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Rare Earth Metal Complexes of a Mesogenic Schiff-Base, N,N'-di-(4-decyloxysalicylidene)-1', 4'diaminobutane: Synthesis and Characterization

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## Rare Earth Metal Complexes of a Mesogenic Schiff-Base, *N*,*N*'-di-(4-decyloxysalicylidene)-1', 4'-diaminobutane: Synthesis and Characterization

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A mesogenic Schiff-base, N,N'-di-(4-decyloxysalicylidene)-1',4'diaminobutane, (H<sub>2</sub>L) that exhibits smectic-B and nematic mesophases, was synthesized and its structure studied by elemental analysis, mass spectrometry, NMR & IR techniques. H<sub>2</sub>L, upon condensation with hydrated lanthanide(III) nitrates yields Ln<sup>III</sup> complexes of the composition [Ln<sub>2</sub>(LH<sub>2</sub>)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>, where Ln<sup>III</sup> = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. The Pr<sup>III</sup> complex shows smectic-A and nematic phases. The IR and NMR spectral data imply a bidentate bonding of H<sub>2</sub>L in zwitterionic form (as LH<sub>2</sub>) to the Ln<sup>III</sup> ions through two phenolate oxygen atoms, rendering the overall geometry of the complexes possibly to distorted mono-capped octahedra.

Keywords Ln<sup>III</sup> complexes, mesogenic schiff-base, mono-capped octahedron, NMR and IR spectra, zwitterionic coordination

## INTRODUCTION

Schiff-base metal complexes, which are well known to have played a key role in the development of coordination chemistry since nineteenth century,<sup>[1–4]</sup> have been reported<sup>[5]</sup> in large number because they exhibit the phenomenon of mesomorphism. The interest in the synthesis and structural investigations of mesogenic Schiff-base liquid crystals (LCs) originates in their potential applications as "non-linear optical and/or optical storage materials."<sup>[6,7]</sup> Of the metallomesogens, thermotropic LCs have assumed great technological importance owing to their specific applications as advanced functional materials.<sup>[8]</sup> 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 metalcontaining LCs, so-called metallomesogens,<sup>[9,10]</sup> is the presence of magnetic moment which determines the behavior of the LCs in a magnetic field. It is well known<sup>[11]</sup> that magnetic moments, and especially magnetic anisotropy, are inherent properties of fblock metal complexes. In continuation of the earlier work<sup>[12–16]</sup> carried out in our laboratory on systematic structural and spectroscopic studies of 3*d* and 4*f* metal complexes of a series of mesogenic organic Schiff-bases, we now report here the synthesis and spectral studies of a mesogenic Schiff-base, N,N'di-(4-decyloxysalicylidene)-1',4'-diaminobutane (H<sub>2</sub>L) and its rare earth complexes. It has been observed that among all the Ln<sup>III</sup> complexes of the mesogenic Schiff-base (H<sub>2</sub>L) synthesized under the present study, only the Pr<sup>III</sup> complex exhibits mesogenic property.

## **EXPERIMENTAL**

## **Starting Materials**

All the required reagents of analytical grade were obtained from commercial sources and used without further purification: 1-bromodecane, 2,4-dihydroxybenzaldehyde, and 1,4-diaminobutane are from Sigma–Aldrich, USA; all the Ln(NO<sub>3</sub>)<sub>3</sub>.xH<sub>2</sub>O salts are from Indian Rare Earths Ltd. and KI and KHCO<sub>3</sub> are from Merck. The organic solvents obtained from commercial vendors were dried using standard methods<sup>[17]</sup> when required.

#### **Physical Measurements**

The metal contents of the complexes were determined by complexometric titrations against EDTA using xylenol orange as an indicator. Carbon, hydrogen and nitrogen were analyzed on an Exeter Analyzer, Model CE-440 CHN. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL AL-300 MHz FT-NMR multinuclear spectrometer. Infrared spectra were recorded on a JASCO FT/IR (model-5300) spectrophotometer within the 4000–400 cm<sup>-1</sup> 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. Magnetic susceptibility measurements

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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 polarized hot-stage binocular microscope (LOMO, USA) equipped with digital camera (Nikon Coolpix 4500). Differential Scanning Calorimetry studies were made on METTLER DSC-25, Mettler STARe SW 9.00 unit.

### Synthesis and Analysis

The synthesis of *N*,*N*'-di-(4-decyloxysalicylidene)-1',4'diaminobutane (H<sub>2</sub>L), 2, was achieved by proceeding through two major steps, *viz.*, alkylation of 2,4-dihydroxybenzaldehyde with 1-bromodecane, followed by Schiff-base formation. All the experimental details are given in Scheme 1. The Ln<sup>III</sup> 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 adding together THF solutions of the appropriate metal nitrate (2.0 mmol, in 20 mL) and the ligand, H<sub>2</sub>L (1.83 g, 3.0 mmol in 30 mL) under magnetic stirring. The resulting mixture was then stirred continuously for ~3 h at room temperature. The solid product thus separated out in each case was filtered, washed repeatedly with cold methanol and dried over fused CaCl<sub>2</sub>.

## Preparation of 4-decyloxysalicylaldehyde, 1

To a solution of 100 mL of dry acetone, equimolar amounts of 2,4-dihydroxy benzaldehyde (6.91 g, 50 mmol), 1-bromodecane (10.4 mL, 50 mmol) and potassium bicarbonate (5.51 g,  $\sim$ 55 mmol) were added. The mixture was refluxed for  $\sim$ 30 h in presence of KI (0.1–0.2 g) as a catalyst and filtered while hot to remove insoluble solids. Hydrochloric acid (6*N*) was added

to the filtrate until the point of neutralization and the product was then extracted twice with CHCl<sub>3</sub> (100 mL portions). The chloroform extracts were concentrated to obtain a straw-yellow solid which was purified by column chromatography over SiO<sub>2</sub> 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-decyloxysalicylaldehyde in the form of a white solid; yield: 8.63 g, 62%.

## Synthesis of *N*,*N*'-di-(4-decyloxysalicylidene)-1',4'-diaminobutane, 2

The ligand, N,N'-di-(4-decyloxysalicylidene)-1',4'-diaminobutane, was prepared by refluxing absolute ethanolic solutions of 4-decyloxysalicylaldehyde (8.34 g, 30 mmol in 50 mL) and 1, 4-diaminobutane (1.5 mL, 15 mmol) for ~1.5 h in presence of few drops of glacial acetic acid. The resulting mixture was left over night; minute yellow-colored crystalline product, **2**, thus obtained was filtered off under suction, thoroughly washed with cold ethanol and dried at room temperature. Yield: 4.39 g, 60%, as shining yellow-colored microcrystalline solid; m.p. 112°C.

Anal. Calcd for  $C_{38}H_{60}N_2O_4$  (608.89) (%): C, 74.96; H; 9.93; N, 4.60. Found: C, 74.92; H, 9.97; N, 4.63. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>;  $\delta$ ) 0.88 (t, J = 6.9, 3H, -CH<sub>3</sub>), 1.77-1.27 (m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-), 3.56 (s, 2H, -NCH<sub>2</sub>), 3.95 (t, J = 6.6, 2H, -OCH<sub>2</sub>), 6.37 (d, J = 8.1, 1H, Ar-H), 6.38 (s, 1H, Ar-H), 7.06 (d, J = 8.4, 1H, Ar-H), 8.14 (s, 1H, -N=CH), 13.96 (s, br, Ph-OH); <sup>13</sup>C{<sup>1</sup>H}NMR (300 MHz;  $\delta$ , CDCl<sub>3</sub>): 166.0, 163.7, 163.3, 132.9, 112.0, 106.8, 101.8, 68.1, and 57.6; FAB Mass (m/e, fragment, % intensity): the molecular ion as base peak (608, M<sup>+</sup>,100) generates simultaneously two fragments,



SCH. 1. Reaction steps involved in the synthesis of 4-decyloxysalicylaldehyde, 1; *N*,*N*'-di-(4-decyloxysalicylaldene)-1',4'-diaminobutane, 2, (H<sub>2</sub>L), and Ln<sup>III</sup> complexes, 3.

 $M_1-M_2; M_1: 332, C_{10}H_{21}OC_6H_3(OH)CH-N(CH_2)_3CH_2^+, 45\%;$  $M_2: 192, HOC_6H_3(OH)CH-N(CH_2)_3CH_2^+, 25\%;$  IR (cm<sup>-1</sup>, KBr disk): 3448 ( $\nu$ -OH), 1619 ( $\nu$ -C=N), 1286 ( $\nu$ -C<sub>ph</sub>-O).

## Synthesis of La<sup>III</sup> Complex, [La<sub>2</sub>(LH<sub>2</sub>)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>

The La<sup>III</sup> complex was prepared by adding drop-wise THF solution of La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (0.87 g, 2.0 mmol in 20 mL) to a THF solution of the ligand, H<sub>2</sub>L (1.83 g, 3.0 mmol in 30 mL) under magnetic stirring. The resultant solution turned cloudy after ~15 min; stirring was continued for ~3 h at room temperature when a solid product separated out which was filtered, washed repeatedly with cold methanol and dried over fused CaCl<sub>2</sub>. Yield: 74%, 1.84 g, as a light yellow-colored solid; m.p. 225°C (decompose).

Anal. Calcd for La<sub>2</sub>C<sub>114</sub>H<sub>180</sub>N<sub>12</sub>O<sub>30</sub> (2476.52) (%): C, 55.29; H; 7.33; N, 6.79; La, 11.22. Found: C, 55.32; H, 7.28; N, 6.80; La, 11.20. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>;  $\delta$ ): 0.88 (t, *J* = 6.0, 3H, -CH<sub>3</sub>), 1.57–1.25 (m, 16H, –(CH<sub>2</sub>)<sub>8</sub>-), 3.41 (s, 2H, –NCH<sub>2</sub>), 3.44 (t, *J* = 6.6, 2H, –OCH<sub>2</sub>), 6.06 (d, *J* = 6.9, 1H, Ar–H), 6.48 (s, 1H, Ar–H), 6.92 (d, *J* = 6.0, 1H, Ar–H), 8.04 (s, 1H, -N=CH), 12.20 (br-s, 1H, –N<sup>+</sup>H); <sup>13</sup>C{<sup>1</sup>H} NMR (300 MHz; CDCl<sub>3</sub>;  $\delta$ ) 177.9, 164.4, 167.9, 134.4, 114.6, 108.9, 104.5, 67.9 and 57.2; IR (cm<sup>-1</sup>, KBr disk): 3199 ( $\nu$ –N<sup>+</sup>H), 1652 ( $\nu$ –C=N), 1229 ( $\nu$ –C<sub>ph</sub>–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. The infrared spectral data of two representative complexes are given below:

## **RESULTS AND DISCUSSION**

The shining yellow-colored microcrystalline Schiff-base ligand (H<sub>2</sub>L) was found to react with Ln(NO<sub>3</sub>)<sub>3</sub>.*x*H<sub>2</sub>O to yield Ln<sup>III</sup> complexes; the data obtained (elemental analyses, magnetic moments, important physical properties, and general behavior) on the ligand and the complexes are given in Table 1. The analytical data of the complexes indicate 2:3 metal to ligand stoichiometry with the general formula [Ln<sub>2</sub>(LH<sub>2</sub>)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. The ligand (H<sub>2</sub>L) in all the complexes under discussion coordinates to the metal ion in the form of non-deprotonated zwitter-ionic species as evidenced by NMR and IR spectra discussed later while the nitrate groups (both within and outside the coordination sphere) counter balance the positive charge of the Ln<sup>III</sup> ion(s).

## **Magnetic Study**

The  $\mu_{eff}$  values (at R.T.) of all the present Ln<sup>III</sup> complexes (3.72, 3.83, 1.92, 3.80, 11.69, 14.49, 15.22, and 15.30 B.M. for Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, respectively, as

shown in Table 1) have been found to be higher than the reported van Vleck values presumably on account of metal-metal interactions that may be present in all such complexes showing the abnormal  $\mu_{eff}$  values. Jean-Pierre Costes et al.<sup>[18]</sup> in their first example of a polynuclear gadolinium complex observed that  $\chi_{M}T$  increases steadily from 40 to 10 K and then more sharply down to 2 K and attributed that such a behavior was typical of a ferromagnetic interaction between the gadolinium ions; further, in the introduction part of the same publication, they claimed to have reported lately two dinuclear (Er, Er) and (Gd, Gd) complexes which showed a ferromagnetic behavior unambiguously attributable to lanthanide–lanthanide interaction. On these lines, the present complexes may be considered to involve ferromagnetic interaction at the room temperature itself.

## Electronic Spectra

The electronic spectra (qualitative solution-state spectra in a mixed solvent (CHCl<sub>3</sub> and DMSO; 3:1 v/v) in the 200–1100 nm region) recorded for only the Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup>, and Dy<sup>III</sup> complexes show a considerable red shift in the  $\lambda_{max}$  values in comparison with those of their corresponding aquo ions.<sup>[19]</sup> These red shifts are presumably due to the Nephelauxetic effect<sup>[20]</sup> 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 ( $\beta$ ), bonding parameter ( $b^{1/2}$ ), Sinha's parameter ( $\%\delta$ ), and covalence angular overlap parameter ( $\eta$ ), calculated by the procedures as reported in literature,<sup>[21]</sup> suggest a weak covalent nature of the metal-ligand bonds.

The structures and purity of the Schiff-base ligand and of the metal complexes were studied by IR and NMR spectroscopy and elemental analyses. The structure of the ligand was further confirmed by FAB Mass spectrum. The mass spectral features of H<sub>2</sub>L were characterized by the base peak as well as molecular ion peak corresponding to the m/e value of 608, which matches with the molecular weight of 608.89 of H<sub>2</sub>L of the molecular formula,  $C_{38}H_{60}N_2O_4$ . The 100% intensity of the molecular ion peak is as expected for the molecule on the basis of its predominant aromatic character; the major fragment peaks at m/e = 332, 192 are due to  $C_{10}H_{21}OC_6H_3(OH)CH-N(CH_2)_3CH_2^+$  and HOC<sub>6</sub>H<sub>3</sub>(OH)CH–N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub><sup>+</sup>, respectively.

## NMR Spectral Study

A comparison of the NMR spectral [<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}] data (Table 3, Figure 1) of the ligand, with that of the La<sup>III</sup> complex shows that the bonding of the phenolic oxygen of the ligand to the metal ion is substantiated by the fact that the phenolic-OH signal, appearing at  $\delta$ , 13.96 ppm in the ligand, disappears upon complexation. It may be noted that the composition of the La<sup>III</sup> complex, [La<sub>2</sub>(LH<sub>2</sub>)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>, implies coordination of H<sub>2</sub>L as a neutral species; however, it may be inferred from the <sup>1</sup>H NMR spectrum of the compound that the phenolic protons are shifted to the two uncoordinated imino nitrogen atoms, which then get intramolecularly hydrogen-bonded to the metal-bound phenolate oxygen atoms to give rise to the

TABLE 1	Analytical data and general behavior of the $Ln^{III}$ complexes of $H_2L$
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Hol /complex formula	Color vield %	Мп		Found (e	calcd.)%		<i>ц</i> (ВМ) (van
weight (empirical formula)	(solubility)	(C)	С	Н	Ν	М	Vleck values) (h)
H <sub>2</sub> L, 608.89 (C <sub>38</sub> H <sub>60</sub> N <sub>2</sub> O <sub>4</sub> )	Yellow, 60% (a,	112 -	74.92 (74.96)	9.97 (9.93)	4.63 (4.60)		
[La <sub>2</sub> (LH <sub>2</sub> ) <sub>3</sub> (NO <sub>3</sub> ) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> 2476.52	0, C, u, C, 1) Light yellow, 74% (b, d, e)	225 (g)	55.32 (55.29)	7.28 (7.33)	6.80 (6.79)	11.20 (11.22)	Diamagnetic
$(La_2C_{114}H_{180}N_{12}O_{30})$ $[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$ $2480$ 53 (ProC $\dots$ H. $\dots$ N $\dots$ O $\dots$	Light yellow,	245 -	55.16 (55.20)	7.34 (7.32)	6.77 (6.78)	11.31 (11.36)	3.72 (3.40–3.60)
[Nd2(LH2)3(NO3)4](NO3)2 2487 19/Nd-C H N O.	Light yellow,	240 (g)	55.03 (55.05)	7.25 (7.29)	6.79 (6.76)	11.56 (11.60)	3.82 (3.50–3.60)
[Sm <sub>2</sub> (LH <sub>2</sub> ) <sub>3</sub> (NO <sub>3</sub> ) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> 2400 43(Sm <sub>2</sub> C <sub>2</sub> , H <sub>12</sub> N <sub>12</sub> O <sub>2</sub> )	Light yellow,	240 (g)	54.74 (54.78)	7.28 (7.26)	6.74 (6.72)	12.01 (12.03)	1.92 (1.50–1.60)
[Eu <sub>2</sub> (LH <sub>2</sub> ) <sub>3</sub> (NO <sub>3</sub> ) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> 2502.64	10% (b, u, c) Light yellow, 72% (b, d, e)	250 (g)	54.68 (54.71)	7.21 (7.25)	6.71 (6.72)	12.09 (12.14)	3.80 (3.40–3.60)
$\begin{array}{c} (Eu_2C_{114}H_{180}N_{12}O_{30}) \\ [Gd_2(LH_2)_3(NO_3)_4](NO_3)_2 \\ 2512 & 217C4 & C_{11} & M_{12}O_{12} \end{array} \end{array}$	Cream, 65% (d,	260 (g)	54.56 (54.48)	7.21 (7.22)	6.71 (6.69)	12.47 (12.51)	11.69 (7.80–8.00)
2516.56 2516.56	c) Light yellow, 68% (d, e)	265 (g)	54.39 (54.41)	7.19 (7.21)	6.72 (6.68)	12.59 (12.63)	14.49 (9.40–9.60)
$(1b_2C_{114}H_{180}N_{12}O_{30})$ $[Dy_2(LH_2)_3(NO_3)_4](NO_3)_2$ $7573~71(Dy_2C_{11}H_{220}M_{20}O_{22})$	Light yellow,	260 (g)	54.22 (54.25)	7.20 (7.19)	6.69 (6.66)	12.83 (12.88)	15.22 (10.40–10.50)
[Ho <sub>2</sub> (LH <sub>2</sub> ) <sub>3</sub> (NO <sub>3</sub> ) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> 2528.57(Ho <sub>2</sub> C <sub>114</sub> H <sub>180</sub> N <sub>12</sub> O <sub>30</sub> )	10% (u, c) light yellow, 73% (d, e)	260 (g)	54.11 (54.15)	7.15 (7.18)	6.61 (6.65)	13.03 (13.05)	15.30 (10.30–10.50)
	×				e X	•	

Solvents: benzene (a), chloroform (b), dichloromethane (c), pyridine (d), THF (e), hot DMSO (f); decompose (g); Room temperature magnetic moments (BM) measured on Faraday balance (h).

		1	1 -		
Pr <sup>III</sup>			Nd <sup>III</sup>		
Transitions/bonding	$\lambda_{\rm max}~({\rm cm}^{-1})$	$\lambda_{\rm max}({\rm cm}^{-1})$	Transitions/bonding	$\lambda_{\rm max}~({\rm cm}^{-1})$	$\lambda_{\rm max}~({\rm cm}^{-1})$
parameters	aq. ion	complex	parameters	aq. ion	complex
$^{l}G_{4} \leftarrow {}^{3}H_{4}$	9,900	9,681	${}^4F_{3/2} \leftarrow {}^4I_{9/2}$	11,450	11,468
$^{l}D_{2}^{*} \leftarrow$	16,850	16,863	${}^{4}F_{5/2}$ , ${}^{2}H_{9/2}$ $\leftarrow$	12,500	12,484
${}^{3}P_{0} \leftarrow$	20,800	20,661	${}^{4}S_{3/2}, {}^{4}F_{7/2} \leftarrow$	13,500	13,423
			${}^{4}F_{9/2} \leftarrow$	14,800	14,706
			$^{2}G_{7/2}^{*} \leftarrow$	17,400*	17,123
			${}^{4}G_{9/2} \leftarrow$	19,500	19,531
β		0.991			0.996
$b^{1/2}$		0.067			0.045
$\%\delta$		0.908			0.402
η		0.004			0.002
Sm <sup>III</sup>			Dy <sup>III</sup>		
${}^{6}F_{9/2} \leftarrow {}^{6}H_{5/2}$	9,200	9,372	${}^{6}H_{5/2} \leftarrow {}^{6}H_{15/2}$	10,200	10,249
${}^{6}F_{11/2} \leftarrow$	10,500	9,843	${}^{6}F_{7/2} \leftarrow$	11,000	10,977
${}^{4}G_{5/2} \leftarrow$	17,900	17,391	${}^{6}F_{5/2} \leftarrow$	12,400	12,346
${}^{6}P_{7/2}^{*} \leftarrow$	26750*	25,840	${}^{6}F_{3/2} \leftarrow$	13,200	13,123
β		0.974			0.998
$b^{1/2}$		0.114			0.032
$\%\delta$		2.669			0.200
η		0.013			0.001

 TABLE 2

 Electronic spectral data of various metal complexes of H<sub>2</sub>L

\*Hypersensitive band.

zwitterionic structure (= $N^+$ –H····· $O^-$ ) and the macrocycle under this condition is designated as LH2.<sup>[22]</sup> We found that the signal corresponding to the imine hydrogen, -CH-N, was broadened in the La<sup>III</sup> complex ( $\delta$ , 8.04 ppm) when compared with that of the ligand ( $\delta$ , 8.14 ppm). Additionally, a new signal, characteristic of -N<sup>+</sup>H resonance, appears in the spectrum of the complex at  $\delta$ , 12.20 ppm which is not shown by the parent ligand. These observations are in accordance with those made by Binnemans et al., [23] who, while reporting their work on rare earth containing magnetic LCs of the formula,  $[Ln(LH)_3(NO_3)_3]$ , where LH = 4-alkoxy-N-alkyl-2-hydroxy benzaldimine, found that selective irradiation of the signal at  $\delta$  12.29 ppm removed the broadening of the imine signal, thereby inferring that the signal does not correspond to the proton of the -OH group, but to the proton of the  $-N^+H$  group. Thus, it may be confirmed that the present Schiff-base (H<sub>2</sub>L) exists in the metal complex in a zwitter-ionic form, with the phenolic oxygen deprotonated and the imine nitrogen protonated (Scheme 2).

The <sup>13</sup>C{<sup>1</sup>H} NMR spectra show a significant shift of the –NCH signal from  $\delta$ , 166.01 ppm (in the case of H<sub>2</sub>L) to  $\delta$ , 177.85 ppm (in the case of the La<sup>III</sup> complex). Similar shifts were observed in the case of the carbon atoms directly attached to the bonding atoms (phenolate carbons). Other carbons of the metal complex showed only smaller changes in their chemical shift differences on comparing with the neutral ligand. Thus, the NMR spectral data imply bonding through the two phenolate

oxygen atoms of the ligand in the zwitter-ionic form to the La<sup>III</sup> metal ion.

## **IR Spectral Study**

Assignments regarding bonding through specific functional groups have been made by a careful comparison of the vibrational bands in the spectra of the ligand and the metal complexes (Table 4). The broad absorption centered on 3448 cm<sup>-1</sup> in the IR

![](_page_5_Figure_9.jpeg)

SCH. 2. Depiction of migration of phenolic protons to imine nitrogen atoms of the ligand,  $H_2L$ , during the formation of zwitter ion.

TABLE 3 NMR Spectral data\* of H<sub>2</sub>L and the La<sup>III</sup> complex

	Lig	gand	La <sup>III</sup> complex			
<sup>1</sup> H/ <sup>13</sup> C{ <sup>1</sup> H} (multiplicity)	Peak position ( $\delta$ ) ppm	Coupling constant J (Hz)	Peak position ( $\delta$ ) ppm	Coupling constant J (Hz)		
$\Phi$ –OH (s)	13.962	_	_	_		
$-N^+H(br s)$	_	_	12.199	_		
-N=CH(s)	8.141	_	8.044	_		
$-C_6H(d)$	7.073, 7.045	8.4	6.926, 6.906	6.0		
$-C_3\overline{H}(s)$	6.378	_	6.477	_		
$-C_5\overline{H}(d)$	6.368, 6.341	8.1	6.075, 6.052	6.9		
$-C_{1^{\prime\prime}}H(t)$	3.970, 3.948, 3.927	6.6	3.466, 3.444, 3.424	6.6		
$-NC\overline{H}_{2}(s)$	3.564	_	3.409	_		
$-(CH_{2})_{8}(m) \& -C_{2'}H(d)$	1.769-1.269	_	1.570-1.254	_		
$-CH_{3}(t)$	0.901, 0.880, 0.858	6.3	0.898, 0.878, 0.856	6.0		
-NCH	166.01	_	177.85	_		
$-\overline{C_4}$	163.54	_	164.44	_		
$-\overline{C}_2$	163.27	_	167.93	_		
$-\overline{C}_6$	132.45	-	134.38	-		
$-\underline{\mathbf{C}}_{1}$	112.04	-	114.62	-		
$-\overline{C}_5$	106.83	_	108.88	_		
-C <sub>3</sub>	101.80	-	104.52	-		
$-\overline{\mathbf{C}}_{1^{\prime\prime}}$	68.09	_	67.91	_		
$-\overline{C}_{1'}/-C_{4'}$	57.56	_	57.23	_		
$-\overline{C}_{2'}/-\overline{C}_{3'}$	28.48	_	28.98	_		
$-\overline{\underline{C}}_{2^{\prime\prime}}-\overline{\underline{C}}_{9^{\prime\prime}}$	31.89-22.67	_	31.90-22.67	_		
$-\underline{\underline{C}}_{10''}$	14.10	-	14.10	_		

 $\beta$  pectra (300 MHz) recorded in solutions of CDCl<sub>3</sub>; \*spectrum recorded at 22.7°C; <sup>1</sup>H NMR spectral data are given in  $\delta$  (w.r.t. TMS); <sup>13</sup>C{<sup>1</sup>H} R data measured in ppm w.r.t. CDCl<sub>3</sub> signal at 77.00 ppm.

trum of the ligand, characteristic of phenolic O-H stretch-<sup>[24]</sup> may be understood to involve H-bonding (to the ortho =N group presumably of intramolecular type) under the exmental conditions; this band totally disappears in the spectra of the complexes due to the shifting of the phenolic proton to the azomethine nitrogen atom resulting in the formation of zwitter ion. The weak/medium intensity bands centered on 1286 cm<sup>-1</sup> are assignable to phenolic C-O stretching vibration. The strong

Downloaded by [Moskow State Univ Bibliote]	$-\underline{C}_{1'}$ $-\underline{C}_{2'}$ $-\underline{C}_{2'}$ $-\underline{C}_{1'}$ $-\underline{C}_{2'}$ $-\underline{C}_{1'}$ S NMF spec ing, <sup>[1]</sup> spec perir

TABLE 4
IR Spectral data* (cm <sup>-1</sup> ) of $H_2L$ and of $Ln^{III}$ metal complexes

	ν ( <b>O</b> –H)		vasCH	veCH		v (C–O)		ν	(NO <sub>3</sub> )		
H <sub>2</sub> L <sup>1</sup> /complex	phenolic	$\nu$ (N <sup>+</sup> H)	CH <sub>3</sub> /CH <sub>2</sub>	CH <sub>3</sub> /CH <sub>2</sub>	$\nu(C=N)$	phenolic	$v_5$	Ionic	$v_1$	$\nu_2$	v <sub>5</sub> -v
H <sub>2</sub> L	3448 b	_	2,922	2,854	1,619	1,286	_	_	_	_	_
$[La_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3199w	2,926	2,855	1,652	1,229	1,472	1,383	1,290	846	182
$[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3182w	2,925	2,855	1,649	1,225	1,472	1,381	1,289	846	183
$[Nd_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3190w	2,925	2,855	1,649	1,227	1,473	1,381	1,289	845	184
$[Sm_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3178w	2,926	2,855	1,649	1,229	1,472	1,381	1,290	846	182
$[Eu_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3170w	2,926	2,855	1,653	1,229	1,472	1,382	1,291	846	181
$[Gd_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3175w	2,926	2,855	1,653	1,229	1,468	1,378	1,288	845	180
$[Tb_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3173w	2,926	2,855	1,653	1,229	1,472	1,378	1,288	845	184
$[Dy_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3191w	2,926	2,855	1,652	1,229	1,472	1,381	1,291	846	181
$[Ho_2(LH_2)_3(NO_3)_4](NO_3)_2$	-	3193w	2,926	2,855	1,652	1,229	1,470	1,379	1,289	846	181

\*Spectra recorded as KBr pellets; b: broad; as: asymmetric; s: symmetric; w: weak.

![](_page_7_Figure_1.jpeg)

FIG. 1. (a) and (b): <sup>1</sup>H NMR spectra of ligand (H<sub>2</sub>L) and its La<sup>III</sup> complex; (c) and (d): <sup>13</sup>C{<sup>1</sup>H} NMR spectra of ligand (H<sub>2</sub>L) and its La<sup>III</sup> complex.

intensity band occurring at 1619 cm<sup>-1</sup>, assignable<sup>[25]</sup> to  $\nu_{C=N}$  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<sup>III</sup> ion results in migration of the phenolic protons onto the two uncoordinated imino nitrogen atoms, which then get intramolecularly hydrogen-bonded to the metal-bound phenolate oxygen atoms to give rise to the zwitterionic structure, N<sup>+</sup>–H····O<sup>-</sup>. Similar zwitter-ionic behavior has been reported by others for acyclic Schiff-base lanthanide complexes.<sup>[26]</sup> The formation of a zwitterionic form can be rationalized by the tendency of the lanthanide ions to coordinate to negatively charged ligands with a preference for O-donor ligands. By transfer of the phenolic proton to the imine nitrogen, the phenolic oxygen becomes negatively charged thereby facil-

itating coordination to the lanthanide ion. The initial evidence for zwitter-ionic formation was obtained from <sup>1</sup>H NMR spectra while further evidence was given by infrared spectroscopy and, more particularly, by the band frequencies of the C=N stretching vibration. The shift to higher wave numbers upon complexation implies the presence of C–N<sup>+</sup> group<sup>[27]</sup> and the noninvolvement of nitrogen atom in complex formation. Thus, all the present complexes are characterized by a strong band due to C=N stretching vibration at 1649–1653 cm<sup>-1</sup> and a weak broad band at about 3199–3170 cm<sup>-1</sup> due to the hydrogen-bonded N<sup>+</sup>–H····O<sup>-</sup> vibration of the protonated imine.<sup>[27]</sup> Thus, it may be understood that the ligand coordinates to the metal ion *via* the negatively charged phenolic oxygen with no bond formation between the lanthanide ion and the imine nitrogen.

![](_page_8_Figure_1.jpeg)

FIG. 2. Proposed polyhedron (Monocapped Octahedron) for  $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$ : Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho.

The IR spectra of the complexes also show three additional characteristic frequencies of the coordinating nitrate groups ( $C_{2\nu}$ ) in the range of 1473–1468, 1291–1288, and 846–845 cm<sup>-1</sup>.<sup>[28]</sup> 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 at

 TABLE 5

 Transition temperatures and enthalpy changes

Compound	Transition <sup>a</sup>	$T^{\mathrm{b}}/^{\circ}\mathrm{C}$	$\delta H^{\rm b}/{\rm kJ}~{\rm mol}^{-1}$
H <sub>2</sub> L	Cr-Cr	76.97	33.93
	Cr-SmB	82.04	6.45
	SmB-N	105.97	69.54
	N-I	111.00 <sup>c</sup>	_
	N-SmB	108.89	68.35
	SmB-Cr	72.99	38.48
$[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$	Cr-SmA	134.90	23.94
	SmA-N	167.86	50.93
	N-I	242.00 <sup>c</sup>	-

<sup>a</sup>Cr: Crystal, N: Nematic; SmA: Smectic A; SmB: Smectic B; I: Isotropic liquid.

<sup>b</sup>Data as obtained from the first DSC cycle.

<sup>c</sup>Data.as inferred from Polarizing Optical Microscope.

higher energies,  $184-180 \text{ cm}^{-1}$ , may be indicative of a bidentate interaction of the coordinated nitrate anions with the lanthanide ions.<sup>[28,29]</sup> The additional bands observed at  $1383-1378 \text{ cm}^{-1}$  may be attributed to the non-coordinated nitrate groups present outside the coordination sphere of the complexes. At this juncture, a distorted mono-capped octahedron with CN = 7 may be tentatively proposed for the complexes (Figure 2).

## **Optical and Thermal Study**

The mesophases were identified by polarized hot-stage microscopy (POM) and DSC studies. The POM studies imply smectic-B and nematic phases of  $H_2L$  and smectic-A and nematic phases of the  $Pr^{III}$  complex, respectively; the corresponding transition temperatures and enthalpy changes are given in Table 5 while the textures are shown in Figure 3. All the other Ln<sup>III</sup> complexes under present study are found to be non-mesogenic.

![](_page_8_Figure_12.jpeg)

FIG. 3. Optical textures of: (a)  $H_2L$  (*SmB*) at 92°C and (b)  $Pr^{III}$  complex (*SmA*) at 150°C.

## **CONCLUSION**

The mesogenic Schiff-base, N,N'-di-(4-decyloxysalicylidene)-l',4'-diaminobutane, (H<sub>2</sub>L) exhibits smectic-B and nematic phases and coordinates to Ln<sup>III</sup> as a neutral bidentate species to yield seven-coordinate complexes (the polyhedron being possibly a distorted monocapped octahedron) of the general formula, [Ln<sub>2</sub>(LH<sub>2</sub>)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. In all cases, the zwitterionic species of the neutral bidentate ligand, H<sub>2</sub>L, coordinates to the Ln<sup>III</sup> metal ion through two phenolate oxygen atoms. Among the complexes, only the Pr<sup>III</sup> complex exhibits liquid crystalline property (smectic-A and nematic phases).

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