

Growth, Structural and Spectral Characteristics of Single Crystal Nickel Histidinate

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Abstract : Using slow evaporation solution growth technique, single crystals of Nickel histidinate were grown successfully. Structural and spectral analyses of as grown crystals were carried out by X-ray diffraction, Fourier Transform Infrared, UV-VIS-NIR and Nuclear Magnetic Resonance spectral methods. XRD analysis showed that the type of lattice is orthorhombic for nickel histidinate. From IR spectra most of the bond vibrations were found to be coupled vibrations and zwitter ion of the amino acid was also found in the crystals. Spectra observed in the UV-Visible region showed the characteristic absorbance of Histidine molecules and the transition metal ion Ni²⁺ in the grown crystal. NMR spectrum confirmed the coordination of Ni ion with the Histidine and also showed the presence of specific bonds in the grown crystal. These analyses are help to understand the structure of Nickel histidinate single crystal and its spectral behaviors.

Key word: Nickel Histidinate, Slow evaporation method, Zwitter ion, coupled vibrations, coordination.

I. INTRODUCTION

L-Histidine is an amino acid that is used in the biosynthesis of proteins. It is also used in medicine, feed additive, biochemical research, dietary supplement. It can be used in the treatment of gastric ulcer [1].

L-Histidine contains a α -amino group, a carboxylic acid group and an imidazole side chain classifying it as a positively charged amino acid at physiological pH[2]. The imidazole ring of histidine is aromatic at all pH values [3]. It contains six pi electrons: four from two double bonds and two from a nitrogen lone pair. It has raised special interest because the zwitterion displays two tautomeric forms occurring in equilibrium at biological pH [4]. In solution, histidine presents five pH-dependent different protonation states and shows six distinct geometrical conformations [5]. As a consequence, histidine can act as a donor or as an acceptor for the hydrogen bond [6]. In particular, the imidazole of histidine participates in the tuning of the electronic properties of the copper ion, which is involved in catalysis [7, 8]. Temperature modifies the hydrogen bonding in L-Histidine and plays a key role in its stability and vibrational properties [9]. Experiments conducted by J. Sai Chandra et al. [10], A.Senthamizhan et al. [11], M. Mahadevan et al. [12], H.A.Petrosyan et al. [13] P. N. V. V. L. Prameela Rani et al. [14] and C. Alosious Gonsago et al. [15] reveal the suitability of L-Histidine family crystal as an efficient NLO materials for various applications.

The present study deals with the complex crystals of Nickel substituted L-Histidine. The growth of the crystal has been achieved by slow solvent evaporation technique. The grown crystals were characterized by single crystal XRD, powder XRD, FTIR, UV-VIS-NIR and NMR spectral studies.

2. EXPERIMENTAL METHOD

Nickel histidinate crystals were grown by slow evaporation technique at room temperature from aqueous and equimolar solutions of Nickel Sulphate hexahydrate (NiSO₄.6H₂O) and L-Histidine (C₆H₁₀N₃O₂). The good quality crystals were collected about ten days during the slow evaporation process. The photographs of as-grown crystals of Nickel histidinate is shown in Figure 1. The Powder X-Ray diffraction patterns of the prepared Nickel Histidinate crystals were recorded on Bruker AXS D8 Advance X-ray diffractometer. A suitable crystal was selected for single crystal XRD and unit cell parameters were detected using Bruker Kappa Apex II Diffrectometer. Fourier Transformed-Infra Red (FT-IR) spectrum was recorded using Thermo Nicolet, Avatar370 spectrophotometer in the region 400-4000 cm⁻¹. Optical absorption spectrum was taken from Varian, Cary 5000 Spectrophotometer. Nuclear Magnetic Resonance spectrum was recorded on Bruker Advance 111 Spectrometer.



Figure. 1. Single crystals of Nickel histidinate

3. RESULT AND DISCUSSION

3.1. X-Ray Diffraction Analysis

XRD single crystal data shows that the unit cell parameters are $a = 5.225 \text{ \AA}$, $b = 7.408 \text{ \AA}$, $c = 8.599 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and volume of the unit cell is 720.062 \AA^3 . This confirms the grown crystal belonged to the orthorhombic system with a space group $P2_12_12_1$. Powder XRD pattern was also recorded and given in figure 2. Using unit cell parameters and d-spacing, the miller indices of reflecting planes were determined and shown in figure 2.

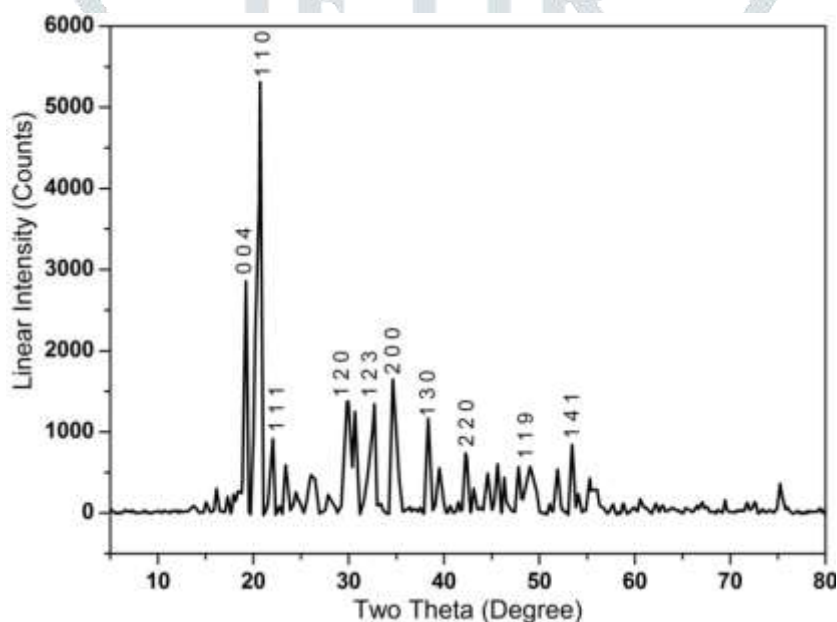


Fig. 2. Indexed Powder XRD pattern of Nickel histidinate single crystal.

3. 2. FTIR Analysis

FTIR spectrum of Nickel histidinate from the range 4000 to 400 cm^{-1} is shown in figure.3. The spectrum shows that most of the vibrations are coupled vibrations, so the peaks are broad in nature. The characteristic assignments of the observed peaks are given in Table 1.

The broad band in the region $2900 \text{ cm}^{-1} - 3500 \text{ cm}^{-1}$ is due to the combinations of asymmetric N-H stretching vibration, symmetric and asymmetric stretching vibrations of C-H bond and O-H stretching vibrations. Similarly the combinational vibrations of zwitter ion i.e. stretching vibrations of amine group and carboxylic group in amino acid, is observed as broad weak intense peak around 2246 cm^{-1} . The peak around 1650 cm^{-1} corresponds to bending vibrations of N-H bond and stretching vibration of C=O bond. The broad and strong peak around 1090 cm^{-1} is due to the stretching vibration of C-O bond in acids and it also corresponds to C-N stretching vibrations in amine. The peak at 615 cm^{-1} is corresponding to the C-H deformation.

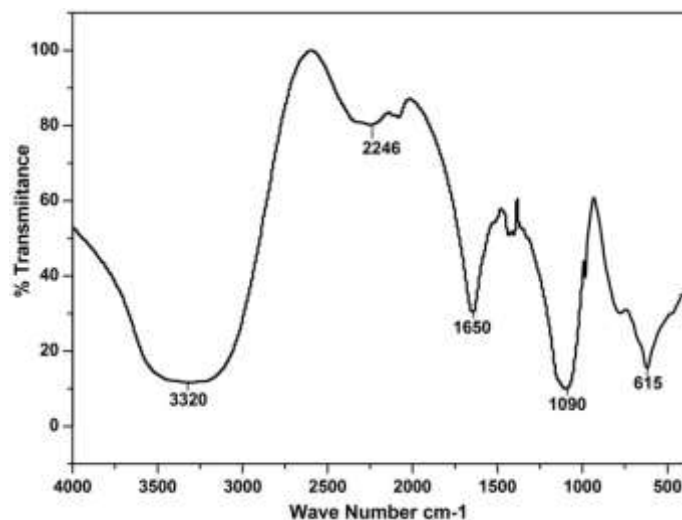


Fig. 3. FTIR spectrum of Nickel histidinate crystal.

Table 1. Assignments on IR bands of Nickel histidinate

Band in cm ⁻¹	Assignments
3320	Symmetric O-H stretching
2246	Vibrations of zwitter ion
1648	N-H bending
1093	C-N stretching
615	C-H out of plane bending

3. 3. UV- VIS - NIR Analysis

UV absorption spectrum was recorded from the region 200nm to 2000 nm and given in Figure.4. It has three absorption peaks approximately centered at 309 nm, 390 nm and 675 nm and at the remaining wavelengths the crystal shows maximum transmittance. The discontinuities in the visible region mainly arise from the absorption of transition metal ion Ni in the crystal. Comparing to the reported value, the absorption of Nickel ion is shifted to its lower wavelength side [16], and the absorption of histidine molecules shifted to its higher wavelength side [17]. This is caused by the coordination of Nickel ion to the Histidine molecules in the grown crystal. The assignment of the absorption peaks are given in Table 2.

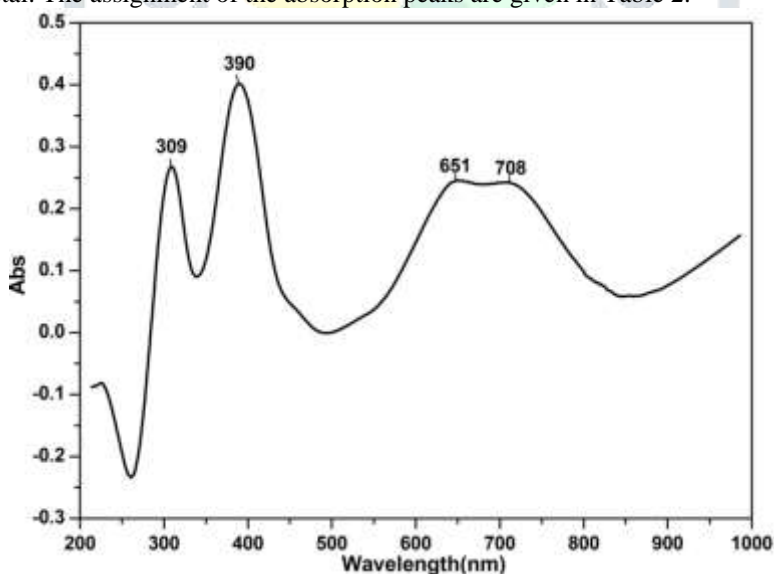


Fig. 4. UV-VIS-NIR spectrum of Nickel Histidinate crystals.

Table 2. Assignments on UV –Vis spectrum of Nickel Histidinate

Wavelength (nm)	Assignment
309	C=C
390	C=N
651,708	Nickel ion

3.4. NMR Analysis

The NMR spectrum of Nickel Histidinate is given in figure.5. There are two broad signals in the upfield side, centered at 2.5 ppm and 3.4 ppm corresponding to $-\text{CH}_2-$ and $-\text{CH}-$ bond respectively. The coordination of the Nickel ion with Histidine, reduces the relaxation times for its imidazole protons leading to the broadening of signals of Histidine protons[18].

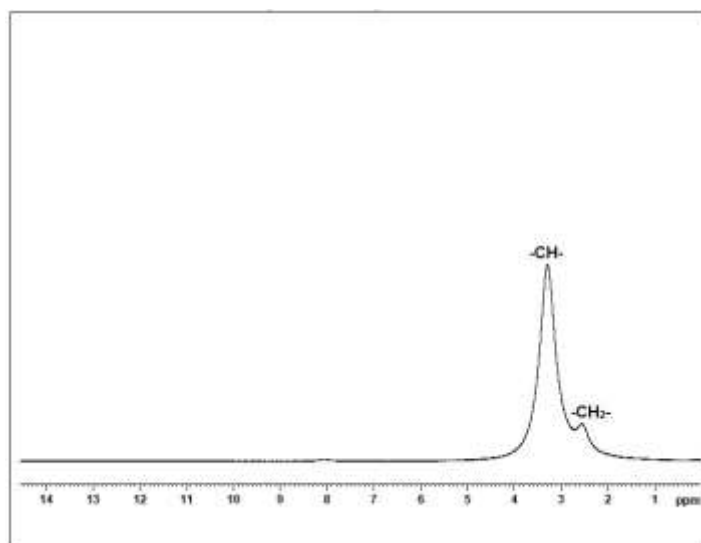


Fig. 5. Proton-NMR spectrum of Nickel Histidinate crystals

IV CONCLUSIONS

The XRD studies concluded that Nickel Histidinate crystallizes in the primitive orthorhombic structure (space group $P2_12_12_1$). The presence of various functional groups and the modes of vibrations in the grown crystals were identified by FTIR studies. UV – Visible and NMR spectrum confirmed the coordination of Ni ion with the Histidine. All the above studies show the structural conformation and the spectral behaviors of Nickel Histidinate single crystal.

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