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

(S. Goswami)

Dated : Calcutta
the 29th August'96

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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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It is my pleasant duty to thank Dr. S. N. Mazumder, Dr. M. Bhattacharjee, Dr.R.N.Dutta Purkayastha,Dr.M.N.Bhattacharjee, Dr.P.C.Paul,Dr.C.R.Bhattacharjee,Dr.V.R.Rao,Dr.P.Srinivas,Dr. S.K.Chetri, Dr.B.Paul, Dr.S.Sarkar,Dr.P.Mathew, Mr.P.Sorkhel, Mr.G.C.Mandal, Mr.D.Dey,Mr.B.Paul, Mr.S.Deb,Mr.S.Purkayastha, Mr.A.Sharma for their cooperation and help during the tenure of my research work. I also wish to acknowledge with thanks the help rendered by Mr.K.N.Mitra and Mr.P.Mazumder.

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

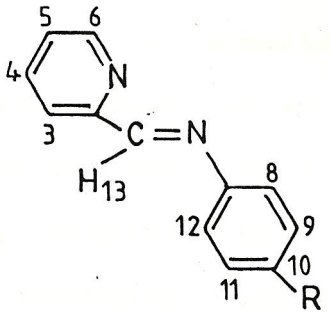
Abstract

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

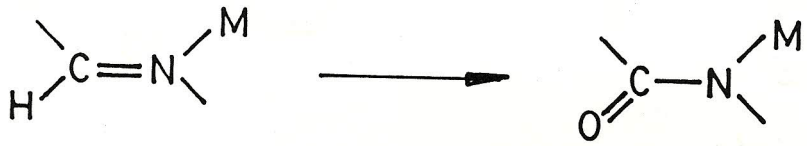
electronic transition energies, ΔE_1 and ΔE_2 ($\Delta E_1 > \Delta E_2$), have been computed using the observed g- values. The ΔE_2 transition in each of the complexes is observed in the range 6800-6155 cm^{-1} while ΔE_1 transition could not be observed due to solvent cut off.

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,

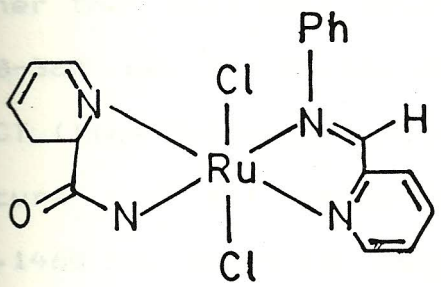
$$-CHO \xrightarrow{[O]} -COOH \xrightarrow{RNH_2} -CONHR,$$

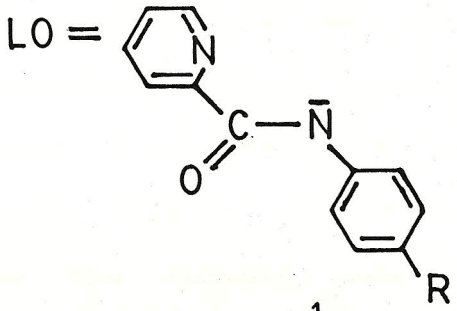


In the present work the conversion (equation 1) follows the reverse sequence,

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

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,

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

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

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

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.

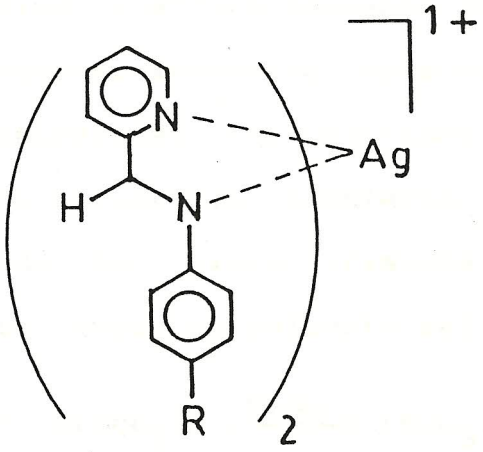
Silver nitrate reacts with boiling ethanolic solution of L(1) in the molar ratio of 1:2 to yield cationic $[AgL_2]^+$ (2), which has been isolated as a crystalline per chlorate salt

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

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(I). 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.

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

$$MCl_2 \cdot 6H_2O + 2AgL_2^+ \longrightarrow ML_3^{2+} + 2AgCl + L$$

Chapter VI describes a generalized synthetic route using silver(I) complexes of L 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 2.086 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.

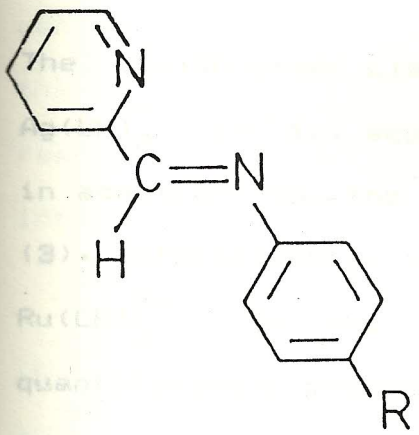
$$[Ru^{III}L_3]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_3]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_2(L^{\bullet})]^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$$

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

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 is also been reported.

The **Chapter VII** describes the synthesis of 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.



R=H : L^1H

R=Me : L^2H

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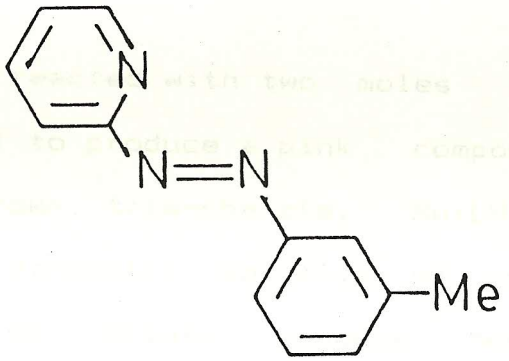

La

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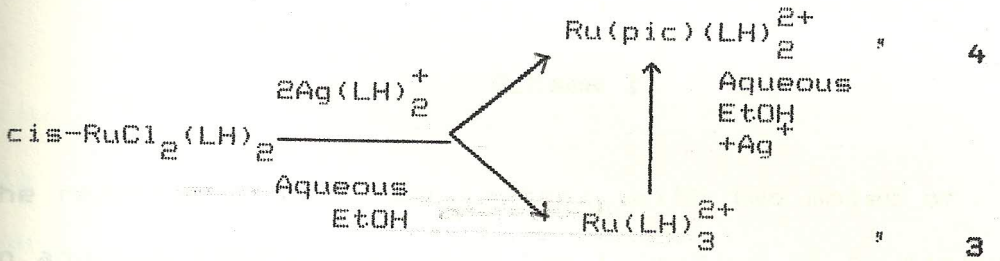
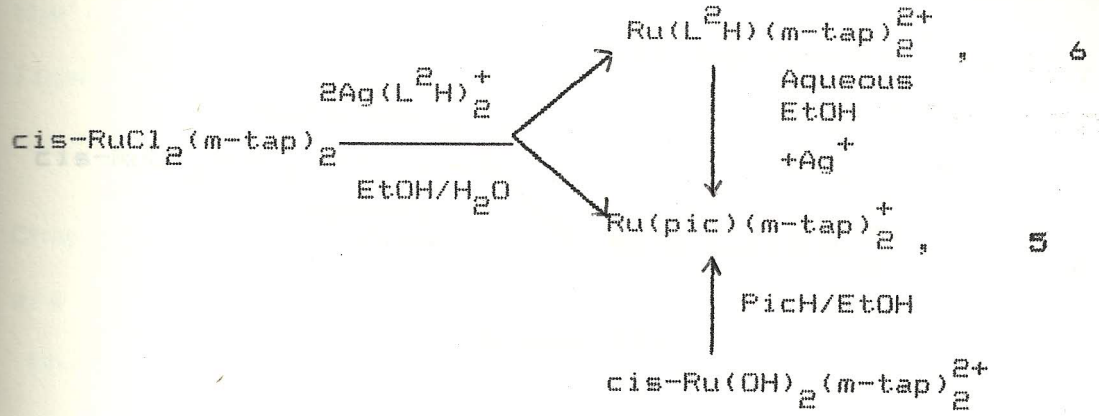
In the process of synthesizing mixed ligand chelated ruthenium complexes of **LH(1)** and 2-(m-tolylazo)pyridine (La,**2**) some interesting products were obtained along with the expected products which are elaborated below (Schemes I-III):



Scheme I

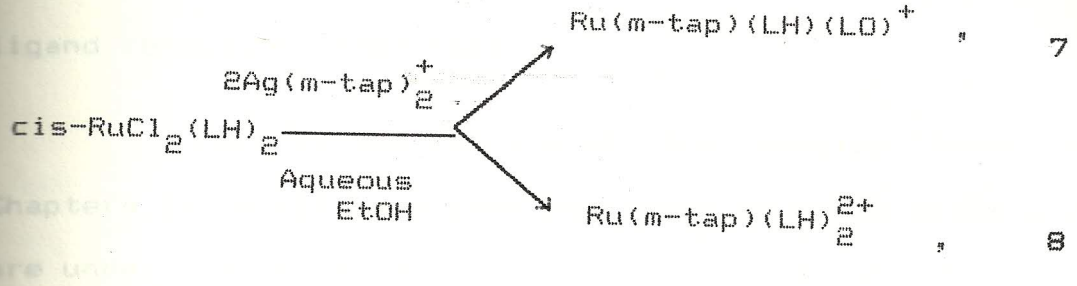
The bluish green cis-$RuCl_2(LH)_2$ reacted with two moles of $Ag(LH)_2^+$ in 1:1 aqueous ethanol to produce a pink compound in addition to the expected brown tris-chelate, $Ru(LH)_3^{2+}$ (**3**). Interestingly, an aqueous ethanolic solution of pure $Ru(LH)_3^{2+}$ in the presence of dilute aqueous $AgNO_3$ 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-$RuCl_2(m\text{-}tap)_2$ 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-$Ru(OH_2)_2(m\text{-}tap)_2^{2+}$ 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 $cis\text{-}RuCl_2(L^2H)_2$ 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.

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