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Synthesis, structures and reactivities of water soluble aromatic thiocarboxamides Fe^{3III} nitrosyl complexes

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Abstract : The new water soluble iron nitrosyls derived from aromatic carboxamide ligands (RCONHCOR') hereafter referred to as LH (where H is dissociable amide proton) have been Structurally characterised on the basis of analytical, spectral (1R, UV and Visible), magnetic and conductemetric studies. The absorption band comeoponding to N-O stretching frequencies u(NO) was observed at 1900-1920 cm^{-1}. These iron nitrosyls [$FeL_2(NO)(MeOH)](ClO_4)_2$ belong to almost {Fe- $NO\}^6$ family.

(**Keywords:** Iron, aromatic carboxamide, wave number, bathochromic shift, magnetic moment)

Introduction

The prominent role of nitric oxide in biological and physilogical processes, as a non innocent ligand in coordination chemistry, occurance of trans effect, as reaction mediator as well as linkage isomerism have led to considerable area of research interest to coordination chemistry as well as biochemists during the past decade[1]. Some of the nitrosyl compounds have been used as NO donors upon illumination to U.V. light. These compounds deserve special attention since they could be most probably be used in photodynamic therpy against cancer[2]. Therefore, research activities have largely been centered at metal nitrosyl species like (L) { M – NO} in view of

(I) Preferential stabilization of one or more redox states of NO, (NO^+, NO^- or $NO^É$) in metal complexes.
(II) Attack of electrophiles or nucleophiles on M – NO^+ center.
(III) Reaction of O_2 with M - $NO^É$ to search biological auto-oxidation processes of free NOÉ.

In continuation of our research work in this area[3] reported previous paper the synthesis and structure of carboxamide Ru(III) nitrosyl complexes. Now, we report synthesis structure and reactivities of water soluble aromatic thiocarboxamide Fe^{III} nitrosyls.

Experimental

All the chemicals used were either chemically pure or AR grade.
(i) The starting materials $[Fe(DMF)_6](ClO_4)_3$, RCONHCOR' (R= 2-pyrrolyl or 2-thiophenyl; R'=OC_2H_5) were prepared according to published procedure[4,5].

(ii) Preparation of complexes : A slurry of $[Fe(DMF)_6](ClO_4)_3$ 0.42g (~0.5mmol) was prepared in 10ml CH_3OH and it was added to a solution of LH (0.2g ~ 1m mol) and sodium hydride (0.025g ~ 1mmol) in 10 ml CH_3OH. The reaction mixture became homogeneous after a stirring of 1h and colour changed to dark red. The stirring continued for about 1h when the precipitate of red coloured complexes $[(L_2Fe(CH_3OH)](ClO_4)$ separated out. It was filtered, washed several times with alcohal, either and dried in vacuum.

This complex (0.30g) was dissolved in 10 ml CH_3CN and the solution was stirred for 10 hrs. To this solution was passed dry NO for 10 min. This solution was kept in refrigerator for over night whereby dark red crystalline complex were

formed. The complexes was separated by filtration, washed with ether and dried in vacuum.

Analyses –

The analyses of iron, chloride and sulpher were carried out by standard procedure[6] carbon, hydrogen, and nitrogen were performed by micro analytical section of Indian Institute of Technology, Kanpur (U.P.), India. The analytical results are given in table-1. The spectral (IR, UV and visible) analyses and magnetic susceptibities measurments were performed in chemistry deptt. B.H.U. Varanasi. The assignment of UV and visible bands are given in table-2

Results and Discussion

The aromatic thiocarboxamides Fe^{III} nitrosyls were synthesized by following reactions:

$$[Fe(DMF)_6](ClO_4)_3 + 2LH \xrightarrow[NaH]{\text{Stirring, 2h in } CH_3OH} [L_2Fe\,CH_3OH](ClO_4)$$

$$[L_2Fe(CH_3OH)] + CH_3CN \xrightarrow[10h]{\text{Stirring}} [L_2Fe(CH_3CN)](ClO_4)$$

$$[L_2Fe(CH_3CN)](ClO_4) + NO \xrightarrow{10\ min.} [L_2Fe(NO)(CH_3CN)](ClO_4)$$

All the complexes are nonhygroscopic, soluble in water and common organic solvents. The molar conductances of complexes in $10^{É2}$ M N.N'- dimethyl for mamide (100 – 110 $OhmÉ^1\,cm^2\,mol^{É1}$) indicates them to be 1 : 1 electrolyte.

The ligands LH = RCSNHCOR' are abbreviated as follows-

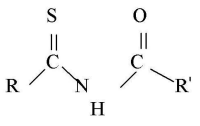


Fig.1

R= 2-Pyrrolyl, R' = OC_2H_5;

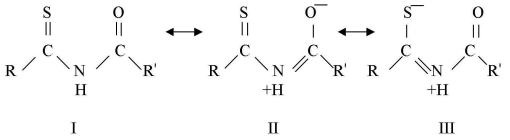
N- Ethoxycarbonylpyrrole- 2-thiocarboxamide (EPS)

R= 2-thiophenyl,

R' = OC_2H_5;

N- Ethoxycarbonylthiophene-2-thioccarboxamide (ETS)

These thiocarboxamide exhibit following resonance structures given below:



I II III

However, in presence of $[Fe(DMF)_6](ClO_4)_3$ and NaH, the ligands thiol form predominates, so both the above ligands, act as anion during the course of reaction. But these thiol forms I or II are not observed under ordinary conditions.

The IR spectra of ligands and complexes were compared inorder to know the mode of linkage of ligands. The characteristic bands of pyrrole (2990, 1550, 1470, 1450, 1140, 1040, 995, 750, 520 and 440 $cm^{É1}$) in EPS and that of thiophenyl group in ETS (3050, 1660, 1590, 750 and 700 $cm^{É1}$) do not shift to a considerable amount (±5 $cm^{É1}$). Further, nitrogen atom of pyrrole and sulpher atom of thiophene are poovly basic[7, 8] due to the involvement of their lone pairs in delocalization of ring.

Thus, it is assumed that bonding in complexes occur via -CONH COÉ- moiety of ligands (LH). The characterstic bands of CH_3OH and CH_3CN were also present at 2315 cmÉ in the spectra of complexes. The characteristic bands of pyridine due to C = C and C = N stretching ring (1430 – 1600 $cmÉ^1$) were present in pyridine nitrosyl complexes.

Reaction of $[L_2Fe(NO)(CH_3CN)](ClO_4)$ [L = EPC or ETC) (~ 0.25 mg) with pyridine (10 ml) resulted a complex $[L_2Fe(NO)(C_5H_5N)](ClO_4)$ as follow-

$$[L_2Fe(NO)(CH_3CN)](ClO_4) \xrightarrow[\text{Stirring, 2h}]{C_5H_5N} [L_2Fe(NO)(C_3H_5N)](ClO_4)$$

(a) Two bands at 3360 cm^{-1} and 3145 cm^{-1} in the spectra of the ligand due to (NH) stretching, disappeared in the spectra of the complexes new band appeared around 3340 cm^{-1}. This could probably be owing to the deprotonation of one of the two H groups during the formation of the complexes. Since the position of this band (3340 cm^{-1}) corresponds to the one found in the spectrum of the pyrrole, it is tacitly assumed that H group of the pyrrole is not deprotonated.

(b) The above brown coloured compound was isolated as microcrystals. Amide I band of free ligands (1680–1720cm^{-1}) undergoes a bathochromic shift (-30 cm^{-1}) and a new band at (1450 –1500 cm^{-1}) appeared in complexes is assigned to u (C=N) of the chelate ring[10] indicating coordination of CO group to the iron (III) through oxygen atom. Bonding of metal ion (electron withdrawing group) with oxygen atom with oxygen atom of carbonyl group of ligand will shift the position of amide bands II and III and the band due to u(CO) of ($C - OC_2H_5$) group towads higher wave number[9]. The broad band at 1500 cmÉ[1] of amide band II, 1260 cm^{-1} amide band (II) and 1190 cmÉ[1] due to u(CO) of ($C- OC_2H_5$) shifted toward higher wave number (±20 cm^{-1}). This further confirms the bonding of metal ion through carbonyl group of ligands also.

(c) Two new bands at 630 cm^{-1}(m) and 600 cm^{-1} appeared in the spectra of ligand, disappeared and new band around 625 cm^{-1} (±5 cmÉ[1]) appeared in the spectra of complexes. These bands are assigned to T(NH). In the complexes NH group deprotonated and hence only one band appeared.

(d) Thioamide band IV) which contains major contribution from (C=S) should appear around 800 cmÉ[1]. In the spectra of the complexes the ligand band at 875 cm^{-1}, that may be due to (C=S), shifted towards the lower wave numbers suggesting the bonding of the metal ion with thiocarbonyl sulphur.

(e) Two new bands around 350 - 470 cmÉ[1] appeared in spectra of complexes are assigned to coupled vibrations having contributions from u(Fe - O) modes.

All the complexes exhibited intense absorption bands at 1890 –1920 cm^{-1}. These bands are assigned to stretching vibration modes of Fe–NO bands, indicating the bonding of nitric oxide with Fe^{III} ion.

Thus on the basis of IR spectral studies, we propose the following tentative structures of Fe^{III} nitrosyl complexes.

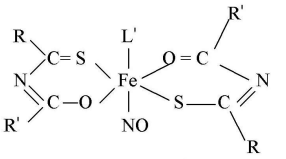


Fig. 2 L' = CH_3OH, CH_3CN; C_2H_5N

R' = OC_2H_5

R = pyrrolye-2 or thiophenyl-2

Electronic Spectra

Electronic spectra of complexes were recorded in 10^{-2} M alcoholic solutions. All the complexes exhibited four absorption bands at nearly same positions. These absorption band along with their assignments are presented in Table-2. These absorption bands are based on molecular orbital diagram applicable to coordinated nitric oxide to metal ions reported else where[11].

NO is a s lewis base and π^* lewis acid, so whenever it is linked to metal through Md $\pi \rightarrow \pi^*$ (NO) bond the positive charge on metal ion decreases and it increases on NO molecules. This bonding mechanism of nitric oxide with metal ion is further enhanced due to presence of s donor and weak p bonder ligand than NO at trans to it.

Table-1
Analytical data, colour, melting point, magnetic moments and molar conductances of complexes

Compounds	Colour	M.P.^{0}c	Magnetic Moments	Found (Coled) %						Lm (ohm^{-1} cm^{-1})
				C	H	N	C1	S	Ru	
$[(EPS)_2Fe(NO)(CH_3OH)]\ ClO_4$	Light red	145	D	34.20 (34.25)	3.56 (3.35)	10.86 (11.75)	6.12 (5.96)	5.56 (5.37)	9.48 (9.40)	110
$[(EPS)_2Fe(NO)(CH_3CN)]\ ClO_4$	Red	130	D	35.64 (35.73)	3.26 (3.14)	13.96 (13.89)	5.78 (5.87)	5.10 (5.29)	9.00 (9.26)	120
$[(EPS)_2Fe(NO)(C_5H_5N)]\ ClO_4$	Brown	150	D	39.08 (39.22)	3.36 (3.26)	13.24 (13.07)	5.68 (5.52)	5.10 (4.98)	8.78 (8.71)	125
$[(ETS)_2Fe(NO)(CH_3OH)]\ ClO_4$	Yellow	148	D	32.56 (32.40)	3.28 (3.17)	6.82 (6.67)	5.76 (5.63)	10.00 (10.16)	8.72 (8.89)	115
$[(ETS)_2Fe(NO)(CH_3CN)]\ ClO_4$	Orange	125	D	33.64 (33.82)	3.14 (2.97)	8.84 (8.77)	5.68 (5.55)	9.90 (10.02)	8.62 (8.77)	120
$[(ETS)_2Fe(NO)(C_5H_5N)]\ ClO_4$	Dark red	140	D	37.12 (37.25)	3.28 (3.10)	8.06 (8.27)	5.34 (5.24)	9.30 (9.46)	8.10 (8.27)	130

Presence of intense band corresponding charge transfer of Fe ($d\pi$) $\rightarrow \pi^*$ (NO) at 460 – 480 nm is assigned to Fe = NO bonds. The position of these bands experiences a bathochromic shift when ligands CH_3OH is changed to CH_3CN to C_5H_5N. Theoretically, five d–d transition bands are possible O in $\{Fe–NO\}^6$ system. These are $^1A_1g \rightarrow {}^3T_1g$, ^3T_2g (spin forbidden) and $^1A_1g \rightarrow {}^1T_1g$, ^1T_2g (spin allowed) but owing to the presence of intense charge transfer bands, the weak bands and $^1A_1g \rightarrow {}^3T_1g$, ^3T_2g are masked and only spin allowed bands are observed at 580-600 nm in all the complexes. These assinments of these bands and other bands are provided in table-2

Table-2
Electronic spectral data of the ligands, complexes and their assignments

Compounds	λ max (nm)	Peak Assignments
E P C	440	n → π^*
	365	π → π^*
$[(EPS)_2Fe(NO)(CH_3OH)]\ ClO_4$	620	$^1A_1g \rightarrow {}^1T_1g$
	550	$^1A_1g \rightarrow {}^1T_2g$
	480	$d\pi \rightarrow \pi^*(NO)$
	430	I L
	360	C T
$[(EPS)_2Fe(NO)(CH_3CN)]\ ClO_4$	600	$^1A_1g \rightarrow {}^1T_1g$
	570	$^1A_1g \rightarrow {}^1T_2g$
	470	$d\pi \rightarrow \pi^*(NO)$
	415	I L
	360	C T
$[(EPS)_2Fe(NO)(C_5H_5N)]\ ClO_4$	605	$^1A_1g \rightarrow {}^1T_1g$
	570	$^1A_1g \rightarrow {}^1T_2g$
	470	$d\pi \rightarrow \pi^*(NO)$
	430	I L
	350	C T
ETC	410	n → π^*
	290	π → π^*
$[(ETS)_2Fe(NO)(CH_3OH)]\ ClO_4$	600	$^1A_1g \rightarrow {}^1T_1g$
	560	$^1A_1g \rightarrow {}^1T_2g$
	480	$d\pi \rightarrow \pi^*(NO)$
	400	I L
	310	C T
$[(ETS)_2Fe(NO)(CH_3CN)]\ ClO_4$	600	$^1A_1g \rightarrow {}^1T_1g$
	550	$^1A_1g \rightarrow {}^1T_2g$
	480	$d\pi \rightarrow \pi^*(NO)$
	360	I L
	320	C T
$[(ETS)_2Fe(NO)(C_5H_5N)]\ ClO_4$	620	$^1A_1g \rightarrow {}^1T_1g$
	560	$^1A_1g \rightarrow {}^1T_2g$
	470	$d\pi \rightarrow \pi^*(NO)$
	380	I L
	340	C T

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