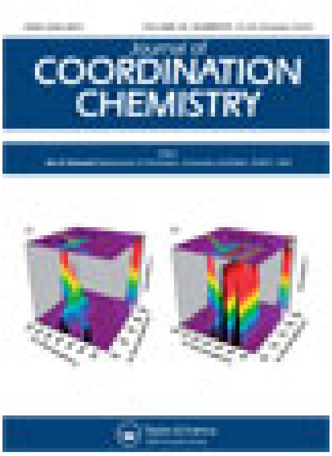

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Complexes of some 4f metal ions of the mesogenic Schiff-base, N,N′-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene: synthesis and spectral studies

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Complexes of some 4f metal ions of the mesogenic Schiff-base, *N,N′*-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene: synthesis and spectral studies

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A mesogenic Schiff-base, *N,N′*-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene, H_2ddsdbz (abbreviated as H_2L), that exhibits a nematic mesophase was synthesized and its structure was studied by elemental analysis, mass spectrometry, NMR, and IR spectral techniques. The Schiff-base, H_2L, upon condensation with hydrated lanthanide(III) nitrates yields Ln^{III} complexes, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. Analyses of the IR and NMR spectral data imply bidentate Schiff-base 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. Polarizing optical microscope and differential scanning calorimetry studies reveal that despite H_2L being mesogenic, none of the Ln^{III} complexes synthesized under this study exhibits mesomorphism.

Keywords: Mesogenic Schiff-base; Ln^{III} Complexes; Zwitterionic-coordination; Mono-capped octahedron; NMR and IR Spectra

1. Introduction

Liquid-crystalline metal complexes, called metallomesogens, are the subject of intense research [1–4]. Liquid crystals with 3d and/or 4f metals have received increasing attention because of the possibility of combining the physico-chemical properties of the metal (color, magnetism, polarizability, redox behavior, etc.) with those of the organic framework [5–9]. Bertolo *et al.* and Chandra *et al.* published [10, 11] complexes of macrocyclic Schiff-base ligands with different size, number, and donors involving coordination with a variety of metal centers. The research groups of Galyametdinov, Bruce, and Binnemans [12–15] reported complexes of Schiff-base ligands with one aromatic ring, but Schiff-base ligands with two and more than two aromatic rings were much less studied [16, 17]. Hence, in continuation of earlier work [18–21] carried out in our laboratory on systematic structural and spectroscopic studies of 3d and 4f metal complexes of mesogenic Schiff-bases, we present here synthesis and spectroscopic

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characterization of some Ln^{III} complexes with a Schiff-base containing three aromatic rings, namely *N*,*N*′-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene (H_2L) (**2**).

2. Experimental

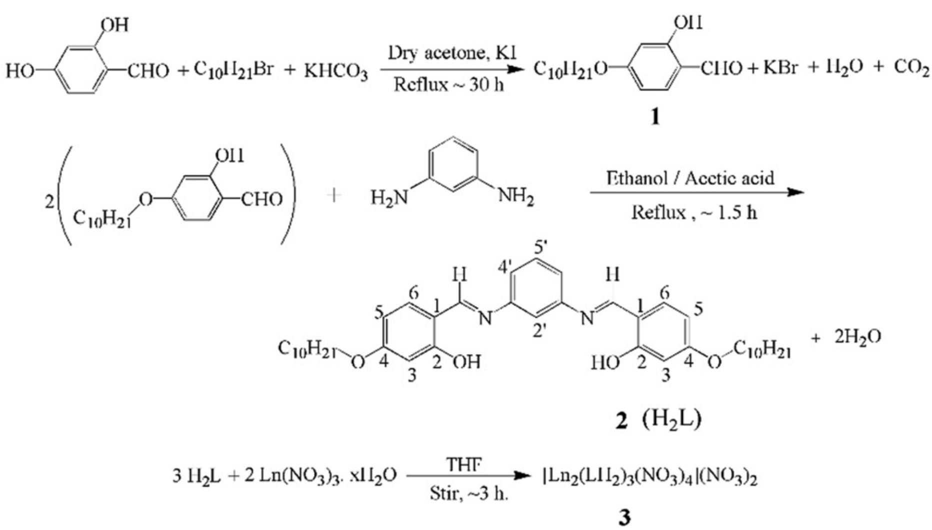
2.1. *Materials*

We obtained reagents of analytical grade (AR) from commercial vendors and used them without purification: 1-bromodecane, 2,4-dihydroxy-benzaldehyde, and 1,3-diamino-benzene are from Sigma-Aldrich, USA; $Ln(NO_3)_3 \cdot xH_2O$ salts are from Indian Rare Earths Ltd., while KI and $KHCO_3$ are from Merck. The solvents obtained from commercial sources were dried using standard methods [22] when required.

2.2. *Synthesis and analysis*

Synthesis of *N*,*N*′-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene (H_2L) (**2**), was achieved by a two-step synthesis, alkylation of 2,4-dihydroxybenzaldehyde with 1-bromodecane followed by condensation with aromatic diamine as per the experimental details given in scheme 1. We prepared 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**) by reacting solutions of the appropriate metal nitrate and H_2L at room temperature.

2.2.1. Preparation of 4-decyloxysalicylaldehyde (1). To a solution of 100 mL of dry acetone we added equimolar amounts of 2,4-dihydroxy benzaldehyde (50 mmol, 6.91 g), 1-bromodecane (50 mmol, 10.4 mL), and potassium bicarbonate (~55 mmol, 5.51 g) and



Scheme 1. Reaction steps involved in the synthesis of 4-decyloxysalicylaldehyde (**1**), *N*,*N*′-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene (H_2L) (**2**), and Ln^{III} complexes (**3**).

refluxed the mixture for ~30 h in the presence of KI (0.1–0.2 g) as a catalyst and filtered while hot to remove insoluble solids; subsequently, we added 6*N* hydrochloric acid to the filtrate until neutralization and extracted the product twice with 100 mL portions of $CHCl_3$. By concentrating the chloroform extracts we obtained a straw-yellow solid 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); evaporation of this purified extract finally yielded 4-decyloxysalicylaldehyde (**1**) in the form of a white solid; yield: 62% (8.63 g).

2.2.2. Synthesis of *N,N′*-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene (H_2L) (2). We prepared *N,N′*-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene (H_2L) (**2**) by refluxing together absolute ethanolic solutions of 4-decyloxysalicylaldehyde (**1**) (8.34 g, 30 mmol in 50 mL) and 1,3-diaminobenzene (1.62 g, 15 mmol in 15 mL) for ~1.5 h in the presence of a few drops of glacial acetic acid. Leaving the resulting mixture overnight yielded a yellow solid, **2**, which was filtered off under suction, thoroughly washed with cold ethanol and dried at room temperature. Yield: 75%, m.p. 105°C. Anal. Calcd for $C_{40}H_{56}N_2O_4$ (%): C, 76.39; H; 8.98; N, 4.45. Found (%): C, 76.33; H, 9.05; N, 4.42. ^{1}H NMR (300 MHz; DMSO-d_6): $\delta = 0.86$ (t, 3H, –CH_3, $J = 6.3$ Hz), 1.72–1.27 (m, 16H, $H^{methylene}$), 4.04 (t, 2H, –OCH_2, $J = 6.6$ Hz), 6.46 (s, 1H, H^3), 6.54 (d, 1H, H^5, $J = 7.8$ Hz), 7.24 (d, 1H, $H^{4'}$, $J = 7.5$ Hz,), 7.36 (s, 1H, $H^{2'}$), 7.46 (d, 1H, $H^{5'}$, $J = 6.6$ Hz), 7.51 (d, 1H, H^6, $J = 9.0$ Hz), 8.89 (s, 1H, –N=CH), 13.38 (s, br, 1H, ph-OH); $^{13}C\{^1H\}$NMR: (75.45 MHz; DMSO-d_6) 163.02 (–NCH), 162.85 (–C_4), 162.46 (–C_2), 148.02 (–$C_{3'}$), 133.73 (–$C_{5'}$), 130.02 (–C_6), 129.22 (–$C_{4'}$), 118.80 (–$C_{2'}$), 112.69 (–C_1), 106.89 (–C_5), 101.20 (–C_3), and 67.62 (–OCH_2). LC/MS mass: the molecular ion (*m*/*e*, 631, 12% intensity) generated simultaneously three fragments, M_1–M_3 (*m*/*e*, fragment, % intensity): M_1: 613, $C_{10}H_{21}OC_6H_3(OH)CH{=}N(C_6H_4)N{=}CHC_6H_3(OH)O(CH_2)_8CH_2^+$, 15%; M_2 (generated from M_1): 571, $C_{10}H_{21}O\text{-}C_6H_3(OH)CH{=}N(C_6H_4)N{=}CH\text{-}C_6H_3(OH)O(CH_2)_5CH_2^+$, 17%; M_3: 276, $C_{10}H_{21}OC_6H_3\text{-}(OH)CH{=}N^+$, 100%; IR (KBr) ($\nu_{max}/cm^{-1}$): $\nu(O–H)_{phenol}$ 3450(br), ν(C=N) 1623(s), $\nu(C–O)_{phenol}$ 1291(s).

2.2.3. Synthesis of $[La_2(LH_2)_3(NO_3)_4](NO_3)_2$ (3). Dropwise addition of THF solution of $La(NO_3)_3 \cdot 6H_2O$ (0.87 g, 2.0 mmol in 20 mL) to a THF solution of H_2L (1.89 g, 3.0 mmol in 30 mL) under magnetic stirring resulted in formation of the La^{III} complex. The resultant solution turned cloudy after ~15 min; a solid product separated upon continuous stirring for ~3 h at room temperature, which was filtered, washed repeatedly with cold methanol, and dried over fused $CaCl_2$. Yield: 66% as yellow solid; m.p. 256°C (decompose); Anal. Calcd for $La_2C_{120}H_{168}N_{12}O_{30}$ (%): C, 56.82; H; 6.68; N, 6.63; La, 10.95; Found (%): C, 56.89; H, 6.70; N, 6.59 and La, 11.01, ^{1}H NMR (300 MHz; DMSO-d_6): 0.86 (t, 3H, CH_3, $J = 5.7$ Hz), 1.72–1.27 (m, 16H, $H^{methylene}$), 4.04 (t, 2H, –OCH_2, $J = 6.3$ Hz), 6.46 (s, 1H, H^3), 6.53 (d, 1H, H^5, $J = 8.4$ Hz), 7.23 (d, 1H, $H^{4'}$, $J = 8.1$ Hz), 7.35 (s, 1H, $H^{2'}$), 7.45 (d, 1H, $H^{5'}$, $J = 7.8$ Hz), 7.51 (d, 1H, H^6, $J = 8.7$ Hz), 8.88 (s, 1H, –N=CH), 13.34 (br-s, 1H, –N^+H); $^{13}C\{^1H\}$ NMR (75.45 MHz; DMSO-d_6): 175.28 (–NCH), 162.82 (–C_4), 168.08 (–C_2), 148.91 (–$C_{3'}$), 133.69 (–$C_{5'}$), 129.78 (–C_6), 129.20 (–$C_{4'}$), 118.76 (–$C_{2'}$), 112.70 (–C_1), 106.85 (–C_5), 101.20 (–C_3), and 67.61 (–$C_{1''}$); IR (KBr) (ν_{max}/cm^{-1}): ν(–N^+H, str.) 3195(w), ν(C=N) 1636(s), $\nu(C–O)_{phenol}$ 1243(m).

We synthesized all the other rare-earth complexes (Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) 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. 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 (KBr) ($\nu_{max}/cm^{-1}$): ν(–N$^+$H, str.) 3205(w), ν(C=N) 1637(s), $\nu(C–O)_{phenol}$ 1228(m); $[Ho_2(LH_2)_3(NO_3)_4](NO_3)_2$: IR (KBr) ($\nu_{max}/cm^{-1}$): ν(–N$^+$H, str.) 3195(w), ν(C=N) 1640(s), $\nu(C–O)_{phenol}$ 1238(m).

2.3. *Physical measurements*

To determine the metal content of the complexes, we carried out complexometric titrations against EDTA using xylenol orange as indicator. Carbon, hydrogen, and nitrogen were analyzed on an Exeter Analyzer, Model CE-440 CHN. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL AL-300 MHz FT-NMR multinuclear spectrometer; infrared spectra (as KBr pellets from 4000 to 400 cm^{-1}) on a JASCO FT-IR (model-5300) spectrophotometer; mass spectrum on a LC/MS (ESI Mode-3000) mass spectrometer, and UV-Vis spectra on a Shimadzu spectrophotometer (model Pharmaspec-UV 1700). We measured molar conductances of the complexes in 0.001 mol L^{-1} solutions, magnetic susceptibility data at room temperature on a Cahn–Faraday balance with $Hg[Co(NCS)_4]$ as the calibrant, and identified the mesophases under polarized binocular microscope (LOMO, USA) equipped with hot-stage and digital camera (Nikon Coolpix 4500). Differential scanning calorimetry (DSC) studies were made on a METTLER DSC-25, Mettler STARe SW 9.00 unit.

3. Results and discussion

3.1. *Magnetic and spectral studies*

The yellow Schiff-base (H_2L) reacts with $Ln(NO_3)_3 \cdot xH_2O$ to yield Ln^{III} complexes; table 1 includes the data obtained (elemental analyses, magnetic moments, important physical properties, and general behavior) on the ligand and the complexes. The analytical data of the complexes imply 2 : 3 metal to ligand stoichiometry with 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. In all the complexes H_2L coordinates as a non-deprotonated zwitterionic species as evidenced by NMR and IR spectra while the counter ions (nitrate groups both within and outside the coordination sphere) balance the positive charge of the Ln^{III} ion(s); the molar conductance data (107–121 Ω^{-1} cm^2 per mole) imply 2 : 1 electrolytic behavior [23].

The μ_{eff} values (at room temperature) of the Ln^{III} complexes (3.93, 3.97, 1.90, 4.87, 11.18, 12.61, 14.56, and 15.31 B.M. for Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, respectively) are higher than the reported van Vleck values; we attribute these higher values to metal–metal interactions in analogy to similar complexes reported [24–26] with abnormal μ_{eff} values.

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} complexes (table 3) in view of their

Table 1. Analytical data and general behavior of the Ln^{III} complexes of H_2L.

H_2L/Complex formula weight (empirical formula)	Color, yield (%) (solubility)	m.p. (°C)	Found (Calcd) % C	H	N	M	μ_{eff} (B.M.) (van Vleck values)[h]	Molar conductance[i]
H_2L, 628.88 ($C_{40}H_{56}N_2O_4$)	Yellow,75%[a,b,c,d,e,f]	105	76.33 (76.39)	9.05 (8.98)	4.46 (4.45)	(–)	–	
$[La_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2536.49 ($La_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 66%[c,f]	256[g]	56.89 (56.82)	6.70 (6.68)	6.59 (6.63)	11.01 (10.95)	Diamagnetic	115
$[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2540.49 ($Pr_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 72%[c,f]	262[g]	56.66 (56.73)	6.72 (6.67)	6.70 (6.62)	11.06 (11.09)	3.93 (3.40–3.60)	109
$[Nd_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2547.16 ($Nd_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 73%[c,f]	268[g]	56.60 (56.58)	6.68 (6.65)	6.59 (6.60)	11.31 (11.33)	3.97 (3.50–3.60)	112
$[Sm_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2568.40 ($Sm_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 70%[c,f]	275[g]	56.35 (56.31)	6.59 (6.62)	6.50 (6.57)	11.81 (11.75)	1.90 (1.50–1.60)	118
$[Eu_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2562.61 ($Eu_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 66%[c,f]	265[g]	56.22 (56.24)	6.56 (6.61)	6.61 (6.56)	11.90 (11.86)	4.87 (3.40–3.60)	121
$[Gd_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2573.18 ($Gd_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 63%[c,f]	278[g]	55.99 (56.01)	6.60 (6.58)	6.47 (6.53)	12.25 (12.22)	11.18 (7.80–8.00)	111
$[Tb_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2576.53 ($Tb_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 71%[c,f]	270[g]	55.91 (55.94)	6.62 (6.57)	6.56 (6.52)	12.35 (12.34)	12.61 (9.40–9.60)	107
$[Dy_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2583.68 ($Dy_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 64%[c,f]	254[g]	55.85 (55.78)	6.50 (6.55)	6.44 (6.51)	12.60 (12.58)	14.56 (10.40–10.50)	118
$[Ho_2(LH_2)_3(NO_3)_4](NO_3)_2$ 2588.54 ($Ho_2C_{120}H_{168}N_{12}O_{30}$)	Yellow, 69%[c,f]	265[g]	55.75 (55.68)	6.49 (6.54)	6.50 (6.49)	12.67 (12.74)	15.31 (10.30–10.50)	113

[a]Benzene; [b]chloroform; [c]THF; [d]dichloromethane; [e]hot ethanol; [f]hot DMSO, DMF; [g]decompose; [h]magnetic moments measured at room temperature; [i]molar conductance values in units of $\Omega^{-1}\,cm^2$ per mole measured at room temperature in $10^{-3}\,mol\,L^{-1}$ solutions in a DMF solvent.

Table 2. IR spectral data (cm^{-1}) of H_2L and of Ln(III) metal complexes.[a]

H_2L/Complex	ν(O–H) phenolic	$\nu(N^+H)$	ν_{as}CH CH_3/CH_2	ν_sCH CH_3/CH_2	ν(C=N)	ν(C–O) phenolic	$\nu(NO_3)$ ν_5	Ionic	ν_1	ν_2	ν_5–ν_1
H_2L	3450b	–	2925	2855	1623	1291	–	–	–	–	–
$[La_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3195w	2925	2854	1636	1243	1462	1385	1287	850	175
$[Pr_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3200w	2927	2856	1640	1242	1465	1384	1292	852	173
$[Nd_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3200w	2926	2855	1642	1244	1463	1385	1289	852	174
$[Sm_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3205w	2925	2855	1637	1237	1473	1385	1292	837	181
$[Eu_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3210w	2925	2855	1643	1237	1472	1385	1295	849	177
$[Gd_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3205w	2926	2855	1637	1238	1475	1384	1293	841	182
$[Tb_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3210w	2926	2855	1640	1238	1472	1384	1293	842	179
$[Dy_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3210w	2926	2855	1638	1237	1472	1384	1293	842	179
$[Ho_2(LH_2)_3(NO_3)_4](NO_3)_2$	–	3195w	2925	2855	1640	1238	1472	1384	1292	846	180

[a]Spectra recorded as KBr pellets; b: broad; as: asymmetric; s: symmetric; w: weak.

Table 3. Electronic spectral data of selected metal complexes of H_2L.

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
Pr^{III}			Nd^{III}		
$^1G_4 \leftarrow {}^3H_4$	9900	9794	$^4F_{3/2} \leftarrow {}^4I_{9/2}$	11,450	–
$^1D_2{}^a \leftarrow$	16,850	16,835	$^4F_{5/2}$, $^2H_{9/2} \leftarrow$	12,500	12346
$^3P_0 \leftarrow$	20,800	–	$^4S_{3/2}$, $^4F_{7/2} \leftarrow$	13,500	13,459
			$^2G_{7/2}{}^a \leftarrow$	17,400	17,182
β		0.994			0.991
$B^{1/2}$		0.055			0.067
$\%\delta$		0.604			0.908
η		0.003			0.004
Sm^{III}			Dy^{III}		
$^6F_{9/2} \leftarrow {}^6H_{5/2}$	9200	9174	$^6F_{9/2}$, $^6H_{5/2} \leftarrow {}^6H_{15/2}$	9100	9099
$^6F_{11/2} \leftarrow$	10,500	10,482	$^6H_{5/2} \leftarrow$	10,200	10,122
$^4G_{5/2} \leftarrow$	17,900	–	$^6F_{7/2} \leftarrow$	11,000	10,989
$^6P_{7/2}{}^a \leftarrow$	26,750	–	$^6F_{5/2} \leftarrow$	12,400	12,346
β		0.998			0.997
$B^{1/2}$		0.032			0.039
$\%\delta$		0.200			0.301
η		0.001			0.001

[a]Hypersensitive band.

ability to show hypersensitive bands; the λ_{max} values of the complexes show considerable red shift in comparison with those of their corresponding aqua ions [27] due to the nephelauxetic effect [28] which is regarded as a measure of covalency of the bonding between the metal ions and the ligands. Various bonding parameters (table 3), namely nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's parameter ($\%\delta$), and covalency angular overlap parameter (η), calculated by procedures reported [29], suggest a weak covalent nature of the metal–ligand bonds.

On the basis of IR, NMR, and electronic spectral data, we propose that the mesogenic Schiff-base, *N,N′*-di-(4-decyloxysalicylidene)-1′,3′-diaminobenzene (H_2L) (**2**),

Table 4. NMR spectral data of H2L and the La(III) complex.[a]

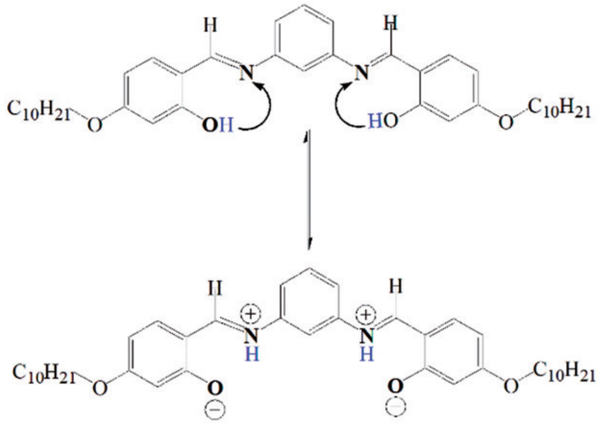
	Ligand		La(III) complex	
$^1H/^{13}C\{^1H\}$ (multiplicity)	Peak position (δ) ppm	Coupling constant J (Hz)	Peak position (δ) ppm	Coupling constant J (Hz)
Φ–OH (s)	13.380	–	–	–
$–N^+H$ (br s)	–	–	13.343	–
–N=CH (s)	8.888	–	8.883	–
$–C_6H$ (d)	7.529, 7.499	9.0	0 7.527, 7.498	8.7
$–C_{5'}H$ (d)	7.467, 7.445	6.6	7.466, 7.440	7.8
$–C_{2'}H$ (s)	7.358	–	7.352	–
$–C_{4'}H$ (d)	7.249, 7.224	7.5	7.247, 7.220	8.1
$–C_5H$ (d)	6.550, 6.524	7.8	6.546, 6.518	8.4
$–C_3H$ (s)	6.458	–	6.456	–
$–C_{1''}H$ (t)	4.057, 4.035, 4.015	6.6	4.058, 4.037, 4.015	6.3
$–(CH_2)_8$ (m)	1.720–1.268	–	1.721–1.267	–
$–CH_3$ (t)	0.880, 0.859, 0.836	6.3	0.879, 0.860, 0.838	5.7
$–N\underline{C}H$	163.02	–	175.28	–
$–\underline{C}_4$	162.85	–	162.82	–
$–\underline{C}_2$	162.46	–	168.08	–
$–\underline{C}_{1'}/–\underline{C}_{3'}$	148.02	–	148.91	–
$–\underline{C}_{5'}$	133.53	–	133.69	–
$–\underline{C}_6$	130.02	–	129.78	–
$–\underline{C}_{4'}/–\underline{C}_{6'}$	129.22	–	129.20	–
$–\underline{C}_{2'}$	118.80	–	118.76	–
$–\underline{C}_1$	112.69	–	112.70	–
$–\underline{C}_5$	106.89	–	106.85	–
$–\underline{C}_3$	101.20	–	101.20	–
$–\underline{C}_{1''}$	67.62	–	67.61	–
$–\underline{C}_{2''}–\underline{C}_{9''}$	30.81–21.56	–	30.78–21.53	–
$–\underline{C}_{10''}$	13.35	–	13.30	–

Spectra (300 MHz) recorded in solutions of DMSO-d_6.
[a]Spectrum recorded at 75.5°C; ^1H NMR spectral data are given in δ (w.r.t. TMS); $^{13}C\{^1H\}$ NMR data measured in ppm w.r.t. DMSO-d_6 signal at 39.50 ppm.

coordinates neutral bidentate to Ln^{III} to yield seven-coordinate complexes, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, possibly in a distorted mono-capped octahedron.

We studied the Schiff-base and metal complexes by IR and NMR spectroscopy and elemental analyses and confirmed the molecular weight of the ligand by LC/MS mass spectrum. The mass spectrum of H_2L shows the base peak ($m/e = 276$, corresponding to the fragment, $C_{10}H_{21}OC_6H_3(OH)CH{=}N^+$), the molecular ion peak with ~12% intensity ($m/e = 631$), and the major fragment peaks ($m/e = 613$ and 571) due to $C_{10}H_{21}OC_6H_3(OH)CH{=}N\text{-}(C_6H_4)N{=}CHC_6H_3(OH)O(CH_2)_8CH_2^+$ and $C_{10}H_{21}OC_6H_3(OH)\text{-}CH{=}N(C_6H_4)N{=}CH\text{-}C_6H_3(OH)O(CH_2)_5CH_2^+$, respectively.

A comparison of NMR spectral [^1H and $^{13}C\{^1H\}$] data (table 4, figure S1 in Supplementary material section) of the ligand, with those of the La^{III} complex, shows that the bonding of the phenolic oxygen of the ligand to metal is substantiated by the phenolic–O<u>H</u> signal, appearing at δ, 13.38 in the ligand, disappears upon complexation. The composition of the La^{III} complex, $[La_2(LH_2)_3(NO_3)_4](NO_3)_2$, implies coordination of H_2L as a neutral species; further, the ^1H NMR spectral data imply that the phenolic protons are shifted to the two uncoordinated imino nitrogen atoms, which then are



Scheme 2. Depiction of migration of phenolic protons to imine nitrogen atoms of H_2L during the formation of zwitterion.

intramolecularly hydrogen-bonded to the metal-bound phenolate oxygen atoms to give zwitterionic structure (=N^+–H···O^-) and the macrocycle under this condition is designated as LH_2 [30]. The signal corresponding to the imine hydrogen, –CH=N, broadened in the La^{III} complex (δ, 8.88) when compared with that of the ligand (δ, 8.89); further, a new signal, characteristic of –N^+H resonance, appears at 13.34 δ which is absent in H_2L. These observations are in accord with those made by Binnemans *et al.* [31], who, while reporting their work on rare earth containing magnetic liquid crystals, [$Ln(LH)_3(NO_3)_3$], where LH = 4-alkoxy-N-alkyl-2-hydroxy benzaldimine, found that selective irradiation of the signal at 12.29 δ 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, H_2L exists in the metal complex in a zwitterionic form, with the phenolic oxygen deprotonated and the imine nitrogen protonated (scheme 2).

$^{13}C\{^1H\}$ NMR spectra show a significant shift of the –NCH signal from δ, 163.02 (H_2L) to δ, 175.28 (in the La^{III} complex); the carbons directly attached to the phenolate showed similar shifts while the shifts of the other carbon signals were of lower magnitude. Thus, NMR spectral data imply bonding through two phenolate oxygen atoms of the ligand in the zwitterionic form to La^{III}.

The broad absorption at 3450 cm^{-1} in the IR spectrum of the ligand, characteristic of $\nu(O–H)_{phenolic}$ [32], 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 formation of the zwitterion. Weak/medium intensity bands centered at 1291 cm^{-1} are assigned to $\nu(C–O)_{phenolic}$. The strong band at 1623 cm^{-1}, assignable [33] to ν(C=N) of azomethine, undergoes a hypsochromic shift (13–17 cm^{-1}) in all the complexes on account of zwitterion formation. Thus, complexation 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···O^-. Binnemans *et al.* [34] reported similar zwitterionic behavior for acyclic

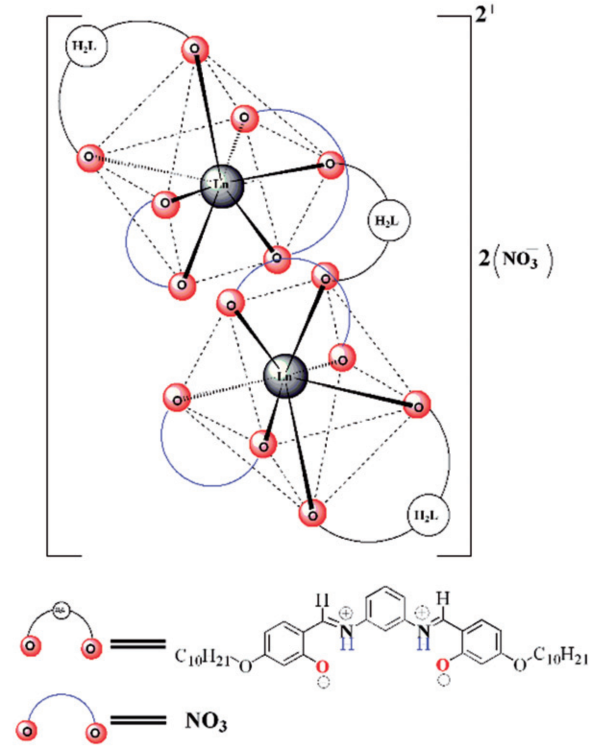


Figure 1. Proposed polyhedron (mono-capped octahedron) for $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$: Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho.

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 ν(C=N) shifting to higher wavenumbers upon complexation, implying the presence of the $C–N^+$ [35] and the non-involvement of nitrogen in complex formation. The present complexes are characterized by a strong band (1643–1636 cm^{-1}) due to ν(C=N) and a weak broad band at 3210–3195 cm^{-1} due to hydrogen-bonded $N^+–H\cdots O^-$ vibration of the protonated imine [35]. Thus, the ligand coordinates to 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 1475–1462, 1295–1287, and 852–837 cm^{-1} [36]. 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 (182–173 cm^{-1}) at higher energies indicates a bidentate coordinated nitrate [36, 37]. Additional bands at 1385–1384 cm^{-1} may be attributed to non-coordinated nitrate present outside the coordination sphere. A distorted mono-capped octahedron with coordination number = 7 may be tentatively proposed for the complexes (figure 1).

Table 5. Thermodynamic data (transition temperatures and enthalpy and entropy changes).

Compound	Transition[a]	T^{b} (°C)	δH^{b} (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
H_2L	Cr–Cr	47.52	10.67	33.29
	Cr–N	94.85	18.20	49.48
	N–I	104.74	1.77	4.69
	I–N	99.00[c]	–	–
	N–Cr	75.41	17.22	49.42
	Cr–Cr	65.67	3.13	9.24

δH (kJ mol^{-1}) = $\Delta H \times$ mw/1000; ΔS (J mol^{-1} K^{-1}) = ΔH (kJ mol^{-1}) $\times$ 1000/TK.
[a]Cr: Crystal, N: Nematic; I: Isotropic liquid.
[b]Data as obtained from the second DSC cycle.
[c]Data as inferred from polarizing optical microscope.

The polarizing optical microscope (POM) studies imply the nematic phase of H_2L and the corresponding transition temperatures, enthalpy, and entropy changes are given in table 5 while the texture is shown in "Supplementary material" section. All Ln^{III} complexes reported here were non-mesogenic. The plausible explanation may be that the thermal energy required to melt the alkoxy chains is so high that the layered structure breaks down before the alkoxy chains are completely molten; in such a situation, the liquid-crystalline properties of the materials are lost.

4. Conclusion

The mesogenic Schiff-base, *N*,*N*′-di-(4-decyloxysalicylidene)-l′,3′-diaminobenzene (H_2L), coordinates to Ln^{III} as a neutral bidentate species to yield seven-coordinate complexes, $[Ln_2(LH_2)_3(NO_3)_4](NO_3)_2$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. Unlike the case with 3d metal ions, the neutral bidentate H_2L coordinates to Ln^{III} in a zwitterionic form through two phenolate oxygen atoms. POM and DSC studies reveal that only H_2L shows mesogenic activity (nematic phase), not the Ln^{III} complexes presumably due to breakdown of the structure of the complexes before the isotropic (clear melting) point.

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