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Reaction of Cis-[Ru Br₂ (DMSO)₄] with some Aromatic Thioamides (RCSNHCOR') in presence of Nitrosyl Ligands and Pyridine

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ABSTRACT

Reactions of RCSNHCOR (R and R' are various type of groups) with cis - $[RuBr_2 (DMSO)_4]$ in presence of nitric oxide and pyridine leads to the formation of new complex of configuration $\{Ru-NO\}^6$ containing pyridine also. The general formulae of the complexes in cis- $[RuBr_2(NO)(LH)(Py)]PF_6$. These complexes have been characterized by elemental, spectral (IR, UV and visible), conductometric and magnetic studies. The presence of v(NO) at 1850-1860 cm⁻¹ supports the presence of a $\{Ru-NO\}^6$ configuration. The electronic properties of complexes is markedly affected by the Br⁻ trans to NO and pyridine in plane.

Keywords: Ruthenium-bromide, Aromatic Thioamide, Trans effect and Charge Transfer Band.

INTRODUCTION

Ruthenium nitrosyl complexes have gained considerable research interest during the past decade and multitudes of ruthenium nitrosyl complexes have been synthesized (Rodrigues et al., 2016). Various types of studies were performed to understand the structure and bonding in ruthenium complexes with noninnocent NO ligand (Eldik et al 2015) in view of potential precursors for the synthesis of N₂ complexes, as models for the investigation of the elementary key steps in the global biogeochemical nitrogen cycle (Tfourni et al 2012), as biological medicinal, environmental, catalytic, therapeutic applications (Rathgeb et al 2014). Given the importance of NO ligand in coordination chemistry, the occurrence of structural trans effect, the role of metal-nitrosyl unit as a reaction mediator or reguation of geometry around the metal ion (Krishnan et al 2017), prompted us to continue our recently initiated study on the interaction of some aromatic thioamides with cis-dichlorotetrakis (dimethyl sulfoxide) ruthenium (II) complexes in presence of nitric oxides as a bench-mark for further investigation of the reactivity of ruthenium nitrosyl complxes (Singh et al 2018). Aromatic thioamides (RCSNHCOR') are known to posses diverse ligating properties, thereby changing both chemical reactivity and structural properties of thioamide complexes induced by alteration in peripheral structure of coordinated ligands (Singh et al 1989, Chauhan et al 1988). With the above objectives, we have previously reported the reaction of little ligands with cis-[RuCl₂(DMSO)4] in presence of nitric oxide. As an extension of our work, we present here the reaction of cis-[RuBr₂(DMSO)₄] with RCSNHCOR' in presence of nitric oxide and characterization of subsequent ruthenium nitrosyl complexes. The study may lead to understand the charge distribution in Ru-NO fragment based on the mode of linkage of auxiliary ligands.

The names and abbreviations of the ligands used are as follows.

R = 4 – tolyl, R' = OEt; N – Carboethoxy-4-toluene thioamide (CTH) R = 2-pyrrolyl, R' = OEt; N-Carboethoxy-2-pyrrolethioamide (ETH) R = 1-pyrrolyl, R' = OEt; N – Carboethoxy-1- pyrrolethioamide (EPH) R = 2-thiophenyl, R' = OEt; N-Carboethoxy-2-thiophenethioamide (ESH) R = 2-pyrrolyl, R' = NH₂; N-Carboamido-2-pyrrolethioamide (ATH) R = 2- pyrrolyl, R' = NHPh; N-Carbophenylamido-2-pyrrolethioamide (PTH)

Experimental

All the chemicals used were either of Analar or chemically pure grade. Solvents were dried before use and all the reactions were carried out under N₂ Atmosphere. Phosphorous, sulphur, bromide and fluoride were determined gravimetrically by standard procedure (Vogel 1973). RCSNHCOR' (Papadopoulas 1973, 1974, 1976) and cis- [RuBr₂(DMSO)₄] (Alessio et al 1988) were synthesized according to the methods reported elsewhere. The IR spectra were recorded in KBr in the range 4000-250 cm⁻¹ on a Perkin-Elmer FT IR spectrophotometer. Electronic spectra were recorded on a cystronic 108 UV and visible spectrometer from 200-900 nm. Magnetic properties of the complexes were studied at room temperature with hlep of Gouy balance. Melting points were recorded on a Fisher-John melting point apparatus. Conductivity of complexes were checked by an Elico conductivity bridge type CM-82T. RuCl₃.XH₂O was purchased from Aldrich chemicals Co and was treated several times with concentrated HCl to prepare the starting material RuCl₃.3H₂O. Nitric oxide was formed by adding concentrated H₂SO₄ on the NaNO₂, passing it through saturated aqueous solution of NaOH and then bubbling through solution/suspension.

Syntheses of Compounds

1. Cis-[RuBr₂ (NO)(CTH)PF₆

A solution of Cis-[RuBr₂ (DMSO)₄] (0.34g~1 mmol) in 15 ml DMSO was mixed with a solution (10 ml) of CTH (0.22g~1mmol) in EtOH/Py (1 : 1) and the resultant mixture was stirred for 1h under N₂ and heated at reflux for 1h. The solution was allowed to cool at room temperature. A dry nitric oxide gas was bubbled in the solution for 1.5h whereby the colour changes to dark brown. A solution (10 ml) of NH₄PF₆ (0.2g~1mmol) in CH₂Cl₂/MeOH (1:1) mixture was added with constant shaking. The volume of solution was reduced to 5 ml and kept in refrigerator (1h) whereby dark known crystals separated, filtered, washed several times with EtOH, Et₂O and dried in vacuo

2. Cis-[RuBr₂ (NO) (ETH)(Py)] PF₆

A solution of cis-[RuBr₂(DMSO)₄] (0.34g~ 1mmol) in 15 ml DMSO was mixed with a solution (10 ml) of ETH (0.20 g~ 1mmol) in EtOH containing two drops of pyridine and resultant solution was refluxed for 0.5h under N₂ whereby light orange colour of solution changed to light brown. The solution was cooled to room temperature. Dry nitric oxide was bubbled for 1h followed by addition of a solution (10 ml) of NH₄PF₆ (0.2g~ 1mmol) in MeOH/CH₂Cl₂ (1:1) mixture. The resultant solution was reduced to small volume (~ 10 ml) at low pressure and kept in refrigerator (2h) whereby known crystal separated, filtered washed several times with EtOH, Et₂O and dried in vacuo.

3. Cis-[RuBr₂ (NO) (EPH)] PF₆

To a warm ethanolic (20 ml) suspension of cis-[RuBr₂(DMSO)₄] (0.34g~ 1mmol) was added ethanolic solution (10 ml) of EPH (0.2g ~ 1mmol) containing few drops of pyridine. The reaction mixture was refluxed for ten minutes, cooled and reduced to small volume (~ 10 ml). A dry nitric oxide gas was passed for 1.5 h followed by addition of a solution (10 ml) of NH₄PF₆ (0.2 g ~ 1mmol) in MeOH/CH₂Cl₂ (1: 1) mixture where by a brown crystals separated, filtered, washed several times with EtOH, Et₂O and dried in vacuo.

4. Cis-[RuBr₂(NO) (ESH)]PF₆

A mixture of cis-[RuBr₂(DMSO)₄] (0.34g ~ 1mmol) and ESH (0.20g~ 1mmol) was refluxed under N₂ in EtOH/CH₂Cl₂ (1 : 1) solution (20 ml) for 1.5 h and cooled. To this solution a dry N₂ gas was bubbled for 1 h followed by addition of a solution (10 ml) of NH₄ PF₆ (0.2 g~ 1 mmol) in MeOH/CH₂Cl₂ (1 : 1) mixture. The solution was shaked well and kept overnight in a refrigerator whereby an orange-brown compound formed filtered, washed several times with EtOH, Et₂O and dried in vacuo.

5. Cis-[RuBr₂(NO) (ATH)]PF₆

A mixture of cis-(RuBr₂(DMSO)₄] (034 g~ 1mmol) in DMSO (10 ml) and ATH (0.17 g~ 1mmol) in CH₂Cl₂ (10 ml) was refluxed for 2h under N₂ and allowed to cool to room temperature. A dry nitric oxide gas was bubbled to this solution for 0.5h followed by addition of a solution (10 ml) of NH₄PF₆ (0.2 g ~ 1 mmol) in MeOH/CH₂Cl₂ (1: 1) mixture. The resultant solution was reduced to 5 ml under low pressure whereby brown compound formed, filtered, washed several times with EtOH, Et₂O and dried in vacuo.

6. Cis-[RuBr₂(NO) (PTH)]PF₆

A mixture of cis-[RuBr₂(DMSO)₄] (0.34 g ~ 1mmol) in 10 ml CH₂Cl₂ and PTH (0.25 g ~ 1 mmol) in pyridine (10 ml) was heated at reflux under N₂ for 2.5 h and allowed to cool at room temperature. To this solution, a dry nitric oxide gas bubbled (1.5 h) followed by addition of a solution (10 ml) of NH₄PF₆ (0.2 g ~ 1 mmol) with constant shaking. It was reduced to 10 ml at low pressure and kept overnight in refrigerator whereby a compound formed, filtered washed several times with EtOH, Et₂O and dried in vacuo.

RESULTS AND DISCUSSION

Nitrosylation of cis-[RuBr₂(DMSO)₄] in presence of variety of ligands LH has been attempted in ethanol/dichloromethane to give new nitrosyl complexes (1-6) containing oxygen, nitrogen and sulphur based ancillary ligands.





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Microanalytical data suggested the formulae given in table 1. They are non hygroscopic, slightly soluble in methanol, chloroform, benzene, more soluble in CH_2Cl_2 , acetone and other halogenated solvents and insoluble in light petroleum and diethyl ether. The molar conductance's of the complexes ranges from 110-120 ohm⁻¹ cm² mol⁻¹ suggested 1: 1 type in dichloromethane. The diamagnetic properties together with analytical data are consistent with preferred geometry which the metal ions generally adopt in some complexes. In order to confirm the proposed formulation of the complexes, spectral studies (IR, UV and visible) have been carried out on these complexes whose results are discussed under the following heads.

Infrared Spectra

The stretching frequency of free nitric oxide is 1870 cm⁻¹. Upon complexation v (NO) may increase or decrease depending on the nature of coligands in the complexes, electronic configuration, overall change on the complex and geometry. In general, the IR stretching frequency of NO decrease with increasing charge from 2377 (NO⁺) through 1875 (NO) to 1450 cm⁻¹ (NO⁻) with the increasing charge on MNO moiety (Mc Cleverly 2004). Thus, electron charge distribution in MNO fragment is very sensitive to the nature of auxiliary ligands. This sensitivity may be a factor in determining the biological significance of these nitrogen (II) oxide complexes. The appearance of a broad intense band at 1850-1860 cm⁻¹ in spectra of complexes (1-6) and at 1840-1850 cm⁻¹ in cis-[RuBr₂ (NO) (LH) (Py)]PF₆ suggested the greater π accepting ability of bromide ligand than chloride ligand. Because of this the π bonding contribution of metal d orbital electrons along MNO moiety decreases thereby weakening M–N bond strength and enhancing NO bond order (Mingos et al 1989, Hayton et al 2002).

The characteristic IR bands of pyrrole moiety (2910, 1550, 1470, 1450, 1140, 1040, 995, 750, 520 and 440 cm⁻¹) (Colthup et al 1975), tolyl group (3030, 2550–2960, 1600, 1580, 1460, 770–730 cm⁻¹) (Cottonet al 1980), thiophenyl group (3050, 1660, 15, 1580, 700-750 cm⁻¹) do not undergo any shift (±5cm⁻¹). This indicates that NH group of pyrrole moiety and sulphur atom of thiophene ring do not participate in bond formation. It is also inconformity with the following facts: (1) nitrogen of the pyrrole ring and sulphur of the thiophene ring are poorly basic due to delocalization of lone pair of electrons in the ring. (2) The deprotonation of pyrrole-2-thiocarboxamide. It is highly unlikely that nitrogen of –NHPh group in PTH would form a bond with metal ion as the lone pair of electron of nitrogen is delocalized in phenyl group. The oxygen of –OEt group is poorly basic so it will not coordinate its lone pair to metal ion. It is, therefore, assumed that bonding in complexes take place with –C(S)NHC(O)– moiety of the ligands and the major shifts in the position of absorption bands are expected to be in thioamide and amide bands.

The donor ability of ligands can be described in terms of following type of resonance structure:

Ordinarily, structure I is predominate when metal is present in zero or preferably lower oxidation states whereas ligand structure II and III persists in higher oxidation states of lighter transition element (Singh et al 1989). IR spectra of the complexes (1–6) have been grouped under three heads :

1. IR Spectra of Cis-[RuBr₂(NO)(LH)Py]PF₆ (LH=CTH, EPH, ESH)

(a) Presence of an intense broad band at 1850 cm⁻¹ an is assigned to v (NO).

(b) An absorption band at 450 cm⁻¹ in assigned to v M–NO.

(c) The absorption band due to v (CO) of free ligands shifted to higher wave number in complexes. So, the possibility of carbonyl oxygen in bond formation with metal atom is ruled out. v (C=S) and thioamide band IV (Mainly due to major contribution of v(C - S)) shift to lower wave numbers with reduced intensity. This supports the bonding through thiocarbonly sulphur.

The thioamide band I (Nakamoto 1963) \Box (NH) + $v\Box$ (CN) shift to lower wave number indicating metal nitrogen bond formation. Thioamide band II ($v(C=N) + \Box$ (NH) + \Box (CH) and thioamide band III (v(C=S) + v (C-N)) (Adams 1968), as expected also shift to lower wave number. The ligands are probably N and S donor in these complexes.

(d) \Box bonding through C = S, C = O and C = N is almost ruled out as single crystal X-ray diffraction analysis of [Cu (PPh₃)₂(LH)Cl] shows the coordination through thione sulphur.

(e) The new bands of medium intensity in the region 340-380 cm⁻¹ may be attributed to coupled vibration of v (Ru – Br) + v (Ru–S) or v (Ru–N) of pyridine atom (Nakamoto 1963).

(f) The characteristic bands of pyridine due to C = C and C = N stretching (ring) (1430-1600 cm⁻¹) shifted to lower wave number (± 15 cm⁻¹), indicating in coordination of pyridine to metal ion (Nakamoto 1963).

Thus, it is concluded that ligands bind metal ion through nitrogen and sulphur.

2. IR Spectra of Cis-[RuBr₂(NO)(LH)(Py)]PF₆

(LH = ATH, PTH)

(a) An intense broad band in the spectra of complexes at 1860 cm⁻¹ shows the presence of nitrosyl group.

(b) An absorption band at 450 cm⁻¹ in spectra of complexes is assigned to v M–NO.

(c) Stretching frequency of carbonyl group around 1720-1730 cm⁻¹ and thioamide band I shifted to lower wave number. Thioamide band II at 1320-1350 cm⁻¹ shifted to lower wave number (+25 cm⁻¹). Ligand band due to v (C=S) group at 1120 cm⁻¹ shifted to higher wave number. Thioamide band III (1070-1000 cm⁻¹) did not shift and thioamide band IV (845-870 cm⁻¹) shifted to lower wave number (-10cm⁻¹).

(d) The new bands of medium intensity in the regions 380-400 cm⁻¹ may be assigned to the coupled vibration of v (Ru-Br) + v (Ru-N) or $v \square$ (Ru-O).

(e) The characteristic bands of pyridine appeared at lower frequency indicating the coordination of metal ion with pyridine.

Thus, on the basis of above IR spectral observation LH bands metal ion through nitrogen of imido group and oxygen of sulphur group (Table-2).

3. Cis-[RuBr₂(NO)(ETH)(Py)]PF₆

(a) In intense absorption band in the spectrum of complex at 1850 cm⁻¹ indicates the presence of nitrosyl group.

(b) An absorption band at 450 cm⁻¹ in the spectrum of complex is assigned to *v* M–NO.

(c) On comparing the IR spectrum of ligand and complexes.

It appears that v (C=O) shifts from 1765 to 1745 cm⁻¹, Thioamide band I shift from 1540 to 1550 cm⁻¹. The thioamide band II at 1340 cm⁻¹ to 1385 cm⁻¹, stretching frequency of C = S group shifts from 1120 to 1100 cm⁻¹. Thioamide band III at 1070 cm⁻¹ does not shift and thioamide band IV at 870 cm⁻¹ shifts to 860 cm⁻¹.

(d) The new bands of medium intensity in the region 340-380 cm⁻¹ may be assigned to the coupled vibration of v (Ru–Br) + v (Ru–O) or v (Ru–S).

(e) The characteristic absorption bands of pyridine were found at lower frequencies indicating the coordination of pyridine to metal ion.

These observation of IR spectral pattern in ligand and complexs, suggested that ETH acts as S and O donor.

UV and Visible Spectra

UV and visible spectra of ligands and complexes were recorded in CH_2Cl_2 from 200-900 nm. The systematic assignments of all the bands or ligands and complexes are given in table 3. The intense absorption bands characteristic of substituted pyrrole ring (235 and 345 nm), substituted thiophene ring (295 and 270 nm) and substituted benzene ring (260 nm) were present in the electronic spectra of ligands (ETH, EPH, ATH and PTH) ESH and (CTH and PTH) respectively. These absorption bands assigned to $\Box \Box \Box \Box \Box$ did not shift when ligand is coordinated to metal ion, suggests that metal ion do not form any bond with these moiety, consistent with IR spectral studies. Further, the UV and visible spectra of ligands (CTH, ETH and PTH) exhibited absorption band in the same solvent at 415-450 nm and 365-390 nm.

These absorption bands are assigned to $n \square \square \square$ and $\square \square \square \square$ transitions. The electronic absorption bands of ligand (EPH, ESH and ATH) in the same solvent appeared at 300-350 nm and 262-292 nm assigned to $n \square \square \square$ and $\square \square$ respectively (Table 3).

The absorption bands of -CSNHCO-moiety assigned to $\Box \Box$ transitions shift to lower wavelength on complexation while that of $n\Box \Box$ shift to longer wave length. In practice the bonding of hetro atom with metal ion would stabilize the orbitals that possess lone pair of electron while destabilize the \Box molecular orbitals. On comparing the electronic spectra of free ligand with corresponding complexes this effect is very much visualized (Arulsamy et al 1984).

UV and visible spectrum of ferrous acetate ion (0.1 M) buffered (pH 5.0) at room temperature and upon saturation with nitric oxide exhibited characteristic absorption bands at 336, 451 and 585 nm. These bands are assigned to the formation of mononitrosylated iron II complex. Upon bubbling N₂ gas to the solution of mononitrosylated iron II ion, these three bands disappear from the spectrum. This shows the great labiality of the complex. The UV and visible spectra of all the complexes also exhibited intense band (\Box =200-250) at 430-450 nm assignable to d \Box (Ru) \Box (NO) transitions. The spectra of all the complexes showed a decrease in the position of d \Box (Ru) \Box (NO) when ligands are CTH, ETH and ESH as compared to ATH, PTH and ETH. These observations suggest that ligand is more effective as N and S donor as compared to N and O or S and O donor atoms.

SN	Compoun	MP	Molar	Yield	Color	Analyses Found (Caled)							
	ds	(°C)	Condu ct ance Ohm ⁻¹ mo ⁻¹ cm ²	(%)		C	Н	N	S	Р	Br	F	Ru
1.	Cis-[RuBr ₂ (NO) (CTH)(Py)] PF ₆	128	110	20	Dark Brown	25.86 (26.01)	2.62 (2.4)	5.4 (5.6)	4.56 (4.33)	4.42 (4.2)	21.48 (21.68)	15.68 (15.44)	13.76 (13.68)
2.	Cis-[Ru Br ₂ (NO) (ETH)(Py)] PF ₆	140	112	22	Orange	21.62 (21.87)	2.26 (2.10)	7.52 (7.8)	4.26 (4.4)	4.28 (4.34)	22.56 (22.44)	15.62 (15.98)	14.02 (14.16)
3.	Cis-[Ru Br ₂ (NO) (EPH)(Py)]PF ₆	136	115	20	Brown	21.52 (21.87)	2.32 (2.10)	7.56 (7.8)	4.32 (4.4)	4.40 (4.34)	22.66 (22.44)	15.82 (15.98)	14.28 (14.16)
4.	Cis-[Ru Br ₂ (NO) (ESH)(Py)] PF ₆	120	115	24	Orange Brown	21.48 (21.37)	2.2 (1.9)	5.42 (5.7)	8.48 (8.7)	4.26 (4.2)	21.80 (21.91)	15.46 (15.61)	13.68 (13.83)
5.	Cis-[Ru Br ₂ (NO) (ATH)(Py)] PF ₆	125	110	25	Brown	19.08 (19.29)	1.82 (1.7)	9.8 (10.2)	4.42 (4.6)	4.68 (4.74)	23.22 (23.39)	16.52 (16.66)	14.48 (14.76)
6.	Cis-[Ru Br ₂ (NO) (PTH)(Py)] PF ₆	110	115	30	Orange	26.38 (26.57)	2.26 (2.10)	9.42 (9.2)	4.38 (4.2)	4.26 (4.07)	20.92 (21.05)	14.90 (15.00)	13.06 (13.28)

 Table 1. Analytical Data, Melting Point, Conductance and Colour of Complexes.

Low spin complexes may exhibit two low energy transitions of very weak intensity $({}^{1}A_{1g} \rightarrow {}^{3}T_{1g}, {}^{3}T_{2g})$ and two higher energy transition of intensity $\varepsilon > 10({}^{1}A_{1g} \rightarrow {}^{1}T_{1g}, {}^{1}T_{2g})$. Presence of absorption bands at 830-860 and 580-620 nm in spectra of all the complexes are consistent with ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ transitions respectively analogous to Ru(II) complexes (Drago 1986).

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Intensity of absorption bands at 460-425 nm and 360-350 nm ($\varepsilon \sim 6 \times 10^3 \text{m}^{-1} \text{cm}^2$) in complexes in complexes suggest that they arise due to LMCT (Legand to Metal Charge Transfer). Further, the intensity of absorption bands at 360-350 and 250-350 nm ($\varepsilon \sim 8 \times 10^3 \text{m}^{-1} \text{cm}^2$) in all the complexes (1–6) suggested that they arise due to IL (Infra Ligand) transitions (Jaworska et al 2004).

Thus, on the basis of spectral (IR and UV-visible), magnetic and conductometric studies on the complexes, we conclude them six coordinate {Ru–NO}⁶ species (Rose et al 2007).

SN	Compounds	v(NO)	ν (NH)	v(C=O)	ν (C=S)	Thioamide Bands			
						Ι	II	III	IV
1.	CTH	-	3220	1765s	1130s	1540s	1360s	1075s	850m
	Cis-[Ru Br ₂ (NO)	1840s	-	1775s	1120m	1500s	1330m	1070s	840m
	$(CTH)(Py)]PF_6$								
2.	ETH	-	3350m	1765s	1120s	1540s	1340s	1070s	870m
			3325m						
	Cis-[Ru Br ₂ (NO)	1850s	-	1745s	1100m	1550s	1385s	1070s	860m
	(ETH)(Py)]PF ₆								
3.	EPH	-	3210m	1730s	1125s	1500s	1320s	1015s	880s
	Cis-[Ru Br ₂ (NO)	1840s	-	1780d	1110s	1480s	1310s	1010m	860s
	(EPH)(Py)]PF ₆								
4.	ESH	-	3240s	1730s	1180s	1510s	1360s	1020s	770s
	Cis-[Ru Br ₂ (NO)	1840s	3380	1740m	1160s	1500s	1350s	1000m	740s
	$(ESH)(Py)]PF_6$		3100br						
5.	ATH	-	3400	1730s	1120s	1580s	1330s	1070s	845s
			3370						
	Cis-[Ru Br ₂ (NO)		3250						
	$(ATH)(Py)]PF_6$	1860s	-	1700s	1130m	1560s	1310s	1070s	835m
6.	PTH	-	3410m	1720s	1120s	1525s	1350s	1000m	870m
			3260m						
	Cis-[Ru Br ₂ (NO)		3160m						
	$(PTH)(Py)]PF_6$	1860s	-	1690s	1140m	1510s	1320s	1000m	860m

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

Table 3. Electronic Spectra of Ligands and 0.25M Solution of Complexes in CH₂Cl₂.

SN.	Compound	Band Position	Assignment
	CTH	450	$n \rightarrow \pi^*$
		310	$\pi \rightarrow \pi^*$
		270	$\pi \rightarrow \pi^*$
1.	Cis-[RuBr ₂ (NO) (CTH)(Py)]PF ₆	850 (105)	$^{1}A_{1g} \rightarrow ^{1}T_{1g}$
		600 (90)	$^{1}A_{1g} \rightarrow ^{1}T_{2g}$
		460 (6 x 10 ³)	LMCT
		440 (2x10 ²)	$d\pi(Ru) \rightarrow \pi^*(NO)$
		360 (8 x 10 ³)	IL
		260 (9 x 10 ³)	$\pi \rightarrow \pi^*$
	ETH	440	$n \rightarrow \pi^*$
		365	$\pi \rightarrow \pi^*$
2.	Cis-[RuBr ₂ (NO) (ETH)(Py)]PF ₆	840 (120)	$^{1}A_{1g} \rightarrow ^{1}T_{1g}$
		590 (130)	$^{1}A_{1g} \rightarrow ^{1}T_{2g}$
		450 (6 x10 ³)	LMCT
		410 (2 x 10 ²)	$d\pi(Ru) \rightarrow \pi^*(NO)$
		350 (8 x 10 ³)	IL
		345 (9.0 x 10 ³)	$\pi \rightarrow \pi^*$ (pyrrole)
		235 (10.0 x 10 ³)	$\pi \rightarrow \pi^*$
		260 (9.0 x 10 ³)	$\pi \rightarrow \pi^*$ (pyridine)
	EPH	350	$n \rightarrow \pi^*$
		290	$\pi \rightarrow \pi^*$
		345	$\pi \rightarrow \pi^*$ (pyrrole)
		235	$\pi \rightarrow \pi^*$ (pyrrole)
3.	Cis-[RuBr ₂ (NO)(EPH)(Py)]PF ₆	830 (105)	$^{1}A_{1g} \rightarrow ^{1}T_{1g}$

	580 (110)	$^{1}A_{1g} \rightarrow ^{1}T_{2g}$
	430 (2.5 x 10 ²)	$d\pi(Ru) \rightarrow \pi^*(NO)$
	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)	$\pi \rightarrow \pi^*$ (pyrrole)
	260 (7 x 10 ³)	$\pi \rightarrow \pi^*$ (pyridine)
ESH	300	$n \rightarrow \pi^*$
	262	$\pi \rightarrow \pi^*$
	345	$\pi \rightarrow \pi^*$ (pyrrole)
	235	$\pi \rightarrow \pi^*$ (pyrrole)

4.	Cis-[RuBr ₂ (NO) (ESH)(Py)]PF ₆	850 (110)	$^{1}A_{1g} \rightarrow ^{1}T_{1g}$
		600 (130)	$^{1}A_{1g} \rightarrow ^{1}T_{2g}$
		440 (3 x10 ²)	$d\pi(Ru) \rightarrow \pi^*(NO)$
		350 (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)
	ATH	350	n→π*
		292	$\pi \rightarrow \pi^*$
		295	$\pi \rightarrow \pi^*$ (Thiophene)
		270	
5.	Cis-[RuBr ₂ (NO) (ATH)(Py)]PF ₆	560 (130)	$^{1}A_{1g}\rightarrow ^{1}T_{1g}$
		620 (120)	$^{1}A_{1g} \rightarrow ^{1}T_{2g}$
		450 (2 x10 ²)	$d\pi(Ru) \rightarrow \pi^*(NO)$
		360 (5 x10 ³)	LMCT
		280 (8 x 10 ³)	IL
		295 (8 x 10 ³)	$\pi \rightarrow \pi^*$ (Thiophene)
		270 (6 x 10 ³)	$\pi \rightarrow \pi^*$
		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-[RuBr ₂ (NO) (PTH)(Py)]PF ₆	830 (110)	$^{1}A_{1g}\rightarrow ^{1}T_{1g}$
		580 (120)	$^{1}A_{1g}\rightarrow ^{1}T_{2g}$
		425 (6 x 10 ²)	LMCT
		430 (2 x 10 ²)	$d\pi(Ru) \rightarrow \pi^*(NO)$
		360 (9 x 10 ³)	IL
		270 (8 x 10 ³)	$\pi \rightarrow \pi^*$ (benzene)
		260 (7 x 10 ³)	$\pi \rightarrow \pi^*$ (Pyridine)

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