



# SYNTHESIS AND CHARACTERIZATION OF PRASEODYMIUM (III) AND NEODYMIUM (III) COMPLEXES CONTAINING 2-METHOXY-6-((2-(PIPERAZIN-1YL) ETHYL IMINO)METHYL) PHENOL AS LIGAND

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## ABSTRACT

A new unsymmetrical Schiff base ligand namely 2-methoxy-6-((2-(piperazin-1-yl)ethylimino) methyl)phenol(L) was derived from the condensation of 1-(2-aminoethyl)piperazine with o-vanilin. The Schiff base metal complexes ( $\text{Ln}^1\text{-Ln}^2$ ) were synthesized and characterized by the elemental analysis, molar conductance, electronic absorption, FT-IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and thermal studies. The IR and NMR spectral data suggested that the ligand was coordinated to metal ion through imine, secondary, tertiary nitrogen atoms and phenolic oxygen atom act as tetradentate (N, N, N, O) modes. The molar conductance data revealed that the metal complexes were 1:1 electrolytes. The presence of coordinated water molecules are inferred from thermogravimetric analysis. Thermal degradation studies show that the final product is the metal oxide. Based on these studies, the complexes are eight coordinated, which have been formulated as  $[\text{Ln}^{\text{III}}(\text{L})(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3)$ , where  $\text{Ln}^1\text{-Ln}^2 = \text{Pr(III)}$  and  $\text{Nd(III)}$ . The Pr(III) and Nd(III) complexes were screened for antibacterial activity against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas auroginosa* and fungal activity against *Candida albicans* and *Aspergillusniger*.

**Key words:** Schiff base, Pr(III), Nd(III), Complexes, Thermal studies, Antimicrobial studies.

## INTRODUCTION

Nowadays coordination chemistry of lanthanide (III) complexes is interesting due to its significant properties like luminescence and supramolecular polymetallic functional assemblies<sup>1-8</sup>. Lanthanide(III) complexes possess distinctive structures in advanced material such as Ln- doped semiconductors<sup>9</sup>, magnetic<sup>10,11</sup>, catalytic<sup>12</sup>, fluorescent<sup>13,14</sup> and nonlinear optical materials<sup>15,16</sup>. Schiff base containing metal complexes have played a vital role in the development of coordination chemistry, resulting in vast number of publications<sup>17</sup>. Only a very few piperazine based Schiff base complexes were reported. On the other hand the

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piperazine offers an aliphatic nitrogen-containing building block<sup>18-26</sup>. Piperazine itself is a good hydrogen-bond acceptor, which together with its metal complexing capabilities, makes it an interesting moiety for supramolecular chemistry<sup>27</sup>. In the present work, we report the synthesis and characterization of Schiff base ligand namely 2-methoxy-6-((2-(piperazin-1-yl)ethylimino) methyl) phenol and its (Ln<sup>1</sup>-Ln<sup>2</sup>) Pr(III) and Nd(III) complexes. The antimicrobial activity for the ligand and Pr(III) and Nd(III) complexes were also ascertained.

## EXPERIMENTAL

### Instrumentation

Elemental analyses (C, H, and N) were performed using an Elementar Vario EL III analyser. The IR spectra were recorded using the KBr disc technique (4000-400) cm<sup>-1</sup> on a Shimadzu FTIR spectrophotometer. The electronic spectra in the range 200-900 nm range were obtained in DMSO on a Shimadzu spectrophotometer. Molar conductances of the Pr(III) and Nd(III) complexes were determined in DMSO using an Elico model 4070 conductivity bridge. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ligand and complexes were measured with Bruker AVANCE III 500 MHz (AV 500). TG-DTA curves of the complexes were recorded on a Perkin Elmer in air atmosphere with a heating rate of 10°C min<sup>-1</sup> between 40°C and 700°C.

### Materials and reagents

All solvents, o-vanillin and 1-(2-aminoethyl)piperazine were procured from Merck and Aldrich. The metal salts Pr<sub>6</sub>O<sub>11</sub> and Nd<sub>2</sub>O<sub>3</sub> were procured from Merck and used as such.

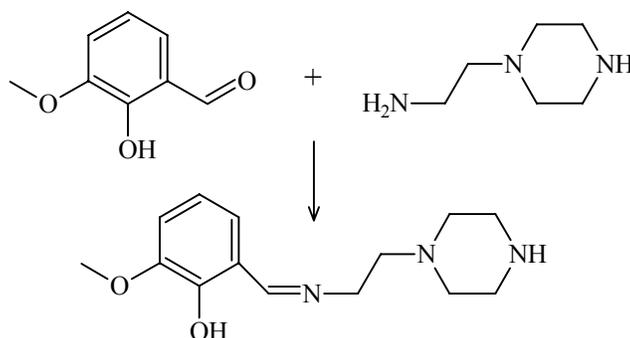
### Synthesis of 2-methoxy-6-((2-(piperazin-1-yl)ethylimino)methyl)phenol ligand (L)

The unsymmetrical tetradentate Schiff base ligand (L) was synthesized by the condensation of 1-(2-aminoethyl)piperazine with o-vanillin in MeOH, in a 1:1 mmol ratio under heating on a water bath at 50°C for 4-5 hr. Then, the solvent was evaporated slowly and a yellow coloured Schiff base was obtained.

### Synthesis of Pr(III) and Nd(III) complexes

The metal(III) complexes were synthesized by the reaction of ligand (L) with the subsequent metal salts. A methanolic solution containing various lanthanide nitrates (0.001 mmol) were added slowly to a solution of Schiff base (0.001 mmol) and the mixture was stirred and heated on a water bath at 50°C for 4-5 hr. They were obtained in good yields and high purity by the slow evaporation of the solvent mixture at atmospheric pressure. The

complexes are stable in air, non-hygroscopic and have decomposed above 270°C, and they are soluble in DMF and DMSO and insoluble in other organic solvents.



2-Methoxy-6-((2-(piperazin-1-yl)ethylimino)methyl)phenol

### Scheme 1: Synthesis of Schiff base ligand

## RESULTS AND DISCUSSION

The physical characteristics, micro analytical and molar conductance data of the ligand and its Pr(III) and Nd(III) complexes are given in Table 1. The newly synthesized piperazine containing Pr(III) and Nd(III) complexes are stable at room temperature in the solid state. The metal complexes are generally soluble in DMF and DMSO and insoluble in other organic solvents. The resulting complexes were characterized using the following physical studies.

**Table 1: Physical and analytical data of Pr(III) and Nd(III) complexes**

Complexes	Mol wt.	Yield (%)	Melting point (°C)	Elemental analysis				Conductance (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
				M	C	H	N	
[Pr (C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> N <sub>3</sub> ) (NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	561.26	78	225	25.11 (26.60)	29.96 (30.70)	3.23 (3.24)	7.49 (7.53)	31.2
[Nd(C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> N <sub>3</sub> ) (NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	564.59	77	200	25.55 (24.64)	29.78 (29.96)	3.21 (3.29)	7.44 (7.50)	23.5

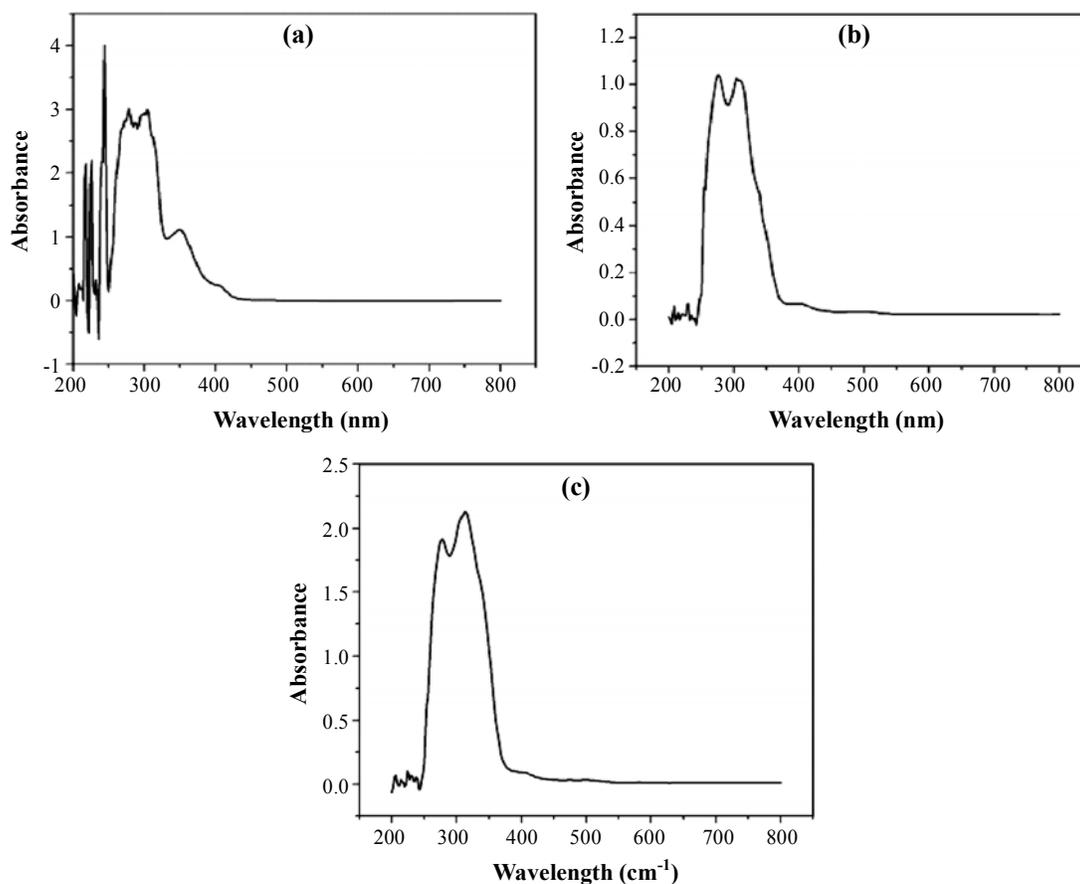
### Molar conductivity measurements

The molar conductivity of Pr(III) and Nd(III) complexes was measured in DMSO at

room temperature. The molar conductivity values of these complexes were in the range of  $25\text{-}55\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , indicating the 1:1 electrolyte nature of these complexes<sup>28</sup>.

### Electronic spectra

The electronic spectra of complexes are shown in Fig. 1. The electronic spectrum of the ligand, shows the  $n\text{-}\pi^*$  transition at 332 nm and the  $\pi\text{-}\pi^*$  transition at 304 nm. The complexes show band in the region of  $n\text{-}\pi^*$  at 290 nm and  $\pi\text{-}\pi^*$  at 278 nm regions. The lanthanum (III) complex has no significant absorption in the visible region, owing to the absence of 4f orbital electrons. The visible spectral bands of the lanthanide complexes were hypersensitive to stereochemistry. This may be probably attributed to the fact that the f-f transitions are very weak and the bands corresponding to this transition are obscured by the strong charge transfer transition bands of the ligand<sup>29</sup>.



**Fig. 1: UV spectrum of (a) Ligand (b) Pr complex (c) Nd complex**

### Infrared spectral studies

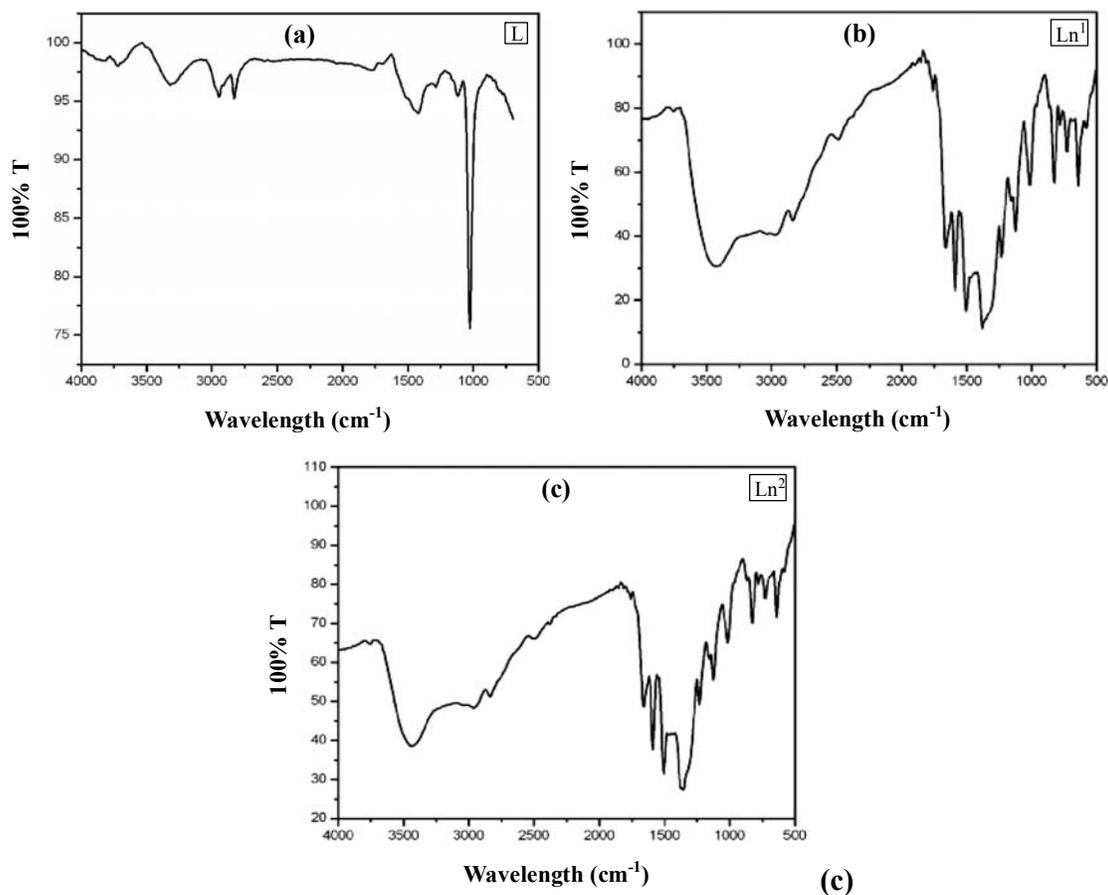
The most pertinent IR absorption bands from the spectra of the complexes, along with their values, are shown in Table 2 and Fig. 2. In the ligand, the C=N band appearing at  $1689\text{ cm}^{-1}$  is shifted to lower frequencies by  $31\text{-}39\text{ cm}^{-1}$  in the corresponding Pr(III) and Nd(III) complexes, indicating that the ligand was coordinated to the metal ions through the azomethine group<sup>30-33</sup>. The ligand show a broad characteristic band of the –OH group in  $3300\text{ cm}^{-1}$ . The disappearance of this band in the spectra of the complexes was indicative of the fact that the deprotonation of the intramolecular hydrogen bonded OH group on complexation and consecutive coordination of phenolic oxygen to the metal ion. The N-H stretching frequency at  $3317\text{ cm}^{-1}$  in free ligand shifted and merged with OH stretching vibrations in all the complexes, which revealed that the secondary N-H atom involved in the coordination. The IR spectra of Pr(III) and Nd(III) complexes show a strong band in the  $3425\text{-}3433\text{ cm}^{-1}$  region, revealing the presence of coordinated water molecule. The Pr(III) and Nd(III) nitrate complexes with respect to nitrate group reveal that the peak around  $1381\text{ cm}^{-1}$  due to ionic nitrate group is present in all the complexes. The magnitude of ( $\nu_4\text{-}\nu_1$ ) and ( $\nu_3\text{-}\nu_5$ ) are  $147\text{-}123\text{ cm}^{-1}$  and  $55\text{ cm}^{-1}$ , indicating the presence of bidentate nitrate groups. From this, we concluded that all the complexes are coordinated with Pr(III) and Nd(III) ions in a bidentate manner<sup>34,35</sup>. The appearance of peak around  $825\text{-}830\text{ cm}^{-1}$  was attributed to the rocking mode of the watermolecule<sup>36</sup>. The presence of coordinated water was also established and supported by TG/DTA of these complexes. The bands in the range  $578\text{-}586$  and  $430\text{-}438\text{ cm}^{-1}$  ranges are assigned to the  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  vibration modes, respectively<sup>37</sup>.

**Table 2: FT-IR data of ligand (L) and Pr(III) and Nd(III) metal complexes**

Compds.	$\nu(\text{O-H})$	$\nu(\text{H}_2\text{O})$	$\nu\text{C=N}$	$\nu\text{N-H}$	$\nu\text{NO}_3$	Ionic nitrate	$\nu\text{M-N}$	$\nu\text{M-O}$
L	3300		1689	3317				
Ln <sup>1</sup>	-	3425	1658	-	1357	1381	438	578
Ln <sup>2</sup>	-	3433	1650	-	1357	1381	430	586

Compds.	$\nu_4$	$\nu_1$	$\nu_2$	$\nu_6$	$\nu_3$	$\nu_5$	$\nu_4\text{-}\nu_1$	$\nu_3\text{-}\nu_5$
L								
Ln <sup>1</sup>	1504	1381	1010	825	780	725	123	55
Ln <sup>2</sup>	1504	1357	1018	825	780	725	147	55



**Fig. 2: IR spectrum of (a) Ligand (b) Pr complex (c) Nd complex**

### NMR Studies

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the ( $\text{Ln}^1\text{-Ln}^2$ ) complexes in  $\text{DMSO-d}_6$  solvent are shown in the Fig. 3. The singlet peak at 8.54 ppm due to azomethine proton shows the formation of Schiff base ligand 2-methoxy-6-((2-(piperazin-1-yl)ethylimino)methyl)phenol. In the complexes ( $\text{Ln}^1\text{-Ln}^2$ ), the up field shift of  $\text{C}=\text{N}$  peak from 8.54 to 8.15 ppm indicates the coordination of imine nitrogen to  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions<sup>38</sup>. The singlet peak at 13.5 ppm show the presence of  $-\text{OH}$  proton in the ligand, which was not observed in these two complexes confirmed the deprotonation and complexation of phenolic oxygen to  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions. The aromatic ring protons form a multiplet in the region of 6.6-7.2 ppm for the ligand, which was slightly affected due to the complexation. The  $^{13}\text{C}$  NMR spectrum of ligand shows imine carbon atom at 162.10 ppm, this peak show upfield shift at 171.11 ppm in the complex.

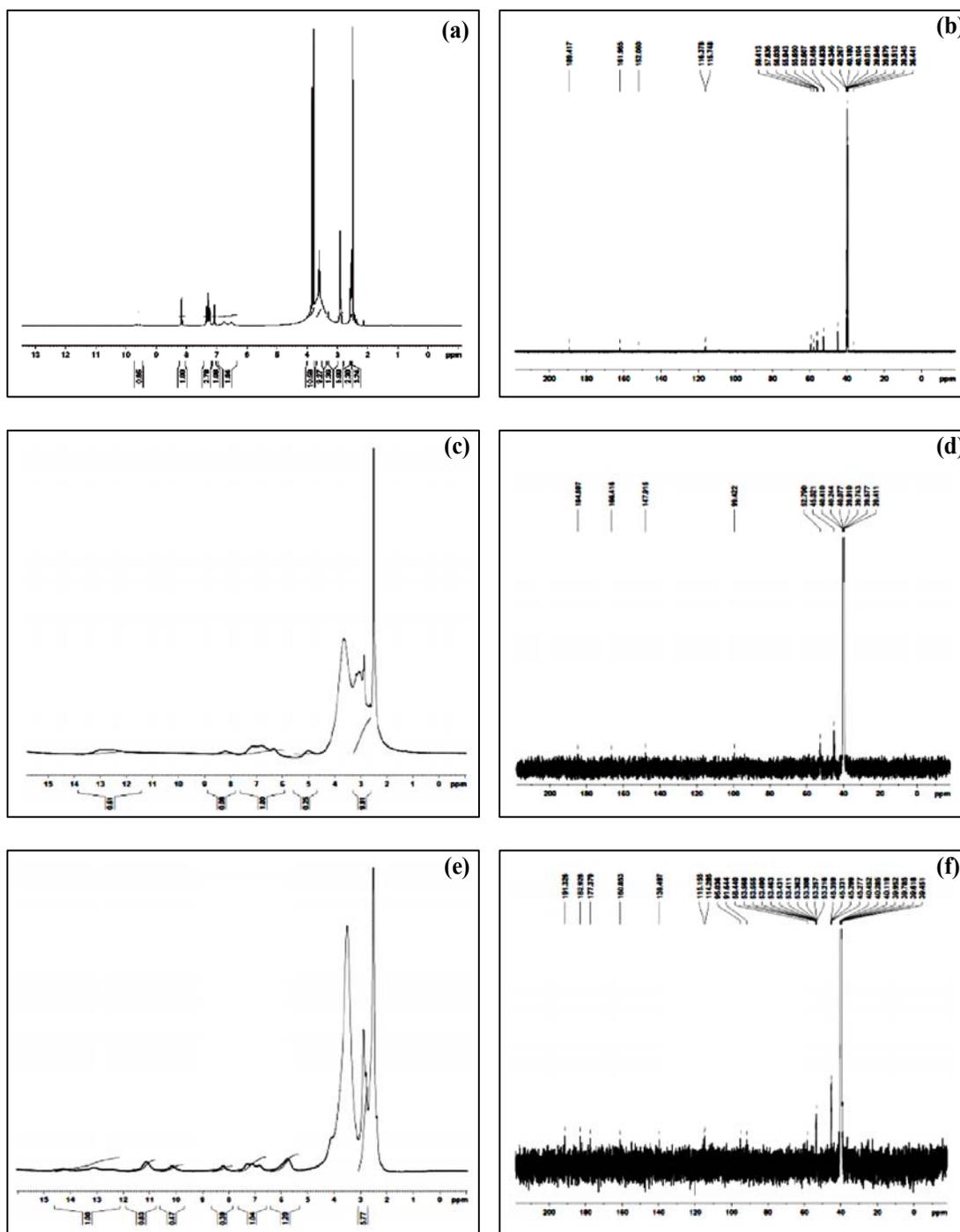


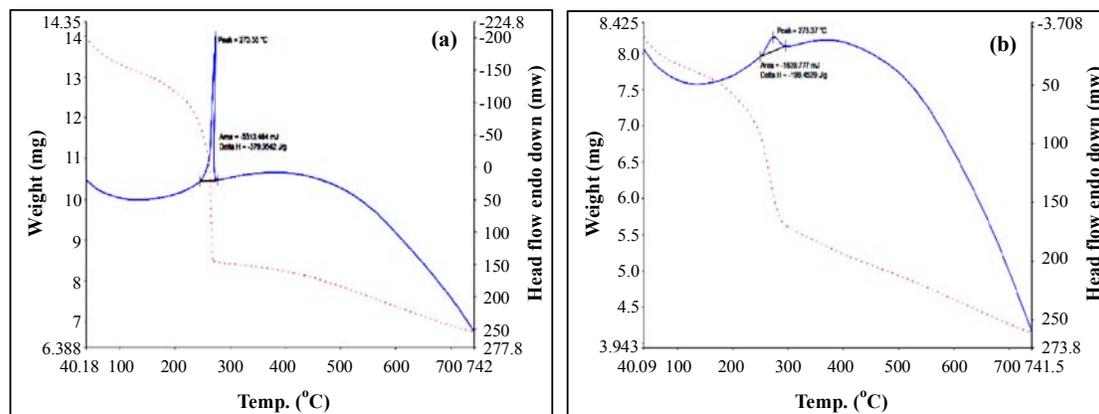
Fig. 3:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of (a) Ligand (b) Pr complex (c) Nd complex

## Thermal analysis

The TG-DTA measurements of Pr(III) and Nd(III) complexes were carried out in air and their thermal data are given in Table 3 and Fig. 4.

**Table 3: Thermal data of Pr(III) and Nd(III) complexes**

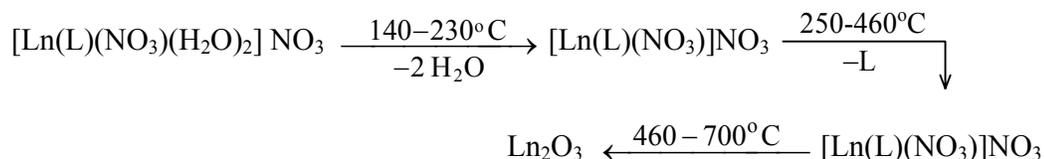
Complexes	DTA Temp. (°C)	Thermo-gravimetry	Weight loss		Nature of the reaction
		Temp range (°C)	Calculated value	Observed value	
[Pr (C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> N <sub>3</sub> ) (NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	-547.11	140-250	6.4	6.5	Dehydration
	+273.55	250-350	46.4	46.8	Loss of ligand
	-265.44	350-700	69.9	69.6	Decomposed to metal oxide
[Nd (C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> N <sub>3</sub> ) (NO <sub>3</sub> )(H <sub>2</sub> O)](NO <sub>3</sub> )	+273.37	140-250	6.4	6.2	Dehydration
	-267.07	250-350	46.1	46.4	Loss of ligand
		300-700	70.2	70.2	Decomposed to metal oxide



**Fig. 4: TG-DTA curve of (a) Pr complex (b) Nd complex**

Generally, the thermal decomposition takes place in three stages. The thermal curves of all the complexes show an endothermic peak in the range 140-230°C corresponds to the dehydration of two water molecules. The loss of water molecules in this range indicates that they were coordinated with the metal ion<sup>39</sup>. Second stage decomposition of ligand in the

temperature range of 250-460°C leads to the formation of Pr(III) and Nd(III) nitrates. Finally, the most stable oxides Pr<sub>6</sub>O<sub>11</sub> and Nd<sub>2</sub>O<sub>3</sub> were formed. The thermal decomposition sequences of the Pr(III) and Nd(III) complexes are shown in the following steps:



### Antimicrobial activity

The results of the antimicrobial activity of the metal complexes against various bacterial and fungal strains determined by the disc diffusion method are presented in Table 4 and Fig. 5. The Pr(III) and Nd(III) complexes show higher activity against four bacterial strains (i.e., *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa*). The zone of inhibition formed by the complexes is greater than the ligand and lesser than the standard Ciprofloxacin. The metal complexes show higher zone of inhibition against two fungal strains (i.e., *Candida albicans*, *Aspergillus niger*). These values are greater than the ligand and lesser than the standard Clotrimazole. From this, we concluded that the metal complexes exhibit greater activity than the ligand.

**Table 4: Antibacterial and antifungal activity of Pr(III) and Nd(III) complexes**

Sample	Inhibition zone diameter (mm/mg sample)					
	Bacteria				Fungi	
	<i>S. aureus</i> G <sup>+</sup>	<i>B. subtilis</i> G <sup>+</sup>	<i>E. coli</i> G <sup>-</sup>	<i>P. aeruginosa</i> G <sup>-</sup>	<i>A. niger</i>	<i>C. albicans</i>
Control	0.00	0.00	0.00	0.00	0.00	0.00
Standard ciprofloxacin (Antibacterial)	30	26	25	28	-	-
Clotrimazole (Antifungal)	-	-	-	-	24	10
L	13	17	14	13	10	12
Ln <sup>1</sup>	15	19	17	16	12	15
Ln <sup>2</sup>	16	18	16	17	13	17

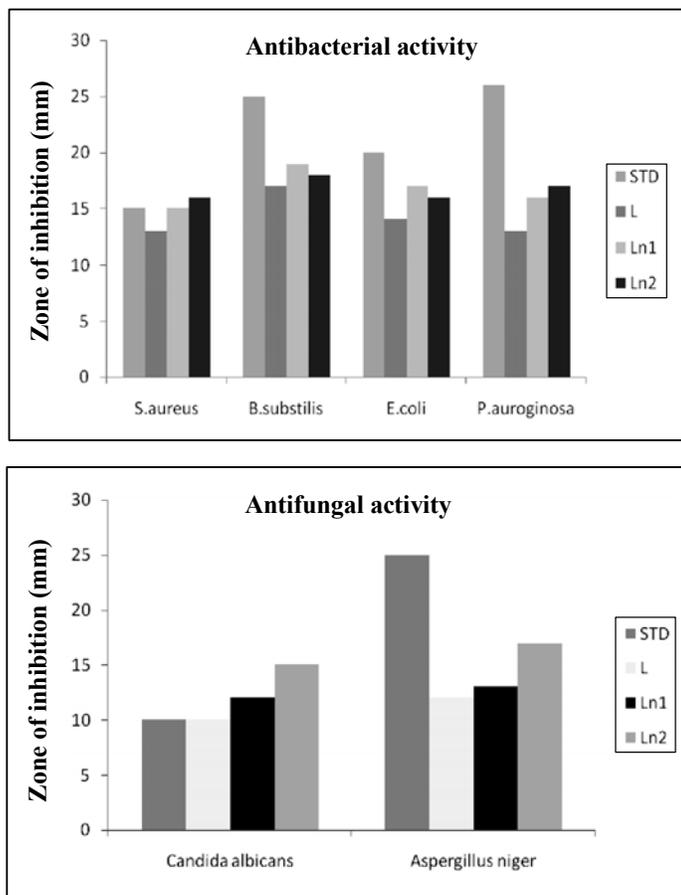
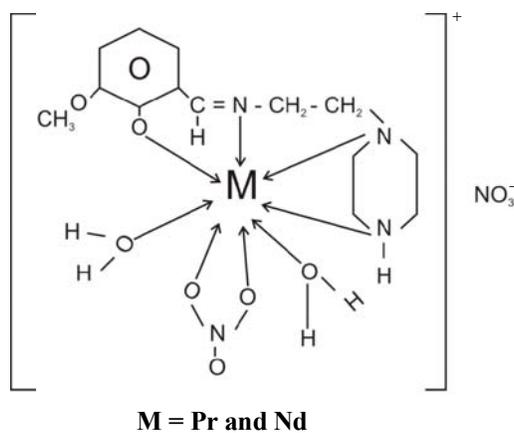


Fig. 5: Antibacterial and antifungal activity of the metal complexes



Scheme 2: The proposed structure for the complexes

## CONCLUSION

The formula assigned for Pr(III) and Nd(III) nitrate complexes namely ( $\text{Ln}^1\text{-Ln}^2$ ), respectively are in accordance with the elemental analysis, conductance and thermal data. The IR and NMR spectral data suggest that the coordinating site are imine, secondary, tertiary nitrogen atoms and phenolic -O atom. The presence of ionic nitrate groups was confirmed by IR spectra. The coordinated water molecules were clearly examined in TG-DTA curves. All these observations lead to the conclusion that Pr(III) and Nd(III) ions are eight coordinated in nitrate complexes. The following probable structure is suggested for all the complexes.

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