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

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ABSTRACT

Pentadentate Schiff base ligand (N,N-bis(2-hydroxy-1-naphthylidene) diethylentriamine) (H₂L) that exhibits a N₂O₂ 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 naphtholic 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. Eu³⁺ and Sm³⁺ 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. 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, light-emitting diodes LED's, plastic lasers and bio-inspired luminescence probes. Among Ln(III) ions, Eu³⁺ and Sm³⁺ 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. 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. This luminescent ligand acts as an 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. 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. This work focuses on the use of H₂L 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, authors have investigated La(III), Pr(III), Nd (III), Sm (III), Eu(III) complexes with (N,N-bis (2-hydroxy-1-naphthylidene) diethylentriamine) ligand (H₂L). 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(ONO₃)₃].6H₂O) [Ln=La,Pr,Nd,Sm,Eu], 2-Hydroxy-1-naphthaldehyde and diethylentriamine 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 using xylene orange 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 10⁻⁴ M, at 25°C using a UV Lambda 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 N₂. 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 (A₂₆₀/A₂₈₀) of 1.8-1.9, indicating that the DNA was sufficiently free of proteins. A concentrated stock solution of DNA was prepared in 5 mM Tris-HCl/50mM NaCl in water at pH 7 and the concentration of CT-DNA was determined per nucleotide by taking the absorption coefficient (6,600 dm⁻¹ mol⁻¹ cm⁻¹) at 260 nm². 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 (Kₒ)²⁺.

\[ [\text{DNA}] (eₐ₋eₕ) = [\text{DNA}] (eₐ₋eₜ) + 1/K (eₐ₋eₚ) \ldots (1) \]

where eₚ, eₜ, and eₕ correspond to the apparent, bound and free metal complex extinction coefficients, respectively. A plot of [DNA] / (eₜ₋eₚ) versus [DNA] gave a slope of 1/(eₚ₋eₜ) and a Y-intercept equal to 1/Kₒ (eₚ₋eₜ); Kₒ is the ratio to the Y-intercept.

2.3. Synthesis of Schiff base ligand (H₂L)

The Schiff base ligand H₂L was prepared²⁰ by mixing 2-hydroxy-1-naphthaldehyde (1.72g; 10 m mol) in 20 ml of hot methanol with diethylentriamine (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 H₂L was dissolved in 20 ml of chloroform²⁰. To this solution, a solution of Ln(ONO₃)₃.6H₂O [Ln=La,Pr,Nd,Sm,Eu] (0.350

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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 CCl₄ 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(H₂L) were synthesized and characterized based on physico-chemical and spectral techniques. The ligand (H₂L) was synthesized by a conventional one-step condensation of 2-hydroxy-1-napthaldehyde and diethylenetriamine. All the complexes were synthesized by reacting [Ln(NO₃ )₃ .XH₂O] (where Ln = La, Pr, Nd, Sm, Eu) with the ligand H₂L yielded a series of complexes correspond to the formula of [LnH₂L(NO₃ )₂₂H₂O]NO₃ .2H₂O. 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 cm² mol⁻¹ as reported for 1:1 electrolytes²⁶. 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 [LnH₂L(NO₃ )₂₂H₂O]NO₃ .2H₂O complexes. The ligand (N,N-bis (2-hydroxy-1-naphthaldehyde) 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

![Infrared spectra in the 1800-400 cm⁻¹ region for the Sm complex (i and ii).](image-url)
The azomethine group is coordinated to the lanthanide ions. In the ligand, the wavelength and the corresponding band assignment for the ligand vibration mode is shifted towards higher frequency region that spectra of ligand and its lanthanide complexes are shown in (Fig.2). The ligand for the isolated ligand. All of the complexes showed very similar infrared frequencies change in profile in the complexes as compared to those observed in the literature.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>F.wt</th>
<th>C(%) found(Calc.)</th>
<th>H(%) found(Calc.)</th>
<th>N(%) found(Calc.)</th>
<th>Yield(%)</th>
<th>( \lambda_{\infty} (\Omega^{-1} \text{cm}^2 \text{mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand H₂L</td>
<td>412.0</td>
<td>75.92(75.91)</td>
<td>6.12(6.08)</td>
<td>10.24(10.21)</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>[La₃L(NO₃)₂]₂H₂O</td>
<td>807.9</td>
<td>35.99(38.61)</td>
<td>2.88(4.08)</td>
<td>9.97(10.39)</td>
<td>50</td>
<td>76.68</td>
</tr>
<tr>
<td>[Pr₃L(NO₃)₂]₂H₂O</td>
<td>809.9</td>
<td>35.96(38.52)</td>
<td>2.87(4.07)</td>
<td>9.96(10.37)</td>
<td>62</td>
<td>99.54</td>
</tr>
<tr>
<td>[Nd₃L(NO₃)₂]₂H₂O</td>
<td>812.5</td>
<td>35.81(38.37)</td>
<td>2.85(4.05)</td>
<td>9.95(10.33)</td>
<td>65</td>
<td>116.52</td>
</tr>
<tr>
<td>[Sm₃L(NO₃)₂]₂H₂O</td>
<td>819.3</td>
<td>35.52(38.08)</td>
<td>2.82(4.02)</td>
<td>9.98(10.25)</td>
<td>60</td>
<td>88.21</td>
</tr>
<tr>
<td>[Eu₃L(NO₃)₂]₂H₂O</td>
<td>820.5</td>
<td>35.46(38.02)</td>
<td>2.82(4.02)</td>
<td>9.99(10.23)</td>
<td>60</td>
<td>87.64</td>
</tr>
</tbody>
</table>

(Calc.): Calculated

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu_{(O-H)} ) (cm⁻¹)</th>
<th>( \nu_{(C=N)} ) (cm⁻¹)</th>
<th>( \nu_{(Ar-O)} ) (cm⁻¹)</th>
<th>( \nu_{(NO_3)} ) (cm⁻¹)</th>
<th>( \nu_{(L-O)} ) (cm⁻¹)</th>
<th>( \nu_{(L-N)} ) (cm⁻¹)</th>
<th>( \lambda_{\infty}(\text{nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand H₂L</td>
<td>3280</td>
<td>1633</td>
<td>1261</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[La₃L(NO₃)₂]₂H₂O</td>
<td>3376</td>
<td>1636</td>
<td>1272</td>
<td>1480</td>
<td>1035</td>
<td>839</td>
<td>1312</td>
</tr>
<tr>
<td>[Pr₃L(NO₃)₂]₂H₂O</td>
<td>3378</td>
<td>1638</td>
<td>1274</td>
<td>1480</td>
<td>1036</td>
<td>840</td>
<td>1313</td>
</tr>
<tr>
<td>[Nd₃L(NO₃)₂]₂H₂O</td>
<td>3376</td>
<td>1637</td>
<td>1272</td>
<td>1480</td>
<td>1036</td>
<td>839</td>
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<td>1273</td>
<td>1480</td>
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<td>839</td>
<td>1313</td>
</tr>
</tbody>
</table>

\( a = n→n^*; b = n→\pi^* ; c = LMCT \)

3.3. UV-Visible spectroscopy of complexes

The UV-visible absorption spectra of the free ligand (H₂L) and its Ln(III) complexes (10⁻⁵ M in DMF) are listed in Table 2. The electronic spectra of the free ligand and its lanthanide complexes are shown in (Fig.2). The ligand (H₂L) 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=C=N) group a conjugated n bond of the aromatic ring. The third band at 305 arises from n→π* transition within the aromatic ring. The absorption bands of the coordinated nitrates (ν(NO₃)) were observed at 1348 cm⁻¹ (ν₁), 1305-1307 cm⁻¹ (ν₂), 839-840 cm⁻¹ (ν₃), and 1312-1313 cm⁻¹ (ν₄). In addition, the separation of the two highest frequency bands (Δν = ν₂ - ν₃) is approximately 169 and 167 cm⁻¹, and accordingly the coordinated NO₃ ion in the complexes is a bidentate ligand²⁶. The vibrational band is present at 1384 cm⁻¹ (ν₃) in IR spectra of complexes indicate the free of ionic nitrate (D₅ₐ symmetry), which is in agreement with the results of the conductivity experiments. Similar changes for all Ln complexation with the ligands²⁶.

3.4. Thermogravimetric analysis

Thermogravimetric (TGA) and differential thermogravimetric (DTA) analysis were carried out for the ligand, H₂L, and its corresponding Ln(III) complexes within the temperature range from ambient temperature up to 900 °C under N₂ 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 H₂L 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$_2$O$_3$ oxide residue which occurred between 371 to 900°C.

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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\(^5\). 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.

**Table 3.** Luminescence data for the Ln complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{ex}) (nm)</th>
<th>(\nu) (cm(^{-1}))</th>
<th>(\lambda_{em}) (nm)</th>
<th>(\nu) (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand (H_2L)</td>
<td>305</td>
<td>32,786</td>
<td>363 (broad)</td>
<td>615 (broad)</td>
<td>(\pi \rightarrow \pi^*)</td>
</tr>
<tr>
<td>([LaH_2L(NO_3)_22H_2O]NO_3.2H_2O)</td>
<td>307</td>
<td>32,573</td>
<td>363 (broad)</td>
<td>27,548</td>
<td>(\pi \rightarrow \pi^*)</td>
</tr>
<tr>
<td>([PrH_2L(NO_3)_22H_2O]NO_3.2H_2O)</td>
<td>307</td>
<td>32,573</td>
<td>364 (broad)</td>
<td>622 (broad)</td>
<td>(\pi \rightarrow \pi^*)</td>
</tr>
<tr>
<td>([NdH_2L(NO_3)_22H_2O]NO_3.2H_2O)</td>
<td>307</td>
<td>32,573</td>
<td>364 (broad)</td>
<td>619 (broad)</td>
<td>(\pi \rightarrow \pi^*)</td>
</tr>
<tr>
<td>([SmH_2L(NO_3)_22H_2O]NO_3.2H_2O)</td>
<td>307</td>
<td>32,573</td>
<td>363 (broad)</td>
<td>617 (sharp)</td>
<td>(\pi \rightarrow \pi^*)</td>
</tr>
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<td>307</td>
<td>32,573</td>
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<td>619 (sharp)</td>
<td>(\pi \rightarrow \pi^*)</td>
</tr>
</tbody>
</table>

*Board; \(^{a}\)Sharp
Table 4. Electronic absorption data upon addition of CT-DNA to the Ln complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Composition</th>
<th>λ(max)</th>
<th>Δλ (nm)</th>
<th>H (%)</th>
<th>$K_b$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{LaH}_2\text{L}(\text{NO}_3)_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$</td>
<td>1:1</td>
<td>398</td>
<td>395</td>
<td>3</td>
<td>+18.02</td>
</tr>
<tr>
<td>$[\text{PrH}_2\text{L}(\text{NO}_3)_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$</td>
<td>1:1</td>
<td>398</td>
<td>396</td>
<td>2</td>
<td>+09.99</td>
</tr>
<tr>
<td>$[\text{NdH}_2\text{L}(\text{NO}_3)_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$</td>
<td>1:1</td>
<td>398</td>
<td>396</td>
<td>2</td>
<td>+19.20</td>
</tr>
<tr>
<td>$[\text{SmH}_2\text{L}(\text{NO}_3)_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$</td>
<td>1:1</td>
<td>398</td>
<td>394</td>
<td>4</td>
<td>+15.78</td>
</tr>
<tr>
<td>$[\text{EuH}_2\text{L}(\text{NO}_3)_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$</td>
<td>1:1</td>
<td>398</td>
<td>395</td>
<td>3</td>
<td>+17.99</td>
</tr>
</tbody>
</table>

Organic ligand H$_2$L; $^{1}$H% = $A_{\text{max}} - A_{\text{neat}}/A_{\text{neat}} \times 100$

3.8. DNA binding studies

The interaction of lanthanide complexes with CT-DNA was investigated using absorption spectroscopy. The electronic spectra of [NdH$_2$L(NO$_3$)$_2$H$_2$O] NO$_3$·H$_2$O in the absence and presence of CT-DNA binding plot are given in (Supplementary Fig. S3). In the presence of increasing amount of CT-DNA, the [NdH$_2$L(NO$_3$)$_2$H$_2$O] NO$_3$·H$_2$O complex showed an decrease in intensity [hypo chromicity (19.20±0.5%) and hypsochromism (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$^{-4}$ 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 $\lambda_{\text{max}}$. The decrease in absorption intensity and significant shift in wavelength is attributed to hypo chromism (red shift) and hypsochromism (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 pentadentate Schiff base ligand H$_2$L and its lanthanide complexes [LnH$_2$L(NO$_3$)$_2$H$_2$O] NO$_3$·H$_2$O (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. During 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 excited 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, Pattpara for providing fluorescence spectral data.

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