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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF Ru(II) COMPLEXESDERIVE FROM BIS(2-HYDROXY-1-NAPHTHALDEHYDE)MALONOYLDIHYDRAZONE

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Abstract:

Ruthenium (II) complexes have been synthesized from reaction of $RuCl_3.3H_2O$ with bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone($napmhH_4$)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 ^{1}HNMR, Electron transfer properties of the monometallic complexes have been studied using cyclic voltammetry technique.

KeyWords:Ruthenium, Monometallic, Spectral and bis(2-hydroxy-1-naphthaldehyde) malonoyldihydrazone (napmhH4)

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.

Further, metal-catalyzed reactions have made a great contribution to the recent growth of organic synthesis and a variety of synthetic methods have been reported using mainly group 8 transition metal complexes in stoichiometric or catalytic amounts.

A survey of literature has disclosed that few ruthenium (II) complexes with monoacylhydrazones and monoaroylhydrazones have been reported **[16]**, yet it has failed to locate any study on ruthenium complexes of the dihydrazones.

In view of the above importance of ruthenium complexes and absence of work on the ruthenium complexes of the dihydrazones, it was of interest to synthesize ruthenium complexes of the bis(2-hydroxy-1-naphthaldehyde) malonoyldihydrazones and to characterize the resulting products. by various physico-chemical and spectral techniques. The stoichiometry of the complexes has been judged mainly from the elemental analysis and thermoanalytical data. The structure of the complexes has been discussed in the light of conductivity, magnetic moment, electronic, IR and ^{1}HNMR spectral studies. Electron transfer properties of the monometallic ruthenium complexes have been studied using cyclic voltammetric technique and discussed in this paper.

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^{0}C on a steam bath. Pyridine, 3-picoline, 4-picoline, KOH, diethylmalonate, hydrazine hydratewere of Merck or equivalent grade and used as received. Malonoyldihydrazine was prepared by reacting diethylmalonate (1 mol) with hydrazine hydrate (2 mol). In order to prepare bis(2-hydroxy-1-naphthaldehyde) malonoyldihydrazone(napmhH_4), malonoyldihydrazine (1.32 g, 10.0 mmol) in dilute ethanol (40 mL) solution was allowed to react with with 2-hydroxy-1-naphthaldehyde (4.40 g, 25.0 mmol) over hot plate at 70 ^{0}C with constant gentle stirring for about 30-45 min. The yellow polycrystalline precipitate **[17]**thus obtained was purified by repeated washing with hot ethanol and dried over anhydrous $CaCl_2$.

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. The FAB mass spectra of complexeswere recorded on a JEOLSX 102/DA-6000 mass spectrometer/ Data system using Argon/Xenon (6 KV, 10mA) as FAB gas. The stoichiometry of the complexes has been judged mainly from the elemental analysis and thermo analytical data. The structure of the complexes has been discussed in the light of conductivity, magnetic moment, electronic, IR and ^{1}HNMR spectral studies.

Electron transfer properties of the monometallic ruthenium complexes have been studied using cyclic voltammetric technique and discussed in this chapter.

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^{II} ($napmhH_4$)Cl(H_2O)] Cl (1)

Orthohydroxy napthaldehyde (1.45 g, 8.43 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 the reaction mixture was reddish. To this reaction mixture was added malonoyldihydrazine (0.5 g, 3.79 mmol) in methanol and refluxed for 1½ h. The solution was filtered in hot condition. Any undissolved residue was rejected by filtration. The filtrate was kept for crystallization. This precipitated green coloured compound which was filtered washed with methanol, ether and dried over anhydrous $CaCl_2$. Yield : 1.54 g (64.3%).

(2) Preparation of [Ru^{II} ($napmhH_4$) Cl (A)] Cl [A = py, (2); 3-pic, (3); 4-pic, (4)]

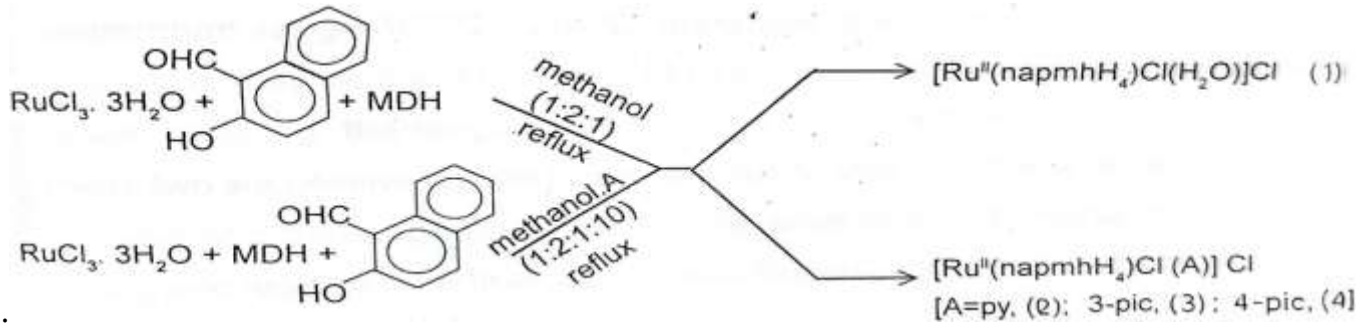
These compounds were obtained by following essentially the above procedure adopting for compound (5) by adding simultaneously pyridine bases to the solution after addition of dihydrazone to the orthohydroxy naphthaldehyde and $RuCl_3.3H_2O$ solution. The green coloured complexes were isolated which was found to have yield in the region 1.85 -1.74 g.

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 **Table2**. 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



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All of these complexes are dark green coloured.The complexes are polycrystalline. These complexes melt with decomposition in the temperature range 225 - 235^0 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 YieldandMolarConductance ofMonometallic RutheniumComplexes derived fromBis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone($napmhH_4$)

Complex	Colour	Decomposition point(^{0}C)	Yield(%)	Molar conductance **(A_M(ohm^{-1}cm^{2}mol^{-1})**
1.[Ru^{II}($napmhH_4$)CI(H_2O)]Cl	Dark green	230	64.3	70.2
2.[Ru^{II}($napmhH_4$)CI(py)]Cl	Dark green	235	69.6	68.9
3. Ru^{II}($napmhH_4$)CI(3-pic)]Cl	Dark green	227	65.4	65.7
4. Ru^{II}($napmhH_4$)CI(4-pic)]Cl	Dark green	225	65.2	68.4

Table 2: Analytical data and magnetic moment data for the Monometallic Ruthenium Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone($napmhH_4$)

Elemental analysis found (calculated %)

complex	Ru	C	H	N	μ_B (BM)
1.[Ru^{II}($napmhH_4$)CI(H_2O)]Cl	16.10 (16.03)	47.69 (47.62)	3.56 (3.49)	8.92 (8.88)	dia
2.[Ru^{II}($napmhH_4$)CI(py)]Cl	14.73 (14.03)	51.98 (52.09)	3.67 (3.62)	10.21 (10.13)	dia
3. Ru^{II}($napmhH_4$)CI(3-pic)]Cl	14.21 (14.33)	52.46 (52.76)	3.87 (3.83)	9.79 (9.93)	dia
4. Ru^{II}($napmhH_4$)CI(4-pic)]Cl	14.27 (14.33)	52.49 (52.76)	3.81 (3.83)	9.81 (9.93)	dia

Table 3: Electronic Spectral data of Ru(II) complexes derived from $napmhH_4$

Complex	λ_{max} (nm) (ϵ_{max} $dm^3mol^{-1}cm^{-1}$)	assignment
1.[Ru^{II}($napmhH_4$)CI(H_2O)]Cl	620(200) 406(1500)	$^1A_{1g} \rightarrow {}^1T_{1g}$ charge transfer
2.[Ru^{II}($napmhH_4$)CI(py)]Cl	645(220) 423(1825)	$^1A_{1g} \rightarrow {}^1T_{1g}$ charge transfer
3. Ru^{II}($napmhH_4$)CI(3-pic)]Cl	630(210) 424(1510)	$^1A_{1g} \rightarrow {}^1T_{1g}$ charge transfer
4. Ru^{II}($napmhH_4$)CI(4-pic)]Cl	632(220) 430(1530)	$^1A_{1g} \rightarrow {}^1T_{1g}$ charge transfer

Thermal Analysis:

Thermal measurements (TGA and DTA) for monometallic ruthenium complexes nos. (2) and (3) were carried out under N_2 atmosphere to give an idea about the suggested formula and the mechanism of

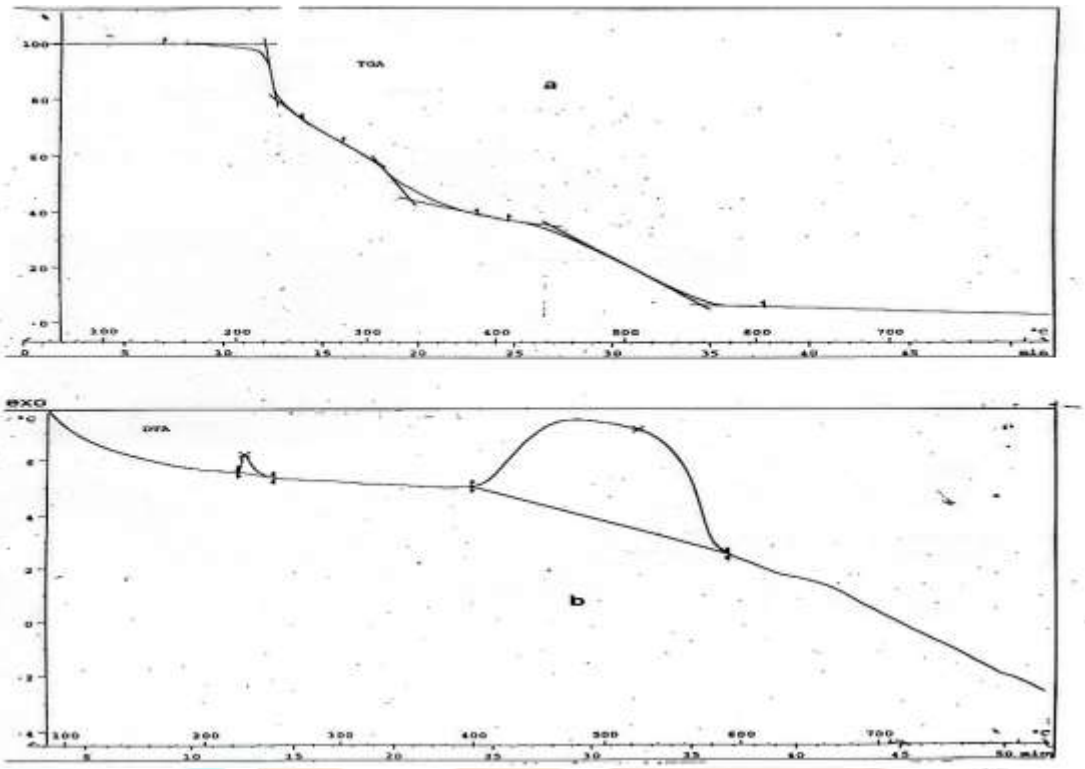

Fig:1. (a) and (b) $[Ru^{II}(napmhH_4)CI(py)]Cl$(2)

decomposition. Thermogram and differential thermogram of the complex no (2) has been shown in Fig:1

The ruthenium (II) complexes $[Ru^{II}(napmhH_4)Cl(py)]Cl$ (2) and $[Ru^{II}(napmhH_4)$ Cl(3-pic)]Cl (3) do not display any weight loss upto 220 ^{0}C indicating absence of lattice water molecule and coordinated water molecule in the complexes. However, weight loss of 19.96% (theo, 19.61%) occured in the range 220 ^{0}C - 237 ^{0}C for complex (6) may be due to removal of one chlorine atom and $2C_4H_2$ from ligand. DTA curve also indicated pyrolysis of ligand in this temperature range. Another weight loss of 11.73% (theo,11.43%) in the temperature range 314^{0}C - 338^{0}C may be due to loss of pyridine molecules. Further, weight loss displayed in the temperature range 448 ^{0}C- 564 ^{0}C may be due to major decomposition of ligand which is also confirmed from the exothermic peak marked at 532 ^{0}C. For complex (7) TGA curve displays 71% weight loss in the temperature range 220 ^{0}C - 282 ^{0}C which may be due to decomposition of major portion of the ligand.

Mass Spectral Study:

Electrospray mass spectrometry is a technique for the characterization of unstable species and intermediates in solution since it allows ions in solution to be transferred to the gas phase with minimal fragmentation **[18].** The mass spectrum of the complex (1) shows a peak at m/z 577.0, which may result from the formation of $[Ru(napmhH_4)\ Cl]^+$.However,for the complex(2),a peak at m/z 653.7 is observed

which may result from the formation of $[Ru(napmhH_4)Cl(py)-H]^+$. The existence of the species in the mass spectra of these complexes indicates their monomeric nature.

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

Molar Conductance:

The molar conductance values 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.

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.

^{1}H NMR Spectra:

Maki and coworkers **[19]** studied ^{1}H NMR spectra of a series of dihydrazones in DMSO-d_6. They assigned the broad signal in the region 11.13-11.72 ppm and 12.23-12.85 ppm to δ NH and δ OH protons, respectively. The signal in the region 8.40-8.80 ppm was assigned to azomethine protons whereas a multiplet in the region 7.10-8.10 ppm to phenyl protons by them. Lal and coworker **[20]** studied the ^{1}H NMR spectra of a series of disalicylaldehyde acyl and aroyl-dihydrazones in DMSO-d_6. They assigned the singlets in the regions 11.72-11.13 ppm, 11.27-11.13 ppm, doublets in the regions 8.31-8.90 ppm and multiplet in the region 6.67-8.20 ppm to phenolic-OH, secondary -NH, azomethine and phenyl protons, respectively.

Dey and workers have synthesized salicylaldehyde 4-methoxy benzoylhydrazone **[21]** and have assigned signals at 11.40 ppm and 12.90 ppm to NH and OH proton respectively.

Table 4: ^{1}HNMR spectra data(in δ) for Bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone($napmhH_4$) and some of its monometallic Ruthenium Complexes .

Ligand/complex	δ (-CH2-)	δ (naphthyl)	δ (CH=N-)	δ (NH)	δ (OH)
$napmhH_4$	3.29	6.98-8.23(m) 3.59	8.84 9.11(d,13 Hz)	10.67 10.80(d,3 Hz)	11.48((d,6 Hz)) 11.82(d,6 Hz)
1.$[Ru^{II}(napmhH_4)CI(H_2O)]Cl$	------	7.20-8.13(m)	8.65(d,9 Hz) 8.88(d,9 Hz)	10.00 10.78	11.68 12.16
2.$[Ru^{II}(napmhH_4)CI(py)]Cl$	------	7.15-8.48(m)	8.88(d,9 Hz) 9.18(d,9 Hz)	10.87 11.54	12.07 12.50
3. $Ru^{II}(napmhH_4)CI(3\text{-}pic)]Cl^a$	3.78 4.05	7.00-8.00(m)	8.90(d,10.5Hz) 9.23(d,10.5Hz)	10.79(d,6Hz) 11.58(d,6Hz)	12.06(d,4.5Hz) 12.50(d,4.5Hz)
4. $Ru^{II}(napmhH_4)CI(4\text{-}pic)]Cl^b$	3.95 4.10	7.15-8.55(m)	8.81(d,8 HZ) 9.32(d,8 HZ)	10.78(d,6Hz) 11.62(d,6Hz)	12.04(d,4 Hz) 12.52(d,4Hz)

a, δ CH_3 for 3- picoline, 2.51; b, δ CH_3 for 4- picoline, 2.58

The ^1H NMR spectrum of napmhH_4 has been recorded in DMSO-d_6 as it is insoluble in CCl_4 and $CHCl_3$. The ^1H NMR spectral data for the complexes have been presented in **Table 4**. The assignment of the signals has been made to various types of protons in the light of literature records. Two proton doublets observed at δ11.48, 11.82 ppm downfield of TMS have been assigned to δ OH protons. The signals observed at δ10.67 and 10.80 ppm are assigned to δNH protons while those at δ 8.84 and 9.11 to δ-CH=N protons, respectively. The multiplet appearing in the region δ 7.03-8.30 ppm has been assigned to naphthyl protons. The dihydrazone shows two signals at δ 3.29, 3.59 ppm assigned to active methylene group (-CH_2-). The appearance of active methylene protons **[22,23]** in the form of two signals suggests enolization of dihydrazone involving them. While the signal at 3.29 is attributed to arise due to methylene protons (-CH_2-), that at 3.59 ppm is atributed to methyne proton (=CH-). The multiplet due to aromatic protons appeared in the δ 6.98-8.23 ppm region.

The complexes (1) to (4) have been characterized by ^1H NMR spectroscopy. The spectra of the ligand and complexes (1) and (2) have been shown in Figs:2-3. The two proton doublets observed at δ 11.48 and 11.82 ppm in free dihydrazone assigned to d OH protons are downfield shifted on complexation. This indicates that the naphtholic -OH groups are not deprotonated even after complexation. The downfield shift of these signals indicates the decrease in electron density over the naphtholic -OH protons. This may result, most probably, from donation of electron from naphtholic OH oxygen to metal centre. The δ NH signals obsreved at δ 10.67 and 10.80 ppm are upfield shifted in the complex (1). This rules out the possibility of coordination of secondary amine nitrogen atom. However, in the remaining complexes the δ NH signals are downfield shifted. This may be due to drainage of electron density from secondary amine nitrogen atoms towards azomethine nitrogen atom during coordination. The complex (6) shows additional signal at 11.82 ppm. This may be attributed to arise due to enolic -OH group resulted from enolization of the complex in solution involving active methylene protons. It appears that this signal is merged with the δ OH and δ NH signals in other complexes in the region δ 10.00 - 12.50 ppm. The azomethine proton signals are downfield shifted in all the complexes except in the complex (1). In all the complexes the signal appear as doublets. Such a downfield shift of azomethine proton signal is caused by drainage of electron density from azomethine nitrogen atoms to the metal centre. However, the upfield shift of azomethine proton signal in the complex (1) indicates that the azomethinenitrogens also received electron density from bivalent metal.

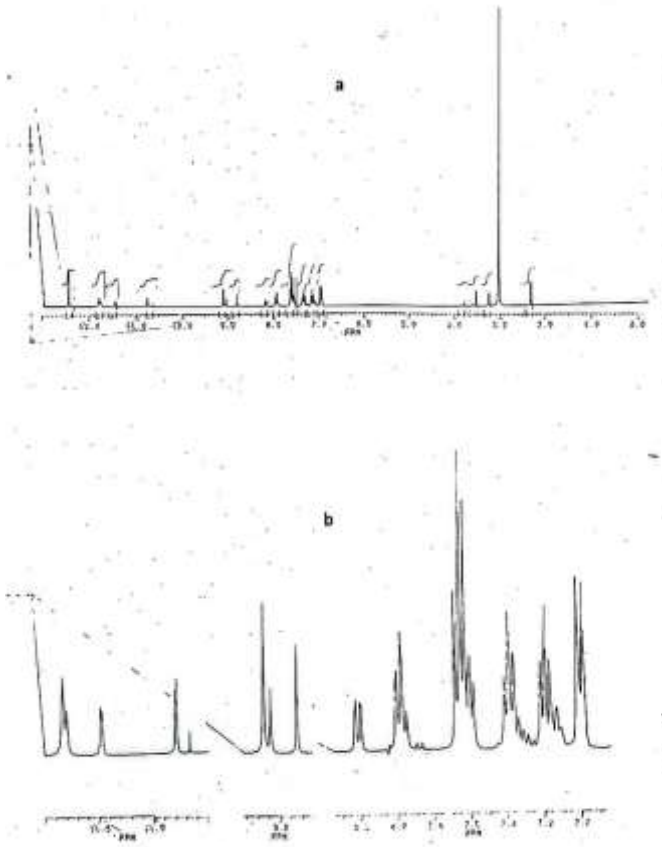

Fig.2. (a) and (b) Bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone

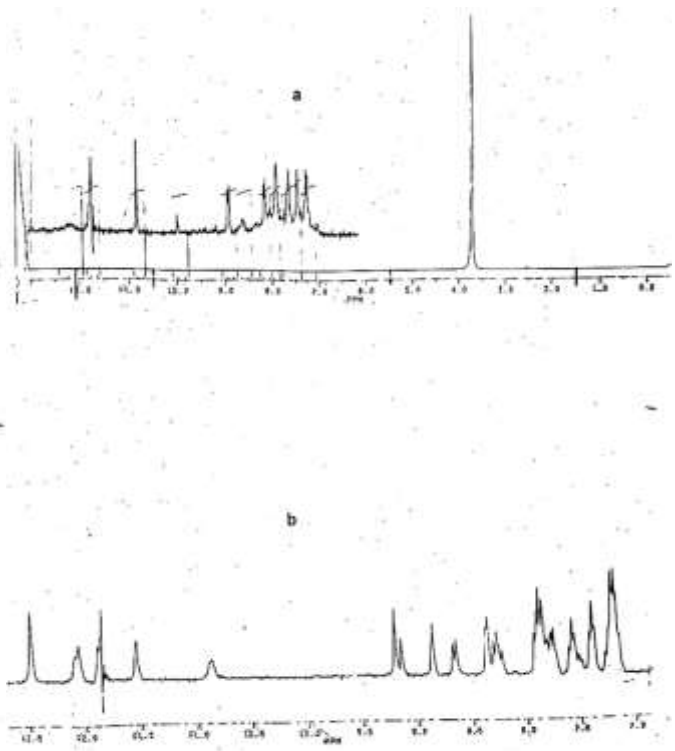

Fig.3.(a) [Ru^{II}(napmhH$_2$)Cl (H_2O)] Cl (1)

(b) [Ru^{II}(napmhH$_2$)Cl (py)] Cl (2)

It may be noted that the azomethine proton signal in the ^{1}H NMR spectra of the complexes (1) to (4) appears as a double. Such a feature of the ^{1}H NMR spectra of these complexes may be related to coordination of dihydrazone to the metal centre in the *anti-cis* configuration. In this configuration, both the azomethine nitrogen atoms and both the naptholic oxygen atoms of the same dihydrazone molecule are bonded to the same metal centre. This introduces steric crowding in the molecule asa resultof one hydrazone part attains axial position while other remains in the equatorial position. In this configuration, the axial azomethine protons absorb at lower field as compared to equatorial azomethine protons which absorbs at higher field. The appearance of doublet in the complexes is a clear indication of the coupling between axial and equatorial azomethine protons.

The pattern of the azomethine proton signals is asymmetric in nature in the complexes (1) to (4). This is the consequence of interchange between the two types of azomethine groups as a result of nitrogen inversion around the metal centre **[24].**

Another important feature of ^{1}H NMR spectra of the complexes is the down field shift shown by methylene protons which appear in the δ 3.75 - 4.10 ppm region although the possibility of interferences with these signals due to signal arising from water absorbed by DMSO-d_6 cannot be ruled out. These signals shift downfield by 0.15-0.20 ppm. Allof these pieces of evidences indicate that probably N_2O_2 coordination chamber is occupied by metal. This is possible only if the dihydrazone coordinates to the metal centre in the *anti-cis* configuration **[25].** This is also supported from the fact that the δ NH, δ OH signals in the complexes (3) and (4) and δ -CH=N signals in all of complexes appear in the form of doublets. Another point of interest

is the methylene proton signals which appear in the form of two resonances. This suggests that the complexes exist in *keto-enol* equilibrium in DMSO solution involving active methylene protons similar to that of free dihydrazone.

Methylproton signal appear at δ 2.32 and δ 2.37 ppm in free 3-picoline and 4-picoline molecules, respectively **[23, 26].** In metal complexes (3) and (4), these signals appear at δ 2.51 and δ 2.58 ppm respectively and thus downfield shifted by 0.19 ppm and 0.21 ppm respectively. This downfield shift is the result of drainage of electron density from Ru(II) atom to ring nitrogen atom which increases the electron density on ring nitrogen atoms making it more electronegative than that in free pyridyl ring.Consequently, ring nitrogen atom withdraws electrons towards itself. Hence, the electron density on all carbon atom decreases. While the decrease in electron density on 2 and 4 carbon atoms is maximum due to o-and p-directing influence, that on 3-carbon atom is minimum. Hence, the downfield shift of methyl proton in 4-picoline is more than that in 3-picoline. Further, two signals are observed in the downfield region in the ^{1}H NMR spectra of the complexes (2) to(4) which may be assigned to 2-pyridyl protons of pyridine, 3-picoline and 4-picoline molecules **[27].** This indicates that the signals due to 2-pyridyl protons of pyridine, 3-picoline and 4-picoline are downfield shifted. Such features associated with the 2-pyridyl protons of pyridine, 3-picoline, 4-picoline confirms flow of electrondensity from ring nitrogen atoms of these donor molecules.

Infrared Spectra:

Some structurally significant IR bands for free dihydrazone and the monometallic complexes have been set out in Table 5. The IR spectra of the complexes nos. (3) has been shown in Fig:4. The ligand band in the region 3600-3300 cm^{-1} due to nOH and n NH become broad on complexation as compared to those in the free ligands. These bands are almost similar to those observed in 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. The ligand bands in the region 3250-3000 cm^{-1} are split into more than two bands showing positive as well as negative shift on complexation

Table 5: Important IR spectra of Monometallic Ruthenium Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone($napmhH_4$)

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.

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 ligands. 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 ligands show two absorption band in1622 -1602cm^{-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

Ligand/Complex	ν (OH)+ ν (NH)	ν (C=O)	ν (C=N)	AmideII+ ν(CO) (naphtholic)	ν (C-O)	ν (N-N)	ν(M-O) (naphtholic)	ν(M-N) (pyridine bases in-plane -ring and out of plane ring deformation	ν (M-Cl)
$napmhH_4$	3467(sbr) 3211(sbr) 3019(sbr)	1684(vs) 1667(vs)	1622(s) 1602(s)	1545(m) 1538(m)	1282(s)	1032(m)	-------	--------	--------
1.[$Ru^{II}(napmhH_4)Cl(H_2O)$]Cl	3435(sbr) 3058(sbr)	1695(vs) 1665(vs)	1625(vs) 1599(vs)	1526(s) 1513(s)	1281(s)	1032(w)	557(w)	--------	323(s)
2.[$Ru^{II}(napmhH_4)CI(py)$]Cl	3462(sbr) 3198(sbr) 3095(sbr)	1689(s) 1676(s)	1624(s) 1600(s)	1553(w) 1530(w)	1281(m)	1032(w)	568(w)	299(m) 631(w)	337(s)
3. $Ru^{II}(napmhH_4)CI(3\text{-}pic)$]Cl	3462(sbr) 3187(sbr) 3067(sbr)	1692(s) 1670(s)	1625(s) 1598(s)	1555 1530	1280(w)	1035(w)	569(w)	287(m) 649(w) 501(m)	316(s)
4. $Ru^{II}(napmhH_4)CI(4\text{-}pic)$]Cl	3450(sbr) 3200(sbr)	1690(vsh) 1675(vs)	1620(s) 1600(s)	1549 1528	1281(m)	1032(w)	563(w)	290(m) 655(m) 510(m)	330(s)

associated with ν>CN band is due to differenceof 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 dihydrazones contain either one or two medium intensity band in the 1538-1545 cm^{-1} region which assigned to [amide II + ν-C-O] (naphtholic)]. These bands are split and undergo positive as well as negative shifts appearing in the region 1513 - 1558 cm^{-1} ,The higher shift of one band indicates noncoordination of >C=O group to the metal centre while negativeshift of the other band indicates coordination of phenolic C-O group to themetal centre.

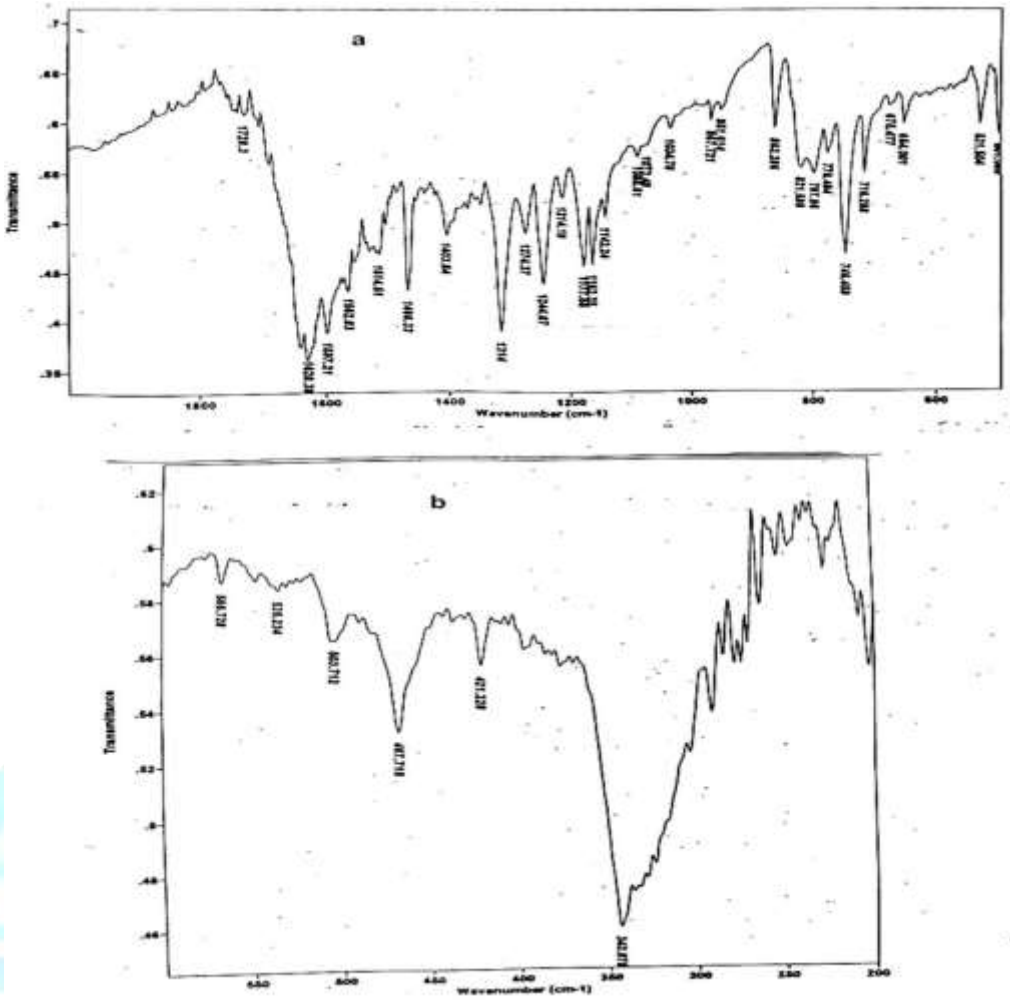

Fig:4. $Ru^{II}(napmhH_4)CI(3\text{-}pic)]Cl$ (3)

The band appearing at 1282 cm^{-1} in the IR spectra of the uncoordinated ligand may be assigned to stretching vibrations of naphtholic C-O group. This band remains almost unshifted in metal complexes indicating bonding through naphtholate atoms albeit weak.

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

The far IR spectra of the complexes (1) to (4) show bands in the region 557-569 cm^{-1}**[28]** which are assigned to νRu-O (naphtholic). However, the νRu-N band is masked by strong bands appearing in the region 316-337 cm^{-1} due to coordinated chlorine atom.

The free pyridine bases absorb at around ~604 and ~405 cm^{-1} due to (in-plane-ring deformation and out-of-plane ring) deformation modes, respectively **[29].** The corresponding band appears in the region 631-650 cm^{-1} and 501-510 cm^{-1} respectively in the spectra of the complexes suggesting the co-ordination of pyridyl ring nitrogen atom to the metal centre. The complexes (6) - (8) show a medium to strong intensity band in the region 287-299 cm^{-1}. This band is assigned to Ru-N stretching frequency due to coordination of pyridiyl ring nitrogen atom to the metal centre **[30].**

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 **[31, 32, 33].** 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 terminalνM-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 **[33]** 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 the complexes (1) to (4) show a sharp vibration in the region 316-337 cm^{-1} which is assigned to the ν(Ru-Cl) stretch **[34].**

Magnetic Moment:

Magnetic susceptibility measurement show that the monometallic ruthenium complexes (1) and (4) are diamagnetic indicating that ruthenium is in +2 oxidation state (low spin d^6, s=o) in these complexes **[35].**

Electrochemical Properties:

The electrochemical properties of the complexes (1) to (4) were studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. Voltammetric data are presented in Table 5.5 and voltammogram for the complexes (2) and (3) are shown in Fig: 5.

The ruthenium(II) complexes (2) to (4) derived from napmhH_4, which are stable in acetonitrile solution, show a reversible one electron oxidation on the positive side of Ag/AgCl (Table 6). This is assigned to the ruthenium (II) - ruthenium (III) oxidation equ. (1).

$$[Ru^{II}(napmhH_4)Cl(A)]Cl \rightleftharpoons [Ru^{III}(napmhH_4)Cl(A)]Cl^+ + e \text{ ----- (1)}$$

A = py(2); 3-pic (3); 4-pic (4)

The one electron nature of the couple has been established by the current height consideration. The D E_p values of these couples lie in the range 52-56 mV and the D E_p values do not change with change in the scan rate. The free ligand napmhH_4 exhibits ligand reduction at a potential of ~ (-1.002 V), the observed reductions for complexes (2) to (4) within the range -0.893 to -0.958 v are, therefore, considered to be the reduction of the coordinated dihydrazone.

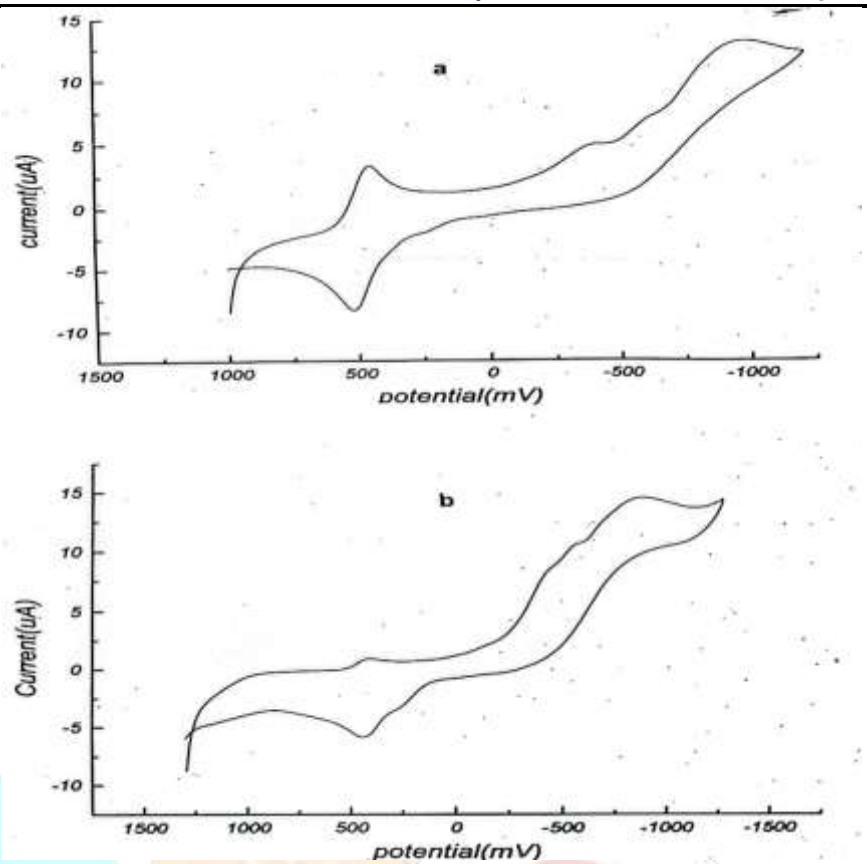

Fig:5 (a) Ru^{II}(napmhH_4)CI(3-pic)]Cl (2)

(b)Ru^{II}(napmhH_4)CI(4-pic)]Cl (3)

For the complexes (2) to (4) derived from napmhH_4, the responses due to Ru(II) - Ru(III) couple appear at 0.489, 0.417 and 0.397 V respectively.

The lower value of oxidation potential for the complexes(2) to (4) 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 (2), increase in electron density over the ruthenium (II) centre lowers the oxidation potential. The same holds true for the complexes (3) to (4).

The complexes (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 - -0.94V for the complex. This reduction is considered to be the reduction of coordinated dihydrazone.

Table 6 : Cyclic Voltammetric data

	Compound	E_{RT}, mV(DE_P, mV)	E_{pc} (mV)
		Ru^{II} - Ru^{III}	
1.	$[Ru^{II}(napmhH_4)$ Cl $(H_2O)]$ Cl	--	-940
2.	$[Ru^{II}(napmhH_4)$ Cl (py)] Cl	+489 (56)	-956
3.	$[Ru^{II}(napmhH_4)$ Cl (3-pic)] Cl	+417 (52)	-906
4.	$[Ru^{II}(napmhH_4)$ Cl (4-pic)] Cl	+397 (53)	-893

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.

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

Conclusion:

This paper describes four ruthenium (II) complexes derived from $napmhH_4$. All of the complexes are monomeric. The dihydrazone coordinates to the metal centre as a neutral tetradentate ligand through protonated naphtholic - OH oxygen atoms and azomethine nitrogen atoms in keto form in *anti-cis* configuration. The metal centres occupy N_2O_2 coordination chamber. In ruthenium (II) complexes, the methyl proton signals are shifted downfield as compared to that in the uncoordinated picolines. This downfield shift of the methyl proton signal has been attributed to the drainage of electron density from Ru (II) atom to pyridyl nitrogen atoms. This has also been confirmed from electronic spectra of the complexes which show high intensity charge transfer band. Ruthenium (II) complexes of $napmhH_4$ show reversible one electron oxidation on the positive side of Ag / AgCl electrode assigned to ruthenium (II)-ruthenium (III) oxidation.

The complexes are suggested to have the structures shown in Fig:6

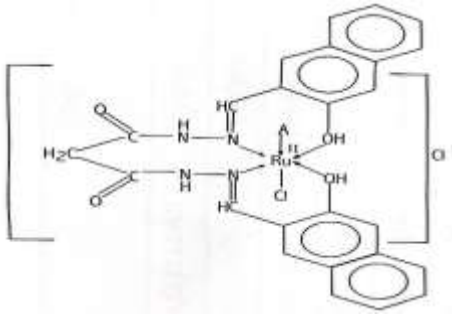

Fig:6 $[Ru^{II}(napmhH_4)$ Cl (A)] Cl

[A= H_2O (1); py (2); 3-pic(3); 4-pic(4)]

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