

Synthesis, Spectroscopic Characterization and Antimicrobial Activities of Some Rare Earth Metal Complexes of Biologically Active Asymmetrical Tetradentate Ligand

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Abstract- The solid complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) with asymmetrical tetradentate Schiff bases derived from 4-methyl-o-phenylenediamine, 3-Acetyl-6-methyl-pyran-2,4-dione and 2-hydroxy-1-naphthaldehyde have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV-visible, FTIR, ¹H-NMR spectra, X-ray diffraction, thermal analysis and screened for antimicrobial activity. The IR spectral data suggest that the ligand behaves as a dibasic tetradentate ligand with ONNO donor atoms sequence towards central metal ion. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal: ligand). The X-ray diffraction data suggest tetragonal crystal system for La(III) complex and orthorhombic crystal system for Ce(III) complex. Thermal behaviour (DSC/TGA) of the complexes was studied and kinetic parameters were determined by Horowitz-Metzger and Coats-Redfern method. The ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* and fungicidal activity were tested against *Aspergillus Niger* and *Trichoderma*.

Keywords- Dehydroacetic Acid; Unsymmetrical Tetradentate Schiff Base; Rare Earth Metal Complexes; Thermal Analysis; Antimicrobial Activity

I. INTRODUCTION

Tetradentate Schiff bases with N₂O₂ donor atoms are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry^[1-5]. A large number of Schiff bases and their metal complexes have been studied because of their interesting and important properties such as their ability to reversibly bind oxygen^[6] and their use in catalyses for oxygenation and oxidation reactions of organic compounds^[7], redox systems in biological processes^[8], Aldol reactions^[9], degradation of dyes through decomposition of hydrogen peroxide and other reagents, in textile industries^[10], reduction of thionyl chloride^[11] and oxidation of DNA^[12]. Also, Schiff bases can be used in degradation of organic compounds^[13] and in radiopharmaceuticals^[14]. Schiff bases of o-phenylenediamine

reported to have variety of applications including biological^[15], clinical^[16] and analytical^[17] fields. Many symmetrical tetradentate bis, Schiff bases of 1, 2-diamines with o-hydroxy aldehydes/ketones have been prepared and studied intensively. However much less attention has been focused on asymmetrical tetradentate Schiff bases derived from 1, 2-diamines and different aldehydes/ketones. In particular, those derived from aromatic 1, 2 diamines have been under-investigated^[18]. It is worthwhile to mention here that asymmetrical Schiff bases of this type are difficult to obtain and not easily isolated.

A search of literature reveals that no work has been done on the rare earth metal complexes of the asymmetrical Schiff bases derived from aromatic 1, 2- diamine, dehydroacetic acid and 2-hydroxy-1-naphthaldehyde. The synthesis of biactive metal complexes of transition metal complexes reported in previous report^[19]. In continuation of our research work on synthesis of biologically active transition metal complexes^[19]. In this communication we report the synthesis of asymmetrical tetradentate Schiff base formed by the condensation of o-phenylenediamine, dehydroacetic acid and 2-hydroxy-1-naphthaldehyde (Fig.1). The Schiff base ligand was allowed to react with La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) ions, in the molar ratio (1:1 ligand : metal ion). The structures of the ligand and its metal complexes were characterized by elemental and thermal analyses, IR, ¹H NMR, electronic, mass spectra, TGA/DSC, XRD and antimicrobial as well as magnetic susceptibility measurements at room temperature.

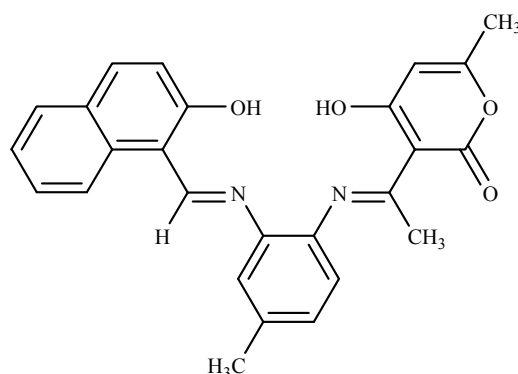


Figure 1 Proposed Structure of Ligand

II. EXPERIMENTAL

All the chemicals used were of analytical grade purchased from Aldrich, Merck and the solvents used were purified by standard methods^[20]. The complexes were analyzed for their metal content by standard methods^[21]. Carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CHNS analyzer. IR spectra were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets. ¹H-NMR spectra of ligand was taken in CDCl₃ using TMS as internal standard. The DSC/TGA and XRD were recorded on SDT Q600 V20.9 Build 20 and Philips 3701 respectively. The UV-vis spectra of the complexes were recorded on Jasco UV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were done on a Guoy balance at room temperature using Hg[Co(SCN)₄] as calibrant. Molar conductance measurements were carried out using 10⁻³ mol/L solution of complexes in nitrobenzene, methanol and DMF at room temperature using Elico CM-180 conductivity meter.

A. General Procedure for the Synthesis of Ligand

Step I

The ligand was prepared by modification of reported method^[22]. A mixture containing 50 mL solution of 0.001 mol (0.168 g) of DHA and 0.001 mol (0.12 g) of 4-methyl-o-phenylenediamine was refluxed in super dry ethanol for about 3 h. Then it was cooled to room temperature and the white coloured intermediate solid compound, mono-Schiff base was obtained with 80% yield.

Step II

0.001 mol of intermediate (0.258 g) was then refluxed with 0.001 mol of 2-hydroxy-1-naphthaldehyde (0.172 ml) in super dry ethanol for 6 h. The precipitate thus formed was filtered, dried in vacuum over CaCl₂ and recrystallised in ethanol (yield 70%).

B. General Procedure for the Synthesis of Metal Complexes

To a hot methanolic solution of the ligand, solution of methnolic metal nitrate was added with constant stirring. The pH of reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 9-10h. The precipitated solid metal complex was filtered off in hot condition and washed with hot methanol, petroleum ether and dried over calcium chloride in vacuum desiccator (yield 48%).

Synthesis of La(III) metal complex.

To a hot methanolic solution (25ml) of the ligand (0.01 mol), solution (25ml) of methnolic solution metal nitrate hydrated [(LaNO₃)₃ 6H₂O] (0.01 mol) was added with constant stirring. The pH of the reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 9-10h. The precipitated solid metal complex was filtered off in hot condition and washed with hot methanol, petroleum ether and dried over calcium chloride in vacuum desiccator (yield 50%).

C. Antimicrobial Activity

The antibacterial activity of free ligand, its metal complexes, the metal salts and control (DMF solvent were tested in vitro against gram +ve bacteria (Staphylococcus) and gram -ve bacteria (E.Coli) by paper disc method^[19]. Sterile (10mm) diameter Whatmann No. 42 paper discs were soaked in different concentrations of the ligand/ complexes (250ppm and 500ppm) in DMF, dried and then placed on the lawn culture of nutrient agar plates. The plates were then incubated for 24h at 37°C and the inhibition zone around each disc was measured. The results obtained were compared with known antibiotics, Ciprofloxin. Three replicates were taken and average value is given. The free ligand, its metal complexes, metal salts and control were screened for antifungal activity against the fungi *Aspergillus niger* and *Trichoderma* at 250ppm and 500ppm levels respectively by mycelia dry weight method^[22]. The culture of fungi were purified by single spore isolation technique. The

glucose nitrate (GN) medium was used for the growth of fungi. The mycelial biomass was then dried along with filter paper in an oven at $65 \pm 5^\circ\text{C}$ to constant weight, cooled and finally weighed. The mycelial dry weight (MDW) was obtained by subtracting the weight of mycelium free filter paper from final dry weight^[23]. Three replicates of each treatment were repeated in all experiments. The MDW was corrected each time by subtracting the dry weight obtained from incubated flask under similar experimental conditions. The yields of MDW in mg are presented in given table. The percentage error was found to be ± 0.01 . The percent decrease in mycelia dry weight to the test compound in each case was calculated and tabulated in terms of average percentage inhibition. The results indicate that the ligand and its metal complexes arrested the growth of fungi.

III. RESULTS AND DISCUSSION

A. Elemental Analysis

Analytical data of the complexes are given in Table I. The values obtained are found in good agreement with the theoretical values calculated for the suggested general formula of the complexes such as $[\text{LnL}(\text{H}_2\text{O})_2\text{NO}_3]$ (where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III)).

TABLE I PHYSICAL CHARACTERIZATION, ANALYTICAL AND MOLAR CONDUCTANCE DATA OF LIGAND AND ITS METAL COMPLEXES

Ligand/Complexes			Found (Calcd.) %			
	F. W.	M.p. °C.	C	H	N	M
(H ₂ L)	426.48	173	74.15 (73.23)	5.15 (5.20)	6.80 (6.57)	
[LaL(H ₂ O) ₂ NO ₃]	661.40	>300	47.21 (47.30)	3.65 (3.70)	6.35 (6.45)	21.00 (21.20)
[CeL(H ₂ O) ₂ NO ₃]	662.61	>300	47.12 (47.25)	3.65 (3.70)	6.34 (6.50)	21.14 (21.27)
[PrL(H ₂ O) ₂ NO ₃]	662.61	>300	47.12 (47.20)	3.65 (3.75)	6.34 (6.50)	21.14 (21.20)
[NdL(H ₂ O) ₂ NO ₃]	666.73	>300	46.83 (46.95)	3.62 (3.70)	6.30 (6.40)	21.63 (21.75)
[SmL(H ₂ O) ₂ NO ₃]	672.85	>300	46.41 (46.50)	3.59 (3.65)	6.24 (6.35)	22.34 (22.50)
[GdL(H ₂ O) ₂ NO ₃]	679.74	>300	45.94 (46.00)	3.55 (3.65)	6.18 (6.30)	23.13 (23.20)

H₂L = Schiff base ligand, 10^{-3} M solution in DMF

B. Molar Conductance

Molar conductance values of lanthanide(III) complexes were measured in dimethylformamide, methanol and nitrobenzene at room temperature and are presented in Table II. These conductance values are much lower than the values reported for 1:1 electrolytes in these solvents^[24]. Therefore, the conductance values suggest that all the complexes are nonelectrolytes and hence, they are neutral complexes.

TABLE II MOLAR CONDUCTANCE AND MAGNETIC MOMENT DATA OF THE LANTHANIDE(III) COMPLEXES

Complexes	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)			Magnetic Moment(BM)	
	DMSO	DMF	C ₆ H ₅ NO ₂	$\mu_{\text{eff}}(\text{obs.})$	$\mu_{\text{eff}}(\text{calc.})$
[LaL(H ₂ O) ₂ NO ₃]	14.50	26.40	8.50	Dia.	Dia
[CeL(H ₂ O) ₂ NO ₃]	15.30	28.70	9.00	2.45	2.55
[PrL(H ₂ O) ₂ NO ₃]	13.70	27.30	8.90	3.52	3.58
[NdL(H ₂ O) ₂ NO ₃]	15.30	29.00	7.20	3.62	3.62
[SmL(H ₂ O) ₂ NO ₃]	14.30	25.70	8.30	1.50	1.62
[GdL(H ₂ O) ₂ NO ₃]	12.50	29.20	9.50	7.90	7.94

C. ¹H-NMR Spectra of Ligand

The ¹H-NMR spectra of free ligand in CDCl₃ at room temperature show the following signals. 2.05-2.15 δ (s, 3H, C₆-CH₃), 2.40-2.55 δ (s, 3H, N=C-CH₃), 4.75 δ (s, 1H, phenolic OH), 5.80 δ (s, 1H, C₅-H), 6.6-7.8 δ (m, aromatic protons), 8.2 δ (s, 1H, N=C-H) and 9.5 δ (s, 1H, enolic OH of DHA moiety). In addition to these peaks, (H₂L₂) shows a peak at 2.30 δ (s, 3H, phenyl-CH₃).

D. Magnetic Behavior

The magnetic moments of the lanthanide metal complexes are given in Table II. The values obtained are very close to the theoretical values calculated for the free metal ions^[25]. The data show that the La(III) complex is diamagnetic and the remaining metal complexes are paramagnetic, as expected. As the magnetic moment values of the complexes are almost the same as those for the respective free lanthanide ions, it is presumed that the 4f electrons are not at all disturbed by the ligand field, and hence,

it is unlikely that the 4f orbitals of the metal ions are involved in coordination in the present complexes.

E. FTIR Spectra

The FTIR spectrum of free ligand shows characteristic bands at 3067, 1691, 1611, 1340 and 1221 cm^{-1} assignable to ν OH (intramolecular hydrogen bonded), ν C=O (lactone carbonyl), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively^[19,22,23]. The absence of a weak broad band in 3200-3400 cm^{-1} region, in the spectra of the metal complexes suggests deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by upward shift in ν C-O (phenolic) to the extent of 25-50 cm^{-1} ^[26]. On complexation, the ν (C=N) band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of the azomethine group is coordinated to the metal ion. This is supported by upward shift in ν (C-N) to the extent of 10-35 cm^{-1} ^[27]. The IR spectra of metal chelates showed new bands in 500-550 and 400-450 cm^{-1} regions which can be assigned to ν (M-O) and (M-N) vibrations respectively^[28]. The IR spectra show a strong band in 3200-3600 cm^{-1} region, suggesting the presence of coordinated water in these metal complexes^[29]. In the spectra of the nitrate complexes, there are two additional bands observed at ≈ 1480 and ≈ 1280 cm^{-1} , which were absent in the spectrum of the free ligand. These bands are assignable to the ν_5 and ν_1 modes of the nitrate ions, respectively. Since the magnitude of the separation between ν_5 and ν_1 is >200 cm^{-1} , it is concluded that the nitrate is coordinated in a bidentate fashion^[30]. The presence of coordinated water is further confirmed by the appearance of non-ligand band in the 810-830 cm^{-1} region, assignable to the rocking mode of water^[31]. The presence of coordinated water is also established and supported by DSC/TG analysis of these complexes. Hence it may be concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

F. Electronic Spectra

The electronic spectra of the ligands and their complexes were recorded in distilled DMF. The electronic spectra of aqueous solutions of the nitrates of Pr, Nd and Sm are compared with the corresponding complexes. The data are summarized in Table II. The data indicate that the energy of f-f transitions in the complexes is slightly reduced compared to the corresponding aquo ions either because of the slight covalent interaction of the 4f orbitals with vacant ligand orbitals, leading to some delocalization with consequent reduction in interelectronic repulsion^[32], or by increased nuclear shielding of the orbitals due to a slight covalent ligand-metal electron drift. The bonding parameter ($b^{1/2}$), the covalency parameter (δ) and nephelauxetic ratio (β) have been calculated using literature procedures^[33-35]. The value of $(1-\beta)$ being less than unity for the complexes, the small and positive values of the bonding parameter $b^{1/2}$ and Sinha's parameter $\delta\%$ suggests the possibility of a partial covalent nature of the metal-ligand bond^[36,37]. Based on the electronic spectral studies, a coordination number of seven around the metal ion may be suggested, as reported for $\text{Nd}(\text{CF}_3\text{COCHCOMe})\cdot\text{H}_2\text{O}$ by Karraker^[38] and for $[\text{Ln}(\text{Hapfh})_2\text{Cl}]\text{Cl}_2$ (Hapfh=acetylpyridine -2-furoylhydrazone) by Singh and Singh^[39].

TABLE III ELECTRONIC SPECTRAL DATA (CM-1) AND RELATED BONDING PARAMETERS OF LANTHANIDE (III) COMPLEXES.

Complexes	Electronic Spectral Bands of $\text{Ln}(\text{NO}_3)_3$	Electronic Spectral Bands of $\text{Ln}((\text{H}_2\text{O})_2\text{NO}_3)$	J-levels	Calculated parameters
$[\text{PrL}(\text{H}_2\text{O})_2\text{NO}_3]$	22371 21413 20800 16900	22123 21276 20576 16638	$^3\text{H}_4 \rightarrow ^3\text{P}_2$ $\rightarrow ^3\text{P}_1$ $\rightarrow ^3\text{P}_1$ $\rightarrow ^1\text{D}_2$	$\beta_{av}=0.9890$ $b^{1/2}=0.0516$ $\delta\%=1.1070$ $\eta=0.0055$
$[\text{NdL}(\text{H}_2\text{O})_2\text{NO}_3]$	19400 17400 13420	19157 17182 13262	$^4\text{I}_{9/2} \rightarrow ^2\text{G}_{9/2}$ $\rightarrow ^4\text{G}_{5/2}, ^2\text{G}_{7/2}$ $\rightarrow ^2\text{S}_{3/2}, ^4\text{F}_{7/1}$	$\beta_{av}=0.9877$ $b^{1/2}=0.0553$ $\delta\%=1.2428$ $\eta=0.0062$
$[\text{SmL}(\text{H}_2\text{O})_2\text{NO}_3]$	27933 24900 24000 21600	27700 24809 23752 21551	$^4\text{H}_{5/2} \rightarrow ^6\text{P}_{3/2}$ $\rightarrow ^4\text{P}_{9/2}$ $\rightarrow ^6\text{P}_{5/2}$ $\rightarrow ^4\text{P}_{13/2}$	$\beta_{av}=0.9938$ $b^{1/2}=0.0752$ $\delta\%=0.6198$ $\eta=0.0030$

G. Powder X-ray Diffraction Analysis

The X-ray diffractogram of La(III), and Ce(III) complexes were scanned in the range 5-80° at wavelength 1.543 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of La(III) complex had six reflections with maxima at $2\theta = 25.83^\circ$ corresponding to d value 3.44 Å. The diffractogram of Ce(III) complex shows eleven reflections with maxima at $2\theta = 12.37^\circ$ corresponding to d value 7.14 Å. The X-ray diffraction patterns of these complexes with respect to major peaks of relative intensity greater than 10% has been indexed by using computer programme^[40]. The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volumes. The unit cell of La(III) complex yielded values of lattice constants, $a=8.04$ Å, $b=8.04$ Å, $c=12.07$ Å and unit cell volume $V=780.52$ (Å)³. In concurrence with these cell parameters, the conditions such as $a=b \neq c$ and $\alpha=\gamma=\beta=90^\circ$ required for sample to be tetragonal were tested and found to be satisfactory. Hence it can be concluded that La(III) complex has tetragonal crystal system. The unit cell of Ce(III) complex yielded values of lattice constant, $a=18.66$ Å, $b=7.77$ Å, $c=3.01$ Å and unit cell volume $V=488.01$ (Å)³. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha=\gamma=$

$\beta = 90^\circ$ required for sample to be orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Ce(III) complex has orthorhombic crystal system. The experimental density values of the complexes were determined by using specific gravity method^[41] and found to be 2.04 and 3.64 g cm^{-3} for La(III) and Ce(III), complexes respectively. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell, the number of molecules per unit cell was calculated by using equation $\rho = nM/NV$ and was found to be two for La(III) and four for Ce(III) complexes respectively. With these values, theoretical densities were computed and found to be 2.05 and 3.65 g cm^{-3} for respective complexes. Comparison of experimental and theoretical density values shows good agreement within the limits of experimental error^[42].

TABLE V XRD PATTERN OF CE(III) COMPLEX

Peak No.	2 θ (observed)	2 θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
1	12.378	12.323	7.1448	7.1766	1	1	0	100
2	19	19.002	4.6672	4.6666	4	0	0	8.94
3	26.955	27.025	3.3051	3.2966	3	2	0	15.14
4	35.667	35.563	2.5157	2.5223	7	1	0	1.68
5	42.458	42.427	2.1273	2.1288	5	3	0	2.65
6	45.487	45.519	1.9928	1.9911	6	3	0	3.29
7	55.218	55.223	1.6621	1.6620	6	3	1	3.99
8	76.208	76.194	1.2482	1.2484	4	6	0	1.99
9	82.407	82.403	1.1693	1.1694	3	6	1	2.68
10	89.576	89.586	1.0934	1.0933	3	7	0	1.58
11	93.604	93.602	1.0566	1.0566	1	2	0	1.91

H. Thermal Analysis

The simultaneous DSC/TG analysis of metal complexes was studied from ambient temperature to 1000°C in nitrogen atmosphere using $\alpha\text{-Al}_2\text{O}_3$ as reference. The TG/DSC curve of Gd(III) complex of ligand, shows three step decomposition. The initial weight loss in TG curve, 5.50% (calcd. 5.30%) corresponds to loss of two coordinated water molecules. The anhydrous complex first show slow decomposition from 250-410°C, with 9.35 % (calcd. 9.12 %) mass loss, a broad exotherm ($\Delta T_{\text{max}} = 407.14^\circ\text{C}$) in DSC may be attributed to removal of coordinated nitrate part of the complex. The second decomposition from 410-650°C, with 22.70 % (calcd. 22.25 %) mass loss and a broad exotherm ($\Delta T_{\text{max}} = 437.83^\circ\text{C}$) in DSC may be attributed to removal of non coordinated part of ligand. The third decomposition from 650-850°C, with 12.80 % (calcd. 12.35 %) mass loss may be attributed to removal of coordinated part of ligand. The mass of final residue corresponds to stable Gd_2O_3 51.47 % (calcd. 50.97 %)

I. Kinetic Calculations

The kinetic and thermodynamic parameters viz n (order of reaction), E_a (energy of activation), z (pre-exponential factor), ΔS (entropy of activation) and ΔG (free energy change) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method^[43] and Coats-Redfern integral method^[44]. The data are given in Table IV. The results show that the values obtained by two methods are comparable. The calculated values of energy of activation of the complexes are relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the complex^[45,46]. The negative values of entropy of activation indicate that the activated complexes are more ordered than the reactants and that the reactions are slow. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transition.

TABLE IV XRD PATTERN OF LA(III) COMPLEX

Peak No.	2 θ (observed)	2 θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
1	22.05	22.07	4.0272	4.0235	0	0	3	7.12
2	25.83	25.83	3.4456	3.4464	2	1	1	100
3	43.17	43.21	2.0938	2.0919	3	2	2	7.38
4	47.67	47.64	1.9061	1.907	4	0	2	14.68
5	58.44	58.44	1.5779	1.5777	3	1	6	6.68
6	99.95	99.95	1.0058	1.0058	0	0	1	7.04
1	22.05	22.07	4.0272	4.0235	0	0	3	7.12

TABLE VI THE KINETIC PARAMETERS OF METAL COMPLEXES CALCULATED BY HOROWITZ-METZGER (HM) AND COATS-REDFERN (CM) METHODS

Complex	Step	n	Method	E _a (kJmol ⁻¹)	Z S ⁻¹ ×10 ⁻⁴	ΔS [#] JK ⁻¹ mol ⁻¹	ΔG [#] (kJmol ⁻¹)	Corelation coefficient (r)
Gd	I	1.1	HM	11.27	15.78	-148.42	19.19	0.9990
			CR	11.11	45.97	-139.83	18.72	0.9980
	II	1.2	HM	10.71	5.20	-162.31	25.31	0.9980
			CR	14.23	9.36	-157.42	24.87	0.9640
	III	0.2	HM	52.69	20.22	-154.76	74.52	0.9980
			CR	13.33	31×10 ⁻⁶	-112.68	68.59	0.9920

J. Antimicrobial Activity

The antimicrobial activity of ligand and metal complexes were tested in vitro against bacteria such as *Staphylococcus aureus* and *Escherichia coli* by paper disc plate method^[19]. The compounds were tested at the concentration 250ppm and 500ppm in DMF and compared with known antibiotics viz ciprofloxin (TableVII). For fungicidal activity, compounds were screened in vitro against *Aspergillus Niger* and *Trichoderma* by mycelia dry weight method^[22] with glucose nitrate media. The compounds were tested at the concentrations 5000 and 1000 ppm in DMF and compared with control. From Table VII, it is clear that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes^[20,47,48]. Such enhanced activity of metal chelates is due to lipophilic nature of the metal ions in complexes^[49]. Such enancement in the activity of metal complexes is due to the chelation which makes a ligand more potent bacterial agent. This increased activity upon chelation is attributed to considerable reduction of the postive charge on metal ion due to its partial sharing with the donor group present in the ligand. The π -electron delocalization over the chelate ring increases the lipophalic character of the central metal atom and favours its permeation through the lipid layers of cell membrane. The tables show that the antimicrobial activity of ligand increases with the introduction of metal ion in its structure by chelation. The data showthat the activity increases slowly from La(III) to Gd(III) complexes. The relation between chelation and toxicity is very complex. Chelation is not only the criterion for antibacterial activity, It is expected to be a function of steric, electronic and pharmacokinetic factors along with mechanistic pathway^[48]. Other factors such as solubility, conductivity, dipole moment, size of metal ion, stability constants of the complexes and their magnetic moments are also reported to affect the microbial activity of the complexes^[23,48].

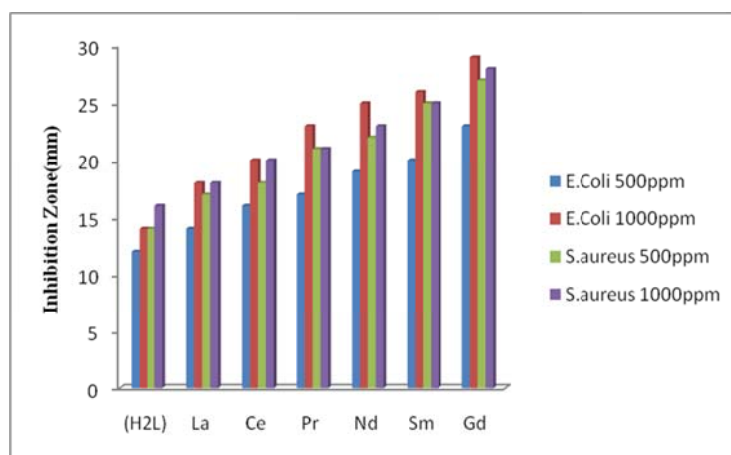
TABLE VII ANTIBACTERIAL ACTIVITY OF LIGAND AND ITS METAL COMPLEXES

Ligand/Complexes	Inhibition Zone (mm)			
	E.Coli		Staphylococcus	
	500ppm	1000ppm	500ppm	1000ppm
Ciprofloxin	29	32	31	35
(H ₂ L)	12	14	14	16
[LaL(H ₂ O) ₂ NO ₃]	14	18	17	18
[CeL(H ₂ O) ₂ NO ₃]	16	20	18	20
[PrL(H ₂ O) ₂ NO ₃]	17	23	21	21
[NdL(H ₂ O) ₂ NO ₃]	19	25	22	23
[SmL(H ₂ O) ₂ NO ₃]	20	26	25	25
[GdL(H ₂ O) ₂ NO ₃]	23	29	27	28

In present complexes, the increasing trend of activity from La to Gd may be attributed to the following factors. First, the increasing size of the metal ions. It has been reported that the antimicrobial activities of heavy rare earth complexes are better than the light rare earth complexes^[50]. Second, the magnetic moments of the metal complexes which show increasing order of μ_{eff} values from La to Gd, except Sm. Lastly, the increase in activity may also be due to the effect of higher stability constants of the complexes. It is general observation that the stability constants of the lanthanide metal complexes with Schiff base increase from La to Gd^[51, 52, 53]. The metal complexes should be highly thermodynamically stable, to reach the site without being dissociated and then react as metal complexes with cells to produce a selective effect^[54]. The increase in activity with concentration is due to the effect of metal ions on the normal process. The action of compounds may involve the formation of hydrogen bond with the active centers of the cell constituents resulting in interference with the normal cell process^[55]. However, the metal complexes do not show any significant antigungal activity against both the fungi *A. Niger* and *Trichoderma*.

TABLE VIII. ANTIFUNGAL ACTIVITY OF COMPOUNDS YIELD OF MYCELIAL DRY WEIGHT IN MG (% INHIBITION)

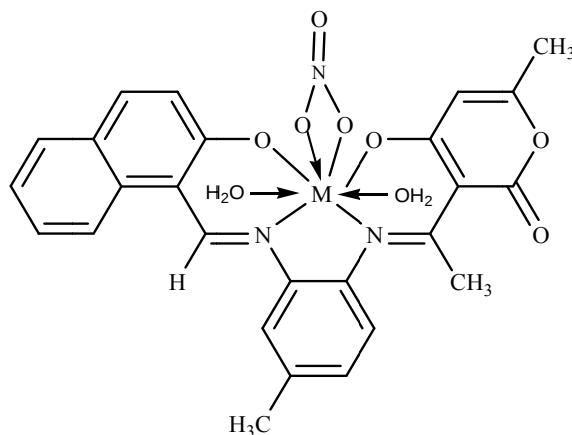
Ligand/Complexes	Inhibition Zone (mm)			
	Aspergillus Niger		Trichoderma	
	500ppm	1000ppm	500ppm	1000ppm
Control	79	79	79	79
(H ₂ L)	52(34)	20(75)	52(34)	20(75)
[LaL(H ₂ O) ₂ NO ₃]	48(40)	17(79)	48(40)	17(79)
[CeL(H ₂ O) ₂ NO ₃]	46(42)	16(80)	46(42)	16(80)
[PrL(H ₂ O) ₂ NO ₃]	43(46)	14(83)	43(46)	14(83)
[NdL(H ₂ O) ₂ NO ₃]	37(54)	12(85)	37(54)	12(85)
[SmL(H ₂ O) ₂ NO ₃]	34(57)	11(87)	34(57)	11(87)
[GdL(H ₂ O) ₂ NO ₃]	32(60)	09(89)	32(60)	09(89)



Graph I Comparative antibacterial activity of Ligand and Metal complexes against E. Coli and S.aureus

IV. CONCLUSION

La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) complexes with N₂O₂ donor Schiff base ligand derived from 4 methyl o-phenylenediamine, 3-Acetyl-6-methyl-pyran-2,4-dione (dehydroacetic acid) and 2-hydroxy-1-naphthaldehyde were synthesized. A comparative study of their physico-chemical properties have been made through elemental analysis, molar conductance, mass, IR, electronic spectra, magnetic moment, TG/DTA, powder XRD and antimicrobial study. The conductance data indicate that all the complexes are 1:1 non electrolytes. The IR data reveal that the Schiff base ligand coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig. 2. Thus lanthanide ions are surrounded by 6-oxygen and 2-nitrogen atoms, thus producing a coordination number of 8 for the lanthanide ions. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. The trend increasing activity of metal complexes from La to Gd is attributed to the increasing size of the metal ions, increasing trend in magnetic moments and increasing order of stability constants of the complexes. DSC/TG reveals thermal stability of complexes. The XRD study suggests tetragonal crystal system for La(III) and orthomboic crystal system for Ce(III) complexes.

Figure 2 Proposed structure of metal complexes
M= La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III)

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