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Copper(II) and Zinc(II) Complexes Synthesized by Green Mechanochemical Method and their Antimicrobial Studies

S. Sani* and I. T Siraj

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Abstract: *Schiff base ligand derived from condensation of 2-hydroxy-1-naphthaldehyde and 2-aminobenzothiazole were synthesized via mechanochemical technique and used for the preparation of Cu(II) and Zn(II) complexes. The Schiff base and complexes were characterized by infrared spectroscopy, powder x-ray diffraction, Thermogravitric/thermal analysis, CHN analysis, solubility test, conductivity measurement and magnetic susceptibility measurement. Infrared spectral study indicated a strong band in the spectra of the Schiff base at 1603 cm^{-1} assigned to azomethine stretching vibration. The azomethine band shifted to 1621 and 1599 cm^{-1} in the IR spectra of Cu(II) and Zn(II) complexes respectively indicating the formation of complex compounds. The decomposition temperatures of the complexes are in the range of 240 - 264 ^oC indicating good thermal stability. Molar conductance values are in the range of 6.34 - 9.8 $Ohm^{-1}cm^2$ mol^{-1}, indicating non electrolytic nature of the synthesized complexes in ethanol. Magnetic susceptibility measurement indicated that Zn(II) complex is diamagnetic while Cu(II) complex is paramagnetic and exhibit magnetic moment of 2.059 BM, the values correspond to the square planar geometry. The theoretical and experimental analytical data of C, H and N for the Schiff base and complexes are in good agreement. The Schiff base ligand and metal complexes have been studied for microbial activity using pathogenic bacteria (Escherichia coli and Staphylococcus aureus) and fungal pathogens (Candida albican and Asperigillus fumigatus) by agar well diffusion method. The results indicated that metal complexes (07 - 19 mm diameter inhibition zones) are more active than Schiff base ligand (07 - 14 mm diameters) against the test organisms.*

Key Words: *Mechanochemistry, Schiff base, azomethine, complexes. antimicrobial activity*

S. Sani
Department of Pure and Applied Chemistry
Usmanu Danfodiyo University, P.M.B. 2346, Sokoto, Nigeria
Email: salihusani016@gmail.com
Orcid id

I. T Siraj
Department of Pure and Industrial Chemistry
Bayero University Kano, P.M.B 3011, Kano, Nigeria
Email: , itsirajo.chm@buk.edu.ng
Orcid id:

1.0 Introduction

Mechanochemical synthesis is a processing technique of solids in which mechanical and chemical phenomena are coupled on a molecular scale. It is possible to produce a desired product using only a mechanical action (high pressure and mechanical stress between reactants and balls) at room temperature or at temperatures lower than traditional solid-state synthesis. This reaction generally involves interaction between solid (Gennari & Andrade-Gamboa, 2018). Synthesis through mechanochemical process can be performed under different conditions such as using a reactive atmosphere (reactive ball milling), under cryogenic conditions (cryomilling), or in a solvent. It has been widely reported that when one of the reactants is a hydrate, generating liquid water during the reaction, or when liquid by-products such as water or acetic acid are generated as condensates during the reaction (Bowmaker *et al*., 2008; Chieng *et al.*, 2011; Friščić, 2010, 2012). Observation of mechanochemical reaction involving milling and pressing of analyte with alkaline halides towards

disks formation for FTIR experiment revealed that the reaction was accelerated when the analyte was in a hydrate form (Fernandez-Bertran & Reguera, 1996). Other experimental conditions can be controlled in order to influence the characteristics of the products (Amrute *et al*., 2021).

Most mechanochemical reactions have been reported to occurred through the application of solvent and their significant in synthesis of catalysts, nanomaterials and pharmaceuticals have been extensively documented (Friščić, 2012; Friscic & Jones, 2009; Shan *et al.,* 2002). However, application of mechanochemical synthetic process in coordination chemistry is welcomed with scanty literature and recent reviews have focused on the synthesis of metal-organic framework compounds (Friščić, 2010; Sani *et al.,* 2019). Controlled addition of small quantity of a liquid to accelerate mechanochemical reactions has been properly addressed as involvement of ‘‘minimal solvent’’ rather than strictly ‘‘solvent-free’’ (James *et al.,* 2012).

Transition metal ions play significant roles in several biochemical processed and their activities can be enhanced when the biologically active ligand is coordinated to a transition metal ion. Metal complexes of Schiff bases derived from heterocyclic compounds containing nitrogen, sulfur and/or oxygen as ligand atoms are known simple structural models of more complicated biological systems (Sakıyan *et al.,* 2004). Inventions of newer, cheaper and more potent analogs of molecules with already well recognized biological activities form a key part of research in the pharmaceutical field. Bring about modifications by manipulating the parent structures serves to enhance the activity of the potent analogs and eliminates adverse effects or toxicity associated with the parent drug.

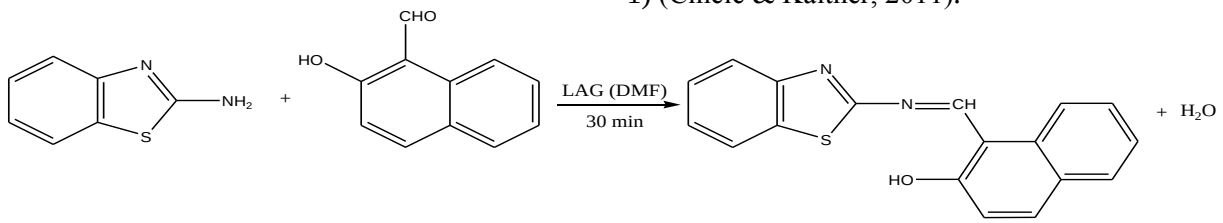
In view of the above, the present work is aimed at synthesizing Cu(II) and Zn(II) complexes derived from 2-aminobenzothiazole Schiff base and their antibacterial and antifungal studies using green mechanochemical method.

2.0 Materials and Methods

PXRD measurements were carried out on a PAN analytical Empyrean X’Pert Pro X-ray diffractometer. Diffractograms were typically carried out from 5–40° with a step size of 0.0167°. Thermal analysis studies of complexes (TGA) were performed using Perkin-Elmer Pyris Diamond TG/ DTA heated in flowing nitrogen (200 $mlmin^{-1}$) at 10^{o} min^{-1}. Elemental microanalyses (C, H, N and S) were determined using a Perkin-Elmer CHNS/O 2400 series II elemental analyzer. IR spectra were recorded on a Perkin-Elmer FTIR Spectrum-400. Melting point were determined using digital melting point MPA100. Electronic absorption spectra were recorded using a Shimadzu UV-Vis 240 spectrophotometer. Magnetic susceptibility measurements were carried out using Sherwood scientific MSB1 magnetic susceptibility balance. Conductivity measurement were carried out using LMCM-20 conductivity meter.

2.1 Synthesis of 1-(benzothiazol-2-yliminomethyl)-naphthalen-2-nol; H_2(L) Schiff base

The Schiff base was synthesized by the reaction of 2-hydroxy-1-naphthaldehyde, (1.722 g; 10 mmol) and 2-aminobenzothiazole (1.502 g; 10 mmol) in agate motor, a small amount of DMF (0.1 ml) was added and the mixture was grinded for 30 min to obtain a brown solid product and dry in air (Scheme 1) (Cinčić & Kaitner, 2011).



Scheme 1: Synthetic reaction of H_2(L) Schiff base

2.2 Synthesis of complexes

2.2.1 1-(Benzothiazol-2-yliminomethyl)-naphthalen-2-nol Copper(II); [Cu(L)$_2$] Complex

Schiff base (H_2(L)) (1 mmol, 0.30438 g) and copper(II) acetate monohydrate (1mmol, 0.1997 g) were weighed in to agate motor. DMF (0.1 ml) was added and the mixture was grinded for 30 minutes to obtain orange powder. The compound was allowed to dried in air at room temperature (Cinčić & Kaitner, 2011).

2.2.2 1-(Benzothiazol-2-yliminomethyl)-naphthalen-2-nol Zinc(II); [Zn(L)$_2$] Complex

Schiff base ($H_2(L)$) (1 mmol, 0.30438 g) and zinc(II) acetate dehydrate (1mmol, 0.2195 g) were weighed in to agate motor. DMF (0.1 ml) was added and the mixture was grinded for 30 min to obtain brownish powder. The compound was allowed to dried in air at room temperature (Cinčić & Kaitner, 2011).

2.3 Antimicrobial sensitivity test

The microbial isolates were obtained from the Department of Chemical Pathology, Aminu Kano Teaching Hospital and were identified using gram staining and biochemical test. The antimicrobial activity was investigated using agar well diffusion method. Different strains of bacteria which included both gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia coli*) and fungi (*Candida albican* and *Aspergillus fumigatus*) were tested.

The Schiff base and the complexes were dissolved separately in dimethylsulfoxide to produce three different concentrations (15, 30 and 60 $mgml^{-1}$) which were placed on the surface of the culture and incubated at 37 ^oC for 24 h (bacterial growth) and 72 h (fungal growth). The diameter of inhibition zone produced by the Schiff base and complexes were compared with that of the referenced drugs using Ciprofloxacin 500 mg (bacterial standard) and Ketoconazole 200 mg (fungal standard) (Vadivel & Dhamodaran, 2016).

3.0 Results and Discussion

The reaction of 2-hydroxy-1-naphthaldehyde and 2-aminobenzothiazole was monitored by powder x-ray diffraction. The reaction proceeds in a slow condition in the absence of any solvent as traces of the starting material were detected even after 80 minutes of net grinding. However, in the presence of small amount of DMF followed by grinding for 30 minutes. The powder X-ray diffraction pattern of Schiff base synthesized in the presence of DMF solvent (Fig. 1) was completely different from the one obtained for the starting materials, which indicated that, the starting materials have been successfully transformed to products. Evidently, a sharp and intense peak observed at 18.932^o and 17.712^o in the powder X-ray diffraction spectra of 2-hydroxy-1-naphthaldehyde and 2-aminobenzothiazole respectively, are absent in the powder X-ray diffraction spectrum of the product. New sharp and intense peaks were witnessed at 13.189^o, 21.051^o and 27.352^o which further confirm the formation of the Schiff base (Cinčić & Kaitner, 2011; Zhong *et al.*, 2012). The powder x-ray diffraction pattern of the complexes also shows different reflections peaks with respect to the reactants (Fig. 2).

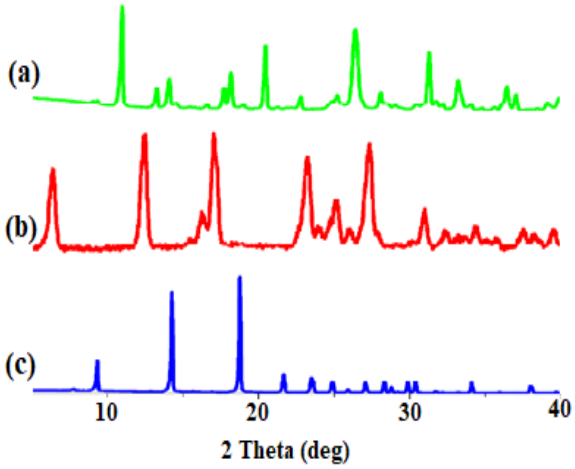


Fig 1. The PXRD Patterns of (a) $H_2(L)$ Schiff base, (b) 2-aminobenzothiazole, (c) 2-hydroxybenzaldehyde showing different PXRD patterns of the Schiff base with respect to the reactants

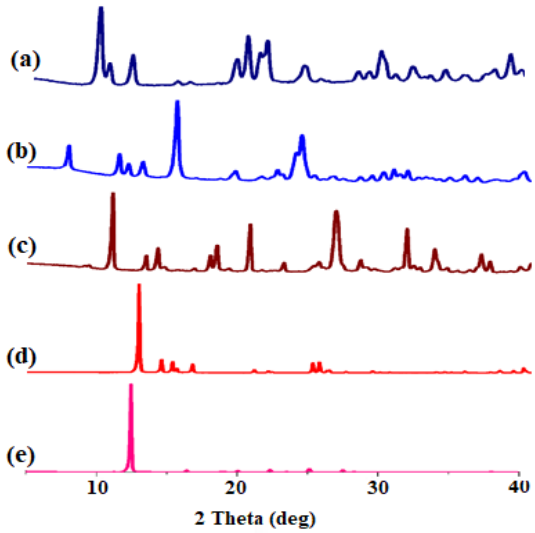


Fig. 2. The PXRD Patterns of (a) $[Zn(L)_2]\cdot 2H_2O$ Complex, (b) $[Cu(L)_2]$ Complex, (c) $H_2(L)$ Schiff base (d) Cu(II) acetate monohydrate, (e) Zn(II) acetate dihydrate showing different PXRD patterns of the synthesized complexes with respect to the derived Schiff base and their respective metal acetate.

The percentage yield of the synthesized Schiff base and its metal complexes ranged from 86.3 - 92.2 %. The Schiff base and metal complexes were coloured.

The colour of complexes are as a result of *d-d* transitions of electrons between energy levels. The Schiff base was found to be crystalline solids with melting point of 124 ºC. Complexes had decomposition temperature higher than Schiff base melting point probably due to complexation which indicated higher stability (Nejo *et al*., 2010). (Table 1)

Table 1: Molecular formula, colour, melting point, decomposition temperature and percentage yield of H_2(L) Schiff base and its complexes

Compound	Molecular Formula	Colour	Melting Point (ºC)	Decomposition Tempt. (ºC)	Yield (%)
H_2(L)	($C_{18}H_{12}N_2OS$)	Brown	124	-	89.6
[Cu(L)$_2$]	[Cu($C_{18}H_{11}N_2OS)_2$]	Orange	-	240	92.2
[Zn(L)$_2$]·2H_2O	[Zn($C_{18}H_{11}N_2OS)_2$]·2H_2O	Brownish	-	264	86.3

The Schiff base and complexes were soluble in polar solvent such as methanol, ethanol, DMSO, DMF and acetonitrile but insoluble in non-polar solvent such as hexane. These suggested the polar nature of the synthesized compounds due to the presence of some polar groups (Table 2).

Table 2: Solubility test of H_2(L) and its complexes in some common solvents

Compound	DMSO	Methanol	Ethanol	Acetonitrile	DMF	Acetone	Hexane
H_2(L)	S	S	S	S	S	IS	IS
[Cu(L)$_2$]	S	S	S	S	S	IS	IS
[Zn(L)$_2$]·2H_2O	S	S	S	SS	S	IS	IS

The strong band observed at 1603 cm^{-1} in the spectrum of Schiff base can be assigned to azomethine (-C=N-) stretching vibration (Jayanthi *et al*., 2017). The azomethine stretching frequency of Schiff base was shifted to 1558 and 1588 cm^{-1} in the spectra of Cu(II) and Zn(II) complexes respectively. This indicates the coordination of metal center with azomethine nitrogen group (Cindrić *et al.*, 2012; Kubaisi & Ismail, 1994). It is expected that coordination of nitrogen to the metal ion would reduce the electron density in the azomethine link and thus change the azomethine absorption (Joseyphus *et al.*, 2006).

More so, new bands that were not found in the spectra of the Schiff base were observed in the spectra of Cu(II) and Zn(II) complexes at 695 and 594 cm^{-1} respectively, corresponding to ν(M-N) band. Additionally, peaks at 460 and 445 cm^{-1} are assigned to ν(M-O) vibrations for Cu(II) and Zn(II) complexes respectively (Nakamoto, 2006; Zhong *et al*., 2012). The presence of M-N and M-O vibration support the participation of N and O atoms in the complexation with metal ions under study.

Table 3: Infrared spectral data of H_2(L) schiff base and its complexes (cm^{-1})

Compound	ν(C=N)	ν(C=N) (Ring)	ν(O–H)	ν(C–O)	M-N	M-O
H_2(L)	1603	1529	3331	1246	-	-
[Cu(L)$_2$]	1558	1540	-	1286	635	460
[Zn(L)$_2$]·2H_2O	1588	1558	3275	1253	594	445

Fig. 3 shows the thermal decomposition process of [Cu(L^1)$_2$] complex in three stages. There was no reasonable mass loss up to 110 ºC which indicate the absence of water of hydration. The TGA shows 20.53% weight loss at 240 ºC with mass loss of 0.41 mg which indicate the decomposition of the first fragment. It conformed to the calculated result of 21.30%. The second step of the decomposition continue from the first and stop at 560 ºC (observed weight loss 54.24%) with mass loss of 1.099 mg. It's also in agreement with theoretical weight loss of 51.77% which indicate the decomposition of the

second fragment. The third decomposition step was observed at temperature 800 ºC. with mass loss of 0.3 mg. The observed weight loss 16.28% is in accordance with theoretical weight loss of 16.89% attributed to the decomposition of third fragment (Nejo *et al.*, 2010).

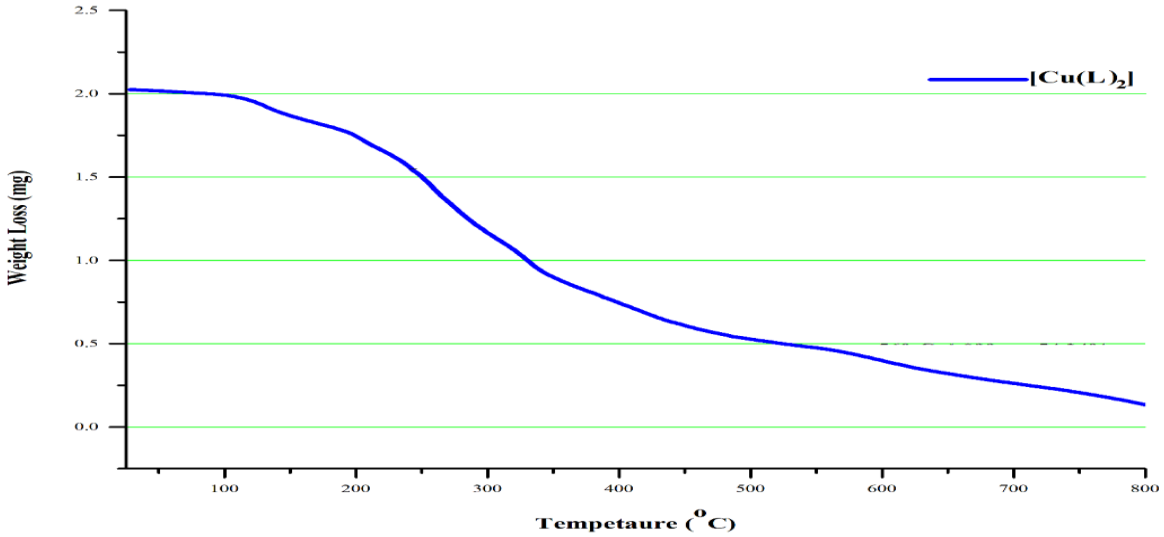


Fig. 3: Thermogravimetric Analysis of $[Cu(L)_2]$ Complex.

The thermogram of $[Zn(L)_2]\cdot 2H_2O$ complex (Fig. 4) shows three decomposition steps within the temperature range 45-800 ºC. The percentage weight loss of 5.35% at 124 ºC which is equivalent to two molecules of water through the calculated result 5.50%. The first decomposition at 264 ºC with estimated weight loss of 24.25% and mass loss of 0.45 mg correspond to weight loss of first fragment, while the second step occurs at temperature 463 ºC with weight loss of 30.24% (0.57 mg mass loss) which is in accordance with the theoretical weight loss of 31.01%. The third decomposition step was observed at 800 ºC. the observed weight loss 33.56% (0.63 mg mass loss) is in accordance with theoretical weight loss of 35.21% attributed to the decomposition of third fragment (Stilinović *et al.*, 2012)

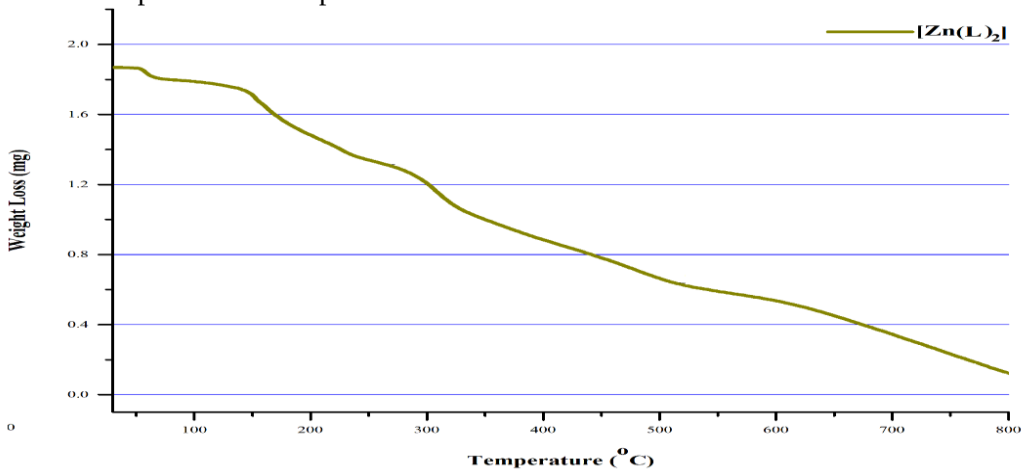


Fig. 4: Thermogravimetric analysis of $[Zn(L)_2]\cdot 2H_2O$ complex

The molar conductivity values in 10^{-3} M solution of the metal complexes in ethanol were measured at room temperature. Table 4 shows the molar conductance (Λ_m) values of the metal complexes. From the results of the analysis Cu(II) and Zn(II) complexes were found to have molar conductance values of 6.34 and 9.80 $\Omega^{-1}cm^2mol^{-1}$ respectively, signifying the non-electrolytic nature, since a value in the range 75 – 90 $\Omega^{-1}cm^2mol^{-1}$ is expected for a 1:1 electrolyte in methanol (Shaker *et al.*, 2009).

Table 4: Molar conductance measurement of metal(II) complexes derived from (H_2L) Schiff base in 10^{-3}M ethanol

Compound	Concentration ($Moldm^{-3}$)	Specific Conductance ($\Omega^{-1}cm^{-1}$)	Molar Conductance ($\Omega^{-1}\,cm^2mol^{-1}$)
$[Cu(L)_2]$	1×10^{-3}	6.34×10^{-6}	6.34
$[Zn(L)_2]\cdot2H_2O$	1×10^{-3}	9.80×10^{-6}	9.80

Magnetic susceptibility measurements show that, $[Cu(L)_2]$ complex is paramagnetic in nature and exhibit a magnetic moment of 2.059 BM as given in Table 5. According to literature the value are in the range conforming to one unpaired electron for square planar geometry (Kalia *et al.*, 2007; Siraj & Kurawa, 2020). Therefore, the square planar stereochemistry for $[Cu(L)_2]$ complex was proposed. The magnetic moment value of $[Zn(L)]\cdot2H_2O$ complex indicates a diamagnetic property, consistent with the zero (0) unpaired electrons of d^{10}. Therefore, the ligand coordinates to Zn(II) ion as a four-dentate chelating agent with a square-planar geometry (Carabineiro *et al.*, 2007; Fitzgerald & Brubaker, 1969; Tas *et al*., 2006; Zaky & Fekri, 2018).

Table 5: Magnetic susceptibility measurement of metal(II) complexes derived from (H_2L) Schiff base

Compound	X_g ($ergG^{-2}g^{-1}$)	X_m ($ergG^{-2}mol^{-1}$)	μ_{eff} (BM)
$[Cu(L)_2]$	$+2.796\ x10^{-12}$	$1.778\ x10^{-3}$	2.059
$[Zn(L)_2]\cdot2H_2O$	$-7.650\ x10^{-12}$	$-4.867\ x10^{-4}$	---

Elemental microanalysis of Schiff base and complexes indicated that the theoretical and experimental analytical data of C, H, N and S for the Schiff base and complexes are in good agreement (Table 6). Slight difference in some of the values are within the acceptable range. The result show 1:2 (metal to ligand) ratio (Tigineh & Liu, 2014).

Table 6: Elemental microanalysis of (H_2L) Schiff base and its complexes

Compound	Found (Calculated) %			
	C	H	N	S
$H_2(L)$	71.69(71.03)	4.04(3.97)	8.96(9.20)	10.72(10.54)
[Cu(L)2]	64.38(64.51)	3.78(3.31)	8.58(8.36)	9.40(9.57)
$[Zn(L)_2]\cdot2H_2O$	64.81(64.33)	4.05(3.30)	7.48(8.54)	9.27(9.53)

Table 7 shows the antibacterial activity of (H_2L) Schiff base and its complexes against bacterial strains, the Schiff base showed least activity against *Escherichia coli* and good activity in complexes, whereas *Staphylococcus aureus* showed moderate to good activity in both Schiff base and complexes compared to the reference drug (ciprofloxacin).

Antifungal strains, against *Candida albican* and *Aspergillus fumigatus* showed inhibition zone ranging between 8-19 mm with the metal complexes having higher zone of inhibition more than the Schiff base (Table 8).

With reference to $[Cu(L)_2]$ complex the effective antifungal activity was not observed against *Candida albican*, however good activity was observed against *Aspergillus fumigatus* (Fig. 5a) and moderate activity in case of $[Zn(L)_2]\cdot2H_2O$ complex (Fig. 5b).

The enhanced activity of metal complexes over the Schiff base was due to coordination which reduces the polarity of metal and thus increasing the lipophilic nature of the metal to the lipid layer of bacterial cell membrane (Chakravarty & Banerjee, 2012; Nishat *et al.*, 2011; Wang *et al*., 2010).

Table 7: Antibacterial activities of $H_2(L)$ Schiff base and its complexes showing the inhibition zones (mm) against the bacterial Isolates

Compound	*Escherichia coli*			*Staphylococcus aureus*		
	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}
Ciprofloxacin (standard)		43			40	
DMSO (Control)	06	06	06	06	06	06
$H_2(L)$	07	07	06	12	10	09
$[Cu(L)_2]$	18	15	12	15	13	10
$[Zn(L)_2]\cdot 2H_2O$	13	10	08	16	14	12

Table 8: Antifungal activities of $H_2(L)$ Schiff base and its complexes showing the inhibition zones (mm) against the fungal Isolates

Compound	*Candida albican*			*Aspergillus fumigatus*		
	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}	60 mgml^{-1}	30 mgml^{-1}	15 mgml^{-1}
Ketoconazole (standard)		28			32	
DMSO (Control)	06	06	06	06	06	06
$H_2(L)$	14	12	10	11	10	08
$[Cu(L)_2]$	07	07	08	17	13	10
$[Zn(L)_2]\cdot 2H_2O$	19	15	11	12	10	09

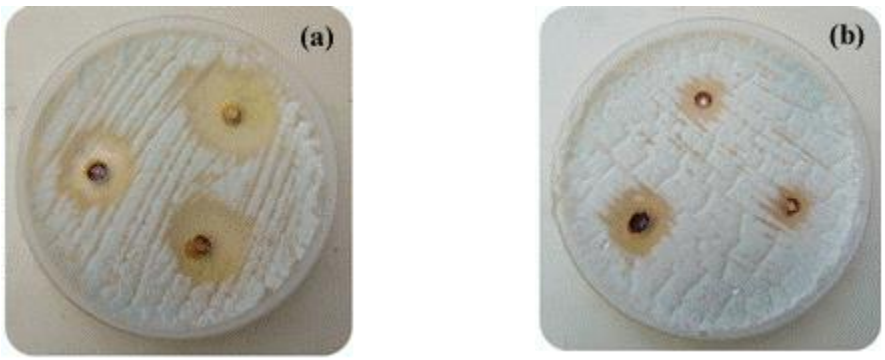


Fig. 5: Showing the antifungal inhibition zones of $[Cu(L)_2]$ complex (a) and $[Zn(L)_2]\cdot 2H_2O$ complex (b) against *A. Fumigatus*

4.0 Conclusion

The Schiff base and their Cu(II) and Zn(II) complexes were successfully synthesized by mechanochemical synthesis. The synthesized compounds were characterized and their antimicrobial activity were evaluated. The study highlights the fact that mechanochemical synthesis is amenable to multi-step synthetic approaches, providing a way to reduce the need for solvents both as reaction media and for purification. From the results, it is envisaged that, the application of this strategy could be extended to prepare a wide range of Schiff bases and related complexes. The method is partly useful in mimicking reactions done using solution and will have a high score over other methods for its green approach. Based on the analyses of the Schiff base and metal(II) complexes carried out, the general molecular structure is proposed as in Figure 6.

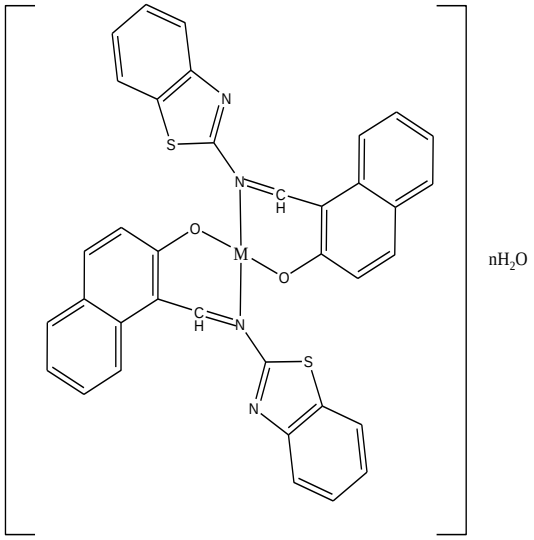


Fig. 6: Proposed structure of $[Cu(L)_2]$ and $[Zn(L)_2]\cdot 2H_2O$ Complexes (M = Cu^{2+} or Zn^{2+} and n = number of water of hydration

5.0 Acknowledgements

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Conflict of Interest

The authors declared no conflict of interest.