Synthesis and spectral characterization of $[CuX_2L]$ Complexes (where $X=Cl^-$, NO^-_3, CH_3COO^-) & L = macrocyclic Schiff base ligands.

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ABSTRACT :

Certain new macrocyclic complexes were synthesis and their structures were proposed on the basis of elemental analysis, IR, photo-electron spectra. The metal to ligand molar ratio of the Cu (II) complexes were found to be 1:1. The Cu (II) shows to be nonelectrolytes by their molar conductivities valve. Their configuration were proposed to be octahedral geometry.

Key word : macrocylic complexes, photoelectron spectra, molar conductance, IR.

INTRODUCTION :

The field of macrocyclic chemistry of metals is developing using rapidly because of its application, in coordination chemistry and bioinorganic chemistry[1-3].

The studies on complexes of Schiff base macrocyclic ligands with different size and member and donor atoms for coordination with a variety of metal centres have been studied[4-7].

A large number of macrocyclic ligand synthesized and yield complexes that exhibit extensive electron delocalization[8].

AIM OF STUDY

The study thus aims at synthesizing Cu (II) complexes by using macrocylic Schiff base ligands.

The namely synthesized copper (II) metal complexes will be characterized by elemental analysis, molar conductivity, UV visible, IR, magnetic moment & XPS data, to establish their structure & geometry[9-12].

EXPERIMENTAL PROCEDURE

Reagent :

E merck (LR grade) & Ranbaxy Solvent were used after purification and drying by conventional methods.

The elemental analysis for C, H, N were determined on a semimicroscale at CDRI Lucknow. Molar conductance of all the complexes were measured at room temperature in acetone by Digisum electron conductivity bridge[13].

The x-ray photo-electron spectra were recorded on a VG scientific ESCA -3 MK-II electron spectrometer

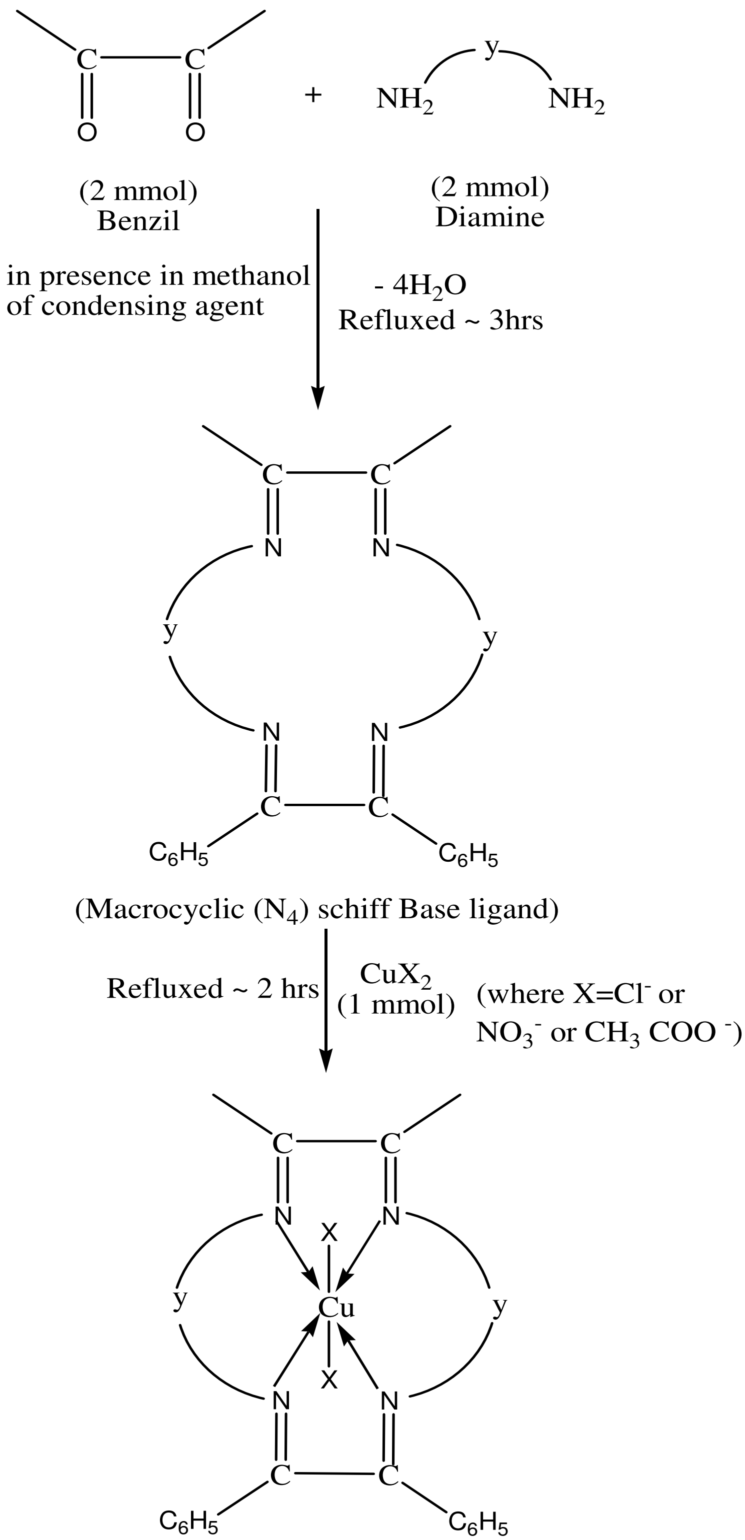
Synthesis of ligand – 2 mmol benzil in dry methanol was fixed into 2 mmol diamine in dry methanol i.e. NH_2 (y) NH_2 (where y = - NHCONH – or – NHCSNH – or – $CH_2CH_2CH_2$ – or – CH_2 CH (CH_3) CH_2 or y = -$CH_2C(CH_3)_2CH_2$– and refluxed for 2 hrs. a solid yellow product was formed giving new macrocylic Schiff base ligands.

Synthesis of metal complexes [$CuLX_2$]

1 mmol of macrocyclic Schiff base ligand (L) in dry methanol was mixed into 1 mmol of CuX_2 solution in dry methanol (where X = Cl^-, NO_3^- or CH_3COO^-) & refluxed for 3 hrs[14-15].

The slight blue solid product was formed which was purified & recrystallized by dry methanol[16].

By scheme-1



Scheme 1

Where,

1. $N_4L^1 = y = -NHCONH-$
2. $L^2 = N_4L^2 = y = -NHCONH-$
3. $L^3 = N_4L^3 = y = -CH_2CH_2CH_2-$
4. $L^4 = N_4L^4 = y = -CH_2CH(CH_3)CH_2-$
5. $L^5 = N_4L^5 = y = -CH_2C(CH_3)_2CH_2-$

RESULT AND DISCUSSION

The elemental analysis C,H & N of all these prepared complexes suggested the general composition [Cu (X_2) L]

Magnetic moment of all these complexes at room temperature were observed in the range 1.90 to 2.60 BM compressing to one unpaired electron.

In IR spectra the pressure of strong band characteristics for the stretching mode of the coordinated >C=N at 1580-16520 cm^{-1}. Group provide strong evidence for the presence of a closed cyclic compound.

The x=ray photoelectron spectra binding energies (ev) data for Cu_2 $P_{1/2,3/2}$ & N_1S (for ligand) have shown in table 3 & 4.

On the basis of elemental analysis, molar conductance, IR, UV visible magnetic moment and XPS data the possible structure.

Table 1 : Analaytical data of [Cu X_2L] complexes (where X = Cl or NO_3 or CH_3COO; L = $L^1 - L^2$ maerocyclic Ligands)

S.No.	Complex	Elimental Analysis % (calculated) found			Molar conductance $ohm^{-1}mol^{-1}cm^2$ in DMF
		C	H	N	
1.	$[CuCl_2L^1]$	32.6 (32.7)	6.4 (6.5)	15.2 (15.2)	30
2.	$[CuCl_2L^2]$	59.2 (59.3)	3.8 (3.9)	9.2 (9.2)	22
3.	$[CuCl_2L^3]$	64.6 (64.7)	5.0 (5.0)	8.6 (8.8)	24
4.	$[CuCl_2L^4]$	65.4 (65.6)	5.3 (5.4)	8.4 (8.5)	28
5.	$[CuCl_2L^5]$	66.2 (66.4)	5.6 (5.8)	8.0 (8.1)	20
6.	$[Cu(NO_3)_2L^1]$	50.2 (50.3)	3.2 (3.3)	19.4 (19.5)	24
7.	$[Cu(NO_3)_2L^2]$	52.2 (52.3)	3.3 (3.4)	16.2 (16.2)	26
8.	$[Cu(NO_3)_2L^3]$	59.4 (59.6)	4.6 (4.6)	12.2 (12.2)	24
9.	$[Cu(NO_3)_2L^4]$	60.6 (60.7)	5.0 (5.0)	11.6 (11.8)	22
10.	$[Cu(NO_3)_2L^5]$	60.4 (61.6)	5.4 (5.4)	11.2 (11.3)	24
11.	$[Cu(CH_3COO)_2L^1]$	57.4 (57.5)	4.2 (4.2)	15.6 (15.7)	22

12.	$[Cu(CH_3COO)_2L^2]$	63.0 (63.2)	4.4 (4.6)	17.2 (17.3)	24
13.	$[Cu(CH_3COO)_2L^3]$	67.2 (67.3)	5.6 (5.6)	8.2 (8.2)	26
14.	$[Cu(CH_3COO)_2L^4]$	68.0 (68.0)	5.8 (5.9)	7.8 (7.9)	27
15.	$[Cu(CH_3COO)_2L^5]$	67.0 (67.1)	5.8 (5.8)	8.2 (8.2)	28

Table 3 : Cu $2p_{1/2}$ and Cu $2p_{3/2}$ binding energies (eV) in [Cu X_2 . L] Complexes

S.No.	Complex	Cu $2p_{1/2,3/2}$	
		Cu $2p_{1/2}$	Cu $2p_{3/2}$
1.	$CuCl_2$	952.4	932.4
2.	$[CuCl_2L^1]$	951.4	931.4
3.	$[CuCl_2L^2]$	951.4	931.4
4.	$[CuCl_2L^3]$	951.4	931.4
5.	$[CuCl_2L^4]$	951.4	931.4
6.	$[CuCl_2L^5]$	951.4	931.4
7.	$Cu(NO_3)_2$	952.8	932.8

8.	$[Cu(NO_3)_2L^1]$	951.6	931.6
9.	$[Cu(NO_3)_2L^2]$	951.6	931.6
10.	$[Cu(NO_3)_2L^3]$	951.6	931.6
11.	$[Cu(NO_3)_2L^4]$	951.6	931.6
12.	$[Cu(NO_3)_2L^5]$	951.6	931.6
13.	$Cu(CH_3COO)_2$	952.8	932.8
14.	$[Cu(CH_3COO)_2L^1]$	951.8	931.8
15.	$[Cu(CH_3COO)_2L^2]$	951.8	931.8
16.	$[Cu(CH_3COO)_2L^3]$	951.8	931.8
17.	$[Cu(CH_3COO)_2L^4]$	951.8	931.8
18.	$[Cu(CH_3COO)_2L^5]$	951.8	931.8

CONCLUSION :

These complexes [Cu (X_2)L] are assigned an octahedral geometry.

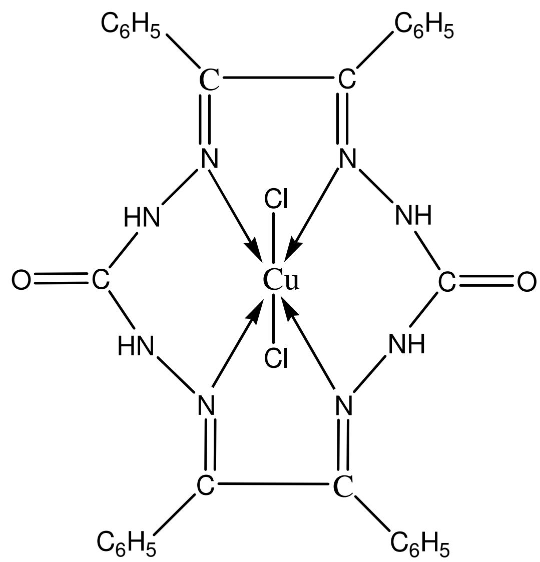


Fig. 11 : [$CuCl_2L^1$]

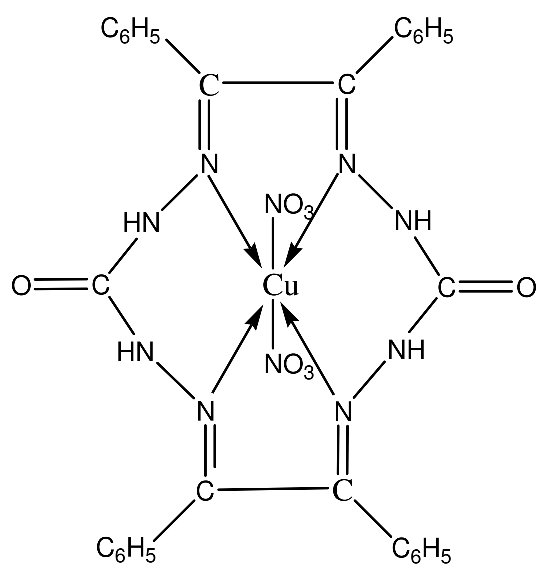


Fig. 23 : [$Cu(NO_3)_2 . L^1$]

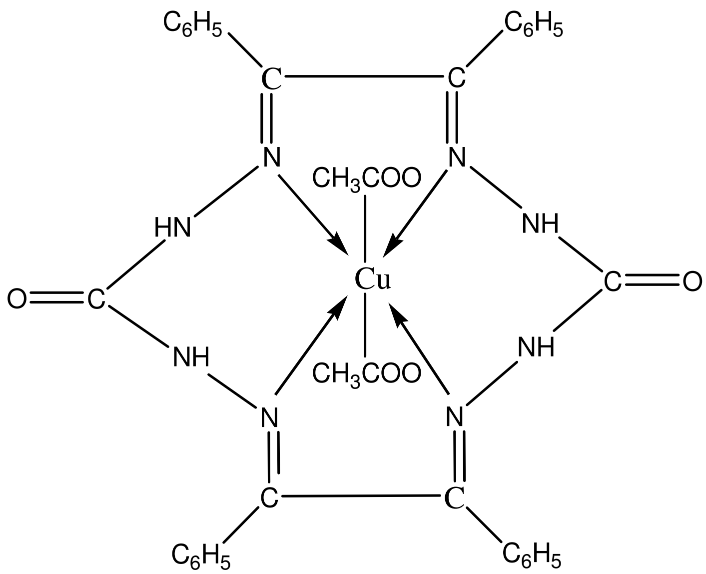


Fig. 35 : [Cu($CH_3COO)_2$. L^1]

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