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Biological Studies of Lanthanide (III) Complexes with Nitrogen-Oxygen donor Schiff base Ligands

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Abstract

Nitrogen-Oxygen donor ligands, 2,3-dimethyl-4-(iminopyridoxyl)-1-phenyl-3-pyrazoline-5-one (L^1), 5-(hydroxymethyl)-4-{(1-Z)-[2-N (2-hydroxylphenyl] ethanimidoyl)- 2-methyl} pyridine-3-ol hydro chloride (L^2) and 5-(hydroxymethyl)-4-{(1-Z)-[2-N(3-hydroxyl-phenyl] ethanimidoyl)-2-methyl} pyridine-3-ol-hydrochloride (L^3) have been synthesized. New lanthanide(III) complexes of the three ligands $[La(L^1)_2(NO_3)_3]$ (a), $[La(L^1)_2Cl_2]Cl$ (b), $[La(L^1)_2ClO_4](ClO_4)_2$ (c), $[La(L^2)_2(NO_3)_2]NO_3$ (d), $[La(L^2)_2Cl_3]$ (e), $[La(L^2)_2(ClO_4)](ClO_4)_2$ (f), $[La(L^3)_2(NO_3)_2]NO_3$ (g), $[La(L^3)_2)Cl_3]$ (h) and $[La(L^3)_2(ClO_4)_2]ClO_4$ (i) are synthesized and characterized by elemental analysis, molar conductivity, magnetic susceptibility measurements and spectroscopic studies. L^1 and L^2 act as tridentate chelating ligand where as L^3 act as a bidentate chelating ligand. The three Schiff base ligands and their metal complexes have been screened for antibacterial activity against six bacteria (*E.coli*, *B. cereus*, *B. subtilis*, *S. aureus*, *S.typhi* and *K. pneumonia*) and four fungi (*A.niger*, *F. moneliforme*, *Pleurotus sajor caju and S.acremonium.*). The antimicrobial studies suggest that the Schiff base ligand L^2 was inactive towards all tested bacteria and fungi while L^1 and L^3 show moderate activity towards a few bacteria and fungi. All metal complexes showed significantly enhanced antibacterial and antifungal activity against microbial strains in comparison with free ligands.

Key words: Complexes, antimicrobial, antibacterial and antifungal activity, Schiff base

Introduction

Schiff base metal complexes are of great interest for many years. It is often used as chelating agents in the field of coordination chemistry. Trivalent lanthanides behave as hard acids and therefore expected to form stronger and

stable complexes with ligands having oxygen or nitrogen-donor atoms [1]. Schiff bases are well known for their anti-cancer and anti-viral activities and its metal complexes have been widely studied because of their anti-fungal, anti-bacterial, anti-cancer, anti-tubercular activities, herbicidal applications, and chelating abilities which attracted remarkable attention [2]. O and N donor atoms in these ligands play a key role as the active sites of various metallo biomolecules. Many reports have indicated the use of organometallics in biosciences [3]. Lanthanide complexes from macrocyclic and macro acyclic ligands have been extensively studied in the past decade. They are used as catalysts in transesterification, radiopharmaceuticals and as fluoroimmuno assay reagents [4]. Owing to the effectiveness of metallo-organic compounds as drugs and powerful antimicrobial agents, these are of great importance [5]. The discovery and development of antibiotics are the influential and victorious achievement in the history of science. This paper reports the synthesis and characterization of Schiff base complexes of lanthanum(III) nitrate, chloride and perchlorate salts from three different ligands and to compare the antimicrobial properties against human pathogenic bacteria and fungi.

Materials and methods

High purity Pyridoxal hydrochloride (Aldrich, USA), 2-Aminophenol, 3-Aminophenol, (E. Merck, India), Nutrient agar, Potato dextrose (Himedia) are purchased and used without further purification. Solvents used are methanol, ethanol, DMF (E. Merck, India). The conductivities of all the complexes measured 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 are recorded on a FTIR spectrophotometer in the range 400-4000cm^{-1} (KBr discs). The electronic spectral data are recorded at 300K in HPLC grade 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 Schiff bases and complexes are analyzed for C, H and N content on a Heracus CHN Rapid Analyzer (1104 28) at SAIF, CUSAT, Kochi. Nutrient agar and Potato Dextrose agar (Himedia) are used as media for bacterial and fungal studies. Human pathogenic bacteria cultures are obtained from Department of Marine Biology, Microbiology and Biochemistry, School of Marine science, CUSAT, Kochi. and from Department of Biochemistry, CUSAT, Kochi. Fungal isolates are obtained from the department of Environmental Science, CUSAT, Kochi. The test was carried out by filter paper disc diffusion method using different concentrations (0.005M. 0.002M and 0.001M) in DMF extract. Sterile Whatman paper discs (5 mm diameter) are soaked each with 100 µl of the extract and placed on bacteria (106 CFU/mL) seeded plate. Cultures are incubated at 37^{0}C for 24h. After incubation of all cultures, zone of inhibitions of bacterial growth are observed. Each experiment was done in 3 replicates and average zone diameter was measured in mm. The fungal culture plates are inoculated and incubated at 25± 20^{0}C and the diameters(in mm) of the inhibition zones after 48 h are measured[6**].**

Synthesis of Schiff bases

2,3-dimethyl-4-(iminopyridoxyl)-1-phenyl-3-pyrazoline-5-one (**L^1**), 5-(hydroxymethyl)-4-{(1-Z)-[2-N(2-hydroxyl phenyl]ethanimidoyl)-2-methyl}pyridine-3-ol-hydrochloride(**L^2**) and 5-(hydroxymethyl)-4-{(1Z)-[2-N(3-hydroxyl phenyl]ethanimidoyl)-2-ethyl}pyridine-3-ol-hydrochloride(**L^3**) are synthesized by adding ethanolic/ methanolic solutions 0.05molar pyridoxal hydrochloride to 0.05molar solutions of 4-aminoantipyrine/ 2-aminophenol/ 3-aminophenol. The reaction mixture was then refluxed on a water bath for about 5–6h, crystalline solid formed was washed with ether followed by acetone and finally recrystallized from absolute alcohol [7].

L^1 Yield 85%, yellow needles, m.p. 278^{o}C, CHN; %C; 58.57(58.81), H; 5.6(5.20), N; 14.38(14.44), UV(DMF); (nm) 275(br), 385(br), IR (KBr/ nujol)ν_{max} (cm^{-1}); 1603, 1649, 1128, 1323, 3550, 1037, 3244, ^{1}H NMR (DMSO,400MHz); δ = 8.3, 2.5, 4.7, 10.13, 3.5ppm.

L^2 Yield 65%; m.p.178^{o}C, CHN; %C; 57.51(55.62), H; 4.41(4.67), N; 10.31(9.98) UV(DMF); (nm) 285(br), 364(br); IR (KBr/ nujol)ν_{max} (cm^{-1}) 1623,1201,1323,3450,1033,3150; ^{1}H NMR (DMSO,400MHz); δ = 8.1,6.7,8.2,8.3,2.9ppm.

L^3 yield 56 %; m.p 150 ^{o};, %C57.65(57.05);, H; 4.85(5.13), N; 10.1(9.50), UV(DMF); (nm) 266, 340; IR (KBr/ nujol)ν_{max} (cm^{-1}) 1602,1317,1203, 3600, 1027, 3100; ^{1}H NMR (DMSO,400 MHz); δ = 8.15,8.24, 6.7,3.4,9.8,3.4ppm.

Synthesis of complexes

All the complexes are prepared by mixing a methanolic/ethanolic solution of $MCl_3/(NO_3)_3/ (ClO_4)_3nH_2O$ with Schiff base suspensions in the same solvent in a 1:2 molar ratio. The resulting mixture was refluxed on a water bath for 5h. Complexes **a, b** and **c** are synthesized in ethanol and complexes **d, e, f, g, h** and **i** in methanol. Solid products separated are collected by filtration, washed with acetonitrile followed by ether, dried *in vacuum* over P_4O_{10} [8]. (Analytical data listed in Table 1).

Physical characterization

The electrical conductance measurement values for complexes **a, b, e** and **h** in DMF is in the range 15-35ohm^{-1}mol^{-1}cm^2 and behave as neutral. The values for complexes **c, d, f, g** and **i** are in the range 140-170ohm^{-1}mol^{-1}cm^2 and behave as 1:2 electrolyte of the type ML_2 [9]. All complexes are diamagnetic, non-hygroscopic and stable at room temperature. The solubility of all the complexes are examined in common organic solvents and found to be soluble in methanol, ethanol, acetone, DMF, DMSO and insoluble in acetonitrile, benzene and toluene.

IR Spectral studies

Very intense and strong vibrational frequency band attributed to −C=N stretching vibration were observed at 1603cm^{-1}, 1623cm^{-1} and 1602cm^{-1} in $\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$ respectively[**10**]. In complexes **a, b** and **c**, these bands were shifted to ~1595cm^{-1}. In complexes **d, e** and **f**, the bands were appeared in the range of 1601-1639cm^{-1} and in complexes **g, h** and **i** , these bands were appeared in the range 1610-1635cm^{-1}.These observations suggests the coordination of the ligands to metal ion *via* azomethine nitrogen [11].

An intense band at 1649cm^{-1} assigned to νC=O stretching frequency observed in $\mathbf{L^1}$ suffer a negative shift of ~25 cm^{-1} and appeared at~1622cm^{-1} in complexes **a, b** and **c.** Another strong and intense frequency band observed at 1384cm^{-1} attributed to the stretching vibrations of the phenolic C-O get shifted to a lower frequency region of 1360-1376cm^{-1} in these complexes. This is a clear evidence for the involvement of these two groups in coordination [11]. New non-ligand bands appeared in the region 450-500cm^{-1} and 400-460cm^{-1} are attributable to M-O bond and M-N bond respectively in these complexes supports complex formation [12].

The typical medium band C-O(pyridyl ring) and C-O(aryl ring) in $\mathbf{L^2}$ appeared at 1323 cm^{-1} and 1201cm^{-1} is found to be shifted to $\pm$ 20cm^{-1} in all complexes ascertaining the participation of both O-H groups in chelation in complexes **d, e** and **f** [9]. In all the complexes, these bands appeared in the range 1301-1334cm^{-1}and 1191-1217cm^{-1} respectively suggesting the involvement of these two groups in coordination. 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 [12]. Occurrence of characteristic bands due to C-O(aryl) stretching frequency at 1245cm^{-1} in $\mathbf{L^3}$ remain unaltered in complexes **g, h** and **i** indicating non-participation of this phenolic group in coordinate bond formation. Another band occurred at 1317cm^{-1} assigned to the C-O (pyridyl ring) in the ligand displayed shift of $\pm$15cm^{-1} in complexes **g, h** and **i** indicate coordination through this oxygen [11].

Characteristic frequency bands of nitrate ions were observed at 1454cm^{-1} (ν_4), 1305cm^{-1} (ν_1) and 1030cm^{-1}(ν_2), of monodentatively coordinated nitrate ion were observed in complex **a** and absence of bands corresponding to ionic nitrate group [12]. This observation in conformity with electrical conductance measurements suggests that the three nitrate groups are present within the coordination sphere. In complex **d**, very high intensity absorptions bands were observed at ~1450-1520cm^{-1}, medium bands at ~1260-1285cm^{-1}, ~1025-1035cm^{-1} and ~750cm^{-1} which are attributed to ν_4, ν_1, ν_2 and ν_3 modes respectively of bidentatively coordinated nitrate group. A band at 1382cm^{-1} is attributed to uncoordinated nitrate group. The separation of ν_4-ν_1 value greater than 200cm^{-1} in complex **d** conclude that nitrate ion is coordinated to the metal ion in a bidentate fashion [12].

In complex **c,** triply split band maxima at 1228cm^{-1}, 1111cm^{-1}, 1033cm^{-1} observed were attributed to ν_8, ν_6, and ν_1 vibrations of perchlorate group of C_{2v} symmetry indicating coordinated perchlorate group. Vibrational frequencies at 940-950cm^{-1} and 468-472cm^{-1} are attributed to ν_2 and ν_4 vibrations of perchlorate of C_{2v} symmetry [13]. Two distinctly split bands were appeared in the range of ~1080-1090cm^{-1} and ~1120-1130cm^{-1} in complex **f** are indicative of coordinated perchlorate of C_{3v} symmetry. The split band at 610-615cm^{-1} and 625-630cm^{-1} support the coordination of perchlorate ion in a monodentate manner. Two unsplit bands in the region ~620-628cm^{-1} and another band in the range ~1100-1115cm^{-1} assignable to the ν_4 and ν_3 modes of perchlorate group of Td symmetry indicate presence of perchlorate group outside the coordination sphere[13].

The triply split band maxima at ~1140-1150cm^{-1}, ~1110-1115cm^{-1} and ~1020-1030cm^{-1} are the ν_8, ν_6, ν_1 modes respectively of coordinated perchlorate of C_{2v} symmetry in complex **i**. In addition, strong bands in the range 928-945cm^{-1} and at 630-635cm^{-1} assignable for ν_2 and ν_3 vibrational modes of bidentatively coordinated perchlorate group of C_{2v} symmetry are also observed. Avery strong and unsplit band at 1078-1095cm^{-1} region were appeared in all complexes attributable to ν_3 mode of perchlorate ion suggesting that there are perchlorate group present outside the coordination sphere. Presence of ionic perchlorate group was further supported by the appearance of strong band in the region 620-624cm^{-1} in all complexes [12]. Frequency bands displayed in the region of 310-325cm^{-1}in complex **b, e** and **h** are attributed to the M-Cl bond [12].

UV spectral studies

UV spectral data of ligands and complexes are presented in Table 2. In ligands, n→π* transitions were appeared at 375nm in $\mathbf{L^1}$, 365nm in $\mathbf{L^2}$, and 340 nm in $\mathbf{L^3}$ and π→π* transitions were appeared at 275 nm in $\mathbf{L^1}$, 285nm in $\mathbf{L^2}$, and 268 nm in $\mathbf{L^3}$. Both bands are shifted to higher/lower energy region in all complexes. Both n→π* and π→π* are blue shifted in complex **a** where as in complex **b**, n→π* is blue shifted and π→π* is red shifted and in complex **c** and **d**, both n→π* and π→π* are red shifted. In complex **e**, π→π* transitions are blue shifted and n→π* transitions are red shifted while in complex **f,** n→π* is blue shifted and π→π* is red shifted. In complex **g**, π→π* transitions are blue shifted, and n→π* transitions are red shifted where as in complex **h** and **i** both transitions n→π* and π→π* are red shifted [13,14]. These observations are the consequences of coordinate bond formation with ligand donor atoms.

NMR Spectral studies

NMR spectral data are presented in Table 3. The entire diamagnetic complexes exhibit signals at lower fields compared to ligands. The downfield shift in the resonance of these protons compared to the ligand are attributed to the decrease of electron density as a consequences of coordinate bond formation with OH and HC=N. In all the ligands, signals of azomethine hydrogen was observed at δ = 8.1-8.7ppm. In complexes, the signals are recorded at δ = 8.3-8.9ppm suggesting coordination through azomethine group. Signals appeared as multiplets at 6.8 to 7.3ppm attributable to aromatic protons also displayed downfield shift in the region δ = 6.9ppm to δ = 7.6ppm in all complexes suggest electronic changes due to coordination [13-15]. The signals appeared as singlet at δ = 10.1ppm in $\mathbf{L^1}$ was attributed to -OH protons. In complexes **b** and **c** this peak was disappeared suggesting deprotonation of OH group and in complex **a**, the peak was appeared with a down field shift suggesting the coordination through this oxygen atom without deprotonation. In complexes **e, g, h** and **i** the peak corresponding to OH proton was appeared without any marginal shift in δ values. A downfield shift in position of δ value of OH was observed in complex **d** also, which is a conclusive evidence for the coordination of phenolic OH in this complex [15].

Biological Activity Studies

The newly synthesized Schiff bases $\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$ and their complexes are screened *in vitro* for their antibacterial activity by disc diffusion method [16] . DMF was used as a negative control and ciprofloxacin was used as positive control. All the bacterial cultures are procured from microbial type culture and sub-cultured in nutrient agar. Positive controls produced significantly sized inhibition zones against the tested bacteria and fungi; however, negative control produced no observable inhibitory effect against any of the test organisms. The antimicrobial studies suggested that the Schiff base $\mathbf{L^1}$ was biologically active towards *B.cereus* and *Salmonella typhimurium* and inactive against other tested bacteria while its nitrate complex **a** show significant activity against all tested organisms with the zone of inhibition ranging from 8-10mm. The chloride and perchlorate complexes **b** and **c** were found to be inactive compared to the nitrate complex. Complexes **a**, **b** and **c** exhibited moderate activity towards *E.coli* (Inhibition zone 10, 7 and 8mm respectively).

$\mathbf{L^2}$ was shown to be inactive against all tested species while a few complexes show enhanced activity. The nitrate analogue **d** was active towards *E.coli* only whereas chloride complex **e** exhibit activity towards *B.cereus*, *S. aureus*, *S.typhimurium* and *E.coli* with zone of inhibition(in mm) 8, 10, 9 and 7 respectively. The perchlorate complex **f** display activity towards all bacteria examined. The growth of *B.cereus* and *S.aureus* are totally inhibited by this complex. (Clear zone 16mm and 18mm).

$\mathbf{L^3}$ was active towards *E.coli*, *B. cereus* and *Klebsiella pneumonia* and the complexes show enhanced activity. Significantly enhanced antibacterial and antifungal activity against microbial strains in comparison to the free ligands was exhibited by the nitrate complex **g**. *B.cereus* and *S.aureus* are the two species most inhibited by complex

g (zone area 16mm and 26mm). Complex **g** can be used as an efficient bactericide against *S.aureus.* All tested species are moderately inhibited by perchlorate complex with zone area ranging from 8-11mm.

A comparison of the Anti bacterial activity of the complexes of L^1, L^2 and L^3

It can be deduced that among the nine complexes evaluated, the nitrate complex of L^3, **g** was shown to have significant activity towards all tested organism. *B.cereus* and *S. aureus* are totally inhibited by this complex. Nitrate complex of L^1, **a** was also active but to a lesser extent compared to that of L^3. L^2 complex **d** was the least active.

It was observed that among the chloride complexes, L^1 complex (**b**) is inactive towards all organisms. L^2 complex **d** was moderately active (7-10mm zone area) towards four of the tested organisms (B.cereus, *S. aureus, S.typhimurium* and *E.coli*) while that of L^3, **h** was active towards three species only(*B.cereus, E.coli* and *S.typhimurium*(zone area 10,10 and 8mm).

Perchlorate complexes of L^2, **f** and that of L^3, **i** are active towards all organisms evaluated but in varying range (Table 4). *B.cereus and S. aureus* are inhibited by **f** with zone area 16mm and 18mm. L^1 complex **c** was inactive.

Antifungal activity

Complexes **a, b, d, e, f, h** and **i** are inactive against all fungi tested. Complex **c** was shown to be an effective toxic agent against all the four fungi tested. Complex **g** show moderate inhibitory activity. The antibacterial activity can be explained as follows. Lipid membrane that surrounds the cell favors the passage of lipid soluble materials due to which lipo-solubility is an important factor, which controls the antimicrobial activity. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocking the metal binding-sites on enzymes of microorganisms. These complexes may disturb the respiration process of the cell and thus block the synthesis of proteins which restrict the further growth of the organism [17]. In addition, the presence of more functional groups like hydroxyl, which can form hydrogen bonding with proteins present in the cell walls of the organism, resulting in interference with the normal cell activities [18]. It can be inferred that L^3 complexes are most powerful intoxicating agents among the three series of complexes examined. The reason may be that L^3 possess free hydroxyl group that can form coordinate bond with trace metals present in the living cell of organisms thereby causing interference in cell reactions and the growth of organism can be inhibited.

Table.1. Analytical data of complexes a–i

Complex	%La obs(calc)	%N obs (calc)	%C obs (calc)	%H obs (calc)
a	12.6(12.1)	15.4(15.4)	50.5(50.4)	4.2 (4.3)
b	13.5(13.9)	10.9(11.1)	47.5(45.6)	5.5(4.8)
c	12.2(12.5)	5.1(5.0)	30.1(28.9)	3.8(3.2)
d	13.6(14.1)	9.9(10.1)	46.1(45.1)	4.1(4.4)
e	15.8(16.8)	6.1(6.8)	39.4(37.8)	3.4(3.8)
f	13.0(13.5)	5.6(5.46)	31.1(30.4)	3.6(3.6)
g	13.1(14.3)	9.9(10.5)	35.0 (33.5)	3.0(3.2)
h	16.0(16.6)	6.4(6.57)	37.3(39.1)	3.3(4.1)
i	12.2(12.5)	5.1(5.0)	30.1(28.9)	3.8(3.2)

Table.2. UV spectral data of complexes a–i (in nm)

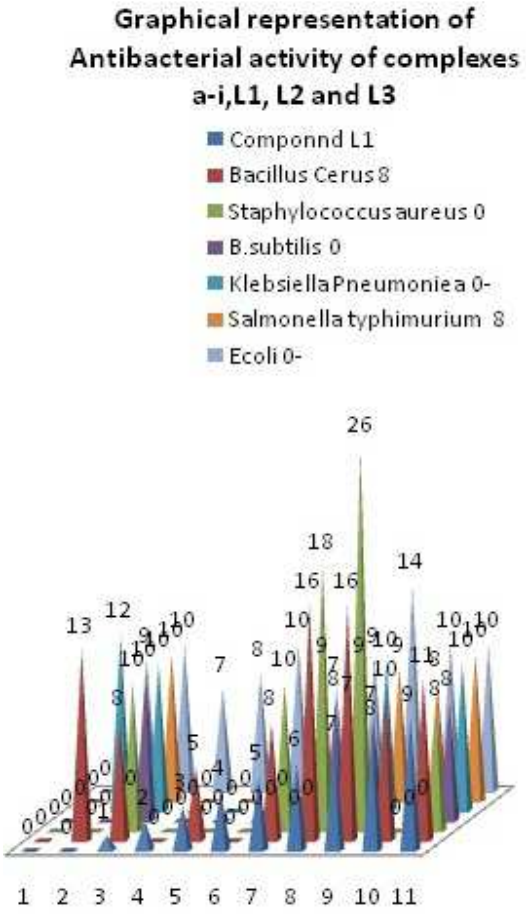
Complex	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
n→π*	365	382	388	369	370	360	350	355	354
π→π*	272	290	279	294	265	290	262	264	265

Table.3.^{1}H NMR spectral data of complexes a–i (in ppm)

Complex	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
HC=N	8.7	8.9	8.6	8.25	8.27	8.26	8.31	8.35	8.37
O-H(alc)	3.9	4.8	4.9	3.6	3.7	3.6	3.4	3.6	3.6
OH(phenolic)	10.3	--	--	-	6.7	-	6.3	6.4	6.6

Table.4. Biological activity of L^1, L^2, L^3 and complexes a–i

Compound	Bacillus Cereus	*Staphylococcus aureus*	B.subtilis	Klebsiella Pneumonia	Salmonella typhimurium	E. coli
	Gram positive			Gram negative		
L^1	8	-		-	8	-
a	8	10	10	10	10	10
b	-	-	-	-	-	7
c	5	-	-	-	-	8
L^2	-	-	-	-	-	-
d	-	-	-	-	-	10
e	8	10	-	-	9	7
f	16	18	8	7	9	9
L^3	13	-	-	12	-	9
g	16	26	7	10	9	14
h	10	-	-	-	8	10
i	11	8	8	10	10	10



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