STUDIES ON THE CHEMISTRY OF RUTHENIUM WITH SCHIFF-BASE AND RELATED LIGANDS

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To My Parents
Who Have Been My Inspiration

इंडियन एसोसियेशन फर दि कल्टिवेशन आफ साइंस
ইণ্ডিয়ান এ্যাসোসিয়েশন ফর দি কালটিভেশন অব সায়েন্স
INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE

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I certify that the thesis entitled, "STUDIES ON THE CHEMISTRY OF RUTHENIUM WITH SCHIFF-BASE AND RELATED LIGANDS", submitted by Mr. Subrata Choudhury 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, while I was in the North-Eastern Hill University, Shillong. 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.

Sreebrata Goswami

Dated : Calcutta
the 29th August'96

(S. Goswami)

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CONTENT

PREFACE

The work presented in this thesis entitled "STUDIES ON THE CHEMISTRY OF RUTHENIUM WITH SCHIFF-BASE AND RELATED LIGANDS", originated from an attempt to develop the Chemistry of Ruthenium with α,α'-diimine ligand N-arylpyridine-2-carboxaldimine (L).

This thesis consists of seven chapters. A brief survey of known coordination chemistry of α,α'-diimine ligand along with the purpose of the present work is outlined in Chapter I. In Chapter II, the synthesis and characterization of the dihalo-bisligated complexes of Ruthenium(II) are described. The reactivity of the complexes toward oxidant is described in Chapter III. Chapter IV deals with the transformation of the coordinated azomethine to amide function and characterization of the trivalent species. Chapter V outlines the synthesis and characterization of the tetracoordinated silver(I) complexes of L. Chapter VI describes the use of Ag-L complexes in synthesis of tris chelated complexes of Ruthenium(II) with L. The concluding Chapter VII describes the transformation of coordinated piconaldimine to picolinamide and picolinate and their characterization.

The present work was initiated in July,1992 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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I am particularly indebted to Dr.S.Bhattacharya, J.U., Calcutta, for his help in computation of EPR data and Ms.R.Dey, I.A.C.S., Calcutta, for emission spectral data. I

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My grateful thanks also go to the Principal,K.N.Govt.College and Department of Education, Government of Meghalaya, for granting me the study leave to undertake the research work.

I wish to express my sincere thanks to my friends for their inspiration. I must also thank Mr.P.P.Dey for his painstaking effort in wordprocessing the entire thesis and Mr.P.Sinha for drawing the figures.

I am short of words to express my sense of gratitude to my parents and other members of my family for their continuous inspiration and constant encouragement.

Date: the 29th August'96.

Subrata Choudhury.

Subrata Choudhury

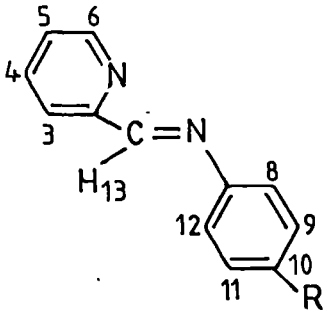
Abstract

STUDIES ON THE CHEMISTRY OF RUTHENIUM WITH SCHIFF-BASE AND RELATED LIGANDS.

ABSTRACT

The present thesis primarily deals with the Chemistry of a α,α'- diimine ligand, N-arylpyridine-2-carboxaldimine (L,1) involving ruthenium. It involves synthesis of new complexes and their thorough characterization. In two cases, structures have been determined by using single crystal x-ray diffraction techniques. Studies of chemical and redox properties of the synthesized compounds form an integral part of the present work. 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 seven chapters.

Chapter I briefly describes the salient aspects of the known coordination of α, α' - diimines. The scope of investigation of the coordination chemistry of the ligand, N-arylpyridine-2-carboxaldimine(L), has been delineated.



L,1

R : L
H : L^1
CH_3: L^2
Cl : L^3

Chapter II describes the isolation and characterization of a group of ruthenium complexes of the type RuX_2L_2 (Cl,Br) which are synthesized by refluxing hydrated RuX_3 (Cl,Br) with the ligand, L, in ethanol.

Owing to the unsymmetrical nature of the bidentate ligand L, five different geometrical isomeric forms are possible. Three of them are isolated by the use of

chromatographic technique. These are characterised with the help of spectroscopic data.

One of the isomers is green which shows a single sharp band for ν_{Ru-Cl} indicating a linear trans grouping for $RuCl_2$ moiety. Rest two isomers are bluish green and violet. Each of them shows a doublet ν_{Ru-Cl} in the range 310 to 290 cm^{-1}.

The geometries of the isomeric complexes are mainly assessed by an examination of high resolution ^{1}HNMR spectra of the complexes. Fortunately all the isomers of RuX_2L_2 display highly resolved ^{1}HNMR spectra which have been completely assigned. Using the ^{1}HNMR data and with the consideration of the models of different isomers it has been possible to assess the geometries of the different isomers of RuX_2L_2.

The solution electronic spectra of the isomeric RuX_2L_2 are dominated by the multiple charge transfer transition in the visible region which are assigned to MLCT [t_2--->π^*(L)] (metal to ligand charge transfer) transitions. Multiple transitions originate from lower symmetry splitting of metal level, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the exited state through

spin-orbit coupling. Transitions in the UV region are due to either intra ligand ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) or charge transfer transitions involving higher energy levels which are higher in energies than the ligand LUMO.

All the complexes display three one-electron nearly reversible to irreversible responses on the positive of SCE. The first quasi-reversible oxidation occurs in the range 0.25-0.50 V is assigned to the Ru(III)/Ru(II) couple.

$$Ru^{III}X_2L_2 + e \rightleftharpoons Ru^{II}X_2L_2$$

The formal potentials for Ru(III)/Ru(II) couple of the cis-isomers is higher than that of the trans isomers. This is due to superior π-interactions in the cis-geometries. The formal potential value of Ru(III)/Ru(II) couple also depends on the nature of the substituent(R) in the ligand. The value decreases with the electron-releasing power of the substituents. The irreversible electron transfer processes at very high positive potentials (~1.8V) are due to ligand based oxidation.

In the **Chapter III** the oxidations of the isomeric bivalent $RuCl_2L_2$ using Cl_2-gas as an oxidant and isolation of the corresponding isomeric trivalent complexes of ruthenium, $[RuCl_2L_2]ClO_4$, are described. Each of the trivalent salts is found to regenerate quantitatively

its corresponding bivalent congener on chemical and electrochemical reductions indicating the conversion, $Ru^{II}Cl_2L_2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Ru^{III}Cl_2L_2^+$, is reversible and stereoretentive.

The yellowish brown micro crystalline salts of $[RuCl_2L_2]ClO_4$, obtained almost in quantitative yields, are highly soluble in redox inert polar organic solvents and behave as 1:1 electrolytes.

The solution electronic spectra of the complexes are characterised by multiple intense absorptions in the visible range due to allowed transitions involving metal and ligand orbitals. A low energy weak absorptions in the range 1625-1450 nm. This low energy transition is due to d-d transition originated from splitting of the t_2-orbitals because of low symmetry and spin-orbit coupling. The energy of the ligand field band is in good agreement with the calculated transition energies using the observed g-values from the respective EPR spectrum.

The magnetic moments of the complexes correspond to low spin d^5 configurations (idealised t_{2g}^5, $s = \frac{1}{2}$). None of the isomers possesses rotational symmetry greater than two fold. Their EPR spectra in frozen acetonitrile-toluene (77K) are accordingly rhombic. The two

electronic transition energies, ΔE_1 and ΔE_2 ($\Delta E_1 > \Delta E_2$), have been computed using the observed g- values. The ΔE_2 transition in each of the complexes is observed in the range 6800-6155 cm^{-1} while ΔE_1 transition could not be observed due to solvent cut off.

Each of the isomers of $[RuCl_2L_2]^+$ displays a reversible, one electron cyclic voltammogram in the potential range 0.3-0.7 V. Under identical conditions the voltammograms (initial scan cathodic) is superimposable on that of the corresponding isomer $RuCl_2L_2$ (initial scan anodic) indicating the process under consideration is reversible and stereo retentive. The formal potential of Ru(III)/Ru(II) couple follow the order: ttt-<cct-<ctc-. Thus the trivalent complex in ctc-geometry is the strongest oxidant. The reduction of the trivalent complex with hydrazine hydrate was examined spectrophotometrically and found to be instantaneous and almost quantitative. In acetonitrile, $RuCl_2L_2^+$ complexes act as mild oxidants.

In **Chapter IV** we describe an interesting ruthenium mediated oxidation of aldimine to amide which is otherwise not obtainable

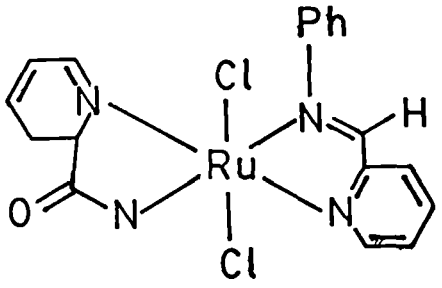
Conversion of an aldehyde function (-CHO) to an amide function (-CONHR) follows the route,

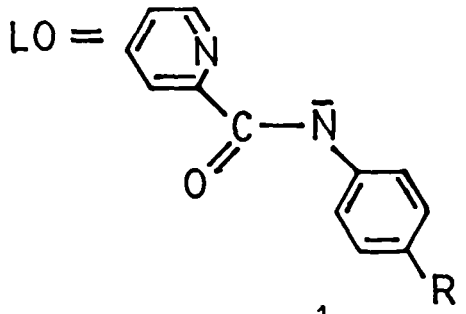
$$-CHO \xrightarrow{[O]} -COOH \xrightarrow{RNH_2} -CONHR,$$

In the present work the conversion (equation 1) follows the reverse sequence,

$$-CHO \xrightarrow{RNH_2} -CHNR \xrightarrow{[O]} -CONHR,$$

A family of isomeric ruthenium amido complexes have been isolated in excellent yields by oxidising the isomeric ruthenium bivalent diimine complexes, $[Ru^{II}(LH)_2Cl_2]$, with aqueous H_2O_2 (also aqueous Ce^{4+}). The complexes of trivalent ruthenium are of the type $[Ru(LO)(LH)Cl_2]$ formed with retention of parental isomeric structure, where LO is N-bonded arylamide bonded to Ru(III) in anionic deprotonated form, LO^-, while the diimine LH is neutral.





$R = H : L^1O$

$R = CH_3 : L^2O$

One of the isomers, trans-$[Ru(L^1O)(L^1H)Cl_2]$ is structurally characterised by the use of X-ray diffraction technique in collaboration. The suitable crystals for the other two isomers could not be developed so far. However, their geometries could be assessed from their spectral data.

All of them displayed a sharp band at ca.1630 cm^{-1} assigned to $\nu_{C=O}$ which is at higher energy compared to that of $\nu_{C=N}$ at ca.1600 cm^{-1}. A single, strong and sharp band in the region 300-305 cm^{-1} has been displayed by the trans-amido isomer assignable to ν_{Ru-Cl} which strongly suggests a linear or nearly linear trans grouping for $RuCl_2$ moiety. A doublet has been observed at the range 290-310 cm^{-1} for other two cis-amido isomers.

The solution electronic spectra of all the complexes are dominated by an intense absorption at ca.500 nm. Other then this more absorptions are observed in the range 280-360 nm. The origin of these absorptions may be due to LMCT (ligand-to-metal charge transfer). A low intensity band occurs for all amido complexes in the near IR region at ca.1460 nm, which is assigned to ligand field transition with in the t_2 shell split by the rhombic nature of the ligand field.

The EPR spectra of the three isomeric Ru(III) amido complexes are rhombic at 77K in frozen acetonitrile-toluene. Both the predicted and observed energies of the band follow the order: trans-<cis-, which is also consistent with ligand filed description of t_2 splitting and this inequality is of diagnostic value for rhombic structure assignment.

The magnetic moment measurement suggests the complexes are of low-spin d^5 configuration (idealised t_{2g}^5; S = $\frac{1}{2}$).

In CH_3CN, the trans- as well as cis-amido isomers of $RuCl_2(LO)(LH)$ display two nearly reversible one electron cyclic voltammetric responses at ca. -0.15V and at ca.1.25V due to stereo retentive Ru(III)/Ru(II) and Ru(IV)/Ru(III) redox respectively. The much lower value of Ru(III)/Ru(II) couple in amide complexes,

$$trans\text{-}/cis\text{-}Ru^{III}(LO)(LH)Cl_2 + e \rightleftharpoons Ru^{II}(LO)(LH)Cl_2^-,$$

than in original diimine complex,(at ca.0.35V), signifies the strong stabilization of the higher oxidation state by the amide ligand.

It has been shown that the transformation of $[Ru(LH)_2Cl_2]$ to the corresponding isomeric $[Ru(LO)(LH)Cl_2]$ proceeds via the formation of $[Ru(LH)_2Cl_2]^+$. The wet solution of $[Ru(LH)_2Cl_2]^+$ spontaneously and quantitatively disproportionate as

$$3\ trans\text{-}/cis\text{-}Ru(LH)_2Cl_2^+ + H_2O \longrightarrow trans\text{-}/cis\text{-}Ru(LO)(LH)Cl_2 + 2\ trans\text{-}/cis\text{-}Ru(LH)_2Cl_2 + 3H^+$$

It is proposed that the water molecule adds to the azomethine function to produce α-hydroxy amine function which is then rapidly oxidised to form the final product.

A preliminary report on the photo induced oxidation of trans-$[Ru(LH)_2Cl_2]$ by molecular oxygen to the corresponding trans-$[Ru(LO)(LH)Cl_2]$ has been also described.

The chemistry of silver complexes of N-arylpyridine-2-carboxaldimine ligand, L(1) is the subject matter of **Chapter V**. The silver complexes of N,N-donors have been shown to be useful synthons for the controlled synthesis of transition metal complexes from their halide salts.

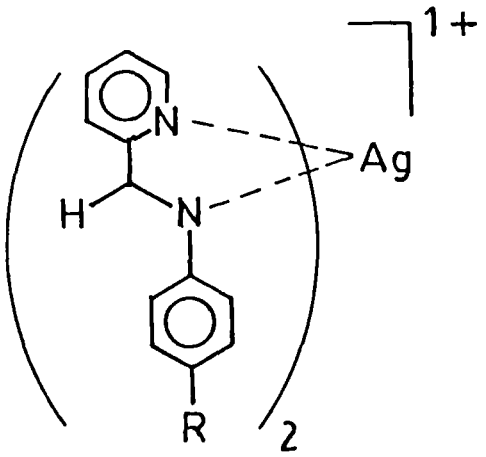
Silver nitrate reacts with boiling ethanolic solution of L(1) in the molar ratio of 1:2 to yield cationic $[AgL_2]^+$ (2), which has been isolated as a crystalline per chlorate salt

$$AgNO_3 + 2L \longrightarrow [AgL_2]^+ + NO_3^-$$

The complex of general type $[AgL_2]ClO_4$ has been formulated by elemental analyses. 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. This shows characteristic absorptions, $\nu_{C=N}$(pyridine) and $\nu_{C=N}$(imine), for coordinated ligand with shifts to lower frequencies compared to free ligand, which suggest that the ligand L is coordinated to silver(1). The high resolution ^{1}HNMR spectra of the complex with different substituted ligands are reported and completely assigned. It has been shown from the ^{1}HNMR data that two ligands in the present silver complex are magnetically equivalent at least in NMR time scale. Based on NMR and IR data it has been proposed that the structure of $[AgL_2]^+$ is tetrahedral.

The solution electronic spectrum of the complex is dominated by intense absorptions in the UV region which may be due to intra ligand transitions.

The stability of the silver compound in chloroform, methanol and acetonitrile have been verified by Beer's Law. These are quite stable in methanol and chloroform



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where as the solutions of them in acetonitrile do not obey Beer's Law.

The reactivities of $[AgL_2]^+$ towards the metal chlorides have been explored and isolation as well as characterization of the resultant complex of the type ML_3^{2+} (M = Fe,Co,Ni) have also been reported.

$$FeCl_3 \cdot 6H_2O + 3AgL_2^+ \longrightarrow FeL_3^{2+} + 3AgCl + 3L$$

$$MCl_2 \cdot 4H_2O + 2AgL_2^+ \longrightarrow ML_3^{2+} + 2AgCl + L$$

Chapter VI describes a generalized synthetic route using silver(I) complexes of I and bpy for the synthesis of a complete series of tris-chelated complexes, $[RuL_n(bpy)_{3-n}]^{2+}$ (n = 0--3)

The direct reaction of hydrated $RuCl_3$ with L in solution failed to afford isolable $[RuL_3]^{2+}$ species. Then the silver(I)-assisted synthetic route was explored for the synthesis of trischelates. The reactions of chloride salts of ruthenium and the silver bis complexes $[AgL_2]ClO_4$ proceeded smoothly in ethanol to yield tris-chelated species, which were isolated as their perchlorate salts

$$RuCl_3 \cdot 3H_2O + 3[AgL_2]^+ \xrightarrow{EtOH} [RuL_3]^{2+} + 3AgCl + 3L$$

$$cis\text{-}[RuCl_2L_2] + 2[AgL_2]^+ \xrightarrow{EtOH} [RuL_3]^{2+} + 2AgCl + 3L$$

$$cis\text{-}[RuCl_2(bpy)_2] + 2[AgL_2]^+ \xrightarrow{EtOH} [RuL(bpy)_2]^{2+} + 2AgCl + 3L$$

$$cis\text{-}[RuCl_2L_2] + 2[Ag(bpy)_2]^+ \xrightarrow{EtOH} [RuL_2(bpy)]^{2+} + 2AgCl + 3bpy$$

The composition of the new compounds, purified by column chromatography, were formulated by elemental analyses. These are diamagnetic (t_2^6) and 1:2 electrolytes in acetonitrile and show characteristic absorptions for coordinated L and bpy, in their IR spectra.

The geometry of the complex $[RuL_3]^{2+}$ was determined by ^{1}HNMR spectroscopy. The methyl signal of $[RuL^2_3]^{2+}$ (L^2 = N-p-tolypyridine-2-carboxaldimine) was observed with the intensities 1:2 at 2.18 and 2.08δ respectively which is characteristic for a meridonal geometry.

The solution electronic spectra of the complexes

are very similar to that of $[Ru(bpy)_3]^{2+}$ in intensity and profile except for the lowest energy transition for $[RuL_3]^{2+}$ which appears at lower energy (480 nm) compared to that of $[Ru(bpy)_3]^{2+}$ (454 nm). Excitation of ethanolic solutions of the complexes at 430 nm at 77K resulted in multiple band emission spectra.

In acetonitrile solution at room temperature, four successive reversible to quasi reversible one electron cyclic voltammetric responses are observed for $[RuL_3]^{2+}$ in the range +1.8 to -2.0 V versus the SCE at a platinum electrode. The response at the positive of SCE is a metal centred process, Ru(III)/Ru(II). Other three cathodic couples represent successive reductions of the three coordinated ligands.

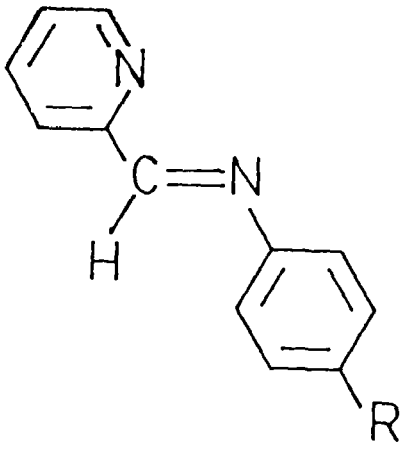
$$[Ru^{III}L_3]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_3]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_2(L^{\cdot})]^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$$

$$[Ru^{II}L(L^{\cdot})_2] \underset{-e^-}{\overset{+e}{\rightleftharpoons}} [Ru^{II}L_3^{\cdot}]^{-}$$

For the cationic complex $[RuL_3]^{2+}$, six successive reductions in principle could occur. Five responses were observed in the experimentally accessible range by employing glassy carbon as a working electrode.

A linear correlation of $\Delta E_{ox/red}$ (the difference of the formal potential of the Ru(III)/Ru(II) couple and the first ligand reduction couple) with MLCT absorption energies has also been reported.

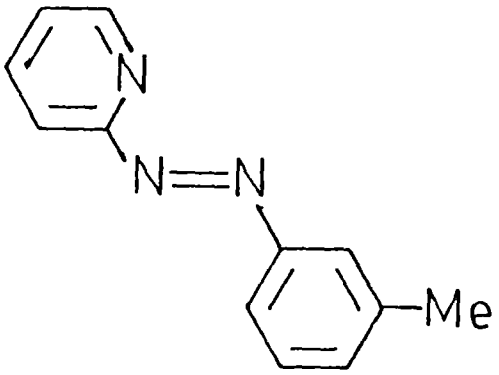
The **Chapter VII** describes the synthesis of tris chelated complexes $[Ru(II)_n(La)_{3-n}]^{2+}$ (La = 2-(arylazo)pyridine, 2-phenylpyridine or aldimine, La = 2-(arylazo)pyridine) based on silver(I) assisted trans-metallation synthetic route.



R=H : L^1H

R=Me : L^2H

1



La

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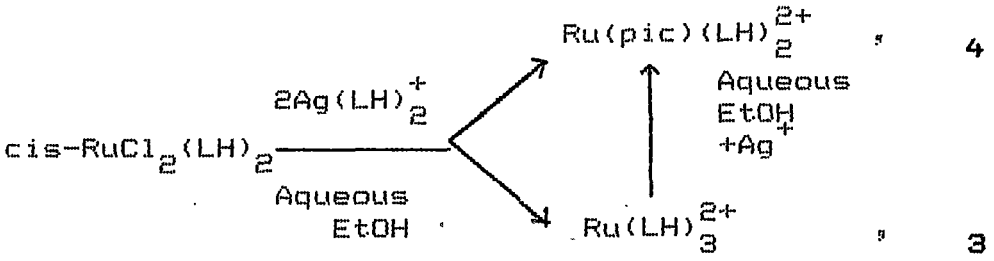
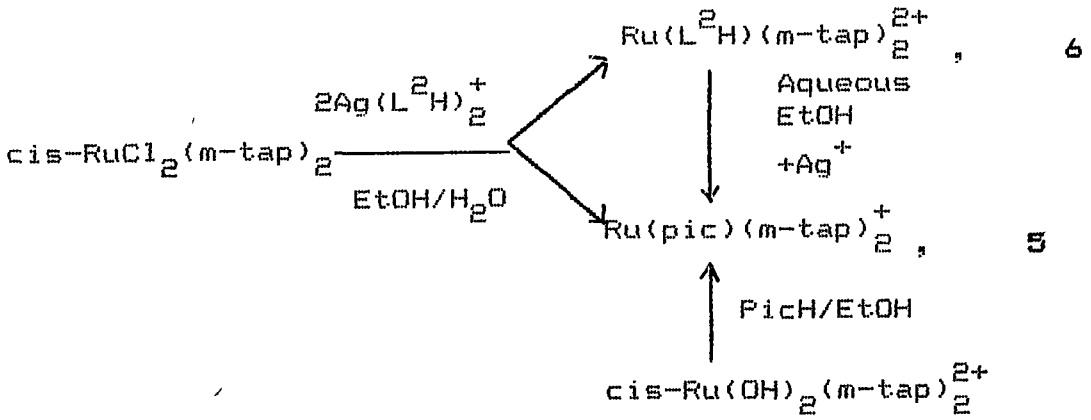
In the process of synthesizing mixed ligand chelated ruthenium complexes of LH(1) and 2-(m-tolylazo)pyridine (La,2) some interesting products were obtained along with the expected products which are elaborated below (Schemes I-III):



Scheme I

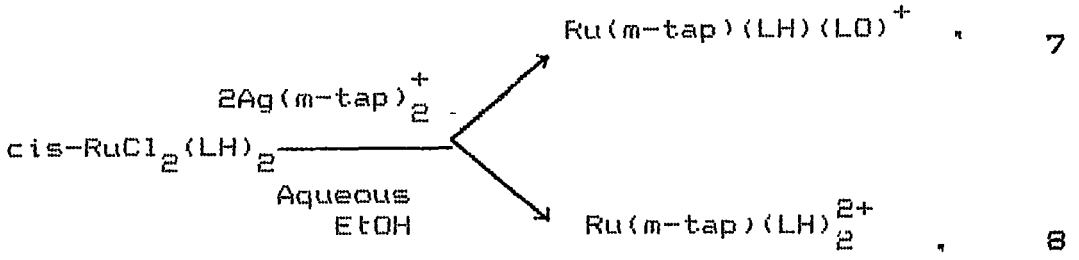
The bluish green cis-$RuCl_2(LH)_2$ reacted with two moles of $Ag(LH)_2^+$ in 1:1 aqueous ethanol to produce a pink compound in addition to the expected brown tris-chelate, $Ru(LH)_3^{2+}$ (3). Interestingly, an aqueous ethanolic solution of pure $Ru(LH)_3^{2+}$ in the presence of dilute aqueous $AgNO_3$ quantitatively produced the pink compound. The pink compound is analysed as $[Ru(pic)(LH)_2]ClO_4 \cdot CH_2Cl_2$ (4) (pic = 2-picolinate anion). The compound 4 is diamagnetic and displayed a moderately strong band at 1650 cm^{-1} indicating the presence of carboxylic function along with the characteristic features of coordinated LH and ionic ClO_4^-. The compound 4 (LH = L^1H) is structurally characterised by the use of x-ray diffraction technique.



Scheme II

The reaction of $cis\text{-}RuCl_2(m\text{-}tap)_2$ with two moles of $Ag(LH)_2^+$ in aqueous ethanol resulted the formation of a mixture of a brown and a violet products. The violet product may be generated by boiling the brown product in aqueous ethanol in the presence of dil $AgNO_3$ solution. Interestingly, the reaction of $cis\text{-}Ru(OH_2)_2(m\text{-}tap)_2^{2+}$ with PicH in ethanol instantaneously produces the violet product in a high yield.

The brown product is analysed and characterised as $[Ru(L^1H)(m\text{-}tap)_2](ClO_4)_2\cdot H_2O$ (6) whereas the violet one is characterised as $[Ru(pic)(m\text{-}tap)_2]ClO_4\cdot CH_2Cl_2$ (5). The compound 5 is 1:1 electrolyte and displays a moderately strong absorption at 1660 cm^{-1} characteristic for carboxylic function which is conspicuously absent in compound 6.



Scheme III

A mixture of a pink and a brown products were resulted when cis-$RuCl_2(L^2H)_2$ reacted with two moles of $Ag(m\text{-}tap)_2^+$ in aqueous ethanol. The pink compound was analysed as $[Ru(L^2H)(L^2O)(m\text{-}tap)]ClO_4 \cdot CH_2Cl_2$ (L^2O = N-p-tolyl-2-picolina--mide) (7). The compound 7 is 1:1 electrolyte and displayed a moderately strong band at 1620 cm^{-1} thereby showing the presence of an amide function. The compounds are characterised by spectral data.

The metal oxidation as well as ligand reductions for the above complexes have been studied voltammetrically in acetonitrile using platinum as the working electrode. It has been observed that the oxidation of the transformed complexes, viz. $[Ru(pic)(LH)_2]^+$, $[Ru(pic)(La)_2]^+$ and $[Ru(LH)(LO)(La)]^+$ occur at lower potential as compared to their parent $[Ru(LH)_n(La)_{3-n}]^{2+}$ complexes. All the complexes show metal-to-ligand charge transfer transitions in the visible range and absorption energies linearly correlate with

the differences between the metal oxidation and the first ligand reduction potentials.

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

Chapter II: Polyhedron, 1992, 11, 3183.

Chapters III: Polyhedron, 1995, in Press

Chapters IV: J. Chem. SOc., Commun., 1994, 57.

Chapter V: Polyhedron, 1994, 13, 1063.

Chapter VI, J. Chem.Soc., Dalton Trans., 1994, 1305.

Chapters VII: Communicated.

Chapter I

CHAPTER I

SCOPE AND THE PURPOSE OF THE PRESENT INVESTIGATION

Abstract:

The metal ion and ligands used in the present work are briefly enumerated in the chapter.

I.1 Preamble

Molecules with carbon nitrogen double bond, C=N, and in particular the α, α' - diimines have attracted much interest for the use as ligands in metal complexes. For example, the century old 2,2'-bipyridine (bpy) molecule belongs to the above class and its complex with Fe(II), $Fe(bpy)_3^{2+}$ has a great analytical value. Its homologue $Ru(bpy)_3^{2+}$ ion, is a complex whose outstanding photo physical, photochemical and redox properties have been widely investigated over the past 15-20 years. Recent comprehensive reviews illustrate the widespread use of this complex and of its derivatives in defferent reactions.

Ruthenium(II) is renowned for forming very inert bonds with imine nitrogen centres[17] and the ligand α-donor strength, as estimated by the protonation constant, pK_{BH^+},[18,19] plays a crucial role in determining the energy of ocrupied metal d-levels and the potential for dissociation. On the otherhand, the accessibility of a redox-active

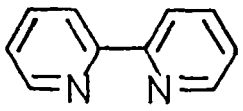
metal-to-ligand charge transfer (MLCT) excited state at low energy depends[20] on the presence of low-lying π^* levels in the coordinated ligand(s). While the former effect causes a stabilization of filled metal d-orbitals and the latter effect leads to a stabilization of ligand centred LUMO's available for charge transfer. Strategies to shift the absorption maximum to lower energy in the above complexes is an important area of research in connection to search[21,22] for effective photocatalysts in the long wavelength region of the solar spectrum. Therefore, attempts towards the synthesis of new compounds, using rationally designed ligands that convey desired properties such as absorption energies and redox potentials to the complexes, seems appropriate.

I 2. Purpose of the Present Work

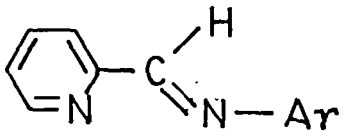
With the background discussed in the last section we set out to explore the synthesis and properties of ruthenium complexes derived from neutral Schiff-base ligand,[23-26] viz. N-aryl-2-pyridinecarboxaldimine,L. Our interests in this area arose due to the following reasons. The ligand, L belongs to α, α'- diimine class and it differs in two major respects from bpy. It has already been established that its lowest π^* is at a lower energy and as a result π - back bonding to L is stronger than bpy. This, has a notable influence on the spectroscopic and redox properties of these complexes. For example, the ruthenium(II) and iron(II) complexes of L absorb[28-30] at much lower energies

$-N=C-C=N-$

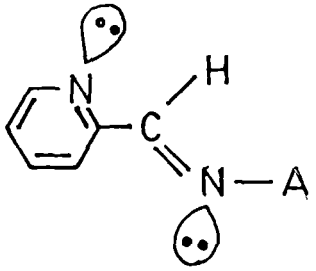
α, α' — Diimine Chromophore



2,2′-Bipyridine



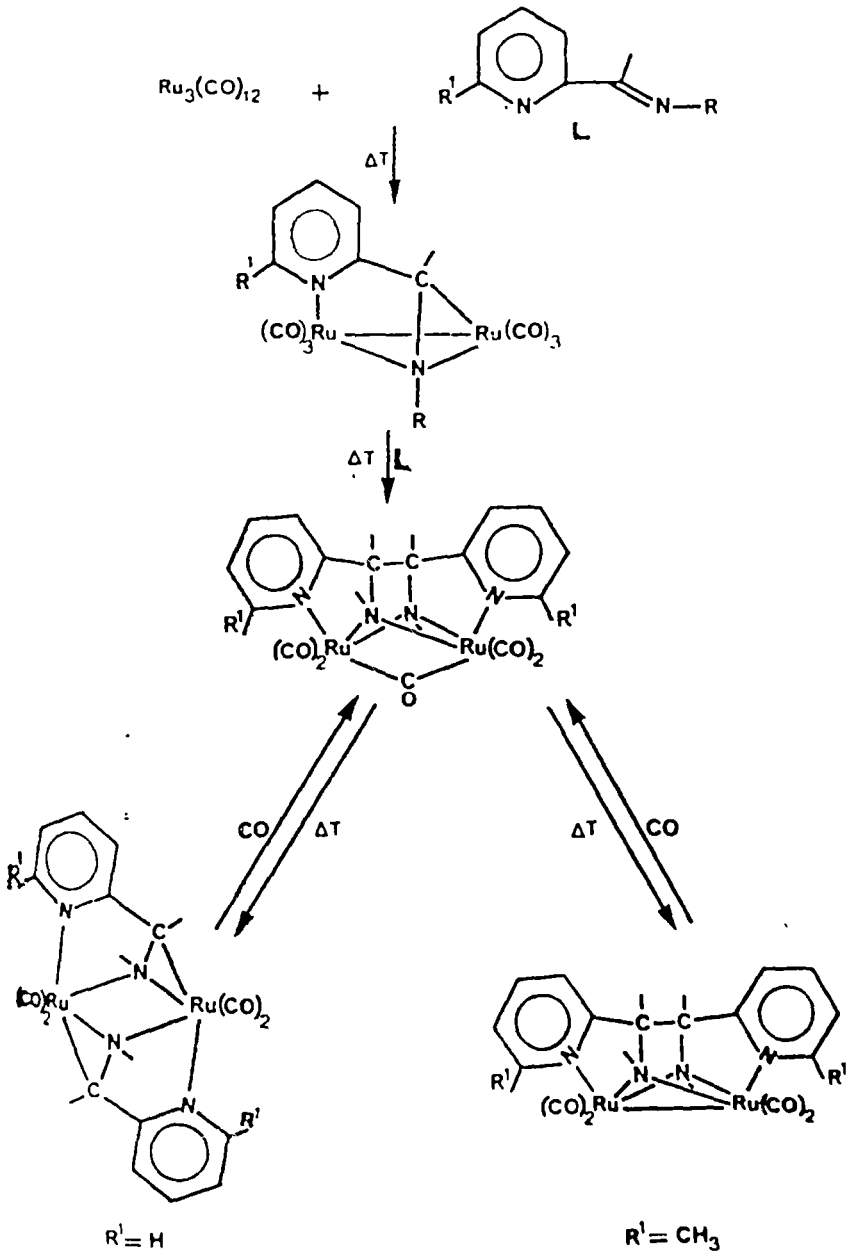
N-Aryl-2-pyridyl Carboxaldiimine (L)



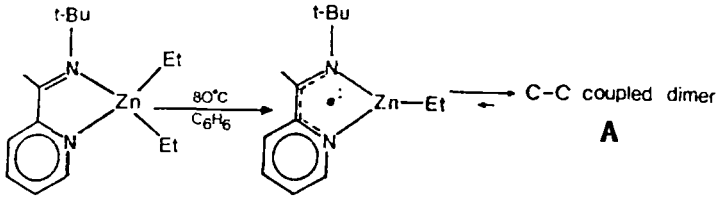
The ground state conformation of L

than the corresponding complexes of bpy. Moreover, the ligand L is more flexible and can coordinate in different ways. Different modes of coordination modes of L have been best exemplified[31-34] in the organometallic complexes of L. Two selective examples of the ligands are shown[35,36] in **Scheme** I[34] and II.[35]

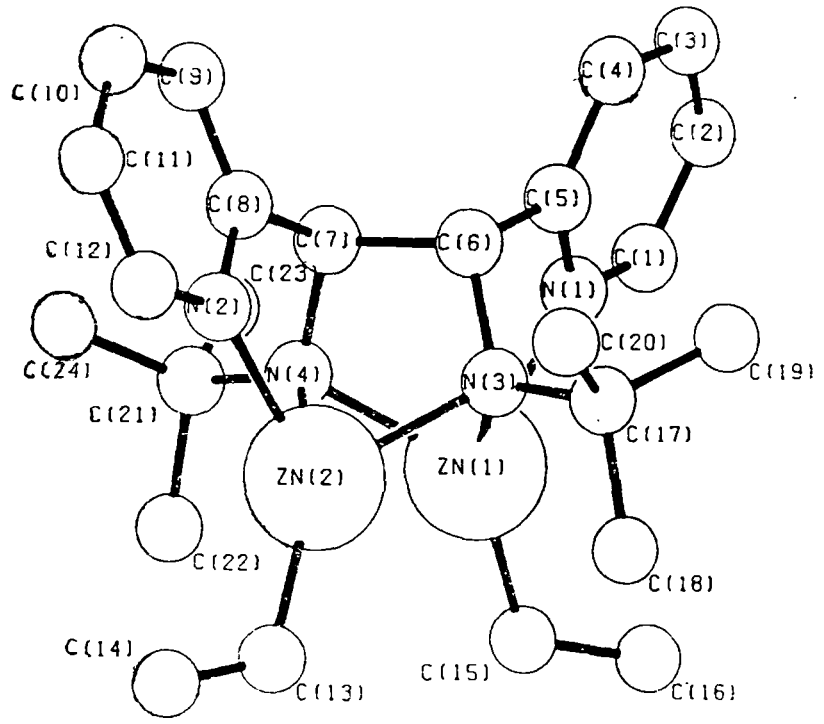
Outside organometallic chemistry, there have been only stray reports on the ruthenium complexes of L. In 1978, Dose and Wilson first reported the synthesis of $[RuL_3](PF_6)_2$ from $K_2[RuCl_5(H_2O)]$. Subsequently, Belser and Zelewsky described[38] the synthesis and properties of a mixed ligand bivalent ruthenium compound. In both the complexes the ligand L binds as a bidentate N,N-donor. The scanty reports in this area is probably due to the lack of suitable synthetic methodologies for the synthesis of above complexes. The work described in the succeeding chapters (II-VII) indeed shows that the coordination chemistry of ruthenium involving L as potentially extensive with many novel features. Efficient, new and direct synthetic routes for the synthesis of above complexes have been developed. Thorough characterization of the complexes have been made based mainly on photochemical data. Some of these properties are not only unusual but also has direct relevances to the design and probable synthesis of efficient redox catalysts. Two novel chemical reactions on these complexes have been followed by the determination of three diamensional X-ray structures (in collaboration) of the products.



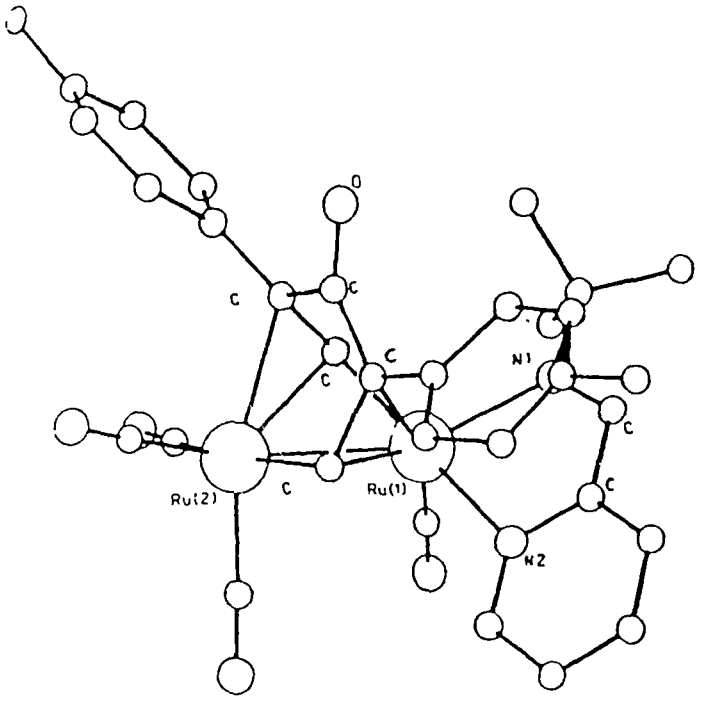
SCHEME I : Reaction Scheme for $Ru_3(CO)_{12}$ and L


t-Bu
Et
N
Zn
Et
N
80°C
C_6H_6
t-Bu
N
Zn—Et
N
C-C coupled dimer
A

SCHEME II


C(10)
C(9)
C(11)
C(8)
C(12)
C(23)
N(2)
C(24)
C(21)
N(4)
ZN(2)
ZN(1)
N(3)
C(22)
C(14)
C(13)
C(15)
C(16)
C(17)
C(18)
C(19)
C(20)
N(1)
C(5)
C(6)
C(7)
C(4)
C(3)
C(2)
C(1)

A



Structure of $Ru_3(CO)_4$ t-Bu-Pyca)(HC-CR)$_2$(CO)

The primary aim of this work may be described in brief by the following points:

(i) Synthesis of new complexes of ruthenium using N-aryl-pyridine-2-aldimine, L as the ligand.

(ii) Characterization of the complexes using spectroscopic techniques.

(iii) Study of redox properties using different electrochemical techniques.

(iv) Study of reactivities of the complexes with special emphasis on redox and ligand displacement reactions.

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Chapter II

CHAPTER II

ISOMERIC COMPLEXES OF RUTHENIUM (II) WITH N - ARYLPYRIDINE - 2 - CARBOXALDIMINES. HIGH RESOLUTION PROTON RESONANCE SPECTRA OF TRANS AND CIS ISOMERS OF RuX_2L_2 (X=Cl, Br) AND COMPARISON OF THEIR PHYSICAL PROPERTIES*

Abstract: *The reaction of N-arylpyridine-2-carboxaldimine [$RH_4C_6NC(H)Py$, L(I)] with hydrated RuX_3 (X=Cl, Br) in boiling C_2H_5OH affords dark crystals of RuX_2L_2. Three geometrical isomers of the compound have been isolated and characterized by analytical and spectroscopic data. The trans isomer of $RuCl_2L_2$ shows a single sharp band for ν(Ru-Cl), where as two bands are observed for the corresponding cis isomers. The high resolution ^{1}HNMR spectra of the isolated complexes are reported and completely assigned. All the complexes have multiple $t_2 \longrightarrow \pi^*(L)$ transitions in the visible region. Each of the complexes display a quasi-reversible oxidative response due to an Ru(III)/Ru(II) couple in the range 0.25-0.50 V vs. SCE at a platinum working electrode. The formal potentials of this couple obey the Hammett linear relationship. The ligand-based irreversible oxidations are also noted.*

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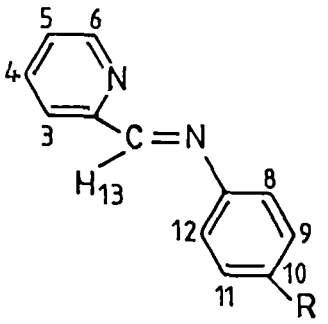
*A part of this work has appeared in *Polyhedron*, 1992, 11, 3183.

II.1 INTRODUCTION

The chemistry of ruthenium complexes of unsaturated nitrogenous ligands is quite extensive.[1-3] However, the Schiff base complexes of ruthenium in general, and bivalent ruthenium in particular, represent[4-10] a relatively unexplored area of chemistry. Our interest in platinum group metal complexes[14-18] of organic ligands with varying degree of σ-basicity and π-acidity led us to explore the ruthenium chemistry of neutral Schiff base ligand system, N-arylpyridine-2-carboxaldimine [L(I)].



L, 1

R : L
H : L^1
CH_3: L^2
Cl : L^3

The ligand L has an α,α'-diimine fragment and it may be noted that most of the α,α'-diimine complexes of ruthenium(II) generally show charge-transfer emission—— a property that helps in mediating[19-21] important photo-induced reactions.

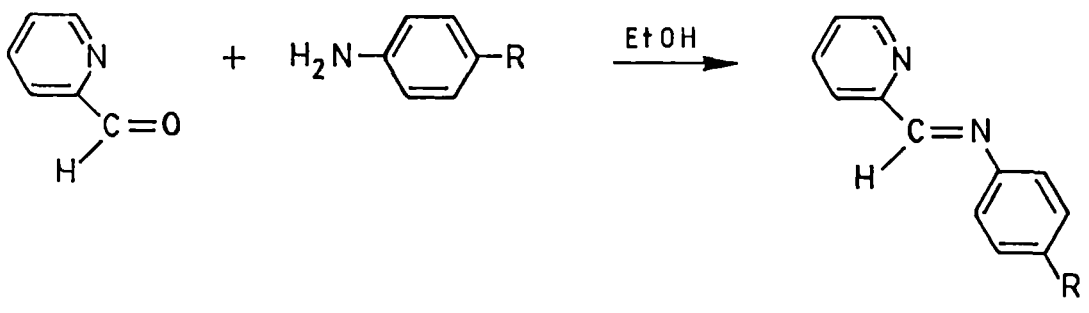
In recent years only a few reports[22-24] of ruthenium complexes of L or related ligands have appeared in the literature. In this chapter we describe the successful synthesis and charcaterization of isomeric bischelated ruthenium(II) complexes of the general type RuX_2L_2 (X=Cl,Br). Stereochemical assessments of the complexes are made on the basis of their spectral data.

II.2 Results and discussion

A. Synthesis and Formulation

(i) Ligands

The three pyridine-2-carboxaldimines(L,1), differing with respect to the substitution on the aryl ring, used in the present work, are abbreviated as L^1- L^3. These were synthesised[24] in high yields by the reaction of 2-piconaldehyde with primary aromatic amines in boiling ethanol (equation 1):



Final purification in each case was performed on a silica gel column.

(ii)Complexes

The above ligands react smoothly with hydrated $RuCl_3$ in 2:1 molar ratio in the presence of excess of LiCl (5 times) in absolute ethanol at reflux to yield an isomeric mixture of $RuCl_2L_2$ and some other unidentified products. The synthetic reaction may be described as follows (equation 2):

$$RuCl_3 \cdot 3H_2O + 2L \xrightarrow{EtOH} RuCl_2L_2 + \text{other products} \qquad 2$$

Addition of excess of LiBr to the reaction mixture prior to the addition of ligands produces the corresponding dibromo compounds.

The synthetic reaction **2** is a partial chloride substitution reaction associated with one-electron metal reduction. The stage at which the reduction of Ru(III) —— Ru(II) occur has not been elucidated. However, metal reduction in ethanol followed by ligand addition may be a plausible path for the formation of the above complexes. Purification and separations of the isomers were performed by column chromatography (see below).

Refluxing $[RuCl_2(Me_2SO)_4]$ with L in EtOH also produces isomeric $RuCl_2L_2$. This reaction (equation 3)

$$RuCl_2(Me_2SO)_4 + 2L \xrightarrow{EtOH} RuCl_2L_2 + 4Me_2(SO) \qquad 3$$

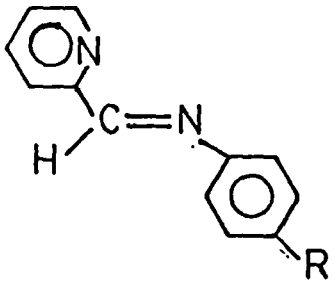
is noteworhty in that Evans et al. found that complete substitution of Me_2SO by a neutral ligand like 2,2'-bipyridine (bpy)does not occur generally in a solvent. We conclude that L must be a better trans-labilising ligand for the above reaction to proceed to completion at the temparature of refluxing EtOH.

(iii) Formulation

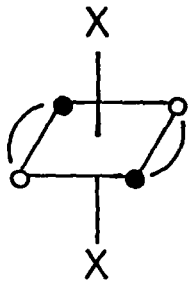
The dihalo complexes are soluble in relatively non-polar solvents like $CHCl_3$, CH_2Cl_2 etc. and are less soluble in polar solvents like CH_3CN, EtOH, MeOH etc. The formulation[25] of the compounds were made based on elemental analyses (Table II.1). These are diamagnetic (t_2^6) and their solutions are non electrolytic. All these data collectively conform to the formulation of the ruthenium complexes as RuX_2L_2 (X=Cl,Br).

B. Possible Isomers

The bischelated RuX_2L_2 containing the unsymmetrical bidentate ligand L, can exist as five geometrical isomers (2 - 6). Out of these two viz. 2 and 3 have trans-RuX_2 orientation whereas rest three, 4-6, have cis-RuX_2 grouping. Considering the coordinated atoms in three pairs, viz. X, X; N^1, N^1 and N^2, N^2 the isomers descriptions 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),

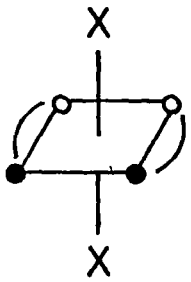


$\equiv$  o N (pyridine)



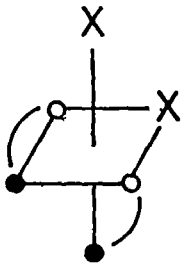
ttt, C_2h

2



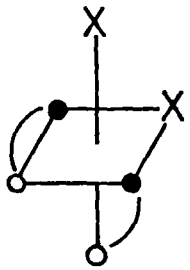
tcc, C_{2v}

3



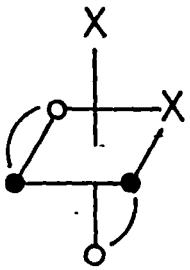
ctc, C_2

4



cct, C_2

5



ccc, C_1

6

6. Idealised point groups for the above geometries are : 2. C_{2h}; 3. C_{2v}; 4. C_2; 5. C_2 and 6. C_1. Both the trans isomers (2 and 3, trans with respect to two X) are expected to be optically inactive unless unusual distorsions make them chiral. The remaining cis isomers (4 - 6) are expected to be chiral.

Out of the five possible geometrical isomers, three have been isolated so far. Their structures have been proven by spectroscopic techniques. These are ttt, ctc and cct. Till date no evidence exists for the occurance of other two isomers from our reaction conditions.

C. Purification and Separation of Isomers

The crude product, RuX_2L_2 obtained from the reaction mixture showed three major spots on a silica gel TLC plate. The purification and isomer separation of RuX_2L_2 were performed by column chromatography on a silica gel column. The green isomer is sparingly soluble in ethanol and thus, deposited in the reaction vessel on cooling. It was collected by filtration and was washed thoroughly with ice-cold ethanol. The filtrate and washings evaporated to dryness and subjected to column chromatography on a silica gel column using different mixtures of $CHCl_3$ and CH_3CN. The first moving green band, was similar to that obtained directly as precipitate from the reaction mixture, was followed by two other major fractions —— one was bluish-green and the other

was violet. There were many overlapping minor bands which were discarded. An uneluted brown product remained at the top of column.

D. Characterisation

(i) Infrared Spectra

Infrared spectral data were collected as KBr discs in the range 4000-250 cm^{-1}. Selected group frequencies are presented in Table.II.2. All the complexes show characteristic absorptions for coordinated L in their IR spectra. In free L ν(C=N) is observed[26] at ca.1625 cm^{-1}. The frequency is lowered in the complexes, ca. 1600 cm^{-1}. The assignment of ν(Ru-X) is made by comparison of the IR spectrum of $RuCl_2L_2$ with those of $RuBr_2L_2$ and free L in the range 400-250 cm^{-1}. The free ligand, L, does not show any absorption below 350 cm^{-1}. All the dichloro complexes exhibit a moderately strong band(s) at ca.300 cm^{-1}, which is conspicously absent in $RuBr_2L_2$. Evidently, this band in the IR spectrum of $RuCl_2L_2$ is due[27] to the ν(Ru-Cl) stretching mode. We could not indentify ν(Ru-Br) which probably lies below our experimentally accessible range. Interestingly, the Ru-Cl stretching mode in green isomer of $RuCl_2L_2$ appears as a single band, whereas those in the bluish-green and violet isomers appear as a two-band structure (Table.II.2,Figure II.1). The singlet nature of ν(Ru-Cl) strongly suggests[27-29] a linear trans grouping of the $RuCl_2$ moiety and the doublet

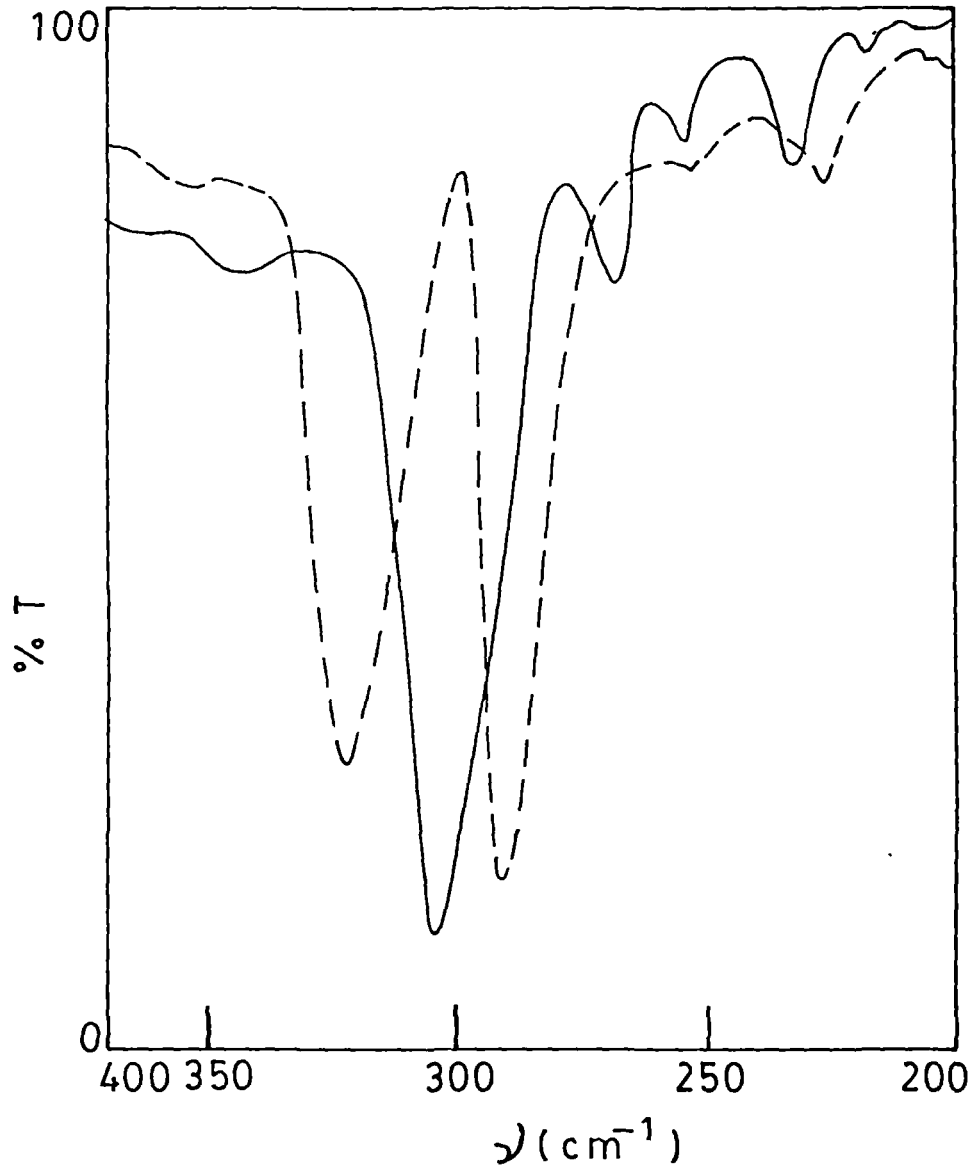


FIGURE II.1 FAR IR SPECTRA OF

(a) ttt-$[RuCl_2L^1_2]$ (——)

(b) cct-$[RuCl_2L^1_2]$ (----)

ν(Ru-Cl) is expected[18,28,27] for a cis-$RuCl_2$ grouping. Thus, from the IR data we conclude that the green isomer is trans with respect to two Cls and the other isomers have a cis-$RuCl_2$ geometry. The dibromo analogues have virtually identical IR spectra in the range 4000-350 cm^{-1}, indicating the gross geometries of the two isomers of $RuBr_2L_2$ are similar to those of $RuCl_2L_2$.

For the sake of comparison a selection of reported ν_{Ru-X} data for Ru(II) and Ru(III) complexes are collected in Table II.3.

(ii) ^{1}HNMR Spectra

The geometries of the isomeric dihalo Ru(II) complexes were mainly assessed by an examination of the high resolution ^{1}HNMR spectra of the complexes. Isomeric $RuCl_2L_2$ ($L=L^1-L^3$) were chosen for this purpose. All of them displayed highly resolved spectra in $CDCl_3$. Three representative spectra of the isomers of $RuCl_2L^2_2$ are displayed in Figure II.2 and data are collected in Table II.4. Different protons are numbered as shown in the structure.

The spectrum of bluish green isomer of $RuCl_2L^2_2$ consists of six aromatic resonances in the range 6.70 to 9.40δ. Two doublet and two triplet resonances, each of which corresponds to one proton signal, in the range 7.60 to 9.40δ are assigned to pyridyl proton signals (Figure II.2,Table II.4). Two more resonances are observed at higher magnetic

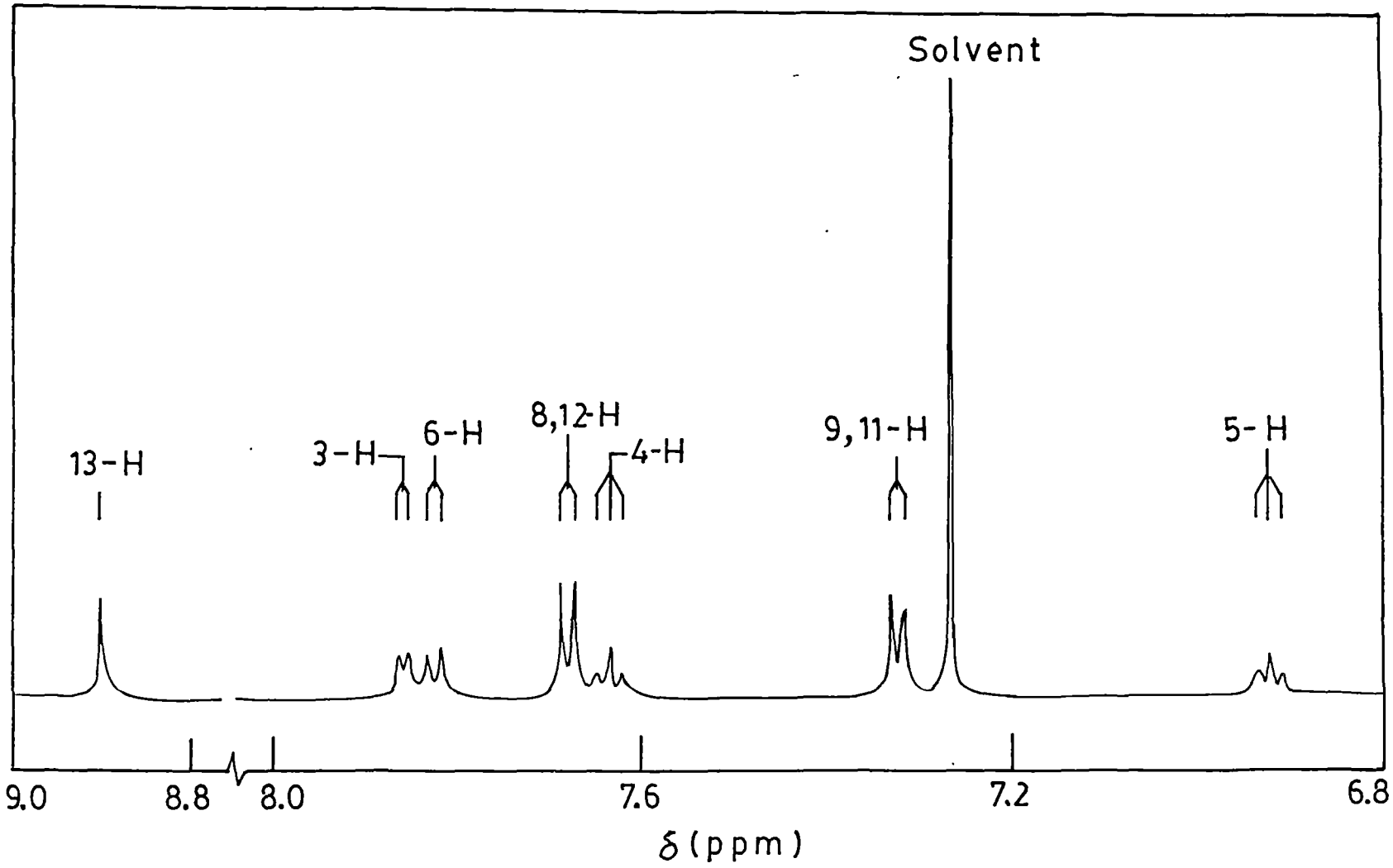


FIGURE II.2a ^{1}HNMR SPECTRUM OF ttt-$[RuCl_2L^1_2]$ IN $CDCl_3$

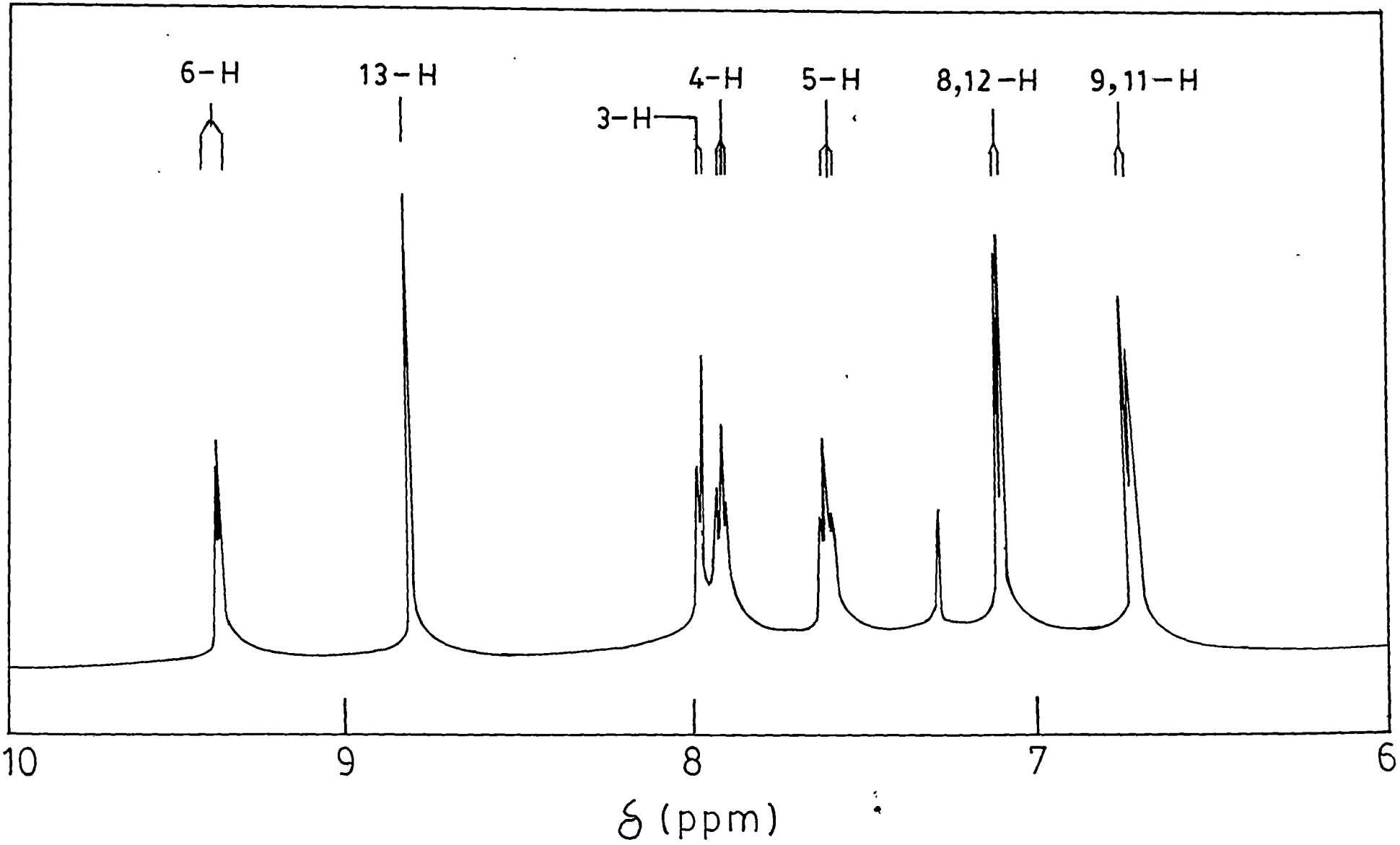


FIGURE II.2b ^{1}HNMR SPECTRUM OF cct-$[RuCl_2L^1_2]$ IN $CDCl_3$

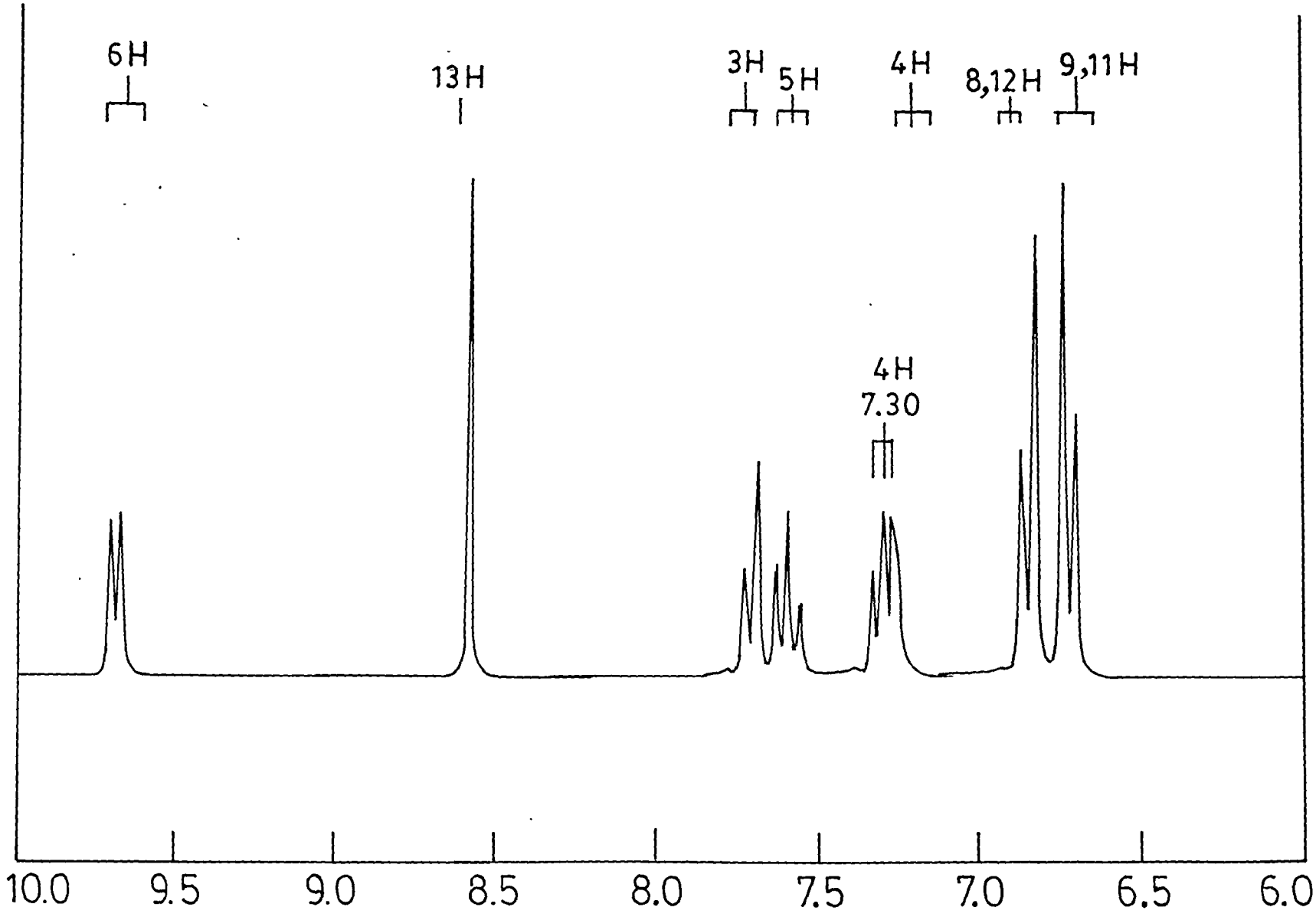


FIGURE II.2c ^{1}HNMR SPECTRUM OF ctc-$[RuCl_2L^2_2]$ IN $CDCl_3$

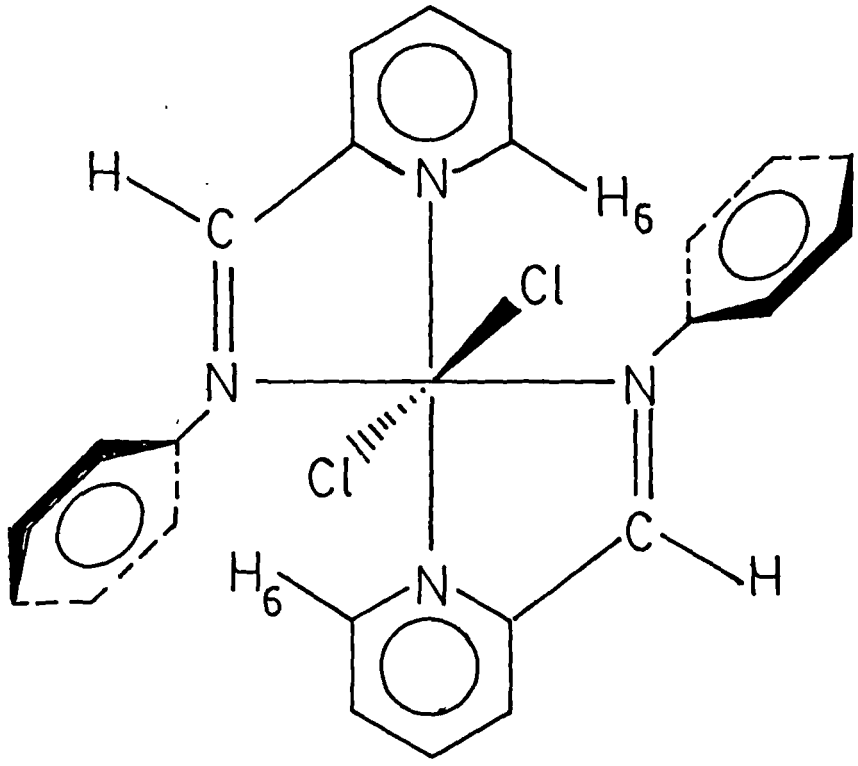
fields. The signal at 7.09δ is a doublet and its area corresponds to two protons. This resonance is assigned to coincident doublets of 8-H and 12-H. Similarly, the doublet signal at 6.71δ due to coincident doublet signals of 9-H and 11-H. This isomer also displays a sharp singlet at 8.78δ assignable to 13-H and the singlet resonance at 2.28δ is assigned to methyl protons.

The violet isomer of $RuCl_2L_2^2$ displays a spectrum similar to that of bluish green isomer. It alsoconsists of six aromatic signals in the range 6.72 to 9.69δ. Two doublet and two triplet resonances, the area of each corresponds to one proton, were observed in the range 7.60 to 9.70δ. These signals are assigned to pyridyl protons (Figure II.2, Table II.4). Two more doubly intense resonances were observed at higher magnetic fields at 6.85δ and 6.72δ. these have been assigned to the coincident pairs of doublets of 8-H, 12-H and 9-H, 11-H respectively. The resonance for 13-H appeared at 8.58 and the other high field sharp singlet resonance at 2.21δ is assigned to methyl resonance.

The spectral pattern of the green isomer of $RuCl_2L_2^2$ is completely different from the other two isomers. Aromatic resonances for the green isomers are observed in the range 6.80 to 7.90δ. Out of the six signals observed in this range, two at 7.32 and 7.68δ are twice as intense as the other four signals. These two signals are due to coincident doublets arising from two pairs of protons, viz. 9-H, 11-H and 8-H,

12-H, respectively. Also a sharp singlet of area corresponding to three protons at 2.48 δ is observed due to methyl resonance. The green isomer shows a sharp singlet at 8.90 ppm, which is assigned to the 13-H resonance.

It may be noted here that the spectra of all the three isomers exhibit one signal for each proton of the ligand L. From this we conclude that the isolated compounds are isomerically pure and the two chelate rings are magnetically equivalent, at least on a NMR time-scale. In practice five geometrical isomers[27,28] are possible (*vide supra*) for the $RuCl_2L_2$ moiety. Of the five possible isomers, one cis(ccc) does not contain any symmetry axis. Thus,the two ligands in ccc geometry should be magnetically inequivalent and should in principle, show twelve aromatic and two methyl resonances. Furthermore, formation of one of the trans-isomers, viz. tcc, is unlikely due to serious steric crowding[27] of the two cis aryl rings. Therefore, the isomers of $RuCl_2L_2$ which have been isolated so far, could have only three geometries, viz. ttt, cct and ctc. Examination of the data presented in the Table II.4 reveals that the pyridyl protons in the green isomers are shielded in general, and 6-H and 5-H in particular, compared to those in the bluish green and violet isomers (Figure II.2). This strongly suggests that the green isomer is the most symmetrical ttt isomer. In this geometry, each of the pyridyl protons are in close proximity (model ttt) to the aryl ring of the second ligand and 6-H


H
C
N
H6
Cl
N
N
Cl
C
H
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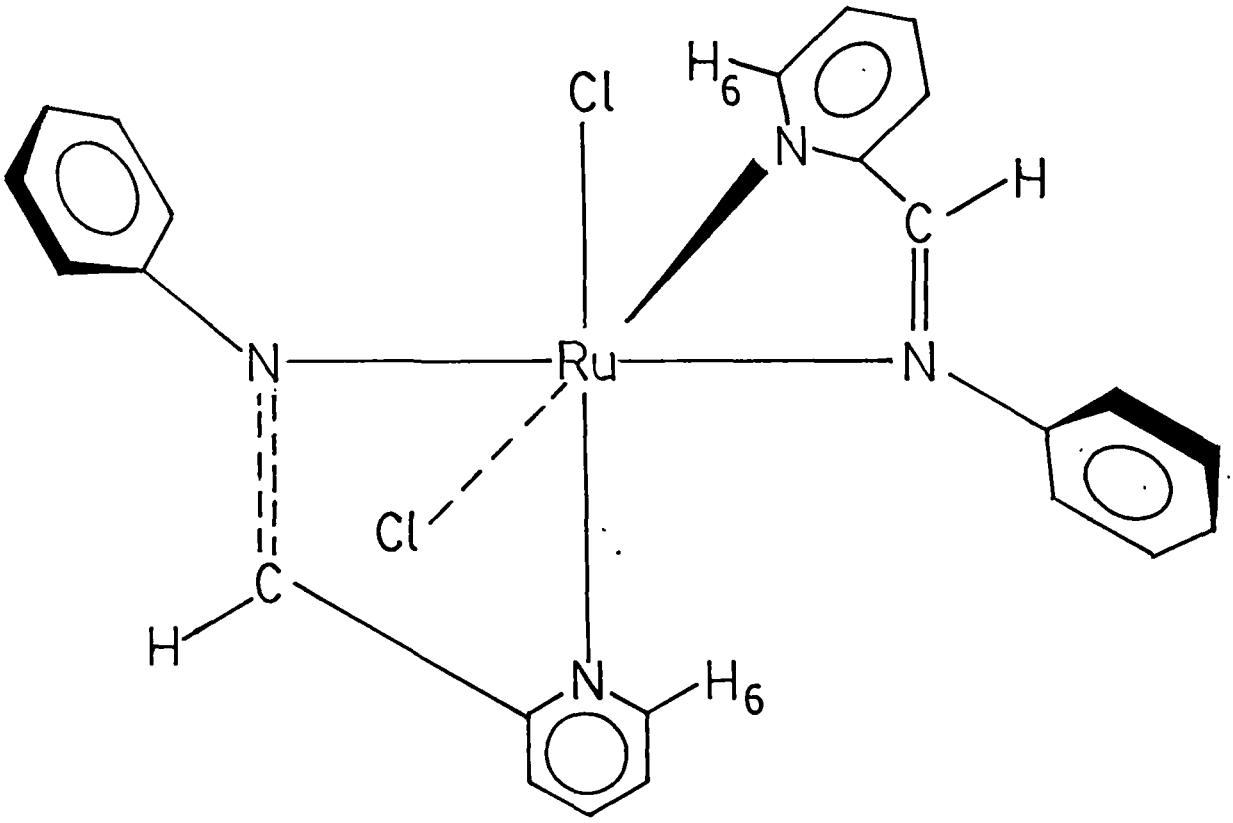
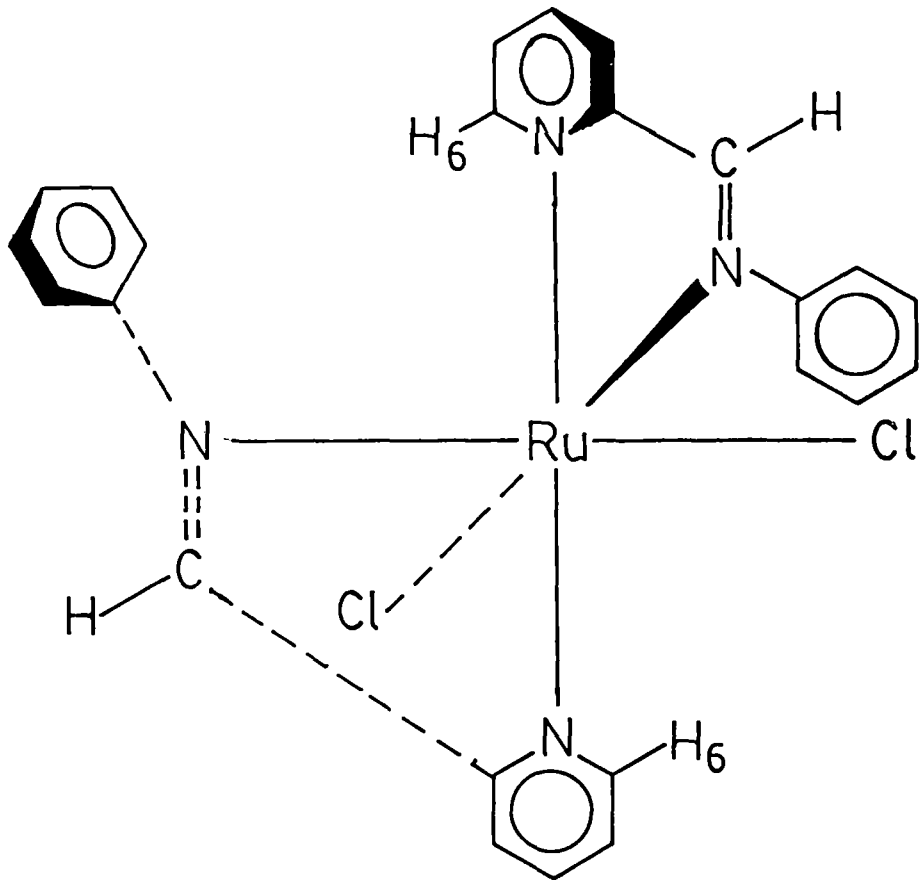
+++ —

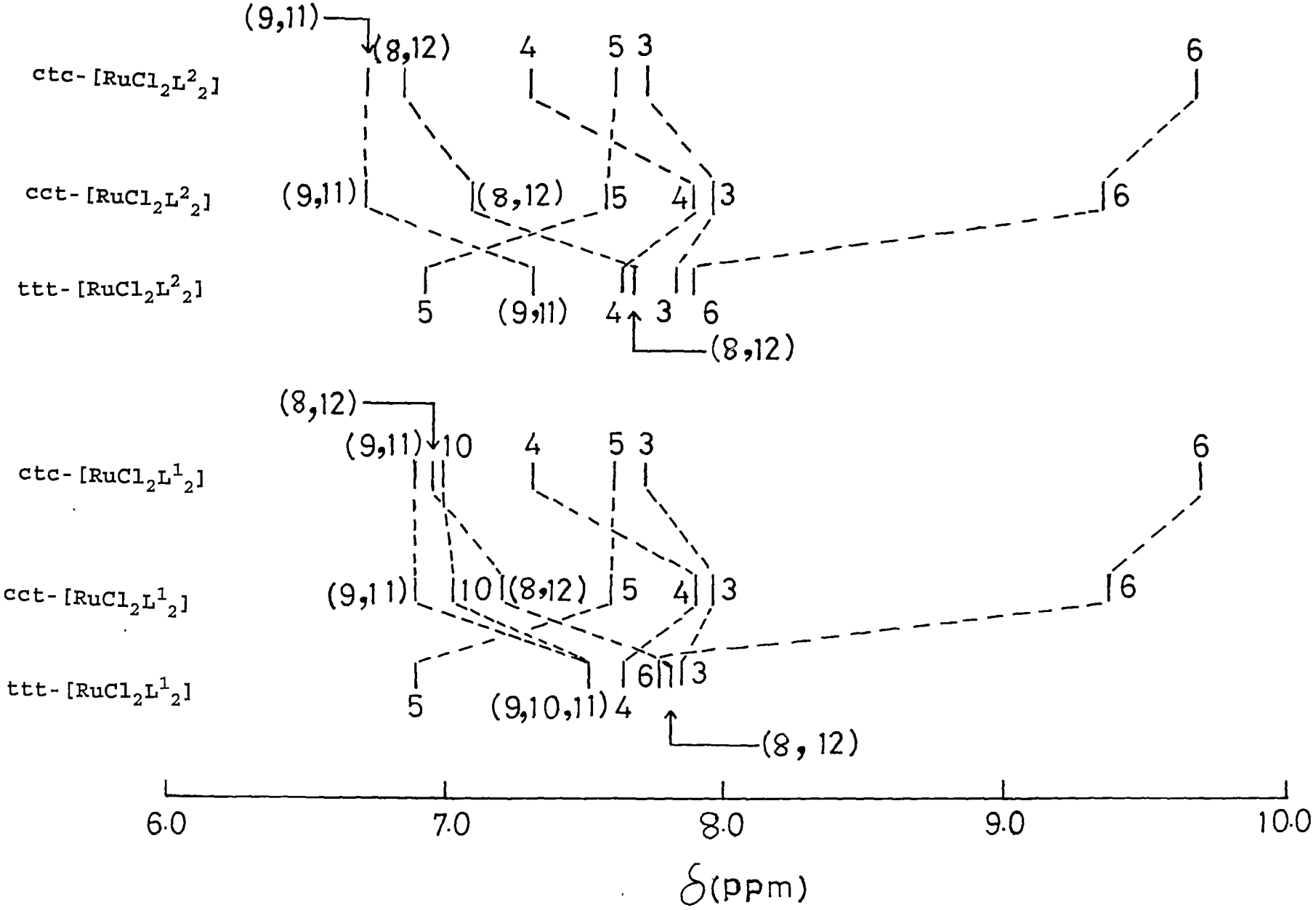


cct–



ctc-

would be closest to the aryl ring. Thus it is expected that 6-H would be shielded by the aryl ring current and would resonate at a higher field (7.86 δ). It is also interesting to note that in the bluish green and violet isomers the 6-H resonances appear at a much lower field at 9.36 δ and 9.69 δ respectively. This result is in accord with the cis - configuration (with respect to two chlorides) where each 6-H is close either to a chloride (ctc) or an imine nitrogen (cct). In these geometries negligible shielding or even deshielding of 6-H would be expected. Therefore, on the basis ^{1}HNMR data it may be concluded that the geometry of green isomer is surely trans, ttt. Interestingly, in the spectrum of violet isomer the pair of protons 8-H, 12-H resonate at higher field (6.85 δ) compared to the same pair in other cis-bluish green isomer (7.09 δ). Considering the models of cct and ctc, it may be seen that in ctc geometry the aryl ring of one ligand is in close proximity and perpendicular to the pyridyl plane and the 8-H, 12-H pair should be shielded by pyridyl ring current. In contrast, in the cct model the aryl ring of one L is away from the pyridyl ring of the other ligand and the pair of 8-H, 12-H resonate at lower field as expected. Moreover, in this geometry the 6-H of one ligand is close to the phenyl ring of other ligand. Therefore, it is logically assumed that the 6-H of the cct-structure should resonate at a comparatively higher field compared to the 6-H resonance of the ctc structure, where 6-H is close to the chlorides. Therefore, based on ^{1}HNMR data we propose that the



^{1}HNMR CORRELATION DIAGRAM

geometry of the bluish-green isomer is cct and that of violet isomer is ctc.

(iii) Electronic Spectra

The electronic spectra of the synthesised complexes were recorded in the range 800-250 nm Major bands of RuX_2L_2 complexes are collected in Table II.5 and the spectra of representative cases are displayed in Figure II.3. Free N-p-tolyl pyridine - 2 - carboxaldimine ligand displays absorption bands at 330 nm (ϵ 3240) and 270 nm (ϵ 5910). These can be respectively assigned to $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions centered primarily on the imine group.

The colour of the ttt-RuX_2L_2 and the cct-RuX_2L_2 is green and bluish-green respectively while that of ctc-RuX_2L_2 is violet. The complexes display multiple bands and shoulders (Table.II.5) in the visible region. The transitions in 700-550 nm region are assigned to metal-ligand charge transfer [$t_2 \longrightarrow \pi^*(L)$] transitions, where $\pi^*(L)$ is the LUMO of the α, α' - diimine chromophore. Transitions of this type are well documented[22,23,38] for the Ru(II) complexes of unsaturated nitrogeneous ligands. The transition under consideration is evidently due to metal-ligand charge transfer (MLCT): $t_2(Ru) \longrightarrow \pi^*(L)$; ttt-$RuX_2L_2$ 675 nm and 620 nm; cct-RuX_2L_2 675 nm and 605 nm: ctc-RuX_2L_2 585 nm. Each of them is associated with shoulders at higher energies. In the present complexes multiple charge transfer

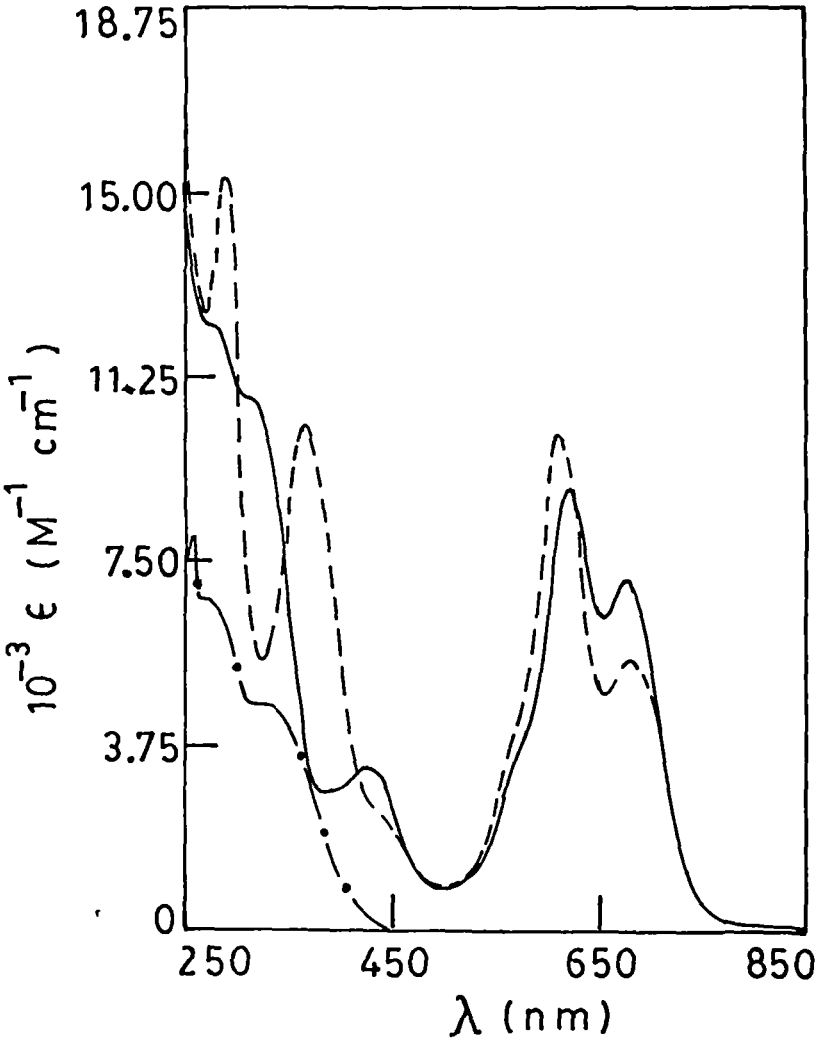


FIGURE II.3 ELECTRONIC SPECTRA IN $CHCl_3$

(a) ttt-$[RuCl_2L^2_2]$ (——)

(b) cct-$[RuCl_2L^2_2]$ (----)

(c) L^2 (-•-•-)

transitions may, primarily originate[34-37] from lower symmetry splitting of metal level, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the excited state through spin orbit coupling.

Some interesting trends in MLCT energies have also been noted here. The higher energy transition (ca.620 nm) together with the shoulder shifts to higher energies on going from a trans to a cis configuration, but the energy of the lowest energy band (ca. 675 nm) remains almost invariant. On the other hand, on changing Cl to Br in a given pair of RuX_2L_2 (X = Cl, Br) the lowest energy band is blue shifted. Transitions in the U.V. region are due to either intraligand ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) transitions or charge transfer transitions involving energy levels which are higher in energies than the ligand LUMO. This may be due to the superior M—L π-bonding in the cis isomers.

E. Electron Transfer Properties

One major objective of the present studies is to characterise the electron transfer behaviour of ruthenium 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,[48,49] differential pulse voltametry[50,51] (DPV) 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^{o}_{298} = formal electrode potential at 298 K.

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

I. Redox Activity of the RuX_2L_2 Species

The RuX_2L_2 complexes are electro active at a platinum working electrode and display three responses,

reversible to irreversible, on the positive side of the S.C.E. The first oxidation occurs in the range 0.20 - 0.50 V involves metal ion, whereas those at very high positive potential(>1.8V), irreversible in nature are believed to be ligand based. It is covenient to discuss the details separately.

(a) The Ru(III) - Ru(II) couple

The results of the cyclic voltammetric experiments are presented in Table.II.6. Representative voltammograms are displayed in Figure II.4.

(i) ttt - RuX_2L_2

All the ttt-RuX_2L_2 species showed one reversible response at ca. 0.30V. At slow scan rates (v $\leq$ 100 mVs^{-1}) and in acetonitrile the response is reversible. This is characterised by $i_{pc} = i_{pa}$; ΔE_p = 80 - 100 mV and $i_{pc}/v^{1/2}$ is a constant. In stirred solution, electrolysis freely occured when the potential is kept fixed on the positive of the anodic peal but at potentials less than the cathodic peak a very little electrolysis was observed. Hence the species are in lower oxidation state and undergo oxidation.

Constant potential coulometry was carried out at a potential 200 mV more positive than E_{pa} (Table II.6) for two representative cases. The coulomb count corresponds to the

transfer of one electron per ruthenium atom in each case.

The cyclic voltammetric response near 0.3 V is thus due to the reversible couple(equation 4), in which the $RuX_2L_2^+$ has ruthenium in the formal oxidation state +3. Since the couple is

$$RuX_2L_2^+ + e \rightleftharpoons RuX_2L_2 \qquad 4$$

electrochemically reversible, RuX_2L_2 and $RuX_2L_2^+$ are likely to have very similar gross structures. The formal potentials, E^o_{298} calculated as the average of the peak potentials are in Table II.6

On increasing scan rate ($v \geq 100$ mVs^{-1}) and particularly on changing the solvent to chloroform, significant deviation (ΔE_p 100) from reversibility is noted (Table II.6). The poorer electrochemical reversibility in chloroform may be due to the low dielectric constant of this solvent (4.8) compared to that of acetonitrile (36.0). Charge separation is hindered when the dielectric constant is low. Moreover,as the oxidised compound $RuX_2L_2^+$ bears one positive charge it is expected that it will be better solvated in more polar solvents. Thus a positive shift of E^o_{298} is expected in going from acetonitrile to chloroform.

(ii) cct and ctc - RuX_2L_2

The results of the cyclic voltammetric experiments are summerised in Table II.6. The general behaviour of these

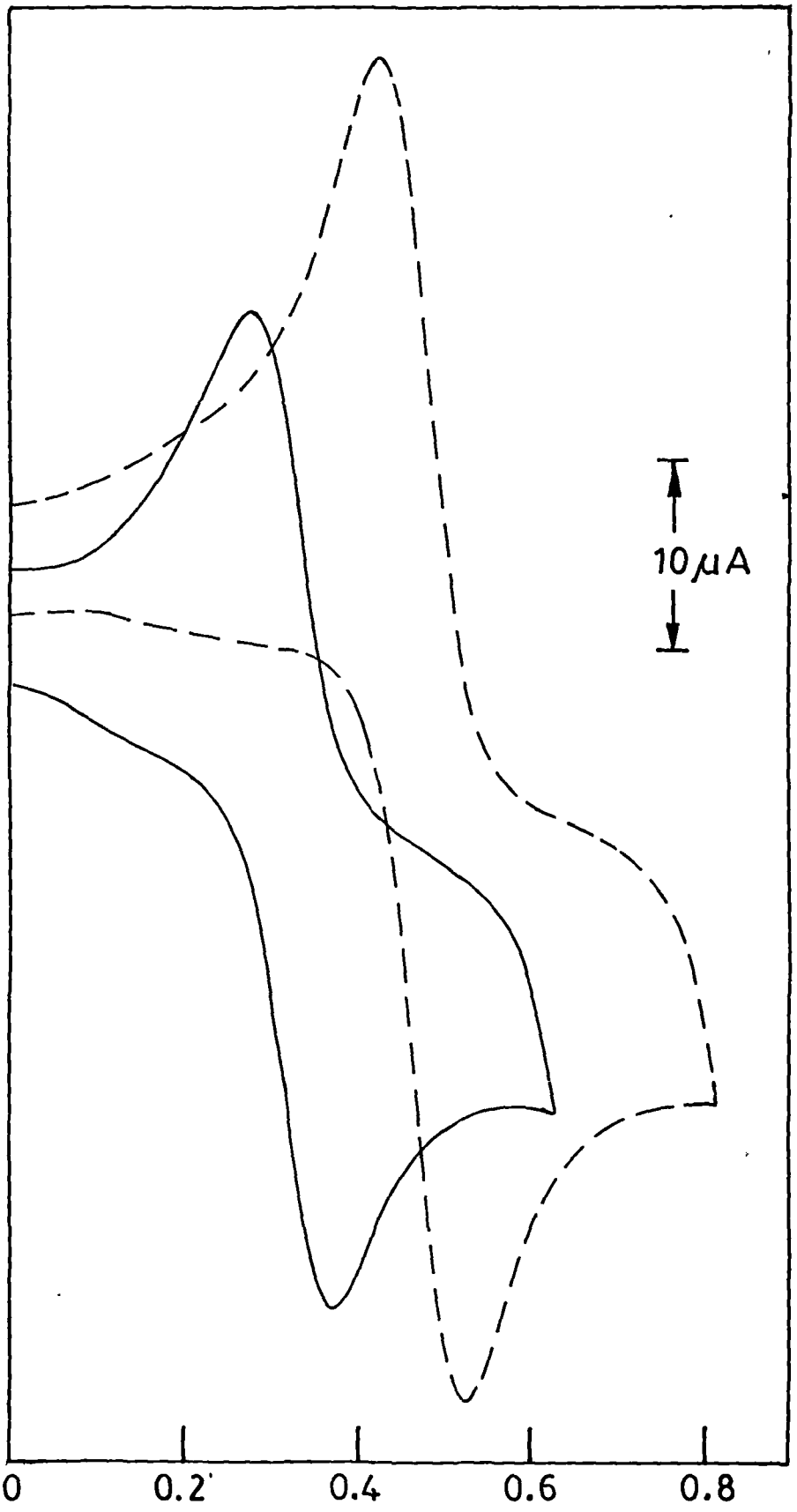


FIGURE II.4a CYCLIC VOLTAMMOGRAMS IN CH_3CN

(a) ttt-$[RuCl_2L^2_2]$ (——)

(b) ctc-$[RuCl_2L^2_2]$ (----)

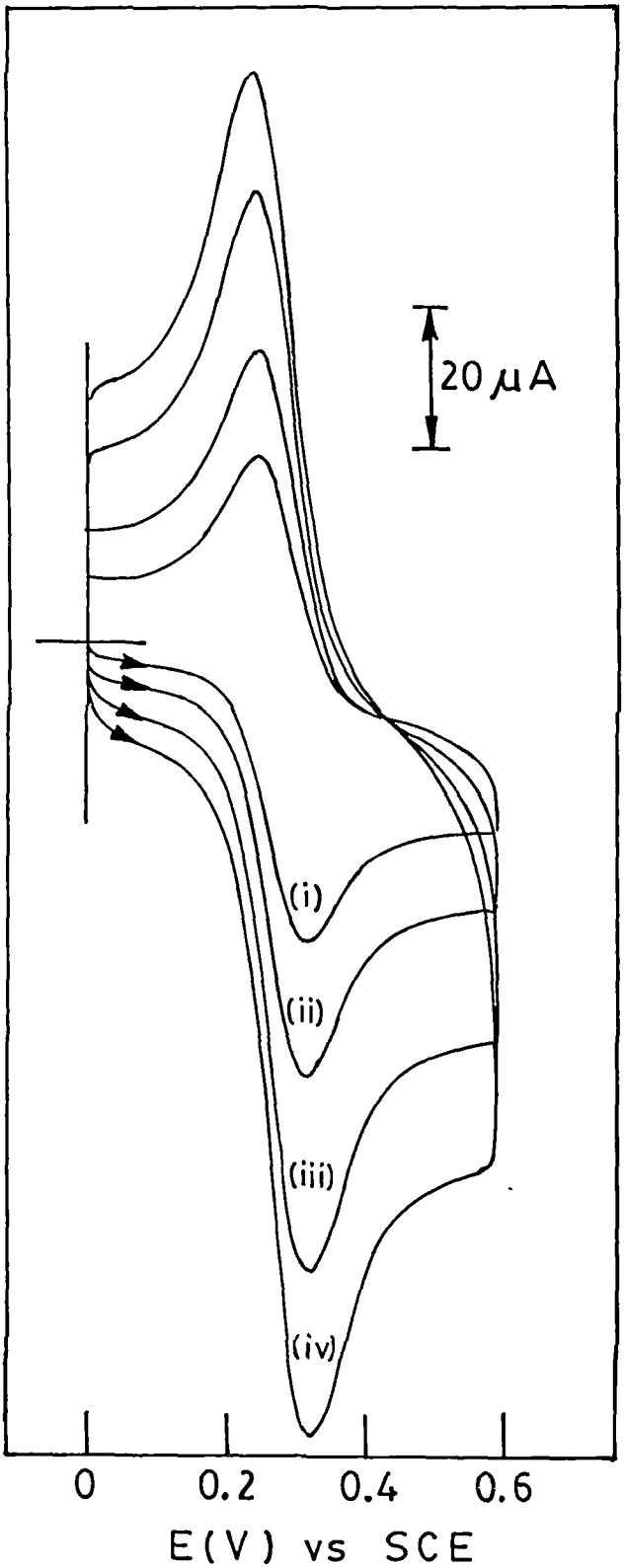


FIGURE II.4b CYCLIC VOLTAMMOGRAM OF ttt-$[RuCl_2L^1_2]$ AT POTENTIALS POSITIVE TO SCE: (i) 20 (ii) 50 (iii) 100 and (iv) 200 mVs^{-1}

two isomers are similar to that of the ttt isomer except that the E^{o}_{298} values are consistently slightly higher than the corresponding trans-analogue. This has been generally observed[27,39-43] in several other cases and this effect is much more pronounced in the complexes of strongly π-interacting ligands. We note here a correspondence between E^{o}_{298} and MLCT energy. Higher the MLCT energy larger is E^{o}_{298}. The order ttt < cct < ctc applies to both MLCT(metal to ligand charge transfer) energy and E^{o}_{298}. This is understandable since the electron is transferred from the t_2 level whose stability increases due to superior metal-ligand π-back bonding in the cis-isomer. The energy of the MLCT band is also controlled by the strength of this bonding. It may be noted that the E^{o}_{298} of Ru(III)/Ru(II) couple in RuX_2L_2 is comparable to that in $RuX_2(bpy)_2$. This similarity indicates that the ligand electrochemical parameter[44] E_L of L is comparable to that of bpy.

(iii) Ligand Oxidation

In addition to the reversible Ru(III)-Ru(II) couple, RuX_2L_2 displays two more irreversible oxidative responses at very high positive potentials (>1.8 V). It may be noted here that the uncoordinated ligand, L^2, also shows two irreversible oxidative responses at 1.54 and 1.93V. It is, therefore, probable that the two successive oxidative responses occurring near 2.0V are due to the ligand based oxidation. The oxidation of coordinated imine linkages has

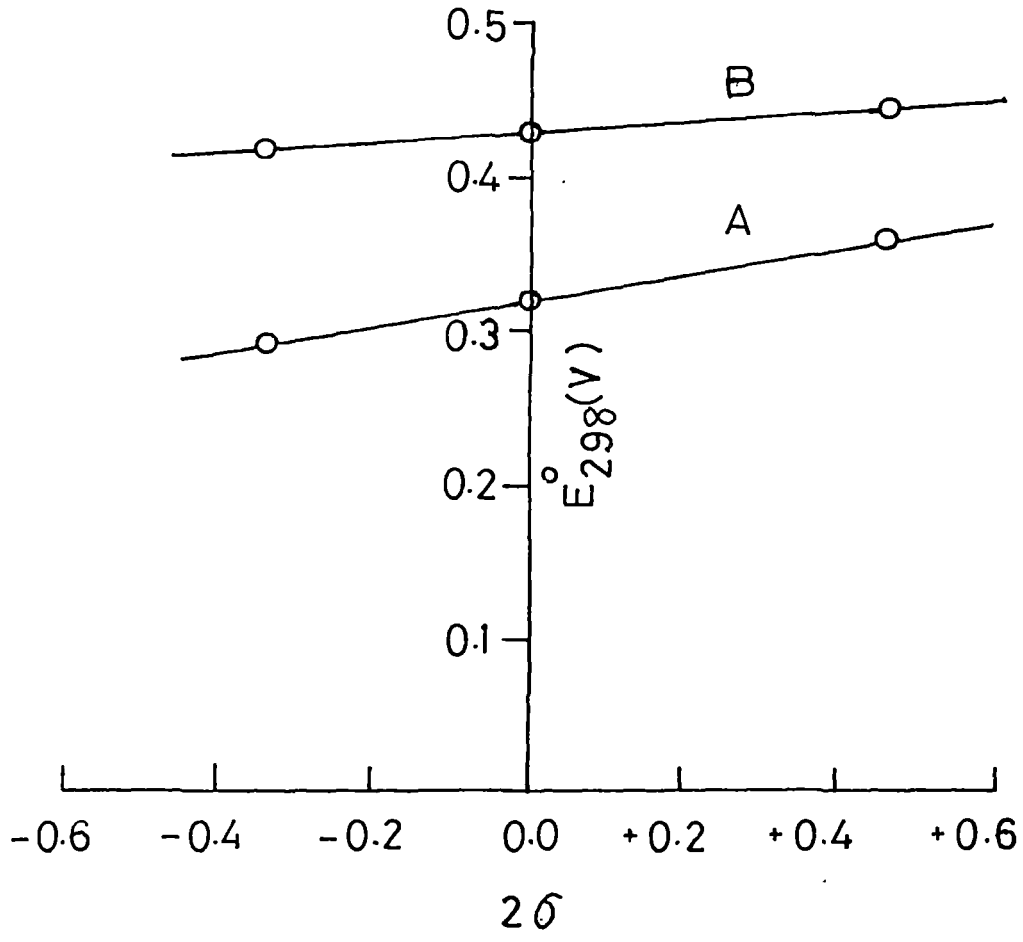


FIGURE II.5 THE PLOT OF E^{0}_{298} vs HAMMETT SUBSTITUENT CONSTANT (σ)

been discussed[38] by others in a related ruthenium(II) system.

Interestingly, the formal potential data also reveal that the E^{o}_{298} of Ru(III)/Ru(II) couples in $RuCl_2L_2$ depend on the nature of substitution (R) in the ligand L. The values decrease[45] with an increase in the electron-releasing power of the substituents. The plot of E^{o}_{298} vs. the Hammett substituent constant[46] (σ) is linear (Figure II.5). Furthermore, the formal potentials of RuX_2L_2 show an increase on changing X from Cl to Br. Qualitatively this is attributed to a stabilization of Ru(II) by increased π-bonding in the dibromo complexes.

EXPERIMENTAL SECTION

A Physical Measurements

(a) Infrared Spectra

Infrared spectra were obtained as KBr discs using a Perkin-Elmer IR-983 (4000-200 cm^{-1}) spectrophotometer.

(b) Electronic Spectra

Solution Electronic spectra were measured in chloroform with a solute concentration of ca 10^{-3} mol dm^{-3} using a Hitachi-320 spectrophotometer. Silica cell of path length 1 cm was used.

(c) ^{1}HNMR Spectra

The measurements were done in $CDCl_3$ with a 500 MHz Bruker FT-NMR Spectropholometer, using TMS as an internal standard.

(d) Magnetic Measurements

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

(c) Electrochemical Measurements[48-51]

The symbols used in electrochemical techniques along with their meaning are described in text (Section II.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±1l by using a precision thermostat. All potentials are uncorrected for junction potentials and are referenced versus saturated colomel Electrode (SCE).

Cyclic Voltammetry

Cyclic voltammetric data were collected using a PAR M-174A polarographic analyser, a 175 universal programmer and a PAR RL0074 XY recorder. Three electrode cell system which includes a planar Beckman model 39273 platinum inlay working electrode, a platinum wire auxiliary electrode and a Saturated Calomel Reference Electrode (SCE) was used in our study. Tetrabutylammonium Perchlorate (TBAP) was 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.

Constant Potential Coulometry

PAR M-173 potentiostat, PAR M-179 digital coulometer and PAR 377A cell system were used in coulometric measurements. The cell system includes a planar wire gauge platinum working electrode, platinum counter electrode and saturated calomel reference electrode. Electrolysis was carried out at a constant potential regulated by the potentiostat and coulomb counts were obtained from digital display and were averages of atleast three independant measurements.

B. Formulation of Compounds

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

C. Solvents

A.R. Grade Benzene, Chloroform, dichloromethane, acetonitrile were used as supplied. Besides, all other solvents used for preparative and analytical work were of reagent grade and used without further purification. For electrochemical work, dried acetonitrile and chloroform were used. Their purification from commercially available sources, 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. 10 gms 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 0.5 h 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}. Throughout 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 Chloroform

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 sealed bottle.

D. Preparation of Compounds

(a) Chemicals

The chemicals and their sources are as follows. Pyridine-2-carboxaldehyde was obtained from Merck,

Schuedhardtt. Phosphoruspentoxide, Silica gel(60 120 mesh) for column chromatography, British Drug House, India. Hydrated Ruthenium trichloride was obtained from Arrora-Matthey Limited, Calcutta. It was digested with concentrated hydrochloric acid as given below.

(b) Ruthenium Trichloride Trihydrate, $RuCl_3 \cdot 3H_2O$

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

(c) Tetra ethyl ammonium perchlorate (TEAP)

It was used as a supporting electrolyte in elctrochemical experiments and prepared as follows:
210g of tetraethyl ammonium bromide was dissolved in 200 ml of water. To the clear solution, a solution of 100 ml $HClO_4$ 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 333 .

(d) Ligands

N-Aryl Pyridine-2-Carboxaldimine

The starting material viz.

Pyridine-2-carboxaldehyde, Aniline, p-Toluidine and p-Chloroaniline were required for the synthesis of the ligands L^1-L^3 respectively. These were generally obtained *in situ* by the condensation of pyridine-2-carboxaldehyde with the appropriate aromatic primary amine in ethanol. The ligand L^2 was prepared as described in the literature. A mixture of 3 g of each pyridine-2-carboxaldehyde and p-toluidine in 30 ml of ethanol was refluxed on water bath for 45 minutes. The solution was then poured in 200 ml of cold water with constant stirring. A yellowish white solid ligand L^2 was obtained, which was filtered and dried. (Yield ca. 90%).

(ø) Complexes

The syntheses of complexes of the type RuX_2L_2 (X = Cl, Br) were achieved using general methods. Yields varied in the range 70-75%. Specific details are given for representative cases.

(1) ttt-,cct-,ctc-Dichlorobis (N-phenylpyridine-2-carboxal--dimine) ruthenium(II)

Ø.Ø52Øg (2 m mol) of $RuCl_3.3H_2O$ and excess of LiCl(2g) were dissolved in 20ml of ethanol and the mixture was refluxed for 15 minutes. To this red-brown solution a mixture of Ø.64g (6 m mol) of pyridine-2-carboxaldehyde and Ø.56g (6 m mol) of aniline in 25ml of ethanol, which was refluxed separately for 30 minutes, was added. Immediately,

a dark violet solution resulted, which was further refluxed for 2h on a water bath. After cooling, dark crystals with a bronze-sheen were filtered off and washed with 5-10 ml of ethanol and then ether. On TLC this compound showed three spots, indicating the presence of ttt-(green,major fraction), cct-(bluish green) and ctc-(violet) isomers of $RuCl_2(L^1)_2$. This precipitate was then subjected to column chromatography on a silica gel column. First a green band was eluted with a 1:10 CH_3CN-$CHCl_3$ mixture. A second band, bluish green in colour, was eluted with a 2:10 CH_3CN-$CHCl_3$ mixture and a third violet band was eluted with a 3:10 CH_3CN-$CHCl_3$ mixture. These compounds were recrystallised from a 1:1 $CHCl_3$-C_6H_{14} mixture.

Another fraction of isomeric $RuCl_2(L^1)_2$ was obtained from the violet filtrate. The filtrate was evaporated to dryness and washed thoroughly with water. The dried residue was then extracted with $CHCl_3$(250 ml). On addition of C_6H_{14} to the concentrated $CHCl_3$ solution (25ml) a dark precipitate was obtained, which was subjected to column chromatography as described above to obtain pure green, bluish green and violet isomers of $RuCl_2(L^1)_2$.

Yield: Green 35%

Bluish green 19%

Violet 20%

(ii) ttt-,cct-Dibromobis(N-phenylpyridine-2-carboxaldimine) ruthenium(II)

These were prepared similarly with the exception that instead of LiCl, LiBr (2g) was added to the solution of $RuCl_3 \cdot 3H_2O$ prior to the addition of an ethanolic solution of the ligand L^1. Isomeric purification was performed using the column chromatographic technique as described before.

Yield: Green 32%

Bluish green 25%

(iii) Preparation of isomeric Dichlorobis (N-p-tolylpyrine-2-carboxaldimine) ruthenium(II) from $RuCl_3$ and preformed L^2

A mixture of 0.26g (1m.mol) of $RuCl_3 \cdot 3H_2O$ and excess LiCl(2g) in 20ml of ethanol was refluxed for 15min. To this a solution of 0.59g (3m.mol) of L^2 in ethanol was added and the mixture was further refluxed for 2h. The rest of the procedure is similar to that described previously.

Yield: Green 32%

Bluish green 16%

Violet 19%

TABLE II.1

Analytical Data of ttt-,cct- and ctc-[RuX_2L_2] (X = Cl, Br)

Compound	Formula	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
ttt-[$RuCl_2L^1_2$]	$C_{24}H_{20}N_4Cl_2Ru$	53.7	53.9	3.7	3.9	10.4	10.4
cct-[$RuCl_2L^1_2$]	$C_{24}H_{20}N_4Cl_2Ru$	53.7	54.0	3.7	3.8	10.4	10.5
ctc-[$RuCl_2L^1_2$]	$C_{24}H_{20}N_4Cl_2Ru$	53.7	53.9	3.7	3.8	10.4	10.5
ttt-[$RuCl_2L^2_2$]	$C_{26}H_{24}N_4Cl_2Ru$	55.3	55.1	4.3	4.3	9.9	9.7
cct-[$RuCl_2L^2_2$]	$C_{26}H_{24}N_4Cl_2Ru$	55.3	55.4	4.3	4.3	9.9	9.8
ctc-[$RuCl_2L^2_2$]	$C_{26}H_{24}N_4Cl_2Ru$	55.3	55.2	4.3	4.4	9.9	9.7
ttt-[$RuCl_2L^3_2$]	$C_{24}H_{18}N_4Cl_4Ru$	47.6	47.7	3.0	3.1	9.2	9.1
cct-[$RuCl_2L^3_2$]	$C_{24}H_{18}N_4Cl_4Ru$	47.6	47.7	3.0	3.1	9.2	9.2
ctc-[$RuCl_2L^3_2$]	$C_{24}H_{18}N_4Cl_4Ru$	47.6	47.5	3.0	3.1	9.2	9.1
ttt-[$RuBr_2L^1_2$]	$C_{24}H_{20}N_4Br_2Ru$	46.1	46.3	3.2	3.2	9.0	8.9
cct-[$RuBr_2L^1_2$]	$C_{24}H_{20}N_4Br_2Ru$	46.1	46.1	3.2	3.2	9.0	8.9
ttt-[$RuBr_2L^2_2$]	$C_{26}H_{24}N_4Br_2Ru$	47.8	47.9	3.7	3.8	8.6	8.5
cct-[$RuBr_2L^2_2$]	$C_{26}H_{24}N_4Br_2Ru$	47.8	47.9	3.7	3.8	8.6	8.6

TABLE II.2

Selected Infrared Spectral Data[a,b] of Complexes

Compound	ν_{max} (cm^{-1})				
	C=N (imine)	C=N (py)	C-H out of plane bending in pyridine ring	C-H Out of plane bending in phenyl ring	Ru-Cl
ttt-$[RuCl_2L_2^1]$	1620	1605	770	690	302
cct-$[RuCl_2L_2^1]$	1620	1605	765	690	310,295
ctc-$[RuCl_2L_2^1]$	1615	1600	765	700	305,290
ttt-$[RuCl_2L_2^2]$	1615	1600	780	700	305
cct-$[RuCl_2L_2^2]$	1620	1605	775	700	310,290
ctc-$[RuCl_2L_2^2]$	1615	1600	770	700	310,295
ttt-$[RuCl_2L_2^3]$	1620	1605	775	690	300
cct-$[RuCl_2L_2^3]$	1615	1600	775	700	310,295
ctc-$[RuCl_2L_2^3]$	1615	1600	780	700	310,290
ttt-$[RuBr_2L_2^1]$	1625	1610	770	690	
cct-$[RuBr_2L_2^1]$	1620	1605	765	700	
ttt-$[RuBr_2L_2^2]$	1625	1610	780	700	
cct-$[RuBr_2L_2^2]$	1620	1605	775	700	

[a] In KBr disc, 4000-200cm^{-1}.

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

TABLE II.3

Ru-Cl stretching Mode(cm^{-1}) for a few reported Ru(II) and Ru(III) chloro complexes.

Compound	ν_{Ru-Cl}	References
$cis-RuCl_2(bpy)_2$	338,319	52
$cis-RuCl_2(Me_2SO)_4$	330,325	53
$trans-RuCl_2([14]aneN_4)^{+a}$	321	54
$cis-RuCl_2(NH_3)_4$	310,285	54
$cis-RuCl_2(HA)_2^b$	363,331	55
$trans-RuCl_2(HB)(B)^c$	358	56
$trans-[RuCl_2(en)_2]Cl\cdot\frac{1}{2}H_2O^d$	325	57
$cis-[RuCl_2(en)_2]Cl\cdot H_2O$	322,311	58

[a] $[14]aneN_4$ = 1,4,8,11-Tetraazocyclotetradecane

[b] HA = Phenylazobenzaldoxime

[c] HB = α-Benzilmonooxime

[d] en = Ethylenediamine.

TABLE II.4

^{1}HNMR Spectral Data for $[RuCl_2L_2]$ in $CDCl_3$

Compound	δ^a(ppm)$_b$ (J,Hz)										
	3-H	4-H	5-H	6-H	8-H	9-H	10-H	11-H	12-H	13-H	10Me
ttt-$[RuCl_2L_2^1]$	7.84 (7.50s)	7.64 (7.60d)	6.92 (6.68d)	7.77 (5.65s)	7.80 (7.60s)	7.56- 7.50	7.56- 7.50	7.56- 7.50	7.80 (7.60s)	8.92^e	
cct-$[RuCl_2L_2^1]$	7.96 (7.40s)	7.90 (7.60d)	7.59 (6.30d)	9.37 (5.00s)	7.20 (7.50s)	6.90 (7.40d)	7.03 (7.20d)	6.90 (7.40d)	7.20 (7.50s)	8.80^e	
ctc-$[RuCl_2L_2^1]$	7.72 (7.70s)	7.31 (4.90d)	7.61 (7.60d)	9.70 (5.50s)	6.95 (8.30s)	6.92 (8.20d)	7.05 (7.20d)	6.92 (8.20d)	6.95 (8.30s)	8.60^e	
ttt-$[RuCl_2L_2^2]$	7.83 (7.45s)	7.63 (7.20d)	6.93 (6.67d)	7.86 (5.60s)	7.68 (8.15s)	7.32 (8.00s)		7.32 (8.00s)	7.68 (8.15s)	8.90^e	2.48
cct-$[RuCl_2L_2^2]$	7.95 (7.50s)	7.89 (7.50d)	7.58 (6.20d)	9.36 (5.30s)	7.09 (7.70s)	6.71 (7.80s)		6.71 (7.80s)	7.09 (7.70s)	8.78^e	2.28
ctc-$[RuCl_2L_2^2]$	7.71 (7.70s)	7.30 (4.90d)	7.60 (7.60d)	9.69 (5.50s)	6.85 (8.30s)	6.72 (8.20s)		6.72 (8.20s)	6.85 (8.30s)	8.58^e	2.21
ttt-$[RuCl_2L_2^3]$	7.88 (7.90s)	7.70 (7.60d)	7.05 (6.60d)	7.87 (5.90s)	7.51 (8.55s)	7.76 (8.40s)		7.76 (8.40s)	7.51 (8.55s)	8.91^e	
cct-$[RuCl_2L_2^3]$	7.99 (7.60s)	7.93 (7.60d)	7.63 (6.50d)	9.35 (5.50s)	7.16 (8.50s)	6.98 (8.40s)		6.98 (8.40s)	7.16 (8.50s)	8.79^e	

[a] Tetramethylsilane is the internal standard

[b] Spin-spin coupling amongst nearest neighbour protons only.

[c] Doublet.

[d] Triplet

[e] Singlet.

TABLE II.5

Solution Electronic Spectral[a] Data of Complexes at 298K

Compound	Vis/UV λ_{max}(nm)(ϵ,$M^{-1}cm^{-1}$)			
ttt-[$RuCl_2L^1_2$]	675(8200),620(10050),570[c]	425(3725),390[c]	290(13250),270(13325)	
cct-[$RuCl_2L^1_2$]	675(6100),605(10870),555[c]	425(2680),	345(10240),280(15540)	
ctc-[$RuCl_2L^1_2$]	586(15000),	361[c](12444),	318[c](22215),	285(25755)
ttt-[$RuCl_2L^2_2$]	675(6960),620(8900), 570[c]	425(3340),390[c]	310(10670),270(12050)	
cct-[$RuCl_2L^2_2$]	675(5475),605(10020),560[c]	425(2500),	360(10200),282(15210)	
ctc-[$RuCl_2L^2_2$]	586(13750),	361[c](11730),	320[c](20735),	285(24950)
ttt-[$RuCl_2L^3_2$]	680(7250),618(8790), 570[c]	425(3370),375[c]	310[c],	280(14610)
cct-[$RuCl_2L^3_2$]	680(5620),608(9500), 560[c]	425(2550),345(10950),		285(17370)
ctc-[$RuCl_2L^3_2$]	586(14630),	361[c](10970),	320[c](21530),	286(23970)
ttt-[$RuBr_2L^1_2$]	665(7360),618(10100),570[c]	425(3550), 385[c]	300(11970),270(12925)	
cct-[$RuBr_2L^1_2$]	665(5320),605(10820),560[c]	420(2925),	365(8150),	280(13300)
ttt-[$RuBr_2L^2_2$]	670(6100),618(10530),570[c]	425(3210), 390[c]		305(11550)
cct-[$RuBr_2L^2_2$]	670(3950),610(9300),560[c]	435(3110),	365(8800),	285(12300)

[a] $CHCl_3$

[c] Shoulder.

Compound L^2 shows absorption at 330(3240) and 270nm(5910)

TABLE II.6

Cyclic Voltammetric Data[a] for RuX_2L_2 at a platinum electrode at the Positive side of S.C.E.

Compound	Solvent	E^{o}_{298}(V)[Ru^{III}/Ru^{II}]	ΔE_p(mV)
ttt-[$RuCl_2L^1_2$][b]	CH_3CN	0.31	100
	$CHCl_3$	0.49	400
cct-[$RuCl_2L^1_2$][b]	CH_3CN	0.33	90
	$CHCl_3$	0.51	200
ctc-[$RuCl_2L^1_2$]	CH_3CN	0.43	100
ttt-[$RuCl_2L^2_2$]	CH_3CN	0.29	120
	$CHCl_3$	0.47	310
cct-[$RuCl_2L^2_2$]	CH_3CN	0.30	100
	$CHCl_3$	0.47	190
ctc-[$RuCl_2L^2_2$]	CH_3CN	0.42	90
ttt-[$RuCl_2L^3_2$]	CH_3CN	0.36	90
	$CHCl_3$	0.55	380
cct-[$RuCl_2L^3_2$]	CH_3CN	0.36	90
	$CHCl_3$	0.55	190
ctc-[$RuCl_2L^3_2$]	CH_3CN	0.44	100
ttt-[$RuBr_2L^1_2$]	CH_3CN	0.40	100
	$CHCl_3$	0.51	390
cct-[$RuBr_2L^1_2$]	CH_3CN	0.40	100
	$CHCl_3$	0.51	170
ttt-[$RuBr_2L^2_2$]	CH_3CN	0.34	120
	$CHCl_3$	0.48	360
cct-[$RuBr_2L^2_2$]	CH_3CN	0.36	100
	$CHCl_3$	0.48	170

[a]Definitions of the symbols used are as in the text, all E values are quoted vs. S.C.E., $v = 50\ mVs^{-1}$

[b]$n = 0.98$ for ttt-[$RuCl_2L^1_2$] and 1.02 for cct-[$RuCl_2L^1_2$], $n = \frac{Q}{Q'}$; where Q' is the calculated coulomb count for the transfer of one electron and Q is the observed coulomb count after exhaustive electrolysis; oxidation in each case was performed at 0.50 V vs S.C.E. in CH_3CN(0.10M[NEt_4][ClO_4])

TABLE II.7

Ligand Based Oxidation[a] of the Complexes at a Platinum electrode at the Positive Side of S.C.E.

Compound	E^{o}_{298} (V)
ttt-$[RuCl_2L^{1}_2]$	1.88, 2.10
cct-$[RuCl_2L^{1}_2]$	1.84, 2.10
ctc-$[RuCl_2L^{1}_2]$	1.83, 2.10
ttt-$[RuCl_2L^{2}_2]$	b
cct-$[RuCl_2L^{2}_2]$	1.84, 2.20
ctc-$[RuCl_2L^{2}_2]$	1.82, 2.20
ttt-$[RuCl_2L^{3}_2]$	b
cct-$[RuCl_2L^{3}_2]$	1.88, 2.30
ctc-$[RuCl_2L^{3}_2]$	1.86, 2.30
ttt-$[RuBr_2L^{1}_2]$	1.86, 2.20
cct-$[RuBr_2L^{1}_2]$	1.84, 2.10
ttt-$[RuBr_2L^{2}_2]$	b
cct-$[RuBr_2L^{2}_2]$	1.81, 2.20

[a] In CH_3CN

[b] Solubility is very low, scanned up to +1.50V.

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Chapter III

CHAPTER III

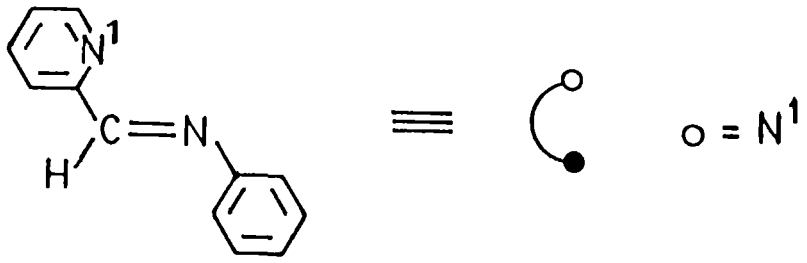
ISOMERIC RUTHENIUM(III) COMPLEXES OF N-PHENYL-2-PYRIDINE CARBOXALDIMINE SYNTHESIS, CHARACTERIZATION AND ELECTRON TRANSFER PROPERTIES*

Abstract: *The geometric isomers of* $[RuCl_2L_2]ClO_4$ *(L = N-phenyl-2-pyridine carboxaldimine) have been isolated by stereoretentive oxidation of corresponding isomeric ruthenium(II) complexes using* $Cl_2(g)$ *as an oxidant followed by addition of sodium perchlorate. The complexes are paramagnetic (low spin* d^5, *S = 1/2) and display rhombic EPR spectra in frozen solution at 77K. The axial (Δ) and rhombic (V) distortion parameters (in the order Δ, V,* cm^{-1}) *are 4340, −3500 (ttt); 4520, −3820 (cct); and 4230, −3710 (ctc). The sign changes correspond to energy inversion of split of* t_2 *components. The electronic transition energies have been computed using the observed g-values. Two predicted optical transitions within the krammer's doublets are experimentally observed or indicated in the near-ir region [ttt- 6330, 2780; cct- 6670, 2810; ctc- 6140, 2780* cm^{-1}*]. In addition to the ligand field transitions, all these complexes also show multiple charge transfer transitions in the visible region. Each of the complexes displays a reversible reductive response due to an Ru(III)/Ru(II) couple in the range 0.3 − 0.5 V vs SCE at a platinum electrode. Chemical reductions of these trivalent complexes, by hydrazine, leads almost quantitatively to the bivalent ruthenium complexes. In acetonitrile,* $RuCl_2L_2$ *complexes act as mild oxidant.*

*A part of this work has appeared in *Polyhedron*, 1995, 0000.

INTRODUCTION

In the preceeding chapter we reported our work[1-6] on the bivalent complexes of ruthenium with L(1). Three geometric isomers of $RuCl_2L_2$ were isolated and characterised. The redox stabilities



L, 1

of all $RuCl_2L_2$ isomers are evidenced by the moderate positive formal potentials of the ruthenium(III)-ruthenium(II) couples. This chapter describes chemical oxidation of the above complexes, isolation and characterization of the trivalent cogeners. The reversibility and relatively easy accessible potentials for the ruthenium(III) - ruthenium(II) couples in isomeric $RuCl_2L_2$ led us to explore the possibility of synthesizing the corresponding trivalent compounds in the pure state. It may be noted in the present context that the

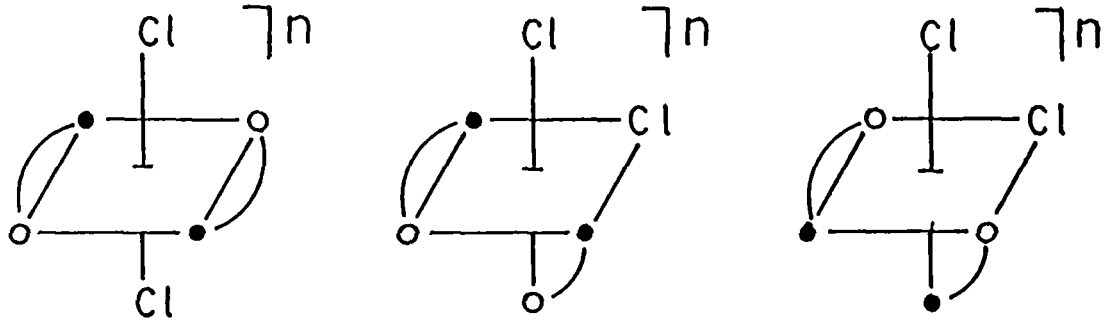
examples of isolable isomeric trivalent ruthenium complexes[7,8] are scarce. In this oxidation state metal-ligand π-interactions become insignificant and the geometry preference of these complexes are totally controlled by steric interactions. Here we also explore the possibilities of using the above compounds as mild oxidants specially in non-aqueous solvents.

Results and Discussion

(A) Synthesis and Geometry

In the last chapter we reported[3] that in the direct reaction of ruthenium(III) chloride with L, the metal ion undergoes reduction with concomitant partial chloride substitution to yield bivalent ruthenium complexes, $RuCl_2L_2$. In order to get an access to the trivalent complexes, preformed $Ru^{II}Cl_2L_2$ was, therefore, chosen for chemical oxidation. Accordingly, an acetonitrile solution of $RuCl_2L_2$ was exposed to Cl_2(g) followed by addition of aqueous $NaClO_4$ led to the synthesis of $[RuCl_2L_2]ClO_4 \cdot H_2O$. The role of aqueous $NaClO_4$ was to bring about precipitation of the product as a perchlorate salt.

The starting complex, $RuCl_2L_2$ thus far been obtained[3,9] in three isomeric forms : green trans-trans-trans (ttt, 2), bluish-green cis-cis-trans (cct, 3) and blue cis-trans-cis (ctc, 4). On oxidation, each of them afforded a characteristic $[RuCl_2L_2]ClO_4 \cdot H_2O$ salt. Interestingly,



n = 0 2 3 4

n = +1 5 6 7

chemical as well as electrochemical reductions of each one of the trivalent complexes (5-7) quantitatively regenerates the parent $RuCl_2L_2$. Thus, the redox reaction involved the above interconversion ($Ru^{II}Cl_2L_2 \rightleftharpoons Ru^{III}Cl_2L_2^+$) is reversible and stereoretentive. Stereoretentivity of the above reaction allows isolation of isomeric $RuCl_2L_2^+$ in three geometries. The examples of such isomeric trivalent ruthenium complexes are scanty in the literature[7,8]. We note here that isomer preference in the trivalent state is primarily steric controlled. As a result, in many cases, oxidations of isomeric bivalent complexes lead to isomerization[10,12] to yield only the trans isomer.

(B) Characterization

The yellowish brown microcrystalline complexes were formulated as $[RuCl_2L_2]ClO_4 \cdot H_2O$ by elemental (C,H,N) analyses of the isolated products (Table III.1). All these complexes behave as 1:1 electrolytes in acetonitrile (Table III.1).

(A) Optical Spectra

IR spectral data were collected as KBr disc in the range 4000 - 250 cm^{-1}. Selected group frequencies are presented in Table III.1.

In free L two absorption bands appear at 1600 and 1630 cm^{-1}, which are due to $\nu_{C=N}$(Py) and $\nu_{C=N}$(imine) respectively. The most significant observation in the IR spectra is the consistant appearance of two strong bands in the region 1590 - 1610 cm^{-1}. The band at lower energy has been assigned to $\nu_{C=N}$(Py). Evidently the higher energy band is due to $\nu_{C=N}$(imine). The shift of $\nu_{C=N}$(imine) to lower energy in the complex compared to free L suggests that the ligand L is coordinated to Ru(III).[13,14]

The complex 5 showed a single, strong and sharp band at 320 cm^{-1} (Table III.1). This is compared with the IR spectrum of free L in the range 400 - 250 cm^{-1}. Free L does not show any absorption below 400 cm^{-1}. Thus, this band in the IR spectrum of complex 5 is assigned to $\nu_{(Ru-Cl)}$ stretching mode. The singlet nature of $\nu_{(Ru-Cl)}$ strongly

suggests[3,15-17] a linear or nearly linear trans grouping for $RuCl_2$ moiety. In other words formation of the trivalent Ru-complex, 5, occurs by the stereoretentive oxidation of its bivalent congener.

In contrast, each of the other two complexes 6 and 7 displays a doublet in the region 290 to 310 cm^{-1} (Table III.1) which is characteristic[16-18] of a cis-$RuCl_2$ geometry. Furthermore, we note here that ν_{Ru-Cl} frequencies in the trivalent complexes (5-7) are systematically higher than those in the bivalent complexes (2-4) indicating stronger Ru-Cl bonds in $[RuCl_2L_2]ClO_4 \cdot H_2O$ complexes.

All three trivalent complexes consistently display bands at 1100 cm^{-1} and 620 cm^{-1}. The structureless broad band at 1100 cm^{-1} is assigned to $\nu_{(ClO_4)^-}$ which suggests the lack of significant perchlorate coordination.[4]

The electronic spectra of the synthesised trivalent complexes were recorded in the range 2000 - 250 nm. Major bands of $[RuCl_2L_2]ClO_4 \cdot H_2O$ complexes are presented in Table III.2 and the spectra of the representative cases are displayed in Figure III.1. The complexes have a characteristic intense band near 500 nm. The trans Ru(III) complex displayed a band at 390 nm whereas in the cases of other two a shoulder is observed at the said region. These allowed transitions[7] are due to involvement of metal and ligand orbitals. A low intensity absorption occurs in all

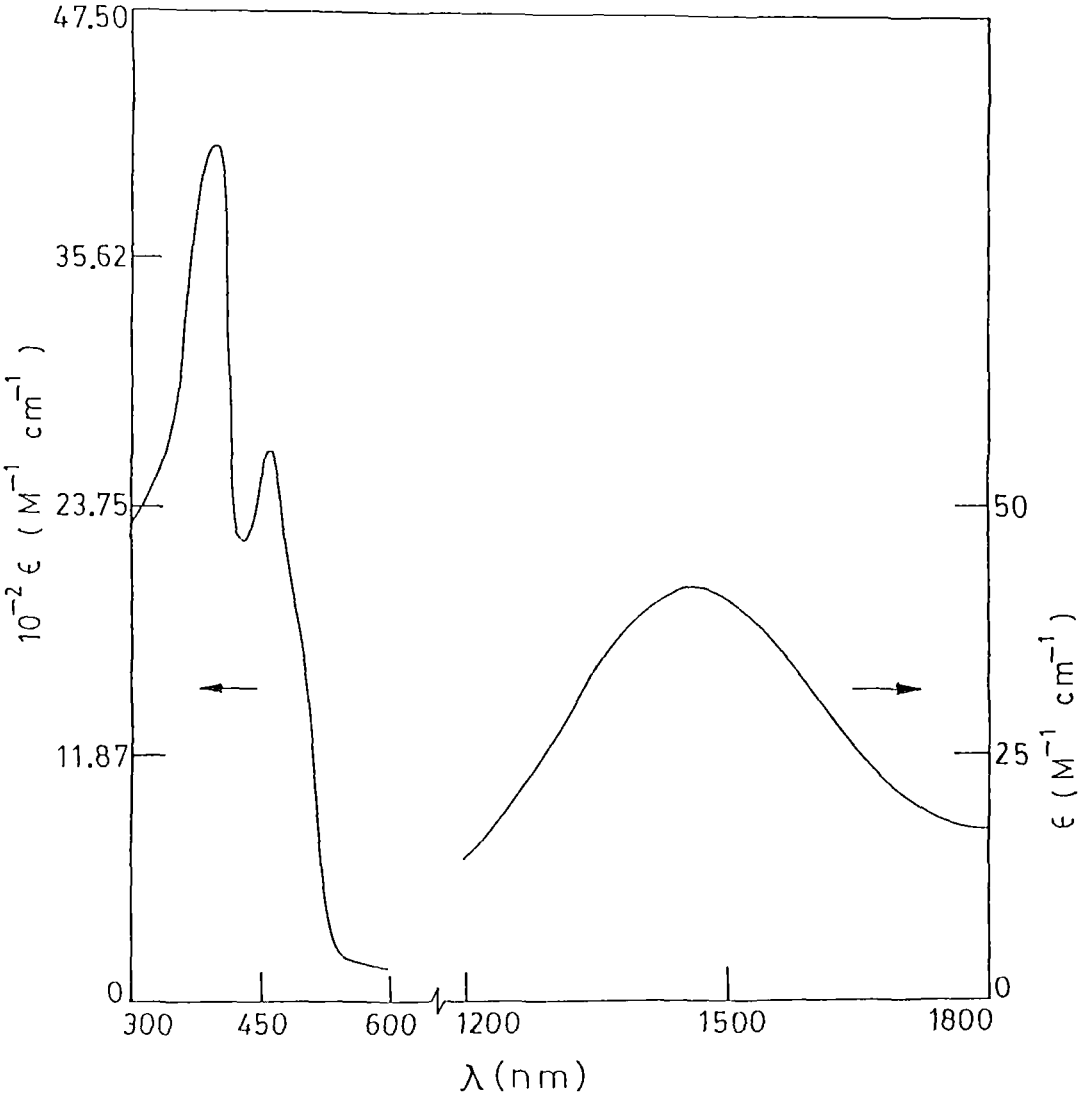


FIGURE III.1 ELECTRONIC SPECTRUM OF ttt-$[RuCl_2L_2]ClO_4$ IN CH_3CN

complexes in the near IR region in the range 1625-1450 nm. This band is assigned to ligand field transition within the t_2 orbitals splitting because of low symmetry and spin-orbit coupling. Interestingly, the energy of the ligand field band is in good agreement with the calculated transition energies using the observed g-values from the respective EPR spectrum.

(B) Magnetic Moments and EPR Spectra :

The magnetic moments of the complexes are collected in Table III.3 which correspond to low-spin d^5 configuration (idealised t_{2g}^5, S=1/2).

None of the isomers possesses rotational symmetry greater than two fold. Their EPR spectra of the complexes were recorded in frozen acetonitrile-touene (77K). The Ru(III) species uniformly displayed three resonances characterising a rhombic structure (Figure III.2). The corresponding g components are designed as g_1, g_2 and g_3 in order of decreasing magnitudes.

The theory of EPR spectra of distorted-octahedral low spin d^5 complexes are documented[19-23] in the literature.

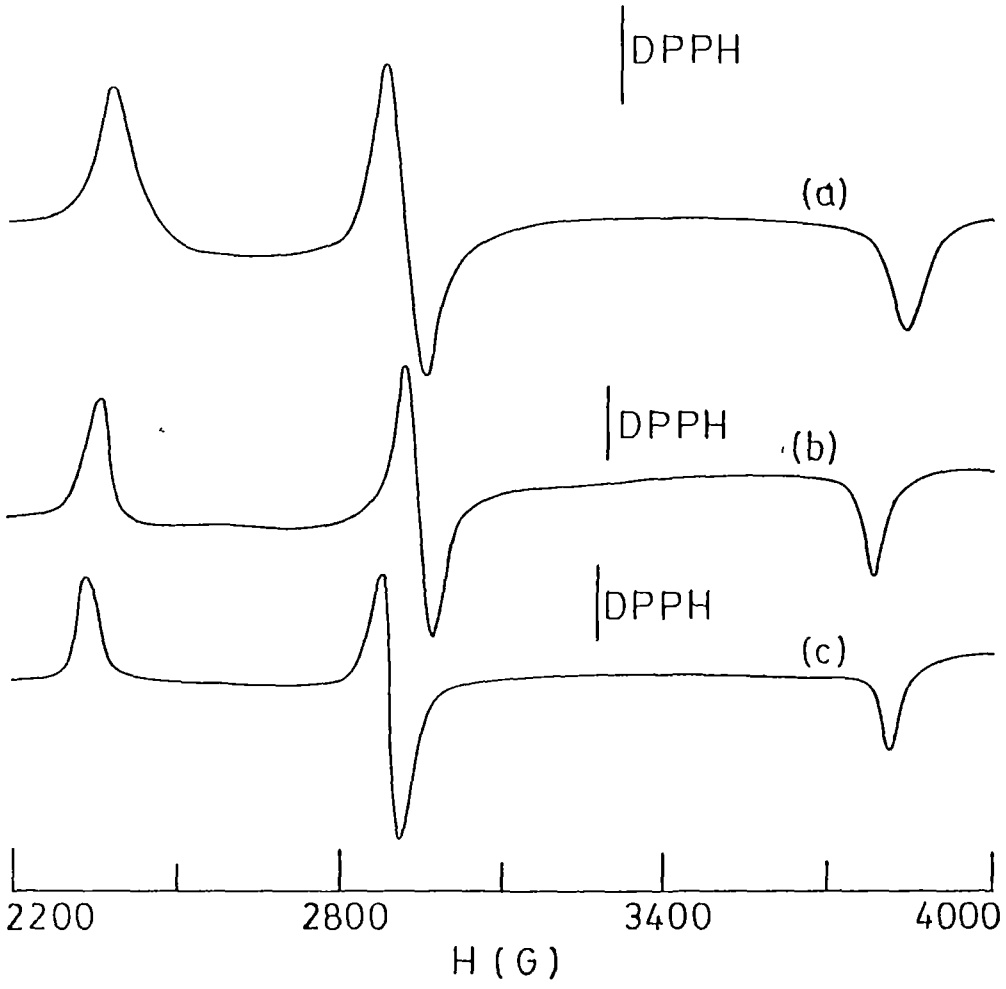
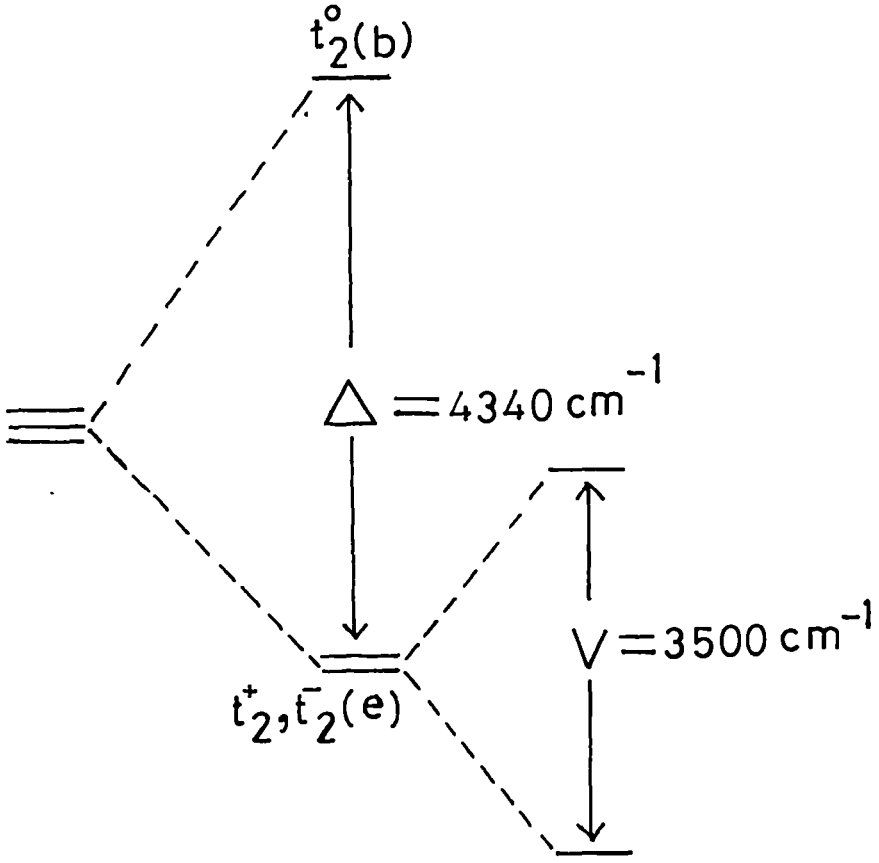


FIGURE III.2 X-BAND EPR SPECTRA IN AN ACETONITRILE-TOLUENE (1:1) GLASS (77K) OF (a) ttt- (b) cct- and (c) ctc-$[RuCl_2L_2]ClO_4$



COMPUTED t_2 SPLITTING OF ttt-$[RuCl_2L_2]ClO_4.H_2O$

Only the essential features of relevance to this work are stated below. The net distortion of pseudo octahedral species can be expressed as the sum of axial (Δ) and rhombic (V) components. The t_2 orbitals consist of the components t_2^o(or,b); t_2^+ and t_2^- (or,e). The axial distorsion, appropriately considered as tetragonal, partly removes t_2 degeneracy, placing t_2^o (or,b) above t_2^+ and t_2^- (or,e) by Δ. The rhombic distortion(V) splits t_2^- and t_2^+ in to nondegenerate components. The components T_2^o, T_2^+ and T_2^- of the T_2 term (spin multiplicity is not shown) undergo corresponding splittings[22]. Under the influence of spin orbit coupling (λ) the components mix, affording three Krammers doublets represented by two identical 3 X 3 matrices as shown.

		$\lvert T_2^- \rangle$	$\lvert \bar{T}_2^o \rangle$	$\lvert T_2^+ \rangle$
		$\lvert \bar{T}_2^+ \rangle$	$\lvert T_2^o \rangle$	$\lvert \bar{T}_2^- \rangle$
$\lvert T_2^- \rangle$	$\lvert \bar{T}_2^+ \rangle$	$\lambda/2$	0	V/2
$\lvert \bar{T}_2^o \rangle$	$\lvert T_2^o \rangle$	0	$-\Delta$	$-\lambda/2^{1/2}$
$\lvert T_2^+ \rangle$	$\lvert \bar{T}_2^- \rangle$	V/2	$-\lambda/2^{1/2}$	$-\lambda/2$

States of β spin are identified by putting a bar on the top.

In the ground Krammers doublets Equations(1,2) where the coefficients p, q and r are real and dependant on Δ, V and λ.

$$\psi_i = p\,|T_2^+\rangle + q|\bar{T}_2^o\rangle + r|T_2^-\rangle \qquad 1$$

$$\psi_{11} = p|\bar{1}_2^-\rangle + q|T_2^0\rangle + r|\bar{T}_2^+\rangle \quad 2$$

EPR g-tensor arising from this doublet can be expressed as in equation 3,4 and 5, where k is the orbital reduction factor assumed to be isotropic.

$$g_x = 2[-2pr - q^2 - 2^{1/2}kq(p+r)] \quad 3$$

$$g_y = 2[2pr - q^2 - 2^{1/2}kq(p-r)] \quad 4$$

$$g_z = 2[-p^2+q^2-r^2+k(p^2-r^2)] \quad 5$$

$$p^2 + q^2 + r^2 = 1.$$

EPR experiment affords only the magnitude of the g values but not their signs. Their corresponds to g_x, g_y and g_z is also unknown. Each correspondence can in principle afford a set of values for p,q,r and k. Meaningful solutions can be sorted out by putting limits on acceptable k values such as 0 < k < 1.5 used in the present analysis. The p,q,r and k values furnish Δ,V and the energies of the ground Krammers doublet, and diagonalization of matrix afford two crystal field transitions ΔE_1 and ΔE_2 ($\Delta E_2 > \Delta E_1$). The availability of experimental ΔE_1 and ΔE_2 values is crucial for choosing the correct solutions through comparison with computed values.[22] The corresponding values of Δ,V and k as well as of p,q and r are then easily extracted. It is to be noted that g_1, g_2 and g_3 are presented on slots of g_x, g_y and g_z having fixed signs.

In the present work ΔE_2 for all the three geometrical isomers have been observed[7,24-26] in the near IR

region in acetonitrile. In the ttt complex a low intensity transition occurs at 6800 cm^{-1}. Between other two cis isomers the cct displays a transitions at 6670 cm^{-1} and ctc at 6150 cm^{-1}. All these are assigned to ΔE_2. ΔE_1 could not be observed since the band maximum falls in the IR region and the solvent, acetonitrile, is not transparent in this region. In view of approximations of the theory, the agreemont between calculated and observed transition energies (Table III.3) is quite satisfactory.

The low molecular symmetry of the complexes is reflected in their EPR spectra. The extent of distorsion from idealised O_h symmetry has been ascertained in terms of axial(Δ) and rhombic(V) components. The distorsions are large enough to make the two ligand field transactions (ΔE_1 and ΔE_2) among the three Trammer's doublets observable in the near IR region. The availability of ΔE_1 and ΔE_2 values led to quantitation of Δ and V with the help of observed g values. The observed k values, a measure of co-valency, are slightly higher than one. This can be due to admixture of excited state (t_2^4e) with t_2^5 configuration. This effect has not been explicitly considered in the model used.

(C) Redox Properties

The electron transfer properties of isomeric salt $[RuCl_2L_2]ClO_4 \cdot H_2O$ were studied cyclic voltammetrically in acetonitrile at a platinum electrode using tetrabutyl

ammonium perchlorate as supporting electrolyte. Potential data are collected in Table III.2 and segmented voltammograms are displayed in Figure III.3. All potentials are referenced to saturated calomel electrode (SCE). The complexes showed ligand based multiple reductive responses which are identical to the responses occuring[1,3] in the corresponding bivalent complexes.We donot consider these any further. Each isomer of $[RuCl_2L_2]^+$ displays a reversible, reductive, one electron cyclic volammogram in the potential range 0.3-0.7V. Under identical conditions, this voltammogram (initial scan cathodic) is superimposable on that of the corresponding isomer of $RuCl_2L_2$ (initial scan anodic). This clearly indicates that the redox process under consideration is reversible and stereoretentive. Exhaustive constant potential electrolyses of isomeric 5-7 were perfoimed at 0.0 V. The coulomb count in each case corresponds to one-electron and the absorption spectrum of solution of electrogenerated bivalent complex matches quantitatively with the corresponding isomer of $RuCl_2L_2$. The formal potentials of the ruthenium(III) / ruthenium(II) couple follow the order : ttt cct ctc. Thus, the trivalent complex in cic geometry (7) is the strongest oxidising agent in this series. This may be rationalised[8] in terms of strongest $d\pi$-$p\pi$ interactions in the corresponding bivalent complex, 4.

The stabilities of the trivalent complexes, $RuCl_2L_2^+$ together with the reduction potentials suggest that they

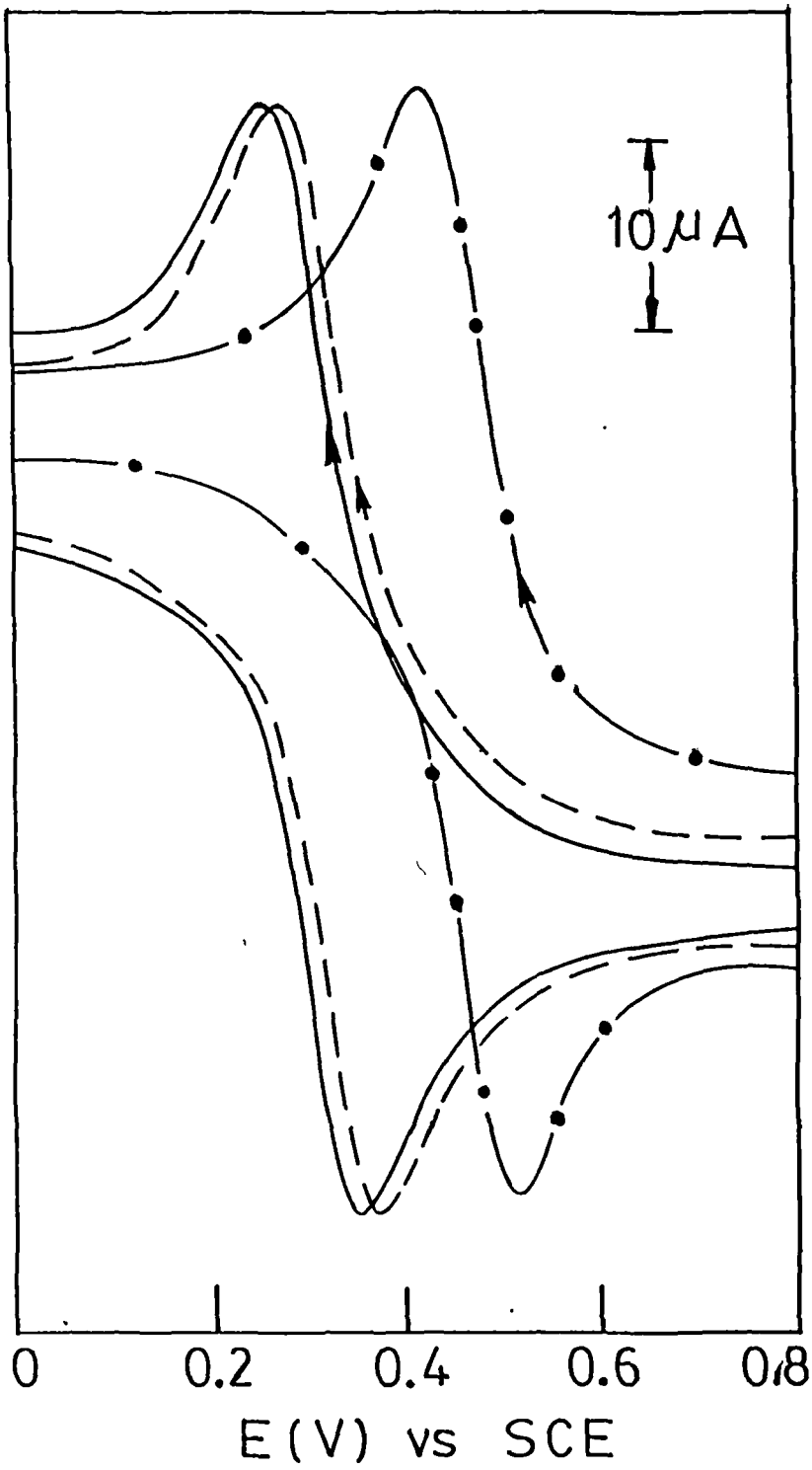


FIGURE III.3 SEGMENTED CYCLIC VOLTAMMOGRAMS OF

(a) ttt- (——) (b) cct- (----) AND

(c) ctc-$[RuCl_2L_2]ClO_4$ (-•-•-) AT 50mVs^{-1} SCAN RATE

might act as moderate one-electron oxidants. Accordingly, two redox reactions were performed which indeed showed that the trivalent complexes successfully take part in the redox reactions.

Addition of a few drops of hydrazine hydrate to the brown solution of isomeric **5-7** in acetonitrile brings about an instantaneous colour change to the corresponding colour of **2-4**. This reaction was followed spectrophotometrically, which showed almost quantitative reduction of the trivalent complex. No attempt has, however, been made to detect the oxidation product(s) of hydrazine. In another experiment equimolar solutions of $Fe^{II}(C_5H_5)_2$ and $Ru^{III}Cl_2L_2^+$ in acetonitrile were mixed together and the resultant solution was examined cyclic voltammetrically. Immediately there was a colour change. In addition to the reversible oxidation wave of $Ru^{II}Cl_2L_2$, a reductive wave at 0.18 V confirmed the generation of $Fe^{III}(C_5H_5)_2^+$ evidently due to the electron transfer in the solution.

EXPERIMENTAL SECTION

A. Physical Measurements

Molar conductivity, Infrared Spectra, Electronic Spectra and Electrochemical Measurements. All described in chapter II.

B. Formulation of Compound

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

C. Materials

The three isomers of Dichlorobis (N-phenylpyridine-2-carboxaldimine) ruthenium(II) were prepared using the methods described in chapter II. Tetrabutyl ammoniumperchlorate (TBAP) was prepared using the same method described in chapter II for tetra ethyl ammonium perchlorate (TEAP). Purification of acetonitrile was done as described in chapter II. Dinitrogen gas was purified by successively bubbling it through the alkaline aquous solution of sodium dithionite and concentrated sulphuric acid. Potassiumpermanganate, concentrated hydrochloric acid, other chemicals and solvents were reagent grade commercial materials.

D. 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 in to solution and evolution of carbon dioxide 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 vaccum over anhydrous calcium chloride.

E. Complexes

The three isomers of $[RuCl_2L_2]ClO_4 \cdot H_2O$ were synthesised using a general procedure. Yields varied in the range 80-90%. Detailed procedure for the preparations of the isomers is given below.

ttt-Dichlorobis (N-phenylpyridine-2-carboxaldimine) ruthenium (III) perchlorate.

A solution of 100mg of the ttt-$[RuCl_2L_2]$ in 25 ml acetonitrile was prepared. To the freshly prepared solutions Cl_2(gas) was bubbled till the colour of the solution changed to light-yellow. The solution was then filtered to remove any insoluble material. To it 5 ml of saturated solution of sodium perchlorate was added and the mixture was left in the refrigerator for about 30 min. Crystalline yellowish brown precipitate, thus formed, was filtered and washed with ice-cold water. The solid mass was then dried in vaccum over P_4O_{10}.

Yield : 80%

TABLE III.1

Analytical, Conductivity and IR data

Compound	Elemental Analysis(%)[a] C	H	N	Λ_M[b] ($ohm^{-1}cm^2mol^{-1}$)	IR[c] (cm^{-1}) $\nu_{C=N}$	ν_{Ru-Cl}
ttt-$[RuCl_2L_2]ClO_4 \cdot H_2O$	44.9 (45.3)	3.0 (3.1)	8.9 (8.8)	135	1602	320
cct-$[RuCl_2L_2]ClO_4 \cdot H_2O$	45.2 (45.3)	3.2 (3.1)	9.0 (8.8)	140	1605	325,310
ctc-$[RuCl_2L_2]ClO_4 \cdot H_2O$	45.1 (45.3)	3.1 (3.1)	8.9 (8.8)	140	1605	320,300

[a] Calculated values are in parenthesis.

[b] In CH_3CN at 298K with a solute concentration of ca. 10^{-3}M.

[c] In KBr disc.

TABLE III.2

Electrochemical and Electronic spectral data

Compound	Electronic spectra[a] λ_{max}(nm) (ϵ, $M^{-1}cm^{-1}$)	Ru^{III}-Ru^{II} couple[b] E^{0}_{298}(V)	ΔE_p(mV)	n[c]
ttt-$[RuCl_2L_2]ClO_4 \cdot H_2O$	1460(43), 500[d], 470(2665), 400(3895)	0.31	70	0.98
cct-$[RuCl_2L_2]ClO_4 \cdot H_2O$	1500(40), 500[d], 457(2760), 390[d], 340(8170)	0.33	65	1.01
ctc-$[RuCl_2L_2]ClO_4 \cdot H_2O$	1625(45), 490[d], 450(2880), 325(8500)	0.47	70	1.01

[a] In CH_3CN at 298K. [b] Conditions : solvent, CH_3CN: supporting electrolyte, $[NBut_4][ClO_4]$ (10^{-1}M); working electrode, platinum; reference electrode, SCE; solute concentration, Ca. 10^{-3}M. Cyclic voltammetric data: $E^{o}_{298} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate, 50 mVs^{-1}. [c] $n = Q/Q'$; where Q' is the calculated coulomb count for the transfer of one electron and Q is the observed coulomb count after exhaustive electrolysis; oxidation in each case was performed at 0.10 V vs. SCE in CH_3CN (0.1 M $[NBut_4][ClO_4]$.) [d] Shoulder.

TABLE III.3

Magnetic moments, EPR g values and derived energy parameters.

Compound	μ_{eff} (BM)[a]	g_x	g_y	g_z	a	b	c	k	$\frac{\Delta}{\lambda}$	$\frac{V}{\lambda}$	Derived Energy parameters (cm^{-1}) $\frac{E_1}{}$	$\frac{E_2}{}$
		g values[b]										
ttt-$[RuCl_2L_2]ClO_4$	1.82	-2.8018	-2.2491	1.7309	0.2048	0.9762	0.0719	1.0958	4.3353	-3.4978	2.7833	6.3324
											(3593nm)	(1579nm)
cct-$[RuCl_2L_2]ClO_4$	1.89	-2.8009	-2.2350	1.7436	0.1994	0.9772	0.0735	1.1039	4.5249	-3.8199	2.8135	6.6690
											(3554nm)	(1499nm)
ctc-$[RuCl_2L_2]ClO_4$	1.85	-2.8120	-2.2632	1.7220	0.2082	0.9755	0.0707	1.1043	4.2258	-3.3140	2.7767	6.1377
											(3601nm)	(1629nm)

$\lambda \approx 1000\ cm^{-1}$ for Ru^{3+}

[a] In the solid state at 298K.

[b] In acetonitrile-toluene (1:1) glass at 77K

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Chapter IV

CHAPTER IV

OXIDATION OF COORDINATED IMINE TO AMIDE. SYNTHETIC AND STRUCTURAL STUDIES ON ISOMERIC $Ru^{II}(LH)_2Cl_2$ [LH = N-ARYLPYRIDINE-2-CARBOXALDIMINE]*

Abstract *The relevant N,N'-coordinating ligands are* $C_5H_4NCH{=}NC_6H_4R$ *(general abbreviation LH, specific abbreviations* L^1H *and* L^2H *for R = H and p-tolyl, respectively) and* $[C_5H_4NC(O){-}N{-}C_6H_4R]$ *(abbreviations LO,* L^1O, L^2O*). Oxidation of trans- and cis-*$Ru^{II}(LH)_2Cl_2$ *by* H_2O_2 *(and also aqueous Ce(IV)) affords in excellent yields amide complexes, trans and cis-*$Ru(LO)(LH)Cl_2$*, with retention of parental isomeric structures. Spectral and magnetic characterization data of the complexes are reported along with the X-ray structure of trans* $Ru^{III}(LO)(LH)Cl_2$*. The conversion* $Ru(LH)_2Cl_2 \longrightarrow Ru(LO)(LH)Cl_2$ *occurs via* $Ru(LH)_2Cl_2^+$*, which reacts with water, affording the amide complex. It is proposed that the water molecule adds to the azomethine function to produce α-hydroxy amine function which is then rapidly oxidised to form the final product. The overall reaction may be represented as follows:*

$$Ru(LH)_2Cl_2 \longrightarrow Ru(LH)_2Cl_2^+ + e$$

$$3Ru(LH)_2Cl_2^+ + H_2O \longrightarrow Ru(LO)(LH)Cl_2 + 2RuCl_2(LH)_2 + 3H^+$$

A crucial reaction condition appears to be the easy accessibility of two oxidation states of the metal ion related by facile transfer of one electron, the higher oxidation state being sufficiently polarising to induce water

binding at the aldimine site. These transformations were also achieved by the photo induced oxidation of the trans- $Ru(LH)_2Cl_2$ *by molecular oxygen.*

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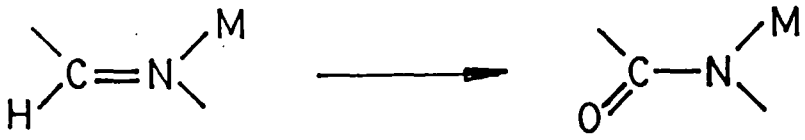
*A part of this work has appeared in *J. Chem. Soc., Chem. Commun.* 1994, 57.

INTRODUCTION

Metal mediated oxidation of organic compounds is a reaction class of fundamental importance in chemistry. The work in this chapter is concerned with a reaction of equation (1)[1,2] where the functional transformation aldimine——>amide occurs. Our objectives of the present work to search for the



reactive systems and to scrutinize the scope and nature of the interesting but little known reaction. The development of the chemistry is accidental, which was observed recently while studying the reactivities of bivalent Ruthenium species of the type $[RuCl_2(LH)_2]$ towards oxidants.[2]

The conversion of common aldehydes to amides follow the route as

$$— CHO \xrightarrow{[O]} — COOH \xrightarrow{RNH_2} — CONHR \qquad 2$$

In the present work we describe the above conversion

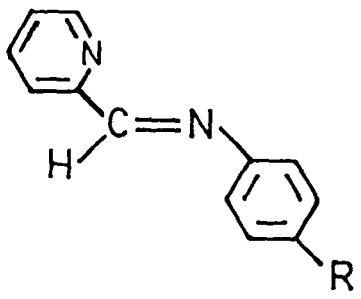
(equation 1) involving a reverse sequence.

$$\text{— CHO} \xrightarrow{RNH_2} \text{— CHNR} \xrightarrow{[O]} \text{— CONHR} \qquad 3$$

A family of isomeric ruthenium amido compounds have been isolated and fully characterised. The three dimensional X-ray structure has been solved for a representative case. A plaussible reaction sequence has been proposed.

Results and Discussion

In the preceeding chapter (II) we described the synthesis, isolation and characterisation of the isomeric bivalent ruthenium complexes of the type $[Ru^{II}(LH)_2CL_2]^3$ [LH = α-diimine, N-arylpyridine-2-carboxaldiimine. The two R groups phenyl (LH = L^1H and p-tolyl (LH = L^2H)] and the trivalent complexes of the type $[Ru^{III}(LH)_2CL_2]^+$ [LH = N-arylpyridine-2-carboxyldimine. The two R groups phenyl (LH = L^1H) and p-tolyl (LH = L^2H)]

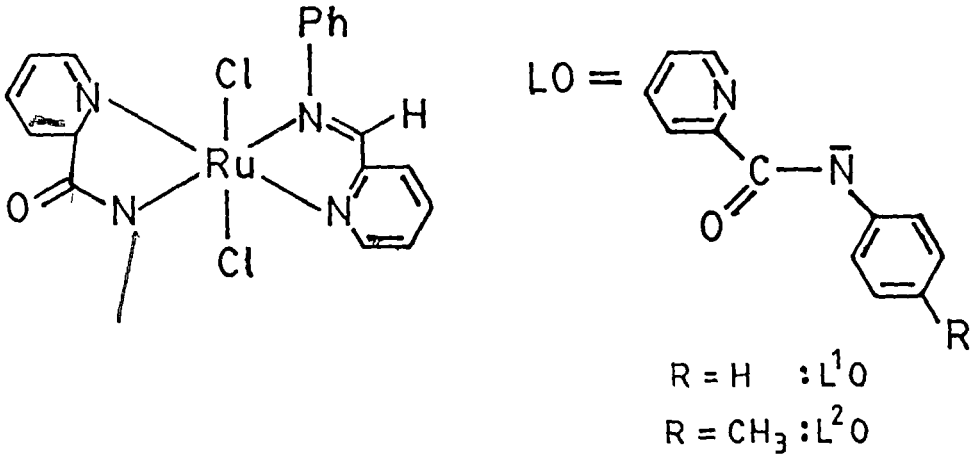


R = H : L^1H

R = CH_3 : L^2H

A. THE REACTION

Oxidation of the isomeric ruthenium bivalent diimine complexes, $[Ru^{II}(LH)_2Cl_2]$, with aqueous H_2O_2 (also Ce^{4+}) afford, in excellent yields, the dark coloured amido complexes of trivalent ruthenium of the type $[Ru(LO)(LH)Cl_2]$ (LO = N - phenyl picolinamide anion with retention of parental isomeric structure.



While LH is neutral, the amide ligand LO is N - bonded to ruthenium(III) in anionic deprotonated form, LO^-. Specific LO's are L^1O (R=H) and L^2O (R = p-tolyl). Even when excess of hydrogen peroxide is used only one imine function of one of the α - diimine ligands is oxidised to amide, the second diimine ligand remains unaffected. Thus $Ru(LO)(LH)Cl_2$ is the only product of oxidation.

B. Characterization

(i) Elemental Analyses

Elemental (C, H, N) analytical data (Table IV.1) agree well with the composition of trivalent ruthenium amido compounds.

(ii) Optical Spectra

I.R. spectra

I.R. spectral data were collected as KBr disc in the range 4000-250 cm^{-1}. Selected group frequencies are presented in Table IV.2 and a representative spectra is displayed in Figure IV.1.

All the three isomeric amido complexes displayed a three band structure in the region 1590-1640 cm^{-1}. The band at lowest energy has been assigned[2,3] to $\nu_{C=N}$(pyridine). The band at higher energy than $\nu_{C=N}$ (pyridine) is due[2,3] to $\nu_{C=N}$ (imine) which is comparatively less intense than $\nu_{C=N}$ (imine) in trivalent ruthenium diimine complexes. The highest energy band is assigned[2] to $\nu_{C=O}$.

A single strong and sharp band is observed in the case of trans amido compound in the region 300-305 cm^{-1} (Table IV.2) which is absent in the I.R. spectrum of free L. Evidently, it is due[4] to ν_{Ru-Cl} stretching mode. The singlet nature of ν_{Ru-Cl} strongly suggest[4,5] the linear or nearly

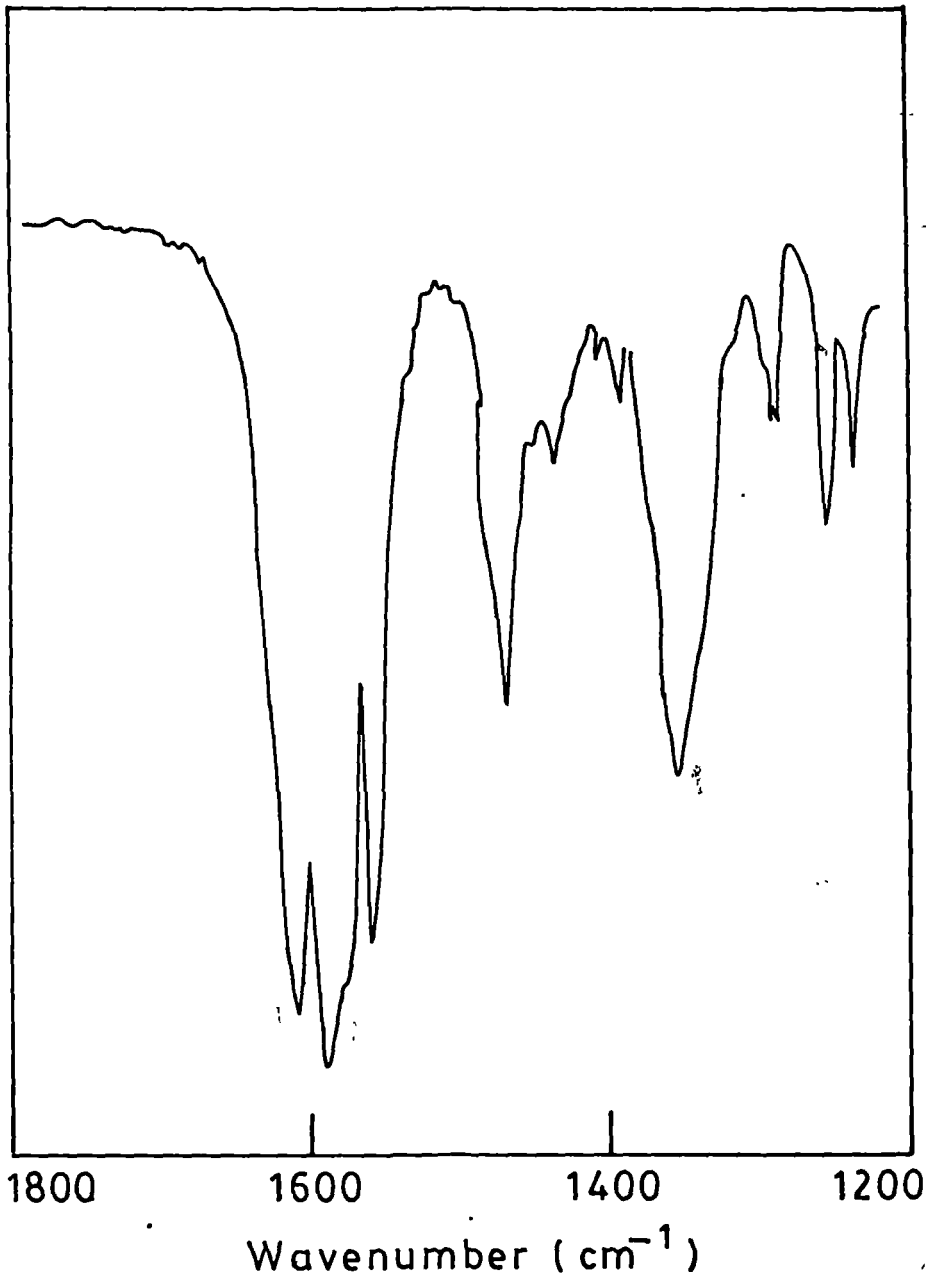


FIGURE IV.1 IR SPECTRUM OF ttt-[Ru(L^1O)(L^1H)Cl_2] IN KBr

linear trans grouping for the $RuCl_2$ moiety and it indicates that the $[Ru^{III}(LO)(LH)Cl_2]$ has been obtained via stereoretentive oxidation of trans-$[Ru(LH)_2Cl_2]$. Other two cis- isomers of amido complexes display a doublet in the region 290-310 cm^{-1}, as expected.[5,6]

(iii) X-ray crystal structure

The imine—— amide oxidation process has been authenticated by structure determination. We tried to grow single crystals for all the three isomeric amido complexes. Unfortunately, till date, we are unable to develop X-ray quality crystals for the cis- compounds. Fortunately, however, single crystals could readily be grown for the ttt-amido compound by slow diffusion of its chloroform solution in toluene.The structural work was carried out by Prof.A.Chakravorty and his group at the Department of Inorganic Chemistry of I.A.C.S. The three dimensional drawings of the worked out structure is displayed in Figure IV.2. Crystal data and selected bond distances and angles are listed (Table IV.3; Table IV.4)

The compound crystallises out as $[Ru(L^1H)(L^1O)Cl_2]PhMe$. The coordination sphere involves RuN_4Cl_2, the two pyridine Nitrogen atoms as well as the two chlorine atoms lie trans to each other. The chelating ligands display an interesting disorder. Even if the complex can be centrosymmetric, the metal atom in the lattice lies on a center of inversion. Thus the molecules are packed in two

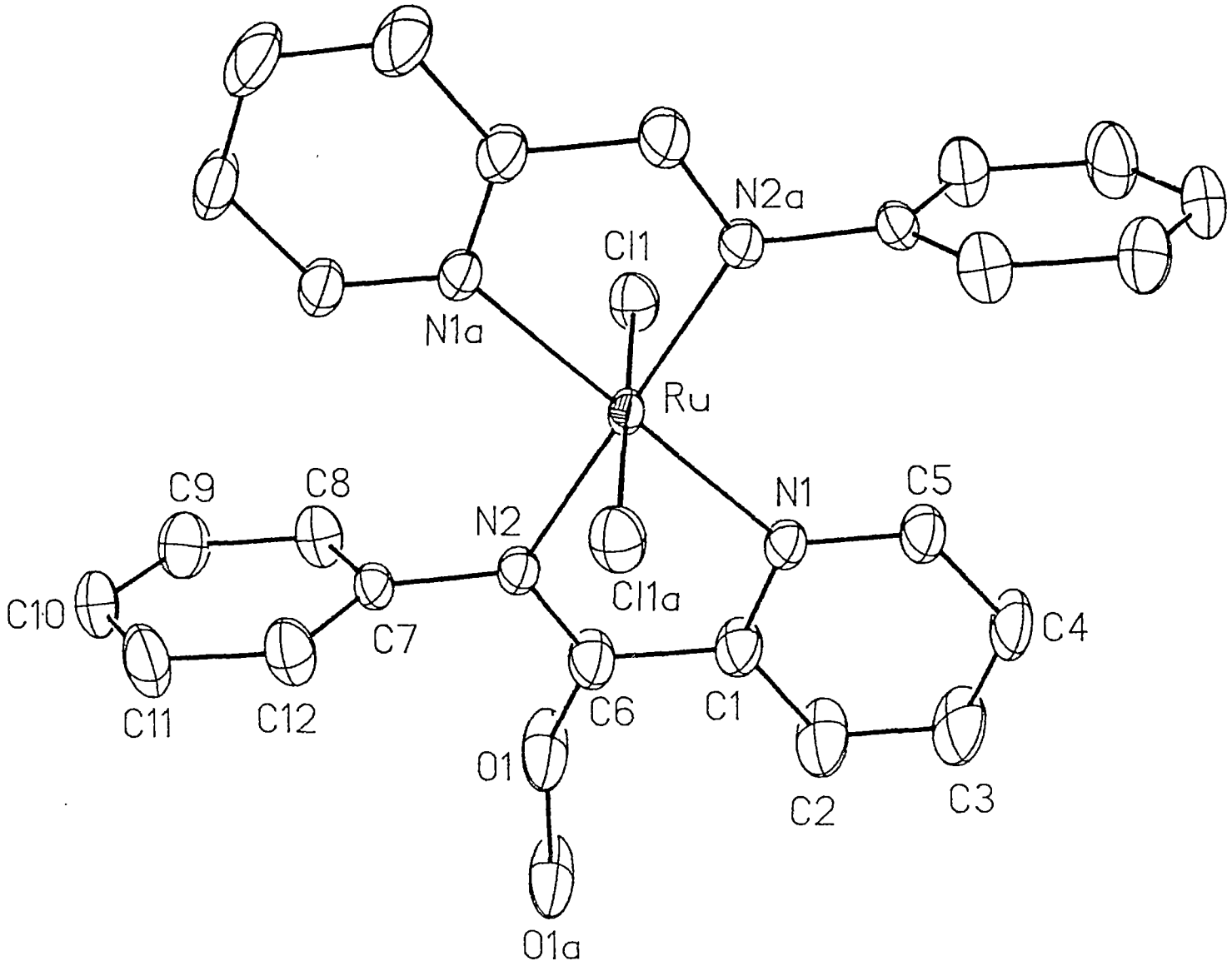


FIGURE IV.2 ORTEP PLOT AND ATOM LABELLING SCHEME FOR

ttt-$[Ru(L^1O)(L^1H)Cl_2]$ IN $[Ru(L^1O)(L^1H)Cl_2].C_6H_5CH_3$

equivalent but opposite orientations such that carbon and nitrogen atoms of the two bidentate ligands are nearly or completely superimposed.

(iv) Electronic Spectra

The electronic spectra of the isomeric trivalent amido complexes of ruthenium were recorded in the range 2200-250 nm. Major bands are presented in Table IV.5 and the spectra of a representative case is displayed in Figure IV.3. The complexes have an intense band near 515 nm. The trans amido complex also displyed another peak at 300 nm together with a shoulder at 350 nm. Whereas in the cases of other two cis-isomers,an intense transition near 500 nm and a shoulder at the uv-region were observed. The origin of the visible range absorption may be due to LMCT(ligand-to-metal-charge transfer) exitation.[7]

Moreover, a low intensity band occurs in all the complexes in near I.R. region at ca.1460 nm. This band is assigned to ligand field transition within the t_2 shell split by the rhombic nature of the ligand field.

(v) Magnetic Moment and EPR Spectra

The magnetic moment has been found to lie in the range 1.82 to 1.89 μ_B for all the three isomeric amido complexes and all of them are of low spin, d^5 configuration (idealised t_{2g}^5; S = 1/2) The EPR spectra of the three isomeric Ru(III) amido complexes are rhombic (Table

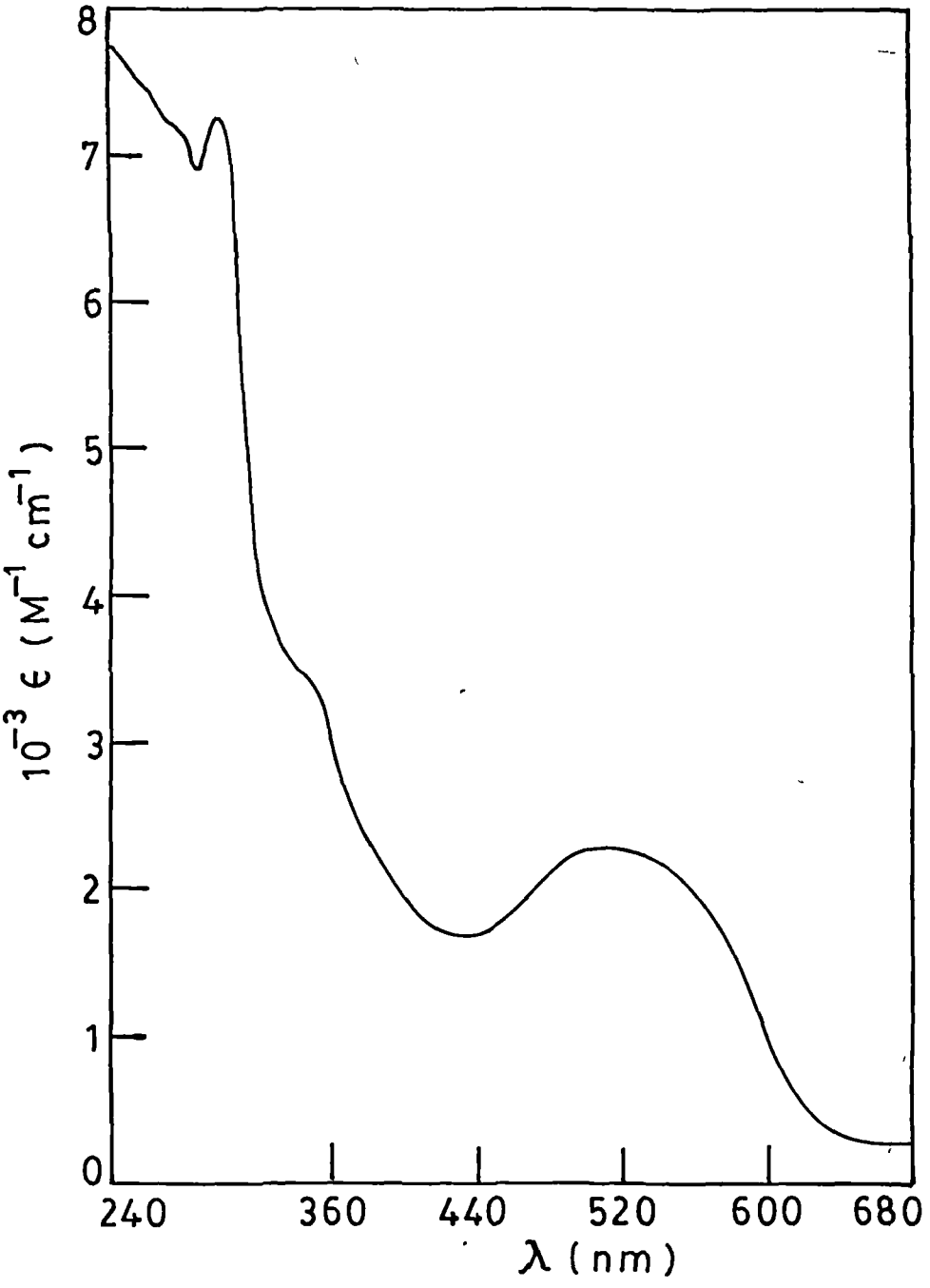


FIGURE IV.3 ELECTRONIC SPECTRUM OF ttt-$[Ru(L^1O)(L^1H)Cl_2]$ IN CH_3CN

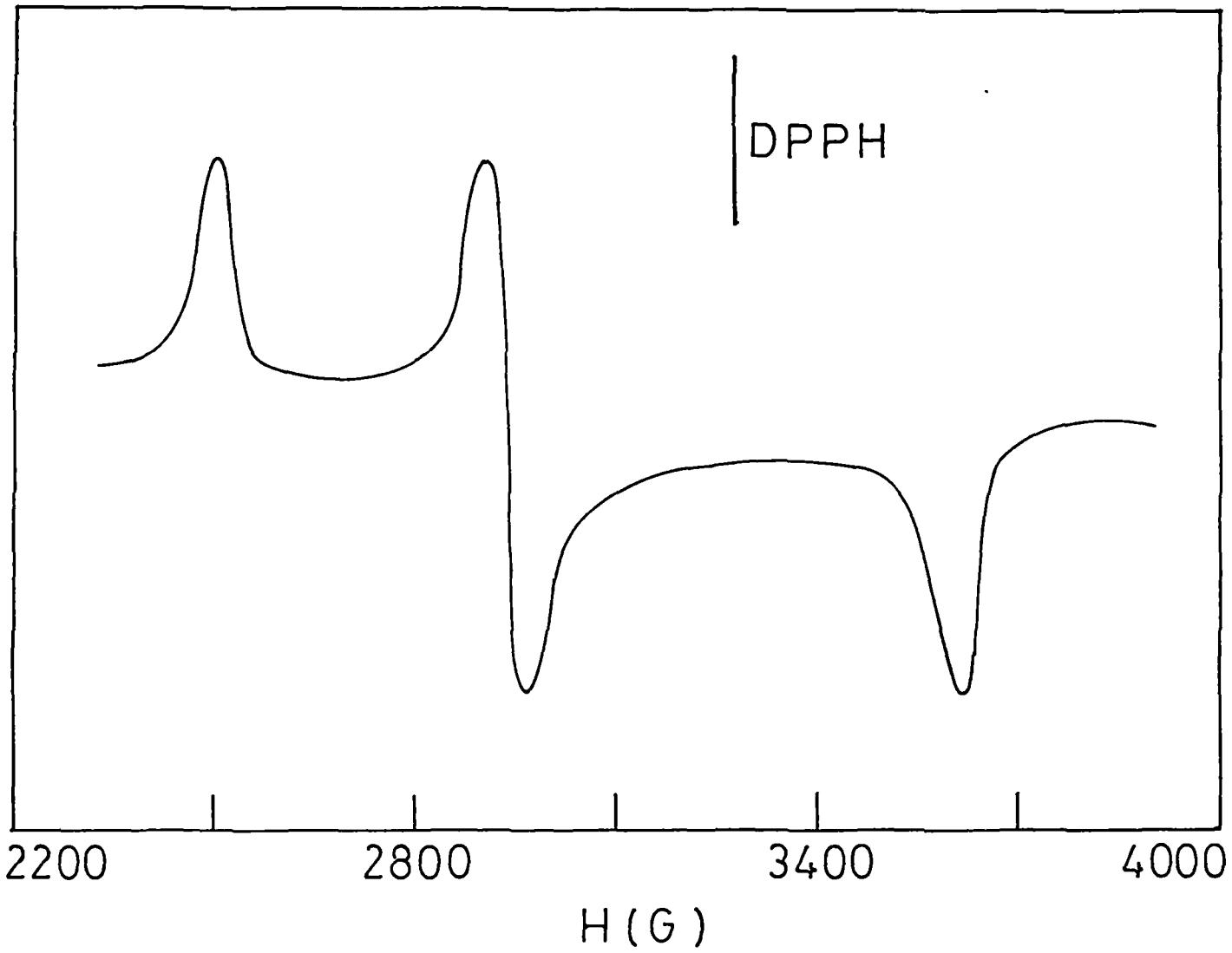


FIGURE IV.4 X-BAND EPR SPECTRUM OF ttt-$[Ru(L^1O)(L^1H)Cl_2]$ IN AN ACETONITRILE-TOLUENE (1:1) GLASS (77K)

IV.6;Figure IV.4) at 77K in frozen acetonitrile-toluene glass.

The spectra have been analysed[8] with help of crystal field g-tensor theory[9-12] of low spin d^5 configuration. The important result is that for each of the complexes the computed energy of the ligand field transitions within the t_2 shell, split by low symmetry components, fits well with the energy of the observed near I.R. band (Table IV.6). For isomeric $Ru(LO)(LH)Cl_2$ complexes both the predicted and the observed energies of the band follow the order trans < cis. This trend is also consistent with ligand field description of t_2 splitting.[13-15] The trans < cis inequality is of diagnostic value for isomeric structure assignment.

(vi) Metal Redox

In CH_3CN(0.1 mol dm^{-3} in the TBAP, Pt-electrode) the trans as well as cis-amido complexes display two nearly reversible one electron cyclic voltammeric responses at ca.-0.15 V and at 1.25 V due to Ru(III)-Ru(II) and Ru(IV)-Ru(III) redox couples, respectively (Table IV.7,Figure IV.5). The original diimine complexes display the one electron cyclic voltammetric responses[3] at ca.0.35V due to Ru(III)-Ru(II) redox couple

$$trans-/cis-Ru^{III}(LH)_2Cl_2^+ + e \rightleftharpoons Ru^{II}(LH)_2Cl_2$$

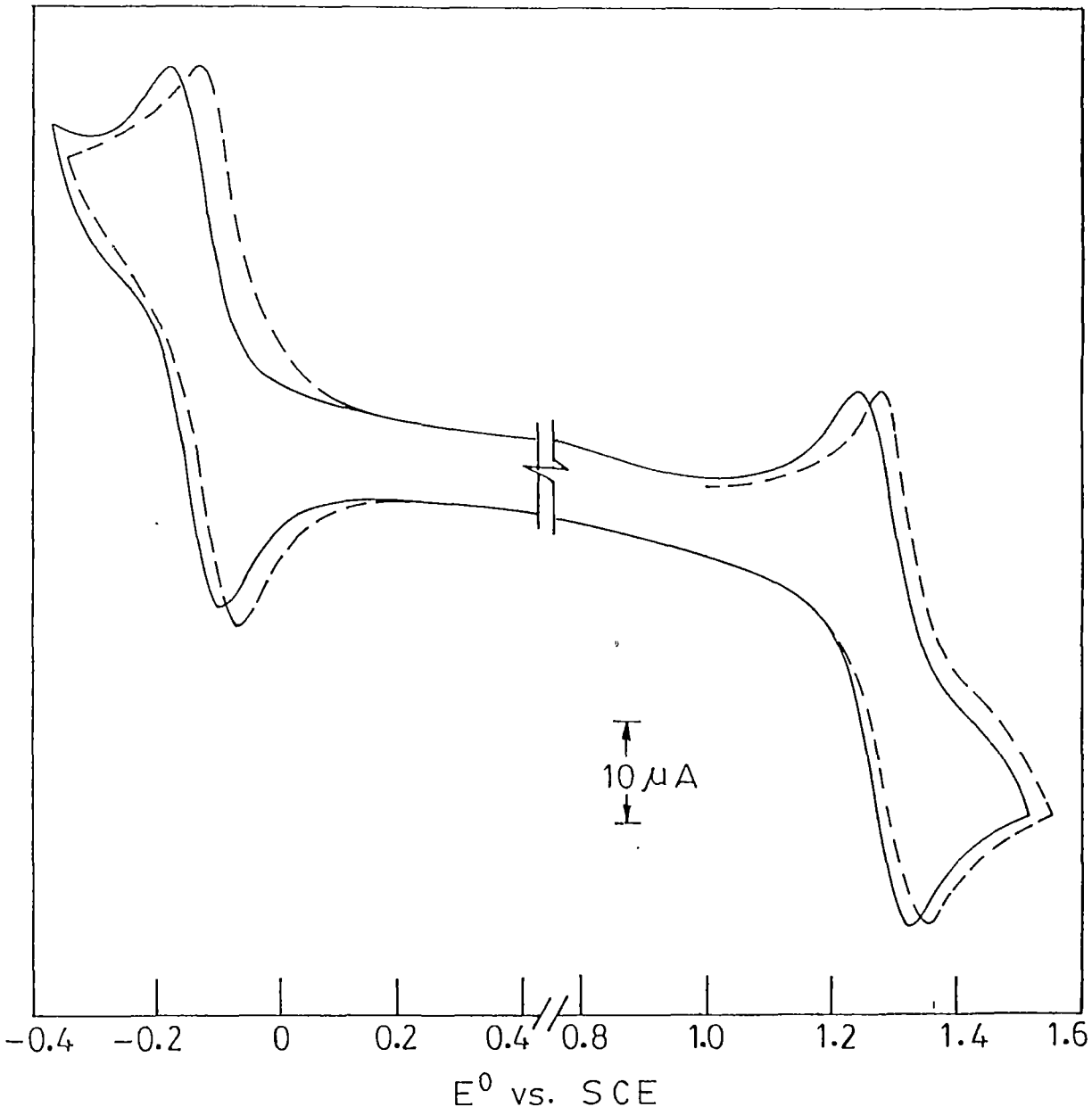


FIGURE IV.5 CYCLIC VOLTAMMOGRAMS OF

(a) ttt-$[Ru(L^1O)(L^1H)Cl_2]$ (——)

(b) ctc-$[Ru(L^1O)(L^1H)Cl_2]$ (----)

The much lower value of Ru(III)-Ru(II) in amide, trans-/cis-$Ru^{III}(LO)(LH)Cl_2^+ + e \rightleftharpoons Ru^{II}(LO)(LH)Cl_2$, then in imine signifies the strong stabilization of the higher oxidation state by the hard amide ligand.[2,16]

The electrochemical data are listed in Table IV.7. The trend of the reduction potential (E^o_{298} Vs SCE) is noted.

Reactions of Isomeric $Ru(LH)_2Cl_2^+$ with water.

In wet solution,[17] $Ru(LH)_2CL_2^+$ reacts on heating spontaneously and quantitatively as,

$$3\text{trans-/cis-}Ru(LH)_2CL_2^+ + H_2O \longrightarrow \text{trans-/cis-}Ru(LO)(LH)Cl_2 + 3H^+ + 2\ \text{trans - /cis-}Ru(LH)_2Cl_2$$

A Reaction Model

The addition of water to the imine function leading to an α - hydroxy amine moiety [C=N ⟶ C(OH)-NH] is a documented pathway for the Schiffbase hydrolysis (to C=O and $-NH_2$). A plausible rationale for the above noted transformation is the close association between Ru(III) α-diimine complex and water which expressed by general equation

$$Ru(LH)_2Cl_2^+ + H_2O \longrightarrow A.$$

The crucial requirement is the adduct A must undergo rapid oxidation before the possible

hydrolysis-related complications could set in. Two electrons are to be transferred and a plausible route may be illustrated as follows:

$Ru(LH)_2Cl_2^+ + A \longrightarrow B + 2H^+ + Ru(LH)_2Cl_2$

$B \longrightarrow C + H^+$

$Ru(LH)_2Cl_2^+ + C \longrightarrow D + Ru(LH)_2Cl_2$

A ——— B Oxidative radical formation

B ——— C Internal redox and proton loss.

C ——— D Metal oxidation

The trivalent complex, $Ru(LH)_2Cl_2^+$ acts as an external oxidant. In the presence of aqueous H_2O_2 or Ce(IV) acts as the external oxidant and the whole of $Ru(LH)_2Cl_2$ is thus converted to $Ru(LO)(LH)Cl_2$ via $Ru(LH)_2Cl_2^+$

$Ru(LH)_2Cl_2 + Ce^{4+} \longrightarrow Ru(LH)_2Cl_2^+ + Ce^{3+}$

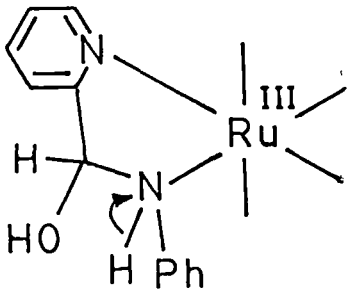
$Ru(LH)_2Cl_2^+ + H_2O + 2Ce^{4+} \longrightarrow Ru(LO)(LH)Cl_2 + 2Ce^{3+} + 3H^+$

$2Ru(LH)_2Cl_2 + H_2O_2 \longrightarrow 2Ru(LH)_2Cl_2^+ + 2OH^-$

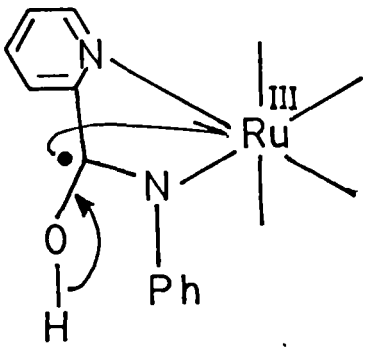
$Ru(LH)_2Cl_2^+ + H_2O + H_2O_2 \longrightarrow Ru(LO)(LH)Cl_2 + 3H^+ + 2OH^-$

ie $Ru(LH)_2Cl_2^+ + H_2O_2 \longrightarrow Ru(LO)(LH)Cl_2 + H_2O + H^+$

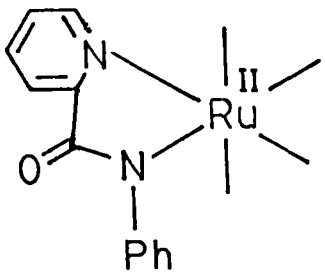
Based on the following discussions it may be concluded that the following general points appear to be crucial for the transformation, coordinated aldimine ——→ amide



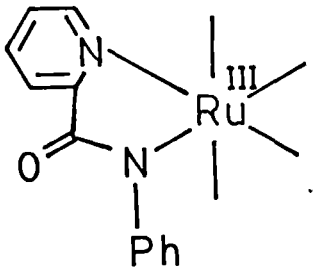
A



B



C



D

(a) The coordinated metal atom should have two easily accessible oxidation states (Ru^{2+}, Ru^{3+}).

(b) The higher oxidation state should have sufficient polarising effect on the aldimine function to make carbon site electrophilic enough to promote water binding.

(c) The water adduct should have the ability to undergo rapid electron transfer at ligand and metal sites.

These provide a working base for expanding the scope of the aldimine —— amide reaction to newer system.

Photo Induced Oxidation of $[Ru(LH)_2Cl_2]$ by Molecular Oxygen. A preliminary report.

In this section we describe photo induced transformation of one of the coordinated imine functions in the trans isomer of $[Ru(LH)_2Cl_2]$ by molecular oxygen.

$$Ru^{II}(LH)_2Cl_2 \xrightarrow{O_2, h\nu} Ru^{III}(LO)(LH)Cl_2$$

The green solution of trans - $Ru(L^1H)_2Cl_2$ in $CHCl_3$ (0.025g in 25 ml $CHCl_3$) was irradiated with a 100 W medium-pressure mercury lamp for a h in air. The solution became red brown. It was evaporated and crystallised from $CHCl_3$-C_6H_{12} (1:1) mixture (yield 85%). The product, analysed[19] as $Ru(L^1O)(L^1H)Cl_2$ (LO = N-phenyl picolinamide). Its spectral and electrochemical properties correspond to an authentic sample[2] of trans-$[Ru^{III}(L^1O)(L^1H)Cl_2]$ prepared by reacting trans-$[Ru^{II}(L^1H)Cl_2]$ with H_2O_2. The starting material,

trans-$Ru(L^{I}H)_2Cl_2$ is stable in daerated conditions and in dark. However, the transformation, trans-$Ru^{II}(LH)_2Cl_2$ ——→ trans-$Ru^{III}(LO)(LH)Cl_2$ was also observable in sunlight but the rate is very slow (ca. 100 h).

The above reaction proceeds smoothly in the presence of air. Therefore, it is reasonable that coordination of molecular oxygen at the metal occurs as the initial step. Recently, it was shown that dioxygen coordination to ruthenium(II) occurs[20,21] at the initial stage in the oxidation of coordinated phenoxazinylate radical. It may be noted here that the reaction, under consideration, is highly specific and occurs only in the trans-$Ru(LH)_2Cl_2$. Neither of the other two geometrical isomers of $Ru(LH)_2Cl_2$ nor the tris chelated complex[22], $[Ru(LH)_3](ClO_4)_2 \cdot H_2O$ reacts under identical conditions. This is probably due to steric demand for the oxygen attack at the central metal ion. The trans planar arrangement of $Ru(LH)_2$ moiety of $Ru(LH)_2Cl_2$ would facilitate the attack of O_2. The bivalent ruthenium dioxygen complex, thus formed, undergoes inner sphere electron transfer to produce transient $Ru^{III}—O_2^{\cdot-}$ which is followed by oxidation of coordinated imine in the presence of light. The role of UV light is to activate the imine function. The succeeding steps in oxygen atom rearrangement is not yet clear to us.

Interestingly, the mixed ligand Ru(III)-amide, **2** is quite stable and does not undergo any further change

even after irradiation for a long time (ca. 5 h). This, observation, in turn, does support our proposition of formation of dioxygen complex at the initial stage. The higher oxidation state of ruthenium (+3) in 2 is not suitable for interaction with O_2 and thus the reaction does not proceed any further.

In summary, it may be stated that the above reaction is one of the rare examples of metal mediated photochemical oxidation reactions with molecular oxygen. The reaction is dependant on the geometry as well as the electronic structure of the compound. Ongoing studies include detailed mechanistic probing of the processes involved and to design other systems to generalize the above reaction.

EXPERIMENTAL SECTION

A. Physical Measurements

Molar conductivity, Infrared and Electronic Spectral Measurements have done as described in Chapter II. Electrochemical measurements were done as described in Chapter II.

B. Formulation of compounds

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

C. EPR Spectra

These were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77K (liquid nitrogen) and the spectra were calibrated with DPPH (g = 2.0037).

D. Materials

The three isomers of Dichlorobis-(N-phenylpyridine-2-carboxaldimine) ruthenium(II) were prepared using the methods described in Chapter II. Tetrabutyl ammonium perchlorate (TBAP) was prepared using the same method described in Chapter II for tetraethyl ammonium perchlorate (TEAP). Purification of acetonitrile and chloroform were done as described in Chapter II. Dinitrogen gas was purified by successively bubbling it through an alkaline aqueous solution of sodium dithionate and concentrated sulphuric acid. Sodium perchlorate($NaClO_4$) was prepared using the same method described in Chapter III. The three isomers of Dichlorobis-(N-phenylpyridine-2-Carboxaldimine) ruthenium(III) were prepared using the method described in Chapter III.

E. Complexes

The three isomeric trivalent ruthenium amidocomplexes, $[Ru(LO)(LH)Cl_2]$, were synthesised using a general procedure. Yields varied in the range 70-75%. Detailed procedure for the prparation of one of the isomers is given below.

trans-[Ru(L^1O)(L^1H)Cl_2] from trans-[Ru(L^1H)Cl_2].

To a suspension of trans-[Ru($L^1H)_2Cl_2$] (100 mg) in chloroform (30 ml) was added 30% aquous H_2O_2 (30 ml) and then the mixture was stirred at room temperature for 2 hrs. The reddish brown chloroform extract was then separated using a separating funnel. The reddish brown residued obtained after solvent removal was purified by column chromatography on silica gel (60-120 mesh) using CH_3CN-$CHCl_3$ (1:10). Finally the compund was recrystallised from $CHCl_3$-C_6H_{14}.

Yield : 75%

F. Reaction of trans-/cis-[Ru(LH)$_2$Cl$_2$]ClO$_4$ with water.

It is performed simply by boiling the solution of [Ru(LH)$_2$Cl$_2$]$^+$ in water and a specific case is described below.

A solution of [Ru($L^1H)_2Cl_2$]$^+$ (50 mg) in water (25 ml) was boiled on water-bath for 1 hr. A dark brown chloroform extract was then obtained from it. The residue obtained after solvent removal was subjected to column chromatography on a silica gel column (60-120 mesh). The first moving green band eluted with CH_3CN-$CHCl_3$ (1:10) was characterised to be the bivalent starting material, trans [Ru($L^1H)_2Cl_2$]. The second reddish brown fraction eluted with CH_3CN-$CHCl_3$ (2:10) correspond to authentic sample of trans-[Ru(L^1O)(L^1H)Cl_2].

G. Crystallography of trans-[Ru(L^1O)(L^1H)Cl_2]

Single crystals of the composition trans-[Ru(L^1O)(L^1H)Cl_2].C_6H_5-CH_3 were grown from the slow diffusion of toluene into a chloroform solution of trans-[Ru(L^1O)(L^1H)Cl_2]. The unit cell dimensions are listed in Table IV.8. The structure was solved by the Patterson heavy-atom method.[23,24] Final cycles of least square refinement converged with discrepancy indices of R=0.0317 and R_w=0.0340. Final positional parameters for selected atoms for the structure are contained in Table IV.9.

H. Photoinduced Oxidation of trans-[Ru(L^1H)$_2$$Cl_2$]

A well thermostated (T=300) solution of trans-[Ru(L^1H)$_2$$Cl_2$] was exposed to a Hg-vapour lamp (100W) for 1 h. The solution was then evaporated to dryness and crystallised from chloroform-toluene.

TABLE IV.1

Analytical Data of $[Ru(LO)(LH)Cl_2]$

Compound	Formula	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
ttt-$[Ru(L^1O)(L^1H)Cl_2]$	$C_{24}H_{19}N_4OCl_2Ru$	52.27	51.86	3.44	4.09	10.16	9.86
cct-$[Ru(L^1O)(L^1H)Cl_2]$	$C_{24}H_{19}N_4OCl_2Ru$	52.27	51.91	3.44	3.91	10.16	9.91
ctc-$[Ru(L^1O)(L^1H)Cl_2]$	$C_{24}H_{19}N_4OCl_2Ru$	52.27	51.67	3.44	3.78	10.16	9.93
ttt-$[Ru(L^2O)(L^2H)Cl_2]$	$C_{26}H_{23}N_4OCl_2Ru$	53.88	52.65	3.97	4.06	9.67	9.13
cct-$[Ru(L^2O)(L^2H)Cl_2]$	$C_{26}H_{23}N_4OCl_2Ru$	53.88	52.93	3.97	4.17	9.67	8.98
ctc-$[Ru(L^2O)(L^2H)Cl_2]$	$C_{26}H_{23}N_4OCl_2Ru$	53.88	53.19	3.97	4.21	9.67	9.17

TABLE IV.2

Infrared Spectral Data of the complexes $[Ru(LO)(LH)Cl_2]$

Compounds	ν_{max} (cm^{-1}),a,b			
	C=N (imine)	C=N(pyridine)	C=O	Ru-Cl
ttt-$[Ru(L^1O)(L^1H)Cl_2]$	1605	1595	1630	320
cct-$[Ru(L^1O)(L^1H)Cl_2]$	1600	1590	1625	325,310
ctc-$[Ru(L^1O)(L^1H)Cl_2]$	1605	1595	1630	320,300
ttt-$[Ru(L^2O)(L^2H)Cl_2]$	1605	1595	1630	315
cct-$[Ru(L^2O)(L^2H)Cl_2]$	1605	1595	1630	320,305
ctc-$[Ru(L^2O)(L^2H)Cl_2]$	1605	1590	1625	315,295

[a] Spectra were recorded in KBr disc (4000 - 250 cm^{-1})

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

TABLE IV.3

Selected Bond Lengths (Å) for [(1-[Ru(L^1O)(L^1II)Cl_2]

Ru Cl(1)	P.334(1)	Ru-N(1)	P.089(3)
Ru-N(2)	P.068(4)	Ru Cl(1A)	2.334(1)
Ru-N(1A)	P.089(3)	Ru-N(2A)	2.068(4)
N(1)-C(1)	1.330(6)	N(1)-C(5)	1.328(7)
N(2)-C(6)	1.296(4)	N(2)-C(7)	1.403(6)
O(1)-C(6)	1.295(11)	C(1)-C(2)	1.384(7)
C(1)-C(6)	1.471(9)	C(2)-C(3)	1.378(14)
C(3)-C(4)	1.346(9)	C(4)-C(5)	1.381(6)
C(7) C(8)	1.382(5)	C(7)-C(12)	1.363(5)
C(8)-C(9)	1.389(8)	C(9)-C(10)	1.355(6)
C(10)-C(11)	1.365(7)	C(11)-C(12)	1.381(8)

TABLE IV.4

Selected Bond Angles (°) for ttt-[Ru(L^1O)(L^1H)Cl_2]

Cl(1)-Ru N(1)	90.1(1)	Cl(1)-Ru-N(2)	89.5(1)
N(1)-Ru-N(2)	77.8(1)	Cl(1)-Ru-Cl(1A)	180.0(1)
N(1)-Ru-Cl(1A)	89.9(1)	N(2)-Ru-Cl(1A)	90.5(1)
Cl(1)-Ru-N(1A)	89.9(1)	N(1)-Ru-N(1A)	180.0(1)
N(2)-Ru-N(1A)	102.2(1)	Cl(1A)-Ru-N(1A)	90.1(1)
Cl(1)-Ru-N(2A)	90.5(1)	N(1)-Ru-N(2A)	102.2(1)
N(2)-Ru-N(2A)	180.0(1)	Cl(1A)-Ru-N(2A)	89.5(1)
N(1A)-Ru-N(2A)	77.8(1)	Ru-N(1)-C(1)	114.2(3)
Ru-N(1)-C(5)	128.7(2)	C(1)-N(1)-C(5)	117.1(3)
Ru-N(2)-C(6)	116.2(4)	Ru-N(2)-C(7)	128.3(2)
C(6)-N(2)-C(7)	115.4(4)	N(1)-C(1)-C(2)	123.1(6)
N(1)-C(1)-C(6)	115.8(3)	C(2)-C(1)-C(6)	121.1(5)
C(1)-C(2)-C(3)	118.6(6)	C(2)-C(3)-C(4)	118.6(5)
C(3)-C(4)-C(5)	119.9(7)	N(1)-C(5)-C(4)	122.7(5)
N(2)-C(6)-O(1)	125.1(8)	N(2)-C(6)-C(1)	115.7(4)
O(1)-C(6)-C(1)	119.2(6)	N(2)-C(7)-C(8)	120.0(3)
N(2)-C(7)-C(12)	120.0(3)	C(8)-C(7)-C(12)	119.7(4)
C(7)-C(8)-C(9)	119.3(3)	C(8)-C(9)-C(10)	120.8(4)
C(9)-C(10)-C(11)	119.4(5)	C(10)-C(11)-C(12)	120.8(4)
C(7)-C(12)-C(11)	119.9(4)		

TABLE IV.5

Solution Electronic Spectral Data of $[Ru(LO)(LH)Cl_2]$

Compounds	λ_{max} nm (ϵ $dm^3 mol^{-1} cm^{-1}$), a,b
trans-$[Ru(L^1O)(L^1H)Cl_2]$	510(2525); 350[b](3750); 280(7350)
cis-$[Ru(L^1O)(L^1H)Cl_2]$	510(3150); 350[b](4700); 290(8130)
cis-$[Ru(L^1O)(L^1H)Cl_2]$	500(2975); 345[b](4320); 290(7090)
trans-$[Ru(L^2O)(L^2H)Cl_2]$	520(2925); 365[b](3850); 300(7550)
cis-$[Ru(L^2O)(L^2H)Cl_2]$	510(3370); 350[b](4350); 290(8160)
cis-$[Ru(L^2O)(L^2H)Cl_2]$	510(3150); 340[b](4160); 300(7920)

[a] In CH_3CN at 298K

[b] Shoulder.

TABLE IV.6

Magnetic moments, EPR g values and derived energy parameters

Compounds	μ_{eff}^{a} (BM)	g values[b]			Derived Energy parameters (cm^{-1})	
		g_1	g_2	g_3	ΔE_1	ΔE_2
ttt-[Ru(L^1O)(L^1H)Cl_2]	1.86	2.6036	2.2174	1.8079	3270 (3058 nm)	6854 (1460 nm)
cct-[Ru(L^1O)(L^1H)Cl_2]	1.82	2.6027	2.2033	1.8106	3250 (3076 nm)	7074 (1413 nm)
ctc-[Ru(L^1O)(L^1H)Cl_2]	1.89	2.6138	2.2365	1.7990	3250 (3076 nm)	6536 (1529 nm)

[a] In solid state at 298 K.

[b] In acetonitrile-toluene (1:1) glass at 77K.

TABLE IV.7

Cyclic voltammetric data[a] at a platinum working electrode for the complexes $[Ru(LO)(LH)Cl_2]$

Compounds	E^{o}_{298} V(ΔE_p mV)	
	Ru^{IV}/Ru^{III}	Ru^{III}/Ru^{II}
ttt-$[Ru(L^1O)(L^1H)Cl_2]$	1.29	-0.14
cct-$[Ru(L^1O)(L^1H)Cl_2]$	1.14	-0.23
ctc-$[Ru(L^1O)(L^1H)Cl_2]$	1.31	-0.141
ttt-$[Ru(L^2O)(L^2H)Cl_2]$	1.28	-0.18
cct-$[Ru(L^2O)(L^2H)Cl_2]$	1.13	-0.22
ctc-$[Ru(L^2O)(L^2H)Cl_2]$	1.30	-0.13

[a] Definitions of the symbols used are as in the text, all E values are quoted vs. SCE. v = 50 mVs^{-1} in CH_3CN (0.1 $M[NEt_4][ClO_4]$)

TABLE IV.8

Crystallographic data for $trans$-$[Ru(L^1O)(L^1H)Cl_2]$

Chem formula	$C_{31}H_{18}N_4OCl_2Ru$
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	9.454(4)
b, Å	9.582(4)
c, Å	9.902(4)
α, deg	69.40(3)
β, deg	75.63(3)
γ, deg	62.96(3)
V, $Å^3$	743.6(5)
Z	1
D_{calc}, gm cm^{-3}	1.62
μ, cm^{-1}	7.36
Crystal dimension, mm^3	0.18 × 0.20 × 0.48
T, °C	295
R, R_w	0.0317 and 0.0340

TABLE IV.9

Selected atomic parameters for (tt-[Ru(L^1O)(L^1H)Cl$_2$]

	X	Y	Z	U(eq)
Ru	0	0	0	31(1)
Cl(1)	-2349(1)	2366(1)	-124(1)	51(1)
N(1)	-1053(3)	-1245(3)	1831(3)	40(1)
N(2)	564(3)	419(3)	1669(3)	39(1)
O(1)	79(12)	124(12)	4126(6)	123(7)
C(1)	-937(5)	-1085(6)	3076(4)	62(2)
C(2)	-1583(9)	-1789(9)	4407(5)	109(5)
C(3)	-2046(8)	-2732(8)	4455(5)	106(4)
C(4)	-2451(6)	-2916(6)	3201(5)	76(3)
C(5)	-1798(5)	-2162(5)	1907(4)	54(2)
C(6)	-38(6)	-129(6)	2965(4)	66(2)
C(7)	1489(4)	1296(4)	1576(3)	38(1)
C(8)	737(4)	2928(5)	1532(4)	53(2)
C(9)	1653(5)	3782(5)	1372(5)	64(2)
C(10)	3269(5)	3031(5)	1265(5)	63(2)
C(11)	3998(5)	1406(6)	1360(6)	70(2)
C(12)	3113(5)	533(5)	1513(5)	58(2)
C(13)	6046(8)	3969(9)	5700(10)	99(4)
C(14)	5986(16)	3837(19)	3334(18)	173(10)
C(15)[b]	6749(19)	3216(10)	4703(20)	108(9)
C(16)[b]	4674(32)	5261(32)	3248(19)	143(18)
C(17)[b]	5148(14)	4708(16)	4271(16)	87(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Site Occupation Factor 0.5.

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Chapter V

CHAPTER V

SYNTHESIS, CHARACTERISATION AND HIGH RESOLUTION PROTON RESONANCE SPECTRA OF $[AgL_2]ClO_4$ (L = N-ARYLPYRIDINE-2-CARBOXALDIMINE) AND THEIR REACTIVITIES*

Abstract: *The N-arylpyridine-2-carboxaldimine (L,I) 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 methods. The complexes are 1:1 electrolytes in methanol. The solutions of the complexes are stable in methanol and chloroform, but dissociate in acetonitrile. The high resolution ^{1}HNMR spectra of silver complexes with different substituted ligands (L^1 - L^3) are reported and completely assigned. It is concluded that both the chelate rings in AgL_2^+ are magnetically equivalent and contain an effective C_2-axis. The chemical reactions of the silver complexes toward chloride salts of iron (II), cobalt(II) and nickel(II) have been examined. In all cases metal exchange reactions take place to yield ML_3^{2+} [M = iron (II), cobalt(II), nickel(II)]. The redox properties of the ML_3^{2+} compounds are briefly examined.*

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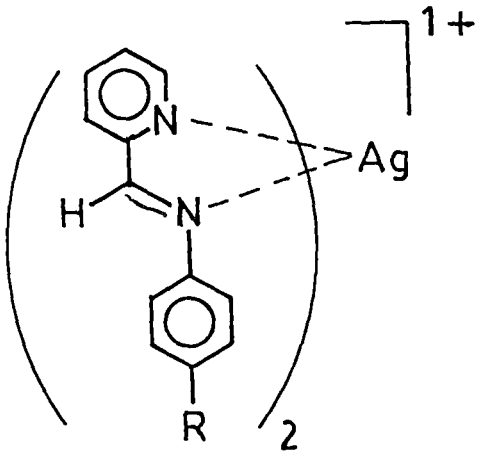
*This work has appeared in *Polyhedron*, 1994, 13, 1063.

INTRODUCTION

We have recently initiated an investigation into the synthesis of silver (I) complexes of neutral N, N-donors in order to use them to synthesise other transition metal complexes from easily accessible metal chlorides. In our initial publications[1,2] we have described the successful use of AgB_2^+ [B = 2,2´- bipyridine or 1,10 - phenanthroline or 2-arylazopyridine][3-5] in the synthesis of some important ruthenium and rhodium complexes. This has encouraged us to initiate research on silver(I) complex of a neutral Schiff base ligand system, N-arylpyridine-2-carboxyldimine (L,1).



2

In the main part of this chapter, we describe the isolation and characterisation of monomeric tetra co-ordinated[6] silver(I) complexes of L. Assessment of structure and the solution stabilities of the complexes have

been made on the basis of spectral data. We also describe here the use of these complexes for the synthesis of some of the known compounds of iron (II), nickel(II) and cobalt(II).

Results and Discussion

A. Synthesis

The three ligands[7] used for the present work were generated *in situ*[8,9] by reacting pyridine-2-carboxaldehyde and the appropriate primary aromatic amine in 1:1 molar proportions in ethanol.

$AgNO_3$ reacts smoothly with an ethanolic solution of L(1) at a boiling temperature in the molar ratio 1:2 to yield cationic complexes $[AgL_2]^+$(2), which have been isolated as crystalline perchlorate salts in high yields from the reaction mixture. Even when metal-to-ligands ratio exceeds 1:2, only bis - ligated 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 compound. The yields of the complexes are quite high (75%). It may be noted here that the corresponding bis complex[4] 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 insoluble in nonpolar benzene hexane etc.

B. Characterisation

The silver(I) complexes of L(1) are obtained as highly crystalline light yellow needles and can be stored for a long time. They are formulated by elemental analyses (C,H,N) and by estimation of silver (Table V.1). The results of estimation Ag^{+}, as well as C,H,N analyses conclusively suggest that the number of ligands (L) per silver ion is two. Further confirmation regarding the presence of Ag(I) ion has been made by magnetic susceptibility measurement. The compounds are diamagnetic (d^{10}) in nature. The molar conductance of $[AgL_2]ClO_4$(2) in methanol (Table V.2) lies between 105 and 110 $ohm^{-1}cm^{2}mol^{-1}$, suggesting[10] a 1:1 type of electrolytic nature of the compounds. These results collectively conform to the formulation of compund as $[AgL_2]ClO_4$.

C. Bonding and Assessment of Structure

(i) Infrared Spectra.

Infrared spectral data of $[AgL_2]ClO_4$ were collected as KBr discs in the range 4000-600 cm^{-1}. Characteristic group frequencies are presented in Table V.3. Some of these bands are found to be useful[11] in identification of the geometry

and bonding of the complexes and are considered here. The broad structure less band[12], $\nu_{ClO_4^-}$ at a ca. 1100 cm^{-1} suggests the lack of significant perchlorate coordination in the solid state. One of most significant observation in the IR spectra of **2** is the consistent appearance of two strong bands at a ca. 1625 and ca. 1600 cm^{-1} which have been assigned[11] to $\nu_{C=N}$(imine) and $\nu_{C=N}$ (pyridine) respectively. Free ligand, L^2, displays[11] absorption due to $\nu_{C=N}$(pyridine) and $\nu_{C=N}$(imine) each at a ca. 1600 and ca. 1630 cm^{-1}, respectively. The shifts of $\nu_{C=N}$ to lower frequencies suggests that the ligand, L is coordinated to silver(I).

(ii) Electronic Spectra

Solution electronic spectra of the silver complexes were studied in three different solvents, viz.-methanol, chloroform and acetonitrile in the uv-visible region to assess their solution stabilities. The data are presented in Table V.4. The electronic spectra of **2** are dominated by two intense absorptions in uv region occuring at ca. 300 and at ca. 220 nm. These intense transitions may be assigned[13] to intraligand $\pi - \pi^*$ transitions. An ill defined shoulder at ca. 380nm in the complex,**2**,was also observable.

The stability of silver complexes in chloroform methanol and acetonitrile have been verified by Beer's law. The intensity of the band at ca. 300 nm does not change with dilution and a plot of absorbance, A, versus concentration,

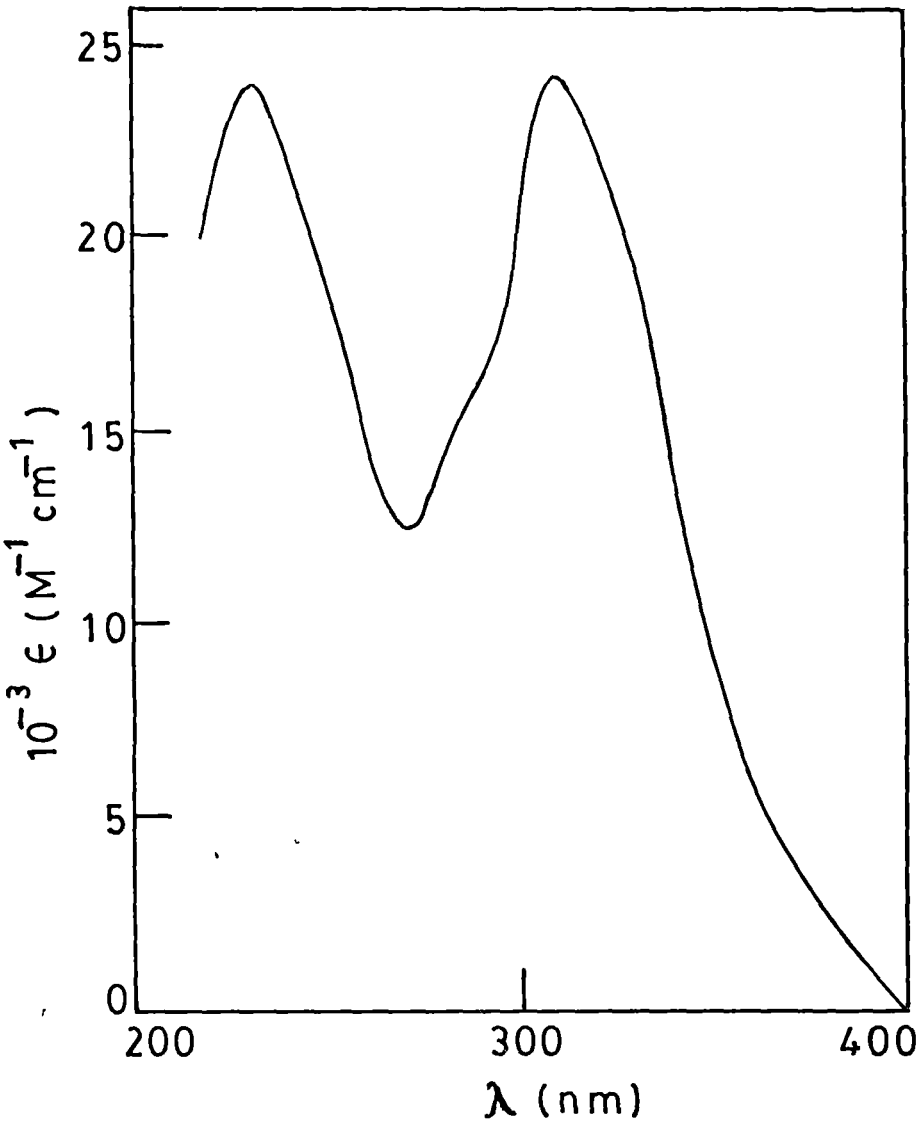


FIGURE V.1 ELECTRONIC SPECTRUM OF $[AgL^2{}_2]ClO_4$ IN CH_3OH

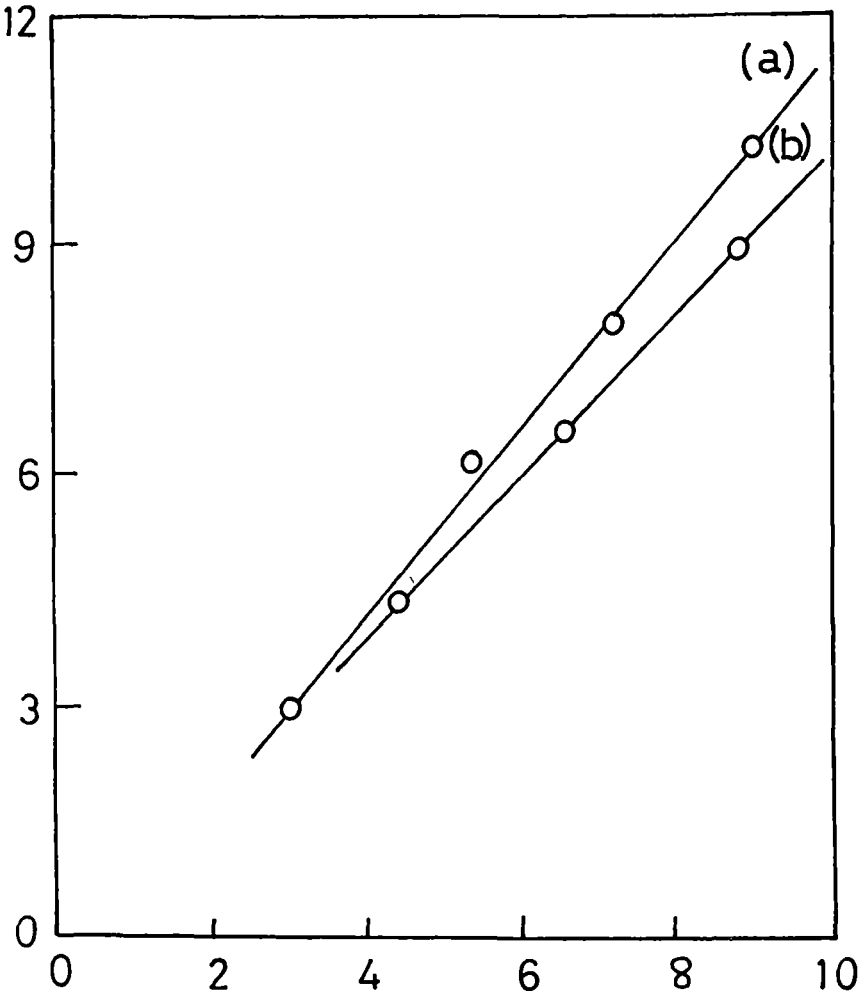


FIGURE V.2 VERIFICATION OF BEER'S LAW IN CASE OF $[Ag(L^1)_2]ClO_4$:

(a) IN CH_3OH AT 302 nm

(b) IN $CHCl_3$ AT 302 nm

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 V.2). Hence, Beer's law is verified and $[AgL_2]^+$ is stable in these solvents. Unlike chloroform and methanol, the solutions of complex, $[AgL_2]^+$ do not obey Beer's law in acetonitrile indicating their instability in acetonitrile.

(iii) ^{1}HNMR Spectra

All the $[AgL_2]^+$ complexes show well resolved ^{1}HNMR spectra in $CDCl_3$ at 400 MHz. Chemical shifts and coupling constant data of free L and the complexes are listed in Table V.5 and the spectra of free L^2 and the complex $[Ag(L^2)_2]^+$ are displayed in Figure V.3. Assignment of individual proton resonances are made on the basis of their relative intensity, spin-spin structure, substitution induced effect and also by comparison of the spectra with those of ruthenium complexes of L. 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 chemical shifts of the pyridyl protons $[AgL_2]^+$ complexes are in the order : δ_{6-H} δ_{3-H} δ_{4-H}, δ_{5-H}. The signals due to individual aryl protons are also 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 appear as coincident doublets in all the AgL_2^+ complexes. The 9-H and 11-H signals appear as coincident

triplets in the complex of L^1, whereas, in the complexes of L^2 and L^3, those appear as coincident doublets as expected. The signal due to 10-H in $[Ag(L^1)_2]^+$ complex appears as a triplet. Further the shift of the 9-H signal to higher field in going from L^1 to corresponding L^2 complex in accordance with the electron releasing character of the methyl substituent. The complex $[Ag(L^2)_2]^+$ also shows a sharp single methyl signal at 2.27ppm.

The overall examination of ^{1}HNMR data reveals the following:

(a) The pyridyl, aryl as well as imine proton resonances of the ligand L shift on coordination. The coordination induced shifts[18] in $[AgL_2]^+$ are due to coordination of L to Ag^+;

(b) In the present group of complexes each kind of proton gives rise to one signal (singlet or multiplet). It is, therefore, certain that each of the compounds exists as a single isomer and the two chelate rings in **2** are magnetically equivalent at least in the NMR time scale. A two fold axis of symmetry is thus required.

The ^{1}HNMR data, presented above, is thus consistent with the tetrahedral geometry of the complexes.

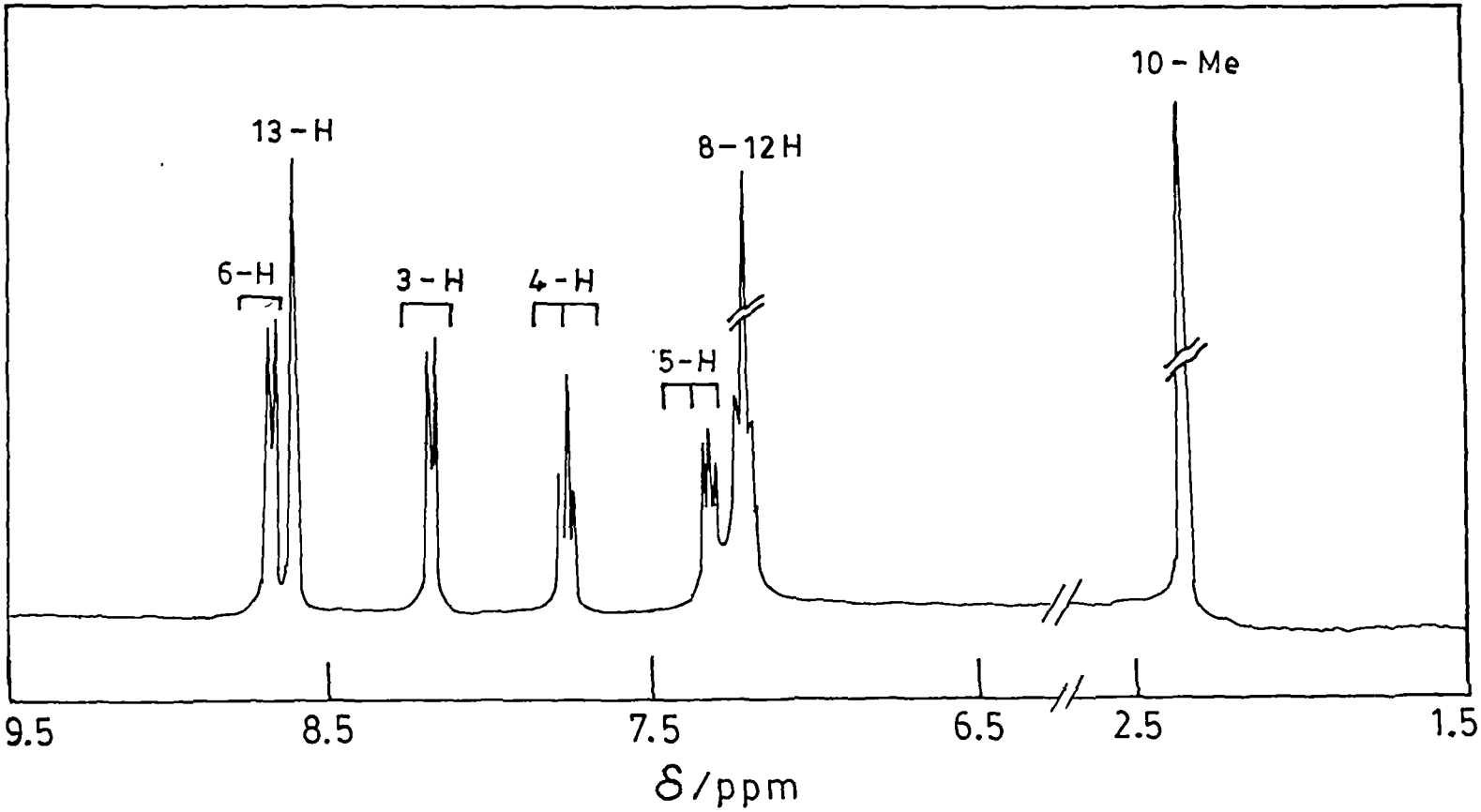


FIGURE V.3a ^{1}HNMR SPECTRUM OF FREE L_2 IN $CDCl_3$

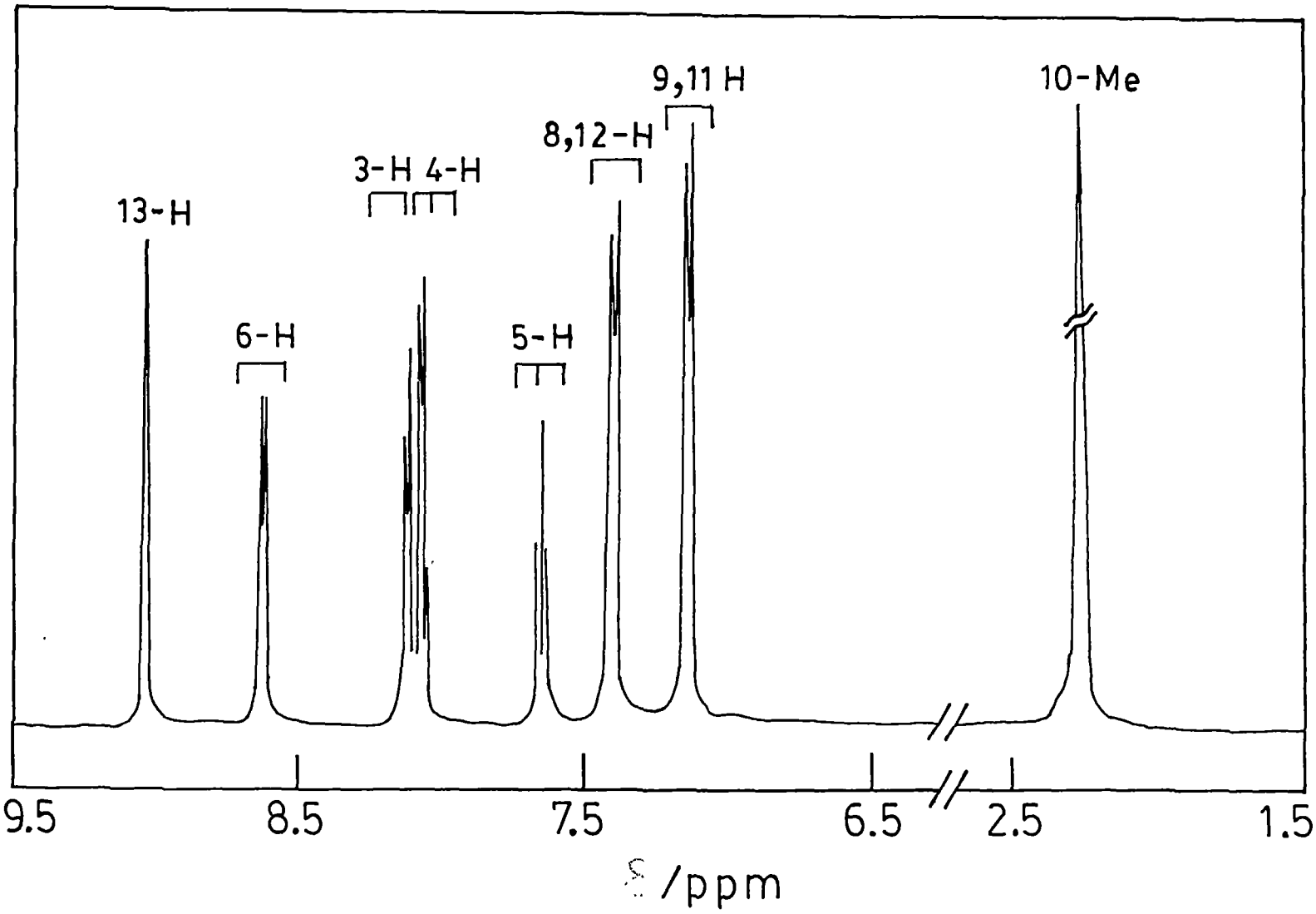


FIGURE V.3b ^{1}HNMR SPECTRUM OF $[Ag(L^{2})_{2}]ClO_{4}$ IN $CDCl_{3}$

D. Chemical Reactivities

In this section we report the reactions of the chlorides of Fe(III), Ni(II)and Cl(II) with AgL_2^+(2). It was anticipated that the interaction of metal chlorides with 2 might lead to metal-L compounds. Accordingly, in line with the synthetic strategy the following reactions were undertaken which led directly to the expected products.

$$FeCl_3 \cdot 6H_2O + 3AgL_2^+ \longrightarrow FeL_3^{2+} + 3AgCl + 3L \qquad 2$$

$$CoCl_2 \cdot 6H_2O + 2AgL_2^+ \longrightarrow CoL_3^{2+} + 2AgCl + L \qquad 3$$

$$NiCl_2 \cdot 6H_2O + 2AgL_2^+ \longrightarrow NiL_3^{2+} + 2AgCl + L \qquad 4$$

All the reactions,(2-4), mentioned above, proceed smoothly in methanol to yield directly ML_3^{2+} and AgCl. The cationic tris chelates have been isolated as their perchlorate salts from solutions. In the case of iron the reduction of iron(III)—— iron(II) occurs in the reaction medium. The high oxidation potential of Fe(III)/ Fe(II) (vide infra) of this complex is no doubt one of the controlling factors for the reduction.

E. Characterisation of the Products (Reactions 2-4)

(a) Formulation

The iron(II) complex is blue violet whereas both cobalt(II) and nickel(II) complexes are orange. Each of them are obtained in a highly crystalline state and in high yields

and are soluble in polar solvents like CH_3CN, C_2H_5OH, CH_3OH etc. They were formulated by elemental analyses (C, H, N) and estimation of iron, cobalt and nickel (Table V.6). The results of estimation of the respective metal and C,H,N analyses conclusively suggest that the number of ligands (L) per metal ion is three. Each of the compound is associated with one molecule of water of crystallisation.

(b) Molar Conductance

The molar conductance of the complexes in methanol (Table V.7) lie between 240 and 250 $ohm^{-1}cm^2mol^{-1}$ suggesting[10] a 1:2 type of electrolytic nature of the compounds. These results collectively conform to the formulation of the compound as $[ML_3](ClO_4)_2 \cdot H_2O$ (M=Fe,Co,Ni).

(c) Infrared Spectra

Infrared spectral data were collected as KBr discs in the range 4000 to 600 cm^{-1}. Selected group frequencies are presented in Table V.7. All the complexes show the characteristic absorptions[11] for $\nu_{C=N}$(imine) and $\nu_{C=N}$(pyridine) in the range 1650 - 1550 cm^{-1} The band at higher energy is due to $\nu_{C=N}$(imine) and the lower energy band is due to $\nu_{C=N}$(pyridine) in the respective compound. The broad structureless band[12], $\nu_{ClO_4^-}$ at ca. 1100 cm^{-1} suggests the lack of significant perchlorate coordination.

(d) Electronic Spectra

Solution electronic spectra of the complexes were studied in acetonitrile in the UV-vis region. The data are presented in Table V.8 and representative spectra are displayed in Figure V.5. The electronic spectra of all the complexes are dominated by absorptions in the UV region occuring at ca. 320, at ca.280 and at ca 230 nm. These may be assigned to intra ligand[13] $\pi-\pi^*$ transitions. Furthermore,in case of iron complex two other absorptions at 570 nm and a shoulder at 530 nm are observed which may be assigned to MLCT (metal-to-ligand charge transfer) [$t_2 \longrightarrow \pi^*(L)$] transitions.

Spectral data for the compounds agree well[11,19,20] with the reported data. Thus we conclude that the compounds are the same as those described earlier.

(e) Redox Properties

The redox properties of the complexes have been studied voltammetrically on the positive of S.C.E. The complexes of iron and cobalt are electroactive and show reversible oxidation responses at ca.1.20 and ca.0.70 V, respectively. Voltammetric data are summerised in Table V.9 and representative voltammograms are displayed in Figure V.6. For comparison, M^{III}/M^{II} couple for $Fe(bpy)_3^{2+}$ and $Co(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) occur at 1.03[21] and 0.03 V[22] respectively. No attempt has been made to isolate ferric or cobaltic compounds in the solid state.

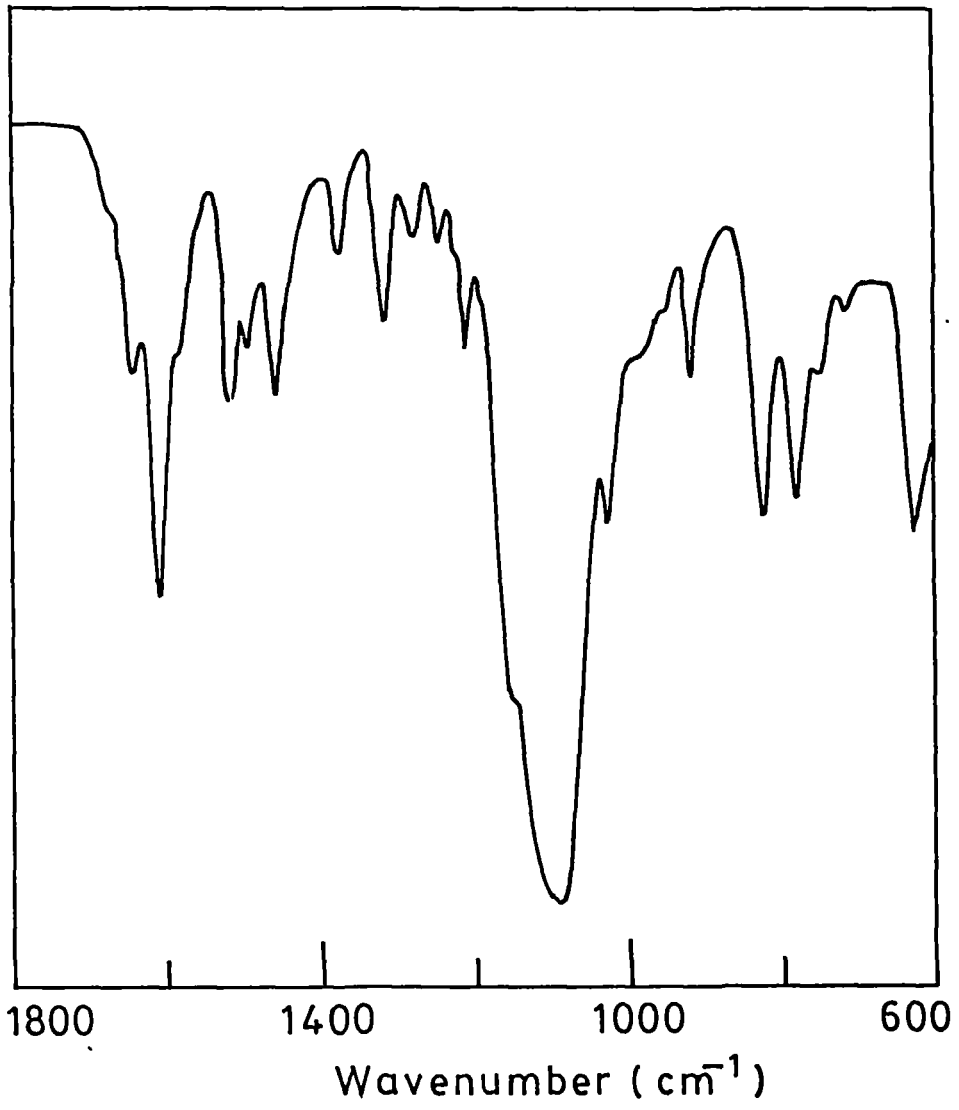


FIGURE V.4 IR SPECTRUM OF $[Co(L^2)_3](ClO_4)_2$ IN KBr

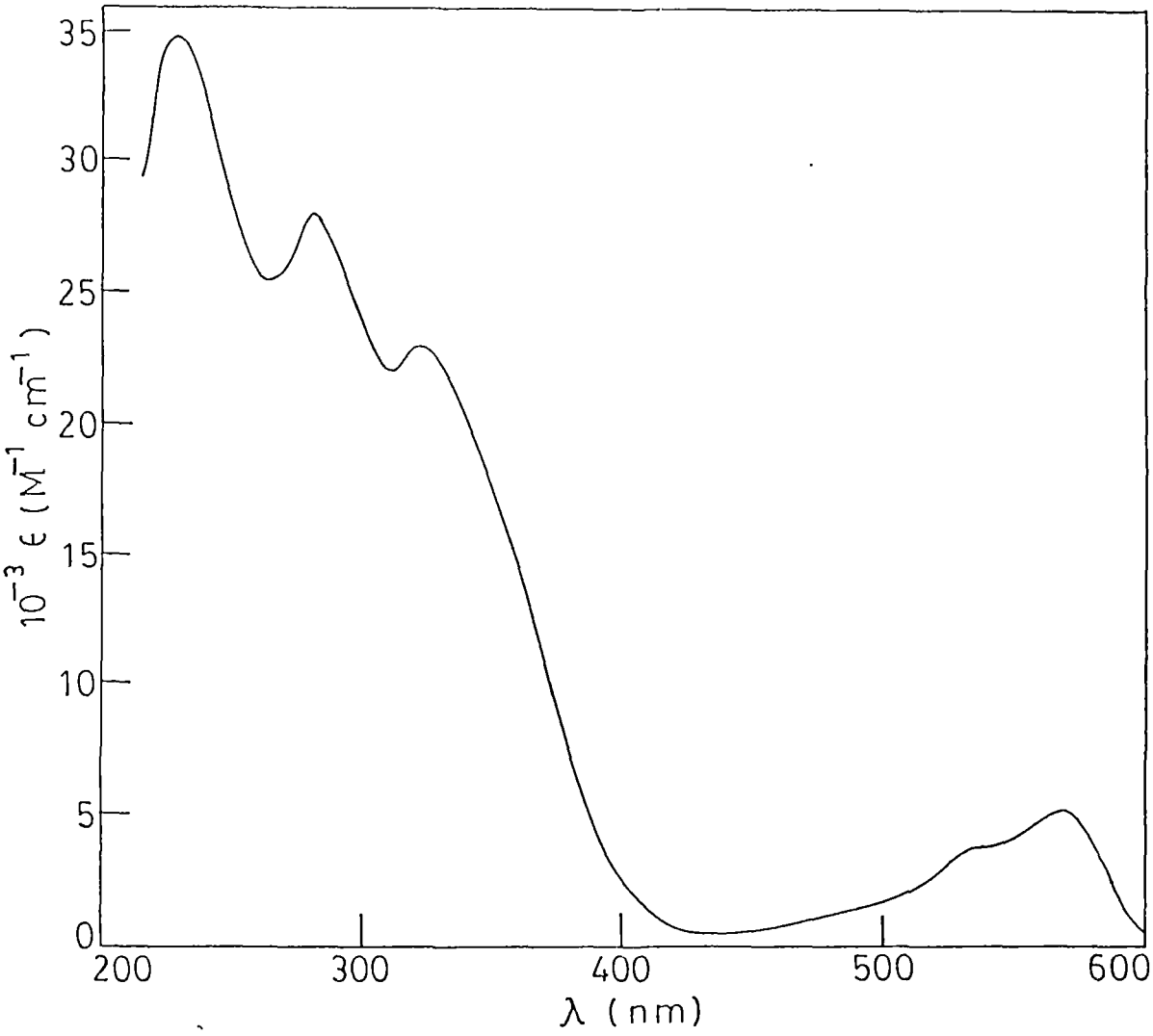


FIGURE V.5 ELECTRONIC SPECTRUM OF $[Fe(L^2)_3](ClO_4)_2$ IN CH_3OH

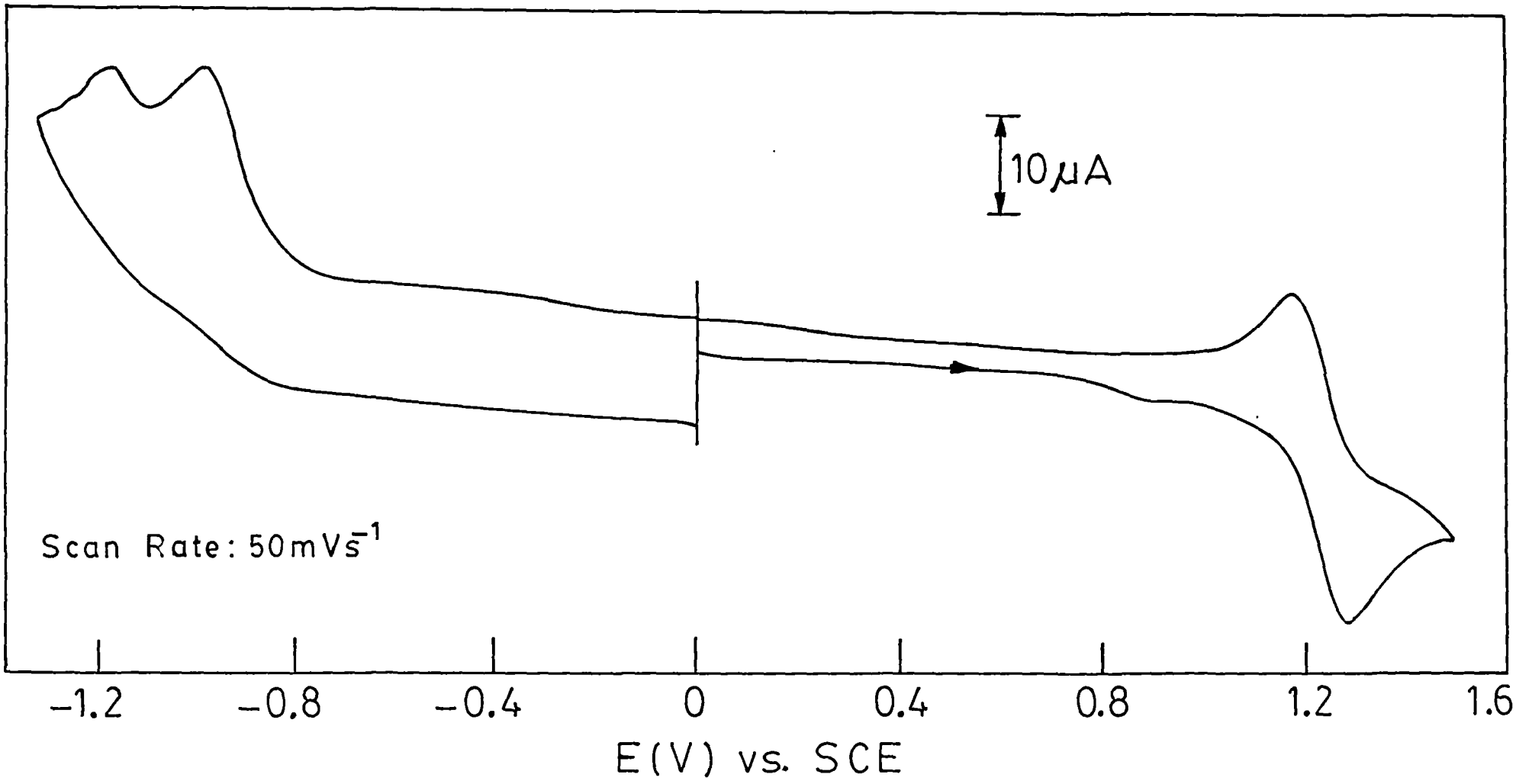


FIGURE V.6a CYCLIC VOLTAMMOGRAM OF $[Fe(L^2)_3](ClO_4)_2$ IN CH_3CN

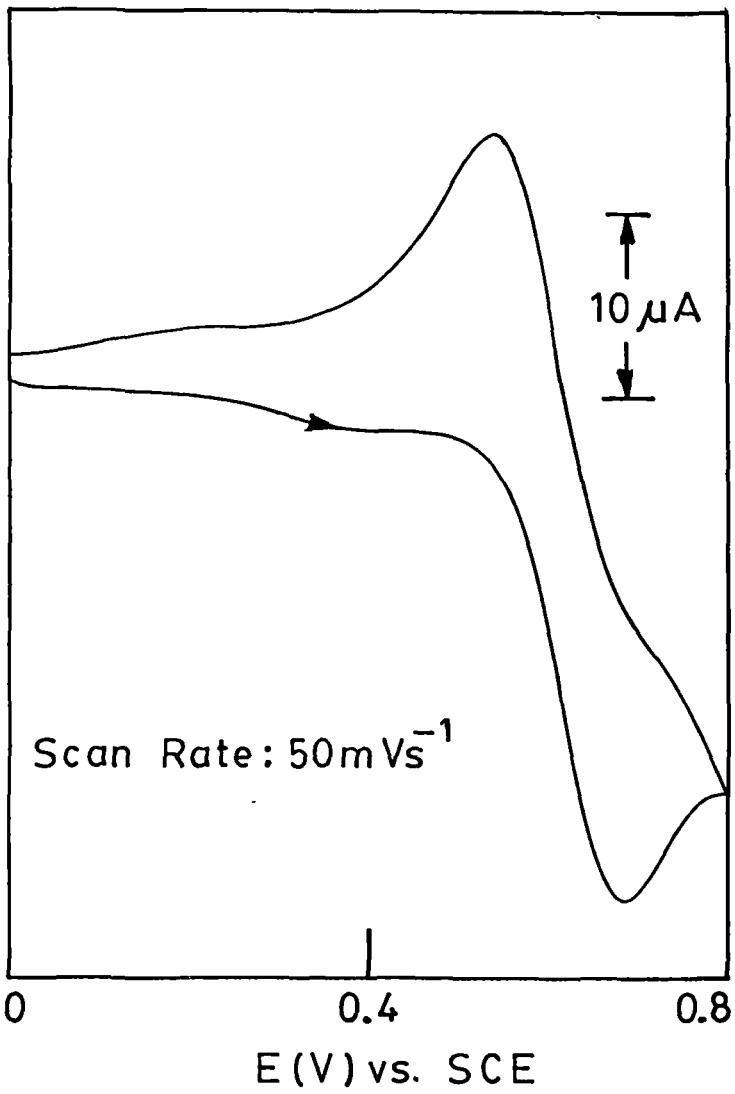


FIGURE V.6b CYCLIC VOLTAMMOGRAM OF $[Co(L^2)_3](ClO_4)_2$ IN CH_3CN

F. Conclusion

It is demonstrated that N-arylpyridine-2-carboxaldimine ligands display high affinity towards silver(I). Stable, tetracoordinated, bischelated complexes of the type $[AgL_2]^+$ are isolated and thoroughlycharacterised 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 I reacts with silver and the stability of the resultant bis complexes, even in solutions, are unprecented for an α, α' - diimine chelating ligand.

Finally it may be concluded that the generalised approach to the synthesis of M-L complexes from easily accessible metal chlorides and 2 has been established. These reactions have led us to some interesting compounds of ruthenium(II), which are described in the succeeding two chapters.

EXPERIMENTAL SECTION

A. Physical Measurements

Melting point measurements, Molar Conductivity, Infrared Spectra, Electronic Spectra, ^{1}HNMR Spectra and Magnetic Susceptibility Measurements.

All described in chapter II and III.

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 V.2.

(i) CH_3OH : 3.06×10^{-5}(3.501), 5.40×10^{-5}(6.176), 7.20×10^{-5}(8.235), 9.01×10^{-5}(10.305) $mol.dm^{-3}$ at λ_{max} 302 nm

(ii) $CHCl_3$: 4.4×10^{-5}(4.425), 6.61×10^{-5}(6.502), 8.82×10^{-5}(0.031), 11.02×10^{-5}(11.035) $mol.dm^{-3}$ at λ_{max} 302 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 analysis of silver. Silver was estimated gravimetrically by precipitating as silver chloride. The detailed procedure is given below.

$[AgL_2]ClO_4$. A known weight (0.400 m.mol) of the compound was taken in a 500 ml. conical flask and it was digested thrice with a mixture of an equal volume of 10M perchloric acid (3 X 10 ml). The colourless residue thus obtained was cooled and extracted four times with distilled water (4 X 50 ml) and filtered. To the filtrate 0.20 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 throughly 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.

Iron, cobalt and nickel were estimated by the reported procedure. While iron was estimated volummetrically using $K_2Cr_2O_7$ as a primary standard, nickel and cobalt were estimated gravimetrically as Ni-DMG and Co-α-nitroso-β-naphthol compounds respectively.

C. Solvents

Commercial ethanol was distilled and used for preparative work. Spectrograde acetonitrile, chloroform and methanol were used for spectral and molar conductance measurements. Distilled water was used for analytical work. Desides 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. Silver nitrate, from Glaxo Laboratories, Bombay. All other Chemicals and solvents used were of reagent grade and were used without futher purification.

(b) Sodium Perchlorate, $NaClO_4$

As dicussed in chapter II.

(c) Ligands[8,9]

The ligand(L) was generally obtained in situ by condensation of 2-pyridine carboxaldimine with appropriate primary amine in ethanol. The preparative method of N-p-tolylpyridine-2- carboxaldimine(L^2) is described in Chapter II.

(d) Complexes

(i) Bis-[N-phenylpyridine-2-carboxaldimine] silver(I) perch-lorate, $[Ag(L^1)_2]ClO_4$

A solution consisting of freshly distilled aniline (1.10g, 0.012 mol) and 2-pyridinecarboxaldehyde (1.26g, 0.012 mol) in ethanol (20 ml) was heated to reflux for 15 minutes. To this yellow solution, a solution of $AgNO_3$(1.00g, 0.006mol) in ethanol (20 ml) was added and again heated to reflux for 2 hrs. The solution was then cooled and filtered to remove insoluble particle. To the cool filtrate an aquous solution of $NaClO_4$ (ca.20g in 10 ml of water) was added and left to crystallise in the dark overnight. A highly crystalline greenish yellow compound was obtained. It was filtered and washed with hexane. The compound was dried in vacuo. Yield : 80%.

(ii) Bis - [N-p-tolylpyridine-2-carboxyldimine] silver(I) perchlorate, $[Ag(L^2)_2]ClO_4$ and bis-[N-p-chlorophenyl pyridine-2-carboxyldimine] silver(I) perchlorate $[Ag(L^3)_2]ClO_4$.

These were prepared similarly using the appropriate primary aromatic amines. Yield: 75 %

(iii) Reactions of $[Ag(L)_2]^+$ with $FeCl_3 \cdot 6H_2O$

The reactions of $FeCl_3 \cdot 6H_2O$ with 3 mols of $[Ag(L)_2]^+$ were performed following a general procedure. Specific details are given for the preparation of $[Fe(L^2)_3](ClO_4)_2 \cdot H_2O$

$FeCl_3 \cdot 6H_2O$ (1.00 g, 0.004 mol) was dissolved in eathnol (25 ml) and to it $[Ag(L^2)_2]ClO_4$ (6.65 g, 0.011 mol) was added and heated to reflux for 2 hours. The mixture was then cooled to room temparature and filtered through a G-4 sintered glass funnel to remove insoluble AgCl. The filtarte was then concentrated to half its initial volume when a violet mass deposited. It was filtered and washed with water and finally with hexane. The produce was then subjected to column chromatography on a silica gel (60-120 mesh) column using different mixtures of CH_3CN-$CHCl_3$ as eluent. The first moving blush yellow band was eluted with 1:20 CH_3CN-$CHCl_3$ mixture and it was discarded. The second moving blue-violet band was eluted with 1:5 CH_3CN-$CHCl_3$ mixture and it was collected. Upon condensation of the blue violet solution, a

violet crystalline compound, $[Fe(L^2)_3](ClO_4)_2 \cdot H_2O$ was obtained. The compound filtered and dried in vacuo. Yield : 70%.

(iv) Reactions with $MCl_2 \cdot 6H_2O$ (M = Co, Ni)

Reactions of $MCl_2 \cdot 6H_2O$ with $[AgL_2]ClO_4$ were carried out following a general procedure given below.

$MCl_2 \cdot 6H_2O$ (M = Co, Ni) (0.004 mol) was dissolved in ethanol(15 ml) and stirred magnetically at room temparature. To this solution, a solution of $[AgL_2]ClO_4$ (0.009 mol) in ethanol (15 ml) was added slowly and the reaction was allowed to continue for 1 hour. The mixture was then filtered through a G-4 sintered glass funnel to remove insoluble AgCl. To this filtrate an aqueous solution of $NaClO_4$ (ca.1g in 10ml of water) was added when an orange crystalline compound, $[ML_3](ClO_4)_2 \cdot H_2O$ was obtained.(the colour of the nickel compound was slightly brighter than its cobalt analogue). The compound was filtered and washed with hexane. It was dried in vacuo. Yield: 85%.

TABLE V.1

Analytical Data of $[AgL_2]ClO_4$

Compound	Formula	%C		%H		%N		%Ag	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Ag(L^1)_2]ClO_4$	$C_{24}H_{20}ClN_4O_4Ag$	50.4	50.1	3.5	3.2	9.8	9.6	18.0	17.8
$[Ag(L^2)_2]ClO_4$	$C_{26}H_{24}ClN_4O_4Ag$	52.0	52.1	4.0	4.1	9.3	9.0	18.0	17.9
$[Ag(L^3)_2]ClO_4$	$C_{24}H_{18}Cl_3N_4O_4Ag$	45.0	44.8	2.8	2.7	8.7	8.7	16.8	16.7

TABLE V.2

Solution Molar Conductivity Data[a] of Complexes $[AgL_2]ClO_4$

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

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

TABLE V.3

Infrared Spectral Data of the Complexes $[AgL_2]ClO_4$

Compound	ν_{max} (cm^{-1})[a,b]				
	C=N(imine)	C=N(pyridine)	ClO_4^{-1}	C-H[d]	C-H[e]
$[Ag(L^1)_2]ClO_4$	1630	1590	1100[c],620	780	675
$[Ag(L^2)_2]ClO_4$	1625	1585	1100[c],620	780	675
$[Ag(L^3)_2]ClO_4$	1620	1585	1100[c],620	780	675

[a]Spectra were recorded in KBr disc (4000 - 600 cm^{-1})

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

[c]Broad

[d]Out-of-plane bedning in pyridine ring

[e]Out-of-plane bending in phenyl ring.

TABLE V.4

Solution Electronic Spectral Data[a] of $[AgL_2]ClO_4$

Compound	λ_{max} nm(ϵ dm^3 mol^{-1} cm^{-1})
$[Ag(L^1)_2]ClO_4$	380[b], 302(24450), 225(23695)
$[Ag(L^2)_2]ClO_4$	380[b], 315(24475), 233(24270)
$[Ag(L^3)_2]ClO_4$	380[b], 300(20590), 230(23685)

[a] In methanol. Solution concentration ca. 10^{-3} mol dm^{-3}

[b] Ill-defined shoulder

TABLE V.5

^{1}HNMR[a] Spectral Data of free L and the Complexes.

Compound	*6-H*	*5-H*	*4-H*	*3-H*	*12-H*	*11-H*	*10-H*	*9-H*	*8-H*	*10-Me*	*13-H*
L^1	8.73[b](8.0)	7.65[c](7.9)	7.95[c](7.1)	8.25[b](8.0)	⟨----------7.17-7.33----------⟩						8.66[d]
$[Ag(L^1)_2]ClO_4$	8.66[b](8.0)	7.66[c](7.8)	8.10[c](7.0)	8.13[b](8.0)	7.45[b](8.1)	7.35[c](8.1)	7.26[c](7.9)	7.35[c](8.1)	7.45[b](8.1)		9.00[d]
L^2	8.70[b](7.8)	7.34[c](7.8)	7.77[c](7.1)	8.18[b](8.0)	7.20-7.26	7.20-7.26		7.20-7.26	7.20-7.26	2.35	8.62[d]
$[Ag(L^2)_2]ClO_4$	8.64[b](7.9)	7.65[c](7.8)	8.09[c](7.0)	8.12[b](8.1)	7.41[b](7.9)	7.15[b](8.0)		7.15[b](8.0)	7.41[b](7.9)	2.27	9.04[d]
L^3	8.71[b](7.8)	7.46[c](7.7)	7.79[c](7.0)	8.26[b](8.0)	7.19-7.36	7.19-7.36		7.19-7.36	7.19-7.36		8.59[d]
$[Ag(L^3)_2]ClO_4$	8.66[b](7.8)	7.65[c](7.7)	8.08[c](7.0)	8.12[b](8.0)	7.37[b](7.9)	7.25[b](8.0)		7.25[b](8.0)	7.37[b](7.9)		9.00[d]

[a] In $CDCl_3$ using $SiMe_4$ as an internal standard

[b] Doublet

[c] Triplet

[d] Singlet

TABLE V.6

Analytical Data of $[ML_3](ClO_4)_2.H_2O$ (M=Fe,Co,Ni)

Compound	Formula	%C		%H		%N		%M(M=Fe,Co,Ni)	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Fe(L^1)_3](ClO_4)_2.H_2O$	$C_{36}H_{32}Cl_2N_6O_9Fe$	52.7	52.8	3.9	4.1	10.3	10.4	6.8	7.0
$[Fe(L^2)_3](ClO_4)_2.H_2O$	$C_{39}H_{38}Cl_2N_6O_9Fe$	54.3	54.4	4.4	4.5	9.8	9.9	6.5	6.7
$[Fe(L^3)_3](ClO_4)_2.H_2O$	$C_{36}H_{29}Cl_5N_6O_9Fe$	46.8	47.0	3.1	3.2	9.1	9.0	6.1	6.3
$[Co(L^1)_3](ClO_4)_2.H_2O$	$C_{36}H_{32}Cl_2N_6O_9Co$	52.5	52.6	3.9	4.0	10.2	10.0	7.2	7.3
$[Co(L^2)_3](ClO_4)_2.H_2O$	$C_{39}H_{38}Cl_2N_6O_9Co$	54.2	54.2	4.4	4.5	9.7	9.8	6.8	6.9
$[Co(L^3)_3](ClO_4)_2.H_2O$	$C_{36}H_{29}Cl_5N_6O_9Co$	46.7	46.8	3.1	3.0	9.1	9.2	6.4	6.6
$[Ni(L^1)_3](ClO_4)_2.H_2O$	$C_{36}H_{32}Cl_2N_6O_9Ni$	52.6	52.5	3.9	4.0	10.2	10.3	7.1	7.0
$[Ni(L^2)_3](ClO_4)_2.H_2O$	$C_{39}H_{38}Cl_2N_6O_9Ni$	54.2	54.3	4.4	4.6	9.7	9.8	6.8	6.8
$[Ni(L^3)_3](ClO_4)_2.H_2O$	$C_{36}H_{29}Cl_5N_6O_9Ni$	46.7	46.8	3.1	3.1	9.1	9.3	6.3	6.5

TABLE V.7

Solution Molar Conductivity[a] and Infrared Spectral[b] Data of the Complexes

$[ML_3](ClO_4)_2.H_2O$ (M=Fe,Co,Ni)

Compound	Λ_M ohm^{-1} cm^2 mol^{-1}	ν_{max} (cm^{-1}) C=N(imine)	C=N(pyridine)	ClO_4^{-1}
$[Fe(L^1)_3](ClO_4)_2.H_2O$	250	1615	1515	1100[c], 620
$[Fe(L^2)_3](ClO_4)_2.H_2O$	250	1620	1560	1100[c], 620
$[Fe(L^3)_3](ClO_4)_2.H_2O$	248	1625	1570	1100[c], 620
$[Co(L^1)_3](ClO_4)_2.H_2O$	240	1615	1600	1100[c], 620
$[Co(L^2)_3](ClO_4)_2.H_2O$	235	1620	1600	1100[c], 620
$[Co(L^3)_3](ClO_4)_2.H_2O$	238	1625	1605	1100[c], 620
$[Ni(L^1)_3](ClO_4)_2.H_2O$	245	1630	1600	1100[c], 620
$[Ni(L^2)_3](ClO_4)_2.H_2O$	242	1625	1605	1100[c], 620
$[Ni(L^3)_3](ClO_4)_2.H_2O$	245	1625	1605	1100[c], 620

[a] In methanol.

[b] Spectra were recorded in KBr disc (4000 – 600 cm^{-1})

[c] Broad.

TABLE V.8

Solution Electronic Spectral Data[a]

of $[M(L^2)_3](ClO_4)_2 \cdot H_2O$ (M=Fe,Co,Ni)

Compound	λ_{max} nm(ϵ $dm^3 mol^{-1} cm^{-1}$)
$[Fe(L^2)_3](ClO_4)_2 \cdot H_2O$	570(5000), 530[b](3570) 320[b](23120), 280[c](27500) 230(34800)
$[Co(L^2)_3](ClO_4)_2 \cdot H_2O$	315(25900), 280(25200) 235(25640)
$[Ni(L^2)_3](ClO_4)_2 \cdot H_2O$	320(21430), 290(19950) 235(27410)

[a] In CH_3CN at 298K.

[b] Shoulder

[c] Broad

TABLE V.9

Cyclic Voltammetric Data[a] of $[ML_3](ClO_4)_2 \cdot H_2O$ (M=Fe,Co)

Compound	E^{o}_{298}(V)$[M^{III}/M^{II}]$	ΔE_p(mV)
$[Fe(L^1)_3](ClO_4)_2 \cdot H_2O$	1.27	140
$[Fe(L^2)_3](ClO_4)_2 \cdot H_2O$	1.20	130
$[Fe(L^3)_3](ClO_4)_2 \cdot H_2O$	1.32	120
$[Co(L^1)_3](ClO_4)_2 \cdot H_2O$	0.66	120
$[Co(L^2)_3](ClO_4)_2 \cdot H_2O$	0.61	180
$[Co(L^3)_3](ClO_4)_2 \cdot H_2O$	0.77	130

[a] In CH_3CN using TBAP (0.1 mol dm^{-3}) as the supporting electrolyte. The values are versus S.C.E.. The reported data correspond to the scan rate v = 50 mVs^{-1}

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Chapter VI

CHAPTER VI

SYNTHESIS ELECTROCHEMICAL AND OPTICAL SPECTRAL PROPERTIES OF MONO-NUCLEAR TRIS CHELATED COMPLEXES OF RUTHENIUM(II) CONTAINING N-ARYLPYRIDINE-2-CARBOXALDIMINE AND 2,2'-BIPYRIDINE LIGANDS*

Abstract: *The synthesis of the tris-chelated complexes, $[RuL_n(bpy)_{3-n}](ClO_4)_2 \cdot H_2O$ [L=N-arylpyridine-2-carboxaldimine, bpy = 2,2'-bipyridine, n=0-3], based on a direct and general synthetic route has been described. For $[RuL_3]^{2+}$, the geometry has been assessed by ^{1}HNMR spectroscopy. All the complexes show metal-to-ligand charge transfer (M.L.C.T.) transitions in the visible range at ca.475 nm. Preliminary results of emission spectra are described briefly. The metal oxidation as well as ligand reduction for the complexes have been studied electrochemically in acetonitrile using different working electrodes. It has been shown, for the mixed l-bpy complexes, that the reductions of coordinated L occur at comparatively lower negative potentials. The correlation between the electrochemical properties and $\nu_{c.t.}$ (absorption) is discussed.*

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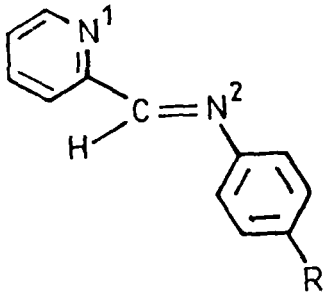
*This work has appeared in *J. Chem. Soc., Dalton Trans.*, 1994, 1305.

INTRODUCTION

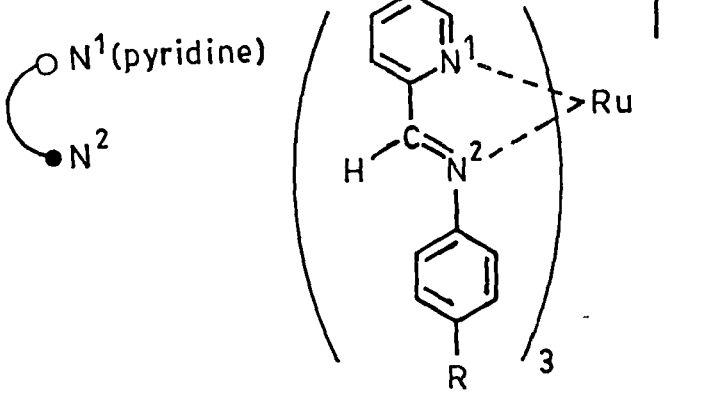
In this present chapter, we describe the synthesis and properties of a series of tris-chelated complexes of ruthenium(II) derived from neutral N-arylpyridine-2-carboxaldimine Schif base ligands, L. Our interest in this area[1-14] arose due to the following reasons.



L

R = H, L^1

R = CH_3, L^2



Firstly, like bpy, ligand L have a α, α'-diimine function. Secondly, it has been already shown that they form stable complexes[15] with ruthenium(II) and finally, the iron(II complexes, $[FeL_3]^{2+}$ absorbs[16-18] at a lower energy than does $[Fe(bpy)_3]^{2+}$.

In recent years only two reports[19,20] o tris-chelated ruthenium(II) complexes of L or related ligand have appeared in the literature. In 1978, Dose an

Wilson[19] first reported the sythesis of $[RuL^2_3](PF_6)_2$ from $L_2[RuCl_5(H_2O)]$. It seems, however, that the compound was not purified and that its properties as described did not correspond to the properties of isomerically pure compound, sythesised by us. A generalised synthetic route using silver(I) complexes of L and bpy is described here, to synthesise a complete series of tris-chelated complexes, $[RuL_n(bpy)_{3-n}]^{2+}$ (n=0-3). The three specific ligands used in this chapter are abbreviated as L^1, L^2 and bpy.

Results and Discussion

A. Synthesis

The direct reaction of hydrated $RuCl_3$ with L (L^1 or L^2) in solution failed to afford isolable $[RuL_3]^{2+}$ species. Ruthenium trichloride underwent partial substitution of Cl^- and an isomeric mixture of $[RuCl_2L_2]$ resulted. We then explored the silver(I)-assisted sythetic route[21-23] for the sythesis of the tris-chelates. The reaction of chloride salts of ruthenium and the silver bis-complexes $[AgL_2]ClO_4$ (L=L^1 or L^2)[23,24] proceeded smoothly in ethanol to yield tris-chelated complexes, which were isolated from the solutions as their perchlorate salts. The sythetic routes may be described by equations 1 - 4

$$RuCl_3 \cdot 3H_2O + 3[AgL_2]^+ \xrightarrow{EtOH} [RuL_3]^{2+} + 3AgCl + 3L \qquad 1$$

$$cis\text{-}[RuCl_2L_2] + 2[AgL_2]^+ \xrightarrow{EtOH} [RuL_3]^{2+} + 2AgCl + 3L \qquad 2$$

$$cis\text{-}[RuCl_2(bpy)_2] + 2[AgL_2]^+ \xrightarrow{EtOH} [RuL(bpy)_2]^{2+} + 2AgCl + 3L \qquad 3$$

$$cis\text{-}[RuCl_2L_2] + 2[Ag(bpy)_2]^+ \xrightarrow{EtOH} [RuL_2(bpy)]^{2+} + 2AgCl + 3bpy \qquad 4$$

The reactions 3 and 4 are particularly useful for the sythesis of mixed ligand complexes, which were, otherwise, not obtainable[19]. In all cases Chromatographic purification of the complexes was required and was performed on a silica-gel column using $CHCl_3$-CH_3CN as eluent (experimental section). It may be noted here that the reaction of $RuCl_3 \cdot 3H_2O$ and $[AgL_2]^+$ in 1:1 molar ratio yields an isomeric mixture[15] of $[RuCl_2L_2]$ as the major product [equation 5]. The properties of isomeric

$$RuCl_3 \cdot 3H_2O + [AgL_2]^+ \xrightarrow{EtOH} [RuCl_2L_2] + AgCl \qquad 5$$

compounds of $RuCl_2L_2$ correspond very well with the authentic compounds, $RuCl_2L_2$, described in Chapter II.

B. Characterisation

The complexes are obtained as highly crystalline, stable dark solids. The compositions of new compounds are formulated by elemental analyses (C,H,N). The magnetic susceptibility measurement revealed that the complexes are diamagnetic (t_2^6) in nature. The molar conductance in acetonitrile lies between 320 and 335 $ohm^{-1}\ cm^2\ mol^{-1}$,

suggesting a 1:2 type of electrolytic nature[25] of the compounds. This results collectively conform to the formulation of the compound as $[RuL_3](ClO_4)_2$.

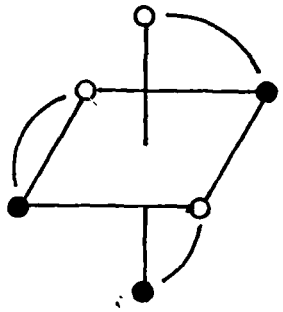
C Bonding and Assessment of Structures

(i) Infrared spectra

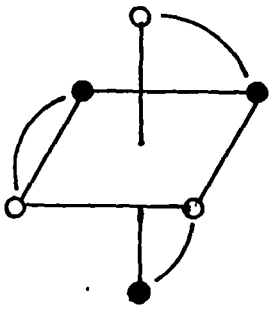
Infrared spectral data of $[RuL_n(bpy)_{3-n}](ClO_4)_2$(n=0-3) were collected as KBr discs in the range 4000-600 cm^{-1}. All of them show characteristic absorptions for coordinated L and bpy[16] in the IR spectra. Selected group frequencies are presented in Table VI.3. The broad structure less bond, $\nu_{ClO_4^-}$ at ca.1100 cm^{-1} suggests the lack of significant perchlorate coordination.

(ii) ^{1}HNMR Spectra and Geometry

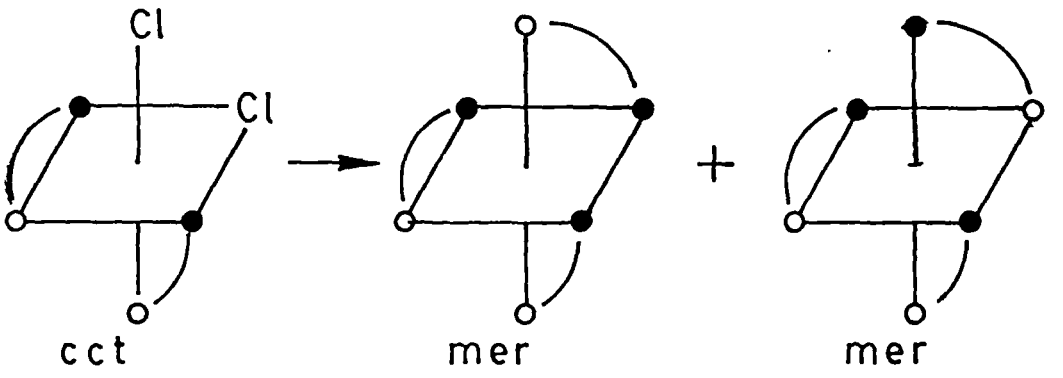
The tris chelated $[RuL_3]^{2+}$ containing an unsymmetrical bidentate ligand L, can exist as *mer* or *fac* geometrical isomers[26,27]. The *fac* form is symmetrical, possesses a C_3 axis of symmetry and in an idealised case the three ligands would be magnetically equivalent whereas the corresponding *mer* isomer, is of C_1 symmetry, and all the three ligands are magnetically inequivalent. In this respect, we selected the tris complex of the methyl substituted ligand, L^2, to take advantage of the methyl resonance, to determine the geometry of $[RuL_3]^{2+}$ by ^{1}HNMR spectroscopy. The ^{1}HNMR spectrum of $[RuL^2_3]^{2+}$ in $CDCl_3$ shows two methyl



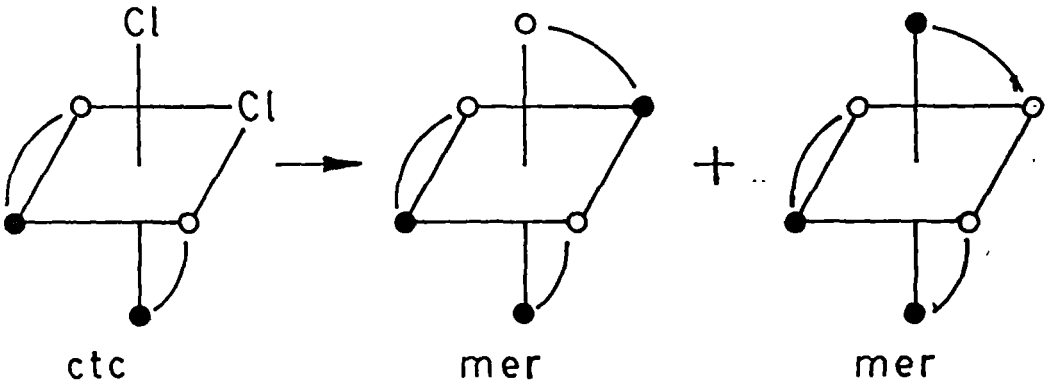
mer-



fac-



cct mer mer



ctc mer mer

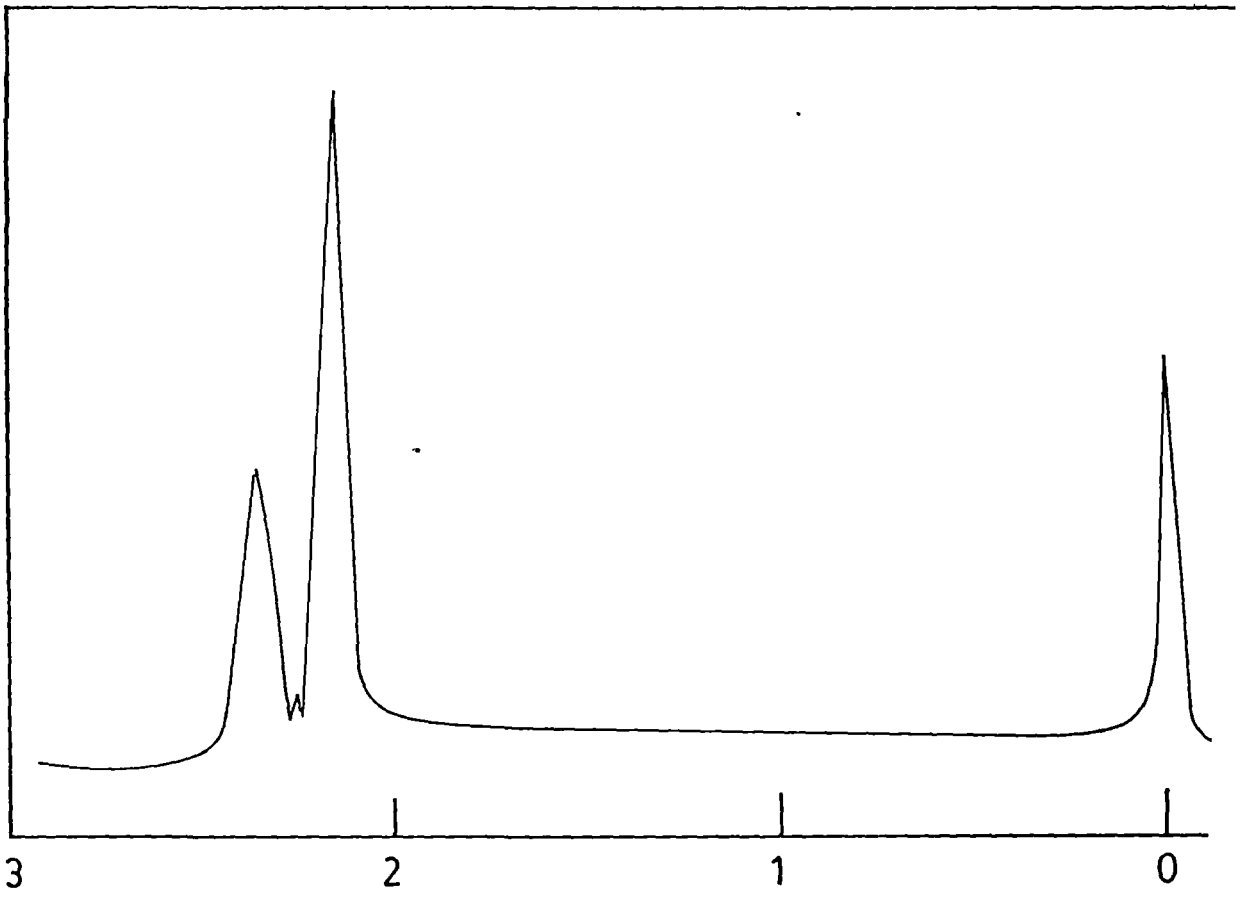


FIGURE VI.1 ^{1}HNMR METHYL SIGNAL OF mer-$[RuL^{2}_{3}](ClO_4)_2.H_2O$

resonances with relative intensities 1:2 at δ 2.18 and 2.08 ppm respectively (Figure VI.1). Meridional tris chelates of unsymmetrical bidentate ligands are well documented[26,28] to display this type of spectrum. We, therefore, conclude that geometry of $[RuL_3]^{2+}$ ($L=L^1$ or L^2) is meridional. The complex pattern of the spectrum in the range 5.60δ - 9.00δ further supports the unsymmetrical *mer* geometry of $[RuL_3]^{2+}$. This result is not incompatible with our expectation since the *fac* form would place the three aryl moieties in close proximity and therefore is most likely to be thermodynamically disfavoured relative to the *mer* isomer where the aryl groups would experience the minimum possible non bonding interactions.

(iii) Electronic Spectra

The absorption spectra of $[RuL^2_n(bpy)_{3-n}]^{2+}$ ($n=0-3$) complexes are shown in Fig.VI.2 and data are collected in Table.VI.4. All appeared to be typical charge transfer (c.t.) spectra with absorption intensities for the lowest energy band ca. $10^4 dm^3 mol^{-1} cm^{-1}$. The low energy transitions which occur in the range 600-400 nm are assigned[15] to metal-to-ligand charge-transfer (M.L.C.T.) transitions. The spectra of the complexes are very similar to that of $[Ru(bpy)_3]^{2+}$ in intensity and profile. Associated with the intense c.t. band is a shoulder at higher energy. The multiple transition in these complexes may arise due to the

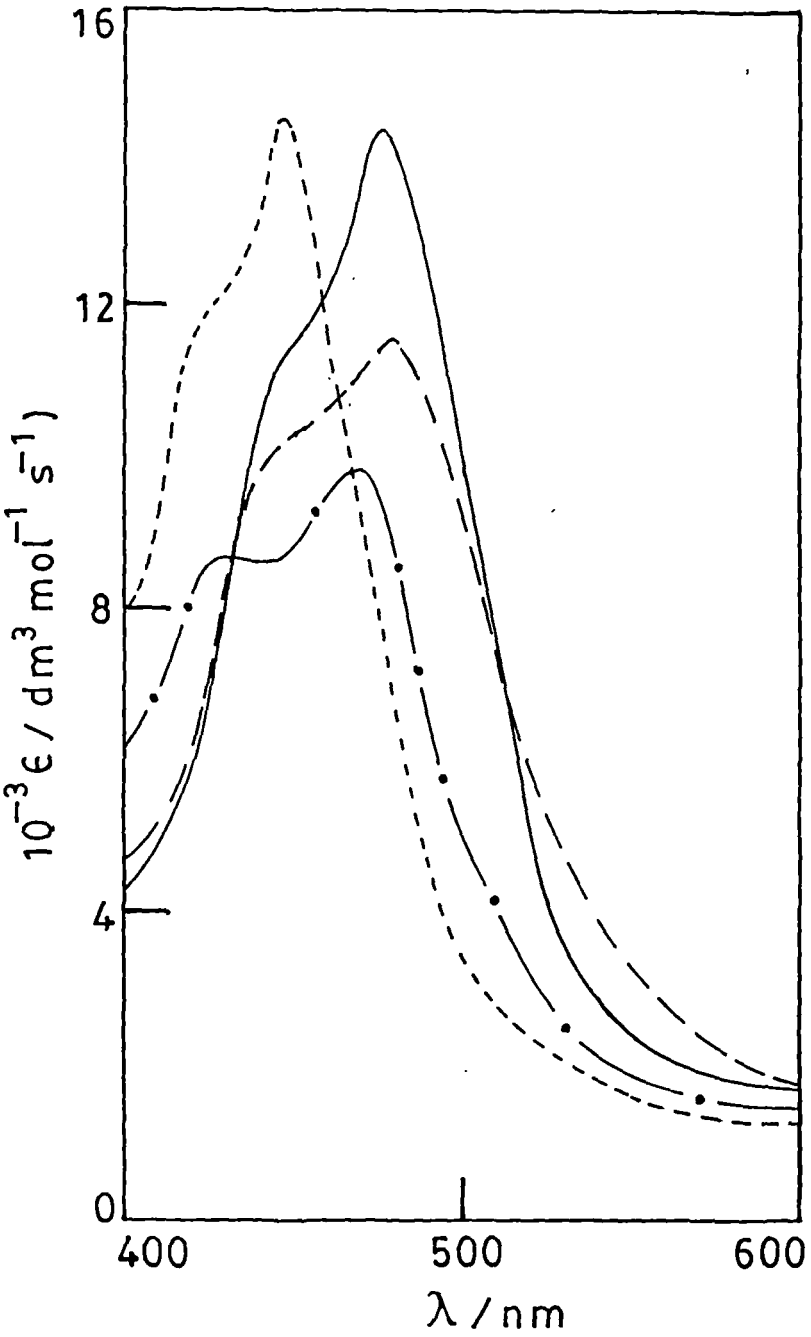


FIGURE VI.2 VISIBLE ABSORPTION SPECTRRA OF

(a) $[RuL^2_3]^{2+}$ (——)

(b) $[RuL^2_2(bpy)]^{2+}$ (----)

(c) $[RuL^2(bpy)_2]^{2+}$ (-•-•-) and

(d) $[Ru(bpy)_3]^{2+}$ (....) IN CH_3CN

presence[29] of different acceptor levels as well as for various other reasons[30-33]. Remarkably the lowest energy transition for $[RuL_3]^{2+}$ (L=L^1 or L^2) occurs at lower energy than that for $[Ru(bpy)_3]^{2+}$. The complex $[RuL^2(bpy)_2]^{2+}$ displays two components in its absorption spectrum in the range 500-400 nm. The feature at longer wavelength (470 nm) is associated with a d(Ru)——π^*(L) transition whereas the band at 430 nm is attributed to the d(Ru)—— π^*(bpy) transition.

We also present some preliminary experimental results on the emmision spectral properties of the above compounds. Unlike $[Ru(bpy)_3]^{2+}$, acetonitrile solutions of mixed ligand complexes and $[RuL_3]^{2+}$ (L=L^1 or L^2) do not emit at room temparature.However, excitation of ethanolic solution of complexes at 430 nm at 77l resulted in multiple band emission spectra. The data have been collected in Table.VI.4.

(iv) Electrochemical Properties

In acetonitrile solution at room temparature, four successive reversible to quasi reversible one electron cyclic voltammetric responses are observed for $[RuL_3]^{2+}$ in the range +1.8 to -2.0 V vs. the saturated calomel electrode (SCE) at a platinum electrode. One of these lies at a positive potential while the other three occur at negative potentials (Table.VI.5.).The uncoordinated ligand L^2 undergoes[15] two sucessive stepwise reductions at -1.42 and -1.88 V and two

oxidative responses are also observable at 1.54 and 1.93 V vs. SCE. Since the oxidative response for $[RuL^{2}_{3}]^{2+}$ occurs at a less positive potential than that of free ligand L^{2}, there is little doubt that the response at ca. 1.44 V for $[RuL^{3}_{2}]^{2+}$ (Figure VI.3) is a metal centred process, $[Ru^{III}L^{2}_{3}]^{3+}$-$[Ru^{II}L^{2}_{3}]^{2+}$. Similar consideration also apply for the Ru-L^{1} system.

We believe[34,35] that the three cathodic couples at the negative of SCE are the successive reductions of the three coordinated ligands (Table-VI.5, Figure VI.4). The redox responses of the $[RuL_3]^{2+}$ system may thus be represented by equation 6.

$$[Ru^{III}L_3]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_3]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_2(L^{\cdot})]^{+}$$

$$\underset{-e^-}{\overset{+e}{\rightleftharpoons}} [Ru^{II}L(L^{\cdot})_2] \underset{-e^-}{\overset{+e}{\rightleftharpoons}} [Ru^{II}(L^{\cdot})_3]^{-} \qquad 6$$

It may be noted here that the first reduction potential of the co-ordinated ligand occurs at a much less negative potential than that for uncoordinated L. This is quite consistent[26,34,36,37] with the available data for complexes of ruthenium(II) containing heterocyclic ligands.

The ruthenium(III)-ruthenium(II) couple in the complexes, $[RuL_n(bpy)_{3-n}]^{2+}$, occurs in the range 1.3-1.5V. The electrode reactions in all cases are almost reversible with ΔE_p = 70-80 mV. It is essential to use anhydrous

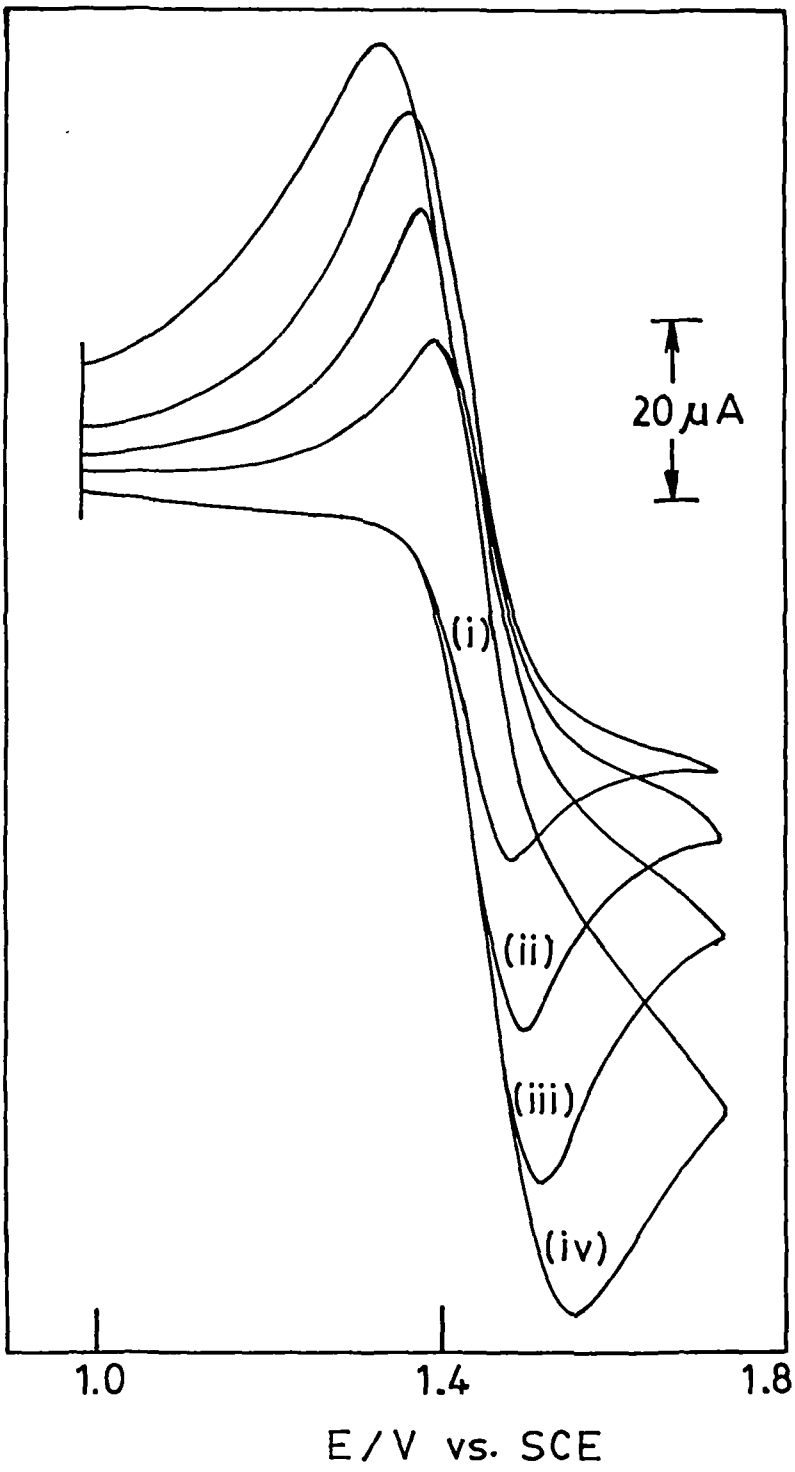


FIGURE VI.3 CYCLIC VOLTAMMOGRAMS OF $[RuL^2_3]^{2+}$ AT DIFFERENT SCAN RA AT POTENTIALS POSITIVE TO SCE: (i) 20 (ii) 50 (iii) and (iv) 200 mVs^{-1}

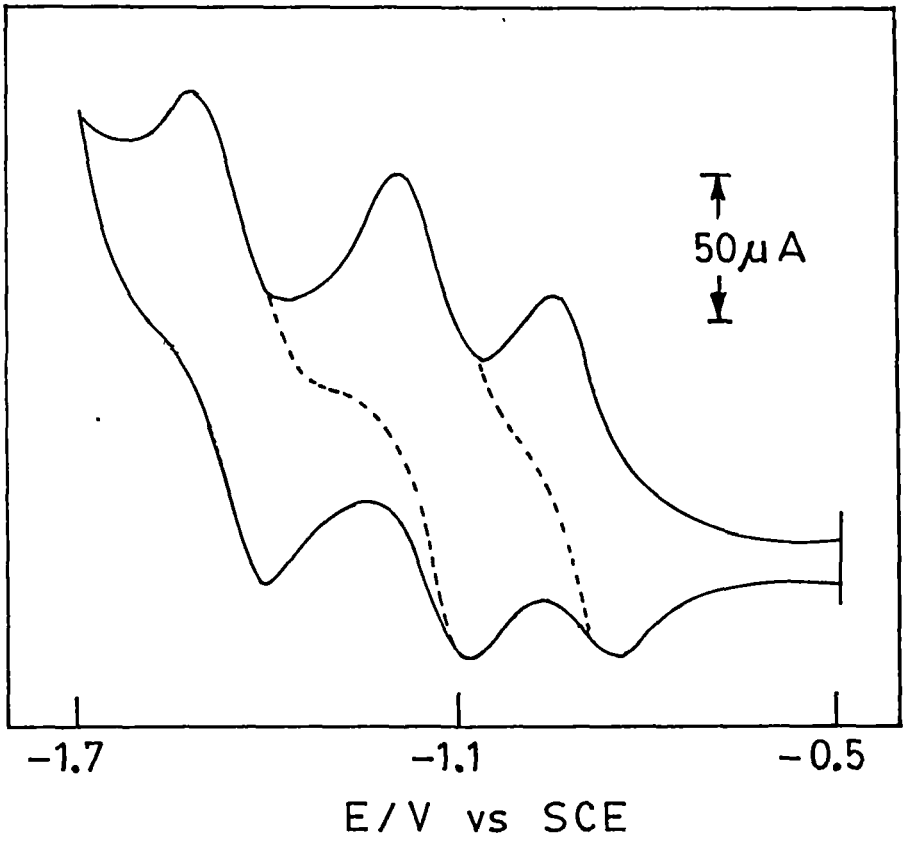


FIGURE VI.4 CYCLIC VOLTAMMOGRAM OF $[RuL^1_3]^{2+}$ AT POTENTIAL NEGATIVE SCE AT A PLATINUM WORKING ELECTRODE

solvent, particularly for complexes containing L, to be able to observe reversible response. The presence of moisture leads to quasireversible to irreversible behaviour where the corresponding reduction wave is either broad or unobserved. This is presumably due to secondary chemical transformations of electrogenerated $[Ru_3]^{3+}$. It has already been shown[38] that electrogenerated[99] trans-$[RuCl_2L_2]^1$ undergoes chemical transformation in the presence of moisture to form trans-$[RuCl_2L(L')]$ ($L' = C_6H_6NC(O)Py$), the mixed-ligand amido complex has been isolated and characterised X-ray crystallographically (Chapter IV).

For the cationic complex, $[Ru_3]^{2+}$ ($L = L^1$ or L^2), six successive reductions, in principle, could occur[24]. We therefore employed glassy carbon as the working electrode for identification of responses at more negative potentials. Five responses were observed for $[Ru_3]^{2+}$ (Table VI.6, Figure VI.5), in the experimentally accessible range (-0.90 to -2.80V). Moreover, for the mixed-ligand complexes, the first reductions may be expected to involve the ligand having the most stable lowest unoccupied molecular orbital (LUMO). We believe this to be L rather than bpy. This proposal is based on the following observations: (i) Each of L and bpy undergoes[15,34] two successive one-electron reductions, (ii) the first two reductions for $[Ru_2^2(bpy)]^{2+}$ occur at less negative potentials than the first reduction potential for $[Ru(bpy)_3]^{2+}$ and (iii) similarly, the first reduction

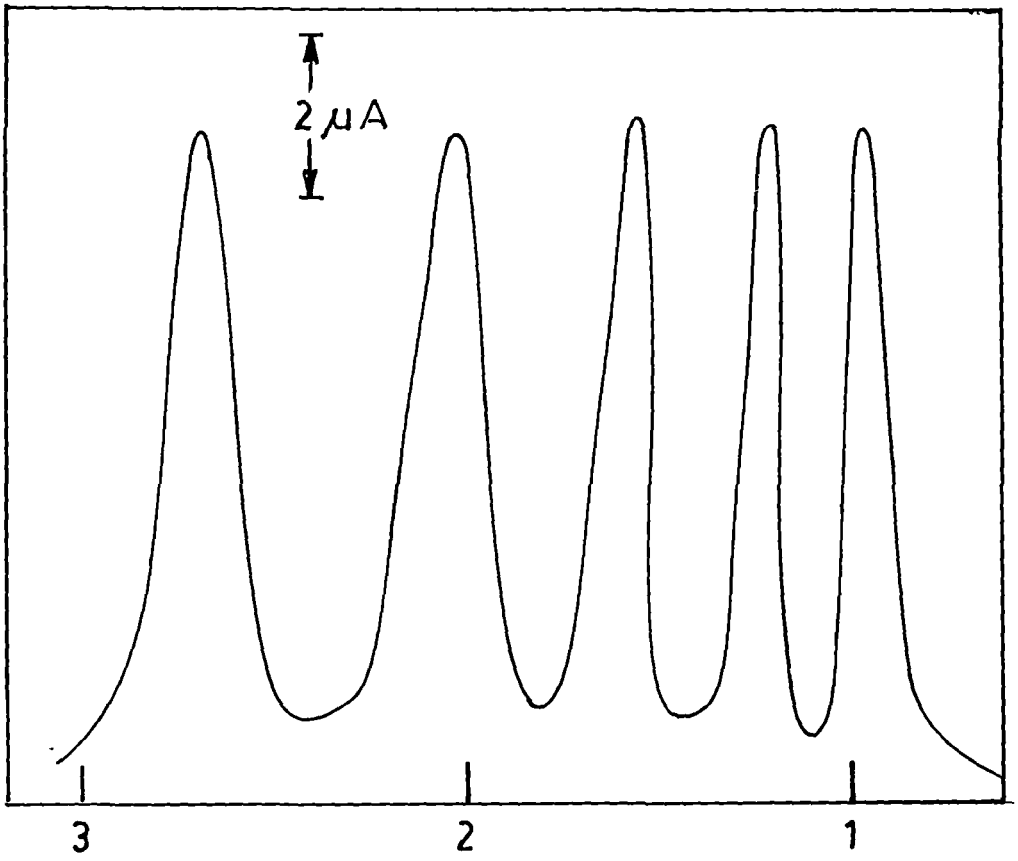


FIGURE VI.5 DIFFERENTIAL PULSE VOLTAMMOGRAM OF mer-$[RuL^1_3](ClO_4)_2$ A GLASSY CARBON ELECTRODE

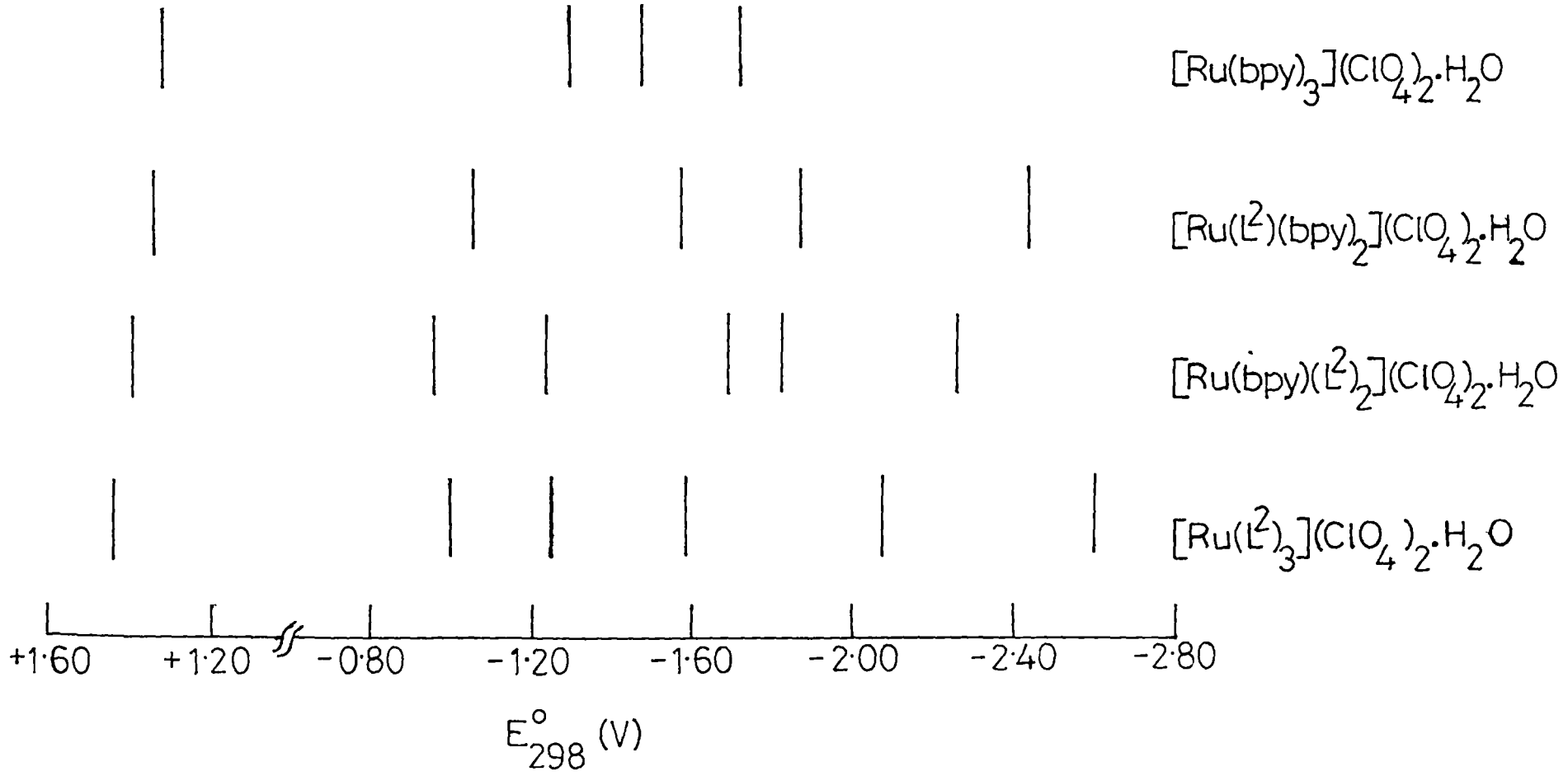


FIGURE VI.6 E^0_{298} CORRELATION DIAGRAM OF $[RuL_n(bpy)_{3-n}]^{2+}$ (n = 0-3)

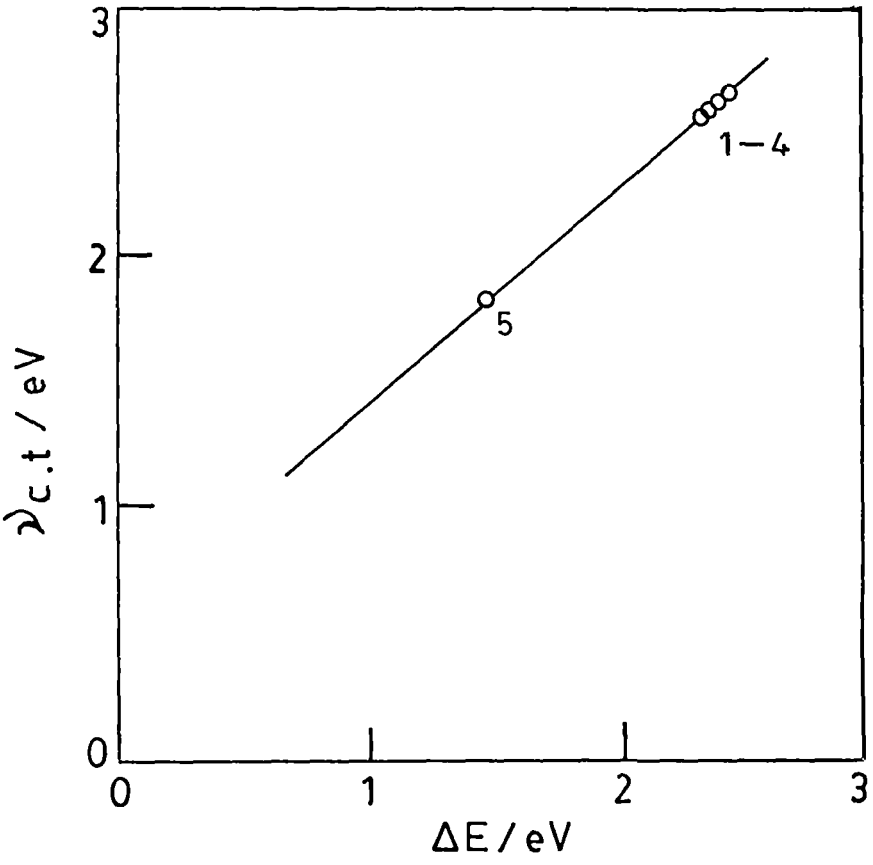


FIGURE VI.7 LINEAR CORRELATION BETWEEN $\tilde{\nu}_{c.t}$ and $\Delta_{ox/red}$ FOR

1. $[RuL^2(bpy)_2](ClO_4)_2.H_2O$
2. $[RuL^1_3](ClO_4)_2.H_2O$
3. $[RuL^2_2(bpy)](ClO_4)_2.H_2O$
4. $[RuL^2_3](ClO_4)_2.H_2O$
5. cct-$[RuCl_2L^2_2]$

potential for $[RuL^{2}(bpy)_{2}]^{2+}$ is much more positive than that for $[Ru(bpy)_{3}]^{2+}$. Out of the six possible reduction for the mixed complexes five are observed for $[RuL^{2}_{2}(bpy)]^{2+}$, whereas for $[RuL^{2}(bpy)_{2}]^{2+}$ in which the reductions are shifted cathodically (Table VI.6, Figure VI.6) only four are observed in the accessible in the voltage window.

It is interesting for the complexes $[RuL_{n}(bpy)_{3-n}]^{2+}$ and $[RuCl_{2}L_{2}]$ that the M.L.C.T.absorption energiesfollow a linear correlation with $\Delta E_{ox/red}$ (Table VI.7), where $\Delta E_{ox/red}$ refers to the difference of the formal potentials of the Ru^{III}–Ru^{II} couple and the first ligand reduction couple.The M.L.C.T. transition for these complexes involves excitation to the π^{*} orbital of L while the first ligand reductions in these complexes also involve the same orbital, as discussed above. A least-squares fit of $\nu_{c.t.}$ against ΔE (Figure VI.6) leads to equation 7

$$\nu = 0.86\Delta E + 0.55 \qquad 7$$

It may also be noted that other examples of ruthenium complexes with similar ligands e.g. the 2, 2'-bipyridine[40,41] and 2-(arylazo)pyridine system,[26,42] also show similar relationships.

Conclusion

The synthesis of isomerically pure tris-chelated ruthenium(II) complexes of α, α'-diimino Schiff-base ligands has been achieved by a general synthetic procedure using the

corresponding silver(I) complexes of L. The spectral as well as the redox properties of the complexes indicate L to have lower energy π^* levels compared to bpy. This is in agreement with the conclusion made recently by Domingey *et al*[35] based on the spectral properties of a group of ruthenium complexes of similar ligands. Studies of the reactivities of these complexes, particularly towards oxidants, are underway.

EXPERIMENTAL SECTION

A. Physical Measurements

Molar conductivity, Infrared and Electronic Spectral Measurements have been done as described in Chapter II Electrochemical Measurements which included cyclic voltammetry and differential pulse voltammetry were done as described in Chapter II. ^{1}HNMR spectral measurements have been done ($CDCl_3$) as described in Chapter II. Solution emmission spectra recorded with a Perkin Elmer MPF-44A fluorescence spectrophotometer and the data were obtained from I.A.C.S., Calcutta.

B. Formulation of Compounds

Complexes were formulated by C,H,N micro-analyses as described in Chapter II.

C Solvents

Solvents used for preparation work and for Spectral and Electrochemical measurements were obtained as described

in the previous chapters.

D. Preparation of Compounds

(a) Chemicals

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

(b) Complexes

(i) The complexes $[AgL_2]ClO_4$ ($L=L^1$ or L^2) were obtained as described in Chapter V. The complex $[Ag(bpy)_2]ClO_4$ was synthesised as before[23,24].

(ii) The complexes, cis-$[RuCl_2L_2]$[15], cis-$[RuCl_2(bpy)_2]$[21] and $[Ru(bpy)_3]ClO_4 \cdot H_2O$[43] were prepared by published procedures.

(iii) **Tris [N-arylpyridine-2-carboxaldimine]Ru(II) perchlorate monohydrate, $[RuL_3](ClO_4)_2 \cdot H_2O$** ($L = L^1$ or L^2) from $RuCl_3 \cdot H_2O$. The compounds were synthesised using a general procedures given below.

To a sample of $RuCl_3 \cdot 3H_2O$ (1 m.mol) dissolved in ethanol (20 ml) was added a solution of $[AgL_2]ClO_4$ (3m.mol) in ethanol (20 ml) and the mixture was heated to reflux for 2 hrs. The solution was then cooled and filtered through a G-4 sintered glass funnel to remove insoluble AgCl. The filtrate was evaporated to dryness over a water bath and the dried

mass was extracted with boiling water (4 x 25 ml). To this water extract an aqueous solution of $NaClO_4$ (ca. 1g in 25 ml water) was added. The reddish brown precipitate thus obtained was filtered and dried in vacuo over P_4O_{10}. This was then subjected to column chromatography on a silica gel (60-120 mesh) column eluting with different mixtures of $CHCl_3$-CH_3CN. A reddish brown band was eluted with $CHCl_3$-CH_3CN (3:2). This was collected and evaporated. Finally it was recrystallised from $CHCl_3$-C_6H_{14}(1:1)

Yield :- $[RuL^1_3](ClO_4)_2$:40%

$[RuL^2_3](ClO_4)_2$:45%

(iv) **Tris.[N-arylpyridine-2-carboxaldimine] Ru(II) perchlorate monohydrate, $[RuL_3](ClO_4)_2.H_2O$ ($L=L^1$ or L^2)** from cis-Dichlorobis [N-arylpyridine-2-carboaldimine] Ru(II), cis$[RuCl_2L_2]$ ($L=L^1$ or L^2). The systheses were performed by using a general procedure given below.

To a suspension of cis-$[RuCl_2L_2]$ (1 m.mol) in ethanol (20 ml) was added a solution of $[AgL_2]ClO_4$ (2 m.mol) in ethanol (20 ml) and the mixture was heated to reflux for 2 hrs. The rest of the procedure was the same as that described in (iii).

Yield:- $[RuL^1_3](ClO_4)_2$: 50%

$[RuL^2_3](ClO_4)_2$: 52%

The analytical and spectral data of the complexes thus obtained corresponded exactly to those of samples prepared by method (iii).

(v) (2,2'-Bipyridine)bis[N-p-tolylpyridine-2-carboxaldimine] Ruthenium(II) perchlorate monohydrate, $[Ru(bpy)L^2_2](ClO_4)_2 \cdot H_2O$.

To a suspension of cis-$[RuCl_2L^2_2]$ (1 m.mol) in ethanol (20 ml) was added a solution of $[Ag(bpy)_2]ClO_4$ (2 m.mol) in ethanol (20 ml) and the reluting mixture was heated to reflux for 2 hrs. It was then filtered through G-4 sintered glass funnel to remove insoluble AgCl. Isolation and purification of the compound from the filtrate was done similarly as described in (iii). Yield:50%.

(vi) Bis-(2,2'-bipyridine)[N-p-tolylpyridine-2-carboxaldimine] Ruthenium(II)perchlorate monohydrate $[RuL^2(bpy)_2](ClO_4)_2 \cdot H_2O$

To a suspension of cis-$[Ru(bpy)_2Cl_2]$ (1 m.mol) in ethanol (20 ml) was added a solution of $[AgL^2_2]$ ClO_4 (2 m.mol) in ethanol (20 ml) and the resulting mixture was heated to reflux for 2 hrs. The rest of the procedure was the same as that described in (v). Yield:50%.

(vii) Reaction of $RuCl_3 \cdot 3H_2O$ with $[AgL_2]$ ClO_4 ($L=L^1$ or L^2) in 1:1 ratio. The reactions were performed by following a general peocedure as described below.

The salt $RuCl_3 \cdot 3H_2O$ (1 m.mol) was dissolved in ethanol (20 ml) and heated to reflux for 10 min. over a water bath. To this red brown solution was added an ethanolic solution of $[AgL_2]ClO_4$ (1 m.mol in 10 ml).

Immediately a dark violet solution resulted which was further heated for 1 hr over a water bath. After cooling the resulting solution was filtered through a G-4 sintered glass funnel. Insoluble white AgCl along with dark crystals of $[RuCl_2L_2]$ were separated from the dark filtrate. The residue was then extracted with chloroform. On slow evaporation of chloroform, dark crystals of isomeric mixtures of $[RuCl_2L_2]$ resulted. Isomeric purification of $[RuCl_2L_2]$ was performed on a silica gel column (60-120 mesh) as described in chapter II. (vide Experimental Section D.e.1.).

Yield:- tlt.$[RuCl_2L_2]$: (L = L^1, 40%, L^2; 45%)
cct.$[RuCl_2L_2]$: (L = L^1, 15%, L^2; 20%)
ctc.$[RuCl_2L_2]$: (L = L^1, 19%, L^2; 21%)

TABLE VI.1

Analytical Data of the Complexes $[RuL_n(bpy)_{3-n}](ClO_4)_2 \cdot H_2O$

Compound	Formula	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
$[RuL^1_3](ClO_4)_2 \cdot H_2O$	$C_{36}H_{32}N_6O_9Cl_2Ru$	50.00	50.15	3.70	3.85	9.70	9.80
$[RuL^1_2(bpy)](ClO_4)_2 \cdot H_2O$	$C_{32}H_{28}N_6O_9Cl_2Ru$	47.30	47.41	3.45	3.51	10.34	10.42
$[RuL^1(bpy)_2](ClO_4)_2 \cdot H_2O$	$C_{28}H_{24}N_6O_9Cl_2Ru$	44.21	44.34	3.16	3.21	10.05	10.21
$[RuL^2_3](ClO_4)_2 \cdot H_2O$	$C_{39}H_{38}N_6O_9Cl_2Ru$	51.65	52.00	4.20	4.10	9.25	9.30
$[RuL^2_2(bpy)](ClO_4)_2 \cdot H_2O$	$C_{34}H_{32}N_6O_9Cl_2Ru$	49.90	50.10	3.95	4.00	9.70	9.85
$[RuL^2(bpy)_2](ClO_4)_2 \cdot H_2O$	$C_{29}H_{26}N_6O_9Cl_2Ru$	47.95	48.05	3.65	3.75	10.15	10.25

TABLE VI.2

Solution Molar Conductivity Data[a] of the complexes

$[RuL_n(bpy)_{3-n}](ClO_4)_2 \cdot H_2O$

Compound	Λ_M $ohm^{-1}\ cm^2\ mol^{-1}$
$[RuL^1_3](ClO_4)_2 \cdot H_2O$	332
$[RuL^1_2(bpy)](ClO_4)_2 \cdot H_2O$	330
$[RuL^1(bpy)_2](ClO_4)_2 \cdot H_2O$	330
$[RuL^2_3](ClO_4)_2 \cdot H_2O$	320
$[RuL^2_2(bpy)](ClO_4)_2 \cdot H_2O$	325
$[RuL^2(bpy)_2](ClO_4)_2 \cdot H_2O$	325

[a] In CH_3CN at 298K. Concentrations are ca. 10^{-3} mol.dm^{-3}

TABLE VI.3

Infrared Spectral Data of the Complexes $[RuL_n(bpy)_{3-n}](ClO_4)_2 \cdot H_2O$

	$\nu_{max}(cm^{-1})^{a,b}$				
Compound	C=N(imine)	C=N(pyridine)	ClO_4^-	C-H[d]	C-H[e]
$[RuL^1_3](ClO_4)_2 \cdot H_2O$	1620	1585	1100[c],620	780	675
$[RuL^1_2(bpy)](ClO_4)_2 \cdot H_2O$	1625	1590	1100[c],620	780	675
$[RuL^1(bpy)_2](ClO_4)_2 \cdot H_2O$	1625	1590	1100[c],620	780	675
$[RuL^2_3](ClO_4)_2 \cdot H_2O$	1615	1580	1100[c],620	780	675
$[RuL^2_2(bpy)](ClO_4)_2 \cdot H_2O$	1620	1585	1100[c],620	780	675
$[RuL^2(bpy)_2](ClO_4)_2 \cdot H_2O$	1620	1585	1100[c],620	780	675

[a] Spectra were recorded in KBr disc (4000 - 600 cm^{-1})

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

[c] Broad.

[d] Out-of-plane bending in pyridine ring.

[e] Out-of-plane bending in phenyl ring.

TABLE VI.4

Solution Electronic Spectral Data of the complexes $[RuL_n(bpy)_{3-n}](ClO_4)_2 \cdot H_2O$

Compound	Absorption[a] λ_{max} nm(ε $dm^3 mol^{-1} cm^{-1}$)	Emission[b] λ_{em} nm
$[RuL^1_3](ClO_4)_2 \cdot H_2O$	480(13760), 445[c](10080), 300(25600), 270(55040)	d
$[RuL^2_3](ClO_4)_2 \cdot H_2O$	480(14310), 445[c](11120), 315(27380), 270(25120)	535, 580
$[RuL^2_2(bpy)](ClO_4)_2 \cdot H_2O$	482(11520), 445(10060), 315[c](17040), 280(32400)	535, 590
$[RuL^2(bpy)_2](ClO_4)_2 \cdot H_2O$	470(9800), 430(8660), 320[c](9325), 285(43540)	540, 590
$[Ru(bpy)_3](ClO_4)_2 \cdot H_2O$	454(14400), 425[c](11630), 305[c](4400), 280(69670)	d

[a] In CH_3CN Solute concentration ca. 10^{-3} mol dm^{-3}

[b] Quantitative spectra were recorded in C_2H_5OH at 77 l.

[c] Shoulder

[d] Not studied.

TABLE VI.5

Cyclic voltammetric data* at a platinum working electrode for the complexes $[RuL_n(bpy)_{3-n}](ClO_4)_2 \cdot H_2O$

	Metal-centred oxidation	Ligand-based reductions		
	E^o_{298}/V (ΔE_p/mV)	E^o_{298}/V (ΔE_p/mV)		
Compound	3+/2+	2+/1+	1+/0	0/1-
$[RuL^1_3](ClO_4)_2 \cdot H_2O$	1.43(75)	0.93(90)	1.16(100)	1.49(110)
$[RuL^2_3](ClO_4)_2 \cdot H_2O$	1.44(70)	0.90(90)	1.19(110)	1.52(110)
$[RuL^2_2(bpy)](ClO_4)_2 \cdot H_2O$	1.40(80)	0.95(90)	1.24(100)	1.70(110)
$[RuL^2(bpy)_2](ClO_4)_2 \cdot H_2O$	1.34(75)	1.04(100)	1.52(110)	1.85(110)
$[RuL(bpy)_3](ClO_4)_2 \cdot H_2O$	1.32(70)	1.30(90)	1.49(100)	1.73(110)

*Cyclic voltammetric experiments were carried out in CH_3CN at 298 K using 0.1 mol dm^{-3} NBu_4ClO_4 as supporting eletrolyte. The reported data correspond to scan rate $v = 50$ mVs^{-1}.

TABLE VI.6

Differential pulse voltammetric data for $[RuL_n(bpy)_{3-n}](ClO_4)_2 \cdot H_2O$ at a glassy-carbon electrode at potentials positive to SCE as 298 K

	Ligand reductions, $-E_p/V$[a,b]				
Compound	2+/1+	1+/0	0/1-	1-/2-	2-/3-
$[RuL^1_3](ClO_4)_2 \cdot H_2O$	0.98	1.22	1.57	2.04	2.70
$[RuL^2_3](ClO_4)_2 \cdot H_2O$	1.00	1.25	1.59	2.08	2.60
$[RuL^2_2(bpy)](ClO_4)_2 \cdot H_2O$	0.96	1.24	1.70	1.83	2.27
$[RuL^2(bpy)_2](ClO_4)_2 \cdot H_2O$	1.06	1.58	1.88	2.44	c

[a] In CH_3CN using 0.1 $mol \cdot dm^{-3}$ NBu_4ClO_4 as supporting electrolyte.

[b] Scan rate = 5 mVs^{-1}, modulation amplitude (ΔE_p) = 10 mV.

[c] Not observed.

TABLE VI.7

Spectroelectrochemical correlation data for the complexes

Compound	E^{o}_{298}/V Metal Oxidation	E^{o}_{298}/V First ligand reduction	ΔE^{o}/V Ox/Red	$\nu_{c.t.}$/cm^{-1} Obs	$\nu_{c.t.}$/cm^{-1} Calc.
$[RuL^{1}_{3}](ClO_4)_2 \cdot H_2O$	1.43	-0.93	2.36	20833	20807
$[RuL^{2}_{3}](ClO_4)_2 \cdot H_2O$	1.44	-0.90	2.34	20833	20668
$[RuL^{2}_{2}(bpy)](ClO_4)_2 \cdot H_2O$	1.40	-0.95	2.35	20746	20737
$[RuL^{2}(bpy)_2](ClO_4)_2 \cdot H_2O$	1.34	-1.04	2.38	21276	20945
$cis\text{-}[RuCl_2L^{2}_{2}]$	0.30	-1.18	1.48	14814	14702

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Chapter VII

CHAPTER VII

A FAMILY OF MIXED LIGAND COMPLEXES OF Ru^{II}-LH [LH = N-ARYL-PYRIDINE-2-ALDIMINE], THEIR REACTIONS, ISOLATION AND CHARACTERIZATION*

Abstract: *Synthesis of the tris-chelated complexes* $[Ru(LH)_n(La)_{3-n}]^{2+}$ *(LH = N-aryl-pyridine-2-aldimine, La = 2-(m-tolylazo)pyridine) based on silver(I) assisted trans-metallation synthetic route, has been described. The complexes,* $[Ru(LH)_3]^{2+}$ *and* $[Ru(LH)(La)_2]^{2+}$ *afford* $[Ru(pic)(LH)_2]^{+}$ *and* $[Ru(pic)(La)_2]^{+}$ *(pic = 2-picolinate ion) respectively, on hydrolysis and subsequent oxidation. When* $RuCl_2(LH)_2$ *was reacted with two moles of* $[Ag(La)_2]^{+}$*, a pink complex of composition* $[Ru(LH)(LO)(La)]^{+}$ *[LO = N-aryl-2-picolinamide] was isolated along with the expected brown complex,* $[Ru(La)(LH)_2]^{2+}$*. Initial oxidation of the metal ion favours LH--> LO conversion. The complexes have been characterized with the help of spectroscopy and X-ray crystallography. The X-ray structure of* $[Ru(pic)(L^1H)_2]ClO_4 \cdot CH_2Cl_2$ *is reported. The metal oxidation as well as ligand reductions for the complexes have been studied voltammetrically in acetonitrile using platinum as the working electrode. It has been observed that the oxidation of the transformed complexes, viz.* $[Ru(pic)(LH)_2]^{+}$*,* $[Ru(pic)(La)_2]^{+}$ *and* $[Ru(LH)(LO)(La)]^{+}$ *occur at lower potentials as compared to their parent* $[Ru(LH)_n(La)_{3-n}]^{2+}$

complexes. All the complexes show metal-to-ligand charge transfer transitions in the visible range and absorption energies linearly correlate with the differences between the metal oxidation and the first ligand reduction potential.

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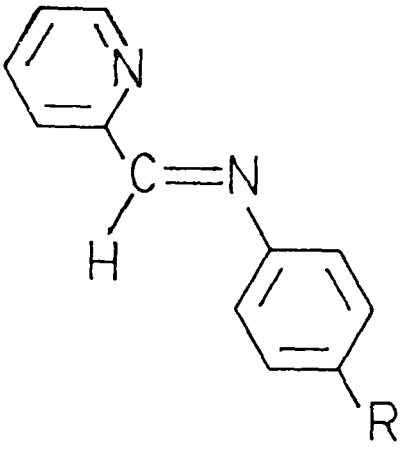
*This work has been communicated.

Introduction

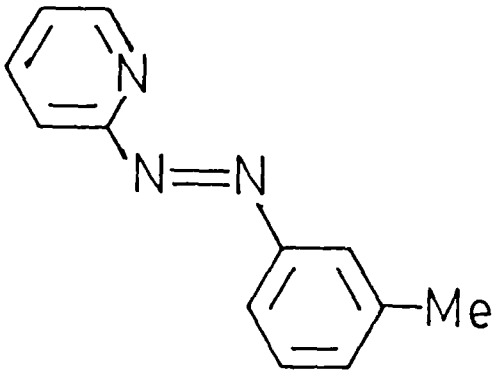
This work stems from our present interest in the ruthenium diimine complexes. This class of compounds are important[1-8] due to their rich redox and optical properties. In this respect, we have been working[9-11] on the synthesis and reactivities of ruthenium complexes of N-aryl-pyridine-2-aldimine (1, LH). These complexes[9-13] are intensely coloured, undergo



R=H : L^1H

R=Me : L^2H

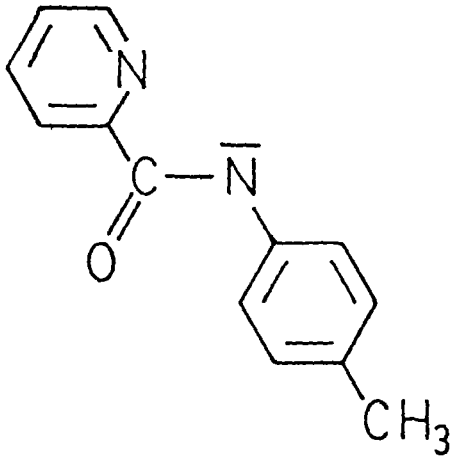
1



La

2

multiple electron transfer and most importantly, these show interesting pattern of chemical as well as photochemical reactivities.



L^2O

In this chapter we report the synthesis and characterization of the tris chelated ruthenium complexes involving LH and La. These may be conveniently synthesized starting from ruthenium bis chelated dichlorides by the use of silver(I) assisted trans metallation reaction route. The study of reactions of ruthenated LH in the above complexes forms an important part of the present work. Interestingly, different products were obtained from apparenly similar type of reactions. All the relevant species have been fully characterized. The reason for transformation selectivity of LH is discussed on the basis of present findings and other results[10,11] from this laboratory and elsewhere.

Results and Discussion

A. The Synthetic Reactions

In the process of synthesizing[9,14-16] mixed ligand tris chelated ruthenium complexes of LH (1) and 2-(m-tolylazo)pyridine (La, 2) some interesting products were obtained along with the expected products, which are elaborated below. The general reaction which has been studied may be represented as follows:

$$cis\text{-}RuCl_2L_2 + 2AgL'_2 \xrightarrow{EtOH} RuL_2L' + 2AgCl + 3L$$

L = LH, La

L' = LH, La

(a) (i) Reaction of cis-$RuCl_2(LH)_2$ and two moles of $Ag(LH)_2^+$

The bluish green cis isomer[10] of $RuCl_2(LH)_2$ was reacted with two moles of silver complex[17], $Ag(LH)_2^+$, in 1:1 aqueous ethanol. In addition to the expected[9] brown tris-chelate, $Ru(LH)_3^{2+}$(3), a pink compound was also formed. Interestingly, an aqueous ethanolic solution of pure $Ru(LH)_3^{2+}$ in the presence of dilute aqueous $AgNO_3$ quantitatively produces the pink compound. The pink product was purified on silica gel column eluting with 1:5 CH_3CN-CH_2Cl_2 mixture. The brown ptoduct was obtained from the column using a more polar solvent (2:3 CH_3CN-CH_2Cl_2 mixture) as an eluent.

(ii) Characterization

The brown compound was identified as[4] $[Ru(LH)_3](ClO_4)_2 \cdot H_2O$(3). Whose characterisation has been discussed in Chapter VI. The pink compound analysed as $[Ru(pic)(LH)_2](ClO_4) \cdot CH_2Cl_2$(4) (pic = 2-picolinateanion). The compound 4 is diamagnetic, 1:1 electrolytic in CH_3CN. The IR spectrum showed all charcateristic features[9,10] of coordinated LH and ionic ClO_4^-. Interestingly, it also displayed a moderately strong band at 1650 cm^{-1} indicating the presence[18,19] of a carboxylic function. Selected characterization data are collected in Table VII.1(a,b,c).

Fortunately, single crystals of 4 (LH = L^1H) could be grown as solvates : $4 \cdot CH_2Cl_2$ and its structure was

successfully solved crystallographically. Molecular views of the complex excluding the solvent of crystallization and the counter anion, ClO_4^- is shown in Figure VII.1. Selected bond distances and bond angles are collected in Table VII.2. The structure solution of 4 unequivocally confirms the composition of 4 as $Ru(pic)(LH)_2^+$. The geometry of the $Ru(LH)_2$ fragment in 4 is trans, cis [trans with respect to two N^1(py) and cis with in the N^2 (imine pair)]. The carboxylic function lies trans to one of the two imine nitrogens. In this manner the three pyridine nitrogens are positioned meridionally. We note here that the parent complex 3 exists[9] in the meridional geometry. Therefore, the transformation 3 —— 4 is stereoretentive.

In the above structure, Ru-N(5) length agrees[20] well with the Ru-N lengths in $Ru(pic)_2(PPh_3)_2$. Interestingly, the four Ru-N lengths in the $Ru(LH)_2$ fragment of 4 are not equal. The Ru-N(4) length is notably shorter than other three Ru-N lengths. This must be due to stronger $d\pi - p\pi$ interactions[13] between Ru(II) and π^* of the imine function containing N(4), which lies trans to the strong σ-donor carboxylic acid function. Moreover, the average Ru-N(imine) length in 4 is shorter[11] by ca.0.03 Å compared to that in trans-$Ru^{III}(LH)(LO)Cl_2$(LO = N-aryl-2-picolinamide). This may be attributed to the superior back-bonding in ruthenium(II) complexes.

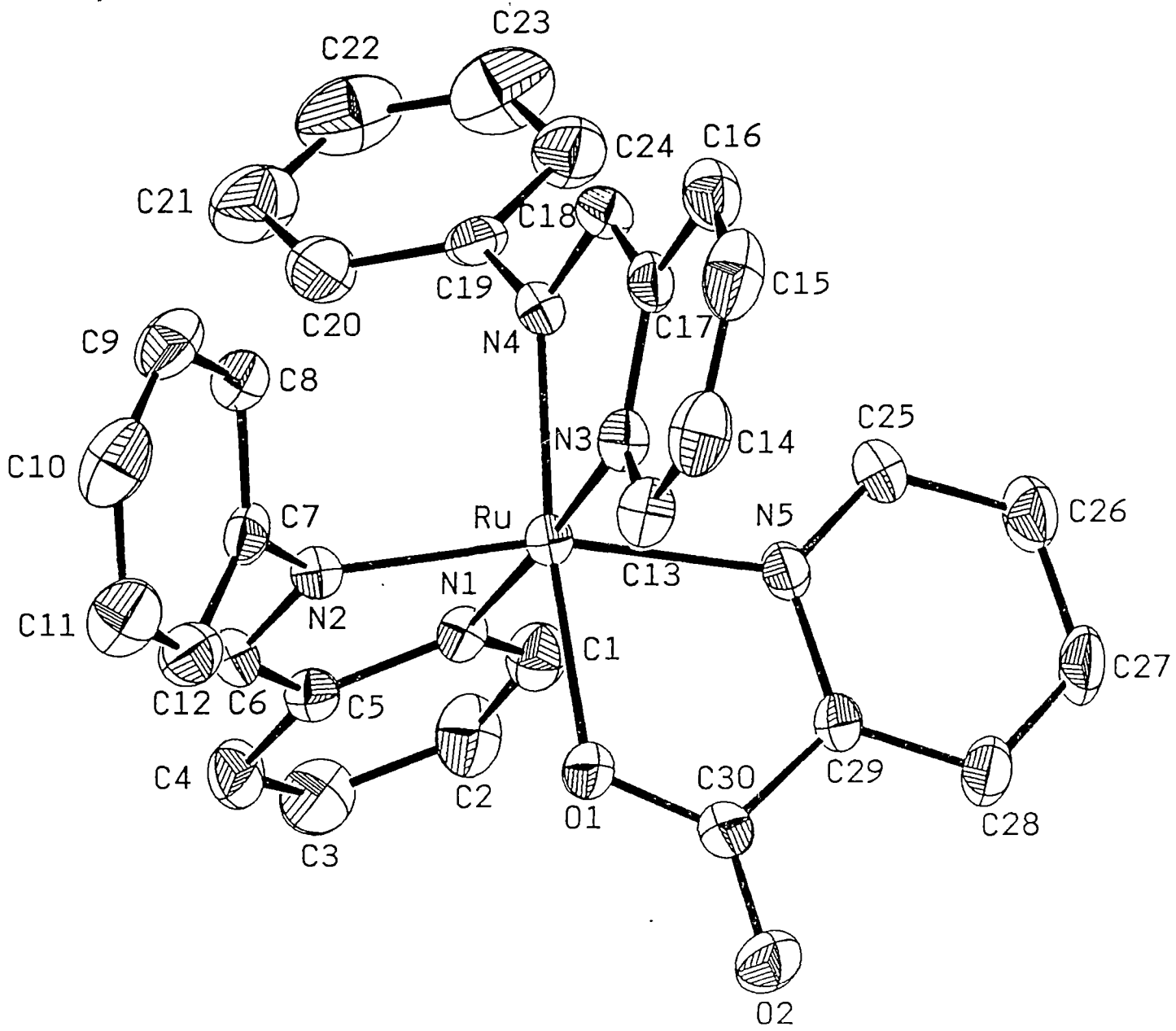
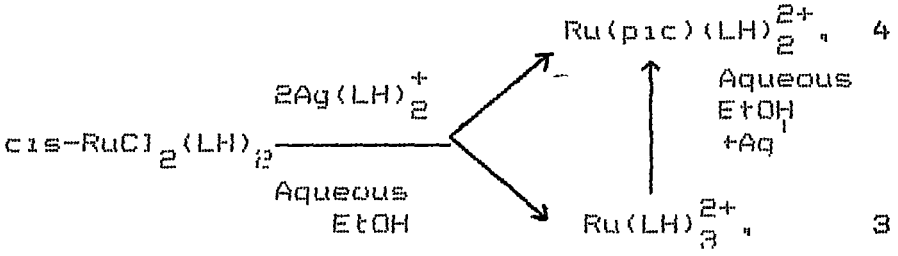


FIGURE VII.1 ORTEP PLOT AND ATOM LABELLING SCHEME FOR $[Ru(pic)(L^1H)_2]^+$ IN $[Ru(pic)(L^1H)_2]ClO_4.CH_2Cl_2$

Finally, it may be noted that the reaction of hydrated $RuCl_3$ and $Ag(LH)_2^+$ in 1:3 mole ratio also resulted in formation of mixture of 3 and 4. The yield of 4 increases with increase of the duration of the reaction.

The reactions, described above, are schematically presented in Scheme I.



Scheme I

(b) (i) Reaction of *cis*-$RuCl_2(m\text{-tap})_2$ and two moles of $Ag(LH)_2^+$

Similar to the prior reaction, this reaction also resulted in the formation of two major products. One of which is violet and the other one is brown in colour. The compounds were purified on a silica gel column by eluting with solvent mixtures of different polarities. The violet compound may be generated by boiling the brown product in aqueous ethanol in the presence of dilute $AgNO_3$ solution. Interestingly, the reaction[18,19] of cis-$Ru(OH_2)_2(m\text{-tap})_2^{2+}$ with PicH in ethanol instantaneously produces the violet product in a high yield.

(ii) Characterization

In this case we have used only methyl substituted ligand, L^2H to take the advantage of monitoring methyl

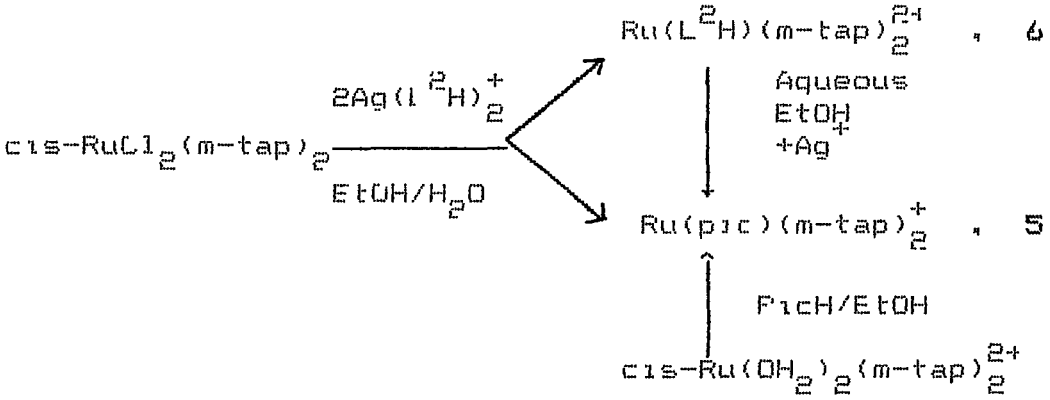
resonances in the less crowded region of the ^{1}HNMR spectrum.

The first moving violet product was eluted with 2:5 CH_2Cl_2-CH_3CN mixture and it analysed as $[Ru(pic)(m\text{-}tap)_2]ClO_4 \cdot CH_2Cl_2$ (5). The brown product, which was eluted with 1:1 CH_2Cl_2-CH_3CN mixture, analysed as $[Ru(L^2H)(m\text{-}tap)_2](ClO_4)_2 \cdot H_2O$, (6). The compound 5 is a 1:1 electrolyte whereas the compound 6 is 1:2 electrolytic in CH_3CN. The compound 5 displayed a moderately strong absorption at 1600 cm^{-1} in the IR spectrum. This band is conspicuously absent in the IR spectrum of 4. Evidently, the 1600 cm^{-1} absorption indicates the presence[18,19] of a carboxylic function in 5 (Table VII.1c).

The ^{1}HNMR spectra of the compounds 5,6 were examined. The aromatic region of both the spectra are complex due to serious overlapping. We therefore, concentrated only on the methyl resonances (Table VII.1.b). The compound 5 displayed two equally intense resonances at 2.15 and 2.05∂. The intensities of two resonances correspond to six protons. The compound 6 also displayed two methyl resonances at 2.21 and 2.12∂, but the ratio of signal intensities is 1:2. Moreover, the total area covered by the two methyl signals of 6 correspond to nine protons. Therefore, it may be concluded that the two equally intense methyl resonances in 5 is due to the presence of two m-tap ligands. In the spectrum of 6 there are three methyl resonances — two of which are overlapping which are attributed[22] to methyl groups of m-tap and the

second signal is due[9] to the p-tolyl group of L^2H. The spectral data, presented above, clearly demonstrate the hydrolytic oxidative cleavage of an imine function occurs in the formation of **5**.

Thus, the reaction is similar to the reaction which is described in section a.



Scheme II

(c) (i) Reaction of cis-$RuCl_2(L^2H)_2$ and two moles of $Ag(m\text{-}tap)_2^+$

In this reaction bluish green cis isomer of $RuCl_2(L^2H)_2$ was reacted with two moles[23] of $Ag(m\text{-}tap)_2^+$ in aqueous ethanol. This reaction also yielded two major products. One of the two products is pink whereas the other one is brown. Unlike other two previously described reactions, the brown product is quite stable in boiling aqueous ethanol. Both the products were purified by using column chromatography technique.

(ii) Characterisation

The pink product was eluted with 1:9 CH_3CN-CH_2Cl_2 solvent mixture and analysed as $[Ru(L^2H)(L^2O)(m\text{-}tap)](ClO_4)\cdot CH_2Cl_2$ (L^2O = N-p-tolyl-2-pirolinamide), (7). The brown product was then eluted with 1:1 CH_3CN-CH_2Cl_2 mixture. Based on the elemental analyses the composition was ascertained as $[Ru(m\text{-}tap)(L^2H)_2](ClO_4)_2\cdot H_2O$ (8). The characterisation of 7 and 8 were unambiguously made based on their physical data.

The compounds 7 and 8 are 1:1 and 1:2 electrolytic, respectively, in acetonitrile. Unlike monopirolinates, the compound 7 did not show any characteristic absorption of carboxylic function. Instead, a moderately strong band at 1620 cm^{-1} in the IR spectrum of 7 confirms the presence[11,21] of an amide function. Fortunately, this compound(7) displayed highly resolved ^{1}HNMR spectrum (Figure VII.2) which was conveniently used for its characterisation. The spectrum consists of well separated, equally intense three methyl resonances between 2.1-2.3δ. This clearly reveals the presence of three tolyl groups in 7. Moreover, there are four doublets of 2H intensities in the range 7.0 and 5.5δ. Such doublets of two proton intensities can only arise from p-substituted phenyl groups. This immediately confirms the presence of two p-tolyl groups in this compound. Rest of the spectrum is complex due to overlapping. The ^{1}HNMR spectrum of 8 is as expected consisting of two methyl resonances, one of which is doubly intense than the other. The spectral data

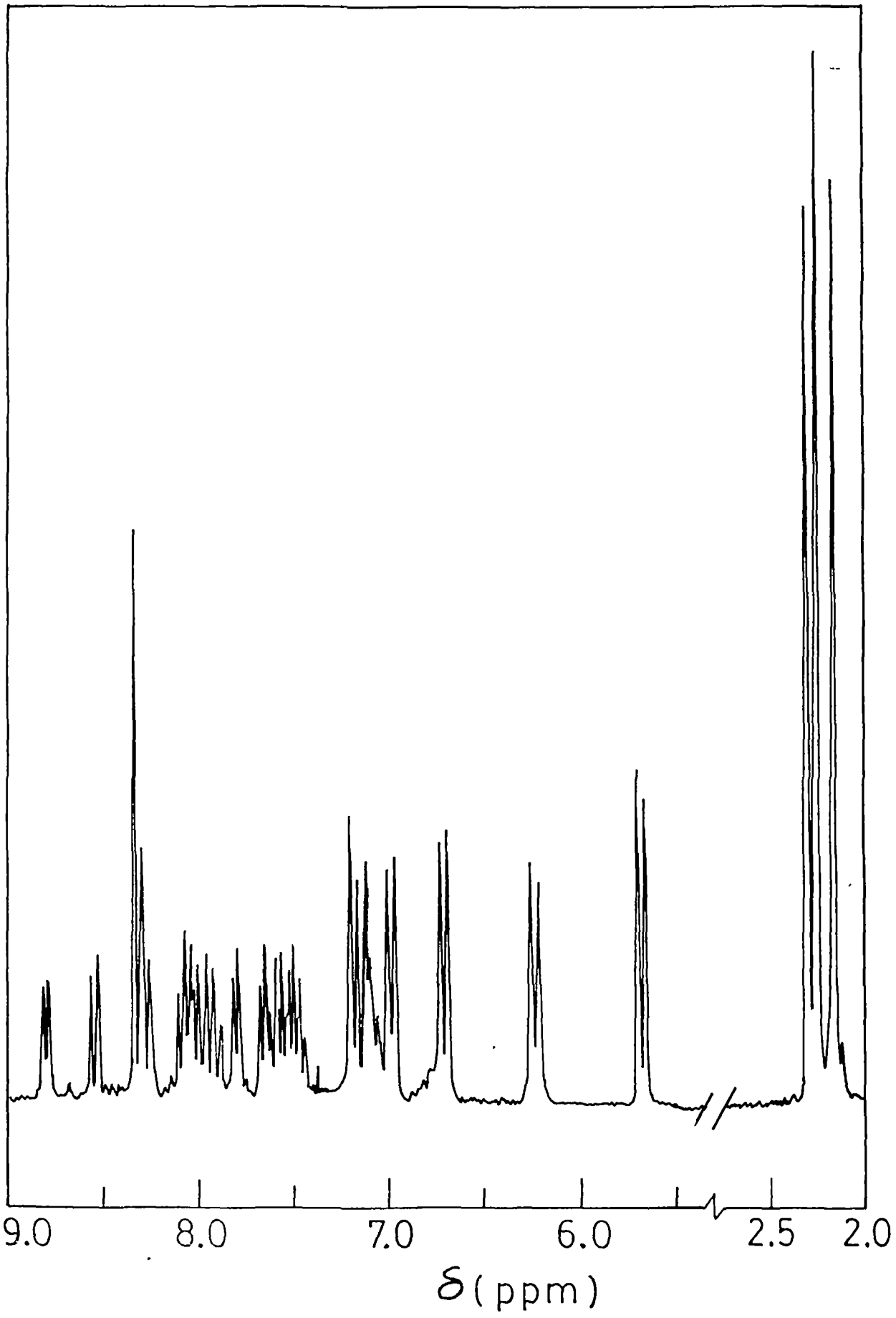
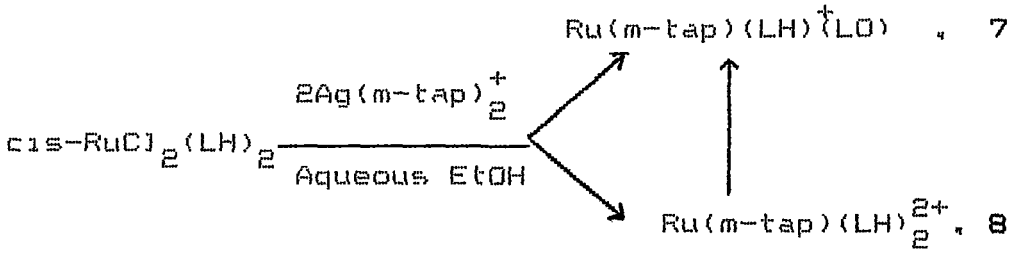


FIGURE VII.2 ^{1}HNMR SPECTRUM OF $[Ru(L^{2}H)(L^{2}O)(La)]ClO_4.CH_2Cl_2$ IN $CDCl_3$

collectively, taken with the analytical data do conform to the proposed compositions of the above compounds.

The reaction, described above, may then be summerised below in Scheme III



Scheme III

We would like to note that a tris chelated compound with three different bidentate ligands as in 7 is extremely rare.[24]

B. The Origin of Transfomation

The reactions described above may be broadly classified in two categories : type (i) LH——pic [reactions (a) and (b)]: type (ii) LH—— LO [reaction (c)]. We first consider the reaction (b) of type (i). In this reaction the starting ruthenium compound does not contain LH. Therefore, the formation of $[Ru(pic)(La)_2]^+$ could, in principle, occur in two ways. Once the coordinated chlorides are precipitated as insoluble AgCl, the solution mixture then contains disolvento complex, $RuS_2(La)_2^{2+}$ (S= solvent) and four moles of free LH. Coordination of LH to $Ru(La)_2^{2+}$ moiety would produce $Ru(LH)(La)_2^{2+}$ (6). Furthermore, hydrolysis[25] of an imine function in a hydroxylic solvent is a common phenomenon.

Thus, hydrolysis of free LH followed by oxidation of the aldehyde function would produce PicH in solution which may then react with the labile disolvento species to form monopicolinate, 5. The second possibility is the same transformation of LH occuring after coordination to $Ru(La)_2$ moiety. We wish to note here that 6 can be easily transformed to 5 and the electrophilicity of LH surely increases upon coordination, which is primary for the hydrolysis of an imine function. Out of the above two possibilities we, therefore, propose that LH—— pic transformation presumably occurs via coordination of LH. This proposal also applies to the reaction (a).

The other type of transformation, LH——LO (type ii) must occur with the coordinated LH since both LH are already coordinated in the starting material. This type of transformation of an imine function has been examplified,[11,21] very recently, in two other ruthenium systems. One such example is the oxidative transformation of trans-$Ru^{II}Cl_2(LH)_2$ to trans-$Ru^{III}Cl_2(LO)(LH)$. It has been shown that initial oxidation of the metal ion followed by partial hydrolysis of coordinated LH and subsequent oxidation of the hydrolysed LH are the steps involved in the above transformation. At this stage, comparison of oxidation power of different reactants of reaction c is necessary for further discussion. We note that La is a very strong[22] π-acceptor. Consequently, $Ag(La)_2^+$ should be a strong oxidant. Furthermore, the oxidation of

cis-$RuCl_2(LH)_2$ may be easily achieved[10] ($E_{1/2}$:0.32V). In the reaction (c), initial oxidation of $RuCl_2(LH)_2$ by $Ag(La)_2^+$ is, therefore, most plausible one. The oxidation of the metal ion then leads to an identical situation where coordinated LH→LO transformation was shown[11] to occur by the electro oxidation of the metal centre. In contrast to the previously reported examples,[11,21] initial oxidation of the metal ion in reaction (c) is not reflected in the oxidation state of the same in the final product. In the present case (7) besidesbeing coordinated to LO, ruthenium is also bound to a very strong π-acceptor, La and a moderate acceptor LH. In the environment of LO, LH and La ruthenium is preferably stabilised in the bivalent state ($E_{1/2}$: Ru^{III}/Ru^{II} 1.0V vide infra).

It may, therefore, be concluded, from the foregoing discussion, that hydrolysis followed by odixation of coordinated LH results in the formation of pic whereas oxidation of the compound followed by hydrolysis would preferentially transform LH to LO.

C. Electrochemical Properties and Redox-Spectra Correlation

Electrochemical properties of the compounds **3-8** were studied cyclic voltammetrically in CH_3CN using TBAP as supporting electrolyte and platinum as a working electrode. The measurements were carried out with the complexes are electroactive, the electrochemical data are presented in

Table VII.3. Representative voltammograms are displayed in Figure VIII.3.

We first consider the three parent chelates viz. 3, 6 and 8. Cyclic voltammogram[9] of the reported compound 3 is already discussed. Each of 6 and 8 displayed an irreversible oxidation wave at a very high oxidation potential (1.6 V) due to Ru(II)——>Ru(III) oxidation. Metal mediated oxidation[11] of coordinated LH has recently been discussed in the literature. For the present complexes the oxidation potentials are very high and consequently the chemical reaction succeeding the electrochemical formation of Ru^{III}-LH is expected to be very fast and thus the reverse waves were absent in the voltammograms of 6 and 8. Both the complexes also display reversible, multiple electron transfer reductive responses on the negative of SCE. These are attributed to the reductions of the coordinated ligands. It may be noted that on moving from 3 to 8 via 6, the metal oxidation potential increases in a parallel direction whereas a reverse trend was observed for the ligand reduction. The above trend is as expected, since La stabilises Ru^{II} better than LH does due to enhance $d\pi$-$p\pi$ back bonding and also undergoes reduction more easily due to presence of lower acceptor orbital.

The two monopicolinates, 4 and 5 showed reversible oxidative and reductive responses on both positive and negative of SCE. Their metal centred redox potentials are

systematically lower than those for the parent diimine compounds. The picolinate ion is a hard ligand, stabilises[18] the higher valent state and thus the above shifts of redox potential is observed. Moreover, on moving from 4 to 5 the $E_{1/2}$ of Ru^{III}/Ru^{II} couple shifts by about 0.56 V presumably due to the better stabilisation of lower valent state by La as noted before. For the similar reason; the ligand reductions in 5 is easier than that in 4. The cyclic voltammogram of the monopicolinamide, 7 consists of a reversible oxidative response at 1.0 V attributed to Ru^{III}/Ru^{II} couple and two reductive couples on the negative of SCE due to the ligand reductions.

Interestingly, the metal redox of 4, 5 and 6 are all reversible whereas those of their parents, 3, 6 and 8 are either irreversible or quasireversible. Irreversiblity in the latter group of complexes are due to metal assisted LH oxidation reaction. Inspite of the fact that both 4 and 6 contains LH as coligand their metal redox responses are reversible. It may, therefore, be concluded that partially transformed products, even if they contain additional LH, are resistant to further oxidation of LH at least in the CV time scale.

The solution absorption spectra of the complexes are recorded in CH_3CN. Representative spectra of the complexes are displayed in Figure VII.4 and the data are collected in Table VII.4. Although the complexes retain

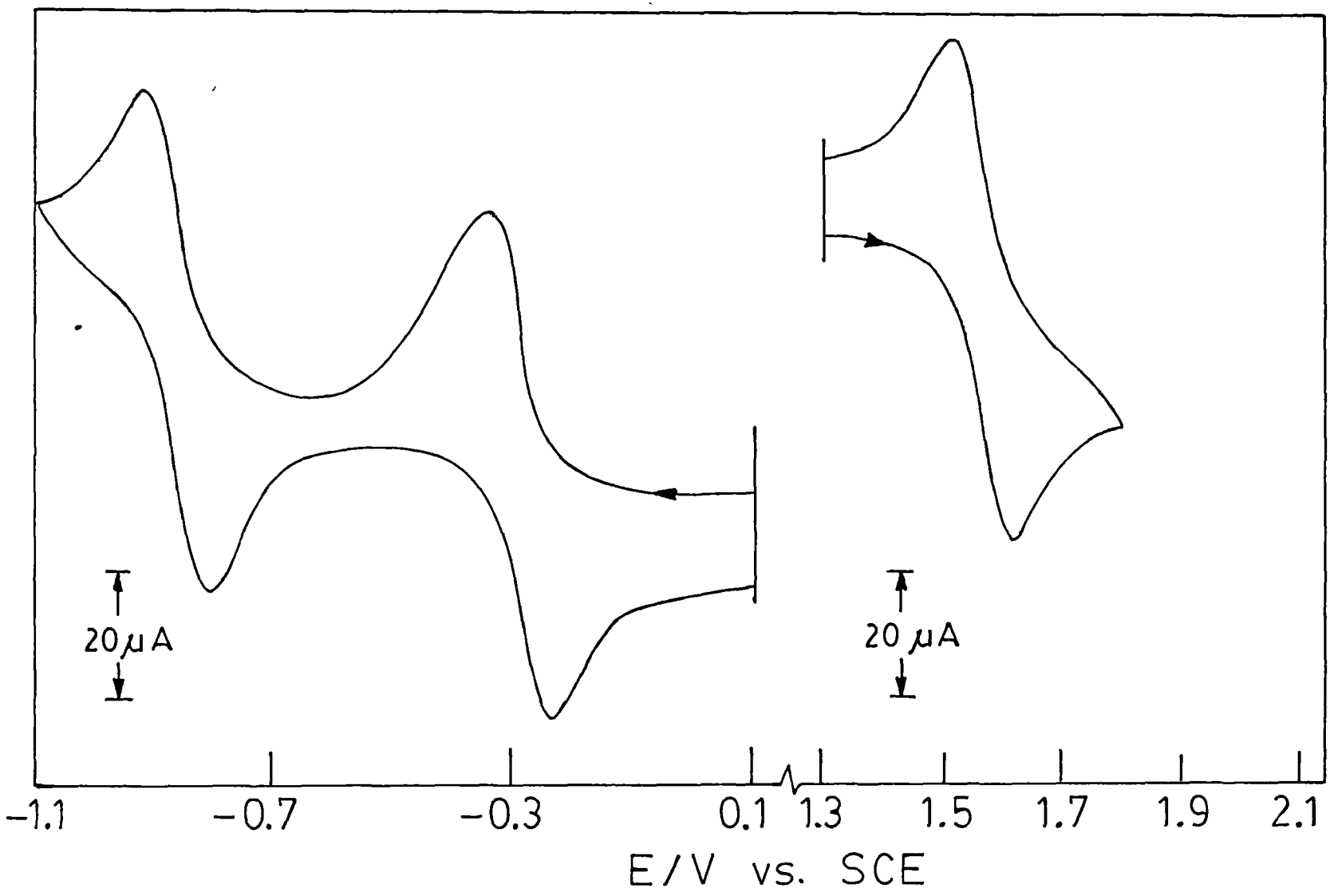


FIGURE VII.3 CYCLIC VOLTAMMOGRAM OF

$[Ru(pic)(La)_2]ClO_4.CH_2Cl_2$ (——) IN CH_3CN

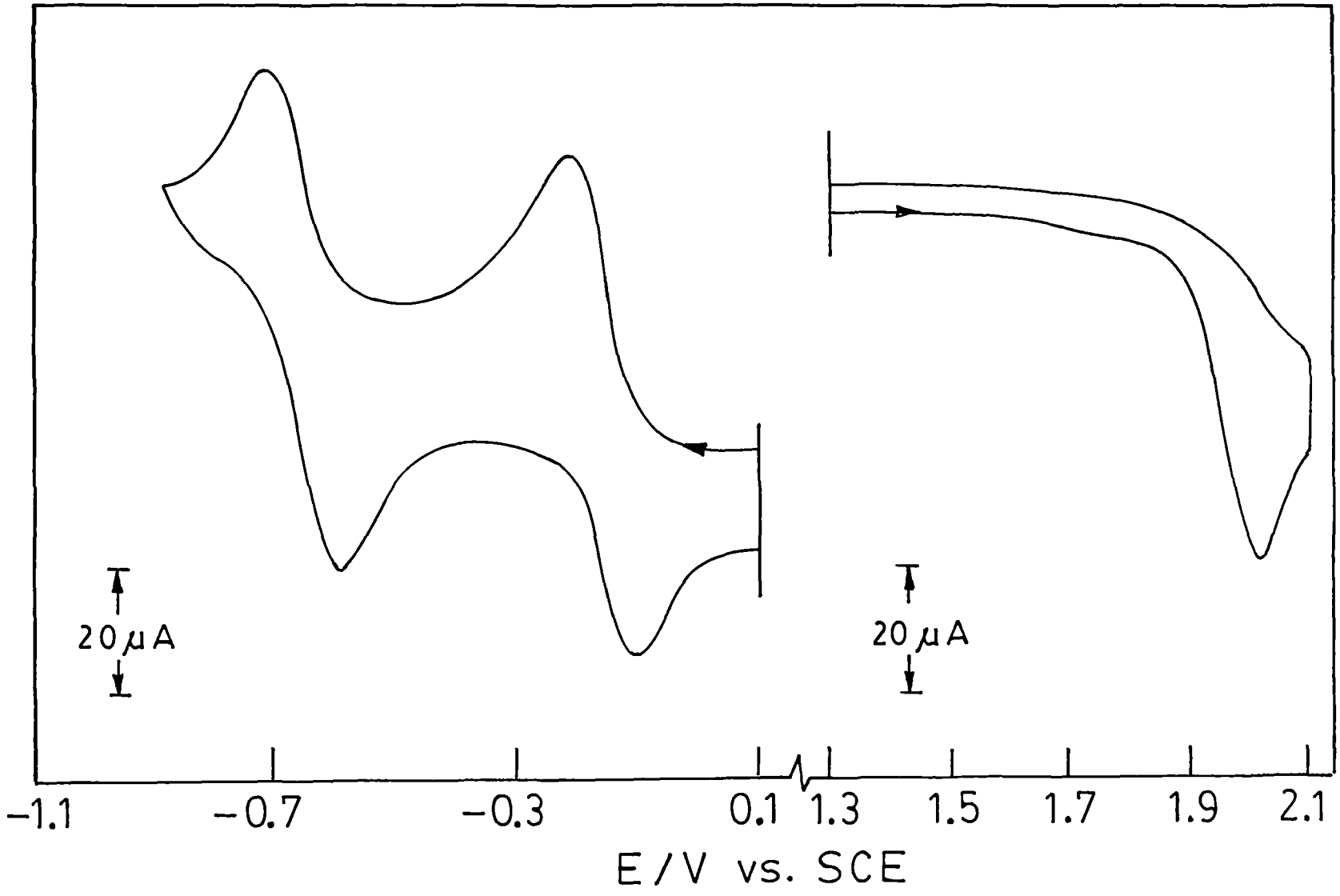


FIGURE VII.3 CYCLIC VOLTAMMOGRAM OF

$[Ru(L^2H)(La)_2](ClO_4)_2.H_2O$ (——)

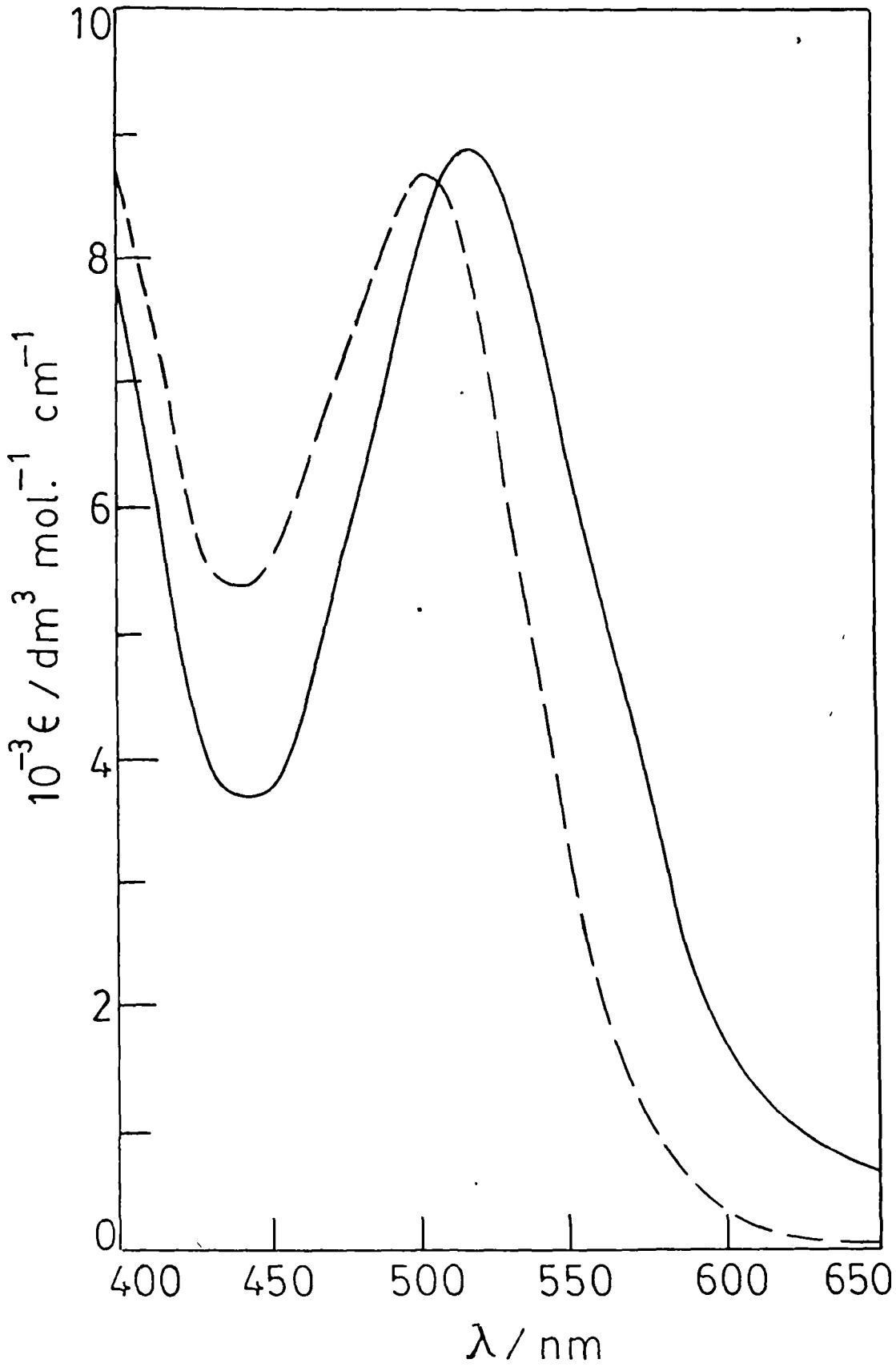


FIGURE VII.4 VISIBLE RANGE ABSORPTION SPECTRA OF

(a) $[Ru(L^2H)(L^2O)(La)]ClO_4.CH_2Cl_2$ (——)

(b) $[Ru(La)(L^2H)_2](ClO_4)_2.H_2O$ (----) IN CH_2Cl_2

fairly intense intraligand transitions in the UV region. The key feature is the intense lower energy transitions occurring in the visible region (520-480 nm) those are assigned[9] to Ru($d\pi$)—— ligand(π^*) MLCT transitions. These transition energies for the parent complexes 3, 6 and 8 are systematically higher than those for the monopicolinates 4, 5 and monopicolinamide, 7. The MLCT absorption energies for all the above complexes, (3-8), interestingly, show a linear correlation[9] with ΔE [where, $\Delta E = E_{1/2}(Ru^{III}/Ru^{II}) - E_{1/2}$ (ligand 0/-1)] [Table VII.5). This correlation, in otherwords, justifies our assignment of MLCT transitions for the complexes.

D. Conclusions

The main findings of this work will now be summarized. The silver(I) assisted trans-metallation route has been shown to be excellent for the synthesis of all possible combination of complexes of formula, $[Ru(LH)_n(La)_{3-n}]^{2+}$ (n = 0-3). The reactions of the coordinated LH in the above complexes show an interesting trend : (i) oxidation of metal ion prior to hydrolysis of ligand results in LH—— LO transformation, (ii) in the absence of any potent oxidant in the reaction mixture the coordinated LH hydrolyses and subsequent oxidation produces 2-picolinate, and (iii) the aforementioned transformations occur to only one of the coordinated diimines.

Finally we wish to mention here that preliminary luminiscence study on the above complexes reveals that the picolinates or the amides have much stronger emission than their parent diimines in the visible region. Our work in this area is continuing.

EXPERIMENTAL SECTION

A. Physical Measurements

Molar conductivity, Infrared and Electronic Spectral Measuremnts have been done as described in Chapter II. Electrochemical measuremenis which includes cyclic voltammetry and differential pulse voltammetry were done as described in Chapter II. Solution electrical conductivity measurements were performed at an Elico CM82T conductivity bridge.

B. Formulation of compounds

Compounds were formulated by C, H, N microanalyses as described in Chapter I

C. Solvents

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

D. Materials

(a) Chemicals

Hydrated Ruthenium Trichloride, $RuCl_3 \cdot 3H_2O$, Sodium Perchlorate, $NaClO_4$ etc and other chemicals required are described in previous chapters.

(b) Complexes

(i) The Complexes, $[Ag(LH)_2]ClO_4$ (LH = L^1H or L^2H) and $[Ag(La)_2]ClO_4$ were obtained as described in previous chapters.

(ii) The complexes, cis-$[RuCl_2(LH)_2]$, cis-$[RuCl_2(La)_2]$ were prepared by reported procedures.

E. Reactions

(a) Reaction of cis-$RuCl_2(LH)_2$ (LH = L^1H and L^2H) and $[Ag(LH)_2]ClO_4$

To a sample of bluish green cis isomer of $RuCl_2(LH)_2$ (0.5 mmol) suspended in ethanol-water mixture (5:1) was added a solution of $[Ag(LH)_2]ClO_4$ (1 mmol) in ethanol (10 cm^3) and the mixture was heated to reflux for 1 h. The solution was cooled and filtered through a G-4 sintered glass funnel. The filtrate was evaporated to dryness. The crude mass was then dissolved in CH_2Cl_2 and subjected to column chromatography on a silica gel column eluting with different mixtures of CH_2Cl_2-CH_3CN. A pink band

of $[Ru(pic)(LH)_2]^+$ was eluted with CH_2Cl_2-CH_3CN (5:1) followed by a brown band of $[Ru(LH)_3]^{2+}$ eluted with CH_2Cl_2-CH_3CN (3:2). These were evaporated and crystallized from CH_2Cl_2-C_6H_{14} (1:1). The compounds were obtained as solvates.

Yield:- $[Ru(pic)(L^1H)_2]ClO_4$: 35%

$[Ru(L^1H)_3](ClO_4)_2$: 25%

$[Ru(pic)(L^2H)_2]ClO_4$: 37%

$[Ru(L^2H)_3](ClO_4)_2$: 26%

(b) Conversion of $[Ru(L^1H)_3](ClO_4)_2$ to $[Ru(pic)(L^1H)_2](ClO_4)$.

To a solution of 0.25 mmol of $[Ru(L^1H)_3](ClO_4)_2$ in ethanol-water mixture (5:1) was added an aqueous solution of $AgNO_3$ (1 mmol in 5 ml. of water) and the mixture was heated to reflux for 2 h. It was then evaporated to dryness and subjected to column chromatography on a silica gel column eluting with different mixtures of CH_2Cl_2-CH_3CN as described in section (a). Yield:-

$[Ru(pic)(L^1H)_2](ClO_4)\cdot CH_2Cl_2$: 76%

$[Ru(L^1H)_3](ClO_4)_2\cdot H_2O$: 19%

(c) Reaction of cis-$RuCl_2(m\text{-}tap)_2$ and $[Ag(L^2H)_2]ClO_4$.

This reaction was similarly performed as the reaction described in section (a) starting from cis-$RuCl_2(m\text{-}tap)_2$ and $[Ag(L^2H)_2]ClO_4$.

Yield:- $[Ru(pic)(m\text{-}tap)_2]ClO_4$: 42%

$[Ru(L^2H)(m\text{-}tap)_2](ClO_4)_2$: 20%

(d)Conversion of $[RuL^2H)(m\text{-}tap)_2](ClO_4)_2$ to $[Ru(pic)(m\text{-}tap)_2]ClO_4$.

This was similarly performed as described in section (c) starting from $[Ru(L^2H)(m\text{-}tap)_2](ClO_4)_2$.

Yield:- $[Ru(pic)(m\text{-}tap)_2](ClO_4)\cdot CH_2Cl_2$: 85%

$[Ru(L^2H)(m\text{-}tap)_2](ClO_4)_2\cdot H_2O$: 9%

(e) Reaction of $[Ru(m\text{-}tap)_2(OH_2)_2]^{2+}$ and PicH was performed as described before.

(f) Reaction of $cis\text{-}RuCl_2(L^2H)_2$ and $[Ag(m\text{-}tap)_2]ClO_4$.

The above reaction was also similarly performed as described in section (a) starting from $cis\text{-}RuCl_2(L^2H)_2$ and $[Ag(m\text{-}tap)_2]ClO_4$.

Yield:- $[Ru(L^2O)(L^2H)(m\text{-}tap)]ClO_4$: 40%

$[Ru(m\text{-}tap)(L^2H)_2](ClO_4)_2$: 17%

F. Crystallography

Single crystals of $[Ru(pic)(L^1H)](ClO_4)\cdot CH_2Cl_2$ were grown at 298K by slow diffusion of hexane into dichloromethane solution of the compound. Diffraction measurements were carried out on a Nonius CAD4 fully automated four-circle diffractometer. The unit cell was determined and refined using setting angles of 25 reflections, with 2θ angles in the range 11.60 to 20.82°.

The unit cell dimension are listed in Table VII.6. Data were collected by θ-2θ scans within the angular range 3-45^{o}. All data reduction and structure refinement were performed using the NRCC-SDP-VAX packages. The structure was solved by the Patterson method. Final cycles of Least-square refinement converged with discrepancy indices of R_f = 0.045 and R_w = 0.035. Final positional parameters for selected atoms of the structure are contained in Table VII.7. Tables containing full listings of atom positions, anisotropic thermal parameters and hydrogen atom locations are available as supplementary material.

TABLE VII.1.a

Analytical Data of the Complexes

Compound	Formula	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
$[Ru(pic)(L^1H)_2]ClO_4.CH_2Cl_2$	$C_{31}N_5H_{26}O_6Cl_3Ru$	48.21	48.32	3.37	3.42	9.07	9.15
$[Ru(L^1H)_3](ClO_4)_2.H_2O$	$C_{36}N_6H_{32}O_9Cl_2Ru$	49.99	50.21	3.70	3.74	9.72	9.61
$[Ru(pic)(L^2H)_2]ClO_4.CH_2Cl_2$	$C_{33}N_5H_{30}O_6Cl_3Ru$	49.52	49.32	3.75	3.72	8.75	8.93
$[Ru(L^2H)_3](ClO_4)_2.H_2O$	$C_{39}N_6H_{38}O_9Cl_2Ru$	51.64	51.52	4.19	4.24	9.27	9.30
$[Ru(pic)(m\text{-}tap)_2]ClO_4.CH_2Cl_2$	$C_{31}N_7H_{28}O_6Cl_3Ru$	46.41	46.35	3.49	3.47	12.22	12.19
$[Ru(L^2H)(m\text{-}tap)_2](ClO_4)_2.H_2O$	$C_{37}N_8H_{36}O_9Cl_2Ru$	48.89	49.01	3.96	3.92	12.33	12.39
$[Ru(L^2O)(L^2H)(m\text{-}tap)]ClO_4.CH_2Cl_2$	$C_{39}N_7H_{36}O_5Cl_3Ru$	52.61	52.32	4.05	4.04	11.02	11.31
$[Ru(m\text{-}tap)(L^2H)_2](ClO_4)_2.H_2O$	$C_{38}N_7H_{37}O_9Cl_2Ru$	50.52	50.52	4.08	4.06	10.80	10.93

TABLE VII.1b

Solution Molar Conductivity Data[a,b] of the Complexes

Compound	Λ_M $ohm^{-1}cm^2\ mol^{-1}$	$\delta^c_{Me/ppm}$
$[Ru(pic)(L^1H)_2]ClO_4$	115	
$[Ru(L^1H)_3](ClO_4)_2$	210	
$[Ru(pic)(L^2H)_2]ClO_4$	120	2.15,2.05
$[Ru(L^2H)_3](ClO_4)_2.H_2O$	219	2.18,2.08
$[Ru(pic)(La)_2]ClO_4.CH_2Cl_2$	126	2.21,2.13
$[Ru(L^2H)(La)_2](ClO_4)_2.H_2O$	221	2.12,2.21
$[Ru(La)(L^2H)(LO)]ClO_4.CH_2Cl_2$	105	2.30,2.25,2.16
$[Ru(La)(L^2H)_2](ClO_4)_2.H_2O$	205	2.21,2.16

[a] Solvent : acetonitrile

[b] Solute concentration : 10^{-3} mol dm^{-3}

[c] In $CDCl_3$ using $Si(Me)_4$ as the internal standard.

TABLE VII.1c

Infrared Spectral Data of the Complexes

Compound	IR(cm^{-1})		
	$\nu_{C=O}$(carboxylic acid)	$\nu_{C=O}$(amide)	$\nu_{C=N}$
$[Ru(L^1H)_3](ClO_4)_2 \cdot H_2O$			1610
$[Ru(pic)(L^1H)_2]ClO_4 \cdot CH_2Cl_2$	1650		1610
$[Ru(L^2H)_3](ClO_4)_2 \cdot H_2O$			1610
$[Ru(pic)(L^2H)_2]ClO_4 \cdot CH_2Cl_2$	1650		1610
$[Ru(L^2H)(La)_2](ClO_4)_2 \cdot H_2O$			1600,1610
$[Ru(pic)(La)_2]ClO_4 \cdot CH_2Cl_2$	1660		1610
$[Ru(La)(L^2H)_2](ClO_4)_2 \cdot H_2O$			1595,1610
$[Ru(La)(L^2H)(LO)](ClO_4)_2CH_2Cl_2$		1620	1595

[a] In KBr disc.

TABLE VII.2

Selected bond distances (Å) and angles (deg) and their estimated standard deviations for $[Ru(pic)(L^1H)_2]ClO_4 \cdot CH_2Cl_2$

Ru-N1	2.046(5)	N2-C6	1.301(8)
Ru-N2	2.045(5)	N4-C18	1.316(8)
Ru-N3	2.048(5)	O1-C30	1.285(8)
Ru-N4	2.022(5)	O2-C30	1.225(8)
Ru-N5	2.079(5)	N2-C7	1.435(8)
Ru-O1	2.073(4)	N4-C19	1.435(8)
N1-Ru-N2	78.34(21)	N2-Ru-O1	87.29(18)
N1 Ru-N3	176.18(20)	N3-Ru-N4	78.91(21)
N1-Ru-N4	99.63(20)	N3-Ru-N5	90.37(20)
N1-Ru-N5	93.29(20)	N3-Ru-O1	93.83(19)
N1 Ru-O1	87.92(19)	N4-Ru-N5	95.60(20)
N1-Ru-N3	98.33(21)	N4-Ru-O1	171.27(19)
N2-Ru-N4	98.48(20)	N5-Ru-O1	79.47(18)
N2-Ru-N5	164.63(20)		

TABLE VII.3

Cyclic voltammetric data[a]

Compound	Metal-centred oxidation	Ligand-based reductions
	$E_{1/2}$/V(ΔE_p/mV)	$-E_{1/2}$/V(ΔE_p/mV)
$[Ru(L^1H)_2](ClO_4)_2.H_2O$	1.43(75)	0.93(90),1.16(100),1.49(110)
$[Ru(pic)(L^1H)_2]ClO_4.CH_2Cl_2$	1.00(75)	1.15(100),1.48(90)
$[Ru(L^2H)_2](ClO_4)_2.H_2O$	1.44(70)	0.90(90),1.19(110),1.52(110)
$[Ru(pic)(L^2H)_2]ClO_4.CH_2Cl_2$	1.00(80)	1.16(100),1.48(100)
$[Ru(L^2H)(La)_2](ClO_4)_2.H_2O$	2.00[b]	0.15(90),0.65(100),1.56(170)
$[Ru(pic)(La)_2]ClO_4.CH_2Cl_2$	1.56(70)	0.28(100),0.85(100),1.71(180)
$[Ru(La)(L^2H)_2](ClO_4)_2.H_2O$	1.81[b]	0.40(90),1.05(100),1.57(120)
$[Ru(La)(L^2H)(LO)]ClO_4.CH_2Cl_2$	0.98(70)	0.92(100),1.27(100)

[a]Cyclic voltammetric experiments were carried out in CH_3CN at 298K using 0.1 mol dm^{-3} NBu_4ClO_4 as supporting electrolyte and platinum as working electrode. The reported data correspond to scan rate v = 50 $mVs.^{-1}$

[b]Irreversible response, the potential corresponds to E_{pa}.

TABLE VII.4

UV/vis spectral data

Compound	Absorption[a] λ_{max} /nm (ϵ/dm^{3}mol^{-1}cm^{-1})
$[Ru(L^1H)_2](ClO_4)_2.H_2O$	480(13760), 445[b](10880), 300(25600), 270(25040)
$[Ru(pic)(L^1H)_2]ClO_4.CH_2Cl_2$	515(10950), 470[b](7300), 315(23400), 270(19040)
$[Ru(L^2H)_2](ClO_4)_2.H_2O$	480(14310), 445[b](11120), 315(27380), 270(25120)
$[Ru(pic)(L^2H)_2]ClO_4.CH_2Cl_2$	515(11100), 470[b](7180), 310(23 660), 265(19175)
$[Ru(L^2H)(La)_2](ClO_4)_2.H_2O$	515(7400), 490[c], 370(17270), 320(15790), 270(15800)
$[Ru(pic)(La)_2]ClO_4.CH_2Cl_2$	545(11980), 360(18620), 310(21250), 250[b](18200)
$[Ru(La)(L^2H)_2](ClO_4)_2.H_2O$	500(8700), 320(22960), 265(23540)
$[Ru(La)(L^2H)(LO)]ClO_4.CH_2Cl_2$	520(8850), 360[c], 315(23720)

[a] In CH_3CN.

[b] Shoulder.

[c] Ill defined shoulder

TABLE VII.5

Redox-Spectra correlation

Compound	$E_{1/2}$/V Metal oxidation	$-E_{1/2}$/V First ligand reduction	ΔE/V O'/Red	$\nu_{c.t.}$/cm^{-1}
$[Ru(L^1H)_2](ClO_4)_2.H_2O$	1.43	0.93	2.36	20833
$[Ru(pic)(L^1H)_2]ClO_4.CH_2Cl_2$	1.00	1.15	2.15	19417
$[Ru(L^2H)_2](ClO_4)_2.H_2O$	1.44	0.90	2.34	20833
$[Ru(pic)(L^2H)_2]ClO_4.CH_2Cl_2$	1.00	1.16	2.16	19417
$[Ru(L^2H)(La)_2](ClO_4)_2.H_2O$	2.00	0.15	2.15	19417
$[Ru(pic)(La)_2]ClO_4.CH_2Cl_2$	1.50	0.28	1.84	18348
$[Ru(La)(L^2H)_2](ClO_4)_2.H_2O$	1.81	0.40	2.21	20000
$[Ru(La)(L^2H)(LO)]ClO_4.CH_2Cl_2$	0.98	0.92	1.90	19230

TABLE VII.6

Crystallographic data for $[Ru(pic)(L^1H)_2]ClO_4 \cdot CH_2Cl_2$

Chem formula	$RuC_{31}H_{26}N_5Cl_3O_6$
fw	772.00
cryst system	Triclinic
space group	P-1
a, Å	11.3737(23)
b, Å	12.527(3)
c, Å	13.255(3)
α, deg	71.978(20)
β, deg	66.052(19)
γ, deg	75.476(18)
V, $Å^3$	1624.1
Z	2
D_{calc}, gm cm^{-3}	1.579
μ, cm^{-1}	7.028
cryst size, mm^3	0.05 x 0.05 x 0.30
λ, Å	0.7107
T, ^oK	298
R_f, R_w	0.045, 0.035
GOF	1.61

TABLE VII.7

Selected atomic parameters and B_{eq} for

$[Ru(pic)(L^1H)_2]ClO_4 \cdot CH_2Cl_2$

	x	y	z	U_{eq} [a]
Ru	0.31889(6)	0.31628(5)	0.24155(5)	2.71(3)
N1	0.4101 (5)	0.2377 (4)	0.1095 (4)	3.0 (3)
N2	0.5055 (5)	0.3476 (4)	0.1874 (4)	3.3 (3)
N3	0.2391 (5)	0.3927 (4)	0.3754 (4)	3.2 (3)
N4	0.3242 (5)	0.1814 (4)	0.3725 (4)	3.0 (3)
N5	0.1343 (5)	0.3068 (4)	0.2520 (4)	3.1 (3)
O1	0.2874 (4)	0.4641 (4)	0.1249 (4)	3.5 (3)
O2	0.1463 (5)	0.5650 (4)	0.0419 (4)	5.6 (3)
C6	0.5810 (6)	0.3240 (6)	0.0903 (5)	3.4 (3)
C18	0.2609 (6)	0.2019 (6)	0.4741 (5)	3.5 (4)
C30	0.1803 (6)	0.4815 (6)	0.1072 (6)	3.8 (4)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid

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Appendix

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