Synthesis and characterization of Schiff base complexes of Cu(II), Ni(II), Co(II) complexes of Schiff base derived from furan 3- carboxaldehyde and 3- amino pyridine

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Abstract- The Schiff base ligand, derived from furan 3- carboxaldehyde and 3- amino pyridine and the Cu(II), Co(II) and Ni(II) complexes were synthesized. The synthesized ligand and its complexes were characterized by elemental analysis, molar conductance, magnetic moment, ^{1}H NMR, IR, UV-Vis and SEM. The analytical data shows that the metal to ligand ratio is 1:2. The molar conductance data revealed that all the complexes are non-electrolytes. Antimicrobial studies indicated that the complexes exhibit more activity than the ligand.

Index Terms- Keywords: ^{1}H NMR, IR, Schiff base ligand, SEM, UV-Vis

I. INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and find extensive application [1- 3]. Schiff bases have played an important role as chelating ligands for a large variety of metal ions. In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance as catalysts in many reaction [4-9]. Also Schiff base complexes derived from heterocyclic compounds have acquired more attention in the field of bioinorganic chemistry because of their biological activities. Some heterocyclic-ketone derived Schiff bases show antibacterial activity and some others can act as antibacterial agent [10- 13]. The present investigation deals with synthesis and characterization of complexes of Cu(II), Ni(II) and Co(II) by Schiff base ligand (L) derived from furan 3 carboxaldehyde and 3- amino pyridine using various techniques.

2. MATERIALS AND METHODS

2.1 Chemicals

GR/AR grade quality chemicals obtained from Merck chemicals were used. All the solvent used were purified by standard methods [14]. The micro analytical data (C, H, N) were collected using Perkin Elmer 2400 instrument.IR spectra were obtained using Schimadzu FTIR 470 IR spectrophotometer.^{1}H NMR spectrum was obtained using Brucker Advance 111,400 MHz spectrometer. Conductance measurements were obtained using systronics-305conductivity meter. Electronic spectra of the ligands and its complexes were obtained using Schimadzu 1601, UV-Visible spectrometer. Powder XRD of complexes were recorded using Brucker AXS DS advance instrument.

2.2 Synthesis of Schiff base ligand

The ligand is prepared by taking equimolar ratio of furan-3-carboxaldehyde and 3-amino pyridine, which are dissolved in ethanol. It is then refluxed for one hour and reaction product is poured into ice. Yellow precipitate formed is filtered and washed with water.

2.3 Preparation of Schiff base metal complexes

The metal complexes were prepared by adding aqueous solution of Cu(II) nitrate, Ni(II) nitrate and Co(II) nitrate to the ligand in ethanol in 1:2 molar ratios and refluxed for about twelve hours at 80^0C. The precipitated solids were washed with ethanol, diethyl ether and hot water and finally dried under vacuum at 90^0C [15-18].

3. RESULTS AND DISCUSSION

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

3.1 Elemental Analysis

The analytical data suggested that all the complexes are mononuclear with the ligand coordinated to the central metal atom. The metal to ligand ratio in all complexes was 1:2[19,20]. The details are given in Table 1.

Table: 1 physical characteristics and analytical data of the complexes.

Compound	Yield%	Colour	Mol. Formula	Mol. Wt.	Elemental Analysis Found (Calcd) %		
					C	H	N
Ligand(L) $C_{10}H_8ON_2$	60	Brown	$C_{10}H_8ON_2$	172	69.76 (69.71)	4.65 (4.63)	16.27 (16.25)
$[CuL_2(NO_3)_2]$	57	Light green	$C_{20}H_{16}O_8N_6Cu$	531.55	45.15 (45.11)	3.01 (2.99)	10.53 (10.51)
$[CoL_2(NO_3)_2]$	59	Brown	$C_{20}H_{16}O_8N_6Co$	526.94	45.54 (45.52)	3.03 (3.01)	10.62 (10.60)
$[NiL_2(NO_3)_2]$	55	Brown	$C_{20}H_{16}O_8N_6Ni$	526.7	45.56 (45.53)	8.75 (8.74)	10.63 (10.61)

3.2 Molar Conductivity

The observed molar conductance data in 10^{-3} M DMF indicate non-electrolytic nature of complexes because their conductivity values were in the range 15-22 ohm^{-1} cm^2mol^-(Table 2), thus all the complexes are non electrolytes. But the conductivity values were slightly higher than for non-electrolytes. This may be due to the partial solvolysis of the complexes in DMF medium [21].

Table 2. Molar Conductance data of the complexes

Compound	Molar conductance Ohm^{-1} cm^2 mol^{-1}
Ligand(L) $C_{10}H_8ON_2$	22
$[Cu\ L_2(NO_3)_2]$	17
$[Co\ L_2(NO_3)_2]$	16
$[Ni\ L_2(NO_3)_2]$	15

3.3. IR Spectra

The IR Spectrum provides the valuable information regarding the nature of functional groups coordinated to the metal atom. The selected IR spectral data of the ligand and complexes given in Table-3. The IR spectra of the ligand showed a broad band in the region 3347 cm^{-1} - 3213 cm^{-1} due to N-H stretching of amine. The absorption band at 1623 cm^{-1} [22] can be assigned to C=N stretching. In all the complexes this bond is shifted to lower frequencies in the range 1638 cm^{-1} – 1622 cm^{-1} up on complexation with metal, which can be attributed to coordination to imine nitrogen to metal centre. The bands in the region 1990-2200 cm^{-1} is due to C- H stretching. The bands in the region 745 cm^{-1} - 707 cm^{-1} is due to M-O stretching frequency. Absorption peaks in the region 1567 cm^{-1} -1549 $cm^{-1}$of complexes is due to C-NO_2 stretching frequency.

Table 3. Selected FT IR frequencies (cm^{-1}) of the ligand and complexes

Ligand/ Complex	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	ν_{C-H}	ν_{M-N}	ν_{C-NO2}
Ligand(L) $C_{10}H_8ON_2$	3347	1344	1623	2114	-	-
[Ni $L_2(NO_3)_2$]	3213	1344	1567	2108	707	1567
[Co $L_2(NO_3)_2$]	3100	1344	1706	2150	752	1552
[Cu $L_2(NO3)_2$]	3200	1365	1622	2105	708	1549

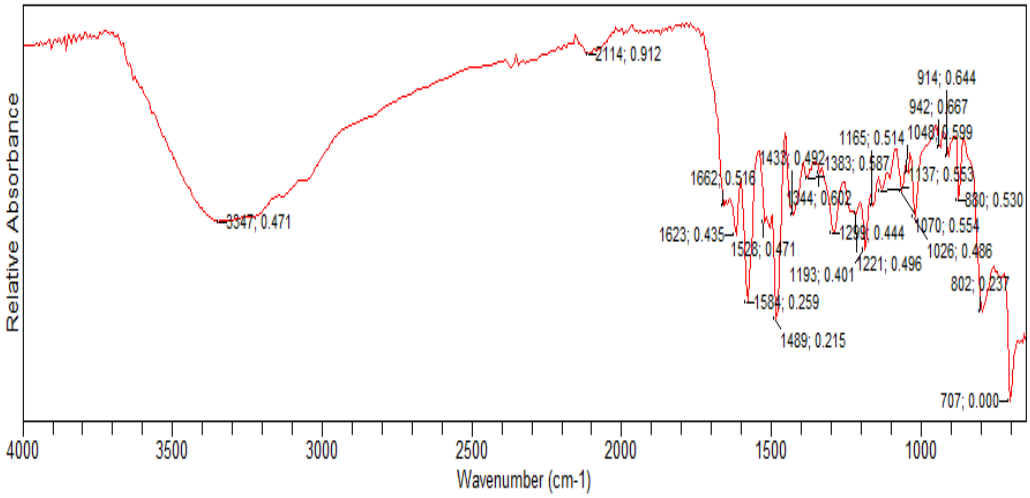

Fig: 1- FTIR Spectrum of Schiff base ligand (L)

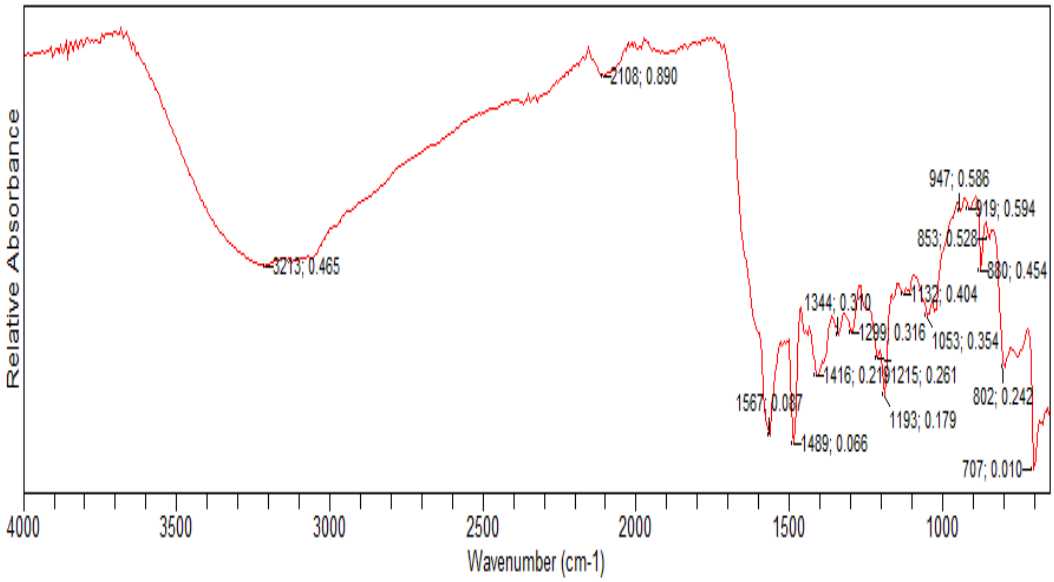

Fig. 2 FTIR spectrum of Ni(II) complex

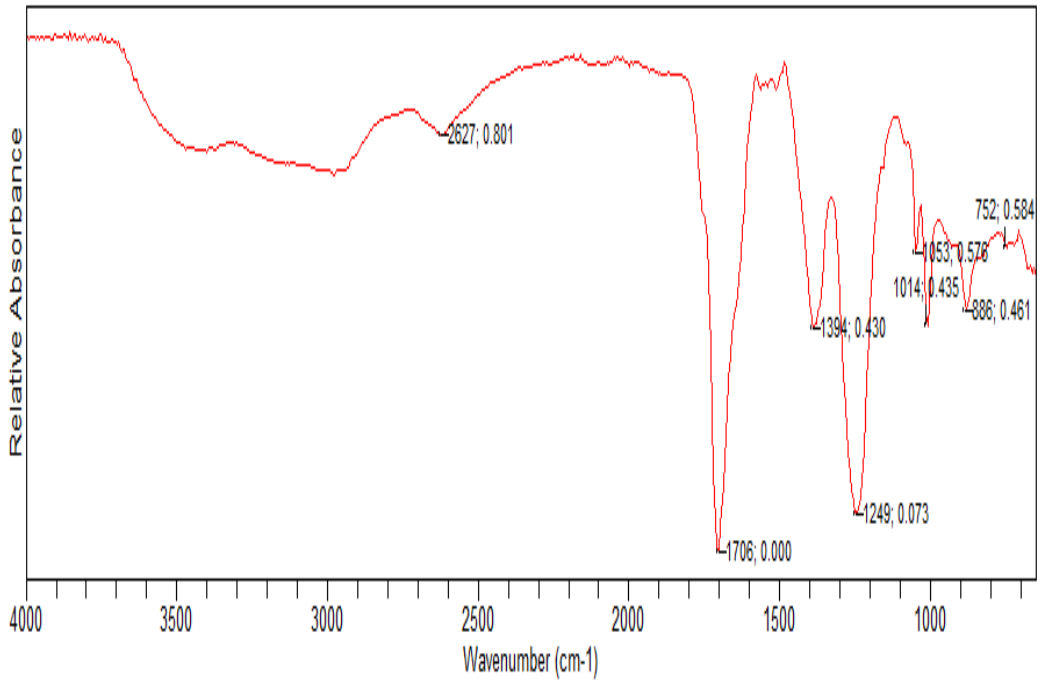

Fig. 3 FTIR spectrum of Co(II) complex

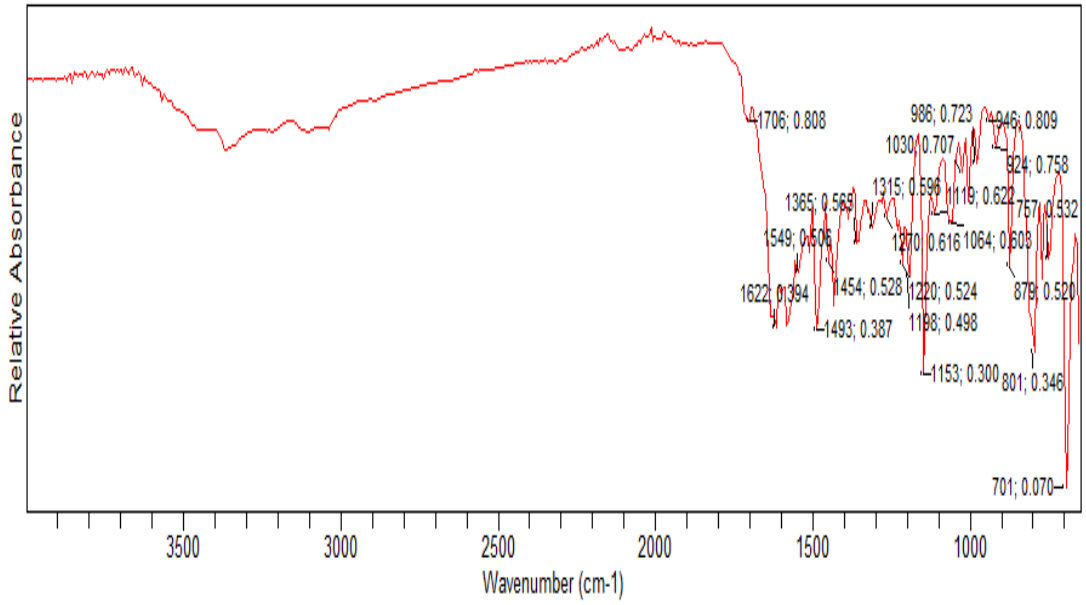

Fig.4 FTIR spectrum of Cu(II) complex

3.4. UV visible spectra

The absorption region assignment and geometry of the ligand and complexes are given in Table.5 The ligand showed a broad band at 330 nm which is assigned to n-π^* transition of the C=N chromophore. On complexation this bond was shifted to the lower wave length suggesting the coordination of imine nitrogen with central metal ion [23]. The UV spectra of the Cu(II) complexes showed three absorption bands at 321nm, 308nm and 263nm giving a hexahedral coordination. The UV spectra of Co(II) and Ni(II) complexes showed absorption bands at 228 nm, 220nm and 278nm, 287nm and 264nm respectively suggesting octahedral coordination for the complexes.

Table 5 UV-Visible Spectra of the ligand (L) and complexes

Ligand/ Complex	$\lambda_{max\ (nm)}$		
Ligand(L) $C_{10}H_8ON_2$	215	210	207
$[Cu\ L_2(NO_3)_2]$	228	220	-
$[Co\ L_2(NO_3)_2]$	278	287	264
$[Ni\ L_2(NO_3)_2]$	321	308	263

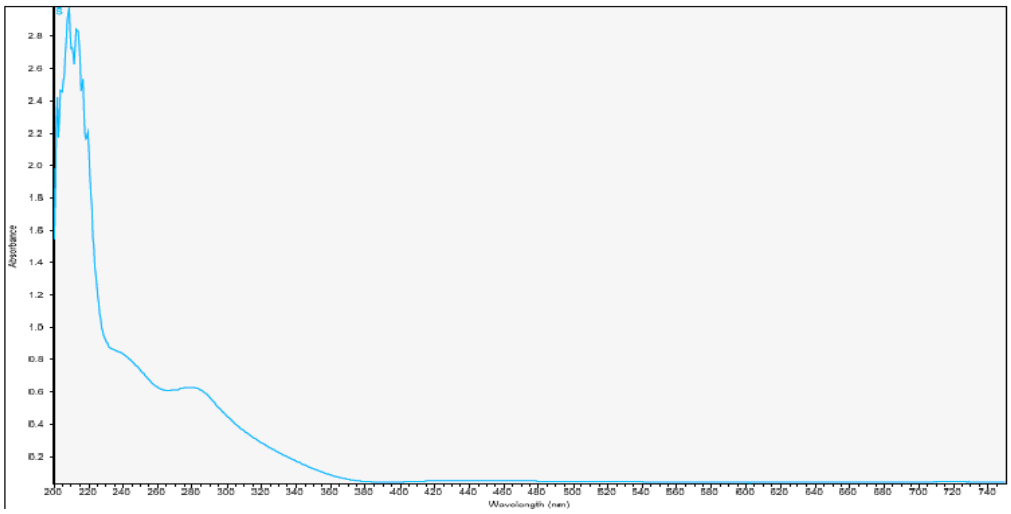

Fig.6 UV visible Spectrum of ligand (L)

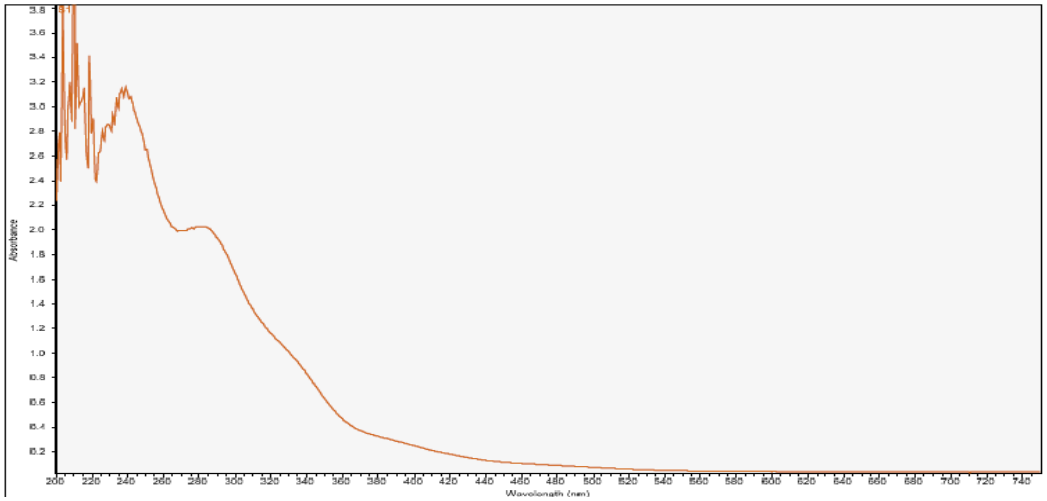

Fig.7 UV visible spectrum of Cu(II) complex

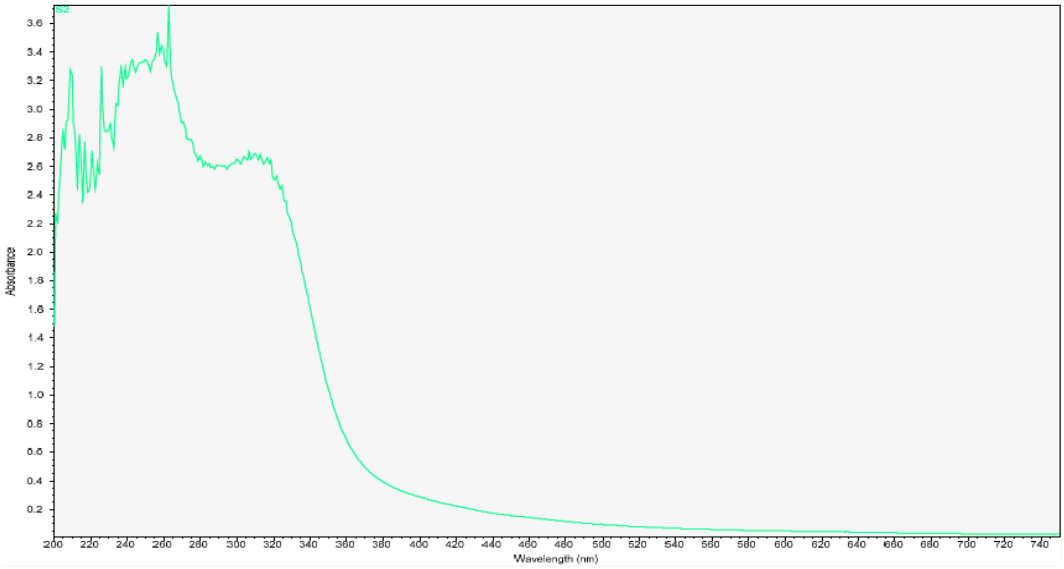

Fig.8 UV Visible spectrum of Ni(II) complex

3.5 Magnetic Susceptibility Measurements (BM)

The magnetic susceptibility values of the complexes are shown in Table 6.

Table 6 Magnetic Susceptibility Measurements (BM)

Ligand/ Complex	Magnetic Susceptibility (BM)
[Cu $L_2(NO_3)_2$]	1.82
[Co $L_2(NO_3)_2$]	2.54
[Ni $L_2(NO_3)_2$	3.1

The Cu(II) complex exhibited magnetic moment of 1.82 BM indicating greater distorted octahedral geometry of the complex. Co(II) complex had magnetic moment of 2.54BM indicated the high spin nature of the complex and have octahedral geometry. The Ni(II) complex exhibited the magnetic moment value of 3.1 BM indicated octahedral coordination.

3.6 ^{1}H NMR Spectra

The ^{1}H NMR Spectra of the ligand shows a peak at δ = 9.81ppm is accommodate to the azomethine proton of the CH=N group. Peaks around δ = 6.7 – 7.59 ppm shows to presents aromatic ring proton. The peak at δ =1.9 -1.06ppm is due to the proton at the furan ring.^{1}H NMR Spectra of the ligand is shown in Fig.9

On complexation a signal appears due to the proton attached to azomethine group at δ = 9.89 ppm. This field shift indicates the deshielding of azomethine proton coordination through the nitrogen atom of the azomethine group.

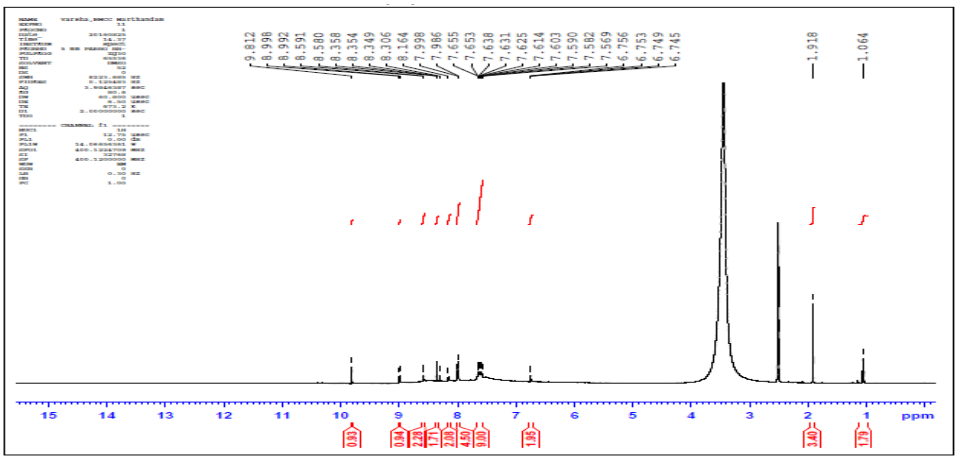

Fig.9 ^{1}H NMR Spectra of ligand

Based on the above results the proposed structure of Ligand (L) and its metal complexes is given below,

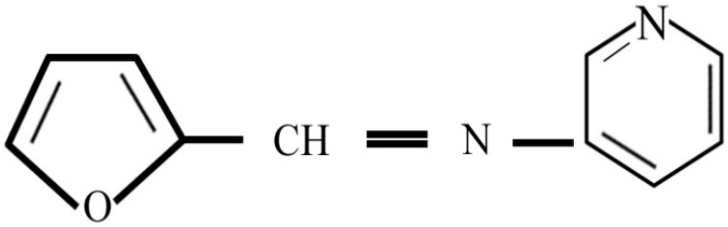

Fig.10 Structure of Ligand L

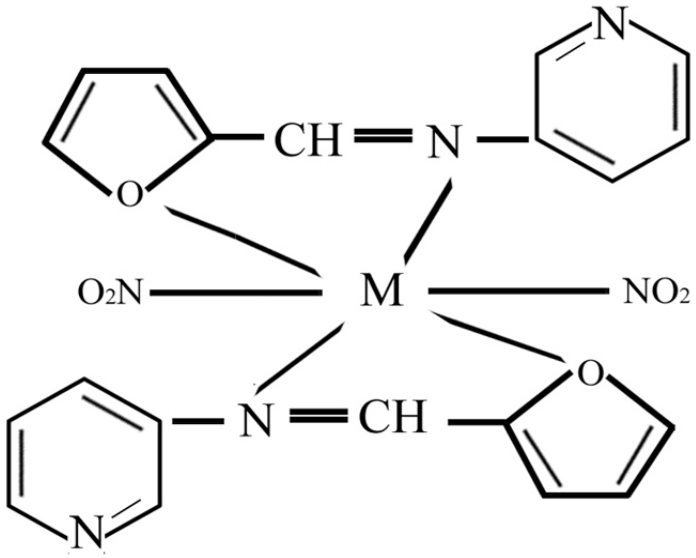

Fig.11 Structure of metal complexes with Ligand L (M=Cu, Co, Ni)

3.7 SEM Analysis

The surface morphology of the complexes has been examined using scanning electron microscope. The SEM images of Cu(II) complex is given below. The SEM images showed that all the complexes are micro crystalline in nature, with rough

and pity surface. Careful examination of the single crystal, clearly indicated the nanoscale size of the single crystal of the complexes [16].

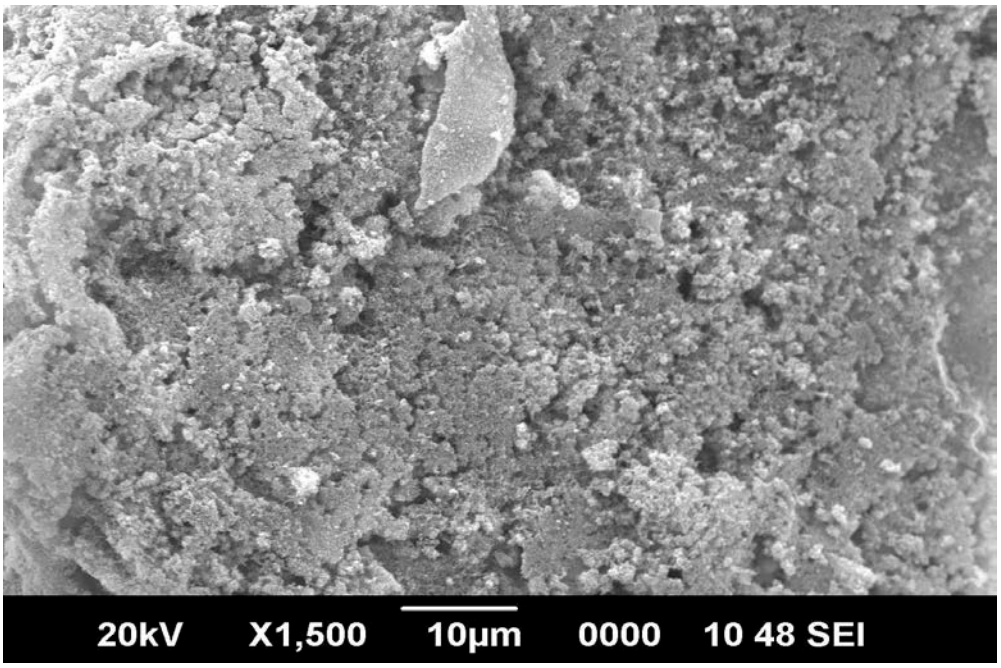

Fig.12 SEM image of Schiff base complex of Cu(II)

3.9. Antibacterial activity

Schiff base complexes of transition metals play vital role in biological study; some of these have now been widely studied for their antimicrobial and anticancer properties [24,25] and extensive investigations in the field of metal complexes have been reported [26,27].

The present investigation suggests that all the metal complexes of the ligand bearing metal ion, phenolic moiety, benzene ring, -N=CH- group have comparatively more biological activity [28]. This study serves as a basis for the chemical modifications directed towards the development of new class of antibacterial agents. Antibacterial activities of the ligand, complexes and standard drugs were screened by disc diffusion method in DMSO as solvent. The results of antibacterial study are given in Table-7. The antibacterial activity was estimated based on the size of inhibition zone in the discs. Under identical conditions the Schiff base complexes of Cu(II) is found to be more active, others exhibit moderate activity

Table.7 Antibacterial activity data of ligand and its complexes.

Ligand/Complex	S. aureus	Styphi	Vcholera
Ligand(L) $C_{10}H_8ON_2$	6mm	-	-
[Ni $L_2(NO_3)_2$]	6mm	7mm	6mm
[Co $L_2(NO_3)_2$]	9mm	8mm	9mm
[Cu $L_2(NO3)_2$]	18mm	14mm	15mm
Positive	30mm	25mm	26mm

3.10 Antifungal activity

The results of antifungal studies reveal that both ligands and complexes do not show anti-fungal properties [29]. The data are given in Table 8

Table.8 Antifungal activity data of ligand and its complexes.

Ligand/Complex	Candida albicans	Aspergilles niger	Candida humilis
Ligand(L) $C_{10}H_8ON_2$	-	-	-
[Ni $L_2(NO_3)_2$]	-	-	--
[Co $L_2(NO_3)_2$]	-	-	-
[Cu $L_2(NO3)_2$]	9mm	8mm	-
Positive	30mm	25mm	26mm

4. CONCLUSION

Schiff base transition metal complexes Cu(II), Ni(II) and Co(II)were synthesised from furan-3- carboxaldehyde using 3-amino pyridine, and characterized on the basis of analytical and spectral data. Elemental analysis shows the metal to ligand ratio is 1:2. Conductivity measurements show all complexes are non-electrolytes. From SEM analysis crystalline nature of complexes is confirmed. Anti-bacterial study shows that all complexes are more active than ligand and Antifungal studies indicates their inactivity towards fungi.

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