XRD ANALYSIS OF TRANSITION METAL COMPLEXES OF SUBSTITUTED HETEROCYCLIC CHALCONES

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ABSTRACT

Five metal complexes of chalcones containing metal ions Cu(II), Co(II), Ni(II), Fe(II) and Zn(II) were synthesized. The ligands were obtained from substituted acetophenone and pyridine / Pyrrole 2-Carboxaldehyde, the ligands are 1-(2'-Hydroxy-3'-Bromo-5'-Chloro Phenyl)-3-Pyridine-2-Propen-1-one (L_2), 1-(2'-Hydroxy-3'-Iodo-5'-Chloro Phenyl)-3-Pyridine-2-Propen-1-one (L_3), 1-(2'-Hydroxy-5'-Chloro Phenyl)-3-Pyrrole-2-Propen-1-one (L_4). The data obtained was preceding using XRD data analysis program. From the experimental measurements, various parameters and Crystal System have been estimated. The XRD analysis revealed that all complexes show good intense and sharp peaks, indicating high crystallinity of complexes.

KEYWORDS: Heterocyclic Chalcones, Transition metal Complexes, XRD analysis.

INTRODUCTION

Chalcones constitute an important group of natural products, chemically they consist of open chain flavonoids in which the two aromatic rings are joined by α, β unsaturated carbonyl system. The presence of a reactive α, β unsaturated keto group in chalcones is found to be responsible for their antimicrobial activity.[1]

In recent years a variety of chalcones have been synthesized and reviewed for their cytotoxic, anticancer, chemo preventive and mutagenic as well as antiviral insecticidal and enzyme inhibitory properties.[2, 3] A number of chalcones having hydroxyl, alkoxy group in different position have been reported to possess antibacterial[4], antiulcer[5], antifungal[6], antioxidant[7], vasodilatory[8], antomitotic[9], antimalarial[10], antileshmanial[11] and inhibition of chemical mediator release, inhibition of leukotriene B4[12], inhibition of tyrosinase[13, 14] and inhibition

of aldose reductase activities.[15] Also chalcones are having the chelating property and they form the stable complexes with the transition metals. The metal complexes of the chalcones are more reactive towards the micro organisms than the corresponding chalcones. Appreciation of these findings motivated us to synthesise new heterocyclic chalcones.

MATERIAL AND METHOD

Experimental: All the melting points were determined in an open capillary tube and are uncorrected. Completion of the reaction was monitored by thin layer chromatography on pre-coated sheets of silica gel-G.

General procedure for the synthesis of Ligands (L$_2$-L$_4$)

A mixture of substituted acetophenone (0.01mol), aromatic carboxaldehyde (Pyridine and Pyrrole 2-carboxaldehyde (0.01mol) and NaOH (0.02mol) were dissolved in methanol solution. The reaction mixture was heated for 2-3 hrs. The progress of the reaction was monitored by TLC. After completion of the reaction the contents were poured in ice water and then acidified by dil. HCl. The solid obtained was filtered, washed with cold water. Then crude product was crystallized from ethanol to give the corresponding product.

Synthesis of metal complexes: The ligand (0. 02 mole) and the metal salt (0.01mole) in 50 ml methanol were refluxed for 2 hours in a reaction flask. The solid mass separated was filtered through a sintered glass crucible (G4) and the residue was washed several times with hot methanol until the washings were free of the excess of ligand.

X-Ray Powder Diffractometer: The X-Ray diffraction technique is a powerful tool to understand the complete molecular structure of a compound.[16] The x-rays interact with innermost electronic cloud in the atoms and suggest internal arrangement of the atoms in the crystal.[17-18]

The procedure in analyzing the powder diffractogram of an unknown sample is consisting of measuring the intensities of the peaks, the diffraction angles θ or 2θ. Once θ is determined it is used for calculating the interplanar spacing d of reflection planes from the values of λ of x-rays used, and then the dimensions of unit cell are determined. Powder diffraction technique is very important method for the identification of unknown compound and applicable to all crystalline substances.

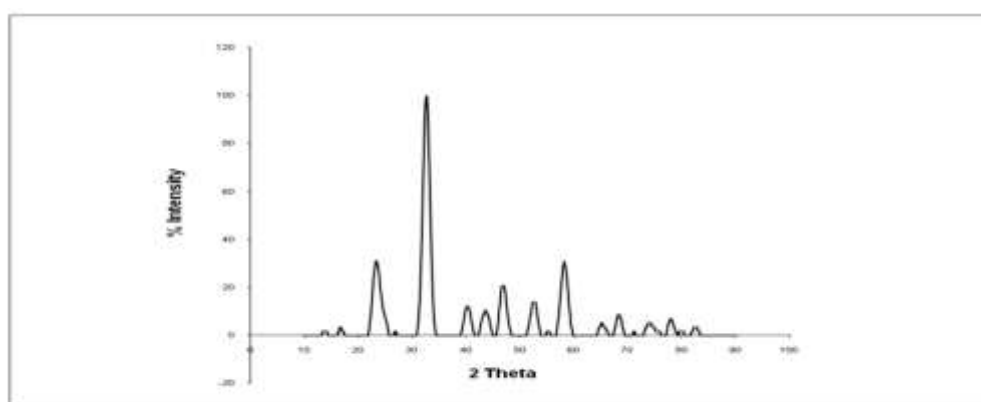**X-Ray Diffraction Study of Cu (II), Co (II), Ni (II), Fe (II) and Zn (II) complexes**

The X-ray powder diffraction of representative metal complexes was scanned on Bruker D8 Diffractometer attached to a digital computer along with graphical assembly in which Cu-K radiation source connected with the tube Cu-Ni-40 Kv/40 mA producing 1.543 A° wavelength radiation was used with scanning rate 2°/ min. each test sample of 200-300 mesh size weighing minimum amount 10 mg was spread in the form of film and spectra were scanned in the range of $2\theta = 10°$ to 80°.

The data obtained was deduced using computer program powder-x. The preliminary data in the form of 2θ and intensity ratio were fed to the computer and corresponding h, k, l values were assigned to each peak. The program calculates the lattice parameters a, b, c (A°) and α, β, γ (degree) along with standard deviation in each. The crystal volume is also obtained from the unit cell data.

Table I: - X-Ray Diffraction Analysis Data

Sr. No.	Compound	Observed Density	Theoretical Density	z	Crystal System	Space Group	% Porosity
1	$Cu(L_2)_2$	1.0197	1.0114	4	Monoclinic	P	0.0082
2	$Ni(L_4)_2(H_2O)_2$	1.9680	1.6256	4	Monoclinic	P	0.021
3	$Co(L_3)_2(H_2O)_2$	1.2378	1.1552	4	Tetragonal	$P_{2/m}$	0.071
4	$Fe(L_3)_2(H_2O)_2$	2.037	1.1921	2	Monoclinic	$P_{2/m}$	0.414
5	$Zn(L_3)_2$	1.2073	1.0114	6	Tetragonal	P	0.1936

These values suggest that each reflex of X-ray diffraction pattern is indexed with perfectness.

Fig. 38: X-ray Diffractogram of $[Cu(L_2)_2].H_2O$

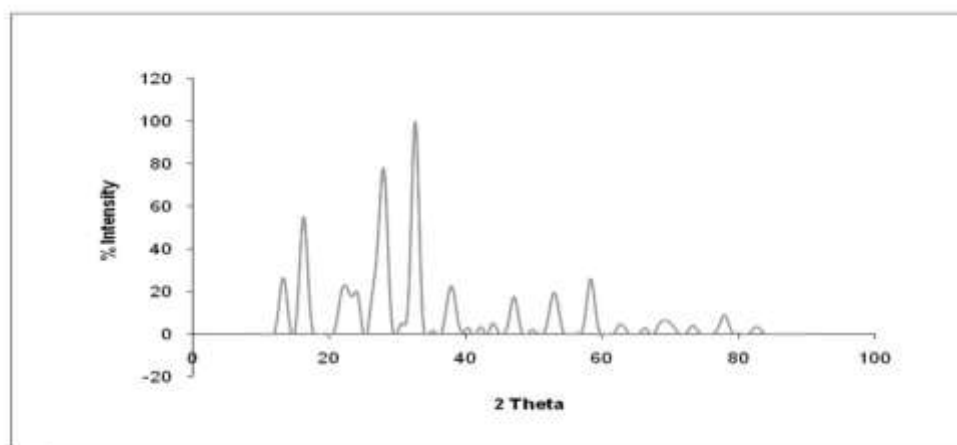**X-Ray Diffraction Study of Cu Complex of $[Cu(L_2)_2]$**

X-ray diffractogram of the **$[Cu(L_2)_2]$** complex are scanned in range $2\theta = 10°$ to 80° and determined the crystal structure of Cu(II) complexes. The X-ray diffractogram of **$[Cu(L_2)_2]$**

shows good intense and sharp peaks, indicating high crystallinity of Cu(II) complex, the standard deviation in lattice parameters for Cu(II) complex is 0.018% The lattice parameter for Cu(II) complex directed to Monoclinic is found to be as expected value of Z(Z=4) The observed density of Cu(II) complex is 1.0197gm/cm^3, while theoretical density from the X-ray data is 1.0114 gm/cm^3.

X-Ray Diffraction Study of Ni(II) Complex of [Ni(L$_4$)$_2$(H$_2$O)$_2$]

The X-ray diffractogram of Ni(II) complex shows good intense and sharp peaks, indicating high crystallinity of Ni(II) complex. The Ni(II) complex is successfully indexed to monoclinic crystal system. The standard deviation in lattice parameter for Ni(II) complex is found to be as expected, which is very well supported by value of Z (Z=4). The observed density of Ni(II) complex is 1.9680 gm/cm^3, while theoretical density from the X-ray data is 1.6256 gm/cm^3. The closeness in the value of observed density and calculated density suggest that each reflux of X-ray diffraction pattern is indexed with perfectness. The X-ray data for Ni(II) complex having metal:ligand stoichiometry as 1:2 have formula factor Z=4. Monoclinic crystal system with Z=4 can be assigned space group P without condition on h, k, l values.


VIIb

Fig. 46: X-ray Diffractogram of [Ni(L$_4$)$_2$(H$_2$O)$_2$]

X-ray Diffraction Study of [Co(L$_3$)$_2$(H$_2$O)$_2$] Complex

X-ray diffractogram of the **[Co(L$_3$)$_2$(H$_2$O)$_2$]** complex is scanned in range 2θ = 10º to 80º and determined the crystal structure of Co(II) complexes. By using the X-ray data, crystal lattice density of complex are calculated. The density of compound was determined by using pyknometric method and the observed value of the density was used to determine formula factor Z for each complexes.

The X-ray diffractogram of **[Co(L₃)₂(H₂O)₂]** shows good intense and sharp peaks, indicating high crystallinity of Co(II) complex. The standard deviation in lattice parameters for Co(II) complex is 0.032% The lattice parameter for Co(II) complex directed to Tetragonal is found to be as expected value of Z(Z=4) The observed density of Co(II) complex is 1.2378 gm/cm^3, while theoretical density from the X-ray data is 1.1552 gm/cm^3.

These values suggest that each reflex of X-ray diffraction pattern is indexed with perfectness.
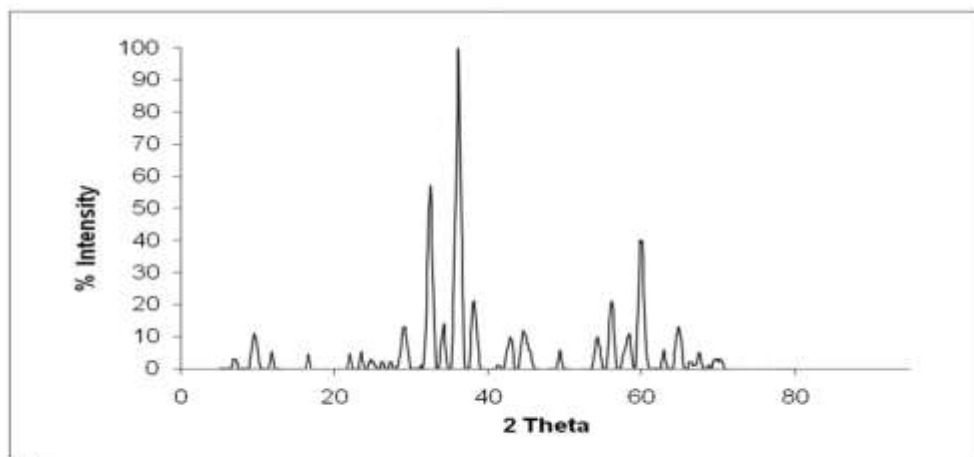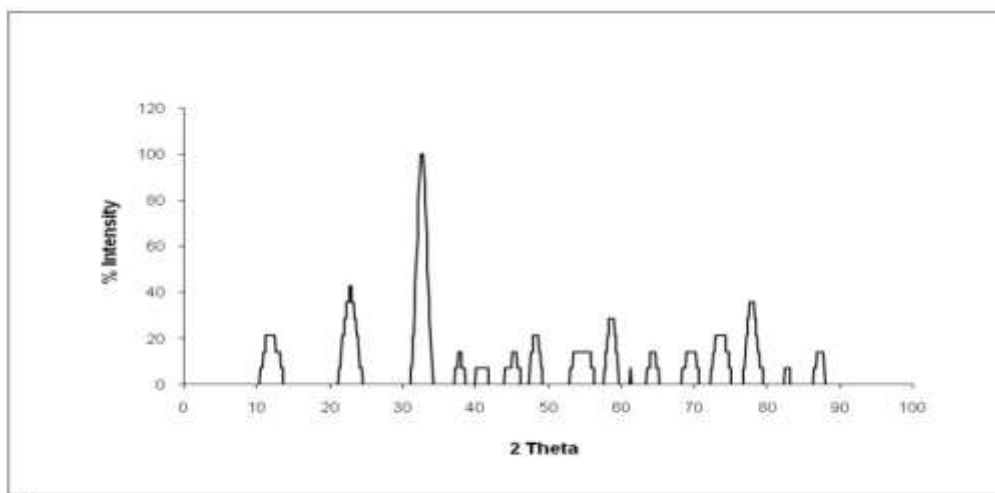

Vlc
Fig. 54: X-Ray Diffractogram of [Co(L₃)₂(H₂O)₂]

X-Ray Diffraction Study of Fe(II) Complex of [Fe(L₃)₂(H₂O)₂]

The X-ray diffractogram of Fe(II) complex shows good intense and sharp peaks, indicating high crystallinity of Fe(II) complex. The Fe(II) complex is successfully indexed to monoclinic crystal system. The standard deviation in lattice parameter for Fe(II) complex is found to be as expected, which is very well supported by value of Z (Z=2). The observed density of Fe(II) complex is 2.037 gm/cm^3, while theoretical density from the X-ray data is 1.1921 gm / cm^3. The closeness in the value of observed density and calculated density suggest that each reflux of X-ray diffraction pattern is indexed with perfectness. The X-ray data for Fe(II) complex having metal:ligand stoichiometry as 1:2 have formula factor Z=2. Monoclinic crystal system with Z=2 can be assigned space group P$_{2/m}$ without condition on h, k, l values.

Vld
Fig. 60: X-ray Diffractrogram of [Fe(L₃)₂(H₂O)₂]

X-Ray Diffraction Study of [Zn(L$_3$)$_2$] Complex

The X-ray diffractogram of **[Zn(L$_3$)$_2$]** shows good intense and sharp peaks, indicating high crystallinity of Zn(II) complex. The standard deviation in lattice parameters for Zn(II) complex is 0.024% The lattice parameter for Zn(II) complex directed to Tetragonal is found to be as expected value of Z(Z=6). The observed density of Zn (II) complex is 1.2073 gm/cm^3, while theoretical density from the X-ray data is 1.0114 gm/cm^3.

These values suggest that each reflex of X-ray diffraction pattern is indexed with perfectness.
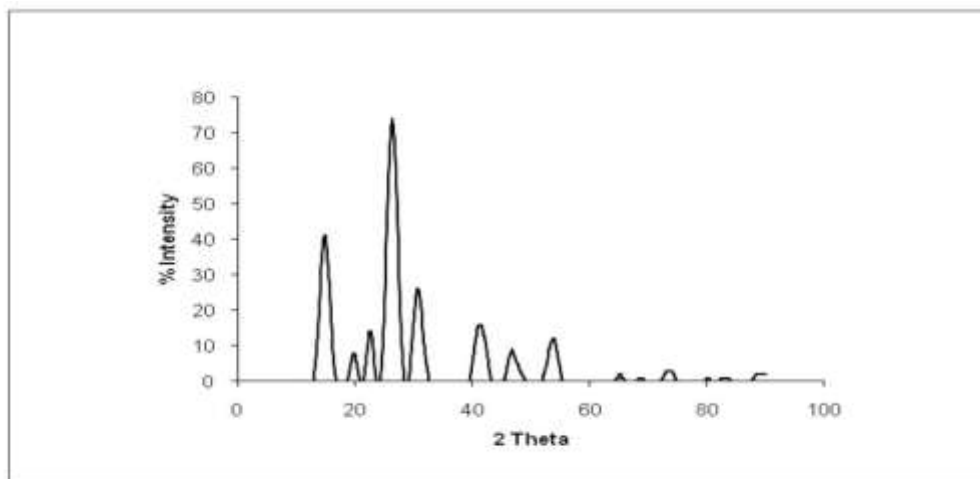
Vle
Fig. 67: X-ray Diffractrogram of [Zn(L₃)₂]

CONCLUSION

The X-ray diffractogram of all complexes show good intense and sharp peaks, indicating high crystallinity of the compounds. The X-ray analysis reveals that the sample is cubic in phases as seen from the presence of extra peaks in XRD pattern.

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