

# Green Synthesis, Characterization and Antimicrobial Activity of Cu(II) Schiff Base Complex

S. Sani, M. A. Kurawa, I. T. Siraj and A. M. Lawal

**Abstract**— Condensation of 2-hydroxy-1-naphthaldehyde and 1,2-phenylenediamine occurs to afford schiff base and its Cu(II) complex in quantitative yield under organic liquid-assisted mechanochemical condition efficiently in the presence of DMF as a liquid-assistant grinding (LGA) solvent. schiff base and its complex were characterized by IR, powder XRD, Differential scanning calorimetry, thermogravimetric analysis and elemental analysis. The analytical data show the composition of the metal complex to be  $[M(L)]$ , where L is the schiff base ligand. IR results demonstrate the tetradentate binding of the schiff base ligand involving two azomethine nitrogen and two phenolic oxygen atoms. The powder XRD studies indicated that Cu(II) complex is less crystalline than the schiff base. The operational simplicity, environmentally friendly conditions and high yield achieved are major benefits that meet the requirements of green production, including saving energy and high efficiency. Structural assignments are based on spectroscopic data. The synthesized schiff base, and metal complex were screened for antibacterial activity using gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia coli*) and antifungal activity using *Aspergillum flavus*. (gram positive) and *Aspergillus niger*. (gram negative) as potential antimicrobials and showed moderate activity. For all the organism tested the complex compound show higher activity than the schiff base. Thus, complexation or chelation increases antimicrobial activity.

**Index Terms**— Schiff base, Liquid-assisted mechanochemistry, powder XRD.

## 1 INTRODUCTION

Traditional synthesis approaches to schiff base complex have been incredibly successful, however, they are innately wasteful, and as raw materials become more limited, it is essential that we struggle to make synthetic chemistry more efficient [1]. The traditional synthesis methods mentioned here are solution-based batch processes, and the inefficiencies related with them arise mainly from the need to use large amounts of solvent in the reaction, with the attendant need for separation of products by chromatography, crystallization, etc. Mechanochemical synthesis involves a reaction between solid reactants, i.e. with no added liquid that might act as a solvent. However, some reactions in this type can result in the generation of liquid during the reaction, e.g. when any one of the reactants is a hydrate, producing liquid water during the reaction, or when liquid by-products such as water or acetic acid are produced as condensates during the reaction [2], [3], [4], [5]. These types of reactions are detected to proceed rapidly under mechanochemical conditions, signifying that the liquid produced during the reaction may accelerate it. The other class of mechanochemical reactions in which a very small quantity of liquid is intentionally added to the reaction mixture. Subsequent studies have revealed that very small quantity of added liquid can dramatically accelerate, and even allow, mechanochemical reactions between solids. In this work, we have investigated the solvent-assisted mechanochemical synthesis of 2-hydroxy-1-naphthaldehyde and phenylenediamine and investigated metal complexation using Cu(II) acetate as

test for two step mechanochemical syntheses. Diamine-type schiff base complexes are of wide interest, example for fluorescent indicators [6], biological mimics [7] 'Jacobsen' epoxidation catalysts [8], extraction of metal ions from water [9] ring-opening poly-merisation catalysts [10], and organic light emitting diode (OLED) applications [11]. Therefore, low-waste routes to such materials are of practical as well as academic interest for research.

## 2 MATERIAL AND METHOD

Grinding in all the reaction was carried out in agate mortar pestle. Chemical used in this study were obtained from Sigma Aldrich with 95% purity.

### 2.1 Synthesis of Schiff base: $[H_2(L)]$

2-hydroxy-1-naphthaldehyde, 2mmol (0.3444g) and 2-phenylenediamine 1mmol (0.1081g) were weighed in to agate motor, a small amount of DMF (0.5-1.0ml) was added to allow the formation of paste during grinding and the mixture was ground for 30min to obtained light brown powder. The solvent was removed from the resulting paste of product by allowing it to stand for some time in the air.

### 2.2 synthesis of Cu(II) Complex: $[Cu(L)]$

$[H_2(L)]$  schiff base (1mmol, 0.4164g) and Copper acetate monohydrate (1mmol, 0.1997g) were weighed in to agate motor, a small amount of DMF (0.5-1.0ml) was added and the mixture was ground for 30min to obtained light green powder. The solvent was removed from the resulting paste of product by allowing it to stand for 12h in the air.

### 2.3 Microbial activity

The antimicrobial activities of the schiff base and its Cu(II) complex in dimethylsulfoxide (DMSO) were performed *in vitro* by serial dilution method. The schiff base and the com-

- S. Sani is currently pursuing PhD. Degree in Inorganic Chemistry at Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria. Also, a Lecturer at Department of Pure and Applied Chemistry Usmanu Danfodiyo University Sokoto, Nigeria. E-mail: salihu\_sani2001@yahoo.com
- M. A. Kurawa is a Professor of Inorganic Chemistry at Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria.
- I. T. Siraj is a Senior Lecturer at Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria
- A. M. Lawal is a PhD. Student at Department of Geology, Bristol University UK. Also, a Lecturer at Federal University Gusau, Nigeria

plex were dissolved separately in dimethylsulfoxide to produce three different concentrations (60, 30 and 15 $\mu\text{gml}^{-1}$ ), which were placed on the surface of the culture and

**Table 1: Physical properties of the schiff base ligand and its metal complex**

Compound	Molecular formula	Colour	Yield (%)	Found (Calculated) (%)		
				C	H	N
[H <sub>2</sub> (L)]	C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	Light brown	88.6	81.13(80.75)	4.39(4.84)	6.44(6.73)
[Cu(L)]	C <sub>28</sub> H <sub>18</sub> CuN <sub>2</sub> O <sub>2</sub>	Light green	84.2	70.54(70.36)	3.49(3.80)	5.63(5.86)

**Table 2: Infrared spectral data of schiff base and its metal complex (cm<sup>-1</sup>)**

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{C})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
[H <sub>2</sub> (L)]	1641	3396	3035	1215	1466	-	-
[Cu(L)]	1633	-	2855	1239	1411	690	457

**Table 3: Energy Dispersive x-ray (EDX) of Cupper(II) complex**

Compound	Element	Weight (%)	Atomic (%)	K Ratio	Line type
[Cu(L)]	C	66.52	72.80	0.17635	K Series
	N	12.52	11.75	0.00415	K Series
	O	19.09	14.86	0.00948	K Series
	Co	2.87	0.59	0.00823	K Series

**Table 4: Thermal analysis of schiff base and its Complex**

Compound	Hydration tempt °C	%Weight loss: observed(calculated)	No. of H <sub>2</sub> O of hydration	Melting point/decomposition tempt (°C)
[H <sub>2</sub> (L)]	-	-	-	126
[Cu(L)]	170	3.70(3.63)	1	325

**Table 5: Antibacterial activities of investigated schiff base and its Complex**

Compound	Escherichia coli: zone of inhibition (mm)			Staphylococcus aureus: zone of inhibition (mm)		
	60 $\mu\text{gml}^{-1}$	30 $\mu\text{gml}^{-1}$	15 $\mu\text{gml}^{-1}$	60 $\mu\text{gml}^{-1}$	30 $\mu\text{gml}^{-1}$	15 $\mu\text{gml}^{-1}$
Schiff base	11	9	-	14	12	10
[Cu(L)]	14	12	10	19	17	15

**Table 6: Antifungal activities of investigated schiff base and its complex**

Compound	Aspergillus flavus: zone of inhibition (mm)			Aspergillus niger: zone of inhibition (mm)		
	60 $\mu\text{gml}^{-1}$	30 $\mu\text{gml}^{-1}$	15 $\mu\text{gml}^{-1}$	60 $\mu\text{gml}^{-1}$	30 $\mu\text{gml}^{-1}$	15 $\mu\text{gml}^{-1}$
Schiff base	11	8	-	12	-	-
[Cu(L)]	13	11	9	18	16	14

incubated at 37°C for two days. The diameter of the zone of inhibition produced by the schiff base and complex were compared with that of the referenced drugs, Ciproflaxacin 500mg for bacteria standard and Ketoconazole 200mg for fun-

gal standard [12], [13].

### 3 RESULTS AND DISCUSSION

The results of the analysis and antimicrobial activity of the schiff base and complex are shown in table 1-6.

A number of schiff bases and metal complexes have been synthesised using the classical method (solution base method). An alternative method having green chemistry approach might lead to the formation of schiff base complex eliminating the generation of the hazardous substances. Herein, the synthesis of schiff base and metal complex using liquid-assisted mechanochemistry, which deals with the use of grinding to promote reactions between solid-solid reactants were demonstrated. Reactions of 1,2-phenylenediamine with 2-hydroxy-1-naphthaldehyde were achieved by simply grinding together the starting materials in the molar ratio 1:2 using DMF as liquid-assisted solvent. The reactions were completed within 25-30 min with good yields comparable with classical methods. The products were compared with the data obtained from classical method

In the FT-IR spectrum of schiff base, the strong band observed at  $1641\text{cm}^{-1}$  can be assigned to the  $\text{-HC=N}$  stretching vibration. The spectrum of schiff base also shows several bands corresponding to aromatic C-H stretching at  $3035\text{cm}^{-1}$ , and aromatic C-C stretching  $1466\text{cm}^{-1}$ . The absorption bands of the aromatic C-O and OH stretching vibration modes are centered at  $1215\text{cm}^{-1}$  and  $3396\text{cm}^{-1}$ , respectively [14]. In the spectra of Cu(II) complex, the HC=N stretching vibration band

is shifted to a lower wave number,  $1633\text{cm}^{-1}$  and this decrease indicates the coordination of the amino group nitrogen to the metal ion [15], [16]. It is expected that, coordination of nitrogen to the metal atom would reduce the electron density in the azomethine link and thus lower the  $\text{-HC=N}$  absorption. The O-H broad band in the schiff base was no longer found in the spectra of investigated metal complex and also phenolic C-O stretching frequency in the complex was shifted to  $1239\text{cm}^{-1}$  indicating deprotonation and coordination of the hydroxyl oxygen to the metal ion. [17].  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  were observed in the far infrared region. These bands were absent in the spectra of the schiff base. The  $\nu(\text{M-N})$  was observed at  $690\text{cm}^{-1}$  as new band in the complex. This occurrence indicates that there is coordination between the metal and the lone pair of electron on the nitrogen atom of the schiff base. Also, bands observed at  $457\text{cm}^{-1}$ , indicates the formation of M-O bond in complex [18].

X-ray patterns of the schiff base and copper(II) complex are recorded in the range of  $5\text{-}40^\circ\text{C}$  ( $\theta$ ), the diffractogram and associated data depict the  $2\theta$  value for each peak relative intensity and inter-planar spacing (d-value). The patterns of the new compounds were completely different from the starting materials. Furthermore, no peak derived from the starting materials were observed, indicating that all starting materials were converted to product. The sharp reflections in the patterns testified to the crystallinity of the LAG products. Base on powder x-ray analysis data, Cu(II) complex is less crystalline than the schiff base, as shown in Figure 2.

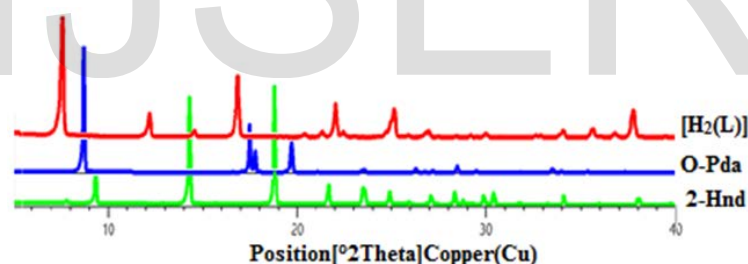


Figure 1: PXRD Patterns of pure 2-Hydroxy-1-naphthaldehyde (2-Hnd), pure 1,2-phenylenediamine (O-Pda) and  $[\text{H}_2\text{L}]$  schiff base.

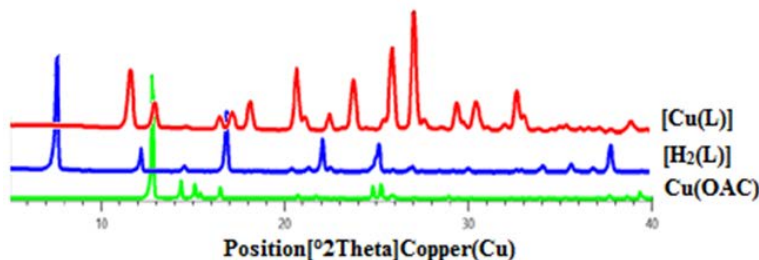


Figure 2: PXRD Patterns of Cupper (II) acetate monohydrate ( $\text{Cu}(\text{OAC})$ ),  $[\text{H}_2\text{L}]$  schiff base and  $[\text{Cu}(\text{L})]$  complex product after 30min LAG of Cupper (II) acetate and  $[\text{H}_2\text{L}]$  schiff base.

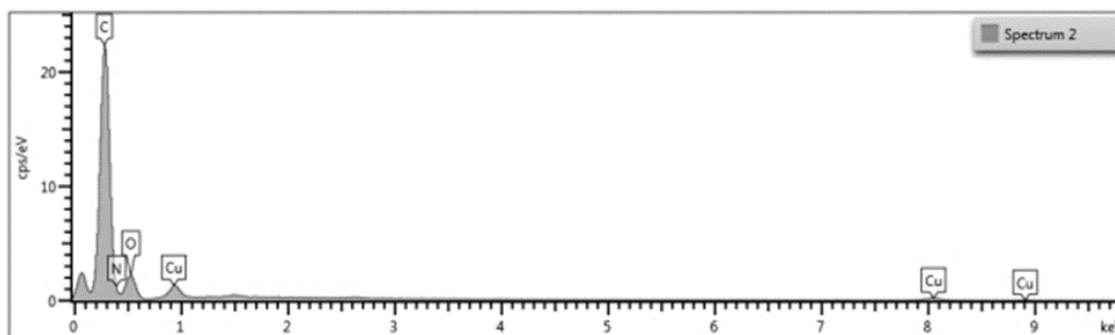


Figure 3: EDX analysis of  $[\text{Cu}(\text{L})]$  complex showing peak due to Carbon, Nitrogen, Oxygen, and Copper.

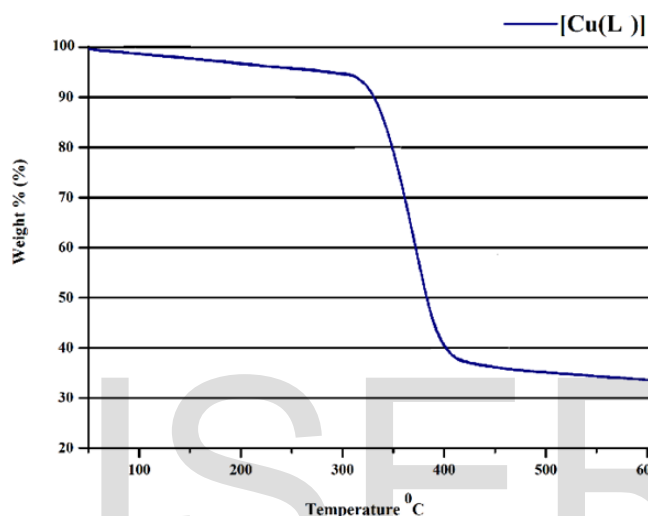


Figure 4: Thermogravimetric analysis of  $[\text{Cu}(\text{L})]$  Complex

EDX can be used to determine which chemical elements present in the sample, and can be used to estimate their relative abundance. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the samples being analyzed (figure 3). Elemental mapping of a sample and image analysis are also possible. EDX results of  $\text{Cu}(\text{II})$  complex showed that, the atomic percentage of Carbon, Nitrogen, Oxygen and Copper are 72.80, 11.75, 14.86, and 0.59% respectively (table 3). The atomic percentage of the component elements were compared in all the points analyzed and the results were found to be in agreement with each other indicating the uniform distribution of the component elements in the sample compound. Furthermore, the result is in conformity with the proposed structure of the complex.

Differential scanning calorimetry (DSC) curve of  $[\text{H}_2(\text{L})]$  schiff base shows one endothermic peak at  $126.3^\circ\text{C}$  which corresponds to the melting point of the schiff base. The simultaneous TGA analysis of the metal complex were studied from ambient temperature to  $600^\circ\text{C}$  under a nitrogen atmosphere (Fig 4). The curve of  $\text{Cu}(\text{II})$  complex exhibits one and relatively long decomposition step, it displays 3.7% weight loss at  $170^\circ\text{C}$  which is equivalent to one molecule of water through the calculated result 3.63%, the decomposition starts at  $325^\circ\text{C}$  and complete at  $412^\circ\text{C}$  (weight loss 58%). The  $[\text{Cu}(\text{L})]$  complex compound was obtained as powder product containing some amounts of residual water by-product as shown by

TGA (Thermogravimetric analysis) (table 4), However, on heating ( $105^\circ\text{C}$ , 36h) complete loss of the water occurred to give a material with satisfactory elemental analysis.

The schiff base and the complex showed moderate microbial activity against the organisms tested. For bacterial strains, *Escherichia coli* show 11mm zone of inhibition in the schiff base and 14mm in the complex at  $60\mu\text{gml}^{-1}$ . For *Staphylococcus aureus* which show highest activity in both schiff base and complex (14 and 19mm respectively) at  $60\mu\text{gml}^{-1}$  (Table 5), the activities of both the schiff base and complex were compared with the reference drug Ciproflaxacin 500mg (45mm zone of inhibition), in both the two bacterial isolates tested  $\text{Cu}(\text{II})$  complex showed higher activity than the schiff base this is probably due to the greater lipophilic nature of complex. Such increased activity of the metal chelate can be further explained on the basis of Overton's concept and Tweedy's chelation theory [19]. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donor group [20], [21] further, it increases the delocalization of  $\pi$  electrons over the whole chelate ring and enhances the penetration of the complex into lipid membrane and those block the metal binding sites on enzymes of microorganisms [22].

Antifungal strains, *Aspergillus flavus* has zone of inhibition 11 and 8mm in the schiff base against the complex with higher inhibition zone of 13 and 9mm at 60 and  $30\mu\text{gml}^{-1}$ . *Aspergillus niger* also show 12mm inhibition zone against 18mm in the



complex at  $60\mu\text{gml}^{-1}$  with the metal complex having higher zone of inhibition more than the derived schiff base (Table 6).

In case of *Apergillus niger*, the effective antifungal activity was not observed against the schiff base at 30 and  $15\mu\text{gml}^{-1}$ , whereas in the *Aspergillus flavus*, it shows no activity against schiff based at  $15\mu\text{gml}^{-1}$ . Cu(II) complex showed moderate activity compared to the reference drug Ketoconazole 200mg (32mm zone of inhibition). Thus, it can be said that, complexation or chelation increases antimicrobial activity as explained by Overton's concept and Tweedy's chelation theory.

## 4 CONCLUSION

The schiff base and its Cu(II) complex have been synthesized and characterized using IR spectroscopy, X-ray diffraction study, Energy dispersive X-ray, Differential scanning calorimetry, Thermogravimetric analysis, and CHN analysis. Antimicrobial studies of schiff base and complex reveal that, the complex show better activity compared to the schiff base.

From the analyses of the schiff base metal (II) complex compound carried out, the general molecular structure is proposed as in Figure 5

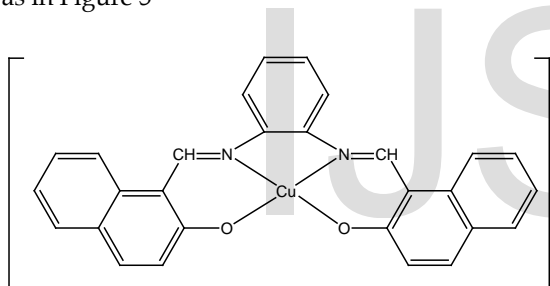


Figure 5: Proposed molecular structure of complex.

## ACKNOWLEDGMENT

Department of Chemistry, University of Malaya, Malaysia, and Department of Microbiology Bayero University Kano, Nigeria, are hereby acknowledged for the kind contribution.

## REFERENCES

- [1] Mason, B. P., Price, K. E., Steinbacher, J. L., Bogdan, A. R. and McQuade, D. T. (2007): "Greener Approaches to Organic Synthesis Using Microreactor Technology" *Chemical Reviews*, 107, 2300-2318
- [2] Friscic, T. (2010): New opportunities for materials synthesis using mechanochemistry. *Journal of Materials Chemistry*, 20, 7599-7605.
- [3] Friscic, T. (2012): Supramolecular concepts and new techniques in mechanochemistry: cocrystals, cages, rotaxanes, open metal-organic frameworks. *Chemical Society Reviews*, 41, 3493-3510.
- [4] Chieng, N., Rades T. and Aaltonen, J. (2011): An overview of recent studies on the analysis of pharmaceutical polymorphs. *Journal of Pharmaceutical and Biomedical Analysis*, 55, 618-644.
- [5] Bowmaker, G. A., Chaichit, N., Pakawatchai, C., Skelton B. W., and White, A. H., (2008). Solvent-assisted mechanochemical synthesis of metal complexes. *Dalton Transactions*, 2926-2928.
- [6] Germain, M. E. and Knapp, M. J. (2008). Turn-on fluorescence detection of  $\text{H}_2\text{O}_2$  and TATP" *Inorg. Chem.*, 47, 9748-9750
- [7] Jones, D. Summerville, D. A. and Basolo, F. (1979). Synthetic oxygen carrier related to biological systems. *Chem. Rev.*, 79, 139-179.
- [8] Jacobsen, E. N., Zhang, W., Muci, A. R., Ecker, J. R. and Deng, L. J. (1991). Highly enantioselective epoxidation catalysts derived from 1,2-diaminocyclohexane. *Am. Chem. Soc.*, 113, 7063-7064.
- [9] In, G., Kim, Y. S. and Choi, J. M. (2008). Study of Solvent Extraction using Salen (Net-2)-2 as a chelating agent for determination of Trace Cu(II) Mn(II) and Zn(II) in water samples. *Bull. Korean Chem. Soc.*, 29, 969-973.
- [10] Idage, B. B. Idage, S. B. Kasegaonkar, A. S. and Jadhav, R. V. (2010). Ring opening polymerization of dilactide using salen complexes as catalyst. *Mater. Sci. Eng., B*, 168, 193-198.
- [11] Bhattacharjee, C. R. Das, G. and Mondal, P. (2011). Photoluminescent Hemidisc-Shaped Liquid Crystalline Nickel (II) Schiff-Base Complexes. *Eur. J. Inorg. Chem.*, 5390-5396.
- [12] Ramon N., Mutijuraj V., Rovichandran S. and kulandaisamy A. (2003): Synthesis, Characterization and Electrochemical Behavior of Cu(II), Co(II), Ni(II) and complexes derived from acetylacetone and panisidine and their antimicrobial activity, *Journal of Chemical Science*, 115(3):161-167.
- [13] Yeamin R. Belayet H. and Saidul Islam M. (2003): Actimicrobial Studies of Mixed Ligand Transition Metal Complexes of Phthailic acid and heterocyclic amine Bases. *Pakistan J. Biological sciences*, 6(17):1494-1496.
- [14] Vadivela, T., Dhamodaranba M. (2015). Synthesis, characterization and antibacterial studies of ruthenium (III) complexes derived from chitosan schiff base. *International Journal of Biological Macromolecules*. biomac-5513; 9
- [15] Al-kubais, A. H., Ismail, K. Z Can. (1994). Nickel(II) and Palladium(II) Chelate of dehydroacetic acid schiff bases derived from thiosemicarbazide and hydrazinecarbodithioate. *J. Chem.* 72. 1785-1788.
- [16] Selwin Joseyphus, R. Justin Dhanaraj, C. Sivasankaran Nair, M. (2006). Synthesis and characterization of some schiff base transition metal complexes derived from vanillin and L (+) alanine. *Transition Met.Chem.* 31. 699-702.
- [17] Reddy V., Patil N., and Patel B. R., (2006). Synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with N, O and S donor ligand" *journal of Indian Council of Chemists*, 23(2) 1-3
- [18] Nakamoto K., Infrared and Raman spectra of inorganic and coordination compounds. 3<sup>rd</sup> Edition (Wile, New York. 1997).
- [19] Tweedy B. G. (1964). Plant extracts with metal ions as potential antimicrobial agents. *Phyto Pathology* 55: 910.
- [20] Kralova K. Kissova K. Svajlenova O. and Vanko J. (2000). Biological Activity of Copper (II) N-Salicylideneaminoacidato Complexes. *Chem.* 58(5):357-361.
- [21] Parekh J. Inamdhar P. Nair R. Baluja S. and Chanda S. (2005): Synthesis and antibacterial activity of some Schiff bases derived from 4-aminobenzoic acid *J. Serb Chem. Soc.* 70(10):1155-1161.
- [22] Vaghiasa Y. Nair R. Soni M. Bulaja S. Chanda S. (2004) Synthesis, structural determination and antibacterial activity of compounds derived from vanillin and 4-aminoantipyrine. *J. Serb.*

*Chem Soc. 69(12): 991-998.*

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