SYNTHESIS, STRUCTURAL ASSESSMENT AND STUDIES OF REACTIVITY OF 2-(ARYLAZO)PYRIDINE COMPLEXES OF RUTHENIUM, RHODIUM AND SILVER

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To

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INDIA

MAY 1992

Dedicated to my mother
and
to the revered memory
of my father

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I certify that the thesis entitled "SYNTHESIS, STRUCTURAL ASSESSMENT AND STUDIES OF REACTIVITY OF 2-(ARYLAZO)PYRIDINE COMPLEXES OF RUTHENIUM, RHODIUM AND SILVER", submitted by Mr. Alok K. Deb for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the award of the Ph.D. Degree. This work has not been submitted for any degree of any other University.

Place: Shillong,
Date : 28 May, 1992

Subrata Goswami
S. Goswami

CONTENTS

PREFACE

The work embodied in this thesis entitled, **SYNTHESIS, STRUCTURAL ASSESSMENT AND STUDIES OF REACTIVITY OF 2-(ARYLAZO)PYRIDINE COMPLEXES OF RUTHENIUM, RHODIUM AND SILVER,** originated from an attempt to develop the transition metal chemistry of 2-(arylazo)pyridines(L).

The thesis consists of six chapters. A brief survery of known coordination chemistry of 2-(arylazo)pyridines is outlined in **Chapter I** along with the scope of the present investigation. In **Chapter II**, the synthesis and characterisation of highly electrophilic new mononitrosyl complexes of ruthenium(II) are described. The reactivities of the ruthenum mononitrosyl complexes, described in Chapter II, towards nucleophiles and reducing agents are the subject matter of **Chapter III. Chapter IV** deals with the synthesis and characterisation of new, stable chelated, tetracoordinated silver(I) complexes of L. **Chapter V** describes the use of Ag-L complexes in synthesis of bis and tris ruthenium(II) complexes of L. Solid-State Thermal Isomerisation of dichlorobis complexes of ruthenium(II) are also described in this Chapter. The concluding **Chapter VI** describes the synthesis structure and electrochemical reduction of 2-(arylazo)pyridine complexes of rhodium(III).

The present work was initiated in August, 1988 in the Department of Chemistry, North-Eastern Hill University, Shillong under the supervision of Dr. S. Goswami.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made whenever the work described as based on the findings of other investigators. I must take the responsibility of any unintentional oversights and errors which might have crept in inspite of all precautions.

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Alok Kumar Deb

ALOK K. DEB

Date : 28 May, 1992

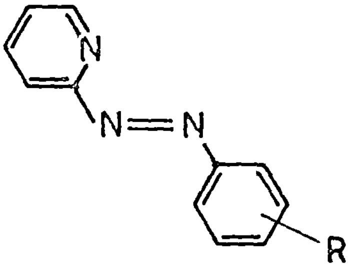
Abstract

Synthesis, Structural Assessment and Studies of Reactivity of 2-(Arylazo)pyridine Complexes of Ruthenium, Rhodium and Silver

ABSTRACT

The present thesis primarily deals with the 2-(arylazo)pyridine (L,1) chemistry of transition metals *viz.* ruthenium, rhodium and silver. It involves synthesis of new complexes and their thorough characterisation. Chemical and redox properties of the synthesised compounds also have been examined in detail. The redox reactions have been studied by using modern electrochemical techniques such as Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV) and Constant Potential Coulometry. The subject matter of the whole thesis has been distributed over six chapters.

Chapter I presents a brief out line about the aspects of the known coordination chemistry of L. The scope of the present investigation is delineated in this back ground.

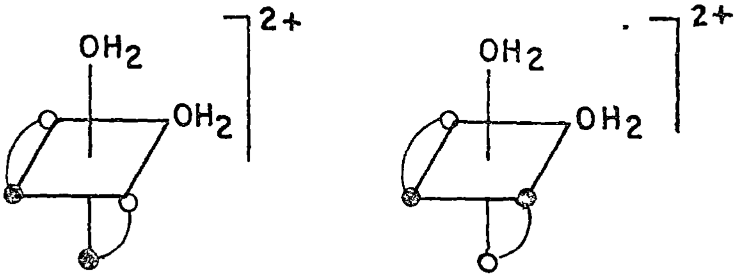


L

R = H : L^1
R = m-Me : L^2
R = p-Me : L^3
R = p-Cl : L^4

1

Chapter II describes the synthesis and characterisation of strongly electrophilic new mononitrosyl complex, *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ (4) and dinitro complex *tc*-$[Ru(NO_2)_2L_2]$(3). The complex, 4 has been synthesised from its dinitro precursor 3. The dinitro complex 3 is, in turn, obtained from a known cationic diaquo complex, *tc*-$[Ru(OH_2)_2L_2](ClO_4)_2.H_2O$ (2). Due to unsymmetrical nature of bidentate L, different geometrical isomeric forms (*tc,cc*) are possible for 2. One of these isomers, *viz. trans, cis(tc)*, has been used as the starting material for the synthesis of the desired nitrosyl complex 4.



tc cc

2

The synthetic route from 2 to 4 via 3 may be represented as follows (equations 1-3)

$$tc\text{-}[Ru(OH_2)_2L_2]^{2+} \xrightarrow{CH_3CN} tc\text{-}[Ru(CH_3CN)_2L_2]^{2+} \qquad (1)$$

2

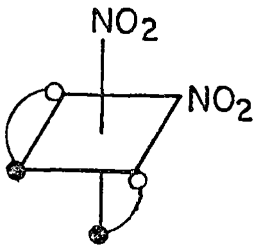
$$tc\text{-}[Ru(CH_3CN)_2L_2]^{2+} \xrightarrow{NO_2^-} tc\text{-}[Ru(NO_2)_2L_2] \qquad (2)$$

3

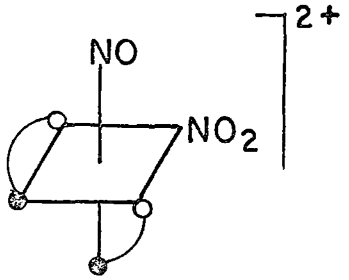
$$tc\text{-}[Ru(NO_2)_2L_2] \xrightarrow{H^+} tc\text{-}[Ru(NO)(NO_2)L_2]^{2+} \qquad (3)$$

3 4

The cationic complex 4 has been isolated as a crystalline perchlorate salt. The spectral data of the intermediates as well as final products clearly reveal that the reactions described in equations 1-3 are stereoretentive. Thus, it has been concluded that the geometries of both 3 and 4 are similar to 2 (*tc*).



3,(tc)



4,(tc)

The nitrosyl complex 4 shows a strong band at *ca*.1950 cm^{-1} in the IR spectrum which is conspicuously absent in the dinitro analogue 3. This band has been assigned to ν_{NO}. Appearance of this band at such a high frequency suggest that formally a linear NO^+ (sp hybridired) is coordinated to a $[RuL_2]^{2+}$ moiety. The ν_{NO} band in 3 appears at *ca*.1360 cm^{-1} whereas the same band in nitrosyl complex 4 shifts to a higher frequency and appears at *ca*.1480 cm^{-1} . These band positions certainly indicates that nitrite ion is coordinated through nitrogen rather than oxygen. A large shift in $\nu_{N=N}$ to lower energy in both 3 and 4 compared to that of free ligand is observed. A trend in the shift of $\nu_{N=N}$ to higher frequency on moving from 3 to 4 is also observed. These results have been rationalised in terms of strong $d\pi(Ru)-\pi^*(L)$ interactions in the present group of complexes.

Solution electronic absorption spectrum of each of the complexes 3 and 4, exhibits allowed metal-to-ligand (MLCT) transition in the visible region (400-550 nm). The MLCT transition in 3 is highly intense and appears at *ca*.540 nm whereas in 4 it is comparatively broader and appears at 410 nm. The appearance of MLCT transition at higher energy in the nitrosyl complex 4 indicates a better metal ——> ligand Π-interaction than that in the corresponding nitro complex 3.

All the complexes are electroactive. All the nitrosyl complexes show a one-electron reversible reduction with formal potential [$E°_{298}(1)$] at *ca*.0.70V. A second one electron irreversible cathodic response with cathodic peak potential [$E_{pc}(2)$] at *ca*.0.17V is also observable. It has been found that electrode reduction potentials in the nitrosyl complex is susceptible to medium effect. It has been concluded that the successive two electron reductions in 4 occurs at the coordinated NO^+ moiety (equations 4 and 5)

$$tc\text{-}[Ru(NO)(NO_2)L_2]^{2+} + e^- \rightleftharpoons tc\text{-}[Ru(NO)(NO_2)L_2]^{+}, E°(1) \qquad (4)$$

$$tc\text{-}[Ru(NO)(NO_2)L_2]^{+} + e^- \longrightarrow tc\text{-}[Ru(NO)(NO_2)L_2], E_{pc}(2) \qquad (5)$$

It may be noted here that the observed reduction potentials in 4 are the highest ever reported in ruthenium mononitrosyl chemistry. The insignificant Π-interaction in the present nitrosyl is surely responsible for such a high reduction potential. The low reorganisational barrier of two electrons transfer, and the strength of the reagents as oxidants make the present nitrosyl complex 4 as a useful nitrosating agent as well as a chemical oxidant.

In case of dinitrocomplex, (3) two oxidative responses at *ca.*1.40 and 1.60V respectively are observed. Out of which the response at a lower positive potential is irreversible whereas the other response is quasi-reversible. It has been argued that oxidation at a higher positive potential is due to electron transfer of Ru(II) species formed by chemical transformation of the transient *tc*-$[Ru^{III}(NO_2)_2L_2]^+$, (3^+).

Chapter III of the thesis includes the reactions of strongly electrophilic ruthenium(II)nitrosyl, *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ (4) towards:

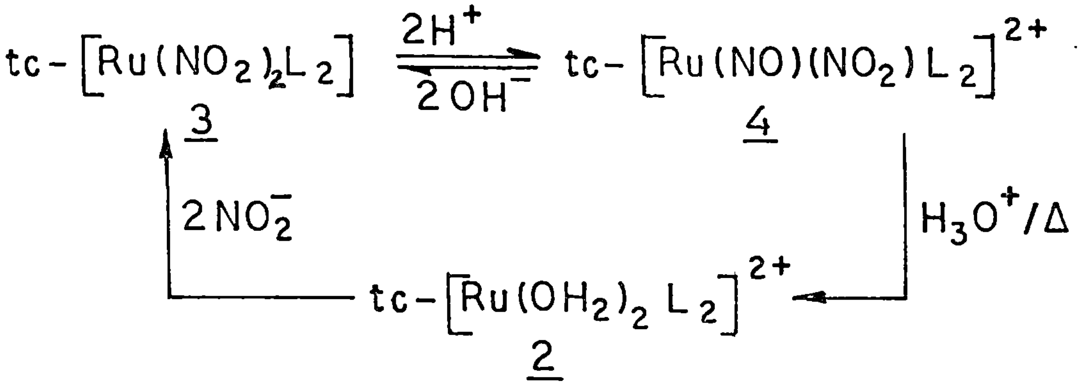
(i) Nucleophiles
(ii) Reducing agents.

(i) Nucleophiles

(a) Acid-Base Equilibrium. The orange ion 4 is predominant in very high acidic medium and instantaneously converts, *tc*-$[Ru(NO)(NO_2)L^2]^{2+}$ (4) to *tc*-$[Ru(NO_2)_2L_2]$ (3), in presence of OH^-. The conversion of 4 to 3 takes place even in moist environment (equation 6). Clearly, coordinated NO in 4 behaves chemically

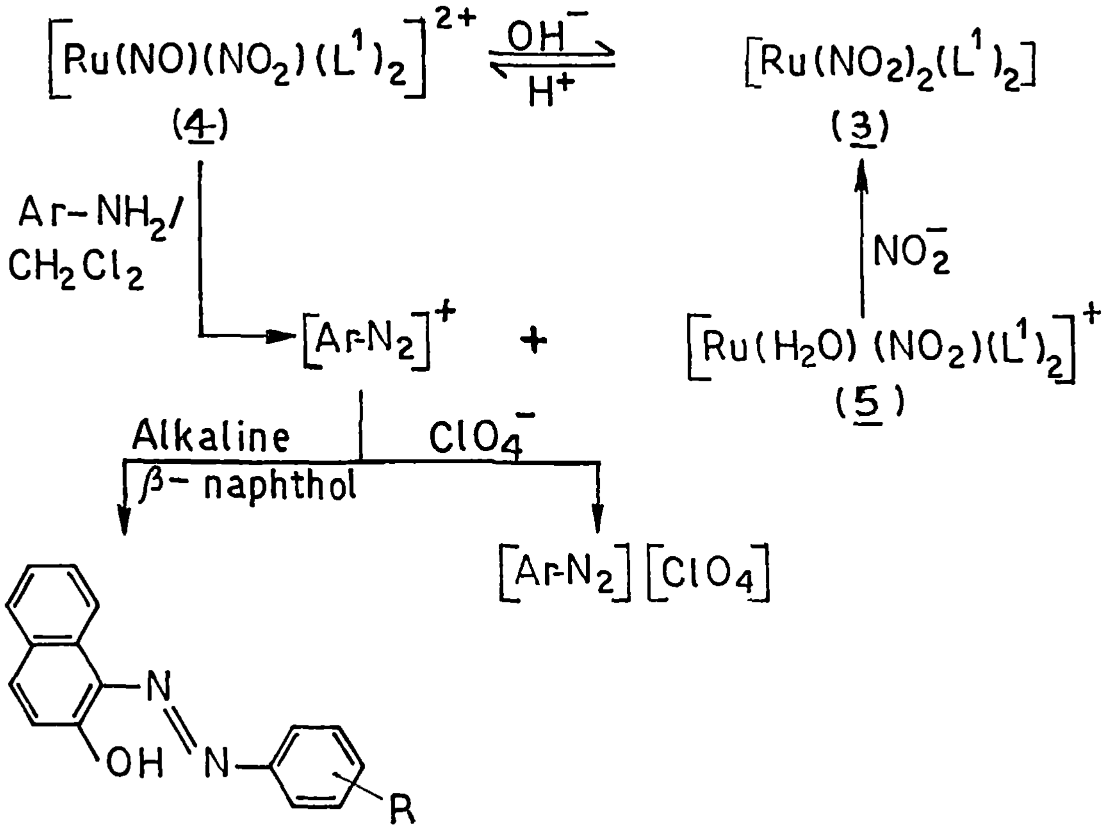
$$\underset{\textbf{4}}{tc\text{-}[Ru(NO)(NO_2)L_2]^{2+}} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\textbf{3}}{tc\text{-}[Ru(NO_2)_2L_2]} \qquad (6)$$

more like NO^+. Instantaneous conversion of 4 to 3 even in a neutral aqueous medium indicates that equilibrium constant, K of equation 6 must be very high. This result has been explained in terms of strong Π-acidity of L. Interestingly, both 3 and 4 reacts with H^+ at a high temperature to yield disolvento complex of ruthenium(II), *tc*-$[RuS_2L_2]^{2+}$ ($S=CH_3CN,H_2O$) This interconversion of 4 to 3 also involving 2 are shown in Scheme 1.



Scheme 1

(b) Diazotisaton of Primary Aromatic Amines. The reactions which have been studied are shown in Scheme 2. The diazotisation reactions of primary aromatic amines are quite fast and are studied in two solvents, viz. acetonitrile and dichloromethane. The results of these reactions are rationalised by following the reaction sequence through the isolation of products at various stages of the reactions. Thus, the diazotisation reaction yield monosolvento compound, *tc*-$[Ru(S)(NO_2)L_2]ClO_4.H_2O$(5) ($S=CH_3CN,H_2O$) along with aryldiazonium cation, $[Ar-N_2]^+$. This has been characterised either by isolation of the cation as its perchlorate salt or by performing the known reaction with alkaline β-naphthol producing azo-dye,1-arylazo-2-naphthol. The reactions with primary aromatic amines are of interest because of its importance



R	Yield(%)
H	45
p-Me	60
p-OMe	55
p-Cl	45

Scheme 2

in connection with the synthesis of aryldiazonium complexes which may be regarded as a model for dinitrogen complexes.

(2) Reductions

(a) Oxidative Coupling. The cationic nitrosyl complex, 4 instantaneously reacts with N,N-dimethylaniline (DMA) in acetonitrile to form N,N,N',N'-tetramethylbenzidine (TMB). Evidently the oxidative coupling reaction 7 is mediated by the strong oxidant 4.

$$2\ \mathrm{DMA} + 2\,tc\text{-}[\mathrm{Ru(NO)(NO_2)(L^2)_2}]^{2+} \longrightarrow \mathrm{TMB} + 2\,tc\text{-}[\mathrm{Ru(CH_3CN)(NO_2)(L^2)_2}]^{+} + 2\ \mathrm{NO} + 2\mathrm{H}^{+} \quad (7)$$

The cationic monoacetonitrile compound 5 together with TMB were purified on a silica gel column. The complex 5 was crystallised as a perchlorate salt and characterised by molar conductance and spectral data. This reaction has also been followed cyclic voltammetrically where it has been shown that 30-35% utilisation of the oxidation equivalent for the coupling reaction 7 has taken place. It is interesting to note that in case of primary amines the present nitrosyl complex has been successfully used as a nitrosating agent whereas in case of a tertiary amine the same nitrosyl complex behaves as an oxidant. The difference in the oxidation potentials of the primary and tertiary amine is no doubt the controlling factor in driving the two reactions.

(b) Formation of Trivalent Ruthenium. Dichlorobis(2,2'-bipyridyl)ruthenium(II), $[\mathrm{RuCl_2(bpy)_2}]$ is quantitatively oxidised to the corresponding ruthenium(III) chelate, $[RuCl_2(bpy)_2]^+$ by *tc*-$[Ru(NO)(NO_2)(L^2)_2]^{2+}$ in acetonitrile (equation 8).

$$tc\text{-}[Ru(NO)(NO_2)(L^2)_2]^{2+} + [RuCl_2(bpy)_2] \longrightarrow$$

$$tc\text{-}[Ru(CH_3CN)(NO_2)(L^2)_2]^+ + [RuCl_2(bpy)_2]^+ \qquad (8)$$

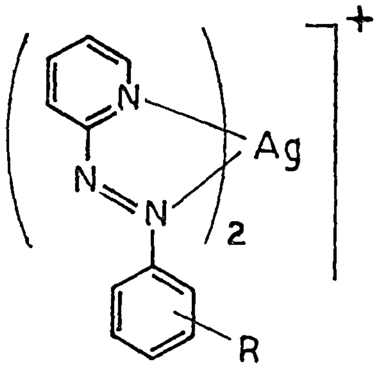
This reaction was followed cyclic voltammetrically.

Chapter IV. The silver chemistry of 2-(arylazo)pyridine ligand, L(1) is the subject matter of Chapter IV.

Silver nitrate reacts in methanol with L in 1:2 proportion to yield cationic $[AgL_2]^+$ (6), which has been isolated as a crystalline perchlorate salt (equation 9).

$$AgNO_3 + 2\ L \longrightarrow [AgL_2]^+ + NO_3^- \qquad (9)$$

The complex has been formulated by elemental analysis. It may be noted here that examples of bis ligated silver(I) complexes are scanty. The complex behaves as a 1:1 electrolyte in methanol. The assessment of bonding in this complex has been made by the examination of the IR spectrum. The position of $\nu_{N=N}$ in the complex was identified by comparison of IR spectra of $[AgL_2]^+$ with those of $[CuL_2]^+$ and free L. It has been observed that the shift of $\nu_{N=N}$ is very small in the IR spectrum of $[AgL_2]^+$ (6) as compared to that of uncoordinated L. This is surely due to negligible $d(\pi) \longrightarrow \pi^*(L)$ interaction. The IR spectrum of $[AgL_2]^+$ nearly superimposes on that of $[CuL_2]^+$. The high resolution ^1H NMR spectra of the complex with different substituted ligands are reported and completely assigned. It has been shown from the ^{1}H NMR data that two ligands in the present silver complex, 6 are magnetically equivalent at least in NMR time scale. Thus, the complex 6 contain an effective C_2-axis. Based on the NMR and IR data it has been proposed that the structure of $[AgL_2]^+$ is tetrahedral.



6

The electronic spectra of complex 6 in chloroform show a small bathochromic shift of $n \longrightarrow \pi^*$ transition as compared to that in free L. This shift is more in polar methanol.

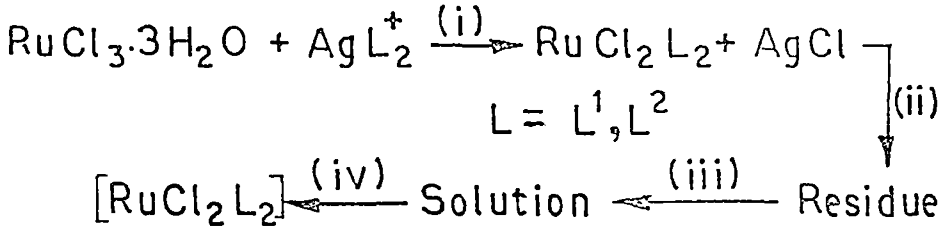
The stability of the silver complex in chloroform, methanol and acetonitrile have been verified by Beer's law. The complex is quite stable in methanol and chloroform whereas solutions of the complex in acetonitrile do not obey Beer's law.

Chapter V. In this chapter we explore the reactivity of silver(I) complex, $[AgL_2]^+$ towards $RuCl_3.3H_2O$ and other chloro complexes of ruthenium(II). Different reactions which have been studied are shown in Schemes 3-5.

The complex $[AgL_2]^+$ reacts with $RuCl_3.3H_2O$ in 1:1 proportion to yield an isomeric mixture of dichloro complexes, $[RuCl_2L_2]$(7) (Scheme 1). Interaction of hydrated $RuCl_3$ or $[RuCl_2L_2]$ and $[AgL_2]^+$ in 1:3 and 1:2 proportion, respectively (Schemes 2 and 3) lead directly to cationic isomeric *tris* chelated ruthenium(II) complexes of L, $[RuL_3]^{2+}$(8). These are isolated as their perchlorates. The reaction described in Scheme 3 has been particularly useful in synthesising the mixed ligand *tris* complexes. For example, $[Ag(L^2{}_2)]^+$ reacts with $[RuCl_2(L^1)_2]$ to yield $[Ru(L^1)_2(L^2)]^{2+}$. The identity of the complexes, thus synthesised, have been established from elemental analyses and spectral data. The advantages of new routes described above are highlighted.

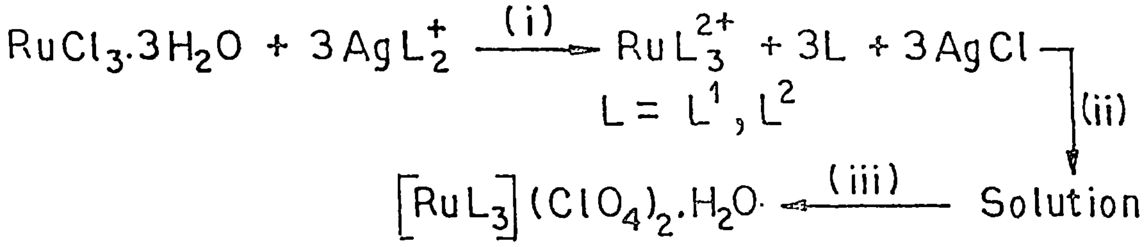
Solid-state thermal isomerisation of the isomeric dichloride complexes, $[RuCl_2L_2]$ have also been studied in this Chapter. These have been followed by different methods *viz.* Thermo Gravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) experiments. It is shown that two, *trans, trans* and *cis, cis* (*cc*) out of the three isomers of $[RuCl_2L_2]$ are converted into the third, *trans, cis* (*tc*) isomer on heating (equation 10).

$$tt/cc\text{-}[RuCl_2L_2] \xrightarrow{\text{heat}} tc\text{-}[RuCl_2L_2] \qquad (10)$$



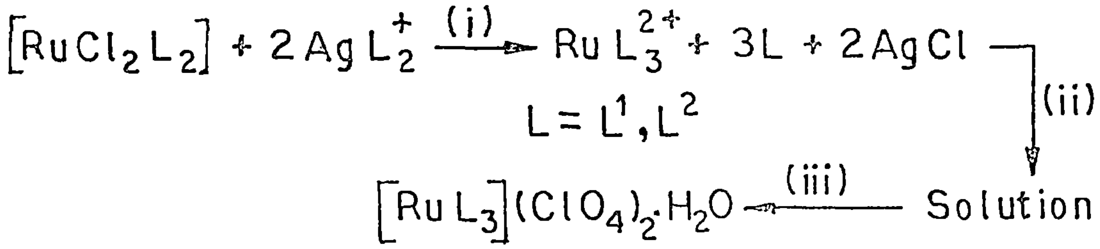
Key: (i) MeOH, Heat; (ii) Filtration; (iii) $CHCl_3$
(iv) Filtration, Hexane

Scheme 3



Key: (i) MeOH, Heat; (ii) Filtration; (iii) Aqueous solution of $NaClO_4$

Scheme 4



Key: (i) MeOH, Heat (ii) Filtration; (iii) Aqueous solution of $NaClO_4$

Scheme 5

Analyses of DSC data reveal that the thermal isomerisation reactions either *tt* → *tc* or *cc* → *tc*, proceed through a similar intermediate, I. (equations 11 and 12).

$$tt \longrightarrow \mathrm{I} \longrightarrow tc \qquad (11)$$

$$cc \longrightarrow \mathrm{I} \longrightarrow tc \qquad (12)$$

The relative thermal stabilities of the different isomers of $[RuCl_2L_2]$ are also briefly noted.

Based on the thermal results, a direct synthetic route to *tc*-$[RuCl_2L_2]$ has also been developed from $[RuCl_2(dmso)_4]$ (dmso = dimethylsulphoxide) and neat L (equation 13).

$$[RuCl_2(dmso)_4] \xrightarrow[ca.230°C]{\text{in neat L}} tc\text{-}[RuCl_2L_2] \qquad (13)$$

The reaction proceeds smoothly at *ca.* 230°C in almost quantitative yield.

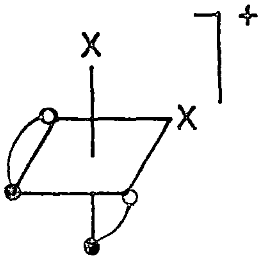
Chapter VI is the concluding chapter of the thesis. It addresses to the synthesis, characterisation and electrochemical reductions of new rhodium(III) complexes of L.

Hydrated RhX_3 (X=Cl,Br,I) reacts in methanol with L in 1:2 proportion to yield $[RhX_2L_2]^+$(9) (equation 14)

$$RhX_3 + 2L \longrightarrow [RhX_2L_2]^+ \qquad (14)$$

This is isolated as a crystalline perchlorate salt and is formulated by elemental analysis and molar conductance data.

Five geometrical isomers are possible for $[RhX_2L_2]^+$. Thin layer chromatographic experiments reveal that the complex exist only in one isomeric form. The stereochemistry of 9 is established using spectroscopic results. A large shift in $\nu_{N=N}$ to lower energy in 9 to that of free L indicate a strong d(Rh) ——> π^*(L) interaction. Where π^*(L) is the LUMO of azoimine chromophore. The dichloro complex also shows moderately strong bands at *ca*.340 and *ca*.320 cm^{-1} due to ν_{Rh-Cl} which are absent in the dibromo and diiodo analogue. Doublet nature of ν_{Rh-Cl} clearly suggests a *cis* $[RhCl_2]^{3+}$ grouping in the dichloride complexes. Dibromo and Diiodo analogues of 9 have virtually identical IR spectra in the range 4000-400 cm^{-1}. High resolution ^1H NMR spectrum of the complex 9 in CD_3CN has been described. The aromatic as well as aliphatic proton signals have been assigned on the basis of their chemical shifts and also by examining the spin-spin splitting patterns of the signals. The ^1H NMR spectrum of the complex displays only one signal (singlet or multiplet) for each proton of the ligand L. This result conclusively suggest that present complex exists only as a single isomer and both the chelate rings are magnetically equivalent. Based on IR and ^1H NMR spectral data it has been proposed that the structure of Rh(III) complex is *trans, cis* 9.



9

The complex 9 exhibits charge transfer (CT) transitions in the visible and UV region.

The complex, under consideration, electroactive and displays four successive reductive responses on the negative side of SCE. ESR studies of the electrolysed solutions clearly indicate that the electrons are added successively to the ligand centres. Four successive electron transfer in the present complex may be represented as follows (equation 15-18):

$$[RhCl_2L_2]^+ + e^- \rightleftharpoons [RhCl_2L'L] \qquad (15)$$

$$[RhCl_2L'L] + e^- \rightleftharpoons [RhCl_2\dot{L}_2]^- \qquad (16)$$

$$[RhCl_2\dot{L}_2]^- + e^- \longrightarrow [RhCl_2\ddot{L}\dot{L}]^{2-} \qquad (17)$$

$$[RhCl_2\ddot{L}\dot{L}]^{2-} + e^- \longrightarrow [RhCl_2\ddot{L}_2]^{3-} \qquad (18)$$

Part of the results of the studies described in Chapters II to VI have been published as noted below and rest are under communication.

Chapter II : *J. Chem. Soc., Dalton Trans.*, 1988, 2051.
Chapter III : *Polyhedron*, 1991, *10*, 1799.
Chapter IV : *Polyhedron*, 1990, *9*, 2251.
Chapter V : *J. Chem. Soc., Dalton Trans.*, 1991, 3249.
Chapter VI : *J. Chem. Soc., Dalton Trans., 1989, 1635.*

Chapter I

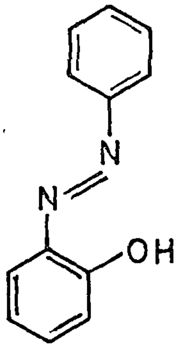
CHAPTER I

A GLANCE INTO THE 2-(ARYLAZO)PYRIDINE COMPLEXES OF TRANSITION METAL IONS AND SCOPE OF THE PRESENT INVESTIGATION

Abstract: *In this chapter the scope of the present investigation is delineated in the background of the known chemistry of 2-(arylazo)pyridine metal complexes.*

I.1 INTRODUCTION

An azo group suitably linked to an aromatic ring carrying an additional donor site is well suited for closure of a chelate ring. Good examples of such a situation are provided by metal complexes of arylazophenols (1)[1-3] and arylazooximes (2)[4-13]



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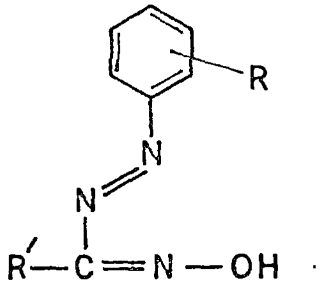


R = H, Me

R′ = Me, Ph, p-Tol

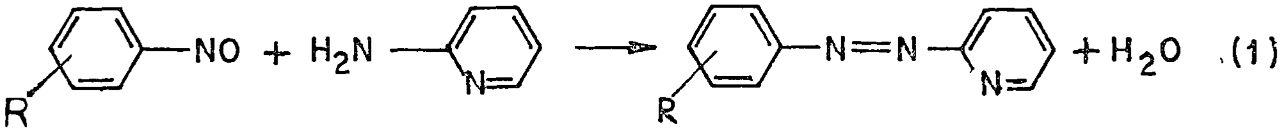
2

whose chelating abilities have been known for many years. The transition metal chemistry of a similar chelating bidentate ligand, 2-(arylazo)pyridine (L,3) has also an extensive literature of recent years.[13,14-42] Very recently, the chemistry of L (3) with non metallic boron has also been reported.[43]

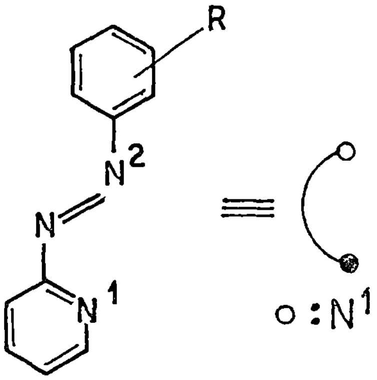
In this thesis we explore the coordination chemistry of ruthenium(II), rhodium(III) and silver(I) involving L. In the succeeding chapters (Chapter II-Chapter VI) several interelated aspects of 2-(arylazo)pyridine (L,3) chelate chemistry of the afforesaid metal ions have been described. The following aspects have been emphasised:

(i) The nitrosyl chemistry of ruthenium containing L and their reactions, (ii) the silver chemistry of L and the use of Ag-L complexes in the synthesis of bis and tris chelates of ruthenium, (iii) the rhodium chemistry of L, and (iv) study of solid-state thermal isomerisation.

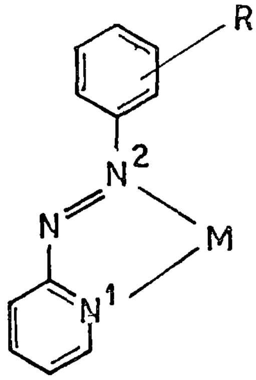
Although, the synthesis[44-46] of 2-(arylazo)pyridine (3) with the help of reaction 1 was reported by Campbell[44] *et al.* in 1953, the properties of 3 as a ligand started developing since 1973.



Till 1980, the progress has been very slow. There were only three reports on Iron(II)[14,15], Nickel(II)[15], and Mercury(II)[16] complexes during this decade. But since 1980, quite extensive and fascinating coordination chemistry of 3, involving platinum group metal ions, in particular, is emerging out of the continuous current activities of different groups around the world. Significant observations of the transition metal chemistry of L are summarised in Table I.1. Important representative structures are also displayed in 5-15. In most of the cases 3 act as a bidentate ligand and bind through pyridine nitrogen (N^1) and one of the azo nitrogens (N^2) to generate the chelate ring 4.



L, 3



4

R = H : L^1
R = m-Me : L^2
R = p-Me : L^3
R = p-Cl : L^4

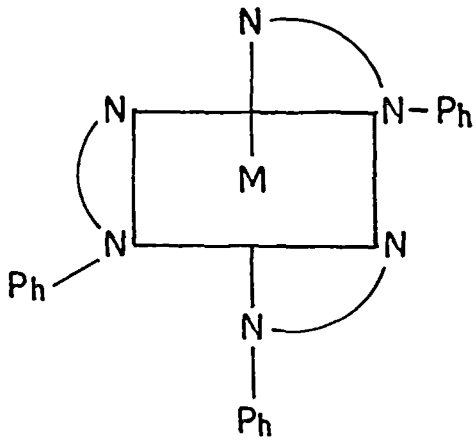
The significance of the present work will be discussed in the appropriate chapters. Our approach has been,

(i) The syntheses and characterisation of new complexes;
(ii) Establishment of their structures using spectroscopic data and
(iii) Examination of their redox activities both chemically and electrochemically.

TABLE I.1

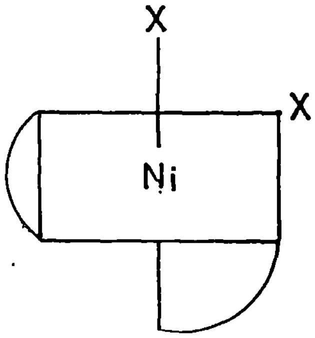
Chelates of 2-(Arylazo)pyridines

Metal ion	System	Structural type and/or any other comments	References
Ni^{2+}	$[Ni(L^1)_3](ClO_4)_2$	Exists in meridional *trans* form (5); from the ν_1 band the D_q of L^1 has been calculated to be 1080 cm^{-1}.	15
	$[NiX_2(L^1)_2].0.5CH_2Cl_2$ X=Cl, Br	In pseudooctahedral geometry the X atoms are *cis* to each other (6).	15
	$[NiI_2(L^1)_2]$	Exists in *trans* planar geometry (7).	15
Fe^{2+}	$[Fe(L^1)_3]I_2$	Exists in meridional *trans* geometry (5); shows metal-to-ligand charge transfer (MLCT) transition at 590 nm; $\nu_{N=N}$ shifts appreciably to lower energy compared to $\nu_{N=N}$ in the free ligand L.	14,15
Hg^{2+}	$[HgCl_2L]$ $L = L^1-L^4$	Formed by reacting $HgCl_2$ with L (8)	16,17
Ru^{2+}	$[RuCl_2L_2]$ $L=L^1-L^2$	Exist in three geometrical isomeric forms: green (γ or *trans,trans,trans:ttt*) (9), blue (α or *cis,trans, cis; ctc*) (10)and blue violet (β or *cis,cis,cis;ccc*) (11); undergoes isomerisation; structures of *ctc* and *ccc* geometries of $[RuCl_2(L^1)_2]$ have been established crystallographically.	18,21-23



M = Ni^{2+}, Fe^{2+}, Ru^{2+}

5



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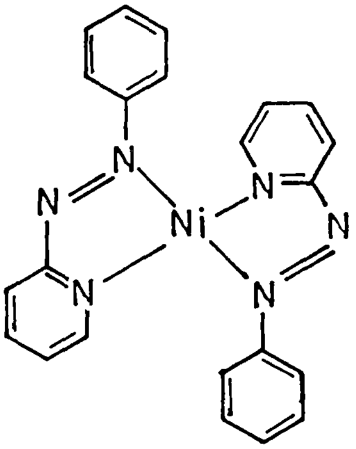

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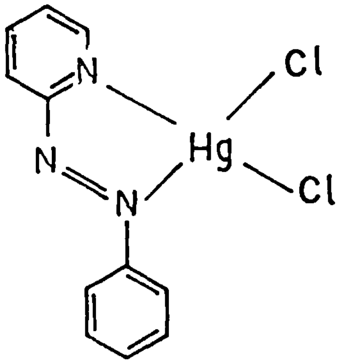

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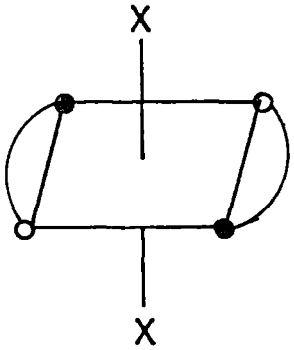
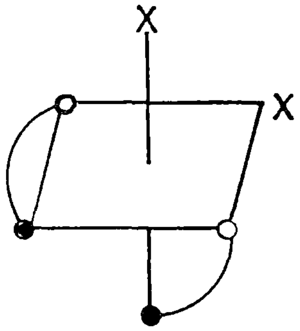
TABLE 1.I (CONTD)

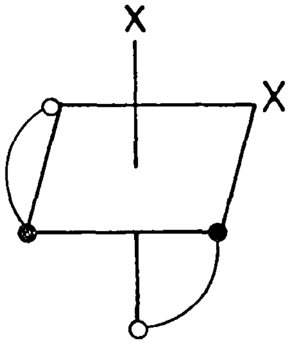
Metal ion	System	Structural type and/or any other comments	References
	$[RuX_2L_2]$ X=Br,I; $L=L^1-L^2$	$[RuBr_2L_2]$ also obtained as *ttt*(9), *ctc*(10) and *ccc*(11) isomers whereas $[RuI_2L_2]$ exists only as *ttt* isomer(9)	21
	$[RuS_2L_2](ClO_4)_2.H_2O$ $S=H_2O$, CH_3CN; $L=L^1-L^2$	Exist both as *ctc* and *ccc* form in which two solvent molecules occupy *cis* position; prepared by silver assisted stereoretentive halide displacement from *ctc* or *ccc*-$[RuCl_2L_2]$	25
	$[Ru(OH)(S)L_2]ClO_4.H_2O$ $S=H_2O$, py; $L=L^1-L^2$	Exist as cis isomer; formed by deprotonation of $[Ru(OH_2)_2L_2]^{2+}$ by NaOH and pyridine bases	25
	$[RuL_3](ClO_4)_2.H_2O$ $L=L^1-L^2$	Exists both as a *meridional* (*mer*,5) and a *facial* (*fac*, 12) isomer; undergoes multielectron transfer reactions at the electrode surface.	27,28
	$[RuX_2(L^1)_2]$ X=CN,N_3	Obtained by anation reaction of an intermediate aquo complex; *ctc* geometry of $[Ru(N_3)_2(L^1)_2]$ has been established crystallographically.	24,28
	$[RuBL_2](ClO_4)_2.H_2O$ $B=L^1,L^2$,bpy,en, tu,btz,py	Formed by stereoretentive displacement of water from $[Ru(OH_2)_2L_2]^{2+}$ by ligand B.	27,28



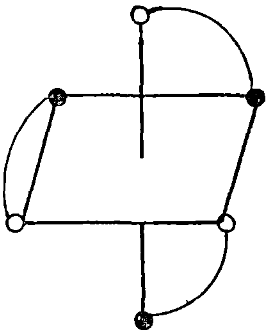
9 (ttt)



10 (ctc)



11 (ccc)



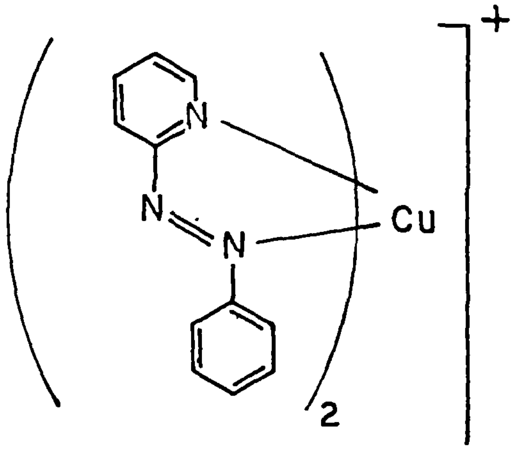
12 (fac)

TABLE I.1 (CONTD)

Metal ion	System	Structural type and/or any other comments	References
	$[RuXPL_2](ClO_4)_2.H_2O$ X=Cl,Br; P=tertiary phosphines;L=L^1-L^2	Obtained by reacting $[RuCl_2L_2]$ with tertiary phosphines (P); substitution of Cl^- by P is stereodynamic	30
	$[Ru(OH_2)(py)(L^1)_2]$ $(ClO_4)_2.H_2O$	Undergoes reversible $2e^-/2H^+$ transfer; catalytically oxidise water to dioxygen	31
Ru^{3+}	$[RuCl_2(L^1)_2]ClO_4.H_2O$	Obtained by stereoretentive oxidation of the corresponding ruthenium(II) isomers with concentrated nitric acid; display rhombic ESR spectra in frozen solutions; strong oxidants and bring about the oxidation of organic as well as inorganic substrates.	32
Os^{2+}	$[OsX_2L_2]$ X=Cl,Br;L=L^1-L^2	Unlike ruthenium, exists only in *ctc* and *ccc* form; No evidence for the existance of *ttt*-$[OsX_2L_2]$ isomer has been obtained; the geometry of *ctc*-$[OsCl_2(L^2)_2]$ has been established crystallographically	33,34
	$[OsDL_2]^{(2-Z)+}$ D^{Z-}=Bidentate ligands *viz.* L^1,L^2, bpy,phen,acac,gly, trp, dbm, ox;Z=0-2; L=L^2	Formed by reacting dibromo-complex,$[OsBr_2L_2]$ with an excess of bidentate ligand, D^{Z-}; each of the complexes undergoes multielectron transfer at the electrode surface	33,34

TABLE I.1 (CONTD)

Metal ion	System	Structural type and/or any other comments	References
Cu^+	$[Cu(L^1)_2]ClO_4$	Exists as gross tetrahedral geometry (13); shows two allowed MLCT bands at 700 nm and 560 nm; a large shift of $\nu_{N=N}$ to lower frequency compared to free L has been observed; undergoes oxidation at a very high positive potentials.	35
Cu^{2+}	$[Cu(L^1)_2](ClO_4)_2$	Exists in gross planar geometry (14); shows a broad ligand field band at 606 nm in CH_3CN	35
Pd^{2+}	$[PdCl_2(L^2)]$	Exists in square planar geometry.	13
	$[PdCl(L^2O)]$ $L^2O=C_5H_4NN_2(O)C_6H_3(CH_3)$	Obtained by oxidation of $[PdCl_2(L^2)]$; the regiospecific oxidation of aromatic $-C_6H_4R$ moiety to $C_6H_3(OH)R$ occurs in the reaction mixture.	13
Re^{5+}	$[ReCl_3ZL]$ $Z=ArC_6H_4N;L=L^1-L^4$	This (15) exemplifies the unusual reducitve azo cleavage reaction mediated by rhenium leading to the complex containing the very rare semibent organoimide function; undergoes oxidation to generate ESR active hexavalent metal complex	38
Cr^{2+}	$[CrCl_2(L^1)_2]$	Obtained as an inert chromium(II) compound; six coordinated with *cis* chlorides, *cis* azo and *trans* pyridyl groups; the overall symmetry is close to C_2; the structure has been determined crystallographically.	39



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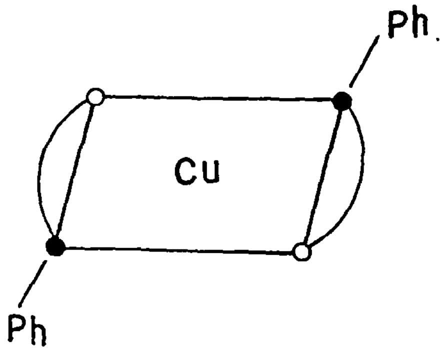

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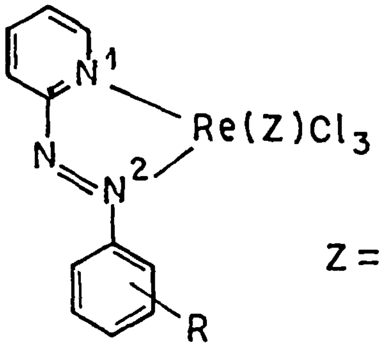

$Z = Ar\,C_6H_4N$

15

TABLE I.1 (CONTD)

Metal ion	System	Structural type and/or any other comments	References
M^o (M=Cr, Mo, W)	$[M(CO)_4(L^1)]$	Diamagnetic air stable solids; obtained by reacting $[M(CO)_6]$ with L^1.	40
	$[M(L^1)_3]$	Obtained from $[M(CO)_6]$; geometry is uncertain	40
M^o (M=Mo, W)	$M(CO)_2(L^1)_2$	Diamagnetic air stable solids	40
Rh^+	$[Rh(nbd)(L^1)Cl].0.5CH_2Cl_2$ nbd=norbornadiene	Obtained from $[Rh(nbd)Cl]_2$; crystallises with two crystallographically independent five coordinate rhodium(I) complexes and one molecule of solvent per asymmetric unit	42
B^{3+}	$[LBF_2]F^*$ $L=L^1-L^4$	Compounds were obtained by reaction of boron trifluoride-diethyl ether with the ligands in 2:1 molar ratio.	43

[*] Only nonmetallic compound of L reported in literature.

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46. The ligand L^3 have been synthesised[45] directly from 2-aminopyridine and p-nitrotoluene using metallic sodium.

Chapter II

CHAPTER II

SYNTHESIS AND CHARACTERISATION OF A NEW MONONITROSYL COMPLEX OF RUTHENIUM(II) CONTAINING 2-(ARYLAZO)PYRIDINE : EXAMPLE OF STRONGLY ELECTROPHILIC NITROSYL*

Abstract: *A high-yield synthetic route to ruthenium(II) mononitrosyl complex of type* $[Ru(NO)(NO_2)L_2]^{2+}$ *(4)* $[L=$*2-(arylazo)pyridine*$]$ *from its dinitro precursor,* $[Ru(NO_2)_2L_2]$ *(3) is described. Complex 4 was isolated as crystalline perchlorate salt. The electronic spectrum of complex 4 and 3 exhibit allowed metal-to-ligand charge-transfer transitions in the visible region, 400-550 nm. The nitrosyl absorbs at a very high wave numbers (* ν_{NO} *ca.1950* cm^{-1}*) in the IR spectrum. All the complexes are electroactive. Secondary oxidation of coordinated nitrite in 3 occurs after electrochemical metal oxidation. In the case of complex 4, two successive one-electron reductions have been observed at relatively high positive potentials.*

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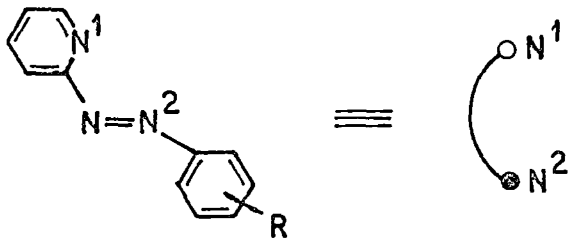
[*] A part of this work has appeared in *J. Chem. Soc., Dalton Trans.*, 1988, 2051.

II.1 INTRODUCTION

The electrophilic behaviour of coordinated nitric oxide (NO) has been of recent interest[1-19] in ruthenium nitrosyl chemistry. It has been shown that those nitrosyls having a sufficiently high degree of nitrosonium ion (NO^+) character and generally showing relatively high ν_{NO} (e.g.>1850 cm^{-1}) are susceptible[1,2] to nucleophilic attack. Synthesis of nitrosyls containing electrophilic NO is, however, an important pre-requisite for studying the above reactions. It is also now known that strong π-acid coligands always favour the binding of NO^+ to a low valent (electron rich) metal centre.[20]

In this chapter we describe the synthesis of mononitrosyl complex of ruthenium(II) from their precursor dinitro complex which contain 2-(arylazo)pyridine (L,1) as one of the coligands. The bidentate nature of L is now well established and it imparts excellent stability[21,22] to ruthenium(II). Although it was recently remarked[23] in passing that it might not be possible to achieve the synthesis of nitrosyl in presence of L because of its very high π-acidity. We thought, the synthesis could be achieved under appropriate conditions. The synthesis of the nitrosyl complex has been achieved starting from dinitro complex of type, $[Ru(NO_2)_2L_2]$. Characterisation of the nitrosyl and their precursor dinitro complex are made on the basis of spectral data. The redox properties of the complex is also reported.

The three ligands used in this chapter are abbreviated as L^1-L^3 (Structure 1).



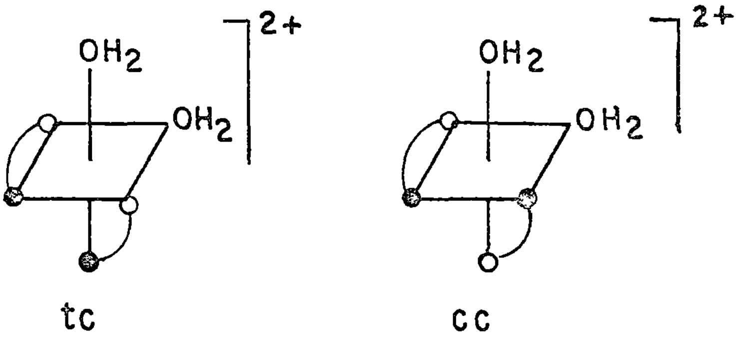
L,1

R	L
H	L^1
m-Me	L^2
p-Me	L^3

II.2 RESULTS AND DISCUSSION

A. Stereochemistry of Starting $[Ru(OH_2)_2L_2]^{2+}$(2) Cation

Due to unsymmetrical nature of the bidentate ligand L(1) the metal complexes of L exist in several geometrical isomeric forms. For example, $[RuCl_2L_2]$ can in principle exist[21,22a] in five geometrical isomeric forms: Isomer stereochemistry of $[RuL_2]^{2+}$ moiety is best defined[24] by considering the relative positions in the pair N^1,N^1 and in the pair N^2,N^2 taken in that order and allowing other ligands to occupy the remaining two octahedral positions. Since the remaining two octahedral positions are automatically fixed by the $[RuL_2]^{2+}$ stereochemistry, we will be considering only the stereochemistry of the $[RuL_2]^{2+}$ moiety for defining various geometrical isomers of $[RuL_2]^{2+}$ complexes. The known diaquo cation, $[Ru(OH_2)_2L_2]^{2+}$ exists[25] in two geometrical isomeric forms. In one of the isomers, of N^1 and N^1 occupy *trans* positions and N^2,N^2 *cis* positions. This isomer is *trans, cis* or simply *tc*(2). Similarly, the other isomer is *cis, cis* or simply *cc*(2).



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One of these isomers, *viz.* *tc*-$[Ru(OH_2)_2L_2]^{2+}$(2) is used as the starting material in the present work.

B. Synthesis

(a) *tc*-$[Ru(NO_2)_2L_2]$(3) from *tc*-$[Ru(OH_2)_2L_2]^{2+}$(2)

A solution of *tc*-$[Ru(OH_2)_2L_2]^{2+}$ in acetonitrile reacts smoothly with an aqueous solution of $NaNO_2$ in 1:2 proportion to yield *tc*-$[Ru(NO_2)_2L_2]$ (equations 1 & 2).

$$\underset{2}{tc\text{-}[Ru(OH_2)_2L_2]^{2+}} \xrightarrow{CH_3CN} tc\text{-}[Ru(CH_3CN)_2L_2]^{2+} + 2H_2O \quad (1)$$

$$tc\text{-}[Ru(CH_3CN)_2L_2]^{2+} \xrightarrow{NO_2^-} \underset{3}{tc\text{-}[Ru(NO_2)_2L_2]} + 2CH_3CN \qquad (2)$$

The compound, *tc*-$[Ru(NO_2)_2L_2]$ is sparingly soluble in acetonitrile-water mixture and thus precipitates on cooling. The product thus obtained is highly crystalline in nature. On TLC it showed single spot confirming the presence of only one isomeric form of the compound. The anation reaction under consideration is a two steps reaction (equations 1 & 2). In the first step stereoretentive solvolysis[25] of violet *tc*-$[Ru(OH_2)_2L_2]^{2+}$ takes place to yield orange *tc*-$[Ru(CH_3CN)_2L_2]^{2+}$ which then undergoes anation reaction to yield a dull red molecular complex of general formula *tc*-$[Ru(NO_2)_2L_2]$. The stereoretentivity of the reactions have been settled on the basis of spectral data (vide infra). It may be noted here that an aqueous solution of 2 with $NaNO_2$ also yields 3 as the major product. TLC experiment of the product 3 obtained from an aqueous solution showed the presence of more than one component. It may be relevant to add that Krause *et al.* also synthesised[23] $[Ru(NO_2)_2(L^1)_2]$ by reacting $[RuCl_2(L^1)_2]$ and excess of $NaNO_2$ at a high temperature. The stereochemistry of the product obtained by them is uncertain.

(b) *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$ (4) from *tc*-$[Ru(NO_2)_2L_2]$ (3)

The direct reaction of Ru(II)-L complexes with nitric oxide (NO) failed to afford tractable RuL(NO) species. The synthetic route by the electrophilic attack of H^+ at a preformed ruthenium nitro complex by acid was then explored. The dinitro compound *tc*-[Ru$(NO_2)_2L_2$] obtained as described above, has been found as a suitable substrate for the synthesis of ruthenium(II) nitrosyl. For preparative conversion of Ru-NO_2 to Ru-NO, dilute aqueous acids are commonly used,[26-28] but this was not effective in affording any characterisable nitrosyl derivative of 3. An ice cold 1:1 mixture of concentrated HNO_3(10M) and $HClO_4$(10M) was, however, found to be the most effective in producing *tc*-[Ru(NO)$(NO_2)L_2]^{2+}$ from *tc*-[Ru$(NO_2)_2L_2$]. From the reaction mixture, it has been isolated as its perchlorate salt, *tc*-[Ru(NO)$(NO_2)L_2](ClO_4)_2$ (4) in a high yield. We note here that this conversion of 3 to 4 may occur by direct nitrosation of coordinated nitrite, (equation 3)

$$\underset{3}{tc\text{-}[Ru(NO_2)_2L_2]} + 2H^+ \longrightarrow \underset{4}{tc\text{-}[Ru(NO)(NO_2)L_2]^{2+}} + H_2O \qquad (3)$$

It may also occur by prior acid-catalysed aquation followed by nitrosation of the aquo complex thus formed (equations 4 & 5)

$$\underset{3}{tc\text{-}[Ru(NO_2)_2L_2]} + H^+ \xrightarrow{H_2O} tc\text{-}[Ru(OH_2)(NO_2)L_2]^+ + HNO_2 \qquad (4)$$

$$tc\text{-}[Ru(OH_2)(NO_2)L_2]^+ \xrightarrow{HNO_2} \underset{4}{tc\text{-}[Ru(NO)(NO_2)L_2]^+} + H_2O \qquad (5)$$

The direct nitrosation path has been observed in other cases[29] and it is probably the path for the formation of present nitrosyl complex. Also it has been observed that 2 does not react with HNO_2 to yield any characterisable nitrosyl complex.

Although, the reaction (3) indicates that dinitrosyl of type, $[Ru(NO)_2L_2]^{4+}$ may also form. To date, we have no evidence for isolable dinitrosyl formation. With the consideration that L is a very strong π-acceptor, this is not surprising. It is significant to note that the synthetic reactions used by us has the advantage that the ligand framework can be established before metal-nitrosyl bond is formed.

Formulation and Assessment of Gross Geometry of $[RuL_2]^{2+}$ Moieties in *tc*-$[Ru(NO_2)_2L_2]$ (3) and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ (4)

The complexes are formulated by elemental analyses (Table II.1). The presence of ionic perchlorate in the nitrosyl complex has been assessed on the basis of IR data (vide infra). All the complexes are diamagnetic as evidenced by the magnetic susceptibility measurements. This indicates that in both the cases the formal oxidation states of ruthenium is +2 (t_2^6). The equivalent molar conductance of the perchlorate salt of 4 lies in the range 260-300 $ohm^{-1}cm^2mol^{-1}$ in CH_3CN (Table II.2) suggesting a 1:2 electrolytic[30] nature of the compound. The dinitro compound is non-electrolytic in acetonitrile (Table II.2).

The problem of stereoretentivity of the reactions (equations 1 & 2) have been resolved by the examination of the ^1H NMR spectra of the compounds. The ^1H NMR spectra of the dinitro complexes (3) of methyl substituted ligands ($L=L^2, L^3$) were used to take the advantage of convenient methyl resonances as a structural probe. A representative spectrum of *tc*-$[Ru(NO_2)_2(L^3)_2]$ is shown in Figure II.1. In $CDCl_3$ each of the compounds, $[Ru(NO_2)_2(L^2)_2]$

TABLE II.1

Analytical Data of *tc*-$[Ru(NO_2)_2L_2]$ and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$

Compound	Formula	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
tc-$[Ru(NO_2)_2(L^1)_2]$	$RuC_{22}H_{18}N_8O_4$	47.22	47.20	3.22	3.10	20.03	20.30
tc-$[Ru(NO_2)_2(L^2)_2]$	$RuC_{24}H_{22}N_8O_4$	49.06	49.20	3.75	3.90	19.08	19.05
tc-$[Ru(NO_2)_2(L^3)_2]$	$RuC_{24}H_{22}N_8O_4$	49.06	49.30	3.75	3.80	19.08	19.15
tc-$[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$	$RuC_{22}H_{18}N_8O_{11}Cl_2$	35.58	35.60	2.42	2.60	15.10	14.95
tc-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$	$RuC_{24}H_{22}N_8O_{11}Cl_2$	37.40	37.30	2.85	2.65	14.55	14.50
tc-$[Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$	$RuC_{24}H_{22}N_8O_{11}Cl_2$	37.40	37.70	2.85	2.65	14.55	14.45

TABLE II.2

Solution Molar Conductivity Data[a,b] of *tc*-[Ru(NO_2)$_2$$L_2$] and *tc*-[Ru(NO)($NO_2$)$L_2$]($ClO_4$)$_2$ at 298K

Compound	Λ_M $Ohm^{-1}cm^2mol^{-1}$
tc-[Ru(NO_2)$_2$(L^1)$_2$]	2.5
tc-[Ru(NO_2)$_2$(L^2)$_2$]	1.0
tc-[Ru(NO_2)$_2$(L^3)$_2$]	1.0
tc-[Ru(NO)(NO_2)(L^1)$_2$](ClO_4)$_2$	265
tc-[Ru(NO)(NO_2)(L^2)$_2$](ClO_4)$_2$	280
tc-[Ru(NO)(NO_2)(L^3)$_2$](ClO_4)$_2$	295

[a] Solvent : acetonitrile. [b] Solute concentration: *ca.* 10^{-3}mol dm^{-3}

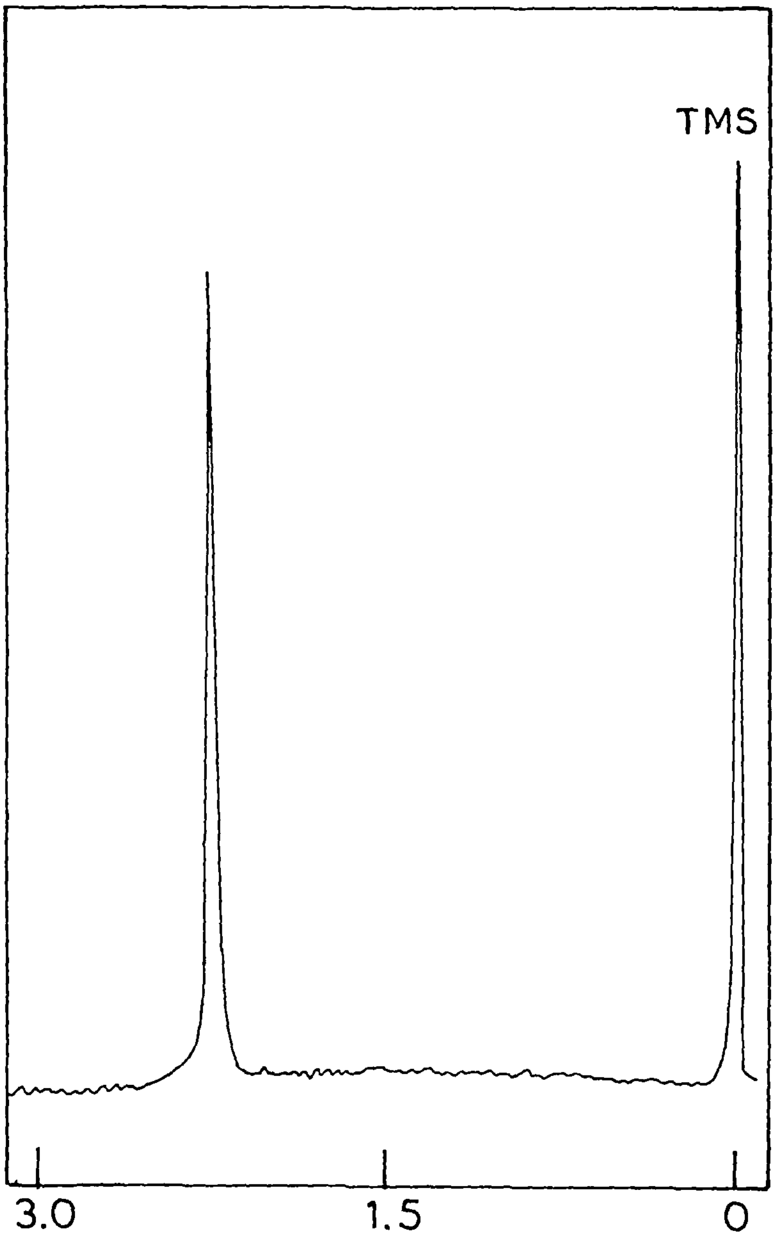
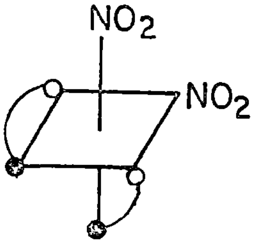


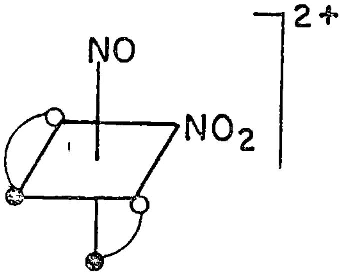
FIGURE II.1. ^{1}H NMR SPECTRUM OF <u>tc</u>-[$Ru(NO_2)_2(L^3)_2$] In $CDCl_3$

and $[Ru(NO_2)_2(L^3)_2]$ shows a single methyl resonance at 2.19 and 2.26 ppm, respectively. It may be noted here that the parent diaquo complexes (2) of L^2 and L^3, *tc*-$[Ru(OH_2)_2L_2]^{2+}$ also show a single methyl resonance[25] at *ca*. 2.15 ppm in $(CD_3)_2SO$. Thus, the two fold symmetry axis after the anation reaction is retained. Furthermore, each of all the three complexes of 3 ($L=L^1-L^3$) shows a doublet resonance at 9.36,9.37 and 9.39 ppm respectively. This response has been assigned[31] to the ortho-pyridyl proton resonance. Appearance of this doublet at such a low field further confirms the *cis* geometry of the dinitro complexes. It may be relevant to add that in the *trans* geometry (*tt*) this proton is shielded by the aryl ring of the second ligand and appears[31] at a higher field. For comparison, 6-H in *tc*-$[RuCl_2(L^2)_2]$ appears at 9.37 ppm whereas in *tt*-$[RuCl_2(L^2)_2]$ it appears[31] at 8.92 ppm.

The nitrosyl complex is obtained by the treatment of H^+ on $[Ru(NO_2)_2L_2]$. Since the reaction of electrophilic H^+ takes place at one of the two peripheral NO_2 groups, it is logical to assume that the gross stereochemistry of $[RuL_2]^{2+}$ in the nitrosyl complex remains the same as the dinitro precursor. Therefore, we conclude that the structures of *tc*-$[Ru(NO_2)_2L_2]$(3) and *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$(4) are as shown below:



3,(tc)

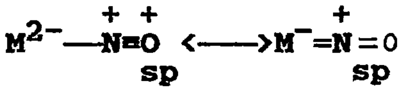


4,(tc)

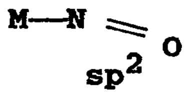
C. IR Spectra : Assessment of Bonding

Infrared data were collected in the range 4000-200 cm^{-1} in KBr disc. Characteristic group frequencies are collected in Table II.3 and representative spectra of *tc*-$[Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$ and *tc*-$[Ru(NO_2)_2(L^2)_2]$ are displayed in Figures II.2 and II.3 respectively. Some of those which are useful in assessing the bonding in these complexes, are discussed below.

(i) ν_{NO}. One of the most significant observations in the IR spectra of **4** is the consistent and systematic appearance of a strong band at *ca*.1950 cm^{-1} (Figure II.2) which is conspicuously absent in the parent *tc*-$[Ru(NO_2)_2L_2]$. Evidently, this is due to the stretching mode[7,29,32] of coordinated NO. A description involving two extreme, bonding formulations is currently used to explain the nature of the M-N-O linkage in most mononuclear complexes. In the sense of formal oxidation state it is now customary to think of linear nitrosyls as derived from NO^+ and bent nitrosyls as derived from NO^-.[33,34] The nitrogen and oxygen atoms in NO^+ are considered to be sp hybridised and the bond order is 3 whereas in NO^- it is sp^2 hybridised and the bond order is 2. In the NO^+ type of linear coordination, π-acceptance is considered to play an important role as it does in metal carbonyls. Thus, for an electron rich metal ion with concomitant π-back bonding results in linear terminal NO, on the other hand an electron poor system prefers to form a bent nitrosyl.



$$M^{2-}\!-\!\underset{sp}{\overset{+}{N}}\equiv\overset{+}{O} \longleftrightarrow M^{-}=\underset{sp}{\overset{+}{N}}=O$$



$$M-\underset{sp^2}{N}=O$$

TABLE II.3

Selected Infrared Spectral Data[a,b] of *tc*-$[Ru(NO_2)_2L_2]$ and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$

Compound	ν_{max} (cm^{-1})						
	C=C + C=N	N=N	NO	NO_2	C-H Out-of plane bending in pyridine ring	C-H out-of plane bending in phenyl ring	ClO_4^-
tc-$[Ru(NO_2)_2(L^1)_2]$	1600	1370		1360	780	700	
tc-$[Ru(NO_2)_2(L^2)_2]$	1600	1365		1355	785	695	
tc-$[Ru(NO_2)_2(L^3)_2]$	1600	1365		1355	780	700	
tc-$[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$	1600	1380	1950	1470	780	695	1100[c],620
tc-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$	1600	1375	1950	1480	780	695	1100[c],620
tc-$[Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$	1600	1375	1955	1455	780	695	1100[c],620

[a] In KBr disc, 4000-200 cm^{-1}. [b] All bands are sharp and strong unless otherwise stated. [c] Broad band.

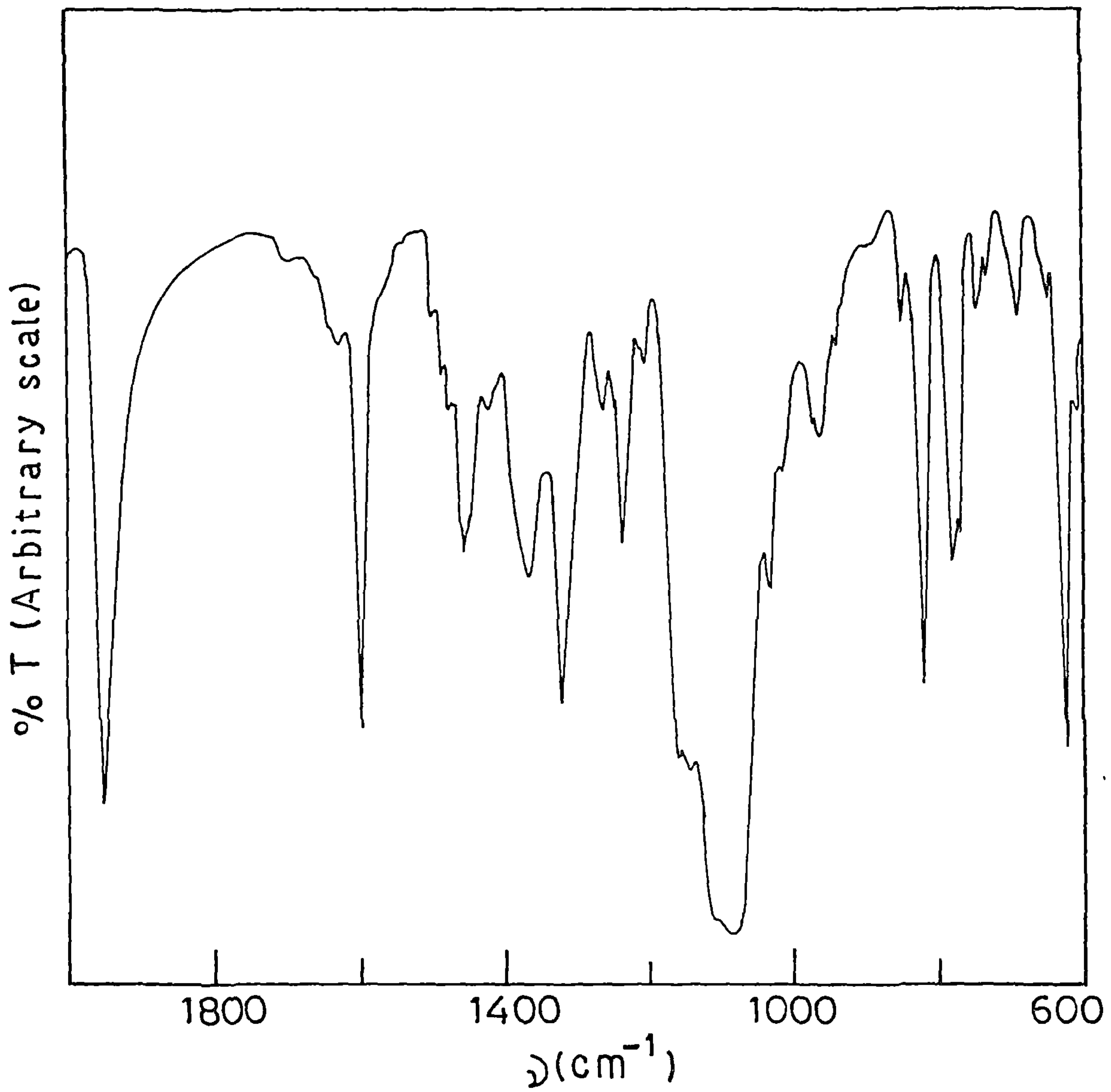


FIGURE II.2. INFRARED SPECTRUM OF <u>tc</u>- [$Ru(NO)(NO_2)(L^3)_2$] $(ClO_4)_2$ IN KBr DISC

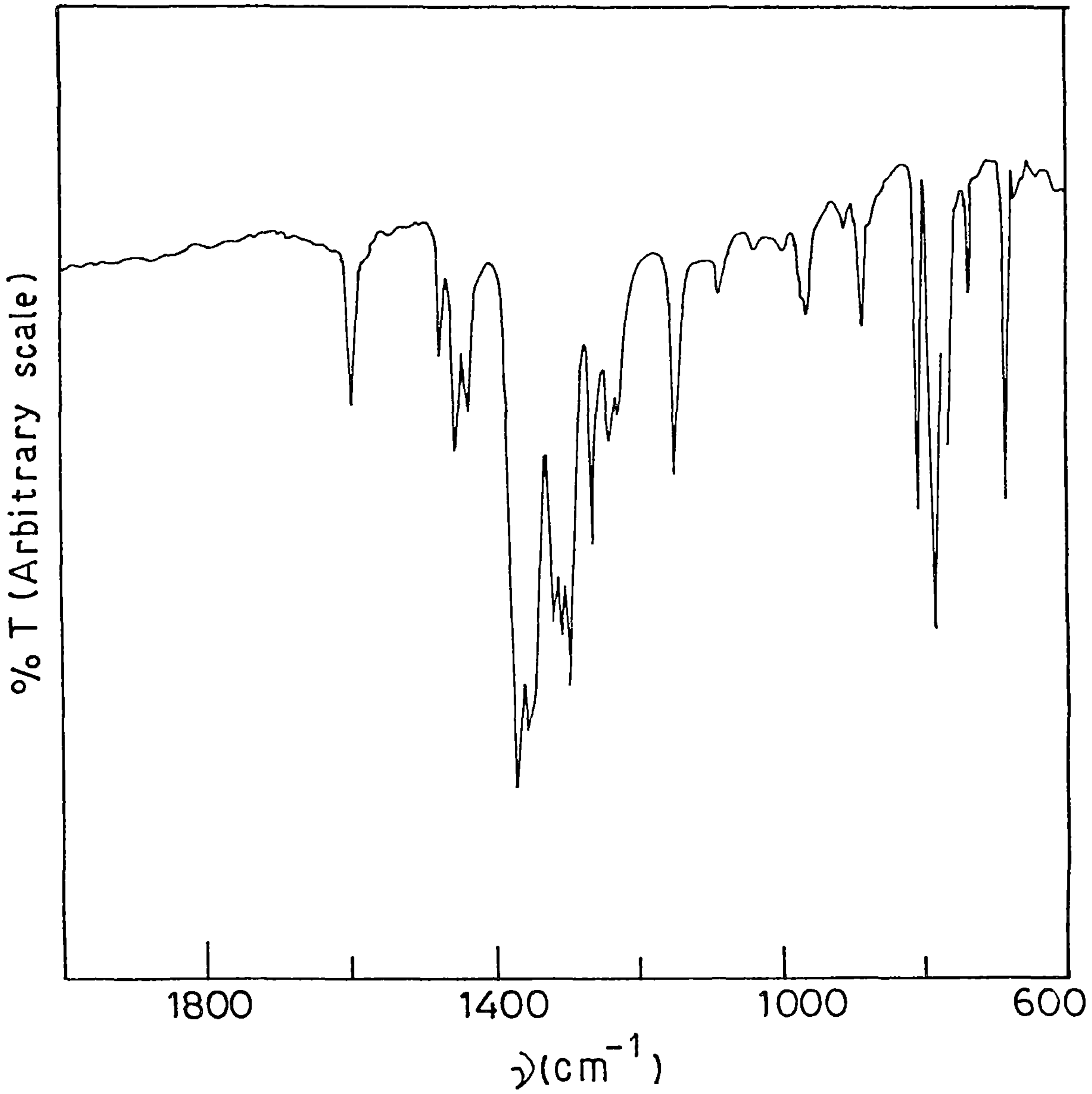


FIGURE II.3. INFRARED SPECTRUM OF tc- $[Ru(NO_2)_2(L^2)_2]$ IN KBr DISC

For compounds of NO^+ and NO^-, ν_{NO} has been observed[1,35] in the ranges 1950-1600 cm^{-1} and 1720-1520 cm^{-1} respectively. The difference in electron density on the coordinated nitrosyls and hence the ν_{NO} are closely related to the π-acceptor functions of the coligands. Such a high value of ν_{NO} (*ca.*1950 cm^{-1}) in the present nitrosyl (4) strongly suggests[36] that formally a linear NO^+ *(sp) is coordinated to a* $[RuL_2]^{2+}$ moiety. *This also in turn* suggest the potential π-acid character of L.

(ii) νNO_2. *tc*-$[Ru(NO_2)_2L_2]$ has a number of NO_2 bands in the region 1300-1400 cm^{-1} (Figure II.3). We assumed there should be some correspondance between the IR spectrum[36] of $[Ru(NO_2)_2(bpy)_2]$(bpy=2,2'-bipyridine) with our nitrite complex. Comparing spectra of the two, it became clear that $\nu_{N=N}$ of L must be one of the two strong bands located at 1370 and 1360 cm^{-1}, rest of which is ν_{asNO_2} but shifted from those in $[Ru(NO_2)_2(bpy)_2]$. We choose the band at *ca.*1360 cm^{-1} as the νNO_2 mode. This band in the *nitrosyl complex* (4) *shifts to a much higher frequency* and is observed at *ca.*1480 cm^{-1} (Figure II.2). For comparison, ν_{asNO_2} bands in $[Ru(NO_2)_2(bpy)_2]$ and in $[Ru(NO)(NO_2)(bpy)_2]^{2+}$ appear at 1332 and 1450 cm^{-1} respectively.[36] The positions of these bands in our complexes clearly indicate that nitrite ion is coordinated through nitrogen[37] rather than oxygen.

(iii) $\nu_{N=N}$. The N=N stretching frequency in free L appears at 1425 cm^{-1}.[38] This frequency is appreciably lowered in both *tc*-$[Ru(NO_2)_2L_2]$ and *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$ (Table II.3). An azo mode at 1425 cm^{-1} (free L) indicates conjugation;[39] the shift to lower energy in the complexes indicates less double bond character in the N=N group. This is a strong evidence for substantial π-bonding to ruthenium through an azo nitrogen in the ruthenium-L complexes. As the Ru-N bond order increases incorporating more π-bonding, the N-N bond order must decrease. Low azo stretching frequencies have also been observed[21,22,38,40] for other azopyridine complexes of electron-rich metal ions. A striking but very reasonable trend in the shift of $\nu_{N=N}$ has been observed in the present group of complexes. The $\nu_{N=N}$ for 3 appears at *ca.*1370 cm^{-1} but the same band shifts to higher energy and appears at *ca.*1380 cm^{-1} in 4. As we move from 3 to 4, an anionic NO_2^- group is replaced by a much stronger π-acceptor NO^+ ligand. As the employed coligand becomes a stronger π-acceptor, there is competition for the ruthenium (t_2) electrons and less π-back donation to L raising the azo bond order resulted. Thus the shift of $\nu_{N=N}$ to higher frequencies on moving from 3 to 4 is as expected.

All the complexes also show[38,40] characteristic IR active bands of the ligand L (Table II.3); *viz.* $\nu_{C=C}$ and $\nu_{C=N}$ at 1600 cm^{-1}, ν_{C-H} out-of-plane bending in pyridine ring at 780 cm^{-1} and ν_{C-H} out-of-plane bending in phenyl ring at *ca.*700 cm^{-1}. A broad structureless band at 1100 cm^{-1} and sharp band at 620 cm^{-1} appear in the complex 4 which was absent in the complex 3. These bands are due[41] to νClO_4^-.

D. Electronic Spectra

Absorption spectral data of solutions of the compound 3 and 4 in dichloromethane and acetonitrile respectively are collected in

Table II.4. Representative spectra for both *tc*-[$Ru(NO_2)_2(L^1)_2$] and *tc*-($Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$ are displayed in Figure II.4 and II.5 respectively. Free ligand L displays absorption bands at *ca.*440 nm (ε, *ca.*700 $dm^3mol^{-1}cm^{-1}$) and at 320 nm (ε,*ca.*19,000 $dm^3mol^{-1}cm^{-1}$). These have been respectively assigned[38] to $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions centered primarily on the azo group. In 3, $\pi \longrightarrow \pi^*$ transition undergoes a slight blue shift and $n \longrightarrow \pi^*$ transition is replaced by an intense absorption at *ca.*370 nm. The origin of this band is not clear to us. This pattern of transitions have been observed[21-25] in several other complexes containing $[RuL_2]^{2+}$ moiety.

More significant are the new allowed bands appearing in the visible region 450-550 nm in 3. We assign this lowest energy transition to metal-to-ligand charge-transfer (MLCT) : $t_2(Ru) \longrightarrow \pi^*(L)$, where $\pi^*(L)$ is the LUMO of the azoimine chromophore. In 4 the MLCT band is comparatively broader and shifts to a higher energy as compared to that of 3. It appears at *ca.*410 nm (Table II.4). The CT band energy is indicative of the metal-ligand interaction. As the t_2 set of the metal becomes more stabilised by this interaction, the metal $t_2 \longrightarrow \pi^*(L)$ separation increases. NO^+ coordination stabilizes t_2 level of ruthenium in 4 better than does by NO_2^- coordination in 3. Assuming the energy of acceptor $\pi^*(L)$ level is unaffected, one would, therefore, expect that ν_{MLCT} 3 should be at a lower energy than ν_{MLCT} 4. This is exactly what we observe in our complexes. Further we note that the MLCT band of 3 is associated with a shoulder at a higher energy, 455 nm (Table II.4, Figure II.4). Such a shoulder is always observed in the *cis* complexes

TABLE II.4

Solution Electronic Spectral Data[a] of *tc*-$[Ru(NO_2)_2L_2]$(3) and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$(4)

Compound	λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})
tc-$[Ru(NO_2)_2(L^1)_2]$	538 (9585), 455 (3355)^b, 355 (18,200)^b, 310 (22,520)
tc-$[Ru(NO_2)_2(L^2)_2]$	540 (9420), 455 (3180)^b, 363 (17,820), 310 (21,000), 290 (17,410)^c
tc-$[Ru(NO_2)_2(L^3)_2]$	538 (9080), 455 (3485)^b, 375 (22,860), 315 (19,630), 290 (16,150)^c
tc-$[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$^{c}	410^d 340^d
tc-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$	410 (9830)^d, 340 (12,150)
tc-$[Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$	415 (10300)^d, 340 (12,350)

---

[a] Solvents: dichloromethane for 3 and acetonitrile for 4. Solute concentrations : *ca*.10^{-3}mol dm^{-3}.

[b] Shoulder. [c] Stability in dilute solution is very low for meaningful quantitative spectrum.

[d] Broad.

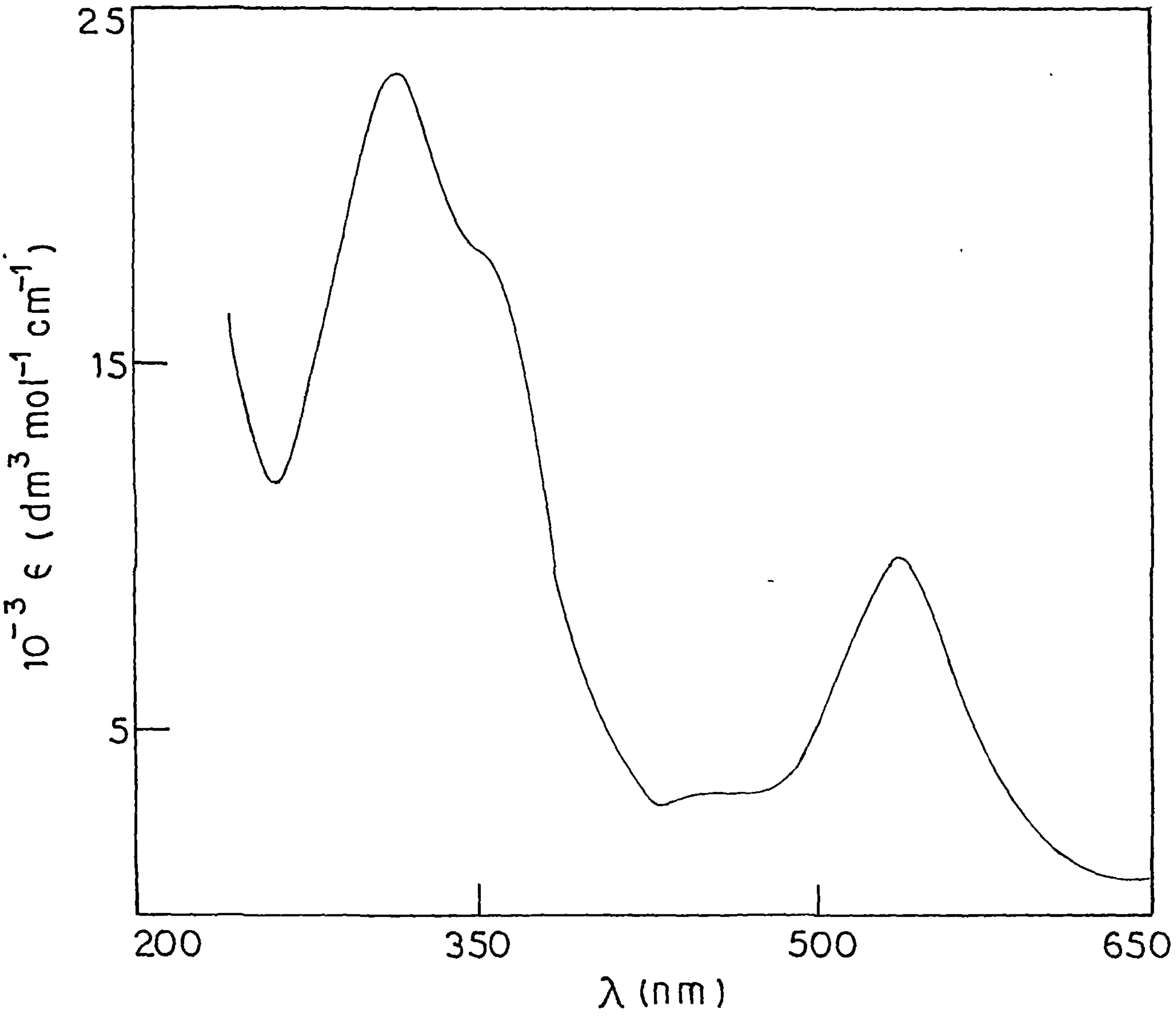


FIGURE II.4. ELECTRONIC SPECTRUM OF <u>tc</u>- $[Ru(NO_2)_2(L^1)_2]$ IN CH_2Cl_2

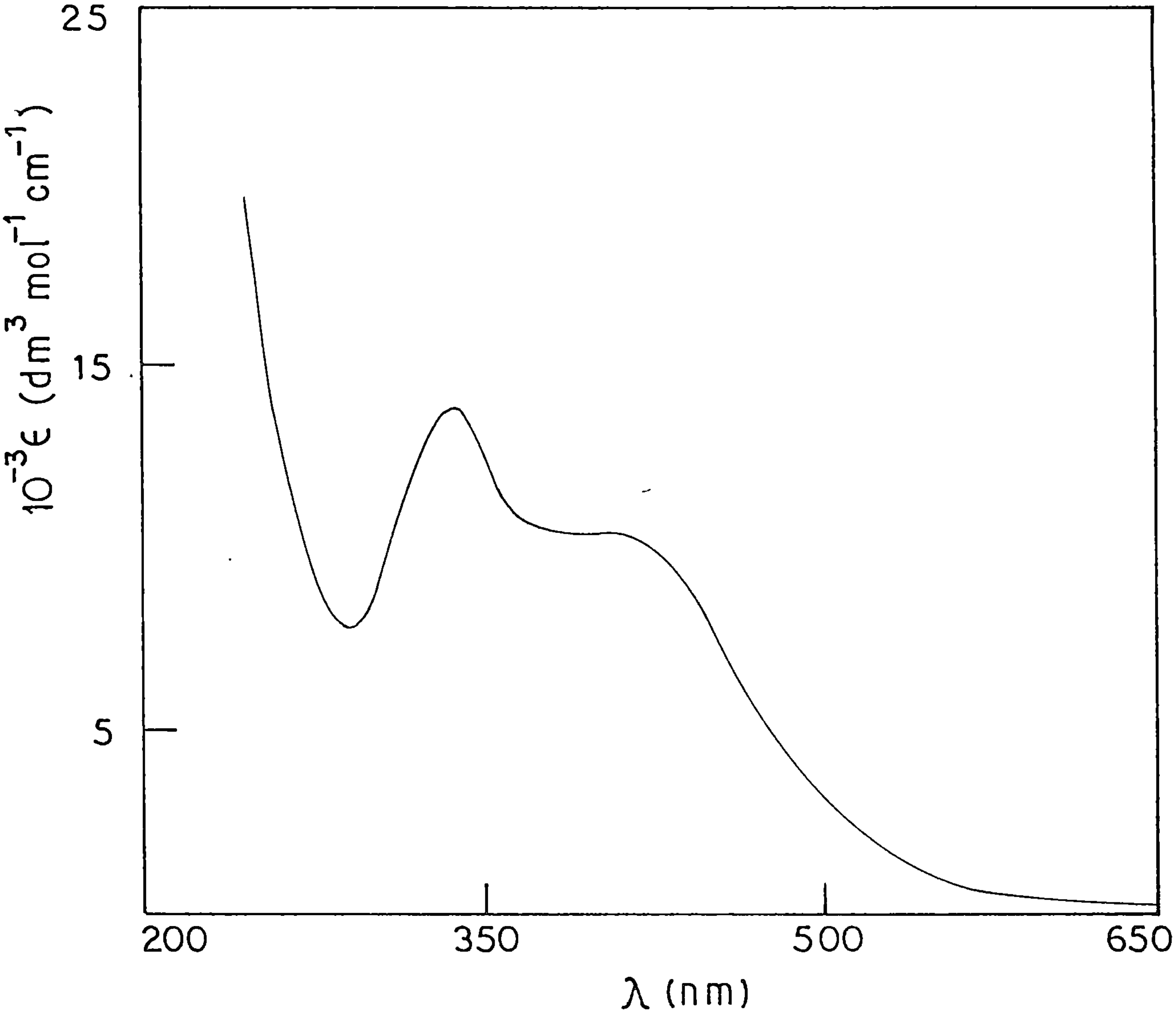


FIGURE II.5

ELECTRONIC SPECTRUM OF tc-[Ru(NO)(NO$_2$)(L^3)$_2$] (ClO$_4$)$_2$ IN CH$_3$CN having $[RuL_2]^{2+}$ fragment. For example, in the earlier reported compounds, *tc*-$[RuCl_2L_2]$, *cc*-$[RuCl_2L_2]$ and *tc*-$[RuXPL_2]^+$ (X=Cl, Br; P=tertiary phosphines) this shoulder appears[21,22a,24] respectively at 460, 480 and 470 nm. The solution spectrum of *tt*-$[RuCl_2L_2]$ does not show[21,22a] any such shoulder. Thus, the assertion that in 3 two NO_2^- groups are *cis* to each other is further strengthened by examining their electronic spectra.

E. Redox Properties

One major objective of the present studies is to characterise the electron transfer behaviour of complexes synthesised by us and to compare the results with those of known systems. To achieve this objective we have extensively used electrochemical techniques such as cyclic voltammetry (CV),[42-52] differential pulse voltammetry (DPV)[53,54] and constant potential coulometry. The electrochemical symbols used throughout the thesis are collected below along with their meaning.

(a) Symbols Used

(i) General

E = applied dc potential

E°_{298} = formal electrode potential

F = faraday = 96,500 coulombs

i = current

i_p = peak current

n = number of electron transferred

v = dc scan rate

(ii) Cyclic Voltammetry

E_{pa} = anodic peak potential

E_{pc} = cathodic peak potential

$\Delta E_p = E_{pa}-E_{pc}$ = peak-to-peak separation

i_{pa} = anodic peak current

i_{pc} = cathodic peak current

(iii) Differential Pulse Voltammetry

E_p = peak potential

Δ = modulation amplitude

The electron transfer behaviour of the complexes in acetonitrile were examined by cyclic voltammetry and differential pulse voltammetry at a platinum working electrode using tetraethylammonium perchlorate (TEAP) as a supporting electrolyte. The electrode potentials reported here were collected at 298 ± 1K and referenced to a Saturated Calomel Electrode (SCE). These are uncorrected for junction contribution. Several one electron reversible to irreversible responses for the complexes **3** and **4** were observed to negative potentials of the SCE (Table II.5) due to ligand reduction localised[22b] at the azo group. These are not considered any further. Our interest here is to study the redox processes which occur at positive potentials of the SCE.

(i) *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$(4)

Typical cyclic voltammograms of *tc*-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$ are displayed in Figures II.6 & II.7 and DPV of the same is shown in Figure II.8. Cyclic voltammetric and differential pulse

TABLE II.5

Cyclic Voltammetric Data[a,b] (298K) of *tc*-$[Ru(NO_2)_2L_2]$ and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ at a Platinum Electrode on the Negative Side of SCE

Compound	$-E°_{298}/V$	$\Delta E_p/mV$
tc-$[Ru(NO_2)_2(L^1)_2]$	0.50	100
	0.92	200
tc-$[Ru(NO_2)_2(L^2)_2]$	0.50	100
	0.92	220
tc-$[Ru(NO_2)_2(L^3)_2]$	0.53	80
	0.91	220
tc-$[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$	0.34	80
	0.51	70
tc-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$	0.38	80
	0.51	70
tc-$[Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$	0.38	80
	0.51	70

[a] Meaning and units of symbols are the same as in text. [b] Cyclic voltammetry was carried out in acetonitrile using 10^{-1}mol dm^{-3} TEAP as a supporting electrolyte. The reported data correspond to scan rate 50 mVs^{-1}. Solute concentration *ca.*10^{-3}mol dm^{-3}.

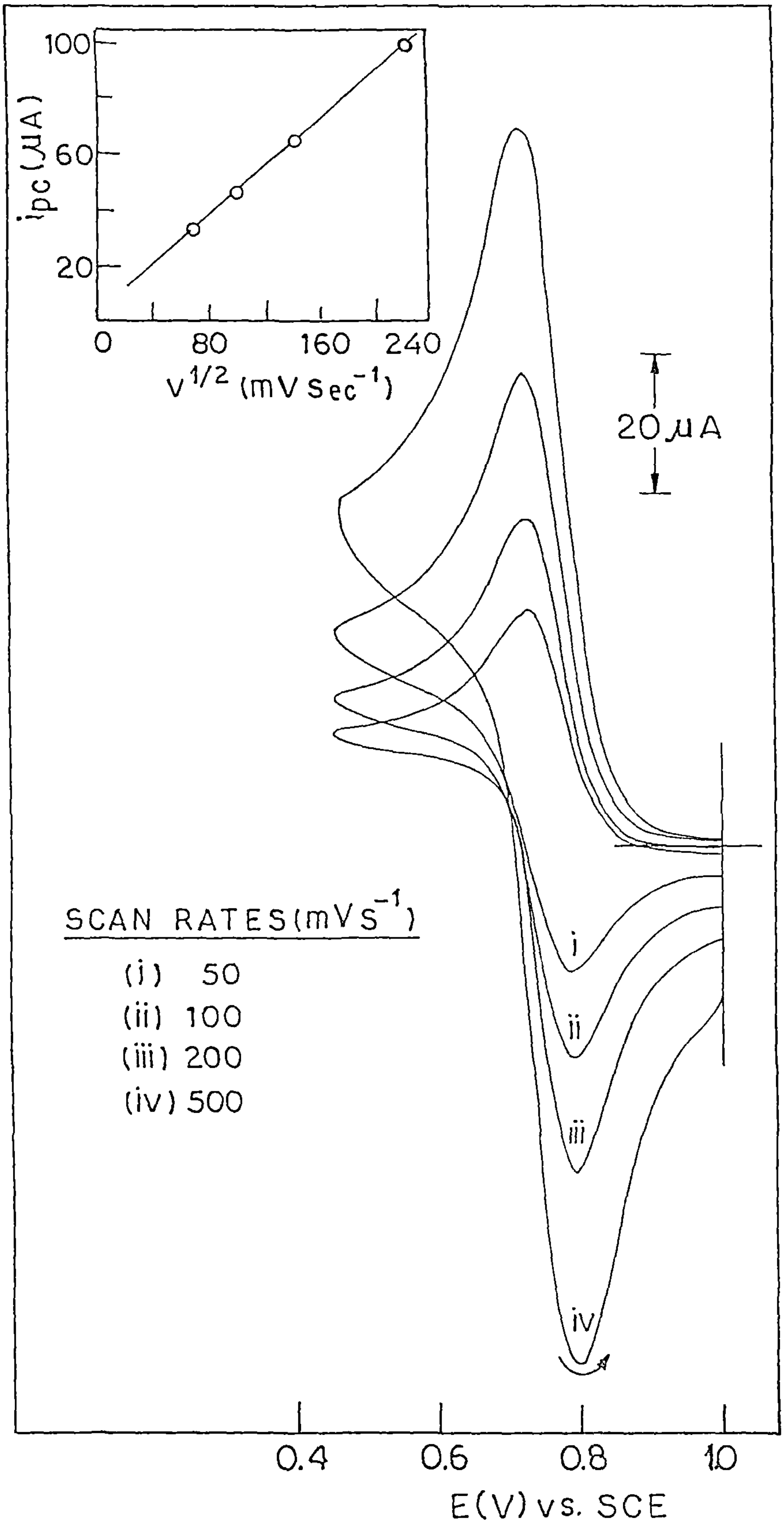


FIGURE II.6

CYCLIC VOLTAMMOGRAMS OF <u>tc</u>- $[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$

IN CH_3CN AT DIFFERENT SCAN RATES

INSET : A PLOT OF i_{pc} VERSUS $v^{1/2}$

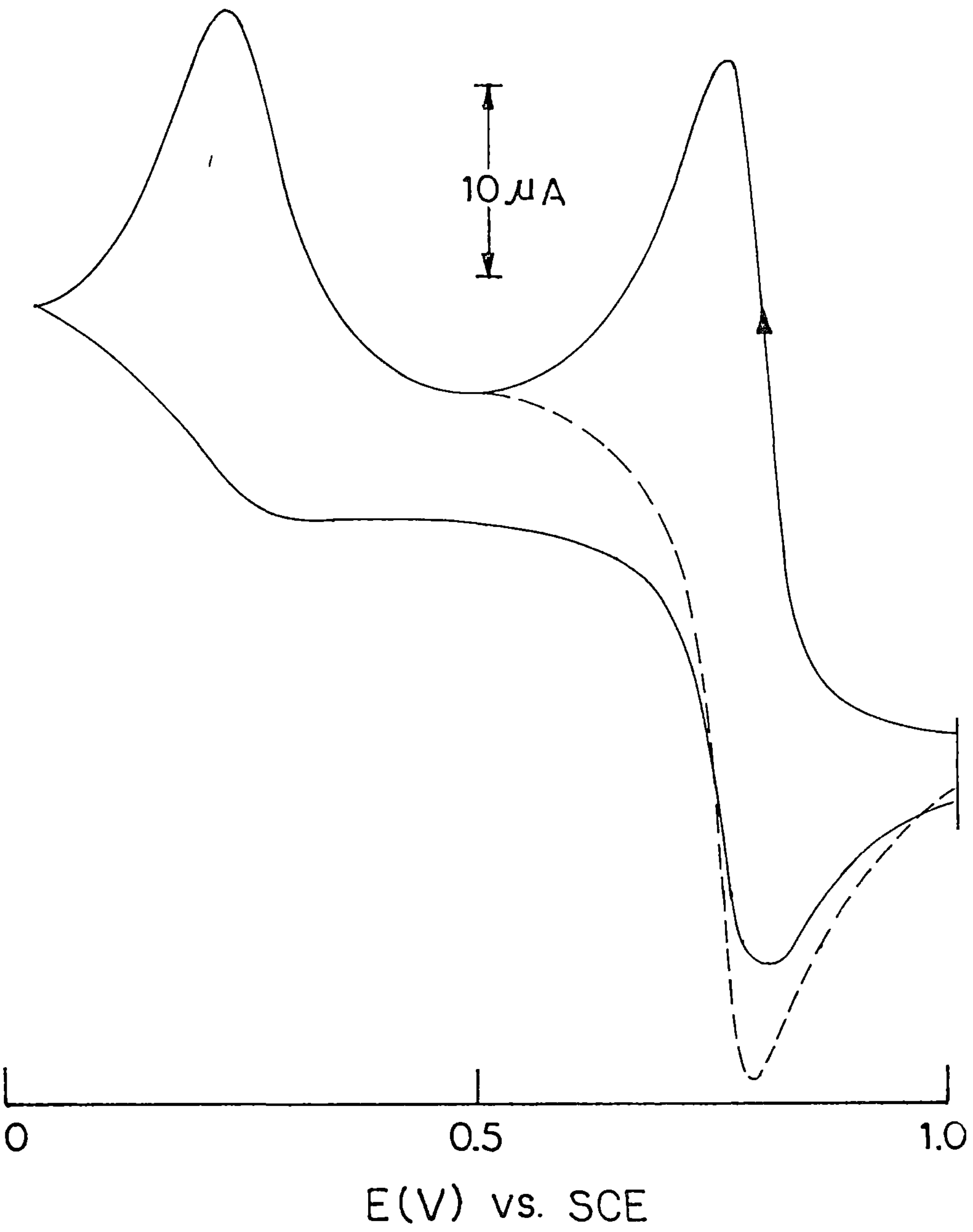


FIGURE II.7

CYCLIC VOLTAMMOGRAM OF tc- [$Ru(NO)(NO_2)(L^2)_2$] $(ClO_4)_2$ AT A 50 mVs^{-1} SCAN RATE IN CH_3CN. THE BROKEN LINE SHOWS THE VOLTAMMOGRAM WHERE THE CATHODIC SCAN IS REVERSED BEFORE REACHING THE SECOND REDUCTION WAVE

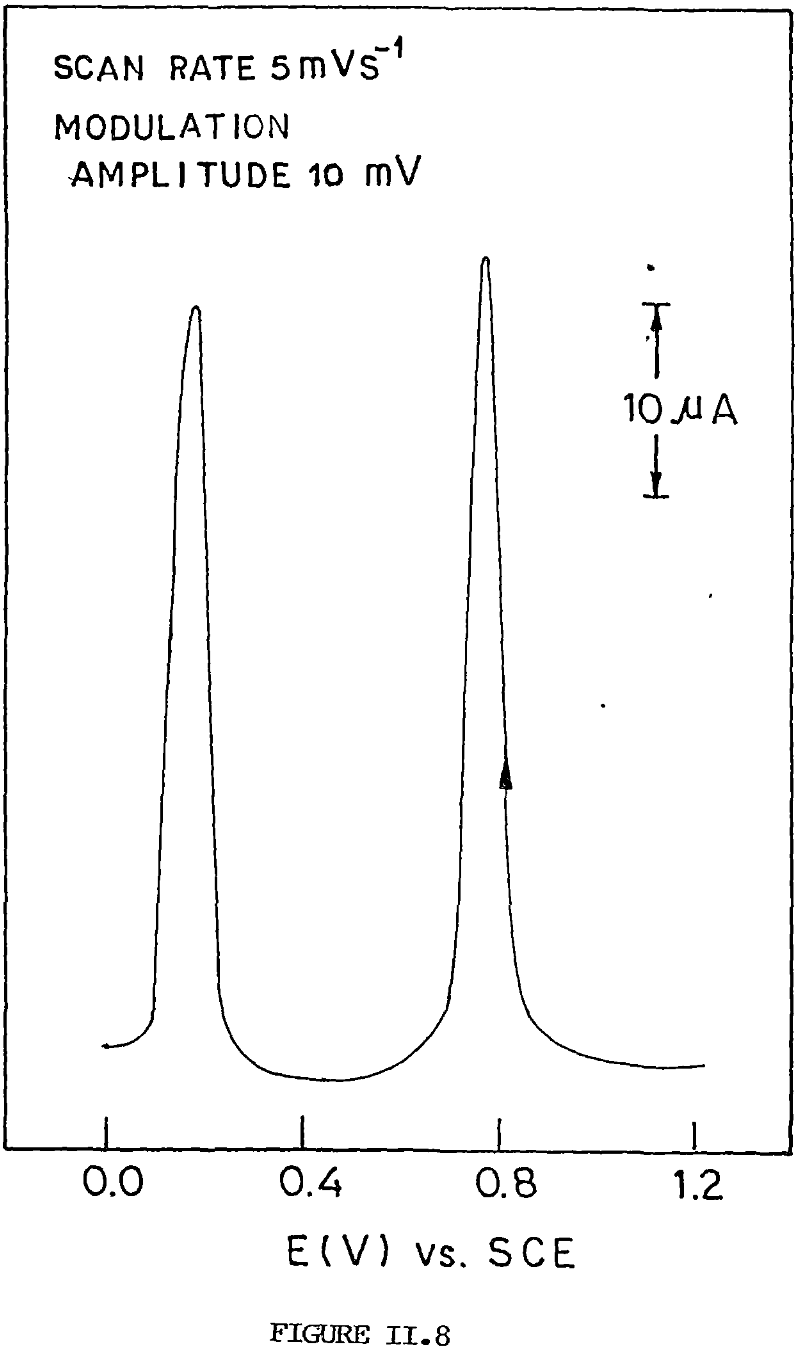


FIGURE II.8

DIFFERENTIAL PULSE VOLTAMMOGRAM OF

tc- [Ru(NO)(NO$_2$)(L^2)$_2$](ClO$_4$)$_2$ IN CH$_3$CN voltammetric data of 4 are collected in Table II.6 and II.7 respectively. All the nitrosyl complex shows a one-electron reversible reduction with formal potential ($E°_{298}$) at *ca*.0.70V (Table II.6). The reversibility of the couple has been established by $i_{pc}=i_{pa}$, ΔE_p=60mV and $i_{pc}/v^{1/2}$ is a constant (Figure II.6). In a stirred solution, electrolysis freely occured when the potential was kept fixed on the negative side of the cathodic peak potential but at potentials more positive than the anodic peak a very little electrolysis was observable. Hence, the couple under consideration is reductive in nature. The $E°_{298}$ value for the reversible wave has been labelled as E°(1). A second one electron irreversible cathodic response with cathodic peak potential (E_{pc}) at *ca*.0.17V, labelled as $E_{pc}(2)$ was also observable (Table II.6, Figure II.7). The ruthenium(II) nitrosyl complex of 2,2'-bipyridine, $[Ru(NO)(NO_2)(bpy)_2]^{2+}$ also undergoes[55] two steps one-electron reductions at 0.33 and -0.56 V vs SCE. It may be noted here that the electrode reduction potentials for the nitrosyl complex 4 are sensitive to medium effect. In acetonitrile, both E°(1) and $E_{pc}(2)$ for *tc*-$[Ru(NO)(NO_2)(L^2)_2]^{2+/+}$ and *tc*-$[Ru(NO)(NO_2)(L^2)_2]^{+/o}$ shift by 80-100mV to a lower positive potentials when the supporting electrolyte was changed from 10^{-1}mol dm^{-3} TEAP to 10^{-1}mol dm^{-3} lithium perchlorate (LIP) (Figure II.9). Specific medium effect might be expected if the electron transfer occurs to and from the periphery of the complex rather than at the central metal d-orbitals. It is now well established that the free nitrosonium cation (NO^+) is an oxidant[56,57] and undergoes electrode reductions. Thus, based on the experimental evidences and also

TABLE II.6

Electrochemical Data^{a,b} (298K) of *tc*-$[Ru(NO_2)_2L_2]$ and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ at a Platinum Electrode to the Positive Potential of SCE.

Compound	v/mVs^{-1}	$E°_{298}/V$	$\Delta E_p/mV$
tc-$[Ru(NO_2)_2(L^1)_2]$	50	1.40^c	
		1.63	70
	100	1.42^c	
		1.63	80
tc-$[Ru(NO_2)_2(L^2)_2]$	50	1.38^c	
		1.60	80
	100	1.38^c	
		1.61	100
tc-$[Ru(NO_2)_2(L^3)_2]$	50	1.35^c	
		1.59	80
	100	1.36^c	
		1.60	90
tc-$[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$	50	0.72	60
		0.17^d	
	100	0.74	80
		0.18^d	
tc-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$	50	0.76	60
		0.18^d	
	100	0.76	80
		0.18^d	

TABLE II.6 (CONTD)

Compound	v/mVs^{-1}	$E°_{298}/V$	$\Delta E_p/mV$
tc-$[Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$	50	0.71 0.15^d	70
	100	0.74 0.16^d	90

[a]Meaning and units of symbols are the same as in text. [b] Cyclic voltammetry was carried out in acetonitrile using 10^{-1} mol dm^{-3} TEAP as a supporting electrolyte. Solute concentration, 10^{-3} mol dm^{-3}. [c]Anodic peak potential (E_{pa}) with no cathodic counterpart. [d] Cathodic peak potential (E_{pc}) with no anodic counterpart.

TABLE II.7

Differential Pulse Voltammetric Data[a,b,c] of *tc*-$[Ru(NO_2)_2L_2]$ and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ in Acetonitrile on the Positive Side of SCE.

Compound	$E°_{298}/V$
tc-$[Ru(NO_2)_2(L^1)_2]$	1.36, 1.64
tc-$[Ru(NO_2)_2(L^2)_2]$	1.37, 1.63
tc-$[Ru(NO_2)_2(L^3)_2]$	1.35, 1.60
tc-$[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$	0.76, 0.18
tc-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$	0.78, 0.19
tc-$[Ru(NO)(NO_2)(L^3)_2](ClO_4)_2$	0.75, 0.16

---

[a] Meaning and units of symbols are the same as in text.

[b] Supporting electrolyte TEAP (10^{-1}mol dm^{-3}), solute concentration *ca.* 10^{-3} mol dm^{-3}.

[c] Scan rate is 5 mVS^{-1}; modulation amplitude (Δ) is 10 mV.

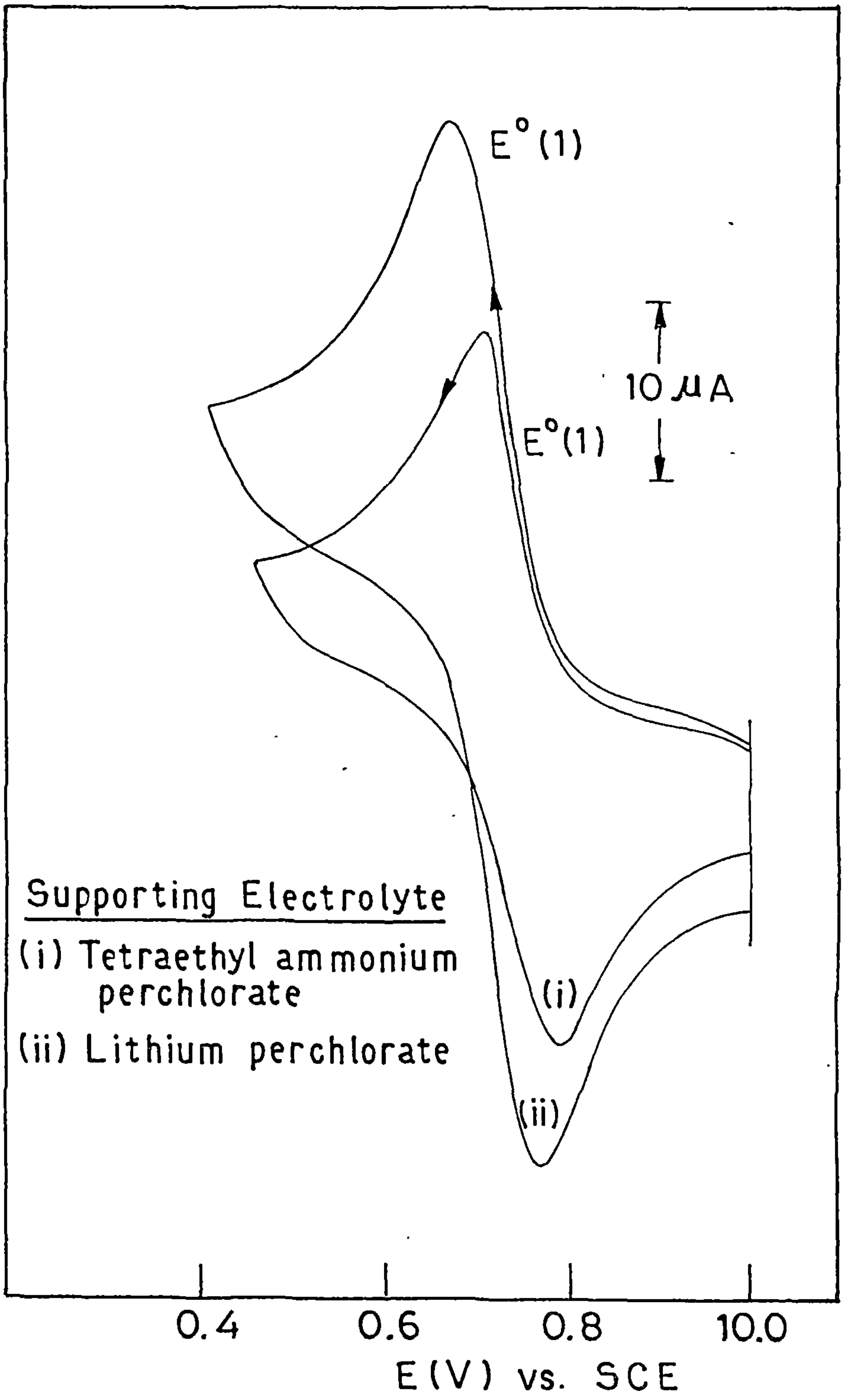


FIGURE II.9

CYCLIC VOLTAMMOGRAMS OF tc- $[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$ AT A 50 mVs^{-1} SCAN RATE IN CH_3CN IN DIFFERENT SUPPORTING ELECTROLYTES by comparison of our data with those of analogous systems[9,55,58,59] lead us to suggest the occurrence of successive two-electron reductions at the coordinated NO^+ moiety (equations 6 & 7)

$$tc\text{-}[Ru(NO)(NO_2)L_2]^{2+} + e^- \rightleftharpoons tc\text{-}[Ru(NO)(NO_2)L_2]^{+}, E°(1) \qquad (6)$$

$$tc\text{-}[Ru(NO)(NO_2)L_2]^{+} + e^- \longrightarrow tc\text{-}[Ru(NO)(NO_2)L_2], E_{pc}(2) \qquad (7)$$

The one electron stoichiometry of the couples E°(1) and $E_{pc}(2)$ are established from the consideration of current height data.

Electron transfer to the nitrosyl group in the present cases is formally a related process in which electrons are added to the levels which are predominantly ligand in character. In this case the barrier of electron transfer must be low and which is also evidenced by the reversibility of the couple 6 [E°(1)]. Irreversibility of the couple 7 [$E_{pc}(2)$] indicates that the two electrons reduced products of **4** is not stable and undergoes chemical transformations. No voltammetric response corresponding to the oxidation of **4** was observable upto 2.0V. The starting nitrosyl complexes have the configuration $(d\pi)^6$ and RuNO is expected to be linear. Additional electrons must enter antibonding levels and if two electrons are added to the NO^+ centre,it should produce NO^-. In fact, coordinated NO^+ to NO_2^- conversion involves donation of an electron pair from O^{2-} to the nitrosyl group. In the nitrite complex, the Ru-NO bond angle is expected to be 120°, the pattern of levels associated with a bent nitrosyl is more appropriate for a nitrite product. Addition of single electron probably leads to a case somewhere between the two extremes.

It is worth mentioning here that the nitrosyl complex (**4**), under consideration, is a quite strong oxidant. The low reorganisational barrier of two electrons transfer, and the strength of the reagents as oxidants make the present nitrosyl as a useful chemical oxidant. The reactions of this complex towards (i) nucleophiles and (ii) reducing agents are described in Chapter III.

(ii) Comparison With Other Ruthenium Nitrosyl Complexes

It is worthwhile to compare the E°(1) and ν_{NO} of **4** with those some of the earlier reported systems (Table II.8). Thus, in the series, *tc*-$[Ru(NO)(NO_2)(L^2)_2]^{2+}$(**4**), $[Ru(NO)(NO_2)(bpy)_2]^{2+}$ (bpy=2,2'-bipyridine), $[Ru(NO)(Cl)(py)_4]^{2+}$ (py=pyridine) and $[Ru(NO)(NH_3)_5]^{3+}$; **4** has the highest ν_{NO} and is a much better oxidant. It is also evident that the replacement of two bpy by two L leads to dramatic augmentation of reduction potentials of the coordinated NO. This is attributed to the much stronger π-acceptor character of L compared to that of bpy. Further, the value of E°(1) of **4** is very close to the reduction potential[60] of uncoordinated NO^+. This implies that the electrophilicity of the coordinated NO in **4** is comparable to that of free NO^+. The insignificant π-interaction of NO in the present nitrosyl is surely responsible for such a high E°(1). To our knowledge, the observed reduction potentials are the highest ever reported in ruthenium mononitrosyl chemistry.

TABLE II.8

Comparison of E°(1) (CH_3CN) and ν_{NO} (KBr) of *tc*-$[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$ with those of some Reported Compounds

Compound	ν_{NO}/cm^{-1}	E°(1)/V	References
NO^+	2220	0.74	32,60,61
tc-$[Ru(NO)(NO_2)(L^1)_2]^{2+}$	1950	0.72	66
$[Ru(NO)(NO_2)(bpy)_2]^{2+}$	1935	0.33	57
$[Ru(NO)(Cl)(py)_4]^{2+}$	1910	0.10	9
$[Ru(NO)(NH_3)_5]^{3+}$	1913	-0.36	58,59

(iii) *tc*-$[Ru(NO_2)_2L_2]$ (3).

The dinitro complexes (3) displays two oxidative responses at *ca*.1.40 and *ca*.1.60V respectively (Table II.6) versus SCE in acetonitrile. Typical cyclic voltammograms of *tc*-$[Ru(NO_2)_2(L^2)_2]$ are displayed in Figure II.10 and the DPV of the same is shown in Figure II.11. The DPV data are given in Table II.7. One electron stoichiometry of the oxidative responses were established from the consideration of i_{pa} data. The first oxidative response occurs at a potential which is responsible for a Ru(II) ---> Ru(III) oxidation (E_{pa} *ca*.1.40V). The oxidation is chemically irreversible.

$$\underset{3}{tc\text{-}[Ru^{(II)}(NO_2)_2L_2]} \longrightarrow \underset{3^+}{tc\text{-}[Ru^{(III)}(NO_2)_2L_2]^+} + e^- \qquad (8)$$

The nature of the voltammogram indicates that further chemical transformations follow the initial oxidation of the metal centre of 3. The second response at a higher potential at *ca*.1.60V is quasi-reversible (Table II.6, Figure II.10) which is no doubt due to electron transfer of ruthenium(II) species formed by secondary chemical transformation of the transient 3^+. The appearance of a second oxidative response at a higher positive potential tempts us to suggest that *tc*-$[Ru(CH_3CN)(NO_2)L_2]^+$ is formed due to disproportionation of *tc*-$[Ru(NO_2)_2L_2]^+$. This type of behaviour is well documented[62,63] in the corresponding bipyridyl chemistry. In this case the first oxidative couple is nearly reversible in the CV time scale but ruthenium(II) complex gradually decomposes and eventually affords a number of products one of which is $[Ru(CH_3CN)(X)(bpy)_2]^+$. In our dinitro complex, the metal

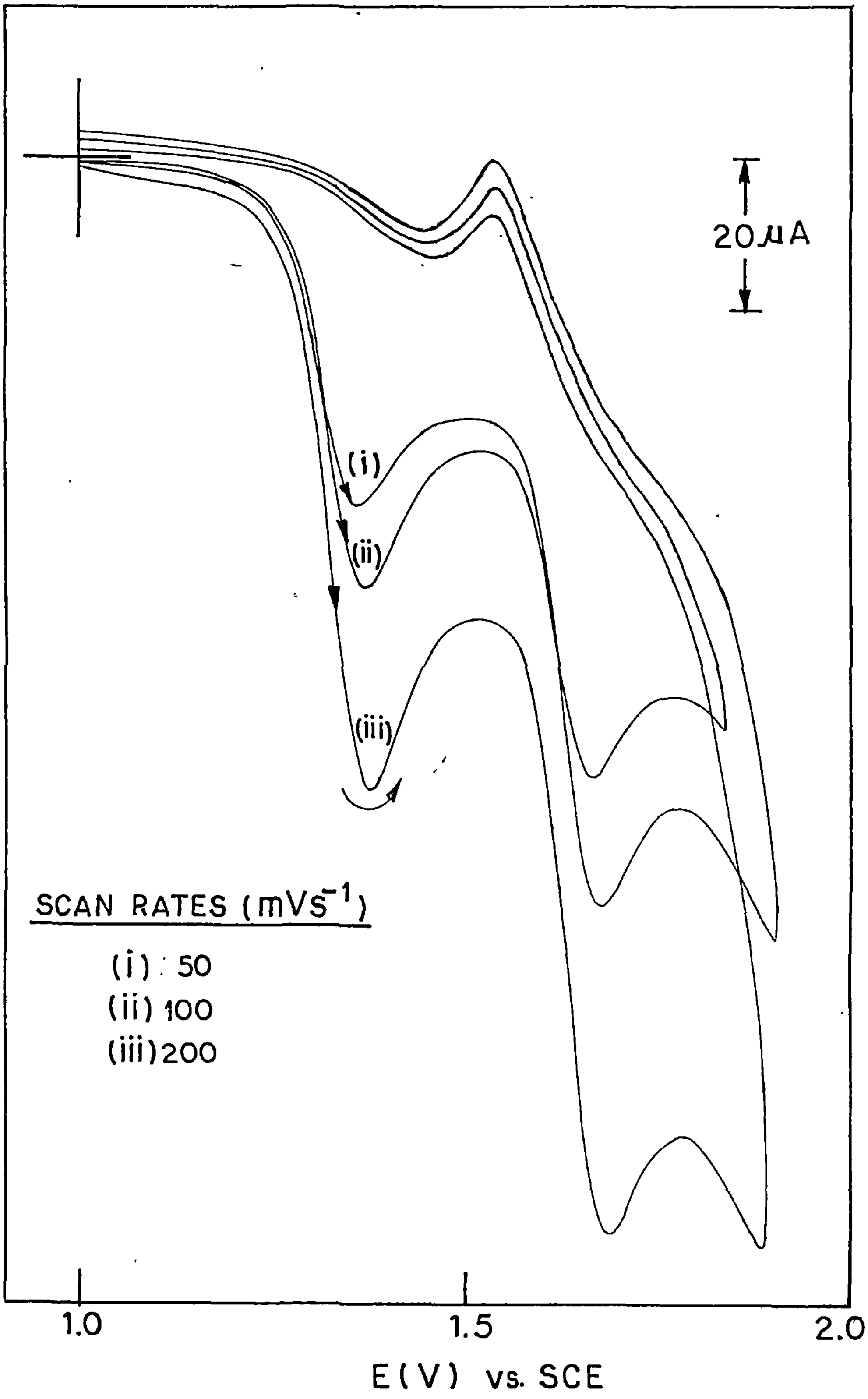


FIGURE II.10

CYCLIC VOLTAMMOGRAMS OF tc- $[Ru(NO_2)_2(L^2)_2]$ IN CH_3CN

AT DIFFERENT SCAN RATES

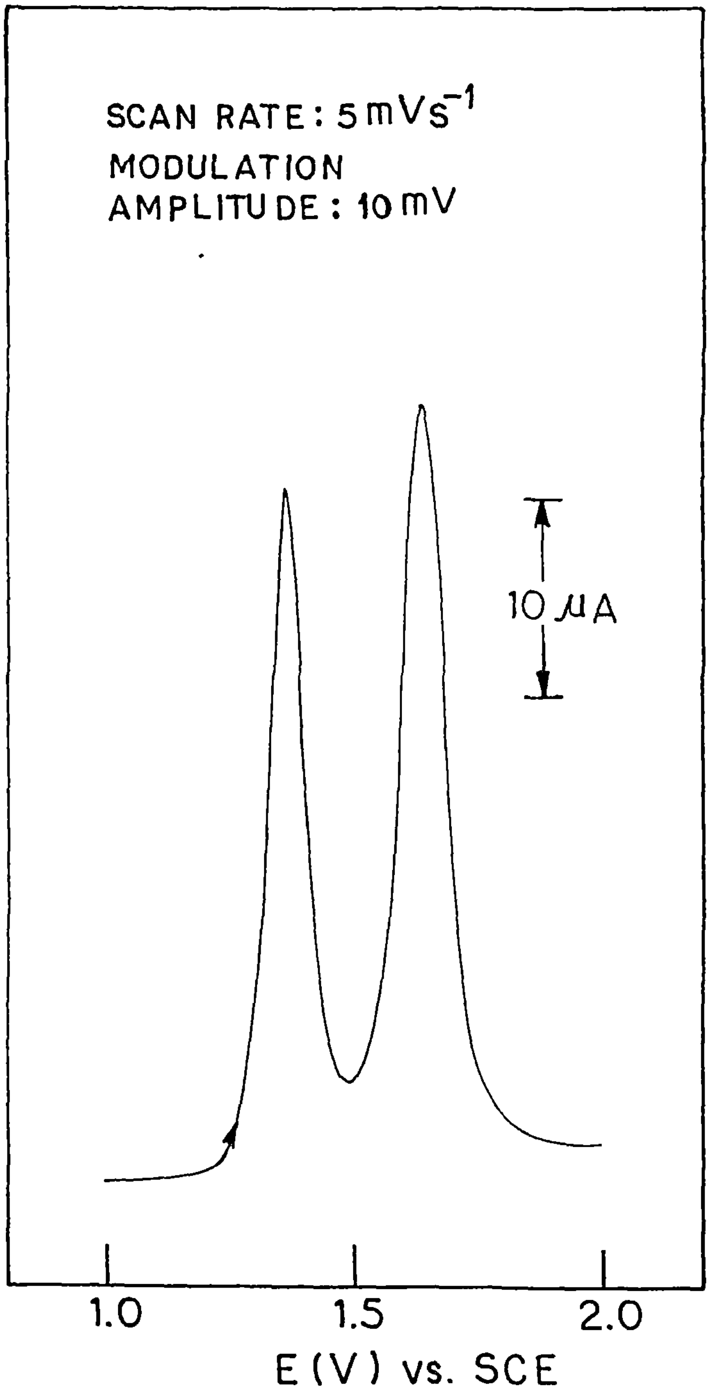


FIGURE II.11.

DIFFERENTIAL PULSE VOLTAMMOGRAM OF tc- $[Ru(NO_2)_2(L^2)_2]$ IN CH_3CN

oxidation takes place at a much higher potential and the reaction succeeding the electrochemical formation of *tc*-$[Ru^{(III)}(NO_2)_2L_2]^+$ (3^+) is expected to be much faster which probably results in complete irreversible nature of the initial oxidative response.

II.3 EXPERIMENTAL SECTION

A.Physical Measurements

(a) Melting Point Measurements

These were measured on a Melting point Apparatus, *Lab. Equip.*

(b) Electrical Conductance Measurements

Electrical Conductivity of Solutions were measured in acetonitrile using a Elico CM82T conductivity bridge with a solute concentration of *ca.* 10^{-3}mol dm^{-3}. Platinised conductivity cell with a cell constant, 1.0 was used for this purpose.

(c) Infrared Spectra

Infrared spectra were obtained in KBr disc using a Perkin-Elmer IR-297 (4000-600cm^{-1}) and a Perkin-Elmer IR-983 (4000-200 cm^{-1}) spectrophotometers.

(d) Electronic Spectra

Solution Electronic Spectra were measured in dichloromethane and acetonitrile with a solute concentration of *ca.*10^{-3} mol dm^{-3} using a Hitachi 330 Spectrophotometr. Silica cell of path length 1 cm was used.

(e) ^{1}H NMR Spectra

The measurements were done in $CDCl_3$ with a Varian EM 390 spectrometer.

(f) Magnetic Measurements

Magnetic susceptibilities were measured with a PAR Vibrating sample magnetometer (Model 155) fitted with a Walker Scientific Magnet (Model L 75 FBAL).

(g) Electrochemical Measurements

The symbols used in electrochemical techniques along with their meaning are described in text (Section II.2.E). PAR 370-4 electrochemistry system was used in all electrochemical measurements. All measurements were done in dinitrogen atmosphere. The data were collected at 298 ± 1K by using a precision thermostat. All potentials are uncorrected for junction potentials and are referenced versus Saturated Calomel Electrode (SCE).

Cyclic Voltammetry

Cyclic voltammetric data were collected using a PAR M-174A polarographic analyser, a 175 universal programmer and a PAR RE0074 XY recorder. Three electrode cell system which includes a planar Beckman model 39273 platinum inlay working electrode, a plantinum wire auxiliary electrode and a Saturated Calomel Reference Electrode (SCE) was used in our study. Tetraethylammonium Perchlorate (TEAP) and Lithium Perchlorate

(LIP) were used as supporting electrolytes. In every case care was taken to obtain a flat current voltage base line over the required voltage range in the absence of the electroactive species.

B. Formulation of Compounds

This was done by C,H,N microanalyses using an Elemetnal Analyser, Haraous CHN-O-RAPID.

C. Solvents

A.R. Grade Benzene, chloroform, dichloromethane, acetonitrile, dimethylsulphoxide and xylene were used as supplied. Besides, all other solvents used for preparative and analytical work were of reagent grade and used without further purification. Commercial toluene was dried[64] as before. For electrochemical work, dried acetonitrile and dichloromethane were used. Their purification from commercially available source, are given below.

(a) Acetonitrile

2 Litres of commercially available acetonitrile was taken in a dry bottle with a guard tube (containing fused calcium chloride), fitted to it. 10g of calcium hydride was added to it. After 24h, the solvent was decanted and was heated to reflux over 5g of P_4O_{10} for 0.5h and distilled. The distilled acetonitrile was then heated to reflux over alkaline permanganate (10g of $KMnO_4$ and 10g of Li_2CO_3) for 15 min prior to rapid distillation. Finally it was redistilled over P_4O_{10}. Through out the process a dry condition was maintained taking necessary precautions. The

acetonitrile so obtained has voltage window of +2.3V to -1.7V at a platinum working electrode.

(b) Dichloromethane

500 ml of the solvent was kept over anhydrous $CaCl_2$ for 10h. The decanted liquid was then thoroughly washed with 10% aqueous $NaHCO_3$ solution. Finally it was distilled over solid $NaHCO_3$ (5g). The voltage window at platinum electrode was +1.5V to -1.5V. Distilled solvent was stored in dark in a sealed bottle.

D. Preparation of Compounds

(a) Chemicals

The chemicals and their sources are as follows. Nitrobenzene, Loba Chemie Industries, Calcutta; m-nitrotoluene, 2-aminopyridine, Koch-Light Laboratories Ltd., England; p-nitrotoluene, phosphorous pentoxide, silica gel (60-120 mesh) for column chromatography, British Drug House, India; silver nitrate, sodium nitrate, merck, sodium carbonate, Glaxo Laboratories (India) Ltd., Bombay; sodium dichromate, Loba Chemie Indoaustranal Co. Bombay. Hydrated Ruthenium trichloride was obtained from Arrora-Matthey Limited, Calcutta. It was digested with concentrated hydrochloric acid as given below.

(b) Ruthenium Trichloride Trihydrate, $RuCl_33H_2O$

5g of commercially available $RuCl_3.XH_2O$ was dissolved in 20 ml concentrated HCl. The solution was evaporated to dryness (*caution*! presence of any nitrous vapour may lead to an impure product). The process was repeated thrice. The residue obtained was $RuCl_3.3H_2O$

(c) Sodium Perchlorate, $NaClO_4$

(*Caution*! All perchlorate salts of metal are potentially explosive. Adequate care must be taken while handling the perchlorates).

Sodium perchlorate was used as anion exchanger of complex salt. 10g of commercially available Na_2CO_3 was treated with excess of perchloric acid till all the Na_2CO_3 goes into solution and evolution of carbondioxide gas ceases. The pH of the solution was maintained at *ca*.7. The solution was concentrated and left for crystallisation. Crystals of $NaClO_4$ thus obtained was filtered and dried *in vacuo* anhydrous calcium chloride.

(d) Lithium Perchlorate, $LiClO_4$ (LIP)

Lithium perchlroate was used as a supporting electrolyte in electrochemical experiments. It was prepared similarly as sodium perchlorate with the exception that 10g of Lithium carbonate was taken instead of sodium carbonate. It was recrystallised from water.

(e) Tetraethylammonium Perchlorate(TEAP)

It was also used as a supporting electrolyte in electrochemical experiments and prepared as follows: 210g of tetraethylammonium bromide was dissolved in 200 ml of water. To the clear solution, a solution of 100ml $HClO_4$ in 20 ml water was added dropwise with constant stirring. A white solid immediately precipitated out. It was filtered and washed with cold water. The solid was recrystallised from water and air dried at 333K.

(f) Ligands

2-(Arylazo)pyridines(L)

The starting material viz. Nitrosobenzene and m-nitrosotoluene were required for the synthesis of ligand L^1 and L^2 repectively. These were synthesised from nitrobenzene and m-nitrotoluene respectively as described in the literature.[65]

(i) 2-(Phenylazo)pyridine(L^1). 5.1g (0.05 mol) of 2-aminopyridine was added to a warm 50% NaOH solution (50 ml). The mixture was gently heated (*ca.*50°C) after adding 15 ml of benzene. 6g (0.05 mol) of nitrosobenzene was then added portionwise. The mixture was stirred at *ca.*50°C for 12h. The resulting solution was then extracted several times with benzene. The dark brown solution was boiled with charcoal and filtered. The concentrated filtrate (*ca.*25 ml) was then subjected to column chromatography on a silica gel column, eluting it with benzene. The lower most green band was discarded while the orange band was collected. The evaporation yielded red coloured liquid of 2-(phenylazo)pyridine (L^1). Yield : 70%.

(ii) 2-(m-tolylazo)pyridine (L^2) was similarly prepared in good yield (65%) by using m-nitrosotoluene instead of nitrosobenzene

(iii) 2-(*p*-tolylazo)pyridine(L^3) 13.7g (0.1 mol) of p-nitrotoluene and 9.4g (0.1 mol) of 2-aminopyridine was added in

150 ml of dry toluene in a 500 ml round bottom flask. To the mixture 4.6g (0.2 mol) of clean sodium was added and stirred vigorously under an atmosphere of nitrogen. The mixture was carefully warmed until a reaction occurred and, after the activity had subsided again heated to reflux for 3h with continuous stirring. The resulting mixture was then filtered hot and the cooled filtrate extracted twice with 25 ml portions of 17% HCl. The acid extract was made basic with NaOH solution (20%) and allowed to stand for 1h. The crude 2-(p-tolylazo)pyrdidine (9.8g) was filtered, washed with water and air dried. It was recrystallised from petroleum ether (90-100°). Red needles of 2-(p-tolylazo)pyridine was obtained. Yield: 8.3g (42%). M.P. 72-74°C.

(g) Complexes

(i) Dichlorotetrakis(dimethylsulphoxide)ruthenium(II), [$RuCl_2(dmso)_4$]. It was prepared by a published procedure reported earlier.[66]

(ii) *tc*-Dichlorobis[2-(arylazo)pyridine]ruthenium(II), *tc*-[$RuCl_2L_2$]. It was prepared by following a published procedure.[21] Specific details for the preparation of tc-[$RuCl_2(L^1)_2$] are given below.

To a suspension of [$RuCl_2(dmso)_4$] (0.48g, 1 mmol) in 300 ml xylene, 0.366g (2 mmol) of L^1 was added and the mixture was heated to reflux for 72h. On cooling, shining crystals of the complex, *tc*-[$RuCl_2(L^1)_2$] deposited. It was collected by filtration and washed with diethyl ether and finally dried *in* *vacuo* over P_4O_{10}. The yield was 80%.

(iii) The Salt ***tc*****-Diaquobis[2-(arylazo)pyridine]ruthenium(II) Perchlorate Hydrate,** *tc*-$[Ru(OH_2)_2L_2]$ $(ClO_4)_2.H_2O$ (2) was prepared by following a published procedure.[25] Specific details for the preparation of *tc*-$[Ru(OH_2)(L^1)_2](ClO_4)_2.H_2O$ are as follows.

To a suspension of 0.250g (0.35 mmol) of tc-$[RuCl_2(L^1)_2]$ in 15 ml methanol, an aqueous solution of silver nitrate (0.119g, 0.70 mmol in 100 ml water) was added and the mixture was heated to reflux for 1h. The solution gradually turned red violet and white precipitate of silver chloride appeared. The reaction mixture was then cooled at room temperature and filtered through a G-4 sintered glass funnel. To the filtrate a large excess of sodium perchlorate (*ca.* 2-4g) followed by 1 ml of 70% aqueous perchloric acid were added. The solution was then kept in refrigerator for overnight when needle shaped dark coloured crystals resulted. These were collected by filtration and dried *in vacuo* over P_4O_{10}. Yield: 75%.

(iv) ***tc*****-Dinitrobis[2-(phenylazo)pyridine]ruthenium(II),**
tc-$[Ru(NO_2)_2(L^1)_2]$ (3). A sample (0.36g, 0.5 mmol) of *tc*-$[Ru(OH_2)_2(L^1)_2](ClO_4)_2.H_2O$(2) was dissolved in 20 ml of acetonitrile and boiled for 15 min. The yellow orange solution was cooled to room temperature. To this an aqueous solution of sodium nitrite (0.5g in 30 ml water) was added and the mixture was heated to reflux for 2h. The solution gradually turned red. It was concentrated to half of its intial volume and kept overnight in a refrigerator. The dark bronze sheen crystals were

collected by filtration and washed thoroughly with water. It was dried *in vacuo* over P_4O_{10}. Yield:90%.

The complexes *tc*-[Ru$(NO_2)_2(L^2)_2$] and *tc*-[Ru$(NO_2)_2(L^3)_2$] were prepared similarly using the appropriate 2. The yields were 85% and 90% respectively.

(v) *tc*-Nitronitrosylbis[2-(phenylazo)pyridine]ruthenium (II)-perchlorate, *tc*-[Ru(NO)$(NO_2)(L^1)_2](ClO_4)_2$ (4).

A sample (0.11g, 0.2 mmol) of *tc*-[Ru$(NO_2)_2(L^1)_2$](3) was treated with 2 ml of concentrated (10 M) nitric acid in a beaker placed on an ice-bath. The mixture was rubbed with a glass rod to make a paste. 2 ml of ice-cold concentrated (10 M) perchloric acid was added dropwise with stirring. The mixture was then diluted with *ca.* 20 ml with ice-cold water. The orange crystals which separated were collected by filtration, washed with minimum volume (*ca.*2 ml) of cold water and dried *in vacuo* over P_4O_{10}. Yield: 90%.

The complexes *tc*-[Ru(NO)$(NO_2)(L^2)_2](ClO_4)_2$ and *tc*-[Ru(NO)$(NO_2)(L^3)_2](ClO_4)_2$ were prepared similarly using the same reaction stoichiometry and conditions starting from the appropriate 3. The yield for each compound was 90%.

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Chapter III

CHAPTER III

ELECTROPHILIC BEHAVIOUR OF COORDINATED NITROSYL: REACTIONS OF OH^-, Ar-NH_2 WITH A HIGHLY ELECTROPHILIC NITROSYL, *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$ [L=2-(ARYLAZO)PYRIDINE] AND ITS ELECTRON TRANSFER REACTIONS*

Abstract: *The electrophilic reactions of highly electrophilic nitrosyl of the type, tc-*$[Ru(NO)(NO_2)L_2](ClO_4)_2$*(4) [L=2-(arylazo)pyridine] has been examined in this chapter. The reactions include acid base behaviour of the coordinated nitrosyl, diazotisation of primary aromatic amines, oxidative coupling of N,N-dimethylaniline and oxidation of a ruthenium(II) complex,* $[RuCl_2(bpy)_2]$ *(bpy=2,2'-bipyridine).*OH^- *instantaneously converts 4 to its dinitro analogue tc-*$[Ru(NO_2)_2L_2]$ *3. It has been shown that the conversion of coordinated* NO^+ *to coordinated* NO_2^- *in the afforesaid complex is chemically reversible. The diazotisation reaction of primary aromatic amines are quite fast and the reactions are studied in two solvents, viz. acetonitrile and dichloromethane. The results of these reactions are*

rationalised by following the reaction sequence through the isolation of products at various stages of the reactions. Thus, the diazotisation reaction yield monosolvento compound, tc-$[Ru(S)(NO_2)L_2]ClO_4.H_2O$ *(S=*CH_3CN,H_2O*) along with aryldiazonium cation,* $[Ar-N_2]^+$ *which has been characterised either by isolation of the cation as its perchlorate salt or by performing the known reaction with alkaline β-naphthol producing azo-dye, 1-arylazo-2-naphthol.*

The complex 4 bring about the oxidative coupling of N,N-dimethylaniline (DMA) to tetramethylbenzidine(TMB) and oxidation of $[RuCl_2(bpy)_2]$ *to* $[RuCl_2(bpy)_2]^+$*. These redox reactions have been studied voltammetrically and the results have been analysed in terms of the electrophilicity of the coordinated* NO^+ *in 4.*

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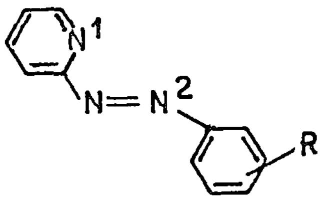
* A part of this work has appeared in *Polyhedron*, 1991, *10*, 1799.

III. 1 INTRODUCTION

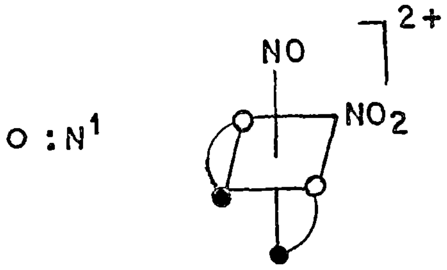
In the previous chapter we have described the synthesis of mononitrosyl complex of ruthenium(II) of the type *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ (4) [L=2-(arylazo)pyridine,1]. It has been shown[1] from its physicochemical data that the nitrosonium ion (NO^+) character of the coordinated nitric oxide in 4 is very high. Given the presence of a strongly electrophilic NO^+ centre in 4, we initiated research on exploring the reactivities of 4. In this Chapter we describe the reactions of 4 towards nucleophiles such as OH^-, primary aromatic amines. The reactions with primary aromatic amines are of interest in the present study because of its importance in connection with the synthesis of aryldiazonium complexes[2-4] which may be regarded[5,6] as a model for dinitrogen complexes.



L,1

R= H : L^1

R = m-Me : L^2



4(tc)

Perhaps the simplest chemical reaction to consider in electrophilic nitrosyl complexes is redox reaction[7,8] at the coordinated NO^+. Redox reactions of *tc*-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$ has also been studied in this chapter. The coordinated nitrosonium ion in **4** has been shown to be relatively strong oxidant and undergoes reversible electron transfer. An understanding of the origin of the electron transfer properties in these complexes are of importance in terms of both electronic structure and chemical reactivity.

III.2 RESULTS AND DISCUSSION

A. Nitrosyl-Nitrite Interconversion. Acid-Base Equilibrium

The ruthenium nitrosyl complex containing 2-(arylazo)-pyridine is converted into nitro complex in solution by the addition of hydroxide ion, OH^- (equation 1)

$$\underset{\mathbf{4}}{tc\text{-}[Ru(NO)(NO_2)L_2]^{2+}} + 2OH^- \longrightarrow \underset{\mathbf{3}}{tc\text{-}[Ru(NO_2)_2L_2]} + H_2O \qquad (1)$$

The nitro complex is in turn reconverted into nitrosyl complex in acidic solutions (equation 2)

$$\underset{\mathbf{3}}{tc\text{-}[Ru(NO_2)_2L_2]} + 2H^+ \longrightarrow \underset{\mathbf{4}}{tc\text{-}[Ru(NO)(NO_2)L_2]^{2+}} + H_2O \qquad (2)$$

The orange *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$ (4) ion is predominant in very high acidic ($[H^+] > 1.0$ mol dm^{-3}) media. Even in moist environments it revert to the corresponding dinitro complex, *tc*-$[Ru(NO_2)_2L_2]$. Clearly, the coordinated nitrosyl in **4** has a high affinity for OH^- and it behaves chemically more like NO^+.

$$tc\text{-}[Ru(NO)(NO_2)L_2]^{2+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} tc\text{-}[Ru(NO_2)_2L_2] \qquad (3)$$

Reaction (3) is chemically reversible and each of the species can be converted to each other by the adjustment of $[H^+]$ of the medium (Figure III.1). Todate we do not have any indication for the existance of isolable dinitrosyl complex even from concentrated acid medium. Unfortunately, the equilibrium constant,K, of reaction (3) could not be measured because of insolubility of 4 in water. However, instantaneous conversion of 4 to 3 even in a neutral aqueous medium indicates that K of equation 3 must be very high. With the consideration that L is a very strong π-acceptor[9-15], the affinity of 4 towards OH^- is in order. The ligand, L (1) reduces π-donation of electron from metal to nitrosyl and thus inturn increasing electrophilicity of coordinated NO.

Reversible conversion between nitrosyl and nitro forms also have been found[16-20] for several nitrosyl complexes and the overall equilibrium constants for coordinated NO^+ to coordinated NO_2^- for those systems have been summarised in Table III.1. Formally, the conversion of 3 to 4 (equation 2) involves oxide ion (O^{2-}) transfer from coordinated nitrite to the Lewis acid H^+. This reaction is analogous to the conversion of free NO_2^- to NO^+ (equation 4)

$$NO_2^- \xrightarrow{H^+} HNO_2\ (NO^+OH^-) \xrightarrow{H^+} H_2NO_2^+(NO^+H_2O) \qquad (4)$$

Thus, the high positive reduction potentials or in otherwords

TABLE III.1

Equilibrium Constants, K at 298K for Reversible Conversion of Coordinated NO^+ to Coordinated NO_2^- for Various Metal Nitrosyl Complexes

Compound	*K*	References
NO^+	2.3×10^{31}	19
$[Ru(bpy)_2(NO)(Cl)](PF_6)_2$	1.6×10^{9}	16
$K_2[Fe(CN)_5NO]$	1.5×10^{6}	17
$K_2[Ir(NO)Cl_5]$	6.0×10^{29}	18
$K_2[Ir(NO)Br_5]$	6.8×10^{27}	18

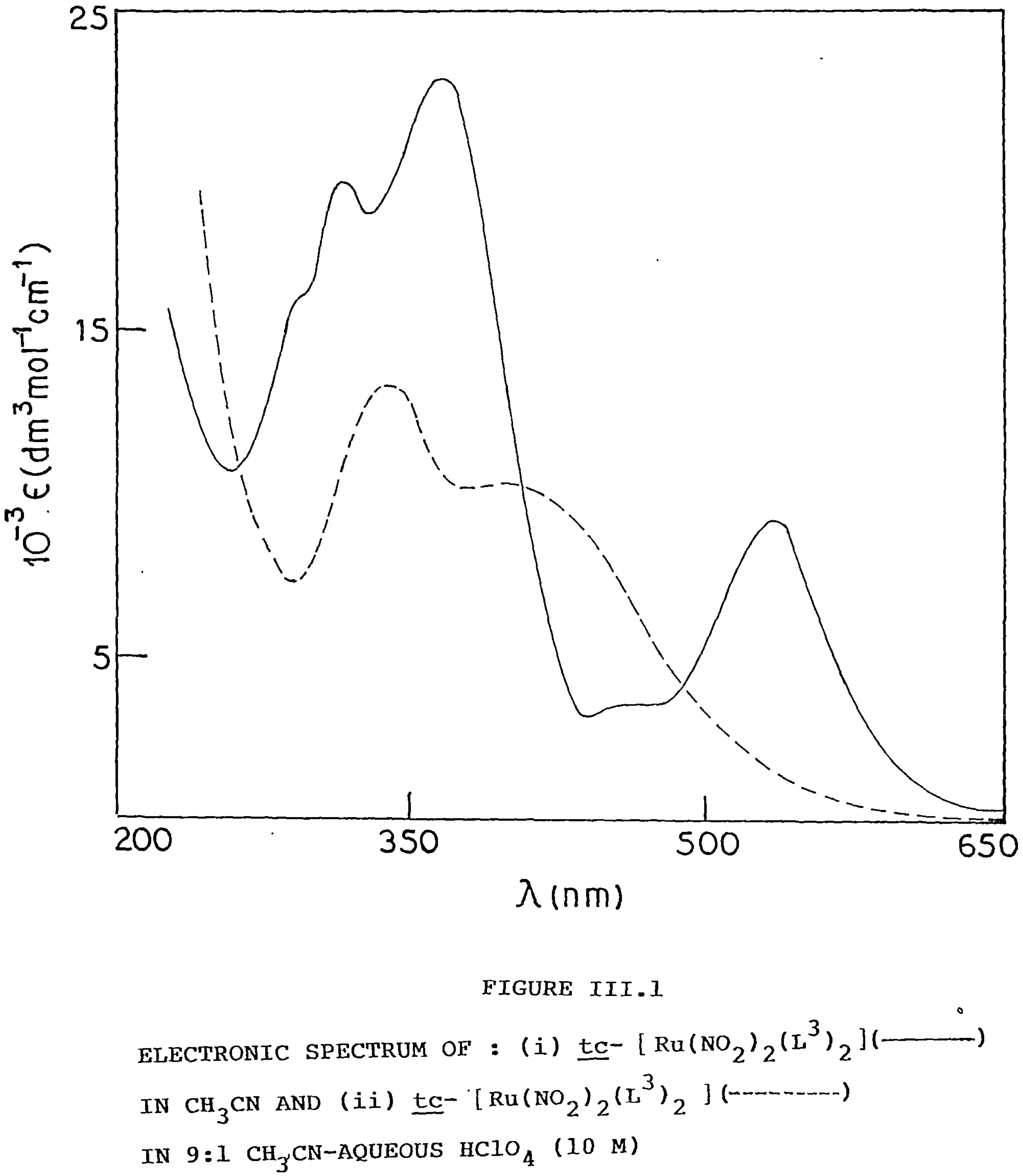


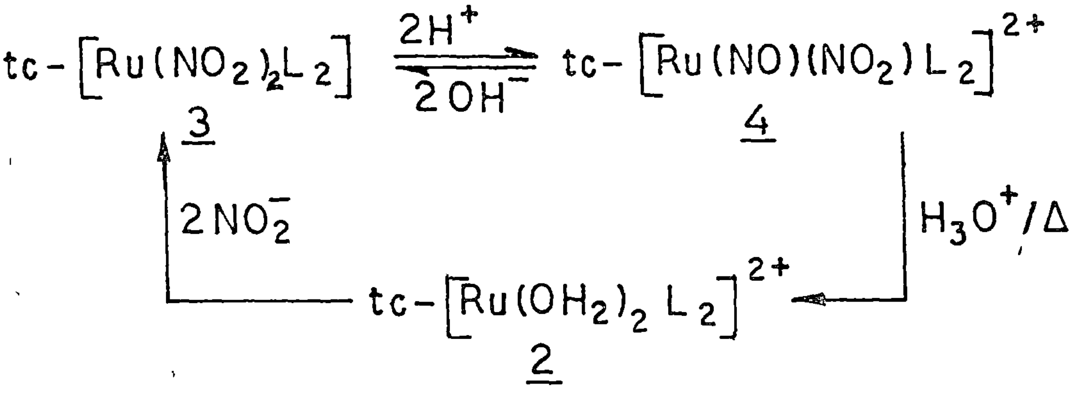
FIGURE III.1

ELECTRONIC SPECTRUM OF : (i) <u>tc</u>- $[Ru(NO_2)_2(L^3)_2]$(———) IN CH_3CN AND (ii) <u>tc</u>- $[Ru(NO_2)_2(L^3)_2]$(- - - - - -) IN 9:1 CH_3CN-AQUEOUS $HClO_4$ (10 M) very high electrophilicity of our nitrosyl is believed to be one of the crucial factors for the facile conversion of *tc*-$[Ru(NO)(NO_2)L_2]^{2+}$ (4) to *tc*-$[Ru(NO_2)_2L_2]$ (3)

In course of our attempts to synthesise nitrosyl complex from its dinitro precursor, we have also examined the action of aqueous acid on 3 at a high temperature. At a boiling temperature the reaction proceeds smoothly to yield a dark violet solution. On addition of an aqueous solution of $NaClO_4$ to the violet solution a crystalline precipitate was obtained.

$$\underset{3}{tc\text{-}[Ru(NO_2)_2L_2]} \xrightarrow{H_3O^+/\Delta} \underset{2}{tc\text{-}[Ru(OH_2)_2L_2]^{2+}} \qquad (5)$$

Spectral data of the isolated compound exactly correspond to that of the known and analysed sample[10] of *tc*-$[Ru(OH_2)_2L_2](ClO_4)_2.H_2O$ (2) and the molar conductance of the compounds are also in order[21] (Vide Experimental Section). It has been found that both aqueous perchloric acid and sulphuric acid convert 3 to 2 but the use of aqueous perchloric acid results in isomerically pure product. A similar product 2 was also obtained from a similar reaction starting from the mononitrosyl complex, (4). This observation tempts us to suggest that the conversion process 3 to 2 proceeds via 4 which may be regarded as an intermediate in the reaction (5). The stability of 4 in aqueous perchloric acid also supports the formation of 4 as an intermediate in the above reaction. The interconversion of 4 to 3 also involving 2 are shown in Scheme 1.



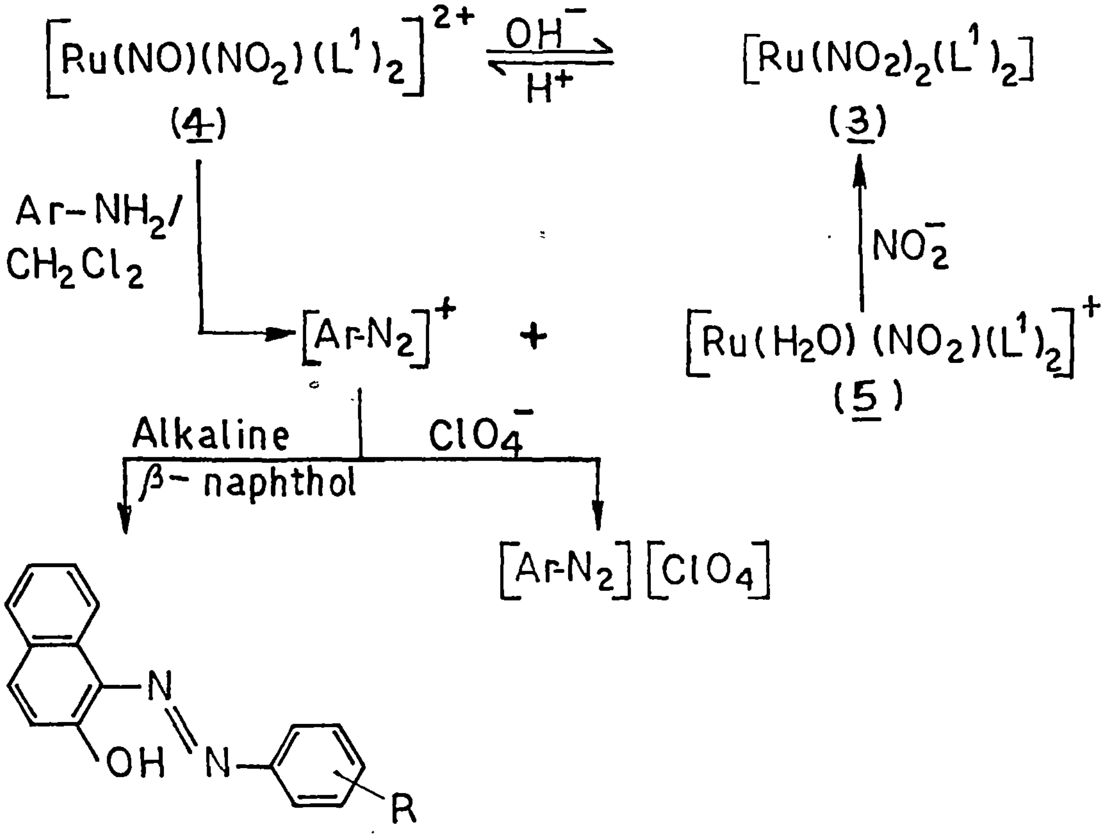
Scheme 1

It is very tempting to view the hydrolysis reactions in Scheme 1 as a process induced by protonation of coordinated NO^+. To date we have no evidence for isolable HNO^{2+} complex in the acid reaction of 4. Our failure to observe any such intermediate upon careful acidification of solution of 4 may indicate either that HNO^{2+} complex intermediate in our compound is unstable and immediately hydrolysed to give solvento complex or that NO^+ character in 4 is so high that the protonation does not take place at all. It is noteworthy to mention that the hydrolysis reaction described in Scheme 1 gives known[10] diacetonitrile compound, *tc*-$[Ru(CH_3CN)_2L_2]^{2+}$ when it is carried out in acetonitrile.

B. Diazotisation of Primary Aromatic Amines

The amines are abbreviated as Ar-NH_2 (Ar=C_6H_5-, $H_3CC_6H_4$-, $H_3COC_6H_4$-, ClC_6H_4-). Reactions of the nitrosyl complex, $[Ru(NO)(NO_2)(L^1)_2](ClO_4)_2$(4) with Ar-$NH_2$ were studied by following the reaction sequence through the isolation of products at various stages of the reactions. The reactions which have been studied are shown in Scheme 2. Strategically, the reactions were conducted in two solvents, *viz.* acetonitrile and dichloromethane, to provide a better insight into the mechanism of the reactions.

The orange solution of **4** in acetonitrile readily reacted with Ar-NH_2 to produce a mixture of *tc*-$[Ru(S)(NO_2)(L^1)_2]^+$ (5) ($S=CH_3CN$) and $[Ar-N_2]^+$. The cationic complex, 5 has been isolated as a crystalline perchlorate salt. The aryldiazonium cation has been identified by IR spectral data (Vide Experimental Section) and also by performing a chemical test with alkaline β-naphthol. Red crystals of the known[22] 1-arylazo-2-naphthol has been isolated from the reaction mixture. This has been identified by elemental analysis and melting point (Table III.2). The metal part has been characterised by elemental analysis (Table III.3) molar conductance [21] as well as by examining the spectral data (Table III.4). It shows a strong band at 1370 cm^{-1} which is assigned[23] to ν_{NO_2} and a weak band at 2300 cm^{-1} assignable to $\nu_{C\equiv N}$ in the IR spectrum (Table III.4, Figure III.2). The electronic spectrum of the complex 5 ($S=CH_3CN$) shows an intense MLCT absorption band at 515 nm in the visible region (Figure III.3). The detail of absorption bands along with their molar extinction coefficients have been tabulated in Table III.4. The same reaction, when performed in the presence of very dilute aqueous perchloric acid (*ca.* 10^{-3}mol dm^{-3}), yielded the aryldiazonium cation in slightly improved yield (yield for each azo dye increased by *ca.*5%) together with a diacetonitrile



R	Yield(%)
H	45
p−Me	60
p−OMe	55
p−Cl	45

Scheme 2

TABLE III.2

Analytical Results and Melting Points of 1-Arylazo-2-Naphthols, $C_{10}H_6OHN_2C_5H_4R$

Compound	Formula	%C		%H		%N		Melting point(°C)
		Calcd	Found	Calcd	Found	Calcd	Found	
$C_{10}H_6OHN_2C_6H_5$	$C_{16}H_{12}N_2O$	77.42	77.30	4.84	4.58	11.30	11.10	130
$C_{10}H_6OHN_2C_6H_4$p-CH_3	$C_{17}H_{14}N_2O$	77.86	77.56	5.34	5.20	10.69	10.55	133
$C_{10}H_6OHN_2C_6H_4$p-OCH_3	$C_{17}H_{14}N_2O_2$	73.38	73.45	5.04	5.03	10.07	10.10	134
$C_{10}H_6OHN_2C_6H_4$p-Cl	$C_{16}H_{11}N_2OCl$	67.96	67.82	3.89	3.80	9.91	9.67	163

TABLE III. 3

Analytical Results of Metal Complexes formed in Diazotisation Reactions

Compound	Formula	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
tc-$[Ru(CH_3CN)(NO_2)(L^1)_2]ClO_4.H_2O$	$RuC_{24}H_{23}N_8O_7Cl$	42.88	42.90	3.42	3.30	16.67	16.52
tc-$[Ru(CH_3CN)_2(L^1)_2](ClO_4)_2.H_2O$	$RuC_{26}H_{26}N_8O_9Cl_2$	40.73	41.00	3.39	3.15	14.62	14.35
tc-$[Ru(H_2O)(NO_2)(L^1)_2]ClO_4.H_2O$	$RuC_{22}H_{22}N_7O_8Cl$	40.70	41.02	3.39	3.50	15.11	15.15

TABLE III.4

Solution Molar Conductivity[a] and Spectral Data of Metal Complexes formed in Diazotisation Reactions

Compound	$\Lambda_M/\mathrm{ohm^{-1}cm^2mol^{-1}}$	IR/Cm^{-1} [b]					UV-Visible[c] $\lambda_{max}/\mathrm{nm}(\varepsilon/\mathrm{dm^3mol^{-1}cm^{-1}})$
		$\nu_{N=N}$	$\nu_{C\equiv N}$	ν_{NO_2}	$\nu_{C=C+C=N}$	δ_{H_2O}	
tc-$[Ru(CH_3CN)(NO_2)(L^1)_2]ClO_4.H_2O$	140	1360	2300[d]	1370	1600	3500[e]	515(6475),350(12,050),310(11,920)[f]
tc-$[Ru(CH_3CN)_2(L^1)_2](ClO_4)_2.H_2O$	300	1365	2295, 2300	-	1600	3500[e]	500(9670),470(6400)[f],365(7910) 310(17,200)[f],280(17,500)
tc-$[Ru(H_2O)(NO_2)(L^1)_2]ClO_4.H_2O$	140	1360	1370	1600	3500[e]		530(8500),470(4750)[f],360(36,950)[f], 325(58,550)[f],312(67015)

[a] Molar conductivity data in acetonitrile with a solution concentration of *ca.*$10^{-3}\mathrm{mol\ dm^{-3}}$. [b] In KBr disc. [c] Solvent : Acetonitrile except for *tc*-$[Ru(H_2O)(NO_2)(L^1)_2](ClO_4)_2.H_2O$ where solvent was dichloromethane. [d] Very weak band. [e] Broad band. [f] Shoulder.

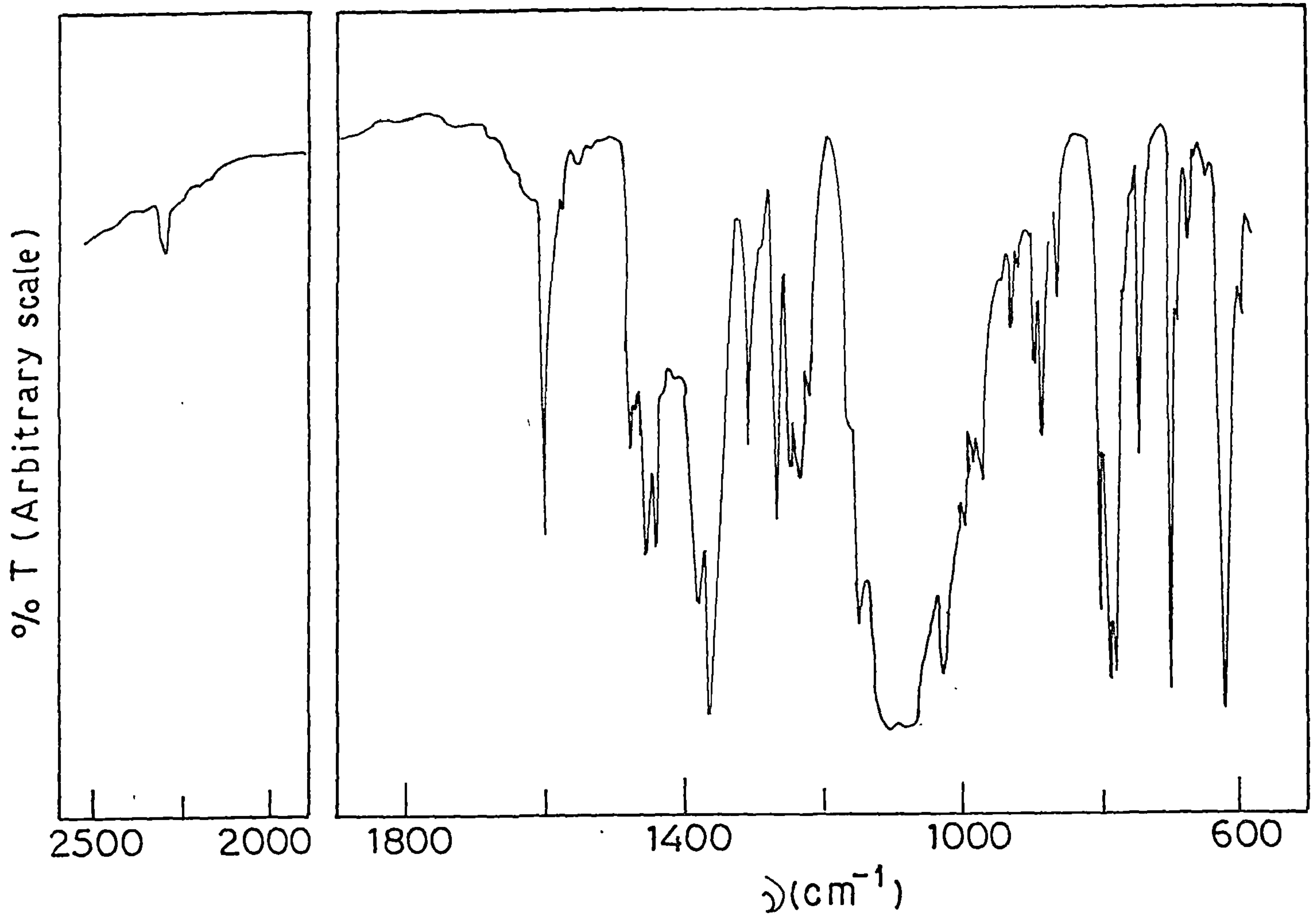


FIGURE III.2

INFRARED SPECTRUM OF <u>tc</u>- $[Ru(CH_3CN)(NO_2)(L^1)_2]$ $ClO_4 \cdot H_2O$ IN KBr DISC

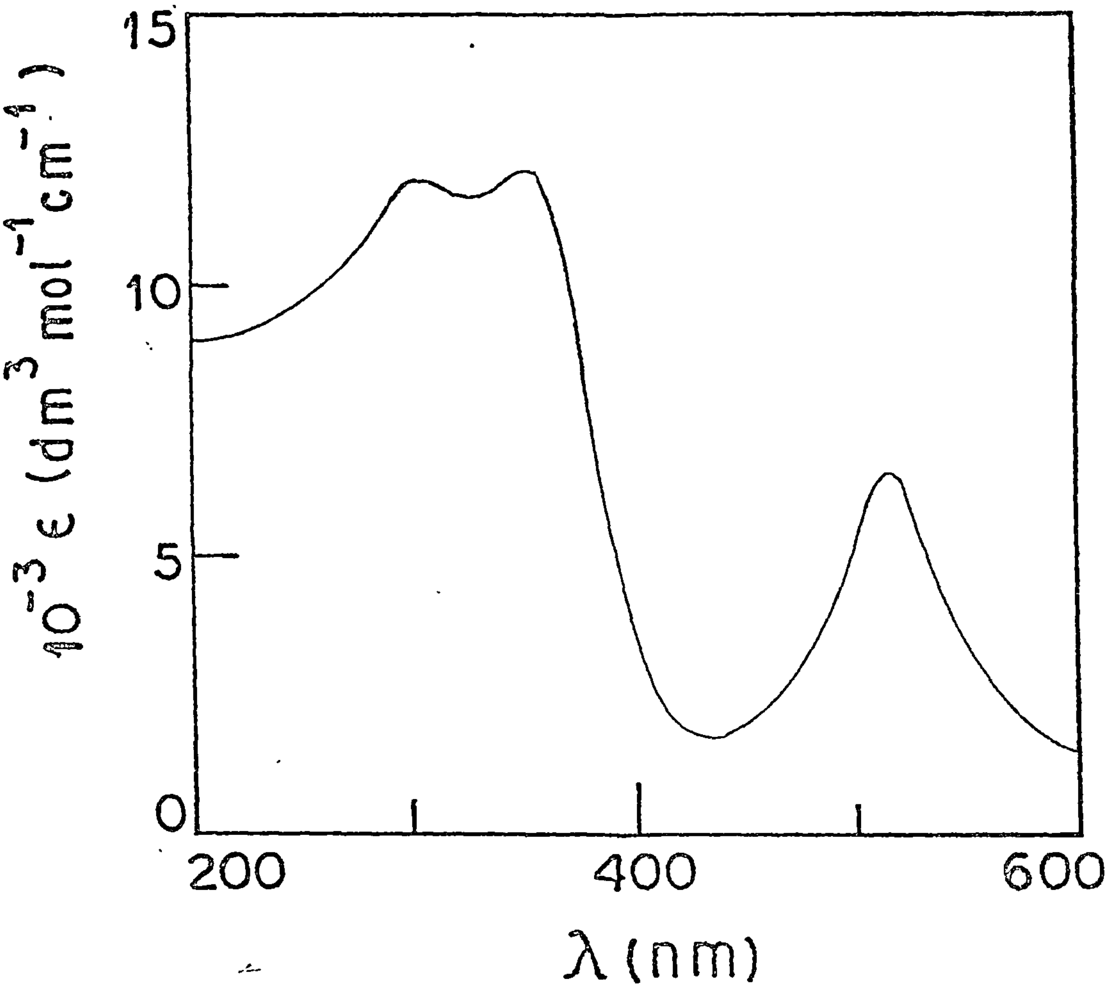
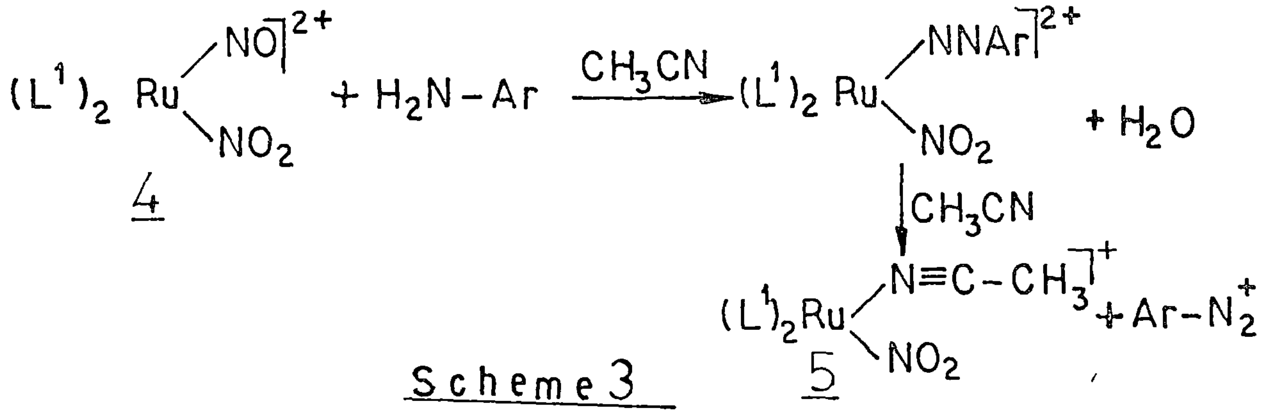


FIGURE III.3

ELECTRONIC SPECTRUM OF tc- [$Ru(CH_3CN)(NO_2)(L^1)_2$] $ClO_4.H_2O$ IN CH_3CN

complex of the type *tc*-[Ru(CH_3CN)$_2$(L^1)$_2$]$^{2+}$(2) (S=CH_3CN). Cationic complex,2 (S=CH_3CN) has been isolated as a perchlorate salt. This has been formulated by elemental analysis (Table III.3), and molar conductance data (Table III.4). This compound shows two $\nu_{C\equiv N}$ modes in the IR spectrum (Table III.4, Figure III.4) indicating a *cis* geometry[10] with respect to the two solvents. The cationic complex, 2 (S=CH_3CN) was further characterised by comparison of its spectral data (Table III.4, Figure III.5) with that of authentic *tc*-[Ru(CH_3CN)$_2$(L^1)$_2$]$^{2+}$, which has been synthesised[10] following the procedure described by Chakravorty and coworkers. The formation of the diacetonitrile compound 2 from the acidic medium was not unexpected since it has already been shown[1] in Section A, that the dinitro complex, *tc*-[Ru(NO_2)$_2$$L_2$](3) is unstable in acidic media and yields disolvento species of the type, *tc*-[RuS_2L_2]$^{2+}$ (2) (S=solvent).

The transformation of 4 to 5 requires firstly diazotisation of the aromatic amines[4] within the coordination sphere of the metal complex followed by substitution of coordinated [Ar-N_2^+] by acetonitrile. The reaction can be represented by Scheme 3.



Scheme 3

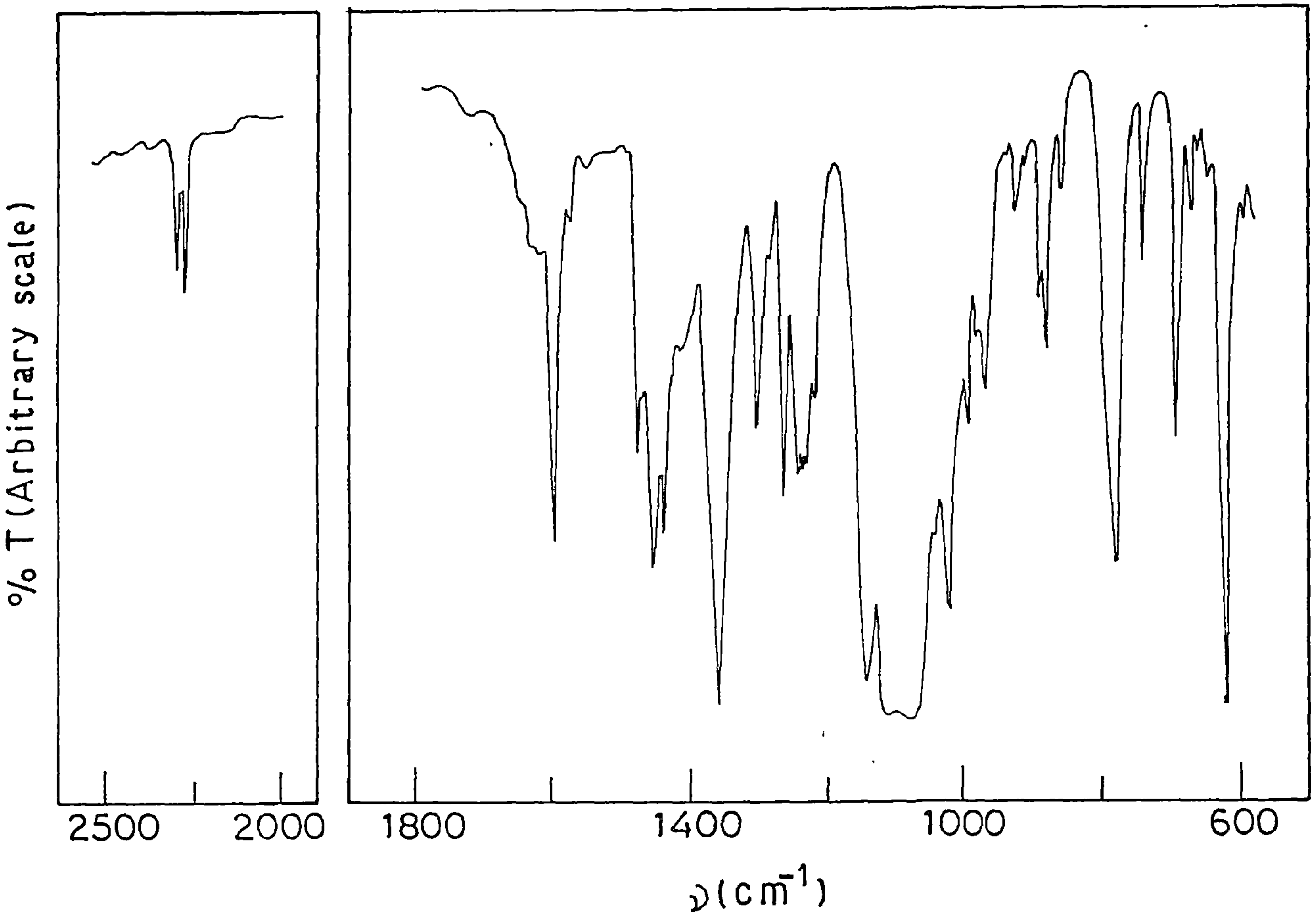


FIGURE III.4

INFRARED SPECTRUM OF <u>tc</u>- [$Ru(CH_3CN)_2(L^1)_2$]$(ClO_4)_2.H_2O$

IN KBr DISC

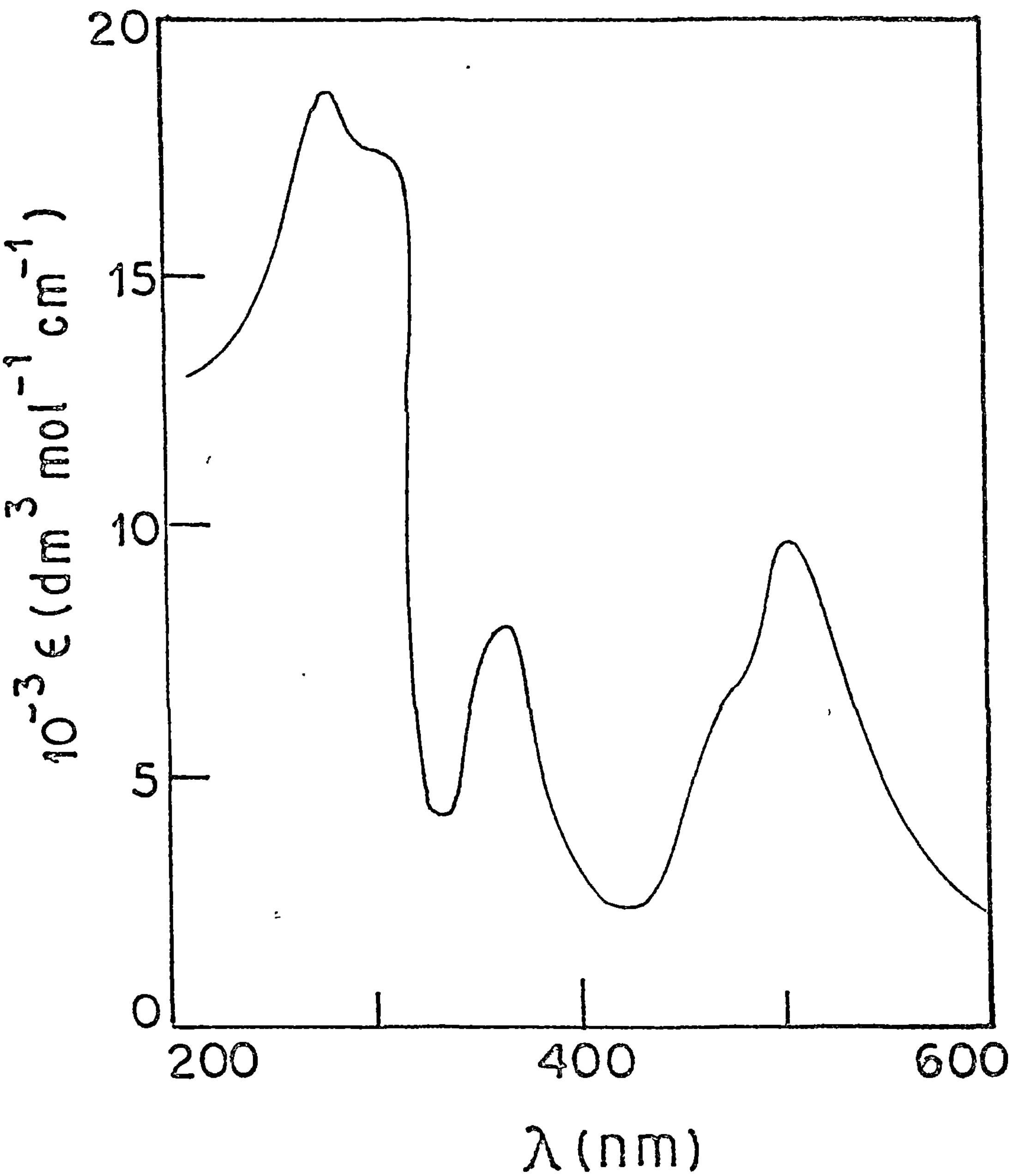


FIGURE III.5

ELECTRONIC SPECTRUM OF <u>tc</u>- $[Ru(CH_3CN)_2(L^1)_2](ClO_4)_2.H_2O$ IN CH_3CN

For purpose of comparison with diazotisation processes in organic chemistry, the stepwise details leading to the net reactions are of interest in that they may involve a series of known intermediates. But in our case we failed to isolate any intermediate.

Keeping the high affinity[10] of acetonitrile for ruthenium(II) in mind, we have examined the same diazotisation reaction in a non-coordinating solvent, dichloromethane with the hope to isolate the coordinated aryldiazonium complex. However, the crude reaction product obtained from the red dichloromethane solution shows a strong band at *ca*.2260 cm^{-1}, indicating the presence[3] of free $[Ar-N_2]^+$ (Figure III.6). It is quite significant to note that the IR spectrum of the crude product shows all the characteristic bands for both coordinated[1] NO_2 and for coordinated[12,24] L^1 (Figure III.6). For example, ν_{NO_2} band appears at *ca*.1370 cm^{-1} and it displays a sharp band at *ca*.1360 cm^{-1} due to $\nu_{N=N}$. Also it shows a sharp band at ca.1600 cm^{-1} assignable[24] to $\nu_{C=C+C=N}$. Analytically, the crude product was always inconsistent. Therefore, we conclude that the isolated product is a mixture of a salt of $[Ar-N_2]^+$ and some ruthenium complex of L. However, extraction of the crude product with water separated $[Ar-N_2{}^+]$ from the metal complex. The residue was soluble in dichloromethane which, on slow addition of hexane, yielded crystalline *tc*-$[Ru(S)(NO_2)(L^1)_2]ClO_4.H_2O$ (5) ($S=H_2O$). The complex 5 ($S=H_2O$), was characterised by elemental analysis (Table III.3), molar conductance[21] (Table III.3) and by spectral data (Table III.4, Figures III. 7 & III.8). A strong MLCT absorption

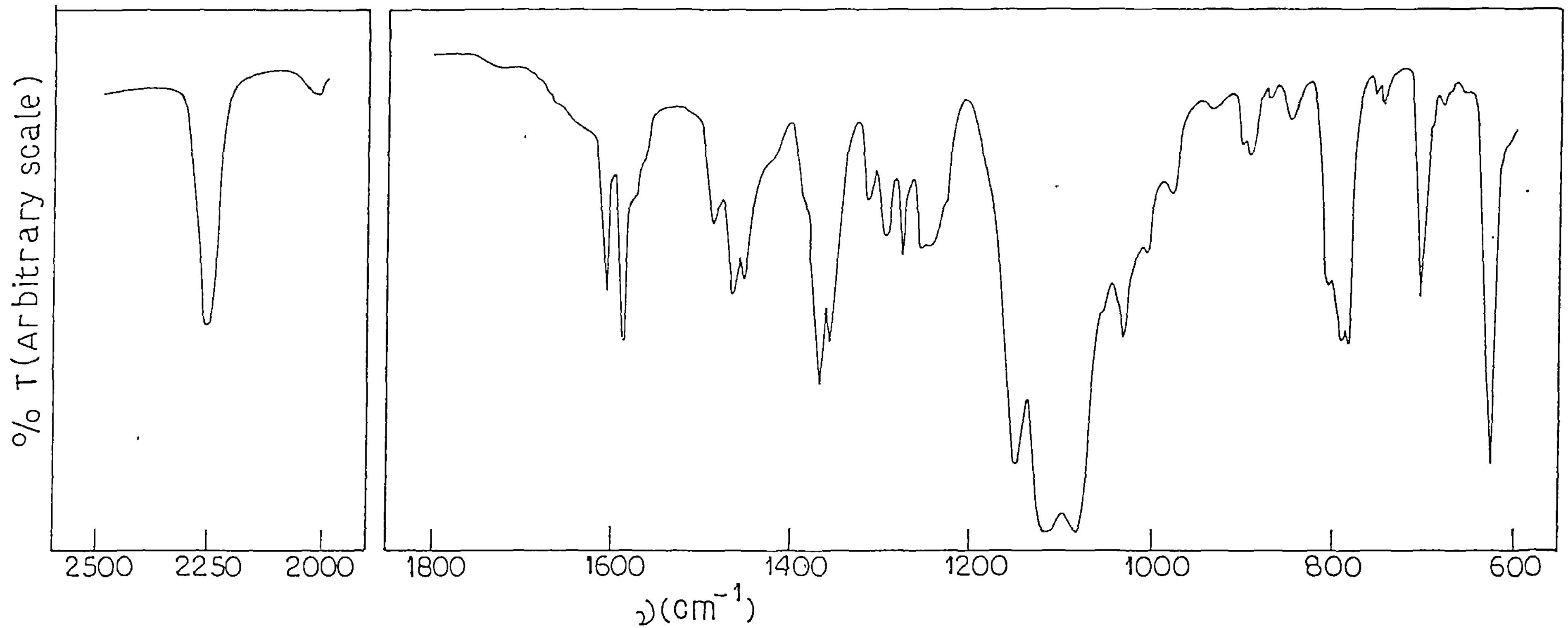


FIGURE III.6

INFRARED SPECTRUM OF A MIXTURE OF <u>tc</u>- [$Ru(H_2O)(NO_2)(L^1)_2$] $ClO_4.H_2O$ AND [$Ar-N_2$] [ClO_4] IN KBr DISC OBTAINED IN DIAZOTISATION REACTION

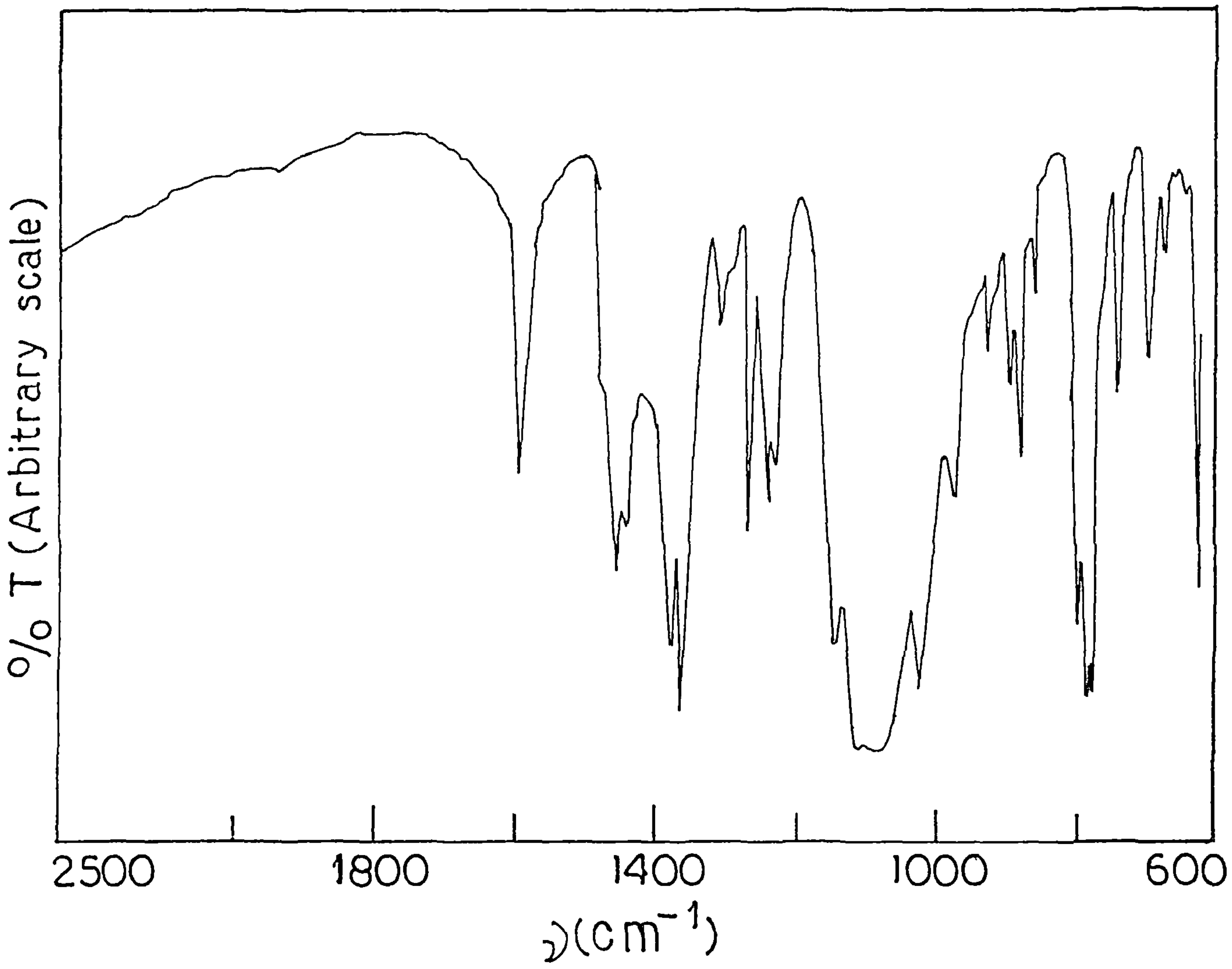


FIGURE III.7

INFRARED SPECTRUM OF tc- $[Ru(H_2O)(NO_2)(L^1)_2]ClO_4 \cdot H_2O$

IN KBr DISC

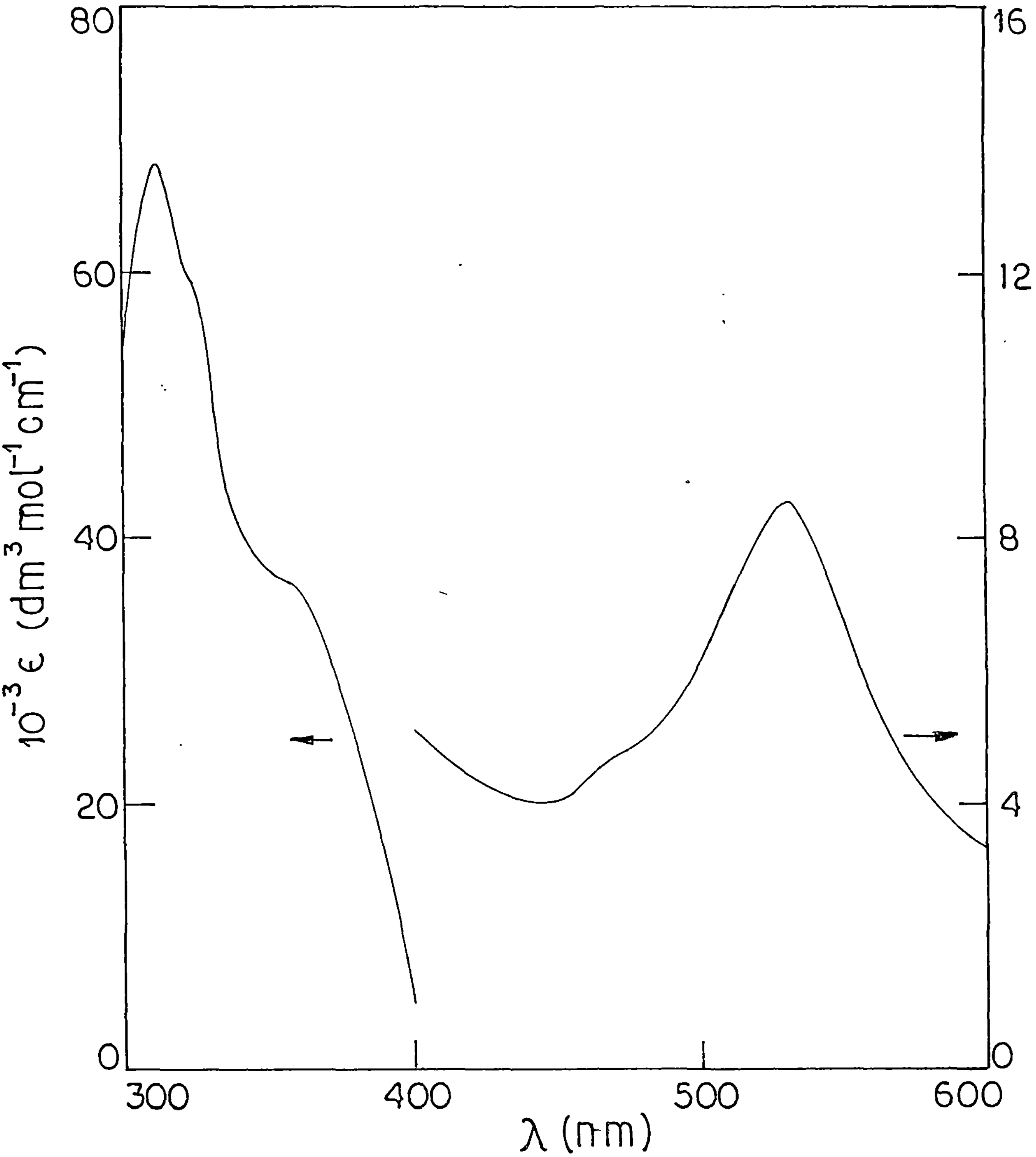


FIGURE III.8

ELECTRONIC SPECTRUM OF tc- [$Ru(H_2O)(NO_2)(L^1)_2$] $ClO_4 \cdot H_2O$ IN CH_2Cl_2

occurred at 530 nm (Figure III.8). Also it is to be noted that the cationic monoaquo complex 5 ($S=H_2O$) produced the monoacetonitrile complex, 5 ($S=CH_3CN$) on treatment with acetonitrile, showing its instability in this solvent. This observation also inturn justifies the formation of the monoacetonitrile complex, 5 ($S=CH_3CN$), in the reaction when it is carried out in acetonitrile.

Free aryldiazonium ions as well as 5 (S=solvent) and 2 ($S=CH_3CN$) are obtained in high yields. The regeneration of 4 can be performed first by treating 5 (S=solvent) or 2 ($S=CH_3CN$) with an aqueous solution of sodium nitrite to obtain the known[1] dinitro complex, *tc*-$[Ru(NO_2)_2(L^1)_2]$ (3), which on treatment with acid produces 4 (Scheme 2). In contrast to the lone example[5,6] of a similar type of reaction, reported previously, free diazonium cations are directly obtained from the reaction of 4 and $Ar-NH_2$. The results could be interpreted by considering the high π-acidity of L^1. It is well documented in the literature that aryldiazonium complexes are generally stabilised[6] by π-back donation. In the present complex, L^1 being a very strong π-acceptor[9-15] reduces the back donation to $[Ar-N_2]^+$ in the intermediate and thus makes it labile towards solvolysis reaction.

The results of the reactions described above are convincing, and one real advantage of such reactions is the possibility of developing a catalytic route for synthetic nitrosation reactions of organic substrates using 4 as the source of NO^+ under mildly acidic or even neutral conditions.

C. Reductions

The electrode reactions of the ruthenium nitrosyl complex of L,**4** has been discussed in the previous chapter. From voltammetry and cyclic voltammetry experiments it has been shown[1,25-27] that the nitrosyl complex undergoes electrochemically reversible one-electron reduction reactions in acetonitrile at *ca.*0.70V and a second irreversible one-electron reduction at *ca.*0.30V (Figure III.9). at at a platinum working electrode. The present ruthenium nitrosyl complex provide an unusual example where electron transfer occurs to and from a coordinated ligand and they are moderately strong oxidants. Two examples are cited below illustrating[28] (i) Oxidative coupling and (ii) oxidation of a ruthenium complex from the bivalent to the trivalent state.

(i) Oxidative Coupling

The cationic nitrosyl complex, *tc*-$[Ru(NO)(NO_2)(L^2)_2]^{2+}$ (4) is converted to the corresponding cationic, *tc*-$[Ru(CH_3CN)(NO_2)(L^2)_2]^{2+}$ (5) complex by N,N-dimethylaniline in acetonitrile. In an electrochemical experiment, a 1mmol solution of **4** in acetonitrile was mixed with 1 mmol of N,N-dimethylaniline (DMA) and the resultant solution was examined cyclic voltammetrically. It shows the characteristic reversible response[29] ($E°_{298}$=0.4V, ΔE_p=60mV) of N,N,N'N'-tetramethyl-benzidine(TMB) evidently formed by oxidative coupling reaction (equation 6, Figure III.10)

$$2\ \text{DMA} + 2\ tc\text{-}\underset{\mathbf{4}}{[\text{Ru(NO)}(\text{NO}_2)(\text{L}^2)_2]^{2+}} \longrightarrow$$

$$\text{TMB} + 2\ tc\text{-}\underset{\mathbf{5}}{[\text{Ru}(\text{CH}_3\text{CN})(\text{NO}_2)(\text{L}^2)_2]^{+}} + 2\ \text{NO} + 2\text{H}^+ \qquad (6)$$

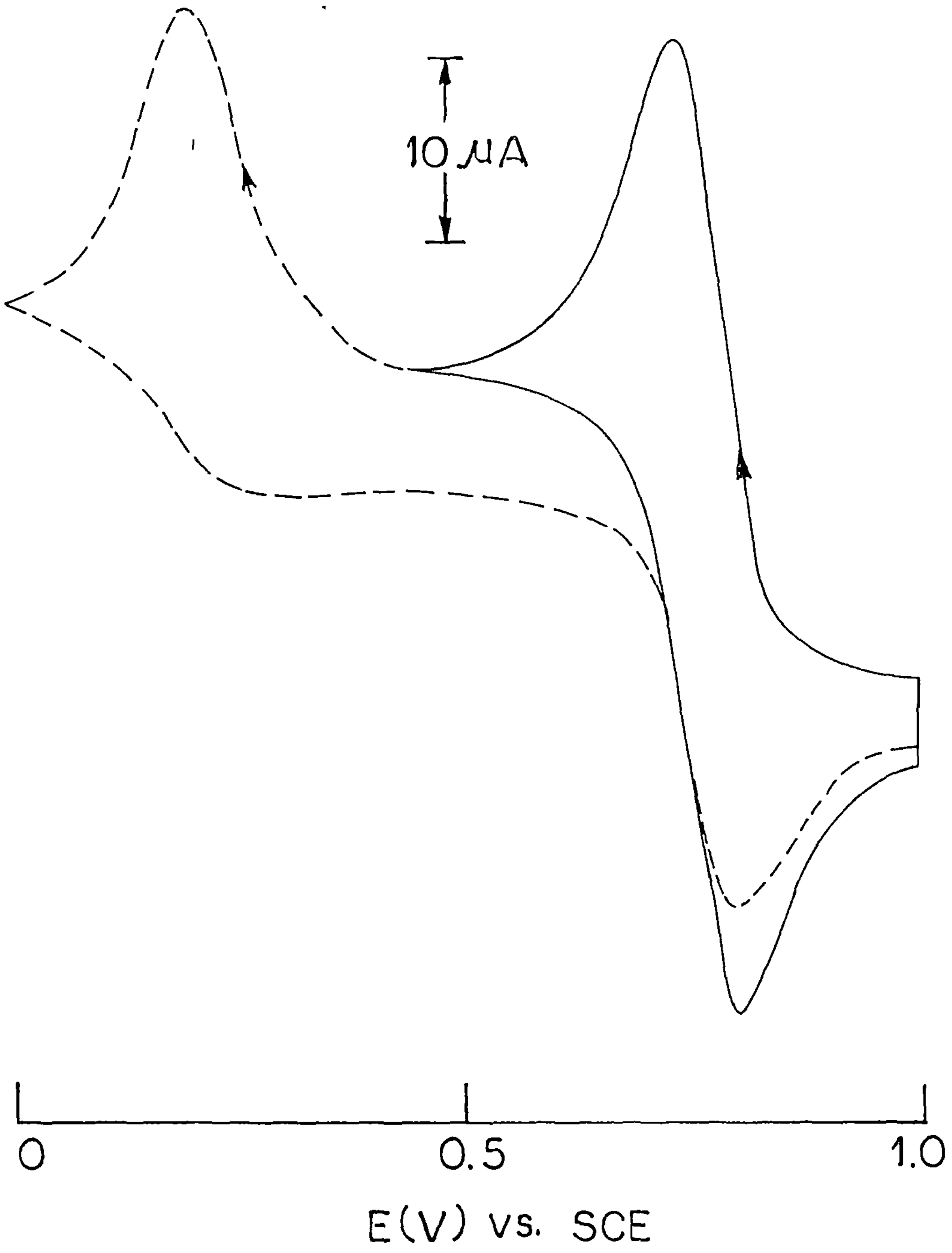


FIGURE III.9

CYCLIC VOLTAMMOGRAM OF tc- $[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$

AT A 50 mVs^{-1} SCAN RATE

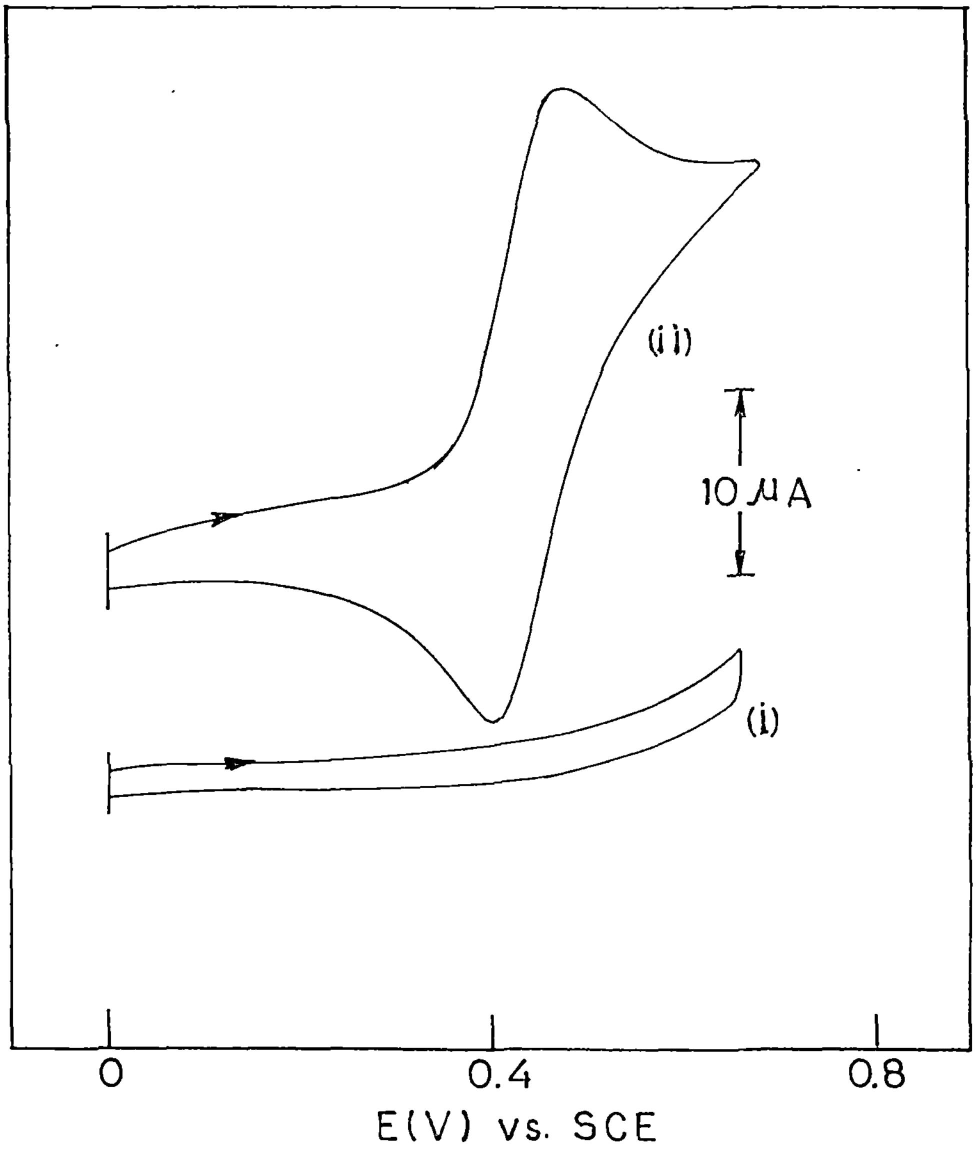


FIGURE III.10

SEGMENTED CYCLIC VOLTAMMOGRAMS OF :

(i) FREE N,N-DIMETHYLANILINE,

(ii) N,N-DIMETHYLANILINE MIXED WITH EQUIMOLAR QUANTITY OF <u>tc</u>- $[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$ IN CH_3CN

The cyclic voltammetric current height of the TMB response corresponds to 35-40% utilisation of the oxidation equivalent for the coupling reaction (Figure III.10). The rest of the amine is evidently lost in side reactions.[30-31] In the preparative scale the reaction (6) was performed in acetonitrile and on column chromatographic purification TMB together with *tc*-$[Ru(CH_3CN)(NO_2)(L^2)_2]^{2+}$ (5) were isolated. The complex 5 was crystallised as perchlorate salt and was characterised by molar conductance and spectral data (vide Experimental Section). Further studies are on to isolate and characterise the other products obtained from the above reaction. It may be noted here that in case of primary amines the present nitrosyl complex has been successfully used as a nitrosating agent whereas in case of a tertiary amine the same nitrosyl complex behaves as an oxidant. The difference in the oxidation potentials[32] of the primary and tertiary amines is no doubt the controlling factor in driving the two reactions. The first reduction potential of **4** [E°(1)] is just enough for the oxidation of DMA whereas it is a weaker oxidant with respect to the primary amines which have been used for studying the diazotisation reactions.

(ii) Formation of Trivalent Ruthenium

Dichlorobis(2,2'-bipyridyl)ruthenium(II), $[RuCl_2(bpy)_2]$ is quantitatively oxidised to the corresponding ruthenium(III) chelate, $[RuCl_2(bpy)_2]^+$ by *tc*-$[Ru(NO)(NO_2(L^2)_2]^{2+}$ (4) (equation 7)

$$\begin{aligned} &tc\text{-}[\mathrm{Ru(NO)(NO_2)(L^2)_2}]^{2+} + [\mathrm{RuCl_2(bpy)_2}] \longrightarrow \\ &tc\text{-}[\mathrm{Ru(CH_3CN)(NO_2)(L^2)}]^{+} + [\mathrm{RuCl_2(bpy)_2}]^{+} \end{aligned} \qquad (7)$$

This reaction was followed cyclic voltammetrically. The cyclic voltammograms of the different mixtures are shown in Figure III.12. A solution prepared by mixing $[RuCl_2(bpy)_2]$ (*ca.* 10^{-3}mol dm^{-3}) with **4** (ca.10^{-3} mol dm^{-3}) shows the characteristic cyclic voltammogram[33,34] of $[RuCl_2(bpy)_2]^+$(Figure III.11) and an additional reversible response at 1.63V (ΔE_p=120mV) was also observable due to the formation of *tc*-$[Ru(CH_3CN)(NO_2)(L^2)_2]^+$ (Figure III.12).Till date the mechanism of the reaction is not clear to us. The origin of the solvento complex 5 (S=CH_3CN) from the reactions (6) and (7) is perhaps one electron reduction of RU^{II}-NO^+ to give Ru^{II}-NO° followed by a rapid solvolysis reaction to form 5 (S=CH_3CN).

III.3 EXPERIMENTAL SECTION

A. Physical Measurements

Melting Point Measurements, Molar Conductivity, Infrared Spectra, Electronic Spectra and Electrochemical Measurements.

All described in Chapter II.

B. Formulation of Compounds

This was done by C, H, N microanalyses. The instrument used was same as described in Chapter II.

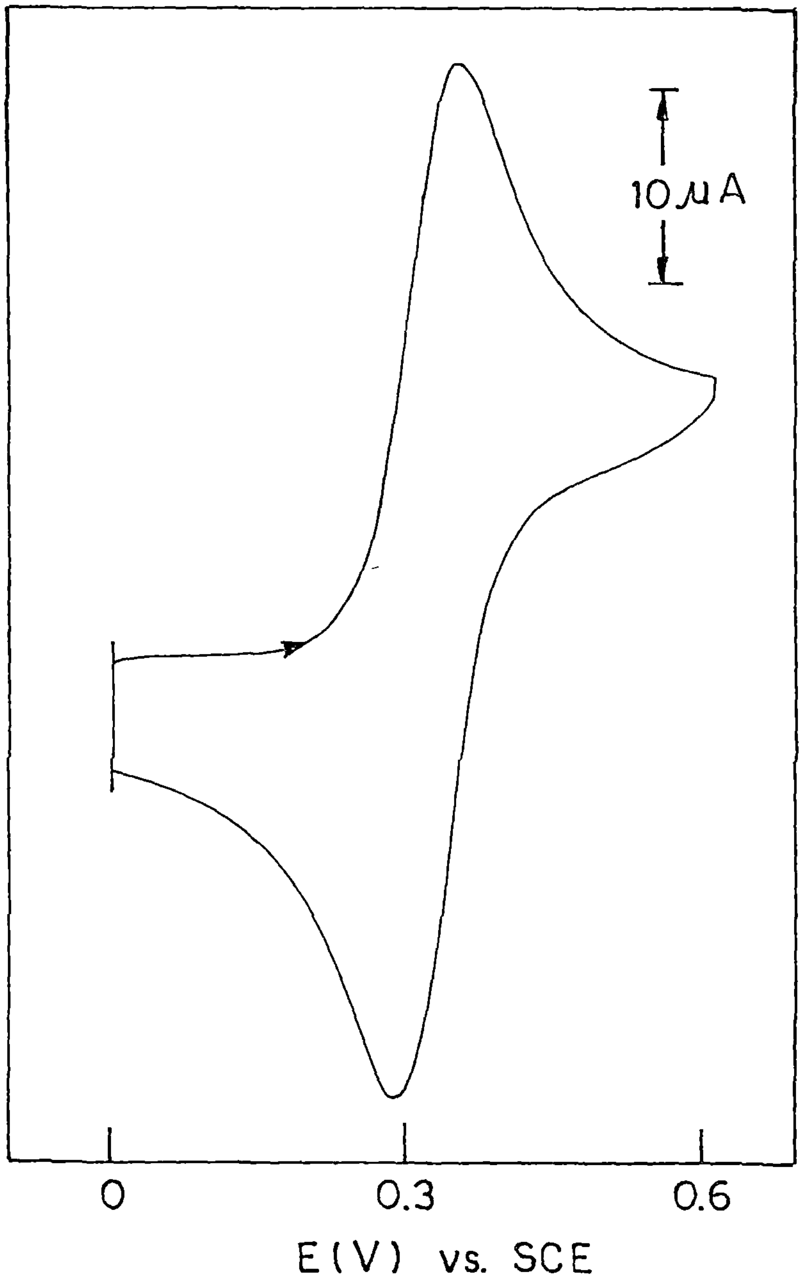


FIGURE III.11

CYCLIC VOLTAMMOGRAM OF [$RuCl_2(bpy)_2$] AT A 50 mVs^{-1}

SCAN RATE IN CH_3CN

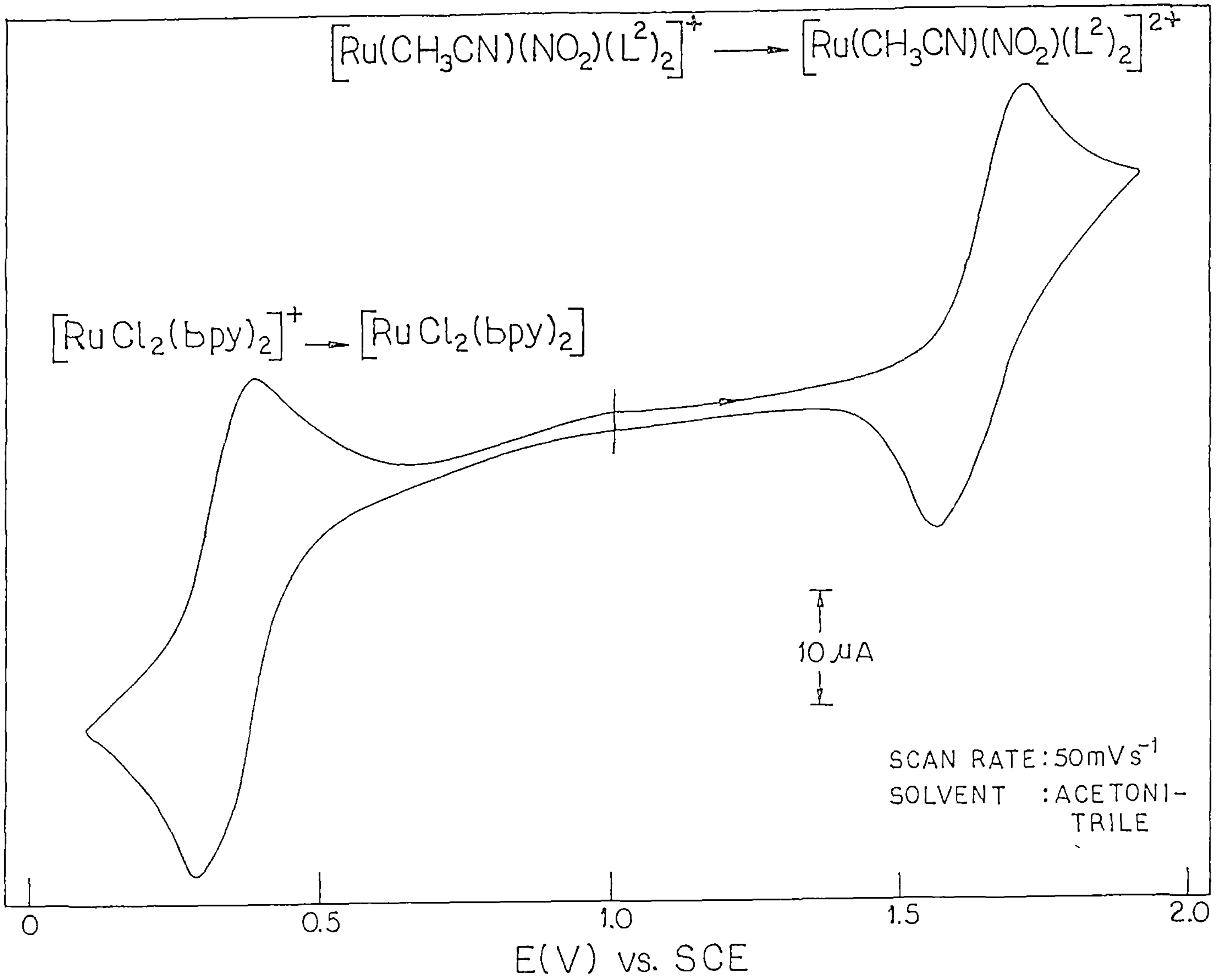


FIGURE III.12

CYCLIC VOLTAMMOGRAM OF A MIXTURE OF tc- $[Ru(NO)(NO_2)(L^2)_2]$ $(ClO_4)_2$ AND $[RuCl_2(bpy)_2]$ IN CH_3CN

C. Solvents

Commercial dichloromethane, purification of which is described in Chapter II. Spectrograde acetonitrile and dichloromethane were used as the solvents in the diazotisation reactions. Purification of acetonitrile for electrochemical work and toluene for synthesis of ligand have been done as described in Chapter II. Besides all other solvents used for preparative and analytical work were of reagent grade and were used without further purification.

D. Preparation of Compounds

(a) Chemicals

The chemicals and their sources are as follows:

Aniline, N,N-dimethylaniline, E. Merck (India) Ltd., Bombay. These were distilled over potassium hydroxide before use. p-Anisidine, p-chloroaniline and p-toluidine, Romali, Bombay. These were of reagent grade and used without further purification. β-Naphthol, Thomas Baker and Co. Bombay; 2,2'-bipyridine, Loba-chemie Indoaustranal Co., Bombay. In addition, all other chemicals and reagents that were obtained are described in Chapter II.

(b) Ligands

Preparations of 2-(phenylazo)pyridine(L^1), and 2-(m-tolylazo)-pyridine(L^2) have been described in Chapter II.

(c) Complexes

(i) *tc*-$[Ru(OH_2)_2L_2](ClO_4)_2.H_2O$, *tc*-$[Ru(NO_2)_2L_2]$ and *tc*-$[Ru(NO)(NO_2)L_2](ClO_4)_2$ complexes were synthesised as described[1] in chapter II.

(ii) *tc*-diacetonitrilebis[2-(arylazo)pyridine] ruthenium(II) Perchlorate Hydrate, *tc*-$[Ru(CH_3CN)_2L_2](ClO_4)_2.H_2O$. It was prepared by following a reported procedure[10]. Specific details for ligand L^1 are given below.

A 0.200g (0.27 mmol) of *tc*-$[Ru(OH_2)_2(L^1)_2](ClO_4)_2.H_2O$ was added to 15 ml of acetonitrile. The mixture was heated to reflux for 30 min. The initial red violet solution gradually turned to yellow orange. The reaction mixture was then cooled to room temperature. On addition of equal volume of water and by keeping it for overnight orange crystalline compound was obtained. These were collected by filtration and dried *in vacuo* over P_4O_{10}. The yield was 0.460g (60%).

(iii) *Cis*-Dichlorobis(2,2'-bipyridyl)ruthenium(II) Dihydrate, ***cis*-$[RuCl_2(bpy)_2].2H_2O$.** It was prepared by following a published procedure[35]. 1.56g (5.97 mmol) ruthenium trichloride trihydrate and 1.87g (12 mmol) 2,2'-bipyridine were heated to reflux together in *ca.*60 ml dimethylformamide for 3h. The volume of the violet solution was reduced to 15 ml when dark crystals started depositing. The mixture was then cooled in an ice bath for several hours. The precipitated solid was collected by filtration and washed several times with cold water. The dark greenish black microcrystalline product is formed in 68% yield

(2.11g). Purity of the product was determined by comparison of its electronic spectrum with published reports.

(d) Complexes formed during the reaction

(i) Conversion of *tc*-[Ru(NO)(NO$_2$)L$_2$](ClO$_4$)$_2$ (4) into *tc*-[Ru(NO$_2$)$_2$L$_2$](3). This was done by following a general procedure. Specific details are given for ligand L^2.

A 8.15 g (0.2 mmol) sample of *tc*-[Ru(NO)(NO$_2$)(L^2)$_2$](ClO$_4$)$_2$ was dissolved in water-acetonitrile (4:1 v/v; 30 ml) and was stirred for 1h at room temperature. Initially the solution was orange but in 30 min it became red. It was then concentrated under reduced pressure to half of its initial volume. The dark crystals were collected by filtration and dried *in vacuo* over P_4O_{10}. Yield : 70%. Spectral data for the compound isolated correspond exactly to that of an analysed sample of *tc*-[Ru(NO$_2$)$_2$(L^2)$_2$] given in Chapter II.

Conversion process for *tc*-[Ru(NO)(NO$_2$)(L^1)$_2$(ClO$_4$)$_2$] to *tc*-[Ru(NO$_2$)$_2$(L^1)$_2$] gives the similar result. Yield : 75%.

(ii) Conversion of *tc*-[Ru(NO$_2$)$_2$L$_2$](3) into *tc*-[Ru(OH$_2$)$_2$L$_2$](ClO$_4$)$_2$.H$_2$O(2). This was done by following a general procedure. Specific details for ligand L^1 are given below.

A sample (0.14g, 0.25 mmol) of *tc*-[Ru(NO$_2$)$_2$(L^1)$_2$] was suspended in 1 mol dm^{-3} aqueous perchloric acid (10 ml) and the mixture heated to reflux for 3h. The solution was then cooled to room temperature and filtered to remove insoluble residues. Crystals of sodium perchlorate (*ca.*1g) were then added with stirring. The mixture was kept overnight in a refrigerator. Dark needle shaped crystals were collected by filtration, washed with the minimum volume (*ca*.5 ml) of cold water, and finally dried *in vacuo* over P_4O_{10}. Yield : 55%. Electronic spectral data for the compound isolated correspond exactly to those for a known analysed sample of tc-$[Ru(OH_2)_2(L^1)_2](ClO_4)_2.H_2O$. Electronic Spectral data are as follows.

λmax (CH_3CN): 500, 476sh, 364, 308sh, 280 and 220 nm (ε,9860, 6800, 17,210, 12,060,16,900 and 22,610 dm^3 mol^{-1} cm^{-1}); Λ_M(CH_3CN, 298K): 300 ohm^{-1} cm^2 mol^{-1} (2) ($L=L^2$): Yield : 50%; λmax(CH_3CN), 500, 476sh, 368, 308sh, 280 and 216nm (ε,10,100, 7040, 17,700, 13,350, 17,800, and 25,410 dm^3 mol^{-1} cm^{-1});ΛM(CH_3CN,295K): 300 $ohm^{-1}cm^2mol^{-1}$).

The same reaction was also carried out in 1mol dm^{-3} aqueous sulphuric acid and the compounds were isolated by addition of saturated aqueous sodium perchlorate solution. The use of aqueous perchloric acid results in an isomerically purer product.

(iii) Conversion of ***tc*****-$[Ru(NO)(NO_2)L_2](ClO_4)_2$(4) into** ***tc*****-$[Ru(OH_2)_2L_2](ClO_4)_2.H_2O$ (2).** This was done similarly using 1 mol dm^{-3} aqueous perchloric acid. Molar conductance and Electronic spectral data corresponds exactly to those in section D.d.(ii) above

2 ($L=L^1$): Yield, 65%
2 ($L=L^2$): Yield, 60%

(iv) Conversion of both *tc*-[Ru(NO$_2$)$_2$L$_2$](3) and *tc*-[Ru(NO)(NO$_2$)L$_2$](ClO$_4$)$_2$ (4) into *tc*-[Ru(CH$_3$CN)$_2$L$_2$](ClO$_4$)$_2$.H$_2$O (2)

The reactions were performed by following a general procedure. Specific details for ligand L^1 are given below.

A sample (0.14g, 0.25 mmol) of *tc*-[Ru(NO$_2$)$_2$(L^1)$_2$) are dissolved in 15 ml acetonitrile and to it 0.5 ml of 10 mol dm^{-3} perchloric acid was added and the solution was heated to reflux for 1h. The solution was then cooled and an equal volume of water was added. On keeping it for overnight orange crystalline compound was obtained. It was collected by filtration, washed with 5 ml water and finally dried *in vacuo* over P$_4$O$_{10}$. Yield : 60%. Electronic spectral data for the compound isolated correspond exactly to those for a known analysed sample of *tc*-[Ru(CH$_3$CN)$_2$(L^1)$_2$](ClO$_4$)$_2$.H$_2$O.(2)(S=CH$_3$CN)

2(S=CH$_3$CN) (L = L^2): Yield, 65%

The complex 4 was similarly converted into 2(S=CH$_3$CN) using 10 mol dm^{-3} perchloric acid

2(S=CH$_3$CN)(L=L^1) : Yield, 70%
2(S=CH$_3$CN)(L=L^2) : Yield, 65%

(v) Diazotisation Reaction. Reaction of *tc*-[Ru(NO)(NO$_2$)(L^1)$_2$](ClO$_4$)$_2$ (4) with Ar-NH$_2$ (Ar-NH$_2$=Aniline, p-anisidine, p-chloroaniline and p-toluidine)

The reactions were performed by using a general procedure. Specific details are given for aniline.

Reaction in acetonitrile. The salt 4 (0.125g, 0.17 mmol) was dissolved in 10 ml of acetonitrile and to it 0.016g (0.17 mmol) of aniline was added. The mixture was stirred for 30 min at room temperature (298K) and then evaporated to dryness using a vacuum pump. The crude product was then extracted with 30 ml (3x10 ml) of ice-cold water and the aqueous solution was collected by filtration. To the above filtrate, an aqueous solution of alkaline β-naphthol was added with continuous stirring over a period of 15 min. Red crystals of 1-phenylazo-2-naphthol were separated and recrystallised from methanol.

The dark tan residue obtained after water extraction was dried and dissolved in dichloromethane. On slow addition of hexane, light brown crystals of *tc*-$[Ru(S)(NO_2)(L^1)_2](ClO_4).H_2O$(5) (S=$CH_3CN$) were obtained, which were filtered and dried in vacuo over P_4O_{10}. Yield : 60%.

Reaction in acetonitrile in presence of aqueous perchloric acid. This was carreid out similarly except *ca.* 10^{-3}mol dm^{-3} aqueous perchloric acid was added together with Ar-NH_2. The metal part was crystallised from a 1:1 acetonitrile/water mixture and left to evaporate at room temperature overnight. The dark crystalline compound was collected by filtration and dried *in vacuo* over P_4O_{10}. Compound tc-$[Ru(CH_3CN)_2(L^1)_2](ClO_4)_2.H_2O$, Yield : 62%. Yield of 1-phenylazo-2-naphthol, 50%.

Reaction in dichloromethane. The salt 4 (0.125g, 0.17 mmol) was suspended in 10 ml of dichloromethane and 0.016g (0.17 mmol) of aniline was added. The mixture was then stirred for 30 min at room temperature (298K) and the red brown solution was then filtered. Brownish-white needles of $[C_6H_5N_2](ClO_4)$ were collected, washed with 5 ml of dichloromethane and finally dried in vacuo over P_4O_{10}. Yield 50% . ν_{max} (KBr): 2260(N≡N), 1590 (C=C), 1100br and 620 cm^{-1} (ClO^-_4).

The cation $[C_6H_5N_2]^+$ could also be extracted with ice-cold water, and on addition of an aqueous alkaline solution of β-naphthol, yielded red crystals of 1-phenylazo-2-naphthol, which were recrystallised from methanol.

The red brown dichloromethane filtrate was concentrated to 10 ml under reduced pressure and slow addition of hexane yielded dark crystals of *tc*-$[Ru(S)(NO_2)(L^1)_2](ClO_4).H_2O$ ($S=H_2O$). These were collected by filtration and dried in vacuo over P_4O_{10}. Yield : 55%.

Conversion of *tc*-$[Ru(S)(NO_2)(L^1)_2](ClO_4).H_2O$ (5) ($S=H_2O$) to *tc*-$[Ru(S)(NO_2)(L^1)_2](ClO_4).H_2O$ (5) ($S=CH_3CN$). 0.100g (0.15 mmol) of tc-$[Ru(S)(NO_2)(L^1)_2](ClO_4).H_2O$ ($S=H_2O$) was dissolved in 15 ml of acetonitrile and stirred at room temperature for 30 min. To the brown solution, an equal volume of water was added and left to evaporate at room temperature overnight. Dark brown crystals of 5 ($S=CH_3CN$) were obtained. The analytical and spectral data correspond exactly to those of the previously isolated compound (5) ($S=CH_3CN$).

(vi) Reaction of *tc*-$[Ru(NO)(NO_2)(L^2)_2](ClO_4)_2$ (4) with N,N'-dimethylaniline. The salt 4 (0.125g, 0.16 mmol) was dissolved in 10 ml acetonitrile and to it 0.020g(0.16 mmol) of N,N'-

dimethylaniline was added. The mixture was stirred for 30 min. at room temperature (298K) and then evaporated to dryness. The crude product was then dissolved in 10 ml of dichloromethane and subjected to column chromatography on a silica gel column. The first yellow fraction was eluted with benzene. The second brownish red fraction was eluted with 1:9 Acetonitrile-dichloromethane solution. A number of other bands are also retained in the column. Separation and identification of different other fractions are underway.

The yellow solution in benzene was concentrated. A yellow crystalline compound was obtained. It was filtered and dried *in vacuum* over P_4O_{10}. Yield : 40%. M.P, 139°C. Found: C,80.10; H, 8.40; N,11.75. Calc for $C_{16}H_{20}N_2$: C, 80.00; H, 8.33; N, 11.67%.

The second brownish red fraction was evaporated to dryness. It was again dissolved in 15 ml of dichloromethane. On addition of equal volume of hexane, a dark crystalline compound was obtained which are collected by filtration and dried in vacuo over P_4O_{10}. Yield : 50%. The compound obtained was *tc*-$[Ru(S)(NO_2)(L^2)_2](ClO_4).H_2O$. ($S=CH_3CN$). Found : C, 44.72; H, 3.98; N, 16.15. Calc. for $C_{26}H_{27}N_8O_7ClRu$: C, 44.60; H, 3.86; N, 16.01%; Λ_M (298K, CH_3CN): 145 $ohm^{-1}cm^2mol^{-1}$; ν_{max}(KBr) : 1370 (NO_2) 2300 (C≡N) and 1365 cm^{-1} (N=N); $\lambda_{max}(CH_3CN)$: 518, 350 and 305 (sh) nm (ε,6600, 12,200 and 12,000 $dm^3mol^{-1}cm^{-1}$).

(vii) Electrochemical Reactions

(a) Oxidative Coupling. A sample of 0.006g (0.008 mmol) of *tc*-

$[Ru(NO)(NO_2)(L^2)_2](ClO_4)$ (4) and 0.200g (0.87 mmol) of TEAP were dissolved in 8 ml of deaerated acetonitrile in an electrochemical cell. To it a solution of 0.001g (0.008 mmol) of N,N-dimethylaniline in 2 ml acetonitrile,was added. The resulting solution was then studied cyclic voltammetrically at a platinum working electrode. A reversible oxidative couple at $E°_{298}$=0.4V (ΔE_p=60 mV) indicating the formation of N,N,N',N'-tetramethylbenzidine (TMB) was observable. A similar experiment, without addition of 4 showed no response in the range 0.0 to 0.60V. The yield of TMB formed in the experiment as stated above, was assessed from the current height data of the reversible couple at 0.4V.

(b) Formation of Trivalent Ruthenium. A sample of 0.011g (0.014 mmol) of 4 and 0.200 (0.87 mmol) of TEAP were dissolved in 10 ml of deaerated acetonitrile in an electrochemical cell. To it 0.007g (0.014 mmol) of $[RuCl_2(bpy)_2]$ was added and the mixture was stirred under nitrogen atmosphere for 5 minutes. The resulting solution showed a reversible reductive response at $E°_{298}$=0.33V (ΔE_p=80mV) indicating the formation of $[RuCl_2(bpy)_2]^+$. Another oxidative response due to oxidation of *tc*-$[Ru(CH_3CN)(NO_2)(L^2)_2]^+$ was also recorded at $E°_{298}$=1.63V (ΔE_p = 120mV). In absence of 4, $[RuCl_2(bpy)_2]$ showed oxidative response at 0.32V.

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Chapter IV

CHAPTER IV

NEW, STABLE, CHELATED, TETRACOORDINATED SILVER(I) COMPLEXES OF THE 2-(ARYLAZO)PYRIDINE LIGAND SYSTEM: SYNTHESIS, CHARACTERISATION AND ASSESSMENT OF BONDING AND STRUCTURE

Abstract: *The 2-(arylazo)pyrdine (L,1) ligands yield bis-chelated silver(I) complexes* $[AgL_2]^+$ *in methanol. The cationic complexes have been isolated as crystalline perchlorate salts which were characterised by elemental analyses and spectroscopic method. The complexes are 1:1 electrolytes in methanol. In contrast to the copper(I) analogue, there is only a small shift of* $\nu_{N=N}$ *to low energy in the IR spectrum of* $[AgL_2]^+$ *as compared to that of uncoordinated L, indicating a negligible* $d\pi$-$\pi^*(L)$ *interactions. The high resolution* ^1H *NMR spectra of silver complexes with different substituted ligands* (L^1-L^4) *are reported and completely assigned and it has been concluded that both the chelate rings are magnetically equivalent and contain an effective* C_2*-axis in each of the complexes. These are quite stable and solutions in methanol and chloroform obey Beer's law.*

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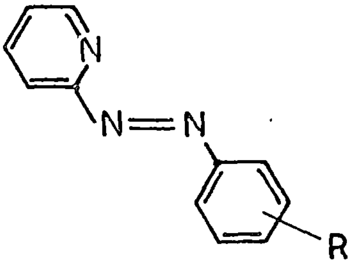
[*] A part of this work has appeared in *Polyhedron*, 1990, *9*, 2251.

IV. 1 INTRODUCTION

The work embodied in this chapter stems from our continued interst in the transition metal chemistry of the azoimine ligand system (L,1) which is well known as a versatile ligand capable of chelating[1-15] a wide range of metal ions. Recently, Datta and Chakravorty have reported[16] the 2-(phenylazo)pyridine chemistry of copper. The richness of this chemistry encouraged us to initiate research on the chemistry of the neighbouring element silver involving L.

Although silver(I) forms a great variety of complexes[17-22] with N-donor ligands and halides, it is evident from a survey of the literature that the reports on stable, monomeric compounds of silver(I) with chelated ligands are scanty.[17,23] Based on the reactivity and stability of the coordination complexes, the silver(I) ion has been characterised as a class B or soft acid. The linear $H_3N\text{-}Ag\text{-}NH_3^+$ ion was reported in 1934 and for many years linear two-coordination[24-26] was believed to be characteristics of silver(I) ion. With further development of silver chemistry, a wide range of geometry has been generally comprehended. For example, in liquid ammonia the linear $Ag(NH_3)_2^+$ ion becomes further solvated[25] to yield the tetrahedral ion $Ag(NH_3)_4^+$. A tetrahedral complex $[Ag(py)_4]ClO_4$ (py = pyridine) has been recently isolated[26] and its X-ray crystal structure determined. The complex is thermally unstable and even at room temperature readily loses two moles of pyridine. With imidazole another structural aspect of silver chemistry becomes highlighted, that of cluster formation of silver(I). The chemistry of monomeric silver(I) complexes of bidentate ligands[27-30] with N,N-donors has grown primarily around 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and related ligands. They are usually isolated in low yields and mostly used as intermediates for the preparation of the corresponding silver(II) complexes.[29,30] Many compounds of silver(I) are also now known with soft donors like, P, As, S, Se etc. but they most adopt either dimeric or polymeric structure[31-37] in the solid state.

With this background we thought it is worthwhile to initiate research on silver(I) with bidentate N,N-donors ligand (L, 1) to consolidate a systematic understanding of the factor determining the geometry of the complex species in the solid state and also in solution. In this chapter we describe the high yield synthesis of stable, monomeric tetracoordinated silver(I) complexes of L(1). Assessment of bonding and structure and the stability of the complexes in solution have been made on the basis of spectral data. Comparisons where relevant, with the corresponding copper(I) complexes[16] are also made. The four specific ligands used in this chapter are abbreviated as L^1-L^4.



L

R = H : L^1
R = m-Me : L^2
R = p-Me : L^3
R = p-Cl : L^4

1

IV.2 RESULTS AND DISCUSSION

A. Synthesis

$AgNO_3$ reacts smoothly with L(1) in boiling methanol in the ratio of 1:2 to yield cationic $[AgL_2]^+$(2), which have been isolated as perchlorate salts from the reaction mixture. Even when metal-to-ligand ratio exceeds 1:2, only bis ligand compounds are formed. The general synthetic route is shown by the equation 1.

$$AgNO_3 + 2L \longrightarrow [AgL_2]^+ + NO_3^- \qquad (1)$$

Recrystallisation of the perchlorate salts from 1:1 methanol-water mixture yielded highly crystalline compounds. The yields of the complexes are quite high (>80%). It may be noted here that the corresponding bis complex[30,38] of bpy and phen, $[Ag(bpy)_2]^+$, $[Ag(phen)_2]^+$ respectively, were obtained only in low yields. The silver-L complexes are highly soluble in common polar organic solvents like acetonitrile, chloroform etc., moderately soluble in water and are insoluble in non-polar benzene, hexane etc.

B. Characterisation

The silver(I) complexes of L(1) are obtained as highly crystalline orange coloured needles. They are stable and can be stored for a long time. They were formulated by elemental analyses (C,H,N) and by estimation of silver (Table IV.1). The results of estimation of Ag^+, as well as C,H,N analyses conclusively suggested that the number of ligands(L) per silver

TABLE IV.1

Analytical Data of $[AgL_2]ClO_4$ and $[CuL_2]ClO_4$

Compound	Formula	%C		%H		%N		%Ag/ %Cu	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Ag(L^1)_2]ClO_4$	$AgC_{22}H_{18}N_6O_4Cl$	46.03	45.58	3.14	3.05	14.65	14.26	18.83	18.90
$[Ag(L^2)_2]ClO_4$	$AgC_{24}H_{22}N_6O_4Cl$	47.88	47.65	3.66	3.55	13.97	13.82	17.96	18.20
$[Ag(L^3)_2]ClO_4$	$AgC_{24}H_{22}N_6O_4Cl$	47.88	47.70	3.66	3.61	13.97	13.82	17.96	18.06
$[Ag(L^4)_2]ClO_4$	$AgC_{22}H_{16}N_6O_4Cl_3$	41.09	40.96	2.49	2.38	13.07	12.95	16.81	16.62
$[Cu(L^2)_2]ClO_4$	$CuC_{24}H_{22}N_6O_4Cl$	51.71	51.55	3.95	3.85	15.08	15.00	11.40	11.25
$[Cu(L^3)_2]ClO_4$	$CuC_{24}H_{22}N_6O_4Cl_2$	51.71	51.60	3.95	3.75	15.08	14.95	11.40	11.26
$[Cu(L^4)_2]ClO_4$	$CuC_{22}H_{16}N_6O_4Cl_3$	44.15	44.05	2.68	2.45	14.05	13.95	10.62	10.38

ion is two. Further confirmation regarding the presence of Ag(I) ion has been made by magnetic susceptibility measurements. The compounds are diamagnetic (d^{10}) in nature. The molar conductance of $[AgL_2]ClO_4$ (2) in methanol (Table IV.2) lies between 105 and 110 $ohm^{-1}cm^2mol^{-1}$, suggesting[39] a 1:1 type of electrolytic nature of the compounds. These results collectively conform to the formulation of the compound as $[AgL_2]ClO_4$.

We have also synthesised the corresponding copper(I) complexes of L(1), $[CuL_2]ClO_4$ ($L=L^1-L^4$) following the procedure described[16] by Datta and Chakravorty. Out of these four complexes, three with ligands L^2-L^4 are new. The analytical results (Table IV.1) and solution molar conductance data (Table IV.2) of the copper(I) complexes, $[CuL_2]ClO_4$ ($L=L^2-L^4$) agree well with their respective composition. A comparison of the infrared spectral data of silver(I) complexes of L with those of corresponding copper(I) complexes have been found to be very useful in the assessment of bonding in Ag(I)-L complexes (vide infra).

C. Bonding and Assessment of Structure

(i) Infrared Spectra. Infrared data were collected in the range 4000-300 cm^{-1} in KBr disc. Characteristic group frequencies are collected in Table IV.3 and a representative spectra for both silver and copper complexes are displayed in Figure IV.1. Some of these bands are found to be useful in identification of the geometry and bonding of the complexes and are considered here. All the complexes show characteristic vibrations[1] due to C=C and

TABLE IV.2

Solution Molar Conductivity Data[a] of complexes $[AgL_2]ClO_4$ and $[CuL_2]ClO_4$ at 298K

Compound	Λ_M $ohm^{-1}cm^2mol^{-1}$
$[Ag(L^1)_2]ClO_4$	105
$[Ag(L^2)_2]ClO_4$	110
$[Ag(L^3)_2]ClO_4$	107
$[Ag(L^4)_2]ClO_4$	108
$[Cu(L^2)_2]ClO_4$	105
$[Cu(L^3)_2]ClO_4$	107
$[Cu(L^4)_2]ClO_4$	106

[a] The solvent used was methanol. Concentrations are *ca*.10^{-3}mol dm^{-3}.

TABLE IV.3

Selected Infrared Spectral Data of free L and Complexes

Compound	$\nu_{max}/(cm^{-1})$[a,b]				
	C=C + C=N	N=N	ClO_4^-	C-H[e]	C-H[f]
L^1 [c]	1590	1425		780[d]	675
$[Cu(L^1)_2]ClO_4$	1590	1375	1100[d],620	780	675
$[Ag(L^1)_2]ClO_4$	1590	1420	1100[d],620	780	675
L^2 [c]	1590	1425		780[d]	675
$[Cu(L^2)_2]ClO_4$	1585	1370	1100[d],620	780	675
$[Ag(L^2)_2]ClO_4$	1585	1420	1100[d],620	780	675
L^3	1600	1425		780[d]	675
$[Cu(L^3)_2]ClO_4$	1600	1375	1100[d],620	780	675
$[Ag(L^3)_2]ClO_4$	1595	1420	1100[d],620	780	675
L^4	1600	1425		780[d]	675
$[Cu(L^4)_2]ClO_4$	1595	1375	1100[d],620	780	675
$[Ag(L^4)_2]ClO_4$	1595	1420	1100[d],620	780	675

[a] Unless otherwise stated, spectra were recorded in KBr disc (4000-200 cm^{-1}). [b] All bands are sharp and strong unless otherwise stated. [c] Spectra were recorded in neat. [d] Broad. [e] Out-of-plane bending in pyridine ring. [f] Out-of-plane bending in phenyl ring.

C=N and vibration of the aromatic rings (Table IV.3). The broad structureless band, νClO_4^-, at *ca.* 1100 cm^{-1} suggests the lack of significant perchlorate coordination[40] in the solid state. Our main objective in studying the IR spectra of silver(I) complexes of 2-(arylazo) pyridines were to study the $\nu_{N=N}$ mode. In general, the N=N stretching mode appears[1] near 1420 cm^{-1} when conjugated and asymmetric[41] (IR allowed). The position of this band in our complexes was identified by comparison of the IR spectra of $[AgL_2]^+$ with those of $[CuL_2]^+$ (Table IV.3) and free L (Table IV.3). A strong absorption of free L (Figure IV.2) was observed at 1425 cm^{-1} which has been assigned[1] to $\nu_{N=N}$. We anticipated $\nu_{N=N}$ in $[AgL_2]^+$ below this region. Interestingly, the vibrational spectra of $[AgL_2]^+$ and the corresponding $[CuL_2]^+$ are nearly superimposable except for a single frequency shift from 1420 to 1375 cm^{-1} (Figure IV.1). The band at 1375 cm^{-1} in $[CuL_2]^+$ has been assigned[16] to $\nu_{N=N}$. Evidently, the band at 1420 cm^{-1} in $[AgL_2]^+$ is also due to $\nu_{N=N}$. The ability of L to act as a strong π-acceptor towards electron rich metal centres are well documented and the diagnostic test[1-15] for this interaction is the shift of $\nu_{N=N}$ to lower frequencies in moving from free L to its complex. The behaviour of $[CuL_2]^+$ is similar to those with other electron-rich metal ions like Fe(II),Ru(II),[2,5,11] Os(II)[3,8] There is a substantial $d\pi(M) \longrightarrow \pi^*(L)$ bonding through an azo nitrogen in all the cases cited above. The small shift of $\nu_{N=N}$ in $[AgL_2]^+$ suggests that the $d\pi-\pi^*(L)$ interaction in the present silver(I) complexes are weak. This is similar to the bonding pattern in other silver(I) complexes with π-acid ligand having phosphorous and sulphur

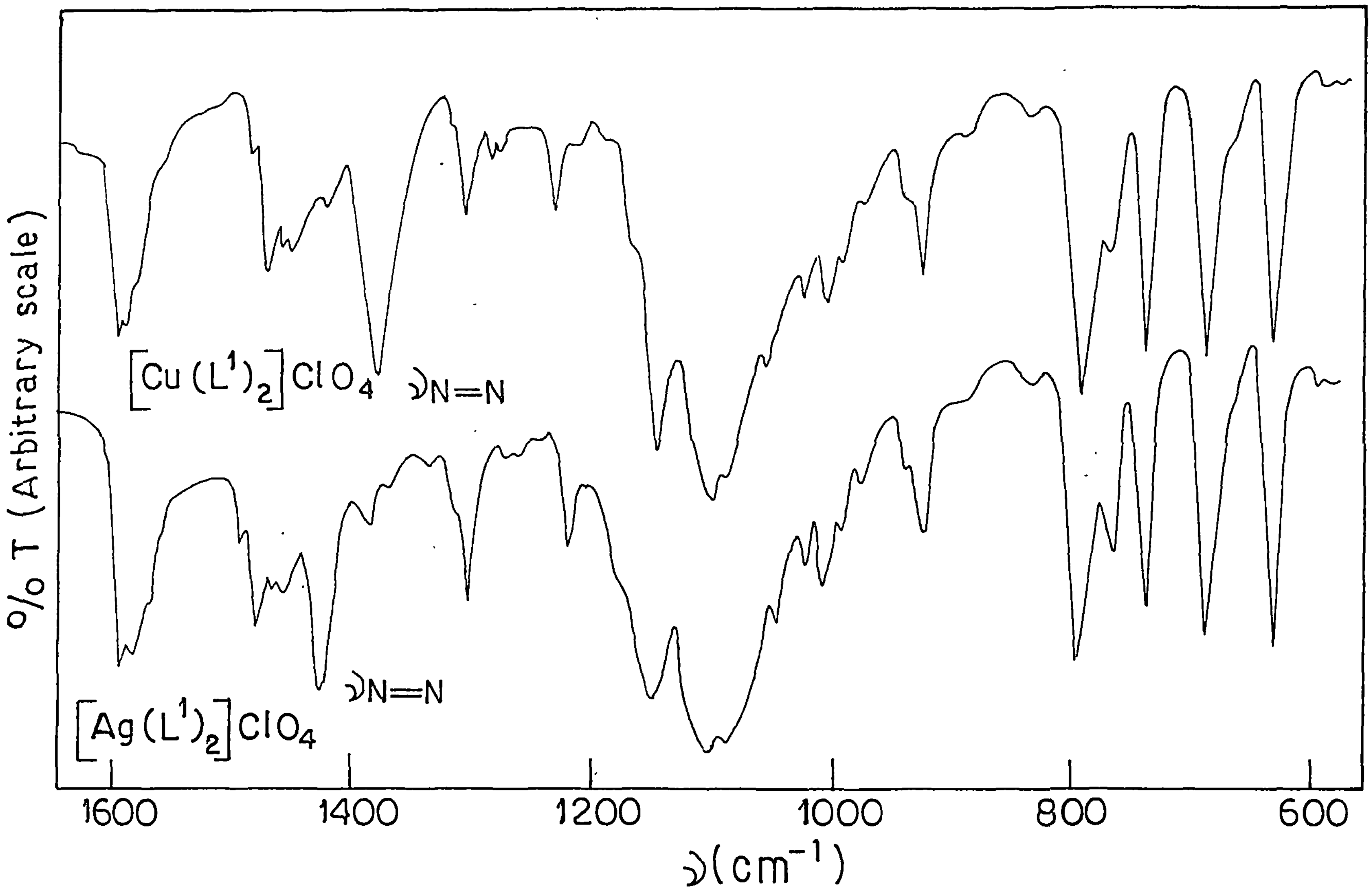


FIGURE IV.1. INFRARED SPECTRA IN KBr DISC

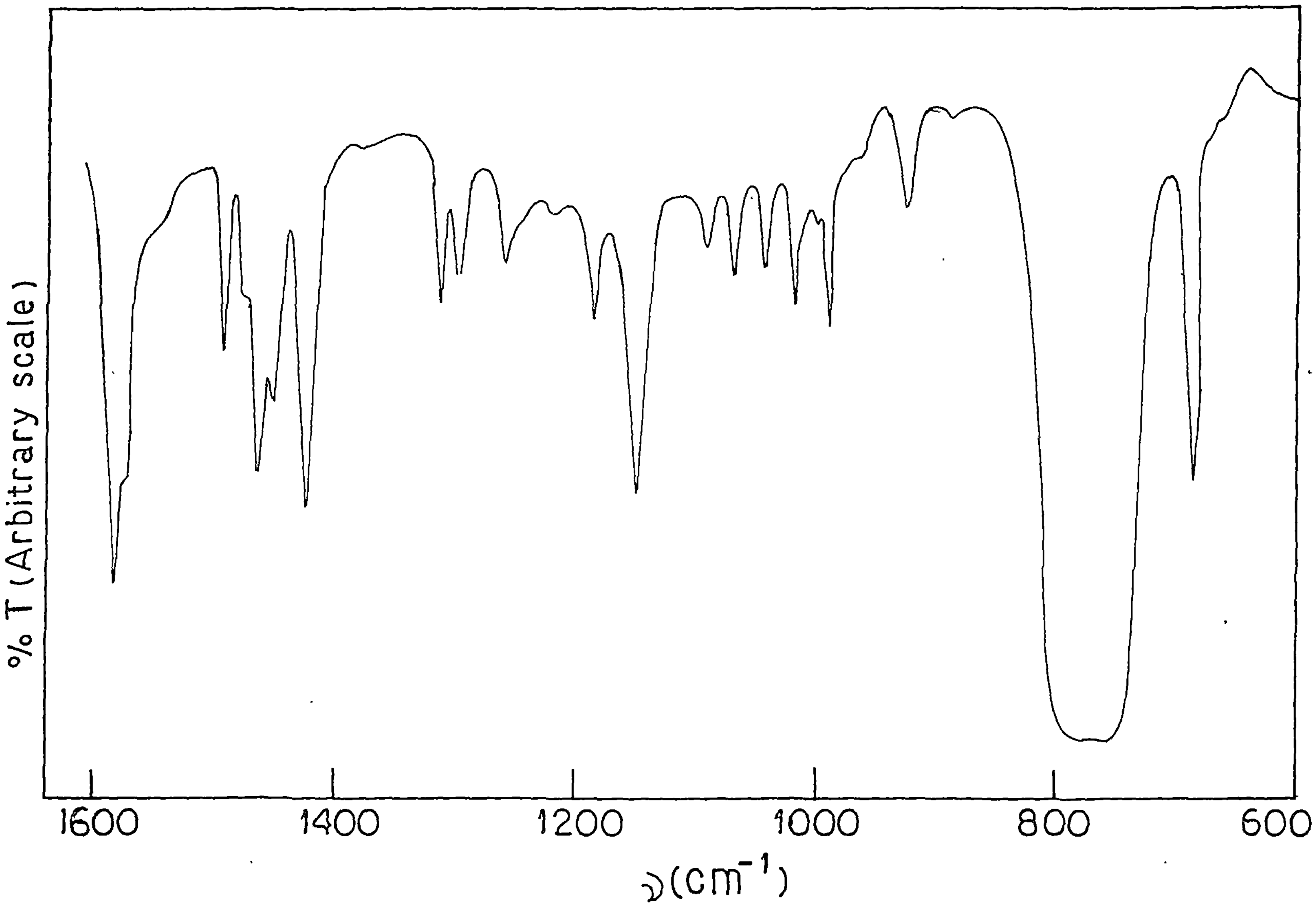
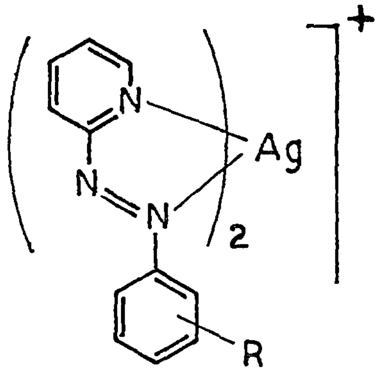


FIGURE IV.2. INFRARED SPECTRUM OF L^1 IN NEAT donors. Near superimposability of the IR spectra of $[AgL_2]^+$ on those of $[CuL_2]^+$ suggests that like $[CuL_2]^+$, the gross stereochemistry of $[AgL_2]^+$ is tetrahedral.



2

(ii) Electronic Spectra. The electronic spectral data of the solutions of $[AgL_2]^+$ in both chloroform and methanol in the visible region are collected in Table IV.4 and a representative spectrum is displayed in Figure IV.3. The electronic spectra of the solutions of 2 were studied mainly to assess their stabilities in two solvents viz. chloroform and methanol, in the visible region. Free L displays absorption band at *ca.* 440 nm which has been assigned[1] to $n \longrightarrow \pi^*$ transitions centered primarily on the azo group. The small bathochromic shift of the absorption maximum to *ca.* 455 nm in the silver complexes compared to that of free L indicates a weak interaction between N^2 and Ag^+. Further, it is to be noted that this shift is more in case of methanol compared to chloroform (Figure IV.3) indicating that,

TABLE IV.4

Solution Electronic Spectral Data[a] of $[AgL_2]ClO_4$ and $[CuL_2]ClO_4$ at 298K in the Visible Region

Compound	Solvent	λ_{max}/nm(ε/dm^{3}mol^{-1}cm^{-1})
$[Ag(L^1)_2]ClO_4$	$CHCl_3$	448(935)
	MeOH	462(990)
$[Ag(L^2)_2]ClO_4$	$CHCl_3$	457(720)
	MeOH	462(825)
$[Ag(L^3)_2]ClO_4$	$CHCl_3$	450(875)
	MeOH	455(1010)
$[Ag(L^4)_2]ClO_4$	$CHCl_3$	455(765)
	MeOH	458(830)
$[Cu(L^2)_2]ClO_4$	MeOH	700(1570),560(5625)
$[Cu(L^3)_2]ClO_4$	MeOH	700(1480),560(5530)
$[Cu(L^4)_2]ClO_4$	MeOH	700(1415),560(5262)

[a] Solute concentrations *ca.* 10^{-3}mol dm^{-3}.

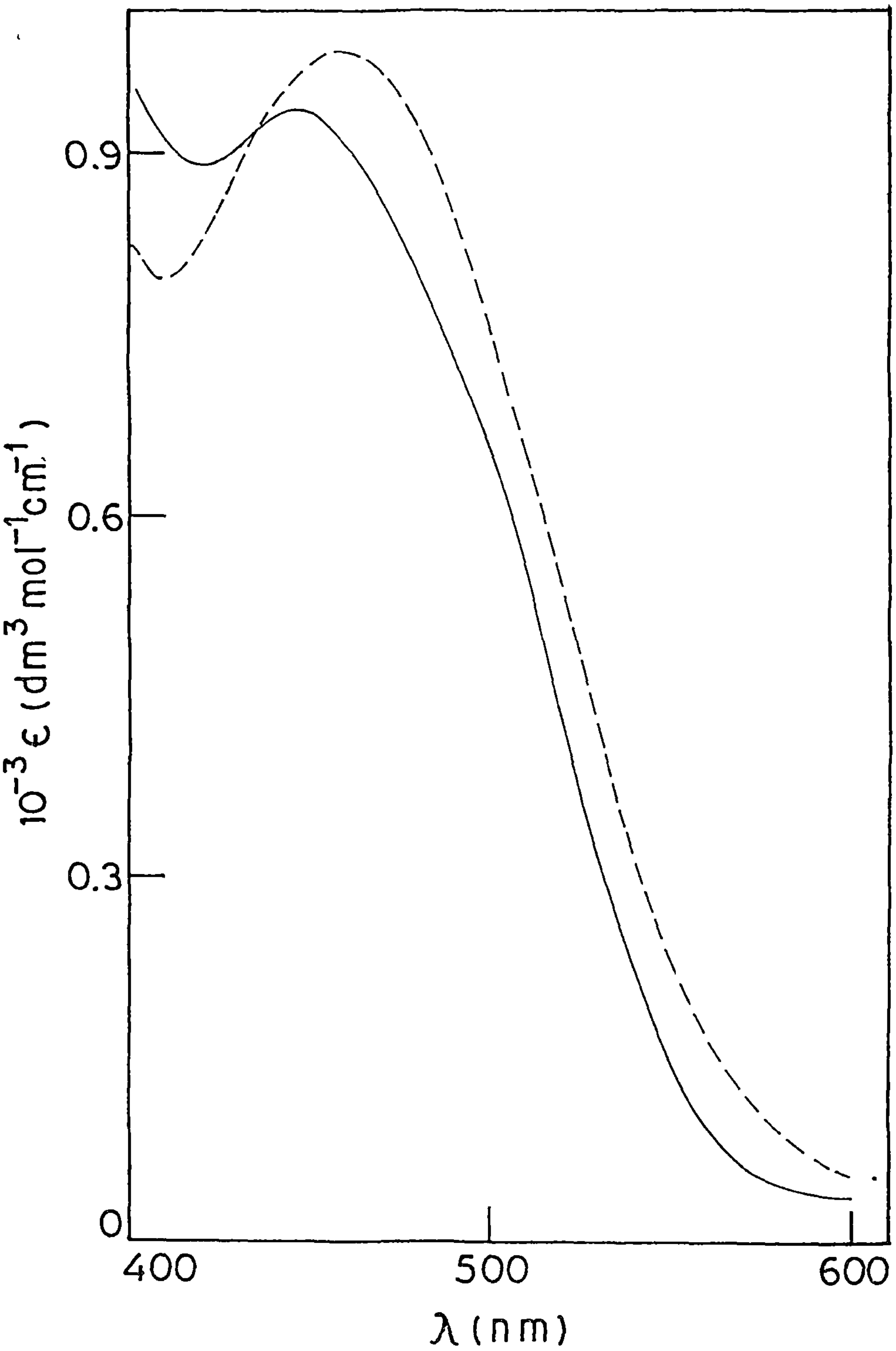


FIGURE IV.3. ELECTRONIC SPECTRUM OF $[Ag(L^1)_2]ClO_4$ (———) IN $CHCl_3$ AND (--------) IN CH_3OH

the interaction of nonbonding electrons is more in the polar solvent. Thus, the electronic spectral data indicate weak interaction between N^2 and Ag^+ which is well consistent with the IR data (vide supra).

The stability of silver complexes in chloroform, methanol and acetonitrile have been verified by Beer's law. The intensity of the band at *ca*.450 nm ($CHCl_3$) and *ca*.460 nm (CH_3OH) does not change with dilution and a plot of absorbance, A, versus concentration, C along abcissa and ordinate respectively gives a straight line passing through origin, the slope of which gives the value of molar extinction coefficient, ε (Figure IV.4). Hence Beer's law is verified and $[AgL_2]^+$ is stable in these solvents. Unlike chloroform and methanol, the complexes, $[AgL_2]^+$ do not obey Beer's law in acetonitrile indicating their instability in acetonitrile.

As in the case of previously reported[16] $[Cu(L^1)_2]ClO_4$, the newly synthesised copper(I) complexes, $[CuL_2]ClO_4$ $[L=L^2-L^4]$ show low energy metal-to-ligand charge transfer transitions (MLCT) at 700 and 560 nm (Table IV.4, Figure IV.5) in methanol due to $t_2(Cu) \longrightarrow \pi^*(L)$ excitation where $\pi^*(L)$ is LUMO of the azoimine chromophore.

(iii) **^1H NMR Spectra.** The proton NMR data in $CDCl_3$ of the complexes 2 are summarised in Table IV.5. Different protons are numbered as shown below.

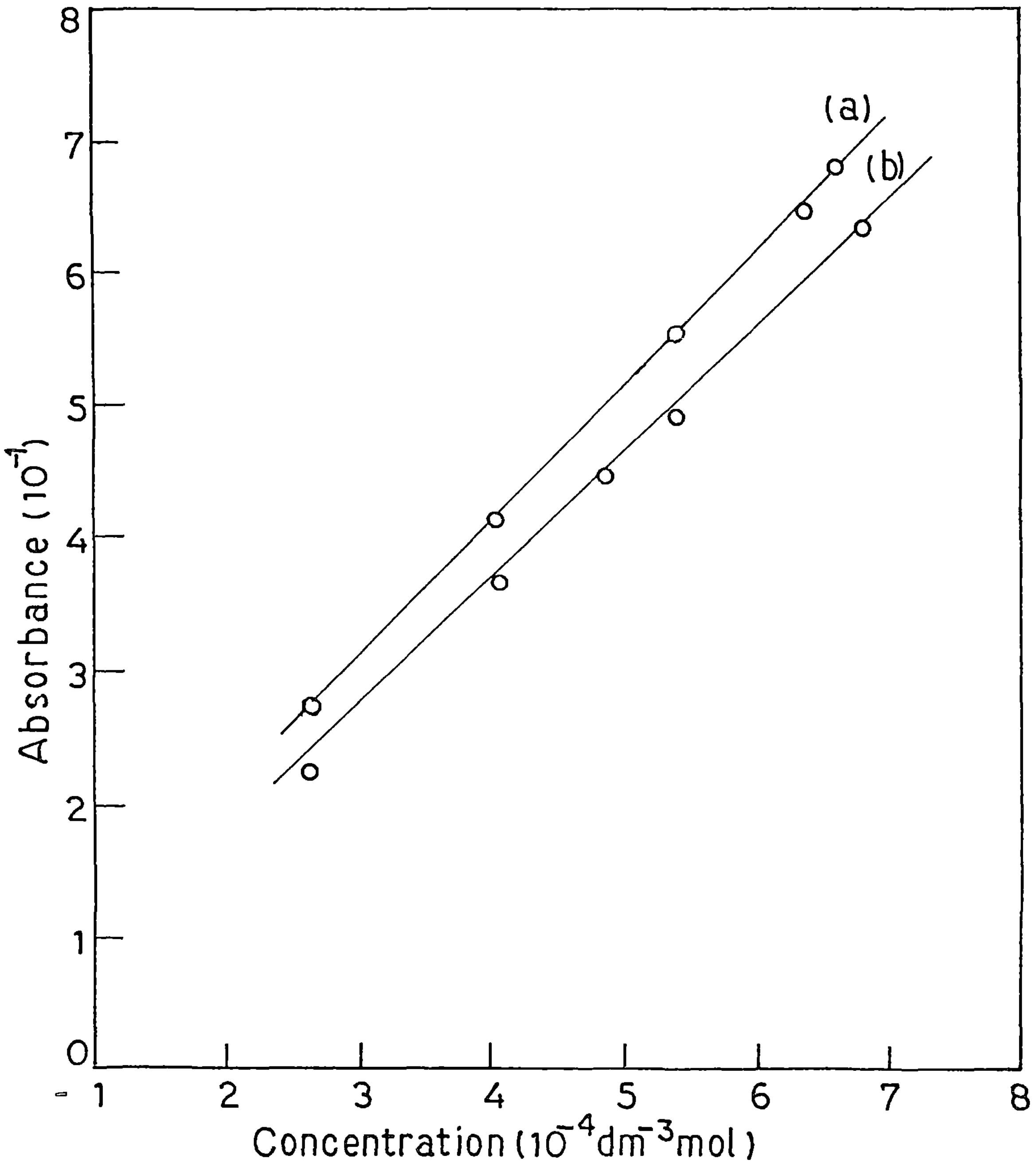


FIGURE IV.4. VERIFICATION OF BEER'S LAW IN CASE OF $[Ag(L^1)_2]ClO_4$:

(a) IN CH_3OH AT 462 nm

(b) IN $CHCl_3$ AT 448 nm

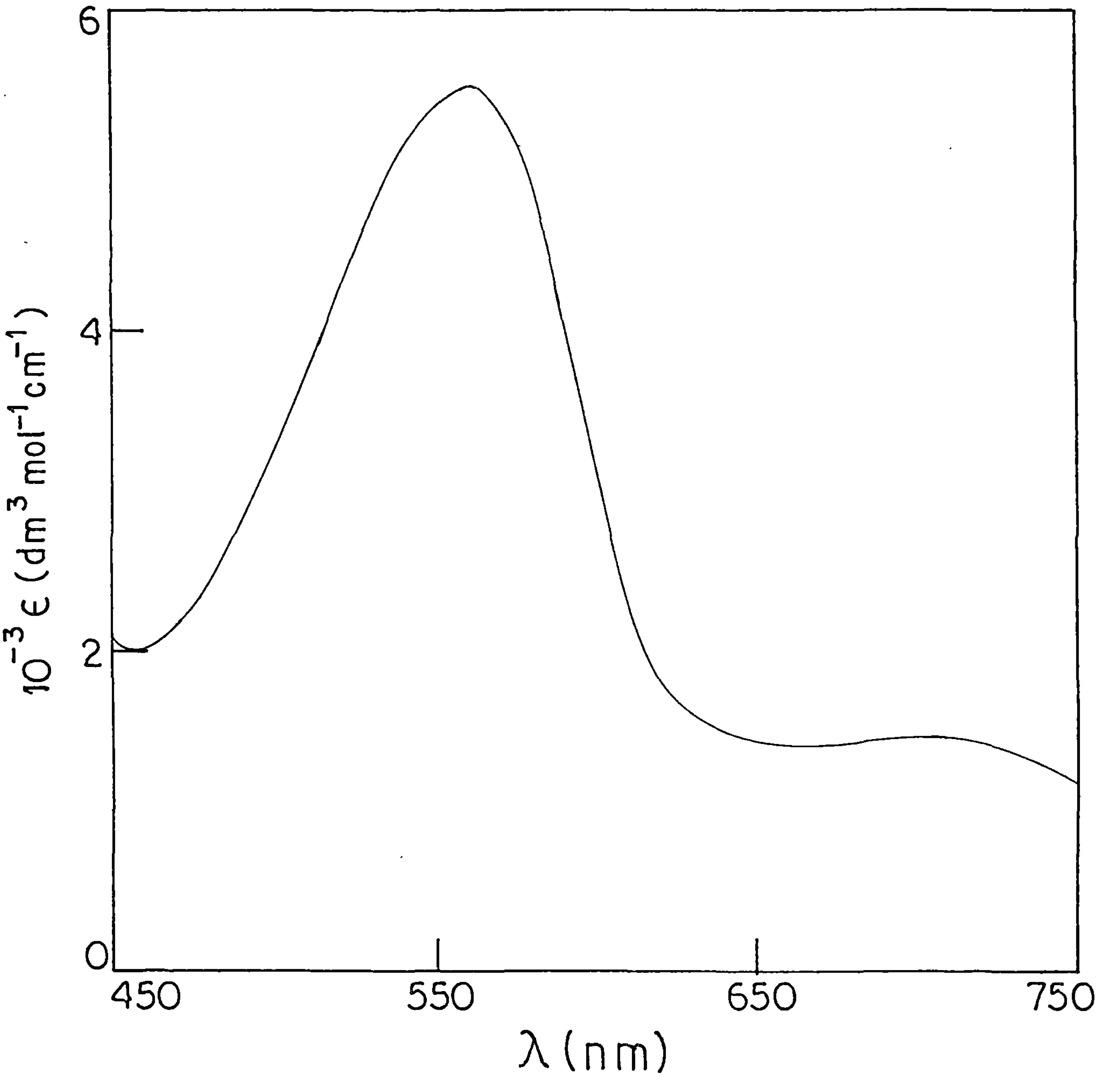


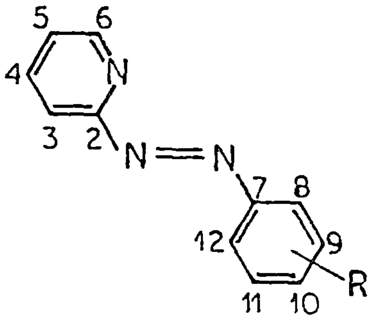
FIGURE IV.5. ELECTRONIC SPECTRUM OF [$Cu(L^3)_2$] ClO_4 IN CH_3OH

TABLES IV.5

^{1}H NMR[a] Spectral data of $[AgL_2]ClO_4$[b]

Compound	δ/ppm										
	6-H	5-H	4-H	3-H	12-H	11-H	10-H	9-H	8-H	9-Me	10-Me
$[Ag(L^1)_2]ClO_4$	8.86	7.85	8.30	8.35	7.83	7.34-7.46	7.34-7.46	7.34-7.46	7.83		
$[Ag(L^2)_2]ClO_4$	8.90	7.63-7.80	8.25	8.30	7.63-7.80	7.26	7.30		7.83-7.80	2.25	
$[Ag(L^3)_2]ClO_4$	8.78	7.71-7.81	8.23	8.30	7.71-7.81	7.18		7.18	7.71-7.81		2.35

[a] In $CDCl_3$ using $SiMe_4$ as internal Standard. [b] Solubility of $[Ag(L^4)_2]ClO_4$ in $CDCl_3$ is low, a resolved spectrum could not be obtained.



L

All the complexes display well resolved ^1H NMR spectra. Representative spectrum is shown in Figure IV.6. The assignments of individual pyridyl ring proton signals were made[14,42-44] on the basis of their chemical shifts and also by examining the spin-spin splitting patterns of the signals. Thus, the signal due to 6-H and 3-H appear as doublets, whereas 5-H and 4-H are triplets in all these complexes. The pyridyl proton signals shift, in general, slightly downfield in these complexes. The chemical shifts of the pyridyl protons of $[AgL_2]^+$ complexes are in the order : $\delta_{6-H} > \delta_{3-H} > \delta_{4-H} > \delta_{5-H}$. Large downfield shifts of the 5-H and 6-H protons in moving from free L to the coordinated L also have been observed. In fact, this is a common feature of the ^1H NMR spectra[44] of the transition metal complexes of L. The signals due to individual aryl protons were also assigned on a similar basis using substituent induced change in splitting patterns and chemical shifts as additional indicators. For examples, 8-H and 12-H signals appear as coincident doublets in the complexes of L^1 and L^3, as expected. The 8-H signal of the corresponding L^2 complex should appear as a separate singlet. Unfortunately, the assignment of the 8-H proton in $[Ag(L^2)_2]^+$ has not been achieved so far because of serious overlap with other signals. Similarly, 9-H and 11-H are equivalent to each other in

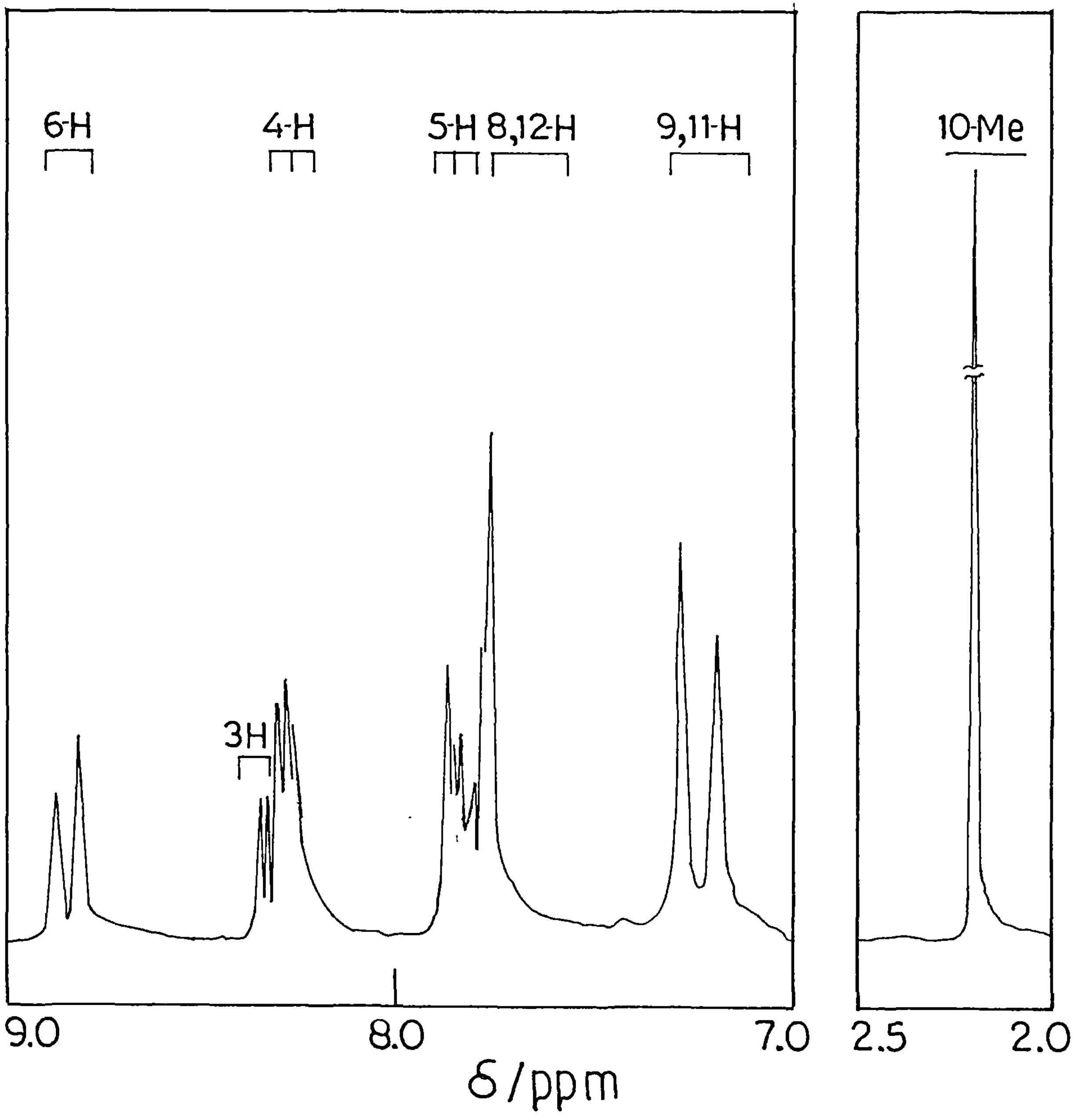


FIGURE IV.6. ^{1}H NMR SPECTRUM OF $[Ag(L^3)_2]ClO_4$ IN $CDCl_3$

$[Ag(L^1)_2]^+$ and appear as triplet whereas in $[Ag(L^3)_2]^+$ these appear as doublets. Further, the 8-H signals are very significantly shifted to higher field in going from L^1 to corresponding L^2 and L^3 complexes in accordance with the electron releasing character of the methyl substituent.

The compounds $[Ag(L^2)_2]^+$ and $[Ag(L^3)_2]^+$ also show a sharp single methyl signal each at 2.25 and 2.35 ppm respectively. It may be noted here that like the methyl protons, all the aromatic protons exhibited only one signal for each proton. From this data it is very likely that both the chelate rings in $[AgL_2]^+$ are magnetically equivalent at least in the NMR time scale and the complexes contain an effective C_2-axis, which is also in agreement with the proposed tetrahedral structure of the complexes.

Conclusion

It is demonstrated that 2-(arylazo)pyridine ligands display high affinity towards silver(I). Stable, tetracoordinated, bis-chelated complexes of the type $[AgL_2]^+$ are isolated and thoroughly characterised with the help of spectroscopic data. We wish to note here that the examples of stable, monomeric tetracoordinated silver(I) complexes are rare. The ease with which L reacts with silver and the stability of the resultant bis complexes, even in solutions, are unprecedented for an α-diimine nitrogen chelating ligand.

IV.3 EXPERIMENTAL SECTION

A. Physical Measurements

Melting Point Measurements, Molar Conductivity, Infrared Spectra, Electronic Spectra, ^{1}H NMR Spectra and Magnetic Susceptibility Measurements

All described in Chapter II.

Beer's Law verification of the solutions of $[Ag(L^1)_2]ClO_4$ have been made spectrophotometrically using the various concentrations(C) as given below. The molar absorbance(A) values are given in parentheses. A plot of A versus concentration C is displayed in Figure IV.4.

(i) MeOH : 2.6678×10^{-4} (0.275), 4.0017×10^{-4} (0.419), 5.3357×10^{-4} (0.563), 6.2694×10^{-4} (0.650) and 6.6696×10^{-4} (0.662) mol dm^{-3} at λ_{max} 462 nm.

(ii) $CHCl_3$: 2.7027×10^{-4}(0.225), 4.0541×10^{-4} (0.366),4.8649×10^{-4} (0.448), 5.4054×10^{-4} (0.482) and 6.7568×10^{-4} (0.632)mol dm^{-3} (0.632) at λ_{max} 448 nm.

B. Formulation of Compounds

Complexes were formulated on the basis of the results of C,H,N microanalyses as described in chapter II and also by chemical analyses of silver and copper. Silver was estimated gravimetrically by precipitating as silver chloride. Copper was estimated volumetrically by titrating against a standard solution of sodium thiosulphate. The detail procedure for estimation of each of silver and copper are given below.

[AgL$_2$]ClO$_4$. A known weight (0.400 mmol) of the compound was taken in a 500 ml conical flask and it was digested thrice with a mixture of an equal volume of 10 M nitric acid and 10 M perchloric acid (3x10 ml). The colourless residue thus obtained was cooled and extracted four times with distilled water (4x50 ml) and filtered. To the filtrate 0.2 N HCl was added with stirring till the precipitation of AgCl is completed. The precipitate was allowed to settle in dark for 2h. It was then filtered through weighed G-4 sintered glass funnel. It was washed thoroughly with distilled water until free from chloride. The precipitate was first dried at 100°C and then at 130-150°C. It was cooled in a desiccator and weighed as AgCl to a constant weight.

[CuL$_2$]ClO$_4$. A known weight (0.400 mmol) of the compound was taken in a 500 ml conical flask. It was then digested thrice with a mixture of equal volume of 10M nitric acid and 10M perchloric acid (3x10ml). The colourless residue thus obtained was again digested with 10 ml of 10M nitric acid. The dried residue was dissolved in distilled water and the volume was made upto 100 ml in a volumetric flask. 10 ml of this solution was pipetted out in a 250 ml conical flask and 1g of solid KI was added. The liberated iodine was titrated with standard (*ca*.0.1N) sodium thiosulphate solution. Percentage of copper is calculated as,

1 ml of N $Na_2S_2O_3$ = 0.06354 g.Cu

C. Solvents

Commercial methanol was distilled and used for preparative work. Spectrograde acetonitrile, chloroform and methanol was used for spectral and molar conductance measurements. Distilled water was used for analytical work. Besides any other solvents used for preparative work are referred in Chapter II.

D. Preparation of Compounds

(a) Chemicals

The chemicals and their sources are as follows: The chemicals required for preparation of ligands and their sources are given in chapter II. *p*-Chloronitrobenzene, British Drug House, Bombay; Silver nitrate, Glaxo Laboratories, Bombay; Copper carbonate, S.d fine chemicals, Boisar. Phosphorous pentoxide, silica gel (60-120 mesh) etc., sources of which are given in Chapter II.

(b) Sodium perchlorate, $NaClO_4$.

As described in chapter II.

(c) Copper(II)perchlorate Hexahydrate, $Cu(ClO_4)_2.6H_2O$

(Caution! All perchlorate salts of metal are potentially explosive. Adequate care must be taken while handling the perchlorates).

Same as $NaClO_4$ except for 10g $CuCO_3$ was taken instead of Na_2CO_3. The compound was obtained in blue crystalline nature.
Yield : Quantitative.

(d) Ligands[45-46]

Preparations of 2-(phenylazo)pyridine (L^1), 2-(*m*-tolylazo)pyridine (L^2) and 2-(*p*-tolylazo)pyridine (L^3) were described in chapter II. The additional ligand, 2-(*p*-chlorophenylazo)pyridine (L^4) used in this chapter was prepared similarly as L^1 using *p*-chloronitrosobenzene instead of nitrosobenzene.

(e) Complexes

(i) Bis[2-(phenylazo)pyridine]silver(I) perchlorate, $[Ag(L^1)_2]ClO_4$. A sample of $AgNO_3$ (0.170g, 1 mmol) in methanol (10 ml) was heated to reflux for 10 min, and to it a solution of L^1 (0.365g, 2 mmol) in methanol (10 ml) was added. The mixture was further heated to reflux for 3h. The reddish brown solution was then cooled and filtered through a G-4 sintered glass funnel. To the cooled filtrate a solution of aqueous $NaClO_4$ (*ca.* 2g in 10 ml of water) was added with constant stirring. A dark coloured compound precipitated and was collected by filtration and washed thoroughly with water. Recrystallisation of the compound from methanol - water (1:1) yielded a highly crystalline, dark brown product which was dried *in vacuo* over P_4O_{10}. Yield 0.46g (80%).

Bis[2-(*m*-tolylazo)pyridine]silver(I) perchlorate, $[Ag(L^2)_2]ClO_4$; bis[2-(*p*-tolylazo)pyridine]silver(I) perchlorate, $[Ag(L^3)_2]ClO_4$; and bis[2-(*p*-chlorophenylazo)pyridine]silver(I) perchlorate, $[Ag(L^4)_2]ClO_4$. These were prepared similarly using the appropriate ligand.

$[Ag(L^2)_2]ClO_4$: Yield, 95%

$[Ag(L^3)_2]ClO_4$: Yield, 80%

$[Ag(L^4)_2]ClO_4$: Yield, 80%

(ii) Bis[2-(arylazo)pyridine]copper(I)perchlorate, $[CuL_2]ClO_4$ (L = L^2-L^4). These were prepared from $Cu(ClO_4)_2.6H_2O$ and appropriate L by following the method described by Datta and Chakravorty[16] for $[Cu(L^1)_2]ClO_4$. Specific details are given for $[Cu(L^2)_2]ClO_4$.

The ligand L^2 (0.75g, 3.80 mmol) was added dropwise to 0.71g (1.90 mmol) of $Cu(ClO_4)_2.6H_2O$ dissolved in 300 ml of 2:1 methanol - water mixture. The mixture was heated to reflux for 48h. The violet solution was then evaporated on a water bath to 10 ml. The gummy mass thus obtained was washed thoroughly with 100 ml water. The mass was then recrystallised from methanol when red violet crystals of $[Cu(L^2)_2]ClO_4$ deposited. These were collected by filtration and then dried *in vacuo* over P_4O_{10}; Yield, 0.64g (60%). Yields of the other complexes are as follows.

$[Cu(L^3)_2]ClO_4$: Yield, 55%

$[Cu(L^4)_2]ClO_4$: Yield, 60%

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Chapter V

CHAPTER V

USE OF SILVER(I) COMPLEXES IN SYNTHESIS. NOVEL AND GENERALISED SYNTHETIC ROUTES TO BIS AND TRIS 2-(ARYLAZO)-PYRIDINE COMPLEXES OF RUTHENIUM(II) AND INVESTIGATION OF SOLID-STATE ISOMERISATION*

Abstract: *Efficient, new and direct synthetic routes to isomeric* $[RuCl_2L_2]$ *and* $[RuL_3](ClO_4)_2.H_2O$ *[L=2-(arylazo)pyridines] complexes, based on the reaction of hydrated* $RuCl_3$ *and* $[AgL_2]ClO_4$*, have been elaborated. The identity of the compounds were established from elemental analyses and spectral data. The advantages of the new methods are highlighted. Solid-state isomerisation of the dichloride complexes has been studied by different thermal methods. It is shown that two (trans, trans and cis, cis) out of the three isomers of* $[RuCl_2L_2]$ *are converted into the third (trans, cis) isomer on heating. Analyses of differential scanning calorimetry data reveal that the thermal isomerisation reactions proceed through a similar intermediate. The relative thermal stabilities of the different isomers of* $[RuCl_2L_2]$ *are also briefly noted.*

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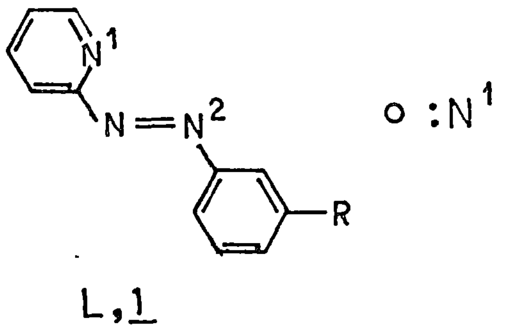
*A part of this work has appeared in *J. Chem. Soc., Dalton, Trans.*, 1991, 3249.

V.1 INTRODUCTION

The ruthenium chemistry of 2-(arylazo)pyridine(L,1) ligands have been an area of considerable interest.[1-11] The reason for this is primarily due to the relevance of this chemistry to catalysis[3], isomerisation[2,9,11] and redox phenomena.[4,5] Quite a number of Ru-L complexes are now known, however, there is no simple and direct synthetic route to such compounds. In general, the dichlorobischelate, $[RuCl_2L_2]$, which is the source material for the synthesis of other Ru-L complexes, is obtained by the reaction of L either with hydrated $RuCl_3$[1] or $[RuCl_2(dmso)_4]$[9] (dmso=dimethylsulphoxide). The existing recommended methods for the synthesis of $[RuCl_2L_2]$ require prolong boiling which leads to isomerisation in most of the reactions. Moreover, there is no direct synthetic method available for the tris complex, $[RuL_3]^{2+}$. It involves[5,9] several steps, which makes the synthesis not only cumbersome but also lengthy. Therefore, there is an obvious need of developing new and direct procedures, those may be of general application, for the synthesis of the title compounds.

The primary goal of this chapter is to report single-pot, high yield synthesis of ruthenium bis and tris chelated compounds of L from $RuCl_3.3H_2O$ with the use of $[AgL_2]ClO_4$. Synthesis and characteristion of the bis chelated silver(I) compounds $[AgL_2]ClO_4$ have been discussed in the previous chapter (Chapter IV). The advantages of our new methods over the existing synthetic procedures are highlighted. Another purpose of this chapter is to study and investigate solid phase thermal isomerisation reactions.[12] These have been followed by

Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) experiments. The dichloride complexes, [$RuCl_2L_2$] are known to isomerise either on heating[9] in high boiling solvents or on nucleophilic substitution reactions.[2,10] Until date, no information as regards the isomerisation of the compounds in the solid state are available. In this chapter we also report the solid state isomeric transformations of a bis ligated ruthenium(II) compound, [$RuCl_2L_2$]. More importantly, the high stereospecificity of the solid state isomerisation reactions in the present case makes the synthesis of a *cis* isomer more simple, fast and straight forward. The two ligands, *viz.* 2-(phenylazo)pyridine, (L^1) and 2-(m-tolylazo)-pyridine, (L^2) have been used for the present study.



L,1

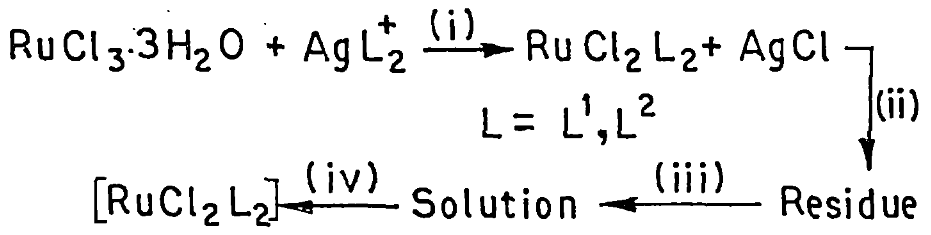
R = H : L^1

R = Me : L^2

V.2 RESULTS AND DISCUSSION

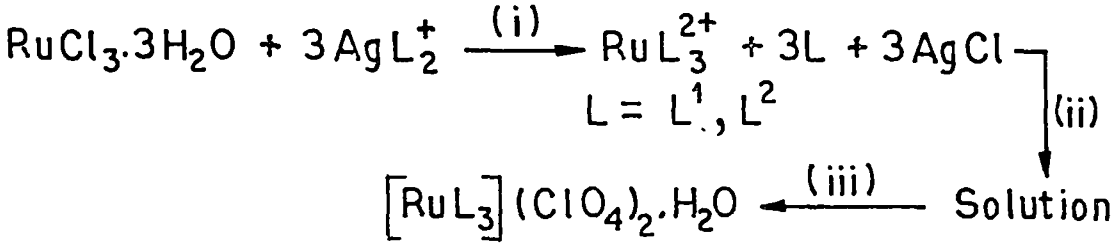
A. Metal Exchange Reaction. Use of Ag-L Complex in Synthesis

Reactions which are studied are shown in Schemes 1-3. In the preceeding chapter (Chapter IV) we have discussed the synthesis of high yield,stable monomeric tetracoordinated silver(I) complexes of L. It is now been possible for us to demonstrate that the newly synthesised silver compound, $[AgL_2]ClO_4$ can be used as a versatile synthone to provide access to Ru-L complexes either from ruthenium trichloride or from the dichlorobis ligated ruthenium complexes. The direct synthesis of bis and tris coordinated Ru-L complexes from $RuCl_3.3H_2O$, as evidenced by Schemes 1 and 2 and that of tris Ru-L complexes from $[RuCl_2L_2]$ (Scheme-3), require stepwise removal of Cl^- followed by coordination of L to the metal centre. Thus, it was anticipated that interaction of either hydrated $RuCl_3$ or $[RuCl_2L_2]$ and $[AgL_2]^+$ in right proportion might lead directly to the desired compound. Accordingly, in line with the synthetic strategy, the reactions stated in the Schemes (1-3) were undertaken, which underwent smoothly to directly to bis and *tris* chelated ruthenium complexes of L. In the reactions stated in the Schemes, the compound $[AgL_2]^+$ not only acts as a source of Ag^+ —— required for a facile halide displacement reaction but also supply required amount of L for the formation of complex of desired composition. It is believed that the reduction of metal centre in each of the reactions (Schemes 1 and 2) are done[1] by the reducing solvent. The *tris* chelates are isolated as their perchlorate salts. The dichlorobischelates, which are sparingly



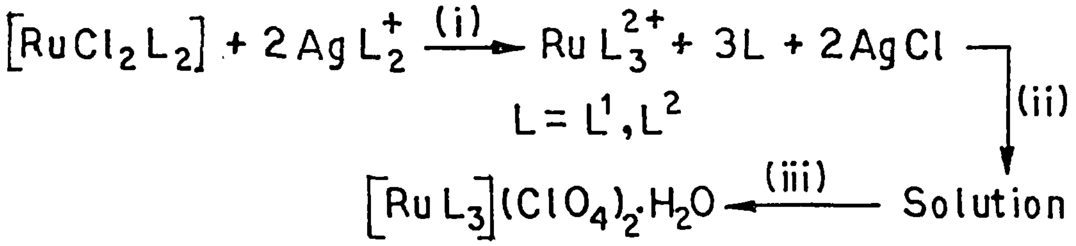
Key: (i) MeOH, Heat; (ii) Filtration; (iii) $CHCl_3$
(iv) Filtration, Hexane

Scheme 1



Key: (i) MeOH, Heat; (ii) Filtration; (iii) Aqueous solution of $NaClO_4$

Scheme 2



Key: (i) MeOH, Heat (ii) Filtration; (iii) Aqueous solution of $NaClO_4$

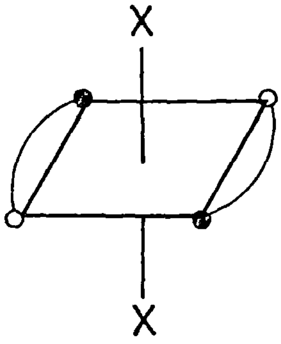
Scheme 3

soluble in methanol, precipitate from the reaction mixture on cooling. In all the cases the compounds are isolated in high yields ca.70%. It may be noted here that excess L could be recovered from the reaction mixtures. The reaction of $[RuCl_2L_2]$ and $[AgL_2]^+$ in boiling methanol (Scheme 3) occurs even at a much faster rate compared to the reaction described in Scheme 2. The yields are almost quantitative (*ca.*90%). It may be noted here that the optimum ratio of the reagents required for the said reaction is $[MCl_2L_2]:[AgL_2]^+$ is 1:2, as expected. We find that this route (Scheme 3) has been particularly useful in synthesising the mixed ligand *tris* complexes. For example, $[RuCl_2(L^1)_2]$ reacts smoothly with $[Ag(L^2)_2]^+$ in 1:2 molar proportion to yield cationic $[Ru(L^1)_2(L^2)]^{2+}$ which is isolated as perchlorate salt. Whereas the standard procedure for the mixed ligand *tris* complex involves a series of consecutive steps starting from metal chloride salt. The mixed ligand *tris* complex *viz.* $[Ru(L^1)(L^2)_2](ClO_4)_2.H_2O$ was also similarly isolated by reacting $[RuCl_2(L^2)_2]$ and $[Ag(L^1)_2]^+$ in 1:2 molar proportion.

The routes of preparation of Ru-L complexes, described above, are straight forward and much more convenient over those reported previously. The existing method for the synthesis of both $[RuL_3]^+$ and $[RuCl_2L_2]$ involve several steps which are not only time consuming but also require extra purification in every steps to remove other contaminated products. The reported preparative routes to bischelates, $[RuCl_2L_2]$, require boiling the reaction mixture for a long time, which invariably leads to isomeric transformations. On the other hand, the synthetic methods developed by us are single step, quite fast, produce compounds of desired composition in high yields and are experimentally facile. Moreover, in the newly adopted methods, the composition of the products can be monitored just by varying the stoichiometric ratio of the reactants. In most of the cases recrystallisation, alone, produce isomerically pure compounds. It may be further noted here that this class of metal exchange reaction has its wide applicability[13] in the synthesis of organo element compounds. To the best of our knowledge, this route has not be explored so far for the synthesis of transition metal compound containing azoimine ligands. The success of this method lies on the facts that in solution $[AgL_2]^+$ complexes are not very stable and Ag^+ has a very high affinity towards Cl^- to form insoluble AgCl, which can easily be removed from the reaction mixture.

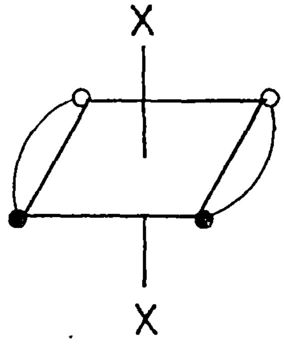
B. Separation and Identification of Isomers

(i) $RuCl_2L_2$: Due to unsymmetrical bidentate nature of L, the dihalobis complexes of type $[RuX_2L_2]$ (X=Cl,Br,I) can in principle exist in five geometrical isomeric forms[1,9,11] (2 - 6). Out of these, two (2-3) have *trans* RuX_2 orientation whereas the other three (4-6) have *cis*-RuX_2. Considering the coordinated atoms in three pairs, *viz*. X, X, N^1, N^1 and N^2, N^2 the isomers are *trans, trans, trans* (*ttt*),(2); *trans, cis, cis*(*tcc*),(3); *cis, trans, cis*(*ctc*), 4; *cis, cis, trans* (*cct*), (5) and *cis, cis, cis*(*ccc*),(6) respectively. It is, however, sufficient to define the relative positions in the N^1, N^1 and N^2, N^2 pairs since the remaining two positions are automatically fixed once the RuL_2 stereochemistry is fixed. Thus, the shorter isomer description, for example, *ttt* is designated as *tt*, and similarly *ccc* as *cc* and



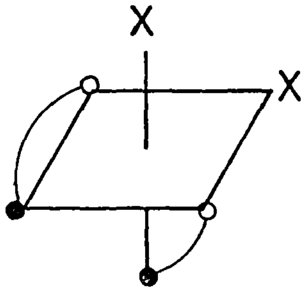
ttt, C_{2h}

2



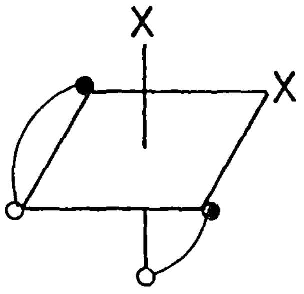
tcc, C_{2v}

3



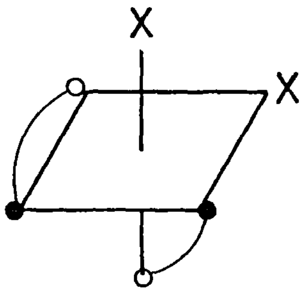
ctc, C_2

4



cct, C_2

5



ccc, C_1

6

so on. Idealised point group descriptions are 2, C_{2h}; 3, C_{2v}; 4, C_2; 5, C_2 and 6, C_1. Of the five possible isomers three have been isolated so far and their structure proven by spectroscopic and X-ray techniques.[14] These isomers are *tt* (2); *tc* (4) and *cc*, (6). Till date no evidence exists for the occurrence of the other two isomers. Reaction stated in Scheme I when carried out at ca.40°C for 15 min. yielded 60-65% 2, 5-8% 4 and 5-10% 6. Purification and isolation of the isomers are done either by solvent extraction or on a silica gel column using $CHCl_3$-CH_3CN mixture as eluent. The analytical results of the complexes thus obtained are quite satisfactory (Table V.1). Spectral data of the compounds are in order[1,4,9] (Table V.2). The geometries of the products are identified by comparing their spectral data with those of authentic samples. For example, in the visible spectra[1] of $[RuCl_2L^1{}_2]$, isomer 2 shows an MLCT transitions at *ca*.635 nm (Figure V.1) whereas 4 and 6 absorbs at *ca*.580 and *ca*.570 nm (Figure V.2) respectively. Moreover the isomer (4) and (6) also associated with a shoulder at *ca*. 460 and 480 nm respectively which are characteristic of these two isomers. In the IR spectra, all the complexes shows characteristic vibrations due to L (Table V.3) which agrees well with the reported compounds.[1,9] The compound 2 shows a single sharp band at *ca*. 325 cm^{-1} due to ν_{Ru-Cl} whereas in case of both 4 and 6 this band appears[1,9] as doublet at *ca*.310 and *ca*.330 cm^{-1} respectively. Singlet nature of ν_{Ru-Cl} in 2 suggest linear trans grouping for the $[RuX_2]^{2+}$ moiety and the doublet nature of ν_{Ru-Cl} in both 4 and 6 confirms that both the chlorine in $[RuX_2]^{2+}$ moiety is in *cis* geometry. In ^1H NMR spectra[15] of

TABLE V.1

Analytical Data of Complexes

Compound	Formula	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
tt-$[RuCl_2(L^1)_2]$	$RuC_{22}H_{18}N_6Cl_2$	49.06	49.25	3.34	3.40	15.61	15.35
tc-$[RuCl_2(L^1)_2]$	$RuC_{22}H_{18}N_6Cl_2$	49.06	49.40	3.34	3.45	15.61	15.45
cc-$[RuCl_2(L^1)_2]$	$RuC_{22}H_{18}N_6Cl_2$	49.06	49.35	3.34	3.35	15.61	15.41
tt-$[RuCl_2(L^2)_2]$	$RuC_{24}H_{22}N_6Cl_2$	50.87	51.05	3.88	3.95	14.84	15.05
tc-$[RuCl_2(L^2)_2]$	$RuC_{24}H_{22}N_6Cl_2$	50.87	50.95	3.88	4.05	14.84	14.90
cc-$[RuCl_2(L^2)_2]$	$RuC_{24}H_{22}N_6Cl_2$	50.87	51.05	3.88	3.95	14.84	15.00
mer-$[Ru(L^1)_3](ClO_4)_2.H_2O^a$	$RuC_{33}H_{29}N_9O_9Cl_2$	45.67	45.85	3.34	3.27	14.53	14.85
mer-$[Ru(L^2)_3](ClO_4)_2.H_2O^a$	$RuC_{36}H_{35}N_9O_9Cl_2$	47.52	47.43	3.85	3.50	13.86	13.75
mer-$[Ru(L^1)(L^2)_2(ClO_4)_2.H_2O$	$RuC_{35}H_{33}N_9O_9Cl_2$	46.92	46.78	3.69	3.65	14.08	13.95
mer-$[Ru(L^1)_2](L^2)](ClO_4)_2.H_2O$	$RuC_{34}H_{31}N_9O_9Cl_2$	46.30	46.15	3.52	3.50	14.30	14.35

[a] Compounds are obtained from $RuCl_3.3H_2O$ or isomeric$[RuCl_2L_2]$.

TABLE V.2

Solution Electronic Spectral[a] and Molar Conductivity[b] Data of Complexes at 298K

Compound	Vis-UV	Λ_M $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
	λ_{max}/nm ($10^{-3}\varepsilon$, $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)	
tt-$[RuCl_2(L^1)_2]$	635(12.200), 400(9.550), 302(16.360)	3.0
tc-$[RuCl_2(L^1)_2]$	580(11.550), 460(2.200)^c, 320(24.100)	3.0
cc-$[RuCl_2(L^1)_2]$	570(10.800), 480(2.100)^c, 340(20.000)	2.5
tt-$[RuCl_2(L^2)_2]$	634(11.600), 415(10.100), 302(16.600)	3.0
tc-$[RuCl_2(L^2)_2]$	580(10.950), 460(2.010)^c, 318(23.900)	2.5
cc-$[RuCl_2(L^2)_2]$	568(10.900), 476(1.900)^c, 335(20.000)	2.5
mer-$[Ru(L^1)_3](ClO_4)_2.H_2O$	492(12.200), 464(10.900)^c,365(32.250).	380
mer-$[Ru(L^2)_3](ClO_4)_2.H_2O$	492(9.740), 462(12.900)^c,372(37.900)	390
mer-$[Ru(L^1)(L^2)_2](ClO_4)_2.H_2O$	492(12.800), 462(12.350)^c,372(34.500)	390
mer-$[Ru(L^1)_2(L^2)](ClO_4)_2.H_2O$	492(11.600), 462(10.555)^c,370(30.415)	395

[a] Solvent : $[RuCl_2L_2]$, dichloromethane and $[RuL_3]^{2+}$, acetonitrile.

[b] Solvent is acetonitrile. Solute concentration *ca*.10^{-3}mol dm^{-3}; [c] Shoulder.

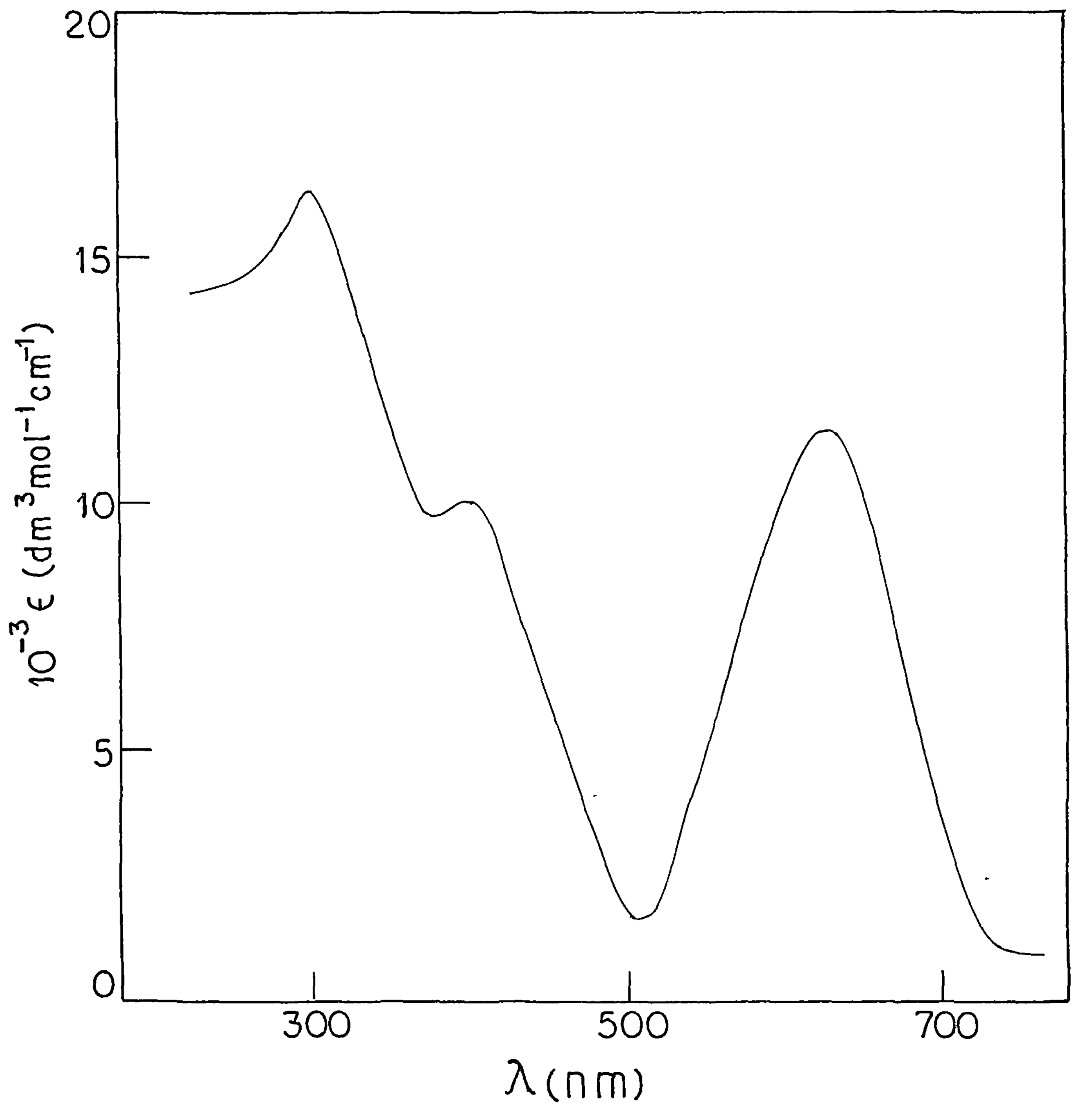


FIGURE V.1. ELECTRONIC SPECTRUM OF tt-[$RuCl_2(L^1)_2$] IN CH_2Cl_2

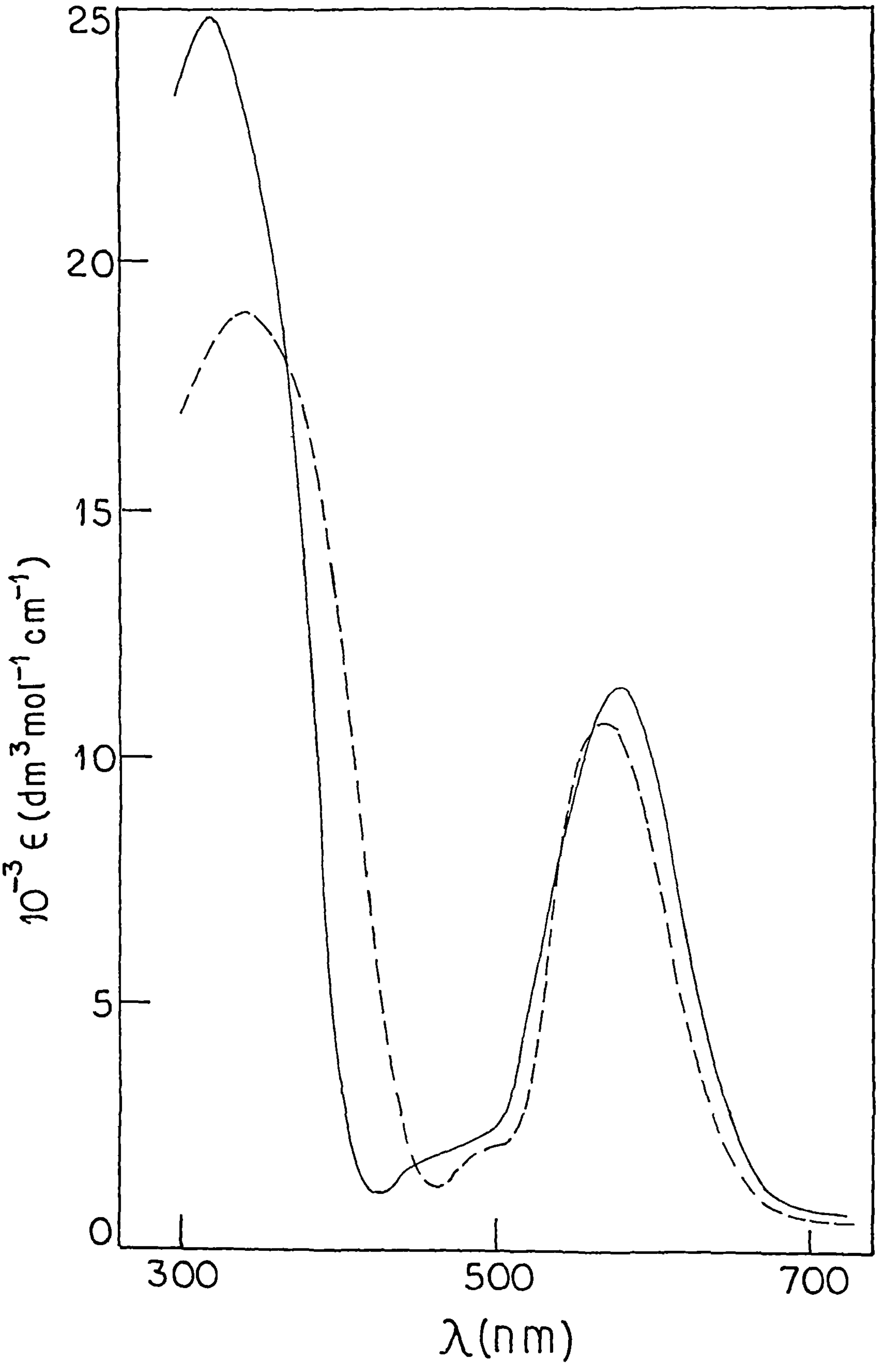


FIGURE V.2. ELECTRONIC SPECTRA OF tc- $[RuCl_2(L^1)_2]$ (———) AND cc- $[RuCl_2(L^1)_2]$ (-------) IN CH_2Cl_2

TABLE V.3

Selected Infrared Spectral Data[a,b] of Complexes

Compound	ν_{max} (cm^{-1})						
	H_2O	C=C + C=N	N=N	C-H Out-of-plane bending in pyridine ring	C-H Out-Of-plane bending in phenyl ring	Ru-Cl	ClO_4^-
tt-$[RuCl_2(L^1)_2]$		1600	1305	770	690	320	
tc-$[RuCl_2(L^1)_2]$		1595	1310	765	690	335,315	
cc-$[RuCl_2(L^1)_2]$		1600	1310	765	700	330,310	
tt-$[RuCl_2(L^2)_2]$		1600	1300	780	700	325	
tc-$[RuCl_2(L^2)_2]$		1605	1300	775	700	325,310	
cc-$[RuCl_2(L^2)_2]$		1595	1310	770	690	325,305	
mer-$[Ru(L^1)_3](ClO_4)_2.H_2O$	3400^c	1600	1355	770	700		1100^c,620
mer-$[Ru(L^2)_3](ClO_4)_2.H_2O$	3400^c	1600	1350	775	700		1100^c,620
mer-$[Ru(L^1)(L^2)_2](ClO_4)_2.H_2O$	3400^c	1610	1355	770	690		1100^c,625
mer-$[Ru(L^1)_2(L^2)](ClO_4)_2.H_2O$	3405^c	1610	1355	765	700		1080^c,620

[a] In KBr disc, 4000-200 cm^{-1}. [b] All bands are sharp and strong unless otherwise stated. [c] Broad.

$[RuCl_2(^2)_2]$ in $CDCl_3$, the green 2 isomer shows a single sharp methyl signal at 2.20 ppm (Figure V.3). More soluble blue isomer 4 also shows a sharp single methyl signal at 2.14 ppm (Figure V.3) confirming the presence of an effective C_2 axis. The other blue isomer 6 shows two equally intense methyl signals (Figure V.3) at 2.21 and 2.40 ppm as expected.

The electrochemical behaviour of the three isomers of $[RuCl_2L_2]$ was also examined cyclic voltammetrically and the values of E^o_{298} compared[1] with those of earlier reported compounds. A representative cyclic voltammogram of the three isomers are shown in Figure V.4. Dichloride complexes in all three geometries undergo one-electron oxidation occuring at > 0.9V versus SCE (couple 1).

$$[RuCl_2L_2]^+ + e \rightleftharpoons [RuCl_2L_2] \qquad (1)$$

tt-$[RuCl_2\ L_2]$ (2) shows one oxidative response at *ca.* 0.9V in acetomitrile whereas the oxidation of *tc* (4) and *cc* (6) isomers occur at *ca.*1.10 and 1.20V respectively (Table V.4, Figure V.4). The reversibility of the couples in each case were examined by $i_{pc} = i_{pa}$; $\Delta E_p = 60$ mV and $i_{pc}/v^{½}$ is a constant. On increasing the scan rate ($v > 100\ mVs^{-1}$) and particularly on changing the solvent to dichloromethane, significant deviation ($\Delta E_p > 60$ mV) from reversibility is observed (Table V.4). As for earlier reported compounds[1,16] a correspondence between E^o_{298} and MLCT energy also observed. Higher the MLCT energy larger is E^o_{298}. The order tt <tc < cc applies to both MLCT energies and E^o_{298}.

(ii) $[RuL_3]^{2+}$. $[RuL_3]^{2+}$ exists[5,17-20] in either facial (7) or

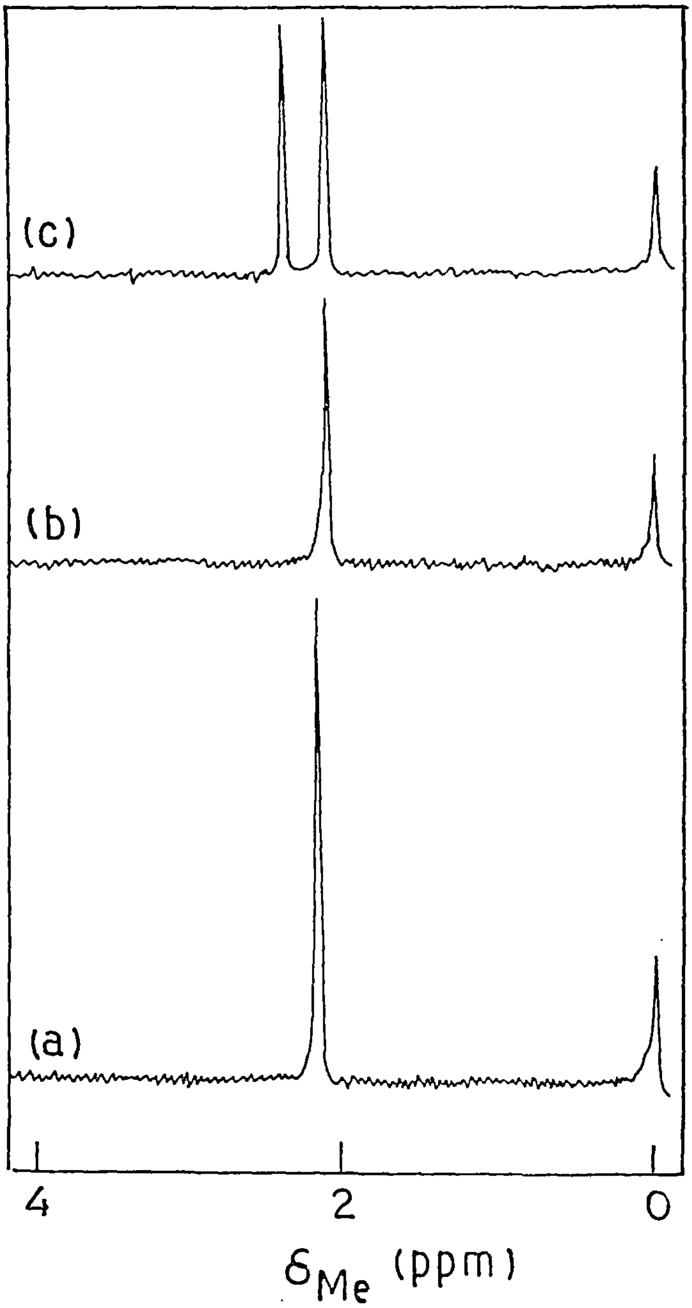


FIGURE V.3. ^1H NMR SPECTRA IN $CDCl_3$: (a) tt- [$RuCl_2(L^2)_2$] , (b) tc- [$RuCl_2(L^2)_2$] , (c) cc- [$RuCl_2(L^2)_2$]

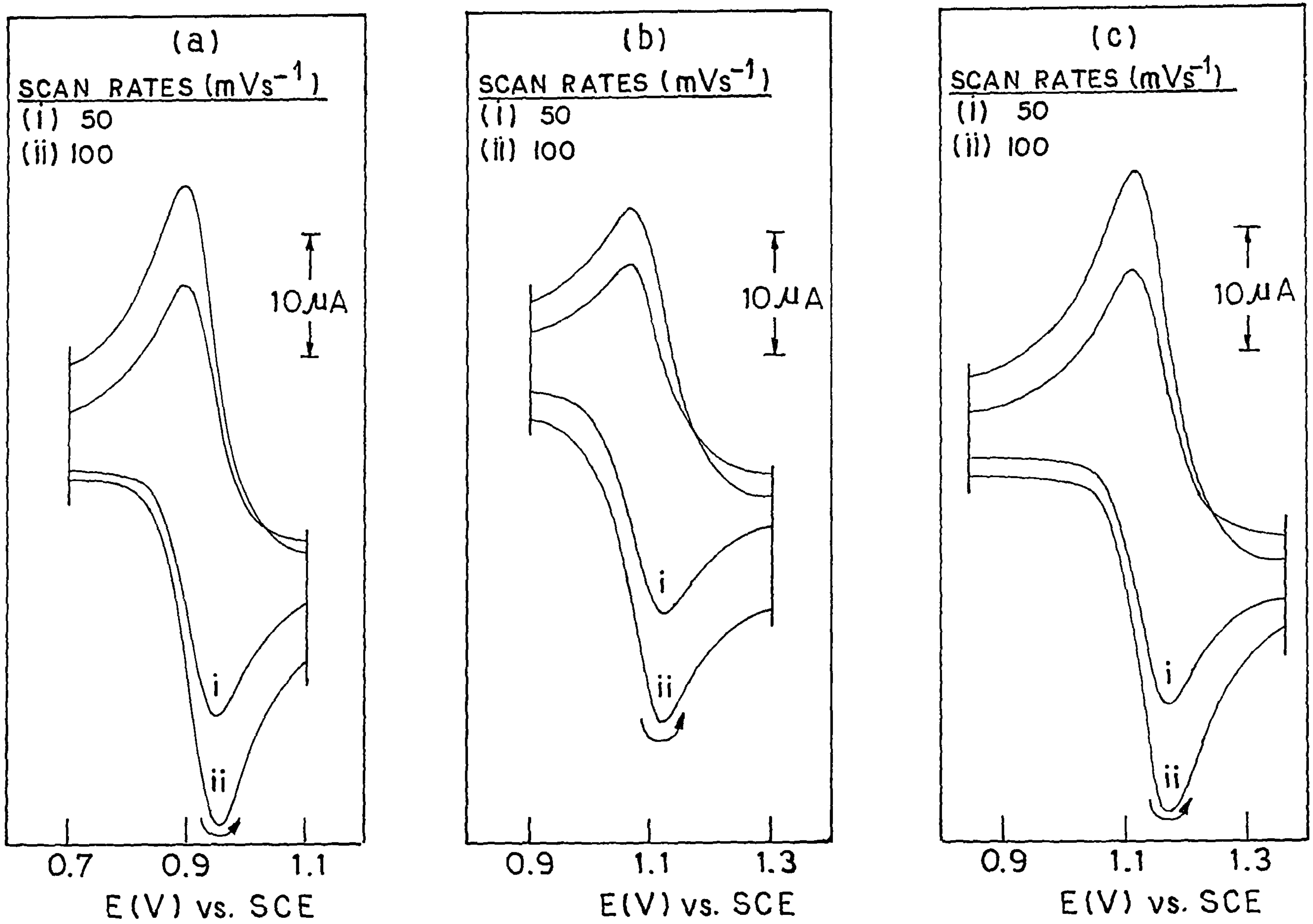


FIGURE V.4. CYCLIC VOLTAMMOGRAMS IN CH_3CN : (a) <u>tt</u>- [$RuCl_2(L^1)_2$] (b) <u>tc</u>- [$RuCl_2(L^1)_2$] , (c) <u>cc</u>- [$RuCl_2(L^1)_2$]

TABLE V.4

Cyclic Voltammetric Data[a,b] (298K) of Complexes on the Positive Side of SCE

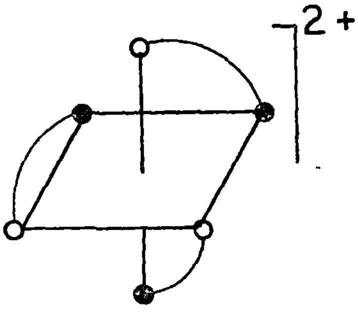
Compound	Solvent	v(mVs^{-1})	E°$_{298}$(V)	ΔE_p(mV)
tt-[$RuCl_2(L^1)_2$]	CH_3CN	50	0.92	60
		200	0.92	70
	CH_2Cl_2	50	0.96	360
		200	0.98	600
tc-[$RuCl_2(L^1)_2$]	CH_3CN	50	1.05	60
		200	1.10	65
cc-[$RuCl_2(L^1)_2$]	CH_3CN	50	1.16	65
		200	1.18	70
tt-[$RuCl_2(L^2)_2$]	CH_3CN	50	0.90	65
		200	0.90	70
	CH_2Cl_2	50	0.92	350
		200	0.93	600
tc-[$RuCl_2(L^2)_2$]	CH_3CN	50	1.10	60
		200	1.10	70
cc-[$RuCl_2(L^2)_2$]	CH_3CN	50	1.20	65
		200	1.20	75

TABLE V.4 (CONTD)

Compound	Solvent	$v(\mathrm{mVs}^{-1})$	$E°_{298}(\mathrm{V})$	$\Delta E_p(\mathrm{mV})$
mer-$[\mathrm{Ru}(\mathrm{L}^1)_3](\mathrm{ClO}_4)_2.\mathrm{H}_2\mathrm{O}$	$\mathrm{CH}_3\mathrm{CN}$	10	2.10^c	
mer-$[\mathrm{Ru}(\mathrm{L}^2)_3](\mathrm{ClO}_4)_2.\mathrm{H}_2\mathrm{O}$	$\mathrm{CH}_3\mathrm{CN}$	10	2.19^c	
mer-$[\mathrm{Ru}(\mathrm{L}^1)(\mathrm{L}^2)_2](\mathrm{ClO}_4)_2.\mathrm{H}_2\mathrm{O}$	$\mathrm{CH}_3\mathrm{CN}$	10	2.23^c	
mer-$[\mathrm{Ru}(\mathrm{L}^1)_2(\mathrm{L}^2)](\mathrm{ClO}_4)_2.\mathrm{H}_2\mathrm{O}$	$\mathrm{CH}_3\mathrm{CN}$	10	2.14^c	

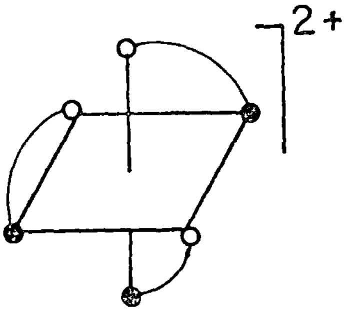
[a] Meaning and units of symbols are the same as in text. [b] Supporting electrolyte, TEAP (10^{-1}mol dm^{-3}); solute concentration, *ca*.10^{-1}mol dm^{-3}. [c] $E°_{298}$ values are obtained from DPV experiments, modulation amplitude (Δ) is 25 mV.

meridional (8) geometry. The product obtained from the reaction



fac,C_3

7



mer,C_1

8

shown in Scheme 2 yielded pure meridional isomer 8 as evidenced by the ^1H NMR spectra. The complexes are obtained as orange coloured crystals. These are characterised by elemental analyses (Table V.1), infrared (Table V.3) and solution electronic spectral and molar conductance[21] data (Table V.2). The electronic spectra of $[RuL_3]^{2+}$ compounds in acetonitrile in the visible region were dominated by one or two allowed CT bands in the range 450-600 nm which are assigned due to $Ru(t_2)$----> $\pi^*(L)$ (Figure V.5, Table V.2). This behaviour of electronic spectra was similar to earlier reported compounds.[5] The geometry of the compound was assessed on the basis of their ^1H NMR data. The methyl signals of L^2 complex was used to probe its stereochemistry. It shows three methyl signals of equal intensity at δ 2.06, 2.20 and 2.27 ppm in $(CD_3)_2SO$ in the pmr spectrum (Figure V.6). Thus all the three ligands in $[Ru(L^2)_3]^{2+}$ are non-equivalent. This is expected[5,21] from a meridional structure where there is no symmetry axis. This observation is in contrast to the earlier experiment where it was reported[5] that

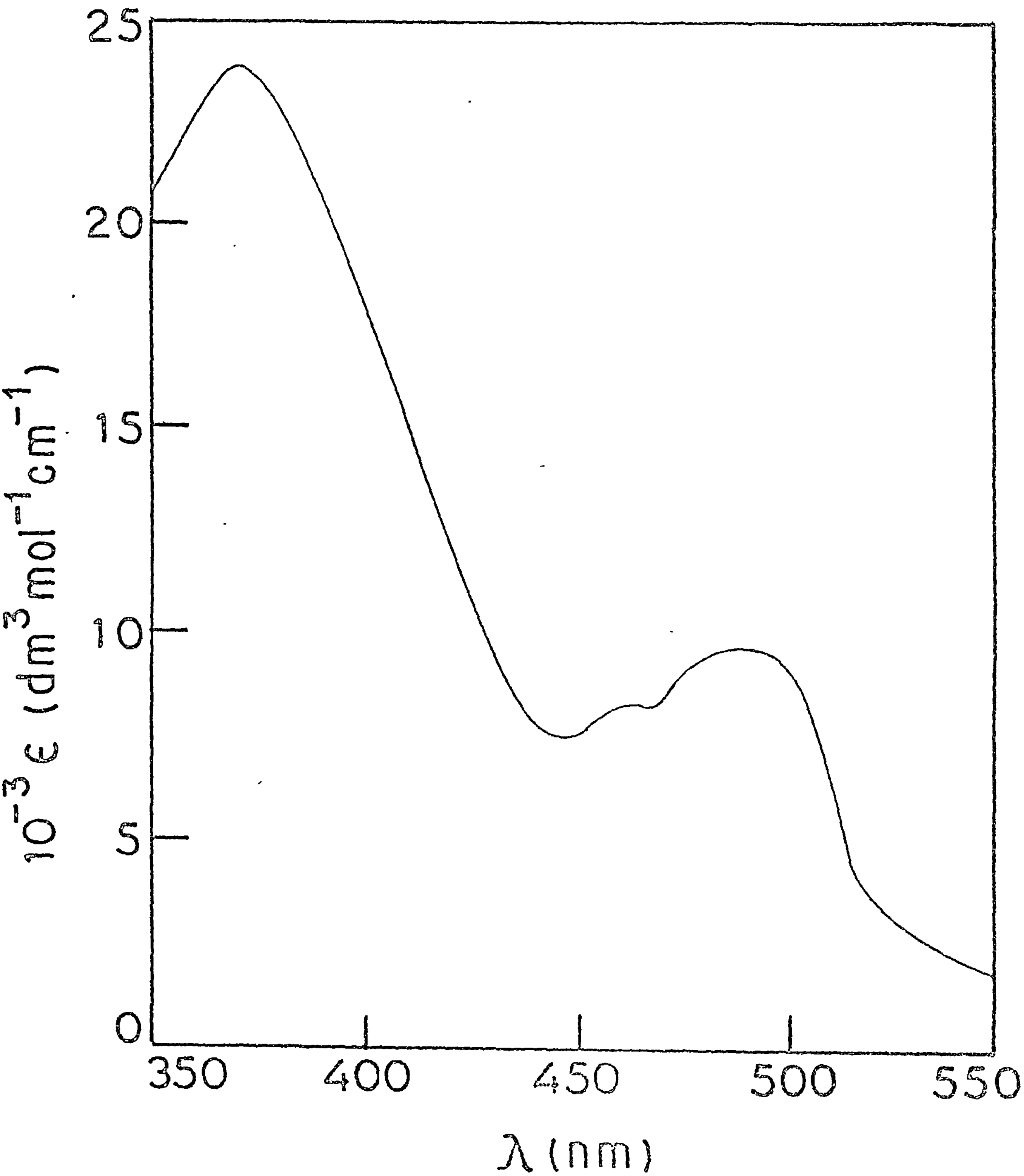


FIGURE V.5. ELECTRONIC SPECTRUM OF mer-[Ru$(L^2)_3$] $(ClO_4)_2\cdot H_2O$ IN CH_3CN

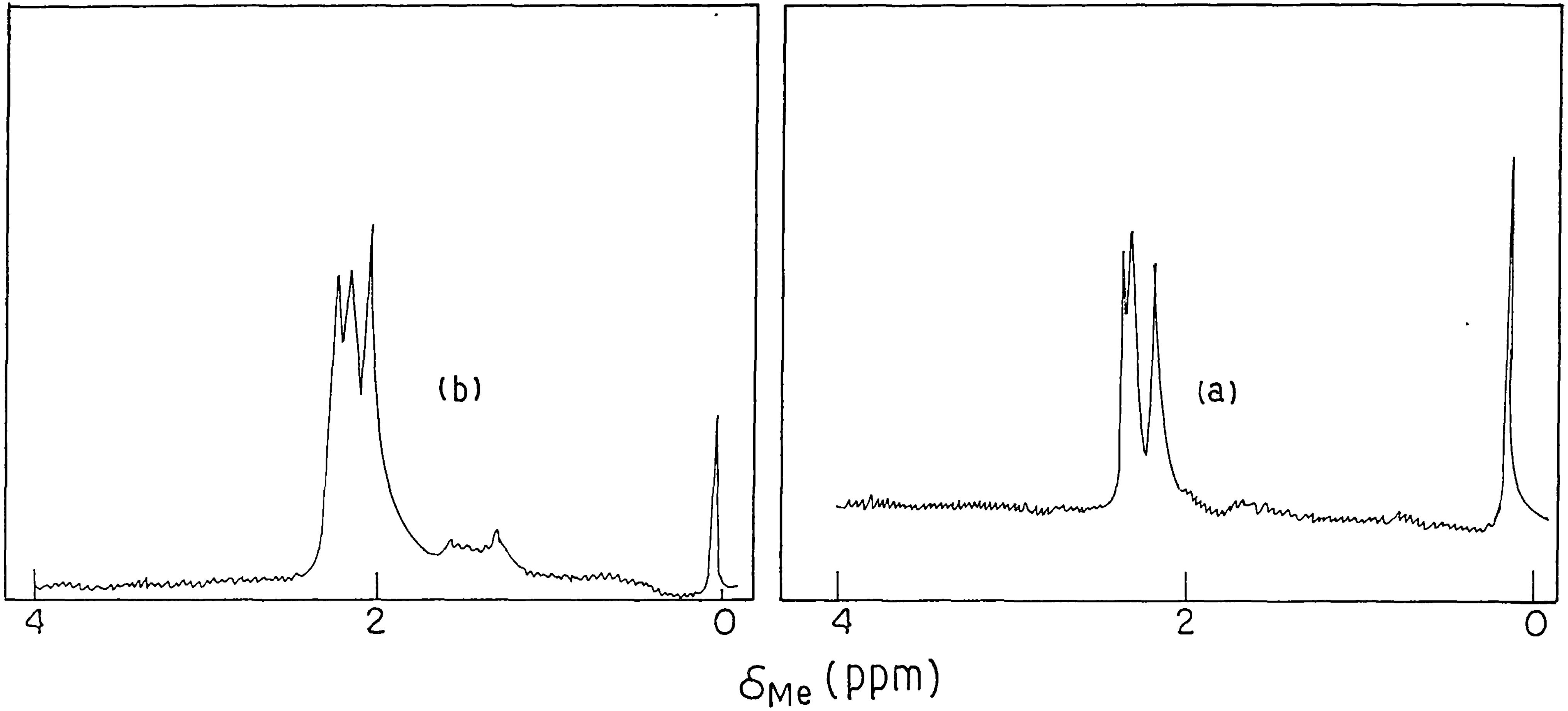
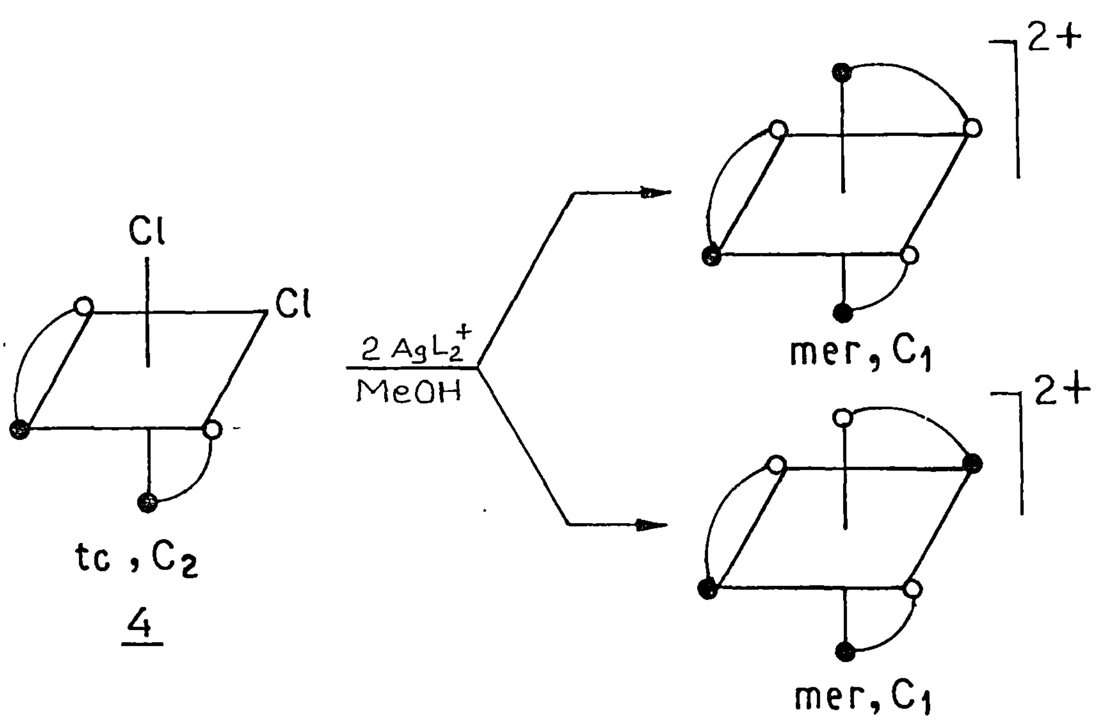
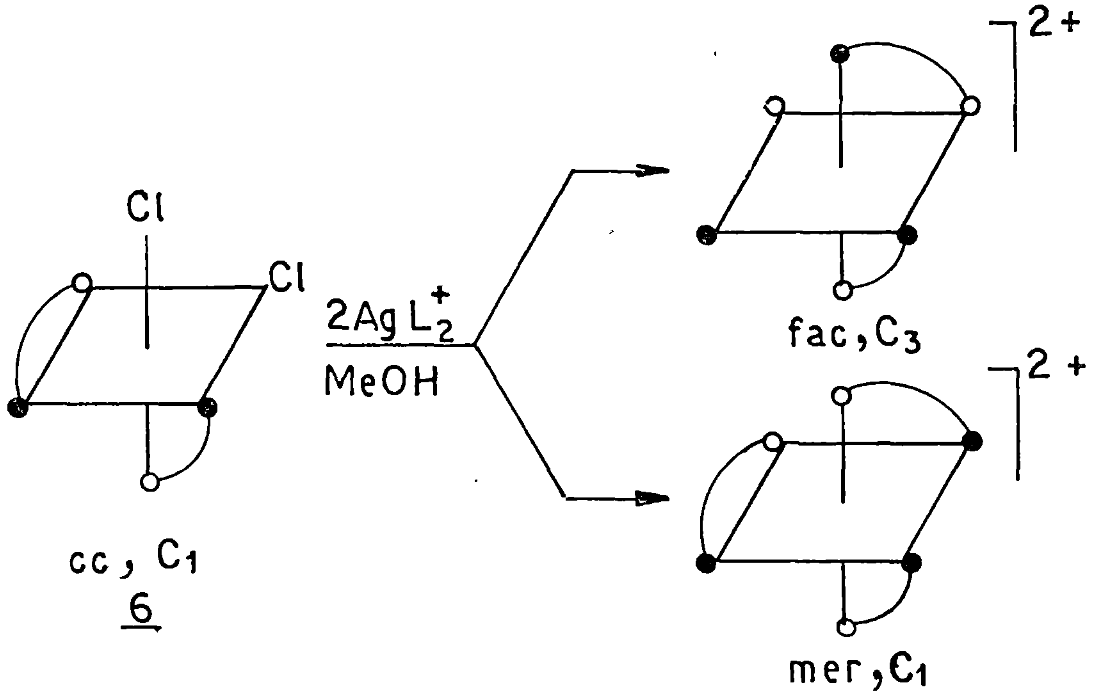


FIGURE V.6. ^{1}H NMR SPECTRA IN $(CD_3)_2SO$: (a) <u>mer</u>-[$Ru(L^2)_3$] $(ClO_4)_2 \cdot H_2O$
(b) MIXTURE OF <u>mer</u>- AND <u>fac</u>- [$Ru(L^2)_3$] $(ClO_4)_2 \cdot H_2O$

in the meridional isomer two methyl signals of relative intensity 1:2 were observed. Based on the ^1H NMR data we conclude that the geometry of the product is meridional. Till date we could not isolate sterically crowded facial isomer of $[RuL_3]^{2+}$(7). The pendant aryl groups of L probably inhibit the formation of the facial isomer. The geometry of the tris complex prepared starting from $[RuCl_2L_2]$ as shown in Scheme 3 depends on the geometry of the starting $[RuCl_2L_2]$ compound. Assuming stereoretentivity of the reaction, the product obtained starting from a *tc* geometry of $[RuCl_2L_2)$ (4) should yield exclusively meridional isomer of $[RuL_3]^{2+}$ (Scheme 4). The product obtained from the reaction described in Scheme 3, starting from *tc*-$[RuCl_2(L^2)_2]$ shows three methyl signals at δ, 2.05, 2.21 and 2.26 ppm in $(CD_3)_2SO$ and hence, it is in meridional geometry. Application of the same reaction to cc-$[RuCl_2(L^2)_2]$ (6) should in principle produce both meridional and facial isomers of $[Ru(L^2)_3]^{2+}$ (Scheme 5). If the chloride displacement is purely statistical two isomers should form in equal amounts. However, crowding of the aryl ring in the facial isomer is likely to make it sterically unfavourable. The product obtained from cc-$[RuCl_2(L^2)_2]$ shows three expected signals of the meridional isomer (Figure V.6) at *ca*.2.03, 2.13 and 2.23 ppm but a new signal of relatively low intensity overlaps with one of the three signals. This new signal is probably arising from facial isomer and its low population is due to the steric factor. Attempted isomer separation on column of alumina or silica gel was not possible due to substrate decomposition.



Scheme 4



Scheme 5

The *tris* complexes display metal centered oxidation[5] at *ca.* 2.15V (Table V.4) whereas ligand base reductions are observed at negative potentials in the range *ca.*-0.08 to -2.06V. A differential pulse voltammogram (DPV) for a representative case has been displayed in Figure V.7.

(iii) Mixed *Tris* chelates, $[Ru(L^1)(L^2)_2]^{2+}$ (9) and $[Ru(L^1)_2(L^2)]^{2+}$ (10). The mixed ligand tris chelates are obtained from tc-isomer of $[RuCl_2L_2]$ by the reaction as shown in Scheme 3. The compounds are characterised by elemental analyses (Table V.1), spectral and molar conductance data[5] (Table V.2 and V.3). The ^{1}H NMR data (δ_{Me}) of the mixed tris chelates are used to probe their stereochemistry. In $[Ru(L^1)(L^2)_2]^{2+}$(9) two intense methyl signals are observed at 2.03 and 2.18 ppm (Figure V.8) demonstrating that two L^2 in 9 is inherently non-equivalent. In case of $[Ru(L^1)_2(L^2)]^{2+}$ (10) single methyl signal at *ca.*2.15 ppm was observable indicating the presence of one L^2 ligand. Interestingly, in case of $[Ru(L^2)_2(bpy)]^{2+}$ (bpy=2,2'-bipyridine) (11) only one methyl signal is observed. Thus the two fold axis in the starting *tc*-$[RuCl_2(L^2)_2)]$ is retained in case of symmetrical bidentate bpy ligand. Moreover it has already been shown that, from a similar reaction *mer*-$[Ru(L^2)_2]^{2+}$ is only obtained from the *tc* geometry of $[RuCl_2(L^2)_2]$. Therefore, we conclude that the synthetic reaction described in Scheme 3 is stereoretentive. The electrochemical behaviour[5] of both 9 and 10 are alike to those of $[Ru(L^2)_3]^{2+}$ and the data are summarised in Table V.4.

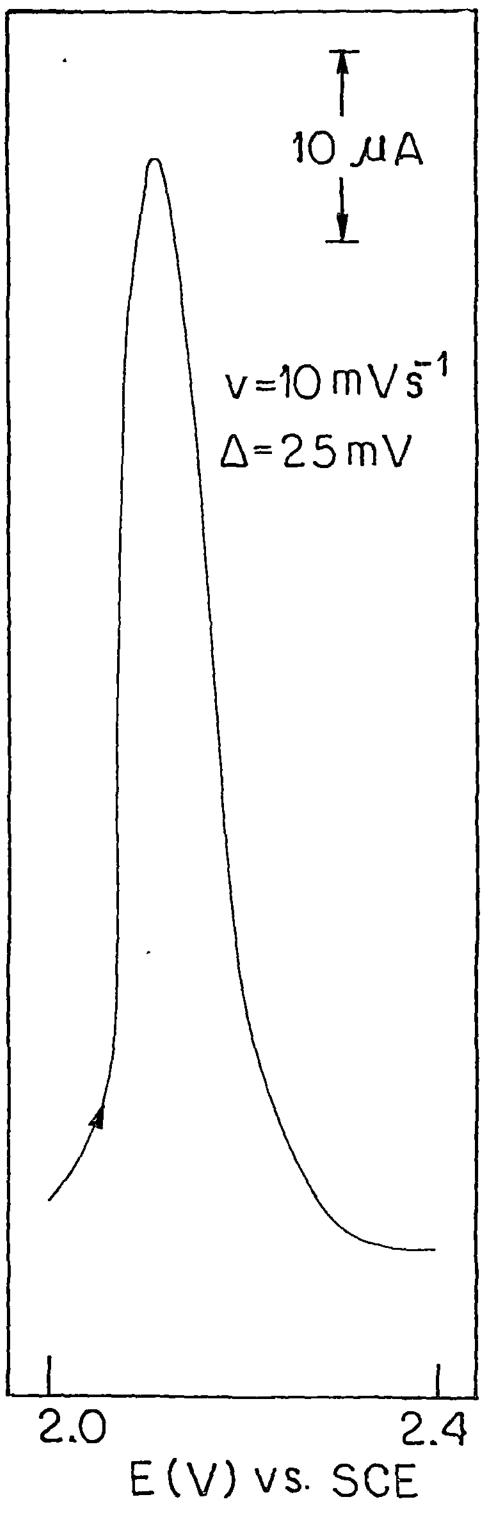


FIGURE V.7

DIFFERENTIAL PULSE VOLTAMMOGRAM OF mer-[$Ru(L^1)_3$] $(ClO_4)_2 \cdot$ H_2O IN CH_3CN

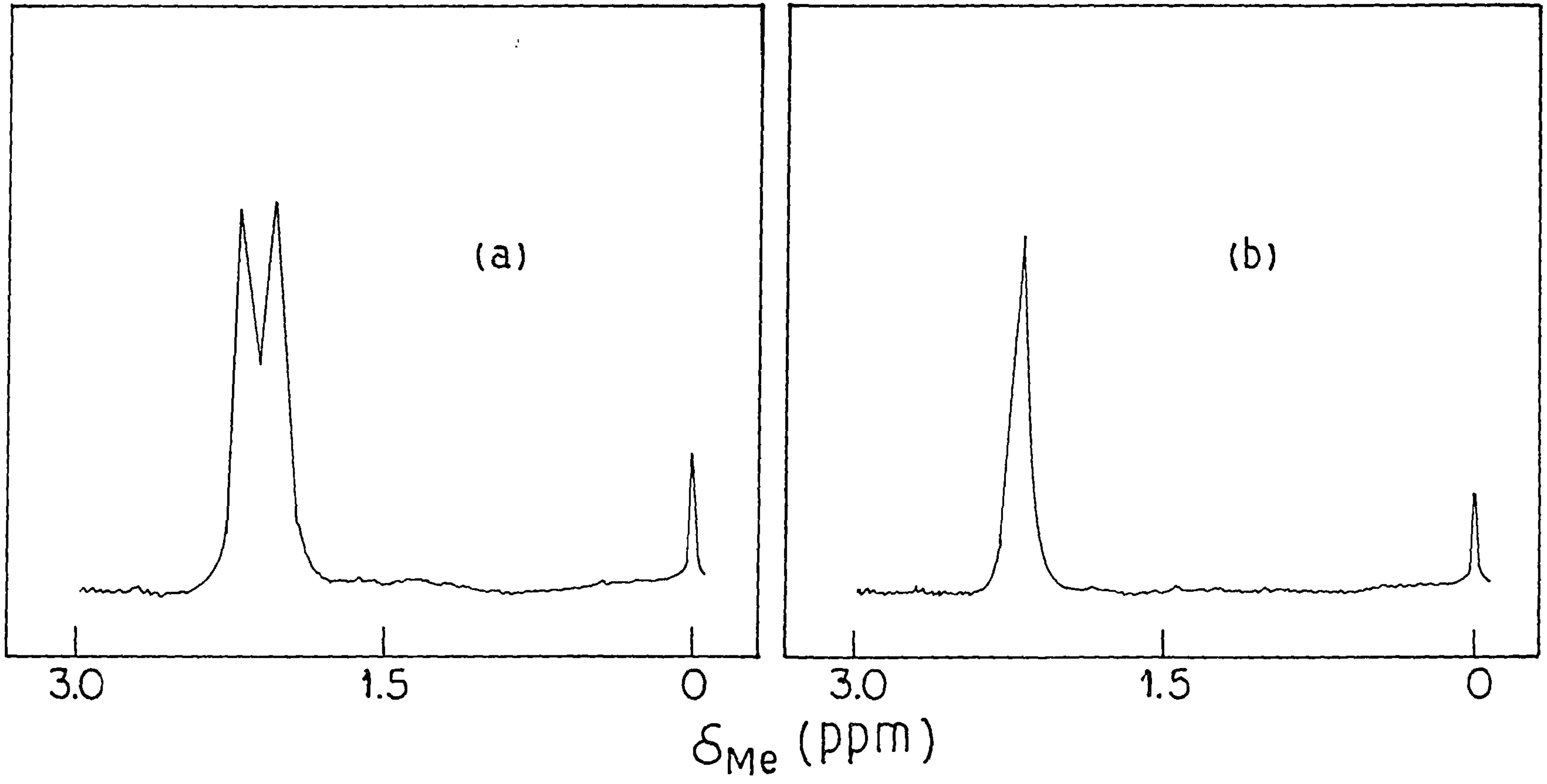


FIGURE V.8. ^1H NMR SPECTRA IN $(CD_3)_2SO$: (a) <u>mer</u>-[$Ru(L^1)(L^2)_2$] $(ClO_4)_2$$\cdot$$H_2O$ AND (b) <u>mer</u>-[$Ru(L^1)_2(L^2)$] $(ClO_4)_2$$\cdot$$H_2O$

C. Solid-State Thermal Isomerisation

It has been observed that both pure *tt* (2) and *cc* (6) isomers of $[RuCl_2L_2]$ or isomeric mixture of $[RuCl_2L_2]$ produce *tc*-$[RuCl_2L_2]$ (4) on heating in solid state. These transformations are quite fast and the yield is almost quantitative (*ca*.90%) (Reaction 2).

$$tt/cc\text{-}[RuCl_2L_2] \xrightarrow{\text{heat}} tc\text{-}[RuCl_2L_2] \qquad (2)$$

Thermolysis of isomeric mixture of $[RuCl_2L_2]$ at *ca*.270°C leading to pure *tc*-$[RuCl_2L_2]$ appears to be an useful way of accessing the compound in *tc*-geometry. In order to gain some insight into the isomerisation process of $[RuCl_2L_2]$ species in the solid state, we investigated solid-phase thermal reaction in the temperature range 30-300°C. This has been followed by TG, DTA and DSC experiments. The TG curve in both cases 2 and 6 remain flat upto 300°C. The DTA curve of 6 shows an exothermic peak at 255°C whereas in case of 2 an exothermic transition was recorded at 285°C. In both the cases the spectral data of the compounds isolated after the transitions were identical to the corresponding *tc* isomer (4). It may be noted here that the DTA curve of 4 is flat in the aforesaid temperature range, indicating that the isomer is stable upto 300°C. The results of DSC experiments for *tc*-$[RuCl_2(L^1)_2]$(2) and *cc*-$[RuCl_2(L^1)_2]$(6) are shown in Figure V.9. The *tt* isomer undergoes an exothermic irreversible transition (227-269°C, $\Delta H = -13.1$ KJ mol^{-1}) whereas in *cc* isomer (6) the transition occurs from 265-269°C ($\Delta H = -10.9$ KJ mol^{-1}) to form the *tc* isomer 4. In each case the DSC

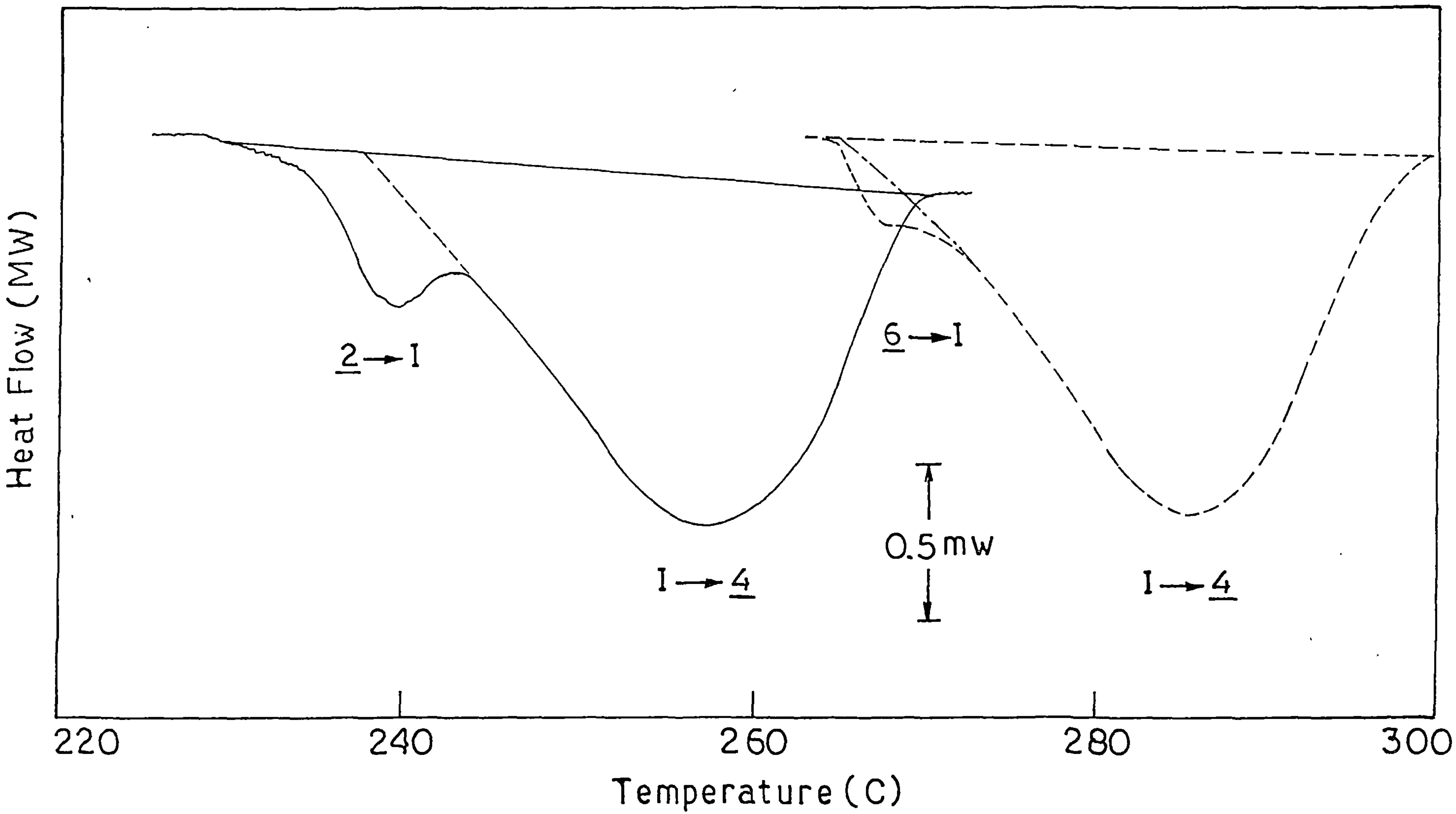


FIGURE V.9. DIFFERENTIAL SCANNING CALORIMETRY (DSC) CURVES OF $[RuCl_2(L^1)_2]$ SHOWING THE TRANSFORMATIONS $\underline{2} \longrightarrow \underline{4}$ (———) AND $\underline{6} \longrightarrow \underline{4}$ (------------)

curve (Figure V.7) is associated with a small peak at a lower temperature indicating that the transitions (2 or 6 to 4) involve two step and go through an intermediate I (equations 3 and 4).

$$2 \longrightarrow I \longrightarrow 4, \; \Delta H = -13.1 \text{ KJ mol}^{-1} \qquad (3)$$

$$6 \longrightarrow I \longrightarrow 4, \; \Delta H = -10.9 \text{ KJ mol}^{-1} \qquad (4)$$

It is interesting to note here that the area bounded by the curve for the second step of transformation (i.e. I——> 4) of reaction 3 is almost equal to that of reaction 4. This implies that heat liberated once the intermediate I is formed, is same for both the reactions. The observation, in turn, tempts us to predict that the isomerisation reactions, under consideration go through a similar intermediate I. The temperature required for a 6——> 4 conversion is higher than a 2——> 4 conversion. This means that *cc* isomer require higher activation energy to form the intermediate I. The very fact, that the isomerisation process under consideration are exothermic reveals that tc isomer 4 is the most thermally stable isomer.

The information hitherto obtained, helped us in designing a solid-state synthetic route to *tc*-$[RuCl_2L_2]$ from $[RuCl_2(dmso)_4]$ (dmso = dimethylsulphoxide) and L. The reaction of $[RuCl_2(dmso)_4]$ in neat L at 230°C proceeds smoothly to produce *tc*-$[RuCl_2L_2]$ (equation 5) in almost quantitative yield. The reaction is very fast and is over in less than 5 min.

$$[RuCl_2(dmso)_4] \xrightarrow[\text{ca.}230°C]{\text{in neat L}} tc\text{-}RuCl_2L_2 \qquad (5)$$

It may be relevant to add that complete displacement of dmso from [$RuCl_2(dmso)_4$] in acetone is very slow[9] (*ca*.72h) and produces compound in *trans* geometry, which on further heating[9] (*ca*.18h) in high boiling xylene yields compounds in *cis* (*tc*) geometry.

Conclusion

It is demonstrated that the synthesis of both bis and tris chelated ruthenium complexes of L can easily be achieved directly from $RuCl_3.3H_2O$ with the use of [AgL_2]ClO_4. The composition of the products can be monitored just by varying the stoichiometric ratio of the reactants. The synthetic route developed by us are experimentally facile and seems to be general for the synthesis of transition metal complexes of polypyridyl and related ligand systems and the strategy used can be regarded as a paradigm for the synthesis of similar type of compounds. The dichloride complexes **2** and **6** undergo solid-state thermal isomerisation reaction to produce thermally most stable isomer **4**. We wish to note[22-24] here that, to our knowledge, these are the first ever examples of solid-state geometrical thermal isomerisation reactions in ruthenium chemistry. Our further studies on the applicability of this method to synthesise other M-L compounds are underway.

V. 3. EXPERIMENTAL SECTION

A. Physical Measurements

Melting Point, Molar Conductivity, Infrared and Electronic Spectral Measurements have been done as described in Chapter II. Electrochemical measurements which includes cyclic voltammetry and differential pulse voltammetry were done as described in Chapter II. ^1H NMR spectral measurements have been done ($CDCl_3$ and $(CD_3)_2SO$) as described in Chapter II. Solid-state thermal investigations were carried out with a Perkin-Elmer DSC-7 differential scanning calorimeter and a Shimadzu DT-30 thermal analyser. The thermal data were obtained from I.A.C.S., Calcutta.

B. Formulation of Compounds

Complexes were formulated by C,H,N microanalyses as described in Chapter II.

C. Solvents

Solvents used for preparative work and for Spectral and Electrochemical measurements were obtained as described in the previous chapters.

D. Preparation of Compounds

(a) Chemicals

Hydrated Ruthenium Trichloride, $RuCl_3.3H_2O$; Sodium Perchlorate etc. and other chemicals required for preparation of ligands are described in Chapter II.

(b) Ligands

Preparation of 2-(phenylazo)pyridine (L^1) and 2-(m-tolylazo)pyridine are given in Chapter II.

(c) Complexes

(i) The salt $[AgL_2]ClO_4$ were obtained as described in Chapter IV.

(ii) **Dichlorotetrakis(dimethylsulphoxide) ruthenium(II),** $[RuCl_2(dmso)_4]$. It was prepared by a published procedure[25] reported earlier.

(iii) **Isomers of Dichlorobis[2-(arylazo)pyridine] ruthenium(II),** $[RuCl_2L_2]$ (Isomers *tt, tc* and *cc*) were prepared by following a published procedure. Specific details for *tt*-$[RuCl_2(L^1)_2]$, *tc*-$[RuCl_2(L^1)_2]$ and *cc*-$[RuCl_2(L^1)_2]$ are given below.

***tt*-$[RuCl_2(L^1)_2]$**[9]. A 4g (8.26 mmol) sample of $[RuCl_2(dmso)_4]$ and 3.04*g* (16.60 mmol) of L^1 were mixed with 400 ml of acetone, and the mixture was refluxed with stirring for *ca.*17h. Upon cooling of the mixture, the green solid was isolated by filtration, washed with acetone and diethyl ether, and dried (75% of Crude material). The sample was then dissolved in minimum amount of chloroform (*ca.*250 ml). On addition of an equal volume of hexane green flakes of *tt*-$[RuCl_2L^1_2]$ was obtained which was collected by filtration and dried *in vacuo* over P_4O_{10}. If TLC shows more than one green spot, the sample was recrystallised again. Yield, 70%.

***tc*-$[RuCl_2(L^1)_2]$**[9]. Described in Chapter II (vide Experimental Section D.g.ii.)

***cc*-$[RuCl_2(L^1)_2]$**[11]. A suspension of 0.200g (0.36 mmol) of *tt*-$[RuCl_2(L^1)_2]$ in 20 ml of dichloromethane and 20 ml of ethanol was stirred at room temperature (20-25°C) with 0.060*g* (0.75 mmol) of NaOH (solid) until all the starting complex had reacted (checked by TLC, about 3h). The solution was cooled in an ice-bath, and 12 drops of concentrated Hydrochloric acid were added. The mixture was concentrated in vacuum to 10 ml and equal volume of diethyl ether was added. After the mixture was allowed to stand overnight at room temperature, the precipitate was collected by filtration, washed with 3 ml of ethanol and 30 ml of water, and dried *in vacuo* over P_4O_{10}. Yield 0.170g (85%).

The complexes *tt*-$[RuCl_2(L^2)]_2$, *tc*-$[RuCl_2(L^2)]_2$ and *cc*-$[RuCl_2(L^2)]_2$ were prepared similarly by taking L^2 instead of L^1.

(iv) Reaction of $RuCl_3.3H_2O$ with $[AgL_2]ClO_4(L=L^1,L^2)$ in 1:1 molar proportion. The reactions with $[AgL_2]^+$ were performed by using the general procedure described below.

The salt $RuCl_3.3H_2O$ (1 mmol) was dissolved in methanol (15 ml) and to it a solution of $[AgL_2]ClO_4$ (1 mmol) in 15 ml methanol was added. This mixture was warmed over water bath *ca*.40°C for 15 min and then cooled. A green precipitate separated. It was filtered through a G-4 sintered glass funnel and washed three times with portions (10 ml) of methanol and dried in vacuum. It was then extracted with the minimum volume (50 ml) of dichloromethane to remove insoluble AgCl. On addition of hexane to the green solution, green flakes of *tt*-$[RuCl_2L_2]$ (2) were obtained. The complex was filtered off and dried in vacuo over P_4O_{10}.

The methanolic filtrate and washings obtained above were concentrated to *ca*.15 ml and on addition of an equal volume of water an isomeric mixture of $[RuCl_2L_2]$ separated which was collected by filtration. It was dried and subjected to chromatography on a silica gel column using different mixtures of dichloromethane-acetonitrile as eluent. The first green band was eluted with $CH_3CN-CH_2Cl_2$ (1:10). The other two bands, viz. blue and blue violet, were eluted respectively with 2:10 and 3:10 $CH_3CN-CH_2Cl_2$. All the bands collected were crystallised by addition of hexane. The analytical and spectral data for the synthesised compounds correspond exactly to those of authentic samples of $[RuCl_2L_2]$. Yields of the different isomers are as follows.

Green band, *tt*-$RuCl_2(L^1)_2$: 70%; Blue band, *tc*-$RuCl_2(L^1)_2$: 10%; Blue violet band, *cc*-$RuCl_2(L^1)_2$: 8%

From a similar experiment starting from $[Ag(L^2)_2](ClO_4)$ and $RuCl_3.3H_2O$ the following complexes were obtained:

tt-$[RuCl_2(L^2)_2]$:70%; *tc*-$[RuCl_2(L^2)_2]$: 10%; *cc*-$[RuCl_2(L^2)_2]$: 8%

(v) Reaction of $RuCl_3.3H_2O$ with $[AgL_2]ClO_4$ ($L=L^1-L^2$) in 1:3 Molar Proportion. The reactions were performed by using the general procedure described below.

A sample of $RuCl_3.3H_2O$ (1 mmol) was dissolved in methanol (15 ml) and to it a solution of $[AgL_2](ClO_4)$ (3 mmol) in methanol (15 ml) was added and the mixture was heated to reflux for 1h. The mixture was cooled and filtered through a G-4 sintered glass funnel to remove insoluble AgCl. The filtrate was concentrated to *ca.*10 ml and an equal volume of diethyl ether was added. The brown precipitate of $[RuL_3](ClO_4)_2.H_2O$ thus formed was collected by filtration. The colour of the filtrate was orange. The product on recrystallisation from water yielded a highly crystalline brown compound. Analytical, spectral and molar conductance data for the synthesised complexes compare very well with those of authentic samples of *mer*-$[RuL_3](ClO_4)_2.H_2O$.

The orange filtrate obtained was evaporated to dryness and then extracted with hexane. The orange hexane solution on evaporation yielded free L. Yield, *mer*-$[Ru(L^1)_3](ClO_4)_2.H_2O$: 70%

A similar experiment starting from $[Ag(L^2)_2]ClO_4$ (3 mmol) and $RuCl_3.3H_2O$ (1 mmol) yielded *mer*-$[Ru(L^2)_3](ClO_4)_2.H_2O$ in 70% yield.

(vi) Reaction of $[RuCl_2(L^2)_2]$ with $[Ag(L^2)_2]ClO_4$ in 1:2 molar proportion. To a suspension of *tc*-$RuCl_2(L^2)_2$ (0.56g, 1 mmol) in 15 ml methanol was added a solution of $[AgL^2)_2]ClO_4$ (1.203g, 2 mmol) in 15 ml methanol and heated to reflux for 30 min. The procedure followed was then exactly similar to that described in section (v) above. The product obtained was *mer*-$[Ru(L^2)_3](ClO_4)_2.H_2O$ in 85% yield and the analytical, spectral and molar conductance data corresponds exactly to that of authentic sample of *mer*-$[Ru(L^2)_3](ClO_4)_2.H_2O$.

The reaction of *cc*-$[RuCl_2(L^2)_2]$ and $[Ag(L^2)_2]ClO_4$ was performed similarly as described above. It yields a mixture of *mer* and *fac*-$[Ru(L^2)_3](ClO_4)_2.H_2O$. Yield, 90%. The analytical spectral and molar conductance data compare very well with that of authentic sample reported previously.

(vii) Synthesis of Mixed-Ligand Tris Complexes from tc-$RuCl_2L_2$

($L=L^1-L^2$). The syntheses of this class of complexes were performed by using a general procedure. A representative example is described below.

mer-[Ru(L^1)(L^2)$_2$](ClO_4)$_2$.H_2O. To a suspension of *tc*-[RuCl_2(L^2)$_2$] (0.566g, 1 mmol) in 15 ml of methanol was added a solution of [Ag(L^1)$_2$]ClO_4 (1.150g, 2 mmol) in 15 ml methanol, and the mixutre was heated to reflux for 30 min. The rest of the procedure is the same as that described in section (vi) above. Yield: 85%. *mer*-[Ru(L^1)$_2$(L^2)](ClO_4)$_2$.H_2O was similarly prepared by taking *tc*-[RuCl_2(L^1)$_2$] and [Ag(L^2)$_2$]ClO_4 in 1:2 molar proportion. Yield: 85%.

Analytical, Spectral and Molar Conductance data agrees well with the reported compounds.

(viii) Solid-State Thermal Isomerisation. *tt*-[RuCl_2(L^1)$_2$] ——> *tc*-[RuCl_2(L^1)$_2$]. A sample of *tt*-[RuCl_2(L^1)$_2$] (0.538g, 1 mmol) was placed in a round bottom flask (50 ml) fitted with a condenser. It was then heated slowly in an oil-bath. The temperature was raised to 250°C and maintained for 5 min. During heating the conversion of green flakes into dark shiny crystals was observed. The solid mass was extracted with the minimum volume (*ca*.100 ml) of dichloromethane. The volume was then reduced to 25 ml and on addition of hexane dark shiny crystals of *tc*-[RuCl_2(L^1)$_2$] separated which were collected by filtration and dried *in vacuo* over P_4O_{10}. Yield: 90%. The conversion of *cc*-[RuCl_2(L^1)$_2$]——> *tc*-[RuCl_2(L^1)$_2$] was similarly performed. The temperature required for this conversion is 280°C. Yield: 90%.

(ix) Reaction of [$RuCl_2(dmso)_4$] in neat L^1. The complex [$RuCl_2(dmso)_4$] (0.484g, 1 mmol) and L^1 (0.366g, 2 mmol) were thoroughly mixed in a round bottom flask (50 ml) fitted with a condenser and heated on an oil-bath at *ca.*200°C for 15 min. The dark mass was extracted with the minimum volume of dichloromethane (*ca.*100 ml). The deep blue solution was then reduced to 25 ml and 50 ml of hexane was added. Dark shiny crystals of *tc*-$RuCl_2(L^1)_2$ separated, were collected by filtration and dried *in vacuo* over P_4O_{10}. Yield, 90%. Analytical, spectral data of the compound are in order with the authentic *tc*-[$RuCl_2(L^1)_2$].

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Chapter VI

CHAPTER VI

SYNTHESIS, STRUCTURE, AND ELECTROCHEMICAL REDUCTION OF 2-(ARYLAZO)PYRIDINE COMPLEXES OF RHODIUM(III)*

Abstract: *The syntheses of new halogenorhodium(III) 2-(arylazo)pyridine(L) complexes of the type* $[RhX_2L_2]ClO_4.H_2O$ *(X=Cl,Br,I; aryl=Ph,* C_6H_4*-Me m or p) are described. The geometry of the complexes have been assessed on the basis of their spectral data. From their high resolution* ^1H *NMR and spectral data it has been shown that the complexes are cis, trans, cis in the following sequence: Cl, Cl; N (pyridine), N(pyridine); and N(azo), N(azo). They are electroactive and display several cyclic voltammetric reductive responses on the negative side of a saturated calomel electrode (SCE). ESR studies of the electrolysed solutions indicate that the electrons are added successively to the ligand centre.*

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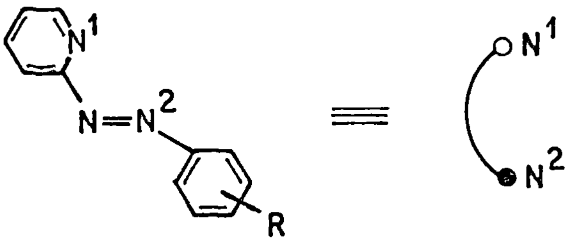
*A part of this work has appeared in *J. Chem. Soc., Dalton Trans.*, 1989, 1635.

VI.1 INTRODUCTION

In recent years complexes of the 2-(arylazo)pyridine ligand system, L(1) with platinum group metal ions have been intensively studied.[1-15] Important phenomena like catalysis,[1] organic hydroxylation,[2] isomerisation,[3-6] and reaction at electrodes[7,8] spearhead the research activity in this area. In comparison, the chemistry of rhodium with L is scarce. Very recently, Krause *et al* have reported[16] a mixed ligand Rh(I) complex of L. The structure of the complex has been established crystallographically. As part of our interest in such complexes, we have initiated research on rhodium chelates of 2-(arylazo)pyridine ligand system. In this chapter we describe the synthesis, characterisation, structural elucidation and electron transfer behaviour of a group of bischelated dihalogeno complexes of rhodium(III). Comparisons, where relevant, with the known rhodium(III) complexes are also made. The three specific ligands used in this chapter are abbreviated as L^1-L^3.



L,1

R	L
H	L^1
m-Me	L^2
p-Me	L^3

VI.2 RESULTS AND DISCUSSION

A. Syntheses and Formulation of Chelates

The synthesis of 2-(arylazo)pyridine ligand[17] (L,1) has been discussed in the preceeding chapters. The reaction between hydrated $RhCl_3$ and L in 1:2 molar ratio proceeds smoothly in boiling methanol. The cationic dihalogenorhodium(III) complexes have been isolated as perchlorate salts. Recrystallisation from dichloromethane-hexane (1:1) yielded highly crystalline products. Even when L to $RhCl_3.3H_2O$ ratio exceeds 2:1, only dihalogenobiscomplex is formed. Addition of LiBr or NaI to the reaction mixture, prior to the addition of ligand, L yield the corresponding dibromo or diiodo analogues respectively. While the chloro complexes have generally been prepared, the bromo and iodo complexes were synthesised only in the case of ligand L^2. The general synthetic route may be represented as shown in equation 1.

$$RhX_3 + 2L \xrightarrow{MeOH} [RhX_2L_2]^+ \qquad (1)$$

The yields of the chloro and bromo complexes are quite high (70-90%) but that of the iodo is low (25%). It is believed that the steric crowding of the two bulky *cis* iodide coligands (vide infra) is the controlling factor for such a low yield in case of diiodide complex.

The complexes are all diamagnetic (t_2^6) as expected. They are soluble in common polar organic solvents, moderately soluble in water and insoluble in non-polar benzene, hexane etc. The complexes were formulated by elemental analyses (Table VI.1). From the molar conductance data (Table VI.2), it has been found that the complexes are 1:1 electrolytes[18] in acetonitrile. These along with analytical data lead unequivocally to the formulation of the rhodium(III) chelates as $[RhX_2L_2]ClO_4.H_2O$(2). The presence of lattice water is confirmed from IR data.

B. Spectra and Stereochemistry

Like $[RuX_2L_2]$ complexes, the dihalogenobis complex of rhodium(III), $[RhX_2L_2]^+$ also in principle may exist[3,11] in five geometrical isomeric form. Possible geometries of the five isomers of $[RuX_2L_2]$ are displayed in Chapter V. The stereochemistry of the synthesised complex has been assessed on the basis of spectral data.

(a) Infrared Spectra

Infrared data were collected in the range 4000-200 cm^{-1} in KBr disc. Characteristic group frequencies are collected in Table VI.3 and representative spectra are displayed in Figure VI.1 and VI.2. Some of these frequencies are found useful in identifying the symmetry and electronic structure of the complexes and are considered here.

(i) $\nu_{N=N}$: π-acidity of L. All the dihalogeno complexes show a sharp band at *ca.*1300 cm^{-1} (Table VI.3, Figure VI.1 and VI.2) which has been assigned[3,6] to $\nu_{N=N}$ of the coordinated ligand. In case of free ligand, L $\nu_{N=N}$ appears[19,20] at 1425 cm^{-1}. This lowering of $\nu_{N=N}$ on moving from free L to the rhodium(III)

TABLE VI.1

Analytical Results of $[RhX_2L_2]ClO_4.H_2O$

Compound	Formula	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
$[RhCl_2(L^1)_2]ClO_4.H_2O$	$RhC_{22}H_{20}Cl_3N_6O_5$	40.15	40.65	3.05	2.65	12.80	12.95
$[RhCl_2(L^2)_2]ClO_4.H_2O$	$RhC_{24}H_{24}Cl_3N_6O_5$	42.00	43.20	3.50	3.25	12.25	12.10
$[RhCl_2(L^3)_2]ClO_4.H_2O$	$RhC_{24}H_{24}Cl_3N_6O_5$	42.00	41.15	3.50	3.25	12.25	12.10
$[RhBr_2(L^2)_2]ClO_4.H_2O$	$RhC_{24}H_{24}Br_2ClN_6O_5$	37.20	38.50	3.10	2.90	10.85	11.35
$[RhI_2(L^2)_2]ClO_4.H_2O$	$RhC_{24}H_{24}I_2ClN_6O_5$	33.15	33.05	2.75	2.95	9.65	10.25

TABLE VI.2

Solution Molar Electrical Conductivity[a] Data of $[RhX_2L_2]ClO_4.H_2O$ in Acetonitrile at 298K

Compound	Λ_M ($ohm^{-1}cm^2mol^{-1}$)
$[RhCl_2(L^1)_2]ClO_4.H_2O$	120
$[RhCl_2(L^2)_2]ClO_4.H_2O$	110
$[RhCl_2(L^3)_2]ClO_4.H_2O$	120
$[RhBr_2(L^2)_2]ClO_4.H_2O$	110
$[RhI_2(L^2)_2]ClO_4.H_2O$	115

[a] Solute concentration *ca.*10^{-3}mol dm^{-3}.

TABLE VI.3

Selected Infrared Frequencies of $[RhX_2L_2]ClO_4.H_2O$ in KBr Disc

	$\nu_{max}(cm^{-1})^a$						
Compound	H_2O^b	C=C + C=N	N=N	C-H Out-of-plane bending in pyridine ring	C-H Out-of-plane bending in phenyl ring	Rh-Cl	ClO_4^-
$[RhCl_2(L^1)_2]ClO_4.H_2O$	3410	1600	1305	760	700	340,330	1100^c,620
$[RhCl_2(L^2)_2]ClO_4.H_2O$	3410	1605	1310	770	705	340,325	1100^c,620
$[RhCl_2(L^3)_2]ClO_4.H_2O$	3405	1605	1310	770	690	350,320	1100^c,620
$[RhBr_2(L^2)_2]ClO_4.H_2O$	3410	1600	1310	770	695		1090^c,620
$[RhI_2(L^2)_2]ClO_4.H_2O$	3405	1600	1310	770	700		1090^c,620

[a] All bands are sharp and strong unless otherwise stated. [b] Broad and strong. [c] Broad.

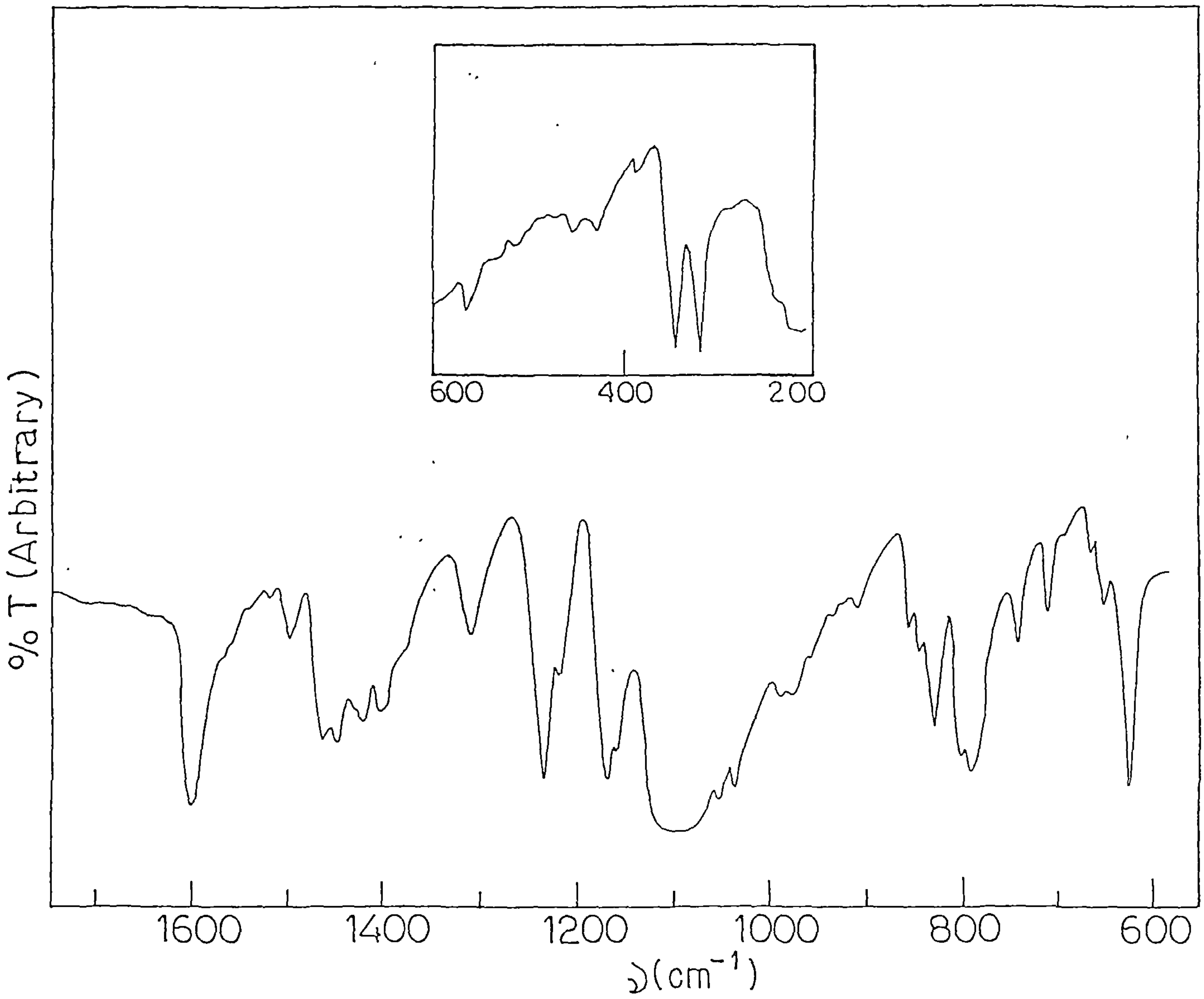


FIGURE VI.1

INFRARED SPECTRUM OF $[RhCl_2(L^2)_2]ClO_4.H_2O$ IN KBr DISC

INSET: FAR INFRARED SPECTRUM OF THE SAME IN KBr DISC

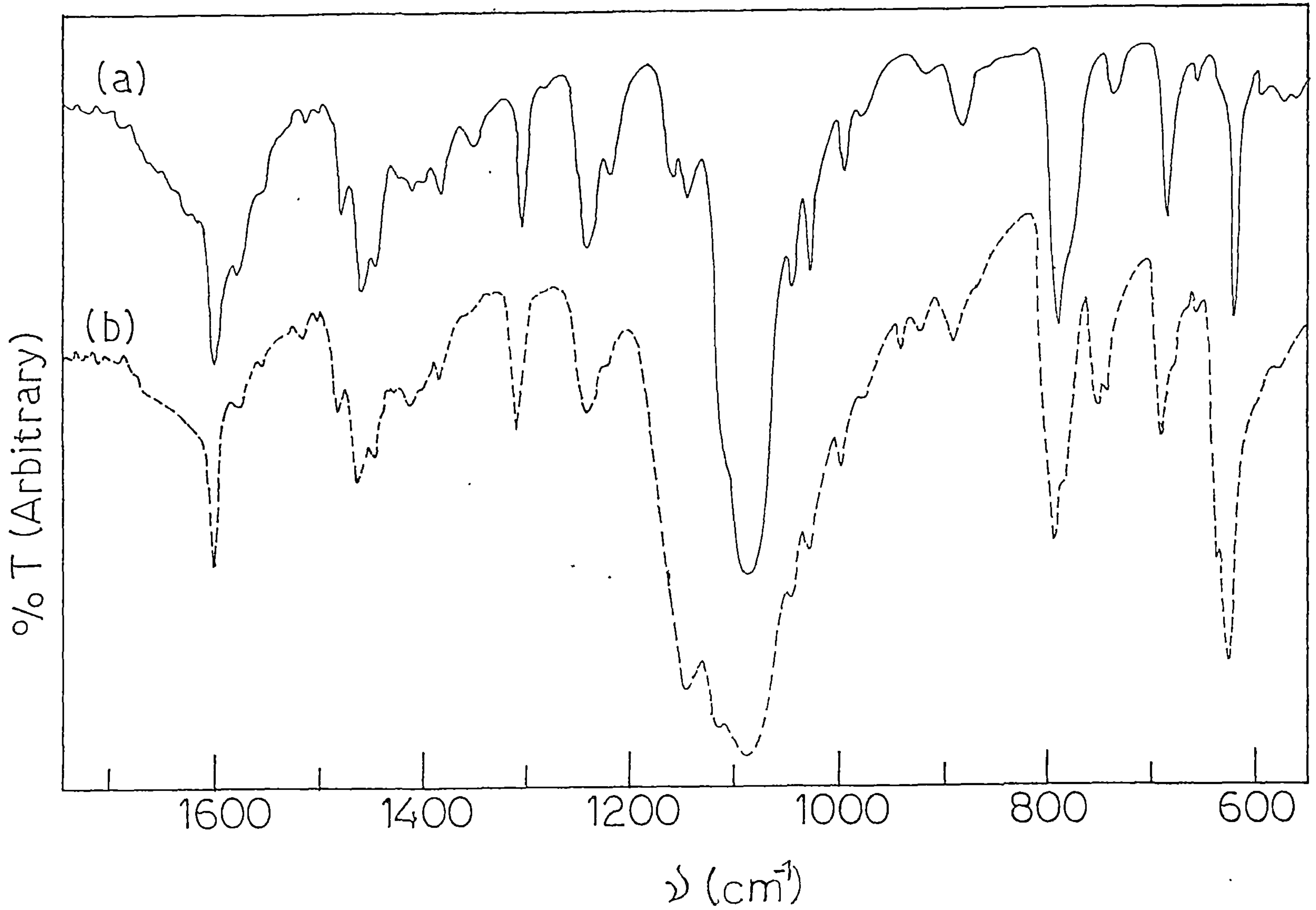


FIGURE VI.2

INFRARED SPECTRA OF : (a) [Rh $Br_2(L^2)_2$]$ClO_4.H_2O$ AND

(b) [$RhI_2(L^2)_2$]$ClO_4.H_2O$ IN KBr DISC compounds, $[RhX_2L_2]^+$ is attributed to the presence of extensive d(Rh) $\longrightarrow$ π^*(L) interaction in the ground state of the complex where π^*(L) is the LUMO of the azoimine chromophore. A similar shift in $\nu_{N=N}$ has also been observed in the L complexes of several electron rich metal ions[3,4,11,15,19,21-23] (Table VI.4). Evidently L has a dominant π-acidic character. This has been reflected in the electrochemcial reduction potentials discussed in Section D of this Chapter.

(ii) ν_{Rh-X}: Isomer Identification. The stereochemistry of the $[Rh-X_2]^+$ moiety in the rhodium(III) complexes have been determined by IR data. The dichloro species show moderately strong bands at *ca.* 340 and 320 cm^{-1} (Table VI.3, Figure VI.1) which are absent in the dibromo and diiodo analogues. These bands are evidently due to ν_{Rh-Cl}. We could not identify ν_{Rh-X} (X=Br,I). These probably lie below our experimental accessible range. A number of workers have assigned[24-27] Rh-Cl stretching mode for Rh(III) complexes in this region (Table VI.5). It may be noted here that *cis* geometry of $[RhX_2L_2]^+$ should have two IR active Rh-Cl stretching modes whereas the *trans* $[RuX_2]$ grouping should have only one IR active[3] mode. The doublet nature of ν_{Rh-Cl} in our compounds (Figure VI.1) clearly indicate[24,28] that the two halides are *cis* to each other. This proposal of *cis* geometry of $[RhX_2L_2]^+$ has been further strengthened by examination of high resolution ^1H NMR spectra which has been discussed below.

(iii) Other Infrared bands. Like the corresponding ruthenium-L complexes, the rhodium complexes display many infrared group

TABLE VI.4

Azo Strtetching Frequencies of Some Reported 2-(Arylazo)pyrdine Metal Complexes

Compound	$\nu_{N=N}/cm^{-1}$	References
$[FeI_2(L^1)_3]$	1353	19
$[NiI_2(L^1)_2]$	1418	19
$[Cu(L^1)_2]ClO_4$	1375	21
$[Cu(L^1)_2](ClO_4)_2$	1412	21
$[HgCl_2(L^1)]$	1420	22
$[CrCl_2(L^1)_2]$	1323	23
tt-$[RuCl_2(L^1)_2]$	1290	3,11
$[RuCl(PPh_3)(L^1)_2]ClO_4.H_2O$	1325	4
tc-$[OsCl_2(L^1)_2]$	1280	15

TABLE VI.5

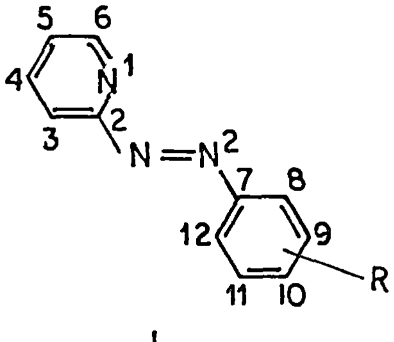
Rh-Cl Stretching Mode (cm^{-1}) for a few Reported Rhodium(III) Chlorocomplexes

Compound	ν_{Rh-Cl}	References
cis-$[RhCl_2(bpy)_2]Cl.2H_2O$	356,349	24
cis-$[RhCl_2(o\text{-}phen)_2]Cl.3H_2O$	346,325	24
cis-$[RhCl_2(py)_4]Cl.5H_2O$	362,351	24

frequencies characteristic[19] of L (Table VI.3). These have already been discussed earlier (Chapters IV and V). We donot discuss these any further. The structureless band at *ca*.1100 and a sharp band at 620 cm^{-1} suggest[29] the lack of significant perchlorate coordination in the solid state. The existence of lattice water[30,31] is confirmed by the appearance of a very broad band at *ca*.3500 cm^{-1} and a weak band at *ca*.1630 cm^{-1} in the IR spectra.

(b) ^1H NMR Spectra

High resolution ^1H NMR data in CD_3CN were obtained for all the dichloro complexes. All the dichloro complexes display highly resolved ^1H NMR spectra. A representative case of $[RhCl_2(L^2)_2]ClO_4.H_2O$ is displayed in Figure VI.3. Chemical shift and spin-spin splitting data are given in Table VI.6. The signals from the protons of pyridine rings are readily assigned[32-35] on the basis of their chemical shifts and also by examining the spin-spin splitting patterns of the signals. The pattern consists of two doublets and two triplets. The protons of the ligand are lebelled as shown below.



L

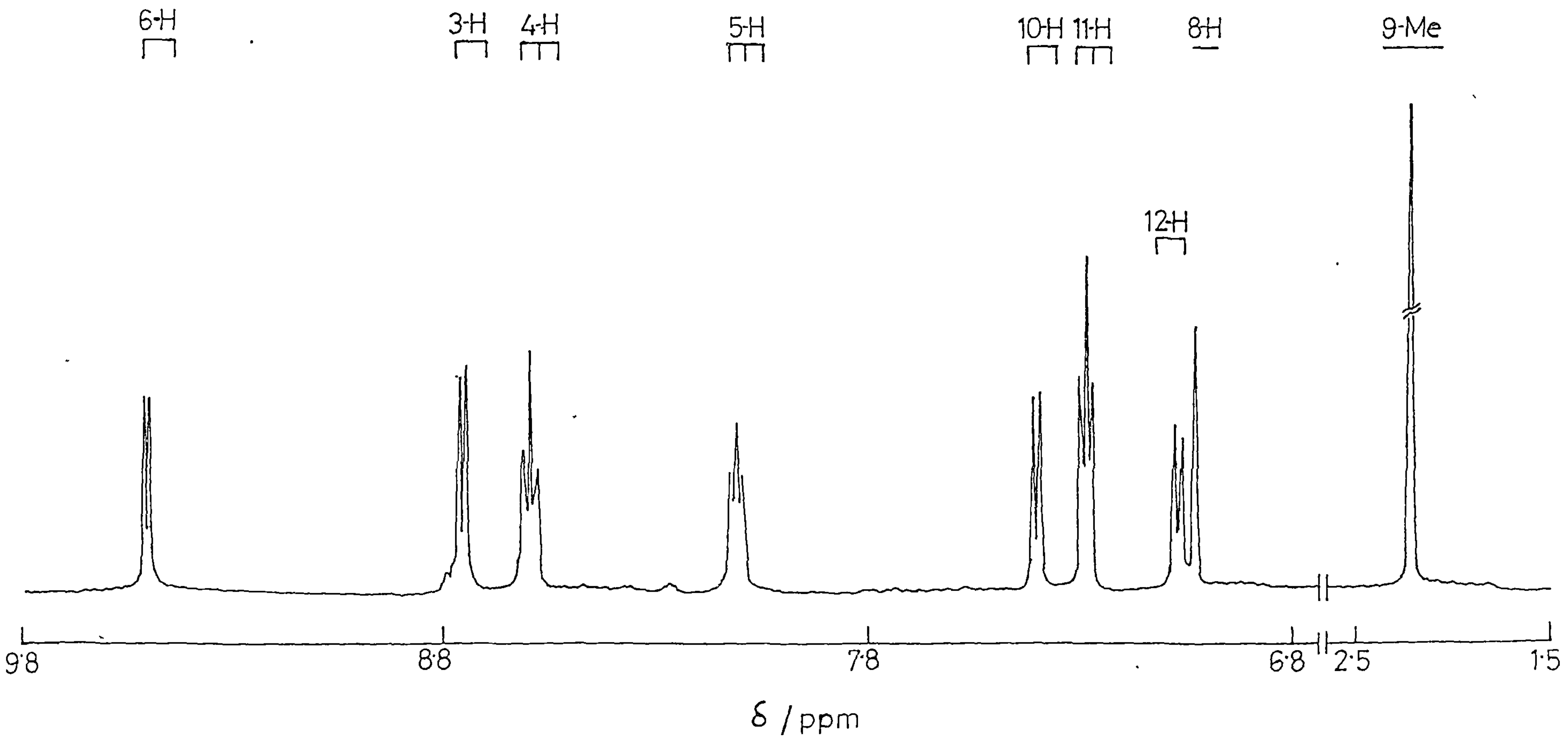


FIGURE VI.3. ^{1}H NMR SPECTRUM OF $[\mathrm{RhCl_2(L^2)_2}]\mathrm{ClO_4.H_2O}$ IN $\mathrm{CD_3CN}$

TABLE VI.6

^1H NMR Spectral Data of $[RhX_2L_2]ClO_4.H_2O$[a] in Acetonitrile

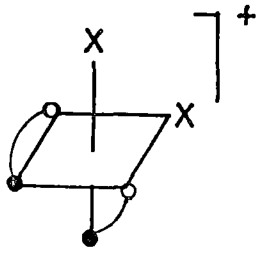
Compound	δ/ppm (J/Hz)[b]										
	6-H	3-H	4-H	5-H	8-H	9-H	10-H	11-H	12-H	9-Me	10-Me
$[RhCl_2(L^1)_2]ClO_4.H_2O$	9.50(5.2)[c]	8.69(8.1)[c]	8.59(7.8)[d]	7.99(6.5)[d]	7.21(7.9)[c]	7.41(7.9)[d]	7.50(7.5)[d]	7.41(7.9)[d]	7.21(7.9)[c]		
$[RhCl_2(L^2)_2]ClO_4.H_2O$	9.51(5.5)[c]	8.75(7.8)[c]	8.60(7.9)[d]	8.11(6.6)[d]	7.02[e]		7.40(7.7)[c]	7.28(7.8)[d]	7.06(8.0)[c]	2.21[e]	
$[RhCl_2(L^3)_2]ClO_4.H_2O$	9.50(5.4)[c]	8.72(7.7)[c]	8.58(7.8)[d]	8.11(6.4)[d]	7.16(8.1)[c]	7.48(8.8)[c]		7.48(8.8)[c]	7.16(8.1)[c]		2.35[e]

[a] For $[RhX_2(L^2)_2]ClO_4.H_2O$ (X=Br,I), well resolved spectra could not be obtained. $[RhBr_2(L^2)_2]ClO_4.H_2O$ gives a single methyl signal at 2.20 ppm whereas $[RhI_2(L^2)_2]ClO_4.H_2O$ gives a single methyl signal at 2.40 ppm; [b] $SiMe_4$ as the internal standard; [c] Doublet; [d] Triplet; [e] Singlet.

Thus, the 6-H is a doublet with a relatively low J value (*ca.*5 Hz), 4-H and 5-H are triplets and 3-H is a doublet. The chemical shifts of the pyridyl protons follows the order: $\delta_{6-H}>\delta_{3-H}>\delta_{4-H}>\delta_{5-H}$. The phenyl ring protons are assigned on a similar basis using substituent induced change in splitting patterns and chemical shifts as additional indicators. For example, 8-H and 12-H signals are coincident doublets in L^1 complex whereas the same 8-H signal appears as separate singlet in the corresponding L^2 complex. Also, 9-H and 11-H signals appear as coincident triplets in L^1 complex whereas these appear as coincident doublets in its L^3 analogue. Further, the 8-H signals are very significantly shifted to a higher field[35] in moving from L^1 to a L^2 complex, in accord with the electron releasing character of the methyl substituents. The complexes of L^2 and L^3 show a single methyl signal at *ca.*2.20 ppm.

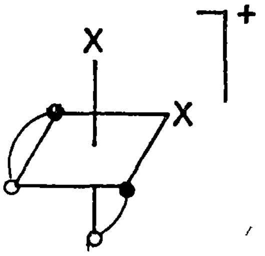
The ^1H NMR spectra of the complexes display only one signal (singlet or multiplet) for each proton of the ligand L.Thus, it is very likely that present complexes exist only a single isomer and both the chelate rings in $[RhCl_2L_2]^+$ are magnetically equivalent, at least in NMR time scale. For a symmetrical structure of $[RhCl_2L_2]^+$ and assuming a free rotation of the aryl ring seven and six aromatic resonances are expected respectively for the complexes of L^1 and L^3. This exactly what we observed in the ^1H NMR spectra. It is also interesting to note that the signal due to 6 H resonate at a low field (9.50 δ) in the complexes. This is in accord with the *cis* geometry[35] where 6-H proton is pointed either to a chlorine or imine nitrogen which would result in negligible shielding or even deshielding of the 6-H proton. On the other hand, a *trans* geometry of $[RhCl_2L_2]^+$ would require 6-H proton to be highly shielded[36] by the phenyl ring of the second ligand and expected to resonate at a higher field. For comparison, 6-H signal of the *trans*-$[RuCl_2(L^1)_2]$ appears[35] at 8.92δ and for a *cis* $[RuCl_2(L^1)_2]$, resonates at 9.39δ, which is almost similar to the chemical shift of 6 H proton in the present compounds. The infrared and ^1H NMR data taken collectively imply that the gross stereochemistry of the dichlororhodium(III) complex, $[RhCl_2L_2]^+$ could be either of the two symmetric *cis* structures 2 or 3. We note that in the ct isomer, (3) the trans N^2, N^2 pair compete for the same metal dπ orbital. This is expected to weaken back-bonding in this isomer compared to *tc*(2) and *cc* isomers where the N^2,N^2 pairs are *cis*. Indeed the isomer 3 does not exist in the cases of Ru(II) and Os(II). Thus we propose that the gross stereochemistry of the present dichlororhodium(III) complex, $[RhCl_2L_2]^+$ is as shown in Structure 2.

It may be noted here that dibromo and diiodo analogues have virtually identical IR spectra in the range 4000-400 cm^{-1}. Therefore, it is concluded that the gross stereochemistry of the dibromo and diiodo compounds are similar to their dichloro analogue 2.



2

X = Cl, Br, or I
• = N^2



3

(c) Electronic Spectra

Electronic spectra of the complexes in acetonitrile were recorded in the region 800-220 nm. Highly intense allowed charge-transfer transitions, which have been observed in the visible and UV region, are collected in Table VI.7. Representative spectra are displayed in Figure VI.4 and VI.5. Free ligand,L display absorption bands at *ca.*440 nm (ε,*ca.*700 dm^3mol^{-1} cm^{-1}) and *ca.* 320 nm (ε,*ca.* 19,000 $dm^3mol^{-1}cm^{-1}$). These can be respectively assigned[37] to $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions centered primarily on the azo group. The higher energy transitions in the complexes[24,26,38,39] charge-transfer transitions primarily centre in the orbitals predominantly ligand in character. The highly intense lowest energy transition at *ca.*360nm (ε,*ca.*20,200 $dm^3mol^{-1}cm^{-1}$) is due to CT transition. The origin of this is not clear to us.

C. Electron Transfer Properties: Redox Reaction

The electron transfer behaviour in acetonitrile solution of the dihalogenobisrhodium(III) compounds of L,$[RhX_2L_2]^+$ were examined by cyclic voltammetry in the range + 2.0 to -20V, versus a saturated calomel electrode (SCE), using platinum as the working electrode. The cyclic voltammetric data are collected in Table VI.8. Representative voltammograms are also displayed in Figure VI.6-VI.9. Comparisons, where relevant, with the analogous systems[40,41] are made.

All the redox couples observed in this study are designated by increasing Roman numerals I through IV proceeding towards more

TABLE VI.7

Electronic Spectral Data of $[RhX_2L_2]ClO_4.H_2O$ in Acetonitrile at a Room Temperature (298K)

Compound	λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})
$[RhCl_2(L^1)_2]ClO_4.H_2O$	360(21,560),305(11,190)[a],220(38,160)[a]
$[RhCl_2(L^2)_2]ClO_4.H_2O$	370(16,645),305(9,010)[a],225(29,990)[a]
$[RhCl_2(L^3)_2]ClO_4.H_2O$	385(19,220),295(11,560),230(27,050)[a]
$[RhBr_2(L^2)_2]ClO_4.H_2O$	375(21,390),230(43,850)[a]
$[RhI_2(L^2)_2]ClO_4.H_2O$	360(17,820),245(34,780)

[a] Shoulder.

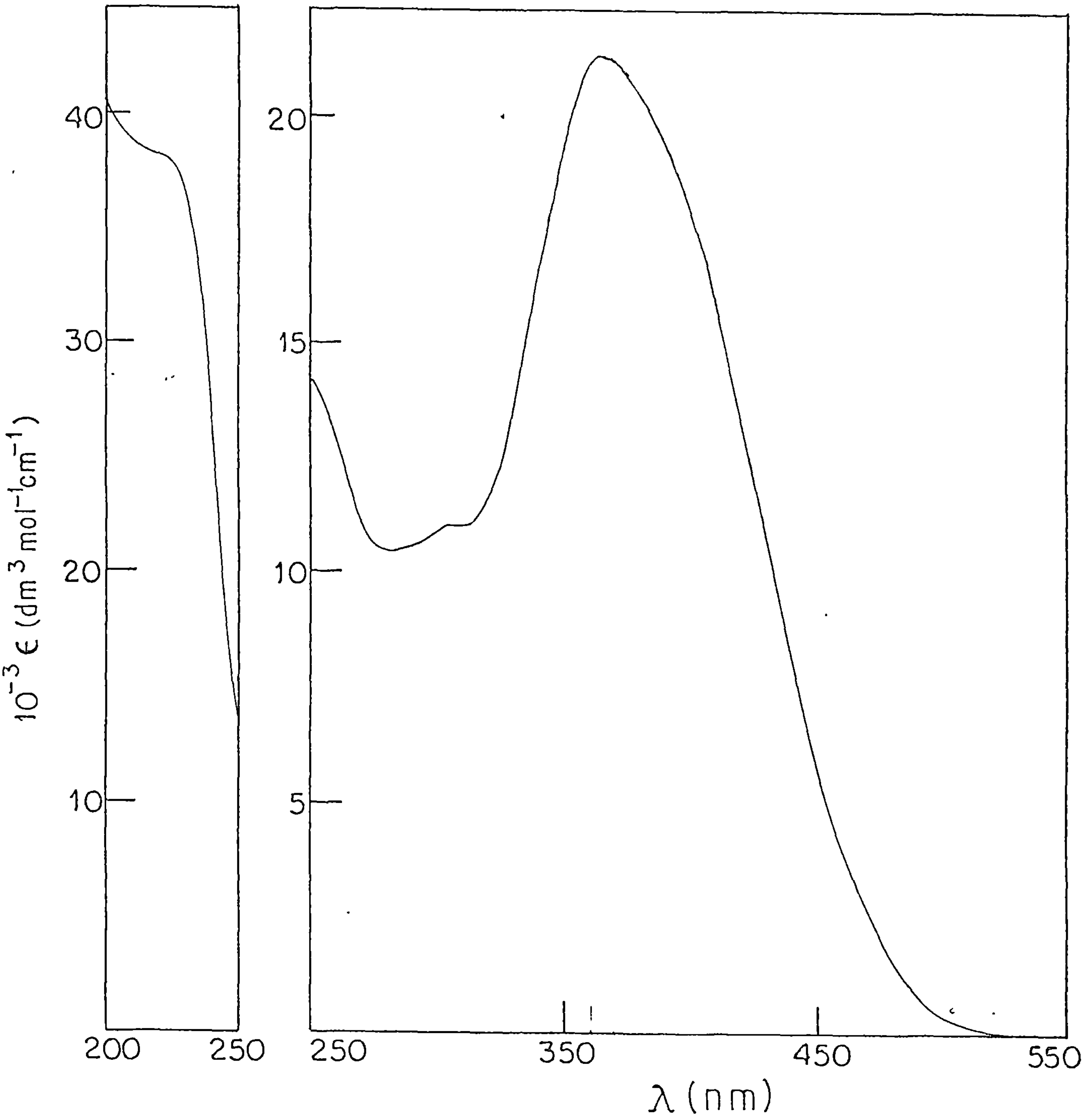


FIGURE VI.4

ELECTRONIC SPECTRUM OF [$RhCl_2(L^1)_2$] $ClO_4.H_2O$ IN CH_3CN

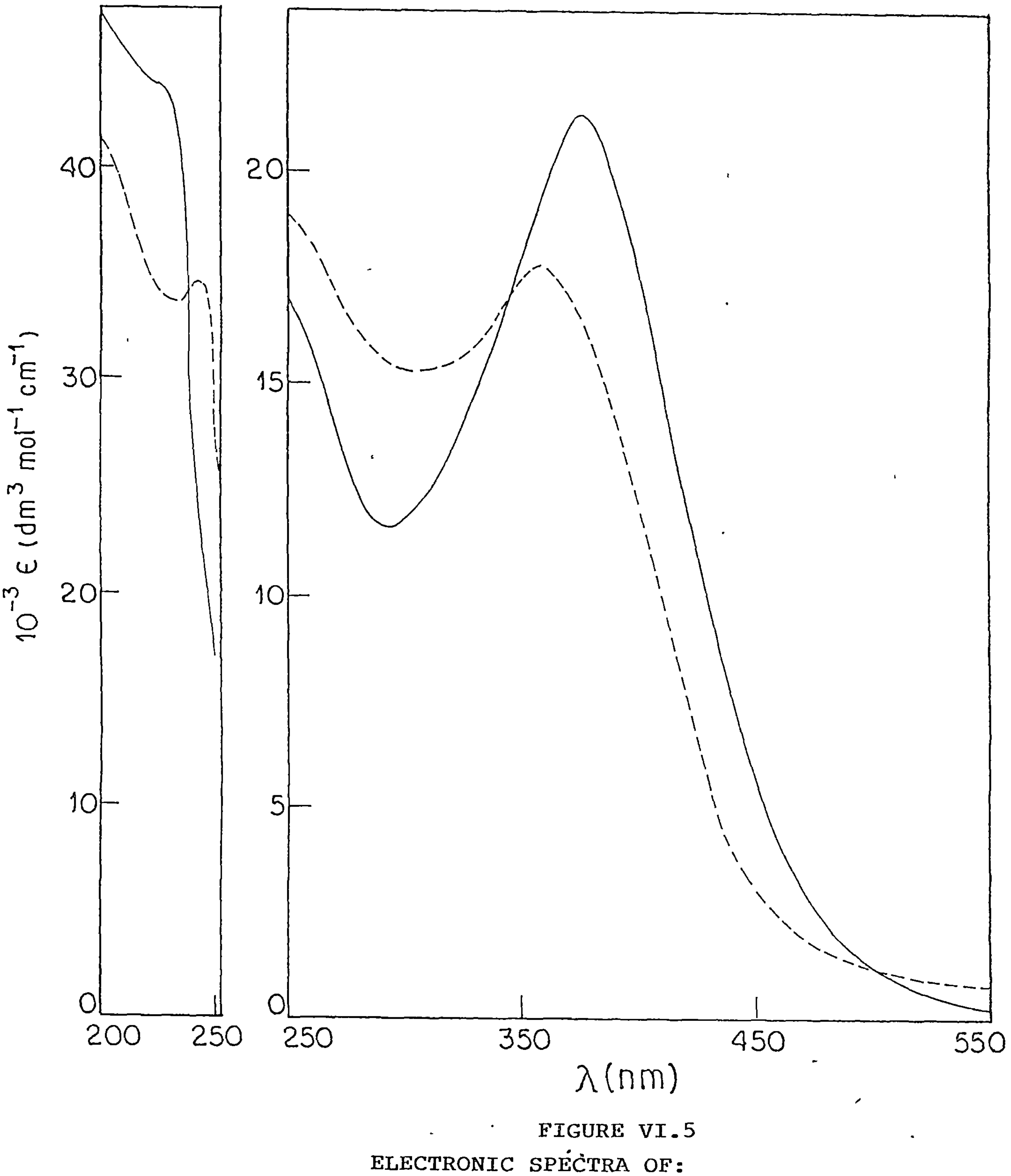


FIGURE VI.5

ELECTRONIC SPECTRA OF:

(i) $[RhBr_2(L^2)_2]ClO_4.H_2O$ (——) AND

(ii) $[RhI_2(L^2)_2]ClO_4.H_2O$ (------) IN CH_3CN

TABLE VI.8

Cyclic Voltammetry Data[a,b] of $[RhX_2L_2]ClO_4.H_2O$

Compound	v (mVs^{-1})	E°$_{298}$/E$_{pc}$ (V)	ΔE$_p$ (mV)
$[RhCl_2(L^1)_2]ClO_4.H_2O$	50	-0.02	70
		-0.34	120
		-1.05[c]	
		-1.36[c]	
$[RhCl_2(L^2)_2]ClO_4.H_2O$	50	0.03	70
		-0.24	130
		-1.00[c]	
		-1.36[c]	
	100	0.03	75
		-0.24	140
		d	
		d	
$[RhCl_2(L^3)_2]ClO_4.H_2O$	50	0.00	60
		-0.35	90
		-0.99[c]	
		-1.40[c]	
$[RhBr_2(L^2)_2]ClO_4.H_2O$	50	0.03	60
		-0.19	140
		-0.95[c]	
		-1.38[c]	

TABLE VI.8 (CONTD)

Compound	v(mVs^{-1})	E°$_{298}$/E$_{pc}$(V)	Δ_{Ep}mV)
$[RhI_2(L^2)_2]ClO_4.H_2O$	50	0.02 -0.22 -0.98[c] -1.36[c]	70 120

[a] Meaning and units of symbols are the same as in text.

[b] In CH_3CN using 10^{-1} mol dm^{-3} TEAP as supporting electrolyte.

[c] Irreversible cathodic response.[d] Not studied.

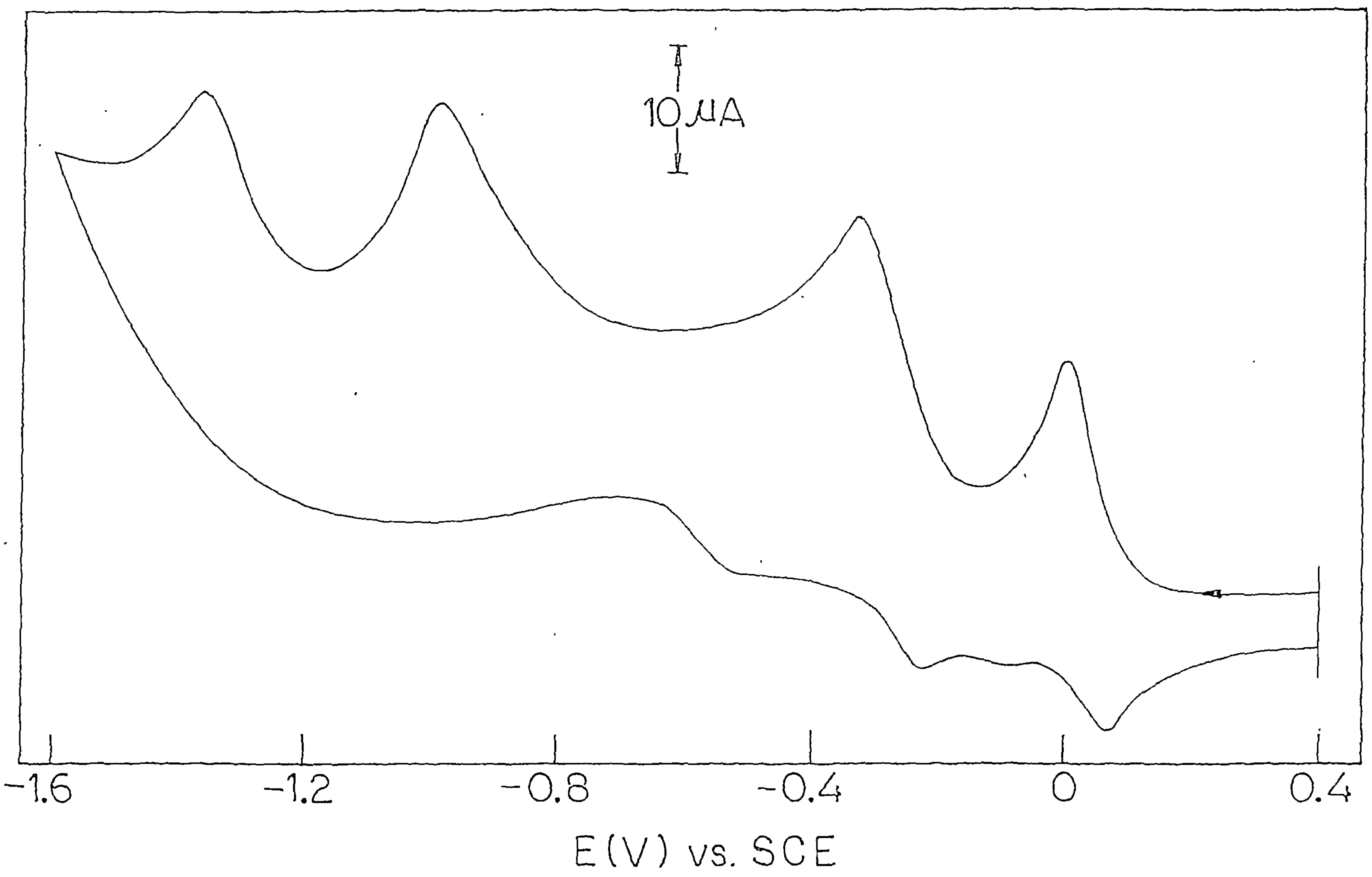


FIGURE VI.6. CYCLIC VOLTAMMOGRAM OF $[RhCl_2(L^2)_2]ClO_4.H_2O$ IN CH_3CN AT A 50 mVs^{-1} SCAN RATE

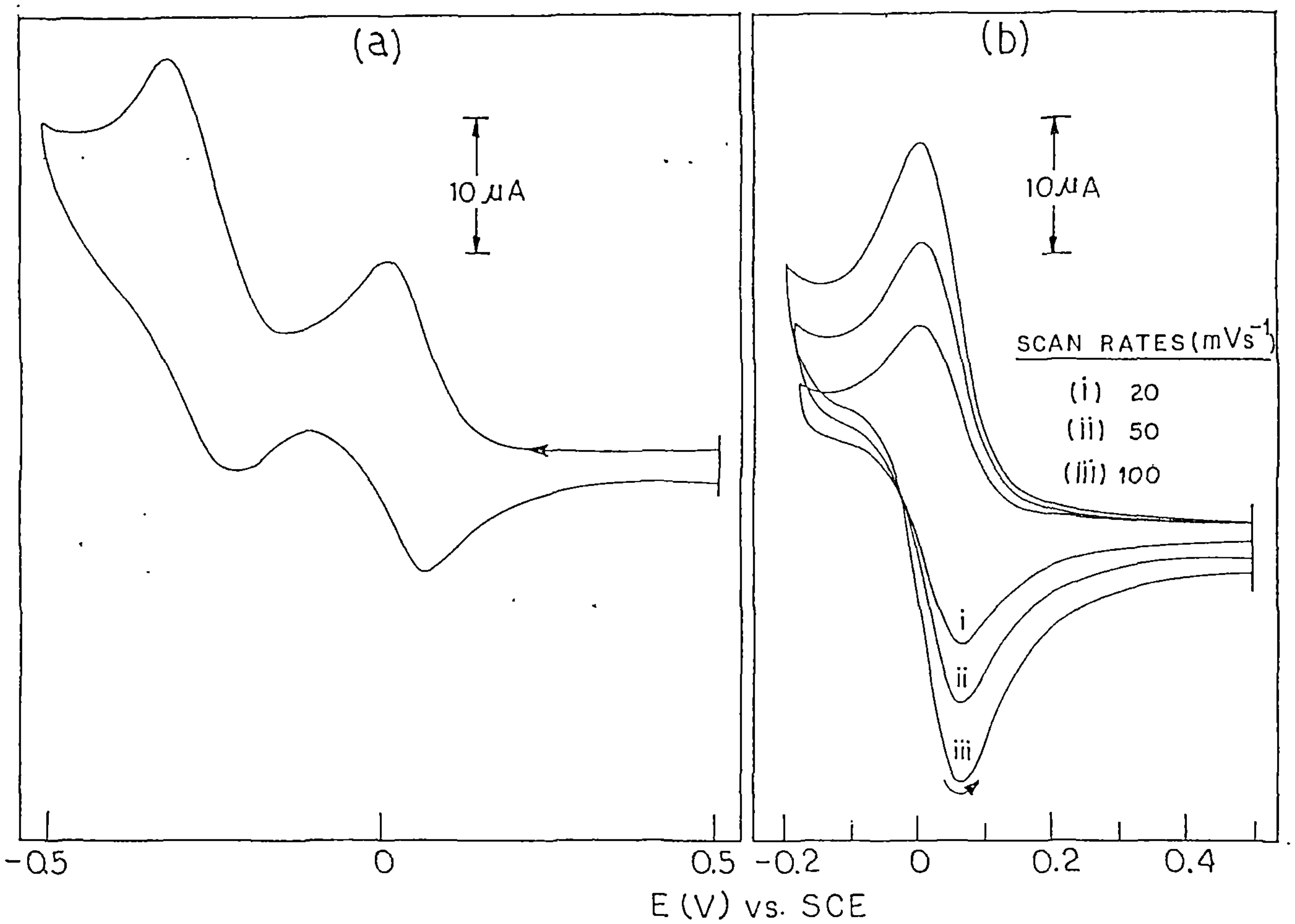


FIGURE VI.7. (a) CYCLIC VOLTAMMOGRAM OF $[RhCl_2(L^2)_2]ClO_4.H_2O$ IN CH_3CN AT A 50 mVs^{-1} SCAN RATE SHOWING FIRST AND SECOND REVERSIBLE REDUCTIONS

(b) CYCLIC VOLTAMMOGRAMS OF $[RhCl_2(L^2)_2]ClO_4.H_2O$ IN CH_3CN AT DIFFERENT SCAN RATES. REVERSAL OF SCAN WAS MADE BEFORE THE OCCURRENCE OF SECOND ELECTRON TRANSFER

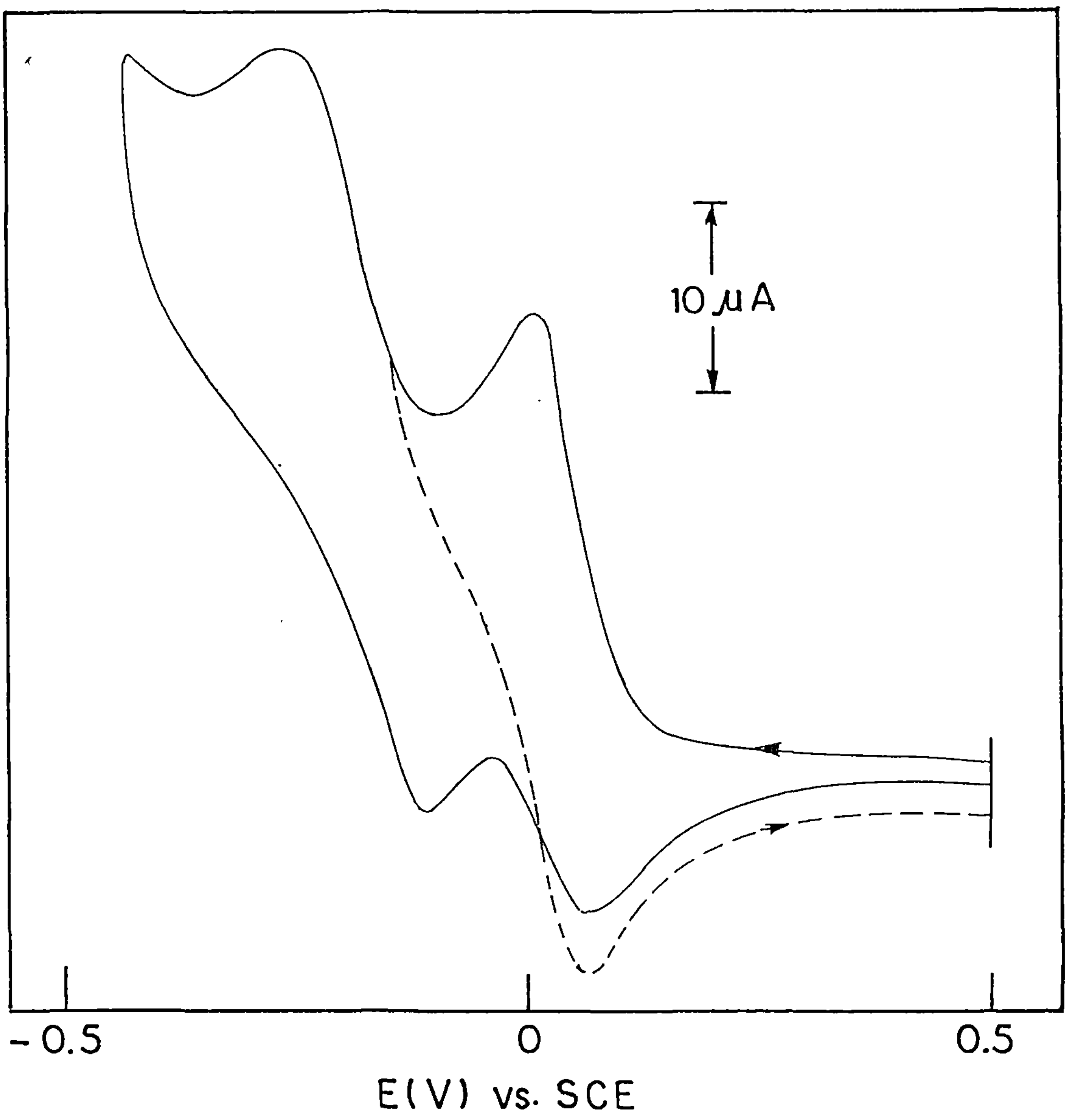


FIGURE VI.8

CYCLIC VOLTAMMOGRAM OF [$RhBr_2(L^2)_2$] $ClO_4.H_2O$ IN CH_3CN AT A 50 mVs^{-1} SCAN RATE. THE DOTTED LINE REPRESENTS THE REVERSAL OF CATHODIC SCAN BEFORE REACHING THE SECOND REDUCTION WAVE

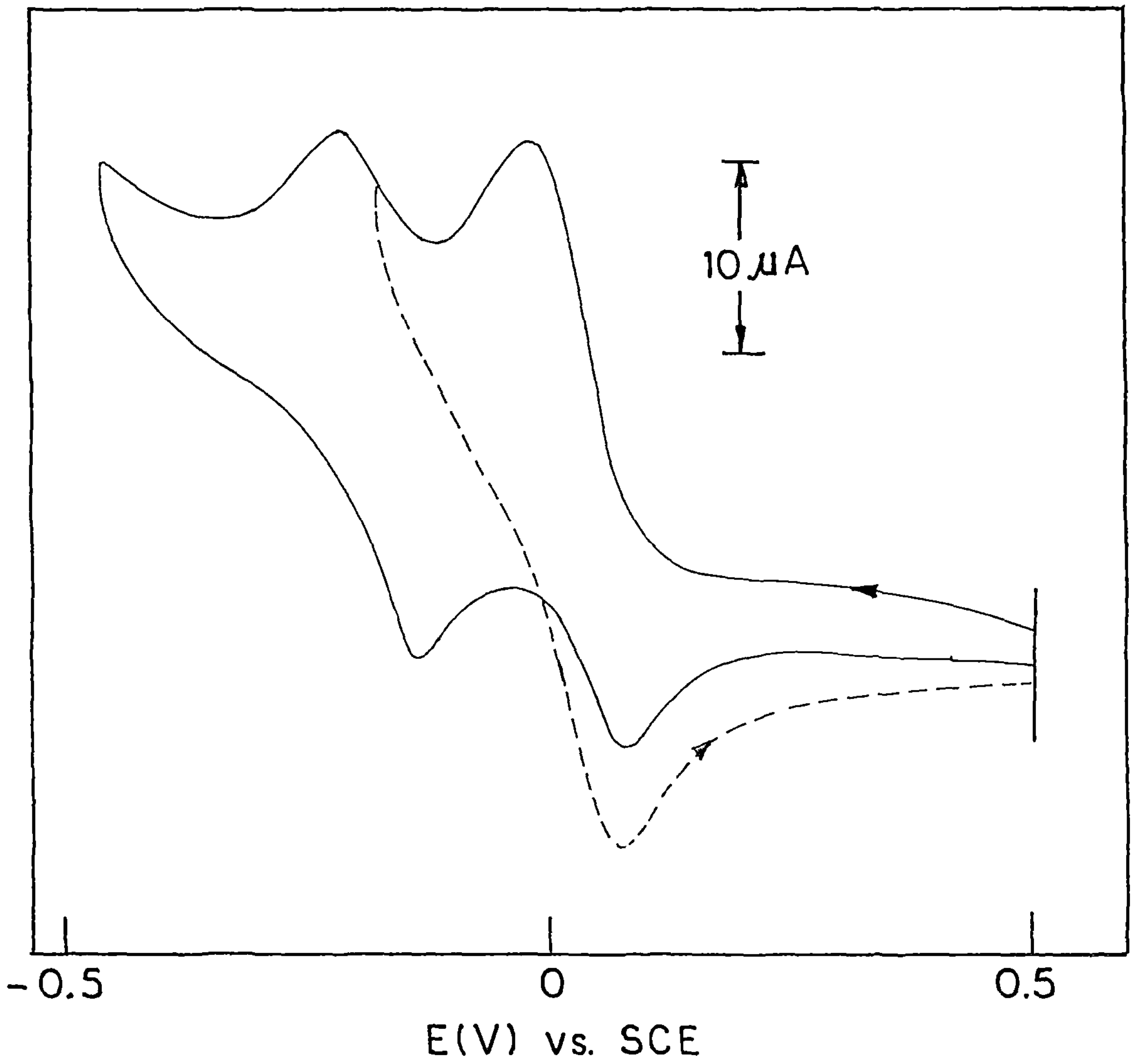


FIGURE VI.9. CYCLIC VOLTAMMOGRAM OF [$RhI_2(L^2)_2$] $ClO_4.H_2O$ IN CH_3CN AT A 50 mVs^{-1} SCAN RATE. THE DOTTED LINE REPRESENT THE REVERSAL OF CATHODIC SCAN BEFORE REACHING THE SECOND REDUCTION WAVE negative potentials. Four reductive responses are observable (Table VI.8, Figure VI.6 and VI.7) in each case. It is essential to use anhydrous solvents to be able to observe all the reductions. Presence of moisture leads to the collapse of the third and fourth reductive responses (III) and (IV) into two one electron transfer processes of unclear origin. The responses I and II are reversible whereas rest two viz.III and IV are irreversible in nature . The third and fourth electron reduced products of $[RhCl_2L_2]^+$ do not appear to be stable and on scan reversal multiple anodic responses of unclear origin were observed.

The colour of the acetonitrile solution of complex 2 (X=Cl) at the initial potential (+0.3V) was pale yellow but a purple colour is observed to develop at the electrode surface shortly after passing the potential corresponding to the least negative reversible wave, $E^{\circ}(1)$ at *ca*.0.0V. At more negative potentials three more responses at *ca*.-0.3V, *ca*.-1.0V and *ca*.-1.36V are also observable, of which the responses at negative potentials (*ca*.-1.0V & *ca*.-1.36V) are irreversible.

Properties of the reduced solutions of $[RhCl_2L_2]^+$. The coulometrically produced solutions obtained by electrolysis[42] of $[RhCl_2(L^2)_2]ClO_4.H_2O$ (2) at -0.1 and -0.4V are respectively purple and brown. Hydrazine also reduces $[RhCl_2(L^2)_2]^+$ to a purple solution. The reduced products are unstable and their isolation in the pure state has not been possible. However, we have managed to record the ESR spectra of the reduced solutions by performing the electrolysis at 260K and quickly freezing (acetonitrile, 77K) the electrolysed solutions. The parent complex (2) is diamagnetic and ESR silent. However, the solutions of the reduction products obtained by electrolysis at two different potentials (at -0.1 and -0.4V) shows highly intense, symmetric and sharp ESR signals[43] with g values at 1.9975 and 2.0006 respectively, as shown in Figure VI.10. In the presence of an aqueous solution of hydrazine, $[RhCl_2(L^2)_2]^+$ shows a similar ESR spectrum (Figure VI.10). These results strongly suggest that the unpaired electrons in the reduced products, $[RhCl_2(L^2)_2]$ and $[RhCl_2(L^2)_2]^-$ are localised[44,45] in orbitals of predominantly ligand character.

The free ligand L displays[8] two quasireversible cyclic voltammetric responses with peak-to-peak separation in the range 120-150mV. Since, no other reduction is observed, the non-generate LUMO is well separated from the next UMO.

$$L + e^- \rightleftharpoons L^-, \quad E^\circ_{298} = -1.31V \qquad (2)$$

$$L^- + e^- \rightleftharpoons L^{2-}, \quad E^\circ_{298} = -1.57V \qquad (3)$$

On comparison of potentials of couples (2) and (3) with those of free bpy[46] (bpy = 2,2'-bipyridine) on the one hand and aromatic azo ligands[47] on the other, it emerges that the electron accepting LUMO of L is primarily azo in character and the couples (2) and (3) essentially correspond to processes (4) and (5) respectively

$$[-N{=}N-] + e^- \rightleftharpoons [-N{\overset{.}{=}}N-]^- \qquad (4)$$

$$[-N{\overset{.}{=}}N-]^- + e^- \rightleftharpoons [-N-N-]^{2-} \qquad (5)$$

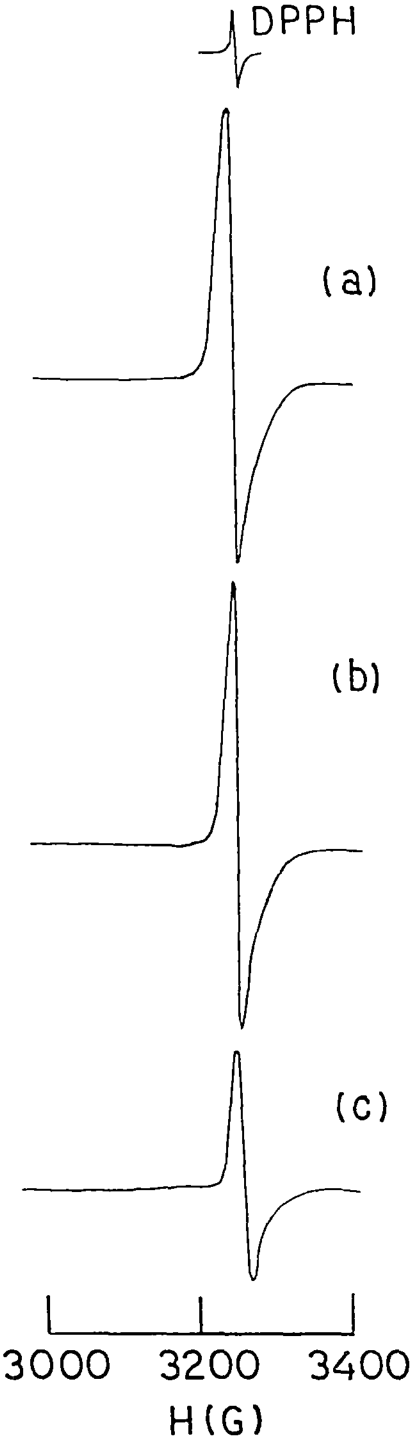


FIGURE VI.10
ESR SPECTRA (G = 10^{-4}T) OF FROZEN
CH_3CN (10^{-1}mol dm^{-3} TEAP) SOLUTIONS
AT 77K : (a) $[RhCl_2(L^2)_2]$,
(b) $[RhCl_2(L^2)_2]^-$ and (c) $[RhCl_2(L^2)_2]^+$
IN A DILUTE CH_3CN SOLUTION OF HYDRAZINE

Due to the high positive charge of the metal ion, Rh^{3+}, the formal potential for the first reduction of L in the complex is uniformly more positive by 1.3V than that of free L. In comparison, the Ru^{2+} analogue of L, tc-$[RuCl_2L_2]$ undergoes first reduction[11] at *ca.*0.5V vs. SCE. In the bis-ligated Rhodium(III) complexes, (2) four successive ligand reductions could thus occur in principle. This is exactly what we observed in our experiment. The spin multiplicity of the various reduced species are not known to us. However, in view of the small difference between successive reduction potentials, it is reasonable to assume that electrons are added successively to L retaining a high spin configuration. This has been shown below (equations 6-9).

$$[RhCl_2L_2]^+ + e^- \rightleftharpoons [RhCl_2\dot{L}\ L],\ E°_{(I)} \tag{6}$$

$$[RhCl_2\dot{L}\ L] + e^- \rightleftharpoons [RhCl_2\dot{L}_2]^-,\ E°_{(II)} \tag{7}$$

$$[RhCl_2\dot{L}_2]^- + e^- \longrightarrow [RhCl_2\ddot{L}\ \dot{L}]^{2-},\ E°_{(III)} \tag{8}$$

$$[RhCl_2\ddot{L}\ \dot{L}]^{2-} + e^- \longrightarrow [RhCl_2\ddot{L}_2]^{3-},\ E°_{(IV)} \tag{9}$$

It may be noted here that $|E°_{(I)} - E°_{(II)}|$ is much lower than $|E°_{(II)} - E°_{(III)}|$. This result probably suggest that first two electrons are added to the two degenerate orbitals, predominantly L in character. Addition of the third and fourth electrons (equations 8 and 9) require higher energies due to the presence of one electron in each one of the two orbitals of the ligand. A similar type of behaviour has also been observed[8] in a ruthenium(II) tris complex of L, $[RuL_3]^{2+}$.

Our experimental data described above clearly show that the first and second electron reductions of $[RhCl_2L_2]^+$ take place at the ligand centres.[7,8] Our proposal regarding the third and fourth electron reduction levels are not certain in absence of ESR data of the third and fourth electron reduced products. It however appears to be a most plausible one. Unfortunately, controlled potential coulometry experiments at more negative potentials (<-1.0V) were vitiated by substrate decomposition.

VI.3 EXPERIMENTAL SECTION

A. Physical Measurements

Melting point Measurements, Molar Conductivity, Infrared Spectra, Electronic Spectra and Magnetic Susceptibility Measurements etc. are described in Chapter II. High resolution ^1H NMR spectra were recorded with the help of 500 MHz FT-NMR spectrometer. The data were obtained from T.I.F.R. Bombay. Electrochemical measurements were done as described in Chapter II. In addition constant potential coulometry experiment was also performed using model 179 digital coulometer. X-band ESR spectra were recorded with a Varian E -109C spectrometer fitted with a quartz Dewar for measurements at 77K. The spectra were calibrated with the help of diphenylpicrylhydrazyl (DPPH) (g=2.0037). The spectra was obtained first by electrolysis of the solution at 260K and then quickly freezing (acetonitrile, 77K). The data were obtained from I.A.C.S., Calcutta.

B. Formulation of Compounds

Formulation of compounds were done by C,H,N micro-analyses as described in Chapter II.

C. Solvents

Preparation of solvents for preparative work as well as spectral and electrochemical measurements are described earlier (Chapter II).

D. Preparation of Compounds

(a) Chemicals

The salt $RhCl_3.3H_2O$ was obtained from Loba-chemie Indoaustranal Co. LiBr was obtained from Thomas Baker (Chemicals) Pvt. Ltd. Bombay; KI, Sarabhai M. Chemicals, Baroda; Hydrazine, Qualigens, Bombay.

All other chemical required for preparation of ligands are described in Chapter II. Preparation of $NaClO_4$ was described in Chapter II.

(b) Ligands

Synthesis of ligands L^1-L^3 are previously described (Chapter II).

(c) Complexes

(i) Dichlorobis[2-(Phenylazo)pyridine]rhodium(III) perchlorate monohydrate, $[RhCl_2(L^1)_2]ClO_4.H_2O$.

A sample of $RhCl_3.3H_2O$ (0.103g, 0.4 mmol) was dissolved in 20 ml methanol and to it 2-(phenylazo)pyridine (L^1) (0.209g, 1.1 mmol) was added. The mixture was heated to reflux for 3h. It was then cooled to room temperature and filtered. An aqueous solution of $NaClO_4$ (2g in 50 ml water) was added to the filtrate with stirring. A green yellow precipitate appeared. The mixture was then concentrated to half its initial volume by heating on a water-bath. The cooled solution was filtered and the precipitate was collected and washed thoroughly with water. Recrystallisation of the precipitate from dichloromethane-hexane (1:1) yielded the greenish yellow crystalline product. Yield: 84%.

(ii) Dichlorobis[2-(m-tolylazo)pyridine]rhodium(II) perchlorate monohydrate, $[RhCl_2(L^2)_2]ClO_4.H_2O$ and

(iii) Dichlorobis[2-(p-tolylazo)pyridine]rhodium(III) perchlorate monohydrate, $[RhCl_2(L^3)_2]ClO_4.H_2O$. These were prepared similarly using the appropriate ligand. Yields were as follows:

$[RhCl_2(L^2)_2]ClO_4.H_2O$: 89%
$[RhCl_2(L^3)_2]ClO_4.H_2O$: 85%

(iv) Dibromobis[2(m-tolylazo)pyridine]rhodium(III) perchlorate monohydrate, $[RhBr_2(L^3)_2]ClO_4.H_2O$.

To a solution of $RhCl_3.3H_2O$ (0.100g, 0.40 mmol) in 20 ml methanol, (1.0g) LiBr was added. The mixture was heated to reflux for 1h. 2-(m-tolylazo)pyridine(L^2) (0.24g, 1.20 mmol) was added and heated to reflux for another 2h. The solution then cooled to room temperature and was filtered. An aqueous $NaClO_4$

solution (2g in 50 ml water) was added to the filtrate with stirring. A reddish brown precipitate appeared. The mixture was then concentrated to half its initial volume by heating on a water bath. The cooled solution was then filtered and the precipitate was collected and washed thoroughly with water. Recrystallisation of the brown precipitate from dichloromethane-hexane (1:1) yielded an orange crystalline compound. Yield, 68%.

(v) Diiodobis[2-(m-tolylazo)pyridine]rhodium(III) perchlorate monohydrate, $[RhI_2(L^2)_2]ClO_4.H_2O$

This was prepared similarly to the dibromo analogue using KI(1g) instead of LiBr. A dark brown crystalline compound was obtained. Yield, 25%.

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Appendix

LIST OF PUBLICATIONS

1. **Synthesis, Characterisation, and Reactivity of New Mononitrosyl Complexes of Ruthenium containing 2-(Arylazo) pyridines : Examples of Strongly Electrophilic Nitrosyls**
   Alok K. Deb, P.C. Paul, and S. Goswami
   J. Chem. Soc., Dalton Trans., **1988, 2051.**

2. **Synthesis, Structure, and Electrochemical Reduction of 2-(Arylazo)pyridne Complexes of Rhodium(III)**
   Alok K. Deb and S. Goswami
   J. Chem. Soc., Dalton Trans., **1989, 1635.**

3. **New, Stable, Chelated, Tetracoordinated Silver(I) Complexes of the 2-(Arylazo)pyridine Ligand System : Synthesis, Characterization and Assessment of Bonding and Structure**
   Alok K. Deb, S. Choudhury, and S. Goswami
   Polyhedron, **1990, *9,* 2251.**

4. **Reactions of Primary Aromatic Amines with Strongly Electrophilic NO Coordinated to a Ruthenium Complex of 2-(Phenylazo)pyridine** Alok K. Deb and S. Goswami
   Polyhedron, **1991, *10,* 1799.**

5. **Use of Silver(I) Complexes in Synthesis of Bis- and Tris-2-(Arylazo)pyridine Complexes of Ruthenium(II) and Investigation of Solid-State Isomerisation**
   Alok K. Deb, Maushumi Kakoti, and S. Goswami
   J. Chem. Soc., Dalton Trans., **1991, 3249.**

In a Related Area

6. **A Novel and Generalised Approach to the Synthesis of ML_3^{n+} [M=Ru(II), Rh(III); L=2,2'-Bipyridine, 1,10-Phenanthroline and 2-(Arylazo)pyridine; n=2,3]**
   M. Kakoti, A.K. Deb, and S. Goswami
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