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# MICROWAVE-ASSISTED SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF COPPER (II) COMPLEX WITH SALICYLALDEHYDE AND P-CHLOROANILINE SCHIFF BASE

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***ABSTRACT***
***Transition Metal Complex of Cu(II) with Schiff base N-salicylidene-4-chloroaniline were synthesized by the use of microwave machine. The mixture of 2-hydroxybenzaldehyde (salicylaldehyde) 1.04ml, (0.01mol) and 4-chloroaniline 1.27g (0.01mol) were taken in 50ml beaker and mixed thoroughly. The mixture was irradiated in a microwave oven at a power of 160W for 3 minute. The synthesized complex was characterized by solubility test, melting point, infrared spectra, electrical. The solvents used were Dimethyl sulfoxide (DMSO), Dimethyl formamide (DMF), chloroform, ethanol and water. The value obtained in the spectra of the Schiff base showed a band at 1610.2cm$^{-1}$ which is assigned to azomethine V(C=N-), while for the metal complex was found to be 1628.8cm$^{-1,}$ The shifting of the band of V(C=N) stretching vibration in the spectra of the Schiff base and metal complex in the region 1610.2cm$^{-1}$ to 1628.8cm$^{-1}$ indicated that the complexation has taken place. The infrared spectra suggested that the Schiff base behaves as a bidentate ligand. The value of molar conductivity is 25 Ohm$^{-1}$cm$^{2}$mol$^{-1}$, which indicated that the complex is electrolyte and the values are in the range of 20.4 – 33.5 Ohm$^{-1}$cm$^{2}$mol$^{-1}$. The Schiff base and its metal(II) complex were tested for antibacterial activity against microorganism using Bacillus cerus and candida albican. The results of the tests indicated moderate antimicrobial activity against the tested organism when compared with the standards (Ciprofloxacin and Fluconazol), and this activity increases by increasing concentration. The Metal Complex showed higher activity than free Ligand due to chelation.***
***Keywords: Microwave oven, Salicylaldehyde, 4-Chloroaniline, Antimicrobial, Azomethine.***

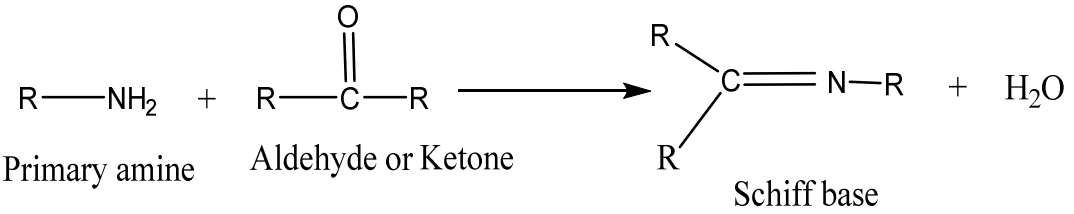
## INTRODUCTION

Microwave chemistry is the science of applying microwave radiation to chemical reactions. Microwave synthesis represents a major breakthrough in synthetic chemistry methodology; a dramatic change in the way chemical synthesis is performed. Conventional heating, long known to be inefficient and time consuming, has been recognized to be creatively limiting too. Microwave synthesis gives the chemists more time to expand their creativity, test new theories and develop new processes. Instead of spending hours or even days synthesizing a single compound, chemists can now perform the same reaction in minutes. The problem associated with waste disposal of solvents has been overcome by performing reactions without a solvent under microwave irradiation. Coupling of microwave irradiation with the use of mineral-supported catalyzed reactions, under solvent-free conditions, provides clean chemical processes with the advantage of enhanced reaction rates, higher yields, greater selectivity, and greater ease of manipulation. Thus microwave synthesis acts as a potential tool for green chemistry (Ravichandran and Karthikeyan, 2011; Hayes, 2002).

Microwave irradiation provides an alternative to the conventional methods, for heating or introducing energy into the system. It utilizes the ability of mobile electric charges present in liquid or conducting ions in solid to transform electromagnetic energy into heat. Microwave radiations are electromagnetic waves. This technology opens up new opportunities to the synthetic chemist in the form of new reactions that are not possible using conventional heating (Krstenansky, 2000 and Sekhon, 2010).

Microwaves can accelerate the rate of reaction, provide better yields and higher purity, uniform and selective heating with lower energy usage, achieve greater reproducibility of reactions and help in developing convenient and cleaner synthetic routes. Microwave-assisted synthesis can be suitably applied to the drug discovery process (Charde *et al.,* 2012), Organic synthesis, Inorganic synthesis, Synthesis of nanotechnology products, Polymer synthesis, Peptide synthesis, Synthesis of radiopharmaceuticals (Grewal *et al.,* 2013) etc.

Schiff bases are compounds containing carbon nitrogen double bond generally known as azomethine or imine linkage. They were named after their discovery in 1864 by an Italian naturalized chemist, Hugo Joseph Schiff (Tidwell, 2008). They are structure based compounds in which the oxygen atom of the carbonyl group (C=O) of an aldehyde or ketone is replaced by the nitrogen of primary amine (Cimerman *et al*., 2000).




**Scheme 1: General reaction for the formation of Schiff base**

Schiff bases of salicylaldehydes have also been reported as plant growth regulators antimycotic activities (Ismail *et al.,* 2017), (Monsanto *et al.,* 2015) and antimicrobian (Hamada *et al.,* 1991)

**GREEN CHEMISTIRTY**

The term Green Chemistry is being worldwide used to describe the design of chemical products and processes that reduce or eliminate the use or generation of substances hazardous to human health (Sheldon, *et al.,* 2007). The beginning of green chemistry is frequently considered as a response to the need to reduce the damage of the environment by man-made materials and the processes used to produce them. A quick view of green chemistry issues in the past decade demonstrates many methodologies that protect human health and the environment in an economically beneficial manner (Wardencki *et al.,* 2005). Green Chemistry is not different from traditional chemistry in as much as it embraces the same creativity and innovation than has always been central to classical chemistry (Manmohan *et al.,* 2012). Green Chemistry would like to increases the efficiency of synthetic methods, to use less toxic solvents, reduce the stages of the synthetic routes and minimize waste as far as practically possible. In this way, chemical synthesis will be part of the effort for sustainable development.

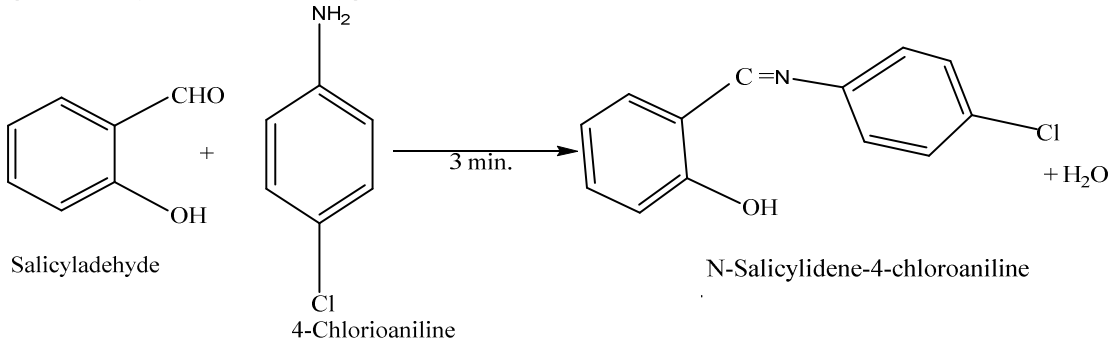
**MATERIALS AND METHODS**

The chemicals and reagents used were of analytical grade purchased and used without further purifications and some are: Salicylaldehyde ($C_7H_6O_2$, 1.04ml, 0.01mol), p-chloroaniline ($C_6H_6ClN$, 1.27g, 0.01mol), Copper (II) chloride ($CuCl_2$, 170.48g/mol) and Ethanol ($C_2H_6O$, 46.07g/mol).

**SYNTHESIS OF LIGAND**

The mixture of 2-hydroxybenzalaldehyde (salicylaldehyde) 1.04ml, (0.01mol) and 4-chloroaniline 1.27g (0.01mol) was taken in 50ml beaker and mixed thoroughly. The mixture was irradiated in a microwave oven at a power rate of 160W for 3 minute. After completion of the reaction, the reaction mixture was poured in to ice water, the yellow solid obtained was filtered, washed, dried and recrystallized from ethanol (Grewal *et al.,* 2013 and Abirami *et al.,* 2014). The yield of the synthesized ligand was calculated using equation below.

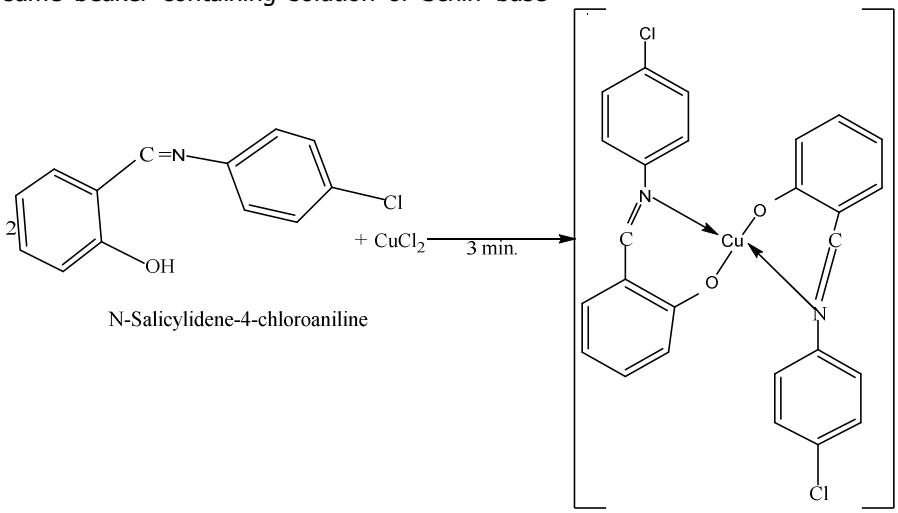
$$Percentage\ yield = \frac{Experimental\ yeild}{Theoretival\ yeild} \times 100$$




**Scheme 2: Synthesis of Schiff Base Ligand**

## SYNTHESIS OF METAL COMPLEX

4.03g (0.02mol) of the Schiff base ligand, N-Salicylidene-4-chloroaniline solution was transferred in to 50ml beaker, 1.7g (0.01mol) of Copper (II) chloride was also transferred in to the same beaker containing solution of Schiff base ligand and mixed thoroughly, the mixture was irradiated in a microwave oven at a power of 160 W for 3 minutes (Grewal *et al.,* 2013 and Abirami *et al.,* 2014). The yield of the synthesized complex was calculated using above equation.




**Scheme 3: Synthesis of Copper(II) Complex**

## RESULTS AND DISCUSION

The reaction between 2-hydroxybenzalaldehyde (Salicylaldehyde) and 4-chloroaniline Schiff base ligand produced (N-salicylidene-4-chloroaniline) which is bright yellow crystalline solid with the percentage yield of 77.8%. It was found that the metal complex has comparatively higher melting point than the Schiff base ligand, this indicate the higher stability of the compound after binding with metal. The Schiff base ligand and its metal(II) complex are soluble in some common organic solvents such as Dimethyl sulfoxide (DMSO), Dimethyl formamide (DMF), and chloroform, slightly soluble in ethanol and insoluble in water as shown in (Table 1). The value obtained in the spectra of the Schiff base showed a band at 1610.2cm$^{-1}$ which was assigned to azomethine V(C=N-) stretching vibration and another band at 3086.2cm$^{-1}$ which was assigned V(O-H) stretching vibration (Table 3). The shifting of the band of V(C=N) stretching vibration in the spectra of the metal complex in the region 1610.2cm$^{-1}$ to 1628.8cm$^{-}$ as shown in (Table 3) indicated that the complexation has taken place. The results of the tests indicated moderate antimicrobial activity against the tested microorganisms when compared with the standard (*Ciprofloxacin and Fluconazol*), and this activity increases by increasing concentration. And also the metal complex showed higher activity than free ligand, due to the effect of the metal ions on the normal metabolic function of the cell. The findings are similar to that reported by Achut *et al.* (2010). Measurement of molar conductance of complex in 10$^{-3}$M dimethyl sulpoxide determined as reported by Geary (1971) are in the range of 20.4 – 33.5 Ohm$^{-1}$cm$^{2}$mol$^{-1}$ which are relatively low, indicating their non-electrolytic nature.

**Table 1: Solubility of the Ligand and the Complex in some common Solvents.**

| Compound | Water | Ethanol | Chloroform | DMF | DMSO |
|---|---|---|---|---|---|
| Schiff base | IS | S | S | S | S |
| Complex | IS | SS | S | S | S |

**KEY:** S = Soluble, IS = Insoluble, SS = Slightly soluble.

**Table 2: Colour, Percentage yield, and melting point of Schiff base and the Complex**

| Compound | Colour | %yield | Melting point (°C) |
|---|---|---|---|
| Schiff base | Bright yellow | 77.8 | 185 |
| Complex | Dark green | 73.7 | 205 |

**Table 3: IR Spectra of the Schiff base and Complex**

| Compound | υ (C=N) $cm^{-1}$ | υ (O-H) $cm^{-1}$ |
|---|---|---|
| Schiff base | 1610.2 | 3086.2 |
| Complex | 1628.8 | 3209.2 |

**Table 4: Conductivity Measurement of Complex in dimethyl sulpoxide.**

| Complex | Concentration $Moldm^{-3}$ | Specific Conductance $Ohm^{-1}\ cm^{-1}$ | Molar Conductance $cm^2\ mol^{-1}$ | $Ohm^{-1}$ |
|---|---|---|---|---|
| $[CuL_2]$ | $1.0\times10^{-3}$ | $25.0\times10^{-6}$ | 25.0 | |

**Table 5: Results of zone of inhibition for the ligand and metal complex**

| Test microbes | Concentration | | | Control | |
|---|---|---|---|---|---|
| **Ligand** | **200µg** | **100µg** | **50µg** | **CPX** | **FLU** |
| *Bacillus cerus* | 14.00 | 7.00 | 0.00 | 34.00 | |
| *Candida albican* | 0.00 | 0.00 | 0.00 | | 35.00 |
| **Complex** | | | | | |
| *Bacillus cerus* | 0.00 | 0.00 | 0.00 | | |
| *Candida albican* | 59.00 | 30.00 | 15.00 | | |

KEY: CPX: Ciprofloxacin, FLU: Fluconazol

**Table 6: Result of minimum inhibitory and bacteriocidal concentration of ligand and complex**

| TEST MICROBE | (MIC) | | | (MBC) | | | CONTROL |
|---|---|---|---|---|---|---|---|
| **Ligand** | **200µg** | **100µg** | **50µg** | **200µg** | **100µg** | **50µg** | |
| *Bacillus cerus* | _ | + | +++ | + | ++ | +++ | _ |
| *Candida albican* | ++ | +++ | +++ | +++ +++ | | +++ | _ |
| **Complex** | | | | | | | |
| *Bacillus cerus* | +++ | +++ | +++ | +++ +++ | | +++ | _ |
| *Candida albican* | _ | _ | _ | _ | _ | + | _ |

**KEY:**

**- :** No growth or turbidity
**+ :** Less growth
**++** : Dense growth
**+++ :** Heavy growth

MIC : Minimum inhibitory concentration
MBC: Minimum bacteriocidal concentration

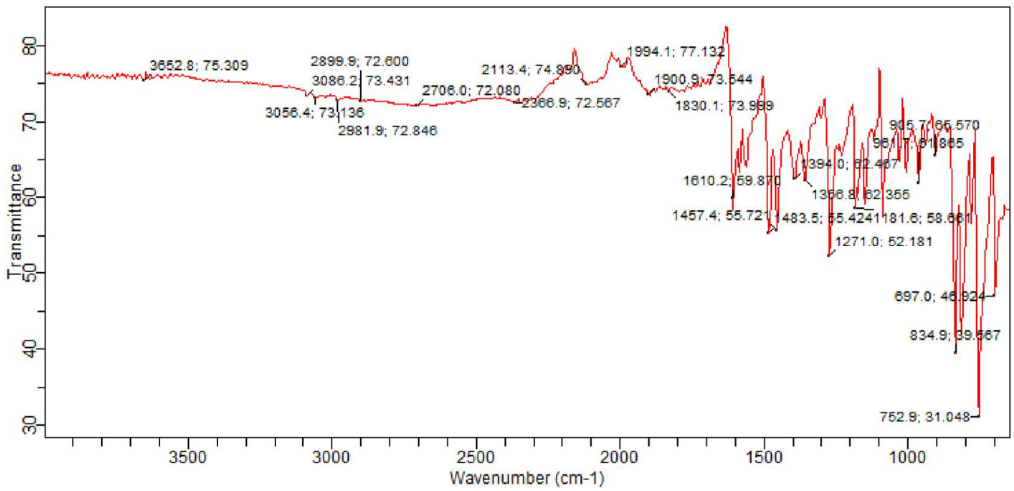



**Fig. 1: FTIR of saliylaldhyde and p-chloroanaline schiff base ligand**

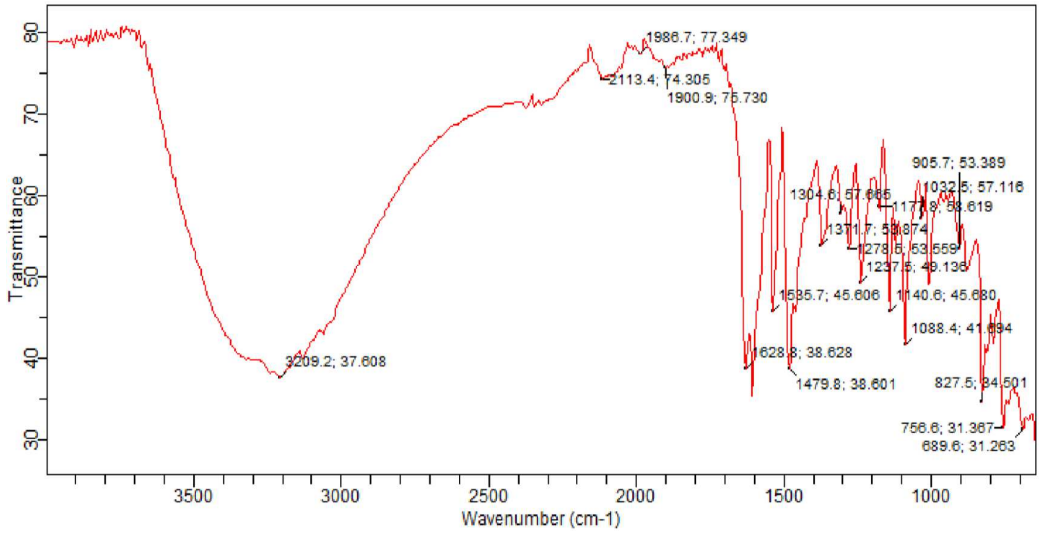



**Fig. 2: FTIR of salicylaldehyde and p-chloroanaline metal complex with copper**

## CONCLUSION

The Schiff base and its corresponding transition metal complex of Cu(II) were synthesized and characterized successfully. The Schiff base act as a bidentate ligand and the metal - ligand ratio was found to be 2:1 in the prepared complex. The Schiff base and its metal complex are soluble in some organic solvents such as chloroform DMSO and DMF etc. Also the antimicrobial activity was tested on both the Schiff base and the metal complex, it is active on the complex and inactive on the ligand. The value of the molar conductance indicated that the metal complex is non-electrolyte.

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