journal of
experimental sciences

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RRST-Biochemistry

Synthesis, Spectral and Antimicrobial Studies of Lanthanide (III) Nitrate Complexes with Terdentate ONO Donor Hydrazones

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Abstract

Few lanthanide (III) nitrate complexes with hydrazones obtained by the condensation of 3-[m/p (hydrazino carbonyl)] phenyl sydnone and hydroxy aryl aldehyde or ketones have been synthesized and characterized by elemental analysis, molar conductance measurements, magnetic moments, Infrared, electronic and ^{1}HNMR spectral studies. The spectral studies show that the hydrazones reacts in enol form and as dibasic terdentate ONO donor nature. From the results the coordination number eight for lanthanide ion in the complexes is proposed. The thermal behaviour, stability ranges, percentage of weight loss, percentage of residue obtained after decomposition of Ln (III) nitrate complexes has been studied. Further more the antimicrobial activity of the ligand and its complexes as inhibiting agents has been screened in *vitro* against two kinds of pathogenic bacteria *Salmonella paratyphi*, *Bacillus cirroflagellosus* and pathogenic fungi *Aspergillus niger*, *Candida albicans*.

Key Words: Lanthanide (III) nitrate complexes and antimicrobial activity

Introduction

Hydrazones and their metal complexes have been found to be potential application in industry and biology[1]. The coordination chemistry of lanthanide is fascinating because they have a tendency to form complexes with coordination number greater than six, even up to twelve. As early as 1979 Thomas et al[2]., have reported eleven coordinated lanthanum (III) nitrate complexes with bis (hydrazone) type ligand derived from 2, 6- diacetylpyridine. Some seven and eight coordinated complexes have also been reported [3-5] with similar ligands and various lanthanides. The coordination number eight is found to be most common among the lanthanides. The study of complexes of hydrazones is interesting from the structural point of view. It is their ability to exist in keto, enol or in special cases mixed keto enol form depending on experimental conditions. IR spectroscopy in extensively used to study these compounds. When the ligand reacts in the keto form one would expect the =NH and >C=O stretching vibrations, where as absence of these vibrations may indicate enol form of the ligand. The present study concerned with synthesis of some lanthanide (III) nitrate complexes of hydrazones derived from 3-[m/p (hydrazino carbonyl)] phenyl sydnone and hydroxy aryl aldehyde or ketones, henceforth abbreviated as LH₂ (I).

Materials and Method

The chemicals used for the analysis of ligands and complexes were of AR/reagent. The solvents were dried and distilled before use according to standard procedure. Lanthanum nitrate penta hydrate $La(NO_3)_3 \cdot 5H_2O$ (99%) was obtained from BDH Chemicals Ltd., other lanthanides were procured from Indian Rare Earth Ltd., as oxides (99.9% pure). The corresponding metal nitrates were prepared by dissolving a slight excess of respective oxide in hot 50% (v/v) nitric acid. The solutions evaporated to a small volumes diluted with water and evaporated again nearly to dryness. The residues were extracted with water and process of evaporation was repeated three times to remove the excess acid resulting in crystals of lanthanide nitrates used for preparation of the complexes.

Preparation of 3- [m/p (hydrazino carbonyl)] phenyl sydnone [6].

3-[m/p [(carbethoxy)] phenyl sydnone 2.34 gm (0.01mol) was dissolved in 60-70 ml absolute alcohol. To this was added 100% hydrazine hydrate 2ml (0.04mol) and refluxed on steam both for four hours. Then the solvent was evaporated and the residue crystallized from methanol dioxane mixture.
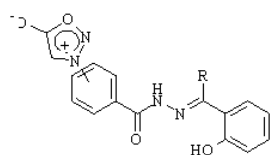
Preparation of hydrazone ligand (LH₂)

The hydrazone ligand (LH₂) was prepared by refluxing 3-[m/p (hydrazino carbonyl)] phenyl sydnone and hydroxy aryl aldehyde or ketone in 1:1 mole ratio for two hours. The solvent was evaporated and the solid separated was crystallized from methanol (yield 60.70%).

Preparation of the complexes:

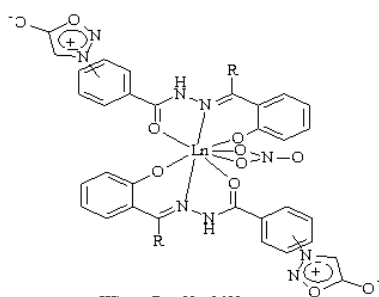Lanthanide (III) nitrate (0.02 mol) dissolved in 20 ml of dry alcohol was mixed with respective hydrazone (0.04 ml) dissolved in the same solvent (20 ml) with constant stirring, The mixture was refluxed on a water bath for about four hours and then pH of the mixture was raised to 6.5 by adding dropwise alcoholic ammonia. The coloured complex thus formed was filtered washed with dry alcohol and dried in vacuum at room temperature.

The metal content determined by complexometric EDTA titration using xylenol orange as indicator[7] at pH 6. The nitrate present in the complexes is determined using a nitron reagent. The elemental analysis (C. H and N) of complexes was recorded on Elemental analyzer, Heraeus Carlo Erba 1108. Conductance measurements were made using $10^{-3}M$ solution of complex in DMF using Elico conductivity bridge type CM-82 provided with a cell having cell constant $0.51cm^{-1}$. The electronic spectra of complexes in DMF solution were recorded on Hitachi 150-20 spectrophotometer in the range of 800 to 200nm IR spectra were recorded in the range of $4000\text{-}200cm^{-1}$ on PerkinElmer-783 model in KBr pellets. ^1H NMR spectra were recorded in DMSO-d_6 on a Bruker AC 300F (300 MHz) spectrometer using TMS as an internal standard. The magnetic susceptibility data at room temperature were obtained by using a model 300 Lewis coil force magnetometer of George Associates Inc. make using a CAHN 2000 electrobalance and a APD make close cycle cryostat working in the range 300-12K. Thermogravimetric (TG) and derivative thermogravimetric (DTG) were carried out for representative complexes in the range of room temperature to about 800°C in dry air atmosphere maintaining a heating rate of 10°C /min.

Where R = H - L^1H_2
CH$_3$ - L^2H_2
C$_2$H$_5$ - L^3H_2

I-Structure of the ligand

Where R = H - L^1H_2
CH$_3$ - L^2H_2
C$_2$H$_5$ - L^3H_2

and Ln = La, Pr, Nd, Sm and Gd

II. Proposed Structure of the complex

Biological activity
Antibacterial activity:

The antibacterial activity of the ligand and its complexes were assayed simultaneously against *Salmonella paratyphi* (Sp), *Bacillus cirroflagellosus* (Bc) by cup plate method. Nutrient broth was prepared by dissolving peptone (10g), yeast extract (5g), sodium chloride (10g) in 1000ml distilled water. The pH of the medium is adjusted to 7.0 and the solution is autoclaved at 121°C at 15 lb pressure for 20mins. One day prior to the experiment, the cultures of *Salmonella paratyphi* (Sp), *Bacillus cirroflagellosus* (Bc) were inoculated in nutrient broth to revive the cultures and incubated for about 18hrs at 37°C.

Each test compound was dissolved in DMF (5ml) to give a solution concentration 1000mg /ml. The 0.1ml of this solution was used for antibacterial testing and Cotrimoxazole was used as standard.

Transfers 1ml of the overnight incubated cultures into the Petri dishes then add the nutrient agar medium, which was cooled to 45-50 °C with gradual shaking for uniform distribution of the culture. Allow it to solidify then cup hole of 10mm diameter were bored carefully with a sterile cork borer. Now add 0.1 ml (100mg) of drug solution then these plates are kept in cold room for 1-2 hrs to facilitate the drug diffusion. Incubate the Petri dishes at 37°C for 24-48 hrs and then calculate the extent of inhibition by measuring the width of zone in millimeters.

Antifungal activity

The antifungal activity of the ligand and its complexes are tested against pathogenic fungi Aspergillus *niger* and *Candida albicans* by cup plate method. Prior to the tests above mentioned fungi were inoculated in potato dextrose broth at 27°C for 24-36 hrs. Potato dextrose broth was prepared by dissolving 250g boiled potato peel filtrate and 20g dextrose in 1000ml distilled water pH was adjusted to 5.6 and sterilized in autoclave.

Then fungal medium was prepared by dissolving peptone (6g), potassium dihydrogen phosphate (3g), yeast extract (6g), sodium chloride (6g) and dextrose (5g) in distilled water. The pH of the media is adjusted to 6.0 by adding 1N solution of sodium hydroxide then add agar (20g) and the solution is autoclaved at 121°C at 15 lb pressure for 20mins.

Transfer 1ml of the overnight incubated cultures into the Petri dishes then adds the fungal medium, which was cooled to 45-50 °C with gradual shaking for uniform distribution of the culture. Allow it to solidify then cup hole of 10mm diameter were bored carefully with a sterile cork borer. Now add 0.1 ml (100mg) of drug solution then these plates are kept in cold room for 1-2 hrs to facilitate the drug diffusion. Incubate the Petri dishes at 37°C for 36-48 hrs and then calculate the extent of inhibition by measuring the width of zone in millimeters and Flucanazole was used as standard.

Results and Discussion

All the lanthanide (III) nitrate complexes are non-hygroscopic, coloured crystalline in nature and insoluble in organic non polar-solvents but soluble in organic polar solvents, like DMF and DMSO. From elemental analysis data (Table 1) reveal that the lanthanide (III) nitrate complexes have a metal to ligand ratio 1:2. The molar conductance of all the complexes has been recorded in DMF at 10^{-3} M concentration. The molar conductance values are much less than expected for 1:1 electrolytes and hence all the complexes are treated as non-electrolytes[8]. Therefore the molar conductivity data suggest that the nitrate ion present within co-ordination sphere in the complexes. Lanthanum (III) nitrate complexes are diamagnetic but other tripositive lanthanide ion complexes are paramagnetic.

16

Table 1:Analytical & Physical data of Ln (III) nitrate complexes with hydrazones

Complex	Colour	Analysis (%) : Found (calculated)					μ_{eff} (BM)
		M	C	H	N	Nitrate	
[La (L^{1}H)$_2$NO$_3$]	White	16.32	44.87	2.58	13.16	7.28	diamagnetic
		(16.40)	(45.34)	(2.60)	(13.22)	(7.32)	
[Pr (L^{1}H)$_2$NO$_3$]	Green	16.07	44.82	2.61	13.14	7.22	3.76
		(16.59)	(45.23)	(2.59)	(13.19)	(7.30)	
[Nd (L^{1}H)$_2$NO$_3$]	Yellow	16.26	44.36	2.50	13.02	7.22	3.92
		(16.92)	(45.05)	(2.58)	(13.14)	(7.27)	
[Sm (L^{1}H)$_2$NO$_3$]	Brown	16.98	44.32	2.42	12.96	7.16	2.64
		(17.51)	(44.74)	(2.56)	(13.05)	(7.22)	
[Gd (L^{1}H)$_2$NO$_3$]	Brown	17.89	43.92	2.46	12.71	7.14	7.21
		(18.17)	(44.38)	(2.54)	(12.94)	(7.16)	
[La (L^{2}H)$_2$NO$_3$]	White	15.16	46.21	2.86	12.62	7.02	diamagnetic
		(15.87)	(46.63)	(2.97)	(12.80)	(7.08)	
[Pr (L^{2}H)$_2$NO$_3$]	Green	15.98	45.82	2.92	12.36	7.05	3.78
		(16.06)	(46.52)	(2.96)	(12.77)	(7.07)	
[Nd (L^{2}H)$_2$NO$_3$]	Yellow	16.10	45.86	2.92	12.52	7.00	3.90
		(16.39)	(46.35)	(2.95)	(12.72)	(7.04)	
[Sm (L^{2}H)$_2$NO$_3$]	Brown	16.53	45.86	2.91	12.42	6.92	2.62
		(16.96)	(46.04)	(2.93)	(12.63)	(6.99)	
[Gd (L^{2}H)$_2$NO$_3$]	Brown	17.06	46.01	2.81	12.42	6.91	7.19
		(17.60)	(45.67)	(2.91)	(12.54)	(6.94)	
[La (L^{3}H)$_2$NO$_3$]	White	15.02	46.82	3.26	12.24	6.89	diamagnetic
		(15.38)	(47.84)	(3.32)	(12.40)	(6.86)	
[Pr (L^{3}H)$_2$NO$_3$]	Green	15.38	48.34	3.29	12.39	6.88	3.74
		(15.57)	(47.74)	(3.31)	(12.37)	(6.85)	
[Nd (L^{3}H)$_2$NO$_3$]	Yellow	15.22	48.18	3.24	12.31	6.64	3.95
		(15.88)	(47.56)	(3.30)	(12.33)	(6.82)	
[Sm (L^{3}H)$_2$NO$_3$]	Brown	16.06	46.94	3.19	12.06	6.56	2.66
		(16.44)	(47.24)	(3.28)	(12.25)	(6.78)	
[Gd (L^{3}H)$_2$NO$_3$]	Brown	16.36	47.09	3.25	12.08	6.56	7.24
		(17.07)	(46.89)	(3.26)	(12.16)	(6.73)	

The observed magnetic moments are compared with the theoretical spin orbital coupling values (the Hunds values) and the values calculated from Van Vleck formula[9] of the respective lanthanide ion. These values agree with each other for all the lanthanide (III) nitrate complexes except samarium (III) nitrate complexes. This indicates the non involvement of 4f-orbitals in the bond formation. In the complex of samarium (III) nitrate a little deviation from Van Vleck values indicates little participation of 4f electrons in bond formation. In the samarium (III) nitrate complex a slight higher values observed may presumably be due to temperature dependent magnetism[10-11] on account of low *J-separation*.

Electronic Spectra

The electronic spectra of ligand and their corresponding lanthanide (III) complexes are recorded in DMF in the region 200-900 nm The ligands show bands in the ranges 265-310, 360-380 and 390-410nm and in the corresponding lanthanide (III) nitrate complexes, bands around 290 and 400 nm are observed. In the region from 200-480 nm the bands are quite intensive both for the ligands and corresponding complexes. Thus the weak f-f transitions occurring in this region due to the metal ion in the complexes are obscured in the intense ligand bands. Also the ligand band remains largely unaffected on the complexation. No absorption band due to f-f transition of lanthanide (III) ions could be located in the visible region in the spectra of all these complexes. This is probably due to the fact that the f-f bands are weak and are obscured by the intense charge transfer bands.

Infrared spectra

The important IR frequencies of the complexes are produced in Table-2. The IR spectra of ligand show a sharp and strong intensity bands around 3120-3105cm^{-1} and 1702-1690cm^{-1} assigned to ν(C-H) of sydnone and ν(C=O) of sydnone respectively. The strong band due to azomethine function and amide carbonyl ν(C=O) appeared around 1650-1640 and 1675-1660cm^{-1} respectively. The IR spectra of ligand show a broad medium intensity band in the region 3450-3430cm^{-1} due to phenolic-OH[12],and the band due to ν(C-O) phenolic is located in the region 1530-1520cm^{-1}. All of the ligands as well as the corresponding complexes show broad medium intensity bands in the region 3310-3200 cm^{-1} which may be assigned to ν($^-$NH). The band around 1650-1640cm^{-1} in the spectra of the ligand is assigned to ν(C=O) which in the complex is found to appear around 1630-1605cm^{-1} with a shift

of around 15-25 cm^{-1} similarly the bands occurring around 1625-1610cm^{-1} in the spectra of the ligands may be assigned to ν(C=N) which is also shifted on complexation and appears around 1585cm^{-1} in the complexes. The absence of ν(O-H) band in all the complexes suggest that involvement of oxygen of the phenolic group in the bond formation via deprotonation, The new phenolic band in complexes show a positive shift around 10-15cm^{-1} as compared with ligands confirms the involvement of deprotonated phenolic oxygen in complexation. These observations clearly indicate the existence of the ligands in the keto form. The present lanthanide (III) nitrate complexes show six absorption band in the regions 1500-1470, 1300-1280, 1020-1005, 860-840, 765-750, and 695-685 cm^{-1} assigned to respectively to $\nu_4, \nu_1, \nu_2, \nu_6, \nu_3,$ and $\nu_5,$ vibrations of

the coordinates C_{2v} nitrate group. The magnitude of $\nu_4 - \nu_1$ and $\nu_3 - \nu_5$ are in the range of 200-190cm^{-1} and 70-55cm^{-1} respectively indicates the nitrate group is in bidenate fashion. Apart from these two other non ligand bands are also observed. These are weak bands, one band observed in the range of 505-475cm^{-1} which may be attributed to ν(M-O) [13] and the other around 440-418cm^{-1} which may be assigned to ν(M-N) [14] vibrations. The band due to ν(M-O) usually occurs at higher frequency than ν(M-N) [15] and ν(M-O) band usually broad and strong than the ν(M-N) band. This may be due to large dipole moment change in the vibrations of M-O band in comparison to that in the M-N band[16].

Table 2: Important IR frequencies (cm^{-1}) of the complexes

Complex	ν(C=N) Azomethine	ν(C=O) Hydrazine	ν(C=O) Phenolic	NO$_3^-$ frequencies						ν(M-O)	ν(M-N)
				ν_4	ν_1	ν_2	ν_6	ν_3	ν_5		
La(L^{1}H)$_2$NO$_3$	1590	1602	1542	1478	1498					496	436
La(L^{2}H)$_2$NO$_3$	1598	1585	1538	1496	1284					502	426
La(L^{3}H)$_2$NO$_3$	1602	1582	1532	1500	1300					488	440
Pr(L^{1}H)$_2$NO$_3$	1592	1580	1536	1482	1280					498	420
Pr(L^{2}H)$_2$NO$_3$	1601	1588	1540	1486	1296					502	424
Pr(L^{3}H)$_2$NO$_3$	1598	1582	1536	1492	1284					476	436
Nd(L^{1}H)$_2$NO$_3$	1596	1584	1542	1470						505	428
Nd(L^{2}H)$_2$NO$_3$	1600	1582	1538	1486						482	418
Nd(L^{3}H)$_2$NO$_3$	1602	1585	1534	1498	(1280-1300) In random order	(1005-1020) In random order	(840-860) In random order	(750-765) In random order	(685-695) In random order	496	426
Sm(L^{1}H)$_2$NO$_3$	1592	1578	1532	1478						492	430
Sm(L^{2}H)$_2$NO$_3$	1596	1580	1540	1492						504	432
Sm(L^{3}H)$_2$NO$_3$	1593	1590	1538	1500						493	426
Gd(L^{1}H)$_2$NO$_3$	1599	1585	1542	1496						486	438
Gd(L^{2}H)$_2$NO$_3$	1600	1600	1540	1492						494	436
Gd(L^{3}H)$_2$NO$_3$	1602	1580	1538	1488						475	440

Table 3: ^{1}H NMR spectral data of the ligand (L^{1}H$_2$) and La (III) complex

L^{1}H$_2$	La –complex	Assignments
7.5(s)	7.4(s)	-CH of sydnone ring
12.1(s)	-	-OH (phenolic) proton
11.2(s)	11.3(s)	-NH (of-CONH) proton
7.9(s)	7.84(s)	-N = CH- azomethine proton
8.01 – 8.59 (m)	7.97-8.5(m)	- aromatic (protons)

s = singlet   m= multiplet

^{1}H NMR spectra

The proton NMR spectral data of the ligand and its La (III) nitrate complexes is given in Table-3. ^{1}H NMR spectrum of ligand L^{1}H$_2$ shows a singlet at δ 7.5due to C-H proton of sydnone ring. A fine singlet due to phenolic –OH was observed as a singlet at δ12.1(s, H, -OH). Proton of the NH (of- CONH-) resonated as a singlet at δ11.2(s, 1H) where as proton of C-H (of azomethine) appeared at δ7.9(s, 1H). Eight aromatic protons have appeared as multiplet in the region δ8.01 – 8.59

(m, 8H, ArH). The spectrum of lanthanum (III) complex of ligand L^{1}H$_2$ shows a singlet at δ7.4 (s, 1H) due to C-H of sydnone ring. Another singlet at δ 7.84 (s, 1H) is due to proton on the azomethine carbon. This downfield shift indicates that co-ordination through nitrogen of azomethine group to the metal ion, proton of the NH (of –CONH) has resonated as a singlet at δ11.3 (s, 1H). A fine singlet due to phenolic –OH was observed at δ12.1 (s, 1H) in case of ligand has disappeared in complex indicates the co-ordination via deprotonation. Eight aromatic protons have appeared as multiplet in the region δ

7.97– 8.5 (m, 8H, ArH). This data confirms the complexation of ligand with metal ion.

Thermal studies

The thermal behaviour of representative lanthanide (III) nitrate complexes including stability ranges, peak temperature, percentage of weight loss and percentage of residue (Table-4) obtained after decomposition process has been studied. The complex decomposition proceeds in two major steps. The lanthanum (III) nitrate complex [La (L^{1}H)$_2$NO$_3$] undergoes decomposition in two stages. The first step is from around 403K to about 673K. The weight loss in this range of the temperature corresponds to the loss of one nitrate and one ligand molecule.

In the second stage the weight loss corresponds to the loss of another ligand molecule. The decomposition starts from around 673K and continues up to around 963K, after which a plateau is obtained which indicates the formation of stable La$_2$O$_3$. The weight of La$_2$O$_3$ agrees with the calculated values. In the Gadolinium (III) nitrate complex [Gd (L^{2}H)$_2$NO$_3$] the first stage occurs in the temperature range 393K to 703K the weight loss indicates the loss of one nitrate and one ligand molecule, in the second stage the weight loss in the temperature range 703K to 993K indicates the loss of another ligand molecule beyond 993K a plateau is obtained which indicates the formation of Gd$_2$O$_3$, The weight of Gd$_2$O$_3$, agrees with the calculated values.

Table 4: Thermal data of representative lanthanide (III) nitrate complexes under study

Complex	Process	Decomposition temp-range (K)	Peak temp(K)	Decomposition product	Weight Loss %		No.of moles	Residue		Nature
					obs	Calcd		Obs	Calcd	
[La(L^{1}H)$_2$NO$_3$]		403-673	510	L^{1}H and NO$_3$	46.08	45.34	1 and 1			
	First stage decomposition of co-ordination sphere									
	Second stage decomposition of co-ordination sphere	673-963	848	L^{1}H	38.32	38.01	1	38.68	38.46	La$_2$O$_3$
[Gd(L^{2}H)$_2$NO$_3$]	First stage decomposition of co-ordination sphere	393-703	502	L^{2}H and NO$_3$	43.89	44.65	1 and 1			
	Second stage decomposition of co-ordinate on sphere	703-993	853	L^{2}H	37.32	37.71	1	41.14	40.58	Gd$_2$O$_3$

Table 5: Antibacterial & Antifungal activity of complexes (Zone of inhibition in mm)

Sl.No.	Complex	Antibacterial		Antifungal	
		B.c	S.p	A.n	C.a
1	[La (L^{1}H)$_2$NO$_3$]	12	13	14	11
2	[La (L^{2}H)$_2$NO$_3$]	13	13	13	13
3	[La (L^{3}H)$_2$NO$_3$]	12	13	14	12
4	[Pr (L^{1}H)$_2$NO$_3$]	17	19	16	15
5	[Pr (L^{2}H)$_2$NO$_3$]	16	18	17	16
6	[Pr (L^{3}H)$_2$NO$_3$]	17	18	16	15
7	[Nd (L^{1}H)$_2$NO$_3$]	16	18	16	14
8	[Nd (L^{2}H)$_2$NO$_3$]	15	17	15	16
9	[Nd (L^{3}H)$_2$NO$_3$]	16	17	16	14
10	[Sm (L^{1}H)$_2$NO$_3$]	10	11	12	13
11	[Sm (L^{2}H)$_2$NO$_3$]	11	12	12	12
12	[Sm (L^{3}H)$_2$NO$_3$]	12	13	11	12
13	[Gd (L^{1}H)$_2$NO$_3$]	12	13	12	10

14	[Gd (L^{2}H)$_2$NO$_3$]	11	13	14	12
15	[Gd (L^{3}H)$_2$NO$_3$]	17	15	14	15
16	Cotrimoxazole	25	22	-	-
17	Flucanozole	-	-	24	23

B.c=Bacillus cirroflagellosus;S.p=*Salmonella paratyphi;*A.n=Aspergillus niger; C.a=Candida albican

Antimicrobial Studies

Hydrazones with lanthanides have shown remarkable biological activity mainly antibacterial activity[17] and pharmacological activity[18]. The compounds were tested for their in vitro antibacterial activity against *Salmonella paratyphi* and *Bacillus cirroflagellosus* and antifungal activity against *Aspergillus niger* and *Candida albicans* by the cup plate method[19]. It is evident from the bacterial and fungal screening data (Table-5), that the activities of the ligands have not profoundly increased on complexation with lanthanides except in some cases Sm (III) and Gd (III) complexes are moderately active against *Bacillus cirroflagellosus* Pr (III) and Nd (III) complexes are moderately active against *Salmonella paratyphi.* Overall the ligands and complexes are less active as compared to the standards Cotrimoxazole and Flucanozole used in the present study.

From the foregoing discussion it is concluded that the ligand react in a keto form based upon analytical and spectral studies. The IR and molar conductance data suggests that nitrate ion is coordinated bidentately to the lanthanide ion. The co-ordination number eight for lanthanide ion in the complex of the type [Ln(LH)$_2$NO$_3$] (Ln=La, Pr, Nd, Sm and Gd) has been proposed (II).

Acknowledgement

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