

# Preparation and Characterization of Some New Mixed Ligand with Complexes of Copper (II)

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**Abstract:** This paper involved, The coupling reaction of 4-methoxyaniline, 4-acetylaniline, 4-nitroaniline, and 4-methylaniline, after the diazotization reactions with 4,5-diphenylimidazole as coupling component in alkaline ethanolic solution were maintained to give four azo dyes (L<sub>1-4</sub>), namely, 2-[(p-Xphenyl)azo]-4,5-diphenylimidazole (X= CH<sub>3</sub>O-, CH<sub>3</sub>CO-, -NO<sub>2</sub> and -CH<sub>3</sub> for L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, and L<sub>4</sub>, respectively) and its characterized study after precipitation and re-crystallized use available an analytical spectroscopic, including F.T.I.R, UV-Vis spectrophotometer, C.H.N for the elements, also mass spectrometry and thermal analysis of the two samples of azo ligand. New mixed ligand complexes of these heterocyclic azo-ligands were prepared with Cu(II) transition metal salt. A series of a new copper(II) complexes [Cu(L<sub>1</sub> or L<sub>2</sub> or L<sub>3</sub> or L<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] (1a-4a) their characterized by available techniques such as elemental analysis, determination of metal content M%, molar conductances, magnetic moment measurements, IR and UV-Vis spectral studies. The arylazo-4,5-diphenylimidazole dyes acts as a neutral bidentate ligands, coordinating through(N3) nitrogen atom of imidazole and the other nitrogen atom of azo group which is the farthest of heterocyclic molecule to form five member metallo-cyclic ring. The analytical and spectral data showed that the complexes have octahedral geometry, and they are non-electrolytic in DMSO.

**Keywords:** spectral, magnetic, molar, non-electrolytic, moment.

## 1. INTRODUCTION

Copper is a bioelement and an active site in several metalloenzymes and proteins<sup>(1-4)</sup>. Copper (II) complexes have been widely explored for versatility of coordination, exquisite colors, technical application, spectroscopic properties, and biochemical significance. Octahedral copper(II) complexes of mixed electron donor ligands have been studied due to applications as molecular material<sup>(5-9)</sup>. Imidazole is a five-membered, hetero-aromatic compound containing  $\pi$ -acid imine ( $-C=N-$ ) group<sup>(10)</sup>. The heterocyclic nitrogen compounds especially imidazole derivatives have special importance because of their ubiquity in chemistry and biology<sup>(11,12)</sup>. The formation of azo dyes usually involves the reaction between a diazo species with coupling components<sup>(13)</sup>. This class of organic compounds receive attention due to their use as models for biological systems<sup>(14,15)</sup>. One group of conjugated imidazoles is constructed by combining with an aryl azo ( $Ar-N^+\equiv N$ ) molecular unit<sup>(16-18)</sup>. These classes of organic compounds act, in general, as a bidentate chelator ligands to explore the transition<sup>(19,20)</sup> and non transition metal chelates chemistry<sup>(21,22)</sup>. Additionally, it is well known that some functionalized 2-arylamidazole derivatives were applied for analytical separation and determination of some metal cations<sup>(23-30)</sup>. In the present article, we wish to report the preparation and identification of new Cu (II) mixed ligand complexes of arylazo-4, 5-diphenyl-imidazole derivatives with triphenylphosphine.

## 2. EXPERIMENT

### I. Materials and method:

All reagents and solvents were of the analar/spectroscopic grades and used without further purification, except of 4,5-diphenyl imidazole was prepared as described earlier<sup>(31,32)</sup>. Melting points were determined in an open glass capillary tube using a Stuart melting point SMP10 and are uncorrected. Elemental analyses (C. H. N) were carried out using a C.H.N.O

EA 3000 instrument. The metal contents of the complexes was measured using atomic absorption technique by Shimadzu AA-6300. IR spectra were recorded on a Shimadzu 8000 FT-IR spectrophotometer in the (4000-400)  $\text{cm}^{-1}$  range using KBr discs. Electronic spectra were obtained on a Shimadzu 1800 UV spectrometer using ethanol as solvent in the (1100-200) nm range. Magnetic susceptibilities were determined by faraday method at room temperature using Balance Magnetic (MSB-MKI) apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constant<sup>(33)</sup>. Molar conductance of the transition metal complexes were determined in ethanol using conductivity meter Alpha-800 at 25°C, the concentration of the solutions was ( $10^{-3} \text{ mol L}^{-1}$ ).

## II. Preparation of arylazoimidazole ligands ( $L_{1-4}$ ) :

The azo imidazole ligands Fig.1, were prepared as in the procedure described for 2-arylo-4,5-diimidazole dyes<sup>(34)</sup>. The details are given as follows;

*p*-X-Aniline (1.23, 1.35, 1.38 and 1.07 g for X =  $-\text{OCH}_3$ ,  $\text{CH}_3\text{CO}-$ ,  $-\text{NO}_2$  and  $-\text{CH}_3$ , respectively, 10 mmol) was dissolved in 30 mL distilled water and 3.5 mL of hydrochloric acid ( $11.5 \text{ mol L}^{-1}$ ). This solution was diazotized below 5°C with 11 mL of aqueous ( $1.0 \text{ mol L}^{-1}$ ) sodium nitrite. A drop of the reaction mixture is tested from time to time with starch-iodide paper until nitrous acid persists in the solution during a 30 min interval. The resulting diazonium chloride solution was added drop wise with vigorous stirring to 4,5-diphenyl imidazole (2.2 g, 10 mmol) dissolved in 150 mL alkaline ethanol cooled below 5°C. After leaving in the refrigerator for 24 hour, the mixture was acidified with diluted ( $0.1 \text{ mol L}^{-1}$ ) hydrochloric acid until (pH = 7). The product was separated by filtration, purified by crystallization from hot ethanol, then dried in the oven at 50°C for several hrs.

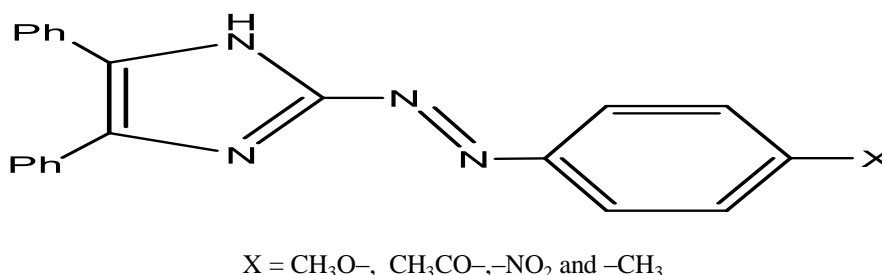


Figure 1: Structural formula of azo imidazole legends

## III. Preparation of copper (II) complexes:

Copper (II) complexes **1a-4a** were prepared from Copper(II) nitrate using the molar ratio (1:1:2:2) of metal,  $L_1$  or  $L_2$  or  $L_3$  or  $L_4$ ,  $\text{PPh}_3$ , and azide.

## IV. Copper(II) complexes 1a-4a:

A methanolic solution (20 ml) of azo dye (1 mmol, 0.354 g,  $L_1$ ; 1 mmol, 0.366 g,  $L_2$ ; 1 mmol, 0.369 g,  $L_3$ ; 1 mmol, 0.338 g,  $L_4$ ) was added dropwise to a solution (30 ml) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (1 mmol, 0.241 g) in the same solvent followed by  $\text{PPh}_3$  (2 mmol, 0.524 g) and  $\text{NaN}_3$  (2 mmol, 0.130 g) in warm methanol. The resultant mixture was stirred for 2 h, solid complexes precipitated, were collected by filtration, washed several times with 1:1 ethanol :water mixture and air dried.

## 3. RESULTS AND DISCUSSIONS

The prepared ligands and their copper (II)-azo complexes gave good yield. Many spectral studies carried out such as :

### I. IR spectrum analysis:

The IR spectral analysis of ligand is in good arrangement with the synthesis ligand. The  $\nu(\text{N}=\text{N})$  frequency of  $L_1$ ,  $L_2$ ,  $L_3$  and  $L_4$  at  $1450\text{-}1460 \text{ cm}^{-1}$  shifts to lower frequency ( $18\text{-}25 \text{ cm}^{-1}$ ) in the complex, indicating participation of one nitrogen of azo in complex formation<sup>(50-51)</sup>. This was also supported by appearance of a new band at  $\sim 435 \text{ cm}^{-1}$  due to the  $\nu(\text{M}-\text{N})$ . The azido complex 1a, 2a, 3a and 4a exhibit a strong sharp stretch corresponding to  $\nu(\text{N}_3)$  at  $\sim 2036 \text{ cm}^{-1}$ , Table (1) and Figures (2-5)

TABLE.1: Selected IR data for Ligands and their mixed ligand complexes

S.	N-H	(C-H)	(C-H)	C=N	N=N	C-O	C=O	NO <sub>2</sub>		PPh <sub>3</sub>		N <sub>3</sub>	M-N	
		Ar.	Al.											
L1	3417	3055	2970	1651	1460	1240	-	-	-	729	694	-	-	
L2	3257	3150	2996	1606	1450	-	1660	-	-	730	694	-	-	
L3	3389	3059	-	1600	1453	-	-	1340	1516	730	696	-	-	
L4	3425	3026	2900	1599	1458	-	-	-	-	725	694	-	-	
1a	3419	3055	2900	1597	1436	1382	-	-	-	1496	730	694	2036	434
2a	3394	3059	2870	1585	1430	-	1660	-	-	1470	730	696	2044	437
3a	3406	3057	-	1585	1438	-	-	1335	1514	1475	725	694	2036	435
4a	3429	3053	2925	1585	1437	-	-	-	-	1480	745	694	2036	435

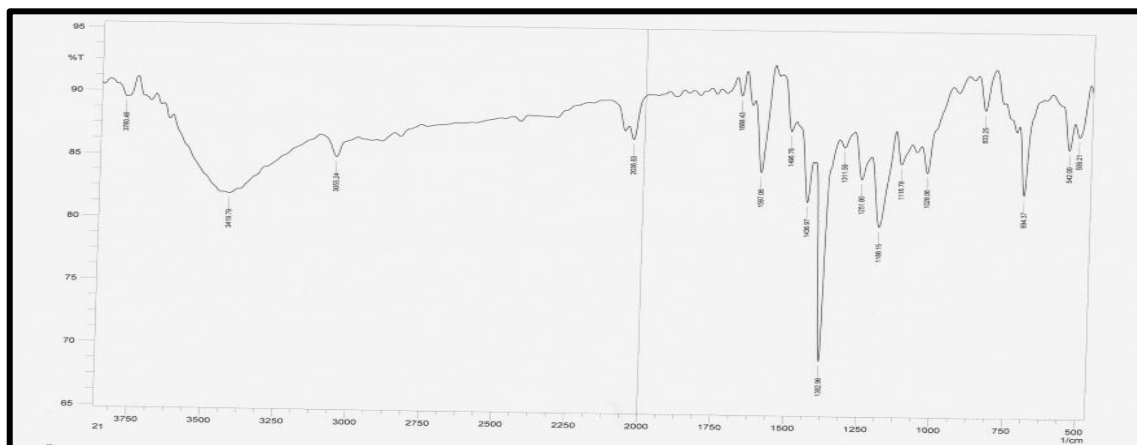


Figure 2: IR spectrum of [Cu(L<sub>1</sub>)(PPh<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] Complex

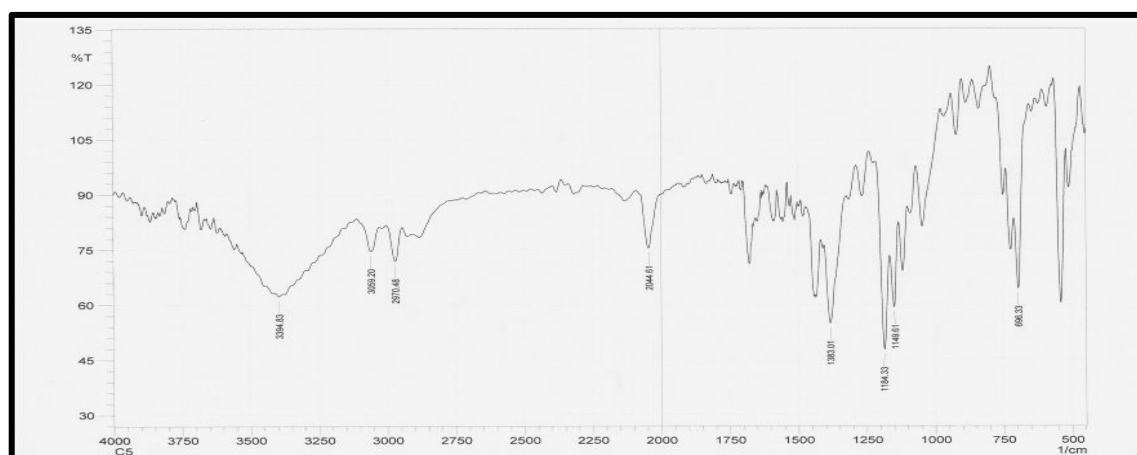


Figure 3: IR spectrum of [Cu(L<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] Complex

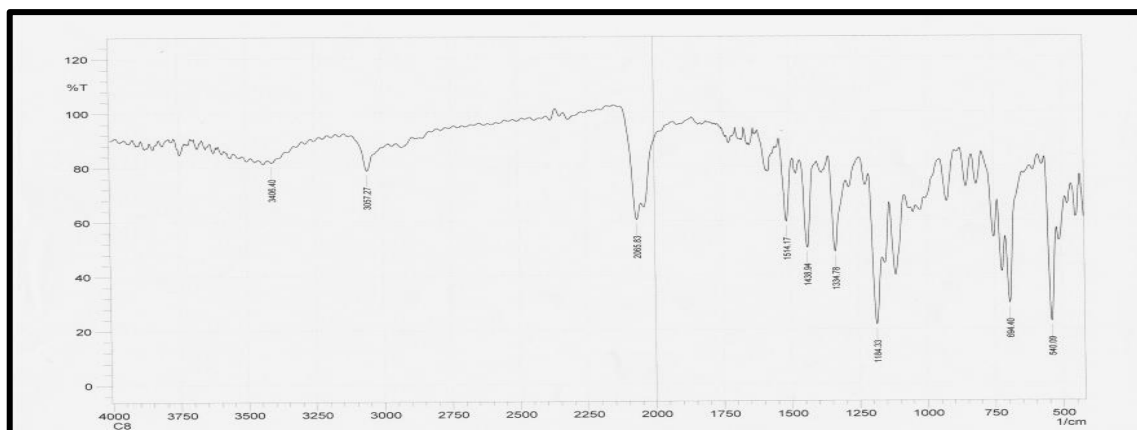


Figure 4: IR spectrum of [Cu(L<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] Complex

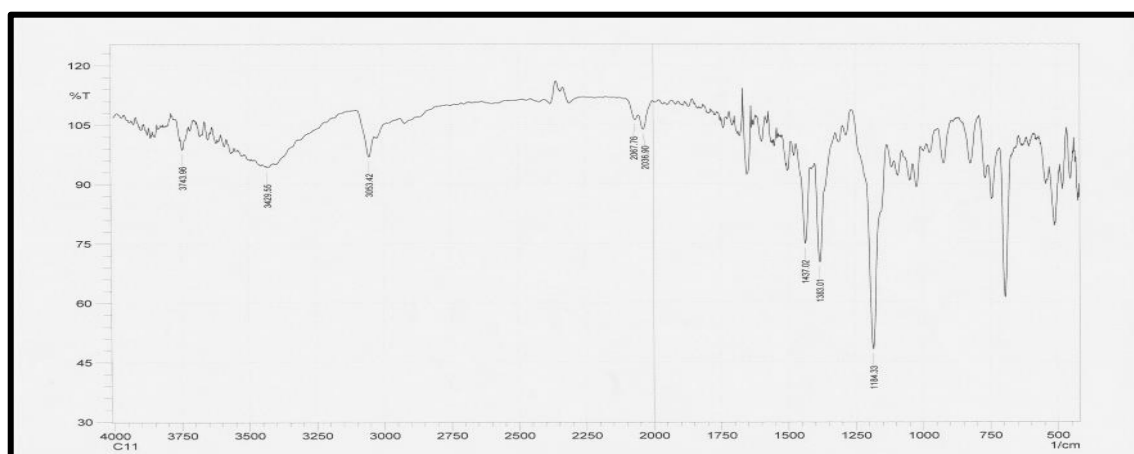


Figure 5: IR spectrum of [Cu(L<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] Complex

**II. U.V- visible Spectra and Magnetic Moment:**

Absorption spectra of the ligands in U.V. and visible region shows (266, 292, 287, 286 nm) is attributed to  $\pi \rightarrow \pi^*$  transition due to presence of conjugation in the ligand molecule<sup>(52)</sup>. (414, 458, 446, 414 nm) are corresponding to  $n \rightarrow \pi^*$ . The absorption spectra ligand peaks are obtained along with the absorption maxima due to d-d transition. The d-d transitions are La-Porte forbidden transitions therefore they are weak in intensity. The position of ligand bands are shifted which may be due to interaction of ligand with metal ion. The spectra of Cu(II) complex only two absorption bands are obtained at  $\lambda_{max}$  629-683 nm and 710-724 nm and are attributed to the transition  $2B1g \rightarrow 2Eg$  and  $2B1g \rightarrow 2B2g$ , respectively<sup>(53)</sup>. The positions of these bands in the spectra of metal complexes are consistent with the expected distorted octahedral. Table (2)

Table . 2. Data of Electronic spectra of complexes, and magnetic moment

S.	Compound	( $\pi \rightarrow \pi^*$ ) <sub>(1)</sub> (n.m)	( $\pi \rightarrow \pi^*$ ) <sub>(2)</sub> (n.m)	C.T. (n.m)	$\mu_{eff}$ B.M.
1a	[Cu(L <sub>1</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	246	300	494	1.74
2a	[Cu(L <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	-	304	526	1.74
3a	[Cu(L <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	236	300	552	1.74
4a	[Cu(L <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	-	302	496	1.77

### III. The elemental analysis :

The prepared ligands and their copper(II)-azo complexes gave good yield. The elemental analysis shown in the Table.(3) indicates that, all the metal complexes have 1:1:2:2 stoichiometry with respect to **L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub>: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O :PPh<sub>3</sub> : NaN<sub>3</sub>**, and are dark colored amorphous substances. The ligands and their complexes were insoluble in water but soluble in most organic solvents<sup>(35-40)</sup> such as methanol, ethanol, acetone, chloroform, DMF, DMSO and pyridine giving stable solutions<sup>(41-49)</sup> at room temperature. The elemental analysis and other measurements shown in the Table.(3)

**Table. 3: The analytical and physical data of the ligands and their complexes**

S.	Chemical Formula	M. Wt	m.p. °C	Yield%	Color	(Found) / Calculated (%)			
						C	H	N	M
L1	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> O	354.40	102-103	73	Deep orange	74.43 74.56)(	5.03 5.11)(	15.62 15.81)(	-
L2	C <sub>23</sub> H <sub>18</sub> N <sub>4</sub> O	366.42	204-205	77	Orange	75.11 75.39)(	4.79 4.95)(	15.08 15.29)(	-
L3	C <sub>21</sub> H <sub>15</sub> N <sub>5</sub> O <sub>2</sub>	369.38	209-211	75	Light orange	67.07 68.28)(	4.01 4.09)(	18.73 18.96)(	-
L4	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub>	338.41	225-226	70	Light orange	77.78 78.08)(	5.21 5.36)(	16.29 16.56)(	-
1a	C <sub>58</sub> H <sub>48</sub> N <sub>10</sub> OP <sub>2</sub> Cu	1026.56	185-187	79	Deep brown	67.64 67.86)(	4.59 4.71)(	13.38 13.64)(	6.08 6.19)(
2a	C <sub>59</sub> H <sub>48</sub> N <sub>10</sub> OP <sub>2</sub> Cu	1038.57	136-138	75	Violet	68.10 68.23)(	4.45 4.66)(	13.18 (13.49)	5.86 6.12)(
3a	C <sub>57</sub> H <sub>45</sub> N <sub>11</sub> O <sub>2</sub> P <sub>2</sub> Cu	1041.53	116-117	78	Deep violet	65.42 65.73)(	4.18 4.35)(	14.52 14.79)(	5.89 6.10)(
4a	C <sub>58</sub> H <sub>48</sub> N <sub>10</sub> P <sub>2</sub> Cu	1010.56.	220	78	Deep brown	68.61 )68.93(	4.61 )4.79(	13.54 )13.86(	6.13 )6.29(

### IV. Conductivity measurement:

The conductivity values of the chelate complexes in ethanol at concentration of (10<sup>-3</sup> mol L<sup>-1</sup>) are in unit (S. cm<sup>2</sup>. mol<sup>-1</sup>). This indicates that they are non electrolytes<sup>(28)</sup>. The results of conductivity measurements are presented in Table.4.

Table. 4 : Data of Molar conductivity of complexes.

S.	Complex	$\Lambda_m$ (s.mol <sup>-1</sup> .cm <sup>2</sup> ) In (DMSO)
1a	[Cu(L <sub>1</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	11.58
2a	[Cu(L <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	13.33
3a	[Cu(L <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	12.54
4a	[Cu(L <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]	12.96

V. Mass spectrum:

The most important peaks in the mass spectral data of tow ligands, The base peak of ligand at 368, 338 m/z is due to the mother ion of L<sub>3</sub> and L<sub>4</sub> respectively. The different competitive fragmentation pathways of ligand give the peaks at different mass numbers at 340, 310 m/z product from rearrangement loss of N<sub>2</sub> from the azo group<sup>(54)</sup> in both tow ligands (L<sub>3</sub> and L<sub>4</sub> respectively). Also we found in two mass spectral data of tow ligands peaks at 220 m/z corresponding to 4,5-diphenylimidazole<sup>(55)</sup>. In (Fig.6 ) and (Fig.7 )

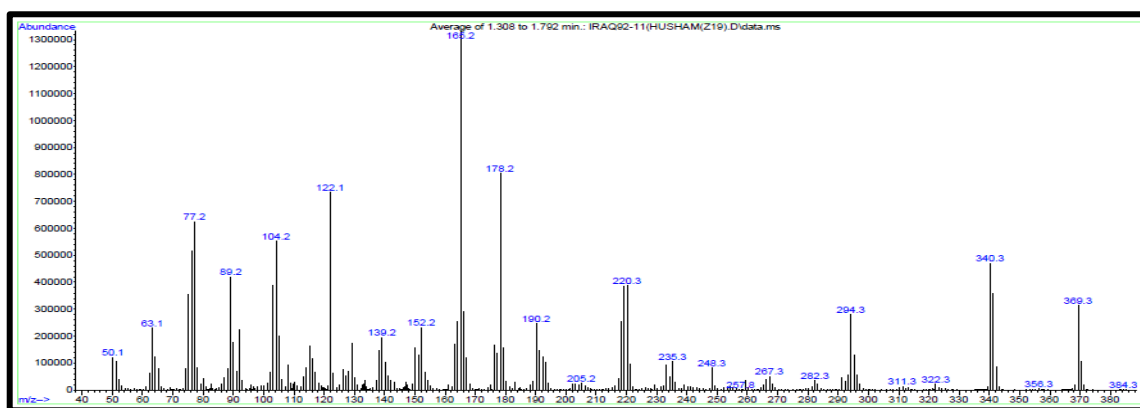


Figure 6: mass spectrometry of (L<sub>3</sub>)

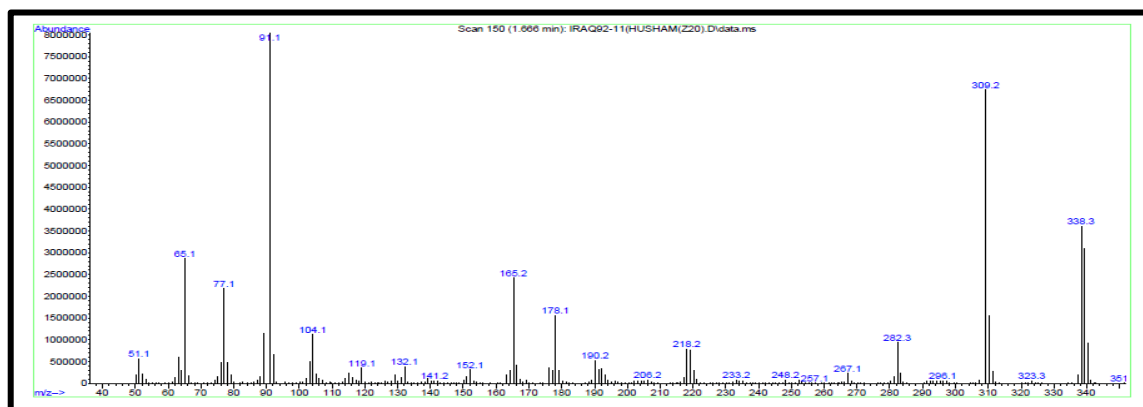
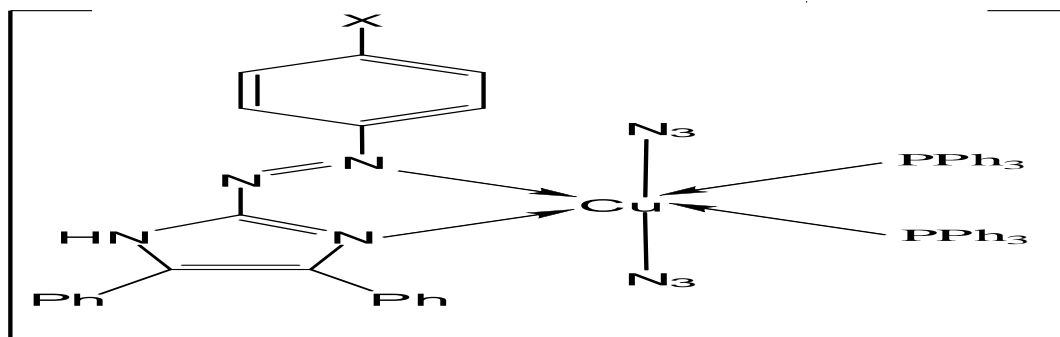


Figure 7: mass spectrometry of (L<sub>4</sub>)

#### 4. CONCLUSIONS

In the present study, the preparation and identification of Cu(II) mixed ligand complexes of azo imidazole compounds with  $\text{PPh}_3$ ,  $\text{N}_3^-$  and  $\text{NCS}^-$  as co-ligand have been carried out by elemental analyses, UV-Vis and IR spectral studies. Electronic spectral data and magnetic susceptibility measurements support octahedral geometry of the complexes.



X =  $-\text{OCH}_3 = \text{L}_1$  or  $-\text{COCH}_3 = \text{L}_2$  or  $-\text{NO}_2 = \text{L}_3$  or  $-\text{CH}_3 = \text{L}_4$

Figure 8: The suggested geometry of Cu(II) Chelate complexes

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