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Synthesis and Spectral characterisation of biologically relevant Cu (II) complexes of Schiff base

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Abstract: Few copper (II) complexes of the ligands L_1 = [(p-methyl anilino) -p- methoxy phenyl acetonitrile] and ligands L_2 =[(p-methoxy anilino) -p- methoxy phenyl acetonitrile] have been synthesized . The ligand has been prepared by Strecker's method which included the reaction of p-methoxy benzaldehyde with p-toludine and p-anisidine respectively. The ligands L_1, L_2 act as the primary ligand and nitrate act as a secondary ligand. The data obtained has been preceding using XRD data analysis program Origin 6.0 Professional and XANES by Athena. From the experimental measurements, various parameters- lattice parameter, particle size, chemical shift, edge width, ENC, Percentage covalency have been estimated. Particle size and chemical shift are found to be in the range of nanometers 0.7 to 0.5 and 5 - 10 eV respectively. The XRD analysis revealed the crystalline nature of the complexes and XANES shows the ionic nature of the sample prepared.

***Keywords**: Schiff based complex, TLC, XRD, XANES, p-methoxy benzaldehyde, α-aminonitrile.*

I INTRODUCTION

Nitrile, α-aminonitrile compounds and their derivatives are subjective to have special attention due to their applications. They act as potential ligands for a large number of metal ions it's derivatives are biological active used as herbicides great pharmacological agents and are used in biological synthesis of chemical compounds by its microbial metabolism in some organisms [1]. Complexes containing more than a metal centre represent the synthetic models of ferromagnetic interaction between the metal centres which can explain oxidation- reduction processes in biological systems in addition to their catalytic and biological activities [2].Besides that, some aminonitriles were used to prepare racemic compounds[3].A search through literature reveals that there is no work has been done on the XRD of transition metal complexes of the L. Keeping this in view, the present paper describes the results of the synthesis and the XRD characterization- of new metal complexes of some transition metal ions Cu (II) of L [(p-methyl anilino) –p- methoxy phenyl acetonitrile] .

The notion of the present work is to synthesize the Schiff base metal complex in order to investigate spectroscopically and to study their crystalline structure at the local scale. The purpose of finding the parameters by XANES is to make a platform to study future in biological activity on the basis of that one can predict the chemical behaviour of sample on the basis of parameters.

The present paper has eight sections, in which Section 1 provides brief introduction and the importance of the Cu (II) complexes of Schiff base. Section II, III, IV, V and VI provides the materials & methodology, experimental techniques for the preparation, characterization of the ligands and their metal complexes using X Ray Diffraction Spectroscopy and XANES, respectively. Section VII gives details of the results and discussion and finally Section VIII presents the conclusions drawn from the ongoing investigations.

II. METHODOLOGY

MATERIALS :-All reagents used were analytical grade purity. All metal salts of Cu (II) 99% (Merck), p-methoxy benzaldehyde 99% (Merck), glacial acetic acid 99% (Merck), concentrated H_2SO_4 99% (Merck), ethanol absolute 99% (Fluka) were used as received from the suppliers. p-toludine and p-anisidine sulfonic acid were supplied by R K Synthesis ltd. All chemicals have been prepared by Strecker's method [4].

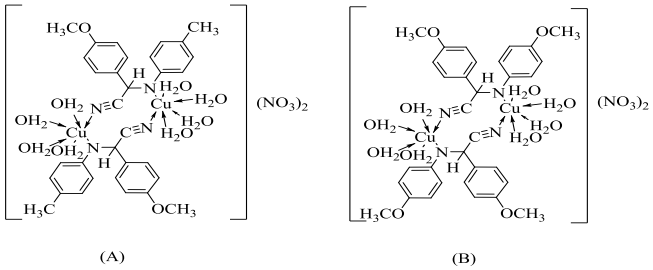
III PREPARATION OF LIGAND (L)

The aldehyde p-methoxy benzaldehyde 0.05 moles was dissolved in 50 ml of glacial acetic acid, toludine sulfonic acid was added in small portions to bring the pH to 2, followed by the additions of 0.05 moles of the amine. The pH was adjusted to 3-4 by adding concentrated H_2SO_4 drop wise.

KSCN 0.05 mole was added to the mixture which was kept stirring. The end of the reaction was checked by the disappearance of the starting material (the amine) and development of a higher spot on T.L.C. The reaction mixture was poured on ice and made slightly alkaline with ammonia. The solid product was filtered, washed with water and dried.

IV PREPARATION OF COMPLEX OF LIGAND L

A solution of a salt of the metal (II) in absolute ethanol was added to an ethanolic solution of the ligand with a continuous stirring. The molar ratio of the reactants was 2:2. Precipitation of the complex took place immediately. The product was filtered off, washed several times with ethanol and dried under vacuum[5].



(A) (B)

Fig.1. Structure of metal complexes (A) [*Octaaqua-di-μ-{(p-methyl anilino)-p-methoxy phenyl acetonitrile} dicopper(ll)]Nitrate*] and (B) [*Octaaqua-di-μ-{(p-methoxy anilino)-p-methoxy phenyl acetonitrile} dicopper(ll)]Nitrate*]

V X-RAY DIFFRACTION

The sample is irradiated with a beam of monochromatic x-rays over a variable incident angle range. The X-rays were produced using a sealed tube and the wavelength of X-ray as 0.154nm (Cu K-alpha) having voltage 40kV and current 100mA.The X-rays has been detected using a fast counting detector based on silicon strip technology (Bruker Lynx Eye detector). Interaction with atoms in the sample results diffracted x-rays when the Bragg equation is satisfied[6]. The XRD patterns were recorded on Bruker D8 Advanced X-ray diffractometer. XRD is a resourceful, non-destructive technique that gives the perfect information about the chemical composition and crystallographic structure of materials[7]. The samples were characterized at room temperature by X-ray diffraction using Cu Kα radiation. The pattern has been indexed using Joint Committee for Powder Diffraction (JCPDF) software.

VI X-RAY ABSORPTION NEAR EDGE STRUCTURES (XANES)

The X-ray absorption spectra at the K-edge of copper and it's mixed ligand copper (II) complexes have been recorded at the Dispersive Extended X-ray Absorption Fine Structure (DEXAFS) beam line, by Applied Spectroscopy Division, BARC. This beam line BL-8 has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation source. To select a band of energy from the white synchrotron beam, a bent crystal (Si 111) polychromator is used in this beamline, which is horizontally dispersed and focused on the sample. A position sensitive CCD detector is used to record the transmitted beam intensity from the sample, thus the whole EXAFS spectrum around an absorption edge takes place in a single shot. The experimental data have been analysed using the available computer software packages Athena, Hephaestus and Origin 6.0.

VII RESULT & DISCUSSION

All the samples are characterized at room temperature by X-ray diffraction using Cu Kα radiation. The diffraction pattern of the complexes is recorded between 2θ ranging from 10° to 80°. The particle size of the samples is estimated using the Scherrer's formula[8].

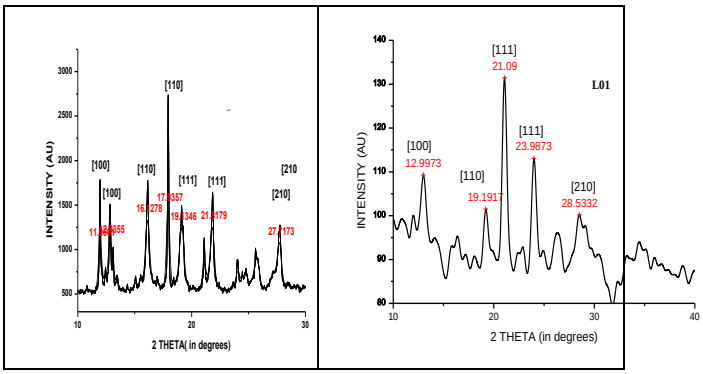


Figure 2: X-Ray diffraction pattern of metal (II) complexes of L.

L_1 (Ligand):- ($C_{16}H_{16}N_2O$) [(p-methyl anilino)-p-methoxy phenyl acetonitrile]

L2 (Ligand):-($C_{16}H_{16}N_2O_2$)[(p-methoxy anilino)-p-methoxy phenyl acetonitrile]

The particle size is given by Scherrer's equation

$$t = \frac{0.9\lambda}{B\cos\theta} \quad \text{..... (4.1)}$$

Where t is the crystal thickness (in nm), B is half width (in radians), θ is the Bragg angle and λ is the wavelength. The particle size corresponding to each diffraction maxima is determined from the measurement of the half width of the diffraction peak (FWHM).

Lattice parameter for simple cubic crystal structure is determined by

$$a^2 = \frac{h^2 + k^2 + l^2}{4\sin 2\theta} \quad \text{.....(4.2)}$$

The value of Lattice parameter and the particle size are shown in 'table 1' for both the complexes.

Table-1

Calculated Lattice Parameter and particle size of metal (II) Complexes of series I

S.No.	Complexes	Lattice Parameter a(nm)	Particle Size t (nm)
1.	$[Cu_2(L_1)_2(H_2O)_8](NO_3)_2$	.04	0.7
2.	$[Cu_2(L_2)_2(H_2O)_8](NO_3)_2$	0.03	0.5

The The range of particle size (a) for the series is 0.03 to 0.04 (nm)

$$a_{[Cu2(L2)\ 2(H2O)8](NO3)2]} < a_{[Cu2(L1)\ 2(H2O)8](NO3)2}$$

The range of thickness (t) for the series is 0.53 to 0.72 (nm)

$$t_{[Cu2(L2)\ 2(H2O)8](NO3)2]} < t_{[Cu2(L1)\ 2(H2O)8](NO3)2}$$

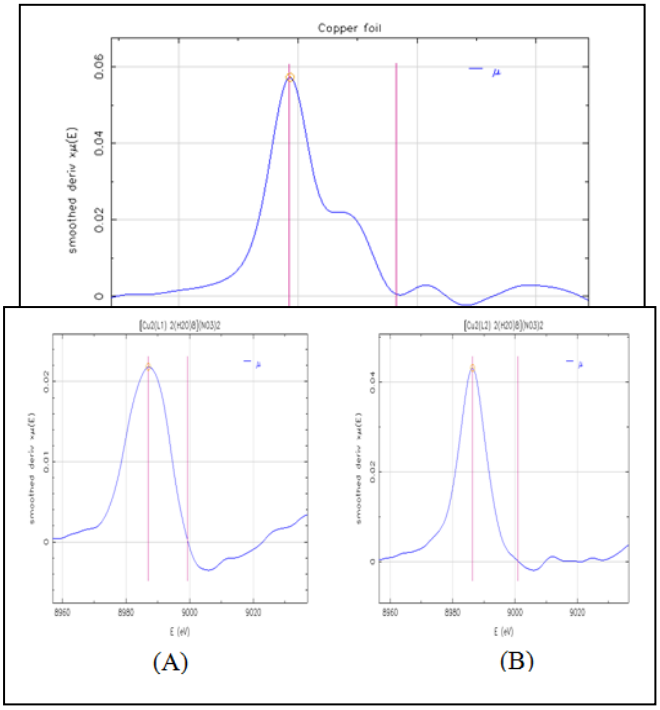


Figure 3 ; Derivatives of the Copper foil & its Complexes

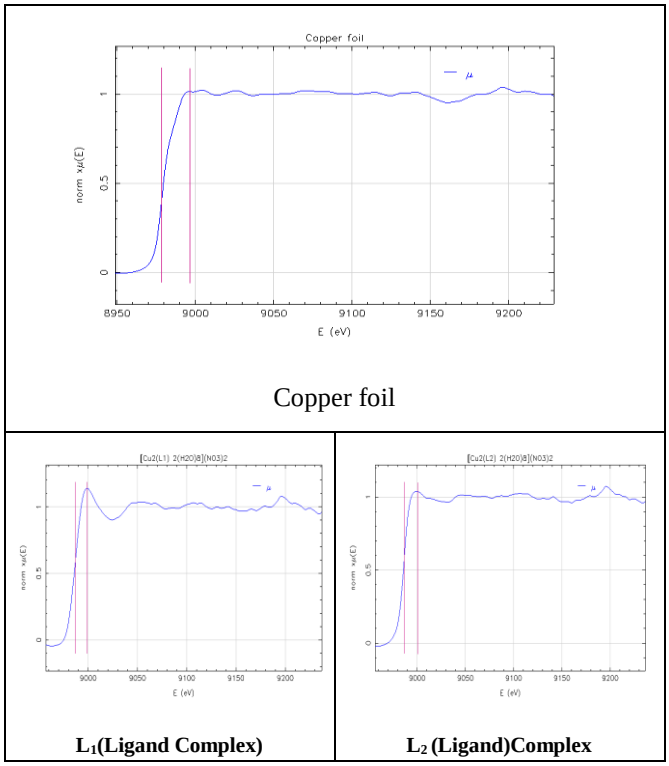


Figure 4 ; Normalised graphs of the Copper Foil & its Complexes

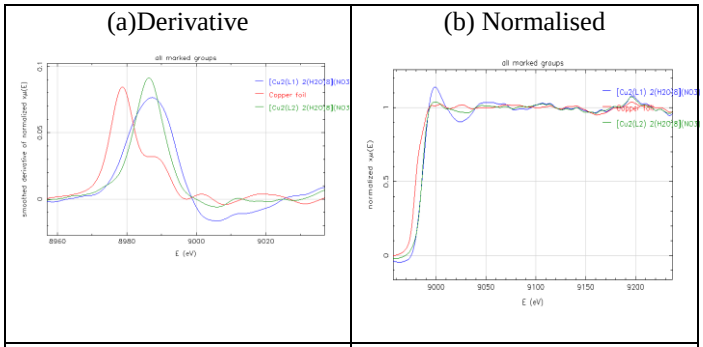


Figure 5 Comparative spectra of Copper & it's Complexes

The range of Chemical shift and Shift of principal absorption maxima is 7.8 to 8.4eV and 20.7 to 22.4 eV respectively. For the complexes, the range of the shift of the principal absorption maximum is between 20.7 to 22.4 eV. Edge widths decreased with respect to pure metal foil almost 6-3 eV. i.e (B) complex is less ionic than the (A) .The chemical shift has been used to determine the effective nuclear charge of the absorbing atom. For all the complexes, the range of effective nuclear charge is between 0.58-0.54 electron/atom. The chemical shift has also been used to determine the percentage covalency on the absorbing atom. For both the complexes, the range of percentage covalency is between 43 - 50 % approx. The shift of the principal absorption maximum

has been obtained. The shift of the Principal absorption maximum is inversely proportional to the ionic character for these complexes.The edge-width has also been obtained for the complexes. It is clear that the edge-width is inversely proportional to ionic character for these series of complexes[9]. For both the complexes, the range of edge-width is between 12.4 – 14.6 eV. i.e B is less ionic than A.which is also verified by shift in principal absorption maxima values.

Table 2
XANES parameter of the Copper & its complexes

Complexes	E_K (eV)	E_A (eV)	Chemical shift (eV)	Shift of principal Absorption maxima (eV)	Edge - width (E_A-E_K) (eV)	ENC Electron / Atom	% covalency
Copper metal	8978.6	8996.5	-	-	17.9	0	61.8
[Cu_2(p-Methyl ben) (p-Tolu)](NO_3)$_2$	8986.9	8999.3	8.4	20.7	12.4	0.58	42.6
[Cu_2(p-Methoxy ben) (p-Ani)](NO_3)$_2$	8986.4	9000.9	7.8	22.4	14.6	0.54	50.2

VIII. CONCLUSION

In summary, copper (II) metal complexes were prepared with chemical active ligands, namely nitrile and α-aminonitrile derivatives using a standard method named Strecker's metod at room temperatures. The XRD pattern is indicative of crystalline in nature which is confirmed by the main peaks positioned Obtained for synthesised complexes. B te multiple peak in pattern it sows te sample is polcrstalline. XRD analysis informs about the particle size in **(nm) &** lattice parameter in **(nm)** for [*Cu (II)*] complexes. The range of particle size (a) for the samples: 0.03 to 0.04 (nm) & the range of thickness (t) is 0.5 to 0.7 (nm) approx respectively.

$$\mathbf{a}_{[Cu2(L2)\ 2(H2O)8](NO3)2} < \mathbf{a}_{[Cu2(L1)\ 2(H2O)8](NO3)2}$$
$$\mathbf{t}_{[Cu2(L2)\ 2(H2O)8](NO3)2} < \mathbf{t}_{[Cu2(L1)\ 2(H2O)8](NO3)2}$$

The main conclusion is that the behaviour of the same metal salt is different with the different ligand ($C_{16}H_{16}N_2$) [(p-methyl anilino) -p-methoxy phenyl acetonitrile] & ($C_{16}H_{16}N_2O$) [(p-methoxy anilino) -p-methoxy phenyl acetonitrile] from aldehyde group. After complex formation each sample has different lattice parameter as well as their thickness. The lattice parameter is least in Copper complex with ligand L_2 while it is highest for the copper with L_1 Similarly for the thickness . The X-ray analysis reveals that the sample is cubic in structure as seen from the presence of extra peaks in XRD pattern. All the peaks match with the software JCPDF.

The chemical shift for the complexes is positive means it needs more energy for excitation than pure metal . The order of chemical shift in each of complexes may also be taken as representative of the relative ionic character of the bonding[10] in these complexes i.e later complex is less ionic than first one .The values of the chemical shifts lie in between 7.8 to 8.4 eV which suggests that copper is in oxidation state +2[11].

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