SYNTHESIS, CHARACTERIZATION, LUMINESCENCE AND DNA BINDING PROPERTIES OF Ln (III)-SCHIFF BASE FAMILY

S. VIDYA SAGAR BABU[†], *K.S.V.KRISHNA RAO*[§]* *YONG ILL LEE*[‡]*

[†] *Department of Chemistry, Sri Krishnadevaraya University, Aanantapuramu-515 003, India.*
[§] *Department of Chemistry, Yogi Vemana University, Kadapa-516 003, India.*
[‡]*Department of Chemistry, Changwon National University, Changwon, South Korea.*

ABSTRACT

Pentadentate Schiff base ligand(N,N-bis(2-hydroxy-1-naphthylidene) diethylenetriamine) (H_2L) that exhibits a N_3O_2 donor set. Five rare earth complexes lanthanide (III), praseodymium (III), neodymium(III), samarium(III)and europium (III) complexes are synthesized and characterized based on elemental analyses, molar conductance, infrared, ultraviolet, thermo gravimetric, X-ray powder diffraction and mass spectral studies. Molar conductivity data suggests that the complexes are 1:1 electrolytics. Infrared spectral data suggest that the ligand binds through two naptholic oxygen atoms, two azomethine nitrogen atoms and one primary amine. IR studies reveal that the complexes contain both coordinating and ionic nitrate ligands. Thermal decomposition studies indicate the presence of two nitrate ions and two water molecules in the inner coordination sphere. Eu^{3+} and Sm^{3+} complexes exhibit luminescence properties. Further, the binding properties of these complexes with calf-thymus DNA have been investigated using absorption spectrophotometry.

Keywords: Rare earth complexes, X-ray powder diffraction, Luminescence, DNA binding.

1. INTRODUCTION

Recently, lanthanide ions, Ln(III) with organic ligands have attracted much attention because of their unique luminescence and magnetic properties[1]. Due to these properties, the use of lanthanide-based probes are becoming more common in a wide variety of photonic applications such as luminescence spectroscopy, planar waveguide amplifiers[2-5], light-emitting diodes LEDs[6], plastic lasers and bio-inspired luminescence probes[7-10]. Among Ln(III) ions, Eu^{3+} and Sm^{3+} have intense long-lived and line-like emission in the visible region that enables them to be promising applications from display devices to biological assays[11]. Unfortunately, the low extinction coefficients of free lanthanide ions result in very inefficient light absorption, which makes direct excitation impossible. However, the luminescence properties of lanthanides can be improved by means of organic ligands containing suitable chromophores coordinated to the lanthanides[12]. This luminescent ligand acts as antenna by efficiently absorbing light in the UV region and transforming the absorbed energy to the emitted level of the lanthanide ion. Moreover, the ligand can protect the lanthanide from vibrational coupling that may quench the luminescence[13]. In addition to the spectroscopic and magnetic properties, the biological activities of the lanthanide complexes such as antitumor, antimicrobial, antivirus, anticoagulant action, from arteriosclerosis, luminescent bio probes, etc., have been investigated in the last few years[14,15]. This work focuses on the use of H_2L ligand which have selective ability to coordinate to lanthanide ions thus protect them from deactivation caused by interaction with solvent molecules and enhance their luminescence by providing proper conjugate absorption groups suitable for energy transfer. Due to the importance of the Schiff base ligands in the various fields of separation and biomedical science[16-19], authors have investigated La(III), Pr(III), Nd (III), Sm (III), Eu(III) complexes with (N,N-bis (2-hydroxy-1-naphthylidene) diethylenetriamine) ligand (H_2L). The coordination behavior has been investigated by correlating with the luminescence properties of these complexes in solutions at room temperature. In addition, the binding properties of these complexes with CT-DNA have been investigated using absorption spectrophotometry.

2. EXPERIMENTAL

2.1. Materials and methods

Lanthanide salts, {$[Ln(NO_3)_3 6H_2O]$Ln=La,Pr, Nd, Sm Eu}, 2-Hydroxy-1-napthaladehyde and diethylenetriamine were purchased from Sigma Aldrich. All other solvents and reagents used were of analytical grade. The metal content of the complexes was determined by titration with EDTA[20] using xylenol oranges as an indicator. Elemental analysis was carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Molar conductivity was measured in dimethyl formamide(DMF) solution, concentration of 10^{-4} M, at 25 °C using ELICO conductivity meter equipped with CM162 conductivity cell. Infrared spectra were recorded on a Perkin-Elmer FT-IR model 100 spectrophotometer in the region of 4000-400 cm^{-1} using KBr pellets. The spectra were recorded at room temperature with 2 cm^{-1} resolution. UV-visible spectra were recorded in DMF solution, concentration of 10^{-5} M, at 25 °C using a UV Lamda 50 Perkin-Elmer UV-visible spectrophotometer. Fluorescence spectra (scanned from 200 to 900 nm, with a spectral resolution of 0.2 nm, slit widths ~2.5nm) were recorded instrument model Perkin Elmer precisely LS-55 fluorescence spectrophotometer with 1 cm quartz cell at room temperature. The light source and detectors were 450W xenon lamp and R955 photomultiplier tube, respectively. The thermal analysis was performed on a Perkin-Elmer Spectrum 2, Pyris STA 6000 thermo balance analyzer operating at a heating rate of 10°C/min in the range of ambient temperature up to 900°C under N_2. X-ray diffractometer (XRD) Philips: PW1830. Electron ionization-mass spectrometer, model: AUTOSPEC-M, Micromass, UK.

2.2. DNA binding experiments

A solution of CT-DNA in 0.5mM NaCl/5mM Tris-HCl (pH 7.0) gave a ratio of UV absorbance at 260 and 280 nm (A_{260}/A_{280}) of 1.8-1.9, indicating that the DNA was sufficiently free of proteins[21]. A concentrated stock solution of DNA was prepared in 5 mM Tris-HCl/50mM NaCl in water at pH 7and the concentration of CT-DNA was determined per nucleotide by taking the absorption coefficient (6,600 $dm^3\ mol^{-1}\ cm^{-1}$) at 260 nm[22]. Stock solutions were stored at 4 °C and were used after no more than 4 days. Doubly distilled water was used to prepare buffer solutions. Solutions were prepared by mixing the complex and CT-DNA in DMF medium. After equilibrium was reached (ca.5 min) the spectra were recorded against an analogous blank solution containing the same concentration of DNA. The data were then fitted into Eq.1 to obtain the intrinsic binding constant (K_b)[23].

$$[DNA]/(\varepsilon_A - \varepsilon_B) = [DNA] / (\varepsilon_B - \varepsilon_F) + 1/K\ (\varepsilon_B - \varepsilon_F) \ldots\ (1)$$

where ε_A, ε_B and ε_F correspond to the apparent, bound and free metal complex extinction coefficients, respectively. A plot of $[DNA] / (\varepsilon_A - \varepsilon_F)$ versus [DNA] gave a slope of $1/(\varepsilon_B - \varepsilon_F)$ and a Y-intercept equal to $1/K_b\ (\varepsilon_B - \varepsilon_F)$; K_b is the ratio to the Y-intercept.

2.3. Synthesis of Schiff base ligand (H_2L)

The Schiff base ligand H_2L was prepared[24] by mixing 2-hydroxy-1-napthaladehyde (1.72g; 10 m mol) in 20 ml of hot methanol with diethylenetriamine (0.54ml; 5 mmol) in 10 ml of methanol. The resulting reaction mixture was taken in a 100 ml round bottom flask and heated under reflux on water bath for 1 h. On cooling the reaction mixture, a crude yellow product was obtained. Then, the product was collected by filtration, washed with cold ethanol and dried. Finally, the product was recrystallized from hot ethanol. Yield: 60 % ; m.p. 253 °C.

2.4. Synthesis of Ln(III) complexes

A 0.350 m mole (0.143g) of $H_2L$was dissolved in 20 ml of chloroform[25]. To this solution, a solution of $Ln(NO_3)_3.6H_2O$ [Ln=La,Pr,Nd,Sm, Eu] (0.350

e-mail:drksvkrishna@yahoo.com

m mole) in 10 ml acetonitrile was added drop wise. The reaction mixture was stirred for 4h, and the yellow precipitate formed was filtered, washed with CCl_4 and dried in *vacuo*. The complex was recrystallized by slow diffusion of diethyl ether into a methanol solution of the complex. Yield: 70%.

3. RESULTS AND DISCUSSION

In the present investigations, Ln(III) complexes of Schiff base ligand(H_2L) were synthesized and characterized based on physico-chemical and spectral techniques. The ligand (H_2L) was synthesized by a conventional one-step condensation of 2-hydroxy-1-napthaladehyde and diethylenetriamine. All the complexes were synthesized by reacting $[Ln(NO_3)_3.XH_2O]$ (where Ln = La, Pr, Nd, Sm, Eu) with the ligand H_2L yielded a series of complexes correspond to the formula of $[LnH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$. All complexes are stable at room temperature, non-hygroscopic, insoluble in water and diethyl ether, but slightly soluble in methanol, ethanol, ethyl acetate, chloroform, benzene and readily soluble in dimethylforma amide and DMSO. The elemental analysis, compound formula, weight, yield%, and molar conductivity data of the complexes are given in Table 1.

3.1.Molar conductance

Molar conductivity values for all complexes in DMF solution at 25 ˚C, tabulated in Table 1, are in the range of 76-117 Ω^{-1} cm^2 mol^{-1} as reported for 1:1 electrolytes[26]. The values suggest ionic nature of the complexes.

3.2.Infrared spectroscopy

Important IR spectral bands Fig.1 data of the samarium complex are present in Table 2. The comparison of the IR spectra of the free ligand and $[LnH_2L(NO_3)_2 2H_2O]NO_3.2H_2O$ complexes.The ligand (N,N-bis (2-hydroxy-1-naphthylidene) diethylenetriamine) significant broad bands were obtained at 1633 cm^{-1} corresponding to imine ν(>C=N−) stretching frequency. Condensation of all the primary amine groups has been confirmed from the absence of the (=N-H) stretching bands in the region 3150-3450 cm^{-1} [27]. The spectra of all the complexes contain strong peaks characteristic of ν(>C=N−) bands, indicating the complexation of the lanthanide ions. Indeed, upon coordination to the metal center, the imine

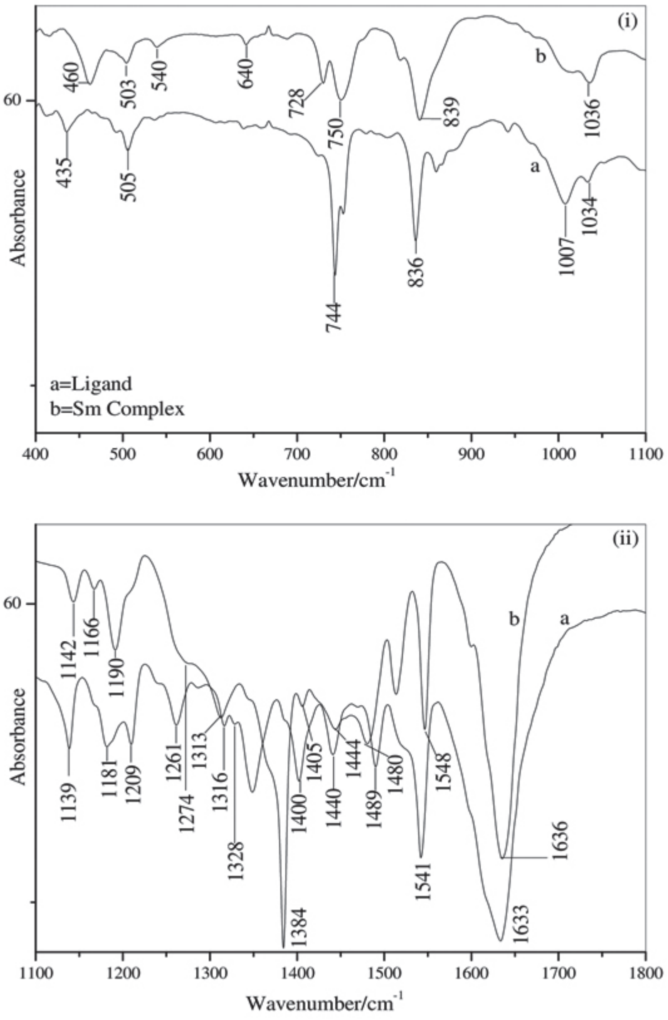

Fig1. Infrared spectra in the 1800-400 cm^{-1} region for the Sm complex (i and ii).

Table 1. Elemental analytical data and molar conductance values for the Ln complexes.

Compound	F.wt	C(%) found(Calc.)	H(%) found(Calc.)	N(%) found(Calc.)	Yield(%)	Λ_m (Ω^{-1} cm^2 mol^{-1})
Ligand H_2L	412.0	75.92(75.91)	6.12(6.08)	10.24(10.21)	60	-
$[LaH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	807.9	35.99(38.61)	2.88(4.08)	9.97(10.39)	50	76.68
$[PrH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	809.9	35.96(38.52)	2.87(4.07)	9.96(10.37)	62	99.54
$[NdH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	812.5	35.81(38.37)	2.85(4.05)	9.95(10.33)	65	116.52
$[SmH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	819.3	35.52(38.08)	2.82(4.02)	9.98(10.25)	60	88.21
$[EuH_2L(NO_3)_2\ 2H_2O]\ NO_3.2H_2O$	820.5	35.46(38.02)	2.82(4.02)	9.99(10.23)	60	87.64

(Calc.): Calculated

Table 2. Important IR bands (cm^{-1}) and UV-visible absorption bands for the Ln complexes.

Complex	ν (O-H)	ν (C=N)	ν (Ar-O)	ν (NO_3^-)						ν (Ln-O)	ν (Ln-N)	λ_{max}(nm)
				ν_1	ν_2	ν_3	ν_4	ν_{1-4}	ν_0			
Ligand H_2L	3280	1633	1261	-	-	-	-	-	-	-	-	305^a,402^b
$[LaH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	3376	1636	1272	1480	1035	839	1312	169	1384	641	460	307^a,421^b,362^c
$[PrH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	3378	1638	1274	1480	1036	840	1313	167	1384	642	462	307^a,421^b,362^c
$[NdH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	3376	1636	1272	1480	1036	839	1313	167	1384	642	463	307^a,421^b,362^c
$[SmH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	3378	1636	1274	1480	1036	839	1313	167	1384	640	460	307^a,421^b,362^c
$[EuH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	3378	1635	1273	1480	1037	839	1313	167	1384	643	461	307^a,407^b,381^c

a = $\pi \rightarrow \pi^*$; b = $n \rightarrow \pi^*$; c = LMCT

ν(>C=N−) stretching frequency in the IR spectra dropped from 1633 cm^{-1} in the free ligand, to 1636, 1638, 1636, 1636 and 1635 cm^{-1} in the related La(III), Pr(III), Nd(III), Sm(III) and Eu(III) complexes. In the H_2L ligand, the phenolic ν(O-H) vibration band appeared at 3280 cm^{-1} while the coordinated vibration mode is shifted towards higher frequency region 3376-3378 cm^{-1} that was due to the intramolecular hydrogen bonds of free ligand. The staying of ν(O-H) in the complexes indicates that the phenolic O-H oxygen is coordinated to the metal ion without deprotonation. The bands near 1600 cm^{-1} and 1260 cm^{-1} are associated with the ν(C=N) and ν(C-O),respectively. The stretching frequencies change in profile in the complexes as compared to those observed for the isolated ligand. All of the complexes showed very similar infrared spectra above 400 cm^{-1} and, therefore, far-infrared spectra were recorded (400 cm^{-1}) in an attempt to assign ν(Ln-O) and ν(Ln-N) vibrational modes. ν(C=N) and ν(C-O),respectively. There is a paucity of such assignments in the literature[28,29] though it appears that ν(Ln-O) and ν(Ln-N) might be expected in the 640-643,460-463 cm^{-1} region. This shift and the appearance of the band at 460-463 cm^{-1} which is assigned to ν(Ln–N) confirm that the nitrogen of the azomethine group is coordinated to the lanthanide ions[28].

The absorption bands of the coordinated nitrates (C_{2v}) were observed at about 1480 cm^{-1}(ν_1), 1035-1037 cm^{-1}(ν_2), 839-840 cm^{-1}(ν_3), and 1312-1313 cm^{-1}(ν_4). In addition, the separation of the two highest frequency bands[$\Delta\nu = \nu_1$-ν_4] is approximately 169 and 167 cm^{-1}, and accordingly the coordinated NO_3^- ion in the complexes is a bidentate ligand[29]. The vibrational band is present at 1384 cm^{-1}(ν_0) in IR spectra of complexes indicate the free of ionic nitrate (D_{3h} symmetry), which is in agreement with the results of the conductivity experiments. Similar changes for all Ln complexation with the ligand[30-33].

3.3. UV-Visible spectroscopy of complexes

The UV- visible absorption spectral data of the maximum absorption wavelength (l_{max}) and the corresponding band assignment for the ligand and its Ln(III) complexes(10^{-5} M in DMF) are listed in Table 2 . The electronic spectra of ligand and its lanthanide complexes are shown in (Fig.2). The ligand (H_2L) shows three absorption bands with maxima at 305, 402 and 421 nm. The bands at 402 and 421 nm, are assigned to n–π* transitions of conjugation between the lone pair of electrons of (>C=N–) group a conjugated π bond of the aromatic ring [34-39]. The third band at 305 arises from π-π* transition within the aromatic ring. The new absorbance band observed at 362 nm complexes was attributed to the electron transfer from lanthanide metal ion and the coordinated ligand i.e M→L charge transfer band. This change is essentially variant for each of the lanthanide complexes (La(III), Pr(III), Nd(III), Sm(III) and Eu(III) and is attributed to metal coordination by the ligand. The higher energy band in the free ligand is observed as a single band upon complexation without much shift in frequency. Based on analytical and spectral data a general structure (Fig.3) is tentatively assigned to the lanthanide complexes.

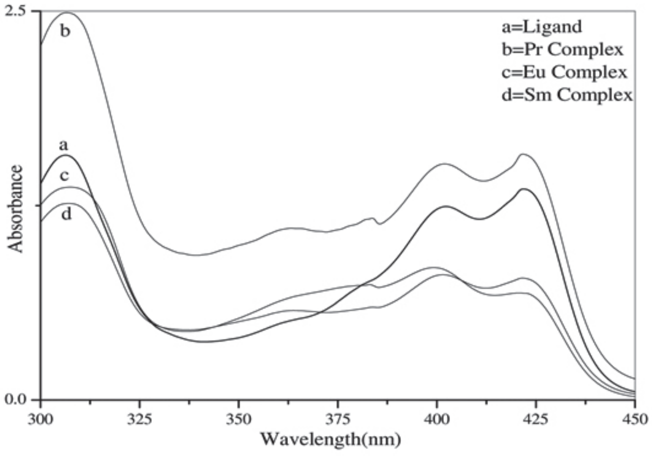

Fig 2. UV-Visible absorption spectra for the Ln complexes

3.4.Thermogravimetric analysis

Thermogravimetric (TGA) and differential thermogravimetric (DTA) analysis were carried out for the ligand, H_2L, and its corresponding Ln(III) complexes within the temperature range from ambient temperature up to 900 °C under N_2 flow. The correlation between the different decomposition steps of Ln(III) complexes with the corresponding weight losses are discussed in terms of the proposed formula of the Ln(III) complexes. TGA results showed that the ligand H_2L is thermally stable up to 240 °C and its decomposition starts at 250°C and finishes at 499°C with one decomposition step (Supplementary Fig.S1). The TGA curve of Sm(III) complex shows (Fig.4), that the Sm(III) complex undergoes multi-stage changes. The first stage, mass loss percentage was 4.5%

is consistent with theoretical value (4.3%). The decomposition temperatures of these hydrates ranging between 113 to 210°C suggests that the presence of a water molecule in the Sm(III) complex bonded in the inner coordination sphere. The second stage of decomposition in the range 210 to 277°C due to loss of one nitrate ion with a weight loss of 8.2% has theoretical value (8.0%). Third stage occurs decomposition 277 to 371°C could be attributed to the loss of another two inner nitrate ions with a weight loss of 16.5% is consist with theoretical value(16.2%). The fourth step processes corresponds to the loss of the ligand molecule and formation of stable Ln_2O_3 oxide residue which occurred between 371 to 900 °C.

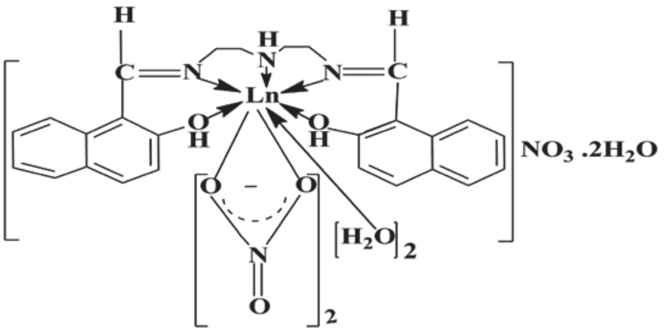

Fig 3. Proposed structure for the rare earth complexes (Ln = La, Pr, Nd, Sm and Eu)

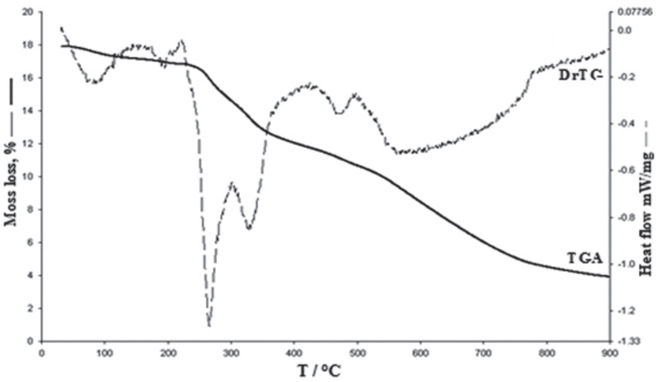

Fig.4. Differential thermal gravimetric analysis cures for the Sm complex

3.5. X-ray powder diffraction studies

X-ray diffraction studies of the powder sample were carried out as it could not be possible to grow suitable crystals for complete X-ray analysis. The observed interplanar spacing values (‘*d*’ in A˚), have been measured from the diffractogram of the $[SmH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$ complex with respect to major peaks having relative intensity at wavelength = 1.54178 and the Millar *i*ndices, *h, k, l* have been assigned to each *d* value and 2*θ* angles are reported in Fig.5 (Supplementary Table.S1). The system belongs to ‘*Orthorhombic*’ form. The direct unit cell dimensions determined are: *a* = 7.9928 A˚; *b* = 9.0910A˚; *c* = 10.8580A˚; v = 788.9775(A˚)^3; α = β = γ = 90º. Based on the experimental evidences, the average crystallite or grain size varies from 22 to 34 nm. The system exhibits nano crystallite phase.

3.6. Mass spectral studies

In the present investigation, the mass spectrum of H_2L showed the formation of a molecular ion peak at m/z: 412 (sodium ion base peak m/z: 434) corresponding to the total molecular weight of the ligand(SupplementaryFig. S2). The molecular ion peak is not detected in the recorded mass spectra of the discussed Ln(III) complexes. The obtained mass spectra indicates relatively neodymium complex and exhibited a large number of peaks possibly due to extensive fragmentation.

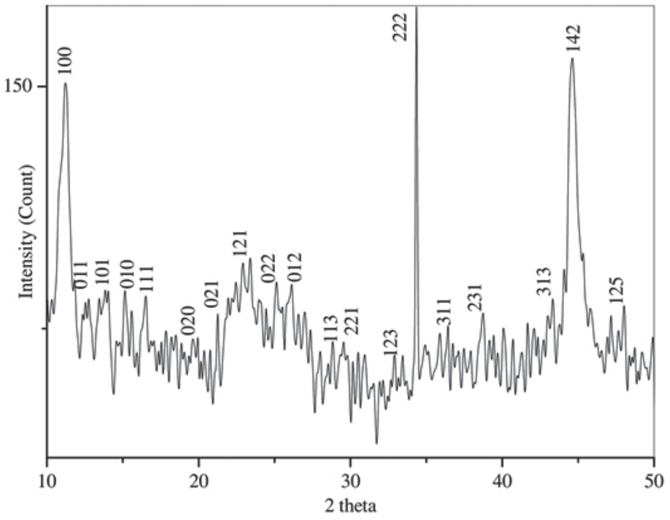

Fig.5. Powder X-ray diffraction spectrum for the Sm complex.

3.7. Luminescence spectroscopy of complexes

The fluorescence spectra (Fig.6) of the ligand and its Ln(III) complexes (1.0× 10^{-5} M in DMF solution) were recorded at the room temperature. The details of the emission characteristic of the ligand and its Ln(III) complexes are listed in Table 3. The emission spectrum Fig.6 of the free ligand H_2L exhibits broad fluorescence band centered at 363 nm attributed to π-π* transitions. Inspection of emission spectra (λ_{exc}= 307nm) shown in Fig.6 together with the data listed in Table 3, indicate that 363 nm attributed to π-π* transitions[35-41]. Inspection of Eu,Sm,Nd and Pr complexes exhibit the characteristic emission spectra of the Ln(III) ions respectively. This indicates that the ligand H_2L is a good chelating organic chromophore and can be used to absorb and transfer energy to the Ln(III) ions.

Under the excitation of 307 nm the emission spectrum of the Eu(III) complex **e** displays luminescence characteristic of Eu(III) emission peak in the region 610-635 nm corresponding to$^5D_0 \rightarrow {}^7F_2$ (619 nm) transition. Samarium (III) complex **d** also emission peak in the range 610-630 nm, luminescence characteristic of Sm (III) transition these transitions are assigned to $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (617nm) transitions[35-42].

The intense broadband that corresponding to the excitation of the organic chromophore ($S_0 \rightarrow S_1$) transition. The emission spectrum of praseodymium **b** and neodymium **c** complexes displays two luminescence bands π→π* at 364, 619 and 622 nm corresponding to the $^3P_0 \rightarrow {}^3F_2$ for Pr(III) and $^4I_{9/2} \rightarrow {}^4G_{5/2}$ for Nd(III) transition respectively. The intensity sequence of the peaks is $I_{4I9/2 \rightarrow 4G5/2}$ $_{>}I_{3P0 \rightarrow 3F2}$ transition, respectively[42].

H_2L is a good organic ligand that can absorb and transfer energy intramolecular from the triplet state of the ligand H_2L to excited state of the Ln(III) ions. At the same time the energy gap between the triplet state of the ligand and the emitting level of the Ln(III) ions only favors the energy transfer process for Eu(III), Sm(III), Nd(III) and Pr(III) ions[43-45]. Although different paths have been suggested for the energy transfer from T_L to the resonance state of Ln(III) ions in lanthanide complexes. The favorite mechanism involves strong absorption of UV energy that excites the ligand to the exited singlet state (S_L), followed by an energy migration via non-radiative intersystem crossing to the T_L. The energy is then transferred intermolecularly from the T_L to a resonance state of the Ln(III) ion, from which the luminescence in the visible region occurs. To luminescence, the T_L level must be nearly equal or lie above the resonance energy level of the Ln(III) ions. If the energy gap between the T_L and the lowest resonance energy level of the Ln(III) ion is low then the back transfer from the lanthanide ion to the ligand can occur which reduces the intensity of the luminescence. Our results of the luminescence experiments were consistent with the proposed mechanism for intermolecular energy transfer[46,49].

For the case of La(III) has no 4f electron and no excited states below the T_L, which is much higher in energy than the S_L and T_L of the ligands. Therefore, the energy absorbed by the ligand cannot be transferred to either La(III) ion by an intermolecular energy transfer process, however relaxes through its own lower energy levels. Therefore the emission bands observed in the emission spectra of La(III) complex at 363 nm respectively, are due to the fluorescence of the ligand. The red shift in the fluorescence band of the ligand in Ln(III) complexes compared with the free ligand can be attributed to coordination of Ln(III) ions to the ligand. This results in increasing of the delocalization of electrons and reducing the energy gaps between the molecular orbitals of the ligand[50]. The luminescence intensities of Eu(III),Sm(III) complexes show strong luminescence than the Nd(III), Pr(III) systems, which indicates that the triplet state energy is more suitable for the luminescence of Eu(III) ion than Sm(III) ion.

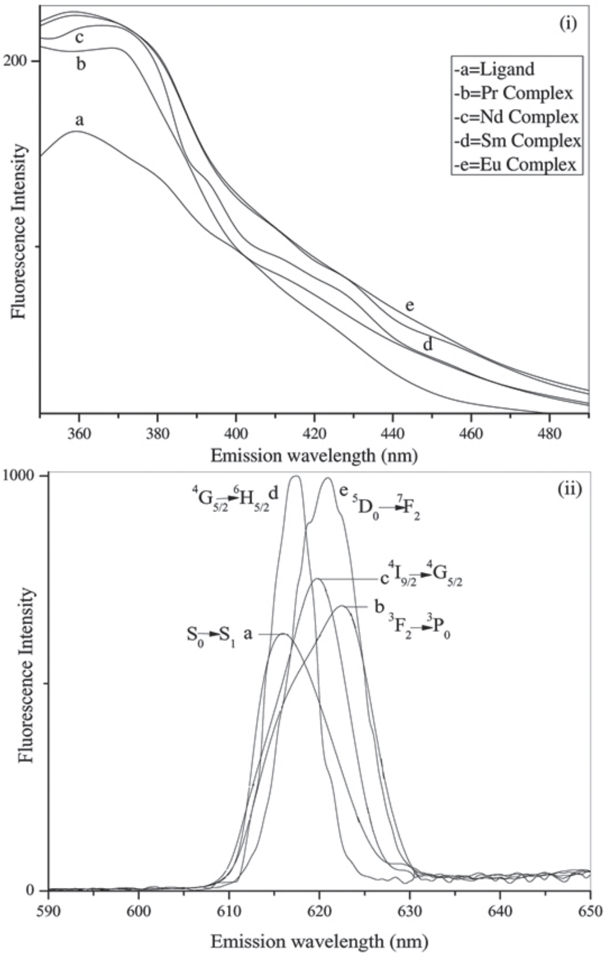

Fig.6. Fluorescence spectrum excited and emission for the Ln complexes (i and ii).

Table 3. Luminescence data for the Ln complexes.

Compound	λ_{ex} (nm)	ν(cm^{-1})	λ_{em} (nm)	ν(cm^{-1})	Assignment
Ligand H_2L	305	32,786	363(broad) 615(broad)	27,548 16,260	π→π* $S_0\rightarrow S_1$
$[LaH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	307	32,573	363(broad)	27,548	π→π*
$[PrH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	307	32,573	364(broad) 622(broad)	27,472 16,077	π→π* $^3F_2\rightarrow{}^3P_0$
$[NdH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	307	32,573	364(broad) 619(broad)	27,472 16,155	π→π* $^4I_{9/2}\rightarrow{}^4G_{5/2}$
$[SmH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	307	32,573	363(broad) 617(sharp)	27,548 16,207	π→π* $^4G_{5/2}\rightarrow{}^6H_{5/2}$
$[EuH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	307	32,573	364(broad) 619(sharp)	27,472 16,155	π→π* $^5D_0\rightarrow{}^7F_2$

[a]Board; [b]Sharp

Table 4. Electronic absorption data upon addition of CT-DNA to the Ln complexes.

Complex	Composition	λ(max)		Δλ (nm)	H (%)[b]	K_b (M^{-1})
	(Metal : Ligand)[a]	Free	Bound			
$[LaH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	1:1	398	395	3	+ 18.02	8.2×10^5
$[PrH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	1:1	398	396	2	+ 09.99	1.3×10^5
$[NdH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	1:1	398	396	2	+ 19.20	7.4×10^5
$[SmH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	1:1	398	394	4	+ 15.78	2.7×10^5
$[EuH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$	1:1	398	395	3	+ 17.99	5.3×10^5

[a]Organic ligand H_2L; [b]$H\% = A_{free} - A_{bound} / A_{free} \times 100$

3.8. DNA binding studies

The interaction of lanthanide complexes with CT-DNA was investigated using absorption spectroscopy. The electronic spectra of $[NdH_2L(NO_3)_2 2H_2O]NO_3.2H_2O$ in the absence and presence of CT-DNA binding plot are given in (Supplementary Fig.S3). In the presences of increasing amount of CT-DNA, the $[NdH_2L(NO_3)_2 2H_2O]NO_3.2H_2O$ complex showed an decrease in intensity [hypo chromicity (19.20±0.5%) and hypsochromic shifts [maximum (2±1) nm] for their blue shift absorption maxima. The value of K_b evaluated for the complex using Eq.1 is found to be 7.4×10^5 M^{-1}. On addition of CT-DNA to the Ln(III) complexes, there is decreasing in molar absorptivity as well as a significant shift in λ_{max}. The decrease in absorption intensity and significant shift in wavelength is attributed to hypo chromism (red shift) and hypso chromism (blue shift), which suggests that the complex is bound to CT-DNA strongly. During these titrations, the change in the absorption values with increasing amount of CT-DNA was used to evaluate the intrinsic binding constants (K_b) for the complexes. The values of K_b evaluated for the complexes using equation 1. Data are presented in (Table 4). This may be attributed to the presence of a phenyl ring in the ligand that facilitates. Therefore, the complexes may be regarded as efficient intercalators of DNA [51-53].

4. CONCLUSIONS

A pentdentate Schiff base ligand H_2L and its lanthanide complexes $[LnH_2L(NO_3)_2\ 2H_2O]NO_3.2H_2O$ (where, Ln = La, Pr, Nd, Sm and Eu were synthesized and characterized. Under UV light excitation, the Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} complex exhibits characteristic luminescence of trivalent metal ions, which indicates that the ligand is a good organic chelator to absorb and transfer energy to metal ions. The complex constructed by a N_3O_2 chromophore, constituted by two imine nitrogen atoms and one secondary nitrogen atom from the amine part and two phenolic hydroxyl groups. Two nitrate ion acts as bindentate ligands. In addition, the participation of two water molecules in the coordinate Ln(III) complexes [with a coordination number of 11]. The energy gap between the lowest triplet state level of the Schiff base and lowest exited state level of Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} favor to the energy transfer process for Ln(III) complexes. The intrinsic DNA binding constants (K_b) of these complexes (10^5) are quite high. Therefore, the complexes may be regarded as efficient intercalators of DNA.

ACKNOWLEDGEMENTS

The authors Dr.S.V.B are thankful to UGC, New Delhi for award of Post-Doctoral Research Fellowship F.31-11(SC)/2009(SA-III). Authors also thank SSSIHL Deemed University, Puttaparthy for providing fluorescence spectral data.

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