



## Rare earths complexes of single arm N – aryl Schiff base ligand

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### ABSTARCT

A synthesized ligand N – ( 2 – hydroxyphenyl) – 4 – n – butylsalicylaldimine ( $H_2L$ ) was used to prepare a series of mononuclear lanthanide complexes of the type  $[LnH_2L(HL)_2Cl]$  ( $Ln = LaIII, CeIII, SmIII$  and  $GdIII$ ). The ligand and complexes were characterized by  $^1H$ ,  $^{13}CNMR$ , elemental analysis (CHNO), FT-IR spectroscopy, GC-mass, Magnetic susceptibility Molar Conductivity and Thermo gravimetric analysis (TGA). Investigation of complexes suggest that two ligand molecules behaves as tridentate and the third one as bidentate as it present in zwitter ionic form with an additional one chloride ion to complete nine coordination geometry.

**Keywords:** Salicylaldimine; Schiff base; mononuclear complexes; Lanthanides

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### INTRODUCTION

The coordination chemistry of lanthanide ions has been widely investigated in recent years because of both the useful magnetic and optical behaviors of these ions. It could exhibit coordination numbers 6–12, with 8 or 9 being ubiquitous [1]. Wide variety of ligands such as Schiff bases ligands have been employed for the synthesis of new classes of lanthanide mesogens [2 – 5]. In this regard Schiff base metal complexes have played a key role to the gradual development of the Ln(III) coordination chemistry, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [6,7]. 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 [8, 9]. The salicylaldimine fragment is well recognized as a good promesogenic unit as the azomethine linkage is stabilized by intramolecular hydrogen bonding in addition to being a good donor site for coordination with metals [10 – 13].

In this paper series of lanthanide complexes of the new Schiff base [ N-(2-hydroxyphenyl)-4-n-alkyl salicylaldimine] were synthesized and investigated.

## MATERIALS AND METHODS

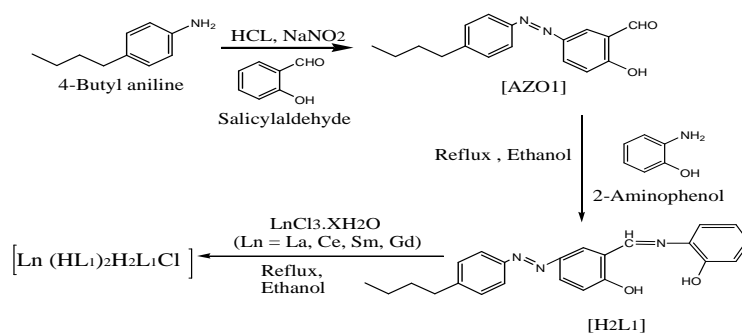
All chemicals were supplied from BDH and Fluka and used without any modification. FTIR spectra were recorded on a Perkin Elmer 100 Series FT-IR spectrometer. <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on JEOL ECA400 FT NMR and JEOL ECX500 FTNMR spectrometer systems using d<sup>6</sup>-dmso as a solvent. Tetramethylsilane (TMS) was used as an internal standard for <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) Mass spectra were recorded by EIMS using a direct injection probe on a Shimadzu GCMS-QP5050A spectrometer. HRESIMS spectra were recorded on Shimadzu UFLC-IT-TOF Mass Spectrometer. Magnetic susceptibility measurements were carried out by employing Magway MSB MK<sup>-1</sup> susceptibility balance at room temperature. Molar conductivity of the complexes were measured in DMSO as a solvent in 0.001 M solutions using a CON 510 bench conductivity meter. TGA were carried out using Mettler Toledo TGA851 and STA 6000 (Perkin Elmer) in the temperature range up to 1000°C. All measurements were carried out at Faculty of Science, UPM University, Malaysia.

### Experimental:

**Preparation of 4-butylphenyl azo:** To 33.5 mmol of 4-n-butyl aniline dissolved in 6M HCl (15mL), 23 mmol of NaNO<sub>2</sub> dissolved in cold water (15mL) was added drop wise in an ice bath under constant mechanical stirring. 33.5 mmol of salicylaldehyde dissolved in (10%) NaOH (15mL) was added gradually. The reaction mixture temperature was kept at (0-5)°C, then dilute acetic acid was added. A brownish orange precipitate was obtained, filtered, washed with water and recrystallized from (ethanol/benzene) (1:1). Yield: 64%; m.p = 75-76°C. Elemental analysis: Calc. for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (282): C, 72.34%; H, 6.38%, N, 9.92%, O, 11.34%; Found: C, 72.84%; H, 6.88%; N, 10.02%; O, 11.4%.

**Synthesis of N-(2-hydroxyl phenyl)-4-n-butylsalicylaldimines (H<sub>2</sub>L):** (0.109g, 1mmol) of 2-amino phenol in ethanol (20mL) and (0.282g, 1mmol) of butylsalicylaldimines in ethanol (20mL) were mixed under reflux for 1h, left aside at room temperature for overnight. Orange flat crystals were formed, filtered and recrystallized from (ethanol/chloroform) (1:1) Yield: 83%; m.p=175-176°C, elemental analysis: Calc. for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> (373): C, 73.99%; H, 6.16%, N, 11.26%; O, 8.57%; Found: C, 74.09%; H, 6.66%; N, 11.36%; O, 8.77%.

**Synthesis of the Complexes:** All complexes were prepared by adding gradually 1 mmol of (LnCl<sub>3</sub>.XH<sub>2</sub>O), where Ln=La, Ce, Sm and Gd, dissolved in ethanol (20mL) to 3mmol (1.12gm) of ligand (H<sub>2</sub>L) at room temperature. Stirred under reflux for 48 hrs. The resulting precipitate was filtered off and recrystallized from hot ethanol then dried in vacuum oven for 24h at 70°C. Yield% 65 – 80.



Scheme 1 synthesis of ligand (H<sub>2</sub>L) and complexes

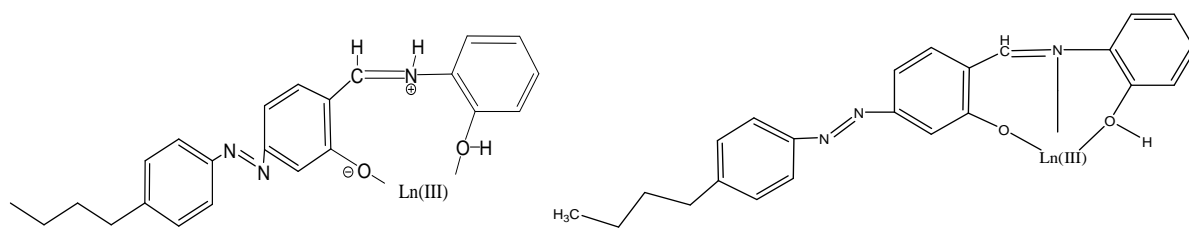
Table 1 some physical properties of lanthanide complexes

Complexes	M.wt.	m.p. °C	Elemental analysis % Found (%Calc.)			
			C	H	N	O
LaC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	1291	160	64.62 (64.13)	5.33 (5.18)	10.03 (9.75)	7.64 (7.43)
CeC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	1292	220	64.67 (64.08)	5.33 (5.18)	10.02(9.75)	7.63 (7.43)
SmC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	1302	155	64.95 (64.44)	5.28 (5.14)	9.90 (9.67)	7.56 (7.37)
GdC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	1309	175	63.89 (63.25)	5.24 (5.11)	9.89 (9.62)	7.53 (7.33)

## RESULTS AND DISCUSSIONS

**IR spectra:** The spectrum of *N*-(2-hydroxyl phenyl)-4-*n*-butylsalicylaldimines)[H<sub>2</sub>L<sub>1</sub>] showed an absorption band at 3659 cm<sup>-1</sup> attributed to phenolic (ν O-H<sub>1</sub>) and at around 3250 cm<sup>-1</sup> for phenolic(ν O-H<sub>2</sub>). The strong intensity band occurring at 1607 cm<sup>-1</sup> assignable to ν(C=N) of the azo methine moiety, while ν(N=N) appeared at 1509 cm<sup>-1</sup>. Two weak/medium intensity bands showed at 1153-1135cm<sup>-1</sup> assigned to the two phenolic ν(C-O). Absorption bands for ν(C-H, aromatic), ν(C-H, aliphatic) and ν(C=C,aromatic) were recorded at 3037cm<sup>-1</sup>, 2925-2855cm<sup>-1</sup> and 1463 cm<sup>-1</sup> respectively(14).

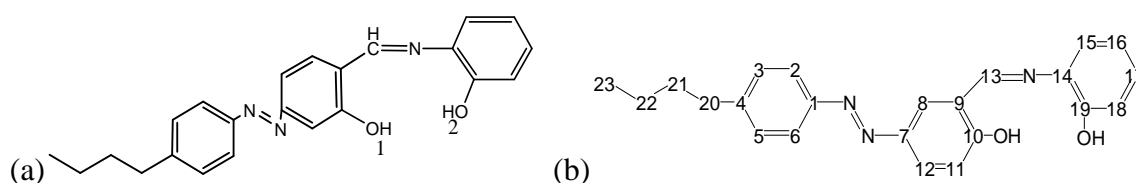
For Lanthanide complexes two bands appeared at 1610 and 1600cm<sup>-1</sup> probably attributed to two types of ν(CH=N). The vibration at higher frequency is due to the coordination through oxygen atom, while the lower value clearly indicated coordination of the complexes take place through the deprotonated phenolic oxygen (OH<sub>2</sub>) and azomethine nitrogen atoms [15], resulting two types of coordination; a bidentate way (through two phenol oxygen) and a tridentate way (two phenol oxygen and imine nitrogen) [16] (Figure 1). The elemental analysis results suggest that three ligand molecules and one chloride ion are present in each complex and these results were supported by <sup>1</sup>HNMR spectral data [17, 18]. The phenolic band ν(OH<sub>1</sub>) was disappeared with the observation of new broad band (due to the interaction with OH<sub>2</sub> band) at 3174 – 3350 cm<sup>-1</sup> probably attributed to the formation of N – H bond by the immigration of phenolic proton to the azomethan nitrogen forming a zwitter ion. The formation of zwitter ion can increase the tendency of LnIII ion to coordinate to the negatively charged oxygen atom [19]. New bands were recorded at 420 – 480 and 523 – 575cm<sup>-1</sup> attributed to Ln – O and Ln – N bonds respectively

Figure 1 proposed two way of coordination of H<sub>2</sub>L in complexes

**Table 2 Major Infra – red absorption bands of H<sub>2</sub>L and complexes (cm<sup>-1</sup>)**

Compound	$\nu(\text{OH}_1),$ $\nu(\text{OH}_2)$	$\nu(\text{N}^+ - \text{H})$	$\nu(\text{C}-\text{N}^+),$ $\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})_{\text{ph.}}$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
H <sub>2</sub> L <sub>1</sub>	3659 3250	-----	1607	1153, 1135	-----	-----
LaC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	~3300 (OH <sub>2</sub> )	3236	1619, 1600	1161, 1112	575, 548	478, 440
CeC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	~3300 (OH <sub>2</sub> )	3236	1620, 1600	1161, 1107	575, 548	478, 440
SmC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	~3300 (OH <sub>2</sub> )	3265	1618, 1600	1661, 1112	548, 523	480, 442
GdC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	~3300 (OH <sub>2</sub> )	3174	1616, 1600	1161, 1110	548, 523	480, 420

<sup>1</sup>H, <sup>13</sup>CNMR spectra: Spectra of the ligands H<sub>2</sub>L and La(III) complex were recorded using d<sub>6</sub>-dmsO as a solvent. H<sub>2</sub>L showed two signals at 13.96 and 10.02 δ for OH<sub>1</sub> and OH<sub>2</sub> respectively. Singlet signal for –CH=N at 8.49 δ clearly indicates that the magnetic environment is equivalent for such proton. Multiples signals of aromatic protons appeared 7.8-7.2 δ, while the nine aliphatic protons peaks of CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> recorded at 3.8-0.9 δ. <sup>13</sup>CNMR spectral data of the ligand H<sub>2</sub>L<sub>1</sub> showed the following assignments: δC1 (151.80), C2 (122.17), C3 (129.21), C4 (130.88), C5 (129.21), C6 (122.17), C7 (144.47), C8 (129.46), C9 (122.47), C10 (163.08), C11 (118.25), C12 (123.86), C13 (162.80), C14 (117.21), C15 (118.3), C16 (127.7), C17 (126.6), C18 (127.71), C19 (158.20), C20 (35.63), C21 (33.54), C22 (22.42), C23 (14.03), see figure 2.

Figure 2; (a) H<sub>2</sub>L, (b) <sup>13</sup>CNMR lable

Only spectrum for LaIII complex was recorded using d<sub>6</sub>-dmsO as a solvent, due to the paramagnetic properties of the other lanthanide ions. The phenolic-OH<sub>1</sub> signal was disappeared and new signal observed at 11.34 δ attributed to (–N<sup>+</sup>H) resonance which is not shown by the parent ligand. This could assign to the movement of one phenolic proton in coordinated ligand to the imine nitrogen, to give rise to the zwitter ionic structure (–N<sup>+</sup>–H...O<sup>-</sup>) (19). Signal for (OH<sub>2</sub>) recorded at 10.06 δ as weak broadened peak, this indicates the the involvement of oxygen atom in the coordination [15]. This observations were supported by Binnemans and others which they indicate clearly the correspondence of these signals to two types of coordination as a result of zwitter ionic structure [16, 20, 21].

Two signals for azomethine proton CH=N were recorded at 8.94 δ and 8.11 δ compared to only one signal at 8.49 δ for free ligand, which suggest the presence of two types of (CH=N) and indicated the existence of two forms of ligands in the complexes; a bidentate through two phenolic oxygen without the involvements of nitrogen atom in the coordination as the ligand exists in the complex as zwitter ionic form and tridentate through the deprotonated phenolic oxygen and azomethine nitrogen along with hydroxyl group [8, 22, 23]. Little shift were recorded for other signals due to the coordination effect (see figures 3 and 4).

**Mass spectra:** The mass spectral features of the ligand was described by base peak as well as molecular ion peak that agreeing with the  $m/e$  value of 373 (Figure 5), which matched with the molecular weight of the ligand ( $C_{23}H_{23}N_3O_2$ ). The main fragment peaks were  $m/z$  [fragment, intensity%] 374 [M+1,30], 373 [M, 100], 316 [M-C<sub>4</sub>H<sub>9</sub>,10], 212[M-C<sub>4</sub>H<sub>9</sub>C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>, 60]. The CHN analysis results were consistent with a stoichiometry with the empirical formula [LnL<sub>3</sub>]. However it is difficult to observe the compositions of the complexes from CHN microanalysis alone. The molecular ion peak of the Ce(III) complex appeared at an  $m/z$  value of 1292, [CeH<sub>2</sub>L(HL)<sub>2</sub>Cl], followed by a peak at 885 [(ML<sub>2</sub>)<sup>+</sup>], suggesting losing one ligand unit (L+Cl) upon fragmentation then loose of another unit before the dissociation of ligand itself (Figure 6).

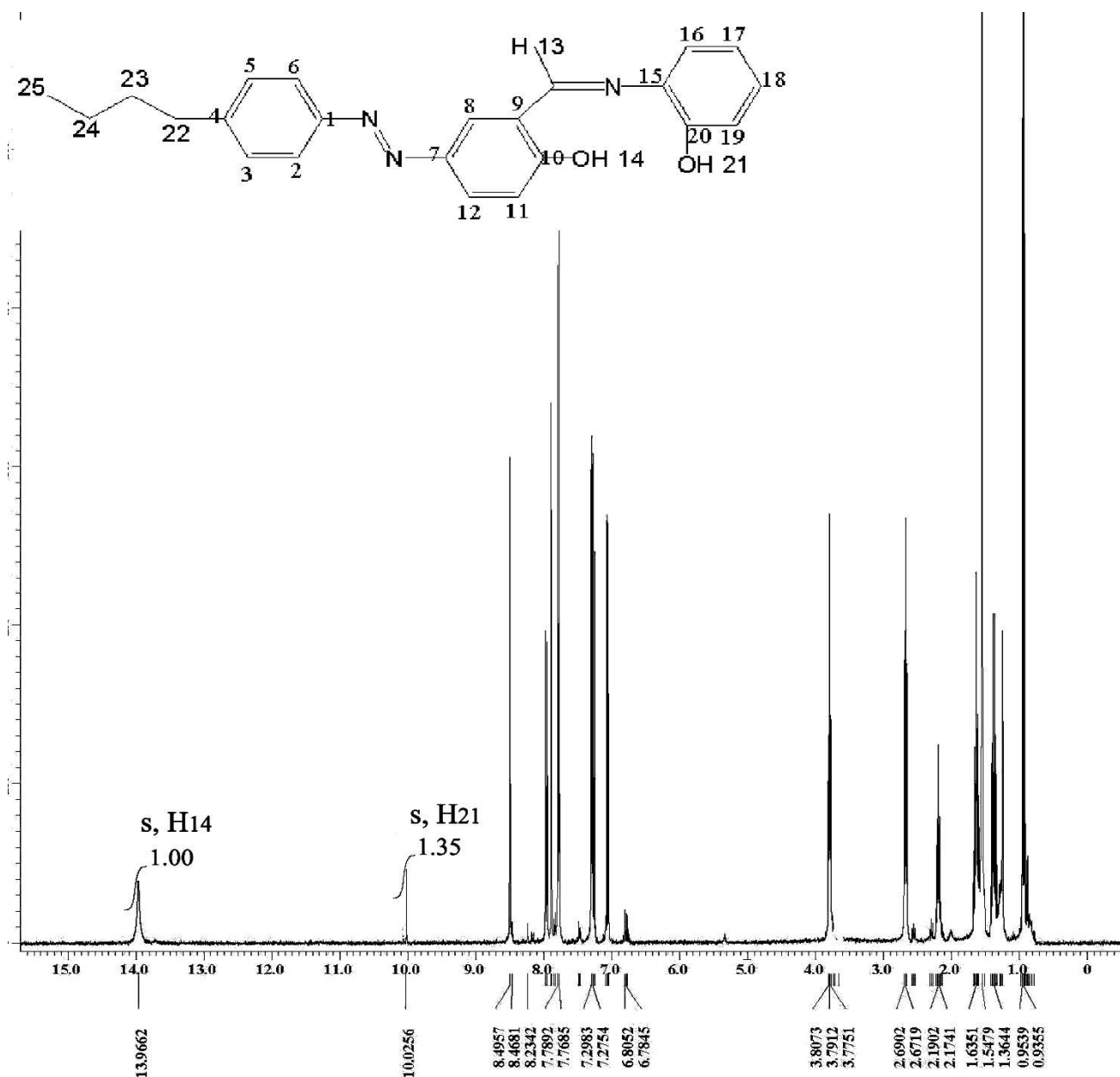


Figure 3 <sup>1</sup>H NMR of the H<sub>2</sub>L





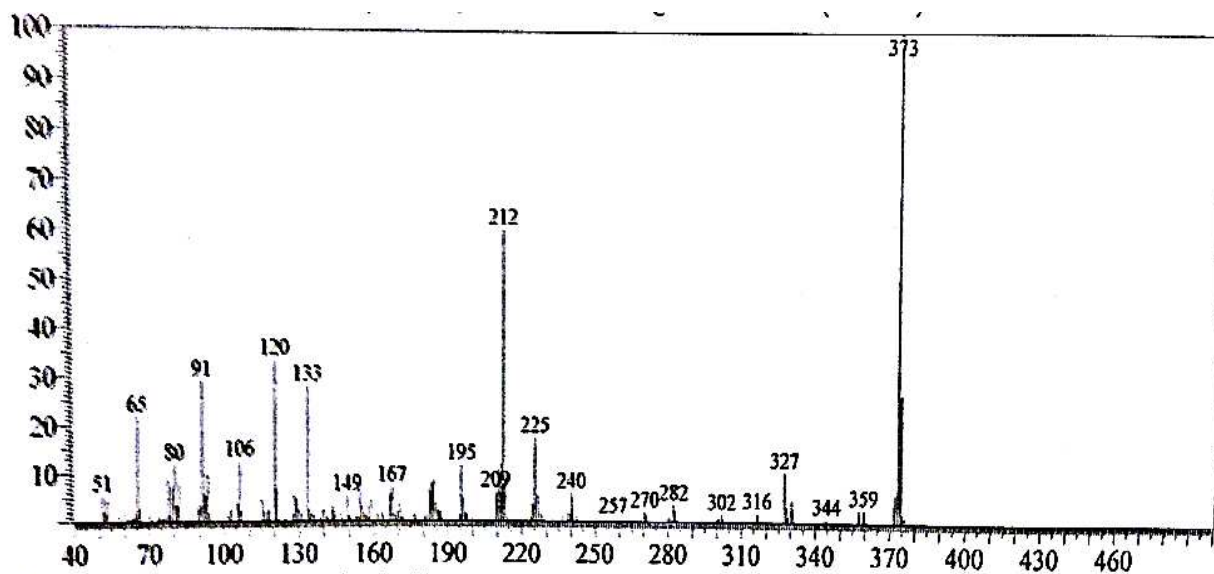
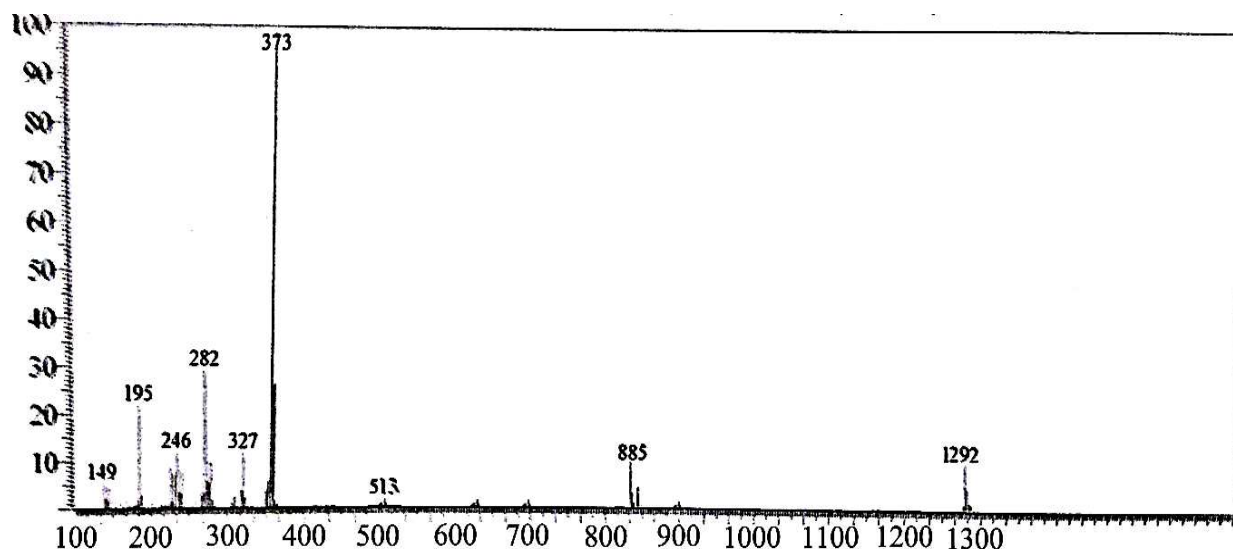
Figure 5 Mass spectrum of H<sub>2</sub>L

Figure 6 Mass spectrum of CeIII complex

**Magnetic measurements:** The magnetic moment data of Ln (III) complexes show that lanthanum (III) chloride complex is diamagnetic in nature while all other complexes are paramagnetic, as expected. Magnetic moment of 2.54 B.M. was recorded for CeIII complex due to the presence of one electron. However, in the case of samarium (III) complex (1.54B.M.), a slight variation from VanVleck values is observed due to low  $J-J$  separation which leads to thermal population of higher energy levels. In GdIII complex a magnetic moment of 7.90 B.M was recorded which suggest a maximum number of unpaired electrons are 7, with all the electrons have parallel spin. This property is important for the use of gadolinium complexes as contrast reagent in MRI scans [24, 25].

**Molar conductivity measurements:** The molar conductivity measurements for the complexes were carried out using a concentration of  $10^{-3}$ M and DMF as a solvent. All complexes showed a behavior

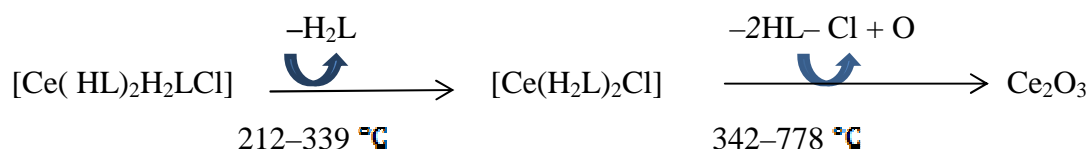
of non-electrolyte type indicating the presence of chloride ions inside the coordination sphere, and these results agree with the suggested configurations of the lanthanide complexes [Table 3].

**Table 3** Magnetic moment and Molar conductivity data of Ln(III) complexes.

Complexes	$\mu_{\text{eff}}$	$\mu_{\text{eff}}$ (Van Vleck)	Molar conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	Geometry
LaC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	0.00	X = $-0.18 \times 10^{-6}$ c .mg sec	11.00	Tctp*
CeC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	2.53	2.54	8.02	Tctp
SmC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	1.54	0.85	12.34	Tctp
GdC <sub>69</sub> H <sub>67</sub> N <sub>9</sub> O <sub>6</sub> Cl	7.90	7.94	9.05	Tctp

\**Tricapped trigonal prisim.*

**Thermo gravimetric analyses of H<sub>2</sub>L and complexes:** Thermo gravimetric analyses were carried out under nitrogen atmosphere at the heating rate of 20°C min<sup>-1</sup> for the ligand H<sub>2</sub>L and its complexes to examine their thermal stability. As shown in figure 7 the TG plot of H<sub>2</sub>L displayed two resolved and well defined decomposition steps. The first decomposition step occurred in the temperature ranges 177–402°C, with a net weight loss of 60.77% (1.59 mg), probably due to elimination of C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> moiety. The second decomposition step occurred in the temperature range 408–498°C with a net weight loss of 5.17 % (0.13 mg) due to the loss of CH<sub>3</sub> moiety to leave an organic residue C<sub>9</sub>H<sub>10</sub>N with a net weight (0.94 mg). Thermal spectrum of the CeIII complex revealed that it is stable up to 212°C and do not show any weight loss below this temperature which indicated that the complex are devoid of lattice and coordinated water in the coordination sphere, see figure 8. The TGA curve shows that the first weight loss was 28.81% (0.85 mg), corresponding to one molecule of H<sub>2</sub>L occurred between 212–339°C. The second and third molecules of ligand eliminated simultaneously between 342–778°C, the observed weight loss was 57.28 % (1.69 mg). Further mass loss recorded up to 778 °C indicates the formation of metal oxide (Scheme 2).



Scheme 2 thermal decomposition of CeIII complex



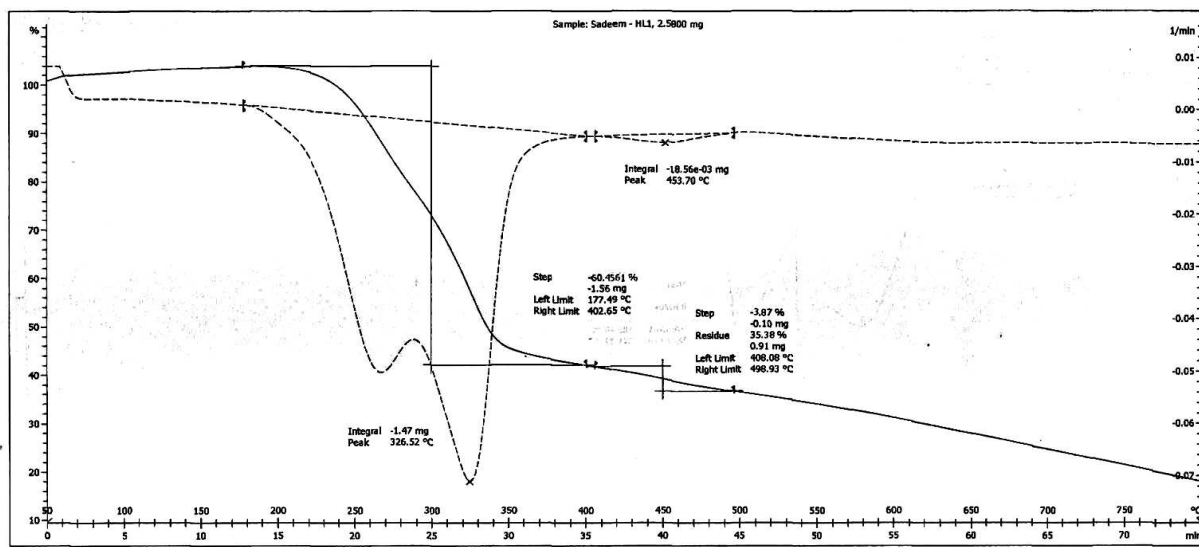
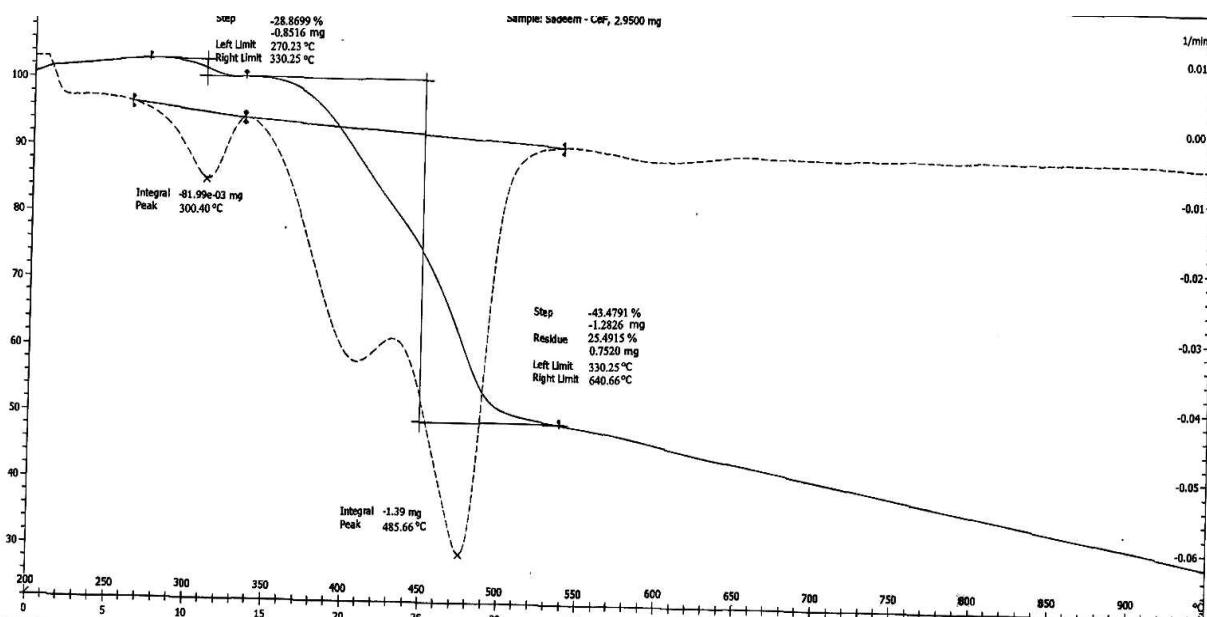
Figure 7 TGA for H<sub>2</sub>L

Figure 8 TGA for CeIII complex

## CONCLUSION

Lanthanide complexes with single arm N-aryl Schiff base ligand (H<sub>2</sub>L) of the formula [LnH<sub>2</sub>L(HL)<sub>2</sub>Cl] were synthesized and characterized. Two forms of ligands exist in the complexes; a bidentate through two phenolic oxygen and tridentate through the deprotonated phenolic oxygen and azomethine nitrogen along with hydroxyl group, see figure 9.

## ACKNOWLEDGEMENT

The authors would like to thank University of Putra Malaysia for using equipments and physical measurements and Al-Mustansiriyah University for the financial support

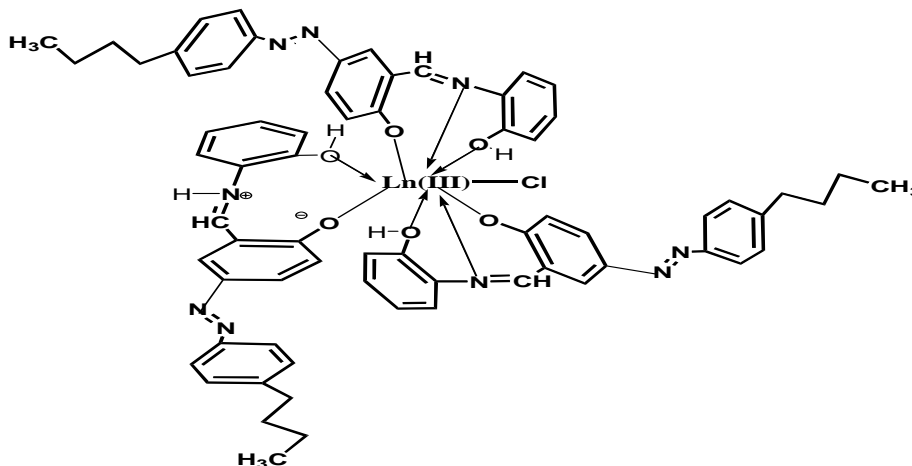


Figure 9 suggested structure configuration of lanthanide complexes

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