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Scientific paper

Synthesis and Spectral Studies of Some Homo Dinuclear Lanthanide(III) Complexes of a Mesogenic Schiff Base

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Abstract

A mesogenic Schiff base, *N,N'*-di(4-decyloxysalicylidene)-1',8'-diamino-3',6'-dioxaoctane (H_2L) and a series of homo dinuclear lanthanide(III) complexes of the type $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) were synthesized and characterized by elemental analysis, mass spectrometry, FTIR, and NMR spectral techniques. The IR and NMR spectral evidences imply bonding of a neutral bidentate H_2L species through two phenolate oxygen atoms in its zwitterionic form to Ln^{III}, rendering the overall geometry of the complexes as a seven-coordinate polyhedron – possibly distorted mono-capped octahedron. Differential scanning calorimetry (DSC) and polarizing optical microscopic (POM) studies reveal mesogenic properties (smectic-X, smectic-A and nematic mesophases) in the ligand over a wide range of temperature but none mesomorphism in the Ln^{III} complexes synthesized under this study. Luminescence studies exhibit emissions of H_2L and Tb^{III} complex.

Keywords: Mesogenic Schiff base; Ln^{III} Complexes; Zwitterionic-coordination; Mono-capped octahedron; Luminescence

1. Introduction

Lanthanide(III) complexes have received much attention due to their potential scientific applications in design of various luminescent metallomesogens,[1,2] chemosensors,[1,3] and photoluminescence materials and devices.[4] Schiff base ligands having N and/or O donor atoms may assemble coordination architectures in which the Ln^{III} ions can promote Schiff base condensation.[5] Mesomorphisms (an anisotropic liquid) in Schiff base ligands, may be obtained by their careful design in which the molecular order is in between the crystalline and isotropic liquid state.[6] By incorporating Ln^{III} ions into the mesogenic Schiff base, one can obtain useful metallomesogens for the design of emissive LCDs.

The mesogenic properties of the ligands may often be influenced by the nature of coordinated metal ions.[7,8] A metallomesogen has the greater tendency to exhibit intermolecular dative coordination in solid state.[7,9] The design of metallomesogens is rather difficult because of their high coordination numbers incompatible with the structural anisotropy, the basics for showing liquid crystalline behavior.[9] However, the columnar type of Ln^{III} ion containing metallomesogens was first synthesized by Piechocki *et al.*,[10] in 1985 followed by the first calamitic Ln^{III} ion containing metallomesogens by Galyametdinov *et al.*,[11] in 1991. Lanthanide(III) complexes with high coordination number may be obtained by choice of nitrate as the counter-ion because it can coordinate in a bi-dentate fashion. In continuation of our earlier work on metallomesogens,[12-17] we now report here synthesis and spectral studies of a mesogenic Schiff base (having terminal alkoxy chain next to benzene ring) and of some homo dinuclear Ln^{III} complexes.

2. Experimental

2. 1. Starting Materials

All the required reagents of analytical grade (AR) were obtained from commercial sources and used without further purification; 1-bromodecane, 2,4-dihydroxybenzaldehyde and 1,8-diamino-3,6-dioxaoctane are from Sigma–Aldrich, USA; all the $Ln(NO_3)_3$ 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.[18]

2. 2. Synthesis

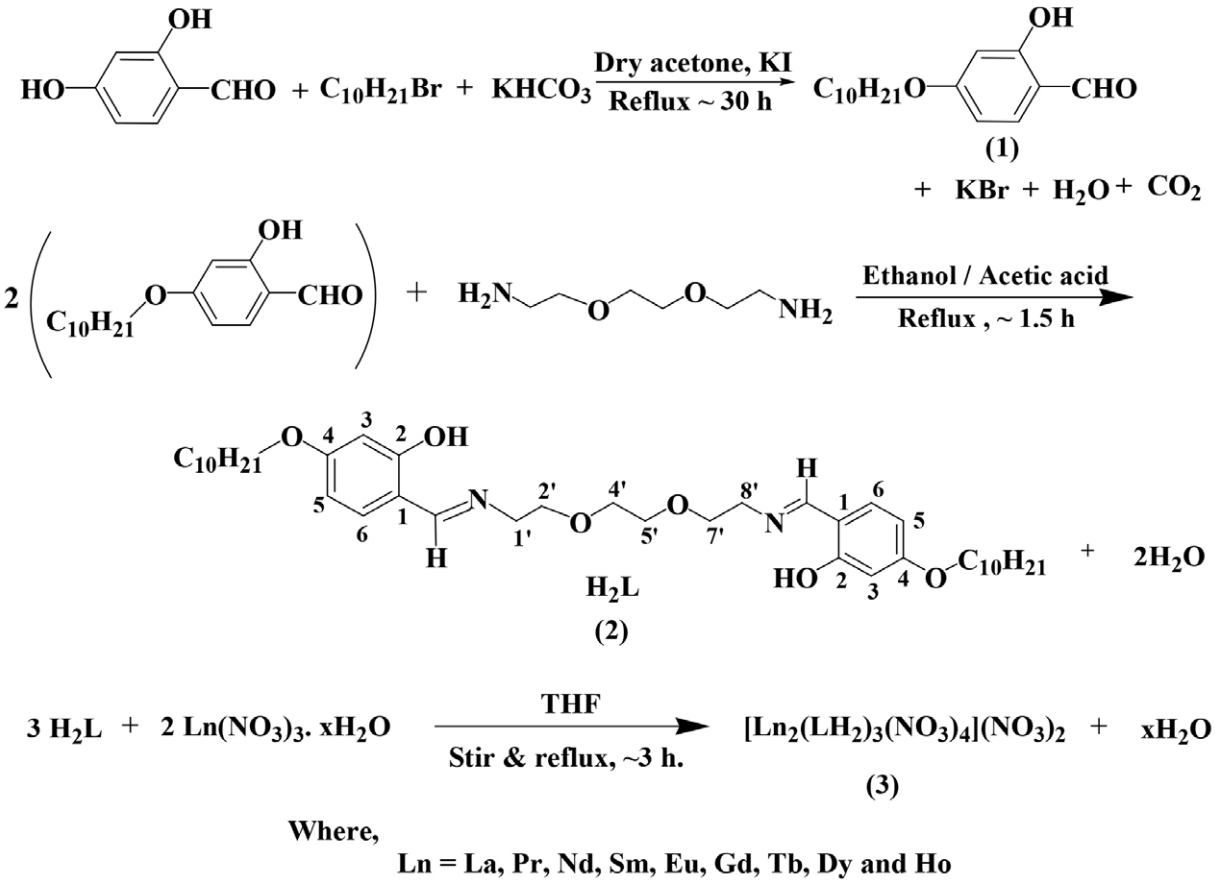
Experimental details given in Scheme 1 show synthesis of *N,N'*-di-(4-decyloxysalicylidene)-1',8'-diamino-3',6'-dioxaoctane (H_2L), **2**, by a two-step process, alkylation of 2,4-dihydroxybenzaldehyde with 1-bromodecane followed by condensation with 1,8-diamino-3,6-dioxaoctane. The Ln^{III} complexes, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho), **3**, were synthesized by reacting the H_2L and appropriate metal nitrate in solution state at room temperature.

2. 2. 1. Preparation of 4-decyloxysalicylaldehyde, 1

Equimolar amounts of 2,4-dihydroxybenzaldehyde (50 mmol, 6.91 g) and 1-bromodecane (50 mmol, 10.4 mL) were mixed with 100 mL of dry acetone and added potassium bicarbonate (55 mmol, 5.51 g). The reaction mixture was refluxed for 30 h in the presence of KI (0.1–0.2 g) as a catalyst. Insoluble solids were removed through hot filtration and subsequently, the filtrate was made neutral by adding 6N hydrochloric acid little at a time and extracted the product twice with 100 mL portions of $CHCl_3$. A straw-yellow solid was obtained upon concentration of the chloroform extracts which was purified by column chromatography over SiO_2 by eluting first with n-hexane and then with a mixture of n-hexane and chloroform (v/v, 1/1). The product, 4-decyloxysalicylaldehyde (**1**) was obtained in the form of a white solid upon evaporation of this purified extract; yield: 68% (9.47 g).

2. 2. 2. Synthesis of N,N'-di-(4-decyloxysalicylidene)-1',8'-diamino-3',6'-dioxaoctane (H_2L), 2

A mixture of absolute ethanolic solutions of 4-decyloxysalicylaldehyde, **1**, (8.34 g, 30 mmol in 50 mL) and 1,8-diamino-3,6-dioxaoctane (2.22 g, 15 mmol in 15 mL) was refluxing together for 1.5 h in the presence of a few drops of glacial acetic acid. Yellow colored solid, **2**, was obtained after the resulting mixture left overnight which was filtered off under suction, thoroughly washed with cold ethanol and dried at room temperature. Yield: 74% (7.43 g), m.p.165 °C. Anal. Calcd for $C_{40}H_{64}N_2O_6$ (%): C, 71.82; H; 8.64; N, 4.19.



Scheme 1. Reaction steps involved in the synthesis of 4-decyloxysalicylaldehyde, **1**; *N,N'*-di-(4-decyloxysalicylidene)-1',8'-diamino-3',6'-dioxaoctane (H_2L), **2,** and Ln^{III} complexes, **3.**

Found (%): C, 71.85; H, 9.65; N, 4.21. ^{1}H NMR (300 MHz; DMSO-d_6; J (Hz), ppm) (Figure S1) δ = 0.85 (t, J = 5.7, 3H, –CH_3), 1.73–1.26 (m, 16H, –$(CH_2)_8$ –), 3.51 (t, J = 6.6, 2H, –NCH_2), 3.96 (t, J = 6.3, 2H, –OCH_2), 6.28 (d, J = 11.4, 1H, Ar–H), 6.33 (s, 1H, Ar–H), 7.19 (d, J = 8.7, 1H, Ar–H), 8.32 (s, 1H, –N=CH), 13.80 (s, br, 1H, Ph–OH); ^{13}C{^{1}H}NMR: (75.45 MHz; DMSO-d_6; ppm) (Figure S2) δ = 165.39, 163.82, 162.36, 132.45, 111.70, 105.56, 101.40, 67.27; FAB Mass (m/e, fragment, % intensity): the molecular ion as base peak (668, M^+, 100) generates simultaneously four fragments, M_1-M_4; M_1: 349, $C_{10}H_{21}OC_6H_3(OH)CH{=}NC_2H_4OCH_2CH_2^+$, 28%; M_2: 321, $C_{10}H_{21}OC_6H_3(OH)CH{=}NCH_2CH_2O^+$, 25%; M_3: 305, $C_{10}H_{21}OC_6H_3(OH)CH{=}NCH_2CH_2^+$, 35%; M_4 (generated from M_3): 164, $(OH)C_6H_3(OH)CH{=}NCH_2CH_2^+$, 25%; IR (cm^{-1}, KBr disk): 3458 (ν–OH), 1628 (ν–C=N), 1150 (ν–C_{ph}–O).

2. 2. 3. Synthesis of La^{III} Complex, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, 3

Mixing of THF solutions of H_2L (2.01 g, 3.0 mmol in 30 mL) and of $La(NO_3)_3\,6H_2O$ (0.87 g, 2.0 mmol in 20 mL) under magnetic stirring turned the resultant solution cloudy after 15 min. A light yellow colored solid separated upon continuous stirring for 3 h at room temperature was filtered off under suction, washed repeatedly with cold methanol, and dried over fused $CaCl_2$ in a desiccator. Yield: 65% (1.73 g) as yellow solid; m.p. 245 °C (decompose); Anal. Calcd for $La_2C_{120}H_{192}N_{12}O_{36}$ (%): C, 54.25; H, 7.28; N, 6.33; La, 10.46; Found (%): C, 54.30; H, 7.30; N, 6.37 and La, 10.51; ^{1}H NMR (300 MHz; DMSO-d_6; J (Hz), ppm) (Figure S3) δ = 0.88 (t, J = 5.4, 3H, –CH_3), 1.71–1.29 (m, 16H, –$(CH_2)_8$–), 3.54 (t, J = 6.3, 2H, –NCH_2), 3.98 (t, J = 6.3, 2H, –OCH_2), 6.34 (d, J = 6.6, 1H, Ar–H), 6.36 (s, 1H, Ar–H), 7.22 (d, J = 8.7, 1H, Ar–H), 8.36 (s, 1H, –N=CH), 9.27 (s, br, 1H, –N^+H); ^{13}C{^{1}H}NMR: (75.45 MHz; DMSO-d_6; ppm) (Figure S4) δ = 166.07, 162.61, 164.02, 132.75, 111.67, 105.64, 101.56, 67.35; IR (cm^{-1}, KBr disk): 3046 (ν–N^+H), 1658 (ν–C=N), 1124 (ν–C_{ph}–O).

All the other Ln^{III} 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 while the NMR data of the ligand (H_2L) and the La^{III} complex are presented as supplementary data. Infrared spectral data of the ligand and complexes are given in Table 2; the data of two representative complexes are given below: $[Gd_2(LH_2)_3(NO_3)_4](NO_3)_2$: IR (cm^{-1}, KBr disk): 3026 (ν–N^+H), 1654 (ν–C=N), 1124 (ν–C_{ph}–O); $[Ho_2(LH_2)_3(NO_3)_4](NO_3)_2$: IR (cm^{-1}, KBr disk): 3038 (ν–N^+H), 1654 (ν–C=N), 1124 (ν–C_{ph}–O).

2. 3. Physical Measurements

The Ln^{III} ions in the complexes were determined complexometrically by titrating against the standard EDTA solution using xylenol orange as a metal ion indicator. The elemental contents (C, H and N) were analyzed on an Exeter Analyzer, Model CE-440 CHN. Bruker Av III HD (DRX) 300 MHz FT-NMR multinuclear spectrometer was used to record the ^{1}H and ^{13}C NMR spectra while Bruker IFS66 FTIR spectrometer recorded IR spectra 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 10^{-3} 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 optical textures using an Olympus BX60 Polarizing Optical Microscope (POM) equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller (heating and cooling rates of 2 °C/min). Differential Scanning Calorimetry (DSC) studies were made on a Mettler-Toledo DSC822e module (scan rate 10 °C/min under a helium flow, aluminum cups). Fluorescence measurements were recorded at room temperature in a mixed solvent of $CHCl_3$/DMSO solutions (3:1 v/v; 10^{-4} mol L^{-1}; λ_{ex}, 380 nm) on a Perkin Elmer LS-45 luminescence spectrometer (10 nm slit width on both excitation and emission).

3. Results and Discussion

3. 1. Properties of the Complexes

The analytical data on elemental analyses, general behavior and some important physical properties of the Ln^{III} complexes are given in Table 1. The Ln^{III} complexes synthesized under the study are of the type $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$ indicating 2:3 metal to ligand stoichiometry with nitrate groups present both outside and within the coordination sphere. The molar conductivity measurements in 10^{-3} M DMF solutions (110–125 Ω^{-1} cm^2 mol^{-1}) of the Ln^{III} complexes imply 2:1 electrolytic behavior.[19]

3. 2. FAB-mass Spectral Study of H_2L

The formation of the Schiff base ligand (H_2L), in addition to the IR and NMR spectral techniques to be discussed later, was further confirmed by the FAB mass spectrum. The molecular ion peak as well as base peak that corresponds to the *m/e* value of 668, matches with the molecular weight of the ligand (668.95) having the molecular formula, $C_{40}H_{64}N_2O_6$. 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* = 349, 321, 305, 164) are due to $C_{10}H_{21}OC_6H_3(OH)CH{=}N$-

Table 1. General and analytical data of H_2L and of Ln^{III} metal complexes.

H_2L/complex formula weight (empirical formula)	Colour, yield	m.p. (°C)	Found (Calcd.)% C	H	N	M	μ_{eff}(van Vleck) value, B.M.
H_2L, 668.95 ($C_{40}H_{64}N_2O_6$)	Yellow, 74%	165	71.85 (71.82)	9.65 (9.64)	4.21 (4.19)	–	–
$[La_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2656.68 ($La_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 65%	245[d]	54.30 (54.25)	7.30 (7.28)	6.37 (6.33)	10.51 (10.46)	Diamag.
$[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2660.69 ($Pr_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 66%	242[d]	54.15 (54.12)	7.28 (7.27)	6.38 (6.32)	10.66 (10.59)	3.90 (3.40-3.60)
$[Nd_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2667.35 ($Nd_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 72%	238[d]	54.10 (54.03)	7.28 (7.26)	6.28 (6.30)	10.90 (10.82)	3.94 (3.50-3.60)
$[Sm_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2679.59($Sm_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 69%	240[d]	53.82 (53.79)	7.26 (7.22)	6.30 (6.27)	11.30 (11.22)	1.87 (1.50-1.60)
$[Eu_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2682.80 ($Eu_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 74%	255[d]	53.75 (53.72)	7.23 (7.21)	6.32 (6.27)	11.37 (11.33)	4.56 (3.40-3.60)
$[Gd_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2693.37($Gd_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 70%	258[d]	53.49 (53.51)	7.23 (7.19)	6.29 (6.24)	11.71 (11.68)	10.84 (7.80-8.00)
$[Tb_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2696.72 ($Tb_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 67%	260[d]	53.47 (53.45)	7.21 (7.18)	6.28 (6.23)	11.86 (11.79)	11.84 (9.40-9.60)
$[Dy_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2703.87 ($Dy_2C_{120}H_{192}N_{12}O_{36}$)	Light yellow, 70%	257[d]	53.35 (53.30)	7.20 (7.16)	6.27 (6.22)	12.09 (12.02)	12.47 (10.40-10.50)
$[Ho_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2608.73 ($Ho_2C_{120}H_{192}N_{12}O_{36}$)	Light Yellow, 68%	258[d]	53.22 (53.21)	7.19 (7.14)	6.26 (6.21)	12.25 (12.18)	14.36 (10.30-10.50)

d = decomposition

$C_2H_4OCH_2CH_2^+$, $C_{10}H_{21}OC_6H_3(OH)CH{=}NCH_2CH_2O^+$, $C_{10}H_{21}OC_6H_3(OH)CH{=}NCH_2CH_2^+$, and $(OH)C_6H_3(OH)CH{=}NCH_2CH_2^+$ species respectively.

3. 3. IR Spectral Studies

The important infrared spectral data of H_2L and its Ln^{III} complexes are presented in Table 2.

The broad absorption, centered at 3458 cm^{-1} and characteristic of $\nu(O–H)_{phenolic}$,[20] involving considerable H-bonding, disappears in spectra of the complexes due to shifting of the phenolic proton to the azomethine nitrogen, resulting in formation of the zwitterion. The weak/medium intensity bands of the H_2L centered at 1150 cm^{-1} are assigned to $\nu(C–O)_{phenolic}$. The strong intensity band appearing at 1628 cm^{-1}, which is assignable[21] to ν(C=N) of azomethine, undergoes a hypsochromic shift in all the complexes on account of zwitterion formation. Thus, the complexation of the H_2L to Ln^{III} results in 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, $N^+–H\cdots O^-$. Such zwitterionic behavior is in consistent with the study of Binnemans *et al.*,[22] who also reported similar observation for acyclic Schiff base lanthanide complexes. The band frequencies of ν(C=N) shifting to higher wave numbers upon complexation, also provide further evidence implying the presence of the $C–N^+$ and the non-involvement of nitrogen in complex formation.[23] Further, the present complexes are

Table 2. IR Spectral data* (cm^{-1}) of H_2L and of Ln^{III} metal complexes

H_2L/Complexes	ν(O–H) *phenol*	ν (N^+H)	ν(C=N)	ν(C–O) *phenolic*	$\nu(NO_3)$ ν_5	Ionic	ν_1	ν_2	$\nu_5 - \nu_1$
H_2L	3458 b	–	1628 s	1150 m	–	–	–	–	–
$[La_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3046w	1656	1124	1470	1386	1290	794	180
$[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3042	1654	1118	1469	1386	1294	794	175
$[Nd_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3040	1654	1126	1470	1380	1292	791	178
$[Sm_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3042	1654	1124	1470	1382	1292	792	180
$[Eu_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3030	1654	1124	1468	1381	1288	793	181
$[Gd_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3026	1654	1124	1467	1372	1290	791	177
$[Tb_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3036	1654	1122	1471	1378	1294	792	177
$[Dy_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3028	1654	1126	1472	1378	1292	793	180
$[Ho_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3038	1654	1124	1470	1382	1290	794	180

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

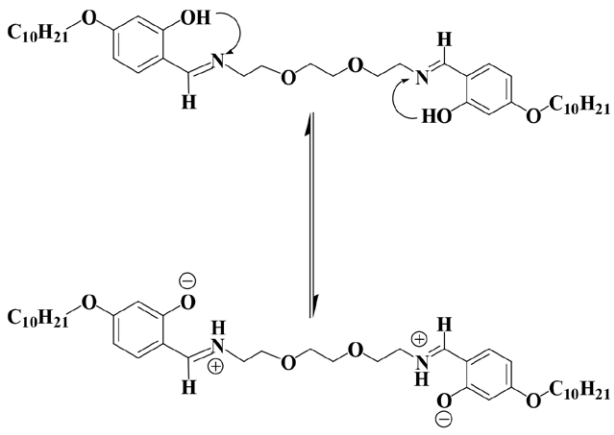
characterized by a strong band at 1656–1654 cm^{-1} due to ν(C=N) and a weak broad band at 3046–3026 cm^{-1} due to H-bonded N^+–H···O^- vibration of the protonated imine.[23] Thus, the above evidence supports for none involvement of bonding between lanthanide and the imine nitrogen; instead the ligand coordinates to the Ln^{III} ions *via* the negatively charged phenolic oxygen.

The Ln^{III} complexes also exhibit three additional characteristic bands of the vibrational modes of the coordinated nitrate groups (C_{2v} symmetry) at 1472–1467, 1294–1288, and 794–791 cm^{-1}.[24] Besides, the mono- and bidentate chelating nitrates in the complexes may be distinguished on the basis of the profile and separation of the modes associated with asymmetric nitrate vibrations. Accordingly, a bidentate coordinated nitrate is indicated by the magnitude of splitting (181–175 cm^{-1}) at higher energies.[24,25] The non-coordinated nitrate present in the ionization sphere is supported by additional bands at 1386–1372 cm^{-1}.

3. 4. ^{1}H and ^{13}C NMR Spectral Studies

A comparison of ^{1}H NMR spectral data of the ligand with that of the La^{III} complex shows the phenolic –OH signal (δ, 13.80) that appear in the ligand, disappears later upon complexation. Further, the ^{1}H NMR spectral data imply the shifting of phenolic protons to the two uncoordinated imino nitrogen atoms, which give zwitterionic structure (=N^+–H···O^-) by intramolecularly hydrogen-bonding to the metal-bound phenolate oxygen atoms; as such is designated as LH_2.[26] Besides, the La^{III} complex (δ, 8.36) shows a signal corresponding to the imine hydrogen, –CH=N, that got broadened when compared with that of the ligand (δ, 8.32). Further, the La^{III} complex shows a new signal, characteristic of –N^+H resonance, at 9.27 δ while such a signal is absent in the ligand. The results are in accordance with similar observations made by Binnemans *et al.*,[27] on metallomesogens, [Ln(LH)$_3$(NO$_3$)$_3$], where LH = 4-alkoxy-N-alkyl-2-hydroxy benzaldimine. Thus, the metal complex has its Schiff base ligand existing in a zwitterionic form, with the phenolic oxygen deprotonated and the imine nitrogen protonated (Scheme 2), as supported evidently by IR and NMR spectral data.

The ^{13}C{^{1}H} NMR spectral data show a significant shift of the –NCH signal (δ, 165.39 in case of H_2L and δ, 166.07 in the La^{III} complex) implying the two phenolate oxygen atoms of H_2L bonded to La^{III} in the zwitterionic form. The carbons directly attached to the phenolate group showed similar shifts while those for the other carbon signals were of lower magnitude.



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

3. 5. Magnetic and Electronic Spectral Studies

The μ_{eff} values (at room temperature) of all the Ln^{III} complexes (Table 1) under the present study have been found to be higher than the reported van Vleck values. These abnormal μ_{eff} values, attributed to metal–metal interactions, are in good agreement with similar complexes reported in literatures.[28-30]

The electronic spectra of only the Pr^{III}, Nd^{III}, Sm^{III}, and Dy^{III} complexes (Table 3) were recorded in qualitative solution state from 200 to 1100nm, in view of their ability to show hypersensitive bands. The considerable red shifts in the λ_{max} values of the above complexes compared to those of the corresponding aqua ions,[31] are attributed to

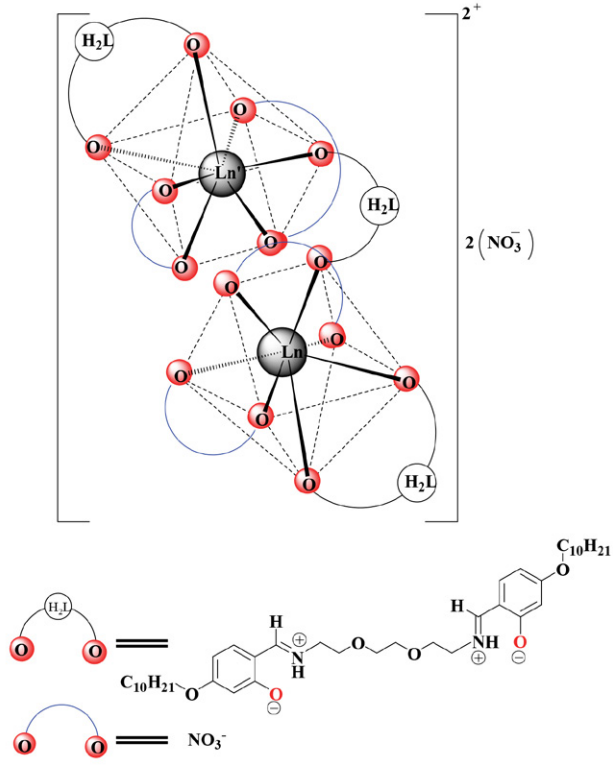


Figure 1. Proposed Polyhedron (Mono-capped Octahedron) for [$Ln_2(LH_2)_3(NO_{3)4}](NO_3)_2$: Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho

Table 3. 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	9800	$^4F_{3/2} \leftarrow {}^4I_{9/2}$	11,450	11,435
$^1D_2{}^* \leftarrow$	16850*	16,840	$^4F_{5/2} \leftarrow$	12,500	12,484
$^3P_0 \leftarrow$	20800	20,760	$^4S_{3/2}, {}^4F_{7/2} \leftarrow$	13,500	13,430
			$^4F_{9/2} \leftarrow$	14,800	14,694
			$^2H_{11/2} \leftarrow$	15,900	15,850
			$^2G_{7/2}{}^* \leftarrow$	17,400*	17,196
			$^4G_{7/2} \leftarrow$	19,100	19,015
β		0.993			0.995
$b^{1/2}$		0.059			0.050
$\%\delta$		0.705			0.503
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	10,352	$^6F_{9/2} \leftarrow$		
$^4G_{5/2} \leftarrow$	17,900	–	$^6H_{5/2} \leftarrow$	10,200	10,156
$^6P_{7/2}{}^* \leftarrow$	26,750*	26,197	$^6F_{7/2} \leftarrow$	11,000	10,952
$^4D_{7/2}$	29,100	29,185	$^6F_{5/2} \leftarrow$	12,400	12,392
			$^4F_{7/2} \leftarrow$	25,800	25,828
β		0.991			0.998
$b^{1/2}$		0.067			0.032
$\%\delta$		0.908			0.200
η		0.004			0.001

* Hypersensitive band.

the Nephelauxetic effect,[32] which is 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 (%δ), and covalency angular overlap parameter (η), calculated by the procedures as reported,[33] suggest a weak covalent nature of the metal–ligand bonds.

Based on the above spectral evidences, the seven-coordinate geometry, possibly in a distorted mono-capped octahedron (Figure 1) may be proposed to all the present complexes in which the mesogenic Schiff base, *N,N*'-di-(4-decyloxysalicylidene)-1',8'-diamino-3',6'-dioxaoctane (H_2L), **2**, coordinates to the Ln^{III} ions in a neutral bidentate fashion.

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

Ligand	Transition[a]	T^b (°C)	ΔH^b (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
H_2L	Cr – SmX	91.84	10.62	29.11
	SmX– SmA	116.96	10.52	26.98
	SmA – N	131.93	16.52	40.80
	N – I	162.85	6.09	13.97
	I – N	148.53	2.39	5.67
	N – SmX	141.73	1.12	2.70
	SmX – Cr	89.96	20.20	55.65

[a] Cr: Crystal; SmX: Smectic-X; SmA: Smectic-A; N: Nematic; I-Isotropic liquid [b] Data as obtained from the DSC cycle

3. 6 Optical and Thermal Studies

The DSC (recorded in the second heating and cooling cycle with heating rate of 10°C/min) and POM (heating and cooling rates of 2 °C/min) were employed to study liquid crystalline (mesogenic) properties of the ligand and those of the Ln^{III} complexes. The corresponding transition temperatures, enthalpy, and entropy changes are given in Table 4.

The POM study revealed optical textures of the H_2L (Figure 2) implying smectic-X (*SmX*), smectic-A (*SmA*) and nematic (*N*) mesophases while none of the Ln^{III} complexes reported here exhibited mesomorphism. The non-mesomorphism in the Ln^{III} complexes may be attributed to very high thermal energy required to melt completely the alkoxy chains of the complexes. Under the

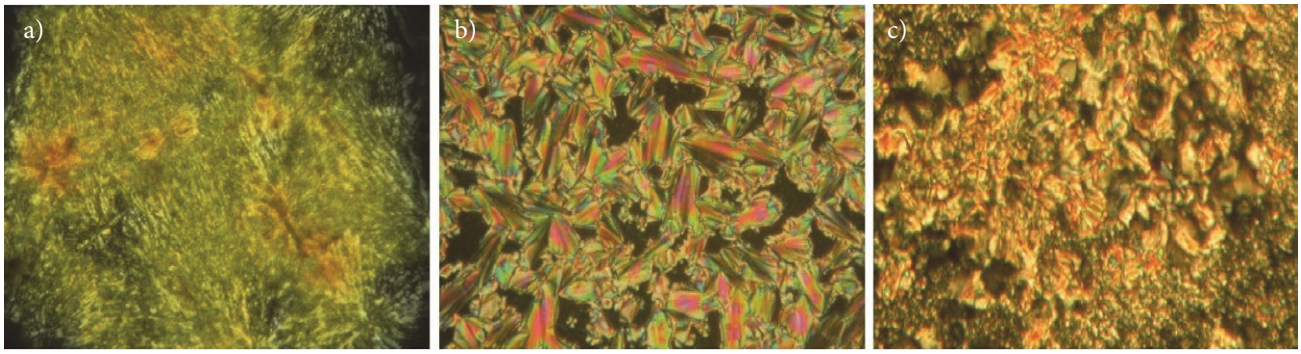


Figure 2. Optical textures of Schiff base (H_2L): (a) Smectic-X (*SmX*), (b) Smectic-A (*SmA*) and (c) Nematic (*N*)

given situation of high energy level, the layered structure in the complexes breaks down prior to the alkoxy chains, losing thereby the mesogenic properties of the materials.[27]

3. 7. Luminescence Studies

The H_2L shows fluorescence (Figure 3a) with an emission band at 410 nm due to intra-ligand transition and the Tb^{III} complex (Figure 3b) with four typical metal-centered emission bands at 490 nm ($^5D_4 \rightarrow {}^7F_6$), 547 nm ($^5D_4 \rightarrow {}^7F_5$), 620 nm ($^5D_4 \rightarrow {}^7F_3$), and 685 nm ($^5D_4 \rightarrow {}^7F_0$) respectively.[34]

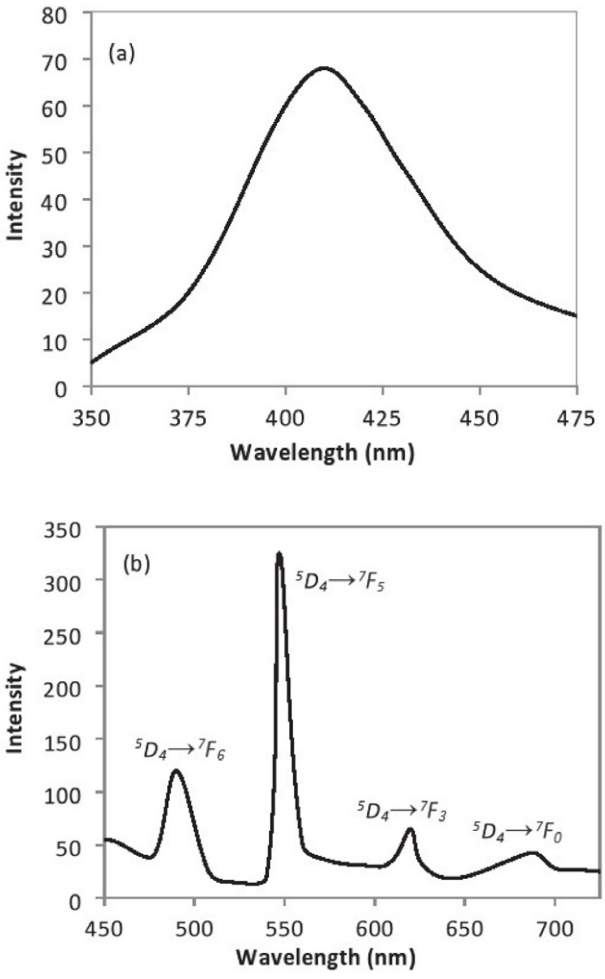


Figure 3. The fluorescence spectra of (a) H_2L and (b) Tb^{III} complex.

Under the same experimental conditions, the observed fluorescence intensities of the Sm^{III}, Eu^{III} and Dy^{III} complexes were observed to be weak (spectra not shown) and their emission spectra also did not show any bands characteristic of metal-centered emission. Thus, it may be inferred that the H_2L is likely to be a suitable organic chelator to absorb energy and transfer the same to Tb^{III} ion, implying the well-known intramolecular energy transfer mechanism exhibited by lanthanide Schiff base complexes.[35]

4. Conclusion

The mesogenic (*SmX, SmA* and *N*) Schiff base, *N,N'*-di-(4-decyloxysalicylidene)-1',8'-diamino-3',6'-dioxaoctane (H_2L), coordinates to Ln^{III} ions (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) as a neutral bidentate species to yield seven-coordinate non-mesogenic complexes of the formula, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, the polyhedron being possibly distorted mono-capped octahedron. The neutral bidentate H_2L coordinates to Ln^{III} in a zwitterionic form through two phenolate oxygen atoms along with bonding of nitrato groups in similar bidentate fashion. Luminescence of the H_2L and Tb^{III} complex arises due to intra-ligand and metal-centered emissions respectively.

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Povzetek

Sintetizirali smo mezogeno Schiffovo bazo, *N,N*'-di(4-deciloksisaliciliden)-1',8'-diamino-3',6'-dioksaoktan (H_2L) in serijo homo dvojedrnih lantanoidnih(III) kompleksov tipa $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, in Ho) ter jih okarakterizirali z elementno analizo, masno spektrometrijo, FTIR in NMR spektroskopijo. IR in NMR analizi nakazujeta vezavo nevtralne dvovezne H_2L zvrsti preko dveh fenolatnih kisikovih atomov v zwitterionski obliki na Ln^{III}, kar vodi do kompleksa s koordinacijskim številom sedem – verjetno popačen oktaeder s sedmim donorskim ligandom nad stransko ploskvijo. DSC in polarizacijski optični mikroskop (POM) razkrijeta mezogene lastnosti (smektična X, smektična A in nematična mezofaze) liganda v širokem temperaturnem območju, vendar nobenega mezomorfizma pri Ln^{III} kompleksih, sintetiziranih pri tej študiji. Študij luminescence pokaže emisije pri H_2L in Tb^{III} kompleksih.