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Synthesis, Characterization and Antimicrobial Studies on Some Trivalent Lanthanide Metal Complexes with a Bidentate O, N Donor Mixed Ligands

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Abstract: ***A new divalent mixed ligand Schiff base and some lanthanide (III) complexes such as La (III), Pr(III), Ce(III), Nd(III), Gd(III) Sm(III), Dy(III) and Tb(III) complexes were synthesized derived from condensation of salicylaldehyde with 4-methoxyphenylamine and 2-hydroxy-3-methoxybenzaaldehyde with 4-methoxyphenylamine in alcoholic medium forming 2-(E)-[4-methoxybenzylideneamine] phenol (L^1) and 2-(E)-[4-methoxyphenylimino methyl] -6-methoxy phenol (L^2) respectively. The synthesized mixed ligands and lanthanide (III) complexes were characterized by elemental analysis, FTIR, ^{1}HNMR, UV-visible and molar conductance, x-ray diffraction, magnetic susceptibility and antimicrobial studies. These analytical and spectral data revealed that ligand coordinates with central lanthanide (III) ions by its two imines nitrogen atoms and two phenolic oxygen atoms and two water molecule the general formula of the complex is [LnL^1& L^2 $(H_2O)_2$ NO_3] . The ligand metal complex obtained by (1:1:1) (L^1 : metal: L^2) molar ratio. The result obtained by antibacterial, antifungal activity indicates that the antifungal are highly biologically active Aspergillus Niger at 500 ppm and at 250 ppm against Fusarium Oxysporum than that of antibacterial activity. All the complexes showed low conductivity i.e. Non electrolytic behavior in nature.***

Key words: Mixed ligands, antibacterial and antifungal activity, x-ray diffraction studies

1. Introduction

A series of lanthanide (III) with a Schiff base ligand used for accelerating the organic and inorganic reactions. In the Schiff base oxygen, nitrogen were electron donating ligands and able to coordinate metal through imines nitrogen. Several studies showed that the presence of lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine (-N=CH-) group is of considerable chemical, biological, analytical and industrial important. Chelating ligands containing O and N donor atoms shows broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions [1, 2]. Aromatic hydroxyaldehydes form stable complexes and the presence of a phenolic hydroxyl group at their ortho-position imparts an additional donor site in the molecule making it bidentate. Such a molecule coordinates with the metal ion through the carbonyl oxygen and deprotonated hydroxyl group. The chelating properties of Schiff bases derived from ortho-hydroxyaldehyde and Ketenes are well established [3-5].

In view of the coordinating ability of Schiff bases derived from ortho-hydroxyaromatic aldehyde along with their biological activity. Schiff bases are reported to show antibacterial, antifungal activity [6], anticancer activities [7]. In the present study, Schiff bases mixed ligand 2-(E)-[4-methoxybenzylideneamine]phenol (L^1) and 2-(E)-[4-methoxyphenylimino methyl] -6-methoxy phenol (L^2) and their metal complexes used as biological agents against gram-positive such as *Staphylococcus aureus, Bacillus substilis* and antifungal activity gram-negative such as *Aspergillus Niger, Fusarium Oxysporum.*

2. Experimental

2.1. Materials and methods

Lanthanide (III) nitrates obtained from Rare Earth Ltd. (India) were used without further purification. Salicylaldehyde, 2-hydroxy-3-methoxybenzaaldehyde and 4-methoxyaniline was obtained from Alfa Acer Chemicals and solvents were obtained from Aldrich Chemical Company. The powders XRD were characterized by recorded on Perkin Elmer TA/SDT-2960 and Philips 3701, respectively. ^{1}H-NMR spectra of ligand and metal complexes were recorded on a spectra were taken in d_6-DMSO & the chemical shifts were given in parts per million (ppm) with respect to tetramethylsilane (TMS) used as internal standard. UV-Visible spectra were recorded in DMSO solution Concentration of 10^{-6} m, at 25°C and wavelength was reported in (nm) using a UV-visible Spectrophotometer. The magnetic measurements were carried out at room temperature with a Gouys balance and Mercury tetrathiocyanato Cobalt (II) was used as a standard for calibration.

2.2. Synthesis of Schiff base ligand

The synthesis of Schiff base ligand was prepared by modification of reported method [8]. The synthesis of 2-(E)-[4-methoxybenzylideneamine] phenol (L^1) in 50 ml solution of ethanol contain 0.001mol of salicylaldehyde (0.122g), and 0.001mol of 2-hydroxy-3-methoxybenzaaldehyde (0.152 g) were continuous stirred for 4 hours at room temperature at show in figure-I. The gray color was obtained. The ligands were collected, filtered by using Buckner funnel, washed with ethanol and dried in the desiccators. Purity of the ligands was checked by TLC plates. The product was

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purified and recrystallised with a hot ethanol. The yield of ligand L^1 were obtained 80%.

The synthesis of 2-(E)-[4-methoxyphenylimino methyl] -6-methoxy phenol (L^2) in 50 ml solution of ethanol contain 0.001mol of 2-hydroxy-3-methoxybenzaaldehyde (0.152 g) and 0.001mol of 4-methoxyphenylamine (0.123 g) were continuously stirred for 4 hours at room temperature at show in figure-II. The orange color was obtained. The ligands were collected, filtered by using Buckner funnel, washed with ethanol and dried in the desiccators. Purity of the ligands was checked by TLC plates. The product was purified and recrystallised with hot ethanol. The yields of ligand L^2 were obtained 78%.

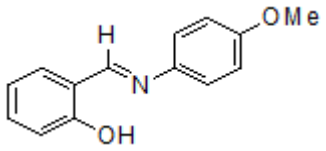


Figure 1: Structure of Schiff base ligand 2-(E)-[4-methoxybenzylideneamine] phenol (L^1)

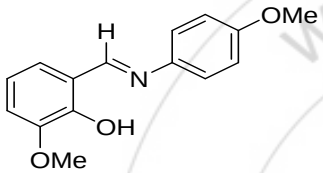
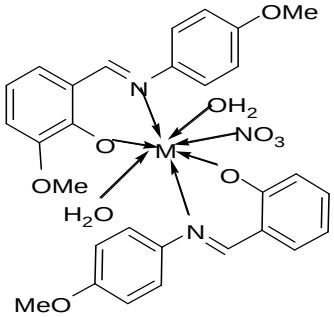


Figure 2: Structure of Schiff base ligand 2-(E)-[4-methoxyphenylimino methyl] -6-methoxy phenol (L^2)

2.3. Synthesis of metal complexes

Synthesis of lanthanide (III) complexes, the mixture of (0.01mol) ligands 2-(E)-[4-methoxybenzylideneamine]phenol (L^1) and 2-(E)-[4-methoxyphenylimino methyl] -6-methoxy phenol (L^2) dissolve in 25ml hot ethanol solution simultaneously and other lanthanide (III) nitrate (0.01mol) 25 ml of hot ethanol was added under constant stirring for 3 hours at room temperature .The precipitated complexes were filtered off washed with ethanol, diethyl ether and dried under vacuum over anhydrous calcium chloride ($CaCl_2$). Decomposition points of lanthanide (III) complexes were greater than 200°C.



M = La (III), Ce (III), Pr (III), Nd (III), Sm (III), Gd (III),), Tb (III) and Dy (III).

Figure 3: Proposed structure of mixed ligand complexes

3. Result and Discussion

3.1. ^{1}H-NMR spectra of ligands

The ^{1}H-NMR spectra of mixed ligands (L^1& L^2) in $CDCl_3$ at room temperature shows in Figure -I. The signals at 10.85δ (s, 1H, phenolic OH), 7.5-9.3δ (m 7H, Ar-H), 7.4δ (s, 1H, N=C-H), 3.94δ (s 3H, OCH_3). In Figure -II shows the signals 13.91δ (s1H, phenolic OH), 6.8-7.3δ (m 7H, Ar-H), 8.6δ (s1H, N=C-H), 3.8-3.9δ (s6H, OCH3). It should be noted that the phenolic proton have always given a singlet in off-set at high δ values, thus confirming its involvement in an intramolecular hydrogen bond with the neighboring nitrogen atom [9].

3.2. Elemental analysis

The ligands are soluble in ethanol, DMSO, DMF, DCM, $CHCl_3$ and $CDCl_3$ the yield, melting point, colors molecular weight and molar conductance, magnetic susceptibility data of the compounds are presented in the Experimental section table 1 and 2. The mixed ligands (L^1&L^2) addition of metal like La (III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) Tb(III), and Dy(III) nitrite dissolve in ethanol the solution of the ligand gave different colored complexes. The newly synthesized mixed ligand complexes are very stable at room temperature in the solid state. While all the mixed ligand complexes are insoluble in organic solvent like diethyl ether, methanol, they are soluble in DMSO, DMF, $CDCl_3$.

3.3 Molar conductance

Molar conductivity data for all the complexes in DMF solution at room temperature are in range 11-129 cm^2 mol^{-1} reported for 1:1 electrolytes [10]. Conductance measurements of 10^{-3} M solutions of the complexes in DMSO were carried out on a conductivity meter by using conductivity cell Type Cd-10, cell K=1.0±10%. The conductivity values were suggests in Table (3) all the lanthanide (III) complexes showed low conductivity i.e. non electrolytic behavior.

3.4 Magnetic Measurement

Study on unpaired electron of lanthanide (III) complexes by using magnetic susceptibility measurements of the powdered complexes were carried out by employing Guoy's balance method at 28 ^{0}C temperature. Mercury tetrathiocyanato Cobalt (II) was used as a standard for calibration. The μ_{eff} ions was calculated of effective magnetic moment of the using following formula

$\mu_{eff} = 2.83 (\chi_m T)^{1/2}$ B.M.

χ_m = molar susceptibility, T = absolute temperature and B.M. = bourse megatons the μ_{eff} of the metal ions was calculated in the present lanthanide (III) complexes were summarized in Table (3). The data shows that lanthanum complexes were diamagnetic in nature, as expected from its closed shell electron configuration and absence of unpaired electrons.[11] All other triple positive charged lanthanide complexes are paramagnetic due to the presence of 4f-electrons, which are effectively shielded by *5s2* and *5p6* electrons[12]

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Table 1: Analytical data of ligands L^1 and L^2

Ligands	M. Wt.	Color	M.P	Yield (%)	Elemental analysis (%) found (cal.)			
					C	H	N	O
$C_{14}H_{13}NO_2(L^1)$	227.25	Gray	85^0C	90	73.02 (73.30)	5.77 (5.71)	6.16 (6.11)	14.08 (14.00)
$C_{15}H_{15}NO_3(L^2)$	257.28	Orange	90^0C	85	70.02 (70.11)	5.88 (5.52)	5.44 (5.40)	18.66 (18.60)

Table 2. Physical characterization, analytical data of mixed ligand Lanthanide (III) complexes

Metal Complexes	M.Wt.	M.P/Dec Temp(°C)	Color	Yield (%)	Elemental analysis found (calculated)				
					C	H	N	O	M(Ln)
$[La(L^1\text{-}L^2)(H_2O)_2\ NO_3]$	721.47	250	Yellow	58	52.90 (52.40)	4.45 (4.40)	4.25 (4.21)	17.06 (17.00)	21.16 (21.20)
$[Ce(L^1\text{-}L^2)(H_2O)_2NO_3]$	722.68	205	Yellow	57	52.80 (52.70)	4.74 (4.62)	4.25 (4.41)	16.98 (16.74)	21.24 (21.30)
$[Pr(L^1\text{-}L^2)(H_2O)_2NO_3]$	723.47	≥250	Yellow	58	52.74 (52.80)	4.73 (4.82)	4.24 (4.21)	16.96 (16.73)	21.33 (21.50)
$[Nd(L^1\text{-}L^2)(H_2O)_2NO_3]$	726.81	205	Orange	57	52.47 (52.60)	4.71 (4.59)	4.22 (4.23)	16.87 (16.91)	21.73 (21.56)
$[Sm(L^1\text{-}L^2)(H_2O)_2NO_3]$	732.93	210	Yellow	55	51.99 (51.94)	4.66 (4.69)	4.18 (4.22)	16.72 (16.65)	22.44 (22.85)
$[Gd(L^1\text{-}L^2)(H_2O)_2NO_3]$	739.82	203	Orange	60	51.46 (51.77)	4.62 (4.49)	4.14 (4.43)	16.55 (16.46)	23.23 (23.39)
$[Tb(L^1\text{-}L^2)(H_2O)_2NO_3]$	714.49	≥250	Red	60	51.34 (51.93)	4.61 (4.88)	4.13 (4.41)	16.51 (16.42)	23.42 (23.45)
$[Dy(L^1\text{-}L^2)(H_2O)_2NO_3]$	745.07	200	Orange	57	51.07 (51.00)	4.58 (4.38)	4.11 (4.09)	16.42 (16.71)	23.82 (23.50)

Table 3: Magnetic moment and Molar conductance data of mixed ligand Lanthanide (III) nitrate complexes at room temperature.

Metal Complexes	Magnetic moment (BM)		Molar conductance Mho(cm^{-2} mol^{-1})
	μ_{eff} (observed)	μ_{eff} (calculated)	DMSO
$[La(L^1\text{-}L^2)(H_2O)_2\ NO_3]$	Diamagnetic	Diamagnetic	34.01
$[Ce(L^1\text{-}L^2)(H_2O)_2NO_3]$	2.42	2.53	27.01
$[Pr(L^1\text{-}L^2)(H_2O)_2NO_3]$	3.60	3.72	32.04
$[Nd(L^1\text{-}L^2)(H_2O)_2NO_3]$	3.73	3.92	24.01
$[Sm(L^1\text{-}L^2)(H_2O)_2NO_3]$	1.35	1.45	27.00
$[Gd(L^1\text{-}L^2)(H_2O)_2NO_3]$	7.82	7.94	27.89
$[Tb(L^1\text{-}L^2)(H_2O)_2NO_3]$	9.46	9.52	30.01
$[Dy(L^1\text{-}L^2)(H_2O)_2NO_3]$	10.25	10.42	26.20

3.5. FTIR Studies

A study and comparison of infrared spectra of free ligands (L^1 and L^2) and their respective lanthanide (III) complexes (Table-4) these ligands behave as neutral bidentate and lanthanide (III) metals are coordinated through N and O of two azomethine groups and two aqua ion. The strong band observed at 1602 and 1613 cm^{-1} region in the free ligands have been assigned to ν (-C=N-) vibrations of azomethine groups. After complexation these bands were shifted to higher wave number by 14 cm^{-1} indicates a stronger double bonds character of the imines bonds and coordination other azomethine nitrogen atoms to the lanthanide (III) ion [13, 14]. The phenolic –OH indicate in the presence of Ph-OH (ν_{OH}) group respectively 1244 and 1243 cm^{-1} present in L^1 and L^2. In the mixed ligands complexes both peaks were shifted towards lower frequency at 1507-1569, 1243-1244 cm^{-1} respectively i.e. azomethine-N and deprotonated –O atom indicating both were involved in the chelation [15]. All the mixed ligands Schiff base complexes show an additional peak in the region 2835-3059, 816-848, and 727-787 cm^{-1} due to νOH stretching, rocking and wagging mode of coordinated water molecules respectively. All the mixed ligands Schiff base complexes show a peak in the region of 2979-3059 cm^{-1} aromatic –C-H bonding. The lanthanide (III) metal nitrate complexes the occurrence of two additional strong absorption bands around at 1496 and 1290 cm^{-1}, which were absent in the free ligands. The presence of non-ligand band in 816-847 cm^{-1} region, assignable to the rocking mode of water [16]. The IR spectra show a strong band in the 3060-3604 cm^{-1} region, suggesting that the presence of coordinated water in the lanthanide (III) complexes [17]. The FTIR spectra of metal chelates showed new bands in 525-575 cm^{-1} range assigned to (M-N) and 400-450 cm^{-1} range assigned to (M-O) mode [18].

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Table 4: Major FTIR spectral data for the L^1 and L^2 ligands and mixed ligand Lanthanide (III) nitrate complexes (cm^{-1}).

Ligands/Complexes	C-H Aromatic	ν (C=N)	ν (Ar-O)	ν (M-O)	ν (M-N)	ν (C=C)	ν (C-O)	ν_1 NO_3	ν_2 NO_3
$C_{14}H_{13}NO_2(L^1)$	2841	1602	1244	-	-	1490	1150	-	-
$C_{15}H_{15}NO_3(L^2)$	2835	1613	1243	-	-	1466	1194	-	-
$[La(L^1\text{-}L^2)(H_2O)_2NO_3]$	3059	1636	1257	423	575	1467	1130	1496	1275
$[Ce(L^1\text{-}L^2)(H_2O)_2NO_3]$	3059	1637	1257	426	575	1494	1130	1494	1277
$[Pr(L^1\text{-}L^2)(H_2O)_2NO_3]$	2989	1637	1257	435	510	1477	1152	1477	1279
$[Nd(L^1\text{-}L^2)(H_2O)_2NO_3]$	3060	1636	1255	446	574	1480	1147	1480	1280
$[Sm(L^1\text{-}L^2)(H_2O)2NO_3]$	2979	1636	1256	421	511	1481	1148	1481	1283
$[Gd(L^1\text{-}L^2)(H_2O)2NO_3]$	2979	1636	1255	436	575	1482	1147	1482	1287
$[Tb(L^1\text{-}L^2)(H_2O)2NO_3]$	2979	1636	1257	438	576	1479	1172	1496	1286
$[Dy(L^1\text{-}L^2)(H_2O)_2NO_3]$	3058	1623	1256	442	550	1482	1147	1482	1290

3.6. Electronic Spectra

The study of electronic spectra of the lanthanide (III) complexes in a shift band position towards the lower wave numbers as compared to those of the metal salts. The bands observed in the case of Ce(III),Pr (III), Nd(III) and Gd(III) complexes could be assigned to the transition from $^2F_{5/2}$, $^3H_4$, $^4I_{9/2}$ and $^4H_{5/2}$ (ground state levels) to the excited state level of J-levels respective $4f^n$ configurations. The present data (Table-5) also show that the nephelauxetic ratio (β) for different J-levels vary considerably. The (1-β) values are used to calculated Sinha's Percentage covalency parameters (δ %) [19]. another bonding parameter b½ which measures the amount of 4f-orbitals ligand-orbital mixing in these compounds and the angular overlap parameter (η) were also calculated. The values b½, δ% and η have been calculated by the expressions of Tandon et.al [20]. The positive values for (1-β) and δ % in these coordination compounds Table-4 suggest that the bonding between lanthanide (III) ion and mixed Schiff base ligand is covalent as compared with the bonding between metal and an two aqua ion. The values of parameter of bonding (b½) and angular overlap parameter (η) were found to be positive indicative covalent bonding.

Table 5: Electronic spectral data (cm^{-1}) and their related bonding parameter of lanthanide (III) nitrate complexes.

Ln^{3+}	Band position of $Ln(NO_3)$	Band Position of Metal complexes	J-Levels	β	1-β	$b^{1/2}$	δ%	η
Ce^{3+}	27855	27745	$^2F_{5/2}\rightarrow{}^2D_{3/2}$	0.9960	0.004	0.044	0.4.16	0.0048
	27700	27070	$^2F_{5/2}\rightarrow{}^2D_{5/2}$	0.9772	0.0228	0.167	2.3331	0.1518
	26843	26483	$^2F_{5/2}\rightarrow{}^2D_{7/2}$	0.9665	0.0335	0.1294	3.4661	0.1845
	26540	26235	$^2F_{5/2}\rightarrow{}^2D_{9/2}$	0.9885	0.0115	0.0758	1.1633	0.105
Pr^{3+}	22217	22010	$^3H_4\rightarrow{}^3P_2$	0.9906	0.0094	0.0685	0.9489	0.0971
	21230	21121	$^3H_4\rightarrow{}^3P_1$	0.9948	0.0052	0.0509	0.5227	0.0720
	21801	21410	$^3H_4\rightarrow{}^3P_0$	0.9820	0.018	0.0948	1.8329	0.1347
	16912	16624	$^3H_4\rightarrow{}^1D_2$	0.9829	0.0171	0.0948	1.8329	0.1347
Nd^{3+}	19220	19110	$^4I_{9/2}\rightarrow{}^2G_{9/2}$	0.9942	0.0058	0.0533	0.5833	0.0626
	17470	17270	$^4I_{9/2}\rightarrow{}^4G_{5/2},{}^2G_{7/2}$	0.9885	0.0114	0.0754	1.1532	0.103
	13540	13345	$^4I_{9/2}\rightarrow{}^2G_{3/2},{}^4F_{7/2}$	0.9855	0.0144	0.0848	1.4611	0.1204
	12600	12420	$^4I_{9/2}\rightarrow{}^4F_{5/2},{}^4H_{9/2}$	0.9857	0.0142	0.0842	1.4406	0.1195

3.7. X-ray diffraction study

The powder x-ray diffraction of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Tb(III) complexes were mixed Ligands complexes scanned in the range of 5-75^0 at wavelength 1.540598Å. The diffractogram and associated data depict the 2θ value each peak, relative intensity and inter-planar spacing (d-values) summarized show in Table- 6. The above indexing method also yields Miller indices (h k l), unit cell parameters & unit cell volume. Moreover, the newly synthesized mixed ligand complexes were evaluated for their in x-ray diffraction data suggest monoclinic crystal system for La(III), Ce(III) complex and orthorhombic crystal system for Pr(III), Nd(III), Gd(III), Dy(III), Tb(III) complex and tetrahedral crystal system for Sm(III) complex. In x-ray diffractogram of figure-IV shows that percentage of intensity vs. 2θ values in the systematic arrangement of mixed ligand complexes. The x-ray diffraction pattern of these complexes with respect to major peak having relative intensity greater than 10% has been indexed by computer program [21]. The experimental density values of the complexes were determined by using specific gravity method [22].

They'd' values of reflections were obtained using Bragg's equation.

$$n\lambda = 2d\sin\theta$$

To calculate the unit cell volume of La (III) and Ce (III) complexes for monoclinic crystal system by the following equation was used.

$$V = abc\sin\beta$$

To calculate the unit cell volume of Pr (III), Nd (III), Gd (III), Tb (III) and Dy (III) complexes for orthorhombic crystal system by the following equation was used.

$$V = abc$$

To calculate the unit cell volume of Sm (III) complex for tetragonal crystal system by the following equation was used.

$$V = a^2c$$

Table 6: Lattice constant, Unit cell Volume, Crystal system and Inter-planar spacing of lanthanide (III) nitrate complexes.

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Unit cell of Ln(III) complexe	Lattice Constant			Unit cell Volume	Edge length	Inter axial angle	Crystal system	2θ	d-value
	a (Å)	b (Å)	c (Å)	V ($Å^3$)					(Å)
La(III)	15.29	9.82	8.05	702.44	$a \neq b \neq c$	$\alpha = \beta = 90 \neq \gamma$	monoclinic	41.29	2.18
Ce(III)	10.39	10.35	7.53	471.10	$a \neq b \neq c$	$\alpha = \beta = 90 \neq \gamma$	monoclinic	47.28	1.92
Pr(III)	17.52	14.56	5.40	1380.31	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	orthorhombic	43.12	2.09
Nd(III)	15.82	11.52	8.52	1535.73	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	orthorhombic	46.17	1.96
Sm(III)	9.124	9.124	9.35	778.54	$a = b \neq c$	$\alpha = \beta = \gamma = 90$	tetragonal	44.10	2.05
Gd(III)	17.26	14.32	10.24	2533.71	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	orthorhombic	34.02	2.61
Tb(III)	8.245	9.458	7.523	586.69	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	orthorhombic	49.00	1.83
Dy(III)	9.124	9.123	7.756	645.70	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90$	orthorhombic	50.89	1.79

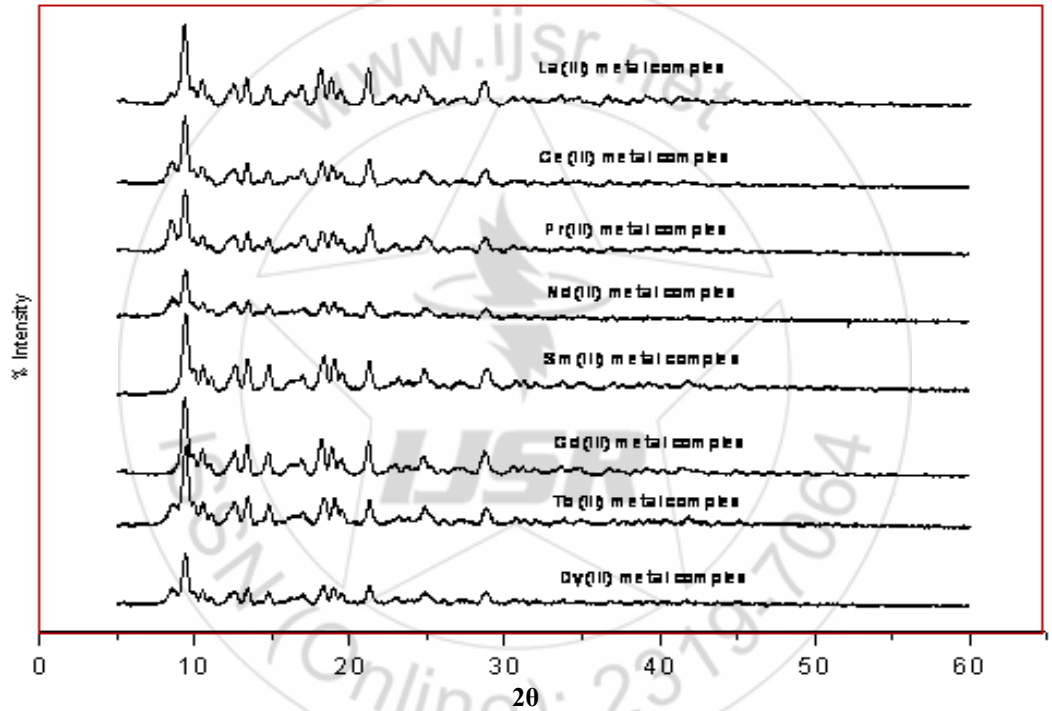


Figure 4: X-ray diffractogram of La (III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Tb(III)complexes.

3.8. Antibacterial and Antifungal activity

The antibacterial activity of the newly prepared ligands and some mixed ligand complexes were tested in vitro against bacteria by paper disc plate method [23]. The mixed ligands metal complexes have been tested for their antibacterial activity against *Staphylococcus aureus* and *Bacillus substilis* and antifungal activity *Aspergillus Niger* , *Fusarium Oxysporum* at the same concentration 250 ppm & 500 ppm. The obtained result show that good antibacterial activity are presented in Table-7. The mixed ligands and its metal La(III),Ce(III),Pr(III), Nd(III),Sm(III),Gd(III) and Dy(III)complexes shows highly active as compared to its ligands with zone of inhibition 13-17 mm, 13-18 mm, 13-17 mm, 11-15 mm, 12-15 mm, 15-16 mm, 11-17 mm and respectively. The mixed ligands Tb (III) complexes have exhibited good activity with the zone of inhibition 14-21mm when compared to the standard drugs ciprofloxacin. The results show antibacterial activity of Schiff base mixed ligands and its metal complexes of following increasing order Tb(III) > Gd(III) > L^1 > Ce(III) > La(III) ≈ Pr(III) > Sm(III) > Dy (III) > L^2

The antifungal activity result revealed that the mixed ligands metal like La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) complexes have exhibition shows highly activity with the zone of inhibition 16-19 mm, 22-24 mm, 20-24 mm, 14-20 mm, 16-26 mm, 22-24 mm, 14-24 mm, 15-23 mm as compared to the standard drug ciprofloxacin. The antifungal activity of Schiff base ligand & the mixed ligand complexes of following order's Ce(III) ≈ Gd(III) >Pr (III) > Sm(III) > La(III) >Dy (III) > Tb(III) > Nd(III) > L^2 > L^1. From the result obtained, it clear that the antibacterial activity of metal salts is high. Inhibition by metal complexes is found to be higher than that of a free ligand and corresponding metal salts against the same organism under

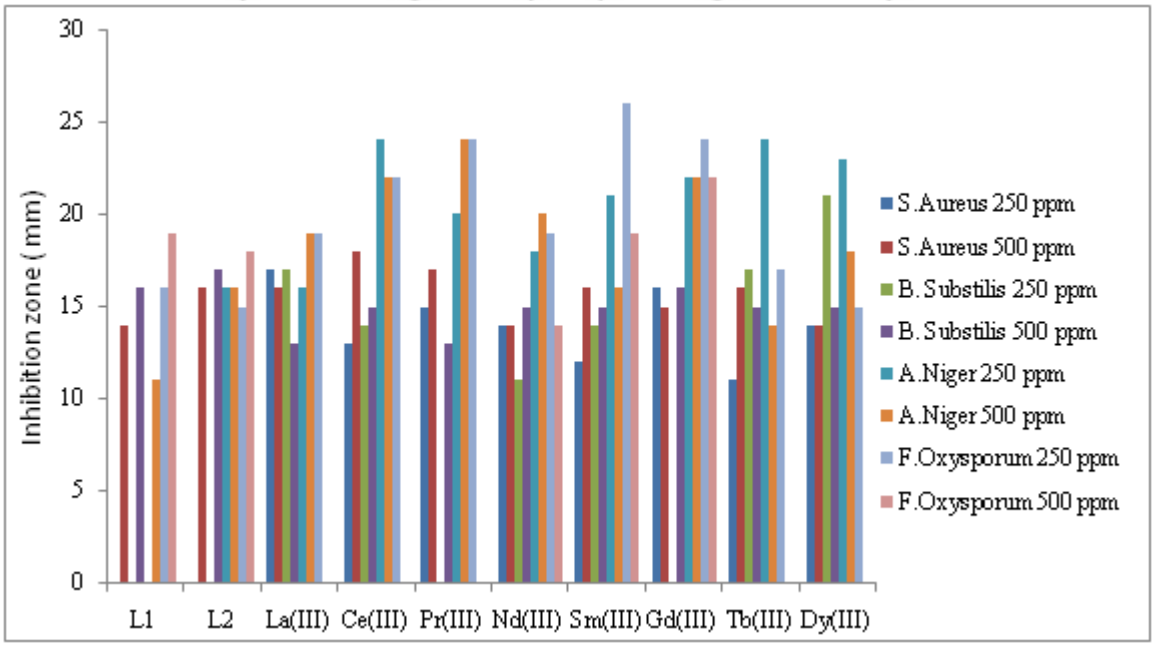
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experimental conditions. The metals salt used for the synthesis of complexes exhibit negligibly high antimicrobial activity [24, 25]. The comparative study of all compounds both ligands and mixed ligand metal complexes shows higher antifungal activity like *Aspergillus Niger* at 500 ppm and at 250 ppm against Fusarium Oxysporum.

Table 7: Antibacterial and Antifungal activity of L^1 and L^2 ligands and mixed ligand lanthanide (III) nitrate complexes [Diameter of inhibition Zone in (mm)]

Compounds	Antibacterial activity				Antifungal activity			
	Staphylococcus aureus		*Bacillus Substilis*		*Aspergillus Niger*		*Fusarium Oxysporum*	
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm
$C_{14}H_{13}NO_2(L^1)$	00	14	00	16	00	11	16	19
$C_{15}H_{15}NO_3(L^2)$	00	16	00	17	16	16	15	18
$[La(L^1\text{-}L^2)(H_2O)_2NO_3]$	17	16	17	13	16	19	19	00
$[Ce(L^1\text{-}L^2)(H_2O)_2NO_3]$	13	18	14	15	24	22	22	00
$[Pr(L^1\text{-}L^2)(H_2O)_2NO_3]$	15	17	00	13	20	24	24	00
$[Nd(L^1\text{-}L^2)(H_2O)_2NO_3]$	14	14	11	15	18	20	19	14
$[Sm(L^1\text{-}L^2)(H_2O)_2NO_3]$	12	16	14	15	21	16	26	19
$[Gd(L^1\text{-}L^2)(H_2O)_2NO_3]$	16	15	00	16	22	22	24	22
$[Tb(L^1\text{-}L^2)(H_2O)2NO_3]$	11	16	17	15	24	14	17	00
$[Dy(L^1\text{-}L^2)(H_2O)_2NO_3]$	14	14	21	15	23	18	15	00
ciprofloxacin	10	12	16	10	16	11	22	09

Figure.V. Antibacterial and antifungal result of L^1 and L^2 ligands and mixed ligands lanthanide (III) complexes at 250 ppm and 500 ppm.



4. Conclusion

The newly synthesis ligand and mixed ligand metal complexes like La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Tb(III) complexes with bivalent N & O donor Schiff base ligand derived from 4-methoxyphenylanaline, Salicylaldehyde and 2-hydroxy-3-methoxybenzaaldehyde were synthesized. The result obtained by antibacterial, antifungal activity indicates that the antifungal are highly biologically active Aspergillus Niger at 500 ppm and at 250 ppm against Fusarium Oxysporum than that of antibacterial activity. All the complexes are low molar conductivity in nature. The x-ray diffraction study indicate that monoclinic crystal system for La(III), Ce(III) complex and orthorhombic crystal system for Pr(III), Nd(III), Gd(III), Dy(III), Tb(III) complex and tetrahedral crystal system for Sm(III) complex.

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