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Synthesis and Spectroscopic Investigations of Cu (II) doped Ni L-Histidine Hydrochloride Monohydrate Crystals

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ABSTRACT

*Copper doped Ni L-Histidine Hydrochloride monohydrate crystals Cu(**ll**)-**Ni LHICL** are grown at room temperature using slow evaporation techniques. The Cu(II) doped crystals are characterized by spectroscopic techniques such as X-Ray diffraction studies, Electron Paramagnetic Resonance (EPR), Optical Absorption and FT-IR studies. The powder diffraction patterns of prepared crystals have been recorded and lattice cell parameters are evaluated as a = 1.5300, b = 0.8834, c = 0.7036 nm. From EPR studies, g and hyperfine splitting parameters for Cu(II) ion in the host are determined as* $g_{ll} = 2.2918$ *,*$A_{ll} = 123\times10^{-4}$ *and* $g_{\perp} = 1.9644$*,* $A_{\perp} = 78\times10^{-4}$ *indicates that octahedral symmetry. The Optical absorption studies also confirm the octahedral symmetry transition metal ions in the host crystal. Crystal field and inter electronic parameters are evaluated. The FT-IR spectrum exhibit characteristic vibrations of the crystal indicating bond formation between the metal ion and the amino acid.*

Keywords: Crystal field, Spin Hamiltonian parameters, Optical Absorption Spectrum, L-Histidine hydrochloride monohydrate, FT-IR, XRD.

INTRODUCTION

Metal-amino acid studies are very useful to know the structural, electronic, and magnetic properties and they can provide valuable information to understand the properties of metal ions in metalloproteins. Metal ions are biologically important with amino acids [1] Metal ions may act synergistically with peptides promoting their biological activity, example Gly-L-His-L-Lys, a growth modulating tripeptide from human plasma [2] but there is no full clarification of the coordination of such compounds. Now a special attention is directed towards transition metal complexes of the Histidine containing peptides [3]. The structural stability of amino acid crystals is one of many lines of current research. L-Histidine is one of the protein forming amino acid, playing a fundamental role in several biological mechanisms including the formation of hemoglobin [4]. Amino acids are very necessary in biological bodies, and complex readily with the first transition series ions such as nickel ion. There is a wealth of information on the structures of transition metal complexes with amino acids (including nickel and alanine) in the literature [5]. Ni(II) is potentially inhibits synthesis of macromolecules such as RNA and proteins [6] and it has been reported that nickel metal acts as a cofactor of several enzymes [7]. Nickel being an essential part of some enzymes therefore functions in association with some molecules in the biological systems [8]. The nickel complexes are found to be effective antibacterial agents than commercial streptomycin and Ampicillin drugs [9].

Copper metalloproteins are involved in various biological functions such as electron transfer, oxygen transport, or substrate oxidation. These functions are the consequence of the redox properties of the copper ion modulated by the protein ligands and selection of substrates by the active site [10]. Histidine has been found to act as both a bidentate and tridentate ligand in copper-histidine crystal structures[11]. Copper, Histidine interactions play an essential role in biological systems and proteins containing copper ions are involved in important physiological processes such as respiration, iron transport, oxidative stress protection, blood clotting and pigmentation[12]. Histidine is a tridentate ligand that has an amino, imidazole and carboxylate group as metal ion binding sites but only a metal ion with an octahedral coordination sphere can form a tridentate chelate [13]. Crystal structure of Zinc(D,L-Histidine)$_2$ complex has been reported with Cu(II) ion dopant [6] in which bis Histidine was shown to be a bidentate ligand with Zinc(II) ion bound to imidazole and amino nitrogen and to carboxylate oxygen. Copper is the most abundant transition metal present in living systems, and Cu(II) ions are well-known to play a key role in the working mechanism of several important metalloenzymes, such as galactose oxidase and superoxide dismutase [14].Early studies of Cu(II) doping on pure L-histidine hydrochloride monohydrate (LHICL) are available [15,11]. Complexes of amino acids with inorganic salts are promising materials as they tend to combine the advantages of the organic amino acid with that of the inorganic salts [16]. Amino acids play an important role in many physiological activities of the human body and are helpful in understanding the biological functions of macromolecules such as proteins. In particular, transition metals such as Mn, Fe and Cu are involved in many redox processes requiring electron transfer, and play an important role in the folding and bio functionality of proteins [17]. Amino acids are very active for efficient and new materials for NLO applications since the discovery of second harmonic generation (SHG) in quartz crystal by Franken et al [18]. A major role is being played by NLO materials in photonics including optical information processing, telecommunication sensor protector applications and optical data storage. Some of the organic materials exhibit good NLO properties due to their flexibility in structural modifications which lead to an unlimited number of crystalline structures[19-23]. Inorganic NLO materials, on the other hand, exhibit higher mechanical strength, thermal stability and good transmittance[24-26]. Thus, combining the advantages of organic and inorganic materials, research is focused on semi-organic NLO crystals for obtaining the best suited crystals for NLO applications.

Doping can be modifying the physical properties of materials for technological applications. Certain transition metal ions often modify the growth habit of a crystal when incorporated into the lattice [27-30,9]. Structural studies of many transition metal complexes showed that the amino acids coordinate in various ways, depending upon the metal ion, its oxidation state and the primary structure of the amino acid [21].The EPR spectroscopy of transition metal ions in crystals is used to find the local site symmetry and distortions with the ligand [31]. Copper ions have an unpaired spin, and their electronic properties were studied by electronic paramagnetic resonance (EPR) spectroscopy. This technique may offer a detailed view of the coordination of the ligands and the chemical bonding of the ion. Electron paramagnetic resonance (EPR) spectroscopy has along history of the study of copper-doped crystalline systems [32].The primary aim of these were to obtain accurate and unambiguous g copper hyperfine A and quadruple tensors to both define the coordination of the doped metal ion and to understand how the observed spectral characteristics relate to electronic structure. Results from single-crystal experiments where doped copper replaced other transition ions in crystalline amino acid models have shown that the site can be identified by alignment of the g and copper hyperfine tensor axes with the ligand bond directions in the host [33].

The EPR results are compared with the structure of Zn(L-asp) and the electronic properties of the copper ions reported [31]. The synthesis, spectrochemical properties, structure, stability, thermochemical study and characterization of complexes of Cu(II), Ni(II), Co(II) and Zn(II) with Histidine, glycine, alanine and other amino acids have previously been reported [34-40].Hence no work is done on Cu(II) doped Nickel L-Histidine. The present work is to synthesize and characterize Cu(II) doped in Ni LHICL crystals by spectroscopic studies like X-Ray diffraction (XRD), Electron Paramagnetic Resonance(EPR), Optical absorption and FT-IR techniques to understand oxidation states of the doped metal ion, the site symmetry and bonding nature.

MATERIALS AND METHODS

Crystals of Cu^{2+}dopedNi L-histidine hydrochloride monohydrate, here after called Ni LHICL, were grown by slow evaporation at room temperature from the aqueous, equimolar and equivolume solutions containing nickel chloride hexahydrate ($NiCl_2.6H_2O$) and L-histidine hydrochloride monohydrate ($C_6H_{10}N_3O_2Cl.H_2O$) by adding 0.01 mol % of copper chloride as dopant to the growth solution for growing Cu (II)-Ni LHICL crystals in about thirty days by slow evaporation. Powder X-Ray diffraction spectrum of the crystals was recorded on PHILIPS Make PW1830 X-RAY Diffractometer, Polycrystalline EPR spectrum was recorded at room temperature on JEOL- JES-FA 200 EPR spectrometer, crystals of 2 mm thickness were selected for optical absorption spectra recorded on JASCO V670 spectrophotometer in the region 200 and 1200 nm. FTIR spectra were recorded using KBr pellets on Thermo Nicolet 6700 FTIR spectrophotometer in the region 400- 4000cm^{-1}.

RESULTS AND DISCUSSION

Powder XRD studies of Cu(II) doped Ni LHICL crystals: Powder X-ray diffraction studies carried out on Cu(II)-Ni LHICL crystals revealed sharp, clean patterns, indicative of highly crystalline phases. The powder XRD pattern of the grown crystal was shown in fig.1. Lattice cell parameters were evaluated using Nakamoto Programme for Cu(II)-Ni LHICL crystals, a = 1.5300nm, b= 0.8834nm, c= 0.7036nm at room temperature and showed in table. 1. These values agreed well with the reported values of pure LHICL crystal cell parameters, a = 1.5317nm, b = 0.8929nm, c = 0.6851 nm indicating doping and complexation did not change the crystal structure to a greater extent [41].

Table :1 d-spacing and h k l values obtained for of Cu(II) doped Ni LHICL Crystal. Sys.Orthorhombic, Lambda= 1.54056, a=1.5300nm, b=0. 8834nm, c=0. 7036nm

d-spacing A		Indices			2Theta	
obs.	calc.	h	k	l	obs.	calc
7.57	7.65	1	1	0	11.68	11.55
6.10	6.39	1	0	1	14.69	13.84
5.66	5.78	2	1	0	15.62	15.30
5.03	5.17	2	0	1	17.60	17.10
4.41	4.41	3	1	0	20.11	20.08
3.77	3.74	0	2	1	23.52	23.76
3.67	3.63	1	2	1	24.20	24.47
3.49	3.51	4	1	0	25.45	25.35
3.34	3.42	1	0	2	26.65	25.96
3.10	3.19	2	0	2	28.71	27.89
3.00	3.01	3	2	1	29.71	29.58
2.88	2.89	5	1	0	30.96	30.90
2.66	2.67	5	1	1	33.57	33.47
2.54	2.58	4	0	2	35.18	34.96
2.39	2.39	3	3	1	37.53	37.48
2.30	2.31	1	0	3	39.09	38.86
2.21	1.95	4	1	3	40.67	40.46
2.12	2.10	0	4	1	42.61	42.58
2.04	2.06	6	0	2	44.25	43.91
1.94	1.94	3	4	1	46.65	46.59
1.85	1.87	6	2	2	48.99	48.63
1.79	1.82	1	3	3	50.70	50.03

1.75	1.75	8	2	0	51.95	51.76
1.68	1.68	3	5	0	54.49	54.45
1.65	1.65	9	0	1	55.37	55.32
1.55	1.57	5	3	3	59.29	58.88
1.49	1.50	9	1	2	61.81	61.42
1.46	1.45	4	5	2	63.57	63.47
1.41	1.44	3	3	4	65.85	64.87

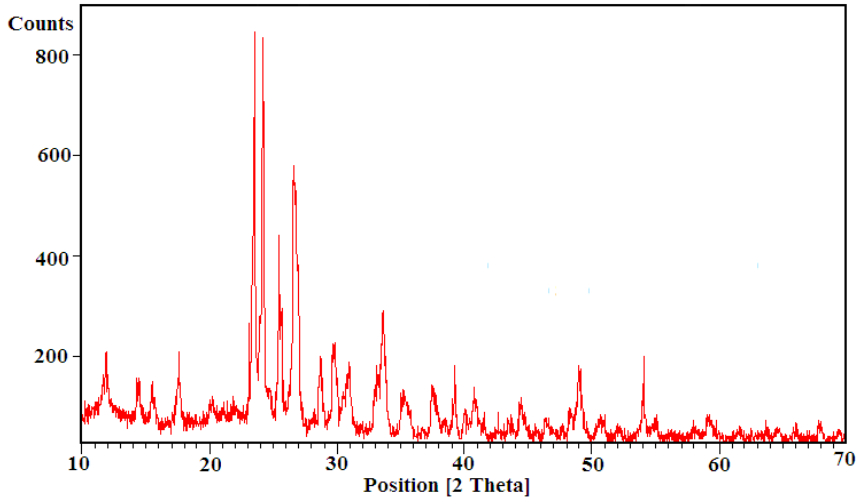

Fig.1 X-RD spectrum of Cu(II) doped Ni LHICL crystal

EPR spectrum of Cu(II) doped Ni LHICL crystals : EPR studies were carried out for Cu(II) doped Ni LHICL at 9.154558GHz and at room temperature. Introduction of Cu(II) ions into the Ni LHICL crystal produced four major lines characteristic of Cu(II) ion with S=1/2 and I=3/2 as showed in fig. 2. Splitting of hyperfine lines was observed during crystal rotations. For Cu(II) ion with single unpaired electron (S=1/2) interacting with its nucleus (I=3/2), the following spin Hamiltonian was used to analyze the EPR spectrum . The spin Hamiltonian and hyperfine splitting values were evaluated based on the following equation.

$$\mathbf{H = g_{II}\,\beta\,H_z S_z + g_{\perp}\,\beta\,(HxSx + H_yS_{y)}) + A_{II}I_zS_z + A_{\perp}\,(I_xS_x + I_yS_y)}$$

Where the symbols stand for their usual meaning [42]. The g and A values calculated from the spectra at room temperature were given in table 2 . The molecular coefficient, α^2, is a measure of covalent nature of σ bonding, calculated using the equation.

$$\boldsymbol{\alpha^2 = A_{II}/0.036 + (g_{II} - 2.0023) + 3/7\,(g_{\perp} - 2.0023) + 0.04}$$

Table. 2 Resonance and Hyperfine splitting values for the Cu(II) doped Ni LHICL at room temperature

Parameters	**Eigen values**					
	g_{II}	$g_{\perp}$	**K**	$\boldsymbol{\alpha^2}$	**α**	$\boldsymbol{\alpha^1}$
g	2.2918	1.9644	0.3295	0.3799	0.6163	0.1899
A (mT)	123 x 10^{-4} cm^{-1}	78 x 10-4 cm^{-1}				

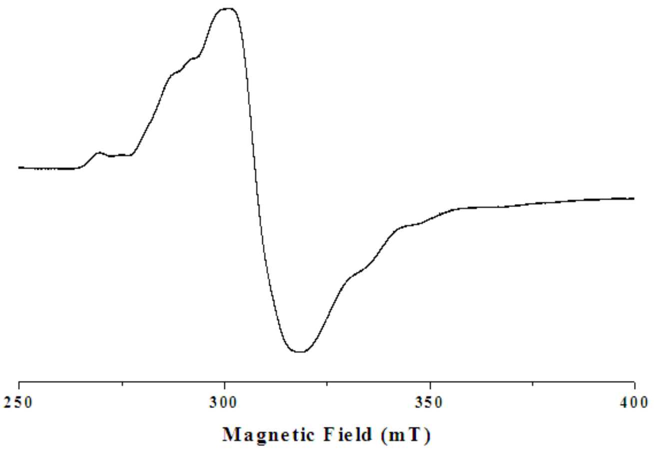

Fig.2 EPR spectrum of Cu(II) doped Ni LHICL crystal ($\nu = 9.152104$ GHz).

given in table. 2. α^1 parameter was also evaluated from the normalization condition on the ground orbital [43].

$$\boldsymbol{\alpha^1 = (1-\alpha^2)^{1/2} + \alpha S = 0.8036}$$

S is the overlap integral between $d_{x^2-y^2}$ orbital and normalized ligand orbital. The value of 'S' is given as 0.085 for a copper complex with nitrogen ligands [44]. The bonding parameters showed that the crystal Cu(II)-Ni LHICL exhibited covalent nature in bonding.

Optical absorption studies of Cu(II) doped Ni LHICL crystals: The Optical absorption spectrum of Cu(II) doped NiLHICL was recorded between 200 and 1200 nm at room temperature and the absorption bands were shown in fig. 3. Cu^{2+} ion has a $3d^9$ configuration with ^2D ground state. In an octahedral crystal field ^2D splits into a triplet $^2T_{2g}$ and a doublet ^2E_g in which $^2T_{2g}$ is of higher energy and ^2E_g is of lower energy due to Jahn-Teller effect. ^2E_g further splits into $^2B_{1g}$ ($d_{x^2-y^2}$) and $^2A_{1g}$ (d_{z^2}) while $^2T_{2g}$ splits into $^2B_{2g}$ (d_{xy}) and ^2E_g (d_{xz}, d_{yz}). The band at 825 nm was assigned for Cu(II) ion corresponding to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$ which was taken as 10Dq band.

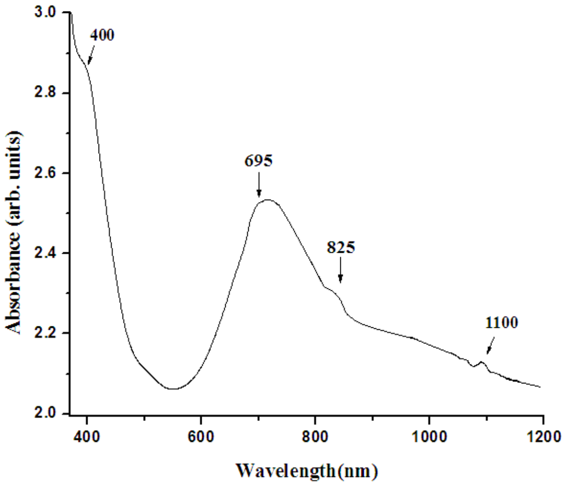

Fig.3 Optical absorption of Cu(II) doped in Ni LHICL Crystal

According to the Jahn-Teller effect, Cu(II) can never have a regular octahedral symmetry due to the generacy of its ground state. The Optical absorption band shifted towards higher frequency in the optical absorption spectrum. The optical absorption spectrum also exhibited three characteristic bands at 400 nm, 695 nm and 1100 nm for Ni(II) ion in the host lattice.

Table 3. Optical transitions for the Cu(II) doped NiLHICL crystals

Transitions From $^6A_{1g}$(S)	**Observed**		**Calculated**
	Wavelength (nm)	**Wavenumber (cm^{-1})**	**Wavenumber (cm^{-1})**
For Cu(II)	825	-	-
For Ni(II)			
$3A_{2g}$(F)→$3T_{1g}$ (F)	400	25118	25150
$3A_{2g}$(F)→$3T_{1g}$ (P)	695	14426	14437
$3A_{2g}$(F)→$3T_{2g}$ (F)	1100	9088	9050

These bands were due to spin allowed transitions which were intense and were assigned for three transitions : $^3A_{2g}$(F) → $^3T_{2g}$(F), $^3A_{2g}$(F) → $^3T_{1g}$(F) and $^3A_{2g}$(F) → $^3T_{1g}$(P) [45] . Based on these assignments energy matrices ($d^8$and d^9) were solved for different values of inter-electronic repulsion parameters B, C and Crystal field parameter Dq. The following values were obtained for Ni(II): Dq = 905 cm^{-1},B = 710 cm^{-1} and C = 3790 cm^{-1}. The observed and calculated band head positions of Cu(II) doped NiLHICL crystals were shown in table. 3.

FT-IR spectra of Cu(II) doped Ni LHICL crystals : FT-IR spectroscopy was effectively used to identify the functional groups in the grown crystal. FT-IR spectrum of the Cu(II) doped Ni LHICL crystals at room temperature and was shown in fig. 4. The NH_3^+ stretching and characteristic of hydrogen bonding region shows broad bands in the range 3500-2500 cm^{-1}. The N-H stretching vibration of the amino group in L-histidine gave rise to an amide band between 3310 and 3270 cm^{-1}. The amide band is usually part of a Fermi resonance doublet with the second component absorbing weakly between 3100 and 3030 cm^{-1} [46]. The CH_2 group of histidine produced peaks at 2612 cm^{-1} and 3009 cm^{-1} due to its symmetric and asymmetric stretching modes respectively. The peak at 1577cm^{-1} was attributed to the skeletal vibrations of histidine ring. The values were shown in table 4. These values were compared with the values of pure L-Histidine [47] and doped L-Histidine hydrochloride monohydrate crystals [48].

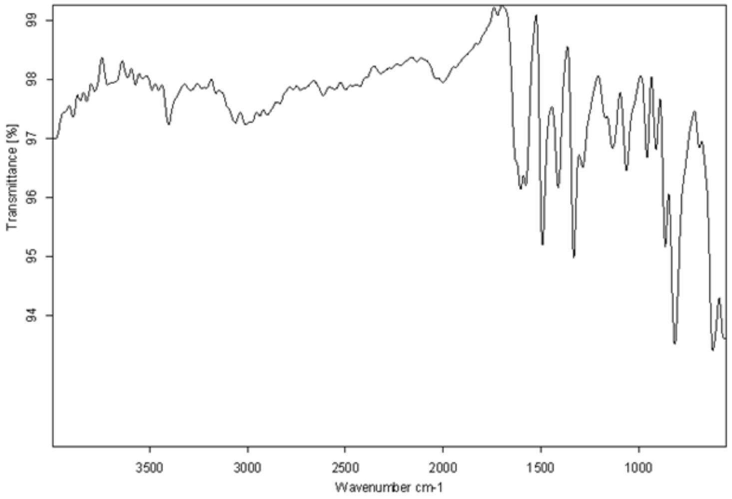

Fig.4 Infra red spectra of Cu(II) doped Ni LHICL Crystal

APPLICATIONS

The studies of synthesis and characterization of Cu(II) doped in Ni LHICL crystals is to understand oxidation states of the doped metal ion, the site symmetry and bonding nature.

CONCLUSIONS

Cu (II)Ni LHICL Crystals were grown at room temperature from aqueous solution and were characterized using Powder XRD, EPR, Optical absorption and FTIR studies. The powder XRD pattern showed that the lattice cell parameters for pure crystal and doped crystal did not vary much indicating the slight changes that took place in the crystal lattice. The slight deviation of evaluated cell parameters confirm the incorporation of transition metal ions in to the host lattice.

Table:4 Observed Vibrational modes of Cu(II) doped Ni L-histidine hydrochloride monohydrate crystals.

Wavenumber (cm^{-1})	**Assignments**
3716	O-H stretching of water
3292	H_2O symmetrial stretching
3145,3009	C-H asymmetrical stretching
2997	NH_3 symmetrical stretching
2612	C-H symmetrical stretching
1722	C=O stretching
1577	Skeletal vibrations of Histidine ring
1494	C-H deformation
1411	symmetric mode of $-COO^-$ and C-N stretching
1332	C-C-H in plane deformation
1286,1134	N-H bending
1062	C-C-N asymmetric stretching
957	C-H bending
865	C-H out of plane bending
689	C-C in plane bending
621	C-H bending , inplane ring deformation

The analysis of the optical absorption spectra confirmed the coordination of Ni(II) and Cu(II) ions with the amino acid molecule and the site symmetry was distorted octahedral in the host lattice. The crystal field and Racah parameters were determined. From the EPR spectral studies, spin-Hamiltonian and hyperfine splitting parameters were evaluated which confirmed the distorted octahedral geometry for Cu(II) ions in the host lattice. From the evaluated parameter, s by correlating EPR and optical results, partial covalence between Cu(II) ions and the ligands was proposed**.** Various vibrational modes of Cu(II)-Ni LHICL crystals from FTIR studies related to stretching modes of NH_3^+, COO- groups, and in-plane C-H deformation of imidazole ring confirmed the presence of amino acid.

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