

Synthesis and characterization of new ruthenium - aromatic thioamide nitrosyls

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ABSTRACT

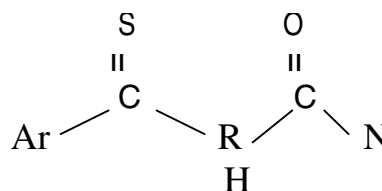
Reactions of aromatic thioamides, LH, with $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ yields $[\text{Ru}(\text{NO})\text{Cl}_3(\text{LH})]$. The complexes have been characterized by analytical, IR, U.V and Visible spectral and magnetic measurements. The presence of $\nu(\text{NO})$ at $1830\text{-}1840\text{ cm}^{-1}$ indicates a $\{\text{Ru NO}\}^6$ configuration.

Key words: Synthesis, ruthenium and thioamide nitrosyls.

INTRODUCTION

Nitrosyl is a versatile ligand for coordination and organometallic compounds¹⁻⁵. The chemistry of metal nitrosyl complexes has become a focus of intensive research⁶ due in part to the important roles of nitric oxide in biological systems⁷. In this connection, the study of metal nitrosyls that release NO under photochemical conditions has attracted much attention^{8,9}. Ru nitrosyls appear as promising candidates for NO generation because they are photolabile but thermally stable under physiological conditions. Prakash and coworkers synthesized a Ru nitrosyl compound with a Polydentate aminothiolate ligand that can release NO upon irradiation with visible light¹⁰. This prompts us to explore the chemistry of Ru nitrosyl complexes in sulphur rich environment.

Aromatic thioamides ArCSNHCOR are potentially mono, bi/tri-dentate ligands whose coordination behaviour was investigated¹¹⁻¹⁴. The compounds are comparable to monothio- β -diketones, because in both the classes Keto-enol tautomerism is possible, and the enolic hydrogen is ionizable. This paper deals with the reactions of $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ with aromatic thioamides. The names and abbreviations of the reagents reported are as follows



Ar= 4- tolyl, R= OEt; N- Carboethoxy-4-toluenethioamide (Hctt)

Ar= 2-pyrrolyl, R=OEt; N-Carboethoxy-2pyrrolyle thioamide (Hcept)

Ar= 1-pyrrolyl, R= OEt; N- Carboethoxy-1-pyrrolylethioamide(Hcpt)

Ar= 2 thiophenyl, R=OEt; N-Carboethoxy-2-thiophenethioamide (Hcett)

Ar= 2-pyrrolyl, R=NH₂; N-Carboamido-2-pyrrolylethioamide(Hcapt)

Ar= 2-pyrrolyl, R=NHPh; N-Carbophenylamido-2-pyrrolylethioamide(Hcppt)

EXPERIMENTAL

All the chemicals used were either chemically pure grade or Analar grade. $[\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2]$ and ligands were prepared by the reported methods¹⁵⁻¹⁸. All the solvents were dried before use. Sulphur and halogens were estimated by the standard procedure¹⁹. IR spectra were recorded with a Perkin-Elmer FT IR

spectrophotometer in KBr DISC. Electronic absorption spectra were obtained on cystronic 108 uv-vis spectrometer from 200-900nm. C,H and N analysis were performed in microanalytical laboratory of I.I.T kanpur.

Preparation of Complexes

[Ru(NO)Cl₃(LH)] (LH=Hctt, Hcett)

A suspension of [Ru(NO)Cl₃(PPH₃)₂] (0.19g, 0.25mmol) and one equivalent of LH (0.56,0.25mmol) in 20ml DMF was heated at reflux

Table 1: Analytical data and colour of the complexes

Compound	m.p (°c)	Magnetic moment	Found (Calcd) %					Mode of linkage
			C	H	N	Cl	S	
[Ru(NO) Cl ₃ (Hctt)]	208	D	28.94 (28.66)	3.20 (2.82)	16.42 (6.08)	23.28 (23.12)	7.12 (6.94)	N and S
[Ru(NO) Cl ₃ (Hcept)]	195	D	22.42 (22.04)	2.86 (2.29)	8.98 (9.64)	23.82 (24.45)	7.56 (7.34)	S and O
[Ru(NO) Cl ₃ (Hcpt)]	185	D	22.32 (22.04)	2.44 (2.29)	3.80 (9.64)	24.64 (24.45)	7.68 (7.34)	N and S
[Ru(NO) Cl ₃ (Hcett)]	160	D	21.64 (21.21)	2.22 (1.98)	6.56 (6.18)	23.86 (23.53)	14.24 (14.14)	N and S
[Ru(NO) Cl ₃ (Hcpt)]	165	D	17.04 (17.71)	2.28 (1.72)	14.12 (13.7)	26.56 (26.19)	8.06 (7.87)	N and O
[Ru(NO) Cl ₃ (Hcppt)]	180	D	30.2 (29.84)	2.84 (2.27)	2.1 (17.68)	22.64 (22.07)	7.08 (6.63)	N and O

D= Diamagnetic

Table 2: Characteristic IR bands of ligands and complexes

Compounds	νNO	νNH	νCO	νCS	Thioamide bands			
					I	II	III	IV
Hctt		3220	1765s	1130s	1540s	1360s	1075s	850w
Ru (NO) Cl ₃ (Hctt)	1830	-	1770s	1115m	1500s	1320m	1060s	840m
Hcept		3350m	1765s	1120s	1540s	1340s	1070s	870m
Ru (NO) Cl ₃ (Hcept)	1830	3325m	1745s	1100m	1555s	1385s	1070s	865m
Hcpt		3210m	1730s	1125s	1480s	1310s	1015s	860s
Ru (NO) Cl ₃ (Hcpt)	1840	-	1790s	1115s	1480s	1310s	1010m	850s
Hcett		3240 br	1730s	1180s	1510s	1360s	1020s	770s
Ru (NO) Cl ₃ (Hcett)	1835	3500 3100 br	1750m	1150m	1500s	1345s	1000m	720s
Hcpt		3400m 3370m 3250m	1730s	1120s	1580s	1330s	1060s	845s
Ru (NO) Cl ₃ (Hcpt)	1840	-	1690s	1130m	1550s	1310s	1070s	860s
Hcppt		3410m 3260m 3160m	1720s	1120s	1525s	1350s	1000m	860m
Ru (NO) Cl ₃ (Hcppt)	1840		1680s	1140m	1510m	1320s	1010m	870m

for 2-3h, during which the colour changed from dark green to orange brown. The solvent was pumped off, and residue was washed with Et₂O and then extracted with CH₂Cl₂. On adding Et₂O-hexane (20ml,1:1 vlv), a crystalline precipitate of the complex formed. It was filtered, washed with Et₂O and dried in vacuo. yield 0.07g, 65%.

[Ru(NO)Cl₃(LH)] (LH= Hcept, Hcpt)

A mixture of [Ru(NO)Cl₃(PPh₃)₂] (0.19g,0.25mmol) and one equivalent of ligand LH (0.05g, 0.25mmol) was heated in DMF (20ml) at reflux for 3h, during which the colour changed from dark green to orange red. The solvent was pumped off, and the residue was purified by column chromatography (silica gel) using CH₂Cl₂- hexane (1:1) as eluant yield 0.07g, 65%.

[Ru(NO)Cl₃(LH)] (LH=Hcpt, Hcppt)

A suspension of [Ru(NO)Cl₃(PPh₃)₂] (0.19g, 0.25mmol) and one equivalent of ligand LH (0.42g,0.06g respectively, 0.25mmol) in 20ml acetone was heated at reflux for 6h. The solvent was removed and residue was extracted with CH₂Cl₂. On adding Et₂O-hexane (20ml,1:1 VIV), afforded pale reddish brown precipitate. It was filtered washed with Et₂O and dried in vacuo. Yield, 0.04g, 0.08g respectively, 70%.

RESULTS AND DISCUSSION

Treatment of [Ru(NO)Cl₃(PPh₃)₂] with one equivalent of LH in refluxing DMF afforded the nitrosyl compounds [Ru(NO)Cl₃(LH)], isolated as air stable solids by the following replacement reaction of PPh₃: [Ru(NO)Cl₃(PPh₃)₂] + LH → [Ru(NO)Cl₃(LH)] + 2PPh₃

The IR spectra show a strong u(NO) band at 1830-1840 cm⁻¹ consistent with other {Ru NO}⁶ system^{20,21}.

Infrared spectra

[Ru(NO)Cl₃(LH)] (LH= Hctt, Hcpt or Hcett)

The band due to ν(C=O) in LH shift to higher wave numbers on complex formation, excluding the possibility of carbonyl oxygen as donor. The ν(C=S) band and the thioamide band IV [mainly due to ν(C=S)] shift to lower wave numbers with reduced intensity. This supports the bonding

through thiocarbonyl sulphur. The thioamide band I (δ(NH) + ν(CN)²² in complexes shift to lower wave numbers indicating metal nitrogen bond formation. Thioamide band II (ν C=N + δ(NH) + δ(CH) and thioamide band III (ν(C=S) + ν(C-N), as expected, also shift to lower wave numbers. The ligands are probably N and S donor in these complexes (Table 2)

Ru (NO) Cl₃(LH)] (LH= Hcpt or Hcppt)

The band due to ν(C=O) in LH shift to lower wave numbers on complex formation which indicates coordination through carbonyl oxygen. The ν(C=S) band and thioamide band IV shift to higher wave numbers. This suggests coordination through N and O in both the complexes.

Table 3: Characteristic uv and visible bands and their assignments

Compound	λ max (nm)	Assignment
Hctt	450	n→π*
	310	π→π*
	270	ILCT
Ru (NO) Cl ₃ (Hctt)	350	IL
	255	CT
Hcept	440	n→π*
	365	n→π*
Ru (NO) Cl ₃ (Hcept)	335 br	I L
	245	C T
Hcpt	300	n→π*
	262	n→π*
Ru (NO) Cl ₃ (Hcpt)	340	I L
	240	C T
Hcett	350	n→π*
	292	n→π*
[Ru (NO) Cl ₃ (Hcett)]	430 br	¹ A _{1g} → ¹ T _{1g}
	350 Sh	I L
	245	C T
Hcpt	350	π→π*
	290	C T
[Ru (NO) Cl ₃ (Hcpt)]	355	I L
	235	C T
	415	n→π*
Hcppt	390	π→π*
	360	CT
	330 br	IL
[Ru (NO) Cl ₃ (Hcppt)]	245	C T

Ru (NO) Cl₃(LH)] (LH= Hcapt)

Compared to unbound LH, $\nu(\text{C}=\text{O})$ shift from 1765 to 1745 cm^{-1} . The thioamide band I shifts from 1540 to 1555 cm^{-1} . The thioamide band II at 1340 cm^{-1} shifts to 1385 cm^{-1} $\nu(\text{C}=\text{S})$ shifts to 1100 cm^{-1} , the thioamide band III at 1070 cm^{-1} , does not shift and the thioamide band IV at 870 cm^{-1} shift to 865 cm^{-1} . This indicates that the Hccept is chelating through S and O. Thus, only Hccept behaves like monothio- β - diketones.

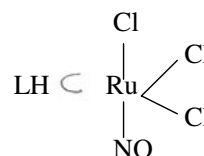
Electronic Spectra

The electronic spectra of ligands and complexes were taken in CH_2Cl_2 and data are given in Table 3. Of the four possible transitions in octahedral ruthenium (II) (t_{2g}^6), ${}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{1g}$, ${}^3\text{T}_{2g}$, ${}^1\text{T}_{2g}$ and ${}^1\text{T}_{1g}$, ${}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{1g}$ and ${}^3\text{T}_{2g}$ are spin forbidden and other two are spin allowed. All the d-d transition

bands are masked by the presence of intense charge transfer bands. However, $[\text{Ru}(\text{NO})\text{Cl}_3(\text{Hcett})]$ show one broad band at 430nm, which is assigned to ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$. one intense band at 380nm each complex is assigned to $d\pi(\text{Ru}) \rightarrow \pi^*(\text{NO})$. The assignments of other bands are given in Table 3

Magnetic Properties

All the complexes are found to be diamagnetic. Thus on the basis of analytical, spectral (ir, uv and visible) and magnetic studies, distorted²³ octahedral structures are proposed for these complexes.

**REFERENCES**

- McCleverty J.A., *Chem. Rev.*, **79**: 53 (1979)
- Richter- Addo G.B, and Legzdins P., *Metal Nitrosyls*, Oxford University Press, New York (1992).
- Eisenberg R. and Meyer, C.D., *Acc. Chem. Res.*, **8**: 26 (1978).
- Mingos D.M.P. and Sharma, D., *Adv. Inorg. Chem.*, **34**: 293 (1989).
- Hayton T.W., Legzdins, P. and Sharp W.B., *Chem. Rev.*, **102**: 935(2002).
- McCleverty J.A., *Chem. Rev.*, **104**: 403 (2004).
- Ignarro L.J., *Nitric Oxide: Biology and Pathology*, Academic Press, San Diego (2000).
- Lorkovic I.M., Miranda K.M., Lee B., Bernhard S., Schoonover, J.R. and Ford, F.C., *J. Am. Chem. Soc.*, **120**: 11674 (1998).
- Tfouni E., Krieger, M., McGarvey B.R. and Franco D.W., *Coord. Chem. Rev.*, **236**: 57(2003).
- Prakash R., Czara A.U., Heinemann F.W, and Sellmann D., *J. Am. Chem. Soc.*, **127**: 13578(2005).
- Singh T. and Singh R.N., *Synth. React. Inorg. Met-org. Chem.*, **19(3)**: 251 (1989).
- Chauhan Veena and Dikshit S.K., *Bull. Chem. Soc. Jpn.*, **60**: 3005 (1987).
- Chauhan Veena and Dikshit S.K., *Synth. React. Met-org. Chem.*, **16(10)**: 1435 (1986).
- Singh Varsha., Pandey D.P, and Singh T., *Orient. J. Chem.*, **22(2)**: 405 (2006).
- Levison J.L. and Robinson. S.D., *J. Chem. Soc(A)*, 2947 (1970).
- Papadopoulos E.P., *J. Org. Chem.*, **38**: 667 (1973).
- Papadopoulos E.P., *J. Org. Chem.*, **39**: 2540 (1974).
- Papadopoulos E.P., *J. Org. Chem.*, **41**: 963 (1976).
- Vogel A.I., "A Text Book of Quantitative Inorganic Analysis", IV Edn, ELBS and Longmans, London, 433, 504, 494 (1985).
- Rose M.J., Fry N.L., Marlow R., Hinck L. and Mascharak, P.K., *J. Am. Chem. Soc.*, 130: 8834 (2008).
- Rose M.J., Patra A.k., Alcia E.A., Olmstead M.M. and Mascharak, P.K., *Inorg. Chem.*, **46**: 2328 (2007).
- Rao CN.R. and Venkataraghavan., *Spectrochim. Acta.*, **18**: 542 (1962)
- Golfeto C.C., Poethsitz G.V., Selistre-d. Araujo S.H., de Arays, M.P., Ellena J., Castellano E.E., Lopes L.G.L., Moreira I.S. and Batista A.A., *J. Inorg. Biochem.*, **104**: 489 (2010).