



## Synthesis, Characterization and Reaction of New Ruthenium Aromatic Thioamide Nitrosyls with Some Nitrogen Donor Ligands

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<http://dx.doi.org/10.13005/ojc/320426>

(Received: November 28, 2015; Accepted: May 05, 2016)

### ABSTRACT

Reactions of  $LH=RCSNHCOOEt$  ( $R=$  4-tolyl, 1-pyrrolyl, and 2-thiophenyl) with  $RuCl_3 \cdot 3H_2O$  and NO leads to the formation of diamagnetic compounds of the formula  $[L_2Ru(NO)(Cl)J]$ . These compounds have been characterised by elemental analysis and IR, UV and Visible and magnetic measurements. The presence of (NO) at  $1835-1855\text{-cm}^{-1}$  indicates a  $\{Ru-NO\}^6$  configuration. The substitution of Cl bounded trans to NO by N-heterocycles bases ( $\alpha$ -picoline,  $\gamma$ -picoline and or pyridine) and  $CH_3CN$  has significant effect on the electronic properties of complexes.

**Keywords :** Ruthenium nitrosyl; Ruthenium; hypsochromic shift.

### INTRODUCTION

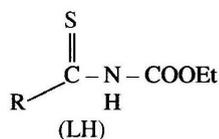
The chemistry of metal nitrosyls that release NO has gained an intensive area of research interest during the recent years, since such species could be used in certain biological processes, like neurotransmission, tumor growth inhibition, hepatic metabolism, cell differentiation and blood pressure regulation.<sup>1,2</sup> The metal nitrosyls that release NO under photochemical condition has attracted much attention. For example NO donors that are capable of releasing NO upon illumination could find use as antitumor agents in Photo Dynamic Therapy

(PDT).<sup>3-5</sup> Non heme iron nitrosyls such as sodium nitropruside  $Na_2[Fe(CN)_5NO]$  and Roussian's salts ( $NH_4[Fe_3S_3(NO)_7]$ ,  $Na_2[Fe_2S_2(NO)_4]$ ) are also known to release NO under photochemical condition. Unfortunately release of NO from these NO donors is dependent on enzymatic reaction, heat or pH and hence target specificity is mostly precluded<sup>6</sup>. Release of auxiliary ligands from metal base NO donors like SNP also leads to deleterious side effect. In contrast, the compounds that release NO strictly upon exposure to light could provide a more selective means of NO delivery. Ruthenium nitrosyls are particularly attractive in this regard owing to their

thermal stability and NO release upon exposure to light.<sup>7-9</sup> The NO release, in most of the octahedral ruthenium nitrosyls having {Ru<sup>II</sup>NO<sup>+</sup>} moiety, can be induced by one electron reduction by photolysis or PDT. In general, it has been found that NO release depends markedly on the *p*-acceptor strength of the ligand coordinated trans to NO and increase in plane ligand field strength.

Despite the large number of ruthenium nitrosyls described in the literature<sup>10-13</sup>, a few examples of ruthenium nitrosyls in sulphur rich environment<sup>14-16</sup> are found to release NO upon irradiation to visible light. This prompts us to explore the chemistry of ruthenium nitrosyls complexes in sulphur rich environment. Further, aromatic thioamides can form stable complexes with transition metal ions.<sup>17-19</sup> The impetus for this and similar work arises from the wide ranging applications of sulphur and nitrogen containing ligands in medicine.<sup>20-22</sup>

The title ligand (LH) is capable of possessing diverse coordinating ability on changing R,



R = 4- tolyl, N-carboethoxy-4-toluenethioamide (Hcct)

R = 1-pyrrolyl, N-carboethoxy-1-pyrroloethioamide (Hcpt)

R = 2- thiophenyl, N- carboethoxy-2-thiophenethioamide (Hcett)

As a part of our continuing investigations on the transition metal complexes of aromatic thioamides, herein we report the synthesis, characterization and possible structures of ruthenium nitrosyls of the title ligand.

## EXPERIMENTAL

### Materials and Measurements

All the chemicals used were either of AR or chemically pure grade. A literature method was used to prepare LH<sup>23</sup>, Elemental analyses (C, H and N) were carried out by Microanalytical section of I.I.T.

Kanpur (U.P.) India. Sulphur chloride, fluoride and boran, were estimated by standard methods.<sup>24</sup> The IR (4000-250 cm<sup>-1</sup>) spectra of the ligand and complexes were recorded in KBr pellets with a Perkin-Elmer FT IR spectrometer. UV and Visible spectra of the ligand and complexes were recorded on a cystronic 108 UV and Visible spectrometer from 200 - 900 nm. RuCl<sub>3</sub>.XH<sub>2</sub>O was purchased from Aldrich chemicals Co. and was treated several times with concentrated HCl to prepare the starting material RuCl<sub>3</sub>. 3H<sub>2</sub>O. All the solvents were purified and or dried by standard techniques and distilled prior to use. Nitric Oxide was generated by dripping concentrated sulphuric acid on NaNO<sub>2</sub>, passing it through a saturated aqueous solution of NaOH and then bubbling through solution/suspension.

### Preparation of Complexes

#### [(cct)<sub>2</sub>Ru(NO)Cl]

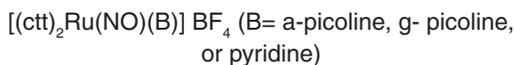
To a 30 ml DMF solution of LH (0.71g, 3.2 mmol) was added slurry of NaH (0.08 g, 3.2 mmol) in 5mL DMF and the resultant solution was stirred for one hour. The colour of solution turned to orange brown when evolution of gas stopped. Solid RuCl<sub>3</sub>.3H<sub>2</sub>O (0.42g, 1.6 mmol) was added to this solution. The color of the reaction mixture changed to red brown immediately. It was refluxed for 5h under N<sub>2</sub> atmosphere and cooled to room temperature and filtered through a sintered glass crucible to remove NaCl. Purified NO gas was allowed to pass and the resultant solution was stirred for 5h, then concentrated to 10 mL. Et<sub>2</sub>O (10 mL) was added to this solution where by a reddish purple crystalline precipitate of the complex was formed. It was filtered off and washed with dry Et<sub>2</sub>O and dried in vacuo. Yield: 0.73g (75%).

#### [(cpt)<sub>2</sub>Ru(NO)Cl]

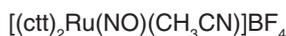
This complex was prepared by the procedure described in 1 except that Hept (0.63 g, 3.2 mmol), NaH (0.08, 3.2 mmol) and RuCl<sub>3</sub>. 3H<sub>2</sub>O (0.42, 1.6 mmol) were used in a total volume of 35 mL dry DMF. It was refluxed for 3h in N<sub>2</sub> atmosphere and filtered off to remove NaCl. The solution was cooled and purified NO gas was bubbled for 1h; the reaction mixture was concentrated to 10mL. Et<sub>2</sub>O 10mL was added to the solution whereby a pale reddish brown crystalline precipitate of the complex was formed. It was filtered and washed with Et<sub>2</sub>O and dried in vacuum. Yield: 0.67g, (75 %).

**[(cett)<sub>2</sub>Ru(NO)Cl]**

This complex was prepared by the same method as described in 1 except that Hcett (0.68g, 3.2 mmol), NaH (0.08, 3.2 mmol) and RuCl<sub>3</sub>·3H<sub>2</sub>O (0.42g, 1.6 mmol) were used in a total volume of 35 mL dry DMF. It was refluxed for 8h in N<sub>2</sub> atmosphere and filtered off in a centered glass crucible. The solution was cooled to 10°C and purified, NO gas was bubbled for 2h. The reaction mixture was concentrated to 10 mL whereby a red brown crystalline precipitate of the complex separated. It was filtered and washed with a little amount of Et<sub>2</sub>O and dried in vacuum yield: 0.67g, (70%).



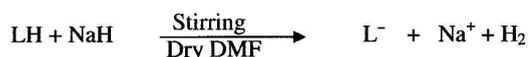
To a 25mL CH<sub>3</sub>CN solution of [(ctt)<sub>2</sub>Ru(NO)Cl] (1mmol) was added 5mL CH<sub>3</sub>CN solution of AgBF<sub>4</sub> (1mmol). This reaction mixture was heated to reflux for 20h. The precipitated AgCl during this time was removed by filtration through a sintered glass crucible. 0.15g of ligands (B) was added to the stirred solution (filtrate). The resultant solution was further stirred for 6h whereby a red brown solution is formed. It was reduced to 10 mL and on adding dry Et<sub>2</sub>O a crystalline precipitate of the complex was formed. It was filtered and washed with Et<sub>2</sub>O and dried in vacuo. Yield: 0.59g, (80%).



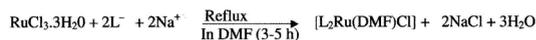
This complex was prepared by the same procedure as described in pyridine complex. The resultant solution was stirred for 6h and concentrated to 10 mL. On adding Et<sub>2</sub>O (10 mL), a yellow brown crystalline complex was formed which was filtered and washed with Et<sub>2</sub>O and dried in vacuum. Yield: 0.45g, (65%).

**RESULTS AND DISCUSSION****Synthesis of the Complexes**

In the present work, the reaction of NaH with stirred solution of title ligand (LH) in dry DMF resulted the deprotonation of ligand. The reaction is given as



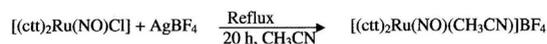
RuCl<sub>3</sub>·H<sub>2</sub>O was allowed to react with deprotonated ligand (L<sup>-</sup>) whereby after prolonged heating the color of the reaction mixture changed to with the formation of 2 equivalents of NaCl



This suggest that [L<sub>2</sub>Ru(DMF)Cl] type species is present in the solution. After passing NO, through the cold solution of this intermediate, desired metal nitrosyls (1-3) were obtained in 70-75% yield



Reaction of chloro complex [(ctt)<sub>2</sub>Ru(NO)Cl] (L = ctt) with AgBF<sub>4</sub> results in the formation of CH<sub>3</sub>CN bonded yellow brown intermediate [(ctt)<sub>2</sub>Ru(NO)(CH<sub>3</sub>CN)]BF<sub>4</sub> type species by halide displacement reaction.



on adding N heterocycles bases B to this yellow brown solution displacement of CH<sub>3</sub>CN by B occurs with the formation of [(ctt)<sub>2</sub>Ru(NO)(B)] .

**IR Spectra**

The ligand LH contains a thioamide<sup>25-27</sup> group (H-N-C=S) and give rise to four characteristic

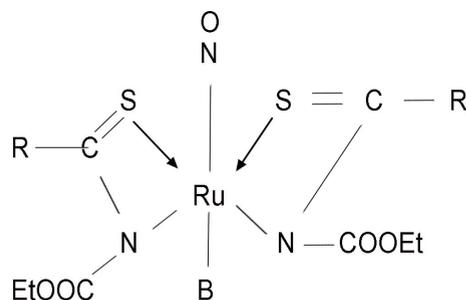


Fig. 1

R = 4 tolyl, 1-pyrrolyl and 2-thiophenyl.

B = Cl, α-pic, γ-pic, py and or CH<sub>3</sub>CN.

Table 1: Analytical data, magnetic properties and colour of the Complexes

Compound	Color	Found (Calc.) %						$\mu_{\text{eff}}$
		C	H	N	S	Halide	B	
1-[(ctt) <sub>2</sub> Ru(NO)Cl]	Reddish purple	43.52 (43.20)	4.14 (3.90)	6.52 (6.87)	10.68 (10.50)	5.96 5.82	- -	DM
2-[(cpt) <sub>2</sub> Ru(NO)Cl]	Pale reddish brown	34.42 (34.2)	3.34 (3.21)	12.24 (12.44)	11.56 (11.48)	6.64 (6.36)	- -	DM
3-[(ceti) <sub>2</sub> Ru(NO)Cl]	red brown	32.32 (32.18)	2.84 (2.68)	7.12 (7.04)	21.68 (21.45)	6.14 (5.95)	- -	DM
4-[(ctt) <sub>2</sub> Ru(NO)( $\alpha$ -pic)]BF <sub>4</sub>	Orange red	44.64 (44.52)	4.18 (4.10)	7.36 (7.41)	8.68 (8.47)	10.20 (10.06)	1.34 (1.43)	DM
5-[(ctt) <sub>2</sub> Ru(NO)( $\gamma$ -pic)]BF <sub>4</sub>	Orange red	44.24 (44.52)	4.02 (4.10)	7.26 (7.41)	8.58 (8.47)	10.30 (10.06)	1.32 1.43	DM
6-[(ctt) <sub>2</sub> Ru(NO)(py)]BF <sub>4</sub>	Orange	43.52 (43.74)	4.1 (3.9)	7.26 (7.5)	8.78 (8.6)	10.36 (10.25)	1.38 (1.45)	DM
7-[(ctt) <sub>2</sub> Ru(NO)(CH <sub>3</sub> CN)]BF <sub>4</sub>	yellow brown	40.78 (40.97)	3.98 (3.84)	7.74 (7.96)	9.22 (9.10)	10.66 (10.8)	1.44 (1.5)	DM

Table 2 : Major IR bands of the ligands and complexes (cm<sup>-1</sup>)

Compounds	Thioamide bands							
	v(NH)	v(NO)	v(CO)	v(CS)	I	II	III	IV
[Hctt] 1-[(ctt) <sub>2</sub> Ru(NO) Cl]	3220 -	- 1842	17685 1770	1130s 1115m	1540s 1500s	1360s 1320m	1075 1060	850 <sub>m</sub> 840 <sub>m</sub>
[Hept] 2-[(cpt) <sub>2</sub> Ru(NO) Cl]	3210 -	- 1848	1740s 1760s	1125m 1115s	1500s 1480s	1320m 1310s	1015s 1010m	880 <sub>m</sub> 860 <sub>m</sub>
[Hcett] 3-[(cett) <sub>2</sub> Ru(NO) Cl]	3240m -	- 1855	1730s 1750s	1180s 1150s	1510s 1500s	1360s 1340s	1020s 1000s	770 <sub>m</sub> 750 <sub>m</sub>
4-[(ctt) <sub>2</sub> Ru(NO)(α-pic)]BF <sub>4</sub>	-	1835	1770s	1115m	1500s	1320m	1060s	840 <sub>m</sub>
5-[(ctt) <sub>2</sub> Ru(NO)(γ-pic)]BF <sub>4</sub>	-	1835	1770s	1115m	1500s	1320m	1060s	840 <sub>m</sub>
6-[(ctt) <sub>2</sub> Ru(NO)(py)]BF <sub>4</sub>	-	1840	1770s	1115m	1500s	1320m	1060s	840 <sub>m</sub>
7-[(ctt) <sub>2</sub> Ru(NO)(CH <sub>3</sub> CN)]BF <sub>4</sub>	-	1845	1770s	1115m	1500s	1320m	1060s	840 <sub>m</sub>

thioamide bands, namely I, II, III and IV having contributions from  $\delta(\text{C-H}) + \delta(\text{N-H})$ ,  $\nu(\text{C=S}) + \nu(\text{C=N}) + \nu(\text{C-H})$ ,  $\nu(\text{C-N}) + \nu(\text{C-S})$  and  $\nu(\text{C-S})$  modes of vibrations respectively (Table 2) The disappearance of  $\nu(\text{NH})$  bands of the ligand (3200-3240)  $\text{cm}^{-1}$  from the spectra of all the complexes indicate the displacement of N-H hydrogen by  $\text{Ru}^{+3}$  and the formation of metal nitrogen bond. All the complexes (1-6) display strong carbonyl stretching frequencies (CO) in the range 1750-1770  $\text{cm}^{-1}$ , indicating a blue shift of (CO) in complexes compared to the free ligand (Table 2). This confirms the coordination of the ligands in their deprotonated forms in these complexes and non involvement of carbonyl group of COOEt in bonding. It is highly unlikely for the oxygen atom of -OEt group to participate in the complex formation. The thioamide band I of the ligands at 1540-1550  $\text{cm}^{-1}$  shift to lower wave number by 20-25  $\text{cm}^{-1}$  in the spectra of complexes. This indicates M-N

bond formation as the thioamide band I has principal contribution from  $\delta(\text{C-H}) + \delta(\text{N-H})$ .

Thioamide band II of the ligands (1340-1400) shifts to lower wave number as a result of coordination through thiocarbonyl sulphur. The thioamide band III is relatively weak in the spectra of the complexes. There is a red shift of 15-20  $\text{cm}^{-1}$  in thioamide band IV (major contribution from  $\mu(\text{C=S})$ ) in the spectra of all the complexes. This further indicates the bonding through thiocarbonyl sulphur. A red shift of 25-55  $\text{cm}^{-1}$  in thioamide band IV usually indicates the bonding through sulphur and a blue shift of 40-90  $\text{cm}^{-1}$  in this band indicates bonding through nitrogen. However, if there is simultaneous coordination through nitrogen and sulphur, there may not be much of the shift in band IV. Hence the small shift in band IV is attributed to simultaneous coordination through nitrogen and sulphur.

**Table 3: UV-Visible and data of the ligand and complexes**

[Hctt]	450	a
	310	b
	270	c
[(ctt) <sub>2</sub> Ru(NO) Cl]	390	d
	345	e
	325	f
	280	g
[Hcpt]	300	a
	262	b
[(cpt)Ru(NO) Cl]	380	d
	358	e
	310	f
	270	g
[Hcett]	350	a
	292	b
[(cett) <sub>2</sub> Ru(NO) Cl]	370	d
	360	e
	320	f
	300	g
[ $\alpha$ - picoline]	375	a
	290	b
	240	c
[(ctt) <sub>2</sub> Ru(NO) ( $\alpha$ -pic)]BF <sub>4</sub>	395	d
	355	e
	325	f
	300	g
	280	f

Two bands around (685-695  $\text{cm}^{-1}$  and (630-660  $\text{cm}^{-1}$  assigned to  $\tau(\text{NH})$  of the ligand disappear in the spectra of complexes, further supports the deprotonation of NH group of the ligand.<sup>19,28</sup>

The appearance of new medium intensity bands in the region 300- 450  $\text{cm}^{-1}$  is strong evidence of coordination by N, S and Cl. These bands have been assigned to coupled vibrations of  $\nu(\text{Ru-N})$ ,  $\nu(\text{Ru-Cl})$  and  $\nu(\text{Ru-S})$ .

A single strong NO stretching band  $\nu(\text{NO})$  is observed for each of the 7 complexes<sup>15,29</sup> (Table 2). These values fall in the expected range for  $\{\text{RuNO}\}^6$  type complexes. In RCS NH COOEt, the electron donating ability of R is expected to be 4-tolyl > 1-pyryl > 2-thiophenyl. Thus, the ligand field strength decreases in the order Hctt>Hcpt>Hcett. The stretching frequencies of NO at 1842, 1848 and 1855 in compound 1,2,and 3 respectively, supports the expectations in the change of ligand field strength as R is varied. The stretching frequencies of NO in compound 4, 5, 6 and 7 are 1835, 1835, 1840 and 1845 respectively. This is smaller than  $\nu(\text{NO})$  in compound 1-3, indicating a better a donor ability of N heterocycles and  $\text{CH}_3\text{CN}$  than chloride<sup>19,30</sup>.

The weak broad band at 3500  $\text{cm}^{-1}$  in the spectra of  $[(\text{ctt})_2\text{Ru}(\text{NO})\text{B}]\text{BF}_4$  (B= pyridine,  $\gamma$ -picoline and  $\alpha$ -picoline are characteristic of pyridine and substituted pyridine, shift towards higher frequency (+80 $\text{cm}^{-1}$ ) . In these complexes, the bands in free pyridine or substituted pyridine at 605-615  $\text{cm}^{-1}$  (in plane ring deformation) and 405-410  $\text{cm}^{-1}$  (out of plane ring deformation) shift to higher frequencies. In the spectra of complexes, there seems to be extensive mixing between the bands of ligands and those of bases, hence the other characteristic frequencies of N-heterocycles did not occur at their standard positions.<sup>19,30</sup>

### UV and Visible spectra

The UV and Visible spectra of the ligands and complexes were recorded in  $\text{CH}_3\text{CN}$  from 200-900 nm. The intensity of the bands ( $\nu=10^2$ - $10^3$ ) indicates that the bands are charge transfer and not d-d transition bands. The systematic assignments of all the bands of ligands and complexes are given in Table 3. The absorption bands at (395-368) are

very much dependent on the ligand field strength and basicity of ligands bound cis to NO. Stronger ligand field strength (Hctt)>Hcpt> Hcett) increases the N-O bond length (decreases  $\nu\text{NO}$ , lesser  $\text{NO}^+$  character). This is nicely supported by  $u(\text{NO})$  values (Table 2). These bands are assigned to  $dp(\text{Ru}) \rightarrow \pi^*(\text{NO})$  (MLCT)<sup>9</sup> There is a red shift (max. 5 nm) of the band at 370 nm by ligands B ( $\alpha$ -pic, 395;  $\gamma$ -pic, 395; py, 390; and CH,CN, 368.) bound cis to NO. This red shift of the CT bands arises from the coordination of more basic N-heterocycles that increase electron density at the metal center and facilitate  $dp(\text{Ru}) \rightarrow p^*(\text{NO})$  transition at lower energy.

The other band at 345-360 nm in assigned to  $dp(\text{Ru}) \rightarrow dp(\text{S})$  on the basis that this transition requires larger amount of energy than  $dp(\text{Ru}) \rightarrow p^*(\text{NO})$ . This is observed empirically, that all the sulphur containing ligands lie at the lower field end of the spectrochemical series<sup>31</sup>. From the general point of view  $-\text{C}=\text{S} \rightarrow \text{M}$  bond of prevailing character should induce a fractional positive charge on the sulphur atom and thereby decrease the bond order of  $-\text{C}=\text{S}$  group, with a consequent decrease of  $\nu(\text{C}=\text{S})$ . On the other hand, subsequent contribution of metal to sulphur  $\pi$  back donation should diminish the sulphur positive charge and increase the bond order of  $-\text{C}=\text{S}$  group. In presence of only a donating N atom of the ligand trans to sulphur, the  $dp(\text{Ru}) \rightarrow dp(\text{S})$  increases<sup>28</sup>. A small downward shift (10-20  $\text{cm}^{-1}$ ) of  $\nu(\text{C}=\text{S})$  compared to free ligand indicates the presence of N atom of one ctt trans to S atom of other ctt. This supports the extensive back donation of electrons from metal filled  $dp$  orbital to sulphur empty  $d\pi$  orbital.

The bands at 300, 350 and 450 nm in free ligands (Hcpt, Hcett, and Hctt respectively), disappear in the spectra of complexes due to stabilization of the lone pair of electrons on complex formation, and similarly the hypsochromic shift in the bands in the spectra of complexes may be explained as that metal ion is bonded through thiocarbonyl sulphur and nitrogen. The bond formation lowers the energy of non bonding orbital as well as  $\pi$  levels, thus now more energy will be required to promote the electron from then n or  $\pi$  level to  $\pi^*$  orbital, hence the observed hypsochromic shift<sup>19</sup>.

The entire compounds are diamagnetic in solid state and solution.

Thus, on the basis of IR, UV-visible and magnetic studies, we proposed the following tentative structures of complexes.

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