

Lanthanide(III) Complexes Incorporating Tridentate ONO-Donor Pyrazolone Ligand: Synthesis, Characterization, Fluorescence and Antimicrobial Studies

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The complexes of La(III), Pr(III), Sm(III), Eu(III), Tb(III) and Dy(III) of general formula $[Ln(L_2)_2(NO_3)_2]NO_3$ have been synthesized with Schiff base of (4-{[(3-hydroxyphenyl)imino]methyl}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one) (L₂) derived from 4-antipyrine carboxaldehyde and 3-aminophenol. The structure of complexes are proposed on the basis of analytical, spectral (FT-IR, UV-visible and ¹H NMR), magnetic and thermal studies. The molar conductance data indicate that the complexes are of 1:1 electrolytic nature. From spectral studies, the lanthanide ions were found to be eight coordinated in these complexes with two nitrate groups behaving in a monodentate manner. The photoluminescence properties of Sm(III), Eu(III), Tb(III) and Dy(III) complexes in dimethyl formamide were investigated. The Schiff base and its lanthanide(III) complexes were screened for their antibacterial activities against seven pathogenic bacteria: *Staphylococcus aureus, Escherichia coli, Aeromonas hydrophila, Klebsiella pneumoniae, Vibrio cholerae, Salmonella typhimurium* and *Bacillus subtilis* by agar disc diffusion method. Most of the complexes were found to exhibit potential activities against a number of pathogenic bacteria.

Keywords: Schiff base complexes, Photoluminescence property, Antimicrobial activity.

INTRODUCTION

The microbial resistance to antibiotics is a big challenge to the researchers and it necessitates the search for new compounds with potential effects against pathogenic micro organisms. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since they have special role in biologically important species [1-3]. Antipyrine [(1,2dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one)] and its derivatives exhibit a wide range of biological activities such as antimicrobial [4,5], antitumor [6], antiviral [7] and analgesics [8,9]. A wide range of metal complexes derived from antipyrine have been reported due to their interesting structural features as well as the biological activity. Pyrazole-based ligands exhibit variable complexing behaviour and a variety of coordination possibilities to metal centers [10]. It has been reported that coordination of organic compound with metal, *i.e.*, chelation causes drastic change in the biological property of the ligand and also the metal moiety [11,12].

Current interest in coordination compounds of lanthanides results from a unique combination of properties of these ions [13,14]. Several lanthanides exhibit strong luminescence emission with narrow line widths, resulting in a high "colour purity" of the emitted light [15,16]. They were extensively used in many areas, such as fluorescence materials [17-19], electro luminescence devices [20,21], fluorescence probes and labels in a variety of biological systems [22-24]. The design of the suitable organic ligands plays a crucial role in the optimization of the photophysical properties of the lanthanide complexes for specific applications [25-28]. Besides their photophysical applications, special interest is also given to the pharmacological properties of rare earth complex drugs [29-31].

In this investigation, we have synthesized La(III), Pr(III), Sm(III), Eu(III), Tb(III) and Dy(III) complexes of the Schiff base 4-{[(3-hydroxyphenyl)imino]methyl}-1,5-dimethyl-2phenyl-1,2-dihydro-3*H*-pyrazol-3-one(L₂).The complexes were analyzed by elemental analysis, UV-visible, FT-IR, ¹H NMR spectra, molar conductance, magnetic and thermal studies. Moreover, the luminescent properties and antimicrobial activities of these complexes were also examined.

EXPERIMENTAL

4-Antipyrine carboxaldehyde and 3-aminophenol (Sigma Aldrich) were purchased and used as such. Lanthanide(III)

nitrate were prepared by dissolving the respective metal oxides (99.9%) in 60% A.R. nitric acid (Merck), followed by crystallization. All complexes were analyzed for their metal content by standard methods [32]. The C, H and N contents in the complexes were determined using Heracus CHN rapid analyzer. The molar conductivities of the complexes were measured in DMF (10⁻³ M) were measured using a Elico CM-180 conductivity meter with a dip type platinum electrodes (cell constant 0.986 cm⁻¹). The IR spectra were recorded in the range 4000– 350 cm⁻¹ on Shimadzu IR470 spectrophotometer. The electronic spectra in the range 190-900nm were recorded using Shimadzu UV–160A. The ¹H NMR spectra were recorded on a Bruker DRX-500 spectrometer using DMSO- d_6 as solvent. The magnetic susceptibility measurements were performed on a Sherwood Scientific Gouy Balance. Thermogravimetric studies of the compounds were carried out on a Perkin Elmer STA 6000 Thermal Analysis system, in the range 15-900 °C with a heating rate 10 °C min⁻¹. Photoluminescence spectral data were drawn using Fluorolog 3 TCSPC fluorescence spectrometer.

The bacterial cultures used in this study-*Staphylococcus* aureus, Escherichia coli, Aeromonas hydrophila, Vibrio cholerae, Klebsiella pneumonia, Salmonella typhimurium and Bacillus subtilis were obtained from department of Microbiology and Biochemistry, School of Marine Sciences, Cochin University of Science and Technology, Kerala, India. The microbiological culture media -nutrient agar and nutrient broth were obtained from Himedia Laboratories Private Limited.

Synthesis of the Schiff base: 4-{[(3-hydroxyphenyl)imino]methyl}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*pyrazol-3-one (L₂): 3-Aminophenol (0.22 g, 2 mmol) was dissolved in 20 mL ethanol and added to 4-antipyrine carboxaldehyde (0.43 g, 2 mmol) in 30 mL ethanol. The 1:1 mixture was refluxed on a boiling water bath for 4 h, the excess of solvent was partially evaporated and yellow solid was separated by adding drops of cold water. It was filtered and washed with water followed by ether. The ligand was then recrystallized from ethanol and dried under vacuum over anhydrous CaCl₂. The purity of the ligand was checked by TLC, infrared and NMR spectra and by elemental analysis. Yield: 71 %, m.p.: 208 °C. ¹H NMR (DMSO-*d*₆) (δ , ppm): 8.83 (s, 1H, phenolic), 8.31 (s, 1H, -CH=N-), 5.9-7.54 (m,-Ph) 3.34 (s, 3H, -N-CH₃), 2.9 (s, 3H, =C-CH₃). IR (KBr, cm⁻¹): ~3370 v(OH), 1641 v(C=O), 1588 v(C=N), 1275 v(ph–O). Anal. calcd. for C₁₈H₁₇N₃O₂ (307.35): C, 70.34; H, 5.6; N, 13.67. Found C, 69.8; H, 5.3; N, 13.7 %.

Synthesis of lanthanide complexes $[Ln(L_2)_2(NO_3)_2]NO_3$ (where Ln = La (1), Pr (2), Sm (3), Eu (4), Tb (5) and Dy (6): All the complexes were synthesized in a similar way by following the **Scheme-I**. The representative procedure for the preparation of Lanthanum complex 1 is described.

The ligand L_2 (0.615 g, 2 mmol) was dissolved in a 1:3 mixture of methanol and ethyl acetate (25 mL) and refluxed with methanolic solution of (10 mL) of La(NO₃)₃·6H₂O (0.433 g, 1 mmol) for 3 h on a boiling water bath. The reaction mixture was cooled to room temperature, the precipitated solid complex 1 was filtered off, washed with hot ethyl acetate and dried under vacuum over anhydrous CaCl₂. The other complexes Pr (2), Sm (3), Eu (4), Tb (5) and Dy (6) were synthesized in the same way by using the appropriate Ln(III) nitrate salts and ligand L_2 taken in 1:2 (metal to ligand) ratio (Scheme-I). The yield and melting point of these complexes were found and tabulated in Table-1.

Antibacterial activity: The synthesized Schiff base and their corresponding Ln(III) complexes were screened for their *in vitro* antibacterial activity against seven pathogenic bacterial strains-*S. aureus, E. coli, A. hydrophila, V. cholerae, K. pneumonia, S. typhimurium* and *B. subtilis* by agar disc diffusion method



Scheme-I: Synthesis route for the synthesis of Schiff base ligand L2 and its Ln(III) complexes

TABLE-1 ANALYTICAL AND PHYSICAL DATA OF Ln(III) COMPLEXES OF L ₂ (COMPLEXES 1 TO 6)									
Complex	Colour	mf		m.p.	Yield	Elemental analysis (%): Found (calculated)			
Complex	Colour	111.1	111. vv .	(°C)	(%)	С	Н	Ν	Ln
$[La(L_2)_2(NO_3)_2]NO_3(1)$	Brown	LaC ₃₆ H ₃₄ N ₉ O ₁₃	936.61	306	61	45.91	3.58	13.2	14.56
						46.02)	(3.6)	(13.42)	(14.78)
$[Pr(L_2)_2(NO_3)_2]NO_3(2)$	Brown	PrC ₃₆ H ₃₄ N ₉ O ₁₃	941.61	328	63	45.68	3.49	13.23	14.81
						(45.9)	(3.6)	(13.4)	(14.96)
$[Sm(L_2)_2(NO_3)_2]NO_3(3)$	Yellowish brown	$SmC_{36}H_{34}N_9O_{13}$	951.05	331	66	45.26	3.42	13.18	15.74
						(45.46)	(3.6)	(13.26)	(15.81)
$[Eu(L_2)_2(NO_3)_2]NO_3(4)$	Brown	EuC36H34N9O13	952.66	307	69	44.94	3.43	12.88	15.58
						(45.38)	(3.6)	(13.2)	(15.95)
$[Tb(L_2)_2(NO_3)_2]NO_3(5)$	Brown	TbC36H34N9O13	959.62	306	65	44.82	3.47	12.78	16.45
						(45.1)	(3.6)	(13.1)	(16.56)
$[Dy(L_2)_2(NO_3)_2]NO_3(6)$	Brown	DyC36H34N9O13	963.20	318	71	44.74	3.49	12.76	16.67
						(44.9)	(3.6)	(13.1)	(16.87)

[33]. 1 mg of each of the test compounds were separately dissolved in 1 mL dimethyl formamide to get stock solution. The standardized inoculums of bacterial suspension $(10^6 - 10^8)$ CFU/mL) is used to spread over the surface of the Mueller Hinton agar plates with a sterile cotton swab to get a uniform lawn culture. The filter paper disc of 5.0 mm diameter which was impregnated with 20 µL of the solution of each of the test compound in DMF. The discs were placed on the previously seeded nutrient agar plates using sterile forceps so that the amount of test material present per disc is 20 µg/disc. The plates were incubated at 37 °C for 24 h and the diameter zones of inhibition (DZI) of bacterial growth around each disc was measured. Streptomycin (20 µg/disc) and DMF were used as standard antibacterial drug and control solvent, respectively. All the tests were performed three times simultaneously to check the consistency in the results and the mean was recorded.

RESULTS AND DISCUSSION

Analytical and physical data: All the complexes 1 to 6 are coloured, non-hygroscopic, microcrystalline solids, soluble in methanol, ethanol, DMSO and DMF, sparingly soluble in acetonitrile, acetone and ethyl acetate but insoluble in water, benzene and ether. The analytical data (Table-1) of the complexes indicates 1:2 (metal:ligand) stoichiometry. The results of elemental analyses (C, H, N and Ln) and some physical properties such as colour, melting point etc of the complexes are presented in Table-1. The data obtained suggest that the complexes may be formulated as $Ln(L_2)_2(NO_3)_3$ where Ln = La, Pr, Sm, Eu, Tb and Dy.

Molar conductance: The molar conductance (Λ_m) of the Ln(III) complexes (**1**) to (**6**) in three non-aqueous solvents, *viz.* DMF, methanol and ethanol (10⁻³ M) were measured at room temperature and listed in Table-2. These values suggest that they are in the range reported for 1:1 electrolytes in the same solvents [34]. These values indicate that two of the nitrate ions are present inside the coordination sphere in all the complexes and one of the nitrate ions exists as ionic. Hence the formula of the complexes may be modified as [Ln(L₂)₂(NO₃)₂]NO₃. Where Ln = La, Pr, Sm, Eu, Tb and Dy.

FT-IR spectra: The important IR bands of the Schiff base ligand L_2 and its lanthanide (III) complexes were summarized in Table-3. The IR spectra of the Schiff base L_2 shows two strong bands at 1641 cm⁻¹ and 1588 cm⁻¹ attributed to the C=O and CH=N stretching vibrations, respectively. In all the complexes v(C=O) bands are red shifted to about 1634-1627 cm⁻¹ and v(CH=N–) bands shifted to 1577-1568 cm⁻¹, suggesting coordination of both groups to the metal ion. This indicates

MOLAR CONDUCTANCE (ohm ⁻¹ cm ² mol ⁻¹) DATA OF Ln(III) COMPLEXES (10 ⁻³ M SOLUTION) OF L ₂									
	*Molar conductance (Λ_m) (ohm ⁻¹ cm ² mol ⁻¹)								
Complex	DMF	Methanol	Ethanol	Type of electrolyte					
1	72.8	89	36.5	1:1					
2	85.8	87	36.7	1:1					
3	82.6	91	36.8	1:1					
4	73.0	92	39.1	1:1					
5	76.4	89	38.2	1:1					
6	84.7	86	38.4	1:1					

these groups are coordinated to metal ion via the carbonyl oxygen and azomethine nitrogen atom. This is supported by a new frequency appearing in the spectra of complexes at 464-452 cm⁻¹ and 503-495 cm⁻¹ due to vibration arising from M-N bond and M-O bond, respectively [28,35]. The presence of a broad band at 3370-3100 cm⁻¹ in the ligand spectrum corresponds to the stretching frequency of phenolic hydroxyl group. This broad band is observed in the spectra of all Ln(III) complexes in the range 3384-3050 cm⁻¹ with a slight shift in the frequency and an increase in the intensity indicating the phenolic OH group is coordinated to the metal ion without deprotonation. This is further confirmed by the shift of phenolic C-O frequency at 1275 cm⁻¹ of the ligand to lower frequencies in all the complexes. In the spectra of complexes, a very strong band observed at about 1384 cm⁻¹ and a medium band at 849-838 cm⁻¹ are attributed to the v_3 and v_2 vibrations, respectively of ionic nitrate of D_{3h} symmetry. The presence of coordinated nitrate ions are indicated by two strong bands at about 1428 and 1315 assigned to the v_4 and v_1 vibrations of the nitrate of C_{2v} symmetry. The frequency separation between v_4 and v_1 may be used to discriminate between the binding modes. Since (v_4-v_1) is found to be in the range 110-119 cm⁻¹, the nitrate ion is coordinated in a monodentate fashion [36]. A representative IR spectrum of Pr(III) complex 2 is given in Fig. 1.

Electronic spectra: The UV-visible absorption spectra of L₂ and the complexes **1** to **6** were recorded in DMF and the main bands were listed in Table-4. The ligand L₂ exhibits an intense absorption band at 291 and 346 nm that can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azomethine group and carbonyl group, respectively. The absorption bands of all the Ln(III) complexes show similarity which indicate similarity of their structures. In all the complexes both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are bands are shifted to lower wavelengths supporting the coordination of L₂ *via* the azomethine nitrogen and the carbonyl oxygen atoms to the central metal ion. In addition

TABLE-3 KEY IR SPECTRAL DATA (cm ⁻¹) OF LIGAND AND ITS LANTHANIDE(III) COMPLEXES											
Commd		v(C=0)	$\mathbf{v}(\mathbf{C}-\mathbf{N})$	N(C O)	Co	v ₃ (NO ₃)	u(I = 0)	u(I n N)			
compu.	V(O-11)	V(C=0)	V(C-N)	V(C-O)	ν_4	ν_2	ν_1	ν_3	ν_2	V(LII-O)	V(LII-IN)
L ₂	3370b	1641s	1588s	1275m	-	-	-	-	-	-	-
1	3380b	1629s	1572s	1240m	1424s	1024m	1311m	1384s	838m	502w	456w
2	3378b	1634s	1575s	1243m	1428s	1024m	1315m	1384s	843m	503w	457w
3	3369b	1627s	1577s	1247m	1431s	1024m	1314m	1383s	849m	495w	452w
4	3375b	1628s	1568s	1246m	1427s	1026m	1315m	1382s	838m	502w	456w
5	3384b	1629s	1575s	1242m	1426s	1023m	1316m	1384s	843m	499w	464w
6	3375b	1634s	1577s	1245m	1432s	1024m	1313m	1384s	840m	502w	456w



Fig. 1. Infrared spectra of (a) Schiff base L₂ (b) [Pr(L₂)₂(NO₃)₂]NO₃ (2)

TABLE-4

UV-VISIBLE ABSORPTION SPECTRA AND								
LIGAND	L_2 AND ITS	Ln(III) COMPLEXES	S S					
Compound	$\lambda_{max}(nm)$	Band assignment	$\mu_{eff.}$ (BM)					
т	291	$\pi \rightarrow \pi^*$						
L_2	346	$n \rightarrow \pi^*$	_					
$[La(L_2)_2(NO_3)_2]NO_3$	281	$\pi \rightarrow \pi^*$						
(1)	335	n→π*	-					
	474	${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{P}_{1}$						
$[Pr(L_2)_2(NO_3)_2]NO_3$	484	${}^{3}H_{4} \rightarrow {}^{3}P_{0}$	2.2					
(2)	278	$\pi \rightarrow \pi^*$	5.2					
	334	n→π*						
	418	${}^{6}\text{H}_{5/2} \rightarrow ({}^{6}\text{P}, {}^{4}\text{P})_{5/2}$						
	451	${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{M}_{17/2}$						
$[Sm(L_2)_2(NO_3)_2]NO_3$	476	${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{I}_{11/2}$	1 15					
(3)	498	${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{M}_{15/2}$	1.15					
	281	$\pi \rightarrow \pi^*$						
	335	$n \rightarrow \pi^*$						
$[E_{\rm H}(L_{\rm c})]$ (NO) 1NO	531	$^{7}F_{0} \rightarrow ^{7}D_{1}$						
(4)	283	$\pi \rightarrow \pi^*$	3.43					
(4)	338	$n \rightarrow \pi^*$						
$[T_{h}(L_{\lambda})(NO_{\lambda})]NO_{\lambda}$	494	$^{7}F_{6} \rightarrow ^{5}D_{4}$						
$[10(L_2)_2(10O_3)_2]10O_3$	282	<i>π</i> →π *	7.78					
(5)	338	n→π *						
	437	${}^{6}\text{H}_{15/2} \rightarrow {}^{4}\text{G}_{11/2}$						
$[Dy(L_2)_2(NO_3)_2]NO_3$	469	${}^{6}\text{H}_{15/2} \rightarrow {}^{4}\text{F}_{9/2}$	10.23					
(6)	280	<i>π</i> → <i>π</i> *	10.25					
	339	n→π *						

to these strong ligand bands, some weak *f*-*f* bands are identified in case of Pr(III), Sm(III), Eu(III), Tb(III) and Dy(III) complexes. The observed *f*-*f* transitions and their tentative assignments are given in Table-4. In the spectrum of Pr complex **2**, two *f*-*f* bands are observed at 474 and 484 nm which are due to the *f*-*f* transitions from the ground electronic state of Pr(III), ³H₄, assigned as ³H₄ \rightarrow ³P₁and ³H₄ \rightarrow ³P₀, respectively. In the spectrum of Sm complex **3**, four medium intensity bands are observed at 418, 451, 476 and 498 nm for the transitions are ⁶H_{5/2} \rightarrow (⁶P,⁴P)_{5/2}, ⁶H_{5/2} \rightarrow ⁴M_{17/2}, ⁶H_{5/2} \rightarrow ⁴I_{11/2} and ⁶H_{5/2} \rightarrow ⁴M_{15/2}, respectively. In case of complexes **4** and **5**, a single *f*-*f* transition of medium intensity is observed at 531 and 494 nm may be assigned to ${}^{7}F_{0} \rightarrow {}^{7}D_{1}$ and ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$, respectively. In complex **6**, two weak bands are found in the UV-visible region. The first peak at 437 nm corresponds to the *f*-*f* transition ${}^{6}H_{15/2} \rightarrow {}^{4}G_{11/2}$ and the second peak at 469 nm can be assigned to ${}^{6}H_{15/2} \rightarrow {}^{4}F_{9/2}$ electronic transition [35-37].

Fluorescence studies: The photoluminescence spectra of ligand L_2 and the complexes 3, 4, 5 and 6 were recorded in DMF (10^{-5} M) at room temperature by exciting band at wavelength $\lambda_{\text{exc}} = 300 \text{ nm}$ and shown in Fig. 2. The emission spectrum of L_2 exhibits a broad emission band at $\lambda_{max} = 470$ nm which presumably due to $(^*\pi \rightarrow \pi)$ transitions. The complexes 3, 4, 5 and 6 upon excitation at λ_{exc} = 300 nm, exhibit fluorescence emission spectra with red shift in the range 492-514 nm with a greater enhancement in the fluorescence intensity (Table-5). The red shift in the fluorescence band of the ligand in the complexes compared to the free ligand can be attributed to coordination of the lanthanide ion to the ligand [38-40]. The magnitude of enhancement in fluorescence intensity depends upon the nature of the coordinated metal ion. In this case it is observed that fluorescence intensity increases in the order Sm(III) (3) > Tb(III) (5) > Dy(III) (6) > Eu(III) (4) > L₂. The enhancement of the ligand fluorescence in these complexes may be considered as a combined effect of ligand fluorescence and contribution from characteristic metal centered luminescence.



Fig. 2. Fluorescence emission spectra of Sm (3), Eu (4), Tb (5) and Dy (6) complexes in DMF solution (10⁻⁵ M)

In addition to the ligand centered fluorescence (${}^{*}\pi\rightarrow\pi$), these complexes also emit characteristic metal-centered luminescence. This can be considered as a result of intramolecular energy transfer taking place between the ligand L₂ and these metal ions in the complexes. The emission spectrum of Sm complex **3** exhibits two weak characteristic metal centered emission bands at 568 and 602 nm corresponding to ${}^{4}G_{5/2}\rightarrow$ ${}^{6}H_{7/2}$ and ${}^{4}G_{5/2}\rightarrow$ ${}^{6}H_{9/2}$, respectively. The Eu(III) complex **4** in addition to ligand centered peak at 494 nm (${}^{*}\pi\rightarrow\pi$) transitions also showed two weak metal-centered emission bands at 570 and 608 nm corresponding to ${}^{5}D_{2}\rightarrow$ ${}^{7}F_{1}$ and ${}^{5}D_{2}\rightarrow$ ${}^{7}F_{2}$ electronic transitions, respectively. The emission spectrum of Tb(III)

TABLE-5
FLUORESCENCE EMISSION SPECTRA DATA OF SCHIFF
BASE LIGAND L ₂ AND ITS Ln(III) NITRATE COMPLEXES
IN DMF (10 ⁻⁵ M) AT ROOM TEMPERATURE

Compd.	λ_{ex} (nm)	λ_{em} (nm)	Assignment	FI (a.u.)
L_2	300	472	π*→π	7183
$[S_{m}(L_{n})(NO_{n})]NO_{n}$		492	π*→π	
$[\operatorname{SIII}(\operatorname{L}_2)_2(\operatorname{INO}_3)_2]\operatorname{INO}_3$	300	568	${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$	29295
(3)		602	${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$	
$(\mathbf{E}_{\mathbf{v}}(\mathbf{I}_{\mathbf{v}}) (\mathbf{N}\mathbf{O}_{\mathbf{v}}) \mathbf{N}\mathbf{O})$		494	$\pi^* \rightarrow \pi$	
$[Eu(L_2)_2(INO_3)_2]INO_3$	300	570	${}^{5}D_{2} \rightarrow {}^{7}F_{1}$	11813
(4)		608	${}^{5}D_{2} \rightarrow {}^{7}F_{2}$	
		497	π*→π	
$[10(L_2)_2(INO_3)_2]INO_3$	300	568	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$	22348
(5)		610	${}^{5}D_{4} \rightarrow {}^{7}F_{3}$	
$[Tb(L_2)_2(NO_3)_2]NO_3$	200	514	π*→π	20120
(6)	500	569	${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$	20120
ET E1 .	•.			

FI = Fluorescence intensity

complex consists of two weak emission bands at 568 and 610 nm corresponds to ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ and ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ electronic transitions, respectively. The Dy complex **6** consists of ligand centered emission around 514 nm and also two weak metal-centered emission band at 569 nm associated with to ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition [41-43].

¹H NMR spectra: The ¹H NMR spectra of the ligand L₂ and the diamagnetic lanthanum complex 1 were recorded in DMSO- d_6 solvent and compared. Both the ¹H NMR signals at 8.3 and 8.83 ppm due to azomethine proton and phenolic proton of the ligand were retained in the spectrum of lanthanum complex 1 with a remarkable downfield shift to 8.42 and 8.9 ppm, respectively. This confirms that both the due to coordination to the metal ion through the azomethine nitrogen and phenolic group are involved in coordination to the lanthanum ion without deprotonation. Also, the multiplet appearing in the range δ = 5.9-7.54 ppm in the ligand L₂ owing to aromatic ring protons shifted slightly downfield to $\delta = 6.3-7.7$ ppm in the complex. This suggests change in the overall chemical environment of the ring protons as a result of coordination with the lanthanum ion. There is also slight upfield shift is observed in case of two singlet peaks corresponding to protons of $N-CH_3$ and $=C-CH_3$ groups which was originally present at 3.34 and 2.9 ppm in the spectra of ligand [35].

Magnetic susceptibility measurements: The magnetic moment data of the complexes are given in Table-4. The result indicates that the magnetic moment values at room temperature fairly agree with Van Vleck values indicating weak interaction of 4*f* electrons in the metal-ligand bond formation [44]. Magnetic measurements revealed that all the compounds were paramagnetic except La(III) complex. Lanthanide(III) complex is diamagnetic as expected by the closed shell electronic configuration with no unpaired electron. Relatively high value in the Sm(III) complexes may be due to the low energy gap between the ground level and the next excited level, which can be populated easily even at room temperature.

Thermogravimetric analysis: Thermogravimetric analysis of the complexes were carried out within a temperature range 30-900 °C in an inert atmosphere to ascertain their relative thermal stability and the presence of any associated water molecules. The thermal analysis data of complexes 1 to 6 is given in Table-6. The thermal decomposition patter of all the complexes is almost same. There is no appreciable mass loss up to 200 °C revealing the absence of water or solvent molecules in the complexes. The first stage of decomposition starts in the range 204-256 °C and ends in the range 309-347 °C with a weight loss of 19.5-19.8 % can be assigned to the loss of three nitrate groups from the inner and the outer coordination sphere of the complex. The rate of mass loss become maximum in the range 306-339 °C as indicated by the DTG peaks. The second stage of decomposition starts in the region 311-349 °C and ends in the range 718-723 °C accompanied by a mass loss of 61.6-63.1 % corresponds to the removal of two ligand molecules. The maximum rate of mass loss occurs in the range 409-424 °C as indicated by the DTG peaks. The residual mass percentage suggests that the final products obtained corresponds to anhydrous lanthanide metal oxide (where Ln = La, Pr, Sm, Eu, Tb or Dy) [45].

Based on the results of above physico-chemical and spectral studies, the following structure has been proposed for the lanthanide(III) nitrate complexes $[Ln(L_2)_2(NO_3)_2]NO_3$ (where Ln = La, Pr, Sm, Eu, Tb and Dy) as shown in Fig. 3.

Antimicrobial studies: The inhibition zones of the Schiff base ligand L_2 and the lanthanide complexes 1 to 6 against seven bacterial species are presented in Table-7. The ligand exhibited moderate activity against *S. typhimurium, K. pneumonia, A. hydrophila* and *B. subtilis* with an inhibition

TABLE-6											
	TG AND DTG DATA OF COMPLEXES 1 to 6										
Complex	Stage of	TG temperature	DTG peak	Mass loss (%)	Assignments	Final					
complex	decomposition	range (°C)	(°C)	Found (calcd.)	Assignments	residue (%)					
1	Ι	256-312	306	19.8 (19.6)	Loss of three molecules of nitrate ions	La_2O_3					
1	II 317-718 418 6		62.5 (63.1)	Loss of two molecules of ligand L ₂	17.7 (17.3)						
2	Ι	242-336	331	19.8 (19.7)	Loss of three molecules of nitrate ions	Pr_2O_3					
2	II	340-721	418	62.2 (62.6)	Loss of two molecule of ligand L ₂	18.2 (17.7)					
2	Ι	220-336	339	19.6 (19.5)	Loss of three molecules of nitrate ions	Sm_2O_3					
3	II	341-723	412	61.8 (62.3)	Loss of two molecules of ligands L ₂	18.6 (18.2)					
4	Ι	208-309	309	19.3 (19.5)	Loss of three molecules of nitrate ions	Eu_2O_3					
4	II	311-721	424	61.9 (62.2)	Loss of two molecules of ligand L ₂	18.8 (18.3)					
=	Ι	204-316	306	19.1 (19.3)	Loss of three molecules of nitrate ions	Tb ₂ O ₃					
3	II	318-720	415	61.6 (61.64)	Loss of two molecules of ligand L ₂	19.3 (19.06)					
6	Ι	236-347	336	19.3 (19.2)	Loss of three molecules of nitrate ions	Dy ₂ O ₃					
0	II	349-723	409	61.7 (61.5)	Loss of two molecules of ligand L ₂	19.5 (19.3)					

TABLE-7 ZONE OF INHIBITION (mm) FOR ANTIMICROBIAL ACTIVITY OF L_2 AND COMPLEXES AGAINST VARIOUS PATHOGENIC SPECIES

	Diameter of zone of inhibition (DIZ, mm)									
Compound				Gram-j	positive					
	E. coli	S. typhi	K. pneumonia	V. cholerae	A. hydrophila	S. aureus	B. subtilis			
L ₂	-	12	10	-	11	-	10			
$[La(L_2)_2(NO_3)_2]NO_3(1)$	18	21	13	16	15	14	12			
$[Pr(L_2)_2(NO_3)_2]NO_3(2)$	12	20	12	14	11	10	8			
$[Sm(L_2)_2(NO_3)_2]NO_3(3)$	10	12	10	10	8	9	-			
$[Eu(L_2)_2(NO_3)_2]NO_3(4)$	13	20	11	17	9	-	-			
$[Tb(L_2)_2(NO_3)_2]NO_3(5)$	10	20	13	-	12	-	-			
$[Dy(L_2)_2(NO_3)_2]NO_3(6)$	13	22	12	-	13	10	7			
DMF	0	0	0	0	0	0	0			
Streptomycin (Std.)	18	20	21	5	18	20	23			
() - no inhibition zonos 1	5 mm - 1000 00	tivo 5 10 mm -	minimum optivity	10.15 mm - mo	dometo estivitvu > 1	5 - high activity				

(-) = no inhibition zone; 1-5 mm = less active; 5-10 mm = minimum activity; 10-15 mm = moderate activity; > 15 = high activity



Fig. 3. Tentative structure of complex $[Ln(L_2)_2(NO_3)_2]NO_3$, where Ln = La, Pr, Sm, Eu, Tb and Dy

zone of 10-12 mm. Most of the metal complexes exhibited better antibacterial activity when compared to the parent ligand with only slight exception in few cases. Complexes 1 and 2 were active against all the bacterial species. Against S. typhimurium, the complexes La (1), Pr (2), Eu (4), Tb (5) and Dy (6) displayed higher inhibition zone in the range 20-22 mm. La complex (1) exhibited highest inhibition of growth against E. coli and A. hydrophila with zone of inhibition 18 mm and 15mm, respectively. Eu complex (4) displayed high activity against V. cholerae with an inhibition zone of 17mm and more potent than standard antibiotic (streptomycin). Against Grampositive species: B. subtilis and S. aureus, La(III) complex showed the maximum inhibition zone of 12 and 14 mm, respectively. From the above observation it is infered that some of the lanthanide complexes exhibited almost similar or even higher activity compared to standard drug (streptomycin) especially against the tested Gram-negative bacterial species: S. typhimurium, E. coli and V. cholere. The higher activity of the complexes compared to free ligand may be attributed to chelation which reduces polarity of the metal ion by partial sharing of the positive charge with donor atoms of the ligand. This increases the lipophilic character of the metal chelates which favours the penetration into the lipid membrane of the cell wall of microorganism, thereby raising the activity of the complex

and restricts further growth of the organism [46,47]. Higher activity observed against the Gram-negative bacteria can be explained by considering the effect on lipopolysaccharide (LPS), a major component of the surface of Gram-negative bacteria. Lipopolysaccharide is an important entity in determining the outer membrane barrier function and the virulence of Gram-negative pathogens. The Schiff base can penetrate the bacterial cell membrane by coordination of metal ion through oxygen or nitrogen donor atom to LPS, which leads to the damage of outer cell membrane [48,49]. A graph showing the activity of ligand and its lanthanide(III) complexes is depicted in Fig. 4.



Fig. 4. Graph showing the antimicrobial activity of Schiff base L_2 and its Ln(III) complexes

Conclusion

In the present work the bidentate Schiff base L_2 and its lanthanide(III) complexes of the type $[Ln(L_2)_2(NO_3)_2]NO_3$ and were characterized by a variety of physico-chemical methods. The lanthanides exhibit a coordination number eight in these complexes. The fluorescence data reveals that Sm(III), Tb(III), Eu(III) and Dy(III) exhibit greater enhancement in fluorescence band of the ligand and also characteristic metal centered luminescence peaks. The ligand and all the complexes were analyzed for their antibacterial activities. Antibacterial results show that most of the synthesized complexes possess a very high antibacterial activity against tested bacteria than the corresponding ligand. These findings indicate that Schiff base complexes lanthanides have much potential practical application for development of luminescence and new therapeutic reagent for diseases on the molecular level.

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