

## 사배위 N<sub>2</sub>O<sub>2</sub> Schiff 염기 리간드와 그 희토류 금속착물의 합성 및 특성

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## Synthesis and Characterization of Tetradentate N<sub>2</sub>O<sub>2</sub> Schiff Base Ligand and its Rare Earth Metal Complexes

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**요 약.** o-phenylenediamine, 3-acetyl-6-methyl-(2H)pyran,2,4(3H)-dione (dehydroacetic acid 또는 DHA) 및 2, 4-dihydroxy benzaldehyde에서 비롯된 4-hydroxy-3-(1-{2-(2,4-dihydroxy-benzylidene)-amino phenylimino}-ethyl)-6-methyl-pyran-2-one (H<sub>2</sub>L)의 La(III), Ce(III), Pr(III), Nd(III), Sm(III) 및 Gd(III) 고체착물을 합성하여 원소분석, 전도도법, 자기수차율, UV-vis, FT-IR, <sup>1</sup>H-NMR, X-선 회절, 열분석으로 특성을 규명하였으며, 항미생물 활성도를 조사하였다. FT-IR 스펙트럼 결과에 의하면 이 리간드는 중성금속에 대해 ONNO 주개원자를 통해 이염기성 사배위 리간드로 행동함을 알 수 있다. 원소분석 결과로부터 이들 착물의 화학량론비는 1:1 (금속: 리간드)임을 알 수 있다. 물리 및 화학적 실험결과로부터 La(III), Ce(III), Pr(III), Nd(III), Sm(III) 및 Gd(III) 착물은 일그러진 팔면체의 기하구조를 가짐을 알 수 있다. X-선 회절 데이터로부터 La(III) 및 Ce(III) 착물은 단사정계, 그리고 Pr(III) 및 Nd(III) 착물은 사방정계를 가짐을 알 수 있다. 이들 착물의 열적 행동(TG/DTA)을 연구하였으며, 속도론적 파라메타를 Horowitz-Metzger 및 Coats-Redfern 방법으로 결정하였다. 리간드와 그 착물의 항박테리아 활성도를 Staphylococcus aureus, Escherichia coli 및 Bacillus Sp.에 대해, 그리고 살균활성도를 Aspergillus Niger, Trichoderma 및 Fusarium oxysporum에 대해 각각 조사하였다.

**주제어:** 디하이드로 아세트산, 비대칭 사배위 Schiff 염기, 희토류 금속착물, 분말 X-선 회절, 생물학적 활성도

**ABSTRACT.** The solid complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) with 4-hydroxy-3-(1-{2-(2,4-dihydroxy-benzylidene)-amino phenylimino}-ethyl)-6-methyl-pyran-2-one (H<sub>2</sub>L) derived from o-phenylenediamine, 3-acetyl-6-methyl-(2H)pyran,2,4(3H)-dione (dehydroacetic acid or DHA) and 2, 4-dihydroxy benzaldehyde have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV-visible, FT-IR, <sup>1</sup>H-NMR, X-ray diffraction, thermal analysis study, and screened for antimicrobial activity. The FT-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 physico-chemical data suggests distorted octahedral geometry for La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) complexes. The X-ray diffraction data suggests monoclinic crystal system for La(III) and Ce(III) and orthorhombic crystal system for Pr(III) and Nd(III) complexes. Thermal behavior (TG/DTA) of the complexes was studied and kinetic parameters were determined by Horowitz-Metzger and Coats-Redfern methods. The ligand and its metal complexes were screened for antibacterial activity against Staphylococcus aureus, Escherichia coli, Bacillus Sp. and fungicidal activity against Aspergillus Niger, Trichoderma and Fusarium oxysporum.

**Keywords:** Dehydroacetic acid, Unsymmetrical tetradentate Schiff base, Rare Earth metal complexes, Powder X-ray diffraction. Biological activity

## INTRODUCTION

Tetradentate Schiff bases with N<sub>2</sub>O<sub>2</sub> donor atoms are well known to coordinate with various metal ions and

have attracted a great deal of interest in recent years due to their rich coordination chemistry.<sup>1-5</sup> Schiff bases of o-phenylenediamine reported to have variety of applications including biological,<sup>6</sup> clinical<sup>7</sup> and analytical<sup>8</sup> fields. Many

symmetrical tetradentate bis-type Schiff bases of 1, 2-diamines with *o*-hydroxy ketones/aldehydes have been prepared and studied intensively. However, much less attention has been focused on unsymmetrical tetradentate Schiff bases derived from 1, 2-diamines and different aldehydes. In particular, those derived from aromatic 1, 2-diamines have been under-investigated.<sup>9</sup> It is worthwhile to mention here that the unsymmetrical Schiff bases of this type are difficult to obtain and are not easily isolated.<sup>10</sup>

Coordination chemistry of lanthanides has become of increasing significance in last few years due to the wide variety of applications of lanthanide complexes in super-molecular photochemistry and in medicine.<sup>11,12</sup> Coordination compounds of the lanthanides are frequently used as catalysts, which is demonstrated by the work of Shiba-ski *et al.*, Kobayashi and Voropai and others.<sup>13-15</sup> One of the oxygen heterocyclic compounds, 3-acetyl-6-methyl-2*H*-pyran 2,4(3*H*)-dione (DHA) was reported to be an excellent chelating agent and possesses promising fungicidal, bactericidal, herbicidal and insecticidal activities.<sup>16-19</sup> It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems.<sup>20</sup> The structural and interesting biological properties of DHA appeals to inorganic chemists working in the field of coordination chemistry. Schiff bases and their metal complexes exhibit a wide range of biological activities and various structural features. In view of the enormous importance of DHA and its metal complexes it is thought worthwhile to synthesise the Schiff base of DHA and its metal complexes.

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, 4-dihydroxy benzaldehyde. In con-

tinuation of our earlier work on synthesis of bioactive transition metal complexes,<sup>21</sup> in this communication we report the synthesis of asymmetrical tetradentate Schiff base formed by the condensation of *o*-phenylenediamine, dehydroacetic acid and 2, 4-dihydroxy benzaldehyde (Scheme 1). The solid complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) with this ligand have been prepared and characterized by different physico-chemical techniques.

## EXPERIMENTAL

Dehydroacetic acid purchased from Merck was used as supplied. *o*-phenylene diamine and 2, 4-dihydroxy benzaldehyde of AR grade were used for synthesis of ligand. AR grade metal nitrates were used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CHNS analyzer. FTIR spectra were recorded on Jasco FTIR-4100 spectrometer using KBr pellets. <sup>1</sup>H-NMR spectra of ligand was obtained in CDCl<sub>3</sub> using TMS as an internal standard. The TG/DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701 respectively. The UV-visible spectra of the complexes were recorded on JascoUV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were determined on a Guoy balance at room temperature using Hg[Co(SCN)<sub>4</sub>] as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10<sup>-3</sup> M solution in DMF.

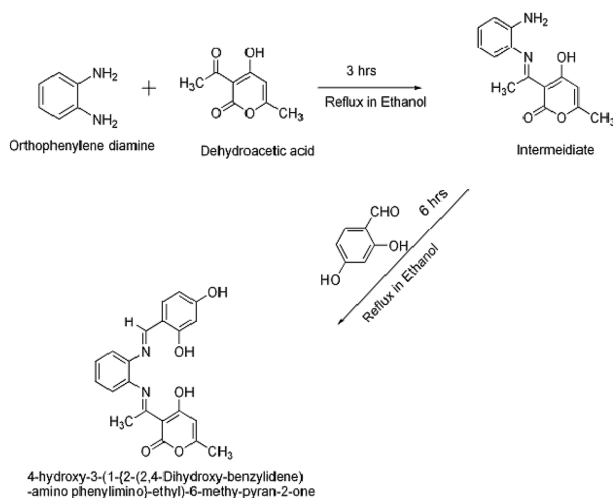
### General procedure for the synthesis of ligand

**Step I:** The ligand was prepared by modification of reported method.<sup>21</sup> In a 50 mL solution of 0.001 mol (0.168 g) of DHA, 0.001 mol (0.108 g) of *o*-phenylenediamine was refluxed in super dry ethanol for about 3 h. Then it was cooled to room temperature. On cooling, 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, 4-dihydroxy benzaldehyde (0.138 g) in super dry ethanol for 6 h. The precipitate thus formed was filtered, dried in vacuum over CaCl<sub>2</sub> and recrystallised in ethanol (yield: 73%).

### General procedure for the synthesis of metal complexes

To a hot solution of ligand (0.01 mol) in chloroform, methanolic solution (25 mL) of metal nitrate (0.01 mol) was added under constant stirring. The pH of the reaction



**Scheme 1.** Synthesis of Ligand.

mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 10-11 hrs. 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%).

### Antimicrobial Activity

The antibacterial activity of free ligand, its metal complexes, the metal salts and control (DMF solvent) was tested *in vitro* against gram + ve bacteria (*Staphylococcus*) and gram -ve bacteria (*E. coli*) by paper disc method.<sup>22</sup> Sterile (10 mm) diameter Whatmann No. 42 paper discs were soaked in different concentrations of the ligand/complexes (250 ppm and 500 ppm) in DMF, dried and then placed on the lawn culture of nutrient agar plates. The plates were then incubated for 24 h 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 values are given in (Table 4 and 5).

The free ligand, its metal complexes, metal salts and control were screened for antifungal activity against the fungi *Aspergillus niger* and *Trichoderma* at 250 ppm and 500 ppm levels respectively by mycelia dry weight method.<sup>23</sup> The culture of fungi was 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 655 °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.<sup>23</sup> 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 (Table 5). The percentage error was found to be 0.01. The percent decrease in mycelia dry weight of

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.

## RESULTS AND DISCUSSION

Physical characteristics, micro analytical, molar conductance data of ligand and metal complexes are given in Table 1. The analytical data of complexes reveals 1:1 molar ratio (metal: ligand) and corresponds well with the general formula  $[ML(H_2O)_2 NO_3]$  [where M=La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III)]. The magnetic susceptibilities of La (III), Ce (III), Pr (III), Nd (III), Sm (III) and Gd (III) complexes at room temperature are consistent with distorted octahedral structure with two water molecules and one nitrate molecule coordinated to metal ion. The presence of two coordinated water molecules was also confirmed by TG-DTA. The metal chelate solutions in DMF show low conductance which suggest their non-electrolytic nature.

### <sup>1</sup>H-NMR spectra of ligand

The <sup>1</sup>H-NMR spectra of free ligand in CDCl<sub>3</sub> at room temperature shows the following signals. δ 2.10 (s, 3H, -CH<sub>3</sub>), 2.55 (s, 3H, N=C-CH<sub>3</sub>), 5.20 (s, 1H, phenolic OH), 5.80 (s, 1H, Ar-H), 6.10-7.20 (m, 8H, Ar-H), 9.20 (s, 1H, N=C-H), 9.50 (s, 1H, enolic OH of DHA moiety).

### Mass Spectra of the ligand

Mass spectral data confirmed the structure of the ligand HL as indicated by the peaks corresponding to their molecular masses.

### Magnetic measurements

The effective magnetic moments (Table 1) of all the complexes indicate their paramagnetic nature except La(III), which is diamagnetic. The values obtained are

**Table 1.** Physical characterization, analytical and molar conductance data of ligand and its metal complexes

Ligand/complexes	F.W.	M.P. Decom. Temp °C	Magnetic moment $\mu_{\text{eff}}$ (B.M.)	Molar conductance. Mho cm <sup>2</sup> mol <sup>-1</sup>	% Found (Calculated)			
					C	N	H	M
(H <sub>2</sub> L)	378.39				66.40(66.50)	4.05(4.7)	7.20(7.40)	
[LaL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	613.31	>300	Dia.	33.04	41.00(41.12)	3.10(3.28)	6.70(6.85)	26.01(26.08)
[CeL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	614.52	>300	2.58	29.00	41.10(41.04)	3.10(3.28)	6.70(6.83)	26.00(26.03)
[PrL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	614.52	>300	3.50	30.06	41.01(41.04)	3.15(3.28)	6.70(6.83)	25.90(26.03)
[NdL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	618.64	>300	3.70	21.04	40.60(40.77)	3.10(3.25)	6.60(6.79)	25.70(25.86)
[SmL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	624.76	>300	1.55	28.05	40.10(40.37)	3.20(3.22)	6.70(6.72)	25.50(25.60)
[GdL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	631.65	>300	7.80	26.05	39.80(39.93)	3.10(3.19)	6.50(6.65)	25.10(25.32)

similar to the Van Vleck and Frank<sup>24</sup> and Hund's values except in case of Sm(III) where slightly higher value was obtained. This is due to low J-J separation, which leads to thermal population of higher energy levels. The values obtained are similar to those of typical lanthanide ions<sup>25</sup> and indicate the non involvement of 4f electrons in bonding due to their very effective shielding by the 5s<sup>2</sup> 5p<sup>6</sup> octet. Gd(III) ion has 4f<sup>7</sup> electronic configuration with <sup>8</sup>S<sub>7/2</sub> single-ion ground state.

### FTIR spectra

The FTIR spectrum of free ligand shows characteristic bands at 3060-3312, 1705, 1663, 1360 and 1224 cm<sup>-1</sup> assignable to intramolecular hydrogen bonded ( $\nu$  OH), lactone carbonyl ( $\nu$  C=O), azomethine ( $\nu$  C=N), aryl azomethine ( $\nu$  C-N) and phenolic ( $\nu$  C-O) stretching modes respectively.<sup>21,26</sup> The absence of a weak broad band in the 3060-3312 cm<sup>-1</sup> region, noted in the spectra of the metal complexes, indicates 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 phenolic ( $\nu$  C-O)<sup>27</sup> to the extent of 30-50 cm<sup>-1</sup>. On complexation, the ( $\nu$  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 ( $\nu$  C-N) to the extent of 10-50 cm<sup>-1</sup>.<sup>28</sup> The FTIR spectra of metal chelates showed new bands in 425-550 cm<sup>-1</sup> range assignable to (M-N)<sup>29-32</sup> and 400-450 cm<sup>-1</sup> range assignable to (M-O) modes.<sup>33</sup> The FTIR spectra showed a strong band in 3150-3600 cm<sup>-1</sup> region, suggesting the presence of coordinated water in these metal complexes. Infrared spectra of the nitrate complexes revealed two additional strong bands around 1491 and 1279 cm<sup>-1</sup>, which were absent in the free ligand.<sup>34</sup> The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830-840 cm<sup>-1</sup> region, assignable to the rocking mode of water.<sup>34</sup> The presence of coordinated water is also established and supported by TG/DT analysis of these complexes. Hence it is clear that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

### Electronic Spectra

The electronic spectra of the aqueous solutions of the nitrates of Pr, Nd and Sm are compared with the corresponding complexes. The data are summarized in Table 4. The data indicates that the energy of f-f transitions in the complexes is slightly reduced compared to the corre-

sponding 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<sup>33</sup> or by increased nuclear shielding of the orbitals due to a slight covalent ligand-metal electron drift. The bonding parameters ( $b^{1/2}$ ), the covalency parameter ( $\delta$ ) and nephelauxetic ratio ( $\beta$ ) have been calculated using literature procedures.<sup>35-37</sup> 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.<sup>38,39</sup> Based on electronic spectral studies, a coordination number of seven around the metal ion has been suggested, as reported for Nd(CF<sub>3</sub>COCHCOMe).H<sub>2</sub>O by Karraker<sup>40</sup> and for [Ln(Hapfh)<sub>2</sub>Cl]Cl<sub>2</sub> (Hapfh=acetylpyridine-2-furoylhydrazone) by Singh and Singh.<sup>41</sup>

### Thermal analysis

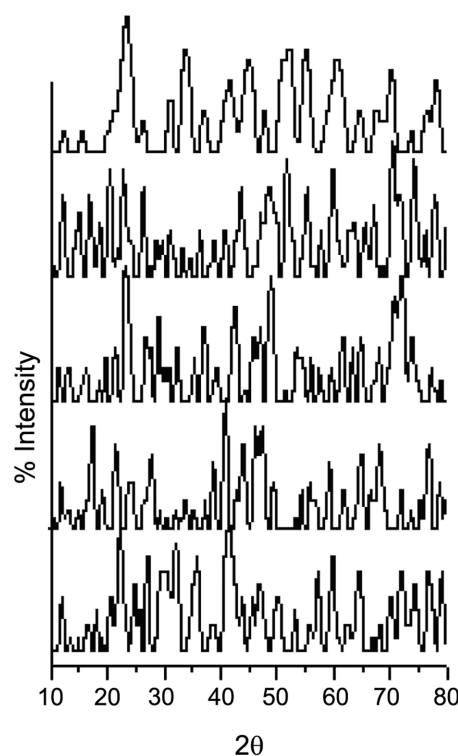
The simultaneous TG/DT analysis of metal complexes was studied from ambient temperature to 1000 °C in nitrogen atmosphere using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference. The La(III), and Sm(III) complexes were chosen for thermal study. On the TG curve of La(III) complex, the first step shows a steep slope between 140-230 °C with a mass loss of 5.7% (calculated 5.86%), indicating the removal of two molecules of coordinated water. An endothermic peak in the range 140-200 °C ( $\Delta T_{max}=170$  °C) on the DTA curve corresponds to the dehydration step. The anhydrous complex first show slow decomposition from 200-300 °C, with 10.00% mass loss, (calcd. 10.10%) and a broad exotherm ( $\Delta T_{max} = 275$  °C) in DTA may be attributed to removal of coordinated nitrate part of the complex.<sup>42</sup> The second step decomposition is from 400 to 600 °C with 22.70% mass loss (calcd 23.00%) which corresponds to decomposition of coordinated part of ligand. A broad endotherm in DTA is observed for this step. The mass of the final residue corresponds to stable oxide, 52.00% (calcd. 52.82%). The TG curve of Sm(III) complex shows first mass loss 5.78% (calcd. 5.76%) in the range 100-225 °C and an endothermic peak in this region  $\Delta T_{max}=195$  °C, which indicates removal of two coordinate water molecules. The anhydrous complex show slow decomposition from 225-320 °C with 10.20% (calcd. 9.92%) mass loss. A broad exotherm  $\Delta T_{max} = 299$  °C in DTA may be attributed to the removal of coordinated nitrate part of the complex. The second step decomposition from 400 to 650 °C with 24.20% mass loss (calcd 23.50%) corresponds to decomposition of coordinated part of ligand. A broad endotherm

in DTA is observed for this step. The mass of final residue corresponds to stable  $\text{Sm}_2\text{O}_3$ , 54.20% (calcd. 55.81%).

### Powder X-ray diffraction

The X-ray diffraction of metal complexes was scanned in the range  $5\text{--}80^\circ$  at wave length  $1.543\text{\AA}$ . The diffractogram and associated data depict the  $2\theta$  value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of La(III) complex had fourteen reflections with maxima at  $2\theta = 41.57$  corresponding to d value  $2.17\text{\AA}$ . The diffractogram of Ce(III) complex shows twelve reflections with maxima at  $2\theta = 40.92^\circ$  corresponding to d value  $2.20$ . The diffractogram of Pr(III) complex had twelve reflections with maxima at  $2\theta = 23.09$  corresponding to d value  $3.08$ . The diffractogram of Nd(III) complex had nine reflections with maxima at  $2\theta = 70.43$  corresponding to d value  $1.33$ . The x-ray diffraction pattern of these complexes with respect to major peaks having relative intensity greater than 10% have been indexed by using computer programme (Powder X-ray data analysis system, Cheng Dong, Institute of Physics, Chinese Academy of Science) 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,  $a = 12.18\text{\AA}$ ,  $b = 4.40\text{\AA}$ ,  $c = 5.58\text{\AA}$  and unit cell volume  $V = 299.4321\text{\AA}^3$ . In concurrence with these cell parameters, the condition such as  $a \neq b \neq c$  and  $\alpha = \gamma = 90^\circ \neq \beta$ . required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded that La(III) complex has monoclinic crystal system. The unit cell of Ce(III) complex yielded values of lattice constants,  $a = 16.49\text{\AA}$ ,  $b = 5.34\text{\AA}$ ,  $c = 5.06\text{\AA}$  and unit cell volume  $V = 746.1900\text{\AA}^3$ . Pr(III) complex yielded values of lattice constants,  $a = 14.91\text{\AA}$ ,  $b = 7.82\text{\AA}$ ,  $c = 7.68\text{\AA}$  and unit cell volume  $V = 897.5200\text{\AA}^3$ . Nd(III) complex yielded values of lattices constants  $a = 10.59\text{\AA}$ ,  $b = 6.86\text{\AA}$ ,  $c = 4.35\text{\AA}$  and unit cell volume  $V = 316.6349\text{\AA}^3$ . Gd(III) complex yielded values of lattices constants  $a = 17.26\text{\AA}$ ,  $b = 7.62\text{\AA}$ ,  $c = 4.10\text{\AA}$  and unit cell volume  $V = 539.8008\text{\AA}^3$ . In concurrence with these cell parameters, the condition such as  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90$  required for crystal to be orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Ce(III), Pr(III), Nd(III) and Gd(III) complexes has orthorhombic crystal system. The experimental density values of the complexes were determined by using specific gravity method (Shoemaker and Garland, 1989) and found to be  $1.24$ ,  $3.32$ ,  $1.65$  and  $4.71 \text{ g cm}^{-3}$  for La(III), Ce(III), Pr(III) and Nd(III) complexes respectively. By



**Fig. 1.** X-ray diffractograms of La(III), Ce(III), Pr(III), Nd(III) and Gd(III) complexes.

using experimental density values, molecular weight of complexes, Avogadro's number, volume of the unit cell, the number of molecules per unit cell were calculated by using equation  $\rho = nM/NV$  and was found to be one for La(III) and four for Ce(III), Pr(III) and Nd(III) complexes. With these values, theoretical densities were computed and found to be  $1.23$ ,  $3.31$ ,  $1.64$  and  $4.70 \text{ g cm}^{-3}$  for respective complexes. Comparison of experimental and theoretical density values showed good agreement within the limits of experimental error.<sup>43</sup>

### Kinetic data

The kinetic and thermodynamic parameters *viz* order of reaction (n), energy of activation ( $E_a$ ), frequency factor ( $\log A$ ), entropy of activation ( $\Delta S^\ddagger$ ) and free energy change ( $\Delta G^\ddagger$ ) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Coats-Redfern integral and Horowitz-Metzer method<sup>30</sup> and the data is given in *Table 2*. The results showed that the values obtained by two methods are comparable. The calculated free energy of activation is relatively low indicating the autocatalytic effect of metal ions on thermal decomposition of the complexes.<sup>31,32</sup>  $\Delta S^\ddagger$  values were negative, which indicate a more ordered activated

**Table 2.** Electronic spectral data (cm<sup>-1</sup>) and related bonding parameters of lanthanide (III) complexes.

Complexes	Band Position of Ln(NO <sub>3</sub> )	Band Position of Metal Complexes	Band Assignments	Calculated parameters
[PrL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	22371	22200	<sup>3</sup> H <sub>4</sub> <sup>3</sup> → <sup>3</sup> P <sub>2</sub>	β <sub>av</sub> =0.9937
	21413	21300	→ <sup>3</sup> P <sub>1</sub>	b <sup>1/2</sup> =0.03949
	21008	20900	→ <sup>3</sup> P <sub>1</sub>	δ%=0.6329
	16920	16800	→1D <sub>2</sub>	γ=0.003165
[SmL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	19267	19190	<sup>4</sup> H <sub>5/2</sub> → <sup>6</sup> P <sub>7/2</sub>	β <sub>av</sub> =0.9936
	17241	17200	→ <sup>4</sup> P <sub>9/2</sub>	b <sup>1/2</sup> =0.03819
	13459	13350	→ <sup>4</sup> P <sub>13/2</sub>	δ%=0.6352
	12484	12350	→ <sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> F <sub>9/2</sub>	η=0.003176
[GdL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	27933	27800	<sup>4</sup> H <sub>5/2</sub> → <sup>6</sup> P <sub>7/2</sub>	β <sub>av</sub> =0.9920
	24875	24700	→ <sup>4</sup> P <sub>9/2</sub>	b <sup>1/2</sup> =0.04384
	21550	21400	→ <sup>4</sup> P <sub>13/2</sub>	δ%=0.7975
	13908	13800	→ <sup>4</sup> F <sub>9/2</sub>	η=0.003988
	10537	10400	→ <sup>4</sup> F <sub>9/2</sub>	

state that may be possible through the chemisorption of oxygen and other decomposition products. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transitions.

**Antimicrobial activity**

The Schiff base ligand H<sub>2</sub>L and its metal complexes were evaluated for antimicrobial activity against bacteria such as *Staphylococcus aureus*, *Escherichia coli* and *Bacillus Sp* by paper disc method.<sup>21</sup> The compounds were

tested at the concentration 0.25 mgmL<sup>-1</sup> and 0.5 mgmL<sup>-1</sup> in DMF and compared with known antibiotics viz. *Ciprofloxin* (Table 4). For fungicidal activity, compounds were screened in vitro against *Aspergillus Niger*, *Trichoderma* and *Fusarium oxysporum* by mycelia dry method with glucose nitrate media.<sup>23</sup> The compound were tested at the concentration 250 and 500 ppm in DMF and compared with control (Table 5). From Tables 4 and 5, it is clear that the inhibition by metal chelates is higher than that of ligand.

The results showed that the free ligand as well as all the metal complexes exhibit antimicrobial activity against

**Table 3.** The kinetic parameters of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CM) methods

Complex	Step	n	Method	E <sub>a</sub> (kJmol <sup>-1</sup> )	Z (S <sup>-1</sup> )	ΔS# (JK <sup>-1</sup> mol <sup>-1</sup> )	ΔG# (kJmol <sup>-1</sup> )	Correlation coefficient (r)
La(III)	I	0.5	HM	18.86	6.510 <sup>5</sup>	-234.72	35.03	0.9995
			CR	26.22	6.810 <sup>8</sup>	-238.18	42.63	0.9957
	II	1.3	HM	63.01	6.310 <sup>2</sup>	-222.18	95.69	0.9985
			CR	45.23	5.410 <sup>2</sup>	-228.45	78.29	0.9992
Sm(III)	I	0.9	HM	16.35	3.110 <sup>8</sup>	-240.96	32.95	0.9975
			CR	22.09	3.210 <sup>8</sup>	-245.24	38.99	0.9999
	II	1.3	HM	31.50	9.910 <sup>-3</sup>	-257.61	69.39	0.9995
			CR	26.53	1.310 <sup>5</sup>	-258.24	64.57	0.9997

**Table 4.** Antibacterial activity of ligand and its metal complexes.

Ligand/Complexes	inhibition zone (mm)					
	<i>E. coli</i>		<i>Staphylococcus</i>		<i>Bacillus sp.</i>	
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm
<i>Ciprofloxin</i>	29	32	31	35	25	27
(H <sub>2</sub> L)	11	14	11	15	10	13
[LaL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	11	15	13	16	11	14
[CeL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	12	16	13	17	12	15
[PrL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	12	18	13	16	11	17
[NdL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	12	18	14	17	11	16
[SmL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	13	19	14	17	11	18
[GdL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	13	19	15	18	12	18

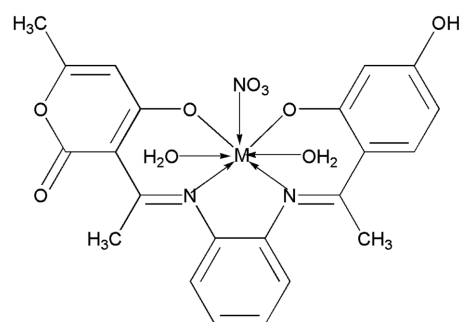
**Table 5.** Antifungal activity of compounds yield, of mycelial dry weight in mg (%inhibition)

Ligand/Complexes	<i>Aspergillus Niger</i>		<i>Trichoderma</i>		<i>Fusarium oxysporum</i>	
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70	68	68
(H <sub>2</sub> L)	47(41)	17(79)	29(59)	17(76)	49(28)	36(47)
[LaL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	40(50)	16(80)	28(60)	17(76)	48(30)	32(57)
[CeL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	39(51)	20(75)	29(62)	15(79)	46(33)	29(58)
[PrL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	40(50)	14(83)	25(65)	14(80)	42(39)	27(61)
[NdL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	38(52)	12(85)	23(68)	12(83)	41(40)	22(68)
[SmL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	37(54)	12(85)	21(70)	10(86)	36(48)	17(75)
[GdL(H <sub>2</sub> O) <sub>2</sub> NO <sub>3</sub> ]	36(55)	11(86)	15(79)	9(88)	34(50)	13(81)

both the strains. The comparative study of the ligand and its metal complexes indicates that the metal complexes exhibit higher antimicrobial activity than free ligand under identical experimental conditions. Antimicrobial inhibitions were compared with that of *Ciprofloxin* as a standard, showing that the activity of all the tested compounds is less than the standard. The metal salts used for the synthesis of complexes exhibit negligibly small antimicrobial activity.<sup>22,23</sup> The remarkable enhancement of activity of ligand after chelation can be explained on the basis of Overtones concept and Tweedy's concept. According to these concepts, chelation tends to make a ligand more potential bacterial agent. The increased activity upon chelation is attributed to the positive charge of metal partially shared with donor atoms present on ligand and possible  $\pi$ -electron delocalization over the whole chelate ring.<sup>44</sup> This, in turn, increases the lipophilic character of the metal chelate and favors its permeation through the lipid layers of the bacterial membranes resulting in interference with normal process. Inhibition was found to increase with increasing concentration of metal complex.<sup>45</sup>

## CONCLUSION

La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) complexes with N<sub>2</sub>O<sub>2</sub> donor Schiff base ligand derived from *o*-phenylenediamine, 3-Acetyl-6-methyl-pyran-2, 4-dione (dehydroacetic acid) and 2, 4-dihydroxy benzaldehyde 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 indicated that all the complexes were 1:1 non electrolytes. The IR data revealed that the Schiff base ligand is coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig. 2. A distorted octahedral geometry were assigned for



**Fig. 2.** Proposed structure of metal complexes where M = La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III).

La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) complexes. The complexes were biologically active and showed enhanced antimicrobial activities compared to free ligand. Thermal study revealed thermal stability of complexes.

The XRD study suggested monoclinic crystal system for La(III) and orthorhombic crystal system for Ce(III), Pr(III), Nd(III) and Gd(III) complexes.

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