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ORIGINAL ARTICLE

Synthesis, spectroscopic characterization and thermal studies of some rare earth metal complexes of unsymmetrical tetradentate Schiff base ligand

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Thermal analysis;
Powder X-ray diffraction;
Biological activity

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-hydroxy-benzylidene)-aminophenylimino}-thyl)-6-methy-pyran-2-one (H_2L) derived from *o*-phenylenediamine, 3-acetyl-6-methyl-(2*H*)pyran,2,4(3*H*)-dione (dehydroacetic acid or DHA) and salicylic aldehyde have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV–visible, FTIR, ^{1}H NMR spectra, X-ray diffraction, and thermal analysis and screened for antimicrobial activity. The FTIR spectral data suggest that the ligand behaves as a dibasic tetradentate ligand with ONNO donar 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 suggest distorted octahedral geometry for La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) complexes. The X-ray diffraction data suggest monoclinic crystal system for La(III) and Ce(III) and orthorhombic crystal system for Pr(III) and Nd(III) complexes. Thermal behaviour (TGA/DTA) of the complexes was studied and kinetic parameters were determined by Horowitz–Metzger and Coats–Redfern methods. The ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus*, *Escherichia coli* and *Bacillus* sp. Fungicidal activity against *Aspergillus niger*, *Trichoderma* and *Fusarium oxysporum*.
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1. Introduction

Tetradentate Schiff bases with N_2O_2 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 (Atkins et al., 1985; Yuan et al., 1993; Ramesh et al., 1996; Ohashi, 1997; Jeong et al., 1996). Schiff bases of *o*-phenylenediamine are reported to have a variety of applications including biological (Singh et al., 1975), clinical (Mahindra et al., 1983) and analytical (Patel et al., 1999) fields.

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Many symmetrical tetradentate bis-type Schiff bases of 1,2-diamines with *o*-hydroxy aldehyde/ketone 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 (Phan et al., 2004). It is worthwhile to mention here that unsymmetrical Schiff bases of this type are difficult to obtain and are not easily isolated (Tan and Ang, 1988). Considering the importance of hydrogen bonding in chemical and biological systems some research groups, in recent literature, reported vibrational modes of carbonyl functionalities such as acetate, carboxyl, and carboxylate and the reactivity of functional groups, namely, carboxy, amide, aldehyde, cyno, isopropyl, nitro and nitrate based on their physical properties such as total dipole moment and heat of formation (Medhat and Eckhard, 2004; Medhat et al., 2005; Medhat and Mahmoud, 2009).

Coordination chemistry of lanthanide has become of increasing significance in the last few years due to the wide variety of applications of lanthanide complexes in supramolecular photochemistry and in medicine (Minhus et al., 2007; Guo et al., 2007). Co-ordination compounds of the lanthanides are frequently used as catalysts, which is demonstrated by the work of Shibaski et al. (1997), Kobayashi and Ishitani (1995) and others (Voropai et al., 2001).

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 (Surya Rao et al., 1978, 1980; Schleiffenbaum et al., 1992; Stanley et al., 1996). It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems (Levai and Jeko, 2006). A search of the literature revealed that no work has been done on lanthanide(III) metal complexes of the asymmetrical Schiff base derived from aromatic 1,2-diamine, dehydroacetic acid and salicylic aldehyde.

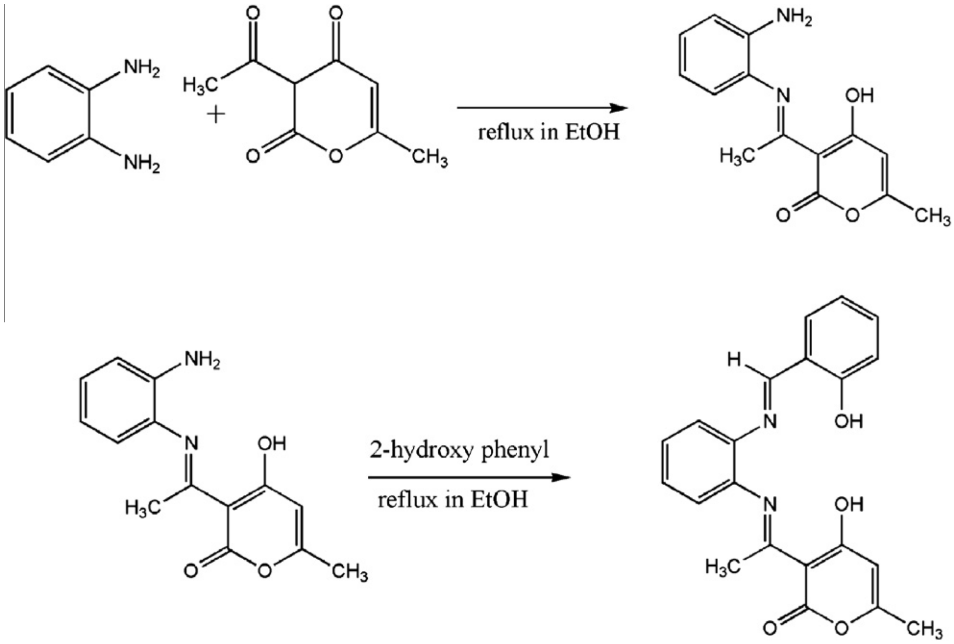
In this paper, we report the synthesis and characterization of lanthanide(III) metal complexes with tetradentate ligand derived from aromatic 1,2-diamine, dehydroacetic acid and salicylic aldehyde.

2. Experimental

Dehydroacetic acid purchased from Merck was used as supplied. *o*-Phenylene diamine and salicylic aldehyde of AR grade were used for synthesis of ligand. AR grade metal nitrate was used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. FTIR spectra were recorded on Jasco FTIR-4100 spectrometer using KBr pellets. ^{1}H NMR spectra of ligand were measured in $CDCl_3$ using TMS as 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 complex were recorded on JascoUV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were determined on a Guoy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

2.1. General procedure for the synthesis of ligand

The ligand was prepared by a reported method (Munde et al., 2009). A typical procedure for the synthesis of Schiff bases was as follows. A 50 mL solution of 0.10 mmol (0.168 g) of dehydroacetic acid, 0.10 mmol (0.108 g) of *o*-phenylenediamine and 0.10 mmol (0.122 g) of salicylic aldehyde in absolute ethanol were refluxed for about 4 h. The precipitate thus formed was cooled to room temperature and collected by filtration, ollowed by recrystallization in ethanol (Yield: 80%) (See Scheme 1).



Scheme 1 Synthesis of ligand.

2.2. 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 reaction mixture was adjusted to 7.5–8.5 by adding 10% alcoholic ammonia solution and refluxed for about 6–7 h. 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 desiccators (Yield = 50%).

3. 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 reveal 1:1 molar ratio (metal: ligand) and correspond 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 TGA–DTA analysis. The metal chelate solutions in DMF show low conductance and this supports their non-electrolyte nature.

3.1. ^{1}H NMR spectra of ligand

The ^{1}H NM*R* spectra of free ligand in $CDCl_3$ at room temperature shows the following signals. δ 2.18 (s, 3H, $-CH_3$), 2.55 (s, 3H, $N{=}C{-}CH_3$), 5.54 (s, 1H, phenolic OH), 5.84 (s, 1H, Ar–H), 6.97–7.53 (m, 8H, Ar–H), 8.65 (s, 1H, N=C–H) and 13.45 (s, 1H, enolic OH of DHA moiety).

3.2. Mass spectra of the ligand

Mass spectral data confirmed the structure of the Ligand HL as indicated by the peaks corresponding to their molecular mass (Fig. 1).

3.3. Magnetic measurements

The magnetic measurements were carried out at room temperature with a Gouy's balance and [HgCo$(SCN)_4$] was used (See Fig. 2) as a calibrant. Results are as shown in Table.1

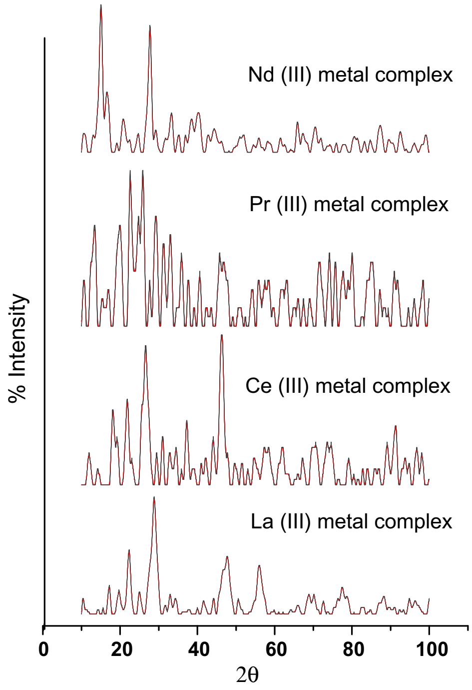


Figure 1 X-ray diffractograms of La(III), Ce(III), Pr(III) and Nd(III) complexes.

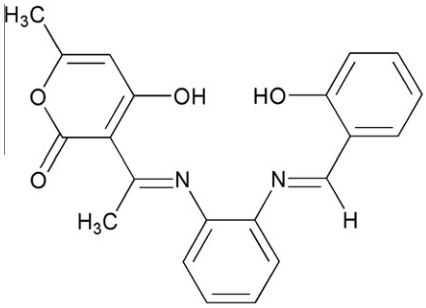


Figure 2 Structure of ligand.

3.4. FTIR spectra

The FTIR spectrum of free ligand shows characteristic bands at 3060–3300, 1703, 1657, 1354 and 1219 cm^{-1} assignable to intramolecular hydrogen bonded (*t* OH), lactone carbonyl (*t* C=O), azomethine (*t* C=N), aryl azomethine (*t* C–N) and phenolic

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

Ligand/complexes	F.W.	M.P./decomp. temp. (°C)	Magnetic moment μ_{eff} (B.M.)	Molar conduc. Mho (cm^2 mol^{-1})	% Found (Calcd.)			
					C	H	N	M
(HL)	362.39	185	–	–	69.12 (69.60)	4.88 (5.01)	7.50 (7.73)	_
[LaL$(H_2O)_2NO_3$]	597.82	> 300	Dia.	33.04	41.60 (42.22)	3.07 (3.37)	6.80 (7.03)	22.40 (23.25)
[CeL$(H_2O)_2NO_3$]	599.03	> 300	2.58	29.00	42.01 (42.14)	3.10 (3.36)	7.10 (7.02)	23.05 (23.41)
[PrL $(H_2O)_2NO_3$]	599.03	> 300	3.50	30.06	42.10 (42.14)	3.01 (3.36)	6.80 (7.02)	23.00 (23.41)
[NdL $(H_2O)_2NO_3$]	603.15	> 300	3.70	21.04	41.95 (41.85)	3.10 (3.34)	6.80 (6.97)	23.50 (23.93)
[SmL $(H_2O)_2NO_3$].	609.27	> 300	1.55	28.05	41.30 (41.43)	3.00 (3.31)	6.80 (6.90)	24.60 (24.69)
[GdL $(H2O)_2NO_3$]	616.16	> 300	7.80	26.05	40.80 (40.97)	3.10 (3.27)	6.81 (6.82)	26.00 (25.54)

(*t* C–O) stretching modes, respectively (Ramarao et al., 1985; Tan et al., 1984). The absence of a weak broad band in the 3060–3300 cm^{-1} 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 (*t* C–O) (Venketeswar Rao and Venkata Narasaiah, 2003) to the extent of 30–50 cm^{-1}. On complexation, the (*t* 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 (*t* C–N) to the extent of 10–50 cm^{-1} (Dash et al., 2002). The FTIR spectra of metal chelates showed new bands in 425–550 cm^{-1} range assigned to (M–N) (During et al., 1965; Nakamoto, 1961, 1978; Ueno and Martell, 1956) and 350–320 cm^{-1} range assigned to (M–O) modes (Percy, 1976). The FTIR spectra show a strong band in the 3150–3600 cm^{-1} region, suggesting the presence of coordinated water in these metal complexes. Infrared spectra of the nitrato complexes revealed two additional strong bands around 1491 and 1279 cm^{-1}, which were absent in the free ligand (Shoemaker and Garland, 1989). The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830–840 cm^{-1} region, assignable to the rocking mode of water (Shoemaker and Garland, 1989). The FTIR data are given in Table 2. The presence of coordinated water is also established and supported by TG/DTA analysis of these complexes. Hence coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

3.5. 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 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 (Percy, 1976), 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 the literature procedures (Sinha, 1966; Ryan and Jorgensen, 1960; Singh et al., 1978) The value of $(1 - \beta)$ being less than unity (Jorgensen, 1967) for the complexes, the small and positive values of the bonding parameter $b^{1/2}$ and Sinha's parameter $\delta\%$ suggest the possibility of a partial covalent nature of the metal–ligand bond (Singh et al., 1978; Ghosh and Pradhan, 1995). Based on electronic spectral studies, a coordination number of seven around the metal ion is suggested, as reported for $Nd(CF_3COCHCOMe)\cdot H_2O$ by Karraker (1967) and for $[Ln(Hapfh)_2Cl]Cl_2$ (Hapfh = acetylpyridine-2-furoylhydrazone) by Singh and Singh (1989).

3.6. Thermal analysis

The simultaneous TG/DT analysis of metal complexes was studied from ambient temperature to 1000 °C in nitrogen atmosphere using α-Al_2O_3 as reference. The La(III), Ce(III), Nd(III) and Sm(III) complexes of ligand H_2L were chosen for thermal study. On the TG curve of La(III) complex, the first step shows a steep slope between 150 and 230 °C with a mass loss of 5.6% (calcd. 6.0%), indicating the removal of two molecules of coordinated water. An endothermic peak in the range 150–200 °C (ΔT_{max} = 182 °C) on the DTA curve corresponds to the dehydration step. The anhydrous complexes first show slow decomposition from 250 to 600 °C, with 19.98% (calcd. 21.15%) mass loss, a broad exotherm ΔT_{max} = 405 °C in DTA may be attributed to the removal of non coordinate part of ligand. The second step decomposition is from 610 to 650 °C, a sharp endotherm in DTA at 617 °C is observed for this step. The mass of final residue corresponds to stable La_2O_3, 59.65% (calcd. 54.19%). The TG curve of Ce(III) complex shows first mass loss 5.5% (calcd. 6.0%) in the range 160–205 °C and an endothermic peak in this region ΔT_{max} = 202 °C indicates the removal of two coordinate water molecules. The anhydrous complex shows slow decomposition from 210 to 650 °C with 40.20% (calcd. 41.10%) mass loss. A broad exotherm ΔT_{max} = 230 °C in DTA may be attributed to the removal of non coordinate part of ligand. The mass of final residue corresponds to stable Ce_2O_3, 49.84% (calcd. 54.79%). In the TG curve of Nd(III) complex, the first step shows a steep slope between 150 and 230 °C with mass loss of 5.13% (calcd. 5.90%), indicating the removal of two molecules of coordinate water. An endothermic peak is shown in this region ΔT_{max} = 212 °C. The second slow step from 250 to 850 °C with mass loss 39.00% (calcd. 38.24%), an exothermic peak ΔT_{max} = 355 °C in DTA may be attributed to the decomposition of non coordinate and coordinate part of ligand. The mass of the final residue corresponds to stable Nd_2O_3, 53.50% (calcd. 55.18%). The TG curve of Sm(III) complex shows two stage decomposition, the first mass loss 5.2% (calcd. 5.9%) in the range 150–230 °C; an endothermic peak in this region ΔT_{max} = 205 °C corresponds to the removal of two molecules of co-ordinate water. The mass of the final residue corresponds to stable Sm_2O_3 59.04% (calcd. 57.23%).

3.7. Powder X-ray diffraction

The X-ray diffraction of metal complexes was scanned in the range 5–100° at wave length 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 16 reflections with maxima at 2θ = 46.30° corresponding to *d* value 1.95 Å. The diffractogram of Ce(III) complex shows 12 reflection with maxima at 2θ = 22.31° corresponding to *d* value 3.98 Å. The diffractogram of Pr(III) complex had 16 reflections with maxima at 2θ = 25.88° corresponding to d value 3.43Å. The diffractogram of Nd(III) complex had 14 reflections with maxima at 2θ = 25.04° corresponding to d value 3.55 Å. The X-ray diffraction pattern of these complexes with respect to major peaks having relative intensity greater than 10% has been indexed by using computer programme. The above indexing method also yields Miller indices (*hkl*), unit cell parameters and unit cell volume. The unit cell of La(III) complex yielded values of lattice constants, a = 8.1289 Å, b = 8.1829 Å, c = 6.0525 Å and unit cell volume V = 402.6603 $Å^3$. The unit cell of Ce(III) complex yielded values of lattice constants, a = 7.3987 Å, b = 9.8488 Å, c = 5.1946 Å and unit cell volume $V = 375.2879$ Å^3. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded that La(III) and Ce(III) complexes have monoclinic crystal system. The unit cell of Pr(III) complex yielded values of lattice constants, $a = 13.7623$ Å, $b = 13.1894$ Å, $c = 4.1115$ Å and unit cell volume $V = 746.1900$ Å^3. The unit cell of Nd(III) complex yielded values of lattice constants $a = 15.1800$ Å, $b = 7.10$ Å, $c = 6.27$ Å and unit cell volume $V = 675.63$ Å^3. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90$ required for sample to be orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Pr(III) and Nd(III) complexes have 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 0.91, 0.97, 1.94 and 2.16 g cm^{-3} for La(III), Ce(III), Pr(III) and Nd(III) complexes, respectively. By 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 the equation $\rho = nM/NV$ and was found to be one, one, four and four for La(III), Ce(III), Pr(III) and Nd(III) complexes, respectively. With these values, theoretical densities were computed and found to be 0.90, 0.96, 1.93 and 2.15 g cm^{-3} for the respective complexes. Comparison of experimental and theoretical density values shows good agreement within the limits of experimental error (Deshmukh et al., 2005) (Fig. 2).

3.8. Kinetic data

The kinetic and thermodynamic parameters *viz* order of reaction (n), energy of activation (E_a), frequency factor (log A), entropy of activation ($\Delta S^{\#}$) and free energy change ($\Delta G^{\#}$) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Coats–Redfern integral and Horowitz–Metzer methods (Nakamoto, 1961). The results show that the values obtained by the two methods are comparable. The calculated free energy of activation is relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the complex (Ueno and Martell, 1956; Nakamoto, 1978). $\Delta S^{\#}$ values were negative, which indicate a more ordered activated state that may be possible through the chemisorptions 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 transition (See Table 3).

3.9. Antimicrobial activity

The antimicrobial activity of ligand and metal complexes was tested *in vitro* against bacteria such as *Staphylococcus aureus, Escherichia coli* and *Bacillus* sp. by paper disc plate method (Mane et al., 2001). The compounds were tested at the concentrations 0.5 and 1 mg mL^{-1} in DMF and compared with known antibiotics *viz* ciproflaxin (Table 5). For fungicidal

Table 2 The kinetic parameters of metal complexes calculated by Horowitz–Metzger (HM) and Coats–Redfern (CM) methods.

Complex	Step	n	Method	E_a (kJ mol$^{-1)}$	A (S^{-1})	$\Delta S^{\#}$ (JK^{-1}mol$^{-1)}$	$\Delta G^{\#}$ (kJ mol^{-1})	Corelation coefficient (r)
La(III)	I	0.3	HM	2.93	1.77×10^3	−169.00	15.48	0.9993
			CR	27.59	5.0119	−177.67	16.13	0.9976
	II	0.3	HM	17.47	2.66×10^6	−173.03	42.97	0.9999
			CR	16.35	1.49×10^6	−157.69	40.85	0.9966
Ce(III)	I	0.55	HM	9.66	1.86×10^6	−169.32	22.34	0.9914
			CR	12.99	9.94×10^6	−155.39	21.30	0.9972
	II	0.55	HM	19.36	4.69×10^6	−167.74	45.54	0.9936
			CR	10.21	1.83×10^6	−156.40	43.77	0.9973
Nd(III)	I	0.50	HM	7.24	9.72×10^2	−175.95	20.12	0.9941
			CR	15.93	5.463×10^3	−163.12	19.94	0.9903
	II	0.50	HM	14.32	5.82×10^2	−171.19	39.50	0.9988
			CR	10.10	3.88×10^2	−162.10	38.16	0.9963
Sm(III)	I	0.55	HM	26.41	5.711×10^5	−154.99	37.08	0.9914
			CR	11.18	1.563×10^3	−148.12	34.06	0.9998
	II	0.55	HM	31.5	8.970×10^3	−163.13	55.49	0.9998
			CR	16.95	1.129×10^3	−139.37	52.00	0.9953

Table 3 FTIR spectra of the ligand (HL) and its Ln(III) complexes (cm^{-1}).

Ligand/complexes	(OH)	(C=O)	(C=N)	(C–N)	(C–O)	(NO_3)	(NO_3)	(M–N)	(M–O)
HL	3060–3300	1703	1657	1354	1219	–	–	–	–
[LaL$(H_2O)_2$ NO_3]	–	1683	1610	1390	1259	1491	1270	452	335
[CeL$(H_2O)_2$ NO_3]	–	1670	1606	1384	1245	1485	1272	450	360
[PrL$(H_2O)_2$ NO_3]	–	1697	1610	1386	1257	1480	1275	460	358
[NdL$(H_2O)_2$ NO_3]	–	1680	1615	1390	1250	1490	1278	470	365
[SmL$(H_2O)_2$ NO_3]	–	1672	1617	1385	1255	1465	1270	472	360
[GdL$(H_2O)_2$ NO_3]	–	1680	1618	1390	1260	1489	1273	470	365

Table 4 Electronic spectral data (cm^{-1}) and related bonding parameters of lanthanide(III) complexes.

Complexes	Band position of Ln(NO_3)	Band position of metal complexes	Band assignements	Calculated parameters
[PrL(H_2O)$_2$$NO_3$]	22,371	22,180	$3H_4 \rightarrow {}^3p_2$	$\beta_{av} = 0.9905$
	21,413	21,213	$\rightarrow {}^3p_1$	$b^{1/2} = 0.04806$
	21,008	20,876	$\rightarrow {}^3p_1$	$\delta\% = 0.9535$
	16,920	16,690	$\rightarrow {}^1D2$	$\eta = 0.0047$
[NdL(H_2O)$_2$$NO_3$]	19,267	19,200	${}^4H_{5/2} \rightarrow {}^{six}P_{7/2}$	$\beta_{av} = 0.9937$
	17,241	17,040	$\rightarrow {}^4P_{9/2}$	$b^{1/2} = 0.0390$
	13,459	13,250	$\rightarrow {}^4P_{13/2}$	$\delta\% = 0.6283$
	12,484	12,250	$\rightarrow {}^4F_{9/2}$	$\eta = 0.0031$
			$\rightarrow {}^4F_{9/2}$	
[SmL(H_2O)$_2$$NO_3$]	27,933	22,855	${}^4H_{5/2} \rightarrow {}^6P_{7/2}$	$\beta_{av} = 0.9941$
	24,875	24,700	$\rightarrow {}^4P_{9/2}$	$b^{1/2} = 0.03773$
	21,550	21,450	$\rightarrow {}^4P_{13/2}$	$\delta\% = 0.5911$
	13,908	13,513	$\rightarrow {}^4F_{9/2}$	$\eta = 0.0029$
	10,537	10,152	$\rightarrow {}^4F_{9/2}$	

Table 5 Antibacterial activity of HL and its metal complexes.

	Inhibition zone diameter (mm)					
	E. coli		*Staphylococcus*		*Bacillus* sp.	
Ligand/complexes	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
Ciprofloxin	29	32	31	35	25	27
(HL)	08	11	11	14	08	12
[LaL(H_2O)$_2$ NO_3]	08	11	12	15	09	13
[CeL(H_2O)$_2$ NO_3]	09	11	12	15	09	13
[PrL(H_2O)$_2$ NO_3]	10	12	13	16	10	14
[NdL(H_2O)$_2$ NO_3]	10	13	14	17	10	14
[SmL(H_2O)$_2$ NO_3]	11	12	14	17	11	14
[GdL(H_2O)$_2$ NO_3]	12	13	15	18	12	16

Table 6 Antifungal activity of compounds yield of mycelial dry weight in mg (% inhibition).

Ligand/complexes	*Aspergillus niger*		*Trichoderma*		*Fusarium oxysporum*	
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70	68	68
(HL)	61(23)	24(70)	40(43)	19(73)	53(23)	37(46)
[LaL(H_2O)$_2$$NO_3$]	55(31)	50(37)	37(48)	16(78)	50(27)	33(52)
[CeL(H_2O)$_2$]NO_3]	50(37)	42(47)	35(50)	15(79)	47(31)	30(56)
[PrL(H_2O)$_2$$NO_3$]	45(44)	40(50)	32(55)	13(82)	44(36)	27(61)
[NdL(H_2O)$_2$$NO_3$]	45(44)	38(52)	29(59)	11(85)	42(39)	23(67)
[SmL(H_2O)$_2$$NO_3$]	40(50)	33(59)	25(65)	10(86)	37(46)	18(74)
[GdL(H_2O)$_2$$NO_3$]	38(25)	23(71)	20(72)	08(89)	35(49)	14(80)

activity, compounds were screened *in vitro* against *Aspergillus niger*, *Trichoderma and Fusarium oxysporum* by mycelia dry weight method (Venketeswar Rao and Venkata Narasaiah, 2003) with glucose nitrate media. The compounds were tested at the concentrations 250 and 500 ppm in DMF and compared with control (Table 6). From Tables 5 and 6, it is clear that the inhibition by metal chelates is higher than that of path ligand and the results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes (Venketeswar Rao and Venkata Narasaiah, 2003; Mane et al., 2001). Such enhanced activity of metal chelates is due to the lipophilic nature of the metal ions in complexes (Mishra and Singh, 1993). 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 center of cell constituents, resulting in interference with the normal cell process (Mohanan and Devi, 2006).

4. Conclusion

In the light of the above discussion we have proposed distorted octahedral geometry for La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume

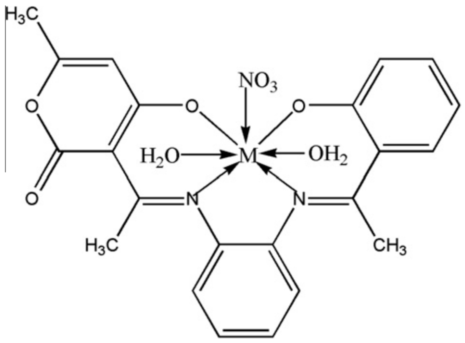


Figure 3 Structure of metal complexes. Where M = La(III), Ce(III), Pr(III), Nd(II) and Sm(III).

that the ligand behaves as dibasic, ONNO tetradentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig. 3. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The XRD study suggests monoclinic crystal system for La(III) and Ce(III) and orthorhombic crystal system for Pr(III) and Nd(III) complexes.

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