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# Syntheses and spectral studies of copper ii sulphate complex with furancarbamide, benzoic acid hydrazaide and its acetone hrdazone derivative

S. A Emmanuel<sup>1</sup>, S. A Thomas<sup>1</sup>, S. O Idris<sup>2</sup>, J. F Iyun<sup>2</sup>

<sup>1</sup>Sheda Science and Technology, Complex Sheda, Abuja <sup>2</sup>Chemistry Department, ABU, Zaria

# ABSTRACT

Chelate of furancarbamide (FUR), benzoic acid hydrazide (BAH) and its acetonebenzoic acid hydrazone (ABH) with copper II sulphate have been prepared. The complexes and ligands were characterized by Fourier transform infrared spectra analysis, electronic spectra analyses, conductivity, melting point, and solubility. The FTIR analysis indicated that the ligand (FUR) coordinated with the metal ions through the carbonyl oxygen, the azomethine nitrogen and amine nitrogen, while (ABH) coordinated through the carbonyl oxygen and azomethine nitrogen. This is an indication that the ligands acted as tridentate and bidentate donors to the metal ions. The electronic spectra showed the complexes as distorted octahedral geometry. The conductivity data showed the complexes as non electrolytes. Elemental analysis indicate that the complex of ABH formed an M:L<sub>2</sub>. X type while FUR complex formed an ML<sub>1</sub>.X type complex.

**Key words:** benzoic acid hydrazide acetonebenzoic acid hydrazone, furancarbamide, copper II sulphate, complex, ligand.

# **INTRODUCTION**

Dinuclear copper complexes are receiving continuous attention primarily due to their structural, magnetic, electron transfer and catalytic properties [1] and as models for metalloenzymes containing dicopper active sites [2]. Tridentate Schiff bases are very effective in producing dinuclear species of metal ions such as copper (II) that prefer square-planar or square-pyramidal geometry. In addition, such ligands can be used to obtain mononuclear hexacoordinated copper (II) complexes that are of considerable interest from the standpoint of their coordination geometry and spectroscopic properties [3]. Seema et al studied the properties of copper (II) complexes of 1-(2-hydroxyl phenyl)-3-(1-hydroxy, 2,4-Dibromophenyl)-2-propen-1-one and 1-(2'-hydroxyl-3'-iodo-5'-mehtyl phenyl)-3-1(1-hydroxy 2,4-Dibromo phenyl)-2-propen-1-one. The complexes gave a square planar geometry as shown by spectroscopic study [4]. Copper (II) complexes have also found use as therapeutic agents. Thus Copper (II) complexes of thiosemicarbazones were synthesized as potential antitumor agents and showed significant improvement in cytotoxic activity against human acute lymphoblastic leukemia CCRF-CEM

cells and colon adenocarcinoma HT-29 cells [5]. In this study copper (II) complex of furancarbamide (FUR) and acetonebenzoic acid hydrazone (ABH) were synthesized and their physicochemical parameters were determined and compared.

# MATERIALS AND METHODS

## Reagents

All the reagents used for this study are of analytical grade and were obtained from Sigma Aldrich Company and BDH. They were used without further purification.

## Methods

Synthesis of furancarbamide ligand by Cherkasov et al, (1970) method as in [8] 40ml of analar grade furfuraldehyde was measured and poured into a 250 ml flat bottom flask, 40g of urea added, followed by 9ml of distilled water. The mixture was heated on a water bath until a temperature of 60°C was reached, 1ml of 20% NaOH solution was then added and heating continued for another 20 minutes. The mixture was cooled on an ice bath and the precipitate filtered and washed with cold water (10-15°C) and then it was dried at a temperature between 40-50°C. The dried powder obtained was washed with n-Hexane and recrystallized twice from methanol- water solution (30/70% v/v) and dried.



Scheme 1: schematic presentation of furancarbamide synthesis

The ligand benzoic acid hydrazide and acetonebenzoic acid hydrazone were synthesized as described by Nwabueze 1996 [10].

7ml (7.07g) of hydrazine hydrate was added in slight excess to 31.6ml ethylbenzoate in a 500ml round bottom flask, 100ml ethanol was then added and the mixture refluxed for 6 hours at  $80^{\circ}$  C. It was poured into a beaker and covered with a watch glass and left to crystallize. The crystals were filtered using a suction pump and recrystallize in ethanol, and dried in a desiccators over calcium chloride.

A schematic representation of the preparation is presented in scheme 2 below.



Scheme 2: Synthesis of hydrazide

7.8g of hydrazide was dissolved in 100ml ethanol 4.14ml (3.3g) added and heated under reflux for 4 hours. The mixture was poured into a beaker, concentrated and left to crystallize. The crystal was filtered and recrystallized in methanol. The pure crystals were dried in a desiccators.



Scheme 2: synthesis of acetonebenzoic acid hydrazone

# Synthesis of metal complexes

5.27g (0.0385mol) of furancarbamide was dissolved in 100ml of boiling distilled water in a 250ml beaker. 4.73g (0.0189mol) of copper II sulphate was dissolved in 50ml of distilled water and added to the ligand solution and heating continued. It was heated for 10 minutes and the removed from heat and filtered immediately. The filterate was concentrated and allowed to cool the resulting precipitate was filtered and dried. It gave a 7.5% yield.

# Preparation of the complex of ABH

The complex of ABH was synthesized by weighing 0.875g (0.005M) in slight excess of ligand dissolved in 70ml ethanol in a 250ml beaker. Then 0.62g (0.009M) copper sulphate dissolved in water was added to the ligand with stirring. The blue crystalline precipitate formed as metal salt was poured into the ligand solution. The crystals were filtered and dried in a dessicator. It gave a yield of about 78.9%

# Preparation of benzoic acid hydrazide complex

0.79g (0.005M) of BAH was weighed and dissolved in 70ml of ethanol in a 250ml beaker. Then 0.72g (0.01M) of copper sulphate was weighed and dissolved in 50ml of distilled water. This was then poured gently into the ligand solution with constant stirring. The resulting crystals were filtered and dried in a desiccator. Yield 69.55%

# **Physical Measurements**

Copper was determined by gravimetric method after removing the organic residue by digesting with a few drops of concentrated nitric acid. Sulphate ion was determined as barium sulphate. The infra red spectra data of ligand and complexes were recorded on Genesis II FTIR spectrometer as kbr discs.

The conductivity was determined on Jenway 4330 conductivity and pH meter. Electronic spectra were determined on Unicam 9700 series UV/Visible spectrometer. Melting point analysis was done on Electrothermal melting point apparatus. The image were taken on Carl Zeiss SEM.

# **RESULTS AND DISCUSSION**

The formation of the complexes from the ligands and copper II sulphate nay be represented by the general equations,

 $\begin{aligned} \text{CuSO}_4 &+ \text{nRCOCNNH}_2 & \dashrightarrow & \text{Cu}(\text{RCOCNNH}_2)_n\text{SO4.nH2O} \text{ (n= 0.5, 1, 2,3; R = cyclo group)} \\ \text{CuSO}_4 &+ \text{nRCONHNH}_2 & \dashrightarrow & \text{Cu}(\text{RCONHNH}_2)_n\text{SO4.nH}_2\text{O} \text{ (n= 0.5, 1, 2,3; R = cyclo group)} \end{aligned}$ 

The analytical data (Table 1) show that the complexes precipitated with 2 molecules of the ligand ABH and BAH while the FUR complex precipitated with one molecule of the ligand. Two and three coordination with respect to the ligand is common among complexes of carboxylic hydrazide [9]. The colour exhibited by the complexes is a probable indication of octahedral geometry for the complexes [6-7]. All the complexes precipitated as crystals and were insoluble in water at ordinary room temperature but dissolved on heating. They were also insoluble in most organic solvents (Table 4).

# Infar red spectra

The band corresponding to  $\Box$  (C=O) vibration found at 1672.03cm<sup>-1</sup> in the ligand (FUR) was lowered in the complex by -26.52cm<sup>-1</sup>. The vibration band due to v(C=N) was found at 1532.58cm<sup>-1</sup> in the ligand but disappeared in the complex. This indicates a strong coordination of this site to the metal ion [11]. Accordingly the carbonyl oxygen and the azomethine nitrogen were most probably involved in the coordination. The band around 3400-3000cm<sup>-1</sup> appeared broad and unresolved in the complex and this may be due to OH or NH of amine nitrogen vibration.

The ligand (ABH) band corresponding to v(C=O) vibration was found around 1638.80cm<sup>-1</sup>. This was increased in the complex by ca 0.96 cm<sup>-1</sup>. The band due to v(C=N) in the ligand observed around 1546.96cm<sup>-1</sup>, while in the complex it was found at 1546.00cm<sup>-1</sup>. The shift in absorption of these bands indicates possible very weak coordination of the ligand through these sites [11]. The band observed around 3000-3400cm<sup>-1</sup> is as assigned to  $v(NH_{*})$ . This was observed in the ligand at 3024.48-3218.34 cm<sup>-1</sup>. It appeared in the complex as a broad unresolved band.

The hydrazide ligand (BAH) showed band corresponding to v(C=O) vibration at 1660.77cm-1. This was lowered in the complex by ca -1.93cm<sup>-1</sup>. The band due to NH vibration appeared in the ligand at 3199.05 and 3025.45cm-1 this was lowered in the ligand by ca -17.39. The shift in the absorption band is an indication that the ligand coordinated to the metal via these sites [9]. There is a band around 3400 which may be due to the water of hydration. The stretching vibration of the sulphato group appeared as a broad singlet with weak shoulder around 1100 cm<sup>-1</sup> in the complexes of ABH and BAH, while in the FUR complex it splits into a doublet form. The splitting is an indication of the involvement of the sulphato group in coordination. The bands due to M-N and M-O were not observed as these appear below the working range of the machine used for this analysis 4000-500cm<sup>-1</sup>



Plate 1: image of copper sulphate at 2um



Plate 2: image of [Cu(ABH)]SO<sub>4</sub> at 2um



Plate 3: image [Cu(fur)]SO<sub>4</sub> at 2um

#### Table 1. Analytical data of complexes

Compounds	Formula	Formula weight	% metal comp	% Anion	%C	%H	%N	Colour	Form
[Cu(L)]SO <sub>4</sub>	$[Cu(C_6H_6O_2N_2)]SO_4$	297.6716	22.0(21.3)	31.50(32.25)	24.2	2.03	9.41	Dark green	Crystal powder
[Cu(ABH)]SO <sub>4</sub>	$[Cu(C_{10}H_{11}N_2O)_2SO_4$	510.015	12.46(12.88)	19.97(18.83)	47.08	4.34	10.98	Blue	Crystalline
[Cu(BAH)]SO <sub>4</sub>	$[Cu(C_7H_9N_2O)_2SO_4, H_2O]$	505.0287	12.56(12.61)	19.75(18.98)	47.56	4.78	11.09	Blue	Crystalline

Values in the brackets are calculated for metal ion and sulphate; C, H, N values are calculated.

Table 2: Electronic Spectra data; Conductivity/Decomposition temp

Sample	Amax of absorption $(cm^{-1})$	stereochemistry	Conductivity µ/siemens	Decomposition temp oC
[Cu(L)]SO <sub>4</sub>	13, 308.5	Distorted Octahedral	0.361	200-212
[Cu(ABH)]SO <sub>4</sub>	11,848.0	Distorted Octahedral	0.351	235-248
[Cu(BAH)]SO <sub>4</sub>	11,458.0	Distorted Octahedral	0.353	215-225
CuSO4	11,500.0	,,		

Compounds	υNH,	υCO	υCN	ΔυCΟ	ΔυCN	Anion
Furfural urea	3323	1672.03	1532.87	-	-	-
[Cu(L)]SO <sub>4</sub>	3560.35, 3486.06, 3003.46	1645.51	-	-26.52	-	1105.25, 986.30
ABH	3218.34; 3024.48	1632.80	1546.96	-	-	-
[Cu(ABH)]SO <sub>4</sub>	3404.47, 3057.27	1654.98	1546.00	+22.18	-0.96	1120.69; 1050.28
BAH	3199.05	1660.77		-1.93		-
[Cu(BAH)SO <sub>4</sub>	3181.69	1658.84				1117.79; 1051.24

#### Table 3: Relevant Infra Red Spectra Data

#### Table 4: Solubility study of complexes and ligand

Sample	H <sub>2</sub> O	Hex	DMSO	ACN	EtOH	MeOH
$[Cu(L)]SO_4$	INS	INS	S	INS	PS	PS
Furancarbamide	S on heating at 100oC	INS	S	INS	PS	PS
[Cu(ABH)]SO <sub>4</sub>	S on heating	INS		INS	INS	INS
ABH	INS	INS	S	INS	S	S
BAH	INS	INS	S	INS	S	S
[Cu(BAH)SO <sub>4</sub>	S on heating	INS	S	INS	INS	INS

### **Electronic spectra**

The electronic spectra of  $[Cu(ABH)_2]SO_4$  showed a maximum absorption band at 11,848cm<sup>-1</sup>,  $[Cu(BAH)_2]SO_4$  showed at 11,458cm<sup>-1</sup>, while  $[Cu(FUR)]SO_4$  showed its band at 13,390.5cm<sup>-1</sup> in DMSO. This is assigned a transition due to d- d. The electronic spectra of Cu (II) compounds are not easily interpreted because of its low symmetry. Virtually all the complexes of copper (II) are either blue or green in colour, but there are exceptions caused by strong ultraviolet band-charge-transfer band tailing off into the blue end of the visible spectrum which cause the substance to appear red or brown [6]. The complexes have the characteristic blue and green colour associated to with copper salts and is assigned a distorted octahedral shape. In hexacoordinated copper (II) complexes, tetragonal distortion from the octahedral symmetry due to the Jahn–Teller distortion is very common. The ligand ABH provided the carboxyl oxygen and the azomethine nitrogen as the coordinating site and formed a bidentate chelate upon complexation with the metal ion the complex having a distorted octahedral geometry. In ethanolic media, reaction of one mole of copper sulphate and 2 mole of ABH and BAH afford the complex a general formula CuL<sub>2</sub>. The electronic spectra feature is comparable with other Schiff base complexes of copper (II) [7].

The conductivity values (Table 2) of the complexes indicate that all the compounds are non electrolytes. The solubility test result showed that the complexes are insoluble in water (except [Cu(ABH)]SO<sub>4</sub>) and other organic solvents (Table 4). They melted or decomposed in the range 200-248°C indicating a possible polymeric nature of the complexes.

#### Scanning electron microscope (SEM) images

The SEM images (Plate 1-3) of the complexes as compared to the copper sulphate showed that the surfaces of the crystals formed by the complexes are different from the copper salt. This is an indication that the ligand changed the surface property of the copper salt. Although the complex of ABH gave a complex with the same colour and stereochemistry with the copper salt but the surface of the compound showed a different morphology compared to the starting salt.

Suggested names for complexes:

[Cu(FUR)]SO<sub>4 =</sub> Furancarbamide copper II sulphate;

 $[Cu(ABH)_2]SO_4 =$  diacetonebenzoic acid hydrazone copper II sulphate;

[Cu(BAH)<sub>2</sub>]SO<sub>4</sub> .H<sub>2</sub>O =dibenzoic acid hydrazide copper II sulphate mono hydrate

### CONCLUSION

The stereochemistry of these complexes are different from the complexes of copper formed from ligands other moiety. Work is on going to determine the characteristics of the ligands with other transition metals. SEM micrograph images of complexes formed compared to copper sulphate salt for ABH and FUR.

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