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Research Article

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Synthesis, characterization and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of 3-pyridine carboxaldehyde and L-tryptophan

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ABSTRACT

The Schiff base complexes of Co(II), Ni(II), Cu(II) and Zn(II) derived from 3-pyridine carboxaldehyde and L-tryptophan. They have been synthesized and investigated by different physicochemical techniques. The resulting complexes were characterized by elemental analysis, molar conductance, IR, XRD and SEM. The low conductance values indicate that all the complexes are non-electrolytes. The metal in the Schiff base complex is hexacoordinated binds through pyridine nitrogen, azomethine nitrogen and nitrate units of metal salt used in the preparation. The synthesized compounds were tested for antimicrobial activity against the bacteria Klebsiella pneumonia, Pseudomonas aeroginosa, E.Coli, Staphylococus aureus, Proteus and Aspergillus niger. The complexes exhibit higher antimicrobial activity than the free Schiff base because of chelation.

Key words: 3-pyridine carboxaldehyde, L-tryptophan, Schiff base, Antimicrobial activity, Nuclease activity

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INTRODUCTION

Compounds which contain pyridine and its derivatives or Schiff bases as ligands have occupied a central role in the development of coordination chemistry and biochemistry. Schiff base ligands forms a stable complex with different transition metal ions. Schiff bases having multidentate coordination sites are known to form complexes with transition metal ions readily [1-6]. In particular, the transition metal complexes have been the subject for thorough investigation because of their extensive application in wide ranging areas from material science to biological sciences [7-9]. The formation of Schiff base intermediate in reactions of biological importance is well documented [10]. Schiff base and their metal complexes have a variety of applications in biological, clinical and analytical fields. Many potent antibacterial and antifungal Schiff base compounds of heterocyclic compounds were reported [11-14]. Some heterocyclic Schiff bases [15-16] can act as antibacterial agent and antifungal agent. The present paper deals with the study of preparation of some Schiff base complexes derived from 3-pyridine carboxaldehyde and L-tryptophan, to elucidate their structure and to show their biological activity on some bacteria and fungi.

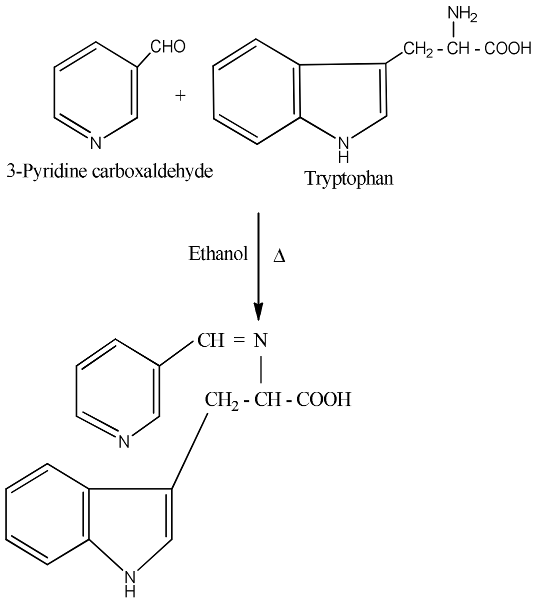
EXPERIMENTAL SECTION

All the chemicals and solvents used were of AR grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Metal salts were purchased from Loba Chemie.

IR spectra of the ligand and their complexes have been recorded in KBr pellets at Shimadzu FT-IR 8201 spectrophotometer in 4000-200 cm^{-1}. Elemental analyses were performed with Perkin Elmer 240 analyzer.

Preparation of Schiff base ligand:

The Schiff base ligand (L_1) was prepared as previously reported [17-18]. Equimolar amounts of tryptophan with 3-pyridine carboxaldehyde was mixed in ethanol and refluxed for 2 hours, then left to cool and the separated Schiff base was recrystallised from ethanol, washed thoroughly with diethyl ether and dried in vacuum.



Ligand(L_1)

Preparation of Schiff base complexes:

Schiff base complexes of ligand L_1 were prepared by the addition of hot ethanolic solutions (60^0C) of ligand L_1 and aqueous solution nitrates of Co(II), Ni (II), Cu(II) and Zn(II) in drop by drop in 2:1 molar ratio. The mixture was stirred for 8 hours at 60^0C. The precipitated solids were washed thoroughly by ethanol and then by diethyl ether. The solid complexes were dried in vacuum desiccator.

Determination of antimicrobial activity:

The in-vitro biological activity of the Schiff base and its metal complexes in DMSO were tested against the bacteria *Klebsiella pneumonia, Pseudomonas aeroginosa , E.Coli, Staphylococus aureus, Proteus* and fungi *Aspergillus niger* by disc diffusion method using nutrient agar as medium and *Amikacin, Flucanazole* as control. The inhibition zone was developed at which the concentration was noted. The antimicrobial activity was estimated based on the size of inhibition zone in the discs [19-22].

RESULTS AND DISCUSSION

All the metal complexes are coloured. They are stable towards air and have high melting point. The complexes are insoluble in water and common organic solvents but are soluble in DMF and DMSO.

Elemental Analysis:

The analytical data suggested that all the complexes are mononuclear with the ligand coordinated to the central metal atom. The stoichiometry [23] and physical characteristic of the complexes are given in Table. 1.1

Table.1.1 Analytical and Physical data of the ligand (L_1) and complexes

Compound	Colour (Yield %)	Empirical formula	Melting point (^{0}c)	Elemental analysis calculated (found) %			
				C	H	N	M
$C_{17}H_{15}N_3O_2$ (L_1)	Pale yellow (70%)	$C_{17}H_{15}N_3O_2$	162-166	69.62 (53.59)	5.12 (5.00)	14.33 (14.20)	-
$[(Co(L_1)_2(NO_3)_2]$	Brown (20%)	Co $C_{34}H_{30}N_8O_{10}$	217-219	53.06 (41.30)	3.90 (3.30)	14.56 (14.29)	7.66 (6.98)
$[(Ni(L_1)_2(NO_3)_2]$	Pale green (45%)	Ni $C_{34}H_{30}N_8O_{10}$	215-218	53.07 (54.10)	3.90 (3.01)	14.57 (14.41)	7.64 (7.57)
$[(Cu(L_1)_2(NO_3)_2]$	Blue (55%)	Cu $C_{34}H_{30}N_8O_{10}$	207-212	52.74 (51.90)	3.88 (3.60)	14.48 (14.01)	8.21 (8.64)
$[(Zn(L_1)_2(NO_3)_2]$	Dirty white (40%)	Zn $C_{34}H_{30}N_8O_{10}$	220-222	52.62 (51.91)	3.87 (3.99)	14.44 (13.95)	8.43 (8.99)

Molar Conductivity:

The molar conductivity values are given in Table.1.2. The molar conductivity values were in the range 16-21 ohm^{-1} cm^2 mol^{-1}. The low conductivity of complexes suggests the nitrato groups also involved in coordination and values were slightly higher for non-electrolytes. This may be due to partial solvolysis of the complexes in DMSO medium [24].

Table.1.2 Molar conductance data of ligand (L_1) and complexes

Ligand /Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})	Nature
$C_{17}H_{15}N_3O_2$ (L_1)	21	Non-electrolyte
[(Co(L_1)$_2$ (NO_3)$_2$]	18	Non-electrolyte
[(Ni (L_1)$_2$ (NO_3)$_2$]	17	Non-electrolyte
[(Cu(L_1)$_2$ (NO_3)$_2$]	19	Non-electrolyte
[(Zn(L_1)$_2$ (NO_3)$_2$]	16	Non-electrolyte

IR Spectral Studies of ligands and its complexes

The IR spectral data of the ligand (L_1) and its complexes are given in Table.1.3 and the respective spectra are shown in Fig.1.1-1.5. Comparison of IR spectra of Schiff base ligand with that of its metal complexes has been adopted to determine the coordinating atoms of the ligand to metal ions. From the IR spectrum of the ligand, the absorption band at 1655cm^{-1} is due to the absorption of imino group -CH = N-. The absorption band at 3401cm^{-1} is attributed to the N-H stretching vibration of the indole ring. The absorption band at 767cm^{-1}, 681cm^{-1}, 1338 cm^{-1} are due to the vibration of 3-substitued pyridine ring, C-H stretching frequency of CH_2 group, respectively. The FT–IR spectrum of the ligand is compared with the spectra of the complexes. The characteristic absorption bands 1625-1605 cm^{-1} were attributed to –C = N. The absorption bands 2850-2820 cm^{-1}, 3388-3332 cm^{-1}, 2949-2904 cm^{-1} were assigned to C–O, O – H and C– H respectively. The N-H stretching frequency of indole ring is not altered in the complex. Hence the –COOH group and indole nitrogen of tryptophan are not involved in binding. The – C= N bands for the free ligand at 1655 cm^{-1} were also shifted to lower frequencies in the spectra of the complexes. (1625-1605 cm^{-1}) suggesting coordination of both the nitrogen atoms to metal [25]. The absorption at 745-739 cm^{-1} is due to the coordination of nitrato group (M-N bond) with the central metal atom [26]. Thus in this metal-Schiff base complex system [M(L_1)$_2$(NO_3)$_2$] stiochiometric complex is formed and the metal binds the ligand L_1 through pyridine nitrogen, azomethine nitrogen and nitrate unit of metal salt used in the preparation. Thus metal in this Schiff base complex is hexa coordinated.

Table.1.3 Selected FT – IR frequencies (cm^{-1}) of the ligand $L_1$and complexes.

Ligand/complex	$\upsilon_{O-H}H_2O$	υ_{C-O}	υ_{C-H}	$\upsilon_{C=N}$	υ_{M-N}
$C_{17}H_{15}N_3O_2$ (L_1)	-	2832.63	2979.93	1655.49	–
[(Co(L_1)$_2$ (NO_3)$_2$]	3332.35	2847.23	2946.54	1605.17	745.85
[(Ni (L_1)$_2$ (NO_3)$_2$]	3385.58	2850.71	2949.12	1607.29	745.18
[(Cu(L_1)$_2$ (NO_3)$_2$]	3388.98	2820.15	2904.97	1625.11	739.08
[(Zn(L_1)$_2$ (NO_3)$_2$]	3388.06	2850.76	2922.60	1611.48	745.44

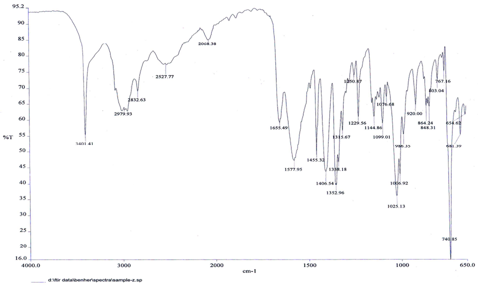


Fig.1.1 FT- IR spectrum of ligand(L_1)

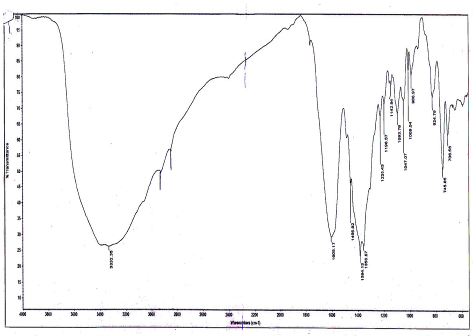


Fig.1.2 FT-IRspectrum of Co(II) complex

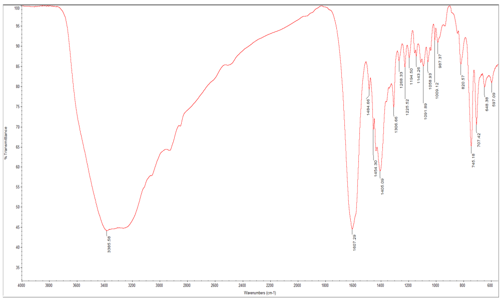


Fig.1.3FT-IR spectrum of Ni (II) complex

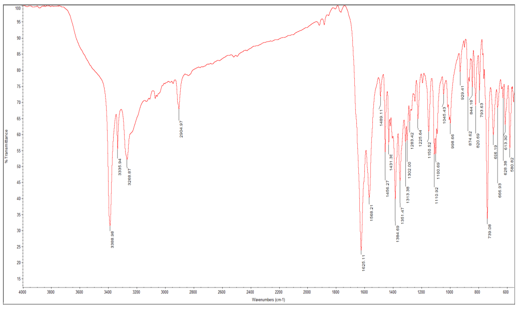


Fig.1.4 FT-IR spectrum of Cu(II)complex

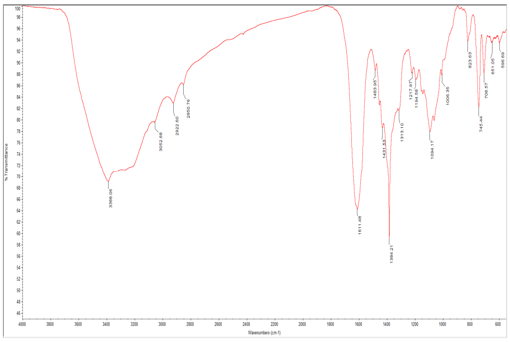


Fig.1.5 FT-IRspectrum of Zn (II) complex

Based on the observations in elemental analysis, vibrational spectral studies, the proposed structure of metal-Schiff base complexes [M $(L_1)_2(NO_3)_2$] was given in Fig. 1.6

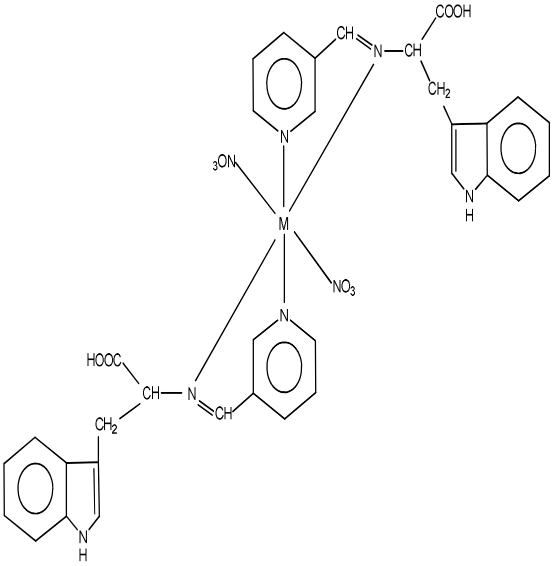


Fig.1.6 Proposed structure of Schiff base complex of Co(II), Ni(II), Cu(II) and Zn(II) ions of ligand L_1
M = Co(II), Ni(II), Cu(II) and Zn(II)

XRD Analysis:

The powder XRD for the Cu(II) complex was performed. The diffractogram was given in Fig.1.7.The grain size of the complex is calculated using Scherer's formula. The calculated grain size is 4.71 nm. This value suggested that the complex is in nano crystalline state.

$$\text{Particle size (d)} = \frac{K\lambda}{\beta \cos \theta}$$

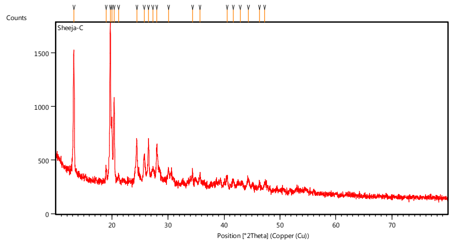


Fig.1.7 XRD spectrum of Cu(II)complex

SEM Analysis:

The surface morphology of Cu(II) complex has been studied using SEM and the respective images are given in Fig.1.8. SEM study reveals that all the complexes are crystalline in structure. The crystals are very clear, rough and pitted needle shaped surface are also seen. The particle size calculated from Scherer's formula showed that the complex is microcrystalline in nature with a size 4.71 nm.

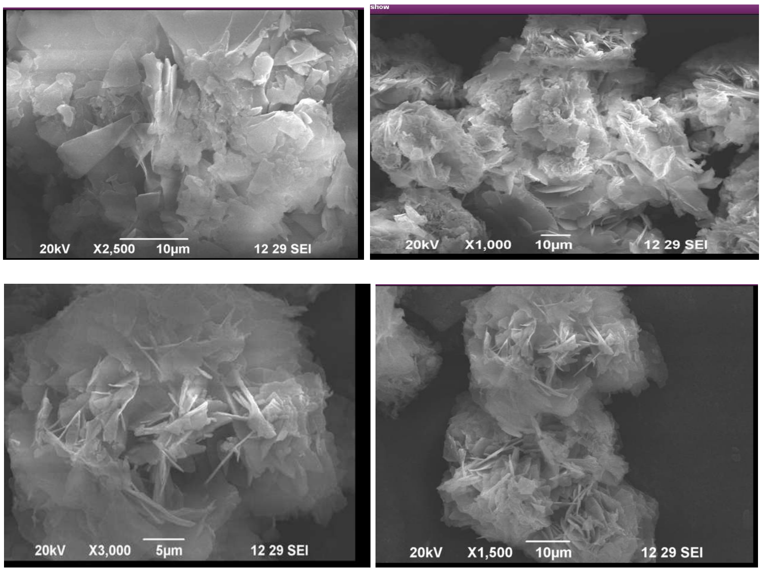


Fig.1.8 SEM images of Schiffbase of Cu(II) complex

Antimicrobial activity:

The results of antibacterial activity substantiate the findings of earlier researchers that biologically active compounds become active and less biologically active compounds become more active upon coordination. Such enhancement in biological activity of metal complexes can be explained on the basis of Overtone's concept and chelation theory [27]. The antimicrobial activity significantly increased on coordination [28].

Table 1.4 Antimicrobial activities of ligand L_1 and complexes

Ligand/ Complex	**Antibacterial activity (mm)**					**Antifungal activity (mm)**
	Klebsiella pneumonia	*Pseudomonas aeruginosa*	*E. Coli*	*Staphylococcus aureus*	*Proteus*	*Aspergillus niger*
$C_{17}H_{15}N_3O_2(L_1)$	9	10	9	7	10	10
$[(Co(L_1)_2 NO_3)_2]$	8	9	11	9	10	11
$[(Ni (L_1)_2 NO_3)_2]$	10	9	11	11	10	10
$[(Cu(L_1)_2(NO_3)_2]$	9	7	8	10	9	10
$[(Zn(L_1)_2 (NO_3)_2]$	8	8	9	10	11	8
Amikacin	20	25	18	28	23	-
Flucanazole	-	-	-	-	-	28

The present investigation suggest that all the metal complexes of the ligand bearing metal ion, pyridine ring, -N = CH- group, have comparatively more biological activity. This antibacterial activity serves as a basis for the chemical modification directed towards the development of new class of antimicrobial agents.

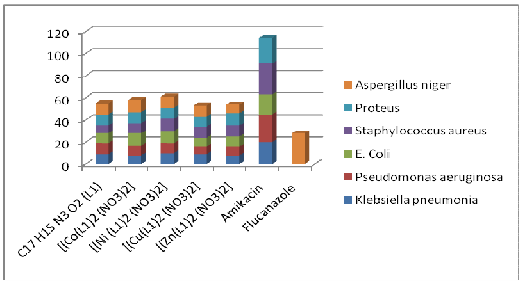


Fig.1.9 The variation of antimicrobial activity of ligand (L_1) and its complexes

CONCLUSION

The Schiff base ligand synthesized from 3-pyridine carboxaldehyde and L-tryptophan formed stable complexes with transition metal ions such as Co(II), Ni(II), Cu(II) and Zn(II) in ethanol. The ligand and their complexes were characterized using spectral and analytical data. From the spectral and stoichiometric analysis, a hexacoordinated nature was assigned for the metal complexes. Antimicrobial study showed that all the complexes have moderately active.

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