

# Synthesis, Characterization and X-ray Spectroscopic studies of copper (II) complexes with pyrimidine based ligand derivatives

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**Abstract - Synthesis, characterization and X-ray K-absorption spectra of copper (II) complexes with Pyrimidine based ligand have been studied in the present communication. Using Seifert X-ray generator and Cauchouis type bent crystal X-ray Spectrograph of 0.4m radius has done X-ray studies. In the present study elemental analysis, XRD, SEM, IR Spectra, <sup>1</sup>HNMR and Electronic spectra and the K-absorption parameters like chemical shift, shift of principal absorption maximum, edge width, percentage covalency, effective nuclear charge have been used to explain the structure of complexes. The aim of this study is to preparation and their structure characterization with copper metal complexes.**

**Keywords: copper (II) complexes, Pyrimidine, XRD.**

## INTRODUCTION

In recent years considerable interest has developed in the coordination chemistry of copper (II) with heterocyclic ligands. Nitrogen, oxygen, and sulphur containing heterocyclic compounds have received considerable attention from the physical, chemical as well as the wide range of pharmacological activities. Pyrimidine-based heterocyclic compounds are of interest as potential bioactive molecules and exhibit analgesic,<sup>[1]</sup> antihypertensive,<sup>[2]</sup> antipyretic,<sup>[3]</sup> antiviral<sup>[4]</sup>, and antiinflammatory activities.<sup>[5]</sup> These are also associated with nucleic acid, antibiotic, antimalarial, anticancer drugs<sup>[6]</sup>. Many of the pyrimidine derivatives are reported to possess potential CNS depressant properties<sup>[7]</sup>. There are few reports concerning pyrimidine condensed with oxygen heterocycles<sup>[8, 9]</sup>. Thus, interest in the metal complexes of pyrimidines has arisen for the following reasons: Firstly, as a result of antitumor activity of some metal complexes<sup>[10]</sup>, Secondly, the growing interest in studies of metal-pyrimidine complexes has led to investigating the bonding mode of the ligand to metal ion, as they possess divergent bonding sites. Moreover, analogues of pyrimidines have been reported to be associated with diverse biofunctions such as immunosuppressant and as anticonvulsant drugs<sup>[11]</sup>. In continuation of our studies on the synthesis and characterization of metal complexes, we have prepared a variety of metal complexes of pyrimidines coordinated to Arylazopyrimidine. The present work is a sequel to investigation of metal ion-ligand ion interactions<sup>[12]</sup>. This paper describes the synthesis, characterization and X-ray absorption studies of this type of complexes. The X-ray absorption spectra are sensitive to the electronic configuration of the absorbing atom, because the spectra occur due to the electronic transition from inner electronic levels to the vacant molecular orbital levels of appropriate symmetry. The position of the X-ray absorption edge in the spectrum depends upon the valency of the absorbing ion, the effective charge on the absorbing atom also on the type and geometry of the complexes<sup>[13, 14]</sup> etc. X-ray absorption spectra have been analyzed in two parts. Near edge X-ray absorption fine structure (NEXAFS) covering energy range up to ~50eV and extended absorption fine structure (EXAFS) that extends to ~1000eV above an absorption edge of the particular sample. NEXAFS is powerful technique for the study of the complexes because much useful information can be obtained on the geometric and electronic structure around X-ray absorption atom<sup>[15]</sup>. It also contains information on bound state electronic transition and multiple scattering resonances associated with a given absorption edge. X-ray absorption spectra are sensitive to chemical condition of the absorbing atom under investigation. The X-ray absorption technique has been devolved as a powerful tool for investigating the geometrical structure of the polyatomic and amorphous materials and complexes. Therefore, much attention has been paid by different workers<sup>[15]</sup> in measuring the change in the position of main edge, and the X-ray parameters. Our XAFS studies on some transition metal complexes provide useful information about the structure of the metal complexes as well as the absorbing atom.

The aim of investigation has to measure X-ray K-absorption spectra of 5 copper complexes namely- Cu (PCL) Cl<sub>2</sub>, Cu (MNL) Cl<sub>2</sub>, Cu (OCL) Cl<sub>2</sub>, Cu (MCL) Cl<sub>2</sub>, Cu (ONL) Cl<sub>2</sub>, here L stands for 6-Methyl-5-arylhydrazono-2thio-4-oxo-pyrimidine and P, O and M are substitute anilines. The study was also intended to provide useful information on the effects of different ligands on the position, shape and fine structure of the K-absorption edge in these copper complexes.

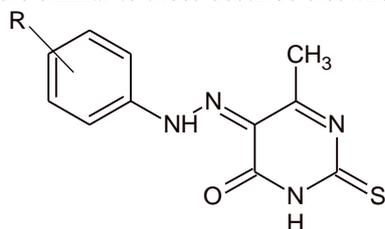
## EXPERIMENTAL TECHNIQUE

### Materials and methods

Elemental analyses (C, H, N, S) were performed by using a Carlo Erba 1160 elemental analyzer. Melting points were recorded in open capillaries and are uncorrected. Grain size of the powdered sample was measured by X-ray diffractometer (Philips X-pert pro diffractometer, PW 1830) at room temperature with CuK $\alpha$  radiation. Surface morphological study was observed by scanning

electron microscopy (SEM, Philips XL 30). IR spectra were recorded using a Perkin-Elmer instrument (using KBr disks, 4000-400 $\text{cm}^{-1}$ ). Electronic spectra were recorded on Shimadzu UV analyzer.

For X-ray absorption studies, the absorption screens were prepared by spreading uniformly the powdered sample of 1sq cm area of cellophane tape. Another piece of cellophane tape was put over it, sealing off the substance in between. The screen which gave the best spectra were found to have generally the thickness of the order of 15 to 30  $\text{mg}/\text{cm}^2$  in the case copper complexes. The thickness and uniformity of the absorption screen play an important role in obtaining good spectrograph. EXAFS study were carried out on Seifert sealed X-ray tube with a tungsten target operating at 16kV and 55mA. A 0.4m radius Cauchois type curved crystal transition spectrograph in its improved form was used to record the spectra. A mica crystal, which is optically pure and free from deformities, was used, as diffracting crystal. the experimental arrangement and the technique for X-ray spectroscopic measurements were similar to those describe elsewhere <sup>[15]</sup>.



**Figure 1.** Structure of the ligand (R=P Chloro, M Nitro, O Chloro, M Chloro, O Nitro)

### Synthesis of the Ligand

All complexes were prepared in a similar way by the usual diazotization process <sup>[16]</sup>.

6-Methyl-5-arylhydrazono-2thio-4-oxo-pyrimidine (ligand) were prepared by dissolving (0.01 mol) of Aniline in a mixture of concentrated hydrochloric acid (3ml) and water (4ml) and cooled to 0-5°C in ice bath. To it a cold aqueous solution of sodium nitrite (0.01mol) was then added. The Diazonium salt so obtained was filtered into a cold mixture of sodium acetate (7gms) and ethylacetoacetate (0.01mol) in ethanol (25ml) the resulting solid is 1-ethoxy-2-arylhydrazono-butene-1, 3dione was washed with water and dry it. Now 1-ethoxy-2-arylhydrazono-butene-1, 3dione of (0.01mol) and thiourea (0.01mol) dissolved in (10ml) Sodium ethoxide mixture (freshly prepared) in a 1 liter round bottomed flask. Then fit a reflux condensers to the flask, introduced a few fragments of broken porcelain pieces for boiling the mixture for 30mins, few crystals are appear after 15 minutes and gradually increase in amount as the refluxing is continued. Cool the flask in ice and filter the solution and dry it.

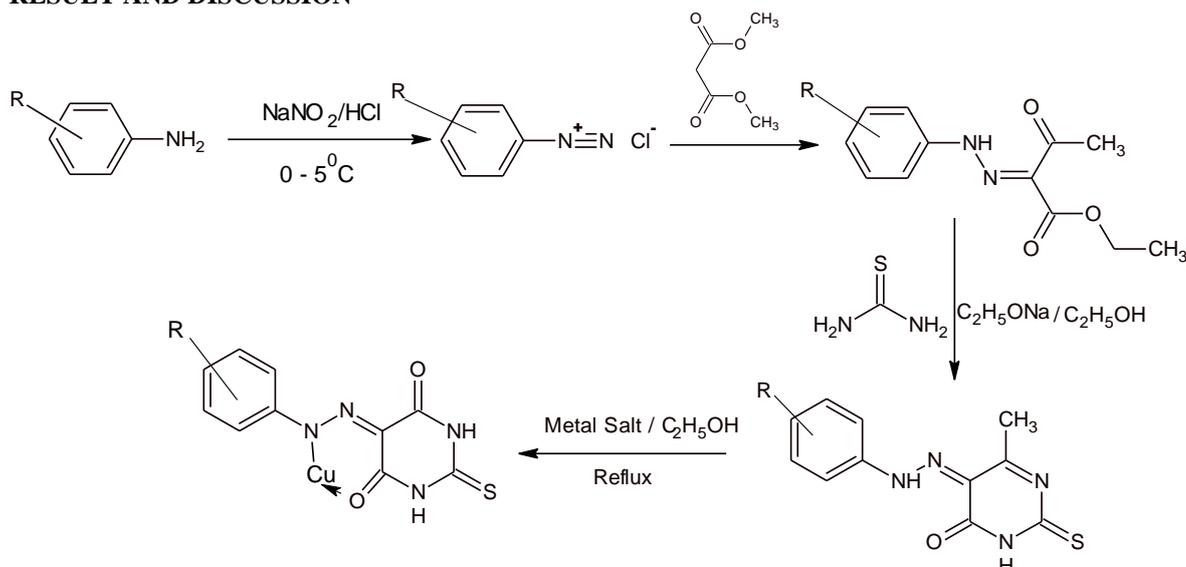
### Synthesis of the complexes

An ethanolic (10ml) solution of ligand (6-Methyl-5-arylhydrazono-2thio-4-oxo-pyrimidine) was mixed with metal Cu (II) chloride in ethanol (10ml) solution keeping Ligand-metal ratio 1:1. The mixture was stirred for  $\approx 1$  hour. Stirring was then continued until the complex precipitated out. The solid product thus formed was filtered, washed several times with methanol and dried in vacuo. In all five prepared complexes, presence of copper is confirmed by X-ray fluorescence (XRF) and X-ray diffraction (XRD). The synthetic and analytical data of the resulting complexes are recorded in Table 1. For metal, hydrogen, sulfur, nitrogen agrees with the theoretical values within the limit of experimental error.

**Table 1.** Analytical data for elemental analysis of complexes

Complex	Molecular Formula	Yield %	Melting Point	Elemental analysis calculated (Found)%				
				C	H	N	S	Metal salt
Cu(PCL)Cl <sub>2</sub>	[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCl)Cl <sub>2</sub> ]	75	220	34 (34.02)	2.85 (2.87)	12.20 (12.22)	6.98 (6.7)	13.84 (13.82)
Cu(MNL)Cl <sub>2</sub>	[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> S)Cl <sub>2</sub> ]	73	240	40.78 (40.77)	3.42 (3.41)	18.29 (18.28)	8.37 (8.36)	16.60 (16.59)
Cu(OCL)Cl <sub>2</sub>	[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCl)Cl <sub>2</sub> ]	65	200	34 (34.02)	2.85 (2.87)	12.20 (12.22)	6.98 (6.7)	13.84 (13.82)
Cu(MCL)Cl <sub>2</sub>	[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCl)Cl <sub>2</sub> ]	82	240	34 (34.02)	2.85 (2.87)	12.20 (12.22)	6.98 (6.7)	13.84 (13.82)
Cu(ONL)Cl <sub>2</sub>	[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> S)Cl <sub>2</sub> ]	78	200	40.78 (40.77)	3.42 (3.41)	18.29 (18.28)	8.37 (8.36)	16.60 (16.59)

## RESULT AND DISCUSSION

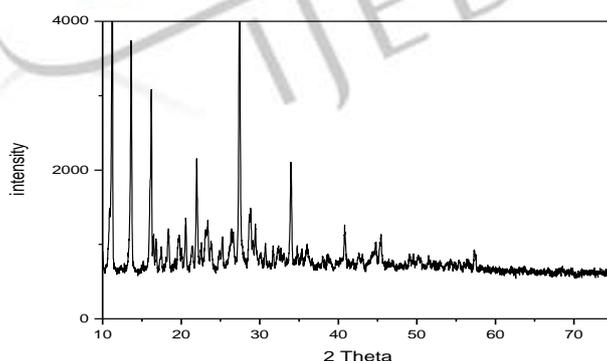


**Synthetic path way for the ligands and metal complexes, here R is- P Chloro, M Nitro, O Chloro, M Chloro, O Nitro.**

Formation of the metal complexes can be represented by the following general equations  $\text{MX}_2 + 2\text{L} \rightarrow [\text{M}(\text{L})_2\text{X}] + \text{X}$ . In this equation, M is Cu (II) and X is Cl and L is [6-Methyl-5-arylhydrazono-2-thio-4-oxo-Pyrimidine]. All complexes are stable at room temperature.

### Spectral Characterization XRD

The sample was characterized at room temperature by X-ray diffraction using Cu K $\alpha$  radiation. The X-ray diffraction patterns of the complexes are indicative of crystalline nature. The diffraction pattern of complexes recorded between  $2\theta$  ranging from  $10^\circ$  to  $75^\circ$ . The crystalline size of the samples is estimated using the Scherrer's formula  $D = k\lambda / \beta_{2\theta} \cos\theta$ , here k is a constant taken to be 0.94,  $\lambda$  the wavelength of X-ray used ( $\lambda = 0.154 \text{ nm}$ ) and  $\beta_{2\theta}$  full width at half maxima of all peaks of the XRD patterns  $\theta$  is Bragg angle. The diffraction patterns have been successfully indexed [17]. The value of the crystalline size is shown in Table 2. The crystalline size was found to be within in the range 22.87-56.53 nm. It is observed that crystalline size is different for every samples, due to change in the R position. The XRD patterns are shown in Figure 2.



**Fig 2. X-ray diffraction patterns of Cu(PCL)Cl<sub>2</sub>**

**Table 2. Values of grain size and band gap energy**

Spectral Features	IR $\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )	$^1\text{HNMR}$ ( $\delta$ ppm)	UV-VIS

Ligand	3487(NH), 1678(C=O), 1585(C=C/C=N), 1263(C=S) 760-540(C-Cl)	2.09(s, 3H,CH3), 10.38(s, 1H,NH), 7.20-8.40(m, 6H,Ar-H)	$\lambda_{\max}$ = 327(nm)
Copper metal	3487(NH), 1683(C=O), 1575(C=C/C=N), 1199(C=S) 760-540(C-Cl), M-O (437) M-N (526), M-Cl (254)	2.09(s, 3H,CH3), 10.38(s, 1H,NH), 7.20-8.40(m, 6H,Ar-H)	$\lambda_{\max}$ = 583(nm)
Cobalt Metal	3487(NH), 1683(C=O), 1575(C=C/C=N), 1199(C=S) 760-540(C-Cl), M-O (437) M-N (526), M-Cl (254)	2.09(s, 3H,CH3), 10.38(s, 1H,NH), 7.20-8.40(m, 6H,Ar-H)	$\lambda_{\max}$ = 476(nm)

### Surface morphology

The SEM images of the samples are shown in the figure 3. From the figure it can be seen that the average length of the crystals for the samples are 2  $\mu\text{m}$  - 6  $\mu\text{m}$  avg particle size respectively. Also, it can be seen that there are some void spaces. The surface morphology changes with change in substituted anilines, all the images having large number of irregular shaped and some having regular crystals are associated with the images shown in figure. The values of grain size measured from SEM images are presented in table 2. It is quite clear from the results that the average grain size estimated by SEM is quite larger than the average grain size measured by XRD.

Cu(PCL)Cl<sub>2</sub>Cu(MNL)Cl<sub>2</sub>Cu(OCL)Cl<sub>2</sub>Cu(MCL)Cl<sub>2</sub>Cu(ONL)Cl<sub>2</sub>

Fig 3. SEM images for copper complexes.

### IR SPECTRA

The IR spectra of all complexes were performed at field between 4000–400  $\text{cm}^{-1}$ , along with tentative assignments. In all the metal complexes the presence of a single medium band in the region 3,250–3,350  $\text{cm}^{-1}$  in the spectra of all complexes may be assigned due to N–H stretch [18, 19]. The bands at 1580-1590  $\text{cm}^{-1}$  due to the azomethine group of the ligand underwent a shift to lower frequency (1581-1495)  $\text{cm}^{-1}$  after complexation, indicating the coordination of hydrazono nitrogen to metal atom and this can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom [20,21]. In addition, the  $\nu(\text{C}=\text{N})$  mode may be coupled with  $\nu(\text{C}=\text{S})$  to give the intense band observed at 1270-1190  $\text{cm}^{-1}$  [22]. The band corresponding to (C=O) at 1680-1690  $\text{cm}^{-1}$  is shifted to lower frequency in the spectra of all the metal complexes. This is clear evidence for coordination by carbonyl oxygen. The vibrations absorption peaks of the  $\nu(\text{M}-\text{N})$ ,  $\nu(\text{M}-\text{Cl})$  and  $\nu(\text{M}-\text{O})$ , which should be at 559-300  $\text{cm}^{-1}$ , as reported by other workers [23, 24] could not be observed since it was beyond the extent of our measurement. Infrared spectral data of the complexes are presented in Table 3.

Table 3. IR data of the Copper metal complexes

Complex	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCI)Cl <sub>2</sub> ]	3493,3203	1684	1572	1572	489	578	300
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> S)Cl <sub>2</sub> ]	3478,3365	1680	1581	1495	430	559	315
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCI)Cl <sub>2</sub> ]	3446,3354	1690	1495	1495	457	596	312
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCI)Cl <sub>2</sub> ]	3487,3444	1681	1495	1495	444	590	320
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> S)Cl <sub>2</sub> ]	3407	1689	1575	1575	463	587	305

### ELECTRONIC SPECTRA

The spectrum of the free ligand exhibits three absorption bands at about 225–260, 330–365, and 440–485 nm region. The complexes yield peaks at approximately 295–370 nm region, which may be attributed to the  $\pi \rightarrow \pi^*$  transitions of the ligand according to their positions and molar absorption coefficient. The absorption and strength of UV spectral in the spectrum of the ligand and complexes are different, indicating that ligand coordinates to metal ions, which is in accordance with the results of IR spectra.

The band gap energies of the samples were calculated from the absorption edges of the spectra. The slope drawn from the start of an absorption edge (the onset of absorbance) and horizontal tangent had drawn on absorption minimum and intercepted each other at some point. The vertical line drawn from this point on wavelength axis gave the absorption edge wavelength. This value of wavelength (nm) was then used in the following relation to know band gap energy,  $E_g$ .

$E_g = hv = hc/\lambda = 1240/\lambda \text{ (nm)} \text{ eV}^{[25]}$ . The values of the band gap energy are different for each complex as shown in Table 2. These values are different due to change in environment of every complex.

### <sup>1</sup>HNMR

To have a better understanding regarding the structure of the pyrimidine ligand and copper (II) complexes, <sup>1</sup>H NMR studies were carried out. Peak assignment was made on the basis of the peak integration and multiplicity. The <sup>1</sup>H NMR spectra of the ligand exhibits peaks at  $\delta(7.6-8.3)$  ppm assigned to the aromatic protons. The signals due to the methyl proton (N=C-CH<sub>3</sub>) were observed at  $\delta(2.5-2.4)$  ppm. The NH protons show the signal at  $\delta(10.8-10.7)$  ppm respectively. On complexation with copper metal there was a shift in the NH proton the peaks were observed at  $\delta(10.5-10.4)$  ppm indicating the bonding of the carbonyl oxygen with the metal ions in these complexes.

### X-ray K-absorption spectral studies

#### (1) Chemical shift

The chemical shift in X-ray absorption spectra is defined as the energy shift of the absorption edge of a metal in a compound or complexes to the edge position in metallic state i.e.

$$\Delta E_K = E_{\text{compound}} - E_{\text{metal}}$$

where,  $E_{\text{Compound}}$  is energy position of the edge of a compound and  $E_{\text{metal}}$  is energy position of edge of metal.

In our investigation we have found that K-absorption edges of five copper complexes are found towards higher energy side. <sup>[26]</sup>

The order of the chemical shift for complexes indicated by their observed value is as follows.

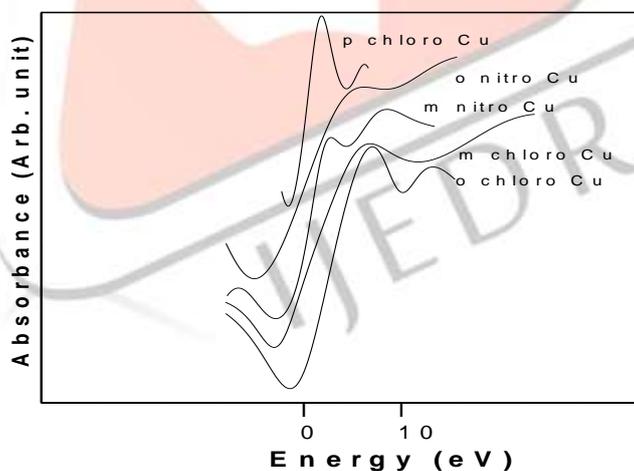


Fig 4. K-absorption discontinuity of five copper complexes

Chemical shift is towards the higher energy side of the metal edge <sup>[26]</sup> and it increases progressively with increases in the valence cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding. When the ligand is attached to copper metal, the chemical shift is higher and its value is ranging from 10.7eV to 13.38 eV. It is well known that the edge shift is proportional to the ionicity, therefore large chemical shift indicating that complexes are more ionic in nature. Further, shift in the case of ionic compound are larger ( $>>10\text{eV}$ ) than those for the covalent compounds ( $<<10\text{eV}$ )<sup>[27]</sup>. Since all these complexes have the central atom in +2 oxidation state surrounded by number of arranged in this same stereo chemical environment. It has been found that such complexes possess high covalent character as compared to other. The role of various bonds attached to the central atom copper ion is prominent in determining the overall chemical shift in metal complexes. Further not only legations of particular type Cu-N, is responsible in imparting ionic or covalent character to the complexes, but their planer/axial positions also contributes to the ionic or covalent character. The values reported here reveal that the copper complexes are covalent in nature. They also surrounded by Cu-N hence this confirms the covalent nature of bonding in the complexes.

**Table 4. The experimental values of chemical shift and other X-ray K-absorption parameters for copper (II) complexes.**

Complex	Edge position $E_K$ (eV)	Chemical shift $\Delta E_K$ (eV) $\sim \pm 0.2$ eV	% Covalency	ENC Electron/atom	Shift of Principal absorption maxima (eV)	Edge Width (eV)
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCl)Cl <sub>2</sub> ]	8991.1	10.7	40	1.03	22.4	11.7
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> S)Cl <sub>2</sub> ]	8991.5	11.1	38	1.04	21.0	9.9
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCl)Cl <sub>2</sub> ]	8991.9	11.5	36	1.09	19.1	7.6
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> SCl)Cl <sub>2</sub> ]	8992.8	12.5	33	1.12	23.5	11.0
[Cu(C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> S)Cl <sub>2</sub> ]	8993.7	13.4	31	1.21	20.1	6.7

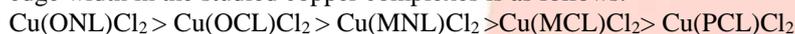
### (2) Shift of principal absorption maximum and Edge width

The X-ray spectroscopic investigations suggest that the order of shift of principal absorption maximum in the studied copper (II) complexes is as follows.



The results reported in the present study shows that, the shift in the principal absorption maximum is on the higher energy side. In the transition metal complexes the principal absorption maximum is known to arise due to the transition of electron from 1s level to vacant higher orbital of appropriate symmetry. For example there are 3 d-d electronic transitions possible <sup>[28]</sup> in a tetragonal complex  $d_{xz} (d_{yz}) \rightarrow d_{x^2-y^2}$ ,  $d_{xy} \rightarrow d_{x^2-y^2}$ ,  $d_{z^2} \rightarrow d_{x^2-y^2}$ . The shift of the principal absorption maximum depends upon the type of overlap between metal and ligand orbital. In our case the results indicated that overlap between the metal and nitrogen will be larger than that between metal and oxygen.

The edge width of K-absorption edge increases with increases in covalent character of the metal ligand bond <sup>[26]</sup>. The edge width of K-absorption edge increases, if the other factor like molecular symmetry etc remains the same <sup>[26]</sup>. The order of edge width in the studied copper complexes is as follows.



The experimental data (Table 4) of edge width of copper metal complexes shows that the edge width varies from 6.74 eV to 11.65 eV. The values reported here shows that these complexes are covalent in nature. The order of the edge width does not match with the order of chemical shift. This is because the edge width does not slowly depend on those factors that are responsible for chemical shift. It is now well established that the octahedral complexes show less edge width values compared to tetrahedral complexes <sup>[27]</sup>. Our values supported octahedral structure. This can also be confirmed when there is no splitting of the main edge in the complexes (see fig 4).

### (3) Chemical shift and percentage covalency-

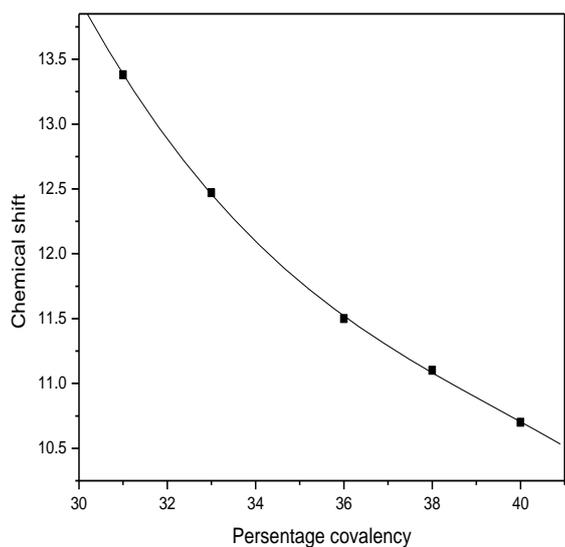
The chemical shift is a measure of degree of covalency. Chemical shift increases with decreases in covalency of copper atom. It can be seen from fig 5a which shows that the relation ship between chemical shift and percentage covalency in metal ligand bonding for copper (II) complexes respectively. By using Clementi's results <sup>[30]</sup> for 1s orbital energy in different oxidation state of copper atom, shift in 1s orbital energy in different oxidation numbers have calculated and a theoretical graph was plotted between shift in binding energy and 1s electron and percentage covalency. The present covalency of metal ligand bonding in copper (II) complexes has been calculated. The results are reported in Table 4 shows that for each complex, increases in covalent nature of bonding causes corresponding shift towards the lower energy side of the metal.

### (4) Chemical shift and effective nuclear charge-

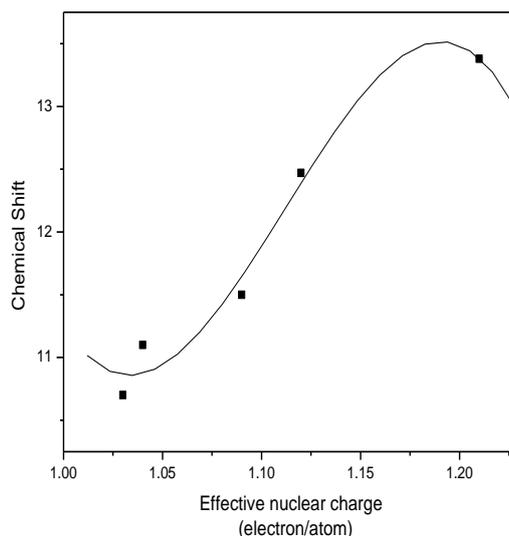
The effective nuclear charge <sup>[28]</sup> on the absorbing ion can be estimated from the measured chemical shift. Effective nuclear charge is the net positive charge experienced by an electron in a multi electron atom, the term effective is used because the shielding effect of negative electrons prevents higher orbital electron from experiencing the full nuclear charge.

The effective nuclear charge <sup>[28]</sup> is a total charge within a certain molecular volume around the nucleus. The effective nuclear charge is correlated with the shift in binding energy (theoretical value) and reported by number of researchers <sup>[26,27,28]</sup>, which can be used to compute effective nuclear charge from observed edge shift. We have used this method for the calculations of effective charge, which can be applied to the complex system. In this method shift in 1s electron energy under different oxidation states of copper is determined using Hartee-Fock-Rothan (HRF) calculations of atomic wave function graph is plotted between shift in binding energy and oxidation number of copper.

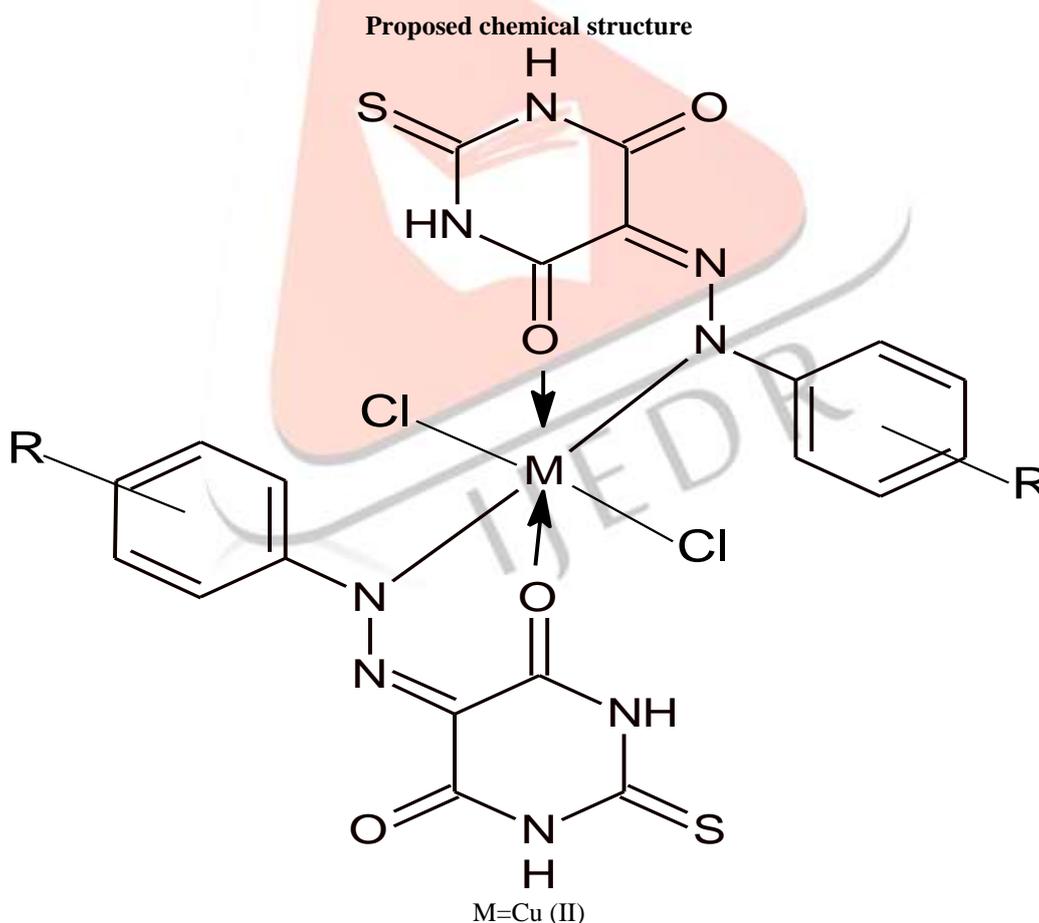
This plot is used to estimate the values of effective nuclear charge corresponding to the measured values of edge shift. The data reported in Table 4 indicate that the effective charge vary from 1.03 to 1.21 electron/atom respectively. This method has been used successfully by various workers <sup>[28]</sup> for computation of effective nuclear charge of the central metal ion. In our present work we observed a parabolic relationship between chemical shift and effective nuclear charge for copper (II) complexes shown in fig5b. Sharma et al <sup>[15]</sup> also observed similar type of relation.



**Fig 5(a) correlation of percentage covalency With chemical shift**



**Fig 5(b) correlation of Effective nuclear charge With chemical shift**



**Figure 6. The proposed chemical structure for the copper metal complexes**

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