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

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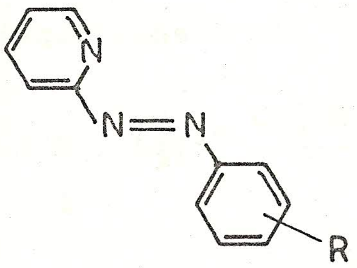
Abstract

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

ABSTRACT

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

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

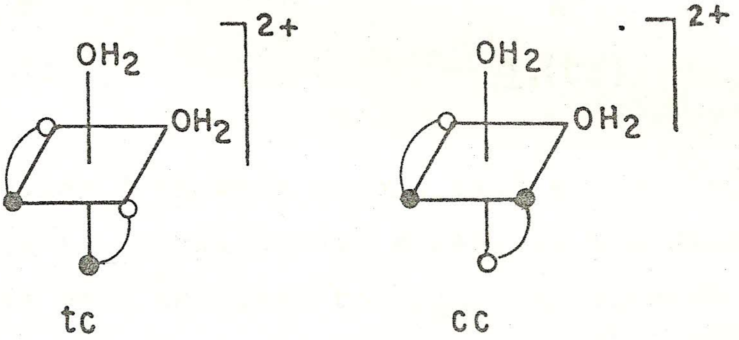


L

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

1

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



2

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

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

2

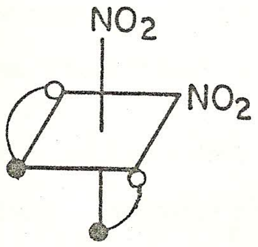
$$tc\text{-}[Ru(CH_3CN)_2L_2]^{2+} \xrightarrow{NO_2^-} tc\text{-}[Ru(NO_2)_2L_2] \quad (2)$$

3

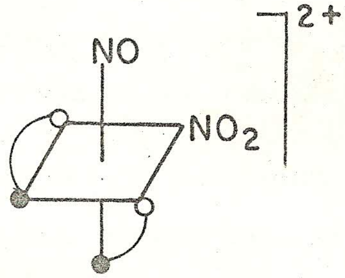
$$tc\text{-}[Ru(NO_2)_2L_2] \xrightarrow{H^+} tc\text{-}[Ru(NO)(NO_2)L_2]^{2+} \quad (3)$$

3 4

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



3,(tc)



4,(tc)

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

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

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

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

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

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

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

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

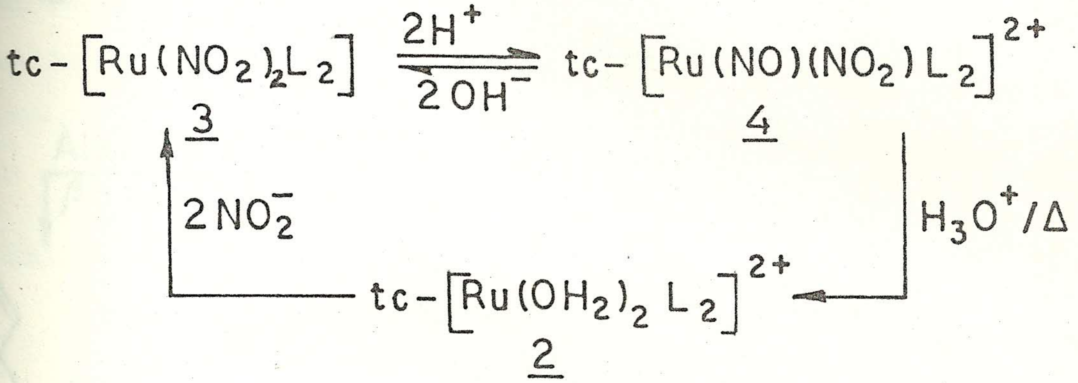
(i) Nucleophiles
(ii) Reducing agents.

(i) Nucleophiles

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

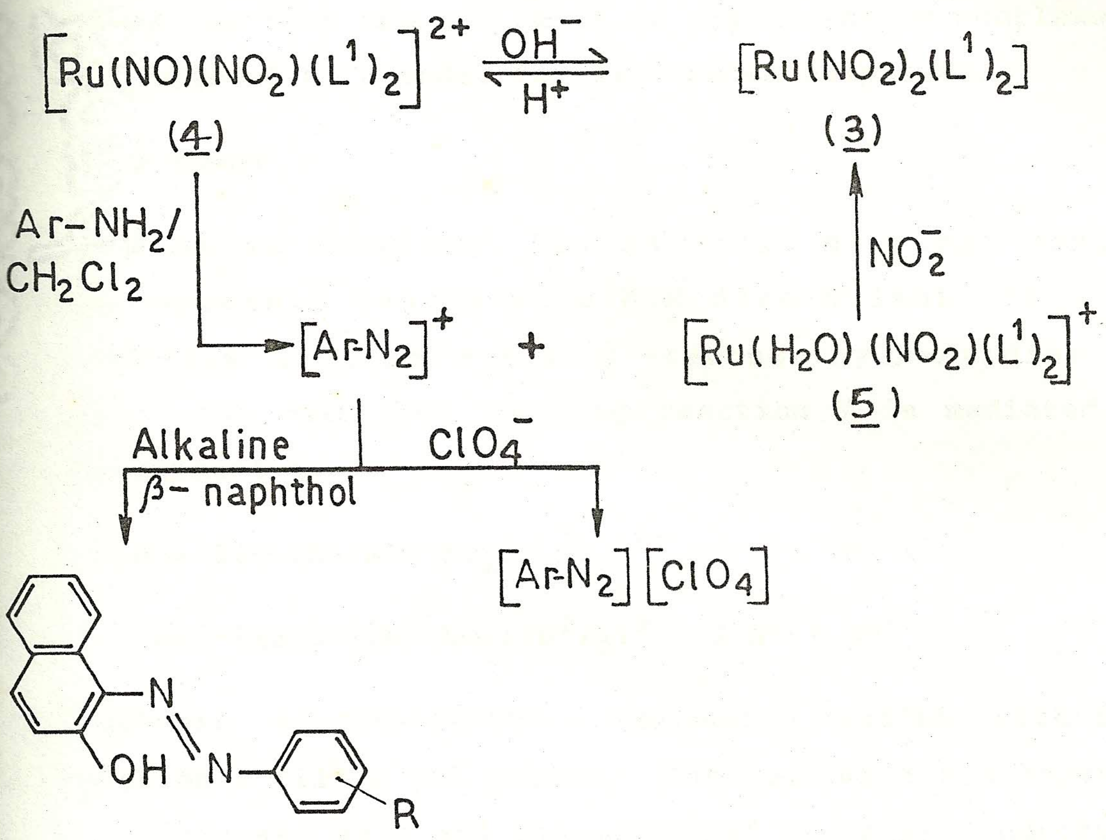
$$\underset{\mathbf{4}}{tc\text{-}[Ru(NO)(NO_2)L_2]^{2+}} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\mathbf{3}}{tc\text{-}[Ru(NO_2)_2L_2]} \qquad (6)$$

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



Scheme 1

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



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

Scheme 2

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

(2) Reductions

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

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

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

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

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

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

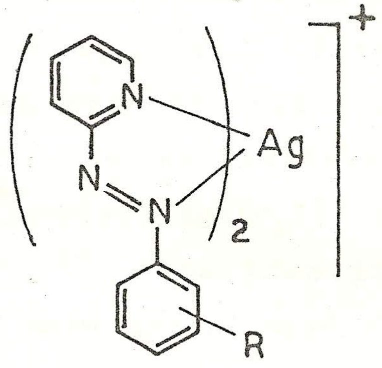
This reaction was followed cyclic voltammetrically.

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

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

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

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



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

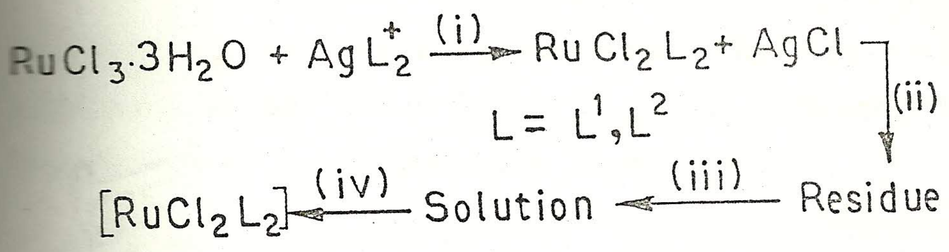
The stability of the silver complex in chloroform, methanol and acetonitrile have been verified by Beer's law. The complex is quite stable in methanol and chloroform whereas solutions of the complex in acetonitrile do not obey Beer's law.

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

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

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

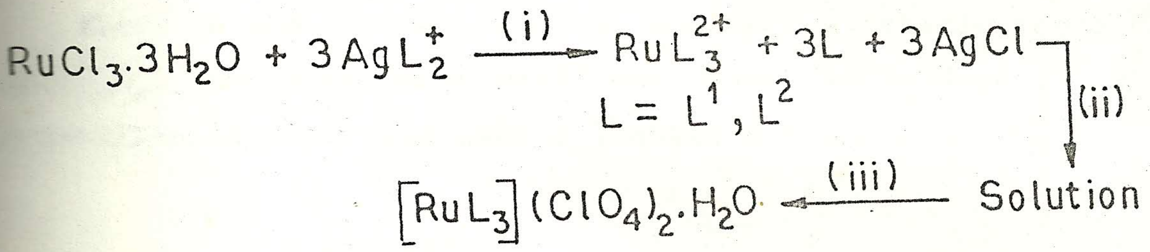
$$\mathit{tt}/\mathit{cc}\text{-}[RuCl_2L_2] \xrightarrow{\text{heat}} \mathit{tc}\text{-}[RuCl_2L_2] \qquad (10)$$



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

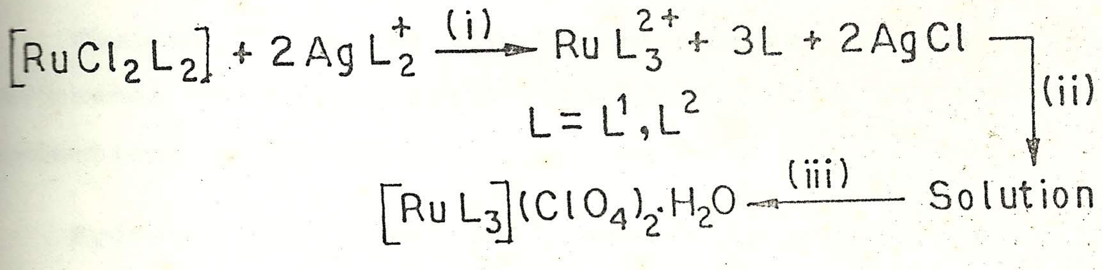
(iv) Filtration, Hexane

Scheme 3



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

Scheme 4



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

Scheme 5

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

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

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

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

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

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

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

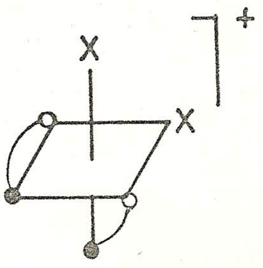
Chapter VI is the concluding chapter of the thesis. It addresses to the synthesis, characterisation and electrochemical reductions of new rhodium(III) complexes of L.

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

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

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

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



9

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

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

$$[RhCl_2L_2]^+ + e^- \rightleftharpoons [RhCl_2L^{\bullet}L] \tag{15}$$

$$[RhCl_2L^{\bullet}L] + e^- \rightleftharpoons [RhCl_2\dot{L}_2]^- \tag{16}$$

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

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

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

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