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SYNTHESIS, CHARACTERIZATION, THERMAL, X-RAY AND ANTIMICROBIAL STUDY OF ZN (II) METAL COMPLEXES OF DEHYDROACETIC ACID BASED NEW SCHIFF BASES

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ABSTRACT

Tetradentate complexes of Zn (II) of Schiff bases derived from DHA, o-phenylenediamine, 4- N, N, Diethyl amino Salicylaldehyde (L1) and Dehydroacetic Acid (DHA), 4-methyl-o-phenylenediamine, 5-bromo Salicylaldehyde (L2) have been synthesized and characterized by elemental analysis, magnetic susceptibility, thermal analysis, X-ray diffraction, ^{1}H-NMR, Mass, IR,UV visible spectra and conductometry. The ligand field parameters have been characterized and found to have octahedral geometry. Thermal behavior (TG/DSC) of the complexes was studied. X-Ray diffraction study reveals monoclinic crystal system. The ligand and its complexes were subjected for antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* and fungicidal activity against *Trichoderma and Aspergillus Niger*.

Keywords: Tetradentate ligand, Dehydroacetic acid, TGA/DSC, X-Ray diffraction.

1. INTRODUCTION

Dehydroacetic Acid (DHA) has antimicrobial effect against bacteria, yeast and molds and used as preservative in food factories & as fungicide with virtuous co-ordination properties [1]. So researchers are infatuated to synthesize metal complexes of Schiff bases choosing it as nucleus. Indicated metal complexes are used in Catalysis [2], DNA cleavage [3], antifungal [4], antitumor [5], antibacterial agents [6]. Zinc has decent co-ordination with N_2O_2 donor Schiff bases. In the present study, tetradentate Zn (II) complexes derived from, DHA, o-phenylenediamine, 4-N, N Diethyl amino Salicylaldehyde (L1) and DHA, 4-methyl-o-phenylenediamine, 5-bromo Salicylaldehyde (L_2) have been synthesized and characterized.

2. MATERIAL AND METHODS

2.1. Reagents and solvents

Dehydroacetic Acid (DHA), o-phenylenediamine, 4-N,N-Diethylamino Salicylaldehyde, 4-methyl-o-phenylene diamine, 5-bromo Salicylaldehyde from Merck of AR grade were used as supplied for synthesis of ligand. AR grade Zinc chlorides used for the synthesis of complexes.

2.2. Synthesis of ligand

In the first step, mono-Schiff base compound was prepared by refluxing 50 ml solution of 10mmol of DHA and 10mmol o-phenylenediamine, 4-methyl-o-phenylenediamine in super dry ethanol for about 3h. The progress of reaction was monitored by thin layer chromatography. Mono-Schiff base thus formed was then refluxed with 10mmol 4-N, N Diethyl amino Salicylaldehyde/5-bromo Salicylaldehyde to prepare asymmetric ligand. Product was then cooled at room temperature and collected by filtration, and recrystallized by ethanol (Yield: L1-87, L2-85 %).

2.3. Synthesis of metal complexes

To a hot methanolic solution (25ml) of the ligand (0.01 mol), methanolic solution (25ml) of zinc chloride (0.01 mol) was added with constant stirring and refluxed for about 3 h. The pH of reaction mixture was adjusted to 7.5-8.5 by adding 10 % alcoholic ammonia. The precipitated solid colored metal complexes was filtered off in hot condition and washed with hot methanol, petroleum ether (40°-60°) and dried over calcium chloride in vacuum desiccators (yield: 65 %).

2.4. Instrumentation

The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. FTIR spectra were recorded on Jasco FTIR-4100 spectrometer using KBr pellets. ^{1}H NMR spectra of ligand were measured in $CDCl_3$ using TMS as internal standard. The TG/DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701, respectively. The UV-visible spectra of the complex were recorded on JascoUV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were determined on a Guoy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant.

2.5. Antimicrobial Analysis

Metal and Ligand complexes were screened for their antimicrobial activity by disc plate method. Antimicrobial activity was tested by disc plate technique involving the cultures of the selected organisms. The test solutions of metal ligand complexes were prepared in sterile dimethyl sulfoxide (DMSO) solvent for the study. The synthesized metal ligand complexes were tested at different concentrations to find out the minimum concentration of the metal complexes required for inhibiting the growth of microbes. The zone of inhibition for the test samples, standard and control (DMSO) was measured.

3. RESULTS AND DISCUSSION

Table 1 indicates physical characteristics, micro analytical and molar conductance data of ligand and metal complexes. Molar ratio of (metal: ligand) is 1:1 and found in good relevance with the general formula $[ML(H_2O)_2]$. Where L= L1, L2.

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

The ^{1}H NMR spectra of free ligand, in $CDCl_3$ at room temperature shows the following signals. L_1 -1.04-1.09 δ (t, 6H, 2×CH_3-CH_2-N), 1.11-1.16 δ (q, 4H, 2×N-CH_2-CH_3), 2.12 δ (s, 3H, C6-CH_3, 2.51 δ (s, 3H, N=C-CH_3), 5.79 δ (s, 1H, C5-), 6.75-7.16 δ (m, aromatic protons), 8.59 δ (s, 1H, N=C-H), 6.18 δ (s), phenolic (OH) hydrogen of phenyl ring) and 9.50 δ (s, 1H, enolic (OH/NH) of DHA moiety) [7]. L_2 - 2.09 δ (s,3H,C6-CH_3),2.11 δ (s, 3H, N=C-CH_3),2.25 δ (s,3H, C4-methyl of phenylring) 5.77 δ (s, 1H, C5-), 6.73-7.03 δ (m, aromatic protons), 8.88 δ (s, 1H, N=C-H),9.76 δ(s), phenolic (OH) hydrogen of phenyl ring) and 15.88 δ (s, 1H, enolic (OH) ofDHA moiety).

3.2. FTIR Spectra

A comparative study of IR data of ligand and its metal complexes is listed in Table 2. It shows major band at 3227-3419, 1687-1690, 1640-1658, 1502-1561, 1351-1353, 1214-1230 cm-1 of L_1 and L_2 are assignable to υ OH, υ C=O (lactone carbonyl), υ C=N (azomethine), C=C, υ C-N (aryl azomethine) and υ C-O (phenolic) stretching modes respectively [8]. Lack of broad band in region of 3200-3400 cm^{-1} in the spectra of metal complexes reveals chelation of phenolic oxygen to the metal ion [9]. Difference of 10-40 cm^{-1} in frequency is observed in case of azomethine υ (C=N) band in metal complexes, with compared to ligand which is 1640-1658 cm^{-1} indicating involvement of azomethine nitrogen in coordination to metal [10]. Metal complexes shows new band in the 530-532 and 471-477 cm^{-1} region can be assigned to υ M-O and M-N vibrations respectively. While (C=C) ring skeletal band is constant in all metal complexes. The presence of coordinated water in metal complexes is confirmed by observing broad band in 3067-3088 cm^{-1} region and a new band at ~860 cm^{-1} that may be assigned for O-H stretching vibration and out of plane bending of water molecule coordinated to complexes [11]. Hence, it is concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule to the zinc metal ions.

Table 1: Physical characterization, analytical and molar conductance data of compounds

CompoundMolecular formula	Mol. Wt.	M.P./ Decomp Temp.^{0}C	Color	Molar conductance. Mho $cm^2 mol^{-1}$	Found (calculated)			
					C	H	N	M
(H_2L1) $C_{23}H_{27}N_3O_4$	433.50	87	Dark Red	----	68.25 (69.27)	6.06 (6.28)	9.23 (9.69)	-----
(H_2L2) $C_{22}H_{19}N_2O_4Br$	454.30	173	Dark Yellow	----	57.44 (58.04)	4.09 (4.21)	6.08 (6.15)	-----
$[L1Zn((H_2O)_2]$	496.87	263	Faint Brown	25.35	60.89 (60.43)	5.21 (5.07)	8.35 (8.46)	13.10 (13.16)
$[L_2Zn(H_2O)_2]$	518.68	267	Faint Yellow	29.54	51.25 (50.94)	3.15 (3.30)	5.34 (5.40)	11.54 (12.61)

Table 2: IR and UV data of ligand and metal complexes

Compound	IR band frequency (cm^{-1})								λmax (nm)	Magnetic Moment (BM)
	ν(OH)	ν(C=O)	ν(C=N)	C=C	C-N	C-O	M- O	M- N		
L1	3227	1687	1640	1502	1353	1230	---	---	263, 332	--
Zn-L1	3056	1685	1621	1502	1360	1214	532	472	328, 447, 613	Diamagnetic
L2	3419	1690	1658	1561	1360	1214	---	---	274, 338	--
Zn-L2	3054	1685	1612	1519	1351	1167	530	477	340, 423, 623	Diamagnetic

3.3. Electronic absorption spectra and Magnetic susceptibility

The electronic absorption spectrum of L1, L2 and its complexes in 10^{-4} M DMSO solution at room temperature along with magnetic susceptibility are listed in Table 2. L1 shows two bands at 263,332 nm these absorption bands assigned for π-π*, n-π*transitions. L2 shows two bands at 274,338 nm suggested the π-π*, n-π* transitions. Both ligands show the value for -C=O, in 263-274 region, and -C=N azomethine π- π* transition in 332-338 nm. Zn (II) complex of L1 shows three bands at 613,447,328 assigned for 6A1g → 4T1g, 6A1g → 4T2g and charge transfer respectively. Zn (II) complex of L2 absorbs at 623, 423,340, for 6A1g → 4T1g, 6A1g → 4T2g and charge transfer respectively. Both complexes are Diamagnetic in nature for d^{10}configuration of Zn (II) [12]. Electronic absorption data along with magnetic properties are in good agreement with high spine octahedral geometry for both Zn (II) complexes.

3.4. Powder X-ray diffraction

Scanning of x-ray diffractogram of Zn(II) metal complexes of L1 and L2 is done at wavelength 1.543 Å in the range 5-100°. The x-ray diffraction pattern of these complexes compared with major peaks of relative intensity greater than 10% has been indexed to their hkl value by using computer program. The diffractogram of Zn(II) complex of L1 had twenty reflections with maxima at 2θ=4.14° corresponding to d value 4.8017Å, lattice constants, a=7.3662 Å, b=9.5623 Å, c = 11.7895 Å and unit cell volume V=718.43318 $Å^3$. The diffractogram of Zn (II) complex of L2 had twenty one reflections with maxima at 2θ = 10.48° corresponding to d value 4.16Å, lattice constants, a=8.9665 Å, b=9.4879 Å, c =16.7895 Å and unit cell volume V=1284.546 $Å^3$. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α =γ = 90° ≠ β required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded that Zn (II), complex of L1, L2 has monoclinic crystal system [13].

3.5. Thermal analysis

The TG/DSC analysis of both Zn (II) complexes was done from ambient temperature to 1000°C in nitrogen atmosphere using α-Al2O3 as reference. The TG curve of Zn-L1 complex show first mass loss 7.91% (calcd.7.45%) in the range 185-220°C and an endothermic peak in this region ΔT min. is 200°C, indicate removal of two coordinated water molecules [14]. The first step is slow decomposition from 220-505°C with 27% mass loss. This can be further confirmed by observing broad exotherm in DSC with ΔTmax. = 434°C indicates non coordinated part of complex. In second step, 37.19 % losses confirmed by ΔTmax. = 690.17°C indicate removal of coordinated part. The TG curve of Zn-L2 show first mass loss 11.91 % (calcd.11.45%) in the range 165-200°C and an endothermic peak in this region ΔTmin. = 190°C, The first step is slow decomposition from 200-450°C with 37% mass loss. This can be further confirmed by observing broad exotherm in DSC with ΔTmax. = 385°C indicates removal of non-coordinated part of complex. In second step 27.29% loss confirmed by ΔTmax. = 630.25°C by stable residue formation.

3.6. Antimicrobial activity

The antimicrobial activity of ligand and metal complexes were tested in vitro against bacteria such as Staphylococcus aureus and Escherichia coli by paper disc plate method [15]. The compounds were tested at the concentration 500ppm and 1000ppm. DMF and compared with known antibiotics viz. Ciproflaxin (Table 3). For fungicidal activity, compounds were screened in vitro against Aspergillus Niger and Trichoderma by mycelia dry weight method [16] with glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with control (Table 4).

From Table 3 and 4, it is clear that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes. Such enhanced activity of metal chelates is due to the increased lipophilic nature of the metal ions in complexes. The increase in activity with concentration is due to the effect of metal ions on the normal cell process.

Table 3: Antibacterial activity of compounds

Test Compound	Inhibition Zone (mm)			
	E.Coli		*Staphylococcus*	
	500 ppm	1000 ppm	500 ppm	1000 ppm
Ciproflaxin	29	32	31	35
(H_2L_1)	09	12	12	15
[$L_1Zn(H_2O)_2$]	13	17	17	19
(H_2L_2)	15	18	17	18
[$L_2Zn(H_2O)_2$]	19	23	21	24

Table 4: Yield of Mycelial dry weight in mg (% inhibition)

Test Compound	*Aspergillus Niger*		*Trichoderma*	
	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70
(H_2L_1)	61	24	40	19
[L_1 $Zn(H_2O)_2$]	53	18	34	08
(H_2L_2)	43	17	24	15
[$L_2Zn(H_2O)_2$]	32	10	22	04

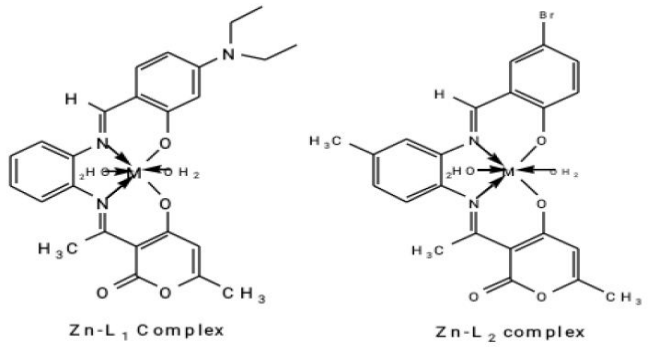

Fig. 1: The proposed structure of the complexes, Where M= Zn

4. CONCLUSION

In the present investigation we have reported synthesis of two asymmetrical ligand and its Zn (II) metal complexes. Spectral study probes chelation by azomethine nitrogen and phenolic oxygen are involved in the coordination with metal ions, proposing high spine octahedral geometry for both Zn (II) complexes. It is assumed that the ligands behave as dibasic and are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The XRD study suggests monoclinic crystal system. Study based on transition metal complexes is an under-developed area of research and is full of opportunities for further progress as Metal Complexation and its significant effects on biological activities.

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Conflict of interest

The authors certify that there is no conflict of interests with any financial organization regarding the material discussed in the paper.

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None declared

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