Synthesis and Characterization of Carboxamide Ruthenium (III) Nitrosyl Complexes

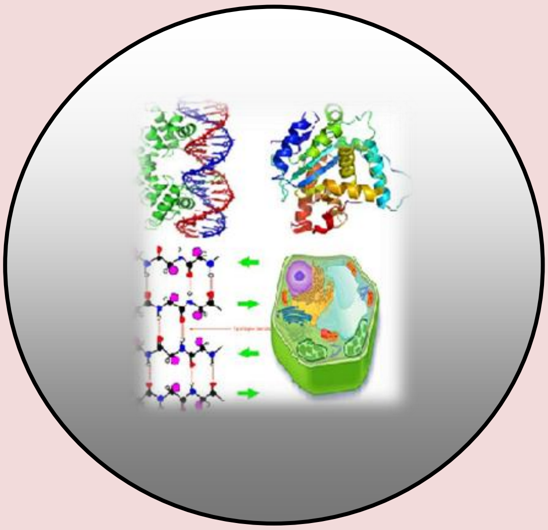
By

K.K. Singh

ISSN 2319-3077 Online/Electronic
ISSN 0970-4973 Print

Index Copernicus International Value
IC Value of Journal 82.43 Poland, Europe (2016)
Journal Impact Factor: 4.275
Global Impact factor of Journal: 0.876
Scientific Journals Impact Factor: 3.285
InfoBase Impact Factor: 3.66

J. Biol. Chem. Research
Volume 37 (1), 2020 Pages No. 188-193

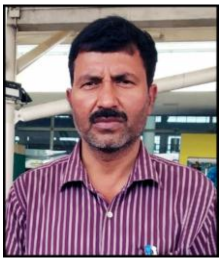


Journal of
Biological and
Chemical Research
An International Peer Reviewed / Referred Journal of Life Sciences and Chemistry

Indexed, Abstracted and Cited in various International and National Scientific Databases

Published by Society for Advancement of Sciences®

J. Biol. Chem. Research. Vol. 37, No. 1, 188-193, 2020
(An International Peer Reviewed / Refereed Journal of Life Sciences and Chemistry)
Ms 37/01/3445/2020
All rights reserved
ISSN 2319-3077 (Online/Electronic)
ISSN 0970-4973 (Print)



Dr. K.K. Singh
http:// www.sasjournals.com
http:// www.jbcr.co.in
jbiolchemres@gmail.com

RESEARCH PAPER
Received: 29/01/2020 Revised: 30/03/2020 Accepted: 31/03/2020

Synthesis and Characterization of Carboxamide Ruthenium (III) Nitrosyl Complexes

K.K. Singh
Department of Chemistry, T.D.P.G. College, Jaunpur (U.P.) 222002, U.P., India

ABSTRACT

New ruthenium- nitrosyl complexes of Carboxamide (RCONHCOR') were synthesized. The molecular formula of these complexes are [RuCl_3 (NO) (RCONHCOR')]. These complexes were Characterized analytical speclral (1R, UV and Visible), magnetic and conductometric measurements. The presence an absorption band at 1940-1950 Cm^{-1} in complex suggest the presence of {Ru-NO}^{6} electron configuration. Based on these studies tentative structures of these complexes have been proposed.

Keywords: Ruthenium nitrosyl, spectral, Carboxamide and electron configuration.

INTRODUCTION

Synthesis and structural characterization of ruthenium complexes have gained considerable area of research interest during the last decade in view of their role in biological processes such as in neuron-signaling, (Ignarro, 2000) Cardiovascular control, defense mechanism against microorganisms and tumor cells. Control and monitoring of release of NO from NO doner metal complexes are crucial for understanding its chemical and biological functions. Light- triggered NO donors have been successfully used for controlled delivery of nitric oxide to biological target (Mascharak et. al. 2004). Numerous compounds have been prepared with the aims of studying these structruce and bonding in ruthenium complexes with NO ligand considering them as a precursores for synthesis of N_2 Complexes as most important steps in biochemical nitrogen cycle.

In view of the diverse application of ruthenium nitrosyls, we synthesized and characterized several ruthenium nitrosyl complexes (Singh et. al. 2011). As a part of our work in this area, we report the synthesis and characterization new carboxamide ruthenium (III) nitrosyl complexes.

Experimental

All the chemicals used were either chemically pure or Analar grade.

(i) $[RuCl_3(NO)(PPh_3)_2]$ was prepared by literature method given elsewbere (Sing et.al.1980)

(ii) All the carboxamides RCONHCOR′ were prepared by the procedure give (Papadopoulos 1973, 1974)

(iii) Preparation of [RuCl$_3$(NO)(RCONHCOR′)] (R= pyrrolyl-1 or pyrrolyl-2; R' = OC_2H_5 or NH_2) 450 mg. of [RuCl$_3$(NO)(PPh$_3$)$_2$) was dissolved in alcohol 15ml. under N_2 with constant stirring. 250mg. of ligand solution in 10 ml. alcohol was added drop wise with constant stirring (1h) and refluxed (15min.) petroleum ether (40-60^0) was added whereby precipitate of complex was formed. It was filtered washed several times with petroleum ether and dried in Vacuum.

(iv) Preparation of [RuCl$_3$ NO R CONHCOR'] (R= Pyrrolyl-1 or pyrrolyl-2, R' = -NHPh) 500mg. of [RuCl$_3$(NO) (PPh$_3$)$_2$) was dissolved with magnetic stirring in 30ml. CH_2Cl_2 and then a solution of ligand 200mg. in 20ml. CH_2Cl_2 was mixed to it. The stirring was continued for 2h and then resultant reaction mixture was kept in ice cold water. A crystalline compound was formed, fultered, washad with ether and dried in vacuum.

(v) [RuCl$_3$(NO)(RCONHCOR')] (R= thiophenyl, R′ = OC_2H_5)

[RuCl$_3$(NO) (PPh$_3$)$_2$) (400mg.) and ligand (250mg.) was refluxed in n-butanol (10ml.) for 2h. The solvent was removed under reduced pressure and remaining oil was dried in vacuo. Water (6ml) was added. The solution was decanted into a beaker and allowed to stand at room temperature. 3 days latter orange crystals were formed, filtered off and dried in vacuum.

Analyses

The analyses of ruthenium, sulphur, chloride wee carried out by the standard methods (Vogel, 1986). Carbon, hydrogen and nitrogen analyses were performed by the micro analytical section of Indian Institute of Technology, Kanpur (U.P.), India. The analytical results are given in table 1.

The IR spectra, magnetic susceptibilities measurements and UV visible spectra of complexes and ligands have been taken in Chemistry Department B.H.U., Varanasi.

RESULTS AND DISCUSSION

A series of ruthenium (III) nitrosyl carboxamide complexes were synthesized by Substitution of ligands (RCONHCOR') to triphenylphosphine in (RuCl$_3$(NO)(PPh$_3$)$_2$].

$$[RuCl_3(NO)(PPh_3)_2] + RCONHCOR' \xrightarrow[\text{reflex}]{\text{Stirring}} [[RuCl_3(NO)(RCONHCOR')]$$

The dark coloured compounds were isolated and analysed. The analytical data are in good agreement with stoichiometry proposed (Table-1). All the compounds are air stable, non hydroscopric, Soluble in most of the common organic Solvents and partially soluble in water. The molar conductances of the complexes in 10^{-2}M N,N'-dimethyl formamide (50-60 Ohm^{-1} cm^2 mol^{-1}) indicates non electrolyte.

The title ligands R CONHCOR' are similar to β-diketones. The principal advantage with these ligand lies in the fact that properties and flexibility of ligands can be varied by changing CH_2 group in β-diketones as well as R and R' by various groups. These ligands are abbreviated as follows:

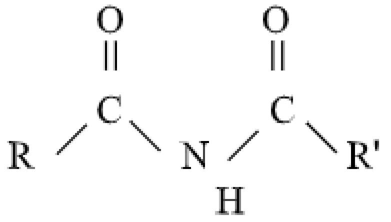
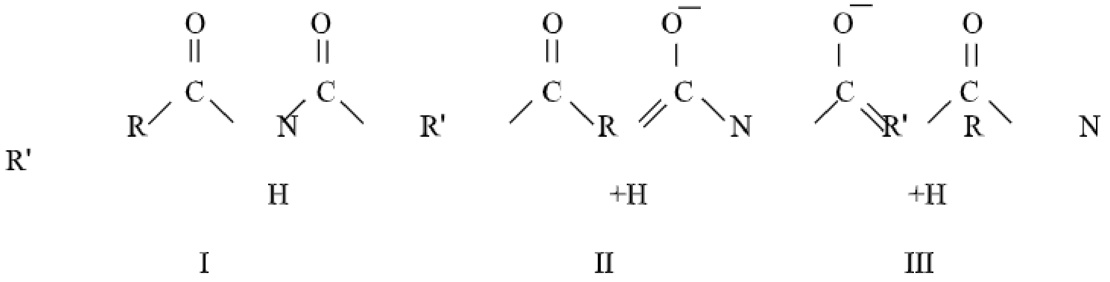


Figure 1.

R= 2-Pyrrolyl, R' = NH_2; N- Carbamoylpyrrole-2-carboxamide (CPC)
R= 2-Pyrrolyl, R' = OC_2H_5; N- Ethoxycarbonylpyrrole-2-Carboxamide(EPC)
R= 2-Pyrrolyl, R' = NHPh; N- Ethoxycarbamoylpyrrole-2-Carboxamide(EPC)
R= 1-Pyrrolyl, R' = OC_2H_5; N- Ethoxycarbonylpyrrole-1-Carboxamide(EPD)
R= 1-Pyrrolyl, R' = NHPh; N- Ethoxycarbamoylpyrrole-1-Carboxamide(EPN)
R= 2-thiophenyl, R' = OC_2H_5; N- Ethoxycarbonylthiophene-2-Carboxamide(ETC)

The complexing abilities of these carboxamides can be best understood in terms of resonance structure given below.



The absence of absorption bands in region 2500-2600 cm^{-1} in the 1R spectra of ligands and complexes suggested that they are present in one form and not in ol form. The absence of absorption bonds owing to υ(OH) and δ(OH) in ligands spectra are also indicative of keto form. So, it is believed that structure-I is dominant in the course of reactions.

The IR bands of pyrrole moiety in CPC, EPC, EPC, EPD and EPN at 2990, 1550, 1470, 1450, 1140, 995, 750, 520, and 440 cm^{-1}, thiophenyl moiety at 3050, 1660, 1590, 750 and 700 cm^{-1} do not undergo any considerable amount of shift after the complex formation because nitrogen atom of pyrrole (Singh et.al. 1980) and thiophenc sulphur atom in thiophenyl ring is poorly basic on account of involvement of lone pair of electron in delocalization processes. Nitrogen atom of – NHPh group will not participate in bonding with ruthenium ion owing to the involvement of lone pair on nitrogen atom in phenyl ring.

Oxygen atom of OC_2H_5 is also poorly basic, so its participation in any type of metal-ligend bonding is too less. Therefore, it is assumed that bonding of ruthenium(III) occurs via-C(O)NH C(O)- moiety of ligand (RCONHCOR').

The IR spectra of ligands exhibited characteristic band at 1680-1720 cm^{-1} due amide band I having major contribution of –CO group in each ligands, shifted lower wave number side (-40 cm^{-1}), indicating coordination through Oxygen of carbonyl group. Bonding of ruthenium ion (electron withdrawing group) with oxygen atom of carbonyl group of ligand will shift amide band II and III and the band due to υ (C- O) of (- C- OC_2H_5) group towards higher wave number (Colthup et.al. 1975).

The broad bands due to amide band II at 1340 and 1270 cm^{-1} and amide band III at 1210 cm^{-1} also shifted towards higher wave number υ(CO) of (-C-OC_2H_5) shifted towards higher wave number (+30 cm^{-1}) present in the spectra of ligands. This also confirms the bonding of ruthenium ion through carbonyl of the ligand.

The IR spectra of complexes $[RuCl_3(NO)(R\ CONHCOR')]$ exhibited bands at 1930-1950 cm^{-1}. These absorption bands are assumed due to stretch frequencies of nitrosyl group in complexes (Prinaka De et.at. 2009) indicating $\{Ru\text{-}NO\}^6$ configuration. The nitrosy π^* MO will monopolise dπ electron of ruthenium ion theirby decreasing the stretching frequency υ(Ru-Cl) trams to it and strenthening Ru-N bond. The presence of absorption band at 600-630 cm^{-1} also reveals the formation of Ru- N bond from nitrosyl group.

The new bands in all the complexes at 600-620 cm^{-1} is assigned to couple vibrations of M-O bonds. The absortion bands of T(NH) of uncoordinated ligand were observed at 600 and 650 cm^{-1} in the spectra of complexes.

Electronic Spectra

Electronic spectra of all the ligand and complexes were recorded in 10^{-2} molar CH_2Cl_2 solutions. These absorption bands along with their assignments are given in table-2. These assignments are based on the molecular orbital diagram applicable to coordinated nitric oxide in complexes elsewhere (Mingos, 1989). Ruthenium ion in octahedral environment of ligands would exhibit theoretically four transition ^1A_1g ^3T_1g, ^3T_2g and $^1A_1g \longrightarrow {}^1T_1g$, ^1T_1g . The two spin forbidden bands are rarely observed owing to very poor intensities. But rest of two spin allowed transitions are generally observed in electronic spectra of ruthenium ion octahedral complexes. However, these transition also are masked some time owing to presence of intense charge transfer bands.

Thus, on the basic of spectral (1R, UV and visible), magnetic, and conductmetric studies the following tentative structures of complexes is proposed.

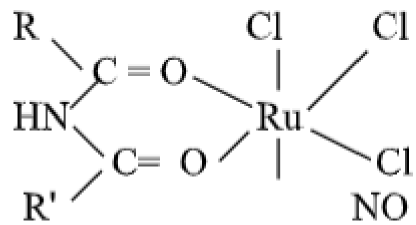


Figure 2.

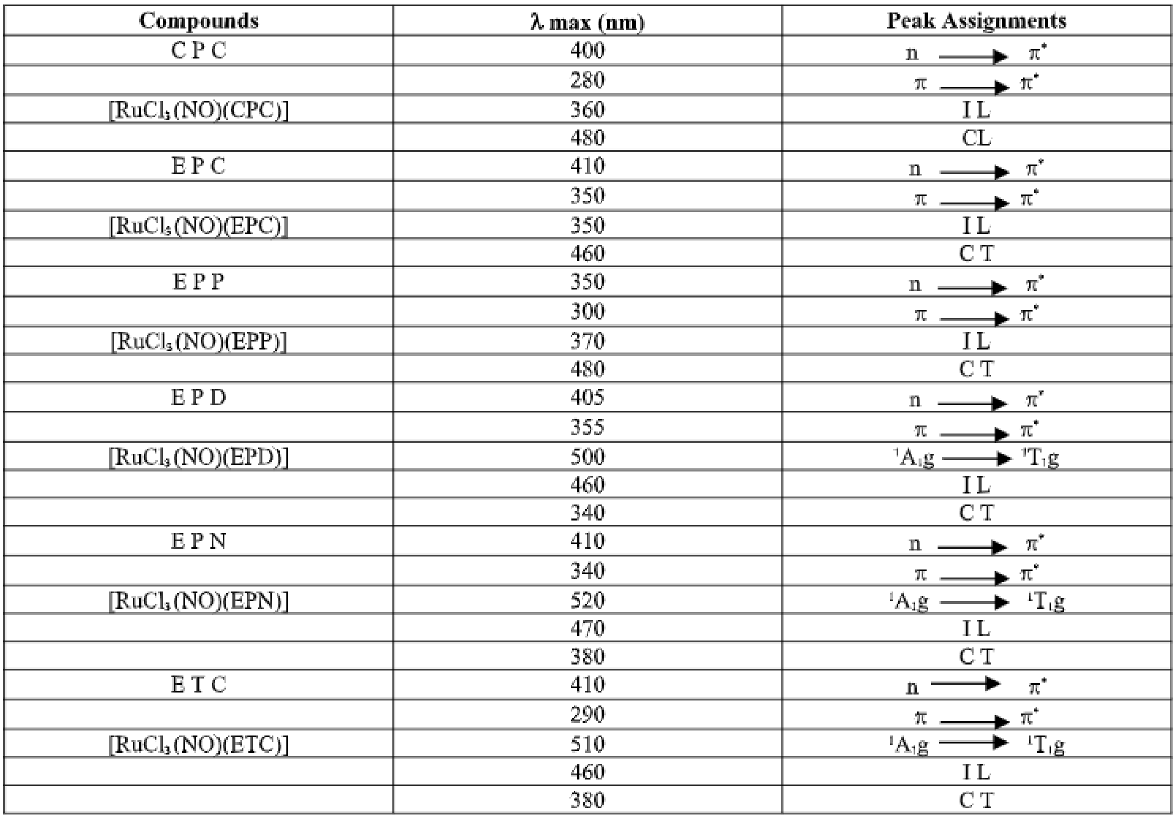
Table 1.

Compounds	Colour	M.P. ^{0}c	Magnetic Moments	Found (Coled) %						Ln $(ohm^{-1} cm^{-1})$
				C	H	N	C1	S	Ru	
[$RuCl_3$NO (CPC)]	Brown	125	D	18.22 (18.43)	1.86 (1.79)	14.26 (14.34)	27.48 (27.27)	-	25.64 25.86	40
[$RuCl_3$ (NO)(EPC)]	Orange	120	D	22.62 (22.88)	2.46 (2.38)	9.86 (10.01)	25.50 (25.38	-	23.88 (24.07)	40
[$RuCl_3$NO (EPP)]	Light Yellow	122	D	30.68 (30.86)	2.46 (2.35)	11.96 (12.00)	22.74 (22.82)	-	21.80 (21.65)	45
[$RuCl_3$ (NO)(EPD)]	Dark Yellow	118	D	22.60 (22.88)	2.56 (2.38)	9.90 (10.01)	25.56 (25.38)	-	23.86 (4.07)	50
[$RuCl_3$ (NO)(EPN)]	Dark Brown	130	D	30.76 (30.86)	2.58 (2.35)	11.92 (12.00)	22.90 (22.82)	-	21.58 (21.65)	35
[$RuCl_3$ (NO)(ETC)]	Orange	110	D	21.88 (21.99)	2.14 (2.06)	6.22 (6.41)	24.54 (24.39)	7.48 (7.33)	23.02 (23.13)	40

ANALYTICAL DATA, COLOUR, MELTING POINT, MAGNETIC MOMENTS & MOLAR CONDUCTANCE

Table 2.

ELECTRONIC SPECTRAL DATA OF THE LIGANDS, COMPLEXES AND THEIR ASSIGNMENTS



Compounds	λ max (nm)	Peak Assignments
C P C	400	$n \longrightarrow \pi^*$
	280	$\pi \longrightarrow \pi^*$
[$RuCl_3$(NO)(CPC)]	360	I L
	480	CL
E P C	410	$n \longrightarrow \pi^*$
	350	$\pi \longrightarrow \pi^*$
[$RuCl_3$(NO)(EPC)]	350	I L
	460	C T
E P P	350	$n \longrightarrow \pi^*$
	300	$\pi \longrightarrow \pi^*$
[$RuCl_3$(NO)(EPP)]	370	I L
	480	C T
E P D	405	$n \longrightarrow \pi^*$
	355	$\pi \longrightarrow \pi^*$
[$RuCl_3$(NO)(EPD)]	500	$^1A_1g \longrightarrow {}^1T_1g$
	460	I L
	340	C T
E P N	410	$n \longrightarrow \pi^*$
	340	$\pi \longrightarrow \pi^*$
[$RuCl_3$(NO)(EPN)]	520	$^1A_1g \longrightarrow {}^1T_1g$
	470	I L
	380	C T
E T C	410	$n \longrightarrow \pi^*$
	290	$\pi \longrightarrow \pi^*$
[$RuCl_3$(NO)(ETC)]	510	$^1A_1g \longrightarrow {}^1T_1g$
	460	I L
	380	C T

ACKNOWLEDGEMENTS

Thanks to Dr. T. Singh for Scientific advice and language corrections.

REFERENCES

Ignarro, L.J. (2000). Nitric Oxide: Biology and Pathology Ed., Academic Press: San Diego.

Afshar, R.K., Patra, A.K., Olmstead, M.M. and Mascharak, P.K. (2004). Synthesis, Structure and reaction of $(Fe\text{-}NO)^6$ nitrosyls derived from polypyridine-carboxamide ligands Photoactive NO donors and reagents for s-nitrosylation of alkylthiols, In org. Chem., 43: 5736-5743.

Singh, T. and Singh K.K. (2011). Synthesis and characterization of some cis $[Ru(NO)XL_2(PPh_3)_2]$ X= neomodentate type complexes of nitrosylruthenium(II). Orient. J. Chem., 27: 155-160.

Jain, K.C., Pandey, K.K., Prasad, R., Singh, T and Agarwala, U.C. (1980). Reactions of Nitrosyl halides and nitrites with ruthenium chlorides hexahydrate, Chloroplatinic acid and Palladum (II) Chlorides in Presence of PPh_3, $AsPh_3$ and $SbPh_3$ Ind. J. Chem., 19A: 1089-1091.

Papadopoulos, E.P. (1973, 1974). Reactions of pyrrole with isothiocyanates. Preparation and reactions of N-ethoxycarbonylpyrrole-2-thiocarboxamide and 2-thiopyrrole-1, 2-dicarboxamide, *J. Org. Chem.*, 38; 667-947. Preparation and reactions of N-ethoxycarbonylthiophene-2-carboxamide and N-ethoxy carbonylthiophene-2-thiocarboxamide, J.org., Chem., 39: 2540-2542.

Vogal, A.I. (1986). A text-book of quantitative inorganic analysis. ELBS, London, 4th Edn., 444.

Singh, T. and Agarwala, U.C. (1980). Complexing behavior of N- ethoxycarbonylpyrrole-2-thiocarboxamide. *Ind. J. Chem.,* 19A: 755-758.

Calthup, N.B., Dal, L.Y. and Wiberty, S.Y. (1975). Introduction to infrared and Raman spectroscopy. Academic, Press. New-Yark, Sanfrancisco, London. 271, 276, 288, 289, 356, 305-307.

De Prinaka Sarpar, B., Magi, S. Das, A.K., Bulak, E., Mobin, S.M., Kaim, Wolfgang and Lahiri, G.K. (2009). Stabilization of $[Ru\ NO]^6$ and $[\ Ru\ No]^7$. Stales in $[Ru^{II}$ (trpy) $(bik)NO]^{n\ +}$ [trpy = 2, 2': 6', 2^{II}-terpyridine, bik = 2, 2' – bis (1-methylimidazolyl) ketone]-formation reactively and Photorelease of metal bound nitrosyl.

Mingos, D.P.S. and Sherman, D.J. (1989). In: A.J. Sykes (Ed.), Advances in inorganic chemistry, Harcourt. Brace and Jovanovich, London, 293-377.

Corresponding author: Dr. K.K. Singh, Department of Chemistry, T.D.P.G. College, Jaunpur (U.P.) 222002, U.P., India
Email: kksingh5678@gmail.com