

**SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF SOME LANTHANIDE (III) COMPLEXES WITH A TRIDENTATE ONO DONOR SCHIFF BASE LIGAND****E. M. Jincy*, P. K. Rejimon** & M. K. Muraleedharan Nair****

* Department of Chemistry, Sree Neelakanta Government Sanskrit College, Pattambi, Palakkad, Kerala

** Postgraduate & Research Department of Chemistry, Maharaja's College, Ernakulam, Kerala

Cite This Article: E. M. Jincy, P. K. Rejimon & M. K. Muraleedharan Nair, "Synthesis, Characterization and Antimicrobial Studies of Some Lanthanide(III) Complexes with a Tridentate ONO Donor Schiff Base Ligand", *International Journal of Applied and Advanced Scientific Research*, Volume 2, Issue 2, Page Number 246-251, 2017.**Abstract:**

Some new lanthanide(III) complexes- La(III), Ce(III), Pr(III) and Nd(III) have been synthesised from Schiff base ligand 4-[(2-hydroxyphenyl)imino]methyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (L_1) whose precursors are 4-antipyrine carboxaldehyde and 2-aminophenol. The metal to ligand ratio (1:2) and the general formula $[Ln(L_1)_2(NO_3)_2]NO_3$ were established by elemental analysis, conductivity measurements, spectral techniques such as IR, UV-Visible, 1H NMR as well as magnetic susceptibility measurements. L_1 behave as a neutral tridentate (ONO) ligand and Ln(III) ion display coordination number eight in all complexes. The Schiff base and complexes were screened for their *in vitro* antimicrobial activities against selected human pathogenic bacteria by agar disc diffusion method. Most of the synthesized complexes were found to be more potent bactericides than the corresponding free ligand.

Key Words: Schiff Base, 4-Antipyrine Carboxaldehyde, Lanthanide (III) Complexes, Spectral Techniques, Antimicrobial Activity & Disc Diffusion**Introduction:**

Antimicrobial resistance is become a global concern that has significant impacts on human health and well-being. Drastic global change has given a momentum to discover compounds with diverse chemical structures and novel mechanism of action [1-4]. Schiff base compounds have been shown to be promising leads for the design of efficient antimicrobial agents as a result of their broad range of biological activities. Rare earth complexes with Schiff base ligands have been extensively investigated due to their structural diversities, interesting coordination behavior and wide range of biological applications [5-7]. In the present work, we have synthesised some Lanthanide complexes with tridentate (ONO) Schiff base L_1 . The coordination behavior of lanthanide(III) ions with L_1 have been studied using elemental analysis, molar conductance, IR, UV-Visible, 1H -NMR and magnetic susceptibility measurements. The antimicrobial efficiency of these complexes against seven different microorganisms has also been studied.

Experimental Materials and Methods:

All chemicals employed in this work were of analytical reagent grade. 2-aminophenol and 4-antipyrine carboxaldehyde were purchased from Sigma Aldrich and nutrient agar from Himedia. Rare earth nitrates $Ln(NO_3)_3 \cdot 6H_2O$ were prepared from Ln_2O_3 (>99.95%) [8]. Schiff base and complexes were analyzed for carbon, hydrogen and nitrogen using Heracus CHN rapid analyzer. All complexes were analyzed for their metal content by standard method [9]. The molar conductivity of the complexes in DMF ($10^{-3}M$) was measured using Elico CM-180 conductivity meter with a dip type platinum electrode (cell constant 0.986 cm^{-1}). The IR spectra of ligand (L_1) and complexes were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ on Shimadzu IR470 spectrophotometer (KBr discs). The electronic spectra in the range $190\text{--}900\text{ nm}$ were recorded using Shimadzu UV-160A. The 1H NMR spectra were recorded on a Bruker DRX-500 spectrometer using $DMSO-d_6$ as solvent. The magnetic susceptibility measurements were carried out on a Sherwood Scientific Gouy Balance. The antimicrobial activity of these complexes against five Gram-negative bacteria -*Escherichia coli*, *Salmonella typhimurium*, *Aeromonas hydrophila*, *Vibrio cholerae*, *Klebsiella pneumonia* and two Gram- positive species *Staphylococcus aureus* and *Bacillus subtilis* were carried out by disc diffusion method.

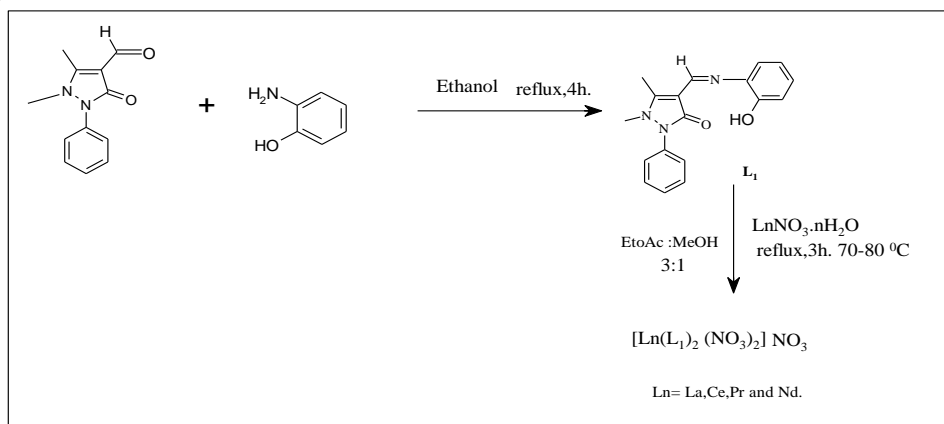
Synthesis of the Schiff base 4-[(2-hydroxyphenyl)imino]methyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (L_1)

4-Antipyrine carboxaldehyde (0.43g) was dissolved in ethanol (20mL) and mixed with solution of 2-aminophenol (0.22 g) in ethanol (20mL). The 1:1 mixture was refluxed on a boiling water bath for about 4 hours, concentrated and the orange red compound was separated by adding few drops of cold water (**Scheme 1**). It was filtered and washed with cold ethanol followed by ether and dried over anhydrous $CaCl_2$. The purity of the ligand was checked by TLC, IR and 1H NMR spectra and elemental analysis. Yield: 71%, mp $169^\circ C$.

1H NMR: (d_6 - $DMSO$) (δ , ppm): 8.76(s, 1H, phenolic), 8.3 (s, 1H, -CH=N-), 6.7-7.6(m, -Ph) 3.32(s, 3H, -N-CH₃), 2.72 (s, 3H, =C-CH₃). IR (cm^{-1} , KBr); ~ 3420 (v OH), 1651 (v C=O), 1591 (v C=N), 1272 (v ph-O). Anal. Calcd for $C_{18}H_{17}N_3O_2$ (307.35) C, 70.34; H, 5.58; N, 13.67. Found: C, 70.1, H, 5.28; N 13.73%.

Synthesis of Lanthanide Complexes (A1)–(A4)

All the Ln(III) complexes (A1)–(A4) of the Schiff base L_1 were prepared by the following general method (Scheme1). A solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, Ln = La, Ce, Pr and Nd) in 10 mL methanol was added to the ligand, L_1 (2 mmol) in 40 mL ethyl acetate, stirred and refluxed on a magnetic stirrer at 70–80°C for three hours. The precipitated solid complex was washed with hot ethyl acetate followed by ether and dried in vacuum over P_4O_{10} .



Scheme 1: Synthesis route for the synthesis of Schiff base ligand L_1 and complexes A1 to A4

In Vitro Antibacterial Activity:

The bacterial cultures used in this study - *Staphylococcus aureus*, *Escherichia coli*, *Aeromonas hydrophila*, *Vibrio cholerae*, *Klebsiella pneumonia*, *Salmonella typhimurium* and *Bacillus subtilis* were obtained from department of Microbiology and Biochemistry, School of Marine Sciences, Cochin University of Science and Technology, Kerala, India. The microbiological culture media -nutrient agar and nutrient broth were obtained from Himedia Laboratories Private Limited. In vitro antibacterial activity were studied by agar disc diffusion method [10]. Several discrete colonies of each of the test organisms in a normal saline and turbidity of the suspension were compared with 0.5Mc Farland standards to obtain 10^6 to 10^8 CFU/mL. The standardised inoculums of bacterial suspension were uniformly spread onto nutrient agar plates using a sterile cotton swab. The plates were dried for 15 minutes and then used for the sensitivity test. 1mg of each of the test compounds were separately dissolved in 1mL dimethylformamide (DMF) to get stock solution. The filter paper disc of 5.0 mm diameter which was impregnated with 20 μL of the solution of each of the test compound in DMF. Then the discs were placed on the on the previously seeded agar plates using sterile forceps. The plates were allowed to stand for 30 minutes to aid diffusion and then incubated at 37°C for 24 hours and the diameter zones of inhibition (DZI) of bacterial growth around each disc was measured.

Results and Discussion:

Characterization of Ligand and Complexes:

The details of physicochemical data of the synthesized complexes are given in Table 1. The complexes are soluble in methanol, ethanol, DMSO and DMF and insoluble in benzene, carbon tetrachloride and nitrobenzene. The molar conductance measurements values for complexes, (A1) to (A4), in DMF (10^{-3}M) reveal that all complexes behave as 1:1 electrolytes [11]. Hence the formula of complexes may be represented as $[\text{Ln}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$. Where Ln = La, Ce, Pr and Nd (Table 1).

Table 1: Analytical and Physical data of the metal complexes

Complex	Colour	Mol. Weight	mp °C	Yield (%)	% found(Calculated)				$^*\Lambda_m(\text{DMF})$ $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$
					C	H	N	Ln	
$[\text{La}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A1)	Brown	936.61	301	62	46.43 (46.02)	3.27 (3.6)	12.86 (13.42)	14.65 (14.78)	74.4
$[\text{Ce}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A2)	Brown	940.82	306	69	45.43 (45.96)	3.16 (3.6)	12.7 (13.4)	14.27 (14.89)	89.8
$[\text{Pr}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A3)	Yellowish brown	941.61	331	61	46.37 (45.9)	3.34 (3.6)	12.92 (13.4)	14.71 (14.96)	87.8
$[\text{Nd}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A4)	Brown	944.94	306	63	45.37 (45.76)	3.23 (3.63)	13.0 (13.34)	14.8 (15.3)	85.2

* 10^{-3}M solution

Infrared Spectra:

The selected FTIR spectra of the Schiff base ligand L_1 and its lanthanide(III) nitrate complexes are listed in Table 2. The IR spectra of the Schiff base L_1 shows two strong bands at 1651cm^{-1} and 1591cm^{-1} attributed to the C=O and $-\text{CH}=\text{N}-$ stretching vibrations. In all complexes $\nu(\text{C}=\text{O})$ bands are red shifted to about $1633\text{--}1639\text{cm}^{-1}$ and $\nu(-\text{CH}=\text{N}-)$ bands are blue shifted to $1598\text{--}1600\text{cm}^{-1}$, suggesting coordination of both groups to the metal ion. This is supported by the appearance of non-ligand bands at $\sim 453\text{--}462\text{cm}^{-1}$ due

to the M-N vibrations and bands at $\sim 503\text{ cm}^{-1}$ are attributed to M-O vibrations. The presence of a broad band in the range $3423\text{--}3100\text{ cm}^{-1}$ in the ligand spectrum corresponds to the stretching frequencies of aromatic hydroxyl substituent. In all the complexes these OH band is also present at $3050\text{--}3373\text{ cm}^{-1}$ with an increase in intensity indicates the coordination of phenolic oxygen to the metal ion without deprotonation. This is further confirmed by the shift of phenolic C-O frequency at 1272 cm^{-1} of the ligand to lower frequencies in the range $1260\text{--}1263\text{ cm}^{-1}$ in these complexes [12-13]. Thus L_1 acts as a neutral tridentate ligand coordinating through carbonyl oxygen, imine nitrogen and phenolic oxygen. The complexes exhibit vibrational frequencies characteristic of both coordinated and uncoordinated nitrate ions. A very strong band at $\sim 1384\text{ cm}^{-1}$ and a medium band at $834\text{--}846\text{ cm}^{-1}$ are attributed to the ν_3 and ν_2 vibrations respectively of ionic nitrate of D_{3h} symmetry. The medium band at $\sim 1427\text{ cm}^{-1}$ and $\sim 1300\text{ cm}^{-1}$ are due to ν_4 and ν_1 vibrations of coordinated nitrate group of C_{2v} symmetry. Since $(\nu_4\text{--}\nu_1)$ is $\sim 120\text{ cm}^{-1}$, the nitrate ion is coordinated in a monodentate fashion [14].

Table 2: Important IR bands (cm^{-1}) of Schiff base L_1 and its metal complexes

Compound	$\nu(\text{O-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	Coordinated (NO_3)			Ionic (NO_3)		$\nu(\text{Ln-O})$	$\nu(\text{Ln-N})$
					ν_4	ν_2	ν_1	ν_3	ν_2		
L_1	3423b	1651s	1591s	1272m	-	-	-	-	-	-	-
(A1)	3348b	1635s	1599s	1263m	1429s	1024m	1314m	1384s	836m	502w	457w
(A2)	3355b	1633s	1598s	1260m	1427s	1031m	1304m	1382s	846m	503w	462w
(A3)	3367b	1637s	1598s	1263m	1432s	1024m	1311m	1384s	836m	503w	457w
(A4)	3373b	1639s	1600s	1260m	1431s	1026m	1313m	1382s	834m	504w	453w

^1H NMR spectra

^1H NMR spectra of diamagnetic lanthanum complex (A1) was recorded in $\text{DMSO-}d_6$ and it was examined in comparison with that of the ligand L_1 (Table. 3)

Table 3: ^1H NMR Spectral Data of the Ligand L_1 and its La(III) complex (A1)

Compound	=C- CH_3	N- CH_3	Ar-H	-N=CH	Phenolic -OH
L_1	2.72,s	3.32,s	6.7-7.5,m	8.3,s	8.76, b
(A1)	2.52,s	3.48,s	6.4-7.6,m	8.4,s	8.8, b

In the ^1H NMR spectrum of (A1), the peaks corresponding to the phenolic hydroxyl and azomethine protons are slightly downfield shifted compared to the free ligand L_1 . This shift confirms the coordination of nitrogen atom of the azomethine and oxygen atoms of the phenolic hydroxyl group without deprotonation which is consistent with the IR spectral data. Moreover, the multiplet appearing in the range $\delta=6.7\text{--}7.5$ ppm in the ligand L_1 owing to aromatic ring protons shifted slightly upfield to $\delta=6.4\text{--}7.6$ ppm in the complex[8,13]. This suggests change in the overall chemical environment of the ring protons as a result of coordination with the lanthanum ion

UV-Visible Spectra:

The UV-Visible absorption spectral data of the Schiff base ligand L_1 and complexes (A1) to (A4) were carried in DMF (10^{-5}M) at room temperature at room temperature in the range $190\text{--}800\text{ nm}$ (Fig.1) and presented in the Table 4.

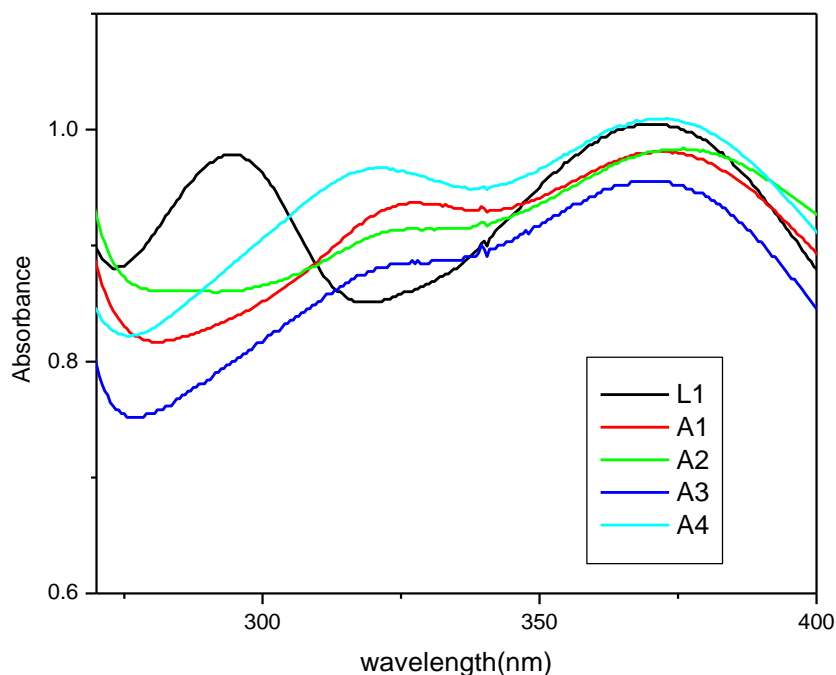


Figure 1: UV-Visible spectra of L_1 and complexes (A1) to (A4)

The electronic spectra of ligand L_1 shows two absorption maxima at 294 and at 375 nm corresponds to $\pi \rightarrow \pi^*$ transitions of azomethine group and $n \rightarrow \pi^*$ transitions of carbonyl group of free ligand. In all the complexes, $n \rightarrow \pi^*$ band is blue shifted to 369-360 nm region while the $\pi \rightarrow \pi^*$ band is red shifted to 321-327 nm [10, 11]. These observations are the consequences of coordinate bond formation with ligand donor atoms. In the visible region, The absorption spectra for weak $f-f$ transitions are observed in the case of Pr(III) and Nd(III), complexes and the tentative assignments for which are given in the table 4. In the absorption spectrum of $[\text{Pr}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A3), three transitions are observed at 487 nm, 476 nm and 449 nm may be assigned to ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ transitions respectively. The spectrum of $[\text{Nd}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A4), exhibit three bands at 472 nm, 524 nm and 582 nm supposed to be arise from ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{11/2}$, ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{9/2}$ and ${}^4\text{I}_{9/2} \rightarrow {}^2\text{G}_{7/2}$, ${}^4\text{G}_{5/2}$, respectively [13,15].

Table 4: The UV-Visible absorption spectra and magnetic moment data of Schiff base ligand L_1 and its complexes A1 to A4.

Compound	λ_{max} (nm)	Band Assignment	Magnetic Moment μ (BM)
L_1	294 375	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
$[\text{La}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A1)	322 363	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
$[\text{Ce}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A2)	321 360	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	2.48
$[\text{Pr}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A3)	449 476 487 327 365	${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	3.42
$[\text{Nd}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$ (A4)	472 524 582 323 369	${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{11/2}$ ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{9/2}$, ${}^4\text{I}_{9/2} \rightarrow {}^2\text{G}_{7/2}$, ${}^4\text{G}_{5/2}$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	3.53

Magnetic Susceptibility Measurements:

The magnetic moments data are listed in Table 4. The lanthanum complex (A1) was found to be diamagnetic as expected while all other complexes exhibit paramagnetic behavior. The magnetic moment data of the complexes indicate that the magnetic moment values agree with those Van Vleck values. The results of magnetic moment determinations indicate the non-involvement of $4f$ electrons of the lanthanide ions in their complexes owing to the shielding of the $5s$ and $5p$ electrons [16].

From these studies, a coordination number eight may be assigned to the metal ion in all these complexes. The tentative structure of the metal complexes (A1) to (A4) is given in Figure 2.

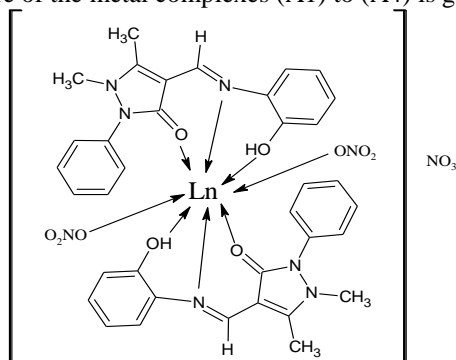


Figure 2: Tentative structure of complex $[\text{Ln}(\text{L}_1)_2(\text{NO}_3)_2]\text{NO}_3$, where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd

In Vitro Antibacterial Activity:

The synthesized Schiff base and their corresponding Ln(III) complexes were screened for biological activity against five Gram-negative bacterial species *Escherichia coli*, *Salmonella typhimurium*, *Aeromonas hydrophila*, *Vibrio cholerae*, *Klebsiella pneumonia* and two Gram-positive species *Staphylococcus aureus* and *Bacillus subtilis* by disc diffusion method [10]. The size of inhibition zone (mm) used for the estimation of antibacterial activity of ligand and complexes is given Table 5. DMF was used as control and streptomycin as a standard drug against respective bacteria. The ligand L_1 exhibited moderate activity against four of the tested bacteria - *S.typhimurium*, *K.pneumonia*, *A.hydrophila* and *B. subtilis* having inhibition zone in the range 9-13 mm. The metal complexes exhibited better antibacterial activity when compared to the parent Schiff base with only slight exception in few cases. The La(III) complex (A1) showed highest activity against *E.coli* and

S.typhimurium with an inhibition zone of 19 mm and 21mm respectively. Against *V.cholerae* the complexes (A1), (A3) and (A4) showed appreciable activity with zone of inhibition in the range 13-17 mm and the maximum inhibition exhibited by Nd complex (A4). All the complexes exhibited moderate activity against *K.pneumonia* *A.hydrophila* and *B. subtilis* with a zone of inhibition of 8-15 mm. Complexes (A1) and (A3) showed moderate activity against *S.aureus*. A graph showing the activity of ligand and complexes is depicted in Figure 3.

The Schiff base ligand L_1 is biologically active and its activity arise from the presence of imine group which is important in elucidating the mechanism of transformation reaction in biological systems. The higher activity of the complexes compared to free ligand may be attributed to chelation which reduces polarity of the metal ion by partial sharing of the positive charge with donor atoms of the ligand. Therefore, chelation increases the lipophilic nature of the central metal atom, which enhances the penetration of the complexes into the lipid membrane of the cell wall of microorganism, thereby raising the activity of the complex and restricts further growth of the organism [17-19].

Table 5: Antibacterial Activity Results of L_1 and complexes A1 – A4

Compound	Diameter of inhibition zone (DIZ) (mm)						
	Tested Bacteria						
	Gram(-) Bacteria					Gram(+) Bacteria	
	<i>E.coli</i>	<i>S.typhi</i>	<i>V.cholerae</i>	<i>A.hydrophila</i>	<i>K.pneumonia</i>	<i>S.aureus</i>	<i>B.subtilis</i>
L_1	-	13	-	10	9	-	10
[La(L_1) ₂ (NO ₃) ₂]NO ₃ (A1)	19	21	15	14	12	14	11
[Ce(L_1) ₂ (NO ₃) ₂]NO ₃ (A2)	12	15	-	15	12	-	10
[Pr(L_1) ₂ (NO ₃) ₂]NO ₃ (A3)	14	18	13	12	11	10	8
[Nd(L_1) ₂ (NO ₃) ₂]NO ₃ (A4)	8	14	17	9	10	-	10
DMF	0	0	0	0	0	0	0
Streptomycin(Std.)	18	20	5	18	21	20	23

Key to interpretation: (-)=no inhibition zone; 1–5 mm = less active; 5–10 mm = minimum activity; 10–15 mm = moderate activity; >15= high activity

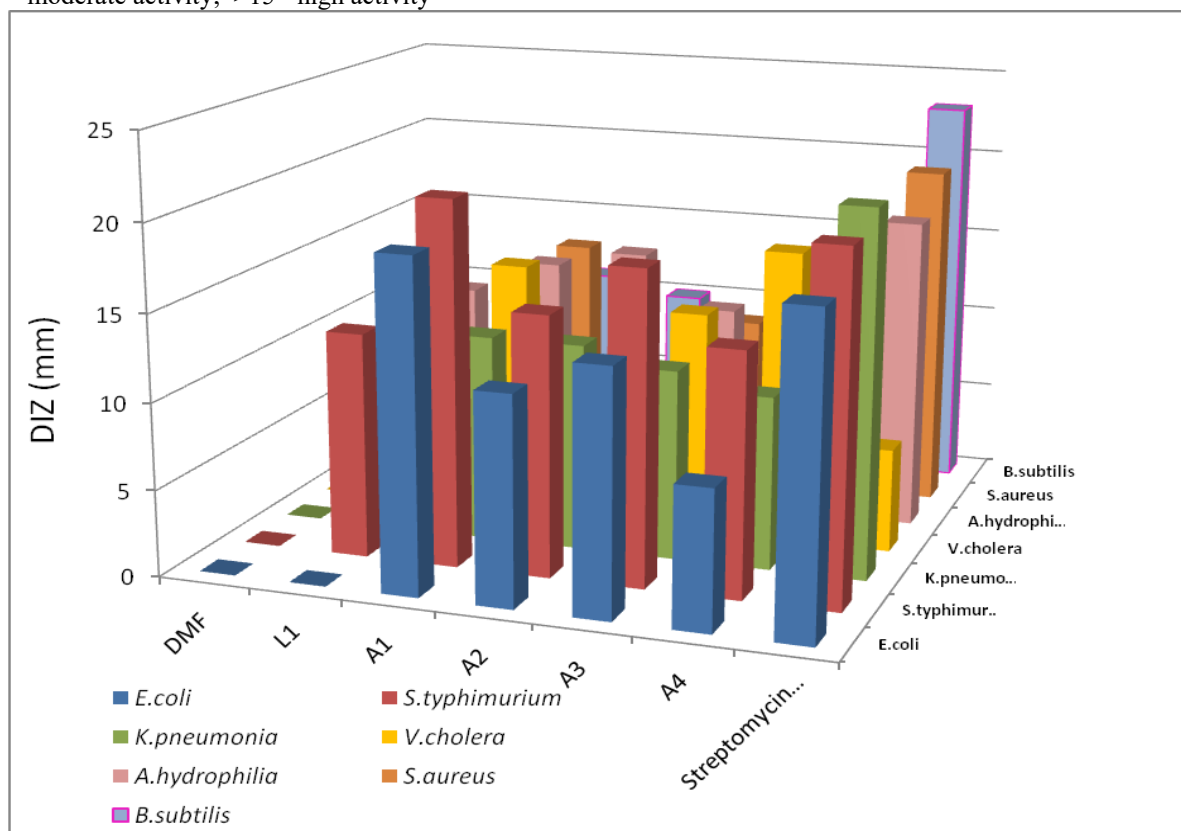


Figure 3: Antibacterial Activity of L_1 and complexes A1-A4

Conclusion:

We have successfully synthesized La(III), Ce(III), Pr(III) and Nd(III) complexes of the tridentate ligand L_1 having general formula $[Ln(L_1)_2(NO_3)_2]NO_3$ and were characterized by variety of physicochemical and

spectral methods. The lanthanides display a coordination number eight in these complexes. The ligand and the complexes were analyzed for their antibacterial activities. Antibacterial results show that most of the synthesized complexes possess a good antibacterial activity against tested bacteria than the corresponding ligand.

Acknowledgement:

The author (JEM) express sincere thanks to UGC, Delhi for financial support and Govt. of Kerala for granting deputation, SAIF, CUSAT Kochi, Mahatma Gandhi University, Kottayam and Department of Chemistry, Maharaja's College, Ernakulum for providing instrumental facility.

References:

1. M.Z. David & R.S. Daum, ClinMicrobiol Rev., 2010, 23, 616 -687.
2. H. de Lencastre, D. Oliveira & A. Tomasz., A. Current Opin Microbiol., 2007, 10, 428-435.
3. P. Przybylski, A. Huczynski, K. Pyta, B. Brzezinski, F. Bartl, Curr. Org. Chem; 2009,13, 124-1483
4. S.P. Anand, A. Doss V. Nandagopalan, Inter J App Biol Pharm Tech., 2011, 2, 453-456.
5. L E Nui, Y Yang, XH Qi, X Liang, Syn. Met-Org.Nano-Met. Chem., 2009, 39, 1-5.
6. K. Mohanan, R. Aswathy, L.P.Nitha, N.E.Mathews , B. S Kumari J. Rare Earths; 2014,32,379-388.
7. Y.M .Song a, J.P. Xu, L. Ding, Q.Hou, J.W. Liu, Z.L. Zhu, J. Inorg. Biochem; 2009, 103 396-400.
8. M.K.M.Nair and P.K.Radhakrishnan, Polyhedron, 1993, 12, 1227-1230.
9. A. I. Vogel, A text book of Quantitative Inorganic analysis ELBS, London 3rd Edn, 1961.
10. Atta-ur-Rahman, Choudhary M.I, Thomsen, WJ;Bioassay Techniques for Drug Development. The Netherlands: Harwood Academic Publishers; 2001, 142-143.
11. W. J. Geary, Coord. Chem. Rev., 1971,7,81.
12. Z.A.Taha, AM Ajlouni, W Al Momani, AA Al-Ghzawi, Spectrochimica Acta Part A; 2011,81, 570 -577
13. G. Ajithkumar, P. K. Radhakrishnan, Synth. React. Inorg. Met.-Org. Nano-Metal Chem., 2002, 32, 831-842.
14. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, part B, fifth ed., Wiley, 1997.
15. W. T. Carnall, K. A. Gschneidner, Jr., L. R. Eyring (Eds.),Handbook on the Physics and Chemistry of Rare Earths, North Holland, Amsterdam;1979, 3,171.
16. J. H. Van Vleck and N. Frank, Phys. Rev., 1929, 34, 1494 -1496.
17. Z.H. Chohan, A. Munawar, C.T. Supuran, Met.-Based Drugs; 2001, 8, 137 -143.
18. A. Kulkarni, S.A. Patil, P.S. Badami, Eur. J. Med. Chem; 2009, 44, 2904 -2912.
19. Z.H. Chohan, H.A. Shad, J. Enz. Inhib. Med. Chem., 2008, 23, 369-379.