

## Synthesis and characterisation of Cu(II) complexes with hetero donor atoms

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(Received: April 12, 2008; Accepted: June 04, 2008)

### ABSTRACT

The present paper deals with the study of synthesis and characterization of Cu(II) complexes with thiazole derivatives, structures were supported by electronic spectra and magnetic susceptibility etc.

**Key words:** Copper complexes, Schiff bases, thiazole derivatives.

### INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and their complexing ability containing different donor atoms is widely reported<sup>1-3</sup>. The chemistry of transition metal complexes containing heterocyclic donor continues to be on interest on account of their biological importance<sup>4-6</sup>. The present study describes the synthetic and structural studies of Schiff bases derived from aldehydes and different amines.

### MATERIAL AND METHODS

All the chemicals and solvents used were of AR-grade. The ligands were synthesized by a general method reported in the literature<sup>7-12</sup>. The physical measurements and analytical methods were the same as those described in literature.

#### Preparation of the compounds

2-(β-Hydroxyl acetyl naphthalimine) thiazole (C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>SO) o-(β-Hydroxyl-1-acetyl naphthalene) benzene sulphonic acid; (C<sub>18</sub>H<sub>15</sub>N<sub>5</sub>O<sub>4</sub>);

2-hydroxy acetyl naphthalene-propnae 1:2-diamine (C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O) o-Tolyl furfural imine (C<sub>12</sub>H<sub>11</sub>NO); 3-propyl-4-amino-5- mercapto-2<sup>l</sup>-hydroxy acetyl naphthylidene (C<sub>17</sub>H<sub>18</sub>N<sub>4</sub>OS). The above compounds were prepared by the condensation of required chemicals, in stoichiometric ratio. (â-Hydroxy-â-acetyl naphthalene; 2-amino thiazole; o-aminobenzene sulphonic acid; propane 1:2-diamine; furfural and o-toluidine. 3-propyl-4-amino-5-mercapto-5-triazole; 1-acetyl-2- hydroxy naphthalene. Characteristic data of the compound is given in table 1.

#### Preparation and isolation of the complexes

##### Bis [2-(β-Hydroxyl Naphthelimine) Thiazole Cu(II) Complex: [Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>]

Ethanolic solution of (95%) of cupric chloride dehydrate (0.04 mole) was mixed with (0.04 mole) ligand solution in ethanol in stoichiometric ratio (1:2) (metal:ligand), light green colour was developed immediately. Now pyridine was added and refluxed on water bath at 60-70°C for two hours and concentrated under vacuum, green crystals formed, were filtered washed with water and dried

under vacuum. The analytical data are given in table 2. Like wise complexes of other ligands with copper salts were isolated.

## RESULTS AND DISCUSSION

### Magnetic susceptibility measurement of copper complexes

$[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{SO})_2]$ ,  $[\text{Cu}(\text{C}_{18}\text{H}_{14}\text{NSO}_4)_2]$   
 $\text{H}_2\text{O}$ ,  $[\text{Cu}(\text{C}_{15}\text{H}_{17}\text{ON}_2)\text{Cl}]\text{H}_2\text{O}$ ,  $[\text{Cu}(\text{C}_{12}\text{H}_{11}\text{NO})\text{Cl}_2]$ ,  
 $[\text{Cu}(\text{C}_{14}\text{H}_{13}\text{NSO})\text{H}_2\text{O}]$

The magnetic data show that all the complexes are normal paramagnetic with  $\mu_{\text{eff}}$  values lying between 1.65-2.15 B.M. These values are fairly in the range observed for Cu(II) complexes containing spin free Cu(II)<sup>(13-15)</sup> ion having planar stereochemistry.

However, this cannot exclude the polymeric nature of the complexes because the polymeric complexes with normal magnetic moments are known in the literature<sup>16-19</sup>. Since the complexes are soluble in common solvents hence the present complexes cannot be polymeric in nature.

In  $[\text{Cu}(\text{C}_{12}\text{H}_{11}\text{NO})\text{Cl}_2]$  complex the magnetic moment (2.15 B.M.) value is slightly in excess over the "spin only" value and this may be due to spin orbit coupling<sup>20</sup>. These results are in agreement with the structural information as reported earlier by Backer *et al.*<sup>21</sup>.

### Electronic spectral studies

#### $[\text{Cu}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{SO})_2]$

The above complex show absorption bands around 760 nm to 330 nm which could be due to the transitions  ${}^2E_g \leftarrow {}^2B_{1g}$  ( $\nu_1$ );  ${}^2B_{2g} \leftarrow {}^2B_{1g}$  ( $\nu_2$ );  ${}^2A_{1g} \leftarrow {}^2B_{1g}$  ( $\nu_3$ ) respectively on the basis of a square planar structure of the copper chelate<sup>22</sup>. The third band at 400 nm could be an intraligand band present in the ligand at 460 nm possibly  $\pi$ - $\pi^*$  transitions.

#### $[\text{Cu}(\text{C}_{18}\text{H}_{14}\text{NSO}_4)_2]\cdot\text{H}_2\text{O}$

Electronic spectral measurements provide the most convincing proof of metal ion geometry. In some cases both the solid state and solution spectra are essential. If the spectra are same, this indicates no change in coordination geometry due to solvent interactions.

Table 1: Chemical analysis of ligands

S. No.	Ligands	Colour	Mpt.	% Analytical Data Found (Calculated)			
				C	H	N	S
1.	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{SO}$	Black	116°C	66.75 (67.16)	4.36 (4.47)	9.88 (10.44)	10.98 (11.94)
2.	$\text{C}_{18}\text{H}_{15}\text{NSO}_4$	Grey brown	225°C	63.20 (63.34)	4.33 (4.39)	4.06 (4.10)	9.35 (9.38)
3.	$\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}$	Deep Reddish brown	87°C	74.10 (74.38)	7.35 (7.43)	10.98 (11.57)	-
4.	$\text{C}_{12}\text{H}_{11}\text{NO}$	Bright black	85°C	77.68 (77.83)	5.86 (5.95)	7.42 (7.56)	8.57 (8.65)
5.	$\text{C}_{17}\text{H}_{18}\text{N}_4\text{OS}$	Dark brown	132°C	66.02 (62.57)	5.12 (5.52)	17.96 (17.17)	10.02 (9.81)

1. 2-( $\beta$ -Hydroxyl acetyl Naphthalimine) Thiazole
2. 0-( $\beta$ -Hydroxyl-1-acetyl naphalene) Benzene sulphonic acid.
3. 2-Hydroxy acetyl naphthalene propane 1:2-diamine
4. 0-Tolyl Furfuralimine
5. 3-Propyl-4-amino-5-mercapto-2hydroxy acetyl naphthylidene

The spectrum of copper chelate shows a low energy band at  $13180\text{ cm}^{-1}$  which has been described as a distorted square<sup>(23-24)</sup> pyramid. Since trigonal bipyramidal copper(II) chelate characteristically shows two bands at  $10400\text{ (}\epsilon\sim 49\text{)}$  and  $13300\text{ cm}^{-1}\text{ (}\epsilon\sim 209\text{)}$  the square pyramidal structure for the above complex seems most probably. Elemental analysis data for the copper(II) complex indicates the presence of one anion and one Schiff base per metal ion which show that the Schiff base coordinated as uninegative ligand.

**[Cu(C<sub>18</sub>H<sub>14</sub>NSO<sub>4</sub>)], [Cu(C<sub>12</sub>H<sub>11</sub>NO)Cl<sub>2</sub>] & [Cu(C<sub>14</sub>H<sub>13</sub>NSO)H<sub>2</sub>O]**

The electronic spectra of the complexes are recorded in the region  $10000\text{--}38000\text{ cm}^{-1}$ . The spectra in this region are expected to contain the ligand field transitions and to give some indication of the stereochemistry about the metal atom<sup>25-26</sup>. The most noteworthy feature of spectra of the complexes are the absence of any significant dependence of the band positions upon the bulkiness of the -R group on the nitrogen. This indicates that any steric strain set up by -R is taken up largely by the organic part of the molecule, while the stereochemistry about the metal is not greatly affected. However, there is difference in the

band spectra largely due to the changes in the ligand fields when the ligands are changed from those having the donor atoms, O, N, S to those having N, O. These results are best explained if the copper atoms are essentially planar, in agreement with the conclusions drawn by the magnetic data.

**Infrared spectra of [Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>SO)<sub>2</sub>], [Cu(C<sub>18</sub>H<sub>14</sub>NSO<sub>4</sub>)<sub>2</sub>], [Cu(C<sub>15</sub>H<sub>17</sub>ON<sub>2</sub>)Cl]H<sub>2</sub>O and, [Cu(C<sub>12</sub>H<sub>11</sub>NO)Cl<sub>2</sub>] Complexes**

The infrared spectra of the ligands show bands at  $1318, 1190, 1170, 1110, 1130, 1080, 1040, 1000, 775$  and  $700\text{ cm}^{-1}$  assigned to the phenyl ring. There is practically no change in the position of these bands on adduct formation.

All the spectra show medium absorption at  $3050, 3010\text{ cm}^{-1}$  due to aromatic (C-H) stretching<sup>27</sup>. In the O-toluyfurfuralimine Cu(II) complex, there are two weak bands at  $2900, 2915\text{ cm}^{-1}$  due to asymmetric and symmetric stretching of the -CH<sub>3</sub> group. These bands continue in the Schiff base complexes.

New bands around  $1600\text{ cm}^{-1}$  appear in the Schiff bases due to the formation of -CH=N band<sup>28</sup>. The lowering in the CH=N frequency from

**Table 2: Chemical analysis of Cu(II) Complexes**

S. No.	Complexes	% Analytical Data Found (Calculated)					Cu
		C	H	N	S	Cl	
1.	[Cu(C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> SO) <sub>2</sub> ]	60.01 (60.25)	3.58 (3.68)	9.25 (9.37)	10.64 (10.71)	-	10.35 (10.62)
2.	[Cu(C <sub>18</sub> H <sub>14</sub> NSO <sub>4</sub> ) <sub>2</sub> ].H <sub>2</sub> O	57.96 (58.10)	3.72 (3.76)	3.74 (3.76)	8.48 (8.60)	-	8.36 (8.54)
3.	[Cu(C <sub>15</sub> H <sub>17</sub> N <sub>2</sub> O)Cl]H <sub>2</sub> O	50.06 (50.27)	5.24 (5.30)	7.64 (7.82)	-	9.80 (9.91)	17.64 (17.73)
4.	[Cu(C <sub>12</sub> H <sub>11</sub> NO)Cl <sub>2</sub> ]	44.84 (45.07)	3.36 (3.44)	4.25 (4.38)	-	22.45 (22.22)	18.89 (19.87)
5.	[Cu(C <sub>14</sub> H <sub>13</sub> NSO)H <sub>2</sub> O]	51.50 (51.77)	4.58 (4.62)	4.26 (4.31)	9.80 (9.86)	-	18.86 (19.56)

1. Bis[2-( $\beta$ -Hydroxyl Naphthelimine) Thiazole] Cu(II) complex
2. Bis[0-( $\beta$ -Hydroxyl-1-acetylnaphalene) Benzene sulphonic acid] Cu(II) Complex.
3. 2-Hydroxy acetyl naphthalene propane 1:2-diamine Cu(II) complex.
4. 0-Tolyl Furfuralimine Coppr(II) complex.
5. 3-Propyl-4-amino-5-mercapto-2'-hydroxy acetyl naphthylidene Cu(II) complex.

the free Schiff base is due to the coordination of -CH=N without<sup>27-28</sup> metal. The other bands in the region 1600 - 1300 cm<sup>-1</sup> are due to ring deformation modes.

All the Schiff except (C<sub>12</sub>H<sub>11</sub>NO) show a strong<sup>29</sup> and sharp band at 3500 ± 20 cm<sup>-1</sup> which may be assigned to the ν(OH). In all the Cu(II) complexes, this band disappears indicates that the proton of the -OH linkage gets linked to copper atom. Further in the complexes there is a shift to lower side in the frequency due to (C-O) stretching (of phenolic-OH). The absence of the n(OH) stretch in the infrared spectra of the complexes and the shift in ν(C-O) indicate the deprotonation of the -OH of the ligand and monobasic character of these ligands<sup>30-31</sup>.

In the region 1700-1400 the ligand (C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>SO) as well as the metal complexes [Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>SO)<sub>2</sub>] show five to six bands, except one which is highly intense and appears at ~1560 and ~1600 cm<sup>-1</sup> in the ligand and the metal complex respectively. The shifting of the band to higher frequency region indicates coordination through sulphur.

In [Cu(C<sub>18</sub>H<sub>14</sub>NSO<sub>4</sub>)<sub>2</sub>] complex the band at 1370 cm<sup>-1</sup> due to -SO<sub>3</sub>H disappeared suggesting deprotonation of the -OH of the SO<sub>2</sub>-OH group.

In the adduct [Cu(C<sub>12</sub>H<sub>11</sub>NO)Cl<sub>2</sub>] the frequency (C-O-C) at 1250 cm<sup>-1</sup> shifted to lower, frequency region 1220 cm<sup>-1</sup>, which indicate that -

**Table 3: Magnetic susceptibility measurement data**

S. No.	Complexes	Temp. °K	Data of Cu(II) Complexes		
			χ <sub>M</sub> ' x 10 <sup>-6</sup> C.G.S. Units	χ <sub>M</sub> x 10 <sup>-6</sup> C.G.S. Units	μ <sub>eff.</sub> B.M.
1.	[Cu(C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> SO) <sub>2</sub> ]	300	1280	1395	1.65
2.	[Cu(C <sub>18</sub> H <sub>14</sub> NSO <sub>4</sub> ) <sub>2</sub> ].H <sub>2</sub> O	300	1442	1635	1.80
3.	[Cu(C <sub>15</sub> H <sub>17</sub> N <sub>2</sub> O)Cl]H <sub>2</sub> O	300	1742	1995	2.00
4.	[Cu(C <sub>12</sub> H <sub>11</sub> NO)Cl <sub>2</sub> ]	300	1965	2170	2.15
5.	[Cu(C <sub>14</sub> H <sub>13</sub> NSO)H <sub>2</sub> O]	300	1810	2140	2.04

**Table 4: Electronic spectral data of Cu(II) complexes**

Complexes	Bands and Transition		
	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub> (λ <sub>1</sub> ) (nm)	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> (λ <sub>2</sub> ) (nm)	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> (λ <sub>3</sub> ) (nm)
[Cu(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> SO) <sub>2</sub> ]	310	585	790
[Cu(C <sub>18</sub> H <sub>14</sub> NSO <sub>4</sub> ) <sub>2</sub> ]	415	570	730
[Cu(C <sub>15</sub> H <sub>17</sub> ON <sub>2</sub> )Cl]H <sub>2</sub> O	445	610	770
[Cu(C <sub>12</sub> H <sub>11</sub> NO)Cl <sub>2</sub> ]	340	530	720
[Cu(C <sub>14</sub> H <sub>13</sub> NSO)H <sub>2</sub> O]	390	660	815

O-atom of (C-O-C) part of the reagent act as a donor site.

By determining the position and number of the reacting sites in the reagent it is concluded

that the adduct possess square planar geometries<sup>32-33</sup>.

**[Cu(C<sub>14</sub>H<sub>13</sub>NO)H<sub>2</sub>O]**

The spectra of the ligand show only one

broad band around 3320 which can be assigned to  $\nu_{\text{NH}}$ . This band is somewhat broader in the spectra of the complex which implies that -NH group is coordinated to the metal ion consequently leading to the lowering of  $\nu_{\text{NH}}$  on coordination. Similarly the  $\text{NH}_2$  bending vibrations [1625, (VS); 1580 (S)

$\text{cm}^{-1}$ ] and  $\nu(\text{C-N})$  vibrations 1340 W; 1320 (S), 1260  $\text{cm}^{-1}$  of the ligand go down in intensity and frequency in the complex. Hence it is concluded that coordination occurs at both the donor sites  $n(\text{NH})$  and  $\nu(\text{NH}_2)$ .<sup>(34,35)</sup>

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