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Synthesis and charecterization of some Lanthanide (III) complexes with N-(furfuralidene)-N′-isonicotinoylhydrazine

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ABSTRACT

*A series of lanthanide nitrato complexes with N-(furfuralidene)-N′-isonicotinoylhydrazine (INH-FF) were synthesized. These complexes were characterized by elemental analysis, conductance, magnetic moment measurements, IR, UV-visible, TGA-DTA and luminescence studies. In these complexes the hydrazone, N-(furfuralidene)-N′-isonicotinoylhydrazine behave as a neutral bidentate ligand with the carbonyl oxygen and azomethine nitrogen as two coordinating sites. All the three nitrate ions also coordinate unidentately with seven coordination for the lanthanide (III) ions with a tentative monocapped octahedral geometry for the complexes. All the complexes have a general formula, [Ln(L)$_2$(NO$_3$)$_3$] where Ln= Pr(III), Nd(III), Sm(III), Gd(III) or Tb(III) and L= N-(furfuralidene)-N′-isonicotinoylhydrazine. Spectroscopic determination of nephelauxetic ratio(β), covalency factor($b^{1/2}$), Sinha parameter(δ%) and covalency angular overlap parameter (**η**) show a weak covalent bond formation between the metal ion and the ligand in the complexes.*

Key words:Lanthanide(III),N-(furfuralidene)-N′-isonicotinoylhydrazine, Nephelauxetic ratio(β), Covalency factor($b^{1/2}$) ,Sinha parameter(δ%) and Covalency angular overlap parameter (**η**) .

INTRODUCTION

Complexes of hydrazones with paramagnetic lanthanide metal ions have attracted close attention because of their novel structural features and relevance to biological processes [1-6]. The study of ligand involving hydrazone is interesting as there is versatility in the co-ordination, the tendency to yield stereochemistries of higher coordination number, the ability to behave as neutral or deprotonated ligand and the flexibility in assuming different conformations.[7] In connection of our work on complexes of hydrazone, we here in report the study of complexes of some lanthanides with the ligand N-(furfuralidene)-N′-isonicotinoylhydrazine (INH-FF) synthesized via. reaction of furfural and isonicotinic acid hydrazide.

EXPERIMENTAL SECTION

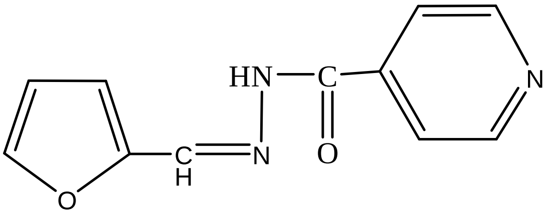
The chemical used were of analytical grade; Furfural (Himedia), Isonicotinic acid hydrazide (Himedia) ,Lanthanide (III) nitrate hexahydrate, (CDH) was used as such.

Physical Measurements

The infrared spectrum was run on potassium bromide phase from 400-4000cm^{-1} range on Shimadzu FTIR 8400S at Department of Chemistry, Manipur University. The electronic spectra of the neodymium(III) and samarium(III) complexes in (DMSO) solution were recorded on Perkin Elmer Precisely,Lambda-35 UV/VIS Spectrometer in the range of 400-900nm at Department of Chemistry, M.U. Magnetic susceptibility measurement of the synthesized lanthanide(III) complexes were carried out at room temperature on Sherwood Scientific Cambridge UK. Conductances were measured on EUTECH CON 510 at 25^{0}C in DMSO. The complexes were analyzed for C, H and N on Elementar Vario EL III Carlo Erba 1108 at Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. TGA and DTA curves were obtained on a Perkin Elmer precisely STA 6000, Simultaneous Thermal Analyzer at Department of Chemistry, Manipur University. The samples were heated in platinum crucibles, in nitrogen atmosphere, within the temperature range 25^{0}C to 940^{0}C. The heating rate was 10^{0}C min^{-1}. Luminescence study was also done in Perkin Elmer precisely LS-55 Fluorescence Spectrometer at Department of Chemistry, Manipur University. Estimation of halide was also done with usual silver nitrate method. Metals were estimated as their oxides.

Preparation of N-(furfuralidene)-N′-isonicotinoylhydrazine (INH-FF)

A mixture of 0.96g of furfural (AR) and 1.3g of isonicotinic acid hydrazide (AR) were dissolved in 25ml of ethanol and 3ml of glacial acetic acid was added to catalyze the reaction. A little more ethanol was added to get a clear solution and the reaction mixture was refluxed for 3 hours. The solution was cooled overnight when the brown N-(furfuralidene)-N′-isonicotinoylhydrazine (INH-FF) crystallized out. The compound was isolated and recrystallised from ethanol and dried in air. (M.P=216^{o}C)



N-(furfuralidene)-N -isonicotinoylhydrazine (INH-FF)

Preparation of lanthanide complexes

Procedure: N-(furfuralidene)-N′-isonicotinoylhydrazine (INH-FF) (0.002M) was dissolved in A.R. ethanol (30ml) by little warming and to this was added lanthanide(III) nitrate hexahydrate(0.001M) (where lanthanide(III)= Pr, Nd, Sm,Gd or Tb). The mixture was refluxed on a steam bath for 4 hours in all the cases, cooled at room temperature and then left in a refrigerator overnight. The resulting yellowish crystals were filtered and washed several times with warm ethanol to remove any excess of the metal nitrate and/or ligand. Finally, the complex was dried in air.

Table :1 Characterization data , Magnetic moments and Molar Conductance of Ln(III) complexes of INH-FF found (calcd.)

Ligand/ Compound	Colour	Metal	C	H	N	μ_{eff} (B.M)	Molar Conductance ($ohm^{-1}cm^2mol^{-1}$) in 0.002M DMSO
$C_{11}H_9N_3O_2$ (INH-FF)	Brown		61.46 (61.39)	4.27 (4.18)	19.33 (19.53)		
$[Pr(C_{11}H_9N_3O_2)_2(NO_3)_3]$	Light yellow	18.73 (18.61)	34.94 (34.87)	2.31 (2.38)	16.62 (16.65)	3.29	23.58
$[Nd(C_{11}H_9N_3O_2)_2(NO_3)_3]$	Light yellow	18.83 (18.97)	34.76 (34.69)	2.25 (2.36)	16.53 (16.56)	3.63	27.94
$[Sm(C_{11}H_9N_3O_2)_2(NO_3)_3]$	Light yellow	19.81 (19.62)	34.56 (34.45)	2.39 (2.35)	16.48 (16.44)	1.84	25.67
$[Gd(C_{11}H_9N_3O_2)_2(NO_3)_3]$	Light yellow	20.39 (20.34)	34.21 (34.14)	2.30 (2.33)	16.25 (16.29)	7.68	22.43
$[Tb(C_{11}H_9N_3O_2)_2(NO_3)_3]$	Light yellow	20.44 (20.51)	34.01 (34.07)	2.34 (2.32)	16.29 (16.26)	9.14	27.21

Table :2 IR spectra (cm^{-1}) bands of Ln(III) complexes of INH-FF

Ligand/Compound	ν(C=O)	ν(C=N)	ν(N-H)	ν(N-N)	$\nu_4(NO_3)$	$\nu_1(NO_3)$	ν(M-N)	ν(M-O)
$C_{11}H_9N_3O_2$	1649	1620	3271	995				
$[Pr(C_{11}H_9N_3O_2)_2(NO_3)_3]$	1625	1577	3234	1022	1470	1344	550	414
$[Nd(C_{11}H_9N_3O_2)_2(NO_3)_3]$	1616	1583	3228	1028	1468	1341	546	422
$[Sm(C_{11}H_9N_3O_2)_2(NO_3)_3]$	1623	1579	3229	1025	1471	1343	541	417
$[Gd(C_{11}H_9N_3O_2)_2(NO_3)_3]$	1619	1586	3234	1024	1469	1344	543	419
$[Tb(C_{11}H_9N_3O_2)_2(NO_3)_3]$	1624	1584	3231	1023	1471	1341	541	418

Table 3: Electronic Spectral data of Ln(III) complexes of INH-FF

Complex	Band max(cm^{-1}) in DMSO	Assignment	Parameters
$[Pr(C_{11}H_9N_3O_2)_2(NO_3)_3]$	i)16890 cm-1 ii)20490 cm-1	$^3H_4 \rightarrow {}^1D_2$ $^3H_4 \rightarrow {}^3P_0$	β=0.9897 $b^{1/2}$=0.0718 **η**=0.0052 δ(%)= 1.040
$[Nd(C_{11}H_9N_3O_2)_2(NO_3)_3]$	i)19,493cm-1 ii)17,153cm-1 iii)13,569cm-1 iv) 12,422cm-1	$^4I_{9/2} \rightarrow {}^2G_{9/2}$ $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ $^4I_{9/2} \rightarrow {}^2S_{3/2}, {}^4F_{7/2}$ $^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	β=0.9838 $b^{1/2}$=0.0636 **η**=0.0082 δ(%)= 1.64

RESULTS AND DISCUSSION

Analytical data, their molar conductance and magnetic moments values of the lanthanide(III) complexes with N-(furfuralidene)-N′-isonicotinoylhydrazine are presented in Table1.The analytical data revealed that the metal to ligand ratio is 1:2 in all these complexes. The molar conductance values of the lanthanide(III) complexes in DMSO at room temperature are much lower than the values reported for the 1:1 electrolyte [8].

Room temperature magnetic moments of the complexes show a slight deviation from Van Vleck values indicating weak interaction of the 4f electrons in metal ligand bond formation [9]. From the above result, these complexes can be formulated as $[Ln(INH\text{-}FF)_2(NO_3)_3]$ where Ln=Pr(III), Nd(III), Sm(III), Gd(III) and Tb(III), and INH-FF= N-(furfuralidene)-N′-isonicotinoylhydrazine.

Infra red:

The ligand N-(furfuralidene)-N′-isonicotinoylhydrazine (INH-FF) has three coordinating sites, the possible co-ordination sites being pyridine-nitrogen, carbonyl oxygen (in keto or enol form) and azomethine nitrogen. The lanthanides on the other hand, are well known for exhibiting a wide array of co-ordination numbers, from six right upto eleven or twelve [10]. The ligand INH-FF can exhibit as tridentate (NNO) or bidentate (NO) donor behavior. However, in our synthesized complexes, the pyridine nitrogen is left out of co-ordination sphere because of the position of nitrogen atom of the pyridine ring. The vibration attributable to the ν(N-H) mode is observed at 3271cm^{-1} for the free ligand and at (3228-3234) cm^{-1} for the complexes. This fact suggests that the ligand INH-FF function as a neutral ligand to the lanthanide ions [11]. For the complexes, the bands assigned to the ν(C=O) and ν(C=N) vibrations are observed at (1616-1625) cm^{-1} and (1577-1586) cm^{-1} respectively whereas the corresponding bands for the free ligand are observed at 1649 cm^{-1} and 1620cm^{-1} respectively[12-16]The shifts of the ν(C=O) and ν(C=N) vibrations of the bands towards lower wave numbers on complexation indicate that carbonyl oxygen and azomethine nitrogen coordinate to the metal ion in all the complexes[13,14,17]. Further, coordination through azomethine nitrogen is also supported by the shifting of ν(>N-N-) bands at 995 cm^{-1} in free ligand towards higher wave number in the complexes at (1022-1028) cm^{-1} [17-20]. Bands observed in the ranges (541-550) cm^{-1} and (414-422) cm^{-1} which are attributed to the stretching vibrations of (Ln-N) and (Ln-O), respectively also confirm the bonding through carbonyl oxygen and azomethine nitrogen [21,22].

The IR spectra of the complexes have five additional bands, which do not have any corresponding bands in the spectrum of the ligand. The two bands observed in the region (1468-1471)cm^{-1} and (1341-1344)cm^{-1} are assigned to ν_4 and ν_1 vibrations, respectively of coordinated nitrate ion. As the difference between ν_4 and ν_1, is ~127 cm^{-1}, the nitrate ions are monodentately coordinated to the lanthanide (III) ions in these complexes [23,24]. These observation in the ir spectra of the ligand and the complexes show that the ligand INH-FF acts as a neutral bidentate ligand coordinating through the carbonyl oxygen and azomethine nitrogen in these complexes. The nitrate ions present in these complexes acts as secondary ligands coordinating unidentately.

Electronic spectra:

The electronic spectra of Pr(III) and Nd(III) complexes were recorded as 0.002M DMSO solutions. The spectral data along with various bonding parameters calculated from the spectral data are given in Table 3. The absorption band associated with the nearly degenerate $^4I_{9/2}\rightarrow{}^4G_{5/2},{}^2G_{7/2}$ transition of the Nd(III) exhibits strong hypersensitive behaviour [25] making it specially suitable for probing the coordination environment around Nd(III) ion. The spectral shape of the hypersensitive transition ($^4I_{9/2}\rightarrow{}^4G_{5/2}, {}^2G_{7/2}$) of $[Nd(INH\text{-}FF)_2(NO_3)_3]$ compare well with the bands of seven co-ordinated Nd(III) complexes reported by Karraker[26]. Compared to the spectra of the aquoneodymium(III) complex, the hypersensitive band mentioned above shows a significant red shift($\Delta\nu$=204cm^{-1}). For other important bands ($^4I_{9/2}\rightarrow{}^2H_{9/2},{}^4F_{5/2}$; $^4I_{9/2}\rightarrow{}^4S_{3/2},{}^4F_{7/2}$; $^4I_{9/2}\rightarrow{}^4G_{7/2},{}^2K_{3/2}$) the red shift is much less. Various spectral parameters like the nephelauxetic ratio β, (β= average value of $\nu_{\text{complex}}/\nu_{\text{aquo}}$)[27], the covalency factor $b^{1/2}$, ($b^{1/2}=1/2[(1-\beta)^{1/2}]$) [28], Sinha Parameter δ(%), $\delta(\%)=[(1-\beta)/\beta]\text{x}100$[27], and covalency angular overlap parameter $\boldsymbol{\eta}$, [$\boldsymbol{\eta}=(1-\beta^{1/2})/\beta^{1/2}$] [28] have been calculated from the hypersensitive transition of the lanthanide(III) spectra(Table 3).

The electronic spectra of Pr(III) complex exhibits bands around 16890cm^{-1}and 20490cm^{-1} in the visible region which may be due to $^3H_4\rightarrow{}^1D_2$ and $^3H_4\rightarrow{}^3P_0$ transitions respectively [9]. Compared to the spectra of the aquo Pr(III) complex, these bands show a slight red shift ($\Delta\nu$=~130cm^{-1}; ~160 cm^{-1}). The other bands in these regions cannot be located as these bands are presumably buried underneath the strong metal- ligand charge–transfer band around 24000cm^{-1}. The values obtained were close to those calculated for similar other Nd(III) and Pr(III) chelates. The β values in the complex are close to unity showing only a slight covalent character of the Ln(III)→ligand interaction; the $b^{1/2}$ values suggest a small participation of 4f orbitals in bonding and along with δ values indicate relative low covalent character of the bond.

Thermogravemetric analysis:

The thermogram curve of the complexes shows the absence of water molecule either in or out of the coordination sphere. The analyses of these curves suggest that above 240^{0}C the compound start to loss mass with partial evaporation of the organic ligand. The residues obtained after heating up to 900^{0}C, to constant weight were very close to those expected for the lanthanide(III) oxides. All these results are in accordance with the composition of the complexes determined by elemental analyses.

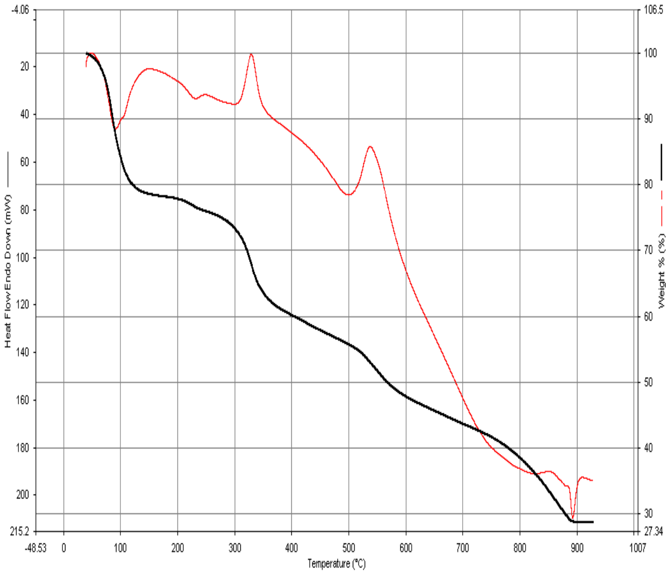


Fig.1 TGA -DTA Thermogram of the [Tb(INH-FF)$_2$(NO$_3$)$_3$] complex

Luminescent study:

The luminescent spectrum of Tb(III) complex with N-(furfuralidene)-N′-isonicotinoylhydrazine excited at 364nm was recorded. The characteristic f – f transitions of Tb^{+3} ion were observed with maxima at 487nm, 545nm, 585nm and 615nm attributable to transitions $^5D_4\rightarrow{}^7F_6$, $^7F_5$, $^7F_4$

and $^7F_3$ respectively [29,30] (Fig.2). The fluorescence intensity of the complex is weaker than that of the Tb(III) ion. This result indicated that the complex have the function of decrease in the fluorescence.

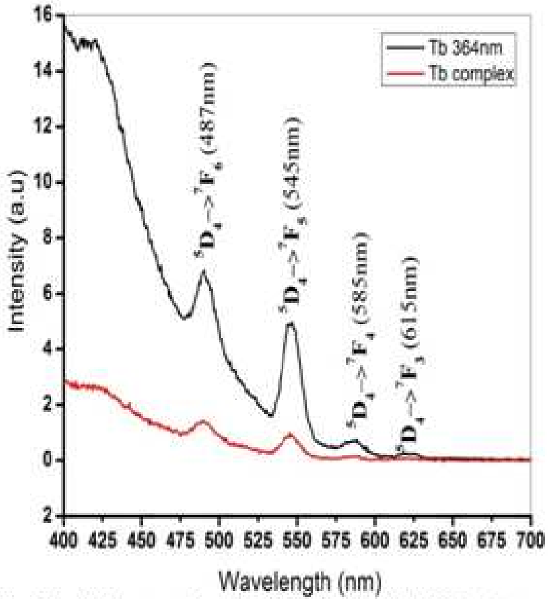
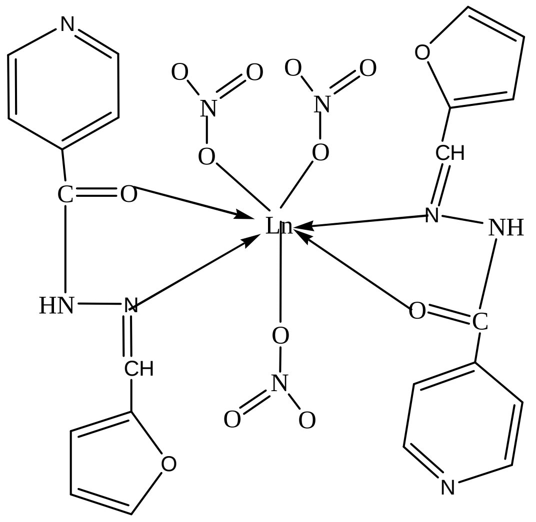


Fig.2 Emission spectrum of the [Tb(INH-FF)$_2$(NO$_3$)$_3$] complex

CONCLUSION

The non electrolytic behavior of the complex suggests that all the three nitrato ions are coordinated to the central lanthanide(III) ion. The infra-red studies reveal that the ligand co-ordinate in a bidentate manner. Thus on this basis, it is revealed that the lanthanide(III) ions is surrounded by two oxygen atom of carbonyl group and two nitrogen atoms of azomethine group and three anionic nitrato ligands producing a coordination number seven for the lanthanide(III) complex with a tentative monocapped octahedral geometry for the complexes. The proposed structure of the complexes is shown below



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