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New coordination compounds of some rare-earth metal complexes with sulfur and nitrogen Schiff bases and their *in vitro* antibacterial and antifungal properties

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A series of rare-earth metal complexes with Schiff bases have been prepared by the interactions of hydrated lanthanide(III) chloride with the sodium salts of 1-(2-thienyl)ethanone hydrazinecarbothioamide (L^1H) and 1-(2-thienyl)ethanonehydrazinecarboxamide (L^2H) in 1:3 molar ratios and characterized by their elemental analyses, molar conductance and IR, NMR (^1H and ^{13}C) electronic and EPR spectral studies. The spectral data suggested that the complexes have a hexa-coordinated environment around the central metal atoms. Elemental analyses and NMR spectral data of the ligands and their metal(III) complexes agree with their proposed structures. The synthesized Schiff bases and their new metal complexes have been screened for *in vitro* antibacterial activity against Gram-negative (*Escherichia coli*) and Gram-positive (*Pseudomonas cepacicola*) bacterial strains and for *in vitro* antifungal activity against *Fusarium oxysporum* and *Macrophomina phaseolina.* All compounds showed significant antibacterial and antifungal activities against microbial species.

Keywords: rare-earth elements; Schiff bases; EPR spectra; antibacterial activity; antifungal activity

1. Introduction

Coordination chemistry of lanthanides was limited initially to strongly chelating ligands with oxygen as donor atoms (*1*). With the development of new synthetic techniques, a significant number of lanthanide(III) complexes, with various types of ligands, were prepared and characterized. A survey of the literature reveals that not only are the lanthanide(III)–nitrogen donor complexes interesting, but they also find applications in organic synthesis and catalysis (*2*). Lanthanide(III) ions are known to exhibit interesting bonding possibilities with various types of ligands. Extensive literature is available on lanthanide complexes containing several polydentate ligands (*3–5*). However, such complexes with biologically active ligands have received comparatively less attention. Lanthanide ions, in view of their electronic configuration and size, are often used as a spectroscopic probe as surrogates for calcium(II) ions in studies of biological systems, as well as promoters in the dyeing industry and as a diagnostic agent in clinical

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medicine (*6–8*). Lanthanide ions in aqueous solution form aquated complexes and hence in aqueous media, any ligand added is in competition with the water molecules that are present in large quantities. Furthermore, displacement of a coordinated water molecule by another ligand is commonly difficult. Thus, only strong ligands which are chelating form lanthanide complexes of sufficient stability. It is well known that the heterocyclic compounds exhibit bactericidal, fungicidal, herbicidal and insecticidal activities. When such heterocyclic ligands are complexed with the metal ions, they exhibit enhanced microbiological activity (*9*). Because of the rapid development and also challenging demands, it has become necessary to synthesize and screen newer compounds for antimicrobial activity. Such a study is highly useful to evaluate the possibilities of using metal complexes against microorganisms and to check their biodegradation in the environment. Lanthanide chelates are increasingly becoming a popular choice for use as luminescent probes and tools in clinical diagnostics, basic research, drug discovery, sensing and imaging.

Heterocyclic compounds are widely distributed in nature and are essential to many biochemical processes. These compounds are worth attention for many reasons, chief among them are their biological activities: many drugs are heterocyclic. Metal chelation is involved in many important biological processes in which coordination can occur between a variety of metal ions and a wide range of ligands (*10*). Many types of ligands are known and the properties of their derived metal chelates have been investigated (*11–13*). Our interest in the chemistry of hydrazine lanthanide complexes with O and N donor ligands comes from their structural importance as well as their interesting biological activities.

Metal complexes of Schiff bases form an interesting class of compounds, which find extensive applications in various fields (*14–17*). Among these complexes, several lanthanide(III) complexes containing Schiff bases have also been reported. However, lanthanide(III) complexes formed from heterocyclic Schiff bases, particularly those containing a thiophene ring system, have received comparatively less attention. Apart from the structural diversities and bonding interactions, the multitude of applications of lanthanide complexes make them an exciting aspect of coordination chemistry (*18–20*).

2. Experimental

2.1. *Materials*

Hydrated lanthanide(III) chlorides and 2-acetylthiophene were purchased from Alfa Aesar and used as received. All the chemicals and solvents used were of analytical grade. All the solvents were dried and distilled before use.

2.2. *Analytical methods and physical measurements*

The metal contents were estimated complexometrically, with EDTA, using Erichrome Black T as an indicator. Sulfur and nitrogen were estimated by Messenger's and Kjeldahl's methods, respectively. IR spectra were recorded on a Perkin-Elmer model 577 grating spectrophotometer, in the range 4000–200 cm^{-1}, in KBr discs. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL-AL-300 FT NMR spectrometer in DMSO-d_6 using TMS as the internal standard. EPR spectra of the complexes were monitored on a Varian E-4X band spectrometer. The electronic spectra were recorded on a Varian–Cary/5E spectrophotometer at SAIF, IIT Madras, Chennai. Molecular weight determinations were carried out by the Rast Camphor method. Magnetic measurements were recorded at room temperature with the Faraday balance using $Hg[Co(NCS)_4]$ as calibrant.

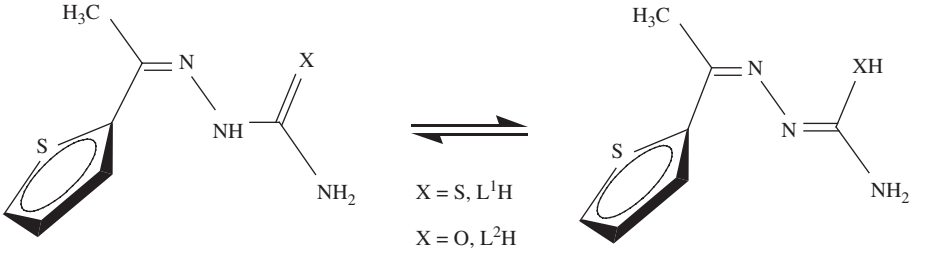

Figure 1. Tautomeric forms of the ligands.

2.3. *Synthesis of the ligands*

Both the ligands 1-(2-thienyl)ethanone hydrazinecarbothioamide (L^1H) and 1-(2-thienyl)-ethanonehydrazinecarboxamide (L^2H) were synthesized as reported in the literature (*21*). The parent ligands exist in the tautomeric forms, as given in Figure 1.

2.4. *Synthesis of the sodium salt of the ligands*

Sodium metal was taken corresponding to the ligand. Then both the sodium metal and the ligand were dissolved separately in a minimum amount of methanol. Ultimately, these two solutions were dissolved to prepare a sodium salt of the ligand. In this process, the sodium metal first reacts with methanol and forms sodium methoxide. This sodium methoxide in the next step reacts with the ligand and replaces an acidic proton from the enolic form of the ligand with the sodium metal, and forms sodium salt of the particular ligand. We can use the ligand as such, but the rate of reaction will be slow when compared with that of the sodium salt. Removal of chloride from the metal chloride is easier with sodium than with hydrogen.

2.5. *Synthesis of the lanthanide(III) complexes*

The methanolic solution of hydrated lanthanide chloride ($LnCl_3 \cdot xH_2O$) was mixed with the methanolic solution of the sodium salt of the ligand in a 1:3 molar ratio. The mixture was then heated under reflux for about 30–36 h. On cooling, the sodium chloride which formed in this reaction was separated out by a separating funnel and then the filtrate was dried in vacuum. The physical properties and analytical data of these complexes are recorded in Table 1. The synthetic route of the complexes is given in Figure 2.

2.6. *Antimicrobial studies*

2.6.1. *Antibacterial activity*

The antibacterial activity of the compounds was determined by the disc diffusion method (*22*). The bacteria were cultured in nutrient agar medium and used as inoculum for the study. Bacterial cells were swabbed onto nutrient agar medium (prepared from NaCl 5.0 g, peptone 5.0 g, beef extract powder 3.0 g, yeast extract powder 3.0 g, agar 20.0 g in 100 ml of distilled water; pH 7.5–0.2) in Petri dishes. The test solutions were prepared in methanol to a final concentration of 500 and 1000 ppm, and then applied to filter paper discs (Whatman No. 4; 5 mm in diameter). These discs were placed on the already seeded plates and incubated at 35 ± 2 °C for 24 h. The zone of inhibition around the discs was measured after 24 h. Tetracycline was used as a standard positive control.

Table 1. Analytical data and physical properties of the ligands and their complexes.

Compound	Color	Melting point (°C)	Found (calcd.) (%) N	S	Ln	μ_{eff} (B.M.)	Mol. wt. found (calcd.)
L^1H	Yellow	155	21.17 (21.08)	32.03 (32.17)	–	–	217.45 (199.30)
L^2H	White	187	23.11 (22.93)	17.38 (17.50)	–	–	172.96 (183.23)
$[La(L^1H)_3] \cdot 3H_2O$	White	180 (d)	15.90 (16.00)	24.22 (24.42)	17.44 (17.63)	Dia.	756.54 (787.84)
$[Pr(L^1H)_3] \cdot 3H_2O$	Off white	175 (d)	15.62 (15.96)	24.12 (24.35)	17.53 (17.83)	3.7	749.43 (789.83)
$[Nd(L^1H)_3] \cdot 3H_2O$	Cream	182	15.67 (15.89)	24.09 (24.25)	17.96 (18.18)	3.62	753.37 (793.17)
$[Sm(L^1H)_3] \cdot 3H_2O$	White	170	15.48 (15.77)	23.89 (24.07)	18.62 (18.81)	1.63	762.26 (799.28)
$[La(L^2H)_3] \cdot 3H_2O$	Creamy white	230	16.89 (17.04)	12.91 (13.00)	18.42 (18.77)	Dia.	699.32 (739.62)
$[Pr(L^2H)_3] \cdot 3H_2O$	White	190 (d)	16.74 (16.99)	12.92 (12.97)	18.79 (18.99)	3.68	698.65 (741.63)
$[Nd(L^2H)_3] \cdot 3H_2O$	Cream	170 (d)	16.56 (16.92)	12.87 (12.91)	19.14 (19.36)	3.51	700.57 (744.97)
$[Sm(L^2H)_3] \cdot 3H_2O$	White	202	16.39 (16.78)	12.76 (12.80)	19.88 (20.01)	1.52	718.02 (751.08)

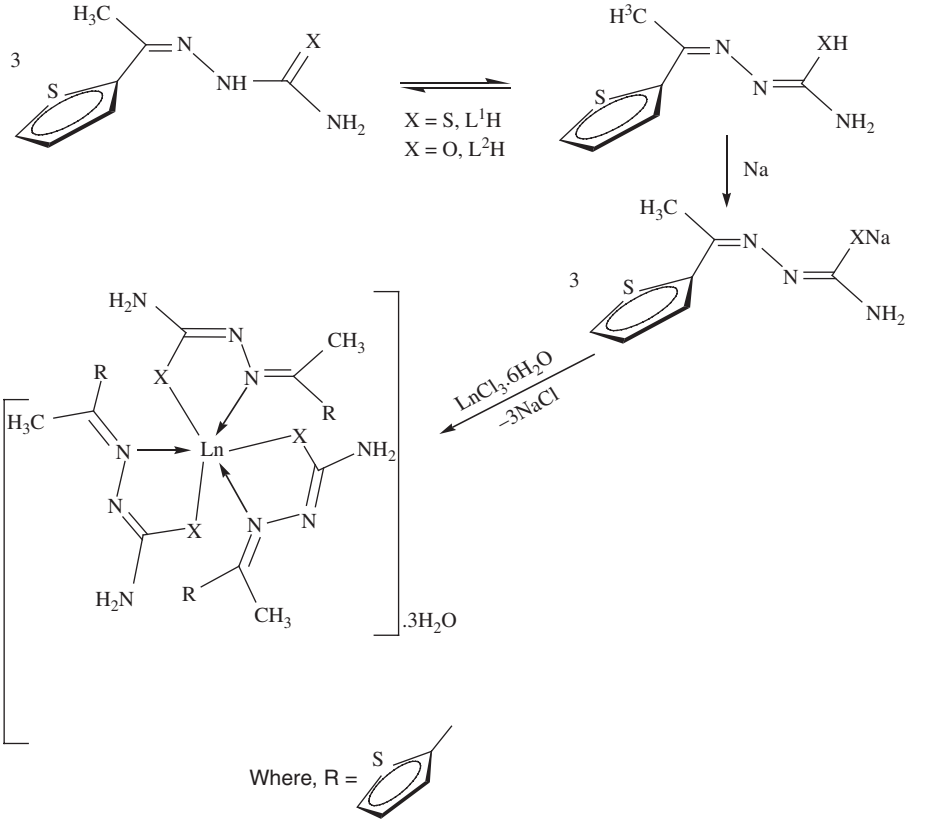

Figure 2. Synthetic route of the complexes.

2.6.2. *Antifungal activity*

Antifungal activities of all the synthesized compounds were screened for *in vitro* growth-inhibitory activity against *Fusarium oxysporum* and *Macrophomina phaseolina* by using the disc diffusion method (*22*). The fungi were cultured in potato dextrose agar medium. Potato dextrose agar medium (prepared from potato 150 g, dextrose 5 g and agar 2 g in 200 ml of distilled water) was

poured into sterilized Petri dishes and allowed to solidify. The dishes were inoculated with a spore suspension of *F. oxysporum* and *M. phaseolina* (106 spores/ml of the medium). The compounds to be tested were dissolved in methanol to a final concentration of 100 and 200 ppm and soaked in filter paper discs (Whatman No. 4; 5 mm in diameter). These discs were placed on the already seeded plates and incubated at $35 \pm 2\,^{\circ}\mathrm{C}$ for 4 days. After 4 days, the inhibition zone that appeared around the discs in each plate was measured. To avoid the activity of the solvent that was used in the test solutions, a solvent-only-treated plate was maintained. Flucanazole was used as a standard.

3. Results and discussion

The reactions of hydrated lanthanide chlorides with monobasic bidentate ligands are shown by

$$\mathrm{LnCl_3 \cdot } x\mathrm{H_2O} + 3\mathrm{LNa} \xrightarrow{\mathrm{MeOH}} [\mathrm{Ln(L)_3}] \cdot n\mathrm{H_2O} + 3\mathrm{NaCl} + (x-3)\mathrm{H_2O},$$

where LNa is the sodium salt of the ligand molecule, Ln = La, PrNd and Sm, $n = 3$ and $x = 6$.

The newly synthesized complexes have been obtained as colored solids that exhibit their solubility in methanol, DMSO and DMF. The monomeric nature of these products has been confirmed by the molecular weight determination. The synthetic route of the complexes is given in Figure 2.

3.1. *Electronic spectra*

The electronic spectra of the ligands and their complexes were recorded using distilled DMSO. The spectra of both ligands L^1H and L^2H show a broad band at 375–382 nm that can be assigned to the $n - \pi^*$ transitions of the azomethine group, which undergoes a blue shift in the complexes (360–365 nm) due to the polarization within the >C=N chromophore caused by the metal–ligand interaction. Two bands in the regions 275–280 and 290–300 nm due to $\pi - \pi^*$ transitions in the ligands remain approximately at the same positions in the spectra of the metal complexes.

The electronic spectra of the complexes are dominated by the ligand bands, with a slight shift to higher or lower energy levels. This slight shift was attributed to the effects of the crystal field upon the interelectronic repulsion between the 4f electrons (*23*). The absorption bands appearing in the spectra of Nd(III), Pr(III) and Sm(III) are due to transitions from the ground levels $^4I_{9/2}$, $^3H_4$ and $^6H_{5/2}$ to the excited J levels of 4f configuration, respectively. The nephelauxetic parameter (β) (*24*), bonding parameter ($b^{1/2}$) (*25*) and Sinha's covalency parameter (δ) (*26*) and angular covalency (η) for the Pr(III), Nd(III) and Sm(III) complexes are presented in Table 2. Sinha's parameter (δ) suggests the degree of covalency and is obtained by

$$\delta = \frac{1 - \beta_{\mathrm{av}}}{\beta_{\mathrm{av}}} \times 100,$$

where β_{av} is the average value of the ratio of $v_{\mathrm{complex}}/v_{\mathrm{aquo}}$. The magnitude of the bonding parameters ($b^{1/2}$) suggests the degree of involvement of 4f orbitals in metal–ligand bonding and is related to nephelauxetic ratio (β) by

$$b^{1/2} = \left[\frac{1 - \beta_{\mathrm{av}}}{2}\right]^{1/2},$$

$$\text{Angular covalency, } \eta = \frac{(1 - \beta_{\mathrm{av}})^{1/2}}{\beta_{\mathrm{av}}^{1/2}}.$$

Table 2. Electronic spectral data of Ln(III) complexes.

Complex	Assignment	V_{max} of Ln^{3+} ion (cm^{-1})	V_{max} of complexes (cm^{-1})	β	$1-\beta$	$b^{1/2}$	δ
$[Pr(L^1H)_3]\cdot 3H_2O$	$^3H_4$–$^1D_2$	17425	17256	0.9903	0.0097	0.0696	0.9795
	$-{}^3P_0$	20951	20842	0.9947	0.0053	0.0514	0.5328
	$-{}^3P_1$	21440	21268	0.9919	0.0081	0.0636	0.8166
	$-{}^3P_2$	22825	22739	0.9962	0.0038	0.0435	0.3814
$[Nd(L^2H)_3]\cdot 3H_2O$	$^4I_{9/2}$–$^4G_{5/2}$, $^2G_{7/2}$	16835	16670	0.9901	0.0099	0.0703	0.9998
	$-{}^2G_{9/2}$	19795	19610	0.9906	0.0094	0.0685	0.9489
	$-{}^4G_{11/2}$	21916	21742	0.992	0.008	0.0632	0.8064
$[Sm(L^1H)_3]\cdot 3H_2O$	$^6H_{5/2}$–$^4I_{13/2}$	21450	21276	0.9918	0.0082	0.064	0.8267
	$-{}^4F_{9/2}$	25836	25652	0.9928	0.0072	0.06	0.7252
	$-{}^4I_{9/2}$	26622	26421	0.9924	0.0076	0.0616	0.7658
	$-{}^6P_{3/2}$	28680	28525	0.9945	0.0055	0.0524	0.553

The intensity of the f–f transitions presents an interesting observation. The intensity of the normal f–f transitions does not show much change. However, the hypersensitive transitions (environment-sensitive transitions) are found to show large changes in the intensity. According to Karraker (*27*), the shape and intensity of these transitions indicate the geometry of the complex. In the present complexes, nephelauxetic ratio (β) is less than 1 and positive values of $b^{1/2}$ and δ indicate slight covalent bonding between the metal and the ligand.

3.2. *IR spectra*

The IR spectra of the free ligands L^1H and L^2H display two sharp bands at 3350–3340 and 3460–3450 cm^{-1} due to ν_{sym} and ν_{asym} vibrations of NH_2 group, respectively, which remain at almost the same positions in the spectra of the complexes, suggesting that the NH_2 group is not involved in chelation. The broad band in the region 3240–3230 cm^{-1} due to νNH vibrations disappears in the spectra of metal complexes, indicating the deprotonation of this group is not in coordination with the metal atom. The band at 1620–1615 cm^{-1} in the spectra of the free ligands due to $\nu(>C{=}N)$ is shifted to a lower wavenumber in the metal complexes, suggesting the coordination through the azomethine nitrogen atom. The bands at 1050 cm^{-1} due to $>C{=}S$ and 1680 cm^{-1} due to $>C{=}O$ are shifted towards lower frequency in the complexes, indicating coordination of sulfur and oxygen to the central metal atom, respectively. The coordination of the azomethine nitrogen and bonding of the thiolic sulfur/ketonic oxygen are supported by the appearance of bands in the 510–550 and 360–420/580–620 cm^{-1} regions in the complexes, which may be assigned to ν(M–N) and ν(M–S)/ν(M–O) vibrations, respectively (Table 3).

3.3. *^{1}H NMR and ^{13}C NMR spectra*

The ^{1}H NMR spectra of both the ligands and their La(III) complexes were recorded in DMSO-d_6 (Table 4). In the spectra of the La(III) complex, the $-NH_2$ signal remains unperturbed at δ 2.72–2.78 ppm, indicating the non-involvement of this group in the complexation. The signal of $-$NH proton in the ligands in the range δ 9.60–9.82 ppm disappears in the spectra of the corresponding complexes. The absence of this signal in these complexes suggest that this proton has been lost via thioenolization and ketoenolization of $>C{=}S$ and $>C{=}O$ groups, and coordination of sulfur and oxygen to the metal atoms, respectively, has taken place. The free ligands show multiplets in the region δ 6.75–8.92 ppm attributable to aromatic protons, which appear almost in the same position in their respective complexes.

Table 3. IR (cm^{-1}) spectral data of the ligands and their corresponding complexes.

Compound	ν(HN)	V (NH_2)		ν(C=S)/ν(C=O)	ν(C=N)	ν(M → N)
		υ_{sym}	υ_{asym}			
L^1H	3240	3350	3460	1050	1620	–
L^1H	3230	3345	3458	1680	1615	–
$[La(L^1H)_3] \cdot 3H_2O$	–	3348	3452	938	1612	510
$[Pr(L^1H)_3] \cdot 3H_2O$	–	3342	3459	942	1609	544
$[Nd(L^1H)_3] \cdot 3H_2O$	–	3340	3450	949	1610	522
$[Sm(L^1H)_3] \cdot 3H_2O$	–	3345	3455	954	1612	526
$[La(L^2H)_3] \cdot 3H_2O$	–	3348	3452	1020	1608	535
$[Pr(L^2H)_3] \cdot 3H_2O$	–	3346	3456	1000	1598	548
$[Nd(L^2H)_3] \cdot 3H_2O$	–	3343	3453	1025	1605	539
$[Sm(L^2H)_3] \cdot 3H_2O$	–	3349	3457	1000	1599	543

Table 4. ^{1}H NMR and ^{13}C NMR (δ, ppm) spectral data of the ligands and their La(III) complexes.

Compound	^{1}H NMR				^{13}C NMR		
	−NH (bs)	$-NH_2$ (s)	$-NH_3$	Aromatic proton (m)	(>C=S)/ (>C=O)	>C=N	Aromatic carbon
L^1H	9.6	2.72	2.23	6.75–8.80	170.32	151.21	159.76, 136.99, 129.15, 127.79
L^2H	9.82	2.78	2.42	6.79–8.76	165.21	153.68	158.72, 137.74, 133.81, 127.82
$[La(L^1H)_3] \cdot 3H_2O$	–	2.7	2.21	6.72–8.90	165.52	156.26	160.62, 137.84, 130.81, 127.94
$[La(L^2H)_3] \cdot 3H_2O$	–	2.77	2.4	6.70–8.92	152.48	158.05	160.66, 138.89, 130.08, 127.99

The $^{13}C\{^1H\}$ NMR spectra of the ligands and their lanthanum complexes were carried out in DMSO-d_6, and the assignments are shown in Table 4. The signals due to azomethine carbon appeared at δ 151.21–153.68 ppm and on complexation they have shown downfield shift to δ 156.26–158.05 ppm due to the resonance and also shown that nitrogen is involved in coordination. The spectra of the ligands exhibit intensive resonance signals at δ 170.32/165.21 ppm due to the C=S/C=O groups, respectively, which undergo downfield shift in the metal complexes, suggesting the involvement of sulfur/oxygen in coordination with the metal atom.

3.4. *Magnetic properties and EPR spectra*

The La(III) complexes are diamagnetic, as expected. The room-temperature magnetic moments of the complexes do not show much deviation from Van Vleck values (*28*), indicating that there is no significant participation of the 4f electrons in bonding because they are well shielded by the $5s^2\ 5p^6$ octet. However, in the case of Sm(III) complexes, a slight variation from Van Vleck values was observed (*29*). Due to the low J–J separation, the energy level between the ground state and the next highest level is only of the order of kT, and the excited states are also populated, leading to anomalous magnetic moments. This is known as the first-order Zeeman effect (*30*). The EPR spectra of metal chelates provide information about hyperfine and superhyperfine structures that are important in studying the metal ion environment in the complexes, *i.e.* the geometry and nature of the ligating sites from the Schiff base. The EPR spectra (both at room temperature and liquid nitrogen temperature (LNT)) were broad, with a similar g value of 1.98, which is nearly equal to the free electron value ($g = 2.00277$). Similar linewidths at both the temperatures indicate that spin–lattice and spin–spin relaxation processes contribute equally to linewidth. Further, the complete absence of zero-field hyperfine splitting and the presence of broad bands indicate that the Ln^{3+} (where $Ln^{3+} = Sm^{3+}$ and Pr^{3+}) ion is located in a rather disordered environment

caused by strain. Thus the spectrum is an average overall possible realization of the crystal field, which can be influenced by the distribution of hydrogen bonds. Random H-bonds between water molecules and complexes induce small distortions, which lead to line broadenings. This phenomenon, called strain, more specifically g-strain for the g-tensor distribution and D-strain for the zero-field splitting distribution, leads to broad asymmetric EPR line shapes (*31*).

3.5. *Bioassay*

The antimicrobial properties of the lanthanide(III) complexes have been reported by several researchers (*32*, *33*). The organisms used for antimicrobial studies are two bacteria, *Escherichia coli* and *Pseudomonas cepacicola*, and two fungi, *F. oxysporum* and *M. phaseolina*. The results of antimicrobial activity show that the metal complexes exhibit antimicrobial properties, and it is important to note that they show enhanced inhibitory activity compared to the parent ligands (Figures 3 and 4). A possible mode of action can be speculated in the light of chelation theory (*34*, *35*). Chelation reduces the polarity of the metal ion considerably, mainly because of the partial sharing of its positive charge with the donor group and a possible π-electron delocalization over the whole chelate ring. The lipids and polysaccharides are some important constituents of cell walls and membranes, which are preferred for metal ion interaction.

Chelation may not be the only reason for antibacterial activity. The higher activity of the metal complexes can be attributed to the involvement of a metal ion in the normal cell processes (*36*). Generally, this can be achieved through the following properties of the metal complexes:

(a) the complex should possess sufficient lipid solubility to permit transport of metal ions across membranes;
(b) the metal complexes should be highly thermodynamically stable, to reach the site without being dissociated; and
(c) they should then react as metal complexes with cells to produce a selective effect.

It has been noted that the complexes with sulfur-containing ligand (L^1H) exhibited more inhibition when compared with the oxygen-containing ligand (L^2H) complexes. The binding capacity

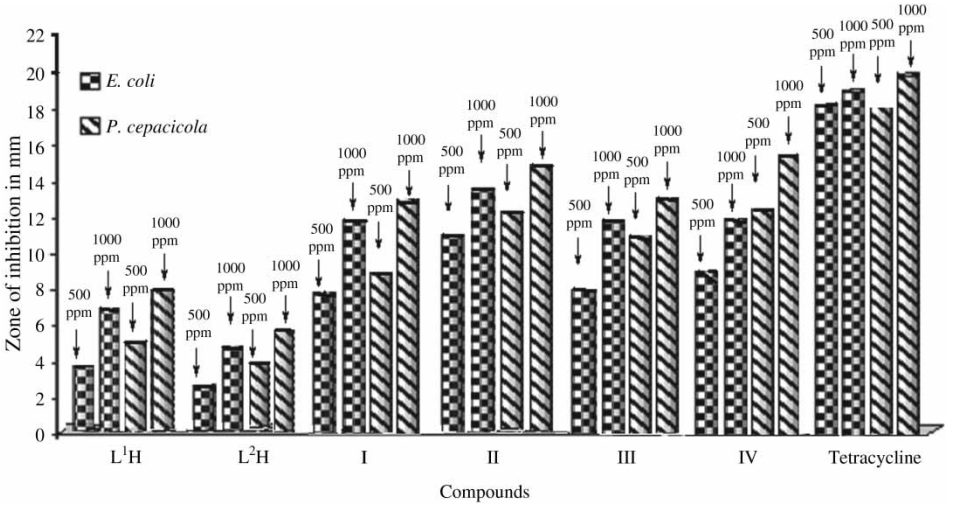

Figure 3. Antibacterial activity of the ligands and their respective complexes.

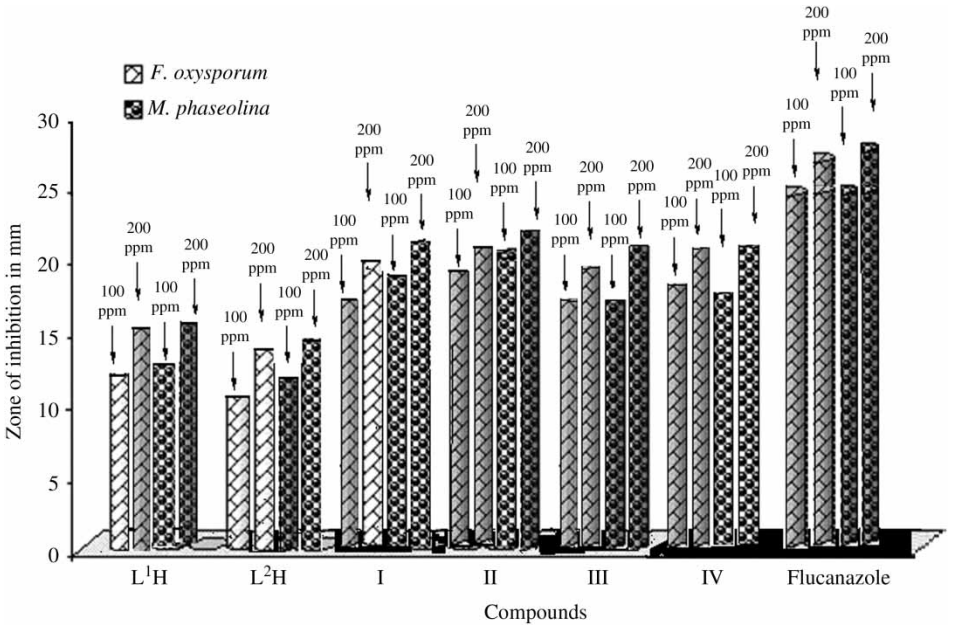

Figure 4. Antifungal activity of the ligands and their respective complexes.

of the oxygen toward the central metal ion is greater than that of the sulfur complex. As a consequence of this, the extent of the metal ion available is reduced for the display of antimicrobial activity. Factors capable of increasing the lipophilic nature and polar substituents attached to the thiophene ring are expected to enhance the antimicrobial properties.

4. Conclusion

On the basis of the analytical data and spectral studies, it has been observed that the ligands coordinated to the metal atoms in a monobasic bidentate manner and thus possess an octahedral geometry. The complexes showed better antimicrobial activities when compared with the parent ligands.

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