

# Synthesis and Spectral Characterization of Cu(II) Tetra Aza Macrocylic Complexes

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## ABSTRACT

A novel family of tetraaza macrocylic Cu (II) complexes Cu LX<sub>2</sub> (where L = N<sub>4</sub> donor macrocylic ligand and X = Cl) have been synthesized. Characterization has been done on the basis of elemental analysis, molar conductance, UV visible, IR, magnetic susceptibility and XPS data. IR spectra and XPS data shows that the ligand behave tetra dentate through 4 N atoms, the XPS data suggest octahedral geometry for Cu (II) macrocylic complexes.

**Key words:** Synthesis, Tetra aza, Macrocylics, Cu (II) Complexes.

## I. INTRODUCTION

Transition metal complexes containing macrocycles are of much interest in reference of structural and coordinational chemistry<sup>1</sup>. Transition metal macrocylic complexes have received much attention as an active part of metalloenzymes<sup>2</sup>

Copper(II) is the most studied transition metal showing electronic configuration Ar[3d<sup>9</sup>4s<sup>0</sup>]. Copper plays a very significant role medically and biologically. Deficiency of copper can lead to a variety of adverse effects such as fragility in bones, loss of lysyl oxidase in cartilage<sup>3-6</sup>. A number of reviews<sup>7-13</sup> have been published on the general biochemistry of copper, electronics aspect of active sites<sup>14,15</sup> and relevant model chemistry of simple copper complexes.

Macrocylic ligands are always attractive in the generation for new chemistry because they offer a wide variety of donor atoms, ionic charge, coordination numbers and geometry of the resultant complexes<sup>16-20</sup>. Aza type ligands appear very promising for potential use as antibacterial, antifungal agents as well as due to their other biological

properties. Complexes with macrocylic ligands are known as to play a significant role either in naturally occurring biological system or as pharmacological agent<sup>21,22</sup>. In this report we report the results of our studies on the synthesis and spectral properties of [CuX<sub>2</sub>L] complexes (where X=Cl<sup>-</sup> and L=macrocylic ligands)

## II. EXPERIMENTAL TECHNIQUES

### Materials and Method

All the solvent used were of E. Merck (L.R. Grade and Ranbaxy). Copper(II) used as chloride salts were of Merck. Solvent were used after purification and drying by conventional methods. The I.R. spectra of the complexes were recorded on perkinelmer 457 spectrometer at room temperature in KBr. X-ray photoelectron spectra were recorded on a VG scientific ESCA-3 MK II electron spectrometer.

### Synthesis of Ligands:

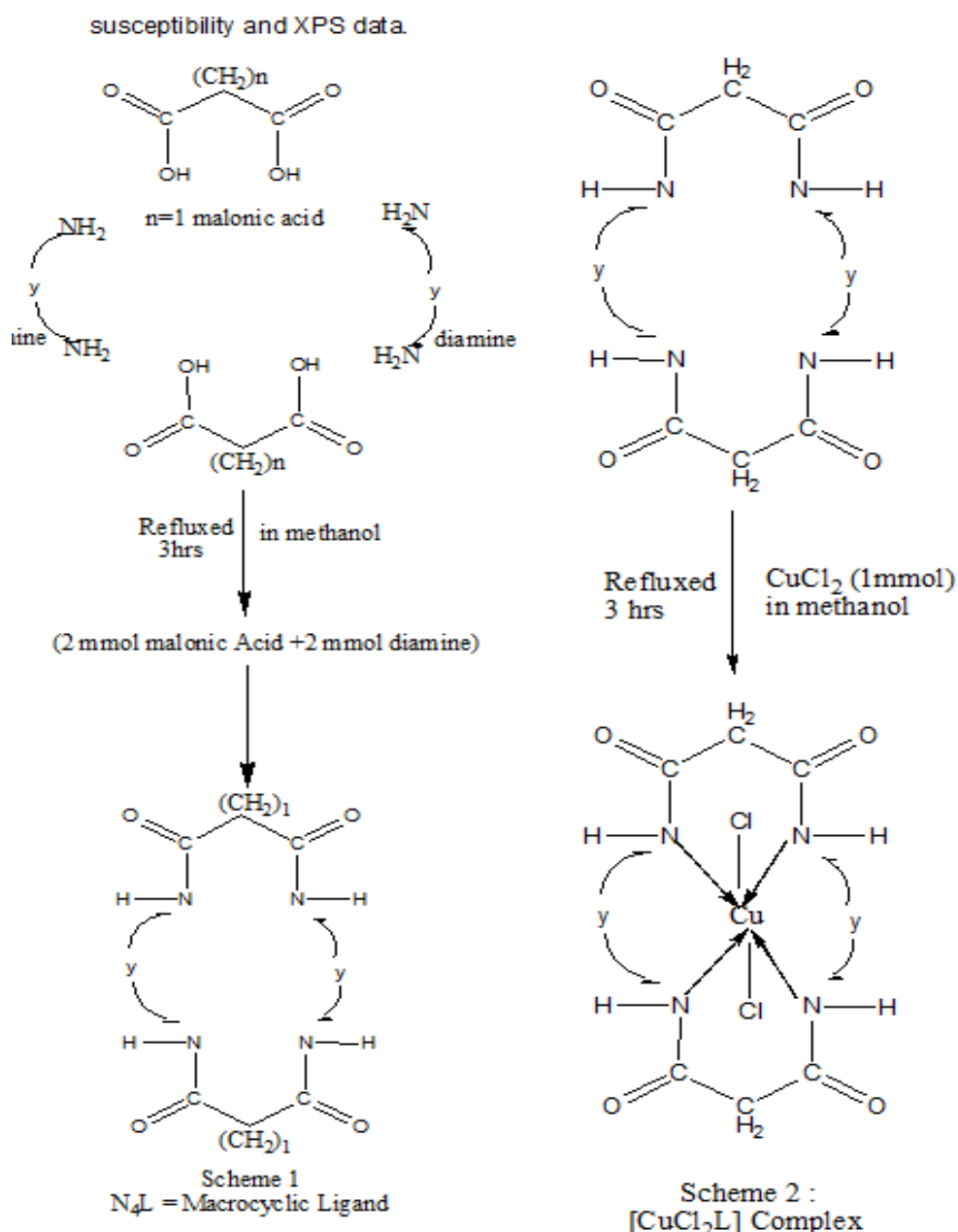
2mmol of malonic acid or succinic acid or glutaric acid in dry methanol was mixed in 2mmol solution in dry methanol of diamines *i.e.* NH<sub>2</sub> (y)NH<sub>2</sub>

Where

$y = -\text{NHCONH}, \text{NHCSNH}$  OR  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{-OR-CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-}$  OR  $-\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{-}$  OR  $-(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$  OR  $-(\text{CH}_2)_6$  OR  $-(\text{CH}_2)_7\text{-}$  OR  $-(\text{CH}_2)_8$  OR  $-(\text{CH}_2)_9\text{-}$  OR  $-(\text{CH}_2)_{10}\text{-OR-}(\text{CH}_2)_{12}$  and refluxed for 3 hours. TLC has suggest formation of a new product.  $\text{N}_4\text{L}^1$  to  $\text{N}_4\text{L}^{12}$  Macrocyclic ligands were synthesized.

### Synthesis Of Complex

In this solution 1mmol  $\text{CuCl}_2$  solution in dry methanol was mixed and again refluxed, found solid product, dried and recrystallised as shown in scheme 1 and scheme 2. These prepared complexes were  $[\text{Cu}(\text{L}^{1-12})\text{Cl}_2]$  which were characterized by elemental analysis, molar conductance, UV visible, IR, Magnetic susceptibility and XPS data.



### III. RESULT AND DISCUSSION

On the basis of elemental analysis data, all the complexes have the general composition<sup>23</sup>  $[\text{CuCl}_2\text{L}^{1-12}]$ .

<sup>12</sup>]. The molar conductance measurements in DMF shows that all the complexes are non electrolyte indicating.

That the ions are coordinated to the metal ion. In IR spectra the presence of a strong band characteristic for the stretching mode at 1580-1620 $\text{cm}^{-1}$ . Spin allowed transitions are expected in the visible and near IR region. Magnetic moment of all the complexes at

room temperature lie in 1.98 to 2.02BM. On the basis of above studies the possible structure of all these prepared complex was  $[\text{CuCl}_2\text{L}^{1-12}]$ . Metal complex have assigned octahedral geometry

**Table 1.** ANALYTICAL DATA OF  $[\text{CuCl}_2\text{L}]$  complexes where L=L1 to L12.

S.No.	Complex	Elemental analysis % (Calculated) found			Molar conductance $\text{Ohm}^{-1} \text{mol}^{-1} \text{Cm}^2$ in DMF
		C	H	N	
1.	$[\text{CuCl}_2\text{L}^1]$	25.0 (25.2)	3.0 (3.1)	29.4 (29.5)	20
2.	$[\text{CuCl}_2\text{L}^2]$	19.6 (19.8)	2.4 (2.4)	23.2 (23.2)	22
3.	$[\text{CuCl}_2\text{L}^3]$	34.2 (34.4)	4.4 (4.5)	13.2 (13.4)	18
4.	$[\text{CuCl}_2\text{L}^4]$	37.4 (37.6)	5.2 (5.3)	12.4 (12.5)	16
5.	$[\text{CuCl}_2\text{L}^5]$	40.2 (40.4)	5.6 (5.8)	11.6 (11.7)	14
6.	$[\text{CuCl}_2\text{L}^6]$	37.2 (37.4)	5.6 (5.7)	12.4 (12.4)	15
7.	$[\text{CuCl}_2\text{L}^7]$	42.8 (42.9)	6.2 (6.3)	11.0 (11.1)	16
8.	$[\text{CuCl}_2\text{L}^8]$	45.0 (45.2)	6.6 (6.3)	10.4 (10.5)	18
9.	$[\text{CuCl}_2\text{L}^9]$	47.2 (47.2)	7.0 (7.1)	10.0 (10.0)	22
10.	$[\text{CuCl}_2\text{L}^{10}]$	49.0 (49.1)	7.4 (7.5)	9.4 (9.5)	20
11.	$[\text{CuCl}_2\text{L}^{11}]$	50.6 (50.7)	7.6 (7.8)	9.0 (9.1)	24
12.	$[\text{CuCl}_2\text{L}^{12}]$	53.0 (53.0)	8.0 (8.2)	9.2 (9.4)	20

**Table 2.** Electronic spectral bands of  $[\text{CuCl}_2\text{L}]$  complexes

S.No.	Complex	$\lambda_{\text{max,UV}} (\text{cm}^{-1})$
1.	$[\text{CuCl}_2\text{L}^1]$	17920; 22320
2.	$[\text{CuCl}_2\text{L}^2]$	17921; 22321
3.	$[\text{CuCl}_2\text{L}^3]$	17820; 22330
4.	$[\text{CuCl}_2\text{L}^4]$	17840; 22340
5.	$[\text{CuCl}_2\text{L}^5]$	17920; 22400
6.	$[\text{CuCl}_2\text{L}^6]$	17842; 22360
7.	$[\text{CuCl}_2\text{L}^7]$	17890; 22320
8.	$[\text{CuCl}_2\text{L}^8]$	17892; 22316
9.	$[\text{CuCl}_2\text{L}^9]$	17916; 22320
10.	$[\text{CuCl}_2\text{L}^{10}]$	17920; 22330
11.	$[\text{CuCl}_2\text{L}^{11}]$	17921; 22340
12.	$[\text{CuCl}_2\text{L}^{12}]$	17860; 22300

**Table 3.** Cu 2p  $\frac{1}{2}$  and Cu 2p  $\frac{3}{2}$  binding energies (eV) in [Cu Cl<sub>2</sub>L] complexes

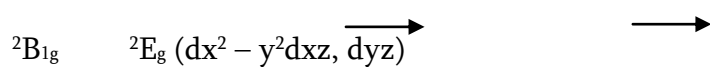
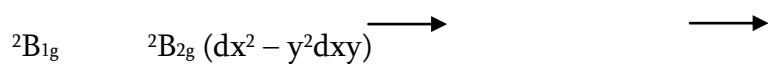
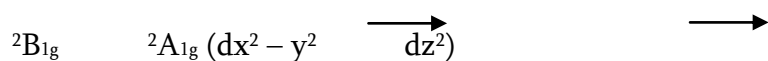
S. No.	Complex	Cu 2p photoelectron peak	
		Cu 2p $\frac{1}{2}$	Cu 2p $\frac{3}{2}$
1.	[CuCl <sub>2</sub> .L]	952.4	932.4
2.	[CuCl <sub>2</sub> .L <sup>1</sup> ]	951.4	932.4
3.	[CuCl <sub>2</sub> .L <sup>2</sup> ]	951.4	932.4
4.	[CuCl <sub>2</sub> .L <sup>3</sup> ]	951.4	932.4
5.	[CuCl <sub>2</sub> .L <sup>4</sup> ]	951.4	932.4
6.	[CuCl <sub>2</sub> .L <sup>5</sup> ]	951.4	932.4
7.	[CuCl <sub>2</sub> .L <sup>6</sup> ]	951.4	932.4
8.	[CuCl <sub>2</sub> .L <sup>7</sup> ]	951.4	932.4
9.	[CuCl <sub>2</sub> .L <sup>8</sup> ]	951.4	932.4
10.	[CuCl <sub>2</sub> .L <sup>9</sup> ]	951.4	932.4
11.	[CuCl <sub>2</sub> .L <sup>10</sup> ]	951.4	932.4
12.	[CuCl <sub>2</sub> .L <sup>11</sup> ]	951.4	932.4
13.	[CuCl <sub>2</sub> .L <sup>12</sup> ]	951.4	932.4

**Table 4.** N1s binding energies (eV) in Ligands and [Cu Cl<sub>2</sub>L] complexes

S.No.	Complex	N1s
1.	L <sup>1</sup>	400.4
2.	[CuCl <sub>2</sub> .L <sup>1</sup> ]	401.8
3.	L <sup>2</sup>	400.4
4.	[CuCl <sub>2</sub> .L <sup>2</sup> ]	401.8
5.	L <sup>3</sup>	400.4
6.	[CuCl <sub>2</sub> .L <sup>3</sup> ]	401.8

7.	$L^4$	400.4
8.	$[CuCl_2.L^4]$	401.8
9.	$L^5$	400.4
10.	$[CuCl_2.L^5]$	401.8
11.	$L^6$	400.4
12.	$[CuCl_2.L^6]$	401.8
13.	$L^7$	400.4
14.	$[CuCl_2.L^7]$	401.8
15.	$L^8$	400.4
16.	$[CuCl_2.L^8]$	401.8
17.	$L^9$	400.4
18.	$[CuCl_2.L^9]$	401.8
19.	$L^{10}$	400.4
20.	$[CuCl_2.L^{10}]$	401.8
21.	$L^{11}$	400.4
22.	$[CuCl_2.L^{11}]$	401.8
23.	$L^{12}$	400.4
24.	$[CuCl_2.L^{12}]$	401.8

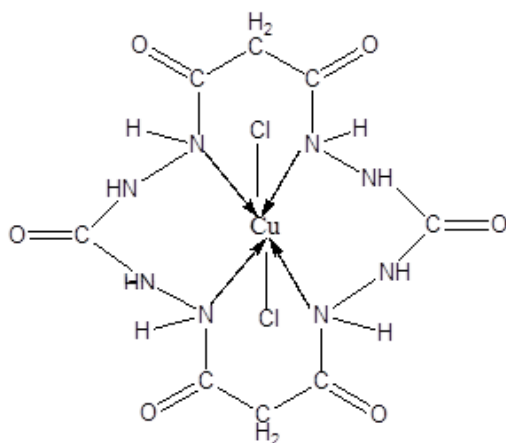
In Table2 These bands have been assigned to the following transitions in order of increasing energy



the x-ray photoelectron spectra have shown binding energies (eV) data for Cu 2p  $\frac{1}{2}$  ;  $\frac{3}{2}$  and N1s photoelectron (Table 3 & 4) respectively. The Cu 2p  $\frac{1}{2}$ ,  $\frac{3}{2}$  photoelectron peak in all these prepared [CuCl<sub>2</sub>.L<sup>1-12</sup>] complexes were found having less binding energy (ev) than in CuCl<sub>2</sub>; suggesting copper metal ion is getting more electron density in [CuCl<sub>2</sub>.L<sup>1-12</sup>] complexes i.e. coordination occur<sup>24</sup>

#### IV. CONCLUSION

On the basis of elemental analysis, molar conductance, IR, UV-visible, magnetic moment and XPS data, the possible proposed structure of these all prepared [CuCl<sub>2</sub>.L<sup>1-12</sup>] metal complexes have assigned as shown in figure 1 suggesting octahedral geometry<sup>25</sup>.



**Figure 13.** [CuCl<sub>2</sub>L<sup>1</sup>]Complex

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