Synthesis, Characterization and Electrochemical Properties of Ru (II, III) Complexes DERIVE FROM Polyfunctional Disalicylaldehyde Malonoyldihydrazone

Dr. Jayanta Chakraborty[1], Dr. Subhendu Banik[2]
[1]*Associate Professor, Department of Chemistry,*
[2]*Associate Professor, Department of Mathematics,*
Tripura Institute of Technology, Narsingharh-799009, Tripura, India.

Abstract- **Ruthenium (II and III) complexes have been synthesized from reaction of $RuCl_3.3H_2O$ with salicylaldehydemalonoyldihydrazone (slmhH$_4$) in methanol medium under various experimental conditions. The composition of the complexes has been established from the data obtained from elemental analyses, thermo analysis and FAB mass spectra. The structural assessment of the complexes has been carried out based on data obtained from molar conductivity, magnetic susceptibility, electronic, IR and ESR, Electron transfer properties of the monometallic complexes have been studied using cyclic voltammetry technique.**

Index Terms- **Ruthenium, Monometallic, Spectral and disalicylaldehydemalonoyldihydrazone (slmhH$_4$)**

I. INTRODUCTION

Ruthenium atom is metal ion which has been selected for the purpose of studying the complex chemistry of the dihydrazones. It has been selected in the present study because of its extensive role in photocatalysis **[1-6]**, photochemistry, catalysis [**7, 2-3,8 -10**], biology **[11-13]** and electrochemistry **[14].** A significant body of research currently exploits, the synthesis of photoactive ruthenium compounds, for the study of their photo chemical, photo physical and electrochemical properties. These investigations have attempted to design and construct new ligand and their corresponding ruthenium complexes capable of performing useful light - induced function **[15].** In these Ru complexes a metal - to - ligand charge transfer (MLCT) state of Ru (II) moiety, (^{3}CT) Ru, is responsible for all its photochemistry.

Ruthenium atom is another metal ion which has been selected for the purpose of studying the complex chemistry of the dihydrazones. It has been selected in the present study because of its extensive role in photocatalysis **[1-6]**, photochemistry, catalysis **[7, 2-3, 8-10],** biology **[11-13]** and electrochemistry **[14].** A significant body of research currently exploits, the synthesis of photoactive ruthenium compounds, for the study of their photo chemical, photo physical and electrochemical properties. These investigations have attempted to design and construct new ligand and their corresponding ruthenium complexes capable of performing useful light - induced function **[15].** In these Ru complexes a metal - to - ligand charge transfer (MLCT) state of Ru (II) moiety, (^{3}CT) Ru, is responsible for all its photochemistry.

Material and method: Commercial grade ruthenium trichloride (1g) is activated by dissolving in concentrated HCl (5 mL) and then evaporating the solution to dryness at 100^0C on a steam bath. Pyridine, 3-picoline, 4-picoline, KOH, diethylmalonate, hydrazine hydrate, salicylaldehyde, were of Merck or equivalent grade and used as received. Malonoyldihydrazine was prepared by reacting diethylmalonate (1 mol) with hydrazine hydrate (2 mol). Disalicylaldehydemalonoyldihydrazone(slmhH$_4$.) was prepared by reacting a warm ethanol solution of malonoyldihydrazine(1 mol) with salicylaldehyde (2 mol) and was suction filtered, washed with ethanol and dried in vacuo (m.p 230°C) [found: C. 59.56; H, 4.64; N, 16.64]. Ruthenium in the complexes was determined by a standard literature method. Carbon, nitrogen and hydrogen were determined micro analytically. Molar conductance of the complexes 10^{-3}M dilution in CH_3OH solution were measured on a Direct Reading conductivity meter -303 with a dip type conductivity cell at room temperature. Infrared spectra were recorded on BOMEM DA-8 FT-IR spectrometer in the range 4000-450 cm^{-1} in KBr discs. The electronic spectra were recorded on a UV 2600 Double Beam UV-Vis Spectrophotometer. ESR spectra was recorded at X-band frequency on a Varian E- 112 X 1Q band spectrometer using DPPH (g=2.0036) as an internal field maker. The FAB mass spectra of complexes were recorded on a JEOLSX 102/DA-6000 mass spectrometer/ Data system using Argon/Xenon (6 KV, 10mA) as FAB gas.

II. PREPARATION OF COMPLEXES

Activation of $RuCl_3$. $3H_2O$

Commercial grade ruthenium trichloride (1g) is activated by dissolving in concentrated HCl (5 mL) and then evaporating the solution to dryness at 100^0C on a steam bath.

(1) Preparation of [Ru^{III}(slmhH$_4$) Cl$_2$] Cl. 0.5 H$_2$O (1)

Salicylaldehyde (0.93 g, 7.62 mmol) in methanol solution (20 mL) was added to $RuCl_3$. $3H_2O$ (1g, 3.82 mmol) and stirred for 10 mins followed by reflux for ½ h. The colour of reaction mixture changed from reddish to green. To this reaction mixture was added malonoyldihydrazine (0.5 g, 3.79 mmol) in methanol (20 mL) and refluxed for 1h. The solution was filtered in hot condition. Any undissolved residue was rejected. The filtrate was kept for crystallization. This precipitated green coloured compound, which was filtered, washed with methanol, ether and dried over anhydrous $CaCl_2$. Yeild: 1.60 g (76%).

(2) Preparation of [Ru^{III} (slmhH$_4$) Cl(py)]Cl$_2$ (2)

Salicylaldehyde (0.93 g, 7.62 mmol) in methanol solution (20 mL) was added to $RuCl_3.3H_2O$ (1g, 3.82 mmol) and stirred for 10 mins followed by reflux for ½ h. The colour of reaction mixture changed from reddish to green. To this reaction mixture was added malonoyldihydrazine (0.5 g, 3.79 mmol) in methanol (20 mL) followed by addition of pyridine (3.02 g, 38.2 mmol) and refluxed for 1 h. The solution was filtered in hot condition. Any undissolved residue was rejected by filtration. The filtrate was kept for crystallisation. This precipitated green coloured compound which was filtered, washed with methanol, ether and dreid over anhydrous $CaCl_2$. Yield: 1.58 g (66%)

(3) Preparation of [Ru^{II} (slmhH$_4$) Cl(A)] Cl [A = 3-pic, (3); 4-pic, (4)]

These compounds were obtained by following essentially the above procedure by adding simultaneously 3-picoline / 4-picoline to the solution after addition of dihydrazone to the salicylaldehyde and $RuCl_3.3H_2O$ solution. The green coloured complexes were isolated and collected as usual. Yield: 1.63 g (66.2%) (3); 1.62 g (64.9%) (4).

III. RESULT AND DISCUSSION

The colour, decomposition point, percentage yield and molar conductance of the complexes are set out in **Table 1.** The analytical and magnetic moment data for the complexes have been presented in **Table 2**. The electronic spectral data for the complexes have been presented in **Table 3** The composition of the complexes have been deduced based on the data obtained from elemental analysis and thermo-analytical data.

In order to isolate complexes, first preformed dihydrazones were allowed to react with $RuCl_3$. $3H_2O$ in CH_3OH either as such or in presence of pyridine bases under reflux. This, however, led to the precipitation of unreacted ligand which were confirmed by colour, and melting point. Hence, ruthenium complexes described in this paper were prepared by an alternative method. In this method, o-hydroxy aromatic aldehydes were refluxed with $RuCl_3$ in methanol for ½ h followed by addition of malonoyldihydrizine in CH_3OH. The resulting reaction mixture was further refluxed for 1½ h. This led to the precipitation of green coloured complexes. The preparation of the complexes is shown in the following schematic diagram.

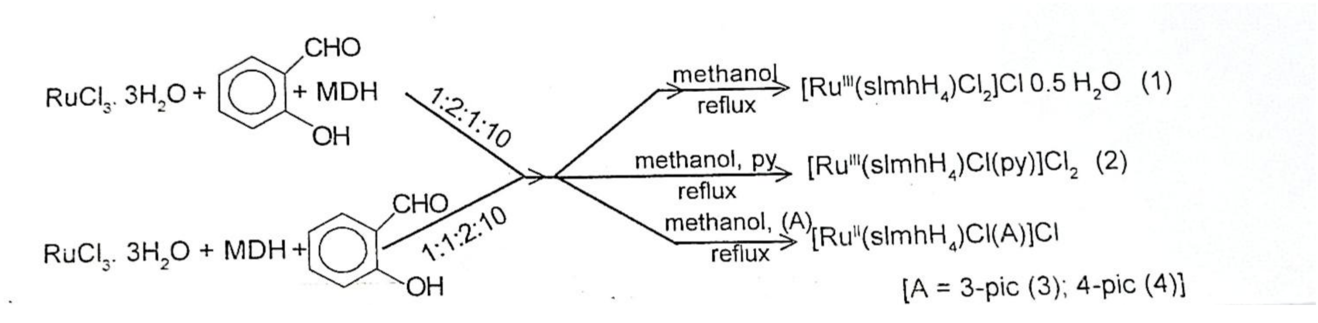

Fig:1

All of these complexes are dark green coloured. The complexes are polycrystalline. These complexes melt with decomposition in the temperature range 225 - 242^0 C. After 30-35 days, complexes melt at room temperature without change in colour. All of the complexes are highly soluble in solvents like CH_3CN, CH_3OH, acetone, ethanol, DMSO and DMF. However, the complexes are insoluble in solvents such as CCl_4, $CHCl_3$, ether and benzene.

Table 1 : Colour, Decomposition Point, Percentage Yield and Molar Conductance of Monometallic Ruthenium Complexes derived from Disalicylaldehyde malonoyldihydrazone (slmhH$_4$)

Complex	Colour	Decomposition point(^{0}C)	Yield(%)	Molar conductance **(Λ_M (ohm^{-1}cm^{2}mol^{-1})**
1.[Ru^{III}(slmhH$_4$)CI$_2$]Cl.0.5 H$_2$O	Dark green	225	76.0	63.5
2.[Ru^{III}(slmhH$_4$)CI(py)]Cl$_2$	Dark green	242	66.0	132.7
3. Ru^{II}(slmhH$_4$)CI(3-pic)]Cl	Dark green	240	66.2	63.9
4. Ru^{II}(slmhH$_4$)CI(4-pic)]Cl	Dark green	235	64.9	69.2

Table 2: Analytical data and magnetic moment data for the Monometallic Ruthenium Complexes Derived from Disalicylaldehyde malonoyldihydrazone(slmhH$_4$)

Elemental analysis found (calculated %)

complex	Ru	C	H	N	μ_B (BM)
1.[Ru^{III}(slmhH$_4$)CI$_2$]Cl.0.5 H$_2$O	18.71 (18.15)	37.01 (36.66)	3.21 (3.05)	10.16 (10.06)	1.78
2.[Ru^{III}(slmhH$_4$)CI(py)]Cl$_2$	16.34 (16.12)	42.02 (42.14)	3.42 (3.35)	11.02 (11.17)	1.76
3. Ru^{II}(slmhH$_4$)CI(3-pic)]Cl	16.61 (16.69)	45.32 (45.62)	3.87 (3.80)	11.63 (11.57)	dia
4. Ru^{II}(slmhH$_4$)CI(4-pic)]Cl	16.56 (16.69)	45.37 (45.62)	3.78 (3.80)	11.67 (11.57)	dia

Table 3: Electronic Spectral data of Ru(III) and Ru(II) complexes

Complex	λ_{max} (nm) (€$_{max}$ dm^{3}mol^{-1}cm^{-1})	assignment
1.[Ru^{III}(slmhH$_4$)CI$_2$]Cl.0.5 H$_2$O	630(630) 473(1460)	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$
2.[Ru^{III}(slmhH$_4$)CI(py)]Cl$_2$	640(200) 470(690)	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$
3. Ru^{II}(slmhH$_4$)CI(3-pic)]Cl	620(190) 440(1700)	$^1A_{1g} \rightarrow {}^1T_{1g}$ charge transfer
4. Ru^{II}(slmhH$_4$)CI(4-pic)]Cl	622(320) 430(1650)	$^1A_{1g} \rightarrow {}^1T_{1g}$ charge transfer

IV. THERMAL ANALYSIS

Thermal measurements (TGA and DTA) for monometallic ruthenium complexes nos. (1), (2), were carried out under N$_2$ atmosphere to give an idea about the suggested formula and the mechanism of decomposition. Thermogram and differential thermogram of the complexes no. (2) has been shown in **Figs: 2**

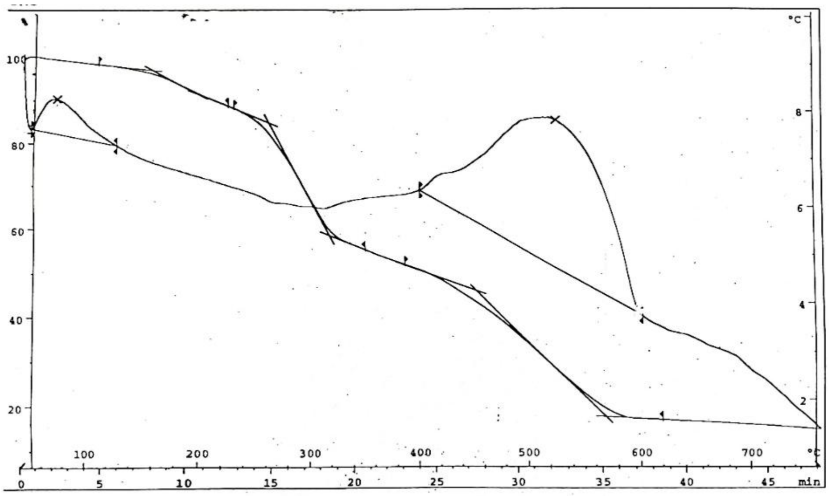

Fig:2.[Ru^{III}(slmhH$_4$)CI(py)]Cl$_2$ (2)

The recorded TGA for [Ru^{III}(slmhH$_4$)Cl$_2$]Cl 0.5 H_2O (1) displays an initial weight loss of 1.63% (theo,1.62%) in the 60^{0}C - 105^{0}C range which is in accord with the loss of 0.5 H_2O molecules and is likely to be due to hydration. This complex also displays three successive weight losses covering the range 188^{0}C - 213^{0}C, 295^{0}C-326^{0}C and 460^{0}C-527^{0}C respectively. The weight loss of 6.93% (theo,6.40%) in the range 188^{0}C-213 ^{0}C is due to one Cl atom in aggrement with the elemental analysis. The rest two ranges are due to pyrolysis of organic ligand. An exothermic peak marks the pyrolysis of the organic residue at 491^{0}C. The final product was found to be Ru_2O_3 [calculated 46.46% (theo, 44.92%)] which is also consistant with the +3 oxidation state of ruthenium. In TGA analysis, the ruthenium complex [Ru^{III}(slmhH$_4$)Cl(py)]Cl$_2$ (2) does not display any weight loss upto 160^{0}C indicating non existence of lattice water molecule. However, in the temperature range 167^{0}C - 207^{0}C, there was 5.45% (5.66%) weight loss. This weight loss may be due to removal of Cl atom. There are two successive weight losses covering the ranges 269 ^{0}C - 325 ^{0}C and 460 ^{0}C - 575 ^{0}C respectively. These two successive weight losses are due to loss of pyridine, N_2 and one Cl and pyrolysis of organic ligand. An exothermic peak at 532^{0}C marks the pyrolysis of the organic residue. The final product was found to be metallic ruthenium [residue 16.75% (theo, 16.12%)].

V. MASS SPECTRAL STUDY

The monometallic ruthenium complex (1), [Ru^{III}(slmhH$_4$)Cl$_2$]Cl.0.5 H_2O was characterized by FAB mass spectrometry .The FAB mass spectrum for the complex (1) has been shown in **Fig 3.** The mass spectrum of complex (1) in methanol shows a peak at m/z, 441 and 513 which may result from the formation of [Ru(slmhH$_4$]$^+$ and [Ru(slmhH$_4$) (Cl$_2$) + H]$^+$ respectively.

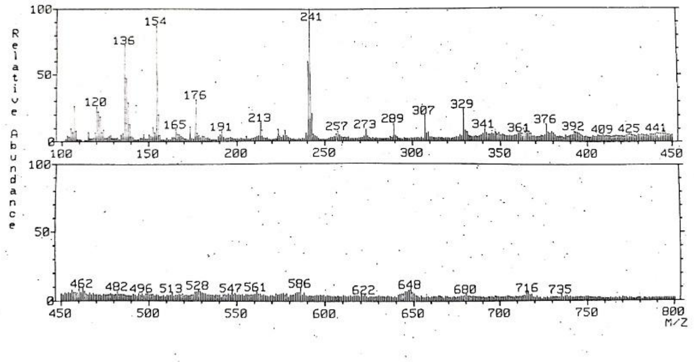

Fig 3: [Ru^{III}(slmhH$_4$)CI$_2$]Cl.0.5 H_2O (1)

The existence of the species in the mass spectra of this complex indicates their monomeric nature.

VI. MOLAR CONDUCTANCE

The molar conductance values [Table 1] for all of the complexes (1) to (4) at 10^{-3} (M) dilution in methanol solution fall in the region 63.5 - 70.2 ohm^{-1} cm^2 mol^{-1} in methanol except for the complex (2), which has molar conductance value of 132.7 ohm^{-1} cm^2 mol^{-1}

A comparison of experimental values of the molar conductance for the complexes with the literature values suggests that they are 1:1 and 1:2 electrolytes in methanol, respectively. Slightly lower values than that required for 1:1 and 1:2 electrolyte may be attributed to low mobility of cationic coordination sphere because of its large size.

VII. INFRARED SPECTRA

Some structurally significant IR bands for free dihydrazone and the monometallic complexes have been set out in Table 4. The IR spectra of the complexes nos. (1) has been shown in Fig 4. The ligand bands in the region 3450-3050 cm^{-1} due to νOH and ν NH become broad on complexation as compared to those in the free ligand. These bands are almost similar to those observed in salicylaldehyde and orthohydroxy acetophenone indicating the presence of OH groups in these complexes. The essential feature of these bands indicates the presence of hydrogen bonding in the complexes. However, it appears that the strength of the hydrogen bonding in the complexes is weakened as compared to that in the uncoordinated ligands. Further, these bands become broad, some times merging with the broad ν (OH) band. Because of such a feature of the ν (NH) band in the IR spectra of the complexes, we have refrained from drawing any conclusion regarding coordination of -NH group in bonding or otherwise.

Table 4: Important IR spectra of Monometallic Ruthenium Complexes Derived from Disalicylaldehyde malonoyldihydrazone($slmhH_4$)

Ligand/Complex	ν (OH)+ ν (NH)	ν (C=O)	ν (C=N)	AmideII+ ν (CO) (phenolic)	ν (C-O)	ν (N-N)	ν (M-O) (phenolic)	ν (M-N) (pyridine bases in-plane -ring and out of plane ring deformation	ν (M-Cl)
$slmhH_4$	3450(m) 3208(s) 3050(s)	1676(s) 1659(s)	1625(s) 1611(s)	1555(m)	1270(s)	1034(m)	-------	--------	----------
1.$[Ru^{III}(slmhH_4)Cl_2]Cl.0.5\ H_2O$	3424(s) 3214(sbr) 3066(sbr)	1720(m)	1603(vs)	1552(vs) 1546(vs) 1538(vs)	1272(s)	1035(m)	567(w) 502(w)	--------	344(s) 334(s)
2.$[Ru^{III}(slmhH_4)Cl(py)]Cl_2$	3448(vs) 3108(m) 3073(m) 3043(m)	1684(m) 1672(m) 1663(m)	1621(v) 1604(s)	1557(m) 1537(m) 1518(m)	1272(m)	1034(m)	562(w)	290(m) 631(w) 460(m)	321(s)
3. $Ru^{II}(slmhH_4)Cl(3\text{-}pic)]Cl$	3422(vs) 3277(sbr) 3087(m) 3024(m)	1685(s) 1675(m)	1618(s) 1600(s)	1558(m) 1519(m)	1275(m)	1034(m)	553(w)	287(m) 648(w) 465(w)	317(s)
4. $Ru^{II}(slmhH_4)Cl(4\text{-}pic)]Cl$	3450(s) 3280(sbr) 3100(m) 3060(m)	1680(s) 1670(m)	1620(s) 1605(s)	1555(m) 1525(m)	1281(s)	1038(m)	560(w)	290(m) 650(m) 470(w)	315(s)

In the IR spectra of all of the complexes (1) to (4) both the >C=O stretching bands are either unshifted in frequency or shifted to higher frequency as compared to those in the free ligand. Further, the intensity of these bands remains almost unaltered as compared to that in the free ligand. Such a feature associated with these bands is related to non coordination of both the >CO group to the metal centre.

The IR spectra of the ligand show two absorption band in1625 -1611cm^{-1} region which are assigned to ν>C=N stretching vibration. These bands retain their character as such and appear almost at the same position in the IR spectra of the complexes, albiet slightly modified in their position. Such a feature associated with ν>CN band is due to difference of bonded species (H^+ or M^{2+} or M^{3+}) to the >C=N group. This also indicates that the bonding between azomethine nitrogen atom and metal centre is weak. The IR spectra of dihydrazone contain one medium intensity band in the 1555 cm^{-1} region which assigned to [amide II + ν-C-O] (phenolic)]. These bands are split and undergo positive as well as negative shifts appearing in the region 1518 - 1558 cm^{-1}·The higher shift of one band indicates noncoordination of >C=O group to the metal centre while negative shift of the other band indicates coordination of phenolic C-O group to the metal centre.

The band appearing at 1270 cm^{-1} in the IR spectra of the uncoordinated ligands may be assigned to stretching vibrations of phenolic C-O group. This band remains almost unshifted in metal complexes indicating bonding through phenolate atoms albeit weak.

From the above discussion, it is evident that the ligand coordinate to the metal ion in keto form as neutral tetradentate ligand through azomethine nitrogen atoms and protonated phenolic oxygen atoms.

The far IR spectra of the complexes (1) to (4) show bands in the region 502-567 cm^{-1} **[16]** which are assigned to νRu-O (phenolic). However, the νRu-N band is masked by strong bands appearing in the region 315-344 cm^{-1} due to coordinated chlorine atom.

The free pyridine bases absorb at around ~650 and ~470 cm^{-1} due to in-plane-ring deformation and out-of-plane ring deformation modes, respectively **[17].** The corresponding band appears in the region 631-650 cm^{-1} and 460-510 cm^{-1} respectively in the spectra of the complexes suggesting the co-ordination of pyridyl ring nitrogen atom to the metal centre. The complexes (2) - (4), show a medium to strong intensity band in the region 287-290 cm^{-1}. This band is assigned to Ru-N stretching frequency due to coordination of pyridiyl ring nitrogen atom to the metal centre **[18].**

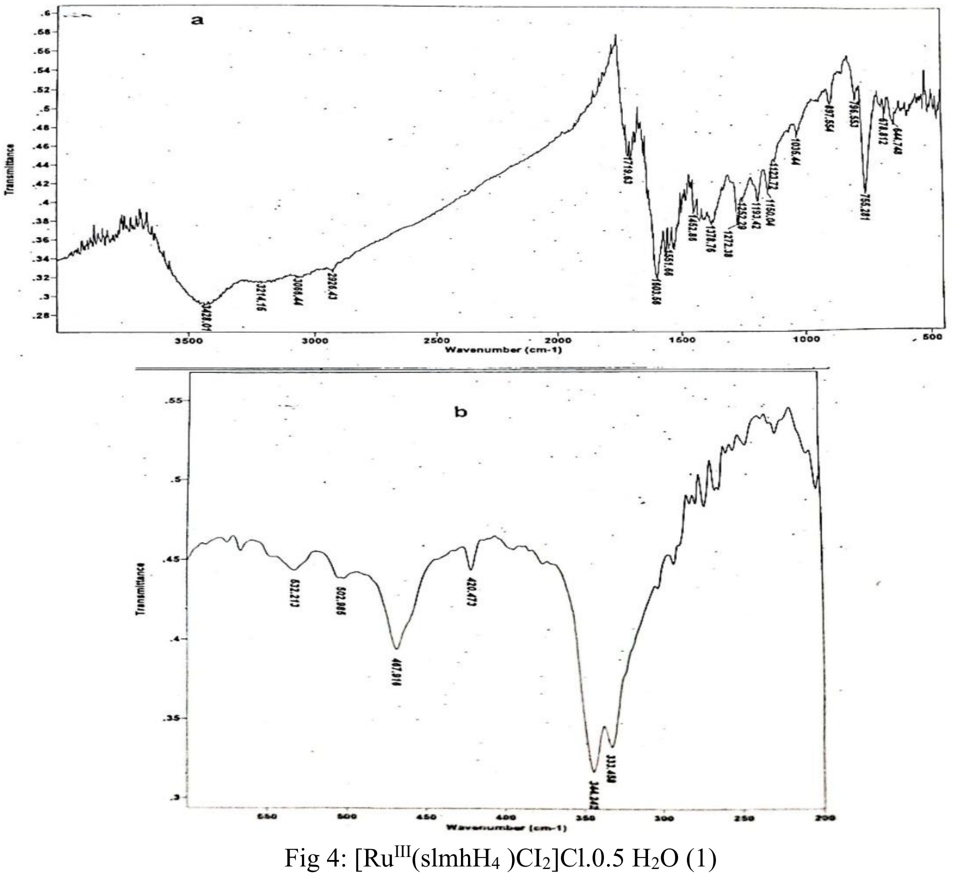

Fig 4: $[Ru^{III}(slmhH_4)Cl_2]Cl.0.5\ H_2O$ (1)

VIII. METAL-CHLORINE STRETCHING FREQUENCY

The metal-halogen stretching vibrations occurring in the low frequency regions, which can easily be identified, provide valuable information regarding the oxidation state and coordination number of the metal ion as well as the stereochemistry of the compound. The νM-X transition metal complexes is dependent upon a number of factors **[19, 20-21].** For example νM-X is lowered as the structure changes from T_d to O_h with the change in coordination number from 4 to 6. There may be two types of M-X bonds viz., terminal and bridging. In general, bridging νM-X modes occur at lower frequencies compared to terminal νM-X modes. If the other things are equal, the νM-X stretching frequency is observed at higher range as the oxidation state of the metal increases. For example, Fe - Cl stretching frequencies **[21]** of tetrahedral $FeCl_4^-$ and $FeCl_4^{2-}$ ions are 385 and 286 cm^{-1} respectively. Further, from low frequency IR spectra of the complexes, it is possible distinguish between cis and trans isomers. IR spectra of complex (1) shows two sharp stretches at 344 and

334 cm^{-1} which correspond to ν(Ru-Cl) and indicate a cis Ru-Cl_2 configuration **[22].** However for the other complexes (2) to (4) show a sharp vibration in the region 315-321 cm^{-1} which is assigned to the ν(Ru-Cl) stretch **[23].**

IX. MAGNETIC MOMENT

Magnetic susceptibility measurement show that the monometallic ruthenium complexes (1) and (2) are one electron paramagnetic [Table 2] which is in accord with the +3 oxidation state of ruthenium (low spin d^5, s=½) **[24].** Other monometallic ruthenium complexes (3) to (4) are diamagnetic indicating that ruthenium is in +2 oxidation state (low spin d^6, s=o) in these complexes **[25].**

X. ELECTRON SPIN RESONANCE SPECTROSCOPY

Electron spin resonance spectra of the complex (1) was recorded in methanol solution at LNT. The spectra of the complex (1) has been shown in Fig 5. This complex shows rhombic spectra with three distinct signals ($g_1 \equiv 2.422$, $g_2 \equiv 2.240$ and $g_3 \equiv 1.956$) in decreasing order of magnitude. The essential features of the spectra indicate that the distortion along the axial direction. The rhombic distortion can be thought of as a combination of axial and rhombic distortion.

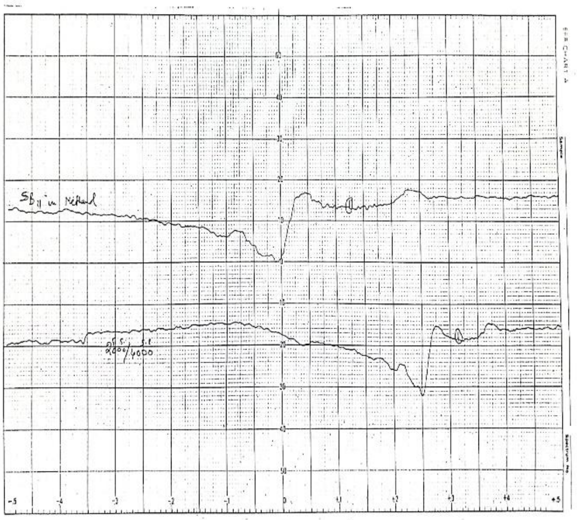

Fig 5: $[Ru^{III}(slmhH_4)Cl_2]Cl.0.5\ H_2O$ (1)

XI. ELECTROCHEMICAL PROPERTIES:

The electrochemical properties of the complexes (1) to (4) were studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. Voltametric data are presented in Table 5. and voltammogram for the complexes (2) is shown in Fig 6. The ruthenium (III) complex $[Ru(slmhH_4)Cl_2]Cl.0.5\ H_2O$ (1) does not show any oxidation- reduction responses on the positive side of Ag/AgCl electrode. However, the ruthenium (III) complex $[Ru(slmhH_4)Cl(py)]\ Cl_2$ (2) shows two voltammetric responses, an oxidative response on the anodic side and a reductive response on the cathodic side, which are, respectively, assigned to the ruthenium (III) - ruthenium (IV) and ruthenium (III)- ruthenium (II) couples.

$$[Ru^{III}(slmhH_4)Cl(py)]Cl_2 \leftrightarrow [Ru^{IV}(slmhH_4)Cl(py)]Cl_2^{+} + e \qquad (1)$$

$$[Ru^{III}(slmhH_4)Cl(py)]Cl_2 + e \leftrightarrow [Ru^{II}(slmhH_4)Cl(py)]Cl_2 \qquad (2)$$

The ruthenium (II) complexes (3) and (4) derived from disalicylaldehyde malonoyldihydrazone show a quasireversible anodic response near 0.38V and one irreversible cathodic response in the potential range -1.034 to -1.076V. The quasireversible anodic response near 0.38V are due to ruthenium(II)-ruthenium(III) oxidation process. The one electron nature of the couple has been established by the current height consideration. Since free ligand $slmhH_4$ exhibits ligand reduction at the potential ~(-0.98V), the observed reductions for complexes (3) and (4) within the range -1.034 to -1.076 V are therefore considered to be the reduction of the coordinated dihydrazone.

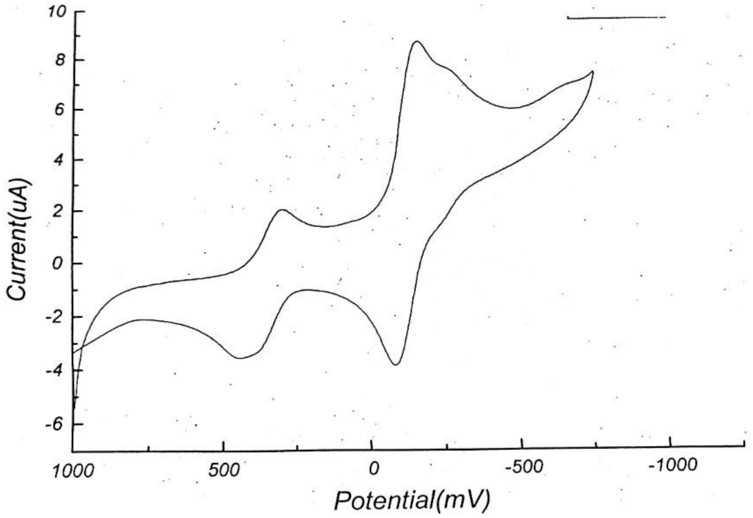

Fig 6: $[Ru^{III}(slmhH_4)CI(py)]Cl_2$ (2)

For complex (3) the responses due to Ru(II) - Ru(III) couple appears at 0.391 V. In the complex (4) the same oxidation couple appears at a lower potential value as compared to that in the complex (3).

The lower value of oxidation potential for the complex (4) than that of the complex (3) can be attributed due to coordination of substituted pyridine bases to the metal centre.

The electron donor capacity of the pyridine bases change in the order :

py < 3-picoline < 4-picoline.

Hence in the complex (4), increase in electron density over the ruthenium (II) centre lowers the oxidation potential. The complex (1) does not show any oxidation - reduction responses on the positive side of Ag/AgCl electrode. However, there are irreversible cathodic responses in the potential range -0.91 V of the complex. This reduction is considered to be the reduction of coordinated dihydrazone.

Table 5: **Cyclic Voltametric data**

Compound	**E_{RT}, mV (ΔE_P, mV)**	**- E_{pc} (mV)**
1. $[Ru^{III}(slmhH_4)Cl_2]Cl. 0.5 H_2O$	--	-910

Compound	**E_{RT}, mV(ΔE_P, mV)**	
	Ru^{III} - Ru^{IV}	Ru^{III} - Ru^{II}
2. $[Ru^{III}(slmhH_4)Cl(py)]Cl_2$	+365(127)	-139 (106)

Compound	**E_{RT}, mV(ΔE_P, mV)**	**E_{pc} (mV)**
	Ru^{II} - Ru^{III}	
3. $[Ru^{II}(slmhH_4)Cl(3\text{-pic})]Cl$	+391(80)	-1076
4. $[Ru^{II}(slmhH_4)Cl(4\text{-pic})]Cl$	+373 (76)	-1034

Solvent acetonitrile, supporting electrolyte, TBAP; Scan rate 100 mVs^{-1}; $E_{RT} = 0.5 (E_{Pa} + E_{Pc})$, where E_{Pa} and E_{Pc} are anodic and cathodic peak potentials, respectively.

$\Delta E_p = E_{Pa} - E_{Pc}$

XII. CONCLUSION

The study describes two Ru(III) complexes and two Ru(II) complexes derived rom slmhH4. All of the complexes are monomeric . The dihydrazones coordinates to the metal centre as a neutral tetradentate ligand through protonated phenolic oxygen atoms and azomethine nitrogen atoms in keto form in *anti-cis* configuration.

The complexes are suggested to have the structures shown in Figs. 7 - 9.

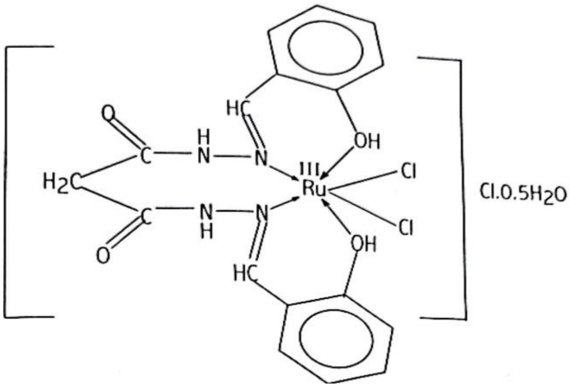

Fig 7:.[Ru^{III}(slmhH_4)CI_2]CI.0.5 H_2O (1)

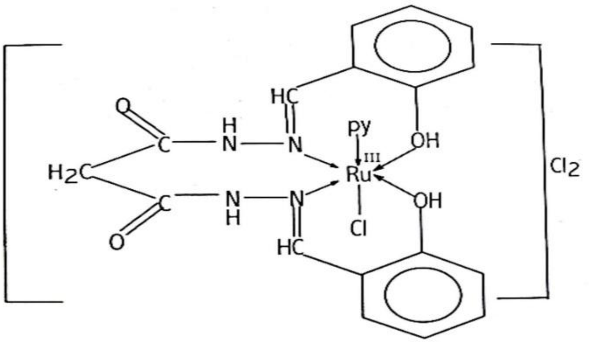

Fig 8: .[Ru^{III}(slmhH_4)CI(py)]Cl_2(2)

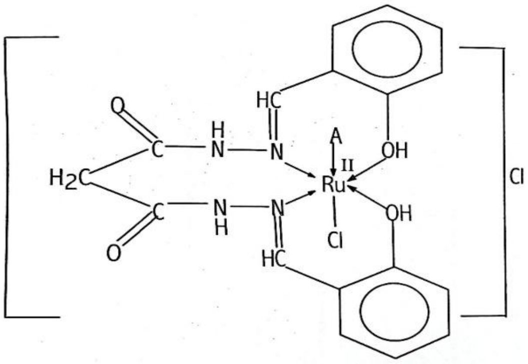

Fig 9: . Ru^{II}(slmhH_4)CI(A)]Cl **[A= 3-pic(3); 4-pic(4)**

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