

Synthesis and Structural Characterization of some Lanthanide(III) Nitrate Complexes with a Mesogenic Schiff-Base, *N,N'*-di-4-(4-heptadecyloxybenzoate)salicylidene-1,3-diaminopropane derived from 2,4-dihydroxybenzaldehyde

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Abstract

Complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) with the Schiff-base, *N,N'*-di-4-(4'-heptadecyloxybenzoate)salicylidene-1,3-diaminopropane, (abbreviated as H₂L) have been synthesized and characterized on the basis of elemental analyses, molar conductance, magnetic, electronic, infrared, ¹H and ¹³C NMR spectral techniques. The nephelauxetic ratio (β), the bonding parameter ($b^{1/2}$), Sinha's parameter ($\% \delta$) and angular overlap parameter (η) have been calculated from the electronic spectra of Pr(III), Nd(III), Sm(III) and Dy(III) complexes. Infrared and NMR spectral data imply a bi-dentate bonding of the Schiff-base in its zwitterionic form (as LH₂) to the Ln(III) ions through two phenolate oxygens, rendering the overall geometry around Ln(III) to distorted square antiprism. Polarized optical microscopy (POM) and differential scanning calorimetry (DSC) shows the liquid crystalline property of the ligand with a nematic (*N*) mesophase. Among the metal complexes, only that of the Gd(III) exhibits smectic B (*Sm_B*) and nematic (*N*) phases.

Keywords: Mesogenic Schiff-base, Ln(III) complexes, zwitterionic-coordination, square antiprism, NMR and IR spectra

Introduction

Metal-containing liquid crystals (metallomesogens) are formed when organic ligands having mesogenic properties co-ordinate to metal ions. The rationale for the incorporation of transition metals into such ligands is the opportunity to combine the properties of liquid crystals (which are anisotropic fluids) with the unique properties of *d*-block and *f*-block transition metals. The incorporation of these transition metal ions allows the tailoring of devices taking advantage of their unique photophysical and magnetic properties, and redox behaviour [1-3].

The design of metallomesogens is a challenge because the presence of a metal center often modifies the mesomorphic behavior of the free ligand [4,5]. On the other hand, transition metals aid in the construction of mesogenic materials with original molecular architectures that cannot be obtained by the use of pure organic systems. There are basically two strategies

for designing lanthanide-containing liquid crystals. One is to synthesize mesogenic ligands leading to mesogenic lanthanide complexes. Secondly, the incorporation of trivalent lanthanide ions into liquid crystals requires the design of an appropriate ligand system, because of the tendency of these ions to adopt a high coordination number (typically eight or nine). Such high coordination numbers seem to be incompatible with the structural anisotropy that is necessary to exhibit liquid crystalline behaviour.

Initially, it was thought that introducing bulky spherical Ln^{III} ions in potentially mesogenic compounds could disrupt the required order to produce mesophases. However, the first lanthanide complex, *bis*(octaalkyloxyphthalocyaninato)lutetium, reported by Piechocki *et al.*, in 1985 [6] opened the prospect for syntheses of many lanthanide complexes amenable to form liquid crystalline phases. Other properties of the Ln^{III} ions can be helpful in liquid crystals, for instance, their varying size along with the series

which can be used to fine-tune the properties of the mesomorphic phases [1]. Additionally, the radius of the metal ion can influence the transition temperatures and even the type of mesophase. This effect has been studied in mesogens of trivalent lanthanide ions [7,8] and divalent transition metal ions [9-11]. By taking advantage of the variation of the coordination number through a proper choice of the metal ion, one can obtain complexes with different metal-to-ligand ratios and molecular geometries, and thus, modifications in the mesophase behavior are expected [8,11,12]. However, in order to study the influence of the metal ion on the thermal behavior of metallomesogens, it is necessary to have ligand systems that are able to form complexes with many different types of metal ions.

Schiff-base metal complexes have drawn the attention of inorganic chemists because of the interesting properties of these complexes [12,13]. Such complexes play an important role in the development of metallomesogens [9,14,15]. The salicylaldimine ligand system has many advantages in the synthesis of metallomesogen because of its considerable flexibility in the synthetic procedure. This allows the preparation of a wide variety of liquid crystalline complexes, whose properties are strongly dependent on the ligand structure and the metal ion used [15]. As a part of our further investigation on systematic structural and spectroscopic studies of 3*d* and 4*f* metal complexes of a series of Schiff-bases [16-20], we now report here the synthesis and structural characterizations of some Ln^{III} complexes with a Schiff-base, *N,N'*-di-4-(4-heptadecyloxybenzoate) salicylidene-1,3-diaminopropane derived from 2,4-dihydroxybenzaldehyde. Besides, the mesogenic properties of the synthesized ligand and Ln(III) complexes are also studied.

Materials and Methods

Starting materials

All reagents were purchased from commercial sources and used without further purification: 1-bromoheptadecane, 4-hydroxy benzoic acid, 2,4-dihydroxybenzaldehyde, *N,N'*-dicyclohexyl carbodiimide (DCC), *N,N'*-dimethylaminopyridine (DMAP), and 1,3-diaminopropane are from Sigma-Aldrich, USA; all Ln(NO₃)₃·xH₂O are from Indian

Rare Earths Ltd. The solvents received were dried using standard methods [21] when required.

Instrumentation

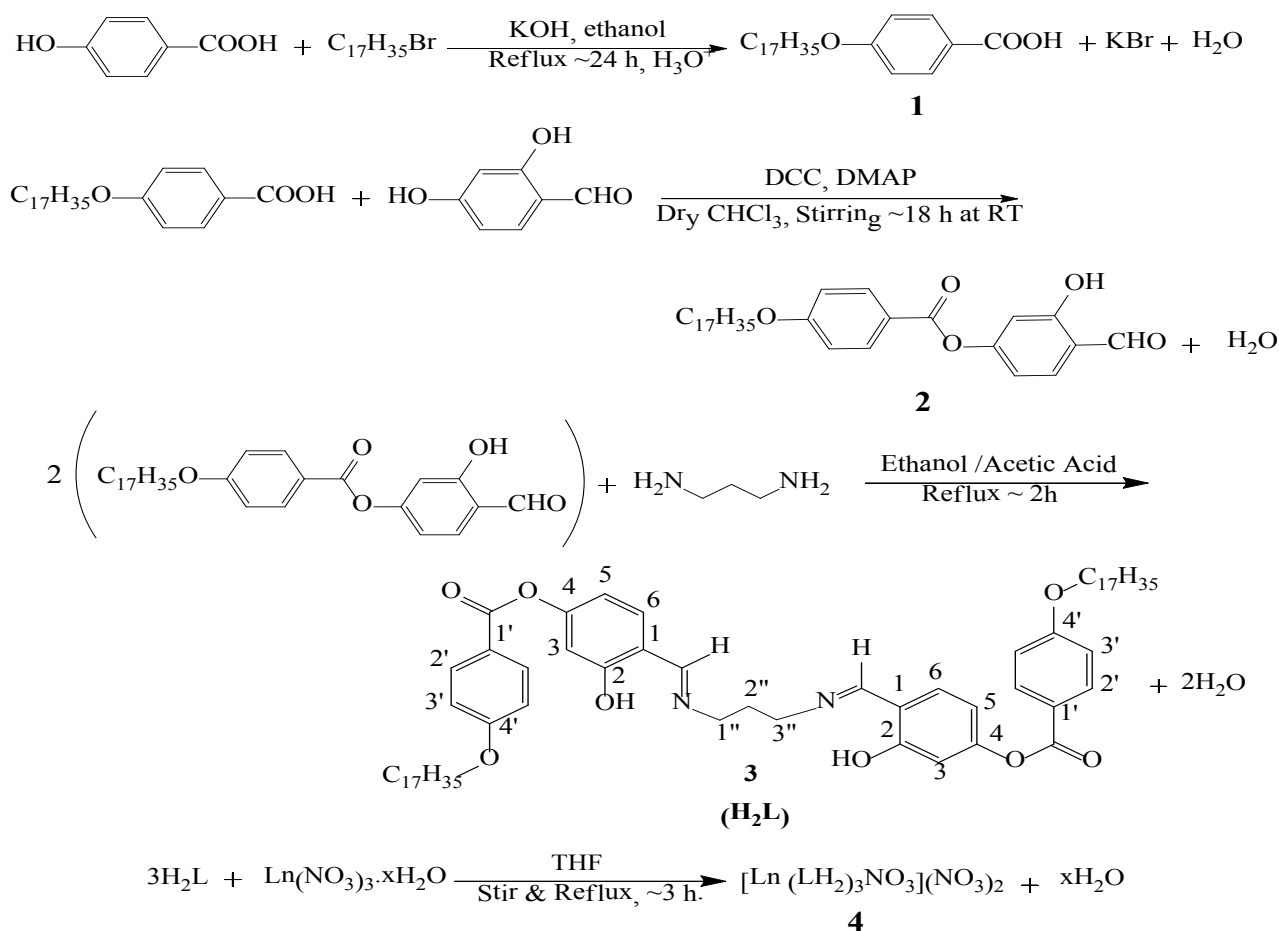
The metal ions were estimated volumetrically by EDTA titration using xylenol orange as an indicator. C, H, and N were determined using a CHN elemental analyzer CE-440. The molar conductance of the complexes was determined in 0.001 M solutions on a digital conductivity meter (Model alpha-06, ESICO International) using a commercial conductivity 'dip cell' of cell constant, 1.03. Magnetic susceptibility measurements were carried out at room temperature on a Cahn–Faraday electrobalance using Hg[Co(NCS)₄] as the calibrant. The electronic spectra were recorded on Shimadzu spectrophotometer, model Pharmaspec-UV 1700 while the IR spectra were recorded on a Bruker IFS66 FTIR spectrometer. The KBr-pellet technique was used to measure the samples. The ¹H and ¹³C NMR spectra were recorded on a Bruker Av III HD (DRX) 300 MHz FT-NMR multinuclear spectrometer. Differential scanning calorimetry (DSC) studies were made on a Mettler-Toledo DSC822e module (scan rate 10 °C min⁻¹ under a helium flow, aluminum cups). Optical textures of the mesophases were observed using an Olympus BX60 polarizing microscope equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller.

Synthesis and analyses

N,N'-di-4-(4'-heptadecyloxybenzoate) salicylidene-1,3-diaminopropane, **3** (Scheme 1), was synthesized from the precursor materials, **1** and **2**, as reported earlier [20]. All [Ln(LH₂)₃(NO₃)₂](NO₃)₂ complexes (Ln=La, Pr, Nd, Sm, Gd, and Dy), **4** (Scheme 1) were prepared analogously by stirring and refluxing solutions of the Schiff-base, H₂L, and the corresponding metal nitrate in 3:1 molar ratio in tetrahydrofuran (THF) medium for ~3 h at 55 °C. The reaction mixture was left overnight in the flask closed with a guard tube. The solid colored complexes that separated in each case were filtered under suction, washed repeatedly with cold ethanol and dried over fused CaCl₂.

Synthesis of *N,N'*-di-4-(4'-heptadecyloxybenzoate) salicylidene-1,3-diaminopropane, **3**

N,N'-di-4-(4'-heptadecyloxybenzoate)salicylidene-1,3-diaminopropane, H₂L, **3** was prepared



Scheme 1: Synthetic steps involved in the synthesis of **1** (4-heptadecyloxybenzoic acid), **2** (4-heptadecyloxy (4'-formyl-3'-hydroxy)-benzoate), **3** (*N,N'*-di-4-(4'-heptadecyloxybenzoate)-salicylidene-1'',3''-diaminopropane, H_2L) and **4** (Ln^{III} complexes).

by refluxing together absolute ethanolic solutions of the heptadecyloxybenzoate ester of 2,4-dihydroxybenzaldehyde (24.84 g, 50 mmol in 100 mL) and 1,3-diaminopropane (1.85 g, 25 mmol in 50 mL) for ~ 2h in presence of a few drops of acetic acid and leaving the resultant solution overnight in the reaction flask at room temperature. The micro-crystalline product was filtered off by suction, thoroughly washed with cold ethanol and recrystallized from a mixture of absolute ethanol and chloroform (1:1 v/v) and dried at room temperature. Yield: 67% (18.05 g) as a yellow colored micro-crystalline solid; m.p. 220 °C. Anal. Calc. for $\text{C}_{65}\text{H}_{94}\text{N}_2\text{O}_8$ (1031.45): C, 75.69; H, 9.19; N, 2.72; found C, 74.59; H, 9.21; N, 2.66%. ^1H NMR: (300 MHz; CDCl_3 ; δ) 0.881 (t, $J = 6.0$, 3H, $-\text{CH}_3$), 1.818-1.261 (m, 30H, $-(\text{CH}_2)_{15}-$), 2.467 (s, 2H, $-\text{CH}_2$), 3.942 (s, 2H, $-\text{NCH}_2$), 4.039

(t, $J = 6.3$, 2H, $-\text{OCH}_2$), 6.800 (s, 1H, Ar-H), 6.959 (d, $J = 8.7$, 1H, Ar-H), 7.273 (d, $J = 8.7$, 1H, Ar-H), 7.691 (d, $J = 7.2$, 1H, Ar-H), 8.114 (d, $J = 8.7$, 1H, Ar-H), 8.359 (s, 1H, $-\text{N}=\text{CH}$), 13.504 (s, br, 1H, Ph-OH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.45 MHz; CDCl_3 ; δ): 165.89, 165.49, 163.64, 162.60, 154.32, 132.35, 128.66, 121.30, 116.53, 114.32, 112.63, 110.58, 68.36, 62.58, 44.64, 22.34 and 14.80

Synthesis of La(III) complex, $[\text{La}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$, **4**

The La(III) complex of the mesogenic Schiff-base ligand, H_2L was prepared by dropwise addition of THF solution (~10 mL) of the $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.44 g, 1 mmol) to a THF solution (~10 mL) of the ligand (3.09 g, 3 mmol) under magnetic stirring. The resultant solution turned cloudy after ~15 minutes implying the starting point of complex formation;

stirring and refluxing were continued for ~3 h when a solid product separated out which was filtered, washed repeatedly with cold methanol and dried over fused CaCl_2 .

Yield: 2.53 g (74%) as a yellow colored solid. mp 244 °C (decomposes). Anal. Calc. for $\text{LaC}_{195}\text{H}_{282}\text{N}_9\text{O}_{33}$ (3419.27): C, 68.50; H, 8.31; N, 3.69; La, 4.06; found: C, 68.28; H, 8.22; N, 3.82; La, 4.12%. ^1H NMR: (300 MHz; CDCl_3 ; δ) 0.875 (t, $J = 5.1$, 3H, $-\text{CH}_3$), 1.867-1.257 (m, 30H, $-(\text{CH}_2)_{15}$ -), 2.687 (s, 2H, $-\text{CH}_2$), 3.986 (s, 2H, $-\text{NCH}_2$), 4.044 (t, $J = 6.3$, 2H, $-\text{OCH}_2$), 6.875 (s, 1H, Ar-H), 6.906 (d, $J = 7.8$, 1H, Ar-H), 6.971 (d, $J = 8.1$, 1H, Ar-H), 7.603 (d, $J = 8.4$, 1H, Ar-H), 8.113 (d, $J = 8.4$, 1H, Ar-H), 9.879 (s, 1H, $-\text{N}=\text{CH}$), 11.238 (br-s, 1H, $-\text{N}^+\text{H}$); ^{13}C $\{^1\text{H}\}$ NMR (75.45 MHz; CDCl_3 ; δ): 163.93, 163.61, 163.21, 195.48, 157.93, 134.92, 132.92, 132.34, 118.60, 114.44, 114.27, 110.89, 68.41, 62.32, 44.54, 22.28 and 14.92

The physical properties and the analytical data of the Schiff-base ligand and all the complexes are given in Table 1 while the IR spectral data are presented in Table 3.

Results and Discussion

Properties of the complexes

The analytical data (Table 1) indicates that the Schiff-base ligand (H_2L) reacts with hydrated Ln(III) nitrates to form Ln(III) complexes indicating 1:3 metal to ligand stoichiometry with the general formula $[\text{Ln}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$. The complexes are stable and soluble in chloroform, DMF, THF, and DMSO. The nitrate groups are present both within and outside the coordination sphere; the molar conductance data ($148\text{--}158 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) measured in 0.001M DMF solution at room temperature imply 2:1 electrolytic nature [22] of the complexes.

Table 1: Analytical data and general behavior of the Ln(III) complexes of H_2L

$\text{H}_2\text{L}/\text{complex}$ formula weight (empirical formula)	Colour, Yield % (Solubility)	m.p. (°C)		Found (Calcd.)%				μ_{eff} (B.M.) ^d	Λ_m^e
		Isotropic point	Hazy phase (meso)	C	H	N	M		
H_2L , 1031.45 ($\text{C}_{65}\text{H}_{94}\text{N}_2\text{O}_8$)	Light Yellow, 70% ^a	220	170-220	74.59 (75.69)	9.21 (9.19)	2.66 (2.72)	-	-	-
$[\text{La}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$ 3419.27 ($\text{LaC}_{195}\text{H}_{282}\text{N}_9\text{O}_{33}$)	Yellow, 74% ^b	244 ^c	-	68.28 (68.50)	8.22 (8.31)	3.82 (3.69)	4.12 (4.06)	diamag.	148
$[\text{Pr}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$ 3421.28 ($\text{PrC}_{195}\text{H}_{282}\text{N}_9\text{O}_{33}$)	Yellow, 76% ^b	242 ^c	-	68.20 (68.46)	8.48 (8.30)	3.60 (3.68)	4.30 (4.12)	3.56	158
$[\text{Nd}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$ 3424.61 ($\text{NdC}_{195}\text{H}_{282}\text{N}_9\text{O}_{33}$)	Yellow, 70% ^b	240 ^c	-	68.10 (68.39)	8.47 (8.30)	3.68 (3.68)	4.38 (4.21)	3.59	154
$[\text{Sm}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$ 3430.73 ($\text{SmC}_{195}\text{H}_{282}\text{N}_9\text{O}_{33}$)	Yellow, 72% ^b	243 ^c	-	67.98 (68.27)	8.26 (8.29)	3.64 (3.67)	4.45 (4.38)	2.56	156
$[\text{Gd}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$ 3437.62 ($\text{GdC}_{195}\text{H}_{282}\text{N}_9\text{O}_{33}$)	Yellow, 70% ^b	246	178-246	67.86 (68.13)	8.32 (8.27)	3.72 (3.67)	4.53 (4.57)	8.16	157
$[\text{Dy}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$ 3442.87 ($\text{DyC}_{195}\text{H}_{282}\text{N}_9\text{O}_{33}$)	Yellow, 68% ^b	250 ^c	-	67.91 (68.03)	8.18 (8.26)	3.58 (3.66)	4.84 (4.72)	10.56	152

^aSolvents: benzene, dichloromethane, chloroform, DMF, THF, DMSO; ^bSolvents: chloroform, THF, DMSO; ^cDecomposed; ^dRoom temperature magnetic moments (B.M.) measured on Faraday balance; ^eThe values of molar conductance (Λ_m), in units of $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, pertain to 0.001 M solutions in DMF measured at room temperature

Magnetic and electronic spectral studies

The magnetic moments (μ_{eff} values at room temperature) of the Ln(III) complexes (3.56, 3.59,

2.56, 8.16 and 10.56 B.M. for Ln = Pr, Nd, Sm, Gd, and Dy respectively) are little deviating from the reported Van Vleck values [23] indicating little participation of

the $4f$ -electrons in bond formation. The slightly higher value obtained in the case of the Sm(III) complex may be attributed to temperature-dependent magnetism on account of low J -separation [24].

Table 2: Electronic spectral data of the selected metal complexes of H_2L

Pr(III)			Nd(III)		
Transitions/ bonding parameters	λ_{\max} (cm ⁻¹) aq. ion	λ_{\max} (cm ⁻¹) complex	Transitions/ bonding parameters	λ_{\max} (cm ⁻¹) aq. ion	λ_{\max} (cm ⁻¹) complex
$^1G_4 \leftarrow ^3H_4$	9900	9834	$^4F_{3/2} \leftarrow ^4I_{9/2}$	11450	11285
$^1D_2 \leftarrow$	16850*	16666	$^4F_{5/2} \leftarrow ^2H_{9/2}$	12500	12474
$^3P_0 \leftarrow$	20800	20430	$^4S_{3/2} \leftarrow ^4F_{7/2}$	13500	13398
			$^4F_{9/2} \leftarrow$	14800	14582
			$^2G_{7/2} \leftarrow$	17400*	17252
			$^4G_{9/2} \leftarrow$	19500	19530
β		0.988			0.993
$b^{1/2}$		0.078			0.059
$\% \delta$		1.215			0.701
η		0.006			0.003
Sm(III)			Dy(III)		
$^6F_{9/2} \leftarrow ^6H_{5/2}$	9200	9160	$^6H_{3/2} \leftarrow ^6H_{15/2}$	10200	10000
$^6F_{11/2} \leftarrow$	10500	10491	$^6F_{5/2} \leftarrow$	12400	12380
$^4G_{5/2} \leftarrow$	17900	17876	$^6F_{3/2} \leftarrow$	13200	13125
$^4M_{15/2} \leftarrow$	20800	20770	$^4F_{7/2} \leftarrow$	25800	25775
$^6P_{7/2} \leftarrow$	26750*	26468			
β		0.997			0.993
$b^{1/2}$		0.039			0.059
$\% \delta$		0.301			0.701
η		0.001			0.003

*Hypersensitive band

We have recorded the electronic spectra (qualitative solution-state spectra from 200 to 1100 nm) of only the Pr(III), Nd(III), Sm(III) and Dy(III) (Table 2) in view of their ability to show hypersensitive bands making it especially suitable for probing the coordination environment around the metal ions; however, no such spectral profile correlation could satisfactorily be made for the present complexes. The hypersensitive bands are particularly susceptible to splitting and intensity changes [25]. Results reveal that the present complexes show a considerable red shift in the λ_{\max} values in comparison with those of their corresponding aquo ions [26]. These red shifts are presumably due to the nephelauxetic effect [27] and

are regarded as a measure of covalency of the bonding between the metal ions and the ligands. Various bonding parameters (Table 2), viz., Nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's parameter ($\% \delta$) and covalency angular overlap parameter (η), calculated by the procedures as reported in the literature [28], suggest weak covalent nature of the metal-ligand bonds.

IR spectral studies

The prominent infrared spectral data of the Schiff-base (H_2L) and its Ln^{III} complexes are presented in Table 3.

Assignments regarding bonding through specific functional groups have been made by a careful comparison of specific vibrational bands of H_2L with the corresponding bands of the metal complexes. The broad absorption at 3445 cm⁻¹ in the IR spectrum of the ligand, characteristic of $\nu(O-H)$ phenolic [29], involves considerable H-bonding (to the ortho $>C=N$ group presumably of intramolecular type) under the experimental conditions; this band disappears in spectra of the complexes due to shifting of the phenolic proton to the azomethine nitrogen, resulting in the formation of the zwitterion. Weak/medium intensity bands centered at 1167 cm⁻¹ are assigned to $\nu(C-O)$ phenolic. The strong band at 1628 cm⁻¹, assignable to $\nu(C=N)$ of azomethine [30], undergoes a hypsochromic shift in all the complexes on account of zwitterion formation.

Thus, complexation to Ln^{III} results in the migration of phenolic protons onto the two uncoordinated imino nitrogen atoms, which then are intramolecularly hydrogen-bonded to metal-bound phenolate oxygen atoms to give the zwitterionic structure, N⁺-H.....O-. Binnemans *et al.* [31] reported similar zwitterionic behavior for acyclic Schiff-base lanthanide complexes. The formation of a zwitterion can be rationalized by the tendency of lanthanides to coordinate to negatively charged ligands with a preference for O-donors by transfer of the phenolic proton to imine nitrogen, the phenolic oxygen becomes negatively charged facilitating coordination to lanthanide. Further evidence was given by the band frequencies of $\nu(C=N)$ shifting to higher wavenumbers upon complexation, implying the presence of the C-N⁺ [32] and the non-involvement of nitrogen in complex

Table 3: The important infrared frequencies (in cm^{-1}) of H_2L and its Ln(III) complexes ^a

$\text{H}_2\text{L}/\text{Complexes}$	$\nu(\text{O-H})$ phenol	ν (N^+H)	$\nu(\text{C=O})$ esteric	$\nu(\text{C=N})$	$\nu(\text{C-O})$ phenolic	$\nu(\text{NO}_3)$				
						ν_5	Ionic	ν_1	ν_2	$\nu_5 - \nu_1$
H_2L	3445 b	-	1734 s	1628 s	1167 m	-	-	-	-	-
$[\text{La}(\text{LH}_2)_3(\text{NO}_3)_2]$	-	3196w	1731	1657	1156	1472	1386	1251	844	221
$[\text{Pr}(\text{LH}_2)_3(\text{NO}_3)_2]$	-	3184	1733	1656	1153	1469	1382	1251	842	218
$[\text{Nd}(\text{LH}_2)_3(\text{NO}_3)_2]$	-	3188	1734	1655	1154	1464	1377	1251	839	213
$[\text{Sm}(\text{LH}_2)_3(\text{NO}_3)_2]$	-	3190	1733	1654	1152	1467	1383	1255	845	212
$[\text{Gd}(\text{LH}_2)_3(\text{NO}_3)_2]$	-	3178	1734	1652	1149	1469	1374	1253	842	216
$[\text{Dy}(\text{LH}_2)_3(\text{NO}_3)_2]$	-	3175	1732	1653	1142	1472	1384	1253	840	219

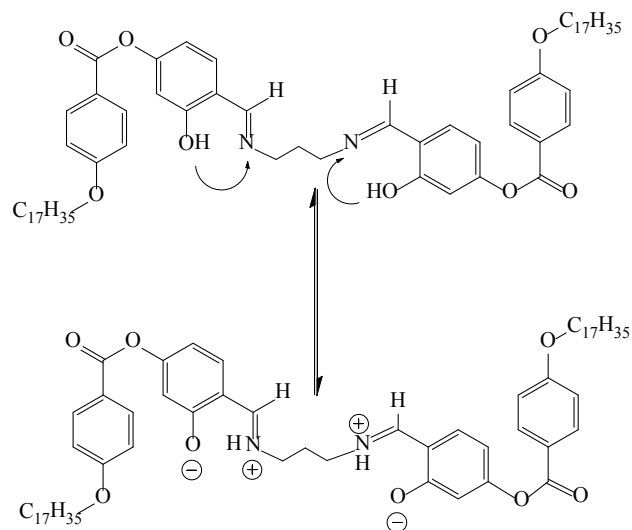
^aSpectra recorded as KBr pellets; b: broad; s: sharp; m: medium

formation. The present complexes are characterized by a strong band due to $\nu(\text{C=N})$ at $1657(2) \text{ cm}^{-1}$ and a weak broad band at $3196(75) \text{ cm}^{-1}$ due to hydrogen-bonded $\text{N}^+\text{H}\cdots\text{O}^-$ vibration of the protonated imine [32]. Thus, the ligand coordinates to the metal via the negatively charged phenolic oxygen with no binding between lanthanide and the imine nitrogen. IR spectra of the complexes also show three additional characteristic frequencies of coordinating nitrate (C_{2v}) at $1472\text{--}1464$, $1255\text{--}1251$, and $845\text{--}839 \text{ cm}^{-1}$ [33]. The profile and magnitude of separation of the modes associated with asymmetric nitrate vibrations have been used as criteria to distinguish between mono- and bidentate chelating nitrates; accordingly, the magnitude of splitting ($221\text{--}212 \text{ cm}^{-1}$) at higher energies indicates a bidentate coordinated nitrate [33,34]. Additional bands at $1386\text{--}1374 \text{ cm}^{-1}$ may be attributed to non-coordinated or ionic nitrate present outside the coordination sphere [30].

¹H and ¹³C NMR spectral studies

A comparison of the NMR spectral data [¹H and ¹³C{¹H}] of the ligand, with that of La(III) complex, shows: (i) the phenolic-OH signal, appearing at δ , 13.504 in the former, disappears upon complexation and (ii) phenolic protons of the coordinated ligand are shifted to the two imine nitrogens, which then get intramolecularly hydrogen-bonded to the metal-bound phenolate oxygens to give rise to the zwitterionic structure ($=\text{N}^+\text{H}\cdots\text{O}^-$). The macrocycle under this condition is designated as LH_2 [35].

The signal corresponding to the imine hydrogen, $-\text{CH}=\text{N}$, broadened in the La(III) complex (δ , 9.879) when compared with that of the ligand (δ ,



Scheme 2: Depiction of migration of phenolic protons to imine nitrogens of the ligand, H_2L , during the formation of zwitter ion

8.359); further, a new signal, characteristic of $-\text{N}^+\text{H}$ resonance, appears in the spectrum of the complex at 11.238δ which is not shown by the parent ligand. These observations are in accordance with those made by Binnemans *et al.* [36], who, while reporting their work on rare-earth containing magnetic liquid crystals of the formula, $[\text{Ln}(\text{LH})_3(\text{NO}_3)_3]$, where LH =4-alkoxy-*N*-alkyl-2-hydroxy benzaldimine, found that selective irradiation of the signal at 12.29δ removed the broadening of the imine signal, thereby inferring that the signal does not correspond to the proton of the $-\text{OH}$ group, but to the proton of the $-\text{N}^+\text{H}$ group. Thus, it may be confirmed that the present Schiff-base (H_2L) exists in the metal complex in a zwitterionic form, with the phenolic oxygen deprotonated and the imine nitrogen protonated (Scheme 2).

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show a significant shift of the $-\text{NCH}$ signal from δ , 162.60 (in the case of H_2L) to δ , 195.48 (in the case of the La^{III} complex). Similar shifts were observed in the case of the carbon atoms directly attached to the bonding atoms (phenolate carbons) while those for the other carbons were of lesser magnitude. The effect of coordination is to strongly influence the carbon shifts particularly of those groups which directly interact with the metal ion [37]. Thus, the NMR spectral data imply bonding only through the two phenolate oxygens of the ligand in the zwitterionic form to $\text{La}(\text{III})$ metal ion. On the basis of the IR, NMR and electronic spectral data it may be proposed that the Schiff-base, N,N' -di-4-(4'-heptadecyloxybenzoate)salicylidene-1'',3''-diaminopropane (H_2L) coordinates to $\text{Ln}(\text{III})$ as a neutral bi-dentate species to yield eight-coordinate complexes of the general formula, $[\text{Ln}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$, where $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$ and Dy , the metal-centered polyhedron being possibly distorted square antiprism (Figure 1).

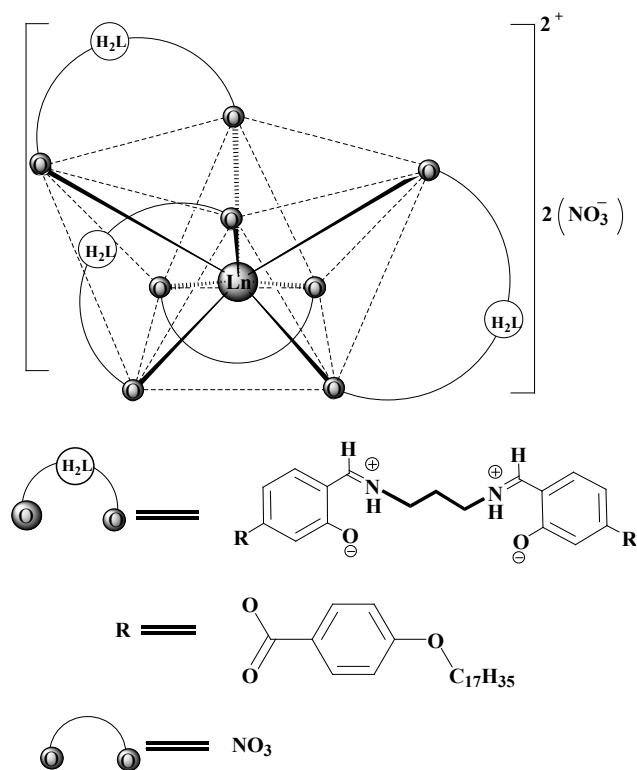


Figure 1: Proposed polyhedron (distorted square antiprismatic) for $[\text{Ln}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$, $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$ and Dy

Mesogenic studies

The mesophases were identified by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) techniques. The corresponding transition temperatures and enthalpy changes are given in Table 4 while the textures are shown in Figure 2. The POM studies imply the nematic phase of H_2L (Figure 2a & b) that exhibits the typical schlieren-texture with two and four brushes or a marbled texture [38].

Table 4: Transition temperatures and enthalpy changes of H_2L and of the $\text{Gd}(\text{III})$ complex

Ligand	Transition ^a	$T^b/^\circ\text{C}$	$\Delta H^b/\text{kJ mol}^{-1}$
H_2L	Cr - N	175.42	3.61
	N - I	211.30	22.97
	I - Cr	192.66	14.81
$[\text{Gd}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$	Cr - Cr	153.37	13.16
	Cr - SmB	174.81	33.55
	SmB - N	229.64	13.41
	N - N	216.04	1.63

^aCr: Crystal, N: Nematic, I: Isotropic liquid, SmB: Smectic B, ^bData as obtained from the first DSC cycle

The nematic liquid crystal phase is characterized by molecules that have no positional order but they tend to point in the same direction. The DSC-thermal data show nematic-isotropic transition of the ligand at 211.30 $^\circ\text{C}$ ($\Delta H = 22.97 \text{ kJ mol}^{-1}$) and isotropic-crystal transition at 192.66 $^\circ\text{C}$ ($\Delta H = 14.81 \text{ kJ mol}^{-1}$) (Table 4).

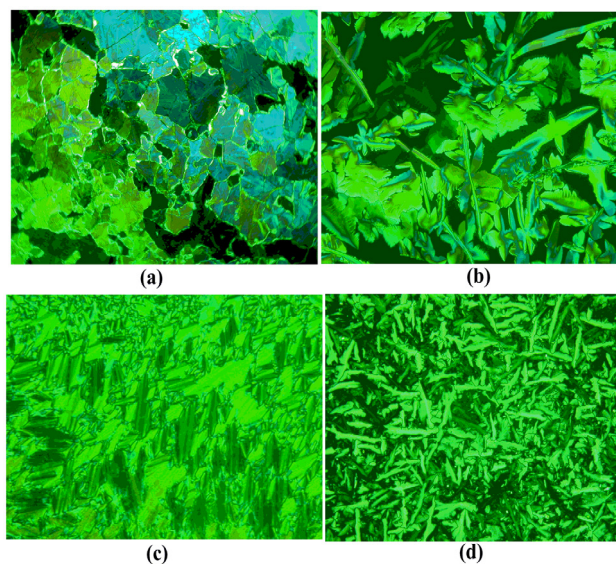


Figure 2: Optical textures of H_2L : (a) Nematic (N) & (b) Nematic (N); and $[\text{Gd}(\text{LH}_2)_3\text{NO}_3](\text{NO}_3)_2$ complex: (c) Smectic B (Sm_B) & (d) Nematic (N)

The mesophase behaviour of the Schiff-base ligand was changed by complex formation with rare-earth metals. Among the Ln(III) complexes, only that of Gd(III) complex exhibits smectic B and nematic phases. The complex also exhibits crystal-crystal transition at 153.37 °C ($\Delta H = 13.16 \text{ kJ mol}^{-1}$) and nematic-nematic transition at 216.04 °C ($\Delta H = 1.63 \text{ kJ mol}^{-1}$). All other Ln(III) complexes under investigation decompose without clearing (between 220 and 250 °C). In a smectic-B phase, the molecules orient with the director perpendicular to the smectic plane, but the molecules are arranged such that the bonds they make with their nearest in-plane neighbors exhibit a sixfold (hexagonal) orientational order [39].

Conclusion

The mesogenic Schiff-base, *N,N'*-di-4-(4'-heptadecyloxybenzoate)salicylidene-1,3-diaminopropane, (H_2L) that exhibits liquid crystalline property (nematic phases), coordinates to Ln(III) as a neutral bi-dentate species to yield eight-coordinate complexes (the polyhedron being possibly distorted square antiprism) of the general formula, $[La(LH_2)_3NO_3](NO_3)_2$, where Ln = La, Pr, Nd, Sm, Gd, and Dy. In all cases, the zwitterionic-species of the neutral bi-dentate ligand, H_2L , coordinates to the Ln(III) metal ion through two phenolate oxygens. Among the Ln(III) complexes, the POM and DSC studies reveal mesomorphism in the Gd(III) complex only.

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