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Synthesis and Characterization of Bioactive Transition Metal Complexes of Cu(II), Co(II) and Ni(II) using 1 naphthyl amine and salicylaldehyde

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Abstract: *The Schiff base complexes Co(II), Ni(II) and Cu(II) of salicylaldehyde and 1 naphthyl amine were synthesized and characterized by elemental analysis, conductivity measurements, electronic, infrared, SEM, spectral measurements and antibacterial studies. The conductance measurements indicate that all the complexes are non-electrolytes. The results indicate that the metal complexes of Ni(II), Co(II) and Cu(II) are hexa-coordinated and have moderate antibacterial activity.*

Keywords: *Antibacterial activity, Elemental analysis, Salicylaldehyde, Schiff base,1 naphthyl amine.*

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I. INTRODUCTION

The Schiff bases are widely studied because of the increasing recognition of their role in biological systems [1]. Schiff-base complexes are used as catalysts in some chemical processes, as biological models for understanding the structures of biomolecules and to emulate the activity of proteins [2]. Schiff bases and their complexes were recently found to have significant antitumor and biological activity [3,4]. The present investigation shows that the synthesis and characterization of schiff base ligand (L) with salicylaldehyde and 1-naphthyl amine and its complexes of Cu(II), NI(II) and Co(II) ions. The above complexes were characterized by elemental analysis, conductance measurements, UV-Visible, IR, SEM, antibacterial and antifungal activity. Thus the result indicates that the complexes are hexa coordinated and also have moderate antibacterial activity. SEM analysis reveals nano crystalline nature of complexes.

II. MATERIALS AND METHODS

2. 1Chemicals

All the chemicals used were of GR/AR grade quality obtained from Merck chemicals. All the solvent used were purified by standard methods [5]. 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-305 conductivity meter. Electronic spectra of the ligands and its complexes were obtained using Schimadzu 1601, UV-Visible spectrometer. Surface morphological studies were obtained using JSM- 6390V scanning electron microscope. Powder XRD of complexes were recorded using Brucker AXS DS advance instrument.

2. 2 Synthesis

The ligand L is prepared by taking equimolar ratio of salicylaldehyde and 1-naphthyl amine, 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 Copper(II) nitrate, Nickel(II) nitrate and cobalt(II)nitrate to the ligand in ethanol in 1:2 molar ratios and refluxed for about twelve hours at 80^{o}C. The precipitated solids were filtered, washed with ethanol, diethyl ether and hot water, and finally dried under vacuum at 90^{o}C [6- 10].

III. RESULTS AND DISCUSSION

All the metal complexes are coloured solids, stable towards air. The complexes are insoluble in water and common organic solvents, but are soluble in DMF, $CDCl_3$ and DMSO.

3. 1 Elemental analysis

The analytical data suggest that all the complexes are mononuclear with the ligand coordinated to the central metal atom and the metal to ligand ratio in all complexes was 1:2, and their formulae have been computed and 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)	61	Brown	$C_{17}H_{13}NO$	248	82.32 (82.25)	5.91 (5.64)	5.83 (5.64)
$[CuL_2(NO_3)_2]$	57	Light green	$C_{34}H_{26}N_4O_8Cu$	683.55	59.71 (59.68)	4.20 (4.09)	4.25 (4.09)
$[CoL_2(NO_3)_2]$	59	Brown	$C_{34}H_{28}N_4O_8Co$	678.94	61.10 (60.90)	4.32 (4.12)	4.82 (4.71)
$[CuL_2(NO_3)_2]$	55	Brown	$C_{34}H_{26}N_4O_8Ni$	678.7	60.41 (60.11)	4.29 (4.12)	4.9 (4.92)

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 15-24 ohm^{-1} cm^2 mol^{-1}(Table 2). The conductivity values indicated that the absence of $–NO_3$ group outside the coordination sphere [11]. 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.

Table 2. Molar Conductance data of the complexes

Compound	Molar conductance Ohm^{-1} cm^2 mol^{-1}
Ligand(L) ($C_{17}H_{13}NO$)	20
$[Cu\ L_2\ (NO_3)_2]$	22
$[Co\ L_2\ (NO_3)_2]$	19
$[Ni\ L_2\ (NO_3)_2]$	17

3. 3 IR Spectra

The selected IR spectral data of the ligand and complexes given in Table- 3. The absorption band at 1633 cm^{-1} ligand can be assigned to C=N stretching. In all the complexes this band is shifted to lower frequencies in the range 1612 cm^{-1} – 1606 cm^{-1} up on complexation with metal, which can be attributed to coordination to imine nitrogen to metal atom. The bands in the region 758 cm^{-1} - 719 cm^{-1} is due to M-N stretching frequency. The bands at 1573 cm^{-1}- 1511 cm^{-1} in complexes is due to C-NO_2 bond [12,13]

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

Ligand/ Complex	$\nu_{C=N}$	ν_{C-O}	ν_{C-N}	ν_{O-H}	ν_{M-N}	ν_{C-NO2}	ν_{H2O}
Ligand(L_1) ($C_{17}H_{13}NO$)	1620	-	1300	1450	-		-
$[Ni\ L_2\ (NO_3)_2]$	1612	1667	1360	-	758	1573	-
$[Co\ L_2\ (NO_3)_2]$	1611	-	1343	-	757	1533	-
$[Cu\ L_2\ (NO_3)_2]$	1606	1667	1305	-	758	1533	

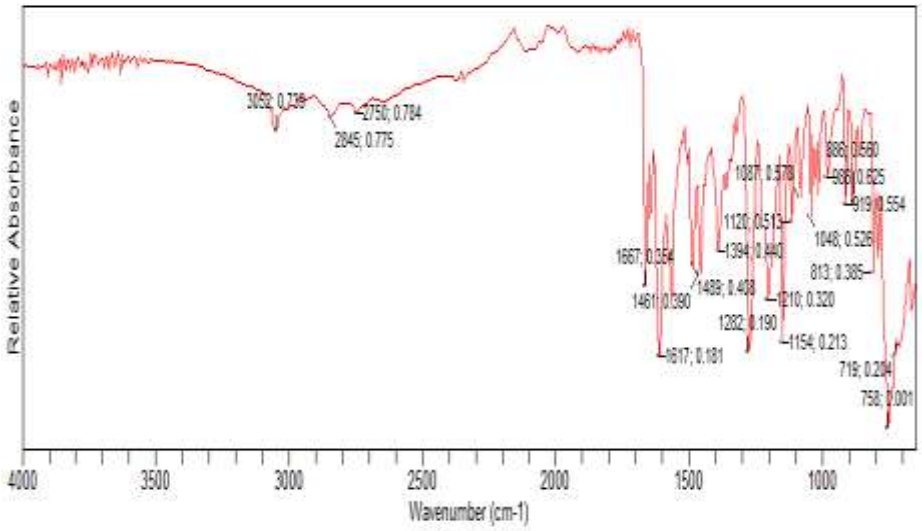

Fig:1-FTIR Spectrum of ligand

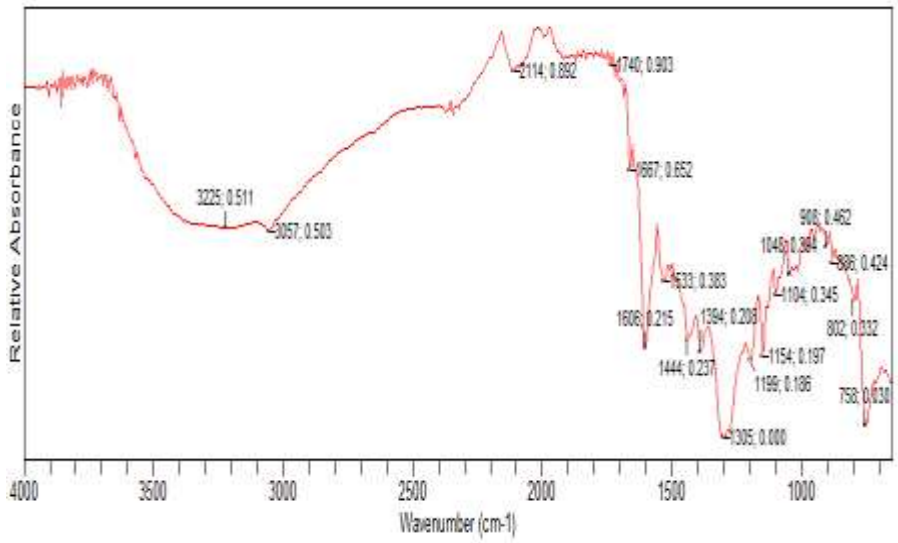

Fig:2-FTIR Spectrum of Ni(II) complexes

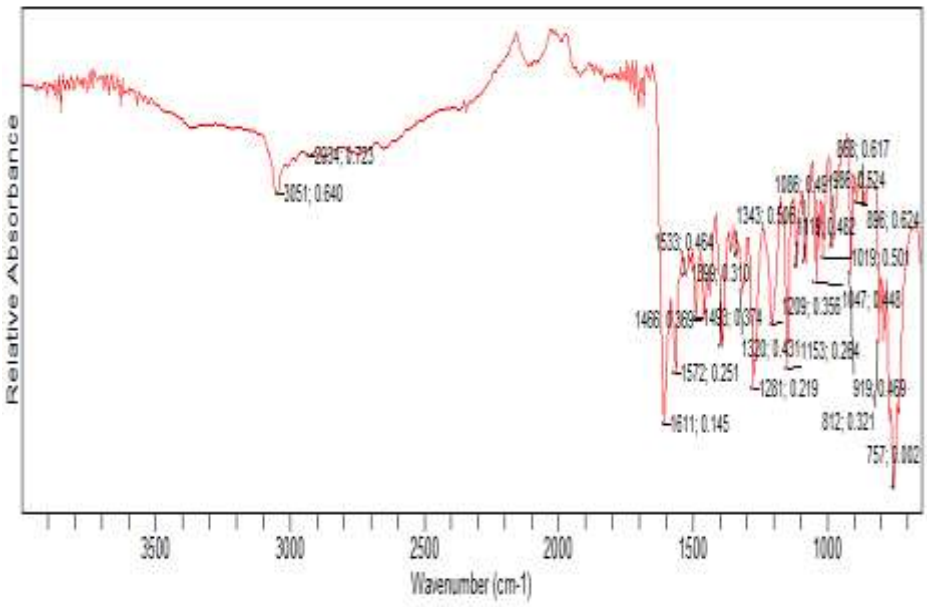

Fig:.3 FTIR Spectrum of Co(II) complexes

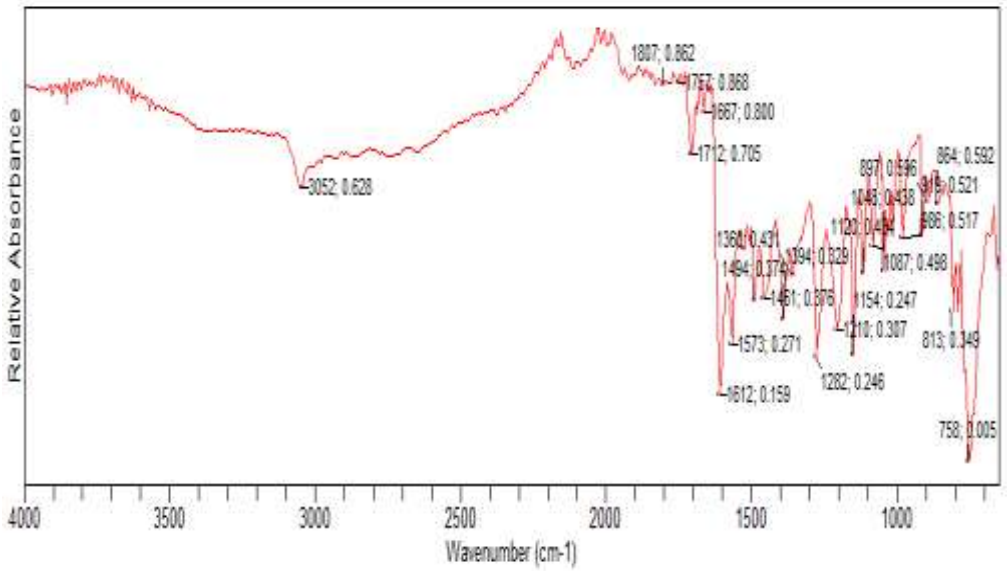

Fig:4 FTIR Spectrum of Cu(II) complexes

3. 4 UV visible spectra

The absorption region assignment and geometry of the ligand and complexes are given in Table 4. The ligand showed a broad band at 333 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. The UV spectra of the Cu(II) complexes showed three absorption bands at 229nm, 235nm and 390nm giving an hexacoordinated geometry. The UV spectra of Co(II) and Ni(II) complexes showed absorption bands at 220 nm, 227nm and 224nm and 301nm, 241nm and 248nm respectively suggesting octacoordinated geometry for the complexes [14,15].

Table 4. UV-Visible Spectra of the ligand(L) and complexes

Ligand/ Complex	**$\lambda_{max\ (nm)}$**		
Ligand(L) ($C_{17}H_{13}NO$)	264	333	322
[Cu L_2 $(NO_3)_2$]	229	235	390
[Co L_2 $(NO_3)_2$]	229	-	-
[Ni L_2 $(NO_3)_2$]	301	241	228

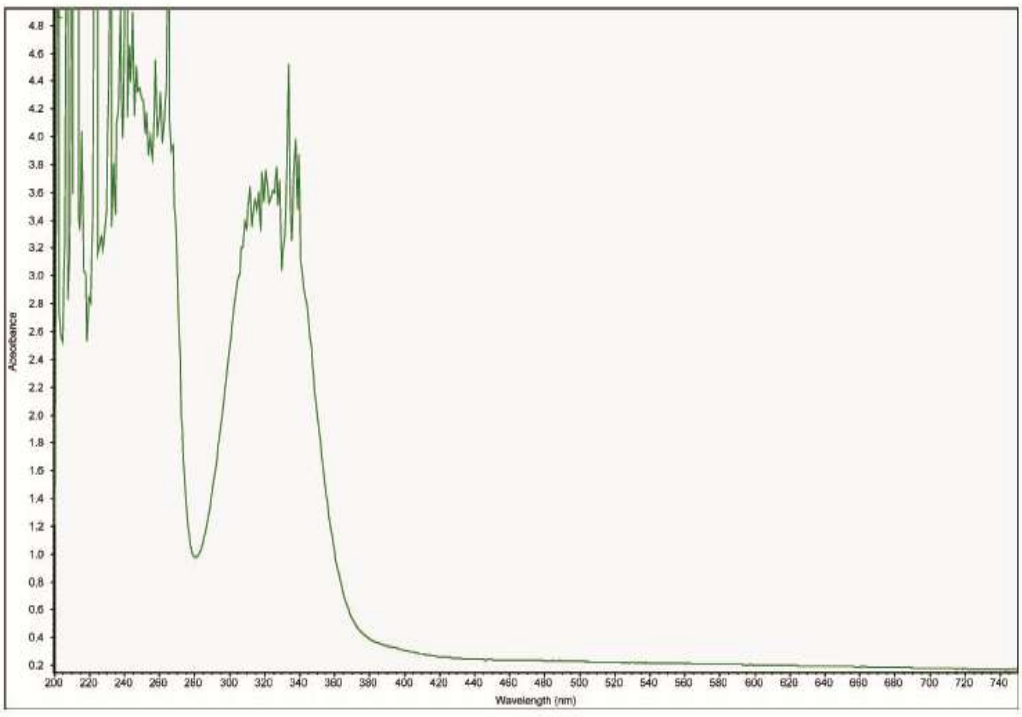

Fig.5 UV spectrum of Ligand

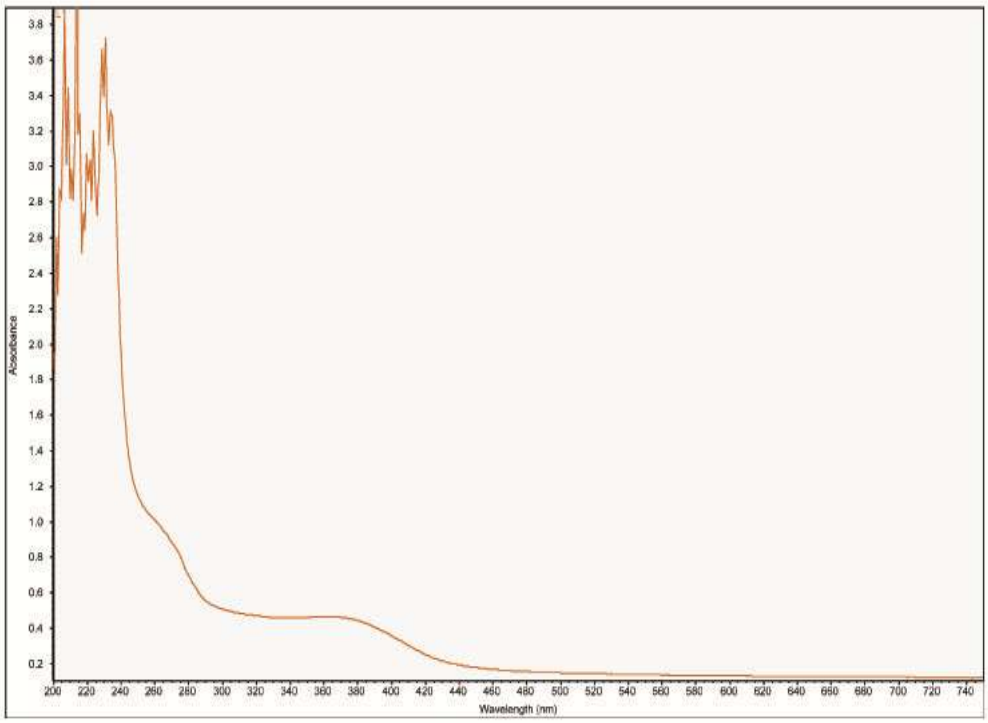

Fig.6. UV visible spectrum of Cu(II) complex

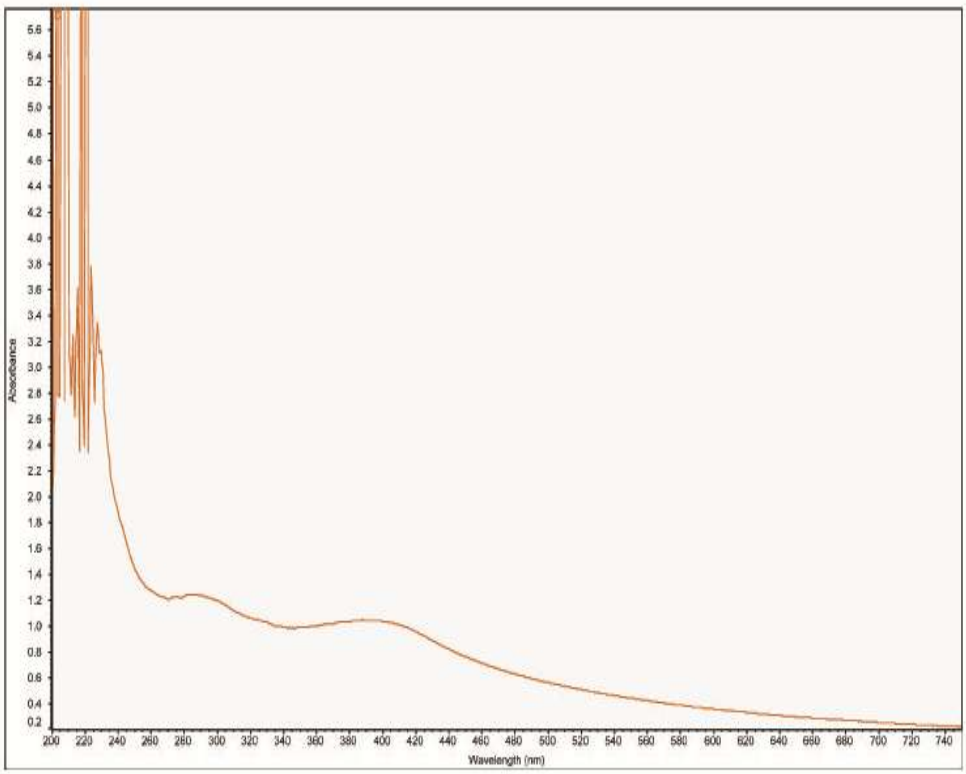

Fig.7. UV visible spectrum of Co(II) complex

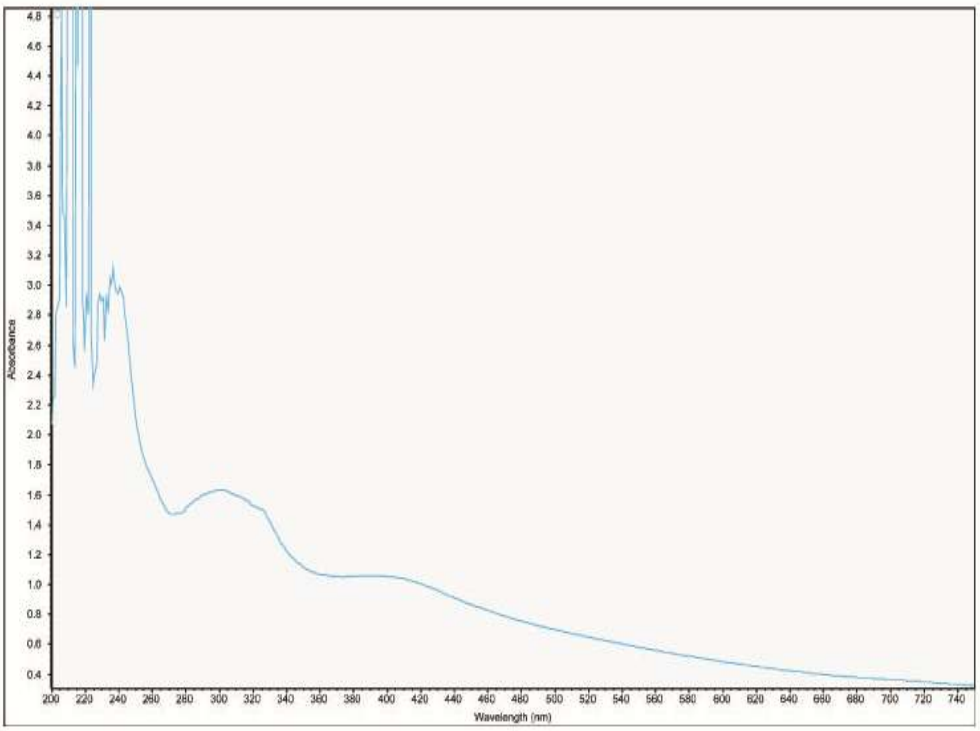

Fig.8 UV visible spectrum of Ni(II) complex

3. 5 Magnetic Susceptibility Measurements (BM)

The magnetic susceptibility values of the complexes are shown in Table.5.

Table. 5 Magnetic Susceptibility values of the complexes

Ligand/ Complex	Magnetic Susceptibility (BM)
[Cu L_2 $(NO_3)_2$]	1.9
[Ni L_2 $(NO_3)_2$]	2.1
[Co L_2 $(NO_3)_2$]	4.7

The Cu(II) complex exhibited magnetic moment of 1.9 BM indicating greater distorted octahedral geometry of the complex. Co(II) complex had magnetic moment of 4.7 BM indicated the high spin nature of the complex and have octahedral geometry. The Ni(II) complex exhibited the magnetic moment value of 2.1 BM indicated octahedral coordination [16].

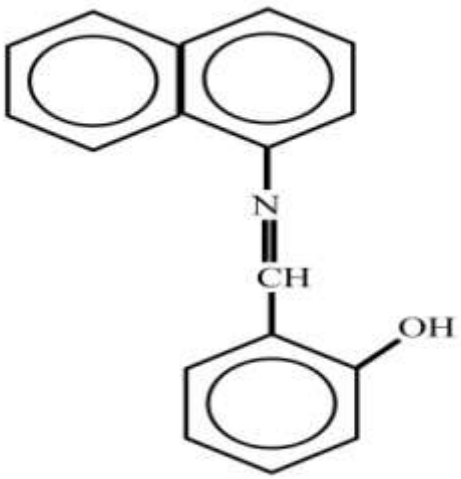

Fig: 9 structure of ligand

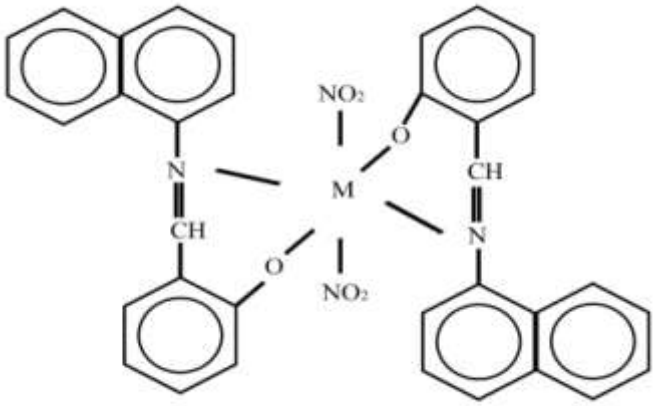

Fig:10 structure of Metal complexes with ligand L (M= Cu, Co, Ni)

3.6 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 bead like appearance. Careful examination of the single crystal, clearly indicated the nanoscale size of the single crystal of the complexes [8].

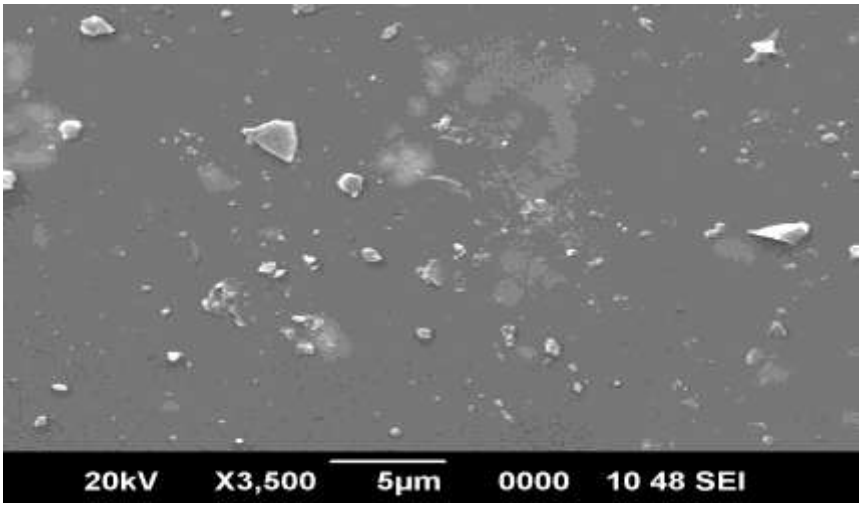

Fig. 11 SEM image of Schiff base complex Cu(II) with ligand L

3. 7 Antibacterial activity

The results of antibacterial activity substantiate the findings of earlier researchers, that biologically in active compounds become active and less biologically active compounds become more active upon coordination. The present investigation suggests that all the metal complexes of the ligand bearing metal ion, benzene ring, -N=CH- group have comparatively more biological activity. 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 solvent. The results of antibacterial study are given in Table: 6. The antibacterial activity was estimated based on the size of inhibition zone in the discs [17- 21].

Table 6. Antibacterial activity data of ligand and its complexes.

Ligand/ Complex	S. aureus	Styphi	Vcholera
Ligand(L) ($C_{17}H_{13}NO$)	6mm	-	-
[Cu L_2 $(NO_3)_2$]	-	6mm	7mm
[Co L_2 $(NO_3)_2$]	10mm	8mm	10mm
[Ni L_2 $(NO_3)_2$]	12mm	12mm	11mm

IV. CONCLUSION

Schiff base transition metal complexes Cu(II), Ni(II), and Co(II) were synthesised from salicylaldehyde using 1- naphthyl amine were clearly described and characterized on the basis of analytical and spectral data. Elemental analysis shows the metal ligand ratio is 1:2. Conductivity measurements show that all complexes are non-electrolytes. SEM analysis clearly indicated the nanoscale size of the single crystal of the complexes. Antibacterial study revealed that all complexes are more active than ligand(L). Cu(II) complex is more active and others exhibit moderate antibacterial activity.

REFERENCE

[1] M. Gielen, E.R.T. Tiekink, Mettallotherapeutic drugs and metal based diagnostic agents. The use of metals in medicine (John wiley & sons, England, 2005).

[2] M.N Hughes, The inorganic chemistry of biological process (2nd edn, Wiley, 1984).

[3] G. Georgier, Polel, Bolg. Akad, Nauk 34(2), 189 (1981).

[4] A. E. Braybstein, "Amino group transfer" Boyer, in P. D. (ed.). "The enzymes", 3rdedn. vol. 9 pt, B, Aced.

[5] A. A. Soliman, G. G. Mohamad, Study of the ternary complexes of copper with salicylidene-2-aminothiophenol and some amino acids in the solid state Thermochimica Acta, 421(1), 2004, 151.

[6] D. P. Singh, R. Kumar, R. Mehani, S. K. Verma, Synthesis and characterization of divalent metal complexes with ligand derived from the reaction of 4-aminopyridine and biacetyl, Journal of Serbian Chemical Society, 71,2006 939.

[7] C. Isac Sobana Raj, C.M. Sofia and M. Antilin Princela**,** Synthesis and Characterization of Bioactive Transition Metal Complexes from Cardanol, Asian J of Research in Chemistry, 7(8), 2014, 711-716

[8] Blessy. C, Isac Sobana Raj C, and Allen Gnana Raj G, Synthesis characterisation and Biological Activities of Co(II), Ni(II) & Cu(II) Complexes with DFMPM and glycine, Der Pharma Chemica,8(18),2016,364-373

[9] Bismi S Prakash, Synthesis and Characterization of Bio Active Transition Metal Complexes of Cu (II) Co (II) and Ni (II) using Natural Sources, Asian Journal of Research in Chemistry, 8(12), 2015, 726- 732

[10] Isac Sobanaraj.C and Anusha, Synthesis and Characterization of Transition Metal Complexes of Cu(II), Co(II) and Ni(II) using Cardanol and 4-aminoantipyridine, Journal of chemical and pharmaceutical research, 7(11), 2015, 485-493

[11] R. N. Rasad and M. Mathur, Journal Indian Chemical society, 88,2011 415 – 419

[12] Tuncel M, Ozbulbul A and Serin S. Synthesis and Characterisation of thermally stable Schiff base polymers and their Copper(II), cobalt(II) and nickel(II) complexes. Reactive and functional Polymers, 68, 2008**:** 292.

[13] Gopalakrishnan S and Sujatha R. Synthesis and thermal properties of Polyurethanes from Cardanol-furfural resin. J. Chem. Pharm. Res. 2(3), 2010:193.

[14] Deepa K, Madhu NT, Radhakrishnan PK. Metal complexes of schiff bases derived from dicinnamoyl methane and aromatic amines, Synth. React. Inorg. Met- Org. Chem, 35,2005, 883.

[15] Selwin Joseyphus R, Justin Dhanaraj C and Sivasankaran Nair M. Synthesis and Characterisation of some Schiff base transition metal complexes derived from vanillin and L (+) alanine. Transition Metal Chemistry. 31; 2006, 699

[16] K. B. Gudasi, M. S. Patil, R. S. Vadavi, R. V. Shenoy, P. S. A. M. Nethaji, X-ray crystal structure of phenyl glycine hydrazide: Synthesis and spectroscopic studies of its transition metal complexes , Spectrochimica Acta A, 67(1),2007, 172-177

[17] K. B. Gudasi, S. Patil, R. S. Vadavi, R. Shenoy, S. A. Patil and M. Nethaji, Synthesis of Cu(II), Ni(II), Co(II), and Mn(II) Complexes with Ciprofloxacin and Their Evaluation of Antimicrobial, Antioxidant and Anti-Tubercular Activity, Transition metal chemistry, 31, 580 (2006).

[18] Z. H. Chohan, H. Pervez, A. Raut, K. M. Khan, C. T. Supwern, Isatin- derived antibacterial and antifungal compounds and their transition metal complexes, J. Enzyme Inhib. Med. Chem., 19(5)), 2004,417-42

[19] Gopalakrishnan S, Nevaditha N T and Mythili C Antibacterial activity of azo compounds synthesized from the natural renewable source, cardanol. J. Chem. Pharm. Res 3(4); 2011: 490.

[20] Mukherjee P K, Saha K, Giri S M, Pal M and Saha B P. Synthesis, Characterisation and antimicrobial studies of Co (II), Ni (II), Cu (II) and Zn (II) complexes of 3-Pyridine Carboxaldehyde and L- tryptophan; Indian. J. Microbiol. 35; 1995: 327

[21] Shivhare S and Mangala Dev Gautam. Synthesis, characterisation and Microbial study of complexes of Cu(II) and Ni(II) with thiosemicarbazone. J. Chem. Pharm. Res. 3(5); 2011: 682.

Jisha.M. J. "Synthesis and Characterization of Bioactive Transition Metal Complexes of Cu(II), Co(II) and Ni(II) using 1 naphthyl amine and salicylaldehyde." IOSR Journal of Engineering (IOSRJEN), vol. 7, no. 8, 2017, pp. 60–67.