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Synthesis and characterization of lanthanide(III) complexes of 21-membered unsymmetrical pentaazamacrocyclic Schiff bases. Identical frame work: Part I

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ABSTRACT

A series of discrete mononuclear lanthanide(III) complexes of **L1** *$[Ln(\mathbf{L1})(NO_3)_2]NO_3.nH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Y; n = 1 for Ce; n = 2 for La, Sm, Gd and Y; n = 3 for Pr, Nd, Eu, and Tb) have been prepared by the condensation of Schiff bases with the precursor compounds namely, 2,6-diformyl-4-methylphenol, 1,5-diamino-3-azapentane and 4,5-dimethyl-1,2-phenylenediamine. All the mononuclear complexes have been prepared in situ by the step-wise condensation from the precursor compounds. The phenolate oxygen atom of the nucleating ligand behaves as a bridging group between the metal. The complexes have been characterized by elemental analysis, IR, UV-Visible, ESI, MALDI-TOF spectra and magnetic studies. The yield of these complexes increases from lighter lanthanides to heavier lanthanides. The fluorescence studies were carried out for europium and terbium complexes. The thermogravimetry studies were carried out for Gd complex of* **L1** *shows a two step thermal decomposition pattern at temperature ranges 300 - 450 and 510 - 620 ^{o}C. The electrochemical studies were carried out for the Ce complex of* **L1** *consists of a reduction wave and an oxidation wave. The results of elemental analysis of the complexes are in good agreement with the theoretical values. The complexes are soluble in methanol, chloroform, DMF, DMSO, and CH_3CN. Conductivity studies reveal that all the complexes are 1:1 electrolytes.*

Key words: Schiff bases, Macrocycles, Lanthanides complexes, Pentaaza macrocycles.

INTRODUCTION

The chemistry of macrocyclic Schiff base complexes have been reviewed in excellent papers [1-6]. Macrocyclic Schiff bases have been widely studied because they can selectively chelate certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of the metal center, and coordinating properties of counterions. Interest in exploring metal ion complexes with macrocyclic ligands has been continually increasing owing to the recognition of their role played by these structures in metalloproteins. Schiff base macrocycles have been great importance in macrocyclic chemistry. They were among the first artificial metal macrocyclic complexes to be synthesized. The metal complexes containing synthetic macrocyclic ligands have attracted a great deal of attention because they can be used as models for more intricate biological macrocyclic systems: metalloporphyrins (hemoglobin, myoglobin, cytochromes, chlorphylls), corrins (vitamin B_{12}) and antibiotics (valinomycin, nonactin). These discoveries have created supramolecular chemistry and its enormous diversity[7-10].Much attention towards macrocyclic lanthanide(III) complexes is made due to their immunotherapy and as contrast enhancing agents in magnetic resonance imaging (MRI) [11-13]. Lanthinade(III) metal ions promote the Schiff's base condensation of the appropriate diamines and the carbonyl precursors resulting in the formation of metal complexes by template method. Synthesis and

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characterization of new mono- and binuclear lanthanide(III) complexes have made an effective impact on bioinorganic chemistry. Coordination chemistry of inorganic complexes with ligands like polyamine, polycarboxylates was also studied [14-16]. A great deal of attention has been paid to the chemical properties of the rare-earth elements, because of their use in magnetic and optical devices as well as in luminescence probes and catalysts in organic syntheses [17]. Herein, I report the synthesis and characterization of lanthanide(III) complexes of 21-membered unsymmetrical pentaaza macrocyclic schiff bases.

EXPERIMENTAL SECTION

Materials

4,5-Dimethyl-1,2-phenylenediamine (Aldrich) was used as such for the synthesis of complexes. 2,6-Diformyl-4-methylphenolwas synthesized by the literature methods [18]. The lanthanide(III) nitrates, namely, $Pr(NO_3)_3.6H_2O$ (99.9 %), $Nd(NO_3)_3.6H_2O$ (99.9 %), $Sm(NO_3)_3.6H_2O$ (99.9 %), $Eu(NO_3)_3.6H_2O$ (99.9 %), $Tb(NO_3)_3.6H_2O$ (99.9 %), and $Dy(NO_3)_3.6H_2O$ (99.9 %) (Indian Rare Earth Ltd.), and $Pr(NO_3)_3.6H_2O$ (99.9 %), $Gd(NO_3)_3.6H_2O$ (99.9 %), $Ho(NO_3)_3.6H_2O$ (99.9 %), $Er(NO_3)_3.6H_2O$ (99.9 %), and $Y(NO_3)_3.6H_2O$ (99.9 %) (Aldrich) were used as such for the synthesis of complexes. *p*-Toluenesulfonyl chloride, *p*-cresol, tetraethylammonium perchlorate (Fluka), lithium hydroxide monohydrate, sodium dichromate dihydrate (LOBA), sodium carbonate, paraformaldehyde, formic acid, sodium hydroxide, sodium acetate, sodium sulfate anhydrous, calcium chloride anhydrous (E. Merck) and 1,5-diamino-3-azapentane were used as purchased. Formaldehyde (38 % *v/v*), glacial acetic acid, hydrochloric acid, sulfuric acid and fuming nitric acid (AR, E. Merck), were used as such. KBr (FT-IR grade) (Aldrich) were used for recording IR spectrum. Acetonitrile, *N,N*-dimethylformamide, chloroform, dichloromethane benzene, toluene (E. Merck), and methanol (SD's) were reagent grade and purified according to the literature method [19]. Diethyl ether, dimethyl sulfoxide, acetone and petroleum ether (60-80 ^oC) (E. Merck) were used as purchased. Double deionized water was obtained by distilling, distilled water over alkaline potassium permanganate.

Physical Measurements

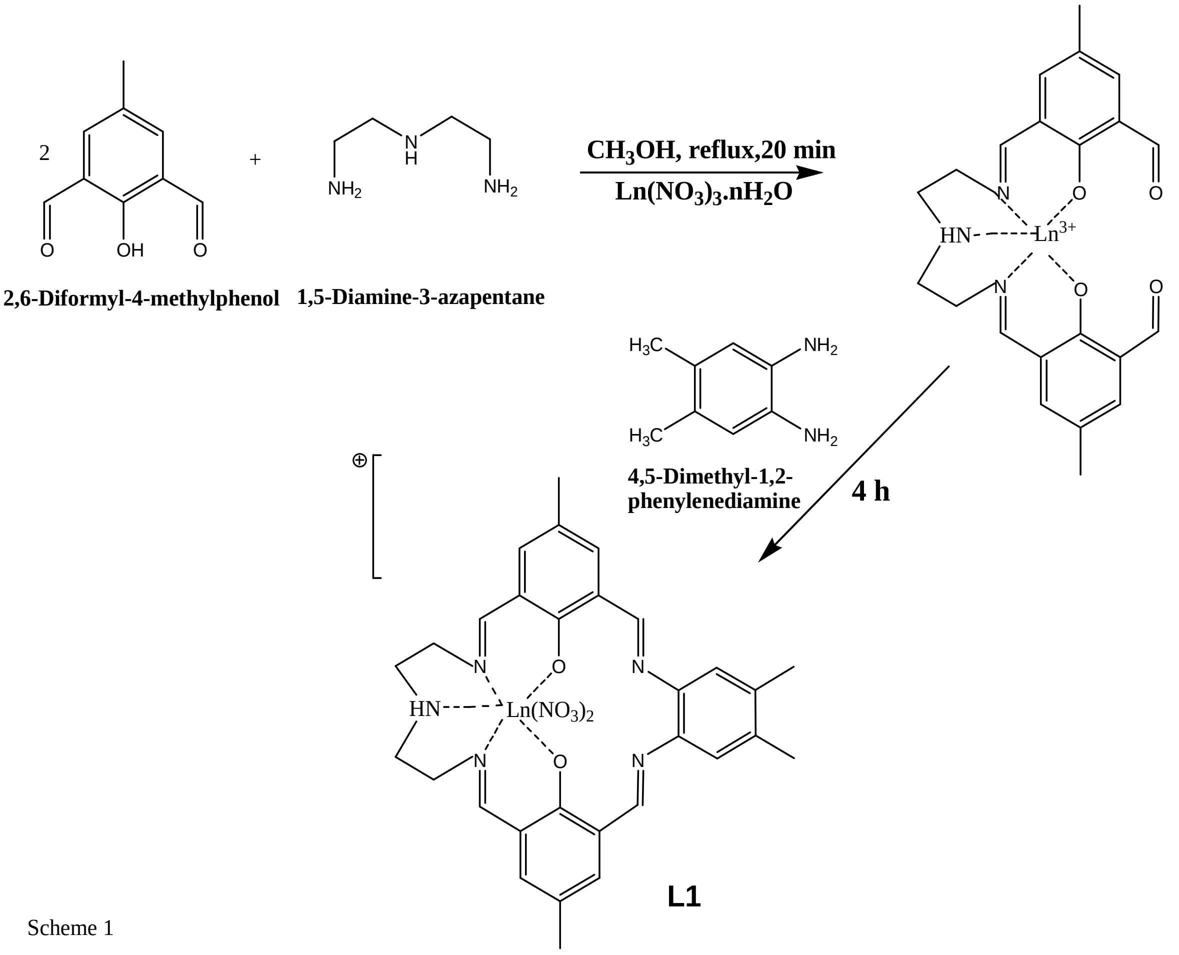
Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 3B UV-Vis spectrophotometer attached to a PC AT-286 and the spectra were recorded in the 900-190 nm range using PECSS software. The spectra of the complexes and the ligand were recorded in acetonitrile at 25 ^oC using a matched pair of Teflon stoppered quartz cells of path length 1 cm. IR spectra were recorded in a Perkin-Elmer RX-I FT-IR spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. CHN microanayses were carried out on a Perkin-Elmer 2400 CHNS/O analyzer and AD-6 Autobalance. Conductivity measurements of the complexes were carried out at 25±1 ^oC in N,N-Dimethylformamide using Elico CM-180 conductivity meter and Elico Type CC-03 conductivity cell (cell constant 1.02 cm^{-1}). Thermogravimetric studies were carried out using Stanton Redcroft STA-780 simultaneous thermal analyzer. The measurements were carried out on the platinum crucibles on sample size between 5 – 15 mg with high purity alumina as the reference. The heating rate was fixed at 10 ^oC/min.The ESI mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole spectrometer. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. The spectra were collected in 6 s scans and the print outs are averaged spectra of 6 - 8 scans.The MALDI-TOF mass spectra were recorded on a Applied Biosystems Voyager-DE PRO system 6316 Mass spectrometer. The accelerating voltage was 20000 V and the spectra were recorded at room temperature. α-Cyano-4-hydroxycinnamic acid was used as the matrix solvent and the mass spectrometer was operated in the positive ion mode.Magnetic susceptibility measurements were carried out on an EG & G PAR MODEL 155 vibrating sample magnetometer at 25 ^oC. The instrument was calibrated using pure nickel. Fluorescence study of the complexes were carried out on a Hitachi 650-40 fluorescence spectrophotometer in acetonitrile or *N,N*-dimethylformamide. Electrochemical studies of the complexes were performed on a EG & G PARC model 273A potentiostat/ galvanostat at 25 ^oC. A three-electrode configuration consisting of glassy carbon disc working electrode, a platinum wire auxiliary electrode, and Ag/AgCl reference electrode was used to record the cyclic voltammograms.

General procedure for the synthesis of lanthanide(III) complexes of L1

2,6-Diformyl-4-methylphenol (0.164 g, 1 mmol) in 20 mL of methanol was added to a stirring solution of the respective hydrated lanthanide(III) nitrate (0.5 mmol) in 20 mL of methanol followed by 1,5-diamino-3-azapentane (0. 05 g, 0.5 mmol) in 20 mL of methanol. The resulting solution was refluxed for 20 min. with stirring and 4,5-dimethyl-1,2-phenylenediamine (0.068 g, 0.5 mmol) in 20 mL of methanol was added dropwise and refluxed for 4 h. After cooling to room temperature (30 ^oC) methanol was removed and the crude compound was extracted with chloroform. Slow evaporation of the chloroform solution gave red-orange microcrystalline compounds, filtered, washed with diethyl ether, and dried in vacuum over anhydrous $CaCl_2$(Scheme 1).

[La(**L1**)$(NO_3)_2$]$NO_3.2H_2O$ *(1)*
Yield 0.185 g (43.3%). Anal. Calc. for $C_{30}H_{37}N_8O_{13}La$: C, 43.06; H, 4.32; N, 13.08, Found: C, 43.17; H, 4.83; N, 13.46%. ESI-MS (*m/z*, M^+): 856 ($C_{30}H_{37}N_8O_{13}{}^{139}La$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ε (L mol cm^{-1}))]: 225 (22, 404), 388 (84, 268). Λ_M (CH_3CN): 131.02 $\Omega^{-1}cm^2mol^{-1}$.

[Ce(**L1**)$(NO_3)_2$]$NO_3.H_2O$ *(2)*
Yield 0.126 g (30.1%). Anal. Calc. for $C_{30}H_{35}N_8O_{12}Ce$ C, 42.91; H, 4.17; N, 13.35, Found: C, 42.25; H, 4.20; N, 13.11%. ESI-MS (*m/z*, M^+): 839 ($C_{30}H_{35}N_8O_{12}{}^{140}Ce$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ε (L mol cm^{-1}))]: 225 (22, 553), 371 (28, 064). Λ_M (CH_3CN): 146.02 $\Omega^{-1}cm^2mol^{-1}$.



Scheme 1

[Pr(**L1**)$(NO_3)_2$]$NO_3.3H_2O$ *(3)*
Yield 0.118g (26.9%). Anal. Calc. for $C_{30}H_{39}N_8O_{14}Pr$: C, 42.00; H, 4.45; N, 12.12, Found: C, 41.87; H, 4.65; N, 12.01%. ESI-MS (*m/z*, M^+): 876 ($C_{30}H_{39}N_8O_{14}{}^{141}Pr$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ε (L mol cm^{-1}))]: 228 (22, 702), 380 (11, 193). Λ_M (CH_3CN): 129.34 $\Omega^{-1}cm^2mol^{-1}$.

[Nd(**L1**)$(NO_3)_2$]$NO_3.3H_2O$ *(4)*
Yield 0.123 g (27.9%). Anal. Calc. for $C_{30}H_{39}N_8O_{14}Nd$: C, 41.77; H, 4.44; N, 12.74, Found: C, 42.07; H, 4.51; N, 13.11%. ESI-MS (*m/z*, M^+): 879 ($C_{30}H_{39}N_8O_{14}{}^{144}Nd$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ε (L mol cm^{-1}))]: 224 (22, 304), 383 (12, 281). Λ_M (CH_3CN): 158.96 $\Omega^{-1}cm^2mol^{-1}$.

$[Sm(\mathbf{L1})(NO_3)_2]NO_3.2H_2O$ ***(5)***
Yield 0.129 g (29.8%). Anal. Calc. for $C_{30}H_{37}N_8O_{13}Sm$: C, 41.52; H, 4.27; N, 12.92, Found: C, 41.05; H, 5.21; N, 12.05%. ESI-MS (*m/z*, M^+): 867 ($C_{30}H_{37}N_8O_{13}{}^{150}Sm$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ϵ (L mol cm^{-1}))]: 230 (22, 901), 380 (12,193). Λ_M (CH_3CN): 122.27 $\Omega^{-1}cm^2mol^{-1}$.

$[Eu(\mathbf{L1})(NO_3)_2]NO_3.3H_2O$ ***(6)***
Yield 0.170 g (38.3%). Anal. Calc. for $C_{30}H_{39}N_8O_{14}Eu$: C, 40.59; H, 4.40; N, 11.63, Found: C, 41.01; H, 4.79; N, 11.01%. ESI-MS (*m/z*, M^+): 887 ($C_{30}H_{39}N_8O_{14}{}^{152}Eu$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ϵ (L mol cm^{-1}))]: 207 (34, 041), 343 (7, 489), 410 (2, 613). Λ_M (CH_3CN): 135.64 $\Omega^{-1}cm^2mol^{-1}$.

$[Gd(\mathbf{L1})(NO_3)_2]NO_3.2H_2O$***(7)***
Yield 0.197 g (45.1%). Anal. Calc. for $C_{30}H_{37}N_8O_{13}Gd$: C, 41.12; H, 4.97; N, 12.81, Found: C, 41.96; H, 5.05; N, 12.12%. ESI-MS (*m/z*, M^+): 874 ($C_{30}H_{37}N_8O_{13}{}^{157}Gd$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ϵ (L mol cm^{-1}))]: 253 (24, 819), 379 (11, 260). Λ_M (CH_3CN): 110.73 $\Omega^{-1}cm^2mol^{-1}$.

$[Tb(\mathbf{L1})(NO_3)_2]NO_3.3H_2O$ ***(8)***
Yield 0.169 g (37.8%). Anal. Calc. for $C_{30}H_{39}N_8O_{14}Tb$: C, 44.67; H, 4.95; N, 13.29, Found: C, 45.01; H, 4.93; N, 12.92%. ESI-MS (*m/z*, M^+): 894 ($C_{30}H_{39}N_8O_{14}{}^{159}Tb$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ϵ (L mol cm^{-1}))]: 230 (45, 153), 370 (10, 898). Λ_M (CH_3CN): 105.64 $\Omega^{-1}cm^2mol^{-1}$.

$[Y(\mathbf{L1})(NO_3)_2]NO_3.2H_2O$ ***(9)***
Yield 0.125 g (31.1%). Anal. Calc. for $C_{30}H_{39}N_8O_{14}Y$: C, 47.67; H, 4.59; N, 13.90, Found: C, 46.01; H, 5.07; N, 12.77%. ESI-MS (*m/z*, M^+): 806 ($C_{34}H_{45}N_7O_{17}{}^{89}Y$). UV-Vis ($CH_3CN$) [$\lambda_{max}$ (nm)(ϵ (L mol cm^{-1}))]: 215 (22, 404), 379 (11, 164). Λ_M (CH_3CN): 116.74 $\Omega^{-1}cm^2mol^{-1}$.

RESULTS AND DISCUSSION

Synthesis of lanthanide(III) complexes of L1

The step-wise condensation of 2,6-diformyl-4-methyl phenol (two equivalents) with 1,5-diamino-3-azapentane (one equivalent) and 4,5-dimethyl-1,2-phenylenediamine (one equivalent) in the presence of hydrated lanthanide(III) nitrate hexahydrate (one equivalent) in methanol under refluxing condition complexes of **L1** are formed in 30 - 45 % yield. Discrete mononuclear complexes $[Ln(\mathbf{L1})(NO_3)_2]NO_3.nH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Y; n = 1 for Ce; n = 2 for La, Sm, Gd, and Y ; n = 3 for Pr, Nd, Eu, and Tb) are obtained in the solid state. The yield of these complexes increases from lighter to heavier lanthanides. The complexes are soluble in methanol, chloroform, DMF, DMSO, and CH_3CN.

Infrared Spectra

The infrared spectra of the complexes of **L1** contain no absorption band characteristic of $-NH_2$ or >C=O function. The strong absorption band observed at ca.1635 cm^{-1} is attributed ν(C=N) vibration [20]. The absorption band appearing at 1545 cm^{-1} is attributed to ν(C=C). The ν(OH) vibration of phenolic proton appears as a broad band at ca. 3400 cm^{-1} probably due to the symmetric and antisymmetric OH stretching vibration of lattice water [21]. The presence of bands at *ca*. 1380 and 816 cm^{-1} are attributed to ionic nitrate groups. The two intense nitrate absorptions due to the asymmetric stretching vibration at appear at ca.1483 cm^{-1} (ν_5) and 1312 cm^{-1} (ν_1) are characteristic of the coordinated chelating nitrate ion [22]. The absorption band appearing at ca.1026 cm^{-1} is attributed to ν_s(NO). The frequency separation between the ν_1 and ν_5 vibration is found to be ca.170 cm^{-1} which is indicative of bidentate coordination of the nitrate ion [23]. The complexes exhibit a sharp and strong absorption band at 1383 cm^{-1} due to the ν(NO)vibration of the free nitrate ion [22]. The infrared spectral data of the complexes are presented in Table 1.

Molar conductivity

The molar conductivity of the lanthanide(III) complexes of **L1** were measured in acetonitrile. The molar conductivities of the complexes show that the complexes are 1:1 electrolyte [24].

Magnetic moments

Magnetic susceptibility measurements of the complexes were carried out at 25 °C. The calculated μ_{eff} values of the Pr(III), Nd(III), and Sm(III), and Gd(III) complexes of **L1** are 3.37, 3.89, and 1.65, and 10.49 B.M., respectively. These values are very close to the van Vleck[25] values for the free lanthanide(III) ions.

Table 1. Characteristic infrared absorption (cm^{-1}) of lanthanide complexes of L1

complex	**assignments**[a]												
	macrocycle						**coordinated**				**ionic nitrate**	**lattice water**	
	ν(OH)	**ν(CH)**	**ν(C=N)**	**ν(C=C)**	**δ(CH)**	**ν(C-O)**	**ν(N=O)**	**$\nu_a(NO_2)$**	**$\nu_s(NO_2)$**	**ν(NO)**		**ν(OH)**	**ρ_r(OH)**
[La(**L1**)$(NO_3)_2$]$NO_3.2H_2O$	3419b,s	2919w	1636	1540sp,s	1456s	1008w	1483	1312	1021sp,w	814w	1384b,s	3419b,s	499w
[Ce(**L1**)$(NO_3)_2$]$NO_3.H_2O$	3433b,s	2921w	1635	1550sp,s	1448s	1008w	1483	1312	1026sp,w	816w	1383b,s	3433b,s	506w
[Pr(**L1**)$(NO_3)_2$]$NO_3.3H_2O$	3420b,s	2922w	1635	1543sp,s	1451s	1008w	1486	1312	1045sp,w	816w	1384b,s	3420b,s	498w
[Nd(**L1**)$(NO_3)_2$]$NO_3.3H_2O$	3408b,s	2919w	1638	1542sp,s	1451s	999w	1491	1312	1026sp,w	816w	1384b,s	3408b,s	499w
[Sm(**L1**)$(NO_3)_2$]$NO_3.2H_2$	3411b,s	2920w	1639	1540sp,s	1451s	999w	1483	1317	1030sp,w	820w	1386b,s	3411b,s	499w
[Eu**L1**)$(NO_3)_2$]$NO_3.3H_2O$	3410b,s	2920w	1635	1540sp,s	1456s	1008w	1484	1317	1026sp,w	816w	1384b,s	3410b,s	498w
[Gd(**L1**)$(NO_3)_2$]$NO_3.2H_2O$	3400b,s	2916w	1636	1541sp,s	1448s	1001w	1483	1317	1029sp,w	816w	1393b,s	3400b,s	500w
[Tb(**L1**)$(NO_3)_2$]$NO_3.3H_2O$	3433b,s	2923w	1623	1539sp,s	1452s	997w	1483	1317	1081sp,w	817w	1384b,s	3433b,s	501w
[Y(**L1**)$(NO_3)_2$]$NO_3.2H_2O$	3408b,s	2920w	1639	1543sp,s	1452s	1000w	1485	1312	1082sp,w	818w	1384b,s	3408b,s	502w

[a] *For reference see the text, abbreviations: sp = sharp, w = weak, b = broad, vs = very strong*

ESI mass spectra

The ESI mass spectra of the complexes contain peaks due to the species $[Ln(\mathbf{L1})(NO_3)_2]^+$, $[Ln(\mathbf{L1})(NO_3)]^+$, $[Ln(\mathbf{L1})]^+$, and $[\mathbf{L1}+H]^+$.The molecular cation $[Ln(\mathbf{L1})(NO_3)_2]^+$ loses the exocyclic ligand (nitrate) resulting the formation of the species $[Ln(\mathbf{L1})(NO_3)]^+$. This fragment further loses the other exocyclic ligand to form the species $[Ln(\mathbf{L1})]^+$ which undergoes demetallation to form $[\mathbf{L1}+H)]^+$. Nitrate ion is removed from $[Ln(\mathbf{L1})(NO_3)_2]^+$ as HNO_3 with a mass loss of 63. In the ESI mass spectra of all the complexes there is an intense peak at m/z 496 corresponding to the species $[\mathbf{L1}+H)]^+$. The ESI mass spectrum of $[Eu(\mathbf{L1})(NO_3)_2]NO_3.3H_2O$ is shown in Figure 1.

Matrix assisted laser desorption ionization-time of flight mass spectra

The MALDI-TOF MASS spectrum of $[Ce(\mathbf{L1})(NO_3)_2]NO_3.H_2O$ confirms the formation of the complex. The complex contains peaks due to the species $[[Ce(\mathbf{L1})(NO_3)_2+H_2]^-(NO_3).H_2O]^+$,$[Ce(H_2\mathbf{L1})(NO_3)+H_2]^+$, $[Ce(H_2\mathbf{L1})+H_2]^+$ and $[H_2\mathbf{L1}]^+$ are 839, 701, 640, and 496, respectively. The intense peak at m/z 496 is due to the species $[H_2\mathbf{L1}]^+$.

Electronic absorption spectra

The Eu(III) complex exhibit three absorptions at 207, 343, and 410 nm and all other complexes exhibit two absorptions, one around 225 nm and the other in the 370-390 nm region.[26] Electronic absorption spectra are recorded for the complexes immediately after preparing the solutions and after standing the complexes in solution over a period of one day, one week, one month, and two months are the same. There is no apparent loss of the metal ion in solution indicating the kinetic inertia of these complexes to metal ion release.

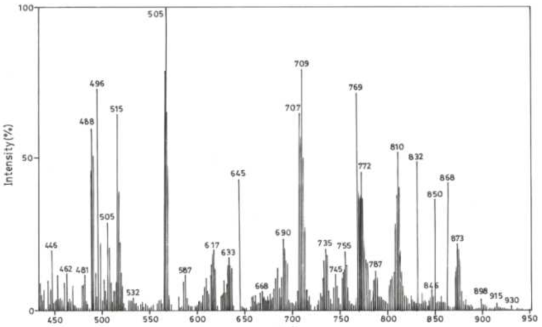


Fig.1 ESI mass spectrum of $[Eu(L1)(NO_3)_2]NO_3.3H_2O$

Electrochemistry

The cyclic voltammogram of $[Ce(\mathbf{L1})(NO_3)_2)]NO_3.H_2O$, consists of a reduction wave and E_{pc} = -1.29 V and an oxidation wave at E_{pa} = -0.982 V (vs Ag/AgCl). The E_{pa} and E_pc values of the complexes are at less negative potentials than the reduction potential of the free metal ion.

Fluorescence studies

The excitation spectrum of $[Eu(\mathbf{L1})(NO_3)_2)]NO_3.3H_2O$, ($\lambda_{emi}$= 461 nm) exhibits a broad band at 359 nm and a sharp band at 453 nm. Upon excitation at the excitation maxima it exhibits an emission band at 685 and 703 nm typical of Eu(III) emission [26,27]. The excitation spectrum of $[Tb(\mathbf{L1})(NO_3)_2)]NO_3.3H_2O$ shows a band at 372 nm, a medium intense peak at 315 nm and a shoulder at 285 nm. Upon excitation at the excitation maxima it exhibits a emission at 545 nm due to the $^5D_4 \rightarrow {}^7F_5$ emission.

Thermal Studies

The thermogram of Gd complex of **L1**shows a two-step thermal decomposition pattern at temperature ranges 300-450 and 510-620 ^oC. At the temperature range of 300-450 ^oC both lattice water and nitrate ion are removed simultaneously and subsequently the ligand undergoes decomposition along with coordinated nitrate ion at the temperature range 510-630 ^oC.

CONCLUSION

The synthesis of lanthanide(III) complexes of **L1** under the same experimental conditions explain the template potential of lanthanide(III) ions in the formation of oxaaza Schiff base macrocycles. The metal ion is coordinated to the three nitrogen and two oxygen donors of the macrocycle and to four oxygen atoms of the two bidentate chelating nitrate ion. The yield of the complexes does not vary appreciably along the series. The presence of a base (LiOH or NaOH) promotes the formation of the monocationic species. The Schiff bases behave as neutral or dianionic ligands according the synthetic procedure employed. The template synthesis is carried out in the absence of base. Similar types of macrocyclic complexes where the phenolic protons remain intact have been reported [28-30]. The formation of the complexes of **L1** with all lanthanide(III) ions is due to the adaptability of this macrocycle to coordinate according to the electronic and geometrical demands of the metal ions.

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