

Ligational Aspects of Some 4f Metal Complexes of a Mesogenic Schiffbase, N,N'-di-(4-dodecyloxysalicylidene)-1',3'-Diaminopropane: Synthesis and Spectral Studies

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Abstract

A liquid crystalline (smectic-F and smectic-A phases) Schiff base, N,N'-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane (abbreviated as H₂L) and a series of lanthanide(III) complexes of the type [Ln₂(LH₂)₃(NO₃)₄](NO₃)₂ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho) have been synthesized and characterized by elemental analysis, mass spectrometry, FTIR, and UV-Vis spectral techniques. The IR spectral data imply a bidentate chelation of the Schiff base in its zwitterionic form (as LH₂) to the Ln^{III} ions through two phenolate oxygens, rendering the overall geometry of the complexes possibly to distorted mono-capped octahedra. The optical and thermal behavior studies (POM & DSC techniques) reveal that despite H₂L being mesogenic, none of the Ln^{III} complexes synthesized under this study exhibits mesomorphism. Fluorescence studies show emissions of H₂L and Sm^{III} complex.

Keywords: Mesogenic Schiffbase; Zwitterionic-coordination; Ln^{III} complexes; Fluorescence; Mono-capped octahedron

Introduction

Metallomesogens are formed by coordination of mesogenic organic ligands with metal ions, where the presence of the metal ion can produce different assembly structures, leading to interesting liquid crystalline properties [1-2]. The ability of different metal ions to arrange the coordinating ligands in a number of different orientations around the central metal ion in its complexes is the reason for the development of different assembly structures [3-4]. Ligands derived from substituted salicylaldimine play an important role in presenting the preferred co-ordination geometries of metal complexes. Multidentate ligands are extensively used in coordination chemistry, since they can be applied in the construction of new frameworks with interesting properties [5-6]. Majority of the metallomesogens

are those complexes derived from salicylaldimine Schiff bases [7-8]. The particular advantage of the salicylaldimine ligand system in the synthesis of metallomesogen is the considerable flexibility of 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 [9].

The potential applications of mesogenic Schiff base liquid crystals as non-linear optical and/or optical storage materials have drawn research interest towards the synthesis and structural investigations of liquid crystalline materials [10-11]. Of the metallomesogens, thermotropic liquid crystals have assumed great technological importance owing to their specific applications as advanced functional materials [9-12]. The design of novel thermotropic LCs involves

suitable selection of a core fragment, linking group, and terminal functionality. One of the most unusual and intriguing properties of metal-containing liquid crystals, so called metallomesogens [5-13], is the presence of magnetic moment which determines the behavior of the liquid crystals in a magnetic field. It is well known that magnetic moments and especially magnetic anisotropy are inherent properties of *f*-block metal complexes [14].

The design of lanthanide-containing liquid crystals is rather difficult because their high coordination numbers seem to be incompatible with the structural anisotropy [15] that is necessary to exhibit liquid crystalline behaviour. However, Galyametdinov and his co-workers synthesized the calamitic lanthanide containing liquid crystal [16] for the first time in 1991 following the discovery of the first columnar liquid crystalline lanthanide complex in 1985 by Piechocki *et. al.*, [17]. Nitrate is often chosen to be the counter-ion which can not only coordinate in a bi-dentate fashion but also allow the lanthanide ion to easily obtain a high coordination number. As a part of our further investigation on systematic structural and spectral studies of 3*d* and 4*f* metal complexes of a series of Schiff bases [18-24], we now report here synthesis and spectral studies of a mesogenic Schiff base, *N,N'*-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane (H_2L) and its Ln^{III} complexes. In this study, none of the Ln^{III} complexes synthesized except the ligand, H_2L exhibits liquid crystalline property.

Experimental

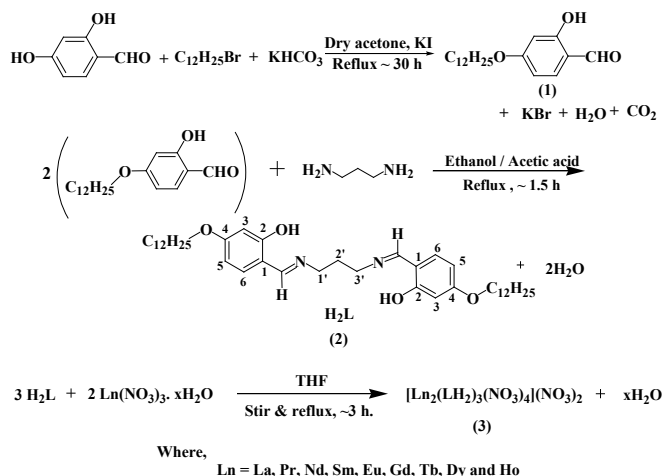
Starting materials

All the reagents and chemicals of analytical grade (AR) were directly imported from commercial sources and used without further purification: 1-bromododecane, 2,4-dihydroxybenzaldehyde and 1,3-diaminopropane are from Sigma-Aldrich, USA; all the $Ln(NO_3)_3 \cdot xH_2O$ salts are from Indian Rare Earths Ltd. and KI and $KHCO_3$ are from Merck. The organic solvents obtained from commercial vendors were dried using standard methods when required [25].

Synthesis

The synthesis of *N,N'*-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane (H_2L), **2**, was achieved by

proceeding through two major steps, *viz.*, alkylation of 2,4-dihydroxybenzaldehyde with 1-bromododecane, followed by Schiff base formation [21-26]. All the experimental details are given in Scheme 1. The Ln^{III} complexes, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$ ($Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy$ and Ho), **3**, were prepared by reacting together the appropriate metal nitrate $[Ln(NO_3)_3 \cdot xH_2O]$ and the ligand, H_2L at room temperature.



Scheme 1. Reaction steps involved in the synthesis of 4-dodecyloxysalicylaldehyde, **1**; *N,N'*-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane, **2**, (H_2L) and Ln^{III} complexes, **3**.

Preparation of 4-dodecyloxysalicylaldehyde, 1

To a solution of 100 mL of dry acetone, equimolar amounts of 2,4-dihydroxy benzaldehyde (50 mmol, 6.91 g), 1-bromododecane (50 mmol, 12.0 mL) and potassium bicarbonate (~55 mmol, 5.51 g) were added. The mixture was refluxed for ~30 h in presence of KI (0.1 to 0.2 g) as a catalyst and filtered while hot to remove insoluble solids. 6N HCl was added to the filtrate until the point of neutralization and the product was then extracted twice with $CHCl_3$ (100 mL portions). The chloroform extracts were concentrated to obtain a straw-yellow solid which was purified by column chromatography over SiO_2 eluting first with n-hexane and then with a mixture of n-hexane and chloroform (v/v, 1/1); evaporation of this purified extract finally yielded 4-dodecyloxysalicylaldehyde in the form of a white solid; yield: 72% (11.03 g).

Synthesis of *N,N'*-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane, **2**

The ligand, *N,N'*-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane, was prepared by refluxing absolute ethanolic solutions of 4-dodecyloxysalicylaldehyde, **1**, (30 mmol, 9.19 g in 50 mL) and 1,3-diaminopropane (15 mmol, 1.11 g in 15 mL) for ~1.5 h in presence of few drops of glacial acetic acid. The resulting mixture was left over night; yellow-colored product, **2**, thus obtained was filtered off under suction, thoroughly washed with cold ethanol and dried at room temperature; yield: 76% (7.43 g) as yellow-colored solid; m.p. 105 °C; Anal. Calcd for C₄₁H₆₆N₂O₄ (650.97) (%): C, 75.65; H, 10.22; N, 4.30. Found: C, 75.55; H, 10.13; N, 4.35. IR (cm⁻¹, KBr disk): 3448 (ν-OH), 1619 (ν-C=N), 1286 (ν-C_{ph}-O).

Synthesis of La^{III} complex, [La₂(LH₂)₃(NO₃)₄](NO₃)₂, **3**

The La^{III} complex was prepared by adding drop-wise THF solution of La(NO₃)₃·6H₂O (0.87 g, 2.0 mmol in 20 mL) to a THF solution of the ligand, H₂L (1.95 g, 3.0 mmol in 30 mL) under magnetic stirring. The resultant mixture was stirred and refluxed continuously for ~3 h, after which it was reduced to a minimum volume on rotary evaporator. Then, addition of acetonitrile followed by magnetic stirring of the mixture for sometime resulted in the formation of yellow precipitate. The solid product thus obtained in each case was filtered, washed with cold methanol and dried over fused CaCl₂ in a desiccator; yield: 75% (1.95 g) as yellow-colored solid; m.p. 234°C (decompose); Anal. calcd for La₂C₁₂₃H₁₉₈N₁₂O₃₀ (2602.76) (%): C, 56.76; H, 7.67; N, 6.46; La, 10.67. Found: C, 56.02; H, 7.69; N, 6.50; La, 10.71. IR (cm⁻¹, KBr disk): 3199 (ν-N⁺H), 1652 (ν-C=N), 1229 (ν-C_{ph}-O).

All the other rare-earth complexes (Ln= Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho) were synthesized in an analogous way by using the appropriate hydrated salt of Ln^{III} nitrate; the physical properties and the analytical data of all the complexes are given in Table 1.

Physical Measurements

The metal contents of the complexes were determined by complexometric titrations against EDTA using xylenol orange as an indicator. C, H and N were analyzed on an Exeter Analyzer, Model CE-440 CHN. Infrared spectra were recorded on a Bruker IFS66 FTIR spectrometer within the 4000–400 cm⁻¹ region using KBr pellets. Mass spectra were recorded on JEOL SX-102 FAB mass spectrometer. UV–vis spectra were recorded on Shimadzu spectrophotometer, model Pharmaspec-UV 1700. 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 made at room temperature on a Cahn–Faraday balance using Hg[Co(NCS)₄] as the calibrant. Mesophases were identified by the textures observed by using an Olympus BX60 polarizing microscope equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller. Differential Scanning Calorimetry studies were made on a Mettler-Toledo DSC822e module (scan rate 10 °C min⁻¹ under a helium flow, aluminum cups). Fluorescence measurements were made in solution state (mixed solvent of CHCl₃/DMSO; 3:1, v/v) on a Perkin Elmer LS-45 luminescence spectrometer with a 10 nm slit width on both excitation and emission.

Results and Discussion

Properties of the complexes

The analytical data and general behavior of the Ln^{III} complexes of H₂L are presented in Table 1.

The analytical data (Table 1) of the complexes indicate 2:3 metal to ligand stoichiometry with the general formula [Ln₂(LH₂)₃(NO₃)₄](NO₃)₂. The nitrate groups are present both within and outside the coordination sphere; the molar conductance data (156–165 ohm⁻¹cm²mol⁻¹) measured in 0.001M DMF solution imply 2:1 electrolytic nature of the complexes [27].

FAB-mass spectral study of the ligand, H₂L

The structure of the Schiff base ligand was confirmed by FAB mass spectrum in addition to the spectral evidences of IR spectroscopy to be discussed later. The

Table 1. General and analytical data of H₂L and of Ln(III) complexes.

H ₂ L/complex formula weight (empirical formula)	Colour, Yield % (Solubility)	m.p.(°C)		Found (Calcd.)%				μ_{eff} (BM) ^d (vanVleck values)	Λ_m^e
		Isotropic point	Hazy phase (meso)	C	H	N	M		
H ₂ L, 650.97 (C ₄₁ H ₆₆ N ₂ O ₄)	Yellow, 76% ^a	105	70-105	75.55 (75.65)	10.13 (10.22)	4.35 (4.30)	-	-	-
[La ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2602.76 (La ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Light Yellow, 75% ^b	234 ^c	-	56.62 (56.76)	7.69 (7.67)	6.50 (6.46)	10.71 (10.67)	Diamag.	162
[Pr ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2606.77 (Pr ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Light Yellow, 74% ^b	232 ^c	-	56.60 (56.62)	7.63 (7.60)	6.40 (6.45)	10.88 (10.81)	2.32 (3.40-3.60)	164
[Nd ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2613.43 (Nd ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Light Yellow, 72% ^b	236 ^c	-	56.59 (56.53)	7.60 (7.64)	6.37 (6.43)	11.12 (11.04)	3.07 (3.50-3.60)	158
[Sm ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2625.67(Sm ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Cream, 72% ^b	240 ^c	-	56.32 (56.26)	7.54 (7.60)	6.36 (6.40)	11.51 (11.45)	1.31 (1.50-1.60)	161
[Eu ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2628.88 (Eu ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Light Yellow, 74% ^b	243 ^c	-	56.12 (56.20)	7.56 (7.59)	6.45 (6.39)	11.60 (11.56)	1.89 (3.40-3.60)	163
[Gd ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2639.45(Gd ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Cream, 70% ^b	245 ^c	-	55.89 (55.97)	7.60 (7.56)	6.32 (6.37)	11.86 (11.92)	5.54 (7.80-8.00)	162
[Tb ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2642.80 (Tb ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Light Yellow 74% ^b	245 ^c	-	55.96 (55.90)	7.61 (7.55)	6.30 (6.36)	12.00 (12.03)	7.98 (9.40-9.60)	165
[Dy ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2649.95 (Dy ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Cream 72% ^b	247 ^c	-	55.68 (55.75)	7.47 (7.53)	6.32 (6.34)	12.32 (12.26)	8.78 (10.40-10.50)	156
[Ho ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂ 2654.81 (Ho ₂ C ₁₂₃ H ₁₉₈ N ₁₂ O ₃₀)	Light Yellow 73% ^b	248 ^c	-	55.70 (55.65)	7.59 (7.52)	6.39 (6.33)	12.48 (12.43)	9.92 (10.30-10.50)	160

^aSolvents: benzene, dichloromethane, chloroform, DMF, THF, DMSO; ^bSolvents: chloroform, THF, DMF, DMSO; ^cDecomposed; ^dRoom temperature magnetic moments (B.M.) measured on Faraday balance; ^eThe values of molar conductance (Λ_m), in units of ohm⁻¹cm²mol⁻¹, pertain to 0.001 M solutions in DMF measured at room temperature

mass spectral features of H₂L were characterized by the molecular ion peak as well as base peak corresponding to the *m/e* value of 650, which matches with the molecular weight of 650.97 of H₂L of the molecular formula, C₄₁H₆₆N₂O₄. The 100% intensity of the molecular ion peak as the base peak is as expected for the molecule on the basis of its predominant aromatic character; the major fragment peaks (*m/e*= 346, 178)

are due to C₁₂H₂₅OC₆H₃(OH)CH=N(CH₂)₂CH₂⁺ and HOC₆H₃(OH)CH=N(CH₂)₂CH₂⁺ species respectively.

IR Spectral Studies

The important infrared spectral data of H₂L and its Ln^{III} complexes are presented in Table 2.

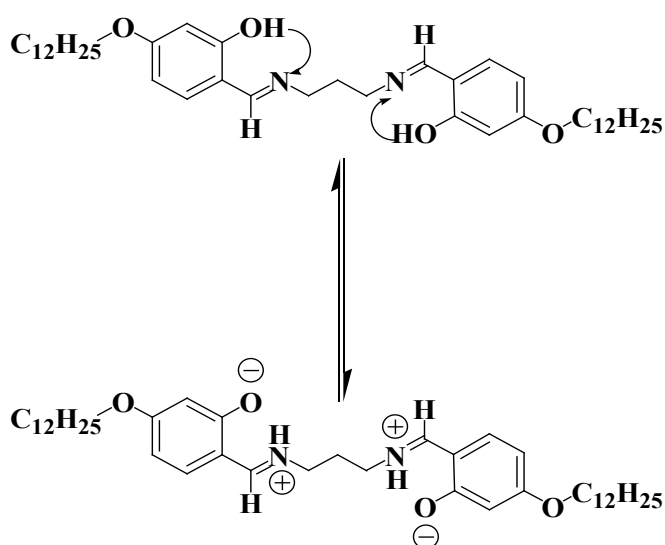
The broad peak centered on 3448 cm⁻¹ in the IR spectrum of the ligand and characteristic of ν (O–H)

Table 2. IR Spectral data* (cm⁻¹) of H₂L and of Ln^{III}metal complexes

H ₂ L/Complexes	ν (O–H) <i>phenol</i>	ν (N ⁺ H)	ν (C=N)	ν (C–O) <i>phenolic</i>	ν (NO ₃)				
					ν_s	Ionic	ν_1	ν_2	$\nu_s - \nu_1$
H ₂ L	3448 b	-	1619 s	1286 m	-	-	-	-	-
[La ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3199w	1652	1229	1472	1383	1290	846	182
[Pr ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3182	1649	1225	1472	1382	1289	844	183
[Nd ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3188	1649	1227	1473	1379	1289	845	184
[Sm ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3190	1649	1229	1472	1383	1290	845	182
[Eu ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3178	1652	1229	1472	1382	1291	842	181
[Gd ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3175	1653	1229	1468	1378	1288	844	180
[Tb ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3173	1653	1229	1472	1378	1288	845	184
[Dy ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3191	1652	1229	1472	1382	1291	846	181
[Ho ₂ (LH ₂) ₃ (NO ₃) ₄](NO ₃) ₂	-	3193	1652	1229	1470	1379	1289	846	181

* Spectra recorded as KBr pellets; b: broad; w: weak; s: sharp; m:medium

[28, 29], totally disappears in the spectra of the complexes due to shifting of the phenolic proton to the azomethine nitrogen atom resulting in the formation of zwitter ion (Scheme 2). The weak/medium intensity band centered on 1286 cm^{-1} is assignable to $\nu(\text{C}-\text{O})_{\text{phenolic}}$ [30]. The strong intensity band occurring at 1619 cm^{-1} , assignable²⁷ to $\nu(\text{C}=\text{N})$ absorption of the azomethine moiety, undergoes a hypsochromic shift in all the complexes on account of zwitter-ion formation. Thus, the complexation to the Ln^{III} ion results in migration of the phenolic protons onto the two uncoordinated imino nitrogens (Scheme 2), which then get intramolecularly hydrogen-bonded to the metal-bound phenolate oxygens to give rise to the zwitterionic structure, $\text{N}^+-\text{H}\cdots\text{O}^-$ [31].



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

The shift to higher wave numbers upon complexation implies the presence of $\text{C}-\text{N}^+$ group [32], and the non-involvement of nitrogen atom in complex formation. Further, all the present complexes are characterized by a strong band due to $\nu(\text{C}=\text{N})$ at $1653\text{--}1649\text{ cm}^{-1}$ and a weak broad band at about $3199\text{--}3173\text{ cm}^{-1}$ due to the hydrogen-bonded $\text{N}^+-\text{H}\cdots\text{O}^-$ vibration of the protonated imine [33]. Thus, the ligand may be considered to coordinate to the metal ion via the negatively charged phenolic oxygen while no binding occurs between the lanthanide ion and the imine nitrogen. The Ln^{III} complexes also exhibit three additional bands around $1473\text{--}1468$, $1291\text{--}1288$ and $846\text{--}842\text{ cm}^{-1}$, which can be assigned to the vibrational

modes of the coordinated (C_{2v}) nitrate groups [34]. The profile and magnitude of separation of the modes associated with asymmetric nitrate vibrations have been used as a criterion to distinguish between mono- and bidentate chelating nitrates. Accordingly, the magnitude of splitting, $184\text{--}180\text{ cm}^{-1}$, at higher energies may be indicative of a bidentate interaction of the coordinated nitrate anions with the lanthanide ions [34-35]. The additional bands observed at $1383\text{--}1378\text{ cm}^{-1}$ may be attributed to the non-coordinated nitrate groups of the complexes.

Magnetic and electronic spectral studies

The room temperature μ_{eff} values (Table 1) of all the Ln^{III} complexes (2.32, 3.07, 1.31, 1.89, 5.54, 7.98, 8.78 and 9.92 BM for $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy},$ and Ho respectively) in the present study have been found to be lower than the reported van Vleck values presumably on account of metal-metal interactions [36-39].

The recorded electronic spectra (qualitative solution-state spectra from 200 to 1100 nm) of only the $\text{Pr}^{\text{III}}, \text{Nd}^{\text{III}}, \text{Sm}^{\text{III}}$ and Dy^{III} (Table 3) were 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 [40]. 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 [41]. These red shifts are presumably due to the nephelauxetic effect [42], and are regarded as a measure of covalency of the bonding between the metal ions and the ligands. Various bonding parameters (Table 3), 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 [43-44], suggest weak covalent nature of the metal-ligand bonds.

Table 3. Electronic spectral data of the selected metal complexes of H₂L.

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	9775	$^4F_{3/2} \leftarrow ^4I_{9/2}$	11,450	11,481
$^1D_2^* \leftarrow$	16850*	16,835	$^4F_{5/2} \leftarrow$	12,500	12,484
$^3P_0 \leftarrow$	20800	20,661	$^4S_{3/2} \leftarrow ^4F_{7/2} \leftarrow$	1,3500	12,423
			$^4F_{9/2} \leftarrow$	14,800	14,684
			$^2H_{11/2} \leftarrow$	15,900	15,949
			$^2G_{7/2}^* \leftarrow$	17,400*	17,094
			$^4G_{7/2} \leftarrow$	19,100	19,011
			$^4G_{9/2} \leftarrow$	19,500	19,531
β		0.993			0.996
$b^{1/2}$		0.059			0.045
% δ		0.705			0.402
η		0.003			0.002
Sm(III)			Dy(III)		
$^6F_{9/2} \leftarrow ^6H_{5/2}$	9200	9174	$^6H_{7/2} \leftarrow ^6H_{15/2}$	9100	-
$^6F_{11/2} \leftarrow$	10,500	9852	$^6F_{9/2} \leftarrow$		
$^4G_{5/2} \leftarrow$	17,900	-	$^6H_{5/2} \leftarrow$	10,200	9756
$^4M_{15/2} \leftarrow$	20,800	20,000	$^6F_{7/2} \leftarrow$	11,000	11,001
$^6P_{7/2}^* \leftarrow$	26,750*	25,907	$^6F_{5/2} \leftarrow$	12,400	12,392
			$^6F_{3/2} \leftarrow$	13,200	13,193
β		0.967			0.989
$b^{1/2}$		0.129			0.074
% δ		03.413			1.112
η		0.017			0.005

*Hypersensitive band

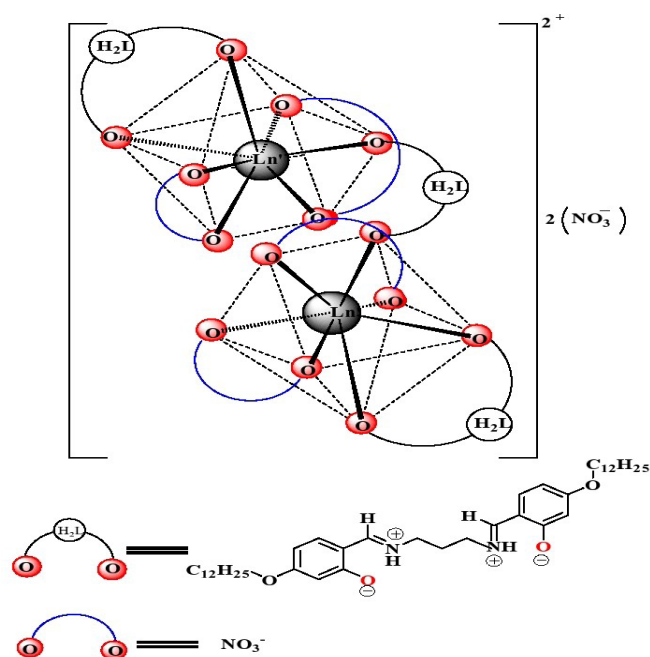


Figure 1. Proposed Polyhedron (Mono-capped Octahedron)

for $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$: $Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy$ and Ho .

On the basis of the IR and electronic spectral data it may be proposed that the mesogenic Schiffbase, *N,N'*-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane (H₂L) coordinates to Ln^{III} as a neutral bi-dentate species to yield seven-coordinate complexes of the general formula, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho, the metal-centered polyhedron being possibly distorted mono-capped octahedron (Fig. 1) [21-26].

Optical and thermal studies

The mesophases were identified by polarized hot-stage microscopy and DSC studies. The POM studies imply smectic-F and smectic-A phases of H₂L; the corresponding transition temperatures, enthalpy and entropy changes are given in Table 4 while the optical texture is shown in Fig. 2.

The present study reveals non-mesomorphism in all the Ln^{III} complexes except the ligand, H₂L. This may

Table 4. Thermodynamic data (transition temperatures, enthalpy and entropy changes).

Ligand	Transition ^a	T ^b (°C)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
H ₂ L	Cr– Sm _F	75.63	7.92	22.72
	Sm _F – Sm _A	93.72	81.40	221.97
	Sm _A – I	101.93	18.09	48.25
	I– Sm _A	100.75	17.85	47.76
	Sm _A – Sm _F	92.41	83.80	229.33
	Sm _F – Cr	70.52	6.82	19.85

^aCr: crystal; SmA: smectic-A; SmF: smectic-F; I: isotropic liquid. ^bData as obtained from the DSC cycle.

be attributed to high thermal energy that is required to melt the alkoxy chains. Under this condition, the layered structure breaks down before the alkoxy chains are completely molten and hence, the liquid-crystalline properties of the materials are also lost [20].

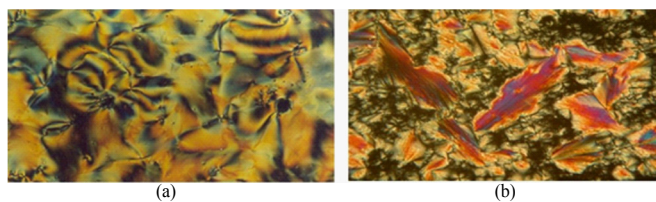


Figure 2. Optical textures of H₂L: (a) Smectic-F (SmF) & (b) Smectic-A (SmA)

Fluorescence studies

Fluorescence emission spectra (with the excitation and emission slit widths of 10.0 nm) recorded in a mixed solvent of CHCl₃/DMSO (3:1 v/v ratio; 1.0 × 10⁻⁴ mol L⁻¹) at room temperature shows an emission band at 435 nm in the case of the ligand, H₂L (Fig. 3a) due to intra-ligand transition. The excitation of the Sm^{III} complex at 386 nm leads to emission of Sm^{III} with four typical emission bands (Fig. 3b) at 468, 560, 598 and 644 nm due to $\pi - \pi^*$ transitions of the ligand and $^4G_{5/2} \rightarrow ^6H_J$ ($J = 5/2, 7/2, 9/2$) transitions [45]. It may be inferred from the above observations that the ligand, H₂L is likely to act as a suitable organic chelator absorbing energy and then transferring some of the absorbed energy to the central Sm^{III} ions, emitting eventually characteristic fluorescence of the Sm^{III} ion.

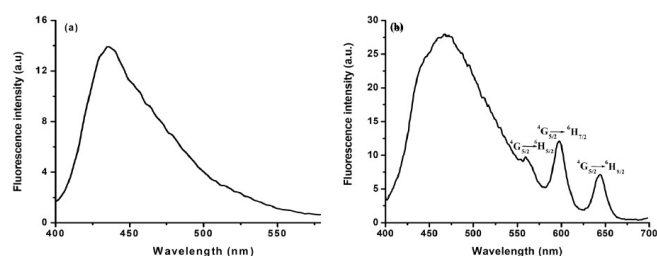


Figure 3. Fluorescence spectra of (a) H₂L and (b) Sm^{III} complex.

Among the emission bands, the band around 598 nm is attributed to the hypersensitive $^4G_{5/2} \rightarrow ^6H_{7/2}$ [46]. The fluorescence of the Sm^{III} complex indicates that the energy level of the triplet state of the ligand, H₂L corresponded to the lowest excited state ($^4G_{5/2}$) level of Sm³⁺ ion. Figure 3(b) also shows that one of the metal centered bands (560 nm) is found to be partially overlapped with the broad band of ligand emission. The well-known intra-molecular energy transfer mechanism shown by lanthanide Schiffbase complexes [47-48], appears to follow between the Schiffbase ligand and the Sm^{III} ion in the present study.

Conclusions

The Schiffbase, *N,N'*-di-(4-dodecyloxysalicylidene)-1',3'-diaminopropane (H₂L), coordinates to Ln^{III} as a neutral bi-dentate species to yield seven-coordinate complexes of the general formula, [Ln₂(LH₂)₃(NO₃)₄](NO₃)₂, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho, the polyhedron being possibly distorted mono-capped octahedron. The zwitterionic-species of the neutral bi-dentate ligand, H₂L, coordinates to the Ln^{III} metal ion through two phenolate oxygens. POM and DSC studies reveal that only H₂L possesses mesogenic property (*SmF* and *SmA*) but none of the Ln^{III} complexes presumably due to breakdown of the structure of the complexes before the isotropic (clear

melting) point. While the fluorescence of the ligand arises due to intra-ligand transition, that of the Sm^{III} complex originates from metal-centered emission.

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