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Microwave Assisted Synthesis of Some Ln(III) Chloride Complexes from 4-Formyl Antipyrine Schiff base: Structural Characterization and Antimicrobial Evaluation

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ABSTRACT

The lanthanide complexes $[La(L_1)_2(Cl)_2]Cl•4H_2O$, $[Sm(L_1)_2(Cl)_2]Cl•4H_2O$, $[Eu(L_1)_2(Cl)_2]Cl•4H_2O$ and $[Dy(L_1)_2(Cl)_2]Cl•4H_2O$ were prepared by reaction between the antipyrine schiff base L_1 and some lanthanide chloride salts through microwave irradiation as a green and efficient method. The lanthanide complexes were characterised based on elemental analysis, molar conductance, FTIR, UV-Visible & ^{1}H NMR spectroscopy, along with magnetic susceptibility and thermogravimetric analysis. The antimicrobial efficacy of the synthesised compounds were assessed with bacteria- *E. coli*, *B. subtilis, A. hydrophila, K. pneumoniae*, *V. cholerae*, and *S. aureus*, as well as fungi like *A.fumigatus*, *A.flavus* and *C.albicans*. Majority of the complexes were discovered to have potential actions against the tested harmful microorganisms.

Keywords: Schiff base, Lanthanide complexes, Antibacterial activity, Antifungal activity.

INTRODUCTION

Schiff base complexes have gained significant recognition in coordination chemistry because of their versatile binding properties, diversity in structure, and potential biological activities. Due to their ability to create complexation quickly, most Schiff bases make good ligands. The coordination of a variety of metallic ions with different geometries and oxidation states may be possible with Schiff bases acting as multifunctional ligands in the interim. The formation of complexes with Schiff bases is possible for lanthanides and d-block metals alike[1].

Antipyrine[2], a well-known antipyretic and analgesic drug, serves as a key moiety in the synthesis of Schiff bases[2]. Antipyrine Schiff base complexes have gained recognition for their impressive biological properties. Antipyrine analogues demonstrate a wide spectrum of biological properties including antimicrobial[2–4], as anticancer[5], antiviral[6–8], antioxidant and anti-inflammatory properties[9,10]. Because they are used in so many diverse domains, new Schiff bases generated from Antipyrine analogues have received a lot of interest these days[11,12]. It is known that their broad-spectrum biological activities have attracted a lot of attention, particularly in medicinal chemistry[10,13]. The metal ion, the Schiff base ligand, and their structural properties all have a significant impact on the bio-activities of Schiff base complexes.

Ln(III)complexes, known for their unique optical and biological properties, are widely used in biology and medicine as diagnostic tools and fluorescence materials.[14] electroluminescent devices[15], fluorescent markers and tags in various biological systems[16,17]. In this context, special emphasis is placed on the therapeutic properties of rare earth complex drugs[17,18].

This paper explores the microwave-enhanced synthesis[19], characterization, and assessment of the bio-activities of the Ln(III) chloride complexes[2,20] of Schiff base resulted from the reaction between 2-aminophenol with 4-antipyrine carboxaldehyde. The coordination behaviour of Ln(III) ions with L_1 has been investigated through elemental analysis, thermal analysis, molar conductance, FTIR, ^{1}H-NMR ,UV-Vis spectroscopic techniques as well as magnetic susceptibility measurements. These lanthanide(III) compounds might introduce a novel class of promising antimicrobial agents.

EXPERIMENTAL

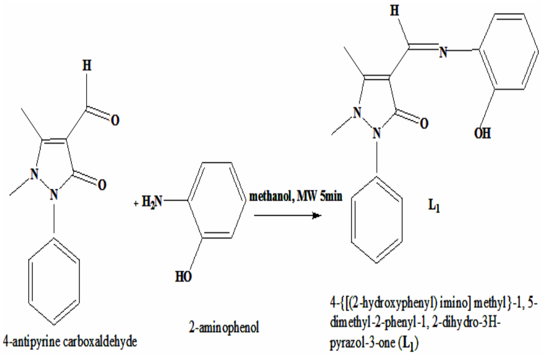
The chlorides of lanthanides, $LnCl_3$ were prepared using standard synthesis methods. Ln_2O_3 was dissolved in 60% (v/v) hot hydrochloric acid, with any residue filtered, and the filtrate was evaporated with a steam bath before the resulting rare earth chlorides were crystallized.[2] Due to their strong hygroscopic nature, the Ln(III) chloride salts were kept within a desiccator in a vacuum with phosphorus(V) oxide. 4-antipyrine carboxaldehyde (≥ 99.8%)[2] and 2-aminophenol (≥ 99%) were obtained from Sigma-Aldrich Chemie in Germany. solvents like methanol, DMF and DMSO were purchased from E.Merck, India.

Carbon, hydrogen, and nitrogen contents[2] were analysed using Elementar model Vario ELIII CHNS Analyzer[2,21]. The percentile metal content in complexes were estimated gravimetrically as Ln_2O_3 by peaceful pyrolysis method. The chloride content in the complex was estimated by Volhard[22] method. Using the Toshniwal Conductivity Bridge and a dip type conductance cell with a platinum electrode, the molar conductances of complexes were determined at room temperature DMF (10–3 M).[2] A Schimadzu IR 470 spectrophotometer was used to record the FTIR spectra of the complexes using the KBr pellet technique, and a Nicolet Magna 550 FTIR[23] instrument was used to record the far-IR spectra of metal complexes using polyethylene pellets in the 500–100 cm^{-1} region[23]. Hitachi 220 A UV-Visible double beam spectrophotometer was used to acquire the electronic spectra, which are in the 190–900 nm range.[19,23] d6-DMSO was used as the solvent in an FT--NMR Bruker AvanceIII spectrometer (400 MHz) to record the ^{1}H NMR spectra. Sherwood-Scientific Gouy Balance was used to measure Magnetic susceptibility measurements.[19,23] TG analysis of the compounds was conducted using thermal analysis system-TGA-DTA Perkin Elmer STA 6000[2] in the temperature 15°C to 900°C.[2]

Microwave-assisted synthesis of Schiff base L_1[19]

Equimolar amounts (1:1) of 4-formyl antipyrine and 2-aminophenol were dissolved in 8–10 mL methanol. The reaction mixture was thereafter subjected to 4-5 min of 350W microwave radiation. An orange-red crystalline solid formed when the solution was gradually cooled. After filtering, the solid was washed with cold methanol and crystallised from the methanol.

Yield: 85%, m.p.: 169°C. The ligand's purity was checked by TLC, infrared[2] spectrum and elemental analysis. Yield: 82%. m.p.:169°. Elemental analysis data for $C_{18}H_{17}N_3O_2$ (molecular weight: 307.35) were found (calculated) as follows: C, 70.34% (70.1%); H, 5.58% (5.28%); N, 13.67% (13.73%)[19].

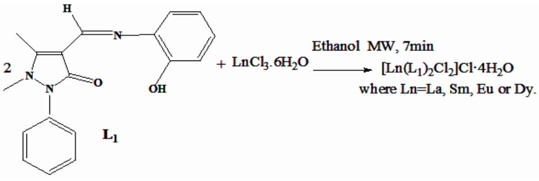


Scheme 1. Microwave-assisted Synthesis of Schiff base L_1[19]

Microwave assisted synthesis of Chloride complexes of Lanthanides $[Ln(L_1)_2(Cl)_2]Cl.4H_2O$ (where Ln = La(C1), Sm(C2), Eu(C3) and Dy(C4))[18]

A mixture of $LaCl_3•6H_2O$(0.371 g, 1 mmol) and Schiff base ligand L_1 (0.615 g, 2 mmol) was ground thoroughly to form a uniform blend. The blend was dissolved in 8-10 mL of ethanol and subjected to microwave irradiation at 350W for 7 minutes. After monitoring reaction completion by TLC, the resulting solid complex (C1) filtered, recrystallized in hot ethanol, dried over anhydrous $CaCl_2$ under vacuum.

The other complexes Sm(C2), Eu(C3), and Dy(C4)), were synthesized similarly by reacting ligand L_1 with the respective lanthanide chloride, $LnCl_3•6H_2O$(Ln = Sm, Eu, and Dy), with a metal-to-ligand ratio of 1:2 (Scheme 2).



Scheme 2. Microwave-assisted Synthesis route for Ln(III) chloride complexes of L_1

Antimicrobial studies

The antimicrobial efficacy of the compounds tested *in vitro* for six bacteria-*B. subtilis*, *A. hydrophila*, *E. coli, K. pneumoniae*, *V. cholerae* and *S. aureus* using the disc diffusion method through the agar medium, and three fungi-*C. albicans, A. fumigatus* and *A. flavus*-cultured on potato dextrose agar. Stock solution was prepared by dissolving 1 mg of each test compound into 1 mL of dimethylformamide (DMF). 5mm filter paper discs saturated in 20 microlitres of each compound placed on the seeded plates for testing. The plates were incubated at 37°C for a duration of 24 h for bacterial strains while 72 h in the case of fungal species[19]. Streptomycin (20 µg/disc) served as the reference standard for antibacterial activity, while Amphotericin-B (20 µg/disc) was used for antifungal activity. DMF was employed as the control solvent.[18,19,24].

RESULTS AND DISCUSSION

All the synthesised complex are coloured solids stable in air, non-hygroscopic, soluble in acetone, methanol, ethanol, DMF, and DMSO; it is sparingly soluble in ethyl acetate but insoluble in ether, water, benzene, and carbon tetrachloride. The physical characteristics and elemental analysis results of L_1[25] and its complexes are consistent with the calculated values (Table 1). The complexes are 1:1 electrolytes according to the molar conductance measurements in DMF (10–3 M).[24,26]. $[Ln(L_1)_2Cl_2]Cl•4H_2O$, is a general formula supported by the data, where Ln represents La(III), Sm(III), Eu(III), or Dy(III).

Table 1: Physicochemical and Molar conductivity data of L_1 & its Ln(III) complexes

Compound	Colour	Formula weight	m.p.°C	Yield(%)	Experimental (Calculated)% C	H	N	Cl	Ln	Λ_m(DMF)$^{-1}$ mol^{-1}cm^2
$L_1C_{18}H_{17}N_3O_2$	orange Red	307.35	169	85	70.1 (70.34)	5.28 (5.58)	13.73 (13.67)	-	-	-
$[La(L_1)_2Cl_2]Cl.4H_2O$ **(C1)**	Reddish Brown	931.27	318	82	45.63 (46.3)	4.75 (4.51)	8.68 (9.01)	10.8 (11.4)	14.35 (14.9)	79
$[Sm(L_1)_2Cl_2]Cl.4H_2O$ (**C2**)	Yellowish Brown	1053.96	327	81	44.1 (45.8)	4.75 (4.45)	8.58 (8.9)	10.83 (11.28)	15.35 (15.9)	81
$[Eu(L_1)_2Cl_2]Cl.4H_2O$ **(C3)**	Brown	1057.29	312	80	44.73 (45.7)	4.39 (4.4)	8.26 (8.89)	10.78 (11.2)	15.68 (16.1)	82
$[Dy(L_1)_2Cl_2]Cl.4H_2O$ **(C4)**	Yellowish Brown	1063.4	318	79	44.57 (45.24)	4.2 (4.4)	8.47 (8.79)	10.73 (11.1)	16.39 (17.02)	69

FT-IR spectra

Table 2 summarizes the characteristic FTIR bands observed for L_1 and its Ln(III) chloride complexes. Two distinctive bands may be seen in FTIR spectra of L_1 at 1651 and 1591 cm^{-1}, respectively. These bands represent the νC=O (carbonyl group stretching vibration) and the νC=N (azomethine group stretching vibration)[2,27]. In complexes C1 to C4, the carbonyl and azomethine bands are observed to shift to shorter wavenumbers, suggesting the coordination between these groups and the central lanthanide ion. The existence of two low intensity bands in the region[19] 457–467 cm^{-1} and 501–505 cm^{-1}, which are attributed to[19] Ln-N and Ln-O bond stretching[19]. L_1 also displays a broad band within the region of 3200–3423 cm^{-1}, which is assignable to stretching vibration of phenolic OH group having intramolecular hydrogen-bond[2,19,28]. In the complexes, this broad-band shifts, indicating that the phenolic oxygen participates in coordination without undergoing deprotonation[27,29,30]. Further evidence for this comes from the shifting of the phenolic C-O frequency of L_1 from 1272 cm^{-1} to lower[19,25,31] frequencies, frequencies, ranging from 1264 to 1256 cm^{-1} in all complexes.[19] Furthermore, a medium band in the 321–328 cm^{-1} region is visible in the far-IR spectra of lanthanide complexes; this band is due to v_{Ln-Cl} vibrations and indicates the establishment of Ln–Cl bond.[2,32,33] All complexes exhibit an IR spectral band in the 3050–3340 cm^{-1} range due to the stretching vibrations in water molecules[34] in the lattice which may overlap with the broad band of the phenolic OH group. Through TG analysis, it is verified that the complexes contain hydration water.[35]

Table 2: FTIR Spectral Data for L1 and Lanthanide Chloride Complexes

Compound	2$\nu_{(O-H)}$	2$\nu_{(C=O)}$	$\nu_{(C=N)}$	2$\nu_{(C-O)}$	2$\nu_{(Ln-N)}$	2 $\nu_{(Ln-O)}$	2 $\nu_{(Ln-Cl)}$
L1	3423b	1651s	1591s	1272m	-	-	-
C1	3340b	1636s	1577s	1264m	459w	501m	326m
C2	3348b	1641s	1573s	1258m	467w	502m	328m
C3	3343b	1639s	1575s	1256m	457w	502m	321m
C4	3341b	1636s	1568s	1261m	457w	504m	321m

s: strong, m: medium, b: broad

Electronic spectral and magnetic moment data

Table 3 summarizes the major bands discovered in the Electronic spectra of the L_1 and C1 to C4[19]. The ligand L_1 exhibits strong absorption bands at 294 and 375 nm, which are associated with the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ electronic transitions in the azomethine linkage and carbonyl group, respectively. Both of these transitions are seen to be somewhat red-shifted in these complexes, suggesting that azomethine nitrogen and carbonyl oxygen have coordinated with the lanthanide ion[19,32]. Along with the prominent ligand bands, weak f-f transitions are also observed in the spectra of complexes of Sm(III), Eu(III), and Dy(III)ions.[17,19,36] Table 3 provides the prominent f-f[19] transition with tentative assignments[2,19].

Table 3 also shows the magnetic moment values of the complexes. As anticipated, lanthanum complex(C1) is diamagnetic, while the other complexes display paramagnetic behaviour. The magnetic moment values for complexes C1 to C4 are close to the Van Vleck values, suggesting[37] that the lanthanide ions' 4f electrons are largely shielded from the chemical environment[27].

Table 3: Electronic Spectral data (DMF)and magnetic moment values of L_1 and Ln(III) complexes C1–C4[20]

Compounds	Absorption bands (nm)	Tentative assignments	μ_{eff} (BM)
L1	(294, 375)	$(\pi\rightarrow\pi^*,\ n\rightarrow\pi^*)$	-
C1	(308, 383)	$(\pi\rightarrow\pi^*, n\rightarrow\pi^*)$	-
C2	(323, 378), 417	$(\pi\rightarrow\pi^*, n\rightarrow\pi^*)$, $^6H_{5/2}\rightarrow(^6P, ^4P)_{5/2}$	1.23
	442, 476, 498	$^6H_{5/2}\rightarrow{}^4M_{17/2}$, $^6H_{5/2}\rightarrow{}^4I_{11/2}$ $^6H_{5/2}\rightarrow{}^4M_{15/2}$	
C3	(314, 374), 531	$(\pi\rightarrow\pi^*, n\rightarrow\pi^*)$, $^7F_0\rightarrow{}^7D_1$	3.42
C4	(308, 378), 437, 469	$(\pi\rightarrow\pi^*, n\rightarrow\pi^*)$, $^6H_{15/2}\rightarrow{}^4G_{11/2}$, $^6H_{15/2}\rightarrow{}^4F_{9/2}$	10.08

^{1}H NMR spectra

^{1}H NMR spectrum of L_1 was obtained in DMSO-d6 (Fig. 1).It showed peaks in the range in the range 8.76ppm and 8.3ppm corresponding to phenolic hydroxyl and azomethine protons respectively.[2] The spectrum of L_1 also shows as sharp singlet (3H) at 2.72 and 3.32 of the groups =C-CH_3 and N-CH_3 of the pyrazolone respectively. The peaks of the azomethine and phenolic hydroxyl protons in the ^{1}H NMR spectra of lanthanum complex C1 show a slight downfield shift, indicating that the azomethine nitrogen and oxygen atoms of the phenolic hydroxyl group coordinate without deprotonation.[17,27]

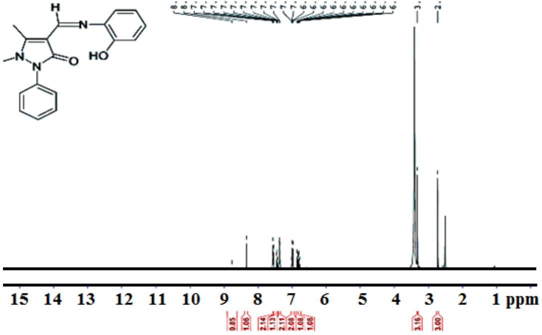


Fig. 1. ^{1}H NMR spectrum of ligand L_1

Thermogravimetric analysis

The thermal behavior of complexes C1 to C4 were examined using thermogravimetric analysis over the temperature ranging 30–900°C under a nitrogen atmosphere[35]. All the complexes exhibit similar decomposition patterns in three main stages. Table 4 presents the TG and DTG data for complexes C1 to C4.

In complex C1, the initial decomposition stage takes place between 52°C and 103°C, where four lattice water molecules are lost, resulting in an estimated mass reduction of 8.1%. The second stage, occurring between 207°C and 534°C, involves the breakdown of one ligand molecule, leading to a weight loss of around 31.8%. The third stage, spanning from 538°C to 778°C, agrees to decomposition of the remaining ligand molecule, with a reduction in weight of approximately 31.2%.[38], leaving anhydrous lanthanum(III) chloride as the residue above 778°C.[39,40] All other lanthanide complexes, C2 to C4, show similar thermal behavior with three stages of decomposition, ultimately yielding anhydrous lanthanide chloride as the final residue at approximately 800°C.

Table 4: Thermal Decomposition data of Complexes C1 to C4

Complex	Stage of decomposition	TG Temperature Range (°C)	DTG peak (°C)	Mass loss % Observed (calculated)	Assignments	Final Residue (%)
(C1)	I	52-103	73	8.1(7.7)	Four lattice water	$LaCl_3$
	II	207-534	289	31.8(32.8)	One ligand molecule	27.6(26.7)
	III	538-778	541	32.5(32.8)	Second ligand molecule	
(C2)	I	56-102	76	8.1(7.6)	Four lattice water	$SmCl_3$
	II	212-464	302	32.4(32.6)	One molecule of L_1	27.8(27.2)
	III	469-752	516	31.7(32.6)	Second molecule of L_1	
(C3)	I	53-103	78	8.1(7.6)	Four lattice water	$EuCl_3$
	II	217-472	308	32.1(32.5)	One molecule of L_1	28.2(27.4)
	III	475-748	498	31.9(32.5)	Second molecule of L_1	
(C4)	I	46-106	74	8.1(7.5)	Four lattice water	$DyCl_3$
	II	234-506	427	31.8(32.1)	One ligand molecule	
	III	508-778	523	31.6(32.1)	Second ligand molecule	28.6(28.2)

Based on the results from the analytical results, a tentative structure (Fig. 2) of Ln(III)[19] chloride complexes, $[Ln(L_1)_2Cl\ ]Cl{\bullet}4H_2O$ (where Ln=La, Sm, Eu, and Dy),with a coordination number eight has been proposed.

$[Ln\ (L_1)_2Cl_2]Cl.4H_2O$ (where Ln = La, Sm Eu and Dy)

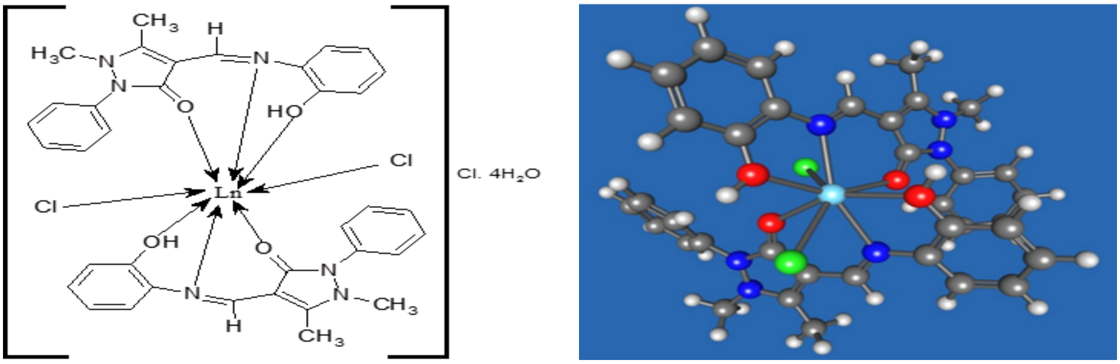


Fig. 2. Proposed Structure of (C1 to C4)

Biological studies

Antibacterial activity

All of the tested compounds demonstrated significant biological activity against various bacteria. The results, detailed in Table 5, show that the complexes exhibited notably superior activity against *V. cholerae*, *E. coli* and *A. hydrophila*, with inhibition zones significantly larger than those observed for the parent ligand and the standard drug, streptomycin[19]. Complexes C1 and C4 displayed exceptional activity in opposition to *V. cholerae*, *Escherichia coli* and *A. hydrophila* with inhibition zones of 30 mm or greater. Notably, complex C4 exhibited the largest inhibition zone of 34 mm against *V. cholerae*. The complexes demonstrated moderate activity against *S.aureus* and *B. subtilis*[25] but showed minimal activity against *K. pneumoniae*.

Table 5 presents the zones of inhibition of the compounds against various microorganisms. Fig. 3a shows the image of inhibition zones of the tested compounds against *A. hydrophila*, while Fig. 3b shows a bar diagram representing the antibacterial activity of L1 and complexes C1 to C4. Chelation, which raises the lipophilic nature of the central metal atom. This makes it easier for the metal to get through the lipid layers of the bacteria,leading to more aggressive destruction and limiting further microbial growth.[41,42]. This could be the reason for the increased bioactivity that lanthanide complexes showed in comparison to the free ligand.[43]

Antifungal activity

Regarding antifungal activity, all of the chloride complexes and the ligand L_1 exhibit very strong activity with a large inhibition zone of 19-26mm against *C. albicans*. Among these complexes, C4 exhibited the highest inhibition zone of 26mm against this fungus much higher than the standard drug Amphotericin B. The complexes C1 and C3 only showed against *A. flavus* and *A. fumigatus* with an inhibition zone of 11-14mm[44,45]. The observations are detailed in Table 5 and visually depicted in Figure 3c.

Table 5: Average inhibition zone (mm) of antimicrobial activities for L_1 and its Ln(III) Chloride complexes[19]

Compound	Inhibition zone (mm)								
	Activity against bacteria						Activity against fungi		
	E. coli	*K. pneumoniae*	*V. cholerae*	*A. hydrophila*	*S.aureus*	*B. subtilis*	*C. albicans*	*A.flavus*	*A.fumigatus*
L_1	-	9	-	10	-	10	21	-	-
C1	32	10	30	30	15	13	22	14	11
C2	24	8	15	12	8	9	19	-	-
C3	33	-	25	23	-	10	23	14	11
C4	32	8	34	22	11	15	26	-	-
DMF	0	0	0	0	0	0	0	0	0
Streptomycin (Std.)	18	20	6	18	21	23	-	-	-
Amphotericin-B	-	-	-	-	-	-	18	16	15

DMF(negative control), Streptomycin: (standard antibacterial drug) and Amphotericin-b(standard antifungal drug)[2,19]

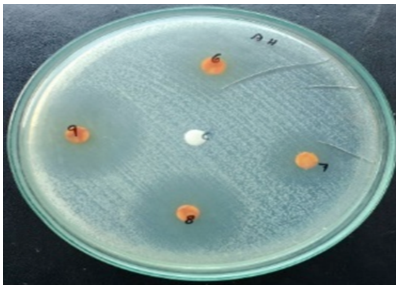


Fig. 3a. Image showing Inhibition zone of complex against *A. hydrophila*

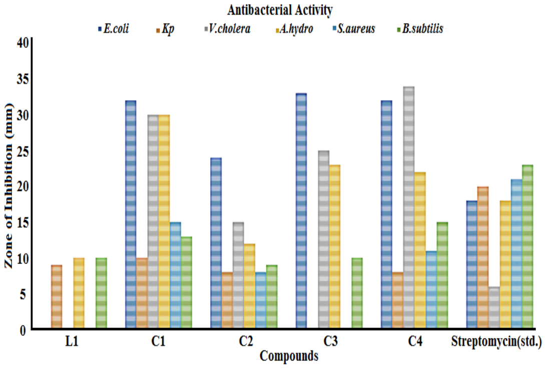


Fig. 3b. Graphical depiction of of L_1 and complexes C1-C4

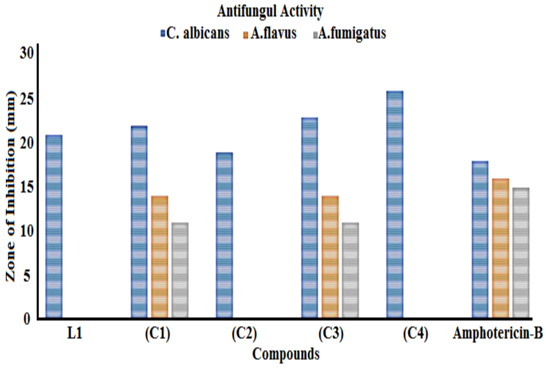


Fig. 3c. Graphical depiction of the antifungal activity of L_1 and complexes C1–C4

CONCLUSION

In this study, some Ln(III) chloride complexes of antipyrine schiff base L_1, formulated as $[Ln(L_1)_2Cl_2]Cl\cdot4H_2O$ (where Ln=La, Sm, Eu, and Dy), were synthesized by microwave irradiation method. Physicochemical and various spectral techniques were used to elucidate the structure of complexes. The antimicrobial properties of L_1 and the complexes were assessed. The metal complexes showed a remarkable improvement in antimicrobial activity concerning the free ligand. With further investigation into their biological properties, these complexes could potentially serve as new antibacterial agents. Notably, the Dysprosium complex exhibited exceptional activity against the majority of the microorganisms that were examined.

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Conflicts of interest

No possible conflicts of interest were declared by the writers.

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