



Reaction of Cis-[RuCl₂ (DMSO)₄] with some Aromatic Thioamides (RCSNHCOR') in Presence Nitric oxide and Pyridine

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ABSTRACT

Reactions of RCSNHCOR' (R and R' are various types of group) with Cis - [RuCl₂ (DMSO)₄] in presence of nitric oxide and pyridine leads to the formation of new complexes of the type cis-[RuCl₂(NO)(RCSNHCOR')(py)]⁺. These cationic complexes were isolated as cis [RuCl₂(NO) (RCSNHCOR') (py)] PF₆ on reacting with NH₄PF₆. The complexes were characterised by elemental analysis, spectroscopic (Infrared, UV-Vis), conductometric and magnetic studies. An intense band at 1840-1850 cm⁻¹ appeared in all the complexes, suggesting a {Ru-NO}₆ type configuration of all these ruthenium nitrosyls presence of chloride ligand trans to NO and pyridine in plane have considerable change in properties of complexes.

keywords: Ruthenium complexes, Carbothioamides, Charge Transfer Band.

INTRODUCTION

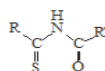
Activation of small molecules like CO, N₂, NO, CS etc. has gain considerable research interest during the past several years. Although the purpose of such investigation was mainly to get a clear understanding of the principal of coordination chemistry, the understanding of several natural processes could also be possible by such a study. NO is well known to play significant role in certain biological & physiological processes in human body as for example cardiovascular control, regulation of blood pressure and neurotransmission¹ etc. Ruthenium nitrosyl compound are known to release NO in aqueous medium under controlled process

and administration of the complexes reduces blood pressure more effectively than sodium nitropruside^{2,3}. The electronic properties of Ru-NO bond can further be modified by changing the coligands in the coordination sphere of ruthenium ion.^{4,5} In order to investigate such an effect, we propose to synthesize ruthenium nitrosyls in presence of aromatic thioamides (RCSNHCOR') and explore their electronic and structural properties. The object of choosing thioamides as ligands lies in the fact that changing R and R' will generally have more pronounced effect on stereochemistry, electronic structures and other properties of complexes. The studies may lead in a semiquantitative way to understand the electron charge distribution

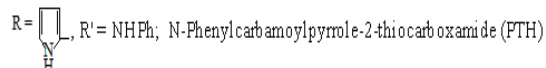
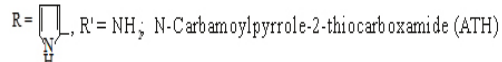
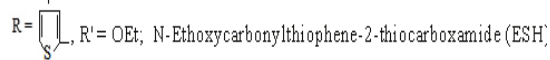
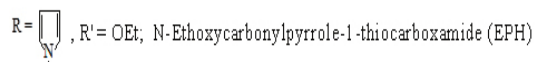
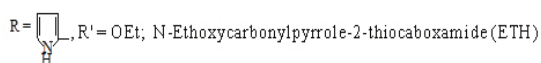


in Ru–NO fragment based on the sensitivity of aromatic carbothioamides and other ligands in the coordination sphere of ruthenium.

The coordinating ability of RCSNHCOR' is varied by changing R and R',^{6,7} so the various ligands used in present work are named and abbreviated as follows :



R = 4-Me C₆H₄, R' = OEt; N – Carboethoxy-4-toluene thiocarboxamide (CTH)



MATERIAL AND MEASUREMENTS

The chemicals used were either chemically pure or AR grade. All the experiments were performed under pure and dry N₂ atmosphere. RCSNHCOR' and cis-[RuCl₂(DMSO)₄] were prepared by the known method⁸⁻¹¹. The starting material RuCl₃·3H₂O was obtained by treating commercially available RuCl₃·xH₂O several times with concentrated HCl. DMSO, acetone, chloroform dichloromethane and diethyl ether were purified dried by standard techniques and freshly distilled before their use. Elemental analysis (C,H and N) were carried out by micro analytical section of B. H. U., Varanasi (U.P), India. Standard methods^{12,13} of analysis were performed to estimate sulphur, chloride, fluoride and phosphorous. Infrared spectra (4000–250 cm⁻¹) of all the ligands and complexes were recorded in KBr pellets by Perkin-Elmer FT IR spectrophotometer. Electronic spectra (200-900 nm) of ligands and complexes were scanned on cystronic 108 UV model spectrophotometer. Magnetic properties were studied by the help of a Gouy balance at room temperature. Melting points of complexes were checked on a Fisher-John melting point apparatus. Conductivity measurements were performed on CM-82 Elico conductivity bridge. NO

was prepared by adding concentrated H₂SO₄ on NaNO₂ and then passing it through a saturated solution of NaOH. The chemical identification of coordinated NO in resultant complexes was made by the reported methods.^{14,15}

Syntheses of Compounds

Cis-[RuCl₂(NO)(LH)(py)]PF₆

1mmol ethanolic solution (10 ml) of ligand LH (CTH, 0.24 g; or EPH, 0.22 g; or ESH, 0.22 g) was added slowly to an ethanolic solution (25ml) of Cis-[RuCl₂(DMSO)₄] (0.25 g~1 mmol) under N₂ followed by addition of pyridine (5ml). The resultant solution was refluxed for 1.5 h, reaching an orange-red colour of solution. This solution was cooled and reduced to 10 ml at low pressure a dry nitric oxide gas was bubbled for about 0.5 h where by the colour of solution changed to orange colour. A solution (10ml) of NH₄PF₆ (0.2 g~1 mmol) in CH₂Cl₂/MeOH mixture was added shaken well, and resultant solution was further reduced to 5 ml. Diethyl ether was added for the precipitation of orange solid product. It was filtered off, washed thoroughly with small quantity of water, diethyl ether and dried in vacuo.

Cis-[RuCl₂(NO)(LH)(py)]PF₆

1 mmol (0.25 g) of Cis-[RuCl₂(DMSO)₄] in 10 ml ethanol and a 10 ml ethanolic solution of LH (ATH, 0.18 g, or ETH 0.20 g) was refluxed for 2 h under N₂ and cooled [RuCl₂(DMSO)₄] under N₂. Next pyridine (5 ml) was added and resultant solution was stirred for about 30 min. and nitric oxide was bubbled for 30 min. while stirring was continued on addition of 10 ml NH₄PF₆ (0.2g~/mmol in CH₂Cl₂/MeOH mixture) solution the orange-red solid that precipitated was filtered off, washed thoroughly with small quantity of water, diethyl ether and dried in vacuo.

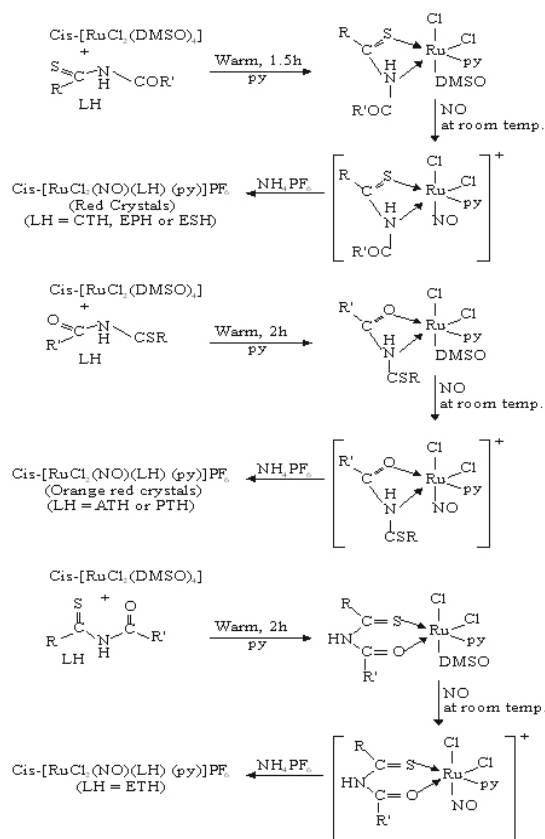
Cis-[RuCl₂(NO)(PTH)(py)]PF₆

1mmol of ligand (~0.25g) was taken in 50 ml warm DMF and stirred for 30 min. whereas an orange turbid solution was obtained. It was filtered, cooled and solvent was removed at reduced pressure to give a 10 ml of ligand solution. Next, this solution was slowly added to continuously stirred solution (10 ml) of [RuCl₂(DMSO)₄] (0.25g~1 mmol) in ethanol followed by addition of pyridine (5 ml). Nitric oxide gas was bubbled for 30 min. and addition of a

solution (5 ml) of NH_4PF_6 (0.2g ~1 mmol in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ mixture) a red brown solid was precipitated. It was filtered, washed with small quantity of H_2O , Et_2O and dried in vacuo.

RESULTS AND DISCUSSION

Starting from $\text{Cis-}[\text{RuCl}_2(\text{DMSO})_4]$ precursor, addition of ligand RCSNHCOR' followed by adding few drops of pyridine and passing NO gas in the resultant solution yielded a set of new nitrosyl complexes containing RCSNHCOR' as a subsidiary ligand.

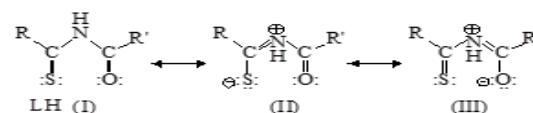


All the compounds are diamagnetic and soluble in CH_2Cl_2 , $(\text{CH}_3)_2\text{CO}$ and H_2O . The analytical data (Table 1) suggest that RCSNHCOR' acts as bidentate in all the complexes. The molar conductance of the prepared complexes was carried out in dichloromethane and results are 1:1 type compounds. The spectroscopic features (IR, UV and visible) and magnetic measurements are in good agreement with proposed formulations of complexes.

Spectroscopic Characterization

In the spectra of complexes the $\nu(\text{NO})$ bands are very close to 1840-1850 cm^{-1} suggesting that NO group in all the complexes are indeed the $\{\text{Ru}(\text{I})-\text{NO}^+\}$ type¹⁶⁻¹⁸. This idea is brought out from molecular orbital approach, which emphasizes the extremely important role of π^* MO of NO in charge transfer from $d\pi$ orbital of metal. Further, the $d\pi$ charge transfer from metal to π^* MO of NO is enhanced when chloro ligand is present trans to NO. The observed stretching frequencies of NO in complexes are in good agreement with the structural trans effect of chloro ligand.

RCSNHCOR' may exhibit three resonance structures as follows



Although I is the preferential structure of the ligand but II and III may also exist under certain condition irrespective of fact that ligand acts as a bidentate or monodentate, it can coordinate with metal ion through any two or one of the three potential donor sites viz, imido N, thiocarbonyl sulphur or carbonyl oxygen atom. The possible mode of coordination of ligands (LH) has been arrived at on the basis of following IR spectral studies. The characteristic IR bands of pyrrole, thiophene and aromatic ring do not undergo any shift in the spectra of complexes (maximum shift $\pm 5 \text{ cm}^{-1}$), indicating as expected, non involvement of pyrrole ring nitrogen, thiophene ring sulphur and aromatic ring in bond formation with metal. In case of bonding through $-\text{C}(\text{S})\text{NHC}(\text{O})-$ moiety of ligand, shift in positions of thioamide and amide bands are expected. The major shifts in these band positions are discussed below.

$\text{Cis-}[\text{RuCl}_2(\text{NO})(\text{LH})(\text{py})]\text{PF}_6$ (LH=CTH, EPH, ESH)

- Free ligand band of $\nu(\text{C}=\text{S})$ and those of thioamide band IV19 (contribution from $\nu(\text{C}=\text{S})$) undergoes downward shift with a decrease in intensity suggesting the bonding of ligand to metal ion through thio carbonyl sulphur atom.
- Thioamide I ($\delta\text{NH} + \nu(\text{C}=\text{N})$), II ($\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{S}) + \delta(\text{C}-\text{H})$) and III ($\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{S})$)

- band²⁰ (1000-1600 cm⁻¹) shifted to lower wave number (Table 2), suggesting the possibility of nitrogen atom of -C(S)NHC(O)- moiety in bond formation with metal ion.
- (iii) The free ligand band due to $\nu(\text{CO})$ shifted to higher wave number, suggesting the non involvement of CO group in coordination with metal ion.
- (iv) Complexes exhibit an intense absorption band at 1840 cm⁻¹, assignable to $\nu(\text{NO})$ ²¹.
- (v) The new bands around 360-480 cm⁻¹ in the spectra of complexes are assigned to coupled vibrations of $\nu(\text{M-S})$ with other bonding modes of ligand molecule.
- (vi) A weak band²² at around 600 cm⁻¹ in IR spectra of all the complexes is assigned to $\nu(\text{Ru-NO})$ vibrations.
- (vii) The characteristic band of pyridine²³ due to C=C and C=N stretching (in ring) (1430-1600 cm⁻¹) shifted to lower wave number (± 15 cm⁻¹), suggesting the coordination of pyridine molecule to metal ion.
- Based on the above IR spectral observation of complexes and its comparison with free ligand, the bonding of LH occurs, possibly through N and S donor atom.

Cis-[RuCl₂(NO)(LH)(py)] PF₆
(LH = ATH, PTH)

- (i) The amide band I (1750 – 1680 cm⁻¹) which arises among to the normal coordinate having major²⁴ contribution from $\nu(\text{CO})$ Shifted to lower wave number on complexation with metal ion, indicating coordination through oxygen of the CO group.
- (ii) Thioamide band²⁴ II and III shift to lower wave number amide bands II and III shifted to higher wave number (± 15 cm⁻¹). This suggests the coordination through N and O atom of the ligands.
- (iii) $\nu(\text{C=S})$ and thioamide band²⁵ IV shifted to higher wave number, excluding the involvement of CS group in bond formation with metal ion.
- (iv) Presence of an intense band at 1850 cm⁻¹ in spectra of complexes, in assigned to stretching vibrate of coordinated NO molecule.
- (v) The broad bands around 430-520 cm⁻¹ in spectra of complexex may be assigned to coupled vibrations of $\nu(\text{Ru-N})$ with other

bonding mode of legand.

- (vi) A weak band at around 5.10 cm⁻¹ in IR spectra of complexes may be assigned to $\nu(\text{Ru-NO})$ mode of vibration²⁶.
- (vii) The characteristic bands of pyridine appeared at lower wave numbers (± 15 cm⁻¹) indicating the coordination of pyridine molecule to the metal ion.

Based on the above observations of IR spectral data, the bonding of ligand is concluded through nitrogen of imido group and oxygen of sulphur group (Table-2).

Cis-[RuCl₂(NO)(LH)(py)] PF₆
(LH = ETH)

- (i) The amide band I at 1775 cm⁻¹ which arises owing to $\nu(\text{CO})$ shifted to lower wave number (~ 40 cm), indicating the bonding of ligand through carbonyl oxygen bonding of metal ion (electron withdrawing group) with oxygen atom of carbonyl group of ligand will shift the position of thioamide bands I and II, amide band II and III and band due to $\nu(\text{CO})$ of the (COOEt) group towards higher wave number. The broad band at 1500 cm⁻¹ (thioamide band I and amide band II, 1310 cm⁻¹, 1260 cm⁻¹ (thioamide band II and amide band III) and at 1190 cm⁻¹ $\nu(\text{CO})$ of (C-OEt) shifted to higher wave numbers (~ 30 cm⁻¹) present in the spectrum of ligand. This further confirms the bonding of metal ion with the carbonyl group and most probably with the sulphur atom of thiocarbonyl group.
- (ii) A downward shift (20 cm⁻¹) in the position thioamide IV band (875 cm⁻¹) of free ligand, suggesting the bonding of metal through thiocarbonylsulphur atom.
- (iii) This complexes exhibit an intense absorption and at 1850 cm⁻¹ is assigned to $\nu(\text{NO})$ of bonded NO.
- (iv) Weak bands around 470-400 cm⁻¹ in the spectrum of complex may be assigned to the coupled vibrations 27,28 of $\nu(\text{Ru-Cl}) + \nu(\text{Ru-O})$ or $\nu(\text{Ru-Cl}) + \nu(\text{Ru-S})$.
- (v) A band of medium intensity at around 590 cm⁻¹ may be attributed the $\nu(\text{Ru-NO})$ vibration.
- (iv) The characteristic bands of pyridine ligand were present at slightly shifted positions (~ 10 cm⁻¹).
- Based on the above observations, the bonding of ligand is concluded sulphur atom of thiocarbonyl and oxygen atom of carbonyl group (Table 2).

Table 1: Analytical Data, Melting Point and Colour of Complexes

SN.	Compounds	Colour	MP (°C)	Molar Conductance ohm ⁻¹ cm ²	Yield (%)	Analyses Found (Calcd)									
						C	H	N	S	P	Cl	F	Ru		
1	Cis-[RuCl ₂ (NO)(CTH)(py)]PF ₆	Orange Red	116	110	26	29.4 (29.55)	2.96 (2.78)	6.32 (6.4)	5.08 (4.96)	5.12 (4.93)	10.84 (10.94)	17.6 (17.5)	15.3 (15.5)		
2	Cis-[RuCl ₂ (NO)(ETH)(py)]PF ₆	Orange	108	115	24	25.68 (25.77)	2.46 (2.33)	8.86 (8.7)	5.06 (4.94)	4.92 (4.8)	11.16 (11.03)	17.12 (17.7)	15.32 (15.68)		
3	Cis-[RuCl ₂ (NO)(EPH)(py)]PF ₆	Red	120	112	25	25.62 (25.77)	2.64 (2.33)	8.52 (8.7)	5.08 (4.94)	4.96 (4.8)	10.92 (11.03)	17.5 (17.7)	15.46 (15.68)		
4	Cis-[RuCl ₂ (NO)(ESH)(py)]PF ₆	Red	95	100	35	25.68 (25.89)	2.32 (2.18)	6.76 (6.52)	10.12 (9.98)	5.86 (4.84)	11.6 (11.8)	17.58 (17.78)	15.62 (15.79)		
5	Cis-[RuCl ₂ (NO)(ATH)(py)]PF ₆	Orange Red	115	110	40	22.6 (22.2)	2.28 (2.02)	11.88 (11.76)	5.52 (5.4)	5.12 (5.21)	12.08 (11.92)	19.22 (19.1)	16.88 (17)		
6	Cis-[RuCl ₂ (NO)(PTH)(py)]PF ₆	Red Brown	105	115	40	30.04 (30.4)	2.56 (2.38)	10.12 (10.43)	4.88 (4.77)	4.76 (4.6)	10.46 (10.58)	16.88 (17)	15.2 (15.05)		

Electronic Spectra

Electronic Spectra of ligands (CTH, ETH, PTH) exhibited absorption band in EtOH at 415 – 450 nm and 365 – 390 nm. These absorption bands are assigned as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. The electronic absorption bands of ligands (EPH, ESH and ATH) in the same solvent appeared at 300-350nm and 262-292 nm assignable to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively (Table-3). The intense absorption bands characteristic of substituted pyrrole ring (235 and 345 nm), substituted thiophene ring (295, 270 nm) and substituted benzene ring (260 nm) were present in the electronic spectra of (ETH, EPH, ATH, PTH), ESH and (CTH, PTH) ligands respectively, these absorption bands assigned as $\pi \rightarrow \pi^*$ transitions did not shift on complexation, suggesting that the metal ion did not interact with the π system of ligands consistent with IR spectral data. The free ligand band characteristic of $n \rightarrow \pi^*$ transition shows a red shift (~15 nm) while that of $\pi \rightarrow \pi^*$ transition shows a blue shift (~10 -15 nm) on coordination of ligand with metal ion (electron withdrawing system). In practice the bonding of hetroatom with metal ion would stabilize the orbitals that possess²⁷ lone pair of electron while destabilize the π molecular orbitals. These effect could be seen in the electronic spectrum of ligand after coordination with metal ion. The comparison of electronic spectra of ligands and corresponding complexes suggested that $n \rightarrow \pi^*$ transition move towards longer wave length while that $\pi \rightarrow \pi^*$ towards shorter wave length constant with the IR spectral interpretations.

UV-Visible spectra of Ru(II) complexes (low spin) generally exhibit²⁹ two low energy transitions of very weak intensity corresponding to $^1A_{1g} \rightarrow ^1T_{2g}$ and $^1A_{1g} \rightarrow ^3T_{2g}$ and at higher energies of comparatively more intensity ($\Sigma > 10$) corresponding to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$. The intensity of two bands around 830-860 nm and 580-620 nm suggested that the bands in all the complexes are due to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ respectively consistent with analogous complexes of Ru(II).

The region above 500nm is dominated by d-d transition and 400-500 nm is dominated by $d \rightarrow \pi^*$ transition while 400-300 nm and below 300 nm are dominated by LMCT and IL respectively. Spectra off all the complexes show an intense band in each at 400-440 nm which would be assigned

Table 2 : Major IR Bands and Comparison of IR Spectra of Ligand and Complexes (cm⁻¹)

SN.	Compounds	$\nu(\text{NO})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{S})$	Thioamide Bands			
						I	II	III	IV
1	CTH	-	3220	1765s	1130s	1540s	1360s	1075s	850m
	Cis-[RuCl ₂ (NO)(CTH)(py)]PF ₆	1840s	-	1775s	1120m	1500s	1330m	1070s	840m
2	ETH	-	3350m 3325m	1765s	1120s	1540s	1340s	1070s	870m
	Cis-[RuCl ₂ (NO)(ETH)(py)]PF ₆	1850s	-	1745s	1100m	1550s	1380s	1070s	865m
3	EPH	-	3210m	1730s	1125s	1500s	1320s	1015s	880s
	Cis-[RuCl ₂ (NO)(EPH)(py)]PF ₆	1840s	-	1780d	1110s	1480s	1310s	1010m	860s
4	ESH	-	3240s	1730s	1180s	1510s	1360s	1020s	770s
	Cis-[RuCl ₂ (NO)(ESH)(py)]PF ₆	1840s	3380 3100br	1740m	1160s	1500s	1350s	1000m	740s
5	ATH	-	3400 3370 3250	1730s	1120s	1580s	1330s	1060s	845s
	Cis-[RuCl ₂ (NO)(ATH)(py)]PF ₆	1850s	-	1700s	1130m	1560s	1310s	1050s	860m
6	PTH	-	3410m 3260m 3160m	1720s	1120s	1525s	1350s	1000s	860m
	Cis-[RuCl ₂ (NO)(PTH)(py)]PF ₆	1850s	-	1690s	1140m	1510s	1320s	990m	870m

Table 3: Electronic Spectra of Ligands and 0.25 m Solution of Complexes in CH₂Cl₂

SN.	Compound	Band Position	Assignment
1	Cis-[RuCl ₂ (NO)(CTH)(py)]PF ₆	450	n→π*
		310	π→π*
		270	π→π*
		850 (125)	¹ A _{1g} → ¹ T _{1g}
		600 (150)	¹ A _{1g} → ¹ T _{2g}
		460 (6 x 103)	LMCT
		440 (2.5x102)	dp(Ru)→π*(NO)
		360 (8 x 103)	IL
2	Cis-[RuCl ₂ (NO)(ETH)(py)]PF ₆	260 (10 x 103)	π→π*
		440	n→π*
		365	π→π*
		840 (125)	¹ A _{1g} → ¹ T _{1g}
		500 (150)	¹ A _{1g} → ¹ T _{2g}
		450 (6 x 103)	LMCT
		410 (2.5 x 102)	dp(Ru)→π*(NO)
		350 (8 x 103)	IL
		345 (9.6 x 103)	π→π* (pyrrole)
		235 (10.4 x 103)	π→π*
		260 (9.6 x 103)	π→π* pyridine

	ATH	350	$n \rightarrow \pi^*$
		290	$\pi \rightarrow \pi^*$
		345	$\pi \rightarrow \pi^*$ (pyrrole)
		235	$\pi \rightarrow \pi^*$
3	Cis-[RuCl ₂ (NO)(ATH)(py)]PF ₆	830 (125)	$^1A_{1g} \rightarrow ^1T_{1g}$
		580 (150)	$^1A_{1g} \rightarrow ^1T_{2g}$
		400 (2.5 x 10 ²)	dp(Ru) $\rightarrow \pi^*$ (NO)
		360 (6 x 10 ³)	LMCT
		280 (8 x 10 ³)	IL
		345 (10 x 10 ³)	$\pi \rightarrow \pi^*$ (pyrrole)
		235 (8 x 10 ³)	$\pi \rightarrow \pi^*$
		260 (7 x 10 ³)	$\pi \rightarrow \pi^*$ pyridine
		345	$\pi \rightarrow \pi^*$
		235	$\pi \rightarrow \pi^*$ pyrrole
4	Cis-[RuCl ₂ (NO) (EPH)(py)]PF ₆	850 (120)	$^1A_{1g} \rightarrow ^1T_{1g}$
		600 (130)	$^1A_{1g} \rightarrow ^1T_{2g}$
		440 (3 x 10 ²)	dp(Ru) $\rightarrow \pi^*$ (NO)
		330 (5 x 10 ³)	LMCT
		260 (8 x 10 ³)	IL
		345 (9 x 10 ³)	$\pi \rightarrow \pi^*$ Pyrrole
		235 (6 x 10 ³)	$\pi \rightarrow \pi^*$
		268 (7 x 10 ³)	$\pi \rightarrow \pi^*$ pyridine
	ESH	350	$n \rightarrow \pi^*$
		292	$\pi \rightarrow \pi^*$
		295	$\pi \rightarrow \pi^*$
		270	$\pi \rightarrow \pi^*$ Thiophene
5	Cis-[RuCl ₂ (NO) (ESH)(py)]PF ₆	560 (130)	$^1A_{1g} \rightarrow ^1T_{1g}$
		620 (140)	$^1A_{1g} \rightarrow ^1T_{2g}$
		440 (2 x 10 ²)	dp(Ru) $\rightarrow \pi^*$ (NO)
		360 (5 x 10 ³)	LMCT
		280 (8 x 10 ²)	IL
		295 (8 x 10 ³)	$\pi \rightarrow \pi^*$ Thiophene
		270 (6 x 10 ³)	
		260 (5 x 10 ³)	$\pi \rightarrow \pi^*$ Pyridine
	PTH	415	$n \rightarrow \pi^*$
		390	$\pi \rightarrow \pi^*$
		270	$\pi \rightarrow \pi^*$ Benzene
6	Cis-[RuCl ₂ (NO) (PTH)(py)]PF ₆	820 (110)	$^1A_{1g} \rightarrow ^1T_{1g}$
		580 (130)	$^1A_{1g} \rightarrow ^1T_{2g}$
		425 (103)	LMCT
		410 (2 x 10 ²)	dp(Ru) $\rightarrow \pi^*$ (NO)
		360 (9 x 10 ³)	IL
		270 (8 x 10 ³)	$\pi \rightarrow \pi^*$ benzene
		260 (7 x 10 ³)	$\pi \rightarrow \pi^*$ Pyridine

to $d\pi(\text{Ru}) \rightarrow \pi^*(\text{NO})$.³⁰⁻³² The energy of transition decreases in complex of CTH, EPH, ESH ligands, than ATH, PTH, ETH, this observation suggested that ligands as N and S donor sites binds metal ion more effectively as compared to N and O or S

and O donor sites. This effect would further lead to stronger M-N bond and weaker N-O bond in complexes, consistent to IR spectral data of M-N and NO stretching frequencies (Table 2).

Intensity of absorption bands at 460-425 nm and 360-350 nm (ϵ max- $6 \times 10^3 \text{ m}^{-1} \text{ cm}^2$) in complexes suggested that these bands appear as a result of LMCT (Ligand to metal charge transfer). Further, the intensity of absorption bands at 360-350 and 280-350 nm (ϵ max- $8 \times 10^3 \text{ m}^{-1} \text{ cm}^2$) in complexes suggested that they arise due to IL (Infra-ligand) transitions³³.

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