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Solid-State Synthesis, Characterization and Antimicrobial Studies of Ni (II), Co (II) and Cu (II) Complexes 1-(4-nitrophenyl)imino]methyl)naphthalen-2-ol

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ABSTRACT

Mechanochemicals synthesis has now been considered as a field of considerable interest for sustainable and green chemistry as a result of its safety, cost effectiveness and high yield. Ni (II), Co (II) and Cu (II) Metal complexes of 1-(4-nitrophenyl)imino]methyl)naphthalen-2-ol have been synthesized. The complexes were synthesized by grinding in an agate mortar with pestle. The complexes were characterized for their decomposition temperature, solubility test, magnetic susceptility, conductivity measurement and their surface functional groups were investigated using the Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra of the free ligand showed a band at 1629cm^{-1} which is assigned to the stretching vibration of the azomethine. The down shifts of this band (1629cm^{-1}) to lower frequencies in the spectra of the metal (II) complexes indicate complexation. The job's method of continuous variation suggested a 1:2 metal-ligand ratio all the Ni (II), Co (II) and Cu (II) complexes. The lower conductivity measurement values (43, 34 and 29 Ohm^{-1}cm^{2}mol^{-1}) revealed the non electrolytic nature of the complexes. The Schiff base and its complexes have been tested for antimicrobial activity against bacterial isolates (*Staphylococcus aureus and Escherichia coli*) and fungal isolates (*Mucor sp and Aspergillus flavus*). All the complexes exhibited appreciable activity on all the isolates.

Keywords: Antimicrobial, Metal Complexes, Schiff base, Solid-state, 2-Hydroxy-1-napthaldehyde

INTRODUCTION

In recent years, solid-state synthesis has possibly gained more attraction because these reactions are sometimes more convenient than using solvent-based synthesis, cost effective and can reduce environmental contamination (Garay *et al*., 2007). In addition, safety may be increased and the reaction processes are considerably simplified (Kidwai, 2001). Mechanochemical reaction promises to be an essential facet of "Green Chemistry" and is of high interest from both the economical and synthetic point of view. Solvent-free reactions possess some advantages over traditional reactions in organic solvents, for example they do not only reduce the burden of organic solvent disposal, but also enhance the rate of many inorganic reactions. In addition, Solid state synthesis of [$CuCl_4$][4,4′- H_2bipy] and [$CuCl_2$4,4′-bipy] was reported when $CuCl_2.5H_2O$ was ground with [(4,4′-H_2bipy)Cl_2] and $CuCO_3$ with [(4,4′-H_2bipy) Cl_2] respectively (Lusi, 2008). Solid-state normally gives high yield and pure product as it is attracting considerable interest in the field of green chemistry or sustainable chemistry because the reaction does not require recovery, storage and disposal of solvent. Besides, the absence of solvents being advantageous, it requires very simple equipment, and more importantly, it provides a faster means of synthesizing complexes (Kaupp *et al*., 2003). Juleikha, (2014) reported the synthesis, spectroscopic and X – Ray Diffraction studies of some Pd(II) complexes with bidentate Schiff bases. These Schiff bases were derived by condensing aldehydes like 2-hydroxy-1-naphthaldehyde, 5-chloro salicyladehyde with amines like 4-Nitro aniline, 4-methyl aniline and 4-methoxy aniline. The complexes were characterized on the basis of elemental analysis, molar conductivity, spectral (IR, 1H and electronic) as well as thermal analysis. All the Pd (II) complexes exhibit square planar geometry with 1:2 (metal:ligand) stoichiometry. The X- ray diffraction studies suggest monoclinic crystal system for these complexes. Solid state reaction is usually achieved via solid-solid or solid-gas and in most cases involve bringing two reactants together to form a product without using the bulk solvent. This is usually achieved when the solid reagents are ground together or exposed to gaseous substances. (Braga *et al*., 2007).

The aim of this paper is to synthesize, characterize and study the antimicrobial activities of Ni (II), Co (II) and Cu (II) complexes of Schiff base derived from 4-nitroaniline and 2-hydroxy-1-napthaldehyde by solid-state method which is now less time consuming, environmentally friendly, low cost and high yield.

MATERIALS AND METHODS

Materials

All reagents are of analar grade purchased from Sigma-Aldrich and used without further purification. All the glassware used in this work were washed with detergent and rinsed with distilled water and dried in an oven at 110^0C. All weighing was carried out using an electric weighing balance AB54 model. The infrared spectral analysis was recorded using SHIMADZU FTIR 8400S model. Conductivity measurement was done using jenway conductivity meter model 4010 in DMSO solvent. Melting point and decomposition temperature were determined using Guoming RY-2 melting tester. The antimicrobial screening was carried out in the microbiology laboratory, Bayero University, Kano. Nigeria.

Methods

Synthesis of the ligand

10mmol of each of the 2-hydroxy-1-napthaldehyde and 4-nitroaniline were grounded in an agate mortar with pestle for 2-5 minutes, which formed a crystalline powdered on further grinding and was dried at 50 ºC as adopted from Kurawa, (2009), (Scheme 1)

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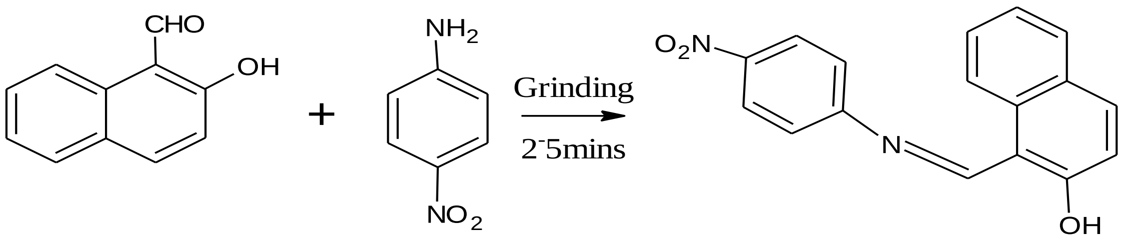


Scheme 1: Mechanochemical Synthesis of the Schiff Base

Synthesis of the Metal complexes

The metal complexes of Co (II), Ni (II) and Cu (II) chloride salts were synthesized by grinding 5mmol of each of the metal salts and 10mmol of the Schiff base in an agate mortar with pestle for 2-5 minutes which gave a crystalline powdered on further grinding and was dried at 50 ºC as adopted from Kurawa, (2009) (Scheme 2).

$$\text{2 Schiff Base } (C_{17}H_{12}N_2O_3) + MCl_2.XH_2O \xrightarrow{\text{Grinding}} \text{Metal Complex}$$

Scheme 2: Mechanochemical Synthesis of the Metal (II) Complexes

Antibacterial Activity

The *in vitro* antibacterial property of the Schiff base ligand and the metal complexes were assayed using two bacterial isolates: *Staphylococcus aureus* and *Escherichia coli*, using disc diffusion method (Aliyu and Sani, 2010).

Antifungal Activity

The *in vitro* antifungal activity of the Schiff base ligand and its metal complexes were studied on two fungi namely; *Aspergillus flavus* and *Mucor sp* using disc diffusion methods (Cheersbrough, 2000).

Determination of Number of Coordinated Ligand

The ligand to metal ratio in the complexes was determined using a continuous variation method (Job's method). (Angelici, 1971). 0.003moldm^{-3} solution of each of the metal (II) salt was prepared and absorbance measured from the UV-visible spectrophotometer. A solution mixtures having a total volume of 16cm^3 in which the mole fraction of each Schiff base is 0.1, 0.4, 0.5, 0.6, 0.8, 0.9 and 1.0. The absorbance of each of these solution mixtures was measured at a maximum wavelength (λ_{max}) of 405nm, 685nm and 523nm for Ni (II), Co (II) and Cu (II) respectively.

RESULTS AND DISCUSSION

The result of the physico-chemical properties and characterization of the Schiff base metal (II) complexes are as presented in Table 1. The metal (II) Chloride Salts reacted with the Schiff Base in 1:2 molar ratios by mechanochemical synthesis and produced crystalline solid complexes. The colour of the Schiff base and the metal (II) Complexes are orange, dark red and dark brown. The melting point of the ligand is 121^0C and the decomposition temperatures are 205, 194 and 184^0C respectively. The high melting and decomposition temperature revealed the stability of the Schiff base and its metal (II) complexes. The molar conductivity values are 34, 43 and 29 Ohm^{-1} cm^2mol^{-1} solution of the complexes in DMSO and this indicates their non-electrolytic nature. (Geary, 1971). The conductivity measurement has frequently been used in structure elucidation of metal chelates i.e. the possible modes of bonding within the limit of their solubility, they also provide a method of testing the degree of ionization of the complexes. (Siddappa and Mane, 2013). The effective magnetic moment values 3.0, 4.6 and 1.4BM for Ni (II) Co (II) and Cu (II) obtained indicates the complexes as paramagnetic and are in the range expected for tetrahedral geometry while that of Cu (II) complex shows a characteristic of the mononuclear, Cu (II) (d^9) one unpaired electron per Cu (II) ion (Mounika *et al*., 2010).

Table 1 Physico-chemical characterization of the Schiff base and Metal (II) Complexes

Compound	**Colour**	**Yield (%)**	**Melting Point ^{0}C**	**Decomposition Temperature ^{0}C**	**Molar conductivity $Ohm^{-1}cm^{2}mol^{-1}$**	**Effective magnetic moment in Bohr Magnetons (μ_{eef}) (BM)**
Ligand	Orange		121	______	_______	
[NiL]	Dark Red	86.60	_____	194	43	3.0
[CoL]	Dark Red	90.01	_____	205	34	4.6
[CuL]	Dark brown	89.11	_____	184	29	1.4

L= 1-{[(4-nitrophenyl)imino]methyl}naphthalen-2-ol

The Schiff base and the complexes are insoluble in most common organic solvent such as methanol, ethanol, Dimethyl formamide and benzene. The ligand and all the complexes are relatively soluble in Dimethylsulfoxide and chloroform except copper complexes which is sparingly soluble in chloroform as shown in Table (2).

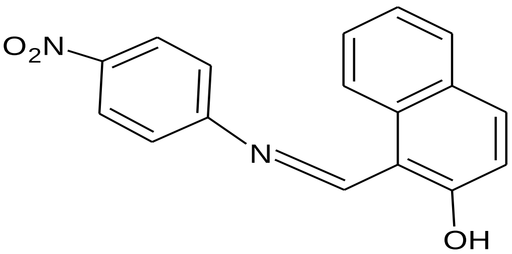
Table 2: Solubility of the Schiff base and the Metal (II) Complexes in some common solvents

COMPOUND	MOH	ETOH	$CHCl_3$	DMF	Benzene	DMSO
Ligand	IS	IS	S	IS	IS	S
$[Co(C_{17}H_{10}N_2O_3)]$	IS	IS	S	IS	IS	S
$[Ni(C_{17}H_{10}N_2O_3)]$	IS	IS	S	IS	IS	S
$[Cu(C_{17}H_{10}N_2O_3)]$	IS	IS	SS	IS	IS	S

L=1-{[(4-nitrophenyl)imino]methyl}naphthalen-2-ol (s= soluble, ss=slightly soluble,Is= insoluble)

FTIR Spectra

The FTIR spectra provide valuable information regarding the nature of functional group attached to the metal atom. (Rajavel *et al*., 2008). The importance band in the FTIR spectra of the Schiff base as well as complexes are shown in the Table 3. A medium intensity band that appears at 1629 cm^{-1} in the ligand which is shifted to lower frequencies in the spectra of the complexes (1610-1620 cm^{-1}) was assigned to C=N stretching, vibration as well as indicating that, the nitrogen of the azomethine group is coordinated to the metals (Sharma *et al*., 1997). A broadband was observed 3358 cm^{-1} in the spectra of the ligand which was assigned to OH vibration frequencies. Assignment of the proposed coordination sites is further supported by the appearance of the medium band in 420-488 cm^{-1} which could be attributed to $_V$M-N respectively (Nakamoto, 1997) and 744-748 cm^{-1} which was assigned to $_V$M-O vibration frequencies. A new broadband in the spectra of the complexes was also observed at 3337-3475 cm^{-1} which indicates the presence of lattice water molecules (Patel and Agwara, 1990). The effective magnetic moment values 3.0, 4.6 and 1.4BM for Ni (II) Co (II) and Cu (II) respectively, indicates the complexes as paramagnetic and are in the range expected for tetrahedral geometry while that of Cu (II) complex shows a characteristic of the mononuclear, Cu (II) (d^9) one unpaired electron per Cu (II) ion (Mounika *et al*., 2010). This is shown in table (1). Based on the result of FTIR, magnetic susceptibility and UV-visible spectrophotometry, the complexes were assigned with tetrahedral geometry. The proposed molecular structure of the Schiff base and its metal (II) complexes are presented as Fig.1.



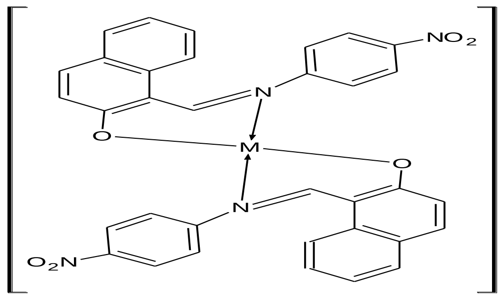


Fig. **1**: Proposed structure of the Schiff Base and metal (II) complexes (M= Co^{2+}, Ni^{2+} and Cu^{2+})

Table 3: Selected Vibration Frequencies of the Schiff base and the Metal (II) Complexes.

Compound	ν(O—H) cm^{-1}	ν(C=N) cm^{-1}	ν(M—N) cm^{-1}	ν(M—O) cm^{-1}
Ligand	3358	1629	__	__
$[Ni(C_{17}H_{10}N_2O_3)]$	3432	1620	475	745
$[Co(C_{17}H_{10}N_2O_3)]$	3387	1619	420	744
$[Cu(C_{17}H_{10}N_2O_3)]$	3475	1610	488	748

L= 1-{[(4-nitrophenyl)imino]methyl}naphthalen-2-ol

Biological Activity

The antimicrobial activities of the complexes and the free ligand tested against two bacterial isolates and two fungal isolates (*Eschericia coli*, *Staphylococcus aureus*, *Mucor sp and Aspergillus flavus*) were carried out and presented in Figs. 2 - 5.

The result of the antibacterial activities of the metal complexes and free ligand tested against *Staphylococcus aureus* aureus revealed that both free ligand and metal complexes shows activities at various oncentrations. The activities increases with increasing concentrations.

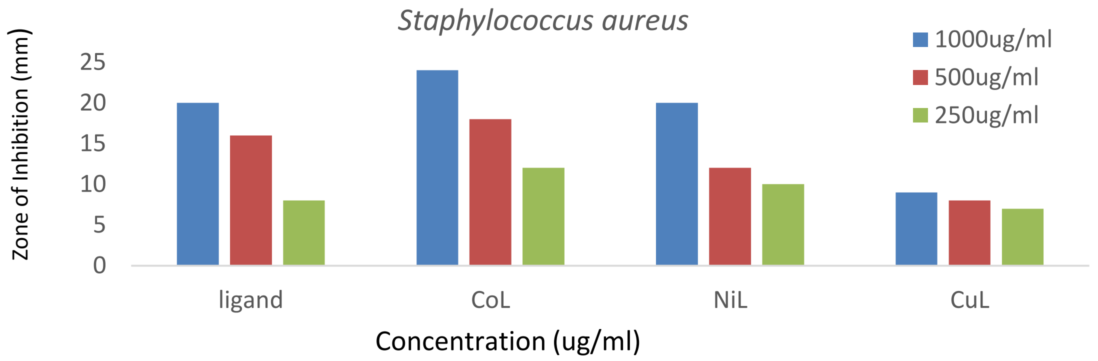


Fig 2: Antimicrobial test of the ligand and CoL, NiL and CuL complexes against *staphylococcus aureus.*

The study for antibacterial activities of metal complexes and free ligand tested against *Eschericia coli* (Fig. 3) shows higher activities at high concentrations and vice-versa. The results also revealed that NiL complexes has no activity against the isolate.

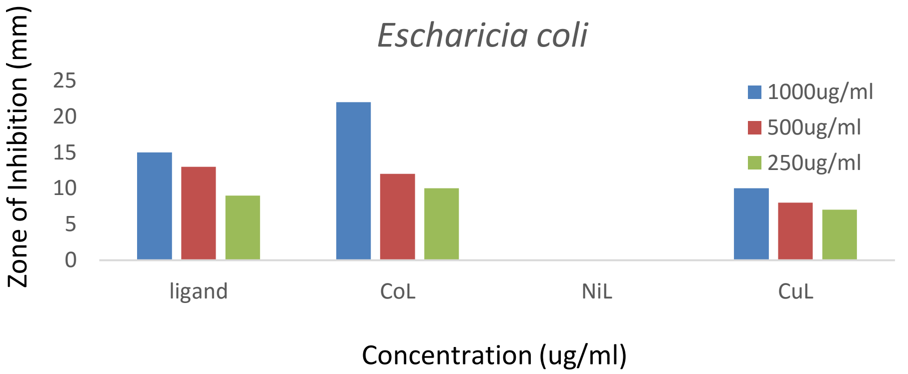


Fig 3: Antibacterial test of the free ligand and CoL, NiL and CuL complexes against *Eschericia coli*

The antifungal activities of the metal complexes and free ligand were carried out against *Mucor sp* and *Aspergilus flavus* and the results were presented in Figs. 4 and 5. The study of antifungal activities of the metal complexes and free ligand against *Mucor sp* shows high activities at higher concentrations and vice-versa. The result also revealed that the free ligand is having least activity which increases after complexing with the metals.

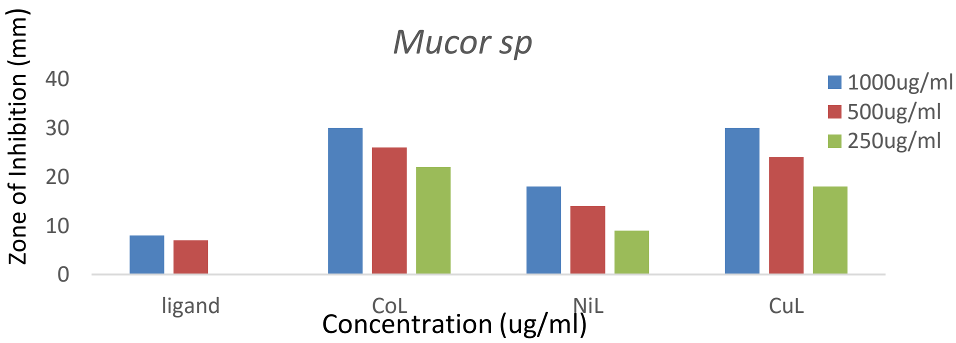


Fig 4: Antifungal test of the free ligand and CoL, NiL and CuL complexes against *Mucor sp*

The activity test of free ligand and metal complexes against Aspergilus flavus (Fig. 5) revealed high activity of the free ligand and metal complexes at higher concentrations and vice-versa.

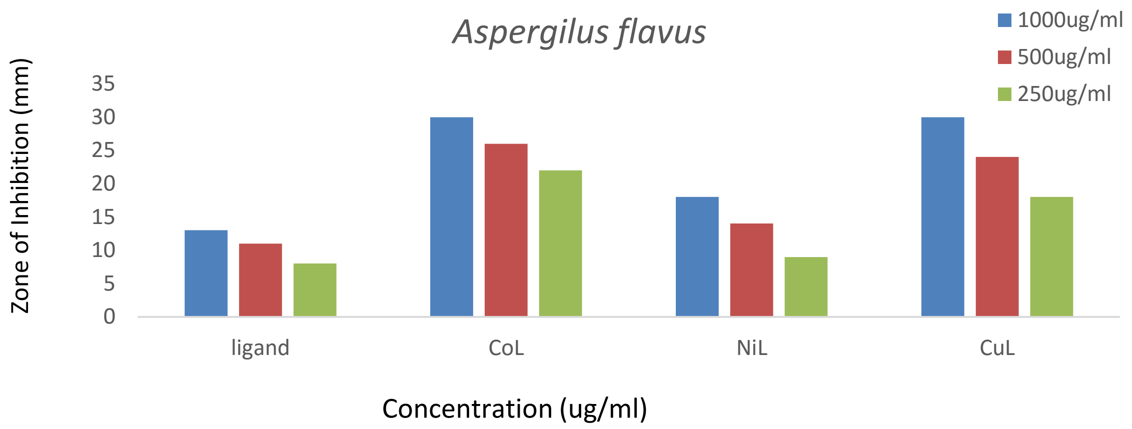


Fig 5: Antifungal test of the free ligand and CoL, NiL and CuL complexes against *Aspergilus flavus.*

CONCLUSION

Metal (II) complexes of Co, Ni and Cu have been synthesized using mechanochemical methods which is cost effective, environmentally friendly and resulting in higher yield of the product. The bidentate ligand coordinates through the nitrogen of the azomethine (-C=N-) and deprotonated oxygen. The high decomposition temperature of the complexes indicates their thermal stability. The complexes are insoluble in most common organic solvents but readily soluble in dimethylsulfoxide (DMSO) and chloroform except Cu (II) complex which is slightly soluble in choroform. Both the ligand and its complexes were tested against some bacterial isolates (*Escherichia coli* and *staphylococcus aureus)* and fungal isolates (*Mucor sp and Aspergillus flavus*) and were found to be active at various concentration except Ni (II) complex which has no activity against *Escherichia coli* and Co (II) and Cu (II) complexes were found to have zero activity against fungal isolate *Mucor sp* as compared with the standards Gentamicin and ceftriasone for bacterial isolate and ketoconazole for fungal isolates.

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