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Research Article

Synthesis and characterization of lanthanide (III) nitrate complexes derived from two isomeric Schiff base ligands and comparative study of their antimicrobial activity

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ABSTRACT

The ligands and complexes were characterized by elemental analysis, molar conductivity, CHN analysis, magnetic susceptibility measurements, and spectroscopic studies such as IR, UV, and NMR. The *in-vitro* biological effects of lanthanide nitrate complexes of two isomeric Schiff base ligands were investigated. A comparative study of the zones of inhibition observed for the ligand and coordinated compounds by disc diffusion method against eight human pathogenic bacteria- *E.coli, K.sps, P.aeruginosa, B.cereus, B.subtilis, S.aureus, S.typhi* and *K. pneumonia*- indicated that the synthesized compounds show higher zones of inhibition than that of the free ligands. The ligands and their metal complexes were also evaluated for their ability to inhibit growth of fungi and algae. Isolates of fungi selected were *A.niger, F. moneliforme, pleurotus sajor caju and S.acremonium.* The cultures of algae, *D. salina, Isochrysis, M.chlorella*, and *Nannochloropsis* were selected for the present study. It is inferred that, increasing the number of chelate rings can increase the lipophilicity of the coordinated complex, which in turn increase antimicrobial activity. Here we report the bio-efficiency of organometallic-based antimicrobials synthesized from two Schiff bases.

Key words: Schiff bases, Lanthanide (III) ion, antimicrobial agent, coordination compounds, lipophilicity

Introduction

The rate of recurrence of acute infections caused by pathogenic microorganisms has increased worldwide and is becoming an important cause of morbidity and death in immune compromised patients in developing countries. The rising dominance of pathogenic microbes that are resistant to the modern antibiotics has resulted in growing concern, especially in the field of health. This leads to our search for new compositions. A great extent of interest have been generated in the study of Schiff bases and their metal incorporated compounds and provide a foundation stone for the building of contemporary coordination chemistry. The interactions of lanthanide metal complexes with Schiff bases have been extensively explored because of its wide variety of possible structures, applications in clinical, analytical, catalytical, industrial and biological fields[1]. Numerous metal complexes derived from lanthanide ions act as antibacterial and anti fungal agents. Accordingly, studies have carried out on the structure and chemical behavior of several metal complexes [2]. Complexes of these metal ions with ligands bearing nitrogen and oxygen donors exhibit great activity towards microorganism. Because of the extensive applications of the special class of lanthanide complexes, we confined our investigations in this field.

Schiff bases are very important as they can bind metal centers involving various coordination modes. Our involvement in the coordination chemistry is to explore the bonding features of the N, O donor Schiff bases and to investigate the variation in biological activities with change in chemical environment of the complexes in the presence of nitrate counter ions.

Materials and Methods

High purity pyridoxal hydrochloride (Aldrich, USA), 2-aminophenol, 3-aminophenol, methanol, ethanol, DMF (E. Merck, India), nutrient agar, potato dextrose (Himedia) were purchased and used as such. The conductivities of all the complexes measured in DMF at room temperature using Thoshniwal Conductivity Bridge with a dip-type conductance cell with platinum electrode having cell constant 0.9658cm^{-1}. The infrared spectra were recorded on a FTIR spectrophotometer in the range 400–4000cm^{-1} (KBr discs). The electronic spectral data were recorded at 300K in HPLC grade DMSO and DMF solutions using a Shimadzu UV 160A spectrophotometer in the range 190–900nm at SAIF, CUSAT, Kochi. NMR spectra recorded on a Bruker DRX -500 spectrophotometer using DMSO–d_6 solvent. The magnetic susceptibility of the complexes was measured at room temperature using Sherwood scientific Gouy balance.

The antimicrobial test was carried out by filter paper disc method using different concentrations (0.005M, 0.002M and 0.001M) in DMF extract[3]. Sterile Whatman paper discs (5mm diameter) were soaked each with 50µL of the extract and placed on bacteria (106CFU/mL) seeded plate. Cultures were incubated at 37^{o}C for 24hrs. After incubation of all cultures, zone of inhibitions of bacterial growth were observed. Each experiment was done in three replicates and average zone diameter was measured in mm. The fungal culture plates were inoculated and incubated at 25±2^{0}C and the diameters (in mm) of the inhibition zones after 48hrs were measured[4]. Algal studies were carried out by spectrophotometric method, the absorbance were measured on 5th, 10th and 15th day [5]. The cultures of algae, fungi and bacteria were obtained from the department of Marine Biology, Microbiology and Biochemistry, School of Marine Science, CUSAT, Kochi.

Experimental

Synthesis of Schiff base ligand I (L^1) and ligand II (L^2)

5-(Hydroxymethyl)- 4-{(1Z)-[2-N(2-hydroxylphenyl]ethanimidoyl)-2-methyl}pyridine-3-ol-hydrochloride (**L^1**) and 5-(Hydroxymethyl)-4-{(1Z)-[2-N(3-hydroxylphenyl]ethanimidoyl)- 2-methyl}pyridine-3-ol-hydrochloride (**L^2**) are synthesized by refluxing pyridoxal hydrochloride (1mmol) in 50mL methanol separately with 2–aminophenol (1mmol) in 30mL methanol and 3- aminophenol (1mmol) in 30mL methanol for 5hrs, allowed to cool. Dark brown solid separated was purified by washing with acetonitrile, followed by acetone, recrystallized from absolute alcohol, dried *in vacuum*, kept over P_4O_{10} in desiccators[6].

$C_{14}H_{16}N_2O_3Cl$ **(L^1)** (Yield: 65%; yellow needles(C_2H_5OH+DMF); m.p.178^{o}C; CHN%: C- 57.51(55.62),H-4.41(4.67), N-10.31(9.98); UVλ_{max}(DMF) = 285nm (br), 364nm (br); IR: (KBr/nujol) *v*max (cm^{-1}) 1623, 1201, 1323, 3450, 1033, 3150; ^{1}H NMR: (DMSO, 400MHz) δ = 8.1, 6.4, 9.1, 2.9 (in ppm).

$C_{14}H_{16}N_2O_3Cl$ **(L^2)** (Yield: 56%; m.p. 150°C; CHN%: C- 57.65(57.05), H- 4.85(5.13), N- 10.1(9.50), UVλ_{max} (DMF): 266nm, 340nm; IR: (KBr/ nujol) *v*max (cm^{-1}) 1602, 1317, 1203, 3600, 1027, 3100; ^{1}H NMR: (DMSO, 400MHz) δ = 8.2, 6.4, 3.4, 9.8(in ppm).

Synthesis of metal complexes

A mixture of **L^1** separately (2mmol) in 40mL methanol and metal salt MNO_36H_2O (1mmol) in 20mL methanol, (where M = La, Ce, Pr and Nd) stirred on a magnetic stirrer for 24hrs, refluxed for 5hrs at 70–80°C on water bath. On cooling, solid product separated was filtered, washed in acetone followed by acetonitrile, dried and stored in a desiccator over P_4O_{10} under vacuum[7]. All the metal complexes are dark brown colored and non-hygroscopic. The characteristics of the complexes are as follows:

$C_{28}H_{34}N_7O_{17}Cl_2La$ ***(a)*** Yield: 62%; m.p.: 258°C, CHN%: C- 46.1(45.1), H- 4.1(4.36) N- 8.85(10.1), La- 13.6(14.1); UV(DMF)λ_{max}: 255nm (br); IR: (KBr/nujol) ν_{max} (cm^{-1}) 1334,1257, 1033,758, 672, 1380, 817; ^{1}H NMR (DMSO, 400MHz); 2.5(br), 3.36(br), 5.1(br,s), 8.3(sh, s), 6.5-7.39(br, m), 10.0(in ppm).

$C_{28}H_{34}N_7O_{17}Cl_2Ce$ ***(b)*** Yield: 65%; m.p.: 255°C; CHN%: C-37.81(36.61), H-4.28(3.62), N- 10.5(10.67), Ce-15.2(15.5); µ-2.55, UV(DMF)λ_{max}: 290nm, 360nm; IR: (KBr/nujol) ν_{max} (cm^{-1}) 1633, 1197, 1301, 430, 470.

$C_{28}H_{34}N_7O_{17}Cl_2Pr$ ***(c)*** Yield: 68%; m.p.: 265°C; CHN%: C- 36.58(39.26),H- 3.6(4.83), N- 10.63(10.61), Pr-15.3(15.8); µ- 2.63; , UV(DMF)λ_{max}: 369nm, 294nm (br), IR: (KBr/nujol) ν_{max} (cm^{-1}) 1515, 1278, 1024, 748, 650,1382, 810.

$C_{28}H_{34}N_7O_{17}Cl_2Nd$ ***(d)*** Yield: 64%; m.p.: 268°C; CHN%: C- 36.3 (36.45), H- 3.60(4.1), N- 10.63(9.8), Nd-15.6(16.1); µ- 3.65; UV (DMF)λ_{max}: 294nm,368nm; IR: (KBr/nujol) ν_{max} (cm^{-1}) 1456, 1258, 1020, 758, 655, 1382, 811.

$C_{28}H_{34}N_7O_{17}Cl_2La$ ***(e)*** Yield: 60%; m.p.: 158°C; CHN%: C- 35.0(33.51), H- 3.03(3.15), N- (9.9)10.52, La-14.3(13.1); UV(DMF)λ_{max}: 350nm, 262nm, IR: (KBr/nujol) *v*max (cm^{-1}) 1276, 1022, 810, 1519, 649, 837, 1382; ^{1}H NMR (DMSO, 400MHz): 3.5, 2.6, 8.9, 6.9, 10.4(in ppm).

$C_{28}H_{34}N_7O_{17}Cl_2Ce$ ***(f)*** Yield: 65%; m.p.: 158°C; CHN%: C- 33.51 (35), H- 3.03(3.15), N- 10.52(9.9), Ce-14.3(13.1); UV(DMF) λ_{max}: 340nm, 268nm; IR (KBr/nujol) ν_{max} (cm^{-1}) 1615,1336,1245, 1190,3600, 3260, 554,463;

$C_{28}H_{34}N_7O_{17}Cl_2Pr$ ***(g)*** Yield: 62%; m.p.: 155°C; CHN%: C- 37.30(38.9), H- 3.45(3.8), N- 9.09(9.0); UV(DMF) λ_{max}: 355nm, 264nm; IR: (KBr/nujol) ν_{max} (cm^{-1}) 1302, 1025, 815, 1434, 736.

$C_{28}H_{34}N_7O_{17}Cl_2Nd$ ***(h)*** Yield: 68%; m.p.: 148°C; CHN%: C- 37.03(39.9), H- 4.07(4.09), N- 9.15(9.5), Nd-15.10(12.8); UV(DMF) λ_{max}: 351nm, 263nm; IR: (KBr/nujol) ν_{max} (cm^{-1}) 1627, 1336, 1245, 1190, 3585, 3245, 550, 465.

Results and Discussions

All complexes are soluble in methanol, ethanol, acetone, DMF, DMSO and insoluble in benzene, carbon tetrachloride and nitrobenzene. The molar conductance data reveals that **L^1**complexes of La, Ce and Pr behave as 1:1 electrolyte and that of Nd as 1:2 electrolyte where as all complexes of **L^2** behave as 1:1 electrolyte[8]. The results of magnetic moment determinations indicate the non-involvement of 4*f* electrons of the lanthanide ions in their complexes owing to the shielding of the 5s and 5p electrons. There is not much influence of the ligand field on 4*f* electrons of the lanthanide ions[9].

IR spectral studies of $L^1$and its complexes

In the IR spectra of **L^1** complexes stretching vibrational frequency band of the azomethine group of **L^1** was shifted to an extent of $\pm$30cm^{-1} and appeared in the range 1601–1639cm^{-1} indicating the involvement of this group in coordination. The typical medium band C-O(pyridyl ring) and C-O(aryl ring) of the ligand is found to be shifted to $\pm$ 20cm^{-1} in all complexes ascertaining the participation of both O-H groups in chelation[10]. In all the complexes,

these bands appeared in the range 1301–1334cm^{-1}and 1191–1217cm^{-1}. Another broad band observed in the region 3200–3400cm^{-1} in the ligand may probably due to the hydrogen bonding between the azomethine nitrogen and phenolic OH in the ligand is disappeared in the complexes[11].

The medium band displayed in the ligand at 1110cm^{-1} remains unaffected, indicating the non-participation of this OH in coordination. A broad medium band in the region 3500–3340cm^{-1} due to the C-OH vibrations indicates the non-coordination of the alcoholic OH. The band appearing at 605cm^{-1} is attributed to the bending of O-H. Existence of this band is a strong support for the nonparticipation of the alcoholic OH in coordinate bond formation. Medium frequency band at 590–710cm^{-1} attributed to the *out-of plane* vibrations of O-H. All these observation suggests that the primary alcoholic OH is non-hydrogen bonded.

All complexes exhibits vibrational frequencies characteristic of both uncoordinated and coordinated nitrate ions. A very strong band at 1384cm^{-1} and a medium band at 823cm^{-1} are attributed to the ν_3 and ν_2 vibrations respectively of ionic nitrate of D_{3h} symmetry. The strong and intense band at ~1517cm^{-1} and ~1280cm^{-1} are due to νN=O (ν_4) and $\nu_{(assm)}NO_2$ (ν_1) respectively are attributed to coordinated nitrate group of C_{2v} symmetry. In all the complexes, ν_1, ν_2, ν_3 and ν_5 were observed in region 1258–1290cm^{-1}, 1025–1035cm^{-1} ,745–755cm^{-1}and ~640–660cm^{-1} respectively[12]. Since (ν_4–ν_1) ~200 cm^{-1}, the nitrate ion is coordinated in a bidentate fashion[13].

The appearance of non-ligand bands at ~458–470cm^{-1} due to the M-O vibrations and bands at ~415–430cm^{-1} are attributed to M-N vibrations[14]. Hence, it is concluded that the Schiff base is expected to act as tridentate chelating ligand, the coordination sites being azomethine nitrogen, and the two phenolic oxygen atoms.

IR spectral studies of L^{2}and its complexes.

A strong sharp band observed at 1602cm^{-1} characteristic of azomethine group suffers a shift of ~+25cm^{-1} indicating a coordination through the azomethine nitrogen. Occurrence of characteristic bands due to C-O stretching frequency at 1245cm^{-1} in the ligand remains unaltered indicating non-involvement of this phenolic group in coordinate bond formation. Another band occurred at 1317cm^{-1} assigned to the C-O (phenolic) of the pyridoxal ring in the ligand displayed shift of $\pm$15cm^{-1} for all the complexes, indicate coordination through this oxygen[10]. A broad band observed at ~3440cm^{-1} in the ligand assigned for the intra–molecular hydrogen bond between the hydrogen atom of the phenolic OH and the nitrogen atom of the azomethine group[21]. In the complexes, there are less broadening and disappearance of this band suggesting that the intra molecular hydrogen bonding might have been lost after complexation. The characteristic frequency band observed at 3600cm^{-1} remain unaffected in all the complexes suggesting the non-participation of the alcoholic OH group in coordination[22].

A characteristic band observed at ~3550cm^{-1} in the complexes of cerium and neodymium suggesting the presence of water molecule. The presence of water is further supported by the appearance of δ(OH) in the region 1360–1370cm^{-1} and another band at ~933cm^{-1} attributed to the out of plane bending of OH [24].

Very sharp and intense bands appeared in the range of 1382–1384cm^{-1} indicates the presence of uncoordinated nitrate ion. The presence of ionic nitrate is further supported by the appearance of medium band in the range of 810–820cm^{-1} of the ν_3 mode. Sharp and strong frequency bands observed in the range 1420–1450cm^{-1} and 1280–1310cm^{-1} are assigned to ν_4 and ν_1 vibrations of coordinated nitrate group. Occurrence of a medium band at ~1025–1038cm^{-1} is ascribed to N-O stretching vibrations of NO_3^- group. A value of 140cm^{-1} in ν_4–ν_1 and a separation <50cm^{-1} in the combination bands (ν_2+ν_5) – (ν_2+ν_6) in the region 1750–1700cm^{-1} is a strong support for monodentate coordination of nitrate ion[15].

Non-ligand bands are appeared in the range 460–470cm^{-1} and 415–440cm^{-1} which are absent in the ligand are attributed to the M-O and M-N bonds, which supports the complex formation [23]. All these observations shows that the coordination sites are azomethine -C=N group and the -C-O (phenolic) group[14].

UV spectral data

In the spectra of the complexes of **L^1**, slight red shifts are observed for n→π* and π→π* transition the region 369–377nm and 287–296nm respectively. In the complexes of **L^2**, $\pi \rightarrow \pi^*$ transitions observed at 268nm are blue shifted to the region 262–264nm and n→π* transitions are red shifted to the region 350–355nm[14]. All these observation suggests bond formation through the donor atoms of the ligands.

The spectral bands associated with the hypersensitive transition of the lanthanide (III) ion which was utilized to study the coordination environment around the metal ion. A comparison of the hypersensitive bands and that of the aqua ions were done for neodymium complex and calculated the bonding parameters [25]. The nephelauxitic ratio β, the covalency factor $b^{1/2}$, angular overlap parameter η and Sinha's covalency parameter δ were calculated and are in the range of (0.9903–0.9966), (0.0289–0.0490), (0.0485–0.0757) and (0.3360–0.5775) respectively, suggesting that the bonding between the metal and ligand is covalent compared to the bonding between metal and water[25].

NMR spectral analysis

In the spectrum of $\mathbf{L^1}$, signal observed at δ = 8.1ppm is attributed to azomethine proton exhibit a low field shift to 8.3ppm for **(a)**. Signals appeared as multiplet at 6.65ppm for aromatic protons also displayed downfield shift in the region δ = 6.95ppm suggest electronic changes due to coordination. The resonance at δ = 9.1ppm in the ligand attributed to -OH proton displayed downfield shift[16] to 10.0ppm.

In the spectrum of $\mathbf{L^2}$, signal observed at δ = 8.2ppm is attributed to azomethine proton exhibit a low field shift to 8.9ppm for **(e)**. Signals appeared as multiplet at 7.25ppm for aromatic protons also displayed downfield shift in the region δ = 7.55ppm. In addition, the signals at 9.67ppm attributed to phenolic proton exhibit a downfield shift to δ = 10.4ppm which appeared as broad signals also support for bond formation through this atom [16].

Antimicrobial Studies

The antimicrobial effects are evaluated as per the guidelines of Committee of Clinical Laboratory Standards. Isolates of bacteria are selected 24hrs before in nutrient broth. Nutrient agar medium is prepared as per the methods described in literature and autoclaved at 120^{o}C and 15kg/cm^2 pressure. This is allowed to cool to 60^{o}C. About 20–25mL sterile agar medium is introduced into petri plates. When attained room temperature, bacterial suspension of 25µL is added, swabbed and kept for 15min for uniform spreading. To the petri plates, the sterile discs of 5mm diameter (purchased from Himedia) are distributed in array, followed by test solution 20–25µL. These plates are covered and allowed [19] to incubate 18-24hrs at 37^{o}C.

The ability of the complexes to inhibit the growth of selected human pathogenic bacteria (Table I), fungi (Table II) and *marine algae* (Table III) are presented. The zone of inhibition values of the free ligand and its complexes indicate that all the metal chelates have higher antimicrobial activity than the free ligand.

Antifungal activity was assessed by a disc diffusion method. The isolates of fungi were transferred from stocks to potato dextrose agar and then sub cultured to enhance sporulation. Seven day-old cultures were covered with 1mL distilled water and the colonies were probed with the tip of a sterile Pasteur pipette to obtain the fungi. The suspensions were transferred to sterile tubes and allowed to sediment for 30min [20].

Sterile algae nutrient medium [17] was inoculated with algal cells. These were incubated for 3 days in an orbital incubator under continuous illumination at normal temperature (24-26^{o}C) a portion of this culture was transferred into fresh sterile algal nutrient medium to prepare a secondary liquid culture. The absorbance was measured for each culture before the addition of test samples. To 5mL of each culture, 1mL test solution was added and absorbance was again recorded. This is the zeroth day reading.

The test solution was kept under illumination for fifteen days and readings were recorded on every five days [5]. Stock cultures of algae were raised in 1000mL Erlenmeyer flasks containing 500mL Walno's medium [17]. Illumination was provided by white florescent light of 2000tux for a period of 12:12hrs.

I. Antibacterial Studies

The results of biological screening of the investigated compounds are reported in table I. It was inferred that the free Schiff base $\mathbf{L^1}$ has been shown to be inactive against all bacterial strains examined where as $\mathbf{L^2}$ exhibit moderate activity against *E.coli, Pseudomonas aeroginosa, B.cereus and Klebsiella pneumonia.* Most of the tested compounds showed remarkable biological activity against different types of gram positive and gram negative bacteria.

Table I. Results of zone of inhibition (mm) of L^1, L^2 and complexes

Compound	E. coli	*P. aeroginosa*	B. cerus	*Klebsiella sps*	*S.aureus*	B.subtilis	K .pneumonia	S. typhi
L^1	-	-	-	-	-	-	-	-
L^2	9	8	13	-	-	-	12	-
a	10	-	-	10	-	-	-	-
b	-	-	-	-	-	-	-	-
c	9	-	10	-	11	-	-	8
d	7	-		-		-	-	
e	14	-	16	-	26	7	10	9
f	6	-	-	-	12	-	-	-
g	18	10	14	-	18	-	14	-
h	-	-	-	-	-	-	-	-

I.1. Activity against *E.coli*

The ligand **L^1**, its complex (***b)*** were inactive against *E.coli* while complexes (***a***), (***c***) and **(*d*)** exhibited moderate activity with inhibition zone diameter 10mm, 9mm, and 7mm respectively. The ligand **L^2** was found to be active against these bacteria with zone diameter 9mm. Among its complexes, (***g***) was shown to have appreciable activity. This is the most potent complex with zone diameter 18mm. Complex (***e***) was also shown to intoxicating effectively against this organism with inhibition zone of 14mm. Complex (***h***) is inactive and (***f)*** has minimum inhibition zone of 6mm.This investigation suggests that quite promising results were obtained from praseodymium complex of **L^2**, (***g)*** that it can be effectively administered against *E.coli*. Lanthanum complex of **L^2, (*e*)** can also be also be used as a toxicant against this organism.

I.2. Activity against *P. aeroginosa*

L^1 and all its complexes in the present investigation obviously show nil activity against this organism while **L^2** and one of its complexes (***g*)** exhibited moderate inhibitory activity with zone diameter 8mm and 10mm respectively.

I.3. Activity against *B. cereus*

L^1 was inactive against this species. Among the four complexes of **L^1**, the only complex which shows moderate activity against this organism was the neodymium complex (**c**). **L^2** and two of its complexes **(*e*)** and **(*g*)** show remarkable activity. The recorded zone of inhibition of **L^2** and the two complexes are comparable. The inhibition diameter for **L^2**, (***e*), (*g*)** are 13mm, 16mm and 14mm respectively**.**

I.4. Activity against *Klebsiella sps.*

The results indicate that both ligands were inactive against this species. Among their complexes, (**a**) is the only one complex which exhibited moderate activity against this species(10mm diameter).

I.5. Activity against *S. aureus*

Both ligands show nil activity against this species. Among the complexes of **L^1,** only (***c***) was moderatively active against this species with zone of inhibition 11mm while complexes **(e)** and **(*g*)** of **L^2** was surprisingly active with inhibition diameter 26mm and 18mm respectively. Complex **(*f*)** show moderate activity (zone of inhibition 12mm).

I.6. Activity against *B.subtilis*

All compounds including **L^1** and **L^2** were inactive against this species except **(*e*)**, the lanthanum complex of **L^2** which show a minimum activity of 7mm zone diameter.

I.7. Activity against *K. pneumonia*

L^1 and all its complexes were shown to be inactive against this bacteria where as **L^2** show a moderate activity with zone diameter of 12mm. Its lanthanum complex **(*e*)** show less activity than the ligand from which it is synthesized (zone diameter 10mm) while its praseodymium complex **(*g*)** show higher activity than **L^2**. Complexes **(*f*)** and **(*h*)** were inactive.

I.8. Activity against S. typhimurium

The results show that only two of the compounds exhibit moderate activity against this bacterium, the praseodymium complex of **L^1, (*c*)** and lanthanum complex of **L^2, (*e*).**The two ligands and all other complexes show nil activity.

Antifungal studies.

Complexes (***a*), (*c*),** (***e***) and (***g***) were selected for antifungal evaluation. The results (table II) suggest that both the uncomplexed Schiff base **L^1** and **L^2** are inactive against all fungi tested. Complexes of **L^1** are also inactive against all fungi tested where as two of the complexes of **L^2** (lanthanum and praseodymium complexes, (***e***) and (***g***)) were shown to exhibit toxicity against all fungi evaluated. Complex **(*e*)** is more effective than (***f***) against *Scopulariopsis acremonium*.

Table II. Fungicidal screening data of L^1, L^2 and complexes

Complound	*Pleujurotus sajor ca*	*scopulariopsis*	*Aspergigillus*	*Moniliforme*
L^1	-	-	-	-
L^2	-	-	-	-
a	--	--	--	--
c	-	-	-	-
e	10	16	8	7
g	8	10	8	6

Algal studies

Compound selected for algal studies (table III) are **L^1, L^2**, **(*a*), (*c*), (*e*)** and **(*g*).** Among the complexes examined, praseodymium complex of **L^2** (***g***) is active against *isochrysis;* all other complexes of both **L^1** and **L^2** are inactive against *Duneliella salina, Marine chlorella, Nanachloropsis oclaba.* In other words, the compounds **L^1, L^2, (*a*), (*c*)** and **(*e*)** allow growth of these algae in their presence.

Table III. Algal screening studies of L^1, L^2 and Complexes

Compound	*Duneliella salina*	*Isochrysis*	*Marine chlorella*	*Nanochloropsis occlaba*
L^1	0.1091	0.0128	0.0162	0.0570
L^2	0.1347	0.0093	0.0177	0.0273
a	0.4318	0.1380	0.1146	0.1611
c	0.3964	0.1316	0.0578	0.1214
e	0.3011	0.0023	0.0232	0.1335
g	0.1946	-0.0013	0.0762	0.0386

The inhibition property of complexes can be explained as follows. The positive charge of the metal ion is shared between the donor atoms of the ligand. There is the possibility of delocalization of the π electron density of aromatic ring also. These two factors positively contribute to increase the lipophilic character. Upon complexation, polarity of metal ion get reduced due to the overlap of ligand orbital and the sharing of positive charge of the metal ions with

donor groups. All these enhances the penetration of complexes into lipid membrane thus restricts the growth of organism.

It is observed that $\mathbf{L^2}$ and its complexes show enhanced activity against most of the organisms than $\mathbf{L^1}$ and its analogues. It can be concluded that $\mathbf{L^2}$ is a bidentate chelate with a free OH group which is absent in $\mathbf{L^1}$. In both complexed and uncomplexed state, the uncoordinated donor atom can form bonds with trace elements present in microorganism which inhibit further growth of the organism [25]. Cell permeability is an important factor that control antifungal activity. The lipid membrane that surrounds the cell favours the passage of lipid soluble materials. This allows the penetration of the compounds into the bacterial membrane, which block further growth of the organism.

Conclusion

The complexes of La, Ce, Pr and Nd synthesized from two different ligands with nitrate as anion. The nitrate ion in complexes of $\mathbf{L^1}$ and $\mathbf{L^2}$ coordinate to the metal ion in different manner. Nitrate ion is coordinated bidentately to the metal ion in complexes of $\mathbf{L^I}$ while in $\mathbf{L^2}$, mono dentatively coordinated. IR data reveals that $\mathbf{L^1}$ act as tridentate chelate, the coordination occurs through the azomethine nitrogen and two phenolic oxygen atoms while $\mathbf{L^2}$ is a bidentately chelating ligand with coordination sites being azomethine nitrogen and phenolic oxygen of the pyridyl ring. IR and NMR spectral studies reveal that the OH of 3-aminophenol has not participated in chelation. Comparative studies of the antimicrobial activity suggest that $\mathbf{L^2}$ and its complexes are more active against most of the organisms evaluated. Complexes of La and Pr of $\mathbf{L^2}$ can be used as potential toxic agents against *E.coli* and *S.aureus*.. Lanthanum complex of $\mathbf{L^1}$ **(*a*)** displayed moderate activity against two of the bacterial strains *E.coli* and *Klebsiella sps* only where as lanthanum complex of $\mathbf{L^2}$**(*e*)** exhibit higher activity against *E.coli, B. Cereus, S.aureus, B.subtilis, S. typhi and Klebsiella pneumonia.* This complex show optimum activity and can be used as an excellent toxic agent against *S. aurous (zone diameter 26mm).* Cerium complex of $\mathbf{L^1}$ **(*b*)** is inactive towards all bacteria while that of $\mathbf{L^2}$ **(*f*)** show minimum activity with *E.coli* and moderate activity with *S.aureus.* Praseodymium complex of $\mathbf{L^1}$**(*c*)** has been found to exhibit moderate activity against *E.coli , B.cereus, S.aureus, S. typhi* where as complexes of $\mathbf{L^2}$ **(*g*)** with this metal has shown to be excellent toxic agent against *E.coli, P.aeroginosa, B.cerus, S. aurous and K. pneumonia*. Neodymium complex of $\mathbf{L^1}$ **(*d*)** exhibit a minimum inhibition zone of 7mm against *E.coli* only. $\mathbf{L^2}$ complex of this metal **(*h*)** is inactive against all tested bacterial strains. A correlation between the structure and biological activity has been established.

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References

1. Bradley, J. Berger. *American Society for Microbiology*, Sept. 2000, 44(9), 2540–2542.
2. Anna G. Matveeva, Alexander S. Peregudov, Evgenij I. Matrosov, Zoya A. Starikova, Sergej V. Matveev, Eduard E. Nifant'ev, *Inorganica Chimica Acta* 362, 2009, 3607–3616
3. Shelke1, V.A., Jadhav1, S.M. , Shankarwar1, S.G., Munde, A.S. , Chondhekar, T.K. *Bull. Chem. Soc. Ethiop*., 25(3), 2011, 381-391.
4. Revanasiddappa, B.C, Subrahmanyam, E.V.S., Satyanarayana, D, *International Journal of ChemTech Research CODEN*(USA): IJCRGG ISSN : 0974-4290, Vol.2, No.1, pp 129-132, 2010
5. Yifeng Chen & Yuhuan Liu & Yingkuan Wang & Roger Ruan, *Appl Biochem. Biotechnol*, 2010, (DOI 10.1007/s12010-009-8866-7)
6. Ram K. Agarwal1, Surendra Prasad, Rajiv Garg, Sushil K. Sidhu. *Bull. Chem. Soc. Ethiop.* 20(1), 2006, 167-172.
7. Kishor Arora, Mukesh Sharma, Sharma, K.P. *E-Journal of Chemistry 6(S1), 2009, S201-S210*
8. Chun-Hui Huang, *Rare Earth Coordination Chemistry*, John Wiley & Sons Asia Pvt.Ltd, 2010.
9. Aida L. El-Ansary, Nora, S., Abdel-Kade, *International Journal of Inorganic Chemistry*, Article ID 901415, 13 pages doi:10.1155/2012/901415, 2012.
10. Mapari A. K, Hate, M. S., Mangaonkar, K. V. *E-Journal of Chemistry* 8(3), 2011,1258-1263

11. Madhu, N.T. , Radhakrishnan, P.K. *Transition Met. Chem*. 25 ,2000, 287.
12. Nakamoto, K. (1986) Infrared and Raman Spectra of Inorganic and CoordinationCompounds, fourth ed., Wiley, New York.
13. Muraleedharan Nair M. K., Radhakrishnan, P. K. *Synth. React. Inorg. Met.-Org. Chem.*, 26, 1996, 263
14. Bi caifeng, Ai xiaokang, fan yuhua, Bi shuangyu xie sitan. *Journal of the Chilean Chemical Society*, 52, (4) 2007, 1291-1293
15. Vimal Kumar, P.M., Radhakrishnan, P.K, *Polyhedron* 30, 2011, 2849–2855
16. Silverstein. R.M, Clayton Bassler .G, Terence C. Morrill, *Spectrometric identification of organic compounds*; Vth edition, John Wiley & sons.
17. Walne, P.R., Studies on food value of nineteen genera of algae to juvenile bivalves of the genera Ostrea , Crassostrea, Mercenaria and Mytilus. Fish. Invest. Lond. Ser. 2. (1970) 26 (5),1-62
18. K. Mounika; B. Anupama; J. Pragathi; C. Gyanakumari; *Journal of Science research*, 2010, 2(3), 513-524
19. K. Praveen; A.Y. Usha; M. Naveen; B. Rajasekhar Reddy; *Journal of Biology, Agriculture and Healthcare* ISSN2225-3208(Paper), 2012, 2(1).
20. A. Esteban; M.L. Abarca; F.J.Cabanes; *Med. Mycol*.; 43: 2005, 61-6.
21. Adem Cinarli1; Demet Gürbüz; Aydin Tavman; A. Seher Birteksöz; *Bull. Chem. Soc. Ethiop*, 2011, 25(3), 407-417.
22. K.U. Ingold; D.R. Taylor; *Canadian Journal of Chemistry*. 1961, 39.
23. Ali E. Sebik; Muharrem Karabork; GokhanCeyhan; Mehmet Tumer; Metin Gigrak; *International Journal of Inorganic Chemistry*, 2012, Volume 2012 Article ID 791219, 11 pages , doi:10.1155/2012/791219
24. J.T.Miller; D.E.Iris; *Canadian. J. of Chemistry*, 1967, 45, 147
25. R.K. Agarwal; R.K. Garg; S.K.Sindhu; *Journal of the Iranian Chemical Society*, 2005, 2(3), 203-211.