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Cu (II), Zn (II) & Cd(II) Metal Complexes with Heterocyclic Schiff Bases: Synthesis, Charactrization and Antimicrobial Study

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Abstract:

Metals complexes of ML_2 type of Cu (II), Zn (II) and Hg (II) were synthesised with Schiff bases prepared by condensation of substituted amino pyridine with 3-acetyl 4-hydroxyquinolin- 2-one. Newly synthesised metal complexes were characterized by various analytical and spectroscopic techniques including elemental analysis, magnetic moment, molar conductance along with electronic, thermal, infrared spectral analysis. Cu (II), Zn (II) and Hg (II) complexes of ligand (L_1) were subjected for their XRD Study. On the basis of magnetic, ESR, XRD and spectral studies octahedral geometry is assigned to Cu (II) Complexes while Zn (II) and Hg (II) Complexes possess tetrahedral geometry. All the synthesized complexes have been evaluated for their antibacterial as well as antifungal activities which has show significant activity for both properties.

Keywords: Metal Complexes, IR spectra, ESR, XRD and Biological Study.

Introduction:

Metal complexes incorporating heterocyclic Schiff bases constitute a significant and well-established domain within coordination chemistry due to their structural versatility and wide-ranging functional applications.[1] Heterocyclic Schiff bases are generally obtained through condensation reactions between heterocyclic amines and aldehydes or ketones, resulting in ligands containing the characteristic azomethine (–C=N–) linkage along with additional donor atoms such as nitrogen, oxygen present in the heterocyclic framework. This combination of donor sites enhances their chelating efficiency, electronic conjugation, and flexibility, enabling effective coordination with metal ions across different oxidation states and coordination environments.[2,3] The incorporation of quinoline and pyridine moiety in Schiff base plays a crucial role in modulating the physicochemical properties of the resulting metal complexes, including their thermal stability, redox characteristics, magnetic behaviour, and spectroscopic features.[4] As a result, quinoline Schiff base metal complexes have been extensively explored for applications in catalysis,[5] electrochemical processes,[6] corrosion inhibition,[7] and materials development.[8] Furthermore, research has demonstrated that metal complexes of Schiff bases of quinoline moiety exhibit notable biological activities, such as antimicrobial,[9]

antifungal,[10] antioxidant,[11] and anticancer effects,[12] often arising from the synergistic interaction between the metal center and the heterocyclic ligand system.

In present investigation we have synthesised metals complexes of Cu (II), Zn (II) and Hg (II) with Schiff bases prepared by condensation of substituted amino pyridine with 3-acetyl 4-hydroxyquinolin- 2-one. The synthesised metal complexes were characterised and subsequently examined for their antibacterial and antifungal properties.

Experimental:

All substances utilised were of analytical reagent quality, and the solvents were purified via distillation prior to use. Infrared spectra were acquired with KBr discs on a Shimadzu IR-470 Spectrometer. The elemental analysis was conducted via the Thermo Fisher Scientific CHN/S/O analyser. The magnetic susceptibilities of complexes were determined at room temperature using the Gouy's method and the Sherwood scientific magnetic susceptibility balance, calibrated with pure water. The molar conductance of metal complexes was measured with a Fisher Scientific conductometer. Molar conductance experiments were carried out at room temperature with 0.001 M complex solutions in DMSO. A Shimadzu thermos analyzer was used to do the thermal analysis. The open capillary method was used to compute melting points and left uncorrected.

Synthesis of Schiff Bases:

3-Acetyl-4-hydroxyquinolin-2-one was synthesized by refluxing Methyl 2-aminobenzoate with ethyl 3-oxobutanoate in the presence of in situ generated sodium ethoxide. Condensation of this compound with substituted aminopyridines yielded the target ligands (L_1–L_2), following the procedure reported in our previous work.[13]

Synthesis of Metal Complexes:

Metal complexes were synthesized by dissolving 0.02 mol of the Schiff bases in 50 mL of ethanol and heating the solution briefly. To this, 0.01 mol of the respective metal salt dissolved in 20 mL of ethanol was added gradually with continuous stirring. The mixture was refluxed for two hours and then cooled. A 10% alcoholic ammonia solution was added dropwise to the cooled reaction mixture until precipitation occurred at the desired pH. The precipitate was digested for one hour, filtered hot, washed successively with hot ethanol and petroleum ether (40–60 °C), and dried in a vacuum desiccator over calcium chloride.

Antibacterial Activity:

The antibacterial potential of the synthesized compounds was investigated using the agar well diffusion technique.[14] Mueller–Hinton Agar (MHA) was used as the growth medium for all antibacterial experiments. Ampicillin served as the reference antibiotic (positive control), whereas dimethyl sulfoxide (DMSO) was employed as the solvent and negative control. All dehydrated media and

antibiotics were obtained from Hi-Media Laboratories, India.

Fresh bacterial cultures were prepared by aseptically transferring test organisms into sterile Mueller–Hinton broth and incubating them at 37 °C for 18 h. The resulting cultures were used as inoculant and evenly spread onto MHA plates. Wells of 10 mm diameter were aseptically created in the agar using a sterile cork borer.

Each well was loaded with 100 µL of the test compound solution to achieve a final concentration of 10 µg per well. Equivalent volumes of DMSO and ampicillin were added to separate wells as negative and positive controls, respectively. The plates were kept at room temperature for 30 min to allow proper diffusion of the solutions and then incubated at 37 °C for 24 h.

The antibacterial activity was tested against *Bacillus subtilis* and *Staphylococcus aureus* (Gram-positive bacteria), as well as *Escherichia coli* and *Salmonella typhi* (Gram-negative bacteria). Following incubation, the zones of inhibition were measured in millimetres, considering only areas showing complete suppression of visible bacterial growth.

Antifungal Activity:

Antifungal screening was carried out using the poison plate method.[15] The fungal species selected for the study included *Aspergillus niger*, *Aspergillus flavus*, *Fusarium moniliforme*, and *Penicillium chrysogenum*. Potato Dextrose Agar (PDA) was used as the culture medium and sterilized by autoclaving at 121 °C for 25 min under a pressure of 15 psi.

Sterilized molten PDA (20 mL) was poured into sterile Petri dishes, followed by the addition of 2 mL of the test compound solution, and mixed gently to ensure uniform distribution. The same procedure was repeated for the positive control (neomycin) and the negative control (DMSO).

Fungal inoculant were prepared by transferring spores from slant cultures into sterile saline solution and mixing thoroughly. The prepared spore suspension was inoculated onto the PDA plates, which were then incubated at room temperature for four days. After incubation, fungal growth was observed and the antifungal activity was evaluated by comparing the results with those of the control plates.

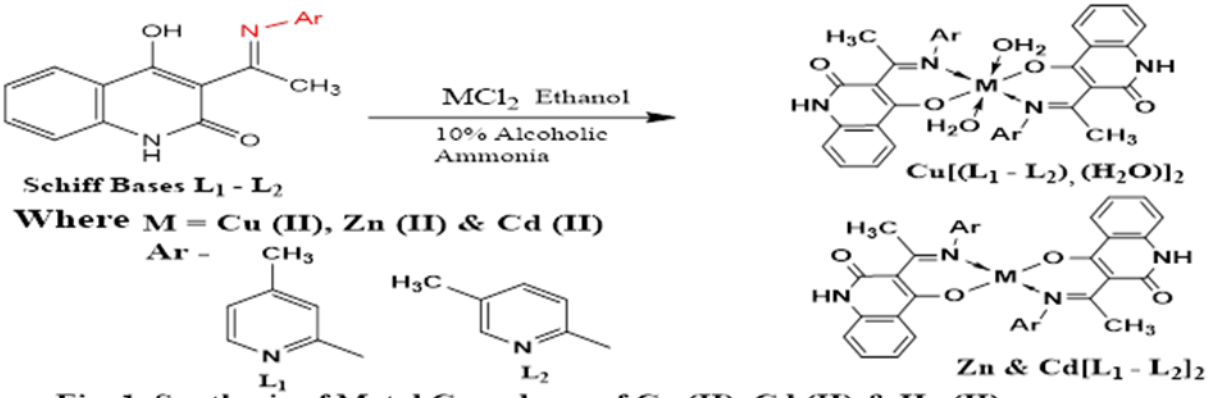


Fig. 1 Synthesis of Metal Complexes of Cu (II), Cd (II) & Hg (II)

Table No. 1 Elemental Analysis of Cu (II), Zn(II) & Cd(II) Complexes

S. No	Complexess	Molecular formula	Colour	M.P.°C	Mol.Wt.	Conductivity μ_v	Elemental analysis Found (Calculated)			
							%C	%II	%N	%M
1	$[Cu(L_1)_2]$	$[Cu(C_{17}H_{14}N_3O_2)_2(H_2O)_2]$	Dirty Green	267	684.21	15.86	59.55 (59.69)	4.65 (4.71)	12.20 (12.28)	9.18 (9.29)
2	$[Cu(L_2)_2]$	$[Cu(C_{17}H_{14}N_3O_2)_2(H_2O)_2]$	Dirty Green	263	684.21	15.82	59.52 (59.69)	4.60 (4.71)	12.19 (12.28)	9.27 (9.29)
3	$[Zn(L_1)_2]$	$Zn(C_{17}H_{14}N_3O_2)_2]$	yellowish White	272	650.02	18.23	62.77 (62.83)	4.37 (4.34)	12.86 (12.93)	10.0 (10.6)
4	$[Zn(L_2)_2]$	$Zn(C_{17}H_{14}N_3O_2)_2]$	yellowish White	277	650.02	18.60	62.77 (62.83)	4.38 (4.34)	12.87 (12.93)	9.80 (10.06)
5	$[Cd(L_1)_2]$	$[Cd(C_{17}H_{14}N_3O_2)_2]$	White	>300	697.05	14.53	58.51 (58.59)	4.00 (4.05)	12.02 (12.06)	16.12 (16.1)
6	$[Cd(L_2)_2]$	$[Cd(C_{17}H_{14}N_3O_2)_2]$	White	>300	697.05	14.69	58.49 (58.59)	4.00 (4.05)	11.95 (12.06)	16.04 (16.13)

Table 2: EPR data of the Cu(II) complexes of the ligand L_1

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	**G**	μ_{eff}
$Cu(L_2)_2$	2.257	2.101	2.15	2.59	1.81

Table No. 3 Electronic Spectral Data of Cu(II) Complexes

Sr. No.	Cu (II) Complexes of Ligand	Absorption Maxima cm^{-1} (nm)		
		V_1	V_2	V_3
1	$Cu(L_1)_2$	11370 (879)	15400 (649)	27777 (360)
2	$Cu(L_2)_2$	11240 (890)	15880 (630)	27777 (360)

Table No. 4 Magnetic Susceptibility Data of Cu (II) Complexes

Sr. No.	Cu (II) Complexes of ligand	χ_M x 10^6 (CGS)	χ_A x 10^6 (CGS)	$\mu_{eff.}$ (B.M.)
1	$Cu(L_1)_2$	1073.48	1372.68	1.81
2	$Cu(L_2)_2$	1103.98	1403.18	1.83

Table No. 5 Infrared Absorption Frequencies (cm^{-1})

Sr. No.	Ligand / Complex	Bond vibrational modes (stretching – ν (cm^{-1}))					
		Lactam	Pyridine	Azo-methine	Enolic	New Peaks	
		(C=O)	(C=N)	(C=N)↓	(C-O)↑	M-O	M-N
1	$Cu(L_1)_2$	1663	1610	1600	1265	486	443
2	$Zn(L_1)_2$	1670	1600	1596	1270	494	441
3	$Cd(L_1)_2$	1662	1607	1594	1275	495	453
4	$Cu(L_2)_2$	1661	1604	1597	1261	488	444
5	$Zn(L_2)_2$	1666	1602	1598	1276	495	445
6	$Cd(L_2)_2$	1663	1601	1593	1271	497	452

Table No.6 Anti- Bacterial and Anti-Fungal Activity

Synthesized Schiff base ligands	Antibacterial Study Zone of Inhibition (diameter in mm)				Antifungal Study Growth of Fungi			
	Gram Positive		Gram Negative		A. niger	A. flavus	F. moniliforme	P. chrysogenum
	S. typhi	B. subtilis	E. coli	S. aureus				
Ampicillin (Reference)	18	19	20	20	-	-	-	-
$Cu(L_1)_2$	13	15	14	14	-	+	-	-
$Zn(L_1)_2$	13	13	12	12	+	+	+	-
$Cd(L_1)_2$	19	19	20	19	++	+	+	-
$Cu(L_2)_2$	13	13	12	12	+	-	+	-
$Zn(L_2)_2$	15	14	13	13	+	+	+	+
$Cd(L_2)_2$	19	19	20	19	+	+	+	+

Moderate growth (++), Reduced growth (+) and No growth (-) of fungi

Result and Discussion:

All copper complexes synthesised in this study exhibit a greenish colour. They exhibit significant solubility in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The low conductivity values of the complexes in DMSO signify their non-electrolytic characteristics.[16]The elemental analysis data of metal complexes confirm the ligand to the metal ratio for Copper complexes as 2:1, proposing a monomeric complex. Zinc complexes are found yellowish white. They remain stable in air and moisture.

The Zn (II) complexes shows melting point in the range of 272-277°C temperature. They are insoluble in non-polar and common polar solvents. At a very low concentration, solutions can be prepared in methanol and DMSO. The molar conductance value of the complexes in DMSO (10^{-3}M) is very low (18.23 - 18.60 $mhos^{-1}$ cm^2mol^{-1}), indicating the non-electrolytic nature of complexes. The metal to ligand ratio was shown as 2:1, predicting a monomeric structure. Cadmium complexes are found colourless. They remain stable in air and moisture. The Cd(II) complexes decomposes at higher temperature (>300^0C). They are insoluble in non-polar and common polar solvents. At a very low concentration, solutions can be prepared in methanol and DMSO. The molar conductance value of the complexes in DMSO (10^{-3}M) is very low (14.53 -14.69 $mhos^{-1}$ cm^2mol^{-1}), indicating the non-electrolytic nature of complexes.[17] The metal to ligand ratio was shown as 2:1, predicting a monomeric structure. The colour, melting/decomposition temperature, conductivity measurement and elemental analysis of Cu (II), Zn (II) and Cd (II) complexes synthesized from ligand $L_1 – L_2$ are presented in the table -1.

The electronic spectra of Cu (II) complexes observed in the present work show absorption bands in three regions. V_1 = 11370-11240 cm^{-1}, V_2 = 15400 - 15880 cm^{-1} and V_3 = 27777cm^{-1}. These observed bands may be assigned to three spin allowed transition $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{lg}$ (F) and $^3A_{2g}\rightarrow{}^3T_{lg}$(F) charge transfer band respectively, which are characteristic of the distorted octahedral field.[18]The electronic spectral data of Cu (II) complex with their L_1 and L_2 ligands are presented in Table -3.

The magnetic moment values μ_{eff} of all Copper (II) complexes in the study were determined to be in the range. 1.81-1.83 B.M., agreeing to two unpaired electrons.[19]Their spectral data are presented in Table -4 while all Zn (II) and Cd (II) complexes are diamagnetic.[20]

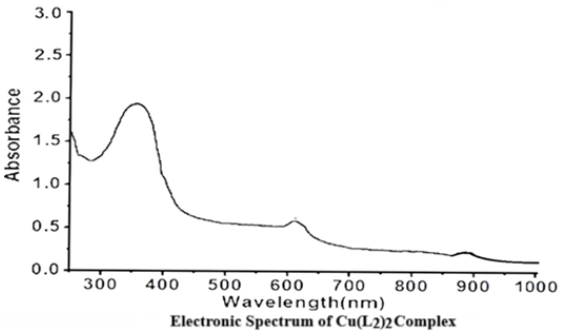
The crystal lattice parameters of the Cu (II), Zn (II) and Cd (II) complexes with ligand L_1 were determined by the X-ray diffraction powder method.[21] The X-ray diffraction patterns of complexes were recorded in the 2θ range from 10° to 80°. The data obtained and reciprocal lattice (*h, k, l)* are listed in the Table – 6 & 7. Based on the results and the literature support, the complexes with ligands are crystalline due to sharp refluxes and have been assigned monoclinic.[22]

In the IR spectra of the corresponding metal complexes are reported in table - 5, medium to weak bands appeared in the region1600-1593 cm^{-1} were assigned to C=N stretching vibration mode.[23] The medium intensity absorption bands in the region 1276-1261 cm^{-1} in the spectra of metal complexes were predictable to enolic C–O stretching frequency.[24] The band assigned to the lactam C=O stretching frequencies in the corresponding complexes were observed in the 1670-1661 cm^{-1}. The metal complexes of Cu (II) in the present research show a broad band in the region

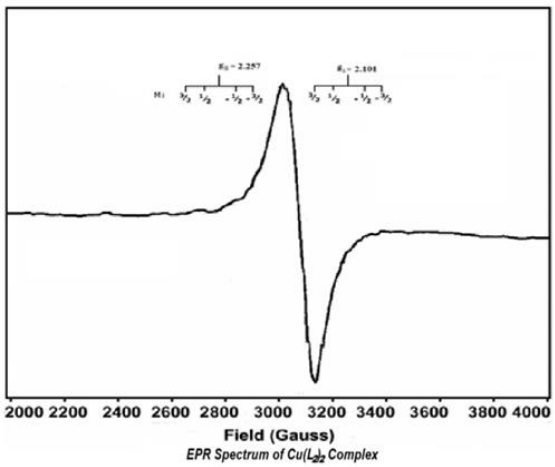
3500-2600 $cm^{-1,}$ which is attributed to the coordinated water present in these complexes.[25] Such bands are not observed in IR spectra of Zn (II) and Cd (II) complexes. However, a peak observed in all the spectra in the range 3431-3249 cm^{-1} is assigned to -N-H stretching.[26]

Based on conductivity, elemental and metal analysis, magnetic moment and electronic spectral data of the complexes, it is proposed that the Cu (II) complexes in the present investigation are having an octahedral configuration while Zinc and Cadmium complexes have tetrahedral geometry.

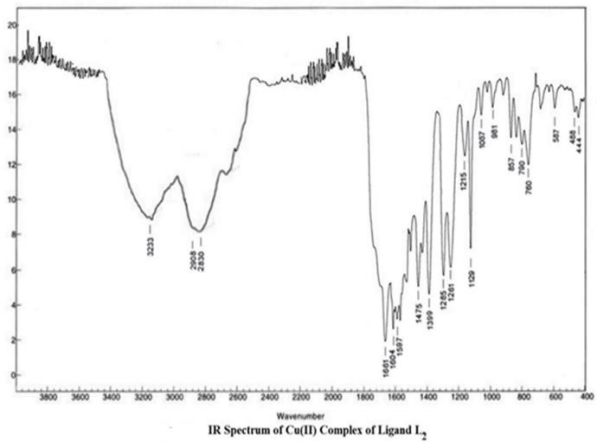
The synthesized complexes of Cu (II), Zn (II) and Cd (II) were subjected for evaluation of anti-microbial activity. The findings are reported in Table 6. Metal complexes of Cu (II), Zn (II) and Cd (II) have demonstrated good antibacterial activity with all bacterial species in the range of 20-12 mm diameter of zone of inhibition. The antifungal test of metal complexes with all ligands revealed that they exhibit significant activity.



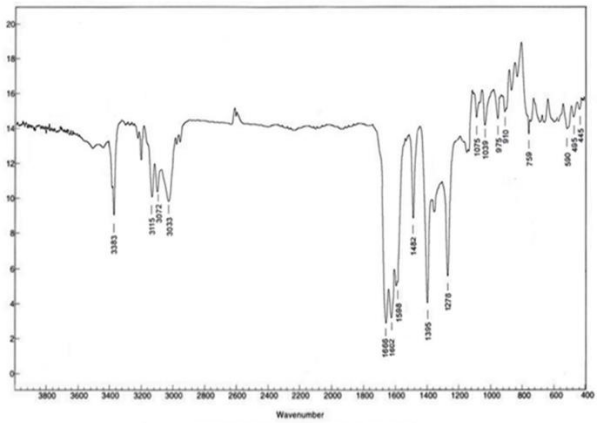
Electronic Spectrum of $Cu(L_2)_2$ Complex



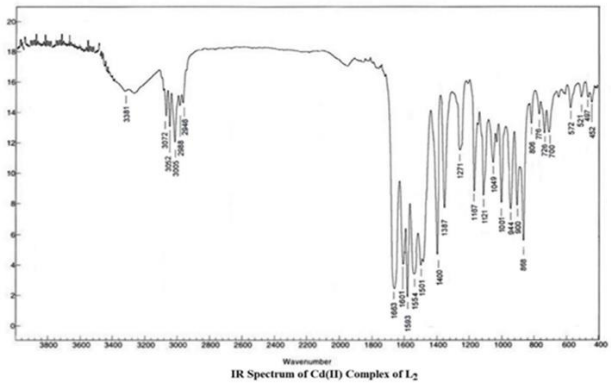
EPR Spectrum of $Cu(L_2)_2$ Complex



IR Spectrum of Cu(II) Complex of Ligand L_2



IR Spectrum of Zn (II) Complex with $Ligand_2$



IR Spectrum of Cd(II) Complex of L_2

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