Synthesis, structural characterization and thermal studies of lanthanide complexes with Schiff base ligand N,N’-di-(4’-pentyloxybenzoate)-salicylidene-1,3-diaminopropane

Sadeem M. Al-Barody and Haslina Ahmad

Cogent Chemistry (2015), 1: 1093920
Synthesis, structural characterization and thermal studies of lanthanide complexes with Schiff base ligand \( \text{N,N}^{+}\)-di-(4'-'pentyloxybenzoate)-salicylidene-1,3-diaminopropane

Sadeem M. Al-Barody* and Haslina Ahmad

Abstract: New mesogen Schiff base ligand \( \text{N,N}^{+}\)-di-(4'-'pentyloxybenzoate)salicylidene-1,3-diaminopropane \([\text{H}_2\text{L}]\) was synthesized by the reaction of substituted 4-pentyloxy(4'-'formyl-3'-'hydroxy)-benzoate and 1,3-diaminopropane in 2:1 molar ratio. Four mononuclear lanthanide complexes of the type \([\text{Ln}(\text{H}_2\text{L})\text{Cl}]\) (\(\text{Ln} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Sm}^{3+} \text{and Gd}^{3+}\) were synthesized and characterized by \(^1\text{H}, ^{13}\text{CNMR}, \text{fourier transform infrared (FT-IR)}\text{ spectroscopy, elemental analysis (C,H,N,O), gas chromatography-mass, magnetic susceptibility and molar conductivity}. \text{Thermal properties of the title compounds were studied using the theogravimetric analysis/differential scanning calorimetry (TGA/DSC) and optical polarizing microscopy (OPM). The ligand and coordination compounds exhibit liquid crystalline properties (smectic A).}

1. Introduction
The coordination chemistry of lanthanide ions has been widely investigated in recent years because of both its useful magnetic and optical behaviors. It could exhibit coordination numbers 6–12, with 8 or 9 being ubiquitous (Chakraborty et al., 2009). Wide variety of ligands such as Schiff bases ligands

ABOUT THE AUTHOR
Sadeem M. Al-Barody is a faculty member in the Department of Chemistry at University of Al-Mustansiriyah. She passed her PhD in Inorganic Chemistry (2014) from the University of Al-Mustansiriyah, Iraq. Her research interests are liquid crystal, aza dyes, aza schiff-base, lanthanides as well as transition metal complexes and dyes sensitized solar cell. She is the author of four publications and book in liquid crystal domain.

PUBLIC INTEREST STATEMENT
The subject of Schiff-base lanthanide(III) complexes has been of interest due to the potential applications of these compounds in different scientific areas. The Schiff-base \(\text{N,N}^{+}\)-di-(4'-'pentyloxy benzoate-salicylidene)-1,3'-diamino propano \((\text{H}_2\text{L})\) and its lanthanide complexes were synthesized and characterized. Investigations of the collected results are consistent with the stoichiometry \([\text{Ln}(\text{H}_2\text{L})\text{Cl}]\) as two forms of ligands exist in the complexes: bidentate through two phenolic oxygen and tetradeinate through the deprotonated phenolic oxygen and azomethine nitrogen to complete seven coordination geometry. All the complexes form a smectic A mesophase and are determined by polarizing microscopy of the complexes. Thermally very stable, the complexes exhibited a fan-like textural pattern characteristic of the enantiotropic SmA mesophase.
have been employed for the synthesis of new classes of lanthanide mesogens (Binnemans & Göller-Walrand, 2002; Bhattacharjee, Datta, Das, & Mondal, 2012; Chakraborty et al., 2012). The lanthanide mesogens also have enjoyed lot of interests owing to unusual geometries and novel properties such as spin crossover, ferro electricity, photo refractivity, contrast agents for magnetic resonance imaging (MRI), luminescent stains for fluoro immune assays, catalysts for the selective cleavage of RNA and DNA, and cancer radio therapeutic agents (Bhattacharjee, Das, Purkayastha, & Mondal, 2011; Kaczmarek, Pospieszna-Markiewicz, Kubicki, & Radecka-Paryzek, 2004; Song, Wang, Zheng, & Liu, 2012; Tsiouri, Hadjiliadis, Arslan, Kariuki, & Plakatouras, 2006; Zucchi & Le Goff, 2012). Transition temperatures of the Schiff base complexes are greatly influenced by the choice of the counterion, and they were able to show that the lanthanide contraction has a distinct influence on the transition temperatures of this type of compound. There is an interest in developing lanthanide-containing liquid crystals, mainly because of the unique magnetic properties of some of the trivalent ions of the lanthanide series (Al-Hamdani, Gassim, & Radhy, 2010). Not only are these ions paramagnetic and have a high magnetic moment but also more importantly, the trivalent lanthanide ions can have a very high magnetic anisotropy. A high value for the magnetic anisotropy is desirable if one wants to switch liquid crystals by an external magnetic field (Bünzl, 2006). Many researchers had studied in detail the complexes of Schiff base ligands with one aromatic ring (Bhattacharjee, Das, Goswami, et al., 2011; Fernandez, de Haan, & Kouwer, 2013). Schiff base ligands complexes with two aromatic rings have been studied much less intensively, (Binnemans et al., 2001) while a new Schiff base ligand contains three aromatic rings and their lanthanide complexes were reported by Binnemans et al. (2002). Schiff base ligands with N, O donor sets have often been used since the Schiff base ligands may assemble coordination architectures directed by the lanthanide (III) ions (Benelli & Gatteschi, 2002; Døssing, 2005; Vigato & Tamburini, 2004). In the study of lanthanide complexes, many different types of ligands are frequently used to link Ln(III). Moreover, the thermodynamic properties of lanthanide complexes are also important for the theoretical study and the practical applications.

The doubly deprotonated ligand contains strong donors, namely phenolato oxygen atoms as well as imine nitrogen atoms bearing excellent coordination ability with transition/inner transition metal ions through its $\text{N}_2\text{O}_3$ donor set (Zheng et al., 2012). As a part of our systematic investigation (Abid & Al-barody, 2014; Abid, Al-Barody, & Ahmad, 2014) on structural and spectroscopic studies of lanthanide metal complexes of a series of mesogenic azo salicylaldimine Schiff-base derivatives, this paper reports the results of investigation on the synthesis, spectroscopic studies and thermal behavior of the mesogenic Schiff-base, $\text{N}_2\text{N}^\prime$-di-(4’-pentyloxybenzoate-salicylidene)-1’3’-diamino propane $[\text{H}_2\text{L}]$, and the corresponding lanthanide complexes.

2. Materials and methods
All chemicals were analytical grade and used without any modification. The C, H, N and O analyses were carried out using a PE2400 elemental analyser (Perkin Elmer, USA). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer 100 Series FT-IR spectrometer (Waltham, MA, USA). $^1$H and $^{13}$CNMR spectra were recorded on JEOLCA400 FT NMR spectrometer (Gangdong-gu, South Korea) using d$_6$—dimethyl sulfoxide (DMSO) as a solvent. Magnetic susceptibility measurements were carried out by employing Magway MSB MK$^-1$ at room temperature. Molar conductivity of the complexes was measured in DMSO as a solvent in 0.001 M solutions using a CON 510 bench Mettler Toledo TGA 851 and conductivity meter. Thermal stability (weight changes) of the samples were recorded by Mettler Toledo TGA851 and STA 6000 (Perkin Elmer, Schwerzenbach, Switzerland) in the temperature up to 1,000°C. The phase transition temperatures determined by using a differential scanning calorimetry (DSC) 7 (Perkin Elmer) equipped with a liquid nitrogen cooling system. Olympus BX50 Optical Polarizing Microscope (OPM, Olympus America Inc., Corporate Parkway, Center Valley, PA, USA) equipped with a LinkamTHMSE-600 hot stage and a Tetramethylsilane (TMS) 92 control unit was used to analyse liquid crystal properties of the ligand and complexes. All measurements were carried out at Faculty of Science, UPM University, Malaysia.
3. Experiment

3.1. Preparation of 4-pentyloxybenzoic acid (1)

Solutions of (80 mmol, 11.05 g) 4-hydroxybenzoic acid in (150 mL) dry ethanol and (160 mmol, 8.97 g) of KOH in (50 mL) dry ethanol were magnetically stirred with simultaneous drop wise addition of (80 mmol, 10.00 mL) 1-bromopentane. The reaction mixture was refluxed for ~14 h under dry atmosphere and allowed to come to room temperature. The solid alkoxy potassium salt thus obtained was separated out by filtration under suction and treated with dilute HCl until the pH of the reaction mixture reached to ~2 h. The crude solid white product was filtered off, washed thoroughly with water and recrystallized successively from solutions of glacial acetic acid and toluene (Zucchi & Le Goff, 2012). Yield: (70%) all the experimental details are given in Scheme 1.

3.2. Preparation of 4-pentyloxy (4′-formyl-3′-hydroxy)-benzoate (2)

Solutions of (50 mmol, 10.40 g in 50 mL) 4-pentyloxybenzoic acid, (50 mmol, 6.90 g in 50 mL) 2,4 dihydroxybenzaldehyde, (55 mmol, 11.35 g in 100 mL) DCC in dry chloroform along with solid DMAP as a catalyst were magnetically stirred at room temperature for ~12 h. The byproduct (dicyclohexyl urea) was filtered off under suction and the solvent was removed on rotavapor.

Table 1. Elemental analysis and some physical properties of the ligand H2L and its lanthanide complexes

| Compound                     | Yield (%) | M. wt. | mp (°C) | (Calculated) found (%) | \(\Lambda_m\) (Ω⁻¹ cm² mol⁻¹) |
|------------------------------|-----------|--------|---------|------------------------|-----------------------------|
| H2L (C₄₁H₄₆N₂O₈)            | 85        | 694    | 169     | (70.89) 70.75 (6.62) 5.80 (4.03) 4.07 (18.44) 18.48 | –                            |
| [La(H2L)LCl]LaC₈₂H₉₀N₄O₁₆Cl | 75        | 1,560  | 145     | (63.07) 63.10 (5.76) 5.80 (3.58) 3.60 (16.38) 16.40 | 10.5                         |
| [Ce(H2L)LCl]CeC₈₂H₉₀N₄O₁₆Cl | 69        | 1,562  | 166     | (62.90) 62.88 (5.76) 5.80 (3.58) 3.54 (16.36) 16.40 | 11.34                        |
| [Sm(H2L)LCl]SmC₈₂H₉₀N₄O₁₆Cl | 85        | 1,572  | 137     | (62.51) 62.57 (5.72) 5.86 (3.55) 3.59 (16.26) 16.30 | 10.13                        |
| [Gd(H2L)LCl]GdC₈₂H₉₀N₄O₁₆Cl | 63        | 1,579  | 220     | (62.23) 62.33 (5.69) 5.75 (3.54) 3.59 (16.19) 16.24 | 12.05                        |
The crude product was recrystallized from hot solution of ethanol and purified by column chromatography over SiO₂ by eluting with a mixture of n-hexane and chloroform (v/v, 1:1); evaporation of this eluent yielded the ester 2, in the form of a white solid (Zucchi & Le Goff, 2012). Yield: (62%).

3.3. Synthesis of $N,N'$-di-(4′-pentyloxy benzoate-salicylidene)-1',3'-diamino propane $[H_2L]$

Absolute ethanolic solutions of (20 mmol, 6.56 g in 100 mL) 4-pentyloxy-(4′-formyl-3′-hydroxy)benzoate and (10 mmol, 0.74 g in 20 mL) 1,3-diaminopropane were refluxed for ~3 h in presence of a few drops of acetic acid. The precipitate was filtered off and recrystallised from (ethanol/ether) (v/v, 1:1), yield: 85%; mp: 168–169°C.

3.4. Synthesis of the lanthanide complexes

To a stirred solution of (2 mmol, 1.2 g) of the ligand ($H_2L$) in (40 mL) ethanol and 1 mmol of the $[LnCl_3\cdotXH_2O = LaCl_3\cdot7H_2O, CeCl_3\cdot7H_2O, SmCl_3\cdot6H_2O$ and $GdCl_3\cdot6H_2O$) in ethanol (50 mL) were mixed and refluxed for 3 h then kept stirring for 72 h at temperature 40–50°C. The yellow precipitate was filtered off, washed with cold ethanol and dried in vacuum oven for 24 h at 70°C. The precipitate was further purified by column chromatography over SiO₂ by eluting with a mixture of (n-hexan: DMF: chloroform) (v/v, 1:1:1) evaporation of this eluent afforded the crystals of the complexes (see Table 1).

4. Results and discussions

4.1. FT-IR spectra

The spectrum of $N$-(2-hydroxyl phenyl)-(4′-pentyloxybenzoate-salicylidene) ($H_2L$) showed an absorption band at 3,285 cm⁻¹ attributed to phenolic $\nu$(OH) the broadness of the band was attributed to the presence of internal hydrogen bond OH···N=C (Abid & Al-barody, 2014). Strong band located at 1,635 cm⁻¹ attributed to $\nu$(C=N). Three Bands appeared at 3,028 and 1,481 cm⁻¹ for aromatic $\nu$(C–H, C=C), $\nu$(C–H) and for aliphatic at 2,957–2,857 cm⁻¹ respectively (Shakya, Singh, & Rao, 2012). The strong bands occurring at 1,722 cm⁻¹ and 1,145 cm⁻¹ in the solution state of the parent ligand may be assigned to $\nu$(C=O) and $\nu$(C–O) stretching modes of aromatic ester. The characteristic response of ether in the infrared is associated with the stretching vibration of the C–O–C system. The bands appearing at 1,246 and 1,064 cm⁻¹ may be assigned to $\nu$(C–O–C) and $\nu$(C–O–C) stretching of aryl alkyl ether (Singh, Kumari, Ravi Kumar, Sridhar, & Rao, 2008). In Ln(III) complexes, the disappearance of phenolic $\nu$(O–H) was observed with the appearance of new broad band around 3,390 cm⁻¹ probably attributed to the formation of N–H bond by the immigration of phenolic proton to the azomethines nitrogen forming a zwitter ion (Figure 1). Similar zwitter ionic behavior has been recorded elsewhere for lanthanide complexes (Singh et al., 2008; Shakya, Singh, & Rao, 2011; Taha, Ajlouni, Al-Hassan, Hijazi, & Faq, 2011). The $\nu$(C=N) in the ligand was split to two bands around 1,663 and 1,618 cm⁻¹ for lanthanide ions complexes probably due to the presence of two types of $\nu$(C=N) stretching and compression vibrations. The vibration at higher frequency is due to the coordination through oxygen atom, while the lower value clearly indicated coordination of the complexes take place through the deprotonated phenolic oxygen (OH) and azomethine nitrogen atoms, (Binnemans et al., 2001; Cifelli, Domenici, & Veracini, 2013) resulting in two types of coordination. A molecular structure suggested for the lanthanide complexes is shown in Figure 2. The deprotonated Schiff's...
The formation of zwitter ion can increase the tendency of Ln(III) ion to coordinate to the negatively charged oxygen atom (Ansari, 2008). New bands were recorded at 550–513 and 474–420 cm⁻¹ attributed to Ln–N and Ln–O bonds, respectively (see Table 2).

4.2. ¹H NMR spectra

NMR spectra were recorded using DMSO as solvent and TMS was used as an internal standard. Chemical shifts were reported in parts per million (ppm) and coupling constants were given in Hertz (Hz). The spectrum of the ligand H₂L showed signal at δ 13.97 ppm and singlet signal for CH=N at δ 8.49 ppm clearly indicates that the magnetic environment is equivalent for such proton. The quintet and the triplet peaks at 3.71 and 2.50 δ ppm were attributed to (–CH₂–C–CH₂–) and (–C–CH₂–C–), respectively. ¹H NMR (500 MHz, DMSO) δ ppm: 0.94 (6H, H₂₃), 1.84–1.39 (m, 12H, H₂₂, 2₁, 2₀), 2.22 (quintet, 2H, H₁₆), 3.80 (t, 4H, H₁₅, H₁₇) 4.05 (t, 4H, H₁₉), 6.76 (dd, 2H, H₈), 6.80 (d, 2H, H₁₂), 6.97 (d, 4H, H₁₃), 7.27 (d, 2H, H₁₁), 8.12 (d, 4H, H₂, 6), 8.49 (s, 2H, H₁₄) ppm (Al-Hamdani et al., 2010; Bhattacharjee, Das, Goswami, et al., 2011; Binnemans et al., 2001, 2002; Bünzli, 2006; Fernandez et al., 2013; Kaczmarek et al., 2004; Tsiouri et al., 2006; Vigato & Tamburini, 2004; Zucchi & Le Goff, 2012), (Figure 2). Only ¹H NMR spectrum for La(III) complex was recorded, due to the paramagnetic properties of the other lanthanide ions. The phenolic (–OH) signal disappeared while the signal corresponding to the imine hydrogen (–CH–N) was shifted upward in the complex to 8.62 δ. New signal, probably characteristic of (–N+H) resonance, appeared at 10.14 δ while the

| Compounds                  | δ(OH) | δ(H₂N) | δ(C=N), (C–N⁺) | δ(C–O) | δ(M–N) | δ(M–O) |
|----------------------------|-------|--------|----------------|--------|--------|--------|
| H₂L (C₄₁H₄₆N₂O₈)          | 3,285 | –      | 1,635          | 1,280  | –      | –      |
| [La(H₂L)LCl] LaC₸₂H₹₀N₄O₁₆Cl | –     | 1,488  | 1,663, 1,618   | 1,275  | 550–513| 474–425|
| [Ce(H₂L)LCl] CeC₸₂H₹₀N₄O₁₆Cl | –     | 1,485  | 1,664, 1,618   | 1,265  | 574–516| 463–436|
| [Sm(H₂L)LCl] SmC₸₂H₹₀N₄O₁₆Cl | –     | 1,487  | 1,663, 1,618   | 1,287  | 560–517| 464–428|
| [Gd(H₂L)LCl] GdC₸₂H₹₀N₄O₁₆Cl | –     | 1,488  | 1,678, 1,617   | 1,230  | 556–515| 465–420|
parent ligand does not show any such signal (Werts, 2005). This could assign to the movement of phenolic protons in coordinated ligand to the two uncoordinated imino nitrogen, to give rise to the zwitter ionic structure (–N\(^+\)-H...O\(^-\)) (Bünzli & Piguet, 2002). These observations have very similar structural properties in comparison with the corresponding complexes of another Schiff’s bases reported recently (Abid et al., 2014; Radecka-Paryzek, Patroniak, & Lisowski, 2005; Tang et al., 2013) indicating clearly that this signal corresponding to the proton of the (–N\(^+\)H) group. Little shift for other signals were recorded due to the coordination effect. The \(^{13}C\)NMR spectra show a shift of the (–NCH) signal from \(\delta\), 165.48 (in the case of \(\text{H}_2\text{L}\)) to \(\delta\), 166.07 in the case of the \(\text{La}(\text{III})\) complex. Similar shifts were observed in the case of the carbon atoms directly attached to the bonding atoms (phenolate carbons) while those for the other carbons were of lesser magnitude (Taha et al., 2011).

4.3. Mass spectra

Mass spectra were recorded using a Direct Injection Probe. The mass spectral features of the ligand \(\text{H}_2\text{L}\) as illustrated in (Figure 3), was described by molecular ion peak at \(m/z = 694\), which matched with the molecular weight of the ligand \((\text{C}_{41}\text{H}_{46}\text{N}_2\text{O}_8)\). The main fragment peaks were \(m/z\) [fragment, intensity %] 694 [M, 10], 623 [M-2(C\(_5\)H\(_{11}\)), 5], 552 [M-2(C\(_5\)H\(_{11}\), 3)], 533 [M-(C\(_5\)H\(_{11}\),OC\(_6\)H\(_4\)), 5], 503 [M-(C\(_5\)H\(_{11}\)),OPhCO\(^+\)], 487 [M-(C\(_5\)H\(_{11}\),OPhCOO\(^-\)), 5], 452 [M-2(OPhHCO\(^+\)), 30], 372 [M-2(C\(_5\)H\(_{11}\),OC\(_6\)H\(_4\)), 5], 312 [M-2(C\(_5\)H\(_{11}\)),OPhCO\(^+\)], 5], 191 [C\(_5\)H\(_{11}\),OC\(_6\)H\(_4\), 25], 142 [2(C\(_5\)H\(_{11}\)), 40], 121 [OHC\(_6\)H\(_4\)CO\(^+\), 100], 96 [HC=NCH\(_2\)CH\(_2\)N=CH\(^+\), 50], 56 [CH\(_2\)CH\(_2\)CH\(_2\)N\(^+\), 30], 69 [CH\(_2\)CH\(_2\)CH\(_2\)N=CH\(^+\), 40]. The mass spectrum of \(\text{Gd}(\text{III})\) complex confirmed the metal/ligand molar ratio 1:2, the mass spectrum was described by molecular ion peak at \(m/z = 1,579\) which confirm the molecular weight \(m/z\) value of 1,581 that agree with the empirical formula of the complex \((\text{GdC}_{82}\text{H}_{90}\text{N}_4\text{O}_{16}\text{Cl})\). The intensity was 100% for the base peak 312 which assign to the cleavage of 2[C\(_5\)H\(_{11}\),OC\(_6\)H\(_4\)CO\(^+\)]. The fragmentation started with the loose first molecule of the ligand before the dissociation of the ligand itself.

4.4. Magnetic measurements

Magnetic susceptibility for the complexes was recorded in the solid state at 298 K using Gouy method in emu/mole units. All the trivalent lanthanide ions, except lutetium, have unpaired f electrons. However the magnetic moments deviate considerably from the spin-only values because of strong spin–orbit coupling (Binnemans & Gündogan, 2002). The magnetic properties of rare earth ions are strongly influenced by this coupling; in particular the magneto-crystalline anisotropy is generally large. As far as the magnetic properties are concerned, the large anisotropic moments arise from the large spin–orbit coupling, making lanthanide ions attractive building blocks in the synthesis of magnetic molecular materials (Miller & Drillon, 2006). The magnetic moment data of \(\text{Ln}(\text{III})\) complex show that lanthanum(III) chloride complexes is diamagnetic in nature while all other complexes are paramagnetic, as expected. Magnetic moment of 2.52 B.M. was recorded for Ce(III) complex due to the presence of one electron. However, in the case of Sm(III) complex, a slight variation from Van Vleck values is observed due to low J–J separation which leads to thermal population of higher energy levels. In Gd(III) complex, a magnetic moment of 7.87 B.M. was recorded which suggests a maximum number of unpaired electrons is 7, with all the electrons have parallel spin. This property is important for the use of gadolinium complexes as contrast reagent in MRI scans (Ansari, 2008; Benelli & Gatteschi, 2002).

Figure 3. Mass spectrum of \(\text{H}_2\text{L}\).
4.5. Molar conductivity measurements

The molar conductivity measurements for the complexes were carried out using a concentration of $10^{-3}$ M and DMSO as a solvent and CON 510 bench conductivity meter (cell constant, $K = 1.0$) built-in temperature sensor (Table 3). All complexes showed a behavior of non-electrolyte type indicating the presence of chloride ion inside the coordination sphere, and these results agree with the suggested configurations of the lanthanide complexes (Tang et al., 2013).

4.6. Thermogravimetric analyses

Thermogravimetric analyses (weight changes) were performed in the temperature range from room temperature up to 1,000°C under air atmosphere at the heating rate of 20°C/min. Thermal properties of the complexes are largely defined by the Schiff’s base ligands, rather than by the lanthanide ions. This is different from what is observed for the Schiff’s base ligands with one aromatic ring. The lanthanidomesogens derived of the two-ring or three-ring Schiff’s base ligands are not very suitable for exploration of their spectroscopic, electric or magnetic properties, due to their high transition temperatures, highly viscous mesophases and low thermal stability (Billard, 2013). Thermal decomposition of lanthanide complexes is very attractive, since it consists of a moderate temperature calcination step and yields high purity oxides without any unwanted byproducts. Recently, synthetic methods for producing oxides with specific morphologies have been reported (Greenwood & Earnshaw, 2012). A thermogravimetric analysis (TGA) curve of Ce(III) complex revealed that the complex is stable up to 123–185°C and do not show any weight loss below this temperature. It is strong evidence, which represent that the complex is devoid of lattice water as well as coordinated water in the coordination sphere (Cifelli et al., 2013). The first weight loss of the complexes was observed 44.43% (0.86 mg), which occurs between the temperatures 150–180°C, corresponding to one molecule of ligand. After the elimination of the first molecule, the decomposition of the second molecule of the complex started simultaneously between the temperatures 185–420°C, and the observed weight loss 46.57% (0.8988 mg) is equivalent to (L) + 0.5 Cl₂. A further mass loss recorded up to 420°C indicates the formation of a thermally stable metal oxide. The last step comprising deionation with simultaneous oxidation of Sm to Ce₂O₃ is found to be very broad in nature, however in majority of the cases all these steps are not generally isolated but overlapped to varying extent and frequently result in fractional losses of the constituent moieties (Hu, Zhang, & Cao, 2003).

4.7. Liquid crystal properties of H₂L and its lanthanide complexes

The mesomorphic behavior of the compounds was probed by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The ligand exhibits SmA phases during heating to isotropic liquid (I) and the reverse cooling process to crystalline solid (Cr). Phase transitions were observed at 101°C (Cr-SmA) and 168°C (SmA-I) (Figure 4). The enthalpy changes for those transitions were 5.8 and 74.8 kJ/mol, on the reverse process, phase transitions happened at 165°C (I-SmA) and 80°C (SmA-Cr). The enthalpies for these transitions were 4.4 and 28.9 kJ/mol. Lanthanide(III) complexes exhibit SmA broken focal-conic fan texture. Therefore, DSC analysis was done for the complexes to determine their phase transition temperature and transition enthalpies value ($\Delta H$). La(III) complex is an enantiotropic liquid crystal exhibiting SmA phases during heating to isotropic liquid (I).

| Complexes             | $\mu_{\text{eff}}$ | $\mu_{\text{eff}}$ Van Vleck | Molar conductivity (Ω⁻¹cm² mol⁻¹) | Geometry       |
|-----------------------|-------------------|-----------------------------|----------------------------------|----------------|
| LaC₈₂H₉₀N₄O₁₆Cl     | 0.0               | X = −0.18×10⁻⁶ cm g s      | 12.50                           | Mcoh* C.N = 7  |
| CeC₈₂H₉₀N₄O₁₆Cl     | 2.65              | 1.55                        | 11.25                           | Mcoh* C.N = 7  |
| SmC₈₂H₉₀N₄O₁₆Cl     | 1.55              | 0.85                        | 12.05                           | Mcoh* C.N = 7  |
| GdC₈₂H₉₀N₄O₁₆Cl     | 7.99              | 7.94                        | 10.07                           | Mcoh* C.N = 7  |

*Monocapped octahedron.
and the reverse cooling process to crystalline solid (Cr). Cr-SmA and SmA-I phase transitions were observed at 127 and 143°C, respectively. The enthalpies for those transitions were 4.9 and 30.7 kJ/mol. On the reverse process, I-SmA and SmA-Cr phase transitions happened at 141 and 112°C, respectively. The enthalpies for these transitions were 4.5 and 40.5 kJ/mol. Upon cooling the complex from isotropic liquid, typical batonnets are formed which coalesce to give rise to a highly birefringent fan-like texture, characteristic of the SmA phase at 112°C (see Figure 5), which quickly

| Symbols                  | Transition temperature (T/°C) and associated transition                                                                 | Enthalpy values (kJ.mol⁻¹) |
|-------------------------|--------------------------------------------------------------------------------------------------------------------------|----------------------------|
| H₂L                     | 101°C (Cr-SmA), 168°C (SmA-I) (heating) 165°C (I-SmA), 80°C (SmA-Cr) (cooling)                                           | 5.8, 79.8, 4.4, 28.9      |
| [La(H₂L)LCl]            | 127°C (Cr-SmA), 143°C (SmA-I) (heating) 141°C (I-SmA), 112°C (SmA-Cr) (cooling)                                          | 4.9, 30.7, 4.5, 40.5      |
| [Ce(H₂L)LCl]            | 145°C (Cr-SmA), 165°C (SmA-I) (heating) 166°C (I-SmA), 146°C (SmA-Cr) (cooling)                                          | 3.5, 50.7, 45.6, 60.1     |
| [Sm(H₂L)LCl]            | 50°C (Cr-SmA₂), 80°C (SmA₂-SmA₁), 135(SmA₁-I) (heating) 137°C (I-SmA₂), 122°C (SmA₁-SmA₂), 80°C (SmA₁-Cr) (cooling)  | 2.7, 45.3, 78.1, 46.4, 60.7, 75.6 |
| [Gd(H₂L)LCl]            | 125°C (Cr-SmA), 218°C (SmA-I) (heating) 220°C (I-SmA), 124°C (SmA-Cr) (cooling)                                          | 46.9, 2.2, 58.1, 1.4      |
reverts to crystalline phase at 89°C. The reversible thermal behavior of the complexes was confirmed by DSC on subsequent heating–cooling runs (Table 4). It is pertinent here to mention that the structurally similar mesogens, N,N\textsuperscript{-}di-(4-butyloxybenzoate)-salicylidene-1,3-diaminopropane, Sadeem M. Al-Barody & Haslina Ahmad, found to be \[\text{Ln(H}_2L\text{)}L\text{Cl}\]. It is clearly indicated that the stoichiometry depends on the number and type of the ligands. Using same lanthanide ions with single arm Schiff base ligand, the stoichiometry was consistent with the stoichiometry \[\text{Ln(H}_2L\text{)}L\text{Cl}\] as two forms of ligands exist in the complexes: bidentate through two phenolic oxygen and tetradentate through the deprotonated phenolic oxygen and azomethine nitrogen to complete seven coordination geometry. In our previous report (Abid & Al-Barody, 2014), using same lanthanide ions with single arm Schiff base ligand, the stoichiometry was found to be \[\text{Ln(H}_2L\text{)}L\text{Cl}\]. It is clearly indicated that the stoichiometry depends on the number and different lengths of the terminal chains on the ligands. All the complexes form a smectic A mesophase and determined by polarizing microscopy of the complexes. Thermally very stable, the complexes exhibited a fan-like textural pattern characteristic of the enantiotropic SmA mesophase.

5. Conclusion

The Schiff-base N,N\textsuperscript{-}di-(4\textsuperscript{-}pentyloxybenzoate)-salicylidene-1,3-diamino propane \[\text{H}_2L\] and its lanthanide complexes were synthesized and characterized. Investigations of the collected results are consistent with the stoichiometry \[\text{Ln(H}_2L\text{)}L\text{Cl}\] as two forms of ligands exist in the complexes: bidentate through two phenolic oxygen and tetradentate through the deprotonated phenolic oxygen and azomethine nitrogen to complete seven coordination geometry. In our previous report (Abid & Al-Barody, 2014), using same lanthanide ions with single arm Schiff base ligand, the stoichiometry was found to be \[\text{Ln(H}_2L\text{)}L\text{Cl}\]. It is clearly indicated that the stoichiometry depends on the number and different lengths of the terminal chains on the ligands. All the complexes form a smectic A mesophase and determined by polarizing microscopy of the complexes. Thermally very stable, the complexes exhibited a fan-like textural pattern characteristic of the enantiotropic SmA mesophase.
Bünzli, J. C. G., & Piguet, C. (2002). Lanthanide-containing molecular and supramolecular polyemeric functional assemblies. Chemical Reviews, 102, 1897–1928. http://dx.doi.org/10.1021/cr010299j

Chakraborty, J., Ray, A., Plet, G., Chastanet, G., Luneau, D., Ziesel, R. F., & Charbonnière, L. J. (2009). Syntheses, characterisation, magnetism and photoluminescence of a homodinuclear Ln(III)-Schiff base family. Dalton Transactions, 46, 10263–10272. http://dx.doi.org/10.1039/b908910a

Chakraborty, L., Chakraborty, N., Choudhury, T. D., Phani Kumar, B. V. N., Mandal, A. B., & Rao, N. V. (2012). Synthesis, mesomorphic and photo-physical properties of few d-and f-block metals coordinated to polar Schiff’s bases. Liquid Crystals, 39, 655–668. http://dx.doi.org/10.1080/02678292.2012.669854

Cifelli, M., Domenici, V., & Veracini, C. A. (2013). Recent advancements in understanding thermotropic liquid crystal structure and dynamics by means of NMR spectroscopy. Current Opinion in Colloid & Interface Science, 18, 190–200.

Dassing, A. (2005). Luminescence from lanthanide(3+) ions in solution. European Journal of Inorganic Chemistry, 2005, 1425–1434. http://dx.doi.org/10.1002/ejic.200500119

Fernandez, A. A., de Haan, L. T., & Kouver, P. H. (2013). Towards room-temperature ionic liquid crystals. Journal of Materials Chemistry A, 1, 354–357. http://dx.doi.org/10.1039/C2TA00133K

Greenwood, N. N., & Earnshaw, A. (2012). Chemistry of the elements. Oxford: Butterworth-Heinemann Elsevier.

Hu, J. M., Zhang, J. Q., & Gao, C. N. (2003). Thermolytic formation and microstructure of IrO2 + Ta2O5 mixed oxide anodes from chloride precursors. Thermochimica Acta, 403, 257–266. http://dx.doi.org/10.1016/S0040-6031(03)00061-3

Kaczmarek, M. T., Pospieszna-Markiewicz, I., Kubiaki, M., & Radecka-Paryzek, W. (2004). Novel lanthanide salicylaldimine complexes with unusual coordination mode. Inorganic Chemistry Communications, 7, 1247–1249. http://dx.doi.org/10.1016/j.inoche.2004.09.022

Miller, J. S., & Drillon, M. (Eds.). (2008). Magnetism: Molecules to materials IV. Weinheim: Wiley.

Radecka-Paryzek, W., Patroniaki, V., & Lisowski, J. (2005). Metal complexes of polyvalent and polyoxazao Schiff base macrocycles. Coordination Chemistry Reviews, 249, 2156–2175. http://dx.doi.org/10.1016/j.ccr.2005.02.021

Shokya, P. R., Singh, A. K., & Rao, T. R. (2011). Homo dinuclear lanthanide(III) complexes of a mesogenic Schiff-base, N,N′-di(4-decyloxyacetyl)salicylidene-1,6-diaminohexane: Synthesis and characterization. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 79, 1654–1659. http://dx.doi.org/10.1016/j.saa.2011.05.030

Shokya, P. R., Singh, A. K., & Rao, T. R. (2012). Synthesis of lanthanide(III) complexes with a mesogenic Schiff-base, N,N′-di(4-decyloxyacetyl)salicylidene-2,6′-diaminopyridine. Materials Science and Engineering: C, 32, 1906–1911. http://dx.doi.org/10.1016/j.msec.2012.05.039

Siniet, A. K., Kumar, S., Ravi Kumar, K., Shidhar, B., & Rao, T. R. (2008). Synthesis and spectral studies of the mesogenic Schiff-base, N,N′-di(4-pentyloxobenzale) salicylidene-1,8-diamo-3,6-dioxoacetone and crystal structure of the Zn(II) complex. Polyhedron, 27, 181–186. http://dx.doi.org/10.1016/j.poly.2007.09.002

Song, X. G., Wang, L., Zheng, Q. F., & Liu, W. S. (2012). Synthesis, crystal structure and luminescence properties of lanthanide complexes with a new semirigid bridging furfurylsalicylamide ligand. Inorganica Chimica Acta, 391, 171–178. http://dx.doi.org/10.1016/j.ica.2012.04.007

Taha, Z. A., Aljouni, A. M., Al-Hassan, K. A., Hijazi, A. K., & Faq, A. B. (2011). Syntheses, characterization, biological activity and fluorescence properties of bis-(salicylaldehyde)-1, 3-propyleneimine Schiff base ligand and its lanthanide complexes. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 81, 317–323. http://dx.doi.org/10.1016/j.saa.2011.06.018

Tong, J., Zhang, J. J., Zhang, D. H., Ren, N., Yan, L. Z., & Li, Y. (2013). Crystal structures and thermodynamic properties of lanthanide complexes with 2-chloro-4, 5-difluorobenzoate and 1, 10-phenanthroline. The Journal of Chemical Thermodynamics, 36, 38–48. http://dx.doi.org/10.1016/j.jct.2012.06.032

Tsiouri, M., Hadjiliadis, N., Arslan, T., Kariuki, B. M., & Plakoutauros, J. C. (2006). Interactions of trivalent lanthanide cations with tetradeutate Schiff bases: New lanthanide(III) complexes from (15,25,N1E,N2E)-N,N-bis(pyridin-2-ylmethylene)cyclohexane-1,2-diamine. Inorganic Chemistry Communications, 9, 429–432. http://dx.doi.org/10.1016/j.inoche.2005.12.018

Vigato, P. A., & Tomburini, S. (2004). The challenge of cyclic and acyclic Schiff bases and related derivatives. Coordination Chemistry Reviews, 248, 1717–2128. http://dx.doi.org/10.1016/j.ccr.2003.09.003

Werts, M. H. (2004). Making sense of lanthanide luminescence. Science Progress, 88, 101–131. http://dx.doi.org/10.3181/003685005783238435

Zhang, J. R., Ren, N., Zhang, J. J., Zhang, D. H., Yan, L. Z., & Wu, K. Z. (2012). Synthesis, characterization and thermochemical properties of four new lanthanide complexes with 3, 5-diisopropylsalicylic acid and 1, 10-phenanthroline. Thermochimica Acta, 547, 31–37. http://dx.doi.org/10.1016/j.tca.2012.08.005

Zucchi, G., & Le Goff, X. F. (2012). Magneto-structural and biomolecular Spectroscopy, 3, 317–323.

Zheng, J. R., Ren, N., Zhang, J. J., Zhang, D. H., Yan, L. Z., & Wu, K. Z. (2012). Synthesis, characterization and thermochemical properties of four new lanthanide complexes with 3, 5-diisopropylsalicylic acid and 1, 10-phenanthroline. Thermochimica Acta, 547, 31–37. http://dx.doi.org/10.1016/j.tca.2012.08.005

Zucchi, G., & Le Goff, X. F. (2012). Magneto-structural and biomolecular Spectroscopy, 3, 317–323.