

# Large Ring Tetraazamacrocyclic Complexes of Cu (II) Derived From 2,3-Pentanedione and Diaminoalkanes

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**ABSTRACT:** Cu (II) complexes of large ring (14 to 32-membered) tetraazamacrocycles are derived from 2,3-pentanedione and aliphatic diamines such as 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; 1,8-diaminooctane and 1,12-diaminododecane formed by template synthesis. The complexes have been characterized by elemental analysis, IR spectra, conductance measurements, and magnetic moments.

**KEYWORDS:** Macrocyclic complexes, Tetraazamacrocycles of Cu (II), IR spectra, Magnetic moments

## I. INTRODUCTION

Fe(II), Co(II), Ni(II) and Cu(II) complexes of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM), a 14-membered N<sub>4</sub> macrocycle, have been synthesized by 2+2 condensation of 2,3-butanedione and 1,3-diaminopropane using metal ion templates.<sup>1-3</sup> Cu(II) complexes of a 12-membered macrocycle derived from benzil and 1,2-diaminoethane also prepared by template procedure.<sup>4</sup> Sulekh Chandra et al.<sup>5</sup> studied the synthesis and characterization of tetraazamacrocyclic ligand and its complexes with Co(II), Ni(II) and Cu(II) in which the ligand acts in a tetradentate manner coordinating through four nitrogen atoms of azomethine groups. Ravinder et al.<sup>6</sup> synthesize the Cu(II) tetraazamacrocyclic complexes and carried out spectral and antibacterial studies in which they found that some complexes are of square planar and some of them are distorted octahedral geometry. A series of mononuclear Fe (II), Co (II), Ni (II), Cu (II) and Pd (II) complexes correspond to tetradentate macrocyclic nitrogen ligand metal (II) complexes, have been synthesized by template condensation reaction.<sup>7</sup> Prasad et al.<sup>8-13</sup> reported Zn(II), Cd(II) and Co(II) complexes of such large ring tetraazamacrocycles and in the present paper the template synthesis of Cu(II) tetraazamacrocycles derived from 2,3-pentanedione and diaminoalkanes such as 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; 1,8-diaminooctane and 1,12-diaminododecane are reported their corresponding formulas and names are [Me<sub>2</sub>Et<sub>2</sub>[14]tetraene N<sub>4</sub>] (2,9-dimethyl-3,10-diethyl-1,4,8,11-tetra azacyclotetradeca-1,3,8,10-tetraene); [Me<sub>2</sub>Et<sub>2</sub>[16]tetraene N<sub>4</sub>] (2,10-dimethyl-3,11-diethyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene); [Me<sub>2</sub>Et<sub>2</sub>[20]tetraene N<sub>4</sub>] (2,12-dimethyl-3,13-diethyl-1,4,11,14-tetra azacycloeicosa-1,3,11,13-tetraene); [Me<sub>2</sub>Et<sub>2</sub>[24]tetraene N<sub>4</sub>] (2,14-dimethyl-3,15-diethyl-1,4,13,16-tetra azacyclotetracos-1,3,13,15-tetraene) and [Me<sub>2</sub>Et<sub>2</sub>[32]tetraene N<sub>4</sub>] (2,18-dimethyl-3,19-diethyl-1,4,17,20-tetra azacyclodotriaconta-1,3,17, 19-tetraene).

## II. EXPERIMENTAL

### Materials

CuCl<sub>2</sub>·2H<sub>2</sub>O (BDH) was of GR/AR grade. 1,3-diaminopropane; 1,4-diaminobutane and 1,6-diaminohexane were obtained from Fluka and distilled before use. 1,8-diaminooctane (Fluka); 1,12-diaminododecane (Fluka) and 2,3-pentanedione (Aldrich) were used as such.

Analytical methods and physical measurements

Carbon and hydrogen were determined on a Coleman C, H Analyser-33 which was standardized by benzoic acid. Copper was determined volumetrically by sodium thiosulphate (Hypo) solution using starch indicator. Nitrogen by Kjeldahl's method and chlorine gravimetrically as AgCl. Infrared spectra were recorded as KBr pellets in the region 4000 to 200 cm<sup>-1</sup> on a NICOLET DXIR spectrophotometer. Magnetic measurements were conducted using a CAHN-2000 magnetic balance. Conductance was measured using a Systronics Direct Reading Conductivity meter 304.

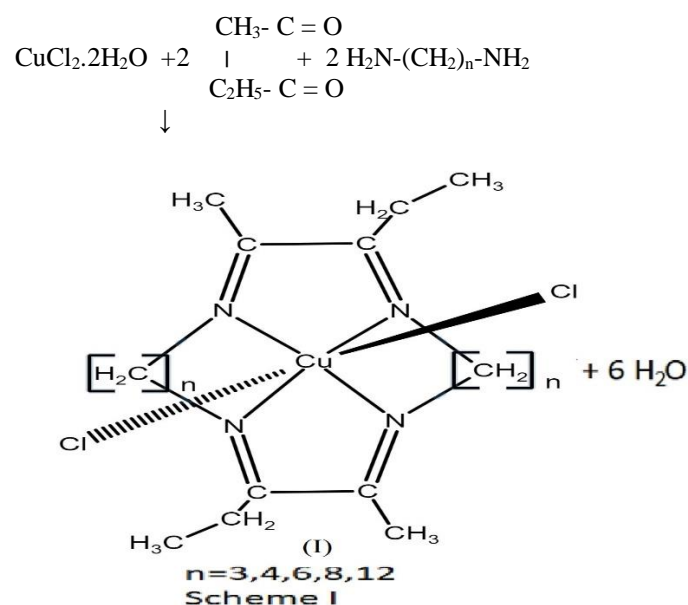
### Synthesis of Cu (II) tetraazamacrocyclic complexes

CuCl<sub>2</sub>·2H<sub>2</sub>O (~4 m mol) was dissolved in 20 ml n-butanol and 2,3-pentanedione (~8 m mol) dissolved in ~30 ml n-butanol was added. To this, a hot solution of 1,3-diaminopropane (~8 m mol in 20 ml n-butanol) was added

dropwise with constant stirring. A solid appeared during the addition and stirring was continued for 3-4 hrs. maintaining the temperature at 60-70 °C. The precipitate was filtered, washed with hot n-butanol and dried in vacuo. Similarly, the reaction of 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,12-diaminododecane with 2,3-pentanedione have been conducted.

### III. RESULTS AND DISCUSSION

Cu (II) complexes of tetraazamacrocycles (I) have been synthesized by 2:2 cyclocondensation of 2,3-pentanedione and different diaminoalkanes viz ,1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane;1,8-diaminooctane or 1,12-diaminododecane in the presence of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Scheme I).



All the complexes are coloured solids and are stable at room temperature. They are soluble in Dimethylsulphoxide (DMSO) but insoluble in most common organic solvents such as chloroform, carbon tetrachloride, methanol, acetone, etc. The elemental analysis and characteristics of these complexes are given in Table-1.

Table –1 Analysis and physical characteristics of tetraazamacrocyclic complexes of Cu (II)

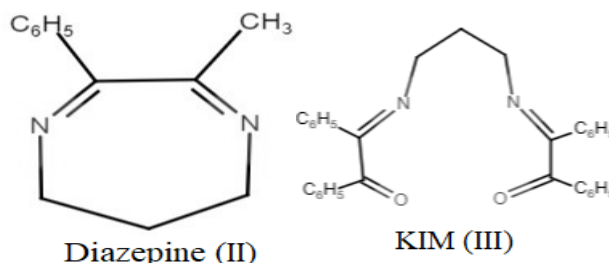
S.No.	Complex	Colour & Decomposition Temperature (°C)	Yield %	Analysis (%) found (calculated)				
				C	H	N	Cu	Cl
1	[Cu (Me <sub>2</sub> Et <sub>2</sub> [14] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	Blue (170)	30	45.45 (46.77)	7.09 (6.86)	13.65 (13.63)	15.40 (15.46)	17.22 (17.25)
2	[Cu (Me <sub>2</sub> Et <sub>2</sub> [16] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	Blue (120)	28	48.65 (49.25)	7.41 (7.34)	12.71 (12.76)	14.32 (14.47)	16.01 (16.15)
3	[Cu (Me <sub>2</sub> Et <sub>2</sub> [20] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	Blue (110)	31	53.21 (53.38)	8.09 (8.14)	11.23 (11.31)	13.00 (12.83)	14.22 (14.31)
4	[Cu (Me <sub>2</sub> Et <sub>2</sub> [24] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	Blue (132)	40	56.05 (56.66)	8.98 (8.77)	9.92 (10.16)	11.48 (11.52)	12.74 (12.86)
5	[Cu (Me <sub>2</sub> Et <sub>2</sub> [32] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	Blue (130)	38	60.97 (61.59)	9.42 (9.67)	8.49 (6.44)	9.49 (9.58)	10.63 (10.69)

Boraey and Gammal<sup>14</sup> pointed out the importance of template synthesis. The template condensation for the preparation of macrocyclic ligands often offers selective routes towards products that are not formed without metal

ions<sup>15</sup>. The template condensation methods lie at the heart of macrocyclic chemistry<sup>16</sup>. Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated during the template reactions<sup>17</sup>. The Transition metal ions are used as the template reactions<sup>18</sup>. The transition metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products<sup>19</sup>.

In general, the metal ion radius and size of the macrocyclic cavity are essential in forming macrocyclic complexes. Stable complexes are formed when the metal ion is of such a size that it can adequately fit in the macrocycle cavity. The selectivity of polyether's towards alkali, and alkaline earth metal ions have been studied as a function of their ring size<sup>20</sup>. For tetraazamacrocycles, ideal ring sizes of metal ions have been investigated, and the M-N distance for which the strain energy in the macrocycle is minimum has been calculated<sup>21-23</sup>. A larger or smaller metal ion would require a change in M-N distance with an accompanying increase in the strain energy of the ligand, causing distortion. The M-N bond length for transition metal complexes of 12- to 16- membered saturated tetraazamacrocycles ranges from 1.8 – 2.4 Å, many macrocycles of varying ring sizes coordinate readily to transition metal ions to give stable complexes<sup>24</sup>.

The complexes synthesized during the present investigation involve macrocycles with larger rings, i.e., containing up to 32-atoms. There will be greater flexibility in such larger rings due to which metal ions smaller than the macrocyclic ring size can be conveniently accommodated, resulting in the formation of stable complexes. A comparison of open chain polyamines and tetraazamacrocycles has been made. It has been suggested that metal ion selectivity is controlled by chelate ring size rather than the macrocyclic ring size<sup>25</sup>. Formation constants of macrocyclic and nonmacrocyclic ligands have been compared. It has been confirmed that chelate ring size is vital in controlling metal ion size-based selectivity and usually overweighs the macrocyclic ring size in this regard<sup>26-29</sup>. Molecular mechanics calculations have also shown that due to the flexibility of the large macrocyclic ring, there is an exceedingly small effect of macrocyclic ring size on the stability of the complexes<sup>30</sup>. During the template synthesis of Fe(II), Co(II), and Ni(II) complexes of MePhTIM, Eggleston, and Jackels<sup>31</sup> have ruled out the possibility of formation of diazepine (III), a heterocyclic product of 1+1 condensation based on <sup>1</sup>H NMR studies. Henery et al.<sup>32</sup> have isolated and characterized a macrocyclic precursor 1,2,8,9-tetraphenyl-diazaduohepta-2,7-diene-1,9-dione (KIM, III) during 2+2 cyclocondensation of benzil and 1,3-diaminopropane in the presence of Co (II).



### Infrared Spectra

Important infrared absorption bands of complexes are given in Table-2.

Table –2 IR, magnetic moment and molar conductance of Cu (II) tetraazamacrocyclic complexes

S.N.	Complex	IR Absorption Bands( $\text{cm}^{-1}$ )		$\mu_{\text{eff}}$ (B.M.)	Molar Conductance ( $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) of $10^{-3}$ M sol.
		$\nu$ C=N	Cu-Cl		
1	[Cu(Me <sub>2</sub> Et <sub>2</sub> [14] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	1580	270	1.83	17.8
2	[Cu (Me <sub>2</sub> Et <sub>2</sub> [16] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	1600	270	1.84	15.2
3	[Cu (Me <sub>2</sub> Et <sub>2</sub> [20] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	1580	270	1.81	16.5
4	[Cu (Me <sub>2</sub> Et <sub>2</sub> [24] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	1600	270	1.82	10.9
5	[Cu (Me <sub>2</sub> Et <sub>2</sub> [32] tetraene N <sub>4</sub> ) Cl <sub>2</sub> ]	1580	270	1.79	-

The Infrared Spectra of the complexes do not exhibit any absorption band at 3200 or 1700  $\text{cm}^{-1}$  indicating the absence of  $>\text{C}=\text{O}$  or  $-\text{NH}_2$  group<sup>33-35</sup>. All the complexes show a medium intensity absorption band in the region 1580-1600  $\text{cm}^{-1}$  which can be assigned to  $\nu$  C=N, indicating the condensation of 2,3-pentanedione and diaminoalkanes. For



TIM complexes<sup>33</sup> of Cu (II)  $\nu$  C=N has been reported at 1600-1620  $\text{cm}^{-1}$ . For Zn(II) complexes of MePhTIM absorption at 1609-1615  $\text{cm}^{-1}$  and 1640-1660  $\text{cm}^{-1}$  were attributed to  $\nu$  C=N (symmetric and asymmetric vibrations)<sup>36</sup>. Chloro complexes show bands at  $\sim 270 \text{ cm}^{-1}$  due to coordinated chloro group. Rana et al.<sup>37</sup> have reported  $\nu$  Cu-Cl at 270  $\text{cm}^{-1}$  in Cu(II) complexes of a 16 -membered tetraazamacrocycle derived from 2,4-pentanedione and m-phenylenediamine. For Cu(II) complexes<sup>38</sup> of an N<sub>6</sub> macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine  $\nu$  Cu-Cl has been reported at 275  $\text{cm}^{-1}$ .

### Conductance

Molar conductance of  $10^{-3}\text{M}$  solutions of the complexes is given in Table-2. Complexes behave as nonelectrolytes in dimethylsulphoxide ( $\Lambda_m$  ranging from 10.9 to 17.8  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) supporting hexacoordination of copper in these complexes<sup>39</sup>. Hexacoordinated Cu(II) complexes of TIM and MePhTIM have been reported.<sup>40</sup> Bhoon and Singh<sup>4</sup> have synthesized six coordinated Cu(II) complexes of a macrocycle derived from benzil and ethylenediamine. Pajunen<sup>41</sup> has reported X-ray structure of six coordinated Cu(II) complex, Diaqo(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) Copper(II) nitrate.

### Magnetic moments

The effective magnetic moments of Cu(II) macrocyclic complexes are given in the Table-2. The observed  $\mu_{\text{eff}}$  values at room temperature ( $\sim 298\text{K}$ ) range from 1.79 to 1.84 B.M. as expected for monomeric and noninteracting copper ions with one unpaired electron. For Cu(II) complexes of 28- membered N<sub>4</sub>O<sub>4</sub> macrocycles  $\mu_{\text{eff}}$  values in the range 1.84-1.94 B.M. have been reported.<sup>42</sup> For Cu(II) complexes of macrocycle derived from benzil and ethylenediamine  $\mu_{\text{eff}}$  values in the range 1.84-1.94 B.M. have been reported.<sup>4</sup> Coltrain and Jackels<sup>40</sup> have been reported magnetic moments in the range 1.80-1.89 B.M.

## IV. CONCLUSIONS

In the present communication, we have synthesized and characterized five large ring (14, to 32 – membered) Cu(II) tetraazamacrocyclic complexes using template synthesis. Based on analytical and spectral data these complexes are assumed to distorted octahedral geometry and their stability is due to the flexibility of large chelate ring.

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