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**COMPLEXATION OF 5,5,7,12,12,14-HEXAMETHYL-1,4,8,11-TETRAAZACYCLODECA-7,14-DIENIUM BROMIDE WITH COPPER ACETATE IN METHANOL AND AQUEOUS SOLUTIONS**

**Pengkompleksan 5,5,7,12,12,14-heksametil-1,4,8,11-tetraazasiklotetradeka-7,14-dienium bromida dengan kuprum asetat dalam metanol dan larutan berair**

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**ABSTRACT**

5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclodeca-7,14-dienium bromide disolvate ((Me<sub>6</sub>N<sub>4</sub>H<sub>4</sub>)Br<sub>2</sub>.2H<sub>2</sub>O) is a 14-membered deprotonated tetraaza macrocyclic salt. Its neutral analogues and their complexes were prepared by templation method under refluxed condition since it was discovered by Curtis in 1961. However, the present diprotonated tetraaza salts react with many metallic salts in both methanolic and aqueous solutions. The complexation involved deprotonation of the diagonally opposite protonated amines and the type of metal salt and solvents also play an important role in the final complex formation. The complexation of (Me<sub>6</sub>N<sub>4</sub>H<sub>4</sub>)Br<sub>2</sub>.2H<sub>2</sub>O with copper acetate in methanol and aqueous solutions gave the expected complex of [Cu((Me<sub>6</sub>N<sub>4</sub>H<sub>2</sub>)Br)Br.2H<sub>2</sub>O]. Pseudo-first order condition for the complexation reaction in water was established.

**Keywords:** Tetraaza, complexes, protonated, complexation, kinetics

**INTRODUCTION**

Several metal complexes with 5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclodeca-7,14-diene (Me<sub>6</sub>N<sub>4</sub>H<sub>2</sub>) as ligand have been prepared by templation method after its unexpected discovery during the recrystallization of bis(ethylenediamine) nickel by Curtis in 1961 (Curtis and House, 1961). The stability and dissociation of the Curtis tetraza-metal complexes in basic solution were also studied and reported (Kasprzyk and Wilkins, 1982; Lu et al., 1999). However, no reaction study between the ligand and metal in solution have been reported since the macrocyclic ligand was formed during the reaction of metal-ethylenediamine complex with acetone. The unexpected discovery of the same ligand but in protonated form in our laboratory (Ismail, 2012) (Me<sub>6</sub>N<sub>4</sub>H<sub>4</sub>)Br<sub>2</sub>.2H<sub>2</sub>O enable us to study the complexation from both synthesis and solution reaction as well. The complexation of the ligand with metal is influenced by the type of metal salts used and the solvent (Podberezskaya et al.,

1986; Yamin et al., 2012). In the present paper we describe the complexation of (Me<sub>6</sub>N<sub>4</sub>H<sub>4</sub>)Br<sub>2</sub>.2H<sub>2</sub>O with copper acetate in methanol and water. For the first time the reaction in aqueous solution was monitored and the conditions for pseudo-first order rate law was established.

**METHODOLOGY**

**Chemical**

All chemicals and solvents were reagent grade purchased from Merck and Aldrich and used as received. The solvents were distilled before used.

**Instrumentation**

Fison CHNS analyzer were model EA 110 was used for microelemental analyses. Infrared spectra (as KBr pellets) were recorded on a Perkin Elmer 400 FT-IR/FT-NIR. Electronic spectra in the 200-800 nm region were recorded on a 1800 Shimadzu spectrophotometer.

The purple crystal having dimension of 0.500 x 0.30 x 0.08 mm was chosen for structure determination. The X-ray data measurements was performed using Bruker D8 Quest diffractometer with graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 301(2) K. A total of 162923 reflections were collected in the range of  $2.791 \leq \theta \leq 25.496^\circ$  ( $-21 \leq h \leq 21$ ,  $-18 \leq k \leq 18$ ,  $-20 \leq l \leq 20$ ) by using an  $\omega$ -2 $\theta$  scan mode, 8205 were unique with  $R_{\text{int}} = 0.1083$ .  $I > 2\sigma(I)$  were used in the succeeding refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were located at calculated positions. The final full-matrix refinement gave  $R_1 = 0.0583$ ,  $wR = 0.1247$ . crystal system monoclinic, P 21/c,  $a=17.860(10)$ ,  $b= 15.4973(11)$ ,  $c=17.2143(14)\text{\AA}$ ,  $\beta=112.066 (10)^\circ$ ,  $V= 4412.8(6)\text{\AA}^3$  and  $Z=8$ .

### Preparation procedures

#### Preparation of ligand

The macrocyclic ligand  $(\text{Me}_6\text{N}_4\text{H}_4)\cdot\text{Br}_2\cdot 2\text{H}_2\text{O}$  was synthesised by following the method described previously<sup>4,7</sup>. 0.01 mol of the ammonium salt and 0.01 mol of ethylenediamine in acetone at 80 °C under constant stirring for 2 h. The solution was then filtered and left overnight at room temperature for crystal growth. Yield: 65%; m.p. 113.4–115.3°C. Anal. Calcd for  $\text{C}_{16}\text{H}_{38}\text{N}_4\text{O}_2\text{Br}_2$  (FW 478.32): C, 40.2%; H, 7.9%; N, 11.1%. Found: C, 38.9%; H, 7.5%; N, 11.6%. NMR:  $^1\text{H}$ ,  $\delta_{\text{H}} 1.49$  (6H, s,  $\text{CH}_3$ ),  $\delta_{\text{H}} 2.06$  (3H, s,  $\text{CH}_3$ ),  $\delta_{\text{H}} 2.80$  (2H, s,  $\text{CH}_2$ ),  $\delta_{\text{H}} 3.42$  (2H, t,  $\text{CH}_2$ ),  $\delta_{\text{H}} 3.69$  (2H, t,  $\text{CH}_2$ ), and  $\delta_{\text{H}} 4.91$  (2H, t,  $\text{NH}_2^+$ ).

#### Preparation of the copper-tetraaza complexes

The complex was synthesized by stirring a 1:1 mixture of copper acetate and ligand in methanol and also separately in water. The solution was then filtered and left at room temperature for evaporation. Yield: 75%; , purple, m.p. 207.4 – 208.3°C. Anal. Calcd for  $\text{C}_{16}\text{H}_{38}\text{N}_4\text{O}_2\text{Br}_2$  (FW 537.83): C, 36.3%; H, 4.7%; N, 10.6%. Found: C, 36.8%; H, 4.4%; N, 9.9%.

#### Spectral course of the reaction

The aqueous solution of the reaction mixture was prepared in 10 ml volumetric flask and an adequate amount was quickly transferred into the 1x1 cm spectrophotometric cell. The

UV-VIS spectrum was recorded at 3 minutes interval until reaction reached completion.

#### Kinetic measurements

Stock solutions of  $(\text{Me}_6\text{N}_4\text{H}_4)\cdot\text{Br}_2\cdot 2\text{H}_2\text{O}$  and copper acetate in water were prepared in 25 ml volumetric flasks and kept in water bath at 28°C for one hour. The calculated amount of ligand and  $\text{Cu}(\text{OAc})_2$  were mixed in 10ml volumetric flask and the flask was filled with distilled water up to the mark. Adequate amount of the solution mixture was quickly transferred into the cell and placed in the thermostatic cell compartment. The kinetic was followed by measuring the absorbance at wavelength of 506 nm. The first order rate law was obtained by plotting  $\ln(A_\infty - A_t)$  against time.

### RESULTS AND DISCUSSION

The spectroscopic data of the ligand agreed very well with the expected structure. The unit cell is also similar to the previously reported (Podberezskaya et al. 1986) and the structural solution gave the structure as shown in Fig.1.



Figure 1. Molecular structure of  $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2\cdot 2\text{H}_2\text{O}$  drawn at 50% probability ellipsoids.

Addition of the ligand  $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2\cdot 2\text{H}_2\text{O}$  into copper acetate solution in methanol and aqueous solutions showed change in colour from blue to purple.

The infrared spectrum (Fig.2) showed stretching frequencies shift of the  $\nu(\text{N-H})$ ,  $\nu(\text{O-H})$ ,  $\nu(\text{C=N})$  and  $\nu(\text{C-N})$  of 3425, 2968, 1669 and  $1163\text{cm}^{-1}$  respectively, compare to those in the free ligand indicating coordination between the copper atom to the four nitrogen atoms of the tetraaza.

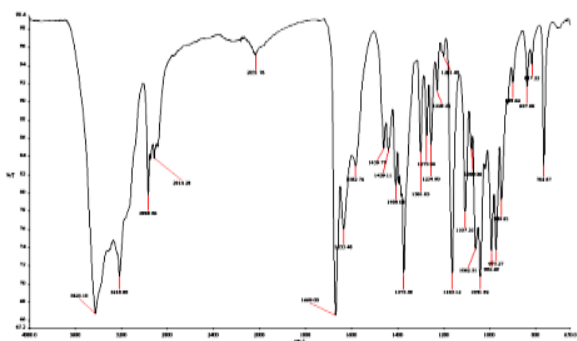


Figure 2. infrared spectrum 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-diene) copper(II) bromide dehydrate

The UV-VIS spectrum of the complex in water showed maximum absorbance at 506 nm compare to  $\text{Cu}(\text{OAc})_2$  of 772 nm. The X-ray study of both crystals obtained from methanol and aqueous solutions showed similar unit cells indicating of the same complex was formed from both solvents of different polarity. In fact the same structure (Fig.3) was reported by Shi & He<sup>8</sup> in 2011 by reacting  $\text{C}_{18}\text{H}_{32}\text{N}_4\cdot 2\text{HBr}\cdot 2\text{H}_2\text{O}$  and  $\text{CuSO}_4$  in methanol as solvent.

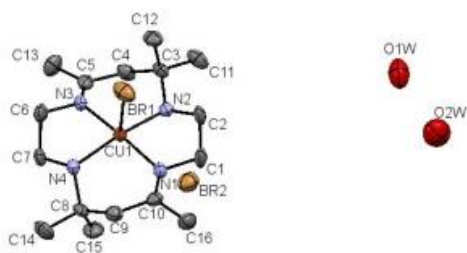


Figure 3. The molecular structure of  $[\text{Cu}(\text{Me}_6\text{N}_4\text{H}_2)\text{Br}]\text{Br}\cdot 2\text{H}_2\text{O}$  drawn at 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

It is clear that the complexation of copper to the tetraaza also involve the deprotonation of two amino protons. One of the two bromo anions coordinated to the central copper resulted in the formation of square pyramidal geometry. In  $[\text{C}_{16}\text{H}_{32}\text{CuN}_4]^{2+}2(\text{ClO}_4)^-$  the counter anion of the salt remains as anions with the complex having square planar geometry (Hasan et al., 2014). However, in a different condition, one of the perchlorate anion coordinated to copper (Bienko et al., 2008) which is analogous to the bromo system. Since most of the complexes were prepared by reflux in organic solvent it is not easy to study the kinetic of the complexation.

However, kinetic studies on the dissociation of the complexes in basic aqueous or mixed aqueous-alcohol solutions and isomerisation of the complexes have been extensively reported (Lee and Hung, 1998; Lu et al., 1981; Maimon et al., 2001). Therefore, to the best of our knowledge this is the first attempt to study the kinetic of complexation of  $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2\cdot 2\text{H}_2\text{O}$  with  $\text{Cu}(\text{OAc})_2$  in aqueous solution. Figure 4 shows the changes in the UV-VIS spectrum during the reaction in aqueous solution. The addition of the ligand into copper acetate solution caused a spontaneous change in the  $\lambda_{\text{max}}$  of copper at 772 nm to a lower value of 718nm and the appearance of new peak at about 506 nm which is similar to the peak of  $[\text{Cu}(\text{Me}_6\text{N}_4\text{H}_2)\text{Br}]\text{Br}\cdot 2\text{H}_2\text{O}$ . The absorbance of the peak at 718nm decreased with time but the peak at 506 nm increased till completion. There is an isosbestic point at 601 nm. The shifted  $\lambda_{\text{max}}$  values after the addition of ligand somewhat vary with the amount of the ligand.

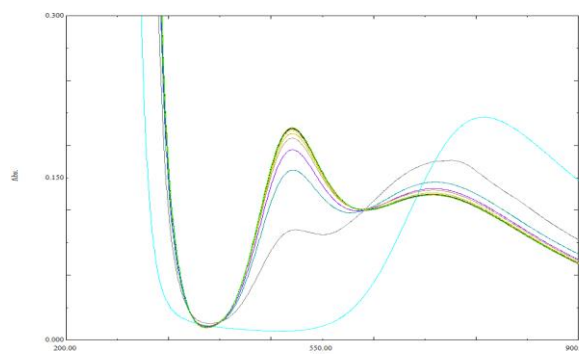
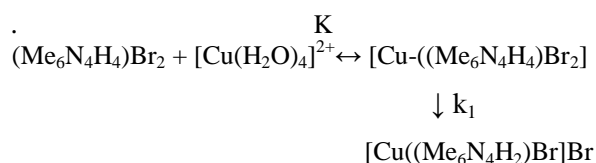


Figure 4. spectral course of the reaction between  $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2\cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{OAc})_2$  in aqueous solution recorded at every 3 minutes interval.  $[(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2\cdot 2\text{H}_2\text{O}]_0 = 0.01\text{M}$  and  $[\text{Cu}(\text{OAc})_2]_0 = 0.001\text{M}$ .

From the spectral course of the reaction we can propose the reaction scheme taking into account the speciation under acidic condition as shown below (Scheme 1).



Scheme 1. Reaction scheme for the complexation

In the scheme, K is a composite constant for the formation of the complex [Cu-ligand] and  $k_1$  is a composite rate constant. On the basis of the above scheme, a rate equation can be deduced as shown below;

If the initial equilibrium is established rapidly, then,

$$d[\text{complex}]/dt = k_1[\text{Cu-ligand}] = k_1K[\text{Cu(II)}][\text{ligand}]$$

where [Cu(II)] and [ligand] are the concentrations of free Cu(II) and ligand respectively, and

$$K = [\text{Cu(II)-ligand}] / [\text{Cu(II)}][\text{ligand}]$$

From the material balance,

$$\begin{aligned} [\text{Cu(II)}]_0 &= [\text{Cu(II)}] + [\text{Cu(II)-ligand}] \\ &= [\text{Cu(II)}](1+K[\text{ligand}]) \end{aligned}$$

Therefore,

$$d[\text{complex}]/dt = k_1K[\text{ligand}][\text{Cu(II)}]_0 / (1 + K[\text{ligand}])$$

where [Cu(II)]<sub>0</sub> is the stoichiometric concentration of Cu(OAc)<sub>2</sub>.

Under condition, [ligand]<sub>0</sub> >> [Cu(II)]<sub>0</sub>

$$\begin{aligned} d[\text{complex}]/dt &= k_1K[\text{ligand}]_0[\text{Cu(II)}]_0 / (1 + K[\text{ligand}]_0) \\ &\approx k_1[\text{Cu(II)}]_0 \text{ if } K[\text{ligand}]_0 \gg 1 \end{aligned}$$

First order plot under condition  $[(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2 \cdot 2\text{H}_2\text{O}]_0 \gg [\text{Cu}(\text{OAc})_2]_0$  showed good straight line up to more than two half lifes (Fig.5).

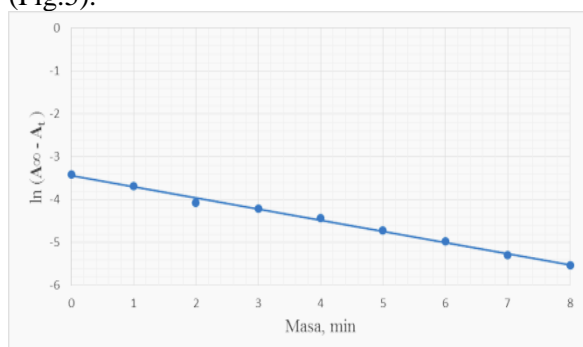


Figure 5. First order plot for the reaction of  $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{OAc})_2$  in aqueous solution.  $[(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2 \cdot 2\text{H}_2\text{O}]_0 = 0.01\text{M}$  and  $[\text{Cu}(\text{OAc})_2]_0 = 0.001\text{M}$ .

## CONCLUSION

Reaction of  $(\text{Me}_6\text{N}_4\text{H}_4)\text{Br}_2 \cdot 2\text{H}_2\text{O}$  with copper acetate in methanol and water gave the same complex of  $[\text{Cu}(\text{Me}_6\text{N}_4\text{H}_2)\text{Br}]\text{Br} \cdot 2\text{H}_2\text{O}$ .

Under excess concentration of the ligand the reaction follows first order rate law. .

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