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Synthesis, characterization, anti-microbial study of 2-amino-N′-[(1E)-1-pyridine-2-ylethylidene]benzohydrazide and its Lanthanide(III) Complexes

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ABSTRACT

A new hydrazone, 2-amino N′-[(1E)-1-pyridine-2-ylethylidene]benzohydrazide (Apbz) and its complexes with rare earth nitrates have been synthesized. These new complexes with the general formula of $[Ln(Apbz)_2 NO_3] \cdot 2NO_3$ *where Ln= La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), and Y(III) were characterized by Spectral (IR,* ^1H *NMR,* ^{13}C *NMR, EPR, UV-Vis, mass), elemental analysis, thermal analysis and molar conductivity. All the complexes are stable in air. The results show that the ligand has coordinated in a tridentate fashion coordinating through pyridine nitrogen, azomethine nitrogen and the carbonyl oxygen.*

Keywords: 2-acetylpyridine, Hydrazone, Lanthanide complexes, Anti-bacterial activity, Anti-fungal activity.

INTRODUCTION

Hydrazones are a versatile class of compounds which present a wide range of biological applications as antimicrobial [1], antitubecular [2], anticonvulsant [3], anti-inflammatory [4], cytotoxic [5] and vasodilator [6] agents. Moreover, Hydrazones derived from 2-acetylpyridine are known to inhibit the proliferation of tumour cells to a greater extent compared to standard anticancer agents [7, 8]. Metal complexes with hydrazones have potential applications as catalysts [9] luminescent probes [10] and molecular sensors [11]. In addition, metal complexes with hydrazones present antimicrobial [12-14], DNA-binding and cytotoxic activities [14]. It has also been shown that metal complexes with hydrazones can be potent inhibitors of cell growth and DNA syntheses [15].

Investigation of molecular complexes of lanthanide ions has attracted significant attention, owing to their broad ranging fluorescent applications in biochemistry, material chemistry, medicine and so forth [16-18]. In our earlier work we have reported the transition metal complexes of title compound, 2-amino N$'$-[(1E)-1-pyridine-2-ylethylidene] benzohydrazide **(**Apbz**)** [19]. In order to understand the mode of coordination with lanthanide ions and the subsequent effect on antimicrobial activity, we report herein the lanthanide complexes of Apbz. The antimicrobial activity of the Apbz and its lanthanide(III) complexes was evaluated against two pathogenic fungi - *Penicillium notatum and Aspergillus niger* and two bacteria - Gram-negative bacterium *Escherichia coli*, Gram-positive bacterium *Bacillus cirroflagellosus* by cup plate method.

MATERIALS AND METHODS

Materials and general methods

All the solvents used were of A.R. grade. Hydrazine hydrate, methyl anthranilate and 2-acetylpyridine were procured from Rankem, Merck and Himedia respectively. *2*-Aminobenzoylhydrazide was synthesized by following the earlier method [20]. The lanthanide nitrates were obtained by heating lanthanide oxides (99.9%) (Indian Rare Earths) with dilute nitric acid (50%) and evaporating the excess acid and dried in vacuum oven.

The title compound 2-amino N$'$-[(1E)-1-pyridine-2-ylethylidene]benzohydrazide (Apbz) was prepared following the literature method[19]. The lanthanide metal complexes of Apbz were prepared by the reaction of ligand with lanthanide metal (III) nitrates in 2:1 molar ratio in methanolic medium and refluxed for 2-3hrs. The resulting solution is concentrated to a small volume and macerated with petroleum ether leading to its solidification. The yellow solid obtained was filtered off, washed with methanol and finally dried in air.

Corbon, Hydrogen and Nitrogen content of the compounds were carried out by using Carlo-Erba Strumentazione (Italy) CHN Analyzer. The metal content of the complexes were determined by complexometric titrations with EDTA using xylenol orange as the indicator. The molar conductance measurements were carried out on Elico Conductivity Bridge, Type CC-01 with cell constant 0.53, provided with dip type conductivity cell, fitted with platinum electrodes. Mass spectra of the ligand and complexes were recorded on a Thermofinnigan 1020 automated GCMS and JEOL SX 102/DA – 6000 mass spectrometer respectively. The IR spectra were recorded on a Nicolet 170 SX FT-IR spectrometer in the 4000–400 cm^{-1} region using KBr discs. The ^{1}H NMR spectra of the ligand and Zn(II) complex (DMSO-d$_6$) were recorded on a Bruker Avance 300 MHz spectrometer operating at 300.13 MHz. Electronic spectra were recorded on a Hitachi 2001 and Cary-Nio-50 Varian spectrophotometer in 200 – 900 nm range in DMSO solutions. Magnetic susceptibility measurements were carried out on a Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant. TG–DTA studies were carried out in the 25–1000 ^{o} C temperature range using a Perkin-Elmer (Pyris Diamond) Analyser in N_2 atmosphere at a heating rate of 10^{o}C/min. The EPR spectra of Gd(III) and Tb(III) complexes were recorded both at room temperature as well as liquid nitrogen temperature on a Varian E-4 X-band spectrometer using TCNE (tetracyanoethylene) as the "g" marker.

Anti-microbial activity

The *in-vivo* biocidal activities of the free ligand, its metal complexes and corresponding metal salts were screened against pathogenic fungi - *Penicillium notatum and Aspergillus niger* and the bacteria - Gram-negative bacterium *Escherichia coli*, Gram-positive bacterium *Bacillus cirroflagellosus* by cup plate method. Fresh solutions of Apbz and its complexes (0.10%) were prepared in DMSO just before use. The biocidal potency of these compounds was estimated by using the radial growth method in duplicate and determined the inhibition zones. DMF was taken as the control and the incubation period for fungi and bacteria was 72 h at 28°C.

Nutrient agar medium was prepared by dissolving peptone (1%), yeast extract (0.6%), beef extract (0.5%), sodium chloride (0.5%) in distilled water. The pH of the solution was adjusted to 7.2 by adding 4% aqueous sodium hydroxide solution. Agar (2.4%) was then added and the whole solution was autoclaved for 20 minutes at 15 psi. Each test sample (5 mg) was dissolved in DMSO (1 ml) and 0.1 ml of this solution (50 μgm) was used for testing. Inoculation medium containing 24 hours grown culture was added aseptically to the nutrient medium and mixed thoroughly to get the uniform distribution. This solution was poured (25 ml in each dish) into petri dishes and then allowed to attain room temperature. Thereafter, punching the set of agar with a sterile cork borer and scooping out the punched part made the cups. The diameter of each cup was 5mm. Norfloxacin and Griseofulvin were used as the standards with DMSO as the solvent control. The entire test samples and the standard were tested at a concentration of 50 μgm. The plates were allowed to stand for an hour in order to facilitate the diffusion of the drug solution and incubated at 37 °C for 48 hours. The zones of inhibition against all the microorganisms were measured in millimeters.

RESULTS AND DISCUSSION

The analytical data [Table 1] indicate that the complexes have 1:2 (Metal: Ligand) stoichiometry. The lanthanide complexes are stable, non hygroscopic and yellow in colour. They are sparingly soluble in ethanol, methanol, soluble in DMSO and DMF but insoluble in benzene, ether and chloroform. The molar conductance values of the complexes in DMSO at 10^{-3}M are in the range of 70.00 - 80.00 $Ohm^{-1}cm^{2}$ moles $^{-1}$, which indicate that they are 1:2 electrolytes [19].

The molecular ion peak at m/z = 254 the mass spectrum of the ligand corresponds to its total molecular weight. The molecular ion peak at m/z =844 in the FAB mass spectrum of $[Sm(Apbz)_2 NO_3]\cdot 2NO_3$ complex [**Figure 1**] supports the proposed composition of the complex.

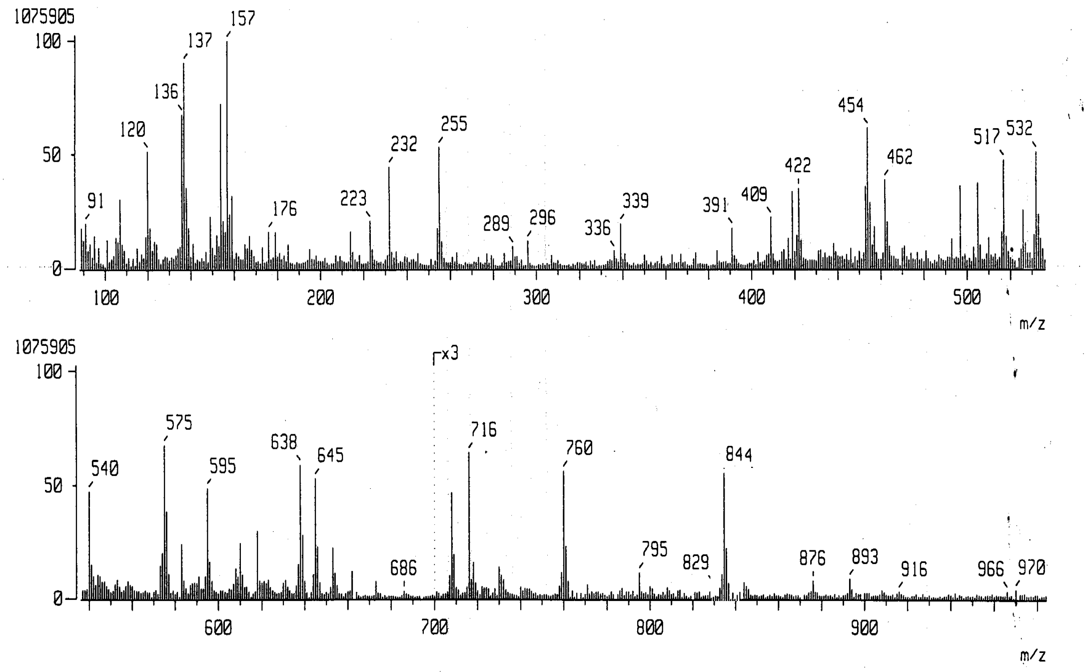

Figure 1: Mass spectrum of $[Sm(Apbz)_2 NO_3]\cdot 2NO_3$

Table 1: Elemental analyses of Apbz and its Ln(III) complexes

SL No	**Compounds**	**Found (calculated %)**				**Effective Magnetic moments (BM)**	**Molar conductance Ohm^{-1} cm^{2} mol^{-1}**
		M	C	H	N		
1	Apbz ($C_{14}H_{14}N_4O$)		66.00 (66.14)	5.58 (5.51)	21.98 (22.05)	-	-
2	$[La(Apab)_2NO_3]\cdot 2NO_3$	16.60 (16.68)	40.39 (40.34)	3.00 (3.36)	18.40 (18.48)	Dia	70.43
3	$[Pr(Apbz)_2NO_3]\cdot 2NO_3$	16.80 (16.88)	40.29 (40.24)	3.30 (3.35)	18.35 (18.44)	3.68	72.46
4	$[Nd(Apbz)_2NO_3]\cdot 2NO_3$	17.29 (17.21)	40.25 (40.09)	3.50 (3.34)	18.30 (18.37)	3.40	75.46
5	$[Sm(Apbz)_2NO_3]\cdot 2NO_3$	17.87 (17.80)	39.70 (39.79)	3.40 (3.31)	18.30 (18.23)	1.60	74.25
6	$[Eu(Apbz)_2NO_3]\cdot 2NO_3$	17.80 (17.96)	39.62 (39.70)	3.25 (3.30)	18.20 (18.20)	3.70	80.05
7	$[Gd(Apbz)_2NO_3]\cdot 2NO_3$	18.40 (18.47)	39.20 (39.47)	3.20 (3.28)	18.00 (18.09)	7.72	80.05
8	$[Tb(Apbz)_2NO_3]\cdot 2NO_3$	18.55 (18.63)	39.30 (39.39)	3.25 (3.28)	18.20 (18.05)	9.80	78.92
9	$[Dy(Apbz)_2NO_3]\cdot 2NO_3$	18.80 (18.97)	39.00 (39.22)	3.25 (3.26)	17.90 (17.98)	10.84	72.12
10	$[Y(Apbz)_2NO_3]\cdot 2NO_3$	11.25 (11.36)	42.85 (42.91)	3.50 (3.57)	19.50 (19.67)	Dia	77.25

Table 2: IR spectral data of Apbz and its Ln(III) complexes

Sl. No.	**Compound**	**NH_2**		**υ(C=O) Amide I**	**υ(C=N) Azomethine**	**υ(Py N)**	**Amide II**	**Amide III**	**Ionic NO_3**	**$-NO_3$ bands**					
		υ_{sym}	**υ_{asym}**							**υ_4**	**υ_1**	**υ_6**	**υ_2**	**υ_3**	**υ_5**
1	APBZ	3430sh	3316sh	1645s	1614s	1582s	1530s	1247sh	-	-	-	-	-	-	-
2	[Ln(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1626s	1586sh	1556m	1523s	1252sh	1384m	1338s	1249m	821w	1030w	742w	669m
3	[Pr(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1615s	1589sh	1547m	1503s	1254sh	1383m	1340s	1250m	822w	1030w	755w	667m
4	[Nd(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1624s	1583sh	1552m	1530s	1254sh	1384m	1338s	1254m	820w	1030w	745w	666m
5	[Sm(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1620s	1584sh	1550m	1524s	1250sh	1383m	1339s	1250m	820w	1031w	750w	671m
6	[Eu(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1627s	1582sh	1550m	1522s	1249sh	1386m	1339s	1249m	825w	1031w	755w	669m
7	[Gd(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1627s	1581sh	1548m	1521s	1249sh	1383m	1319s	1249m	821w	1021w	745w	670m
8	[Tb(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1615s	1582sh	1550m	1524s	1251sh	1384m	1335s	1248m	819w	1042w	742w	668m
9	[Dy(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1629s	1580sh	1549m	1520s	1248sh	1385m	1337s	1248m	822w	1012w	743w	668m
10	[Y(Apbz)$_2$ NO$_3$] ·2NO$_3$	„	„	1629s	1586sh	1556m	1524s	1252sh	1384m	1336s	1252m	825w	1031w	753w	680m

s = strong, sh = sharp, m = medium, b = broad, w =weak

Infrared Spectra

The important IR frequencies of Apbz and its complexes are given in Table 2. A strong band in the spectrum of free ligand at 1645 cm^{-1} is assigned to υ(C=O) (amide I) where as those at 1530 and 1247 cm^{-1} are due to amide II and III, respectively, arising from the υ(C-N) and υ(NH) modes [21]. The strong band at 1614 cm^{-1} is assigned to the azomethine υ(C=N) group. The υ(N-N) is observed at 1012 cm^{-1}[22]. Due to the presence of intramolecular hydrogen bonding between the oxygen of carbonyl and the hydrogen of NH_2, the υ(C=O) is observed at a lower frequency (1645 cm^{-1}) compared to the literature report where in the same was observed at 1700 cm^{-1}. This is proved by its crystal structure [19]. The pyridine ring stretching frequencies appear as a series of bands at 1578, 1554, 1458, 1432 cm^{-1}[23].

The IR spectra of the complexes show the involvement of carbonyl oxygen, azomethine nitrogen and pyridine nitrogen in coordination. In the spectra of complexes, the υ(C=O) band was shifted to lower wave number (16 to 30 cm^{-1}) indicating its coordination to the metal ion [22]. The υ(C=N) band of the azomethine group under goes a negative shift (25-34 cm^{-1}) indicating its involvement in coordination. Additional evidence for participation of υ(C=N) in coordination is given by the slight up word shift of the N-N band in all the complexes [22]. The pyridine ring vibrations at 1578 and 1554 cm^{-1} have merged to give a band in the region 1541-1547 cm^{-1}. The band at 1458 and 1432 cm^{-1} undergo a shift to lower frequency by about 4-15 cm^{-1} and 10-26 cm^{-1} respectively. These changes in pyridine ring vibrations indicate the coordination of the pyridine nitrogen to the metal ion. The coordination of pyridine nitrogen suggests that the ligand rotates across N-N bond, so as to facilitate the coordination through pyridine nitrogen. The crystal structure of the ligand [19] shows that carbonyl oxygen and methyl groups are cis to each other. A strong band around 1384 cm^{-1} indicates the presence of ionic nitrate. The presence of ionic nitrate was also confirmed by conductivity studies. The coordinated nitrate show six absorption bands at 1320, 1252, 819, 1036, 746 and 653 cm^{-1} which are assigned to υ_4, υ_1, υ_6, υ_2, υ_3 and υ_5 vibrations respectively. The difference υ_4- υ_1 and υ_3- υ_5 lies between 68-88 and 90-93 cm^{-1} respectively, indicating the coordination of nitrate group in bidentate fashion [24, 25].

^{1}H NMR and ^{13}C Spectral Studies

H^1 NMR spectra of Apbz and its La(III) complex were recorded in DMSO-d6 solution and the data along with the assignments are compiled in Table 3. Figure 2 gives the numbering system of ligand followed for ^{1}H NMR and ^{13}C assignments. In ^{1}H NMR spectrum of Apbz [19], a sharp peak at 2.44 ppm is assigned to three protons of the methyl group. The NH proton appears as a broad singlet at 15.5 ppm (D_2O exchangeable). The appearance of NH_2 signal down field is due to presence of intermolecular hydrogen bonding between NH_2 and C=O group as also proved by single crystal structure report [19].

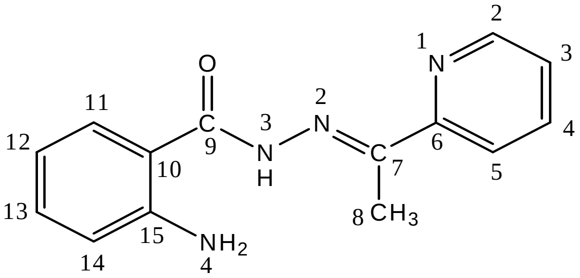

Figure 2: Numbering system of Apbz

The signal due to NH_2 merges with that of H12 and is observed as a multiplet at 6.64 ppm. The aromatic protons are observed between 6.64 - 8.61 ppm. Four doublets at 8.61, 7.83, 7.50, 6.80 ppm are assignable to H2, H5, H11 and H14 respectively. The triplets at 8.12 and

7.24 ppm are due to H4 and H13 respectively, where as multiplet at 7.59 ppm accounts for H3 of pyridine ring. In the ^{1}H NMR spectrum of Ln(III) complex, all the peaks remain almost unchanged [Table 3], [Figure 3].

Table 3: ^{1}H and ^{13}C NMR Spectral Data of Apbz and its La(III) complex

Proton	Apbz	Ln(III) complex	Carbon	Apbz	La(III) complex
H2	8.61 (d, J=4.4)	8.62(d)	C2	148.49	146.39
H3	7.59 (m)	7.59(m0	C3	124.83	122.96
H4	8.12 (t, J=7.5)	8.08(t)	C4	137.36	134.89
H5	7.83 (d, J=8.0)	7.80(d)	C5	121.15	124.26
-	-	-	C6	150.50	151.30
-	-	-	C7	151.58	152.9
CH3	2.44 (s)	2.44(s)	C8	13.21	14.52
-	-	-	C9	156.12	157.22
-	-	-	C10	115.44	115.88
H11	7.50 (d, J=7.4)	7.51(d)	C11	130.16	127.16
H12	6.64 (m)	6.62(m)	C12	117.20	118.00
H13	7.24 (t, J=7.8)	7.21(t)	C13	133.05	130.80
H14	6.80 (d, J=8.1)	6.78(d)	C14	117.7	116.00
-	-	-	C15	149.43	149.16
NH_2	6.64(s)	6.64(s)	-	-	-

s = singlet; d = doublet; m = multiplet

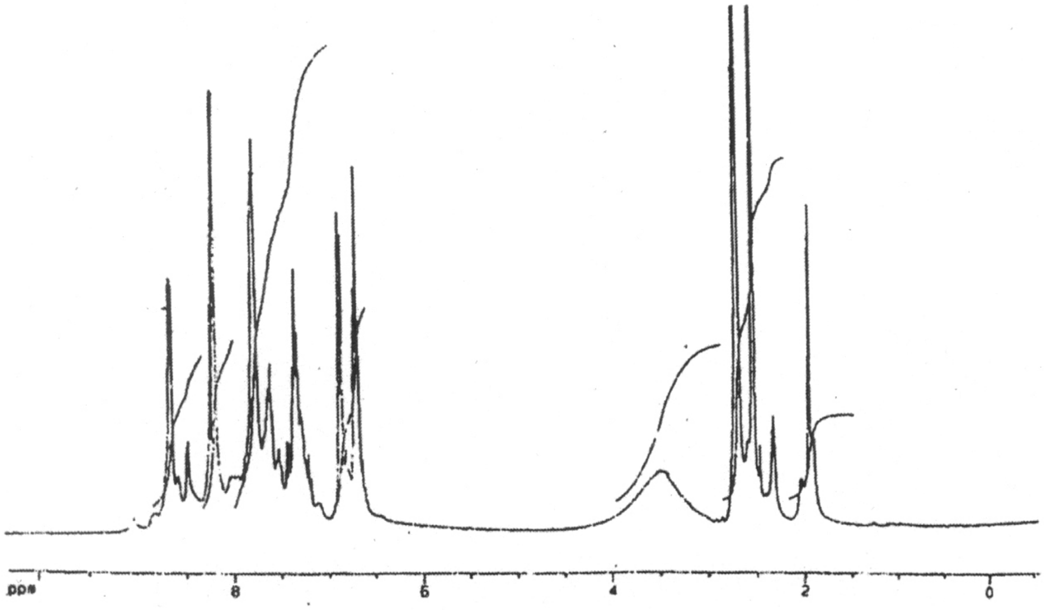

Figure 3: ^{1}H NMR spectrum of $[La(Apbz)_2 NO_3]\cdot 2NO_3$

In ^{13}C NMR spectrum of Apbz [19], the resonance at 148.49, 124.83, 137.36, 121.15 and 150.50 ppm are ascribed to carbons [C2, C3, C4, C5 and C6] of the pyridine ring. The C9(C=O) is observed at 156.12 ppm where as C8 (CH3) resonates at 13.21 ppm. The resonance at 151.58 and 149.43 ppm are ascribed to the carbons bearing the methyl and NH_2 groups respectively.

In the ^{13}C NMR spectrum of the La(III) complex, the C2, C3, C4, C5 and C6 signals of the pyridine ring appear up field at 146.39, 122.96, 124.26, 134.89, 120.55 and 151.30 ppm, indicating the involvement of the pyridine nitrogen in coordination. The C9 (C=O) shows an increase by 1 ppm and is shifted to 157.22 ppm which indicate its ligation to the metal. Similarly C7 and C8 show an increase in frequency and are shifted to 151.30 and 152.9 ppm due to coordination of adjacent azomethine nitrogen to the metal.

Magnetic and EPR spectral studies

The effective magnetic moments [Table 1] of all the complexes indicate that they are paramagnetic in nature except La(III) and Y(III) which are diamagnetic. The values obtained are similar to the Van Vleck and Frank[26], and Hund's [27] values except in case of Sm(III) and Eu(III) where slightly higher values were obtained. This is due to low J-J separation, which leads to thermal population of higher energy levels. The values obtained are similar to those of typical lanthanide ions [28] and indicate the non-involvement of 4f electrons in bonding due to their effective shielding by the $5s^25p^6$ octet.

Gd(III) ion has $4f^{7}$ electronic configuration with $^8S_{7/2}$ single-ion ground state. The energy level of the lowest excited state is vary high with no contribution from orbital angular momentum and the anisotropic effect [29].

The EPR spectra were recorded for $[Gd(Apbz)_2NO_3]\cdot 2NO_3$ complexes at room temperature(RT) as well as at liquid nitrogen temperature (LNT) [Figure 4]. The 'g' values 1.99 (at RT) and 2.04 (at LNT) being almost the same and of similar line widths, indicate that the line widths are independent of temperature [30]. Further, the complete absence of zero-field hyperfine splitting and the presence of broad bands indicate that the Gd(III) ion is located in a rather disordered environment caused by strain. These strains (caused by 'g' strain for the 'g' tensor distribution, D-strain for the zero field splitting distribution) arise due to random hydrogen bonds between water molecules and the complex leading to distortions, which lead to broad resonance EPR lines [31, 32].

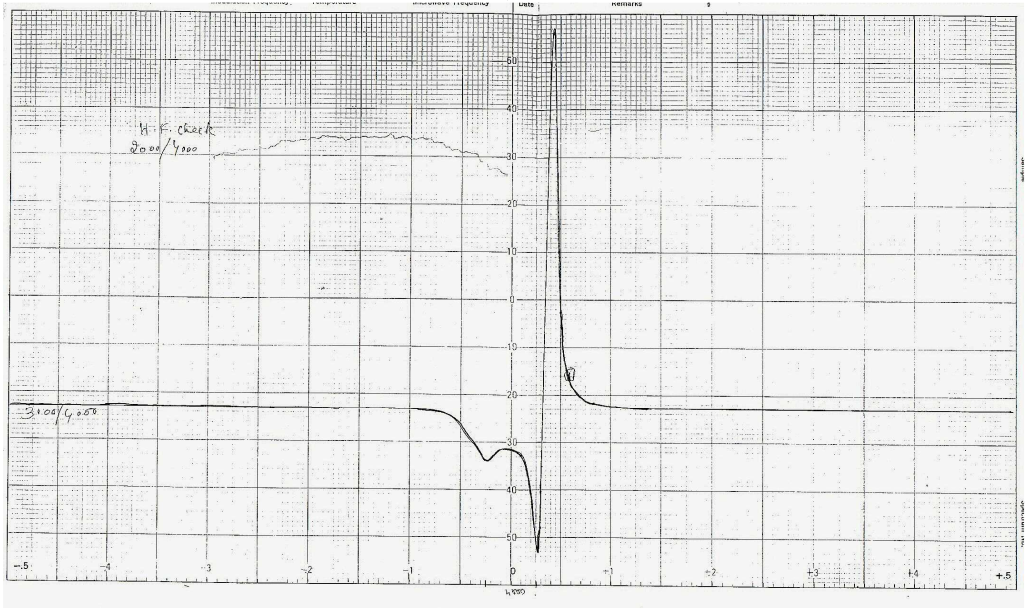

Figure 4: EPR spectrum of $[Gd(Apbz)_2 NO_3]\cdot 2NO_3$

UV-Visible spectra

The electronic spectral data of two representative complexes is given in Table 4 and Figures 5 & 6 show the spectra of $[Pr(Apbz)_2NO_3]\cdot 2NO_3$ & $[Sm(Apbz)_2NO_3]\cdot 2NO_3$ complexes. The free ligand shows an intense band at 32258 cm^{-1} and two weaker bands at 27700 and 38610 cm^{-1} of which the first two are assigned to the n → π* and the latter to the π → π* transitions, respectively. The electronic spectra of the complexes are dominated by ligand bands, with a slight shift to higher or lower energy levels. This slight shift was attributed to the effects of crystal field upon the inter electronic repulsion between the 4f electrons [33].

The nephelauxetic ratio (β), bonding parameter ($b^{½}$), Sinha's covalence parameter (δ%) and angular covalence (η) for the Pr(III) and La(III) complexes have been calculated by literature procedures [34-36].

Comparing the transitions of the complexes to that of the corresponding aqua ions, the electronic spectral bands are found to have shifted to lower energy side (nephelauxetic effect). On comparison of the spectra with that of known compounds, it is concluded that the coordination number of the present complexes is eight.

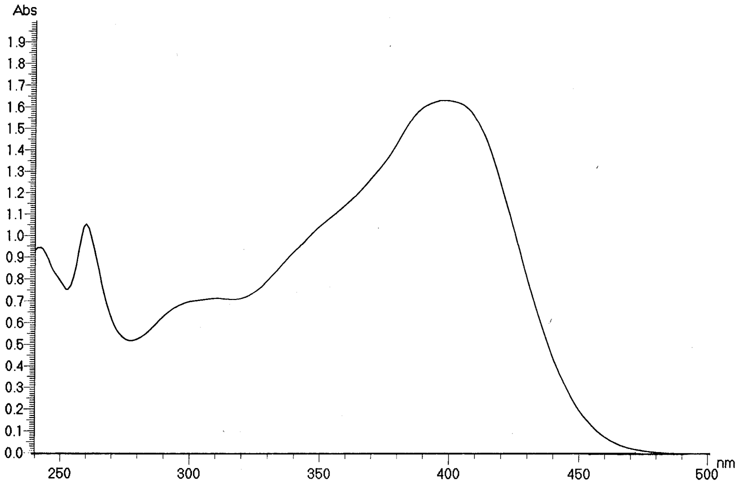

Figure 5: UV Spectrum of [Pr(Apbz)$_2$ NO$_3$]·2NO$_3$

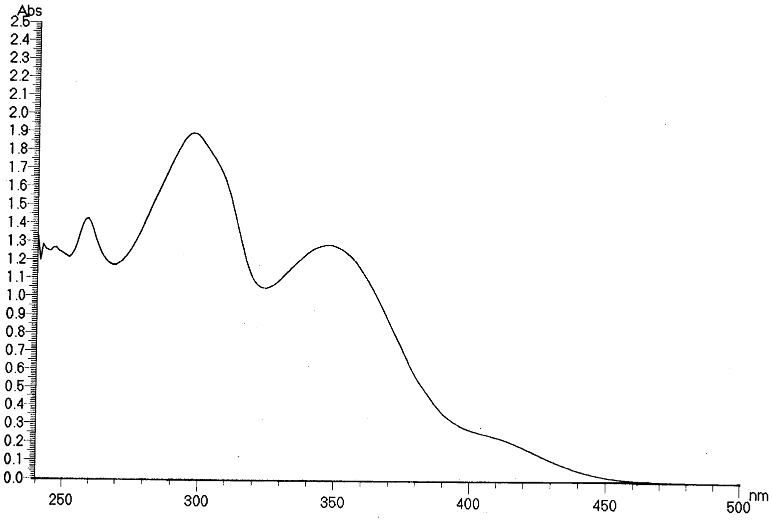

Figure 6: UV Spectrum of [Sm(Apbz)$_2$ NO$_3$]·2NO$_3$

Table 4: UV Visible spectral data of Pr(III) and La(III) complexes

Complex	Assignment	λ_{max} (cm^{-1}) of Ln(III) ion	λ_{max} (cm^{-1}) of Complexes	β	Related parameters
$[Pr(Apbz)_2 NO_3]\cdot 2NO_3$	n→π*	25142	25125	0.99614	$\delta = 0.37338$ %
	π→π*	332046	32258	0.99342	$b^{½} = 0.03049$
		38610	38461	0.99930	η = 0.0.06110
				$\beta = 0.99628$	
$[Sm(Apbz)_2 NO_3]\cdot 2NO_3$	n→π*	28618	28818	0.99305	$\delta = 0.71406$ %
	π→π*	33450	33670	0.99340	$b^{½} = 0.059539$
		38910	38610	0.99228	$\eta = 0.08450$
				$\beta = 0.99291$	

Thermal studies

The thermograms of the representative La(III) and Pr(III) complexes were carried out in nitrogen atmosphere at a heating rate of 10°C/min. In case of $[La(Apbz)_2\ NO_3]\cdot 2NO_3$, the thermogram [Figure 7] exhibits an initial weight loss of 14% (Cal 14.8 %) at 250°C which corresponds to the loss of two ionic nitrate moieties. A further weight loss in the range of 350-800°C corresponds to loss of one coordinated nitrate and two ligand molecules (Obs 67.00% Cal 67.53%). Finally the most stable oxide La_2O_3 is formed on continued heating up to 1000°C. The percentage of metal obtained is in confirmation with the value obtained by metal determinations.

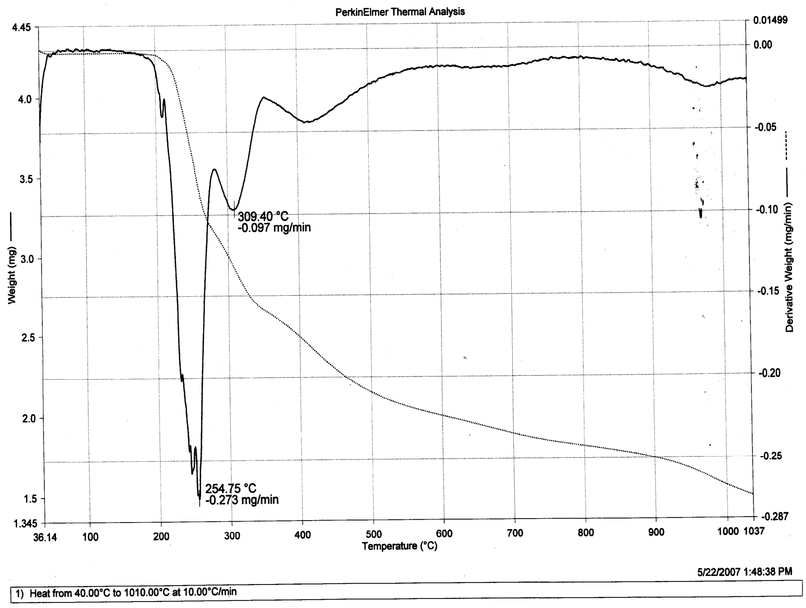

Figure 7: Thermogram of $[La(Apbz)_2\ NO_3]\cdot 2NO_3$

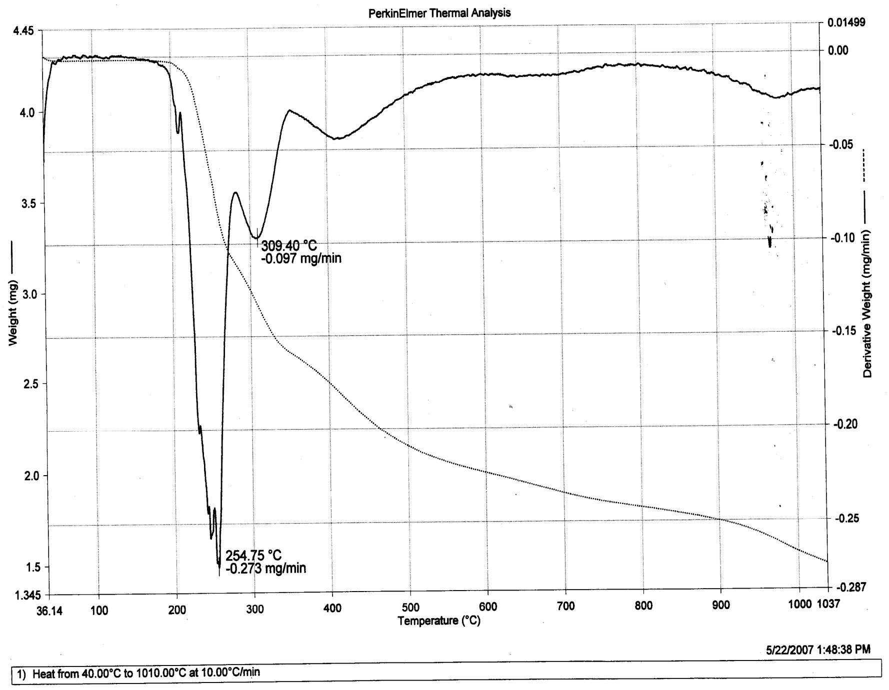

Figure 8: Thermogram of $[Pr(Apbz)_2\ NO_3]\cdot 2NO_3$

In case of $[Pr(Apbz)_2\,NO_3]\cdot2NO_3$, the thermogram [Figure 8] exhibits a loss of 14.50 % (Cal 14.85 %) which corresponds to the loss of two ionic nitrate molecules in the temperature range 250-300°C. A Further weight loss of 68 % (Cal 68.26 %) in the range of 400-800°C corresponds to the loss of one coordinated nitrate and two ligand molecules. Finally the most stable oxide Pr_6O_{11} is formed. The percentage of metal obtained is in confirmation with the value obtained by metal determinations.

Antimicrobial activity

The antibacterial and antifungal activity of the ligand, metal salts and the corresponding complexes were assayed simultaneously against *Pseudomonas aeruginosa* (PA), *Bacillus cirroflagellosus* (BC) and *Penicillium notatum* (PN), *Aspergillus niger* (AN) by cup- plate method [37]. The details of the method employed are given in Instrumentation and Experimental section.

The results of the antibacterial and antifungal study are given in Table 5. The ligand Apbz was less active against, PN, AN, PA and BC. Compared to the ligand, the complexes were moderately active against PA and BC. The enhanced activity of the complexes is due to the synergistic effect that increases the lipophilicity of the complexes. Chelation decreases the polarity of the metal ion, which further leads to enhancement of lipophilicity of the complex. Since the microorganism cell is surrounded by a lipid membrane which favours the passage of lipid soluble materials, increased lipophilicities allows the penetration of complex into, and through the membrane and deactivates the active enzyme sites of the microorganisms [38], however the activity shown is less than that of the standards used. Incase of PN and AN, no change in activity was observed.

Table 5: Antibacterial and antifungal activity data of Apbz And its Ln(III) complexes

Sl No	Compound	Antifungal		Antibacterial	
		PN	AN	PA	BC
1	Apbz	+	+	+	+
2	$[Ln(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
3	$[Pr(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
4	$[Nd(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
5	$[Sm(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
6	$[Eu(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
7	$[Gd(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
8	$[Tb(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
9	$[Dy(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
10	$[Y(Apbz\,)_2\,NO_3]\cdot2NO_3$	+	+	++	++
11	Griseofulvin	+++	+++	-	-
12	Norfloxacin	-	-	+++	+++

Key to interpretation:
**(-) No inhibition zone= inactive; 1-5 mm (+) = Less active;*
6-10mm (++) = moderately active; 11-15 mm (+++) = highly active
PN = Penicillium notatum, AN = Aspergillus niger, PA = Pseudomonasaeruginosa
BC = Bacilluscirroflagellosu

CONCLUSION

Based on NMR and IR spectral data, ligand is behaving in a tridentate fashion coordinating through pyridine nitrogen, azomethine nitrogen and carbonyl oxygen. A conformational change in the structure of the ligand is observed due to rotation about the N–N bond, which facilitate the ligand to coordinate in ONN fashion. Based on the analytical and spectral data, following structure [Figure 9] is tentatively proposed for the lanthanide (III) complexes having the general formula $[Ln(Apbz)_2\ NO_3]\cdot 2NO_3$ where Ln= La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), and Y(III).

The antibacterial activity of the ligand against *Pseudomonasaeruginosa*, *Bacilluscirroflagellosus* has enhanced on complexation, but antifungal activity against *Penicillium notatum* and *Aspergillus niger*, has remained almost the same even on complexation.

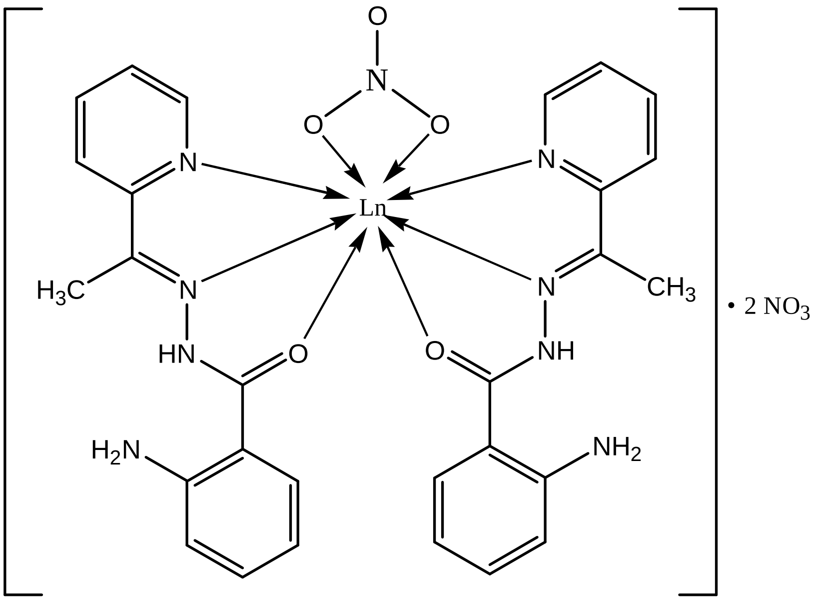

Figure 9: Proposed structure of complex $[Ln\ (Apbz)_2\ NO3]\cdot 2NO_3$

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