

# Study of Binuclear Copper(II) Complexes Derived from Tetra Dentate Mannich Base Complexes

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**Abstract**—Homodinuclear copper(II) complexes have been gaining importance of late owing to their diverse applications in the studies of metalloenzymes and homogeneous catalysis. These studies have revealed the existence of characteristic antiferromagnetic exchange interaction between the two copper(II) centres leading to a lowering in the magnetic moments of these complexes. Sinn and Harris have prepared and characterized various bi- and tri-nuclear copper(II) complexes. Also reported the synthesis and magnetic properties of binuclear complexes of the type  $[Cu(TSB)-Cu(A-A)](ClO_4)_2$ , where TSB=various symmetrical and unsymmetrical tetradentate Schiff bases derived from salicylaldehyde and 2-hydroxyacetophenone, and A-A=tertiary diamines. The present work reports the preparation of complexes of the type  $[Cu(TMB)]$  alongwith synthesis of binuclear complexes  $[Cu(TMB)CuX_2]$  (type I) and  $[Cu(TMB)Cu(A-A)](ClO_4)_2$  (type II), where  $X=Cl^-$  or  $ClO_4^-$ , A-A bidentate ligands such as 2,2'-bipyridyl ( $A^1$ ), 1,10-phenanthroline ( $A^2$ ) and 2-(2'-pyridyl) benzimidazole ( $A^3$ ) and TMB=tetradentate mannich bases obtained by the reduction of the corresponding tetradentate Schiff bases.

## 1. Introduction

Sinn and Harris<sup>(1)</sup> have prepared and characterized various bi- and tri-nuclear copper(II) complexes. Also reported the synthesis and magnetic properties of binuclear complexes of the type  $[Cu(TSB)-Cu(A-A)](ClO_4)_2$ , where TSB=various symmetrical and unsymmetrical tetradentate Schiff bases derived from salicylaldehyde and 2-hydroxyacetophenone, and A-A=tertiary diamines<sup>(1-4)</sup>. The present work reports the preparation of complexes of the type  $[Cu(TMB)]$  alongwith synthesis of binuclear complexes  $[Cu(TMB)CuX_2]$  (type I) and  $[Cu(TMB)Cu(A-A)](ClO_4)_2$  (type II), where  $X=Cl^-$  or  $ClO_4^-$ , A-A bidentate ligands such as 2,2'-bipyridyl ( $A^1$ ), 1,10-phenanthroline ( $A^2$ ) and 2-(2'-pyridyl) benzimidazole ( $A^3$ ) and TMB=tetradentate mannich bases obtained by the reduction of the corresponding tetradentate Schiff bases. Mannich bases used are; TMB<sup>1</sup>=N,N'-ethylene-bis(2-hydroxy naphthylamine); TMB<sup>2</sup>=N,N'-ethylene-bis(2-hydroxy- $\alpha$ -methyl naphthylamine); TMB<sup>3</sup>=N,N'-propyl-ene-bis(2-hydroxy naphthylamine);

TMB<sup>4</sup>=N,N'-propylene-bis(2-hydroxy- $\alpha$ -methyl naphthylamine).

## 2. Experimental Procedure

### 2.1 IR Spectra:

IR spectra were obtained using KBr pellets on a Perkin-Elmer 783 spectrophotometer;

### 2.2 NMR Spectra:

NMR spectra were recorded in  $CDCl_3$  and  $DMSO-d_6$  on a Bruker DMX-300 spectrometer.

### 2.3 X-band ESR Spectra:

ESR spectra of the complexes were recorded at 300 and 77K.

### 2.4 UV-VIS spectra:

The UV-Vis spectra were recorded on a Shimadzu UV-1601 spectrophotometer using DMF as a solvent.

### 2.5 Magnetic susceptibility:

It was measured by Guoy balance using copper sulphate as calibrant.

## 3. Material used:

Reagents such as  $Cu(ClO_4)_2 \cdot 6H_2O$ , 2-(2'-pyridyl)benzimidazole, N,N'-ethylene-bis-1-hydroxy naphthaldimine (TSB) and N,N'-ethylene-bis-(2-hydroxynaphthylamine)<sup>(5)</sup> (TMB) were prepared.

$CuCl_2 \cdot 2H_2O$ , chloroform and ethanol were purchased from Merck and B.D.H. (India) chemicals.

## 4. Solvent used:

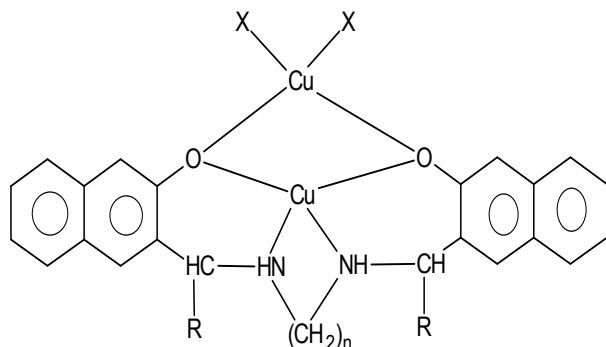
Anhydrous grade ethanol,  $CDCl_3$  and  $DMSO$  were purified according to standard procedures.

## 5. Synthesis :

### 5.1 Synthesis of mononuclear complexes:

To a warm solution of  $CuCl_2 \cdot 2H_2O$  in ethanol (1 mol) was added a solution of tetradentate mannich base (TMB) in ethanol (1 mol) with constant stirring pH of the solution was

raised to 5.5 by the addition of dilute solution of ammonia<sup>(6)</sup>. The separated solid was filtered, washed thoroughly with ethanol, recrystallized from absolute ethanol and finally dried. (Fig. 1)

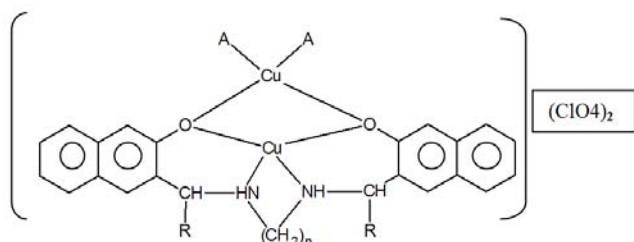


R= H or CH<sub>3</sub>, X= Cl<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>, n=2 or 3

Fig.1

### 5.2. Synthesis of binuclear complexes:

To a solution of [Cu(TMB)] in chloroform (3 mmol) was added a solution of CuCl<sub>2</sub>.2H<sub>2</sub>O or Cu(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O or [Cu(A-A)(ClO<sub>4</sub>)<sub>2</sub>] in absolute ethanol (3mmol). Reaction mixture was refluxed with constant stirring for about 2–3 hr. Resulting solid was filtered, washed thoroughly with a mixture of chloroform and ethanol (1:1), and dried in vacuum.



R=H or CH<sub>3</sub>, A-A= A<sup>1</sup> A<sup>2</sup> or A<sup>3</sup>, n=2 or 3

Fig. 2

## 6. Results and Discussion:

Some binuclear complexes were highly soluble in chloroform–ethanol mixture and, therefore, were isolated by ether extraction and recrystallised from absolute ethanol. The elemental analyses and characterization data of the complexes are presented in Table-1 and Table-2. Tetra dentate mannich base complexes of Cu(II)<sup>(7)</sup> showed single TLC spots and their elemental analyses corresponded to the expected formulae.

Elemental analyses of the binuclear complexes corresponded to the expected formulae.

## 7. Characterization:

### 7.1 NMR–Spectral Studies:

TLC of mannich bases shows single spots confirming purity of the compounds. The elemental analysis of TMB corresponds to the expected formula. In the IR spectra of TMB, there is not band around 1600 cm<sup>-1</sup> corresponding to

vC=N group, confirming complete reduction of >C=N group. A new band due to vN–H appears at 3310 cm<sup>-1</sup> in TMB. NMR spectrum of N,N'-ethylene bis(2–hydroxy naphthylamine) (TSB) shows signals at δ=3.9 and δ=8.3 ppm. Corresponding to ethylene protons and R–C(H)=N– proton, respectively.

### 7.2 Infrared Spectral Studies:

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The IR spectra of the ligand showed a broad band in the region 3200–3600 cm<sup>-1</sup> assignable to intramolecular hydrogen bonded –OH groups. The appearance of this peak in all the spectra of the complexes indicates that the –OH group is free from complexation. The spectrum of the ligand shows two different –C=N bands in the region 1590–1550 cm<sup>-1</sup>, which is shifted to lower frequencies in the spectra of all the complexes (1570–1520 cm<sup>-1</sup>) indicating the involvement of –C=N nitrogen in coordination to the metal ion.<sup>(8)</sup> Accordingly, the ligand acts as a tetradentate chelating agent, bonded to the metal ion via the four nitrogen (–C=N) atoms of the Schiff base.

### 7.3 Magnetic moment studies:

All [Cu(TMB)] complexes are paramagnetic and have magnetic moments corresponding to one unpaired electron. Magnetic moment values of the binuclear complexes at room temperature are lower than the expected spin–only value for one unpaired electron on each copper(II) ion. This is due to the antiferromagnetic interaction between the two copper(II) ions<sup>(9)</sup>. In the complexes involving TMB, lowering in the magnetic moment is slightly more than that in the case of corresponding binuclear complexes [Cu(TSB)CuX<sub>2</sub>] and [Cu(TSB)Cu(A–A)] (ClO<sub>4</sub>)<sub>2</sub>, reported earlier<sup>(10,11)</sup>.

### 7.4 Electronic spectral studies:

In the electronic spectrum of mononuclear complex, [Cu(TMB<sup>1</sup>)], there is a broad band present at 14290 cm<sup>-1</sup>. In the binuclear complex, [Cu(TMB<sup>1</sup>)CuCl<sub>2</sub>], two separate bands arise at 14810 cm<sup>-1</sup> and 10420 cm<sup>-1</sup> for the two different copper(II) centres. Binuclear complex [Cu(TMB<sup>1</sup>)Cu(A<sup>1</sup>)] (ClO<sub>4</sub>)<sub>2</sub> also shows two bands at 17540 cm<sup>-1</sup> and 12500 cm<sup>-1</sup>. The band due to >[Cu(A–A)]<sup>2+</sup> part is observed at higher energy (12500 cm<sup>-1</sup>), than that due to >CuCl<sub>2</sub> part. This is because the diamine creates a stronger field than two chlorides.<sup>(12–14)</sup>

Table 1: Analytical, Electronic Spectral and Magnetic Data for TMB and Its [Cu(TMB)] Complexes

S. No.	Compound	Found (Calc.) %				μ <sub>eff</sub> * (BM)
		Cu	N	C	H	
1.	TMB <sup>1</sup>	–	7.40 (7.52)	77.30 (77.41)	6.35 (6.45)	–
2.	TMB <sup>2</sup> 1/2H <sub>2</sub> O	–	6.70 (6.84)	76.14 (76.28)	7.20 (7.33)	–
3.	TMB <sup>3</sup>	–	7.15 (7.25)	77.60 (77.72)	6.62 (6.73)	–

4.	TMB <sup>4</sup> 1/2H <sub>2</sub> O	–	6.48 (6.61)	76.45 (76.59)	7.43 (7.56)	–
5.	[Cu(TMB <sup>1</sup> )]#	14.50 (14.65)	6.33 (6.45)	66.32 (66.42)	4.92 (5.07)	1.91
6.	[Cu(TMB <sup>2</sup> )]	13.62 (13.76)	6.05 (6.26)	67.58 (67.59)	5.70 (5.63)	1.82
7.	[Cu(TMB <sup>3</sup> )]	14.02 (14.19)	6.13 (6.25)	66.88 (69.03)	5.20 (5.36)	1.93
8.	[Cu(TMB <sup>4</sup> )]	13.22 (13.36)	5.74 (5.88)	68.0 (68.13)	5.80 (5.88)	1.78

\* $\mu_{\text{eff}}$ . Values per Cu(II) ion: 1 B.M. =  $0.927 \times 10^{-23} \text{ Am}^2$ .

#  $\lambda_{\text{max}}$  at 23260 and 14290  $\text{cm}^{-1}$

TMB<sup>1</sup> = (C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>); TMB<sup>2</sup> = (C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>); TMB<sup>3</sup> = (C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>); TMB<sup>4</sup> = (C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>).

**Table 2: Analytical and Magnetic data for binuclear complexes.**

S. No.	Compound	Found (Calcd) %				$\mu_{\text{eff}}^*$ (B.M.)
		Cu	N	C	H	
1.	[Cu(TMB <sup>1</sup> )CuCl <sub>2</sub> ] Bluish black	22.25 (22.37)	4.80 (4.92)	50.60 (50.69)	3.60 (3.87)	0.78
2.	[Cu(TMB <sup>2</sup> )CuCl <sub>2</sub> ] Bluish black	21.25 (21.31)	4.60 (4.69)	52.22 (52.34)	4.24 (4.36)	1.01
3.	[Cu(TMB <sup>3</sup> )CuCl <sub>2</sub> ] Olive green	21.70 (21.83)	4.70 (4.81)	51.43 (51.53)	4.10 (4.12)	0.84
4.	[Cu(TMB <sup>4</sup> )CuCl <sub>2</sub> ] Olive green	20.73 (20.83)	4.45 (4.58)	53.0 (53.10)	4.46 (4.58)	1.19
5.	[Cu(TMB <sup>1</sup> )Cu(ClO <sub>4</sub> ) <sub>2</sub> ] Brown	18.15 (18.25)	3.90 (4.02)	41.29 (41.37)	3.07 (3.16)	0.86
6.	[Cu(TMB <sup>2</sup> )Cu(ClO <sub>4</sub> ) <sub>2</sub> ] Brown	17.46 (17.55)	3.72 (3.86)	42.92 (43.08)	3.48 (3.59)	0.84
7.	[Cu(TMB <sup>3</sup> )Cu(ClO <sub>4</sub> ) <sub>2</sub> ] Olive green	17.76 (17.89)	3.83 (3.94)	42.12 (42.24)	3.29 (3.37)	0.81
8.	[Cu(TMB <sup>4</sup> )Cu(ClO <sub>4</sub> ) <sub>2</sub> ] Olive green	17.12 (17.21)	3.65 (3.79)	43.76 (43.89)	3.70 (3.79)	0.89

\* $\mu_{\text{eff}}$ . Values per Cu(II) ion; 1 B.M. =  $0.927 \times 10^{-23} \text{ Am}^2$

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