

## SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF BIDENTATE SCHIFF BASE COPPER (II) COMPLEXES

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Article Received on  
09 Dec. 2020,

Revised on 29 Dec. 2020,  
Accepted on 19 Jan. 2021

DOI: <https://doi.org/10.17605/OSF.IO/25S6R>

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### ABSTRACT

The Schiff base ligand 2-(4-hydroxy-3-methoxy benzylidene) imino benzhydroxamic acid was synthesized by the condensation of 4-hydroxy-3-methoxybenzaldehyde and 2-amino-benzhydroxamic acid in an alcoholic medium at room temperature. The ligand and copper (II) complexes were characterized by elemental analysis, molar conductance, electronic spectra, IR spectra, NMR spectra, molar conductivity and magnetic susceptibility. The copper (II) complexes are colored and stable in air. In the metal complexes the metal -ligand ratio found to be 1:2. The sharp band appeared at  $1625\text{ cm}^{-1}$  is characteristics of the azomethine group present in the Schiff base

ligand. This band was shifted to lower frequency ( $1580 - 1600\text{ cm}^{-1}$ ) in all the copper complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. The  $\nu(\text{N-OH})$  stretching vibration of the ligand obtained at  $1085\text{ cm}^{-1}$ , which is raised up by  $10-40\text{ cm}^{-1}$  in the complexes suggesting the deportation of (N-OH) hydrogen and coordination of hydroxyamino nitrogen atom in the bond formation with the Cu (II) ions. The molar conductivity data of the complexes in DMF solution indicates they are non-electrolytic nature. All copper (II) complexes are paramagnetic in nature. On the basis of elemental analysis, magnetic susceptibility and electronic spectral data, geometry of complexes was proposed to be octahedral in nature. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base ligand due to chelation.

**KEYWORDS:** Schiff Base, 2-Aminobenzhydroxamic Acid, Vanillin, Copper Complexes, Antimicrobial Activity.

## INTRODUCTION

Schiff bases are the most important class of organic compounds synthesized from the condensation of a primary amine with active carbonyl compounds.<sup>[1-3]</sup> Schiff bases may be represented as  $R-CH=N-R'$  where R and R' may be alkyl, aryl or heterocyclic. Schiff bases of aromatic aldehydes are more stable than aliphatic aldehydes due to effective conjugation. Plants and animals require Cu for normal growth and metabolism. Copper is essential for growth and development of brain, blood cells, blood vessels and maintenance of healthy skin and immune system. The presence of azomethine group, which is responsible for stability, reactivity and biological activity of Schiff bases and their metal complexes.<sup>[4]</sup> Schiff bases and their metal complexes are used in catalyst, antimicrobials, antioxidants, dyes optical materials and analytical chemistry.<sup>[5-9]</sup> Vanillin is used as flavoring agent in sweet foods and beverages. Vanillin is also used as a chemical intermediate in the manufacture of drugs and chemicals. Vanillin Schiff base transition metal complexes have antimicrobial activity. Due to anticlastogenic and antitumor activities of vanillin, it is a best chemical intermediate in the manufacture of drugs such as dopamine, papaverine and aldomet.<sup>[10]</sup> Due to chelation transition metal Schiff base complexes are more stable and have wide applications in antibacterial, antifungal, antiviral, anticancer, and anti-inflammatory. Schiff base ligands acts as chelating ligands and their biological activity enhanced on coordination.<sup>[11-12]</sup> We report here the synthesis, characterization and antimicrobial activity of complexes of Cu(II) containing bidentate Schiff base ligand derived from the condensation of 4-hydroxy-3-methoxybenzaldehyde and 2-amino-benzhydroxamic acid.

## MATERIALS AND METHODS

The chemicals used in the present work were of Anal-R grade and were used without further purification. The elemental analysis (C, H and N) data was obtained using 2400 CHN Perkin-Elmer elemental analyzer. The molar conductivity of the complexes in DMF solution ( $10^{-3}M$ ) were measured by using DI-909 digital conductivity meter. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR spectrophotometer using KBr disc. The magnetic susceptibility data were measured by Gouy method using  $Hg [Co (SCN)_4]$  as a calibrant. The electronic spectra of the complexes were recorded by using Shimadzu model UV-1601 spectrophotometer in DMSO solution.

### Synthesis of schiff base ligand

The Schiff base ligand was prepared in two steps. In the first step 41.6g of hydroxyl amine hydrochloride was gradually added with constant stirring to an ice-cold solution of 48g sodium hydroxide dissolved in 300 ml of water. After that, 45.2g of methyl anthranilate was added to the resulting solution along with enough alcohol for the proper dilution of the solution. The whole solution was allowed to stand for three days at room temperature. Then the solution was distilled under the reduced pressure until sodium salt of hydroxamic acid was precipitated leaving 100 ml of mother liquor in the flask. The salt was filtered by suction and washed with ether. The filtrate was made acidic with HCl and then free hydroxamic acid was precipitated. It was light brown colour and fairly stable at 140<sup>0</sup>C. In the second steps, The Schiff base ligand 2-(4-hydroxy-3-methoxy benzylidene) imino benzhydroxamic acid was prepared by adding 1.52g (0.01 mol) of 4-hydroxy-3-methoxybenzaldehyde in 25 ml ethanol and 1.52g (0.01 mol) of 2-amino-benzhydroxamic acid in 25 ml ethanol. The reaction mixture was refluxed for 2-3 h. The resulting solution produced faint orange crystalline solid on cooling in the freezer. The melting point of Schiff base ligand was obtained to be 54<sup>0</sup>c. The compound found to be stable at upon storage.

### Synthesis of copper (II) complexes

The copper (II) complexes were prepared by mixing (50 ml) ethanolic solution of Cu(II) acetates / chlorides with the (50 ml) ethanolic solution of Schiff base in a metal-ligand ratio 1:2. The resulting mixture was refluxed on water bath for 1-2 h. The complex obtained in each time was cooled, filtered and washed with acetone and recrystallized with ethanol and dried over anhydrous KOH in a desiccator.

**Table 1: Physical Properties and Analytical data of Schiff base and Cu(II) Complexes.**

Compounds	Color	% Analysis Found (Calc)			
		C	H	N	M
Schiff base	Orange	62.81 (62.93)	4.82 (4.89)	9.68 (9.79)	-
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Light green	53.66 (53.77)	4.41 (4.48)	8.30 (8.36)	9.38 (9.48)
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	Parrot green	53.84 (53.93)	4.68 (4.79)	12.47 (12.58)	9.49 (9.51)
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	Green	60.58 (60.64)	4.51 (4.54)	10.54 (10.61)	7.91 (8.02)
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	Light green	62.78 (62.89)	4.21 (4.28)	9.91 (10.00)	7.47 (7.56)
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	Yellowish green	64.89 (64.61)	4.41 (4.48)	9.37 (9.42)	7.08 (7.12)

## RESULTS AND DISCUSSION

The analytical and physical properties of Schiff base and copper (II) complexes are given in Table-1. All copper (II) complexes are coloured and stable in air. The metal ligand ratio in all the metal complexes have 1:2.

**Molar Conductance and Magnetic moment:** Molar conductance and magnetic moment data of copper (II) complexes are given in Table 2. The lower molar conductance values of copper (II) complexes in DMF solution indicate their non-electrolytic nature. Cu(II) is a  $3d^9$  system. The free ion ground state term is  $^2D$ . The ground state term for Cu(II) in weak octahedral is  $^2E_g$ . Cu(II) has one unpaired electron only value for magnetic moment is 1.73 B.M. In weak octahedral field, ground term is  $^2E_g$  and as there is no orbital contribution, there is contribution from first order Zeeman effect. For Cu(II)  $\lambda$  is  $-830\text{ cm}^{-1}$  and  $10 Dq$  is  $13000\text{ cm}^{-1}$ , so  $\mu_{\text{eff}}$  is 1.90 B.M. In distorted octahedral complexes ground state term is  $^2A_{1g}$ , so orbital contribution from first order Zeeman effect is not expected. Hence,  $\mu_{\text{eff}}$  for distorted octahedral Cu (II) complexes are near  $\mu_s$  value only. Thus  $\mu_{\text{eff}}$  for octahedral Cu(II) complexes are expected to be greater than  $\mu_s$  due to spin-orbital coupling, negative value of  $\lambda$  and absence of spin-spin interaction in the complexes.<sup>[13]</sup> The  $\mu_{\text{eff}}$  values of Cu(II) complexes have been found to be in the range of 1.80-1.98 B.M, which suggesting distorted octahedral geometry for these complexes.

**Table 2: Molar Conductance and Magnetic Moment data of Cu(II) Complexes.**

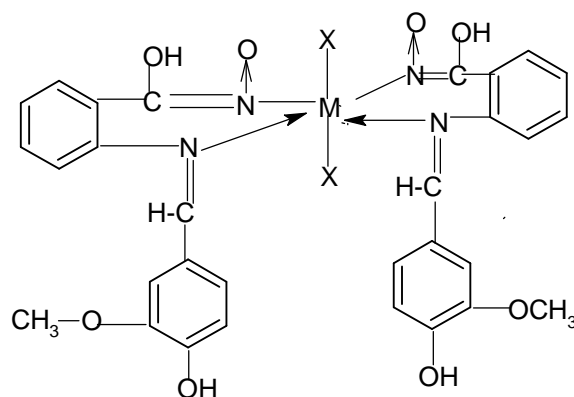
Compounds	Molar conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	$\mu_{\text{eff}}$ (B.M)	Magnetic nature
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	24	1.90	Paramagnetic
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	20	1.85	Paramagnetic
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	23	1.95	Paramagnetic
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	18	1.88	Paramagnetic
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	22	1.92	Paramagnetic

**Table 3: I.R Spectral data of Schiff Base and Cu(II) Complex.**

Compounds	$\nu(\text{OH})$ $\text{cm}^{-1}$	$\nu(\text{C}=\text{N})$ $\text{cm}^{-1}$	$\nu(\text{OCH}_3)$ $\text{cm}^{-1}$	$\nu(\text{M}-\text{N})$ $\text{cm}^{-1}$	$\nu(\text{N}-\text{O})$ $\text{cm}^{-1}$	$\nu(\text{M}-\text{O})$ $\text{cm}^{-1}$	$\nu(\text{OH})+\nu(\text{NH})$ $\text{cm}^{-1}$
Schiff base	3500	1625	2800	-	1080	-	3150
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3540	1600	2780	450	1105	590	3200
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3550	1590	2790	440	1120	-	3250
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ]	3550	1585	2785	455	1110	-	3240
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub> ]	3530	1580	2785	445	1100	-	3230
[Cu(C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> ]	3540	1590	2783	455	1115		3235

**Table 4: Antimicrobial data of Ligand and Cu(II) Complexes:- Diameter of inhibition zone(mm) and activity index(%).**

Compounds	E. coli		S. aureus		A. niger		C.albicans	
	Inhibition zone (mm)	Activity index	Inhibition zone (mm)	Activity index	Inhibition zone (mm)	Activity index	Inhibition zone (mm)	Activity index
Concentration	50 100	50 100	50 100	50 100	50 100	50 100	50 100	50 100
Schiff base	11 14	61.1 66.6	12 14	60 83.3	13 18	61.9 69.2	14 19	70 76
[Cu(L) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	14 18	77.7 81.8	16 20	80 83.3	17 22	80.9 84.6	18 23	90 92
[Cu(L) <sub>2</sub> (Py) <sub>2</sub> ]	14 18	77.7 81.8	16 20	80 83.3	17 22	80.9 84.6	18 23	90 92
[Cu(L) <sub>2</sub> (Quino) <sub>2</sub> ]	14 18	77.7 81.8	16 20	80 83.3	17 22	80.9 84.6	18 23	90 92
Streptomycin	18 22	100 100	20 24	100 100	-	-	-	-
Miconazole	-	- -	-	-	21 26	100 100	20 25	100 100

**Fig. 1: Proposed Structure of Cu(II) Complexes.**

X=Water, ammonia, pyridine, phenyl isocyanide and quinoline. M= Cu(II)

### I.R Spectra

The I.R spectral data of Schiff base ligand and Cu(II) complexes are given in Table 3. The band appeared at  $1625\text{ cm}^{-1}$  is characteristics of the azomethine group present in the Schiff base ligand. This band was shifted to lower frequency ( $1580 - 1600\text{ cm}^{-1}$ ) in all the copper complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes.<sup>[14-17]</sup> From the I.R spectra of copper (II) complexes, it is found that the frequencies due to  $\nu(\text{OH})$  and  $\nu(\text{OCH}_3)$  vibrations remain unchanged. Which indicates the OH and  $\text{OCH}_3$  groups of vanillin are not participate the bond formation with copper ion. The  $\nu(\text{N-OH})$  stretching vibration of the ligand obtained at  $1085\text{ cm}^{-1}$ , which is raised up by 10-40

$\text{cm}^{-1}$  in the complexes suggesting the deportation of (N-OH) hydrogen and coordination of hydroxyamino nitrogen atom in the bond formation with the Cu(II) ions. The coordination of nitrogen atom of azomethine( $>\text{C}=\text{N}$ ) group and hydroxyamino nitrogen atom is further confirmed due to the appearance of a weak and sharp band in the region of  $440\text{--}450\text{ cm}^{-1}$  which was assigned to be due to  $\nu(\text{M-N})$  vibration. The Schiff base ligand 2-(4-hydroxy-3-methoxy benzylidene) imino benzhydroxamic acid was found to be mono anionic bidentate and coordination sites being the nitrogen atom of the azomethine group and hydroxyamino nitrogen atom. In case of aqua complex, separate band for coordinated  $\text{H}_2\text{O}$  is not obtained as it is overlapped by that of coordinated  $\nu(\text{OH})$  vibration. The frequency obtained at  $750\text{ cm}^{-1}$  in aqua complex may be attributed as due to rocking mode of coordinated water. The rocking and the metal oxygen mode of stretching will become infrared active if the metal oxygen bond is sufficiently covalent. In pyridine complex the pyridine vibration show very little shift upon complex formation.

### Electronic absorption spectra

The electronic spectrum of copper (II) complexes was recorded in DMSO at room temperature. Copper (II) complexes show an intense band at  $24800\text{ cm}^{-1}$  and  $26200\text{ cm}^{-1}$  respectively, which assigned to charge transfer from ligand to metal. Other two bands observed by each complex at  $18200\text{ cm}^{-1}$  and  $16500\text{ cm}^{-1}$  due to d-d transition. The electronic absorption spectra of copper (II) complexes were observed at  $15600\text{--}15900$ ,  $15500\text{--}15800$  and  $16000\text{--}16500$  respectively. The electronic absorption spectral data indicating the distorted octahedral nature of the complexes.

### Antimicrobial activity

The synthesized Schiff base ligand and its copper complexes were screened for their in vitro antibacterial activity against *Escherichia. coli* and *Staphylococcus aureus* by disc diffusion method and using streptomycin as control. The antifungal activity against *Aspergillus niger* and *Candida albicans* were tested by well diffusion method and using miconazole as control. The antimicrobial activity profiles of Schiff base ligand and copper complexes against bacteria and fungi are presented in Table 4. The antimicrobial activity of Schiff base ligand is due to azomethine linkage present in it. The antimicrobial data indicated that all the complexes show more activity compared to the free ligand against microorganisms, and this activity is found to be enhanced on coordination with the metal ions. This also can be

explained on the basis of Tweedy's chelation theory and the effect of the metal ion on the normal cell processes.<sup>[18]</sup>

## CONCLUSION

The Schiff base derived from 4-hydroxy-3-methoxybenzaldehyde (vanillin) and 2-amino benzhydroxamic acid and its Cu(II) complexes were synthesized and characterized by micro elemental analysis and different spectroscopic techniques. The Schiff base ligand acts as bidentate. The lower molar conductance values of complexes, suggested their non-electrolytic nature. The band appeared at  $1625\text{ cm}^{-1}$  is characteristics of the azomethine group present in the Schiff base ligand. This band was shifted to lower frequency ( $1580 - 1600\text{ cm}^{-1}$ ) in all the copper complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. The  $\nu(\text{N-OH})$  stretching vibration of the ligand obtained at  $1085\text{ cm}^{-1}$ , which is raised up by  $10-40\text{ cm}^{-1}$  in the complexes suggesting the deportation of (N-OH) hydrogen and coordination of hydroxyamino nitrogen atom in the bond formation with the Cu(II) ion. On the basis of elemental analysis, magnetic susceptibility and electronic spectral data, geometry of complexes was proposed to be octahedral in nature. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base ligand.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this research paper.

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