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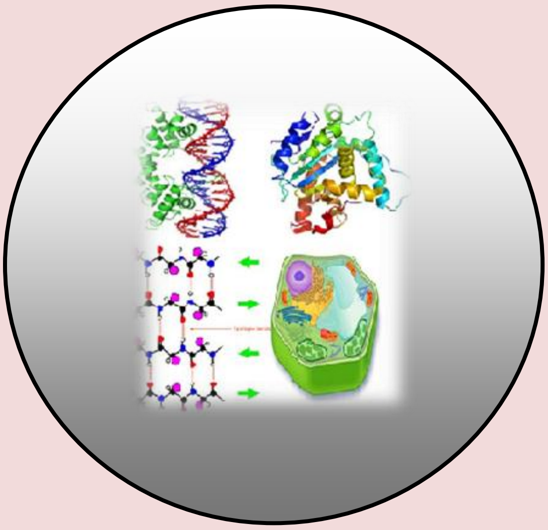

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Synthesis, Structure and Reactivity of Cationic Thiocarboxamide Molybdenum (O) Nitrosyl Complexes

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ABSTRACT

A variety of aromatic thiocarboxamides reacted with tripyridine molybdenumtricarbonyl [Py]$_3$Mo(CO)$_3$] giving [(LH) (Py)Mo(CO)$_3$] (LH=aromatic thiocarboxamides). The nitrosylation of these complexes gave cationic complexes of the type [(LH)(Py)Mo(CO)$_2$NO]PF$_6$. The presence of absorption bands at 1772-1780 cm^{-1} in the IR spectra of all the complexes suggests the [Mo-No]^6 electron configuration. The studies on the structure of these complexes were made on the basin of spectral (IR, UV and visible), magnetic and conductance measurements. Based on these studies tentative structures of these complexes have been proposed.

Keywords: Nitric oxide, thiocarboxamide, molybdenum, absorption bands, π – acceptor.

INTRODUCTION

Nitric oxide has been found to participate in many biological functions including blood pressure, inhibition of platelet aggregation, modification of neurotransmission and antimicrobial activities (Ignarro 2000, Feelish 1996). The increase in the concentration of nitric oxide in the cell can attack on concerous cell which could result in tumor supression (Mascharak et. al., 2004, Arion et.al. 2014). The complexes of molybdenum in lower oxidation states (-2 to +1) have been the area of extensive research during the past two decates (Ehweiner et.al. 2020) owing to their biological importance as nitrate reductase in the flavin part of enzymes, B-acceptor, π-acceptor in presence of carbon monoxide, cyclopentadiene, nitric oxide, Aph$_3$ (A=P, As) and pyridine.

Catalytic applications of transition metal nitrosyls (Pecak et.al. 2021) are of current interest to organometallic and organic chemists.

In view of the diverse and important application of transition metal nitrosyls, we synthesized and studied the structures and reactivity of several ruthenium nitrosyl complexes (Singh et. al. 2011). In this paper, we report the synthesis, structure and reactivity of molybdenum (o) nitrosyl complexes of some aromatic thiocarboxamides.

Experimental

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

(A) $[(Py)_3\ Mo(CO)_3]$ was prepared according to literature method given elsewhere (Abel et.al., 1959).

(B) Aromatic thiocarboxamides were prepared by the procedure given (Papadopoulos 1973, 1974, 1976).

(C) Preparation of $[(LH)(Py)Mo(CO)_3]$: To a 100ml round bottom flask was added $[(Py)_3Mo(CO)_3]$ (0.2g~0.5m mole), aromatic thiocarboxamides (~0.5m mole), and tolune (30 ml). The resulting mixture was stirred under reflux for 1.5h. during which time it darkened. The mixture was cooled to ambient temperature, and solid was collected in a fritted Buchner funnel, rinsed with toluence (30ml) and hexane (30 mol), and dried in an evacuated desiccator to give $[(LH)(Py)Mo(CO)_3]$.

(D) Preparation of $[(LH)(Py)Mo(CO)_3(NO)]PF_6$: To a 100ml round bottom flask was added $[(LH)(Py)Mo(CO)_3]$ (~0.5m mole), $NaNO_2$ (0.25g ~ 3.6 m mole), KPF_6 3.6g ~ 13m mole, and methanol (25ml). Hydrochloric acid (Conc.~2.3ml~27.6m mole) was added dropwise over 40-50second whereby a precipitate of the complex was formed. The mixture was cooled in an ice bath for 15 min. and solid was collected in a fritted Buchner funnel, washed with water (60 ml) and ether (90ml), and dried in an evacuated desiccator.

Analyses

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

The IR spectra, the magnetic susceptibility measurements and the U.V. and visible spectra of the complexes and the ligands have been taken in chemisty deptt. B.H.U., Varanasi. The assignments of major IR bonds are given in table 2. The assignments of UV and visible bands are given in Table-3.

RESULTS AND DISCUSSION

A series of thiocarboxamide complexes were synthesized (scheme-1) by the reaction of aromatic thiocarboxamides with $(Py)_3Mo(CO)_3$.

$$[(\mathrm{Py})_3\mathrm{Mo(CO_3)}] + \mathrm{LH} \xrightarrow[reflux,1.5]{stirring} [(\mathrm{LH})(\mathrm{Py})\mathrm{Mo(CO_3)}]$$

The resultant compound is reacted with $NaNO_2$ and HCl where NOCl (g) is generated in situ forming nitrosyl complexes.

Scheme-2.

$$[(LH)(Py)Mo(CO_3)] \xrightarrow[KPF_6,\text{ room temp.}]{NaNO_2, HCl} [(LH)(Py)Mo(CO)_2)(NO)]PF_6$$

The products were isolated as dark coloured compound. The analytical data are in good agreement with the stoichiometry proposed (Table-1) which the metal ion take in its normally preferred geometry. All the compounds $(LH)(Py)Mo(CO)_3$ are air stable, non hygroscopic, partially soluble in methanol, n-hexane, benzene and soluble in chloroform. The nitrosyl complexes $[(LH)(Py)Mo(CO)_3NO]PF_6$ are soluble in alcohol, pyridine and water. The molar conductances of the complexes in 10^{-3}m N,N' dimethyl formamide (98-102 ohm^{-1} cm^{2} mol^{-1}) (Table-1) indicates 1:1 electrolyte.

The ligands LH = R_1CS NH COR$_2$ are abbreviated as follows :

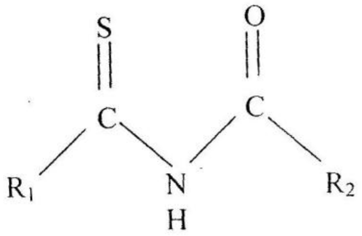
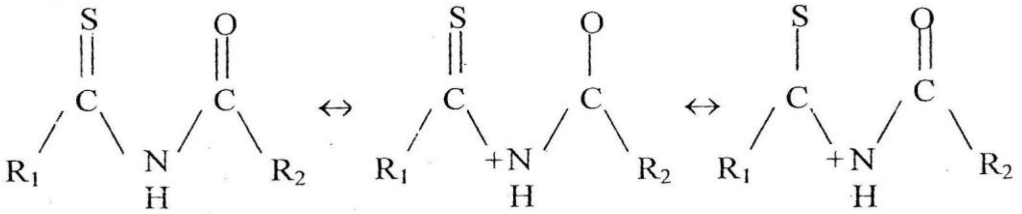


Fig . 1

R_1 = 4 Totyl, R_2 = 0Et; N-ethoxycarbonyltoluene-4-thiocarboxamide (EBH)
R_1 = 2 pyrrolyl, R_2 = 0Et; N-ethoxycarbonyl pyrrole-2-thiocarboxamide (ETH)
R_1 = 1 pyrrolyl, R_2 = 0Et; N-ethoxycarbonyl pyrrole-1-thiocarboxamide (EPH)
R_1 = 2 thiophenyl, R_2 = 0Et; N-ethoxycarbonyl thiophene-2-thiocarboxamide (ESH)
R_1 = 2 pyrrolyl, R_2 = NH_2; N-carbamoyl pyrrole-2-thiocarboxamide (CNH)
R_1 = 2 pyrrolyl, R_2 = NHPh; N-phenyl carbamoylpyrrole-2-thiocarboxamide (PTH)

The donar properties of these thioamides or thiocarboxamides can perhaps be best understood in terms of reronance structure given below. The absence of a weak band in the region 2600 cm^{-1} in spectra of ligand and those of complexes suggested that the ligand and complexes are present in thione form and not in thiol form. Similarly absence of bands due to υ(OH) and δ(OH) in the spectrum of ligand indicated it to be present in keto form. So, it is assumed that structure-I is dominant during the course of reactions.



(I) (II) (III)

The characteristics IR bands of pyrrole moiety in ETH, EPH, CNH and 2990, 1550, 1470, 1450, 1140, 1040, 995, 750, 520 and 440 cm^{-1}) totyl group in EBH (3030, 2550-2960, 1600, 1570, 770 and 730cm^{-1}) thiophenyl group in ESH (3050, 1660, 1590, 750 and 700cm^{-1})

do not undergo any considerable shift since nitrogen atom of pyrrole (Singh et.al. 1980, Chauhan et.al., 1988) ring and sulphur atom of thiophenyl group is poorly basic on account of involvement of lone pair electron in delocalization processes. The deprotonation of pyrrole NH group can take place in highly basic medium in which ligands are unstable. In PTH ligand, nitrogen of -NHPh is poorly basic owing to the delocalization nitrogen lone pair in phenyl ring. Therefore, nitrogen of -NHPH group has least possibility to form a bond wish metal ion. The lone pair of oxygen atom in -OEt group is poorly basic, so it will not participate in bonding with metal ion. Thus, it is assumed that bonding in complexes occur through -C(S) NH C(O)- moiety of ligands (LH) and major shift, in the position of the bands are expected to be in thioamide and amide bands. The characteristics bands of pyridine due to c=c and C=N stretching (ring) (1430-1600) were present in all the complexes. The IR spectra of all the complexes $[(LH)(Py)Mo(CO)_3]$ exhibited two strong absorption bands in the range 1730-1740, 1800-1880 cm^{-1} and complexes $[(LH)(Py)Mo(CO)_3(NO)]PF_6$ exhibited at 1950-1960 cm^{-1}, 2020-2030 cm^{-1} respectively. These absorption bands are assigned to stretching frequency of cis carbonyl groups (Abel, 1959). These stretching frequencies are present at lower positions as compared to υ(CO) in $[(Py)Mo(CO)_3]$ owing to the substitution of Py by ligand having N, O or S and donor atom. Pyridine ligands have weak π bonding ability. As a result of this CO group will monopolise dπ, electron of metal atom to its self thereby decreasing the stretching frequency of carbonyl ligand and increasing M-C bond strength. In nitrosyl complexes $[(LH)(Py)Mo(CO)_2(NO)]PF_6$, one carbonyl has been replaced by NO ligand. Although, it has commonly been found that CO is probably a best π bonding ligand but there is possibility that nitrosyl group or phosphorous trifluoride may some times be a better π-acceptor (Huheey et.al. 2001). The observed frequencies of carbonyl groups in $[(LH)(Py)Mo(CO)_2(NO)]PF_6$ complexes at higher frequencies than $[(LH)(Py)Mo(CO)_3$ suggests that CO receives less and less π electron density and C-O stretching frequency increases accordingly.

The apperance of strong bands at 1782-1780 and 620-650 cm^{-1} in the nitrosyl complexes suggested the presence of $[Mo\text{-}No]^6$ electronic structure of metal atom in the nitrosyl complexes (Maurya et.al., 2006). The shift in the position of thioamide and amide band of ligand in complexes are discussed in the following spectral observations.

IR Spectra of $[(LH)(Py)Mo(CO)_3$ (IH = EBH, EPH, ESH) -

1. The band due to υ(C=O) in LH shifts to higher wave numbers on complexation excluding the possibility of carbonyl oxygen as donor.
2. The υ(C=S) band and the thioamide band IV mainly due to υ(C=S) shift to lower wave numbers with reduced intensity. This support the bonding through thiocarbonyl sulphur (Rao, et.al., 1970).
3. The thioamide hand I (δNH+υCN) in complexes shift to lower wave number indicating metal nitrogen bond formation (Chauhan, et.al., 1988).
4. Thioamide band II (υC=N+δNH+δCH) and thioamide band III (υC=S+υC-N), shift to lower wave numbers.

5. The new bands appeared at 550 and 370 cm^{-1} in all the complexes are assigned due to coupled vibration of υ(Mo-N) and υ(Mo-S). The above facts supports the LH coordination to Mo through N and S (Adam 1968).

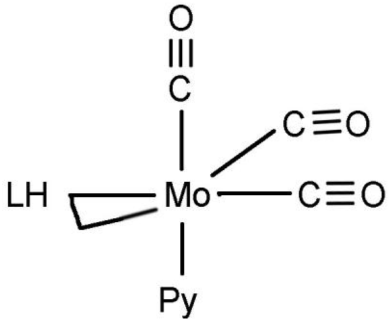
IR Spectra of [(LH)(Py)Mo(CO)$_3$ (LH = CNH, PTH) -

1. The band due to υ(C=0) in LH shift to lower wave number on complexation which indicates coordination through carbonyl oxygen.
2. υ(C=S) and thioamide band IV shift to higher wave number, whereas the thioamide bands II and III shift to lower wave numbers.
3. The bands at 470 and 545 cm^{-1} present in spectra of the complexes is assigned to the contribution from coupled vibrations of υ(Mo-O) and υ(Mo-N). These facts support the bonding through oxygen and nitrogen atoms.

IR Spectra of [(LH)(Py)Mo(CO)$_3$ (LH = ETH) -

1. Compared to unbound LH., υ(C=O) shift from 1765 to 1745 cm^{1} indicating the involvement CO-group of ligand in bond formation.
2. The thioamide bond-I shifts from 1540 to 1550 cm^{-1}.
3. The thioamide band II of ligand at 1340 cm^{-1} shift to 1380 cm^{-1}, thioamide band II of ligand at 1070 cm^{-1} does not shift but the thioamide band IV at 870 cm^{-1}, shift to lower wave number (860 cm^{-1}) indicating the bond formation by CS group of ligand - CSNH CO - moiety, the downward shift of band due to C=S grow from 1120 to 1100 cm^{-1} supports the bonding by CS group to metal ion.
4. The new bands at 470 and 350 cm^{-1} are assigned to the coupled vibrations due to υ(Mo-O) and υ(Mo-S). This indicates that ETH cordinate through sulphur and oxygen.

Thus, on the basis of IR spectral studies, we proposed the following tentative structures of the molybdenum complexes.



Magnetic Measurement

The magnetic susceptibility measurements of these complexes indicate that they are diamagnetic and hence, they should have ground states with a molecular orbital configuration $(^1a_2)^2(^1a_1)^1$ $(^1b_2)^2$ following the molecular orbital diagram reported elsewhere. This result in consistent with low spin [(LH)(Py)Mo(CO)$_2$ NO]$^+$ electronic configuration of Mo(0) in these complexes.

Electronic Spectra

Electronic spectra of the complexes were recorded in 10^{-3} DMA (N,N-dimethylacetamide) solutions. All the complexes exhibited six absorption bands at nearly same position. These absoroption bands along with their assignments are presented in Table-3.

These assignments are based on molecular orbital diagram applicable to have coordinated nitrosyl complexes reported elsewhere (Mingos, 1989).

Molar Conductances

Molar conductances were measured with a toshniwal conductivity bridge type CL01.02. The observed molar conductances values are given in Table-1. The complexes are found in the expected range for 1:1 in N.N'-dimethyl formamide.

Table 1. ANALYTICAL DATA, COLOUR, MELTING POINT, MAGNETIC MOMENTS AND MOLAR CONDUCTANCE.

Compounds	Colour	M.P. ^{0}C	Magnetic Moments	Found (Caled)%							Lm (ohm^{1} cm^{1})
				C	H	N	F	P	S	Mo	
[(EBH)(Py)Mo(CO)$_3$]	Dark Yellow	170	D	47.12 (47.80)	3.84 (3.73)	5.70 (5.80)	-	-	6.56 (7.63)	19.82 (19.91)	
[(ETH)(Py)Mo(CO)$_3$]	Yellow Brown	145	D	42.12 (42.00)	3.40 (3.28)	9.08 (9.19)	-	-	7.12 (7.00)	20.20 (21.00)	
[(EPH)(Py)Mo(CO)$_3$]	Yellow	148	D	42.08 (42.00)	3.46 (3.28)	9.08 (9.19)	-	-	7.04 (7.00)	21.12 (21.00)	
[(ESH)(Py)Mo(CO)$_3$]	Yellow	150	D	40.38 (40.50)	3.12 (2.95)	5.80 (5.90)	-	-	13.40 (13.50)	20.12 (22.25)	
[(CNH)(Py)Mo(CO)$_3$]	Yellowish Brown	160	D	39.12 (39.25)	2.98 (2.80)	13.14 (13.08)	-	-	7.28 (7.47)	22.12 (22.43)	
[(PTH)(Py)Mo(CO)$_3$]	Dark Yellow	170	D	47.48 (47.61)	3.26 (3.17)	11.02 (11.11)	-	-	6.20 (6.34)	19.12 (19.04)	
[(EBH)(Py)Mo(CO)$_2$(NO)]	Brown	160	D	34.08 (34.22)	3.22 (2.98)	6.56 (6.67)	18.24 (18.12)	4.86 (4.92)	15.12 (15.08)	15.32 (15.26)	102
[(ETH)(Py)Mo(CO)$_2$(NO)]PF$_6$	Buff	170	D	29.68 (29.80)	2.66 (2.48)	9.36 (9.28)	18.80 (18.85)	5.24 (5.13)	5.36 (5.30)	15.80 (15.90)	98
[(EPH)(Py)Mo(CO)$_2$(NO)]PF$_6$	Yellow Brown	165	D	29.74 (29.80)	2.56 (2.48)	9.32 (9.28)	18.64 (18.88)	5.36 (5.13)	5.22 (5.30)	15.82 (15.90)	100
[(ESH)(Py)Mo(CO)$_2$(NO)]PF$_6$	Orange	180	D	29.68 (29.98)	2.36 (2.25)	6.82 (6.76)	18.24 (18.36)	15.28 (5.00)	10.36 (10.30)	15.56 (15.46)	99
[(CNH)(Py)Mo(CO)$_2$(NO)]PF$_6$	Light Yellow	145	D	27.22 (27.13)	12.14 (12.08)	12.20 (12.17)	19.76 (19.82)	5.28 (5.40)	5.60 (5.56)	16.82 (16.70)	101
[(PTH)(Py)Mo(CO)$_2$(NO)]PF$_6$	Light Yellow	170	D	35.14 (35.02)	2.56 (2.46)	10.68 (10.75)	17.46 (17.51)	4.84 (4.76)	4.94 (4.92)	14.64 (14.75)	100

Table 2. ASSIGNMENTS OF MAJOR IR BANDS OF THE LIGANDS AND COMPLEXES

Compounds	**υNH**	**υ (C=O)**	**υ (C=O)**	**υ (C=S)**	**Theoamide Bands**			
					I	**II**	**III**	**IV**
EBH	3220	-	1765s	1130s	1540s	1360s	1075s	850m
[(EBH)(Py) Mo(CO)$_3$]	-	1740s 1850s	1770s	1110m	1500s	1330m	1065s	840m
ETH	3350m 3325m	-	1765	1120s	1540s	1340s	1070s	870m
[(ETH)(Py) Mo(CO)$_3$]	-	1740s 1855s	1745s	1100m	1550s	1380m	1070m	865m
EPH	3210	-	1730s	1125s	1500s	1320s	1015s	880m
[(EPH)(Py) Mo(CO)$_3$]	-	1730s 1850s	1790s	1110m	1480s	1310m	1010s	860m
ESH	3240s	-	1730s	1180s	1510s	1360s	1020s	770m
[(ESH)(Py) Mo(CO)$_3$]	3100	1730s 1850s	1750s	1150m	1500s	1345m	1000s	720m
CNH	3400 3370 3250	-	1730s	1120s	1580s	1330s	1060s	845m
[(CNH)(Py) Mo(CO)$_3$]	-	1730s 1890s	1690s	1130m	1550s	1310s	1070s	860m
PTH	3410 3260 3160	-	1720s	1120s	1525s	1350s	1000s	860m
[(PTH)(Py) Mo(CO)$_3$]	-	1740s 1870s	1680s	1140m	1510s	1320s	1010s	870m

Compounds	**υNH**	**υ (C=O)**	**υ (C=O)**	**υ (C=S)**	**Theoamide Bands**			
					I	**II**	**III**	**IV**
[(EBH)(Py)Mo(CO)$_2$(NO)]PF$_6$	-	2030s 1956s	1775s	1768s	1110m	1500s	1065s	840m
[(ETH)(Py)Mo(CO)$_2$(NO)]PF$_6$	-	2030 1950	1780s	1745s	1100m	1550m	1070s	865m
[(EPH)(Py)Mo(CO)$_2$(NO)]PF$_6$	-	2020 1960	1772s	1790d	1110s	1480s	1010m	860s
[(ESH)(Py)Mo(CO)$_2$(NO)]PF$_6$	3500 3100	2025s 1950s	1775s	1750m	1150m	1500s	1000m	720s
[(CNH)(Py)Mo(CO)$_2$(NO)]PF$_6$	-	2030s 1950s	1775s	1690s	1130m	1550s	1070s	860s
[(PTH)(Py)Mo(CO)$_2$(NO)]PF$_6$	-	2020s 1950s	1780s	1680s	1140m	1510s	1010m	870m

Table-3. ELECTRONIC SPECTRAL DATA OF THE COMPLEXES AND THEIR ASSIGNMENTS.

Compounds	λ max	Peak Assignments
[(LH)(Py)Mo(CO)$_3$]	290 330 370 390 425 710	$^1b_2 \rightarrow ^2b_1$ $^1b_2 \rightarrow ^2a_2$ $^1b_2 \rightarrow ^2a_1$ $^1b_2 \rightarrow ^2b_2$ $^1b_2 \rightarrow ^2b_1$ $^1b_2 \rightarrow ^2a_1$
[(LH)(Py)Mo(CO)$_3$(NO)]PF$_6$	300 340 350 380 440 725	$^1b_2 \rightarrow ^2b_1$ $^1b_2 \rightarrow ^2a_2$ $^1b_2 \rightarrow ^2a_1$ $^1b_2 \rightarrow ^2b_2$ $^1b_2 \rightarrow ^2b_1$ $^1b_2 \rightarrow ^2a_1$

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