



Solid State Synthesis, Spectroscopic and X-ray Studies of Cu(II) Schiff base Complex Derived from 2-Hydroxy-3-methoxybenzaldehyde and 1,3-Phenylenediamine

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ABSTRACT

Complex of Cu (II) with Schiff base derived from 2-Hydroxy-3-methoxybenzaldehyde and 1,3-Phenylenediamine have been mechanochemically (liquid-assistant grinding) synthesized and characterized by infrared, powder x-ray diffraction, energy dispersive X-ray and CHN analysis. Evidence from Infrared spectral study indicated a strong band in the spectra of free ligand occurring at 1619 cm⁻¹ which assigned to $\nu(\text{C}=\text{N})$. It shifted to lower frequency region 1587 cm⁻¹ in the complex indicating the involvement of nitrogen atom of azomethine group. The coordination of Schiff base with the metal ion is confirmed by the appearance of low frequency band at 461 cm⁻¹ due to metal-oxygen $\nu(\text{M}-\text{O})$ and at 579 cm⁻¹ due to metal azothemine nitrogen (M-N) band. The Powder-XRD analysis reveals that, the patterns of the ground mixture were entirely different from the starting constituents, indicating that, all the starting materials were transformed to product, furthermore the colour of the complex was different from that of the Schiff base suggesting the formation of coordination compound. The antimicrobial activities of the synthesized Schiff base and complex were tested using serial dilution method, against bacterial strains (*Escherichia coli*, and *Staphylococcus aureus*) and fungal strain (*Aspergillus flavus* and *Aspergillus niger*). It has been observed that the complex has higher activity than the free Schiff base ligand.

Keywords: Mechanochemistry, Power-X-ray, Azomethine, Ligand, Complex.

INTRODUCTION

The development of sustainable and environmentally friendly chemical processes integrating the principles of green chemistry is a challenging quest for chemists. The most important principles are diminishing the use of solvent especially toxic organic solvent, (Sheldon, 2007). Mechanochemistry' can be described as a synthetic methodology induced by the input of mechanical energy and involves reactions in the solid state or in a simple approach, mechanochemistry corresponds to the chemical reactivity achieved by grinding bulk solid reactants either manually, using a mortar and a pestle, or using a ball mill (Braga *et al.*, 2007, Kaupp 2003, Craig 2012). Mechanochemistry involves not only neat grinding (NG), (without addition of solvent), but also liquid-assisted grinding (LAG), which consists on the use of catalytic amounts of a solvent to accelerate the reaction (Bowmaker *et al.*, 2008, Friscic, 2012). Mechanochemistry is rapidly becoming a method of choice in different areas of chemical and materials synthesis, namely: luminescent studies, pharmaceutical, coordination polymers and metal-organic frameworks (MOFs). In fact, recently several coordination compounds have been

prepared by this method and the use of solid-state techniques appears to be a powerful alternative to the commonly used solution- based methods, requiring milder conditions, and shorter reaction times (Andre *et al.*, 2011).

Many coordination complexes have been readily synthesized by simple grinding of transition metal salt with potential ligands (Bahemmat. *et al.*, 2015, Tella, 2016). Also, mechanochemical synthesis of drug metal complexes (Amin, 2014, Tella *et al.*, 2011) and metal organic have also been reported (Pichon *et al.*, 2008, Tella *et al.*, 2015). When two solids are grounded together, the heat generated in the grinding process may be sufficient to induce local melting of the solid reagents. This lead to generation of a hot spot (exothermic) during initial grinding of the solids resulting in the formation of a liquid melt phase (Pichon *et al.*, 2006). However, in literature it was generally observed that, the reaction proceeded via intermediate eutectic liquid melt phase before product formation (Graham, 2013).

We have successfully synthesized Schiff base from 3-methoxy-2-hydroxybenzaldehyde and 1,3-phenylenediamine and its Copper (II) complex mechanochemically (via liquid assistant grinding

LAG). We have also ascertained its antimicrobial activities against some selected bacterial and fungal isolate.

MATERIALS AND METHOD

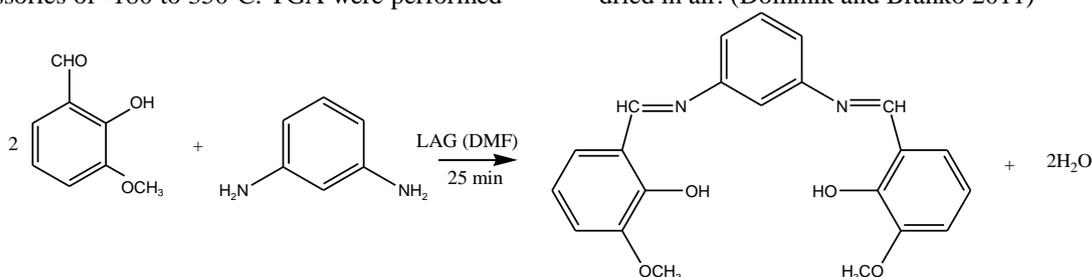
Grinding was carried out in agate mortar with pestle. All reagents used in this study were obtained from Sigma Aldrich UK and were used without further purification. Solid state IR spectra were recorded on a Perkin-Elmer FTIR Spectrum-400. PXRD measurements were carried out on a PAN analytical Empyrean X'Pert Pro X-ray diffractometer. Energy dispersive X-ray (EDX) were determined using FESEM/EDX Hitachi brand model SU8220. DSC were carried out using TA DCS Q20 V24.10 instrument with cooling accessories of -180 to 350°C. TGA were performed

by Perkin-Elmer Pyris Diamond TG/ DTA Heated in flowing Nitrogen (200 mlmin⁻¹). Elemental microanalysis of separated solid chelates for C, H and N were determined using a Perkin-Elmer CHNS/O 2400 series II microanalyser;

SYNTHESIS OF SCHIFF BASE

6,6'-Dimethoxy-2,2'-[1,3-Phenylenebis(nitrilomethylidene)] bis-phenol; [H₂(L)] Schiff base

2-hydroxy-3-methoxybenzaldehyde (6 mmol, 0.9129 g) and 1,3-phenylenediamine (3 mmol, 0.3243 g) were weighed into agate mortar, a small amount of DMF (0.1 ml) was added and the mixture was ground for 25 min to obtain light orange powder. The compound was allowed to dry in air. (Dominik and Branko 2011)



Scheme 1: Synthetic reaction of schiff base

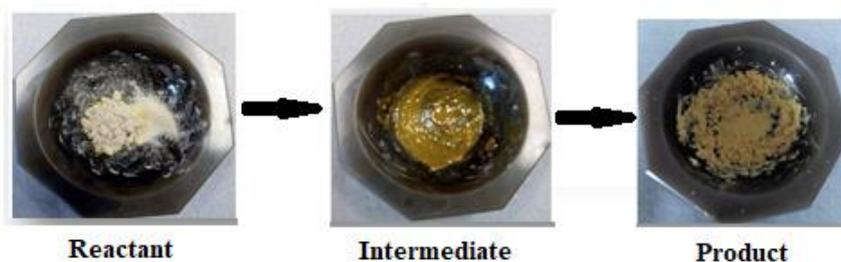


Figure 1: Showing the reactant, intermediate and product of schiff base.

SYNTHESIS OF COMPLEX

6,6' - Dimethoxy - 2,2' - [1,3 - Phenylenebis(nitrilomethylidene)]-bis[phenolato]- N,N',O,O'-Copper(II); [Cu(L)] Complex

The Schiff base (3 mmol, 1.1292 g) and copper acetate monohydrate (3 mmol 0.7473 g) were weighed in to agate mortar, a small amount of DMF (0.1 ml) was added and the mixture was ground for 25 min to obtain dark green powder. It was allowed to dry in air. (Dominik and Branko 2011)

Antimicrobial Sensitivity Test

The antimicrobial activities of the Schiff base and its Cu(II) complex in dimethylsulfoxide (DMSO) was conducted *in vitro* by serial dilution method. The Schiff base and the complex were dissolved separately in dimethylsulfoxide to produce three different concentrations (15, 30 and 60 µgml⁻¹), which were placed on the surface of the

culture and incubated at 37°C for one day. The diameter of inhibition zone produced by the Schiff base and complex were compared with that of the referenced drugs using Ciproflaxacin 500mg (bacterial standard) and Ketoconazole 200mg (fungal standard) (Yeamin *et al.*, 2003, Vadivela and Dhamodaranba 2015).

RESULTS AND DISCUSSION

The Schiff base ligand has an orange colour with 89.5% yield and the elemental analysis results indicate that, the experimental result is very close to the calculated data as shown in Table 1. The FT-IR spectra provide valuable information regarding the nature of functional group attached to the metal atom (Table 2). In order to study the bonding mode of Schiff base to the metal complexes, the IR spectrum of the free ligand is compared with the spectra of the complex. Preliminary identification of ligand was obtained from the absence of the IR bands characteristic for

the amino and carbonyl groups and this is further confirmed by the appearance of new bands due to -C=N- of azomethine. The strong band observed at 1619 cm^{-1} in the spectra of Schiff base can be assigned to -HC=N stretching vibration. The azomethine stretching frequencies in the spectrum of complex is shifted to lower frequencies 1587 cm^{-1} when compared to free ligand. This indicates the coordination of metal center with azomethine nitrogen group. (Al-kubais *et al.*, 1994; Selwin *et al.*, 2006). It is expected that coordination of nitrogen to the metal atom would reduce the electron density in the azomethine link and thus lower the -HC=N absorption. The spectrum of Schiff base [H₂(L)] also shows band corresponding to aromatic C-C stretching at 1452 cm^{-1} and strong absorption at 3467 cm^{-1} which can be assigned to O-H stretching vibration. The phenolic C-O

stretching frequency of Schiff base is seen at 1273 cm^{-1} and the value found to be within the acceptable range as reported in literature (Vadivela, and Dhamodaranba 2015). The phenolic C-O stretching frequency of Schiff base was shifted in the spectrum of complex indicating deprotonation and coordination of the hydroxyl oxygen to the metal ion. (Reddy *et al.*, 2006). The new bands which are not present in the spectrum of Schiff base ligand appeared at 579 cm^{-1} corresponding to M-N and 461 cm^{-1} assigned to M-O vibrations (Nakamoto, 1997). The appearance of M-N and M-O vibration support the involvement of N and O atoms in the complexation with metal ion under investigation (Jain *et al.*, 2005). Therefore, the IR spectral data indicate that the coordination sites of the schiff base to metal ion are -C=N and -C-O.

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

Compound	Molecular formula	Colour	Yeild (%)	Found (Calculated) (%)		
				C	H	N
[H ₂ (L)]	C ₂₂ H ₂₀ N ₂ O ₄	Orange	89.5	70.43(70.20)	5.18(5.36)	7.28(7.44)
[Cu(L)]	C ₂₂ H ₁₈ CuN ₂ O ₄	Dark green	92.2	60.22(60.34)	4.51(4.14)	6.17(6.40)

Table 2: Infrared spectral data of schiff base and its metal complex (cm^{-1})

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{O}-\text{C})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{C})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
[H ₂ (L)]	1619	3467	1119	1273	1452	-	-
[Cu(L)]	1587	3052	1124	1212	1427	579	461

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

Compound	Element	Weight (%)	Atomic (%)	K Ratio	Line type
[Cu(L)]	C	62.26	69.09	0.07249	K Series
	N	13.53	12.88	0.00234	K Series
	O	20.79	17.32	0.00555	K Series
	Cu	3.42	0.72	0.00439	K Series

Table 4: Thermal analysis of schiff base and its Complex

Compound	Hydration tempt °C	%Weight loss: observed(calculated)	No. of H ₂ O of hydration	Melting point/decomposition tempt (°C)
[H ₂ (L)]	-	-	-	135
[Cu(L)]	125	4.2(3.95)	1	205

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

Compound	Escherichia coli: zone of inhibition (mm)			Staphylococcus aureus: zone of inhibition (mm)		
	15 μgml^{-1}	30 μgml^{-1}	60 μgml^{-1}	15 μgml^{-1}	30 μgml^{-1}	60 μgml^{-1}
[H ₂ (L)]	11	15	18	9	11	14
[Cu(L)]	13	19	21	10	12	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)		
	15 μgml^{-1}	30 μgml^{-1}	60 μgml^{-1}	15 μgml^{-1}	30 μgml^{-1}	60 μgml^{-1}
[H ₂ (L)]	7	10	12	-	-	-
[Cu(L)]	10	13	14	-	-	12

The sharp reflections in X-ray diffraction patterns of the synthesized Schiff base and its metal complex reveals the crystalline nature of the compounds. The diffractogram and associated data depict the 2θ value for each peak relative intensity and inter-planar spacing (d-value). Figure 2 shows that, the powder X-ray diffraction patterns (PXRD) of the mechanochemical product was different from the PXRD of the reactants (3-methoxy-2-hydroxybenzaldehyde and 1,3-phenylenediamine).

New intense peaks corresponding to the mechanochemical Schiff base product were observed at $2\theta = 7.798, 13.673, 17.659,$ and 26.472 with d-spacing $11.329, 6.471, 5.018$ and 3.364 respectively. which are absent in the reactants indicating formation of new phase. Quantitative estimation of the 2θ PXRD patterns of the complex were observed at $2\theta = 10.42, 11.19, 18.40$ and 21.46 with d-spacing $8.48, 7.90, 4.82$ and 4.14 respectively (Figure 3)

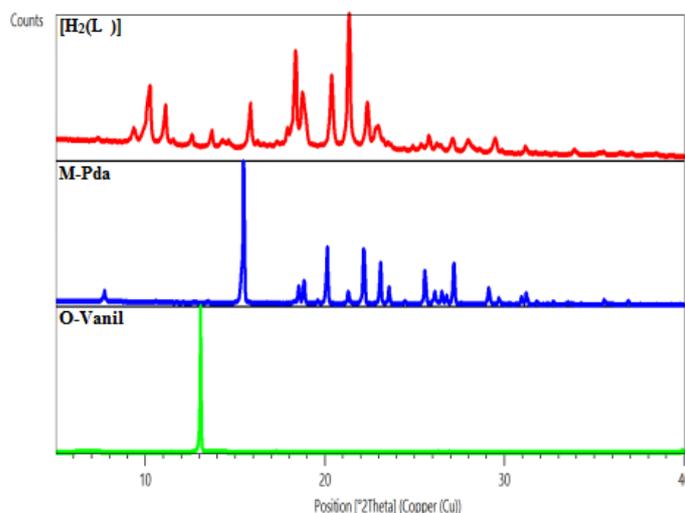


Figure 2: Comparison between PXRD Patterns of 2-Hydroxy-3-Methoxy-benzaldehyde (O-Vanil), 1,3-phenylenediamine (M-Pda) and [H₂L] Schiff base

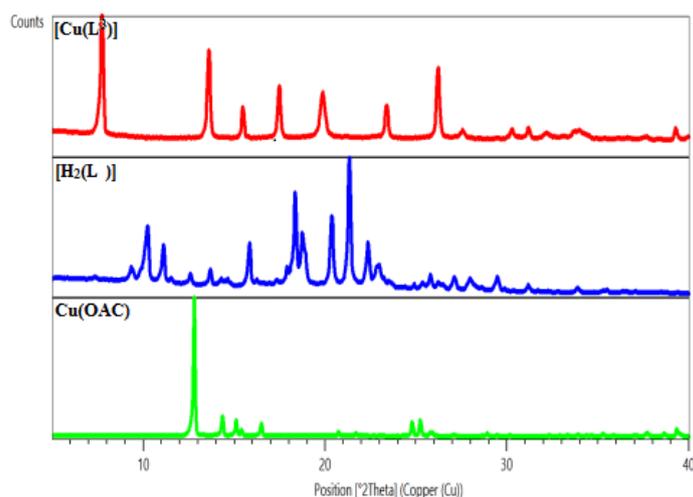


Figure 3: Comparison between PXRD Patterns of Copper (II) acetate monohydrate (Cu(OAC)), [H₂L] schiff base and [Cu(L)] complex product obtained by LAG of Copper (II) acetate and [H₂L] Schiff base

Energy Dispersive X-ray referred to as EDX (Table 3) is an X-ray technique used to identify the elemental composition of materials or chemical characterization of a samples. 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. Elemental mapping of a sample is also possible as showed in Figure 4. EDX results of complex showed that, Carbon has the largest atomic percent 69.09%, followed by oxygen 17.32% then Nitrogen

12.88% and Cobalt 0.72%. The atomic percent of all the four component elements were compared in all the three-point analyzed and the results (atomic percent of C, O, N and Co) were found to be in

agreement with each other indicating the uniform distribution of all the component elements in the sample compound.

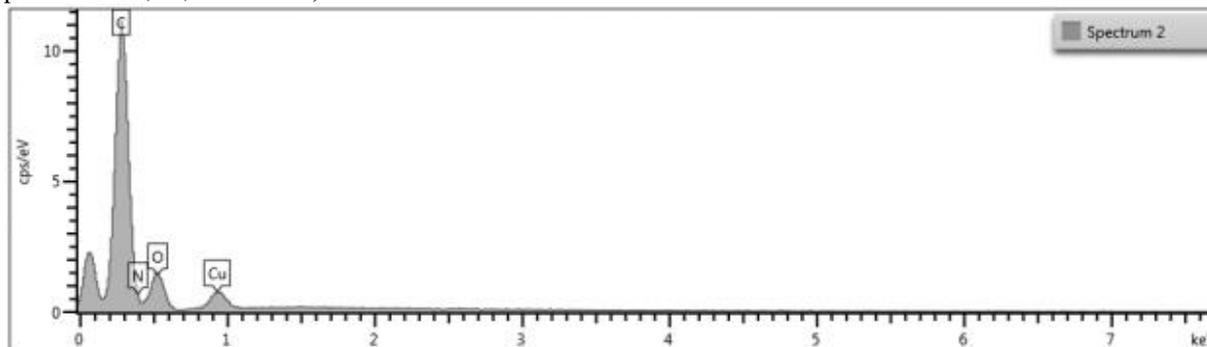


Figure 4: EDX analysis of [Cu(L)] complex showing peak due to Carbon, Nitrogen, Oxygen and Copper in the complex compound

Differential scanning calorimetry (DSC) curve of Schiff base shows one exothermic peak at 135.3°C which corresponds to the melting point of the Schiff base. The simultaneous TGA analysis of the Cu(II) complex were studied from ambient temperature to 600°C under a nitrogen atmosphere (Figure 5). The curve displays 4.2% weight loss (calculated 3.95%) at 125°C which is the same as molecular weight equivalent of one molecule of water and is in

conformity to loss of one water molecule, there are two decomposition stages, the first decomposition amount to 15% weight loss within the temperature range 205-330°C, the last decomposition stage corresponds to 55% weight loss (330-533°C). The results were also confirmed by DTA. Thermal analysis indicate that the complex is more stable than the Schiff base (Table 4).

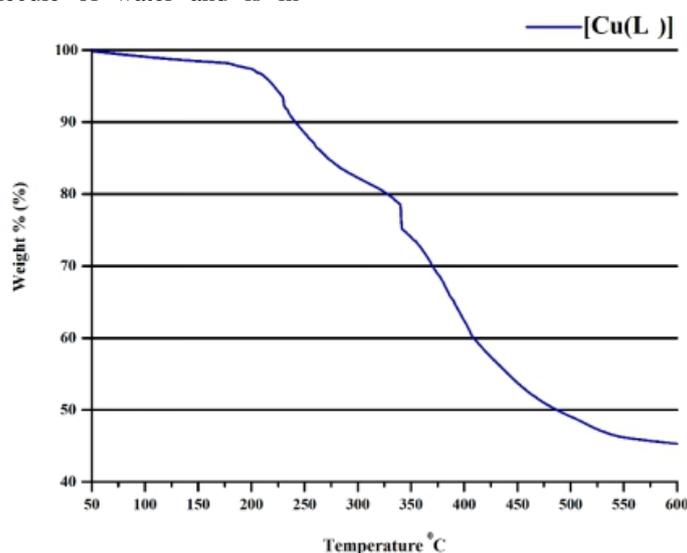


Figure 5: Thermogravimetric analysis of [Cu(L)] Complex, showing 4.2% weight loss at 125°C which is equivalent to 1 molecule of H₂O per molecule of complex

Results of the antimicrobial activity of the complex and Schiff base ligand against the growth of micro-organism are summarized in Table 5 and 6. From the results, inhibition was found to increase with increase in concentration. For antibacterial activity, Cu(II) complex show higher activity against *S. aureus* as compared to *E. coli*. While for fungal sensitivity test the complex show

higher activity against *A. Flavus* as compared *A. Niger*. Cu(II) complex do not show strong concentration dependence of antifungal activity, as compared to antibacterial activities. A comparative study of the Schiff base ligand and its complex indicates that metal complex exhibits higher antimicrobial activity than the free ligand. Such increased activity of the complex is also reported

base on overtone concept and Tweedy chelation theory (Kumar *et. al.*) According to the overtone concept of cell permeability, the lipid membrane surrounding the cell favors the passage of only lipid soluble materials; due to which lipophilicity is an important factor controlling the microbial activity. 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 the positive charge of the metal ion with donor Schiff base ligand.

CONCLUSION

The liquid-assistant mechanochemical synthesis of Schiff base and metal complex

reported in this paper is effective in giving excellent conversion to the product. The Schiff base ligand and its Cu(II) complex were synthesized and characterized by FT-IR, Powder-XRD, EDX, DSC, TGA, and CHN Analysis. The coordination environment around metal center consist of two nitrogen atoms and two oxygen atoms of the Schiff base ligand. Antimicrobial studies reveal that, Cu(II) complex show better activity compared to that of the Schiff base. Thus, it can be said that, complexation or chelation increases antimicrobial activity as explained by Overton's concept and Tweedy's chelation theory. The proposed structure of the metal complex is given as in Figure 6.

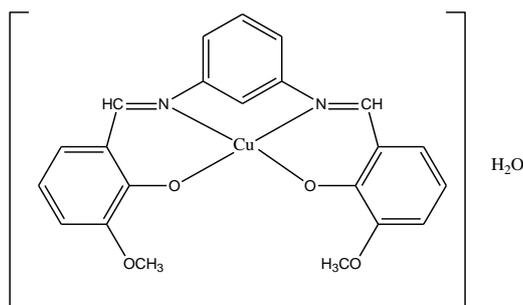


Figure 6: Proposed molecular structure of the complex

ACKNOWLEDGMENT

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