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TEMPLATE SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE(III) COMPLEXES OF 21-MEMBERED UNSYMMETRICAL PENTAAZA MACROCYCLIC SCHIFF BASES BEARING PENDANT ARM. IDENTICAL FRAME WORK: PART II

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Macrocyclic complexes,
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Schiff base macrocycles,
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ABSTRACT: A series of discrete mononuclear lanthanide(III) complexes of $H_2L_1 [Ln(H_2L_1)(NO_3)_2]NO_3 \cdot nH_2O$ ($Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Y$; $n = 1$ 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-azamethypentane 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 mass 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 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.

INTRODUCTION: Macrocyclic compounds have attracted an increasing interest owing to their role in the understanding of the molecular processes that occur in different scientific fields, ranging from chemistry to biochemistry and medicines, from material science to hydrometallurgy^{1-8, 25}. Based on the bonding strength of the ligating groups and the cavity of the ring, macrocyclic ligands can combine with metal ions optionally. Thus this kind of compound offers a direct and similar way to mimic the biological systems, in which biological cycles containing active metal centers are largely involved.

In 1970 Robson and co-workers reported the synthesis of a new compartment macrocyclic system based upon the metal template Schiff-base condensation of 2,6-diformyl-4-methyl phenol with 1,3-diaminopropane in the presence of a range of first row transition metal ions⁹. 2,6-Diformyl-4-methylphenol is a potential precursor to synthesize the compartmental Schiff-basemacrocyclic ligands containing two bridging phenol groups.

Compartmental macrocycles are relevant because they can accommodate two or more metal ions, connected in close proximity by appropriate bridging groups which, if paramagnetic, can interact with each other through the bridging donor atoms of the ligands in a ferromagnetic or antiferromagnetic way. By changing the type of ligand, the distance between the two chambers and/or the paramagnetic centers, it is possible to tune the magnetic interactions. Thus, the

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complexes, in which ferromagnetic interactions occur, may be good building blocks for the preparation of molecular magnets. In addition to that, asymmetric compartmental ligands have been under intense scrutiny because it is expected that well defined bimetallic systems may find interesting applications in several areas of chemical research¹⁰⁻¹³. On the other hand, unsymmetrical macrocycles with two dissimilar lateral chains have been less used¹⁴⁻¹⁹. This type of unsymmetrical macrocycle was first reported by Okawa and Kida¹⁴.

There has been particular interest in the preparation and characterization of coordination compounds with aza-macrocyclic ligands with pendant substituents for the reasons given above²⁰⁻²⁴. The complexation of polyaza-macrocycles are governed mainly by the macrocyclic ring size. *N*-functionalization of these macrocycles may enhance their metal-ion selectivity and the stability of metal complexes depending on coordination properties of the pendant arms²⁰. Pendant-armed macrocycles and their metal complexes have attracted much interest in the past years²⁵⁻³⁰. Synthesis and characterization of Yb-Na dinuclear complex which represents the first example of macrocyclic compartmental complex containing a lanthanide and alkali metal ions with similar pendant arm have been reported by Casellato *et al*³¹. One potential of this area is the concept that, by having pendant arms attached at appropriate positions on the macrocyclic framework, an 'opened crypt and' would result, leading to modified complexation properties over the corresponding clathrochelates or simple macrocyclic precursors²⁶.

I report herein the template synthesis and characterization of lanthanide(III) complexes of 21-membered unsymmetrical pentaaza macrocyclic Schiff bases bearing pendant arm.

MATERIAL AND METHODS: 4,5-Dimethyl-1,2-phenylenediamine (Aldrich) was used as such for the synthesis of complexes. 2,6-Diformyl-4-methylphenol was synthesized by the literature methods³². The lanthanide (III) nitrates, namely, Pr(NO₃)₃.6H₂O (99.9%), Nd(NO₃)₃.6H₂O (99.9%), Sm(NO₃)₃.6H₂O (99.9%), Eu(NO₃)₃.6H₂O

(99.9%), Tb(NO₃)₃.6H₂O (99.9%), and Dy(NO₃)₃.6H₂O (99.9%) (Indian Rare Earth Ltd.), and Pr(NO₃)₃.6H₂O (99.9%), Gd(NO₃)₃.6H₂O (99.9%), Ho(NO₃)₃.6H₂O (99.9%), Er(NO₃)₃.6H₂O (99.9%), and Y(NO₃)₃.6H₂O (99.9%) (Aldrich) were used as such for the synthesis of complexes. *p*-Toluenesulfonyl chloride, *p*-cresol, lithium hydroxide monohydrate, sodium dichromate dihydrate (LOBA), sodium carbonate, paraformaldehyde, formic acid, sodium hydroxide, sodium acetate, sodium sulfate anhydrous, and calcium chloride anhydrous (E. Merck) 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. CDCl₃ (Aldrich), KBr (FT-IR grade) (Aldrich) were used for recording NMR and IR spectra respectively.

Acetonitrile, *N,N*-dimethylformamide, chloroform, dichloromethane benzene, toluene (E. Merck), and methanol (SD's) were reagent grade and purified according to the literature method³³. Diethyl ether, dimethyl sulfoxide, acetone and petroleum ether (60-80°C) (E. Merck) were used as purchased. Double deionized water was obtained by distilling, distilled water over alkaline potassium permanganate. Absolute ethanol was obtained by double distilling rectified spirit over lime and the fraction boiling at 78 °C was collected. Super dry ethanol was obtained by distilling absolute ethanol over magnesium turnings activated by iodine and the fraction boiling at 78 °C was collected. Super dry methanol was also obtained by the same method by collecting the fraction boiling at 65 °C.

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°C 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 microanalyses 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 °C in acetonitrile using Elico CM-180 conductivity meter and Elico Type CC-03 conductivity cell (cell constant 1.02 cm^{-1}). 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. Magnetic susceptibility measurements were carried out on an EG & G PAR MODEL 155 vibrating sample magnetometer at 25 °C. The instrument was calibrated using pure nickel. ^1H NMR spectra were recorded on JEOL 400 MHz ^1H NMR spectrometer in CDCl_3 . Fluorescence study of the complexes were carried out on a Hitachi 650-40 Fluorescence Spectrophotometer in acetonitrile or *N,N*-dimethylformamide.

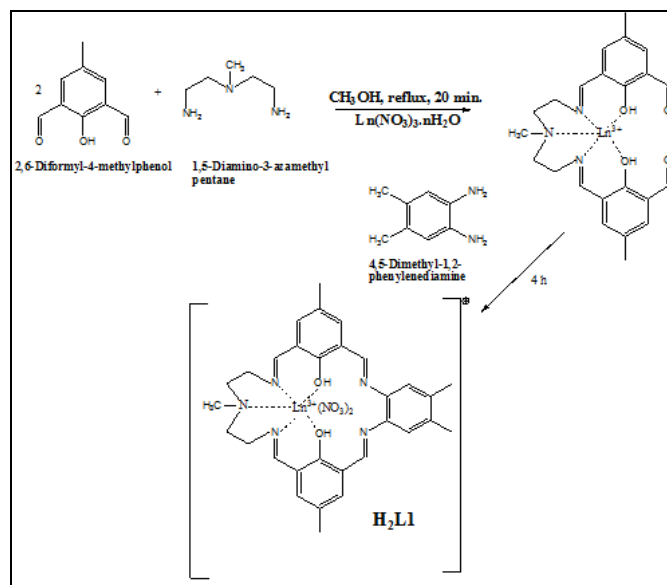
Synthesis of 1,5-diamino-3-azamethylpentane:

1,5-diamino-3-azamethylpentane was synthesized according to the previously reported method³⁴. The amine hydrochloride salt thus obtained was neutralized with base and extracted with CH_2Cl_2 , washed several time with distilled water and dried over P_2O_5 . Under slow evaporation of the solvent a yellow oil was obtained. The 400 MHz ^1H NMR spectrum shows a resonance at 2.32 ppm (3H, NCH_3), 2.80 ppm (t 4H, methylene protons), and 3.20 ppm (t 4H, methylene protons). The ^{13}C NMR spectrum in CDCl_3 has resonances at 36.7 (C2 and C6 carbons), 55.7 (C3 and C5 carbons), and 43.4 ppm (N-CH_3 carbon). In the EI mass spectrum the peak at m/z 117 corresponds to the molecular ion M^+ . Anal. Calcd. for $\text{C}_5\text{H}_{15}\text{N}_3$: C, 51.2; H, 12.9; N, 35.86. Found C, 50.9; H, 12.7; N, 35.65.

Synthesis of lanthanide(III) complexes of 21-membered unsymmetrical pentaazatetraimine macrocycle, 6, 13, 20, 21, 28-pentamethyl-3, 6, 9, 17, 24-pentaaza tetracyclo[24.3.1.1^{11, 15}.0^{18, 23}] monotriaconta-1(30),2,9,11,13, 15(31),16,18, 20, 22, 24,26, 28-tridecaene-30,31-diol ($\text{H}_2\text{L1}$).

The step-wise condensation of 2,6-diformyl-4-methylphenol (two equivalents) with 1,5-diamino-3-azamethylpentane (one equivalent) and 4,5-dimethyl-1,2-phenylenediamine (one equivalent) in the presence of hydrated lanthanide(III) nitrate (one

equivalent) in methanol under refluxing condition complexes of $\text{H}_2\text{L1}$ are formed in 30 - 45 % yield. Discrete mononuclear complexes $[\text{Ln}(\text{H}_2\text{L1})(\text{NO}_3)_2]\text{NO}_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln}(\text{III}) = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Y}$; $n = 1$ for Ce; $n = 2$ for La, Sm, Gd, and Y ; $n = 3$ for Pr, Nd, Eu, and Tb) are isolated in the solid state (**Scheme 1**). The yield of these complexes increases from lighter lanthanides to heavier lanthanides. The complexes are soluble in methanol, chloroform, DMF, DMSO, and CH_3CN .



SCHEME 1: SYNTHESIS OF $\text{Ln}(\text{III})$ COMPLEXES OF $\text{H}_2\text{L1}$

RESULTS AND DISCUSSION:

Infrared spectra:

The infrared spectra of the complexes of $\text{H}_2\text{L1}$ contain no absorption band characteristic of $-\text{NH}_2$ or $>\text{C}=\text{O}$ functions. The strong absorption band observed at ca. 1635 cm^{-1} is attributed to $\nu(\text{C}=\text{N})$ vibration³⁵. The absorption band appearing at 1545 cm^{-1} is attributed to $\nu(\text{C}=\text{C})$. The $\nu(\text{OH})$ 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 water³⁶. The bands at ca. 1380 and 820 cm^{-1} are attributed to ionic nitrate groups. The two intense nitrate absorptions due to the asymmetric stretching vibration of $\nu(\text{NO})$ appearing at ca. 1450 cm^{-1} (ν_5) and 1300 cm^{-1} (ν_1) are characteristic of the coordinated chelating nitrate ion³⁷.

The absorption band appearing at ca. 1037 cm^{-1} is attributed to $\nu_s(\text{NO}_2)$. The frequency separation between ν_1 and ν_5 vibration is found to be

ca.180 cm^{-1} which is indicative of bidentate coordination of the nitrate ion³⁸. The complexes exhibit a sharp and strong absorption band at 1383

cm^{-1} due to the $\nu(\text{NO})$ vibration of the free nitrate³⁷. The infrared spectral data of the complexes are presented in **Table 1**.

TABLE 1: CHARACTERISTIC INFRARED ABSORPTION (CM^{-1}) OF LANTHANIDE(III) COMPLEXES OF $\text{H}_2\text{L1}$

Complex	Assignments ^a												
	macrocycle					coordinated nitrate					ionic nitrate	lattice water	
	$\nu(\text{OH})$	$\nu(\text{CH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\delta(\text{CH})$	$\nu(\text{C}-\text{O})$	$\nu(\text{N}=\text{O})$	$\nu_1(\text{NO}_2)$	$\nu_3(\text{NO}_2)$	$\nu(\text{NO})$		$\nu(\text{OH})$	$\rho_r(\text{OH})$
[La($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 2\text{H}_2\text{O}$	3419 b,s	2918w	1635 sp,s	1545 sp,s	1456 s	999 w	1492	1312	1037	815 w	1384 vs	3419 b,s	472 w
[Ce($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot \text{H}_2\text{O}$	3420 b,s	2922w	1636 sp,s	1539 sp,s	1456 s	998 w	1493	1312	1037	815 w	1384 vs	3420 b,s	472 w
[Pr($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	3433 b,s	2922w	1636 sp,s	1539 sp,s	1456 s	998 w	1498	1322	1031	815 w	1383 vs	3433 b,s	472 w
[Nd($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 2\text{H}_2\text{O}$	3433 b,s	2928w	1635 sp,s	1538 sp,s	1456 s	998 w	1492	1312	1031	820 w	1384 vs	3433 b,s	473 w
[Sm($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 2\text{H}_2\text{O}$	3433 b,s	2921w	1635 sp,s	1539 sp,s	1455 s	998 w	1492	1321	1029	804 w	1383 vs	3422 b,s	473 w
[Eu($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	3412 b,s	2923w	1635 sp,s	1533 sp,s	1463 s	998 w	1498	1317	1031	815 w	1383 vs	3412 b,s	474 w
[Gd($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	3410 b,s	2922w	1637 sp,s	1539 sp,s	1453 s	998 w	1490	1317	1031	820 w	1383 vs	3410 b,s	474 w
[Tb($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	3410 b,s	2919w	1637 sp,s	1539 sp,s	1448 s	1004 w	1490	1312	1037	820 w	1384 vs	3410 b,s	474 w
[Y($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	3424 b,s	2921w	1626 sp,s	1541 sp,s	1454 s	1004 w	1493	1313	1037	820 w	1383 vs	3424 b,s	476 w

^aFor reference see the text, abbreviations: sp = sharp, s = strong, w = weak, b = broad, s = very strong

TABLE 2: COLOR, YIELD, ELEMENTAL ANALYSIS, MOLAR CONDUCTIVITY AND MOLECULAR WEIGHT OF LANTHANIDE(III) COMPLEXES OF $\text{H}_2\text{L1}$

Complex	Color	Yield (%)	Molar Conductance ^a (mho $\text{cm}^2 \text{mol}^{-1}$)	Molecular Weight	Found Calc. (%)		
					C	H	N
[La($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 2\text{H}_2\text{O}$	Maroon red	27.8	141.08	913	45.01 (44.96)	4.95 (5.09)	10.76 (10.83)
[Ce($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot \text{H}_2\text{O}$	black	28.8	142.08	913	42.76 (42.97)	5.01 (5.34)	10.21 (10.91)
[Pr($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	Maroon red	29.1	132.12	890	42.71 (41.64)	4.90 (4.92)	11.10 (11.34)
[Nd($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 2\text{H}_2\text{O}$	Maroon red	38.1	139.42	875	40.96 (40.65)	4.98 (5.03)	9.52 (9.36)
[Sm($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 2\text{H}_2\text{O}$	Maroon red	40.9	140.51	899	46.97 (46.53)	4.01 (3.97)	9.98 (9.48)
[Eu($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	Maroon red	31.1	135.44	901	40.97 (40.38)	3.98 (4.10)	9.95 (9.97)
[Gd($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	Maroon red	28.5	129.23	906	41.06 (40.84)	4.00 (4.08)	10.97 (11.01)
[Tb($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	Maroon red	26.1	125.74	908	42.01 (42.34)	4.52 (4.07)	11.61 (11.93)
[Y($\text{H}_2\text{L1}$)(NO_3) ₂] $\text{NO}_3 \cdot 3\text{H}_2\text{O}$	Maroon red	35.8	143.35	838	45.11 (45.02)	4.90 (4.43)	10.25 (10.97)

^a In acetonitrile

Molar conductivity:

Molar conductivity of the lanthanide (III) complexes of $\text{H}_2\text{L1}$ were measured in acetonitrile. The molar conductivities of the complexes are given in **Table 2** show that the complexes are 1:1 electrolytes³⁹.

Electronic absorption spectra:

Complexes Eu(III) and Tb(III) exhibit three absorptions at 217, 255, and 400 nm and all other

complexes (Ln = La, Ce, Pr, Nd, Sm, Gd, and Y) exhibit two absorptions, one around 214 nm and the other in the 390-400 nm region⁴⁰. These absorptions are due to characteristic of the $\pi-\pi^*$ transition of the azomethine linkage^{41, 42}. There is no apparent loss of the metal ion in solution indicating the kinetic inertia of these complexes to metal ion release. The electronic absorption spectral data is presented in **Table 3**.

TABLE 3: ELECTRONIC ABSORPTION SPECTRAL DATA^a OF THE LANTHANIDE(III) COMPLEXES OF H₂L1

Complex	Absorption bands (nm) (ε, L mol ⁻¹ cm ⁻¹)		
[La(H ₂ L1)(NO ₃) ₂](NO ₃).2H ₂ O	225 (22,404)	388 (84,286)	-
[Ce(H ₂ L1)(NO ₃) ₂](NO ₃).H ₂ O	214 (35,105)	403 (8,252)	-
[Pr(H ₂ L1)(NO ₃) ₂](NO ₃).3H ₂ O	217 (35,432)	397 (7,052)	-
[Nd(H ₂ L1)(NO ₃) ₂](NO ₃).2H ₂ O	210 34,289(0)	255 (18,719)	-
[Sm(H ₂ L1)(NO ₃) ₂](NO ₃).2H ₂ O	214 (22,165)	397 (6,842)	-
[Eu(H ₂ L1)(NO ₃) ₂](NO ₃).3H ₂ O	217 26,374(0)	255 (18,607)	410 (7,534)
[Gd(H ₂ L1)(NO ₃) ₂](NO ₃).3H ₂ O	214 (23,364)	257 (18,752)	-
[Tb(H ₂ L1)(NO ₃) ₂](NO ₃).3H ₂ O	208 (35,611)	256 (18,839)	400 (9,018)
[Y(H ₂ L1)(NO ₃) ₂](NO ₃).3H ₂ O	210 (25,523)	256 (18,680)	-

^aIn Acetonitrile**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), Sm(III), and Eu(III) complexes of H₂L1 are 2.38, 3.89, 1.78, and 3.39 B.M, respectively, which close to the van Vleck[43] values for the free lanthanide(III) ions.

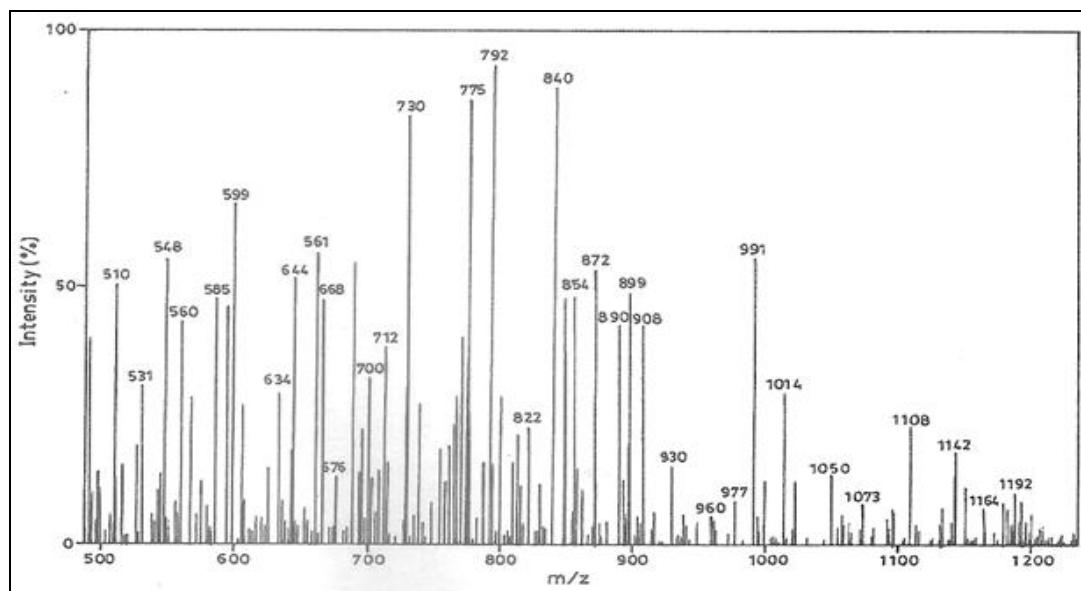
ESI mass spectra:

The ESI mass spectral data of the complexes are presented in **Table 4**. The ESI mass spectra of the complexes contain peaks due to the species [Ln(H₂L1)(NO₃)₂]⁺, [Ln(H₂L1)(NO₃)]⁺,

[Ln(H₂L1)]⁺, and [Ln(H₂L1)+H]⁺. The molecular cation [Ln(H₂L1)(NO₃)₂]⁺ loses the exocyclic ligands (nitrate) resulting in the formation of the species [Ln(H₂L1)(NO₃)]⁺. This fragment further loses the another exocyclic ligand to form the species [Ln(H₂L1)]⁺ which undergoes demetalation to form [(H₂L1)+H]⁺. Nitrate ion is removed from [Ln(H₂L1)(NO₃)₂]⁺ as HNO₃ with mass loss of 63. In the ESI mass spectra of the complexes there is an intense peak at m/z 510 corresponding to the species [(H₂L1)+H]⁺. The ESI mass spectrum of [Tb(H₂L1)(NO₃)₂](NO₃).3H₂O, is depicted in **Fig. 1**.

TABLE 4: ESI MASS SPECTRAL DATA OF LANTHANIDE(III) COMPLEXES OF H₂L1

Complex	Species	m/z
[Sm(H ₂ L1)(NO ₃) ₂](NO ₃).H ₂ O		899
	[Sm(H ₂ L1)(NO ₃) ₂] ⁺	783
	[Sm(H ₂ L1)(NO ₃)] ⁺	721
	[Sm(H ₂ L1)] ⁺	659
	[(H ₂ L1)+H] ⁺	510
[Tb(H ₂ L1)(NO ₃) ₂](NO ₃).3H ₂ O		908
	[Tb(H ₂ L1)(NO ₃) ₂] ⁺	792
	[Tb(H ₂ L1)(NO ₃)] ⁺	730
	[Tb(H ₂ L1)] ⁺	668
	[(H ₂ L1)+H] ⁺	510

**FIG.1: ESI MASS SPECTRUM OF [Tb(H₂L1)(NO₃)₂](NO₃).3H₂O**

Fluorescence studies:

The excitation spectrum of [Eu(**H₂L1**) (NO₃)₂]
NO₃.3H₂O, ($\lambda_{\text{emi}}=461$ 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^{40, 44}. The excitation spectrum of
[Tb(**H₂L1**)(NO₃)₂]
NO₃.3H₂O 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 an emission at 545
nm due to the ⁵D₄ → ⁷F₅ emission.

CONCLUSIONS: The step-wise metal template
condensation of 2,6-diformyl-4-methylphenol, 1,5-
diamino-3-azamethylpentane with 4,5-dimethyl-
1,2-phenylenediamine in the presence of hydrated
lanthanide(III) nitrate readily forms complexes of
H₂L1. The yield of the complexes does not vary
appreciably along the series. However, the yield of
the Sm, Nd, and Y complexes of **H₂L1** vary from
35 - 40 %. The metal ion is coordinated to the
three nitrogen and two-oxygen donor of the
macrocycle and to four oxygen atoms of the two
bidentate chelating nitrate atoms. The Schiff bases
behave as neutral or dianionic ligand according to
the reaction condition. The presence of a base
(LiOH or NaOH) promotes the formation of
complexes containing only one nitrate group and
dianionic Schiff base and in the absence of a base
the macrocycle coordinates on the neutral ligand.
The complexes are soluble in common organic
solvents and aromatic hydrocarbons. Similar type
of macrocyclic complexes where the phenolic
protons remain intact have been reported⁴⁵⁻⁴⁷. The
formation of the complexes of **H₂L1** with all
lanthanide(III) ions is due to the adaptability of this
macrocycle to coordinated according to the
electronic and geometrical demands of the metal
ions.

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