid. Berezin has studied the behaviour in concentrated sulfuric acid in great detail. The phthalocyanine unit is moderately stable towards oxidation, but may be broken down to phthalimide or phthalic acid by a two electron oxidation with ceric or dichromate ions.(101,111) Elvidge(112) has developed the dichromate oxidation as a method for the quantitative determination of the oxidation state of the central metal ion. Under certain circumstances, a one electron oxidation product, having the ring system intact, may be detected. This product is paramagnetic and exhibits an electron-spin resonance spectrum(113,114), typical of a free radical. There has been much interest in the electron-spin resonance spectra of metal phthalocyanine, because information relating to the relative energies of the metal d orbitals, and to the presence or absence of δ and π-bonding, can often be deduced therefore.(115,116)

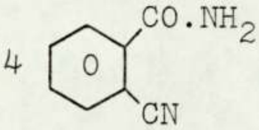
METHODS OF PREPARATION

Phthalocyanine metal complexes may be prepared by various methods, the more general methods(97,98,99,117,118,119) being illustrated in the following equations:

$$\text{PC H}_2 + \text{Mx}_2 \xrightarrow[\text{B.Pt}]{\text{Solvent (eg. quinoline)}} \text{PCM} + 2\text{HX} \qquad (3.1)$$

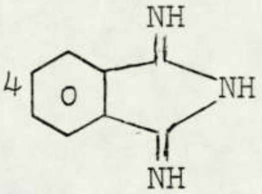


$$+ \text{M} \xrightarrow[\text{dry or solvent}]{300^{\circ}\text{C}} \text{PCM} \qquad (3.2)$$



$$+ \text{M} \xrightarrow[\text{dry}]{300^{\circ}\text{C}} \text{PCM} + 4\text{H}_2\text{O} \qquad (3.3)$$

Reactions (3.2) and (3.3) may also be carried out with metal salts or metal oxides.

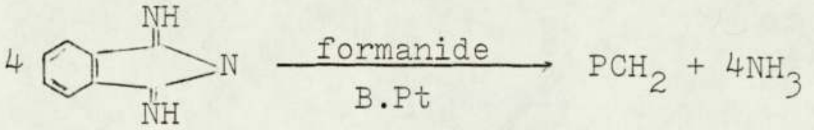


$$+ \text{Mx}_2 \xrightarrow[\text{B.Pt}]{\text{Solvent (eg.formanide)}} \text{PCM}+4\text{NH}_8 \qquad (3.4)$$

$$\text{PCL}_2 + \text{Mx}_2 \xrightarrow[\text{room temp.}]{\text{Solvent}} \text{PCM} + 2\text{Lix} \qquad (3.5)$$

Metal free phthalocyanine may be prepared by a number of routes of which examples are given below:

$$\text{PC Na}_2 + 2\text{H}_3\text{O}^+ \longrightarrow \text{PCH}_2 + 2\text{Na}^+ + 2\text{H}_2\text{O} \qquad (3.6)$$



(3.7)

$$PC\cdot Cu + SO_4H_2 \longrightarrow PC\,H_2 + SO_4Cu \qquad (3.8)$$

Equations (3.1) to (3.8) illustrate basic methods of preparation, but many variations are used, particularly in industry, to obtain an economic yield. Phthalic acid, phthalamide, phthalimide, and phthalic anhydride, together with urea, are often used instead of phthalonitrile, and catalysts such as ammonium molybdate or zirconium tetrachloride may be employed.(120) The reaction between phthalonitrile and metals (finely divided or acid-etched) is usually very vigorous at 250°C - 300°C, sufficient heat being generated to maintain the reaction temperature. This is an illustration of the ease with which the phthalocyanine skeleton, is formed. Even more surprising are the observations that palladium black(121) and gold(122) will dissolve in molten phthalonitrile. Reaction (3.2) between phthalonitrile and finely divided metals, metal hydride, oxide, or chloride is perhaps the most generally employed. For the unstable phthalocyanine complexes such as that of silver(98), the double decomposition reaction (3.5) is to be prefered. Nuclear halogenation often occurs when metal halides are reacted directly with phthalonitrile or O-cyanobenzamide; this may be minimized by the addition of urea, use of basic solvents, or carring out the reaction at a lower temperature.

Purification of the products is best effected by sublimation at 400°C in vacuo. However, not all phthalocyanines will sublime; recrystallization from chlorobenzene, quinoline, or chloronaphthalene may then be employed. Certain more soluble phthalocyanines may be soxhlet-extracted with lower boiling solvents such as acetone or alcohol.

The metal phthalocyanines behave as hetrogeneous catalysts in many reaction systems. Calvin and associates have shown that both metal-free and copper phthalocyanines undergo atomic exchange with molecular hydrogen.(123) Catalyze atomic exchange between hydrogen (and duterium) and water vapour, and catalyze the combination of hydrogen with oxygen at temperatures of 250°C-370°C. Certain metal derivaties, particularly the ferrous and chloroferric complexes, catalyze the decomposition of hydrogen peroxide.(124,125)

The type of metal to nitrogen bonding varies according to the metal. Generally, the transition metals are covalently bound to two anionic nitrogens of the phthalocyanine inner ring and the planar four-coordination completed through the two neutral nitrogen atoms. With non-transitional elements the bond is mainly ionic in character, with no further coordination, and this leads to a much lower order of stability, the metal being displaced from the salt-like compound by treatment with dilute acid. Additional stabilisation is possible where the transition metal has filled non-bonding d orbitals since, although there is no supporting evidence (126), the dxz and dyz orbitals capable of forming π - bonds with the surrounding phthalocyanine macrocyle. This would support the increased bond strength apparent in metal (eg. Pt) to the right of the transition series.

The high fastness to light and the attractive shades offered by the phthalocyanine chromophore have served to stimulate the search for useful water soluble derivatives ever since the first phthalocyanine patent (127) which describes the sulphonation of copper phthalocyanine in oleum. Direct sulphonation gives substitution almost entirely in the three positions, the water-soluble product derived from 4-sulphophthalic anlydride being considerably redder in shade than their sulphonated isomers. This difference is due mainly to aggregation in solution.

Products from the sulphonation of copper phthalocyanine which contains between two and three sulphonic acid groups per molecule have been manufactured for over 25 years as direct dyes for cotton, paper and wool. Copper phthalocyanine tetra-4-sulphonic acid has also been marketed(128). That is one of the compounds whose preparation was attempted in this part of the thesis.

The derivatives obtained through the chlorosulphonation(129) of copper phthalocyanine since a variety of dyes containing both sulphonamide and sulphonic acid groups can be obtained, eg. $[\mathrm{cuPC}\ (\mathrm{SO_3H})_x(\mathrm{SO_2NH_2ly}]$ (130).
The extent of chlorosulphonation can be controlled and the nature of the amine and number of sulphonamide substituents modified to affect such factors as shade, strength and affinity.

Phthalocyanines of some other metals can be similarly chlorosulphonated and at least one dye based on nickel phthalacyanine has been manufactured.(131)

Dyes solubilised by carboxylic acid groups are not so widely used but coppertetra(4)phenylphthalocyanine tetra(5)carboxylic acid, was manufactured by the I.G. as a green dye for cotton.

Ruthenium (11) phthalocyanine has been reported by Kreuger and Kenney(132). It is formed by the reaction of ruthenium trichloride and O-cyanobenzamide, and sublimes with difficulty. It is presumably square planar, although no magnetic data were recorded, and like ferrous phthalocyanine it forms adducts with anline and O-toluidine containing six molecules of base. It is stable in concentrated sulfuric acid but is not oxidized in hydrochloric acid suspension. Much scope for further study of phthalocyanine ruthenium(11) compounds whose preparation was attempted in this part of the thesis.

Phthalocyanine provides a very stable planar tetradentate ligand around metals. It should be possible in such a system to examine the effects of ligands along the Z axis without needing to worry about changes in the x and y axis.

There is also the possibility of studying the molecular orbital interaction in the x and y plane. Such as were studies on Co in vitamine B_{12} coenzyme where there is obviously an extensive molecular orbital interaction between the corrin ring and the cobalt, which means that the oxidation states of cobalt is much less meaningful than is usual for cobalt compounds. Also it is then possible to get quite unusual Z effects. These features should be even more apparent with the second and the third row metal where covalent bonding is more prevalent than for the first row metals.

In the mid to late 1970's there has been a considerable growth of photochemical interest in ruthenium compounds starting with the work of Whitten, who claimed to have catalysed the photochemical cleavage of water(133). Since there is this claim that a ruthenium compound is capable of catalysing the cleavage of water, and also since biologically photosynthesis,uses porphyrin ring compounds chlorophyll, then making the phthalocyanine compounds of ruthenium seem a reasonable way of using a metal for which activity is claimed, and a ligand similar to the biological ligand and attempting to study the effects of the system. If we could get reasonable solubility we could study photochemical or thermal reactions in a system which is related to the other work described in this thesis and yet at the same time is relevant to current areas of Chemical interest.

Although lengthy work was undertaken and is briefly reported here, it turned out to be unsuitable for more detail work primarily because great problems in obtaining complete combustion and therefore reasonable analytical data, occur. Also when we did get sensible analytical data we were unable to obtain water soluble compounds which definately contained ruthenium.

On the advice of my supervisor this work was stopped, since a large amount of the time put in was not being rewarded by useful results nor was there any obvious suggestion that useful compounds would be synthesised given a little more work.

EXPERIMENTAL PROCEDURE

(3.2.1) PHTHALOCYANINOMAGNESIUM(11) MgPC(134)

Lightly-etched(washed with a solution containing 3 % ethylene dibromide in ether), ether-dried magnesium turnings (2g) and dried, recrystallised phthalodinitrile (30g) were heated to 300°C and maintained at this temperature for 4 hours in a three necked flask fitted with an air condenser. The blue-green, molten product was poured off, cooled, ground up to a purple solid and successively extracted with hot benzene, dilute hydrochloric acid, water, ethanol and then dried.
It was recrystallised from boiling pyridine yield 23%.

Analysis			
Found	71.6%C	2.9%H	20.89%N
Expected for MgPC	71.6%C	2.9%H	20.89%N

(3.2.2) METAL-FREE PHTHALOCYANINE (PCH_2)(134)

The purified magnesium phthalocyanine (16g) was slowly added to a mixture of concentrated sulphuric acid (92ml) and distilled water (3.2ml), with stirring at 5°C.
The solution was further cooled in an ice/salt bath to -3°C and stirred for 45 mins. at this temperature.
The resulting green solution was filtered through a coarse glass pad and poured slowly onto crushed ice.

A blue compound with a beautiful purple-reflex separated. This was washed well with water to remove the acid, and with a little ethanol before drying in the oven at 120°C, yield 20%. It is only soluble in 1-chloronaphthalene.

Analysis

Found	74.1%C	3.7%H	21.8%N
Expected for			
$PC{\cdot}H_2$	74.6%C	3.5%H	21.8%N

(3.2.3) PREPARATION OF (PHATHALOCYANINO)CHLORORUTHENIUM (111)MONOPHTHALONITRILATE, $PC.Ru.Cl.C_6H_4(CN)_2$.(134)

Ruthenium trichloride (3.7g) with O-dicyanobenzene (25g) were mixed together by mechanical stirring in a 100 ml hemi-spherical vessel with a flat-flanged lid carring 4 inlets, air condenser, nitrogen-inlet tube and thermometer, the vessel and its contents were brought to 290-300°C by immersion in a bath of molten potassium thiocyanate. The mixture was heated under nitrogen for a fixed time 3 hours or until the mixture solidified. When cool, the product was chipped out of the vessel, and finely ground. At this stage it contained large amounts of free (-O-dicyanobenzene). The crude product was soxhelt extracted with boiling ethanol and then benzene for 2 hours.

Analysis

Found	56.2%C	2.6%H	6.6%Cl	15.5%N

Expected for
$PC.Ru.Cl.C_6H_4(CN)_2$ 61.8%C   2.6%H   4.5%Cl   18.8%N

(3.2.4) PREPARATION OF (PHTHALOCYANINO)RUTHENIUM(11) HEXA-AMILINATE(134) $PC.Ru.6C_6H_5NH_2$.

The product of the previous preparation was placed in an aluminia thimble and continuously soxhlet extracted with anline (250ml) for 12 hours, the dark-green aniline extracts were reduced to small bulk (10ml) by evaporation under high vacuum. The resulting solids were collected on glass sinter-pads, washed thoroughly with ether to remove the residual aniline and then dried at 110°C.

Analysis
Found   67.1%C   3.6%H   16.7%N

Expected for
$PCRu6C_6H_5NH_2$ 69.5%C   5.0%H   16.7%N

(3.2.5) REACTION OF (PHTHALOCYANINO)CHLORORUTHENIUM (111)MONOPHTHALONITRILATE WITH PYRIDINE.

The product obtained from experiment (2.1.3) was soxhlet extracted with boiling pyridine for 20 hours. On addition of ether to the resulting blue-green solution, the product separated as a deep-green solid, washed with ether and dried in vacuo.

Analysis
Found   59.2%C   3.1%H   Cl6.5%   N15.2%

Expected for
$PCRu.6C_5H_5N$ 68.4%C   4.23%H   18.0%N

(3.2.6) REACTION OF (PHTHALOCYANINO)CHLORORUTHENIUM(111) MONOPHTHALONITRILATE WITH OLEUM.

The product obtained from experiment (3.2.3) and oleum (23ml 15%) were heated more than four hours at 170±5°C. The black solution with black precipitate was poured into crushed ice. Then it was diluted to 480ml. The solution is brought to pH 8 with 40% sodium hydroxide solution and then to pH 5 with acetic acid. It was filtered off and the precipitate was washed with water until it became neutral and then washed with alcohol and then dried.

Analysis

Found	53.78%C	2.3%H	11.44%Cl	16.23%N	8.3%S

(3.2.7) REACTION OF (PHTHALOCYANINO)CHLORORUTHENIUM(111) MONOPHTHALONITRILATE WITH OLEUM

Phthalocyaninochlororuthenium(111)monophthalonitrilate (2g) was heated in oleum (20ml) with mercuric sulphate (0.08g) for 4 hours at 150°C. The mixture was poured into crushed ice (500g) and was diluted upto 700ml. The mixture was filtered and the precipitate was collected and washed with water until it became neutral and then was washed with ethanol. This product was identified as unreacted starting material (0.5g). The filtrate was brought to pH 8 with aqueous sodium hydroxide and pH 5 with acetic acid. On gradually evaporation and filtration in different sequences copper sulphate, sodium sulphate, sodium acetate and also a dark grey product were obtained. The grey product was washed with alcohol and ether and dried in vacuo.

Analysis

Found 17.2%C 2.1%H 1.1%Cl 1.2%N 5.5%S'

No suitable solvent or mixed of solvents was found using TLC thenique. Using pH meter titration of 40ml of (0.05 g/lit) of the grey product; water with aqueous solution of sodium hydroxide (0.0966 mole) gave a value of E = 179 for neutralization equivalent. This procedure was attempted with different percentages of oleum but all attempts were unsuccessful.

(3.2.8) PREPARATION OF COPPERPHTHALOCYANINE FROM PHTHALONITRILE AND COPPER(101)

A mixture of phthalonitrile (51.2g) and copper bronze (6.3g) was heated in an oil bath with stirring in a flask. A green colour first formed at 190°C. Then the mass became pasty at 220°C and was too stiff to be stirred at 270°C. At a bath temperature of about 220°C, the internal temperature began to mount rapidly and at times exceeded that of the bath by 45°C. The mass was left for another 5 mins. in the bath, cooled slightly, and ground with alcohol. The finely powdered product was repeatedly boiled with alcohol until it became colourless and contained no phthalonitrile and then dried in vacuo.

The finely ground pigment was dusted into concentrated sulphuric acid (133ml) at room temperature. After an hour, the solution was filtered through sintered glass, the funnel was washed with more acid, and the filtrate and washings poured in a thin steam with thorough stirring on ice (2400g). The precipitate was allowed to coalesce for four hours, collected, washed with boiling water and then alcohol and dried at 100°C.

Analysis
Found 57.7%C 2.54%H 18.79%N

Expected for
PC Cu 66.9%C 2.8%H 19.1%N

(3.2.9) SULPHONATION OF FREE PHTHALOCYANINE (135)

Oleum (7.6ml 15%), phthalocyanine (1g) and mercuric sulphate (0.04g) were heated together for ten hours at 170 ± 5°C with stirring, yielding a dark blue solution containing some precipitate. It was poured into crushed ice (100g) and diluted with water (200ml). The solution was brought to pH 8 with 40% aq sodium hydroxide and then pH 5 with acetic acid. It was filtered and precipitate was collected, washed with water until the filtrate became neutral. The dark blue precipitate identified as free phthalocyanine (0.85g). On complete evaporation of the blue solution traces of a dark blue product was observed from which no analysis was possible.

Analysis of first solid
Found 73.1%C 3.7%H 20.8%N

Expected for PCH_2 74.6%C   3.7%H   21.8%N

This reaction was attempted with 20% oleum and again free phthalocyanine was collected.

(3.2.10) PREPARATION OF SULPHONATED PHTHALOCYANINE

Copper phthalocyanine (2g) and oleum (20ml) and mercuric sulphate (0.08g) were heated at 175°C for 5 hours. The reaction mixture was poured in crushed ice (200g) and diluted with water (400ml). The solution was brought to PH 8 with 50% aqueous sodium hydroxide and then to PH 5 with acetic acid. The mixture contained blue and white crystals. The mixed crystals were separated by filtration and the volume of filtrate was reduced completely and the mixed precipitate were dissolved in 5 molar aqueous sulphuric acid solution (100ml) and filtered. The volume of the dark blue solution was reduced (20ml) and on standing dark blue precipitate was formed (0.8g) it was collected and washed with ether alcohol and then dried.

Analysis

Found	29%C	2.8%H	5.5%N	no end point was detected for sulphor determination.
Expected for $PC(SO_3H)_4$	46.8%c	2.2%	13.7%	153%S'

Conductivity for 0.325g/lit is equal to 1.73×10^{-1} $ohm^{-1}.g^{-1}.Cm^{+2}$ and for 0.0325g/lit is equal to $7.42\times10^{-1}ohm^{-1}.g^{-1}.Cm^{+2}$. Thin layers chromatography using a mixture of ethanol and water in a ratio 4:1 showed only one spot and one spot is also observed in 5 molar aqueous solution of sodium hydroxide.

40ml of 0.75g/lit of the dark blue product was titrated against sodium hydroxide (0.0096N) solution using pH meter a value 217 ± 10 was calculated for neutralisation equivalent which is constant with four sulphonic group per phthalocyanine ligand.

(3.2.11) PREPARATION OF SULPHONATED PHTHALOCYANIN

Copper phthalocyanine (4g) and mercuric sulphate (0.16g) were heated in oleum (40ml) at 170°C. After 8 hours it was poured in crushed ice (400g) and diluted to 800ml with water. The mixture was brought to pH 5 with calcium carbonate and then was filtered to remove excess of calcium carbonate. The volume of filtrate was reduced and some calcium sulphate was filtered off again and on complete evaporation of the second filtrate a dark blue residue was obtained. It was dissolved in cold water, filtered and evaporated to complete dryness and dried in vacuo (4g).

Atomic absorption spectroscopy showed 4,2%Ca and 3.3%Cu and conductivity of (0.075g/lit) of product in water gave a value equal to 5.5 $\text{ohm}^{-1}.\text{g}^{-1}\text{Cm}^{+2}$ same solution shows pH equal to 7.5. Because this product was supposed to be acedic and it was not, it could be a mixture or a Zwitter ion. For further purification this product was dissolved in water and passed through a cation exchange resin (ZeOKAB 225A H form) and then hydrogen sulphide was bubbled through the solution for 10 hours and the solution was left under H_2S atmosphere overnight and then filtered and copper sulphide precipitate was removed. Addition of ethanol to a concentrated solution of compound produced the dark blue precipitate which was washed with ethanol and then dried in vacuo for several days.

Analysis

Found 23.2%C 2.1%H 5.3%N 14.5%S

Column chromatography of this compound using alumina separated only one compound. Atomic absorption - spectroscopy gives values of 0.5%Ca and 0.1%Cu. Conductivity of (0.75g/lit) compound is equal to 0.57 $ohm^{-1}.g^{-1}.Cm^{+2}$ and pH of the same solution shows two peaks at 675nm ($\varepsilon = 2.18g^{-1}Cm^{+2}$) and 660nm ($\varepsilon = 2.02g^{-1}.Cm^{+2}$) and shoulder at 650nm ($\varepsilon = 1.52g^{-1}.Cm^{+2}$) and one peak at 345nm ($\varepsilon = 1.66g^{-1}.Cm^{+2}$). This compound is diamagnetic using Faraday method. Because of the solubility of the product, NMR spectroscopy was not informative. Using pH meter 40ml of (0.75g/lit) compound in water was titrated against aqueous solution of sodium hydroxide (0.0096N) gave a value equal to 361 ± 15.

(3.2.12) REACTION OF SULPHONATED PHTHALOCYANINE WITH FERROUS CHLORIDE

Ferrous chloride (0.16g) in water (40ml) and sulphonated phthalocyanine (0.5g) in water (50ml) were mixed together and refluxed. After 40 hours, the blue solution was filtered. Addition of ethanol on concentrated solution deposited dark blue precipitate which was washed with ethanol and dried in vacuo.

Analysis

Found 50.4%C 1.3%H 7.3%Cl 2.9%N 11.2%S 2.30%Fe

This compound is diamagnetic. The conductivity of (0.75g/lit) of this product is 0.31 $ohm^{-1}.g^{-1}.Cm^{+2}$, no obvious changes were observed in its infrared spectrum from that free ligand. Aqueous solution of the product gives a yellow colour with ceric ammonium nitrate and using 0.5 molar solution of ceric ammonium nitrate as a known concentration of product (0.02g in 10ml) give a molecular weight equal to 1071.

(3.2.13) REACTION OF NICKEL CHLORIDE WITH SULPHONATED PHTHALOCYANINE

Nickel chloride (0.2g) in water (20ml) was refluxed with sulphonated phthalocyanine (0.5g) in water (50ml) for 40 hours. The reaction mixture was cooled and filtered. Some dark blue precipitate (A)was collected on filtration (0.1g) it was washed with water and dried in vacuo. On complete evaporation some dark blue precipitate (B) was formed (0.35g) which was washed with ethanol. This product except water is only soluble in hot DMSO.

Analysis

Found (A) 34.9%C 1.2%H 3.5%Cl 2.2%N S'No end point detected.

(B) 45.5%C 1.3%H 7.6%Cl 2.6%N 4.4%S'

Atomic absorption spectroscopy give 2.3% Ni for product (A) and 4.5% Ni for product (B). Compound A is diamagnetic and compound B is paramagnetic with $x = 13.16x 10^{-6}$. Conductivity of a (0.75g/lit) of compound B in water gave a value of 0.57 $ohm^{-1}.g^{-1}Cm^{+2}$ and the pH of this solution is 4.5. Conductivity of compound A was not measured because of it's insolubility in solvents. Compound A is slightly soluble in hot DMSO and DMF only.

(3.2.14) REACTION OF FERRIC CHLORIDE WITH SULPHONATED COPPER PHTHALOCYANINE

Sulphonated phthalocyanine (0.5g) in water (30ml) was mixed with ferric chloride (0.13g) in water (20ml) and the reaction mixture was heated under reflux for 40 hours. The green solution was then filtered and a green precipitate (c) was collected which was washed with water (0.3g) and dried in vacou. On complete evaporation of solvent a dark blue compound was obtained which was washed with ethanol (0.1g).

Analysis

Found (C) 12.3%C 2.3%H 2.7%Cl 3.7%N 5.1%S'

(D) 9.6%C 1.4%H 2.7%Cl 2.2%N 11.6%S'

using Faraday method compound D is diamagnetic and compound C paramagnetic with $\chi = 37.8 \times 10^{-6}$. The green product C is not soluble in any organic or inorganic solvent. The conductivity of compound D (0.75g/lit) in water is equal to 0.3 $ohm^{-1}.g^{-1}.Cm^{+2}$ and the same solution shows a pH equal to 2.5. No obvious change is observed in their infrared spectra of these products from that of phthalocyanine, determing iron in compound C was not possible because of its insolubility and using concentrated nitric acid produced an insoluble reddish precipitate.

(3.2.15) REACTION OF CUPRIC CHLORIDE WITH SULPHONATED PHTHALOCYANINE

Cupric chloride (0.2g) in water (20ml) was mixed with sulphonated phthalocyanine (0.5g) in water (50ml) and refluxed for 40 hours. The mixture was cooled and filtered. No precipitate was found on filtration, the volume of the filtrate was reduced and on addition of ethanol, unreacted ligand was precipited (0.4g) and cupric chloride was collected on complete evaporation of solvent (1.2g).

(3.2.16) REACTION OF RUTHENIUM TRICHLORIDE WITH SULPHONATED PHTHALOCYANINE

Ruthenium trichloride (0.2g) was refluxed in ethanol (100ml) under nitrogen for one hour. Sulphonated phthalocyanine (0.5g) in degassed water (100ml) was added to the reaction mixture, and the mixture was refluxed under nitrogen for 40 hours. The dark blue solution was filtered under nitrogen and no precipitate was found. Addition of organic solvents on concentrated solution did not produce any precipitate and on complete evaporation of solvent a dark blue precipitate was found, which was washed with degassed ethanol and dried in vacuo.

Analysis

Found	14.1%C	1.5%H	2.5%N	14.8%S

The product was dissolved in water and passed through the cation exchange resin (ZeoKAB,H Form 225A) and the solvent was removed completely and dried in an evacuated oven. The product did not show any sensitivity in exposure to air, the pH of this product (0.75g/lit) is equal to 3 and conductivity of the same solution is equal to $0.5 ohm^{-1}.g^{-1}.Cm^{+2}$. The absorption spectrum of the same solution shows two overlapping peaks at $675nm(\varepsilon=2.32g^{-1}.Cm^{+2})$ and 660 nm $(\varepsilon = 2.32g^{-1}.Cm^{+2})$ and one peak at 635 $(\varepsilon = 2.08g^{-1}.Cm^{+2})$. Thin layer chromatography in a mixture of water and ethanol in ratio 3:2 shows only one spot.

(3.2.17) REACTION OF TRISTRICHLOROEXAKISDIMETHYL SULPHOXIDE-RUTHENIUM(111) WITH SULPHONATED PHTHALOCYANINE

Tristrichlorohexakisdimethylsulphoxide -ruthenium(111) (0.5g) in water (100ml) and sulphonated phthalocyanine

(0.61g) in water (100ml) were heated under reflux for 30 hours. The mixture was filtered and on addition of T.H.F. or acetone on concentrated solution the unreacted ligand was precipited, which was washed with T.H.F. and dried in vacuo. On complete evaporation of filtrate a mixture of ligand and tristrichlorohexakisdimethyl sulphoxide-ruthenium(111) was collected. The first precipitate was identified as unreacted ligand.

(3.2.18) REACTION OF DICHLORO-TRISTRIPHENYLPHOSPHINE RUTHENIUM(11) WITH SULPHONATED PHTHALOCYANINE

Sulphonated phthalocyanine (0.5g) in degassed water (100ml) was mixed with tristriphenylphosphinedichlororuthenium(11) (0.6g) in degassed ethanol (50ml), and the reaction mixture was refluxed under nitrogen for several days. On filtration light brown precipitate was collected and washed with water and dried and identified as tristriphenylphosphinedichloro-ruthenium (11), ligand was obtained by complete evaporation of solvent.

(3.2.19) The above experiment was repeated using propane 2-01 instead of ethanol.

(3.2.20) REACTION OF BLUE SOLUTION (CONTAINING RUTHENIUM (11))IN ETHANOL WITH FREE PHTHALOCYANINE

Ruthenium trichloride (0.25g) in ethanol (100g) and Adams catalyst (0.0002g) was heated at 50°C under hydrogen atmosphere. When the colour of the solution turned blue it was filtered immediately and reduction was continued while its absorbance was measured at wave length 700 nm every quarter an hour. When it reached its maximum absorbance,phthalocyanine (0.6g) was added to the mixture and the reaction mixture was heated under nitrogen at 50°C for 30 hours. Then it was filtered under the nitrogen and the precipitate was washed with ether and ethanol and dried.

Analysis

Found	65.8%C	3.4%H	3.57%Cl	19.36%N

(3.2.21) REACTION OF BLUE SOLUTION IN DMF WITH PHTHALOCYANINE

The previous experiment was carried out and DMF was used instead of ethanol as a solvent and unreacted phthalocyanine was isolated.

(3.3.1) DISCUSSION AND RESULTS:

Continuing our studies of square planar complexes, the preparation of ruthenium (11) complexes containing phthalocyanine as the macrocyclic N_4 ligand system was attempted.

Although there have been several previous reports on the preparation of ruthenium phthalocyanine complexes, most of these have not been well characterized.

Investigation of several possible methods for the preparation of ruthenium phthalocyanine complexes reveals that the reaction of ruthenium trichloride with O-cyanobenzamide, using naphthalene as a dilutant is the most effective one reported in the literature.(136)

In the usual preparation of phthalocyanine compounds, simple metal salts are heated with phthalodinitrile, phlalic acid, phthalic anhydride, phthalimide or phthalamide, producing water insoluble compounds. We have attempted to prepare the complete ligand first and then to insert the metal into the ligand.

Because phthalocyanine provides a very stable planar tetradentate ligand around the metal it is possible in such a system to examine effects on ligands upon the Z axis without worrying about changes in the x and y axis.

If we could get reasonable solubilities for these ruthenium compound then we could study both photochemical and thermal reactions in these systems. To get the desired solubility the sulphonation of either the starting material, phthalonitrile, or the sulphonation of the free ligand could be attempted.

In this thesis attempts to prepare the sulphonated PC ligand using concentrated sulphuric acid or different percentage of oleum are described.

In the case of concentrated sulphuric acid, metal free phthalocyanine decomposes and undergoes decomposition according to the reactions described in literature.(137,138)

$$H_2PC + H_2SO_4 \rightleftharpoons H_2PCH^+ + SO_4^-H \qquad (3.9)$$

$$H_2PC + 3H_3O^+ \rightleftharpoons H_2PCH_4^{4+} + 3H_2O \qquad (3.10)$$

and then conjugation in the ring is destroyed at this stage according to the equation (3.11)

$$H_2PCH_4^{4+} + 8H_2O \longrightarrow 4C_8H_5O_2N + 4NH_4^+ + H_2 \qquad (3.11)$$

Most of the liable metal phthalocyanins react in a similar manner, indicating that demetallation occurs rapidly by the reaction described by equation (3.12)

$$MPCH^+ + 2H_3O^+ \rightleftharpoons M^{++}(aq) + H_2PCH^+ \qquad (3.12)$$

which is then followed more slowly by reaction (3.9) and (3.10).

When free phthalocyanine or the compound we believed to be(phthalocyanino)chlororuthenium(111)monophthalonitrilate were sulphonated using either concentrated sulphuric acid or oleum the phthalocyanine ring cleaved and produced various products mixed up with the products produced during the neutralization and removal of the excess of sulphonating reagent, e.g. $CuSO_4$, $Na\ CO_2.CH_3$ and $Na\ SO_4$.

Sulphonation of copper phthalocyanine in sulphuric acid was also unsuccessful, but when oleum was used a dark blue water soluble compound in reaction mixture was obtained then two different procedures were attempted for the removal of the excess of oleum. In the first attempt excess of oleum was removed by using aqueous sodium hydroxide followed by the addition of acetic acid. This process produced mixtures of sulphonated ligand, sodium acetate, sodium sulphate, and cupric sulphate. All of these compounds have different solubilities in water. Their mixture totally dissolves in water, and when the volume of water is reduced sulphonated phthalocyanine is precipitated and separated. In the second method the excess of oleum was removed using calcium carbonate, and a ligand contaminated with copper and calcium is obtained. When this product is dissolved in water and the solution analysed for Ca and Cu by atomic absorption, and variable results were obtained for a given solution. Since this method for determining Cu and Ca seems to be unstable for this compound, a modification was devised. The solid was heated with a mixture of concentrated sulphuric and nitric acid, fumed down to dryness and then roasted to red heat. Finally the residue was dissolved in dilute nitric acid. This method for the determination of Cu and Ca gave reproducible results.

For further purification calcium is removed using a cation exchanger resin, and copper by bubbling sulphide through an aqueous solution of the ligand for 10 hours, before copper sulphide is filtered off. Subsequently complete evaporation of the water gives the pure ligand without any detectable Cu or Ca contaminations. This compound was submitted for analysis but very poor data was obtained, because of incomplete combustions. When the same sample was analysed at the chemistry Department of Birmingham University it was found that their equipment gave slightly better data for sulphur but even there it seems that the demands made by this material are beyond the limits of their equipment.

Aston Results	29 %C	2.9%H	5.5%N	S not detected
Edgebaston Results	23.2%C	2%H	5.3%N	14.5%S

Because the figure obtained from Aston for sulphur determination was unexpected a solution of the ligand was titrated against an aqueous solution of sodium hydroxide using a potentiometric method for the detection of the end point. A value for the equivalent weight of 218 ± 10 was obtained, which indicates 4 **sulphonic** group per ligand. Fig. (3.5) shows the pH changes with the volume of sodium hydroxide solution added.

Treatment of this sulphonated ligand with iron (11) chloride, nickel chloride or cupric chloride, even after prolonged refluxing yielded only the unreacted ligand. When this ligand was refluxed with iron (111) chloride a green insoluble compound was produced and it was found insoluble in all organic and inorganic compounds. When this new green product was heated in a crucible with concentrated sulphuric and nitric acids, and heated to red heat, a red precipitate was obtained which was not soluble in any organic or inorganic solvent. Therefore the determination of iron for this green compound proved to be impossible.

Analysis

Found 12.3%C 2.3%H 2.7%Cl 3.7%N 5.1%S

From the above experiments it can be concluded that the ligand hole is a suitable size for ferric ion but not for Ni, Cu, or Fe (11).

When $RuCl_3$ was refluxed in ethanol and then refluxed with the sulphonated ligand in water, followed by the complete evaporation of the solvent, a dark blue product was collected. This was then dissolved in water and

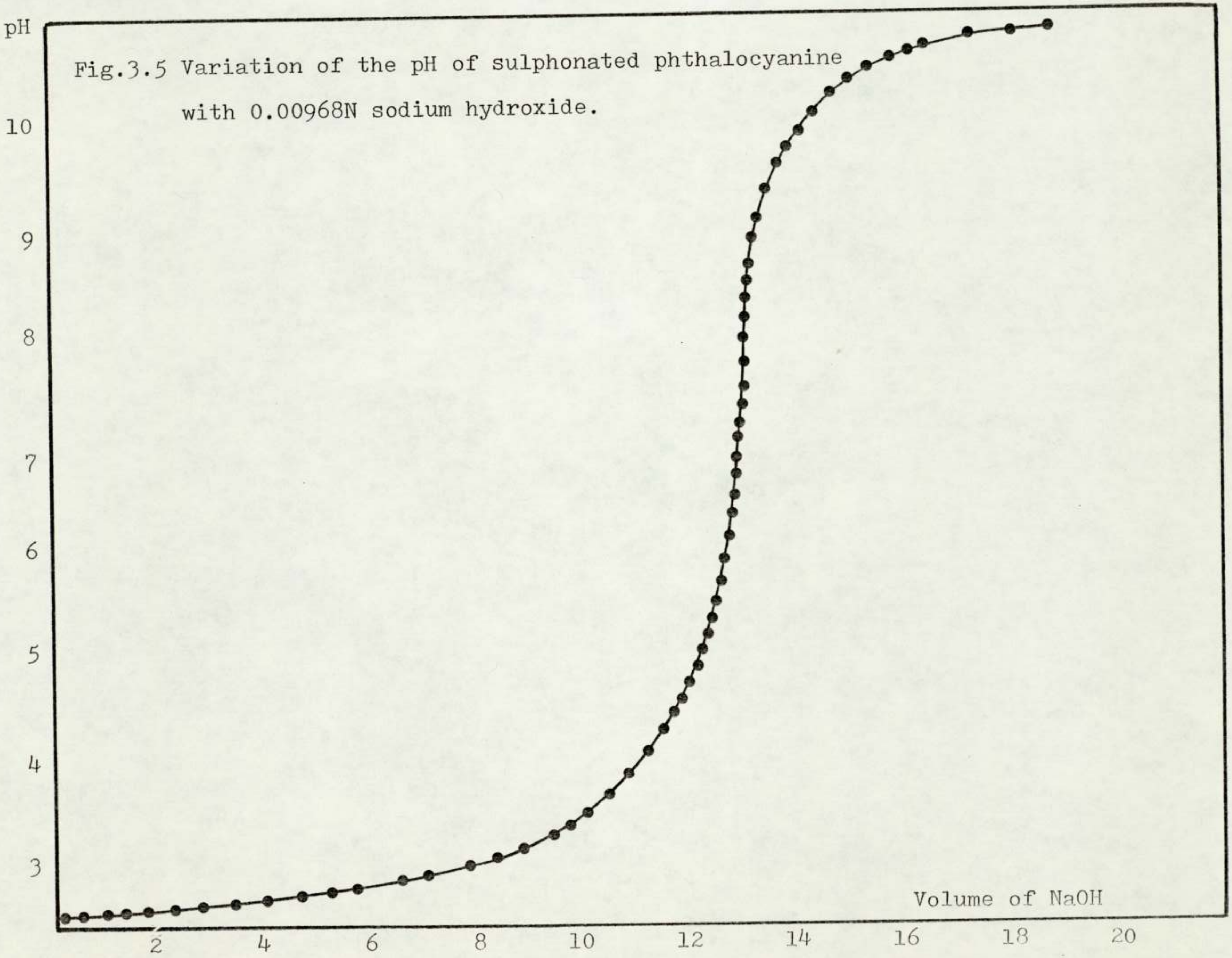


Fig.3.5 Variation of the pH of sulphonated phthalocyanine with 0.00968N sodium hydroxide.

passed through a cation exchange resin. Finally the water was removed and a dark blue compound was obtained again poor analytical data were obtained.

Different ruthenium starting compounds such as $RuCl_2.PPh_3$, $Ru(DMSO)_6.Cl_3$ and blue solution did not react with the sulphonated ligand and unreacted starting materials were collected at the end of the attempted preparations.

A few known compounds were also made, such as magnesium phthalocyanine, and also the preparation of (phthalocyanino)dichlororuthenium(111)monophtjonitrilate was attempted. In the latter case the analytical data is better fitted to the PC.Ru.Cl formula instead of $PC.Ru.Cl.(C_6H_4)(CN)_2$ and it is very difficult to believe any analytical figure. This product also used in attempts at the preparation of (phthalocyanino)ruthenium (111)hexa-anilinate, and the hexa pyridinate.Once again very poor analysis resulted.

One of the great problem in consequence was that it was very difficult to believe any analytical figures, on the grounds that we were never sure whether strange results meant that the compound is impure or merely that the apparatus was not the major contributing factor which in the end forced us to leave this area also the large amount of time being invested was not being rewarded by useful results nor was there any obvious suggestion that useful compounds would be synthesised given a little more work.

CHAPTER FOUR

(4.1.1) INTRODUCTION: REDUCTION OF $RUCl_3$ BY HYDROGEN:

Non aqueous ruthenium chemistry is hampered to some extent by the lack of a suitable starting material, "Commercial ruthenium trichloride" approximately "$RuCl_3.3H_2O$", the commonest starting point for ruthenium work is only soluble in water or the more polar organic solvents and it has the further disadvantage that it is non-stoichciometric, containing Ru (111) and Ru (1V) aquo and hydroxy species.(139) The most of the work in this thesis are concerned with the study of potentially convenient starting compounds, and that this particular chapter deals with reduced blue solution.

The study of ruthenium (11) chemistry thus necessitates reduction in situ or after complex formation, e.g. $RuCl_2$ is not readily accessible(140) and is very unsuitable when isolated.(141) Blue solutions containing ruthenium (11) chloro species have been made by hypophosphite(142) and by electrolytic reduction.(141) The isolation of solids from these blue solutions(143) and by reaction of ruthenium metal(144) with chlorine have been claimed. Refluxing "ruthenium trichloride" in allyl alcohol also gives a blue solution(145); this solution is catalytically very active for inter and intra molecular hydrogen transfer between molecules of allyl alcohol. However, nothing has been isolated from the solution although presumably it contains labile allyl ruthenium (11) species as the addition of pyridine to the solution yields $Ru(Py)_4Cl_2$.(145) Jorgenson(29) measured the electronic absorption spectra of the blue solution in hydrochloric acid and obtained results consistent with the presence of the planar ion $(RuCl_4)^{2-}$. Rechnitz(146) showed, by coulometry, that the electrolytically reduced solution of $K_2(RuCl_6)$ contained ruthenium (11). Adamson(30) has studied the chloride exchange in ruthenium (1V), (111) and (11) solutions, the exchange between free HCl and the anionic ruthenium species being faster the lower the oxidation state. He suggests that the species present in solution may be $(RuCl_4)^{2-}$ but he did however, precipitate a compound analysing roughly for Cs_4RuCl_6.

Halpern and co-workers(147) found that the blue solution made by reduction with titanium (111) chloride in aqueous solution absorbs olefins to form a green solution of 1:1 ruthenium olefin ratio. However, only "activated olefins" such as maleic or fumaric acids can be reduced with molecular hydrogen at 70-90°C. Attempts at hydrogen reduction of the green solution formed with blue solution and non-activated olefins results in the precipitation of metallic ruthenium which then causes heterogenous catalysis. The blue ruthenium (11) solutions were found to absorb carbon monoxide in a two stage reaction going first green and then yellow(147) the green carbonyl species being due to $[Ru(CO)(H_2O)Cl_4]^{2-}$ and the yellow being due to $[Ru(CO)_2Cl_4]^{2-}$ (147).

The so called "blue ruthenium chloro complexes" or the "blue ruthenium (11) chloride" have been the subject of many investigations over the last 25 years. This was first noted by Fourcnoy and Vauquelin in 1804(27) who ascribed it to a compound of osmium Claus(28) observed in 1845 that when ruthenium trichloride was heated with strong reducing agents such as metallic zinc, a deep blue solution was obtained. It was assumed at the time the blue colour was the result of the reduction of ruthenium trichloride to $RuCl_2$, and passed into the literature as such. Joly(148) also observed this deep blue colour when ruthenium trichloride was dissolved in a 25% alcoholic solution. However, he considered this blue solution to be $HORuCl_3$ instead of a reduction product of the ruthenium trichloride. A few years later Gutbier and Trencker(149) refuted Joly and stated that the blue colour was actually due to $RuCl_2$. Remy(150) in 1920 reinvestigated the reduction of ruthenium trichloride, by titrating $RuCl_3$ acid solutions with sodium amalgam, and adopted the hypothesis that the blue solution did result from bivalent ruthenium chloride complexes, Howe,(151) uncertain of earlier work,(152) reinvestigated this system. Preparing his blue solution by an alcoholic reduction, he obtained a solid upon evaporation of the solvent with the stream of hydrogen, which upon analysis had a Cl/Ru ratio of approximately two. An effort was made to determine the oxidation state of this solid by titrating alcoholic solutions with potassium permanganate but satisfactory end points could not be obtained, presumably because of reaction of permaganate with the alcohol present. However, without further evidence he stated that the blue solutions were H_2RuCl_4. Call and Lehmann(153), also prepared these blue solutions from ruthenium trichloride using H_2 in the presence of platinum black as the reductor. During this reduction a ruthenium mirror was produced, along with an intense blue solution, upon evaporation of the solution a solid was obtained which had Cl to Ru ratio 2:1. These authors also attempted to determine the oxidation state of this solid but their method of analysis was only good to approximately 20%.

Other investigators attempted to deduce the oxidation state of the ruthenium in these blue solutions employing both chemical and potentiometric methods, but meaningful results were not obtained, primarly because the authors did not know the oxidation state of their starting material.

More recently Jorgenson(29)has recorded the spectra of these deep blue solutions, and reported an extinction coefficient of approximately 1100 at 690nm, which he assigned as an electron transfer band. He also observed that as the chloride ion concentration increases, this band becomes more intense and shifts to higher wave-lengths. Although Jergenson made no prediction as to either the oxidation state, or the species responsible for the spectrum, Rechnitz(146)assumed that the band at 600nm was due to $RuCl_4^{2-}$ and proceeded to measure the rate at which it apparently reduced water.

Adamson(30)has also studied these blue solutions hoping to show that they were analogous to the ruthenium (111) chloride complexes characterized by Cady(154)and Fine.(155) They were able to elute a discrete band from an anion exchange column with 4 M hydrochloric acid, but no attempt was made to characterise it. These authors did report that in 10-11 molar HCl the magnetic moment of this blue solution was 2.12 to 2.35 B.M., which is unexpected for a low spin d^6 ruthenium (111) complex. The high magnetic moment was explained on the basis of an equilibrium between a low spin octahedral species $RuCl_6^{-4}$and a high spin tetrahedral $RuCl_4^{2-}$, although no additional data was offered to confirm this explanation.

Mercer and Buckley(156)undertook an investigation to characterize the blue solutions using ion exchange techniques they were able to separate three distinct species as well as observe at least two additional anionic species. Spectra was recorded for the species isolated, and characterization was begun.

The most plausible mechanism for the formation of the blue species would involve a disproportion of ruthenium (ll) chloride to form Ru metal and Ru (lll) species the reaction sequence would thus be:

$$Ru^{+2} + n\,H^{+}Cl^{-} \rightleftarrows RuCl_{n}^{2-n} + nH^{+} \tag{4.1}$$

$$RuCl_{n}^{2-n} \longrightarrow Ru^{o} + RuCl_{n}^{3-n} + nCl^{-} \tag{4.2}$$

$$RuCl_{n}^{3-n} + Ru \longrightarrow \text{blue species} \tag{4.3}$$

The ruthenium (ll) species undergoing disproportionation is most likely a ruthenium (ll) chloride in which "n" is greater than one, since uncomplexed ruthenium (ll) has been shown to be stable to disproportionation.

A similar disproportionation mechanism could also explain the observed decomposition of the dimeric ruthenium (lll) chloride complexes in low hydrogen ion. A mechanism such as :

$$Ru_{2}Cl_{3}^{3+} \xrightarrow{\text{low } H^{+}} Ru\ (lV)+Ru(lll)Cl_{n} + (3-n)Cl^{-} \tag{4.4}$$

$$Ru(ll)Cl_{n}+Ru_{2}Cl_{3}^{+3} \longrightarrow Ru(lll)+Ru_{2}Cl_{3}^{+2} \tag{4.5}$$

might be involved in the formation of the blue species as a product of decomposition.

The aqueous chemistry of ruthenium is possibly the most complicated of the transition series. In addition to forming complexes with a large variety of ligands, and existing in a multiplicity of oxidation states, the aqueous chemistry is further complicated by the instability of many of these complexes and the tendency of others to form polymeric species.

The first work of major importance on ruthenium (lV) in acid solution, was conducted by Wehner and Hindman.(157) Working in perchloric acid medium, they were able to prepare uncomplexes ruthenium (lV) by the electrolytic reduction of ruthenium tetroxide. Other investigators employing electrochemical techniques support this conclusion and have postulated that the Ru (lV)species is most likely oxygen bridged.

Investigations on the aqueous chemistry of Ru (lll) chloride complexes have not been as fruitful. Although monomeric K_2RuCl_6, and dimeric $K_4Ru_2Cl_{10}O.H_2O$ salts exist, no chloride complexes of Ru (lV) have been identified or characterized in solution. Wehner and Hindman(158) studied Ru (lV) chloride complexes in perchloric acid by equilibrium and kinetic method. This result indicated that these ruthenium chloride solutions contained at least three species, of which one was neutral and two were anionic. Although they presented evidence for three species, no attempt was made to isolate or characterize them. More recently Mercer and Cox(159) attempted to separate and identify these ruthenium (lV) chloride complexes, using ion exchange and paper electrophoresis techniques.

The aquochlororuthenium (lll) complexes have been isolated and characterized. Rehn and Wilson(160) first separated a number of these complexes by ion exchange techniques. Although they did not identify the species they isolated, they were able to record the absorption spectra of the various fractions eluted from ion exchange columns. Later Cady(154) extended this investigation and isolated, identified $RuCl^{+2}$ and the two isomers of $RuCl_2^{+1}$.

Wehner and Hindman(158) observed the existance of intermediate species which contain ruthenium in the formal oxidation states of (4.2) and (3.5), which at times were atributed to the presence of hydrolitic species. Similar "odd", oxidation states have also been reported between Ru (lll) and Ru (ll). Krauss(161) reported the existance of a blue ruthenium cyanide, $Ru_2(CN)_5$which would contain ruthenium in the formal oxidation state of (2.5). Stephenson and Wilkinson(162) also prepared a ruthenium (2.5), tetra-n-butyratodirutheniumchloride. From magnetic data they postulated that this complex contained ruthenium in an oxidation state of (2.5). This was then varified by Cotton,(163) who conducted an x-ray structure determination of this compound. They reported that the two ruthenium atoms per molecule were crystalographically equivalent with an average oxidation state of (2.5). Nicholson(164) also reports a ruthenium (2.5) complex formed by concentrating an ethanolic solution of ruthenium trichloride and tri-n-butylphosphine, the observed magnetic moment of this complex was reported to be 0.75 B.M/Ru which they claimed was a low spin ruthenium (2.5). My studies on blue solutions should be viewed against the background summarized above.

The work reported here consists of the preparation of the ethanolic blue solution by reduction of Ruthenium trichloride using hydrogen and Adams catalyst. The rate of formation of the blue solution and the effects of temperature and various concentrations of catalyst have been investigated spectrophotometrically. Attempts were also made to prepare new ruthenium (11) compounds from the ethanolic blue solution of ruthenium trichloride but they were unsuccessful.

EXPERIMENTAL PROCEDURE

(4.2.1) PREPARATION OF BLUE SOLUTION IN ETHANOL:

Ruthenium trichloride(165) (0.1g) was dissolved in ethanol (200ml) and a small amount of Adams catalyst (the catalyst is normally prepared in situ by the reaction of platinum dioxide by the hydrogen)(0.0001g) was added to the reaction mixture, together the mixture was degassed using freeze-thaw method. Hydrogen was bubbled through the reaction mixture at room temperature until it became blue (approximately 3hours). The mixture was filtered through a sinter under nitrogen atmosphere and kept under nitrogen in a dry box. Different samples were taken from the filtrate. First a 5mm cell was filled with the blue solution and at the fixed wave-length of 685nm optical density changes with time were measured. A plot of optical density against the gradient at each point produced a straight line. A second sample was filled in dry box in a stoppered cell and its spectrum was obtained immediately and the spectrum of this sample was obtained after remaining 24 hours in the dry box, under nitrogen. No obvious changes were observed in the spectrum. A third sample was also taken from the stock solution, diluted with degassed ethanol while still in the dry box. The spectrum was identical with that of the undiluted sample. This sample also showed the same spectrum as before after 24 hours.

* All samples were withdrawn from the serum-capped stock container using syringes.

(4.2.2) Ruthenium trichloride (0.1g) was dissolved in ethanol (200ml) and Adams catalyst (0.0001g) added. The mixture was degassed and the reaction mixture was hydrogenated at room temperature. Samples were withdrawn from the serum-capped reaction-vessels using syringes, every half an hour, and their spectra were quickly measured. 5mm cells were found to be the most convenient size. The first spectrum showed a maximum around 400nm, but after approximately $1\frac{1}{2}$ hours three maxima had appeared at 680nm, 400nm and 360nm. Only the peak at 680nm regularly increased with time which after approximately 12 hours, its intensity reached the maximum and then began to decrease. (i.e. concentration of Ru(11) decreases).

(4.2.3) The above experiment was repeated and when the solution turned blue it was filtered under nitrogen and left in a dry box, after a while (nearly 6 hours) disproportionation was occured and a metallic mirror covered the reaction vessel.

(4.2.4) Ruthenium trichloride (0.1g) was dissolved in ethanol (200ml) and Adams catalyst (0.0001g) added. The mixture was degassed and hydrogen was passed through it at 30°C samples were withdrawn from the serum-capped reaction-vessel and approximately $7\frac{1}{2}$ hours was required to reach the maximum concentration of Ru(11) as determined at 680nm. It was observed that colour change from brown to green was accelerated, but not green to blue. This experiment was carried out at 40°C and 50°C. At 50°C the maximum intensity at 680 nm was obtained within approximately 2 hours.

(4.2.5) Adams catalyst (0.0001g) in ethanol (200ml) was left in a dry box under nitrogen for forty eight hours. Ruthenium trichloride (0.1g) was added to the mixture in the dry box and then hydrogenation was followed at room temperature. Samples were withdrawn from the reaction-vessel at fixed intervals and the spectra of the sample were measured. After approximately 9 hours the maximum concentration of Ru(11) was obtained. It was concluded that one could not activate the catalyst and that it is not possible to reduce the time of reduction of:

$$\mathrm{Ru(1V)} \longrightarrow \mathrm{Ru(111)} \longrightarrow \mathrm{Ru(11)}$$

by this method.

(4.2.6) Ruthenium trichloride (0.0125g) was dissolved in ethanol (100ml) and Adams catalyst (0.025g) added and the mixture degassed and the hydrogen was bubbled through the reaction mixture at 50°C. Samples were withdrawn at fixed intervals and the spectra of the samples were obtained. It was observed that the amount of catalyst increased the rate of the reaction i.e. (Ru(lV)⟶ Ru(lll)⟶ Ru(ll)), but the maximum concentration of Ru(ll) was not obtained with respect to the previous experiments.

(4.2.7) Ruthenium trichloride (0.0125g) was dissolved in ethanol (100ml) and Adams catalyst (0.001g) was added at room temperature, the mixture was degassed and hydrogen was bubbled through it at 50°C. Samples were withdrawn at fixed intervals and the spectra of the samples were measured. It was also observed that the amount of catalyst used in this experiment increased the rate of reaction but not as much as in experiment (4.2.6) but the maximum concentration of Ru(ll) was higher than that obtained in experiment (4.2.6).

(4.2.8) Ruthenium trichloride (0.1g) was dissolved in ethanol (200ml) and Adams catalyst (0.0001g) added. The mixture degassed and hydrogen was bubbled through it and hydrogenation was performed. When the maximum concentration of Ru(ll) as determined spectrophotometrically, was reached, the reaction mixture was filtered under nitrogen and the stock solution was divided into 6 portions kept in a dry box under nitrogen. The effects on this solution of methylamine, ethylamine, butylamine, benzylamine acetylaceton and bipyridyl were examined separately. The reaction of the blue solution with each of the first four material was rapid and the blue colour quickly changed to green and then yellow. The effect of the last two additives, the chelating ligands was slower (a quarter of an hour) and the colour changed to green and violet respectively for sample 5 and 6.

(4.2.9) Ruthenium trichloride (0.1g) was dissolved in ethanol (200ml) and Adams catalyst (0.0001g) was added to the reaction mixture which was then degassed, and hydrogenation was performed. When the maximum concentration of Ru(11) was obtained, the mixture was filtered under nitrogen and then divided into two parts, which were kept in a dry box. The first flask was filled with carbondioxide and the second one was treated with nitrous oxide and the samples were left under CO_2 and N_2O for one week. On concentration, light viscous brown ligands were obtained, attempts to obtain solid from the viscous ligands were not successful.

(4.2.10) PREPARATION OF BLUE SOLUTION IN WATER.

Ruthenium trichloride (0.3g) was dissolved in water (50ml) and Adams catalyst (0.0003g) was added. The reaction mixture was degassed and hydrogen was bubbled through the solution, the brown colour changed to green and then disproportionation occured. This procedure was attempted unsuccessfully many times with different amounts of Adams catalyst, and only once was it successful. Then it was filtered under a hydrogen atmosphere. Degassed aqueous ethylenediamine (5ml) was added to the filtrate and the colour rapidly changed to violet and then slowly to light yellow. Attempts were made to produce a precipitate from the concentration solution by adding big anions or big cations. These were unsuccessful and on complete evaporation of the solvent a dark yellow oily liquid was obtained.

This procedure was also attempted several times, unsuccessfully, using platinum black and Pd on charcoal.

(4.2.11) Ruthenium trichloride (0.2g) was dissolved in ethanol (400ml) and Adams catalyst (0.0002g) was added to the reaction mixture, which was degassed and treated with hydrogen. When the maximum concentration of Ru(11), determined spectrophotometrically the mixture was filtered under a hydrogen atmosphere and degassed ethylenediamine (5ml) was added to the reaction mixture. The colour of the reaction mixture changed immediately to violet and after 10 minutes precipitate was observed. This was collected by centrifiuging and then washed with alcohol and ether and dried in a desiccator Many attempts were made to identify this violet product but the results were not reproducible, therefore Gel Chromatography for further purification was performed. The G_{10} (sephadex) was dissolved in water, left 20 hours to swell, and then the water evaporated completely and then packed in a column. The violet material was dissolved in water and passed through the column and the eluent was repeatedly examined spectrophotometrically. Two different bands were separated in the column, the first layer, which was brown, passed rapidly through the column, then a yellow layer moved down very slowly. On complete evaporation of the brown layer a very air sensitive brown compound was obtained. This compound in exposure to air became very sticky and looked to decompose. The yellow layer contained little material and immediately after coming out through the column it decomposed to a dark oily material. No attempts were made for identification of the yellow bond.

Analysis
"Brown"
Found 21.9%C 6.5%H 17.0%Cl 23.8%N
IR: 3200, 2000, 1600 and 720Cm^{-1}.

The visible spectrum of the brown compound in water (0.1g/lit) changes with time and the spectrum of the brown compound in oxygen free water is the same as in ordinary water. In it's visible spectrum there is one maximum at 425nm ($\varepsilon = 14g^{-1}.Cm^{+2}$) which increases with time (ε = 17.g.$^{-1}$Cm^{+2}) and one at 325nm (ε = 14g.$^{-1}$ Cm^{+2}) which also increases with time (ε = 14.8g^{-1}.Cm^{+2}). (Note specifically the units in which ε is expressed) The visible spectrum of the solution in water after the addition of a few drops of ethylenediamine didn't show any change with time. The effect of various bases was considered on the solution of this precipitate in degassed ethanol. It was treated with degassed pyridine in ethanol, diphenylamine in degassed ethanol, triethylamine in degassed ethanol, methylamine in degassed ethanol & sodium methoxide in degassed ethanol. It was only very soluble in ethanolic solution of sodium methoxide. This reaction is irreversible and the addition of acetic acid does not reprecipitate any material. The use of cation exchange resin shows that the colour is due to cation.

Its solution in water produced a brown precipitate with sodium perchlorate, and amonium hexafloro-phosphate. The brown product is diamagnetic as determined using Faraday method. The conductivity of this compound in water (0.4g.l^{-1}) is 0.304 Ohm.$^{-1}$g.$^{-1}$Cm^{+2}.

(4.3.1) DISCUSSION AND RESULTS:

Earlier investigations on the blue ruthenium chloride systems have contributed relatively little to the detailed understanding of the Chemistry involved. The principle reason being that in previous studies where quantitative measurements were made on solutions containing the blue species, the results were ambiguous. Primarily this was because they were conducted on solutions containing mixtures of the blue complexes as well as other species of various oxidation states.

Undoubtedly the most useful findings of the research described here are those that enable one to find when and how the maximum concentration of ruthenium(11) can be achieved. Using this information the preparation of some new Ru(11) compounds was attempted.

When the formation of blue solution by reduction of ethanolic solution of ruthenium trichloride was considered spectrophotometrically, with samples being taken from the reaction system at various times, it was observed that there are two peaks which appear in the first two or three hours of the reaction at the ultraviolet end of the visible spectra. These peaks reach a maximum, then they slowly disappear. It is only later as the optical density at 360nm and 400nm is decreasing, that a peak at 680nm, which gives rise to the blue colour begins to appear. This seems in the qualitative interpretation, to imply that firstly an intermediate, probably Ru(lll), is produced which gives the short wave length absorptions and this subsequently reacts further to give the blue absorbing material. The absorption peak at 680nm also goes through a maximum, and if at this stage the Adams catalyst is filtered off, the formation of a ruthenium mirror and the disappearance of blue colour follow, which is indicative of a disproportionation reaction. Therefore a reasonable and qualitative interpretation of these observations is the sequence reaction:

$$\mathrm{Ru(lV)} \longrightarrow \mathrm{Ru(lll)} \longrightarrow \mathrm{Ru(ll)} \qquad (4.6)$$

and in the absence of the Adams catalyst

$$3\mathrm{Ru(ll)} \longrightarrow 2\mathrm{Ru(lll)} + \mathrm{Ru}_{\downarrow} \qquad (4.7)$$

This last reaction may not be just one simple single step, but a complicated series. Presumably if the Adams catalyst is not filtered off then the rereduction of ruthenium(lll) perhaps reduces the rate which this disproportionation is observed to occur.

Although with the Adams catalyst present the black precipitate of ruthenium metal is ultimately observed.

When we attempt to fit the standard kinetic equations to the optical densities at these various wave lengths.

measured as a function of time, it is observed that the peaks which are probably due to Ru(111) obey a first order equation during their decay. The peak at 680nm which is asigned to be Ru(11) also appears to fit a first order curve after a few hours have elapsed. This is probably a simplification for a scheme such as:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (4.8)$$

where $A \longrightarrow B$ is essentially complete.

When the formation of the blue solution by reduction of an ethanolic solution of ruthenium trichloride at room temperature was considered spectrophotometrically the investigation concentrated on the events after Ru(11) began to appear.

Optical densities of four different wave lengths 680nm, 500nm, 400nm and 360nm were plotted against time as shown in Fig.(4.1 a,b). The optical density readings for the two wave lengths 360nm and 400nm were plotted against time. Gradients $(\frac{dD}{dt})$ were obtained and plotted against time. These plots yielded straight lines. This implies a first order rate low. Consideration of the spectra obtained from the reduction of the blue solution at room temperature shows that at least $7\frac{1}{2}$hours is necessary to reach to maximum concentration of Ru(11), as determined by the optical density at 680nm, and after this period the concentration decends. There is the

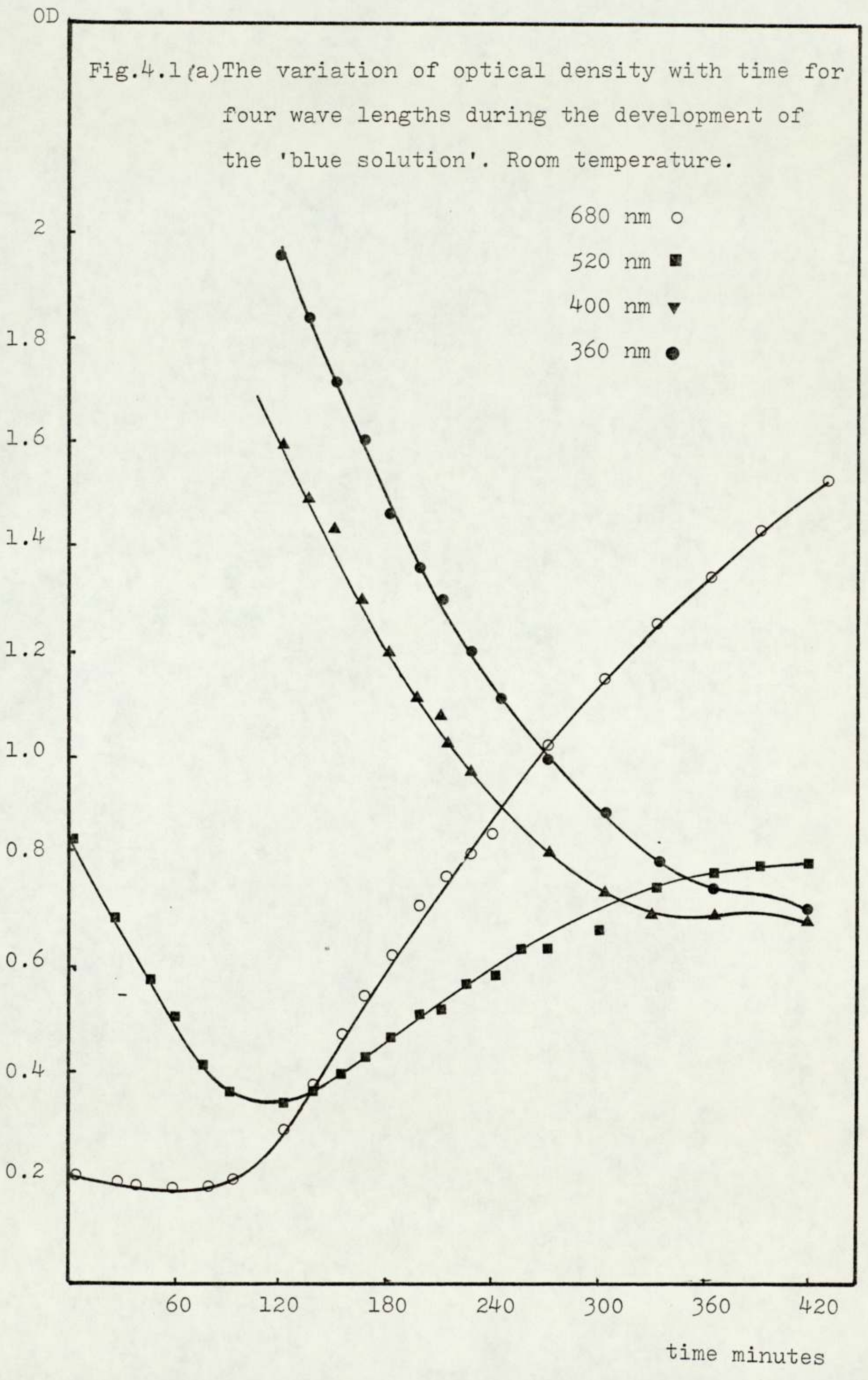


Fig.4.1(a) The variation of optical density with time for four wave lengths during the development of the 'blue solution'. Room temperature.

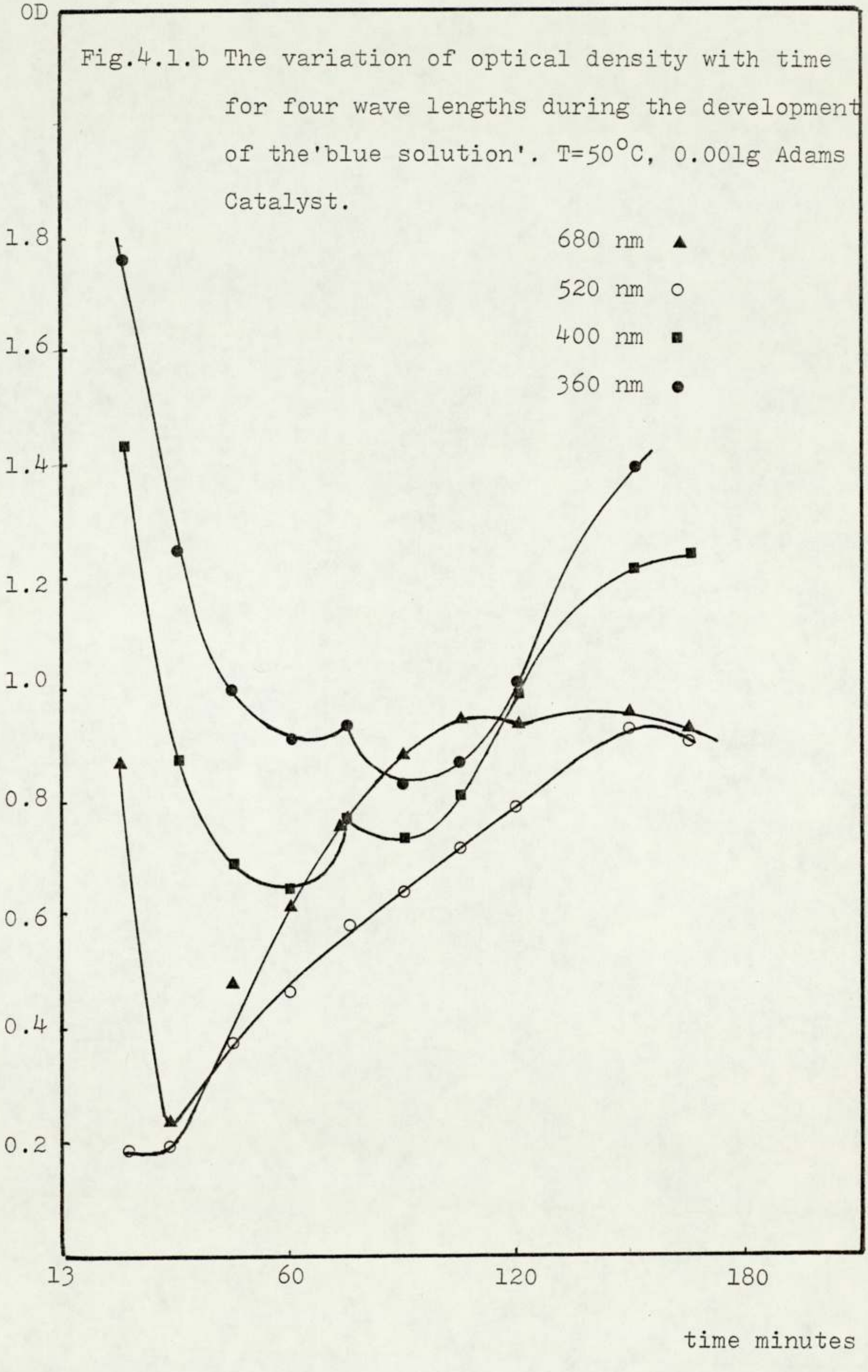


Fig.4.1.b The variation of optical density with time for four wave lengths during the development of the 'blue solution'. T=50°C, 0.001g Adams Catalyst.

possibility of converting one type of Ru(11) complex to another, i.e:

$$Ru_x(11) \longrightarrow Ru_y(11)$$

When the above experiment was repeated at 50°C, the maximum concentration of ruthenium(11) was obtained after approximately 2 hours, after which time the optical density slowly decreases and when the optical densities at the four different wave lengths were plotted against time, those for 360nm and 400nm the reaction again appeared to be first order. In order to evaluate first order plots graphically D_∞ due only to the process occuring over this time range needs to be estimated. Making reasonable estimates for the infinity readings at the wave lengths 360nm and 400nm, reasonable straight lines are obtained when $\log(D_\infty - D)$ is plotted against time and similar but not quite identical rate constants are determined. Also when this set of data is treated with Guggenhime methods, the data is shown to obey the first order rate equation with again comparable rate constants. Table 4.1 shows the rate constants which were obtained at temperature range 50-30°C. The points are described well by the usual Arrhenious equation and the application of this equation, leads to an activation energy of +28.26K.J. mole^{-1}, being determined.

There is no way in which D_∞ at 680nm can be estimated with reasonable accuracy. Since this data goes through a maximum which is then held for quite a long time, so that, obviously there is a subsequent decay process occuring. However, the first order dependence of this process can be checked, if a plot of D_{680} against the e^{-kt} is linear where k is the rate constant determined from the data at 400nm. Such a plot is produced, a good straight line is obtained and therefore it seems that the process which is occuring is one where which ever species is producing absorption at 400nm disappears, yielding only one new product which is responsible for the appearence of the absorption of 680nm. When repeated spectrums are obtained at different times superimposed on each other, the plots do not show a perfect isosbestic point but there is the suggestion of an isosbestic point at 420nm.

Since the decay in the concentration of species producing absorption at 680nm appears to be considerably slower than the process which leads to its formation, it is possible to predict with reasonable accuracy the time which must elapse before the concentration of this species is a maximum from the rate constants already listed in the table(4.1) and determined at 400nm.

Within the table of list of rate constants are also the

TABLE(4.1)

RATE CONSTANTS DETERMINED FROM MEASUREMENTS AT 400nm, 1 ATMOSPHERE PRESSURE H_2.

$T/^{o}C$	$100k/min^{-1}$	Adams catalyst Conc.
30	1.5	$1.0x10^{-3}$
40	2.1	$1.0x10^{-3}$
50	3.0	$1.0x10^{-3}$
50	5.5	$1.0x10^{-2}$
50	5.3	$2.5x10^{-1}$

data at the temperature of 50°C for experiments where different quantities of Adams catalyst being added. This data shows very little change in the rate constants observed as the concentration of the Adams catalyst changes. It seems most reasonable the to speculate that Adams catalyst is not directly involved in the conversion of Ru(lll) $\longrightarrow$ Ru(ll) or at least not in the slow step of the conversion of Ru(lll) $\longrightarrow$ Ru(ll). Clearly hydrogen is likely to be involved in this reduction process. Therefore the most straightforward interpretation is that hydrogen on its own is reacting directly with Ru(lll) without the intermediacy of the catalyst. The alternative has to be that there is some slow step involved in the formation of blue material which does not involve catalyst. That could be Ru(lll) reacting with hydrogen on the catalyst to produce some Ru(ll) species in a fairly rapid reaction, which is then followed by a much slower reaction not involving a catalyst or any preequilibrium. The former explanation is simpler and to be preferred in the absence of any further evidence.

Enough work has been done to find the optimum conditions for the use of blue solutions. To examine the potential usefulness of the blue solution at this stage was broken off because the results was rather disappointing. They did not seem to be offering any marked advantage over the standard chemical reduction methods and processes which are already in the literature.

While we were interested in preparing the dichlorotrisethylenediamineruthenium(11), the blue system was chosen as an attractive potentially precursor because using the standard zinc reduction(166) process one gets $ZnCl_4^{2-}$ as an amine and we were trying to avoid any preparation which would incorporate a second metal in the product, also to avoid the problems of removal of $ZnCl_4^{2-}$. Because of this, some experiments were carried out adding various amines, both monodentate and chelating, to blue solutions in the hope that we would be able to isolate and easily characterize amine complexes of ruthenium. Unfortunately the results were in some ways discouraging. Certainly unidentate amines like methylamine seem to react with the blue solution very quickly, at least as judged by the colour change; where as chelating amines like ethylenediamine, bipyridyl and also acetylacetone reacted much more slowly. This is rather surprising, because normally the chelate effect operating kinetically means that chelate complexes form as rapidly as unidentate complexes, the formation of the first metal-ligand bond is usually rate determining, thus our observation is surprising. If it is general it must mean that while there is one readily available co-ordination site on ruthenium, a second site,cis to the first is not immediately available on the particular ruthenium atom involved, that would tend to support the idea that the blue material is polymeric, as one can envisage polymers such as the Wilkinson$^{(165)}$Pentamer where one site on each ruthenium is immediately available but where one cannot easily obtain a neighbouring site. However, with time one certainly does get changes in the colour after adding chelating ligands to the blue solution. When ethylenediamine is added to the blue solution a colour change is observed and a solid material which is coloured brown is isolated, not as hoped the yellow material. This material is a mixture using a sephadex column a very small amount of yellow material separate out which we presumed to be tris ethylenediamine compound but the yield was too small for complete characterization.

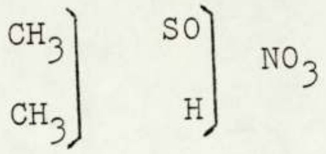
The bulk of the product of this reaction is a very air sensitive brown material which on exposure to air turns very sticky and analysis of this brown material does not seem to correspond to any simple formula that one can envisage the closest fit which we can get to the data seem to be ruthenium to ethylenediamine to chlorine ratio to be 1:3:2 or 1:4:2 but our data does not fit either of those, so we cannot distinguish between them or some other forms. Therefore since clearly this procedure is not a good preparative route to the dichlorotrisethylenediamineruthenium(11), we hoped to make and since the isolation and characterization of this brown material is difficult we ceased on this topic.

CHAPTER FIVE

(5.1.1) INTRODUCTION: DIMETHYL SULPHOXIDE AS A LIGAND

As this part of the thesis deals with dimethyl sulphoxide complexes, a brief review of the field is appropriate.

Dimethyl sulphoxide was first synthesised by Alexandre Saytzeff(167) more than one hundred years ago by oxidation of dimethyl sulphide (DMS) with nitric acid. Solid DMSO.HNO_3, written as:



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rbrace \left.\begin{matrix}SO\\H\end{matrix}\right\rbrace NO_3$$

was isolated, analyzed for, C, H, S and N, then treated with a carbonate to liberate DMSO which was analyzed in turn. During most of the century since its discovery DMSO was of interest to chemists mainly as the first members of the homologous series of sulphoxides and its oxidation-reduction reactions, bond energies, entropies, infrared, ultraviolet and visible spectra were studied.(168) In the late 1950's interest grew slowly in DMSO as a reagent, ligand, solvent and biologically useful compound. By 1960 the number of publications on inorganic and organic applications of DMSO increased very sharply, partly as a result of commercial availability of the solvent. In 1964 Jacob, Bischel and Herschler(169) reported on a number of promising medical uses of DMSO into its proven use in low temperature preservations of living tissues and organisms. At this point the number of publications involving DMSO reached near-flood proportions. Of approximately 1500 papers utilizing DMSO in some way was published between 1867 till the end of 1967.

Because the compound dimethyl sulphoxide has become generally available its solvent action towards inorganic complexes appears to be very promising. That sulphoxide can act as a donor molecule is suggested by some early work of Hofman and Ott,(170) they reported in 1907 that from a reaction mixture consisting of toluene, thionyl chloride and ferric chloride, a crystalline product could be isolated which they formulated as $(CH_3.C_6H_4)_2SO.FeCl_3$. Upon treatment of this compound with warm water they obtained tolysulphoxide. Similar compounds were reported to form from benzylsulphoxide and phenylsulphoxide. Addison and Sheldon(171) reported more recently that when N_2O_4 was used to oxidize alkyl sulphide to sulphoxide addition compounds of the N_2O_4 with the latter could be isolated. For example, with DMSO the 1:1 compound $DMSO.N_2O_4$ was obtained and the author believed that the sulphur is the donor atom. That the oxygen in sulphoxides forms hydrogen bonds has been suggested by Barnard Etal,(172) who reported that the characteristic S-O bond stretching frequencies of sulphons and sulphoxides are lowered by hydrogen bonding in the solvent CH_3OH or $CHCl_3$.

The use of dimethyl sulphoxide(DMSO) as a ligand in the formation of transition metal complexes was first reported by Cotton and Co-workers.(174) Following a thorough vibration analysis of the free ligand(32) they were able to determine whether bonding in the complex was through the sulphur or the oxygen in DMSO by noting whether ν SO, the S-O stretching frequencies increased or decreased on complexation.

In the study of general behaviour of metal tetrafluoride towards a variety of organic donor molecules, Muetterties (175) reported the preparation of the following complexes of DMSO: MF_4.2DMSO, where M=Ti,Zr,Si,Ge,Sn,Mo.

The preparation and partial characterization of crystalline DMSO complexes of twenty two metallic salts representing twelve different metals were reported by Selbin (33) and his co-workers.

James(36) and Ochiai, in their studies on the catalytic hydrogenation properties of ruthenium (11) halides in a variety of solvents(22) reported a simple preparation of ruthenium (11) halide complexes containing coordinated dimethyl sulphoxide, e.g. $RuCl_2(DMSO)_4$, by the reduction of $RuCl_3$ in DMSO by hydrogen. They reported the compound as being an air stable, but that it undergoes very slow air-oxidation in DMSO solutions from which it was isolated. In their IR interperation James and Ochiai assigned the bond at 1100-1120 cm^{-1} region due to νS-O for S coordination and bands in the 930-1023cm region due to

S-O for oxygen bonded DMSO. They have also measured the amount of hydrogen required during the preparative procedure and showed the overall stoicheometry to be:

$$Ru(111) + H_2 \longrightarrow Ru(11) + H^+ \qquad (5.1)$$

Reactions such as (5.1) are of interest because it must involve hydride intermediate. They found the reaction in DMSO to show a first order dependence on ruthenium and an unusual second order on hydrogen, and they have suggested the mechanism.

$$Ru_2^{(111)} + 2H_2 \longrightarrow 2\left[Ru^VH_2\right] \longrightarrow 2Ru^{(III)}H + 2H^+ \qquad (5.2)$$

they also prepared yellow crystals of $RuBr_2(DMSO)_4$ from the reduction of $RuBr_3$ in DMSO by hydrogen and found that the hydrogenation rate was much faster than for the chloride. This was explained as being due in part to a completing hydrogenation of the solvent to dimethyl sulphide catalyzed by the tribromide.

In 1973 Wilkinson(37) and his co-workers prepared the dichlorotetrakisdimethylsulphoxideruthenium(11) by refluxing ruthenium trichloride in dimethyl sulphoxide for a few minutes. They precipitated silver chloride by adding silver nitrate to the aqueous solution of the complex. They have used the dichlorotetrakisdimethylsulphoxide complex as a potentially useful starting material and prepared from it new complexes with carbon-monoxide, nitric oxide, triphenylphosphine, sodium dimethyldithiocarbamatetrihydrate and pyridine as ligands.

Other dimethyl sulphoxide and dimethyl sulphide compounds of ruthenium, specifically $[Ru(DMSO)_6]X_3$, $X=Cl, ClO_4$, yellow and red isomers of $Ru(DMSO)_4Cl_2$, $M[Ru(DMSO)_2Cl_2]$, $M=Na$, Bu_3N, $Ru(DMS)_3Cl_3$ and $[Ru(DMS)_2Cl_3]_2$ have been prepared by Bora(35) and Singh.

Various different procedures were attempted for the preparation of dichlorotetrakisdimethylsulphoxideruthenium(11) during the work described in this part of the thesis and kinetic and mechanistic studies were carried out on the claimed red isomer.

EXPERIMENTAL PROCEDURE:

(5.2.1) PREPARATION OF HEXAKIS(METHYLAMINE)RUTHENIUM (11)IODIDE (176)

Ruthenium trichloride (commercial grade; 0.3g) in distilled water (7ml) and hydrochloric acid (1ml) was mixed with aqueous methylamine (25%,10ml). The mixture was treated with water (10ml) and excess zinc dust (0.4g) was added. The colour of the solution changed from brown to green. This solution was then filtered twice and treated with a saturated aqueous solution of sodium iodide. The grey precipitate which formed, was washed with water, alcohol and then ether.

Analysis			
Found	44.0%C	10.3%H	13.2%N
Expected for $[Ru(CH_3.NH_2)_6]I_2$	47.9%C	10.8%H	13.8%N

IR. 3150, 3250Cm^{-1} doublet, 1595Cm^{-1} singlet.

(5.2.2) PREPARATION OF HEXAKIS(N-BENZYLAMINE)RUTHENIUM (11)CHLORIDE

The above procedure was also used for the attempted preparation of hexakis-N-benzylamineruthenium(11) chloride. The mixture was refluxed under nitrogen for two hours and on addition of saturated sodium chloride a light yellow precipitate was formed.

Analysis				
Found	53.8%C	5.9%H	8.7%N	
Expected for $[Ru(\varphi.CH_2.NH_2)_6]Cl_2$	62.3%C	6.5%H	10.4%N	

(5.2.3) TETRAKIS(DIMETHYLSULPHOXIDE)RUTHENIUM(11) (37)

Ruthenium trichloride (commercial grade 1g) was refluxed in dimethyl sulphoxide (5ml) for 5 minutes. The volume of the solution reduced to half in vacuo. Addition of acetone (20ml) gave a yellow precipitate, which was washed firstly with acetone then with ether. This procedure was very sensitive to the refluxing period. Addition of ether for washing the precipitate produced a very small amount of light brown precipitate in the filtrate.

Analysis				
Found yellow ppt.	18.8%C	3.5%H	19.2%Cl	21.1%S
Expected for $Ru(DMSO)_4Cl_2$	19.8%C	4.9%H	14.6%Cl	26.4%S

(5.2.4) ATTEMPTED PREPARATION OF COMPLEXES BY REACTION OF DICHLORO-TETRAKIS(DIMETHYLSULPHOXIDE)RUTHENIUM(11) WITH AMINES

Dichlorotetrakisdimethylsulphoxideruthenium(11) (0.3g) was dissolved in ethanol (50ml) and treated with an ethanolic solution of ethylamine (9.72g). The solvent was reduced in vacuo and a light yellow precipitate was

formed. The precipitate was centrifuged, washed with ethanol and dried in vacuo. An attempt to obtain more precipitate from the filtrate was unsuccessful. There was insufficient product for elemental analysis.
IR: No band in the region 3000-3500Cm^{-1}, 1600Cm^{-1}.

The procedure was used without success in attempt to prepare complexes from ethanolic solution of N-benzylamine and aqueous solution of ethylamine. When this procedure was attempted with methylamine in ethanol, a grey precipitate was formed on addition of an ethanolic solution of ammonium iodide.

Analysis				
Found	19.1%C	6.5%H	64.4%I	5.2%N
Expected for $[Ru(CH_3NH_2)_6]I_2$	13.3%C	3.5%H	47.1%I	15%N

IR: 3150-3200Cm^{-1}, doublet, 1600Cm^{-1} singlet.

With 1, 2 diaminoethanehydrate a yellow precipitate was found.

Analysis				
Found	31.8%C	6.5%H	66.2%I	4.8%N
Expected for $[Ru(en)_3]I_2$	13.4%C	4.4%H	45.7%I	15.7%N

IR: No band in the region 3500-3000Cm^{-1} and 1600Cm^{-1}.

(5.2.5) REACTION OF POTASSIUMCHLORORUTHENATE WITH DIMETHYL SULPHOXIDE

Potassiumchlororuthenate (10g) in distilled water (1ml) and dimethyl sulphoxide(70ml) was refluxed for more than 24 hours. Crude product was precipitated on cooling (9g). This crude product was refluxed for one hour in dimethyl sulphoxide(100ml) and a brown precipitate (A) (3.4g) and a yellow solution were obtained. A yellow precipitate (B) (4.8g) was obtained from the yellow solution after reducing its volume.

Analysis

Found	A	0.67%C	0.22%H	31.3%Cl	3.9%S
	B	12.2%C	2.86%H	20.1%Cl	18.7%S

Compound A can be S_2C with chloride contamination
I R(B) 1100C m^{-1} singlet 1040C m^{-1} singlet 940C m^{-1} singlet.

(5.2.6) HEXAKIS(DIMETHYLSULPHOXIDE)RUTHENIUM(111) CHLORIDE(36)

Ruthenium trichloride (commercial grade 0.5g) was dissolved in excess dimethyl sulphoxide On warming, the initial deep brown colour of the solution became orange after 24 hours and a very small amount of a yellow crystaline solid formed. Crystals were separated by addition of a mixture of alcohol and ether in ratio 1:3 to the above solution. The mixture was then filtered, washed firstly with ethyl alcohol, then ether and carefully dried in an oven at 100°C, since the product was found to be very sensitive to heat.

Analysis

Found	20.4%C	5.7%H	15.1%Cl	26.3%S
Expected for $[Ru(DMSO)_6]Cl_3$	21.3%C	5.3%H	15.7%Cl	28.3%S

IR: 1460Cm^{-1} singlet, 1305Cm^{-1} with a shoulder at 1285Cm^{-1} 220Cm^{-1}, 1100Cm^{-1}.

TGA 65.6% weight lost at 350°C which corresponds to the loss of six DMSO molecules.

Conductivity in acetonitrile (9.7 x 10^{-5}M) is equal to 99 $52.^{-1}$mol$.^{-1}$Cm^{-1} and conductivity in water (9.7 x 10^{-5}M) is equal to 400 $52.^{-1}$mol$.^{-1}$Cm^{-1}.

(5.2.7) REACTION OF HEXAKISDIMETHYLSULPHOXIDE-RUTHENIUM (111) WITH 1, 2 DIAMINOETHANE.

Hexakisdimethylsulphoxuderuthenium(111)(0.5)was refluxed in ethanol (10ml) and ethylenediamine (10ml) added to the mixture. The system having been previously purged with nitrogen. After 3 hours a white precipitate appeared. The mixture was left overnight, after which time the precipitate was filtered and washed first with ethanol and ether. The product was found to be very sensitive to air.

Analysis

Found	21.5%C	7.2%H	16.3%Cl	19.2%N	7.2%S
Expected for $[Ru(en)_3]$ DMSO Cl_2	22.0%C	6.8%H	16.3%Cl	19.2%N	7.3%S

IR: 3140Cm^{-1} and 3210Cm^{-1}doublet, 1600Cm^{-1}singlet.

This procedure was repeated with methylamine. A very small amount of an ochre coloured solid was formed.

Analysis

Found 17.9%C 5.2%H 18.5%Cl 17.2%N 16.1%S

IR: 3280, 3350Cm^{-1}doublet, 1600Cm^{-1}singlet.

(5.2.8) DICHLOROTETRAKISDIMETHYLSULPHOXIDERUTHENIUM (11) YELLOW(36)

Dimethylsulphoxide (0.7ml) was added to a dark red alcoholic solution of ruthenium trichloride at room temperature. An immediate brown precipitate was formed, which was not soluble in alcohol at room temperature (0.5g in 20ml). A mixture of dimethylsulphoxide and ethanol (1:1,20ml) was added and the reaction mixture was warmed. The brown precipitate dissolved and the colour of the solution became orange. On standing some yellow precipitate appeared, which was collected, washed and recrystalized in ethanol (0.3g). Its conductivity in acetonitrile (1 x 10^{-4}M) is equal to 11 ohm^{-1}mole.$^{-1}$Cm^{-1}.

Analysis

Found	19.3%C	4.5%H	15.3%Cl	26.7%S
Expected for $Ru(DMSO)_4Cl_2$	19.8%C	4.9%H	14.6%Cl	26.4%S

IR: 3500-3400Cm^{-1} broad peak, 1650Cm^{-1}, 1010Cm^{-1}.

(5.2.9) PREPARATION OF DICHLORODIMETHYLSULPHOXIDE RUTHENIUM (11), RED ISOMER(36)

Ruthenium trichloride (0.5g) was refluxed in ethyl alcohol (20ml) for 3 hours, by which time the initial deep red colour of the solution changed to a deep green. Dimethyl sulphoxide(0.8ml) was added and the volume was reduced. On evaporation the colour of the solution changed to red and on cooling orange crystals were obtained. They were washed with cold ethyl alcohol but a considerable amount was found to be insoluble in it. The soluble crystals (C) were obtained by evaporation of ethanol. A small portion of (C) was quickly washed with cold water in an attempt to see whether this procedure could remove any component of (C) which might be present. The resulting solid (D) appears to have identical properties and analytical results, see below. The orange crystals which were not soluble in ethanol allowed to stand under ethanol for one day using a fixed ratio of solid/solvent (0.01g in 5ml). Two different crystals were found, one from being bright yellow (E) and the other red needles (F). The mixture was left for at least 24 hours to let the small quantity of red needles crystals to grow and the two products were separated by hand picking and both then dried in evacuated dessicator.

Analysis

Found	C	19.4%C	4.8%H	23.1%Cl	22.7%S
	D	18.4%C	4.3%H	24.2%Cl	22.6%S
	E	20.0%C	5.3%H	15.25%Cl	26.4%S
	F	19.8%C	4.9%H	25.6%Cl	26.6%S
Expected for $Ru(DMSO)_4Cl_2$		19.8%C	4.9%H	14.68%Cl	26.4%S

I.R (C) and (D) very similar 3500Cm^{-1}, 16200Cm^{-1}, 1400Cm^{-1} 1310-1290Cm^{-1}(doublet) 1100Cm^{-1}, 10010Cm^{-1}, 720Cm^{-1}, 980Cm^{-1}, 720Cm^{-1}, 680Cm^{-1}, 420Cm^{-1}, 390Cm^{-1}, 265 Cm^{-1}

IR (E) in CsI similar to (C) and (D) except 420Cm^{-1}, 380Cm^{-1}, 350-340Cm^{-1}(doublet) 340Cm^{-1}, 300, 265 Cm^{-1}
Not enough samples of (F) for infrared spectrum.

From the empurical formula it is guessed that the compound (C) and (D) have approximately same empurical formula but probably different isomers. Probably $Ru(DMSO)_3Cl_3$.1/2 EtoH. Compound (E) has data very close to $Ru(DMSO)_4Cl_2$.

Ethanolic solutions of this compound gives one maximum at 403nm (ε = 5.4.g.$^{-1}$Cm^{+2}) but with time two maxima at 445nm (5.4g.$^{-1}$Cu^{2}) and 378nm (2.16g.$^{-1}$Cm^{2}) appear together with three isobestic points in the visible region at 386, 441 and 489 nm. It is observed that an increase in the temperature causes a more rapid decrease in optical density. A freshly prepared solution of 'C' in acetonitrile gives one maximum at 412nm (5.0g.$^{-1}$ Cm^{2}) whose intensity decreases with time and shifts to a lower wave length ($\varepsilon = 3.8g.^{-1}Cm^{2}$). Freshly prepared solution of this compound in water gives a maximum at 394nm ($\varepsilon = 4.6g.^{-1}C\,m^{-2}$) and a decrease in optical density is observed with time ($\varepsilon = 3.8g.^{-1}Cm^{2}$).

EQUILIBRIUM AND KINETIC STUDIES ON DEFINED COMPOUND "A"

(5.2.10) For equilibrium studies a solution of the (C) was prepared in ethanol (0.0242g in 50ml ethanol). A standard solution of lithium chloride (0.5mole, 3.0250g in 100ml) in ethanol was also prepared. In a series of flasks 5ml of the ruthenium stock solution were mixed with different concentrations of lithium chloride solution in ethanol. The resulting solutions were kept for one week at a range of temperatures from 25°C-45°C. The optical density of each sample was then determined at fixed wave length 410 nm using 1 cm cell with a water jacket cell holders.

The above procedure was followed several times with different amounts of ruthenium concentrations and different range of lithium chloride concentrations. Table (5.1).

(5.2.11) For the equilibrium studies a solution of the "A" was prepared in ethanol (0.0242 g in 100 ml). A standard solution of dimethyl sulphoxide(0.5mole in ethanol) was also prepared. In a series of flasks 5ml of the ruthenium stock solution were mixed with different concentrations of dimethyl sulphoxide solution in ethanol. The resulting solutions were kept for one week, at a range of temperature from 25°C-45°C. The optical density of each sample was then determined at fixed wave length 410nm using 4cm cell used with water jacket cell holder. Table (5.2). This procedure was also attempted several times with different amounts of ruthenium concentrations and different range of dimethyl sulphoxide concentration.

(5.2.12) In the kinetic studies the effect of chloride ion first was considered at a fixed wave length 410nm and fixed temperature 30°C, the effect of different concentrations of lithium chloride in ethanol was considered and the optical density changes were measured using thermostated cell holders and the rate constants were determined. Table (5.4)

(5.2.13) The effect of a fixed concentration of lithium chloride (0.25mole) in ethanol was considered at fixed wave length 410nm at different temperatures, The optical density changes were measured using a thermostated cell holder and the rate constants were calculated. Table (5.3)

(5.2.14) The effect of dimethyl sulphoxide was considered at a fixed wave length 410nm and fixed temperature 30°C for a wide range of dimethyl sulphoxide concentrations in ethanol and optical density changes were measured and the rate constants were calculated. Table (5.5)

(5.215) The effect of fixed concentration of lithium nitrate in ethanol (0.25mole) at different temperatures 20°C-45°C was considered and the optical density changes were measured using a thermostated cell holder and the rate constants were calculated at fixed wave length 410 nm. Table (5.6)

(5.216) The effect of different concentrations of lithium nitrate in ethanol at fixed wave length 410nm and fixed temperature 30°C was considered and the optical density changes were measured using a thermostated cell holder and the rate constants were obtained. Table (5.7)

(5.2.17) The effect of different concentrations of lithium nitrate in methanol at fixed wave length 410nm and fixed temperature 30°C was considered and the optical density changes were measured using a thermostated cell holder and the rate constants were obtained. Table (5.8)

(5.2.18) The effect of different alcohols; methanol, ethanol, isobutyl and tertiarybutyl was also considered at fixed temperature 30°C and fixed wave length 410nm using a thermostated cell holder. The optical density changes were measured and the rate constants were calculated. Table (5.9)

(5.2.19) The effect of a mixture of lithium chloride and lithium nitrate in different ratios were considered spectrophotometrically at fixed wave length 410 nm and fixed temperature.

(5.2.20) The conductivity changes of "A" in pure ethanol ($2.5 \times 10^{-5} g.l^{-1}$) were followed at fixed temperature 25°C using a thermostated water bath to keep the temperature of the solution constant. It was observed the conductivity increases with time very rapidly for the first 5 minutes and then slowly for another 17 mins.

(5.2.21) The conductivity changes of "A" ($2.5 \times 10^{-5} g.l^{-1}$) in different concentrations of dimethyl sulphoxide in ethanol (0.1, 0.15, 0.18, 0.2, 0.25 M) at fixed temperature 25°C was considered and a rapid increase in conductivity was observed for the first few minutes followed by a slow change for 10 minutes.

(5.3.1) DISCUSSION AND RESULTS:

Attempts at the synthesis of a few primary complexes of ruthenium (11) are described in the experimental part, aiming to use them as a potentially useful starting materials, the method of synthesis employed involves a slight modification to the reported ammine preparation(176). From the only successful preparation it was clear that to obtain reproducible synthesis with reasonable yields vigorous adherence to the procedure laid down in the experimental section had to be followed. Even doubling the quantities of the starting materials in order to prepare larger amounts of the complex in this case gave considerably lower yields.

Since preparation of these compounds using ruthenium trichloride as the only starting material was expensive and can lead to large amounts of byproducts, the preparation of these amine complexes of ruthenium (11) has been tried using dichlorotetrakisdimethylsulphoxide ruthenium(11) as a readily available intermediate step.

The preparation of dichlorotetrakisdimethylsulphoxide ruthenium(11) compound was therefore attempted using different procedures. During the experimental work involved in the various synthesis new and unexpected compounds were observed and different experiments performed for their identifications.

In the preparation of the reported red isomer, which was obtained from the reaction of the ethanolic green solution, obtained from ruthenium trichloride, with dimethylsulphoxide. When the orange crystals obtained were washed with cold ethyl alcohol, it was found that a considerable proportion of the crystals are soluble in ethyl alcohol. The soluble crystals (C) were then regained by evaporation of ethanol. In the infrared of compound (C) peaks due to νS-0 for orange bond and νS-0 for S bonded DMSO were observed as reported in the literature.(36) The empirical formula gives a good fit for Ru(DMSO)$_3$Cl$_3$.1/2Etot. It was also observed that when (C) dissolves in ethanol the optical density of the solution changes with time. A freshly prepared solution of (C) in ethanol gives one maximum at 403nm (ε = 2519mole^{-1}Cm^{-1}) but with time two maximum at 445nm (ε = 1000mole^{-1}C m^{-1}) and 378nm (ε = 2519mole^{-1}C m^{-1}) appears together with three isobestic points at 385, 441, 489nm (Fig 5.1)

Because of the nature of the compound it can be prepared only in small quantity at the time. Although the resulting material from these preparation gave the same analytical analysis, the kinetic and equilibrium data for identical experiments using different batches were found to be variable, within narrow limits. The interpretations of data given below imply that the variation is due to small amounts of impurities such as ionic chloride.

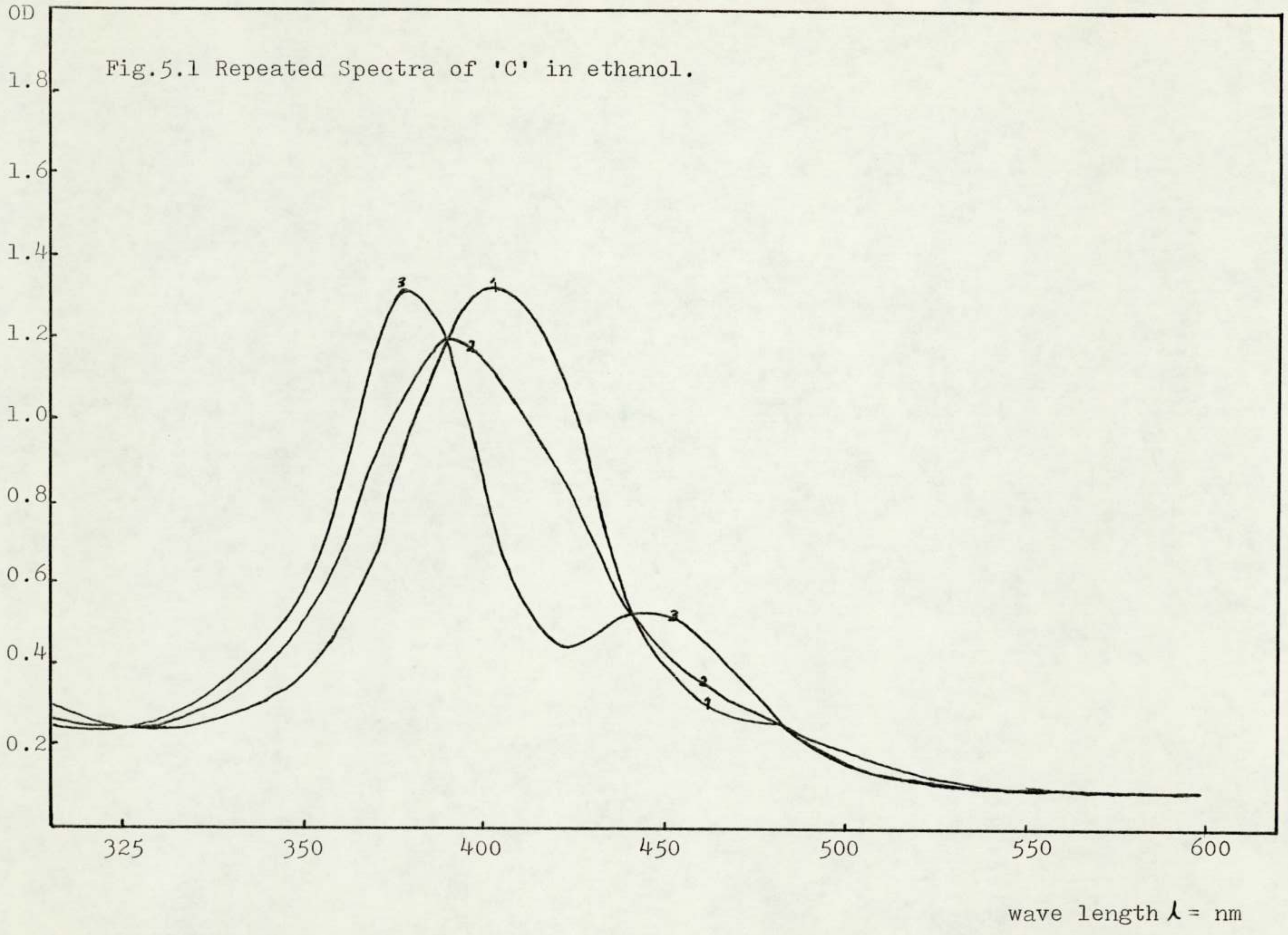


Fig.5.1 Repeated Spectra of 'C' in ethanol.

EQUILIBRIUM STUDIES:

At first we believed that the observed changes in optical density might be due to the dissociation of coordinated chloride, therefore, a set of equilibrium studies were carried out. Observations being made at a wavelength of 410nm, at which the change in optical density is especially pronounced $1.28 < D > 0.48$ for 5.16×10^{-4}M. An equilibrium study was performed in ethanol using added lithium chloride at a range of different temperatures. Table (5.1)

A graph of optical density against the reciprocal of lithium chloride concentration is plotted. Five curves are obtained. These are extrapolated to determine the optical density at infinit concentrations of lithium chloride concentration.

For the equilibrium

$$A + x\mathrm{C\bar{l}} \overset{K_1}{\rightleftharpoons} B$$

if $[T] = [A] + [B]$

and the optical density is given by

$$D = \varepsilon_A \cdot [A] + \varepsilon_B \cdot [B]$$

then we may substitute for $[B]$

$$D = \varepsilon_A [T] + [A] (\varepsilon_A - \varepsilon_B)$$

but

$$[A] = [T] / (1 + K_1 [\mathrm{C\bar{l}}]^X)$$

therefore

$$D = {}_B [T] + (\varepsilon_A + \varepsilon_B) [T] / (1 + K_1 [\mathrm{C\bar{l}}]^x)$$

TABLE (5.1)

TYPICAL DATA FOR THE VARIATION OF OPTICAL DENSITY AT 410nm WITH DIFFERENT ADDED CONCENTRATIONS OF LITHIUM CHLORIDE AT DIFFERENT TEMPERATURES. TOTAL RUTHENIUM CONCENTRATION = 5.5×10^{-4}M.

LiCl/M	T=27.5°C	T=30°C	T=35°C	T=40°C	T=45°C
0.25	0.64	0.70	0.68	0.65	0.71
0.2	0.605	0.67	0.656	0.61	0.68
0.15	0.565	0.628	0.552	0.565	0.63
0.1	0.52	0.55	0.49	0.501	0.582
0.05	0.43	0.465	0.425	0.430	0.485
K_1/M^{-1}	6.3	7.2	4.5	6.4	7.4

Using the observed data for D and $[Cl^-]$ we should be able to estimate the unknown in this equation. An examination of the data of Table (5.1) shows that the variations in optical density are not great enough to give accurate equilibrium constants, but estimates can certainly be made.

The best fits correspond to x=1 and the best values for K_1 are quoted as the final row of Table (5.1). The data do not justify any attempt to calculate ΔH. A casual inspection of the Table shows that the change in optical density with given changes in chloride concentration varies little with temperature. Therefore ΔH is obviously small. Repeat experiments gave similar sets of data. The major problem seems to be that the concentrations of ruthenium allowed by solubility properties are low and that the equilibrium constant is too close to unity to give big changes in the composition of the solutions. However, we may deduce that the equilibrium constant lies within range

$$8 \geq K_1/M^{-1} \geq 4$$

between 25°C and 50°C.

Equilibrium studies were also carried out on the effect of dimethyl sulphoxide in ethanol. Table (5.2) shows the optical density changes at different concentrations.

TABLE (5.2)

TYPICAL DATA FOR THE VARIATION OF OPTICAL DENSITY AT 410nm WITH DIFFERENT ADDED CONCENTRATION OF DIMETHYL SULPHOXIDE AT DIFFERENT TEMPERATURES. TOTAL RUTHENIUM CONCENTRATION = 5.5×10^{-4} M.

DMSO/M	T=25.5°C	T=30°C	T=35°C	T=40°C	T=50°C	$D_{calc.}$
0.5	0.2	0.18	0.195	0.19	0.2	0.185
0.2	0.21	0.2	0.2	0.21	0.2	0.204
0.15	0.212	0.21	0.21	0.22	0.21	0.214
0.1	0.23	0.22	0.22	0.23	0.23	0.232
0.05	0.24	0.23	0.23	0.23	0.22	0.268
0.025	0.31	0.325	0.31	0.307	0.305	0.307
0.01	0.35	0.34	0.36	0.35	0.33	0.348
0.005	0.37	0.37	0.35	0.38	0.37	0.368

From this Table it is obvious that there is little or no variations of the equilibrium constant with temperature, i.e. ΔH is close to zero. No attempt is made therefore to estimate K_2 at the various temperatures.

A treatment similar to that obtained for the effect of added chloride also fits these data. The final column in Table (5.2) gives calculated values for D using the equation.

$$D = \frac{0.228}{1 + 25(\mathrm{DMSO})} + 0.167$$

That is, for the equilibria

$$\mathrm{A} + \mathrm{DMSO} \overset{K_2}{\rightleftharpoons} \mathrm{E}$$

The fit is relatively insensitive to the value of K_2, and so one could say that, over the temperature range studied K_2 is approximately $25\mathrm{M}^{-1}$ with an estimated error of $\pm 10\ \mathrm{M}^{-1}$.

KINETIC STUDIES:

Kinetic studies at fixed concentrations of lithium chloride at different temperature were carried out. Plots of $\log(D_t - D_\infty)$ against time gave straight lines, and rate constants were calculated from these plots. Table (5.3). An activation energy of 92 $\mathrm{K.J.mole}^{-1}$ was calculated from the plot of log K against the reciprocal of temperature.

TABLE(5.3)

VARIATION OF RATE CONSTANT AT FIXED CONCENTRATION OF LITHIUM CHLORINE (0.25 mole) AT DIFFERENT TEMPERATURE DETERMINED AT WAVE LENGTH 410nm.

T/C°	25	30	35	40	45
k/min^{-1}	$5.2x10^{-2}$	$1.3x10^{-1}$	$2.8x10^{-1}$	$5x10^{-1}$	$7.9x10^{-1}$

TABLE(5.4)

VARIATION OF RATE CONSTANT AT 30°C WITH DIFFERENT CONCENTRATION OF LITHIUM CHLORIDE.

LiCl/M	0.25	0.2	0.15	0.1	0.05
k/min^{-1}	0.182	0.15	0.12	0.08	0.05

In kinetic studies the effect of chloride ion at 30°C also considered at different concentrations. Again graphs of log $(D_t - D_\infty)$ against time give straight lines from which rate constants are calculated Table (5.4).

Considering the data for the rate constant in Table (5.4) shows that the reciprocal of the rate constant is dependent on the reciprocal of lithium chloride concentration. We can write.

$$\frac{1}{k_{obs}} = a + \frac{b}{[Cl^-]}$$

or

$$k_{obs} = \frac{[Cl^-]}{a[Cl] + b}$$

For a system such as

$$A + Cl^- \underset{}{\overset{K_1}{\rightleftharpoons}} B$$

$$B = \frac{K_1[Cl^-]}{1 + K_1[Cl^-]} \cdot \left\{ [A] + [B] \right\}$$

therefore, if ruthenium substrate is disappearing via a reaction of B with a rate constant k_3 then

$$k_{obs} = k_3 . K_1 [Cl^-] / (1 + K[Cl^-]$$

which leads to the values at 30°C of

$$K_1 = 2.42\ M^{-1}$$

$$k_3 = 0.455\ min^{-1}$$

It is pleasing to note the similarity of this kinetically determined value of the equilibrium constant to that obtained from equilibrium studies. Their coincidence strengthens the reliability of any scheme passed on this postulated process.

The effect of added dimethyl sulphoxide on a freshly prepared solution has also been studied at $30^{o}C$ and 410nm and graphs of (D_t-D_∞) against time give straight lines from which rate constants are calculated. Table (5.5)

Considering the data for the rate constant in Table (5.5) shows that the reciprocal of rate constants are proportional to the dimethyl sulphoxide concentrations means.

ie. $$k_{obs} = \frac{C}{1 + d\,[DMSO]}$$

if we postulate an equilibrium

$$A + DMSO \underset{}{\overset{K_2}{\rightleftarrows}} E$$

and that a side reaction occurs only via A, k_4, then

$$k_{obs} = K_4 / (1 + K_2\,[DMSO])$$

giving $K_2 = 17.5\ M^{-1}$

and $k_4 = 8.2 \times 10^{-2}\ min^{-1}$ at $30^{o}C$

TABLE(5.5)

VARIATION OF THE RATE CONSTANTS AT DIFFERENT CONCENTRATION OF DIMETHYL SULPHOXIDE AT $T=30^{o}C$, $\lambda=410nm$.

DMSO/M	0.3	0.25	0.2	0.18	0.15	0.1	0.06	0.05
k/min^{-1}	$1.3x10^{-2}$	$1.6x10^{-2}$	$1.9x10^{-2}$	$2.0x10^{-2}$	$2.3x10^{-2}$	$3.0x10^{-2}$	$3.5x10^{-2}$	$4.4x10^{-2}$

TABLE(5.6)

VARIATION OF RATE CONSTANT WITH TEMPERATURE AT FIXED IONIC STRENGTH $LiNO_3 = 0.25M$.

$T/0^{o}$	20.0	25	31	35	40	45
k/min^{-1}	0.033	0.060	0.066	0.10	0.13	0.17

Again, the kinetically derived value of K_2 is in good agreement with that from the equilibrium studies, $(25 \pm 10)M^{-1}$.

For the consideration of the effect of ionic strength, lithium nitrate was chosen to produce a non electrolyte solution in ethanol. At a fixed concentration of lithium nitrate (0.25M), the variation of rate constant with temperature for a freshly prepared solution was investigated. Graphs of $\log(D_t - D_\infty)$ against time were plotted and rate constants calculated. Table (5.6). A graph of log k against the reciprocal of temperature is a straight line with an activation energy of 49.5 K.J. $mole^{-1}$.

Table (5.7) also shows the variation of the rate constant with different concentration of lithium nitrate in ethanol at 30°C. Table (5.8) shows variation of the rate constant with the concentration of lithium nitrate in methanol at 30°C.

Considering the effect of added $LiNO_3$ in ethanol and in methanol, there is essentially independent of ionic strength the reaction can not involve two changed species interacting with each other.

Considering the effect of different alcohols on the rate constant, Table (5.9) shows that there are only small differences in rate constants and therefore it seems

TABLE(5.7)

VARIATION OF RATE CONSTANTS WITH THE CONCENTRATION OF LITHIUM NITRATE IN ETHANOL AT 30°C, λ=410nm.

$LiNO_3$/M	0.25	0.2	0.15	0.1	0.05
k/min^{-1}	0.128	0.104	0.118	0.134	0.133

TABLE(5.8)

VARIATION OF RATE CONSTANTS WITH THE CONCENTRATION OF LITHIUM NITRATE IN MeOH AT T=30°C, λ = 410nm.

$LiNO_3$/M	0.25	0.2	0.15	0.05
k/min^{-1}	0.04	0.035	0.039	0.043

TABLE(5.9)

EFFECT OF DIFFERENT ALCOHOL IN THE RATE CONSTANTS AT FIXED TEMPERATURE 30°C, λ = 410nm.

Solvent	MeOH	EtOH	isobutyl	tertiarybutyl
k/min^{-1}	0.117	0.126	0.050	0.102

unlikely that the solvent takes part in the slow step of the reaction being observed.

When the conductivity changes of (C) in pure ethanol were followed, it was observed that the conductivity increased very rapidly for the first few minutes and then slowly for another twenty minutes. Plot of log $(C_\infty - C_t)$ against time did not produce a straight line (C = Conductivity)

When the conductivity changes of the compound (C) in the presence of different concentrations of dimethyl sulphoxide were followed, the same phenomenon was observed but the rate change was slower. Only when (DMSO)= 0.18M was a straight line obtained from a plot of $\log(C_\infty - C_t)$ against time, giving a rate constant 0.09 min^{-1}. This could have been fortuitous.

The experimental facilities available for the determination of rate constants by conductivity are inadequate for the provision of sufficiently accurate readings over the time scale of this reaction. Therefore, it is impossible to make reliable quantitative statements based on these observations of conductivity data. However, there is obviously an increase in conductivity immediately after solutions are prepared. This change seems to be more rapid than the changes observed spectrophotometrically, and could therefore be assigned to a reaction which was observed at 410nm.

(5.4.1) CONCLUSION:

Considering the analytical data for the compound (A) the empurical formula Ru(DMSO)$_3$.Cl.1/2EtOH looks to be reasonable. In the infrared spectrum of this compound we are able to observe a band at 1100 cm^{-1} due to νS-O for S coordination and bands in the 1001-980cm^{-1}region due to νS-O for oxygen bonded DMSO(36) There are also bands at 390, 340 and 265cm^{-1} indicating both terminal and bridging chlorine atoms(25) The solution of the compound in water immediately produces a precipitate of silver chloride with silver nitrate, indicating the presence of chloride as an anion.

Because the solubility of the compound is very low and the rate of solution is also low, while the conductivity increases rapidly with time for the first few minutes one cannot determine λ_o with any accuracy. An estimate of the initial lower limit for molar conductance of this compound in ethanol is 45 ohm^{-1}.mole^{-1}.cm^{-1} per g atom of ruthenium.

The increase in conductivity with time indicates that ionisation occurs in ethanol, therefore there is the possibility of dissociation of an Ru-Cl bond and the formation of Ru-solvent bond. The conductivity also increases when DMSO is added, in a similar manner, which also suggests the dissociation of Ru-Cl and probably the formation of an Ru-DMSO bond. There is also the possibility that we are dealing with a dimer which in a suitable solvent dissociate into monomeric units, although one might guess that such a process would be slower than the process occuring in the early stages of solution.

Compound (A) is diamagnetic at room temperature. Accepting the above empurical formula compound (A) is unlikely to be a monomer. A dimeric formula might satisfy this observation, if antiferromagnetic interactions were present.

The compound (A) could have various dimeric structures in solid form, two of the likely possibilities are shown in Fig. (5.2) and (5.3).

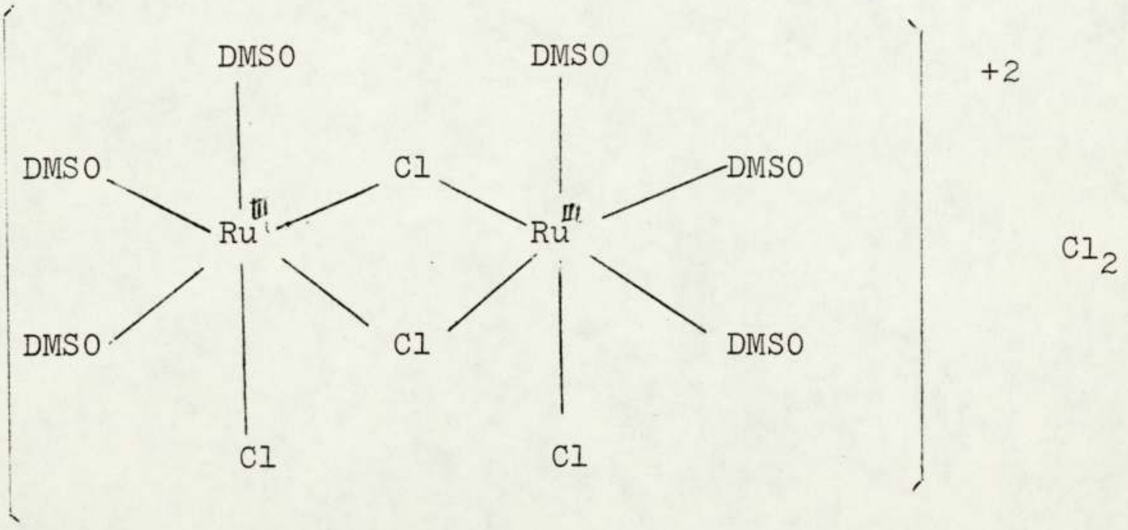


Fig. (5.2)

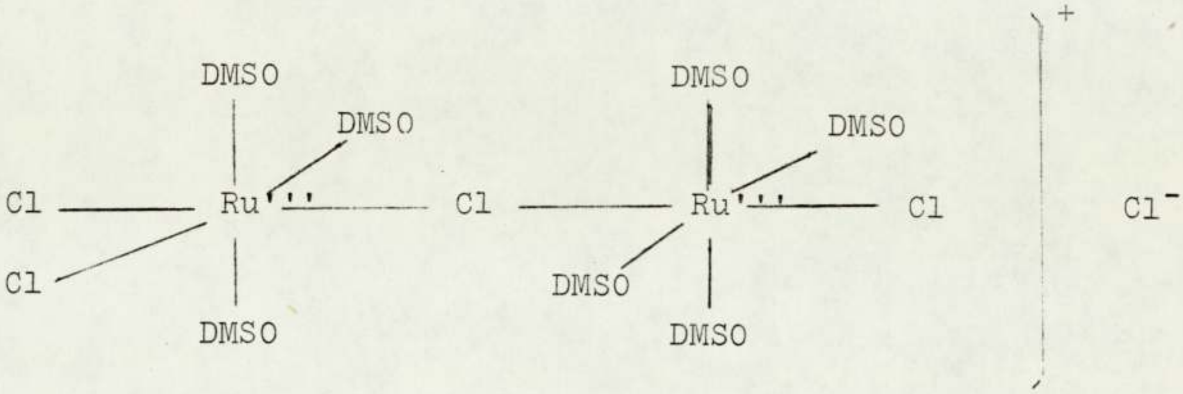
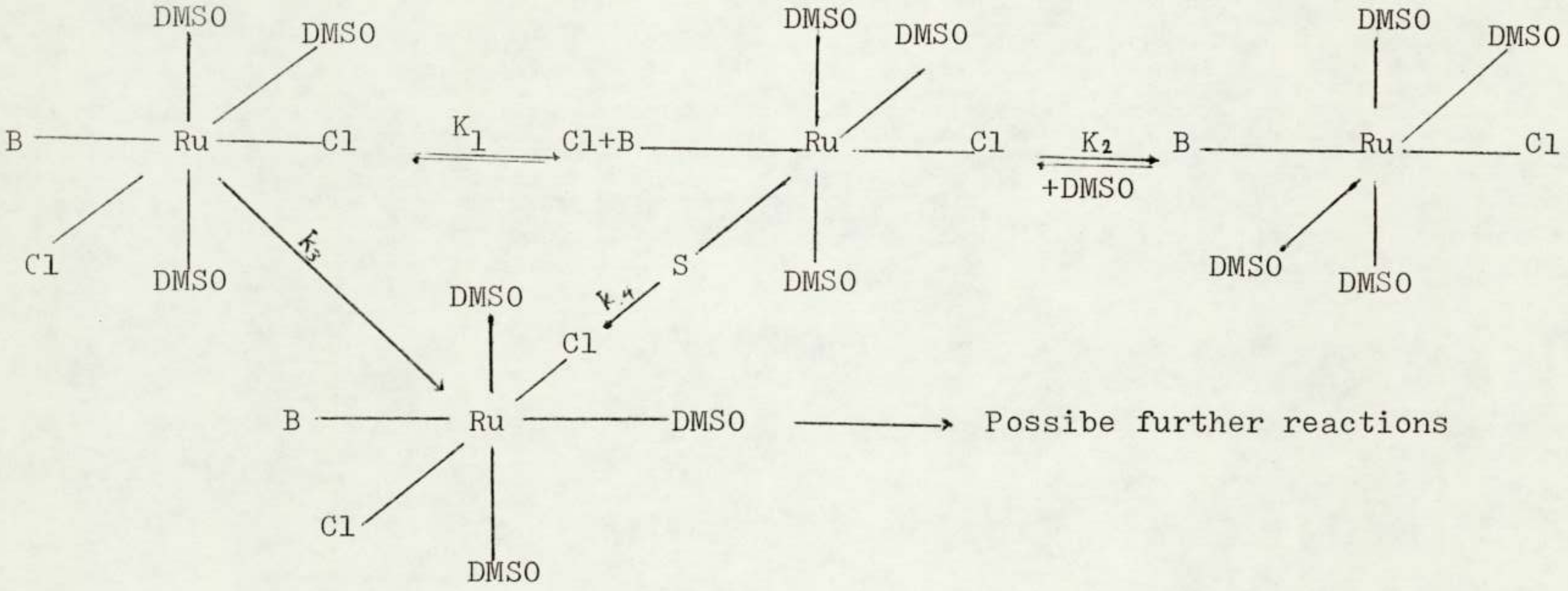


Fig.(5. 3)

It has been previously reported by Yu. N. Kukushkin(176) that dimethyl sulphoxide has a strong trans-influence in platinum (11) complexes, certainly greater than that of chloride. This feature can be used to deduce the more likely possibilities for the structure of the compound (C).

Considering the trans influence of dimethyl sulphoxide we can suggest the mechanism (Fig.5.4). There is the possibility that in solution a chloride ligand trans to dimethyl sulphoxide will substituted first by solvent molecule, while on addition of dimethyl sulphoxide this solvent molecule would be replaced by dimethyl sulphoxide There is no direct evidence to distinguish between dissociation mechanism and an associative one, involving entrance of solvent molecule. The first mechanism is more likely because it does not produce steric hinderence and the rate changes little with a change in alcoholic solvent. There is also the possibility that in



B: represents a bridging ligand between two Ru ion species

S: represents a solvent molecule

Fig.(5.4)

this stage the Ru-bridge bond breaks and further polymerization could be postulated as long as they involve a first order rate low, rather than higher order processes.

The infrared and analytical results of product (D) are identical with the infrared and analytical data of the compound (C), so we can conclude that they are identical. Compound (E) has physical and chemical properties identical to those of Ru(DMSO)$_4$Cl$_2$. Compound (F) has an empurical formula which gives a reasonable fit for the Ru(DMSO)$_3$Cl$_3$ formula, but ofcourse it is different from (C). It would be an isomer of dimeric (C) or a monomer, the yield of (F) was small that no further information was obtained.

In the preparation of dimethyl sulphoxide ruthenium complexes a complicated range of products are obtained our physical studies show some of the possible causes of the range of the product. There are two types of Ru-DMSO bond and two types of coordinated chloride. Also the high trans-influence of DMSO probably implies a high trans-effect of DMSO, which would cause easy cleavage of either terminal or bridging Ru-Cl whichever is trans to DMSO, producing further compounds.

CHAPTER SIX: APPARATUS

INFRARED SPECTRA:

Infrared absorption spectra were taken on a Perkin-Elmer model 457 spectrophotometer, fitted with either NaCl or CSI optics. The compound investigated, were mulled in Nugol or diluted with potassium bromide and pressed into a disc.

ULTRA VIOLET OR VISIBLE ABSORPTION SPECTRA:

Ultra violet absorption spectra were taken on a PYE Unicam SP8-100 or a PYE Unicam SP6-400 spectrophotometer. The solution spectra were measured in the range 1000-200nm. The solution and the solvent for comparison were both contained in 1cm or 0.5cm silica or quartz cells. The cell compartments of these spectrophotometers are equipped with water jackets so that temperature control can be achieved simply by circulating water at the desired temperature through the cell holder.

pH MEASUREMENTS:

pH measurements were made on a EIL pH meter, accurate pH measurements were made on a small volume of solution employing a combination electrode, model EIL, which has an operating range from pH 0 to 14.

ESR SPECTRA:

Electron Spin Resonance Spectra were recorded on a ESR spectrophotometer model JEOL-JES-PEI equipped with a 9400 MHZ oscilator.

CONDUCTIVITY:

The conductivities of the compounds were measured in the range 10^{-3}- 10^{-4} M in different solvents using a Grayshaw Instrument Ltd. conductivity bridge and a cell with platinum electrodes.

MAGNETIC MEASUREMENTS:

Chemically useful information is obtained by proper interpretation of measured values of magnetic moments. These are not measured directly but calculated from the magnetic susceptibility which is measured directly.

The gram magnetic susceptibility X, is calculated from the equation (6.1)(177)

$$\chi . 10^6 = \frac{(\alpha + \beta F^1)}{W} \qquad (6.1)$$

α is a correction due to the volume of air displaced from the Gouy tube and is equal to 0.029 X volume of sample.

β is a constant associate with the apparatus and termed the tube calibration constant.

F^1 is the force on the specimen, ie. $(F-\delta)$, F being the observed force and δ the force on the empty tube.

W is weight of the specimen.

N.B. α, F, and δ are measured in mg and W in g.
Initially a calibrant is used and β evaluated, allowing the calculation of χ for the experimental complex.

The gram magnetic susceptibility is then multiplied by the molecular weight of the complex to give the molar magnetic susceptibility, X_m, the diamagnetic corrections are substracted from X_m to give $X_{m\ corr}$ the corrected molar magnetic susceptibility.

The magnetic moment, μ_{eff} is calculated from the equation (6.2)

$$\mu_{eff} = 2.84\ (X_{m\ corr} \times T)^{1/2} \qquad (6.2)$$

where T is the absolute temperature.
From the experimental value of μ_{eff} the number of unpaired electrons present per metal ion can be obtained.
However an obvious difficulty of this experiment is that to obtain the correct value of μ_{eff} the value of the molecular weight is needed.

Most of the magnetic susceptibilities of the complexes were measured on a Faraday balance, the construction of which is described by Hartley.(178) The basis of this method is that the entire specimen is situated in a region of the magnetic field where the product of the field and the vertical field gradient is constant.

The specimen then experiences a vertical force, which can be measured in the same way as for the Gouy method, with the advantage that it is not dependent on the uniformity of the specimen. The size of the specimen is limited by the extent of the region in which $H \frac{dH}{dx}$ is constant so that the method is unsuitable for ligands and low density solids with low moments.

The formula for the mass susceptibility is the same as that used for the Gouy method though the value of the constant L for the bucket differs.
The mass susceptibility per gram of a substance is given by:

$$X = \frac{Kv + LW}{\mathcal{W}}$$

where K is the volume susceptibility of air + 0.029×10^{-6}

v is the volume specimen (ml)

L is a constant for the bucket involving field strength.

$\mathcal{W}$ is the weight of specimen (g)

W is the apparent increase in weight of the specimen when field is applied (g)

L is obtained by calibration with a material of known susceptibility, Kv is negligible, except for compounds of low density.

The correct position for the specimen must, however, be determined before proceeding with the calibration proper, and the necessary correction for the bucket is first obtained. The vertical position of the bucket can be adjusted by rotating the adjuster in the suspension chain assembly. This should be arranged initially so that the base of the bucket is $2\frac{1}{2}$ mm above the apices of the pole tips. The bucket is then weighed with the magnet 'on' and again with the magnet 'off'. Since vertical displacements are far more critical than in the Gouy method it is essential that the rider of the balance is used for the magnet 'on' weighings to give scale readings as nearly identical as possible. The bucket is then raised by rotating the suspension chain adjuster one turn at a time and the weighings repeated. Five to ten of a suitable calibrant are then placed in the bucket and may be tamped down to prevent subsequent displacement. Weight changes are then noted for the same positions as before and values of W for each position obtained by correcting for the effect of the empty bucket. These values are then plotted against position and the required position is that giving the maximum value of W. The bucket height should now be adjusted to this and should not be subsequently changed. The values of L corresponding to various field strengths can now be found. Since the bucket is at this stage loaded with the calibrant, it is convenient to proceed with measurements on the loaded bucket and to measure the bucket corrections afterwards. The apparent increases in weight are measured for a range of magnet currents, after which the bucket is emptied and corrections obtained for the same magnet currents. W is thus obtained in each case. The weight of the calibrant W is also obtained by difference from weighings already made. Substitution in the equation for the mass susceptibility gives values of L for each of the magnet currents used.

Thermal Gravimetric data were obtained using Stanton Thermobalance (TR,Decimiligram Model) ambient to 1000°C, using static air, with chart-speed 3.

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APPENDIX ONE

Simplest case

$$A \xrightarrow{k_1} B$$

$$A_0 = A+B$$

$$A+B \xrightarrow{k_2} 2B$$

$$-\frac{dA}{dt} = k_1A+k_2A(A_0-A) = -k_2A^2+A(k_1+k_2A_0)$$

let $2Z' = \frac{k_1+k_2A_0}{k_2}$,

$$+\frac{dA}{dt} = +k_2\,(A^2-2Z'A)$$

$$(A-Z')^2-Z'^2 = A^2-2Z'A$$

let $U = A-Z'$ $\quad$ $dU = dA$

Therefore $\frac{dU}{dt} = k_2(U^2-Z'^2)$

$$\int_{A_0-Z'}^{A-Z'} \frac{dU}{U^2-Z'^2} = \int_0^t k_2 dt$$

let $\frac{\alpha}{U-Z'} + \frac{\beta}{U+Z'} = \frac{1}{U^2-Z'^2}$

$\alpha + \beta = 0 \qquad \alpha = -\beta$

$Z'(\alpha-\beta)=1 \qquad \alpha = \frac{1}{2Z'}, \quad \beta = \frac{-1}{2Z'}$

Therefore $\int_{A_0-Z'}^{A-Z'} dU/U-Z' - \int_{A_0-Z'}^{A-Z'} dU/U+Z' = 2k_2Z' \int_0^t dt$

i.e. $\left[\ln(U-Z'/U+Z')\right]_{A_0-Z'}^{A-Z'} = 2k_2Z't$

i.e. $2k_2Z't = \ln(2Z'-A/A)-\ln(2Z'-A_0/A_0)$

which is of the form

$k_{obs}t = \ln(2Z'-A/A)+ \text{constant}$

but $D-D_\infty = \varepsilon A$

therefore $k_{obs}t = \text{constant} + \ln(2\varepsilon Z'+D_\infty -D/D-D_\infty)$

if we now replace the symbol then

$k_{obs}t = (k_1+k_2A_0)t = \text{constant} + \ln(D_0+\frac{\varepsilon k_1}{k_2}-D/D-D_\infty)$ App.1.2

for the purpose of data fitting a new constant Z can be defined and determined.

$Z = D + \varepsilon k_1/k_2$

thus $k_2 = \varepsilon k_{obs}/(X-D_\infty)$

and $k_1 = k_{obs}- k_2(D - D_\infty)/\varepsilon$

APPENDIX TWO

PART I

A more complicated version of the scheme treated in appendix one is

$$E \underset{}{\overset{K_0}{\rightleftarrows}} A + 2L$$

$$A \xrightarrow{k_1} B$$

$$A+B \xrightarrow{k_2} 2B$$

$$C \underset{}{\overset{K_3}{\rightleftarrows}} B + 2L$$

If a solution is made up which initially contains only E at concentration E_0, and if the two equilibria lie far over to the right, then we can approximate

$$L = 2A_0$$

Therefore $A/A+E \;=\; K_0/K_0+4E_0^2$

and $B/B+C \;=\; K_3/K_3+4E_0^2$

$$-d/dt(A+E) = -(K_0+4E_0^2)/K_0.dA/dt = k_1A + k_2AB$$

but $E_0 = (A+E)+(B+C)$

i.e. $B = \left\{E_0-(A+E)\right\}\left\{K_3+4E_0^2/K_3\right\}$

$$\text{or}\quad B = \left\{ K_3+4E_0^2/K_3 \right\}\left\{ K_0+4E_0^2/K_0 \right\}\left\{ K_0E_0/(K_0+4E_0^2) \right\} - A$$

if this realationship is substituted into the differential equation then we have

$$-dA/dt = K_0k_1/(K_0+4E_0^2).A + (K_3+4E_0^2)k_2/K_3.A\left\{ K_0E_0(K_0+4E_0^2) - A \right\}$$

That is, we have a differential equation of the same form as that solved in appendix one, equation (App.1.1) but with different values of the constants involved. The changes of constants are

k_1 is replaced by $K_0k_1/(K_0+4E_0^2)$

k_2 by $(K_3+4E_0^2)k_2/K_3$

and

A_0 by $K_0E_0/(K_0+4E_0^2)$

Therefore the solution of the rate equation here may be written by the appropriate substitutions into (App.1.2) We will still have an equation of the form

$$k_{obs}t = \text{constant} + \ln\,(Z-D/D-D_\infty\ )$$

where

$$k_{obs} = K_0K_3k_1+(K_3+4E_0^2)K_0E_0k_2/K_3(K_0+4E_0^2) \qquad \text{app.2.1}$$

$$Z = D_0 + \varepsilon\, K_0K_3k_1/k_2(K_0+4E_0^2)(K_3+4E_0^2) \qquad \text{app.2.2}$$

and

$$(K_3+4E_0^2)k_2/K_3 = \varepsilon\, k_{obs}/(Z-D\ \ ) \qquad \text{app.2.3}$$

PART II

If the equilibria involve the dissociation of only one ligand, that is

$$E \xrightleftharpoons{K'_0} A + L$$

and

$$C \xrightleftharpoons{K'_3} B + L$$

then the constants in the rate equation (App.1.2) have the values

$$k_{obs} = K'_0K'_3k_1 + (K'_3+E_0)K'_0E_0k_2/K'_3(K'_0+E_0) \qquad \text{app.2.4}$$

$$Z = D_o + \mathcal{E}\, K'_0K'_3k_1/k_2(K'_0+E_0)(K'_3+E_0) \qquad \text{app.2.5}$$

and

$$(K'_3+E_0)k_2/K'_3 = \mathcal{E}\, k_{obs}/(Z-D_\infty) \qquad \text{app.2.6}$$

PART III

If the initial solutions are made up with an added quantity of free ligand, L_0, the form of the rate equation (app.1.2) is still unaltered but the constants again change. Thus in equation (app.2.1) to (app.2.3) thus substitution

$(L_0 + 2E_0)^2$ for the term $4E_0^2$

must be made, while in equations (app.2.4)to (app.2.6) the analogous substitution is

$(L_0 + E_0)$ for E_0

The two alternative mechanistic schemes discussed in Parts I and II can be distinguished. Both show a value of k_{obs} while can increase with E_0 but the variation of the term $k_{obs}/(Z-D_\infty)$ differ as shown in equations (app.2.3) and (app.2.6).